Supporting Information

for the

Article entitled

Living Ziegler-Natta Polymerization by Early Transition Metals: Synthesis and Evaluation of Cationic Zirconium Alkyl Complexes bearing β-Hydrogens as Models for Propagating Centers

authored by

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Experimental details, ^{1}H NMR of compounds **5a-d**, **5f**, **5b***, **5e***, **5e****, **5e*****, **6** and **7**, and details of crystallographic analyses of compounds **3c**, **3e**, **3f**, **3g**, **4a**, **4c-e**, **5e** and **14** (140 pages).

Experimental

Manipulations were performed under an inert atmosphere of dinitrogen using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Diethyl ether (Et_2O) and pentane were distilled from sodium / benzophenone (with a few milliliters of triglyme being added to the pot in the case of pentane). Chlorobenzene was distilled from CaH_2. Benzene-d_6 was likewise vacuum transferred from NaK prior to being used for NMR spectroscopy. Chlorobenzene-d_5 was vacuum transferred from CaH_2 prior to being used for NMR spectroscopy. (η^5-C_5R_5)$ZrMe_2$[$N(R^1)C(Me)N(R^2)$] (**1**), {(η^5-C_5R_5)$Zr(Me)$[$N(R^1)C(Me)N(R^2)$]}[$B(C_6F_5)_4$] (**2**), (η^5-C_5Me_5)$ZrCl_2$[N(Et)C(Me)N(tBu)] (**8**), (η^5-C_5Me_5)$ZrCl(SiMe_2Ph)$[N(Et)C(Me)N(tBu)] (**9**), and (η^5-C_5Me_5)$HfCl_2$[N(Et)C(Me)N(tBu)] (**13**) were prepared as previously reported. ^{1}H NMR spectra were recorded at 400 or 500 MHz and ^{13}C NMR spectra were recorded at 100 or 125 MHz using benzene-d_6 or chlorobenzene-d_5 as the solvent. Elemental analyses were performed by Midwest Microlab.

Preparation of (η^5-C_5Me_5)Zr(R)(Cl)[N(Et)C(Me)N(tBu)] (3): The following is representative for **3a-h** unless otherwise noted: To a –78 °C solution of **8** (500 mg, 1.14 mmol) in 50 ml Et_2O was added a solution of 1.14 mmol of EtMgCl, n-PrMgCl, n-BuMgCl, i-BuMgCl, t-BuLi, or 2-EtBuMgCl in Et_2O. After slowly warming the mixture to RT, the reaction was quenched with 0.5 ml TMSCl, the volatiles were removed *in vacuo*, and the resulting yellow solid was taken up in pentane and filtered. The mother liquor was concentrated and recrystallized at –30 °C to afford yellow crystals with an isolated yield of 80-95%.

(η^5-C_5Me_5)Zr(Et)(Cl)[N(Et)C(Me)N(tBu)] (3a): After EtMgCl addition, mixture was stirred for 1 hr at –78 °C. ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.75 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2 Hz, 1H), 2.58 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2 Hz, 1H), 2.01 (s, 15H), 1.66 (s, 3H), 1.56 (t, ^{3}J=7.6 Hz, 3H),

1.33 (s, 3H), 0.78 (t, ^{3}J=7.2 Hz, 3H), 0.66 (dq, ^{2}J=13.2 Hz, ^{3}J=7.6 Hz, 1H), 0.13 (dq, ^{2}J=13.2 Hz, ^{3}J=7.6 Hz, 1H). Anal. Calcd. for $C_{20}H_3ClN_2Zr$: %C 55.57, %H 8.65, %N 6.48; Found %C 55.64, %H 8.59, %N 6.23.

(η^5-C_5Me_5)Zr(nPr)(Cl)[N(Et)C(Me)N(tBu)] (3b): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.79 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.62 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2 Hz, 1H), 2.13 (m, 1H), 2.01 (s, 15H), 1.67 (s, 3H), 1.54 (m, 1H), 1.33 (s, 9H), 1.22 (t, ^{3}J=7.0 Hz, 3H), 0.80 (t, ^{3}J=7.2 Hz, 3H), 0.59 (ddd, ^{2}J=13.6 Hz, ^{3}J=10.8 Hz, ^{3}J=4.4 Hz, 1H), 0.27 (ddd, ^{2}J=13.6 Hz, ^{3}J=11.2 Hz, ^{3}J=5.6 Hz, 1H). Anal. Calcd. for $C_{21}H_{39}ClN_2Zr$: %C 56.52, %H 8.81, %N 6.28; Found %C 56.50, %H 8.73, %N 6.21.

(η^5-C_5Me_5)Zr(iPr)(Cl)[N(Et)C(Me)N(tBu)] (3c): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.60 (dq, ^{2}J=14.0 Hz,^{3}J=7.2 Hz, 1H), 2.55 (dq, ^{2}J=14.0 Hz,^{3}J=7.2 Hz, 1H), 1.99 (s, 15H), 1.62 (d, ^{3}J=7.2 Hz, 3H), 1.57 (s, 9H), 1.41 (d, ^{3}J=7.2 Hz, 3H), 1.26 (s, 9H), 0.74 (t, ^{3}J=7.2 Hz, 3H), -0.20 (septet, ^{3}J=7.2 Hz, 1H). Anal. Calcd. for $C_{21}H_{39}ClN_2Zr$: %C 56.52, %H 8.81, %N 6.28; Found %C 56.48, %H 8.77, %N 6.20.

(η^5-C_5Me_5)Zr(nBu)(Cl)[N(Et)C(Me)N(tBu)] (3d): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.80 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2 Hz, 1H), 2.61 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2 Hz, 1H), 2.02 (s, 15H), 2.09 (m, 1H), 1.70 (s, 3H), 1.58 (m, 1H), 1.50 (m, 2H), 1.33 (s, 9H), 1.06 (t, ^{3}J=7.2 Hz, 3H), 0.81 (t, ^{3}J=7.2 Hz, 3H), 0.56 (ddd, ^{2}J=13.2 Hz, ^{2}J=10.4 Hz, ^{3}J=4.2 Hz, 1H), 0.24 (ddd, ^{2}J=12.8 Hz, ^{2}J=11.2 Hz, ^{3}J=5.2 Hz, 1H). Anal. Calcd. for $C_{22}H_{41}ClN_2Zr$: %C 57.41, %H 8.98, %N 6.09; Found %C 57.36 %H 8.90, %N 5.89.

(η^5-C_5Me_5)Zr(iBu)(Cl)[N(Et)C(Me)N(tBu)] (3e): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.89 (dq, ^{2}J=14.3 Hz, ^{3}J=7.2 Hz 1H), 2.72 (dq, ^{2}J=14.3 Hz, ^{3}J=7.2 Hz, 1H), 2.24 (nonet, ^{3}J=6.4

Hz, 1H), 2.00 (s, 15H), 1.70 (s, 3H), 1.33 (s, 9H), 1.32 (d, ^{3}J=6.4 Hz, 3H), 1.15 (d, ^{3}J=6.4 Hz, 3H), 0.82 (t, ^{3}J=7.2 Hz, 3H), 0.73 (dd, ^{2}J=13.6 Hz, ^{3}J=6.4 Hz), -0.03 (dd, ^{2}J=13.6 Hz, ^{3}J=6.4 Hz). Anal. Calcd. for $C_{22}H_{41}ClN_2Zr$: %C 57.41, %H 8.98, %N 6.09; Found %C 57.21 %H 8.80, %N 5.91.

(η^5-C_5Me_5)Zr(2-Et-Bu)(Cl)[N(Et)C(Me)N(tBu)] (3f): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.90 (dq, ^{2}J=14.2 Hz, ^{3}J=7.3 Hz, 1H), 2.71 (dq, ^{2}J=14.2 Hz, ^{3}J=7.3 Hz, 1H), 2.01 (s, 15H), 1.83 (m, 1H), 1.71 (s, 3H), 1.70 (m, 2H), 1.57 (m, 1H), 1.35 (m, 1H), 1.33 (s, 9H), 1.05 (t, ^{3}J=7.3 Hz, 3H), 1.03 (t, ^{3}J=7.3 Hz, 3H), 0.66, (dd, ^{2}J=13.5 Hz, ^{3}J=7.1 Hz), -0.08, (dd, ^{2}J=13.5 Hz, ^{3}J=6.2 Hz). Anal. Calcd. for $C_{24}H_{45}ClN_2Zr$: %C 59.02, %H 9.31, %N 5.74; Found %C 58.42, %H 9.25, %N 5.79.

(η^5-C_5Me_5)Zr(tBu)(Cl)[N(Et)C(Me)N(tBu)] (3g): After addition of ^{t}BuLi, mixture was stirred for 4 hours at –78 °C before quenching. ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.95 (dq, ^{2}J=14.4 Hz, ^{3}J=7.0 Hz, 1H), 2.72 (dq, ^{2}J=14.4 Hz, ^{3}J=7.0 Hz, 1H), 2.04 (s, 15H), 1.65 (s, 3H), 1.38 (s, 9H), 1.33 (s, 9H), 0.78 (t, ^{3}J=7.0 Hz, 3H). Anal. Calcd. for $C_{22}H_{41}ClN_2Zr$: %C 57.41, %H 8.98, %N 6.09; Found %C 57.21, %H 8.88, %N 6.05.

Preparation of (η^5-C_5Me_5)Zr(2-*d*-nPr)(Cl)[N(Et)C(Me)N(tBu)] (3b*): In a 50-ml Schlenk tube fitted with a gas tight Kontes Teflon valve, 0.30 g (0.56 mmol) of **9** was dissolved in 15 ml of pentane, after which time, the tube was sealed. After removal from the glove box, the tube was cooled to 77 K, evacuated and resealed. Upon warming to room temperature, the tube was pressurized to 15 psi with propylene, then pressurized to 35 psi with D_2, and resealed. The tube was shaken overnight, during which time the color changed from dark red to yellow, and the volatiles were removed *in vacuo.* Extraction in pentane and filtration through a thin pad of Celite afforded a yellow solution, which upon concentration and cooling to –35 °C afforded

yellow crystals (0.19 g, 79% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.79 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.62 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2 Hz, 1H), 2.13 (m, 0.6H), 2.01 (s, 15H), 1.67 (s, 3H), 1.54 (m, 0.4H), 1.33 (s, 9H), 1.22 (t, ^{3}J=7.0 Hz, 3H), 0.80 (t, ^{3}J=7.2 Hz, 3H), 0.59 (dd, ^{2}J=13.6 Hz, ^{3}J=10.8 Hz, 1H), 0.27 (dd, ^{2}J=13.6 Hz, ^{3}J=11.2 Hz, 1H).

Preparation of (η^5-C_5Me_5)Zr(2-*d*-iBu)(Cl)[N(Et)C(Me)N(tBu)] (3e*): In a 50-ml Schlenk tube fitted with a gas tight Kontes Teflon valve, 0.30 g (0.56 mmol) of **9** was dissolved in 15 ml of pentane and an excess of liquid isobutylene was added, after which time, the tube was sealed. After removal from the glove box, the tube was pressurized to 35 psi with D_2, resealed, and shaken overnight, during which time the color changed from dark red to yellow, and the volatiles were removed *in vacuo.* Extraction in pentane and filtration through a thin pad of Celite afforded a yellow solution, which upon concentration and cooling to –35 °C afforded yellow crystals (0.22 g, 85% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.89 (dq, ^{2}J=14.3 Hz, ^{3}J=7.2 Hz 1H), 2.72 (dq, ^{2}J=14.3 Hz, ^{3}J=7.2 Hz, 1H), 2.00 (s, 15H), 1.70 (s, 3H), 1.33 (s, 9H), 1.32 (d, ^{3}J=6.4 Hz, 3H), 1.15 (d, ^{3}J=6.4 Hz, 3H), 0.82 (t, ^{3}J=7.2 Hz, 3H), 0.73 (dd, ^{2}J=13.6 Hz, ^{3}J=6.4 Hz), -0.03 (dd, ^{2}J=13.6 Hz, ^{3}J=6.4 Hz).

Preparation of (η^5-C_5Me_5)Zr(1-^{13}C-iBu)(Cl)[N(Et)C(Me)N(tBu)] (3e):** Into a 50-ml Schlenk tube fitted with a gas tight Kontes Teflon valve containing a solution of 0.30 g (0.56 mmol) of **9** in 15 ml of pentane was vacuum transferred 1 g of 1-^{13}C-isobutylene. The tube was pressurized to 35 psi with H_2, resealed, and shaken overnight, during which time the color changed from dark red to yellow. The volatiles were vacuum transferred away to recover unreacted 1-^{13}C-isobutylene. Extraction in pentane and filtration through a thin pad of Celite afforded a yellow solution, which upon concentration and cooling to –35 °C afforded yellow crystals (0.20 g, 77% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.89 (dq, ^{2}J=14.3 Hz,

^{3}J=7.2 Hz 1H), 2.72 (dq, ^{2}J=14.3 Hz, ^{3}J=7.2 Hz, 1H), 2.24 (d nonet, $^2J_{CH}$=1.6 Hz $^3J_{HH}$=6.4 Hz, 1H), 2.00 (s, 15H), 1.70 (s, 3H), 1.33 (s, 9H), 1.32 (dd, $^3J_{CH}$=4.4 Hz , $^3J_{HH}$=6.4 Hz, 3H), 1.15 (dd, $^3J_{CH}$=4.4 Hz , $^3J_{HH}$=6.4 Hz, 3H), 0.82 (t, ^{3}J=7.2 Hz, 3H), 0.73 (ddd, $^1J_{CH}$=115.7 Hz, $^2J_{HH}$=13.6 Hz, $^3J_{HH}$=6.4 Hz), -0.03 (ddd, $^1J_{CH}$=115.7 Hz, $^2J_{HH}$=13.6 Hz, $^3J_{HH}$=6.4 Hz).

Preparation of (η^5-C_5Me_5)Zr(1-^{13}C-2-*d*-iBu)(Cl)[N(Et)C(Me)N(tBu)] (3e*):** Prepared in the same manner as above with D_2 in place of H_2 (0.18 g 70% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.89 (dq, ^{2}J=14.3 Hz, ^{3}J=7.2 Hz, 1H), 2.72 (dq, ^{2}J=14.3 Hz, ^{3}J=7.2 Hz, 1H), 2.00 (s, 15H), 1.70 (s, 3H), 1.33 (s, 9H), 1.32 (d, $^3J_{CH}$=4.4 Hz , 3H), 1.15 (d, $^3J_{CH}$=4.4 Hz, 3H), 0.82 (t, ^{3}J=7.2 Hz, 3H), 0.73 (dd, $^1J_{CH}$=115.7 Hz, $^2J_{HH}$=13.6 Hz), -0.03 (dd, $^1J_{CH}$=115.7 Hz, $^2J_{HH}$=13.6 Hz).

Preparation of (η^5-C_5Me_5)Zr(R)(Me)[N(Et)C(Me)N(tBu)] (4): The following is representative for **4a-f** unless otherwise noted: To a –78 °C solution of **3a-f** (1.0 mmol) in 25 mL of Et_2O was added a solution of MeLi (1.0 mmol) in Et_2O. After slowly warming the mixture to RT, the reaction was quenched with 0.5 ml TMSCl, the volatiles were removed *in vacuo* and the yellow solid was taken up in pentane and filtered. The mother liquor was concentrated and the product was recrystallized at –30 °C to afford yellow crystals with an isolated yield of 60-85%.

(η^5-C_5Me_5)Zr(Et)(Me)[N(Et)C(Me)N(tBu)] (4a): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.87 (dq, ^{2}J=13.6 Hz, ^{3}J=6.8 Hz, 2H), 2.70 (bm, 1H), 1.99 (s, 15H), 1.73 (s, 3H), 1.64 (bt, ^{3}J=13.6 Hz, 3H), 1.18 (s, 9H), 1.18 (m, 1H), 0.87 (t, ^{3}J=7.2 Hz, 3H), 0.33 (dq, ^{2}J=13.2 Hz, ^{3}J=7.2 Hz, 1H), 0.10 (s, 3H).

(η^5-C_5Me_5)Zr(nPr)(Me)[N(Et)C(Me)N(tBu)] (4b): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.90 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2 Hz, 1H), 2.70 (b, 1H), 1.99 (s, 15H), 1.98 (m, 2H), 1.74 (s,

3H), 1.23 (t, ^{3}J=7.0 Hz, 3H), 1.18 (s, 9H), 0.88 (t, ^{3}J=6.8 Hz, 3H), 0.88 (m, 1H), 0.27 (m, 1H), 0.14 (s, 3H). Anal. Calcd. for $C_{22}H_{42}N_2Zr$: %C 62.06, %H 9.94, %N 6.58; Found %C 62.00, %H 9.85, %N 6.39.

(η^5-C_5Me_5)Zr(iPr)(Me)[N(Et)C(Me)N(tBu)] (4c): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.77 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.67 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.02 (s, 15H), 1.69 (s, 3H), 1.57 (d, ^{3}J=7.2 Hz, 3H), 1.54 (d, ^{3}J=7.2 Hz, 3H), 1.19 (s, 9H), 0.86 (t, ^{3}J=7.0 Hz, 3H), 0.07 (s, 3H), -0.50 (septet, ^{3}=7.2 Hz, 1H).

(η^5-C_5Me_5)Zr(nBu)(Me)[N(Et)C(Me)N(tBu)] (4d): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.91 (dq, 1H), 2.74 (bm, 1H), 2.01 (m, 2H), 2.00 (s, 15H), 1.75 (bs, 3H), 1.53 (bq, 2H), 1.19 (s, 9H), 1.19 (m, 1H), 1.09 (t, 3H), 0.89 (bt, 3H), 0.27 (b, 1H), 0.13 (bs, 3H).

(η^5-C_5Me_5)Zr(iBu)(Me)[N(Et)C(Me)N(tBu)] (4e): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.97 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2 Hz, 1H), 2.75 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2 Hz, 1H), 2.20 (bm, 1H), 1.98 (s, 15H), 1.80 (s, 3H), 1.27 (d, ^{3}J=6.4 Hz, 3H), 1.23 (d, ^{3}J=6.4 Hz, 3H), 1.19 (s, 9H), 0.85 (t, ^{3}J=7.2 Hz, 3H), 0.41 (dd, ^{2}J=13.2 Hz, ^{3}J=6.4 Hz, 1H), 0.23 (s, 3H), -0.26 (dd, ^{2}J=13.2 Hz, ^{3}J=6.4 Hz, 1H).

(η^5-C_5Me_5)Zr(2-Et-Bu)(Me)[N(Et)C(Me)N(tBu)] (4f): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.98 (dq, ^{2}J=14.1 Hz, ^{3}J=7.1 Hz, 1H), 2.73 (dq, ^{2}J=14.1 Hz, ^{3}J=7.1 Hz, 1H), 1.98 (s, 9H), 1.81 (s, 3H), 1.75 (m, 1H), 1.63 (m, 3H), 1.44 (m, 1H), 1.20 (s, 9H), 1.052 (t, ^{3}J=7.3 Hz, 3H), 1.048 (t, ^{3}J=7.3 Hz, 3H), 0.89 (t, ^{3}J=7.1 Hz, 3H), 0.32 (dd, ^{2}J=14.0 Hz, ^{3}J=7.2 Hz, 1H), 0.21 (s, 3H), -0.34 (dd, ^{2}J=14.0 Hz, ^{3}J=6.8 Hz, 1H). Anal. Calcd. for $C_{25}H_{48}N_2Zr$: %C 64.16, %H 10.35, %N 5.99; Found: %C 62.68, %H 10.03, %N 6.04.

(η^5-C_5Me_5)Zr(2-*d*-nPr)(Me)[N(Et)C(Me)N(tBu)] (4b*): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.90 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2 Hz, 1H), 2.70 (b, 1H), 1.99 (s, 15H), 1.98 (m, 1H), 1.74 (s, 3H), 1.23 (d, ^{3}J=7.0 Hz, 3H), 1.18 (s, 9H), 0.88 (t, ^{3}J=6.8 Hz, 3H), 0.88 (m, 1H), 0.27 (m, 1H), 0.14 (s, 3H).

(η^5-C_5Me_5)Zr(2-*d*-iBu)(Me)[N(Et)C(Me)N(tBu)] (4e*): ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.97 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2 Hz, 1H), 2.75 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2 Hz, 1H), 1.98 (s, 15H), 1.80 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.19 (s, 9H), 0.85 (t, ^{3}J=7.2 Hz, 3H), 0.41 (d, ^{2}J=13.2 Hz, 1H), 0.23 (s, 3H), -0.26 (d, ^{2}J=13.2 Hz, 1H).

(η^5-C_5Me_5)Zr(1-^{13}C-iBu)(Me)[N(Et)C(Me)N(tBu)] (4e):** ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.97 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2Hz, 1H), 2.75 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2Hz, 1H), 2.20 (bm, 1H), 1.98 (s, 15H), 1.80 (s, 3H), 1.27 (m, 3H), 1.23 (m, 3H), 1.19 (s, 9H), 0.85 (t, ^{3}J=7.2 Hz, 3H), 0.41 (ddd, $^1J_{CH}$=114.0 Hz, ^{2}J=13.2 Hz, ^{3}J=6.4 Hz, 1H), 0.23 (s, 3H), -0.26 (ddd, $^1J_{CH}$=114.0 Hz, ^{2}J=13.2 Hz, ^{3}J=6.4 Hz, 1H).

(η^5-C_5Me_5)Zr(1-^{13}C-2-d-iBu)(Me)[N(Et)C(Me)N(tBu)] (4e*):** ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.97 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2Hz, 1H), 2.75 (dq, ^{2}J=14.4 Hz, ^{3}J=7.2Hz, 1H), 1.98 (s, 15H), 1.80 (s, 3H), 1.27 (m, 3H), 1.23 (m, 3H), 1.19 (s, 9H), 0.85 (t, ^{3}J=7.2 Hz, 3H), 0.41 (ddd, $^1J_{CH}$=114.0 Hz, ^{2}J=13.2 Hz, 1H), 0.23 (s, 3H), -0.26 (dd, $^1J_{CH}$=114.0 Hz, ^{2}J=13.2 Hz, 1H).

Preparation of {(η^5-C_5Me_5)Zr(R)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$] (5): The following is representative for **5a-f** unless otherwise noted: To 11 mg (14 μmol) of [$PhNHMe_2$][$B(C_6F_5)_4$] was added a solution of 13 μmol of **4a-f** in 1.0 ml of C_6D_5Cl at –10 ºC to provide a clear, deep yellow solution. See fig. 4 and 6-14 in the supporting information for ^{1}H NMR spectra.

Preparation of {(η^5-C_5Me_5)Hf(R)[N(Et)C(Me)N(tBu)]}[$B(C_6F_5)_4$] (6,7): Prepared in the same manner as **5**. See figs. 15 and 16 in the supporting information for ^{1}H NMR spectra.

Preparation of (η^5-C_5Me_5)Hf($SiMe_2Ph$)(Cl)[N(Et)C(Me)N(tBu)] (10): To a –78 °C solution of **13** (0.50 g, 0.95 mmol) in 100 ml Et_2O was added 5.0 ml (0.95 mmol) of $LiSiMe_2Ph$ (0.19 M in Et_2O). After slowly warming the mixture to RT, the volatiles were removed *in vacuo*, and the resulting brown oil was taken up in pentane and filtered. Removal of the volatiles *in vacuo* afforded a brown oil which could not be further purified (0.55 g, 93%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 7.94 (dd, ^{3}J=7.6 Hz, ^{4}J=1.2 Hz, 2H), 7.27 (t, 3J=7.6 Hz, 2H), 7.13 (tt, ^{3}J=7.6 Hz, ^{4}J=1.2 Hz, 1H), 2.90 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2Hz, 1H), 2.82 (dq, ^{2}J=14.0 Hz, ^{3}J=7.2Hz, 1H), 2.09 (s, 15H), 1.17 (s, 9H), 1.16 (s, 3H), 0.76 (s, 3H), 0.71 (t, ^{3}J=7.2 Hz, 3H) 0.59 (s, 3H).

Preparation of (η^5-C_5Me_5)Hf(1-^{13}C-2-*d*-iBu)(Cl)[N(Et)C(Me)N(tBu)] (11): Into a 50-ml Schlenk tube fitted with a gas tight Kontes Teflon valve containing a solution of 0.38 g (0.61 mmol) of **10** in 15 ml of pentane was vacuum transferred 1 g of 1-^{13}C-isobutylene. The tube was pressurized to 35 psi with D_2, resealed, and shaken overnight. The volatiles were vacuum transferred away to recover unreacted 1-^{13}C-isobutylene. Extraction in pentane and filtration through a thin pad of Celite afforded a yellow solution, which upon concentration and cooling to –35 °C afforded yellow crystals (0.16 g, 48% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.91 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.80 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.05 (s, 15H), 1.66 (s, 3H), 1.32 (d, $^3J_{CH}$=4.4 Hz , 3H), 1.31 (s, 9H), 1.14 (d, $^3J_{CH}$=4.4 Hz, 3H), 0.83 (t, ^{3}J=7.0 Hz, 3H), 0.54 (dd, $^1J_{CH}$=111.1 Hz, $^2J_{HH}$=13.9 Hz), -0.17 (dd, $^1J_{CH}$=111.1 Hz, $^2J_{HH}$=13.9 Hz).

Preparation of (η^5-C_5Me_5)Hf(1-^{13}C-2-*d*-iBu)(Me)[N(Et)C(Me)N(tBu)] (12): To a –78 °C solution of **11** (0.11 g, 0.20 mmol) in 25 mL of Et_2O was added 0.1 ml (0.2 mmol) of MeLi (2.0 M in Et_2O). After slowly warming the mixture to RT, the reaction was quenched with 0.5 ml

TMSCl, the volatiles were removed *in vacuo* and the yellow solid was taken up in pentane and filtered. The mother liquor was concentrated and the product was recrystallized at –30 °C to afford yellow crystals (0.75 g, 71% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 3.00 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.82 (dq, ^{2}J=14.0 Hz, ^{3}J=7.0 Hz, 1H), 2.02 (s, 15H), 1.73 (s, 3H), 1.27 (d, $^{3}J_{CH}$=4.0 Hz , 3H), 1.21 (d, $^{3}J_{CH}$=4.4 Hz, 3H), 1.17 (s, 9H), 0.89 (t, ^{3}J=7.0 Hz, 3H), 0.22 (dd, $^{1}J_{CH}$=109.2 Hz, $^{2}J_{HH}$=13.8 Hz), -0.48 (dd, $^{1}J_{CH}$=109.2 Hz, $^{2}J_{HH}$=13.8 Hz).

Preparation of (η^5-C_5Me_5)Hf(tBu)(Cl)[N(Et)C(Me)N(tBu)] (14): To a –78 °C solution of **13** (0.75 g, 1.43 mmol) in 100 ml Et_2O was added 0.89 ml (1.43 mmol) of tBuLi (1.61 M in tetrahydrofuran). After slowly warming the mixture to RT, the reaction was quenched with 0.5 ml TMSCl, the volatiles were removed *in vacuo*, and the resulting yellow solid was taken up in pentane and filtered. The mother liquor was concentrated and recrystallized at –30 °C to afford white crystals (0.70 g, 89% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 3.09 (dq, ^{2}J=14.4 Hz, ^{3}J=7.1 Hz, 1H), 2.81 (dq, ^{2}J=14.4 Hz, ^{3}J=7.1 Hz, 1H), 2.08 (s, 15H), 1.64 (s, 3H), 1.46 (s, 9H), 1.35 (s, 9H), 0.87 (t, ^{3}J=7.1 Hz, 3H).

Preparation of (η^5-C_5Me_5)Hf(Me)(Cl)[N(Et)C(Me)N(tBu)] (15): To a –78 °C solution of **13** (0.75 g, 1.43 mmol) in 100 ml Et_2O was added 0.53 ml (1.43 mmol) of MeMgCl (2.71 M in tetrahydrofuran). After slowly warming the mixture to RT, the reaction was quenched with 0.5 ml TMSCl, the volatiles were removed *in vacuo*, and the resulting yellow solid was taken up in pentane and filtered. The mother liquor was concentrated and recrystallized at –30 °C to afford white crystals (0.58 g, 80% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 2.82 (m, 2H), 2.07 (s, 15H), 1.57 (s, 3H), 1.28 (s, 9H), 0.82 (t, ^{3}J=7.1 Hz, 3H), 0.23 (s, 3H).

Preparation of (η^5-C_5Me_5)Hf(tBu)(Me)[N(Et)C(Me)N(tBu)] (16): To a –55 °C solution of **(Hf-Me/Cl)** (0.30 g, 0.59 mmol) in 50 ml Et_2O was added 0.31 ml (0.59 mmol) of t-BuLi (1.90

M in pentane). The reaction was stirred overnight at –55 ºC before being quenched with 0.5 ml TMSCl, the volatiles were removed *in vacuo*, and the resulting yellow solid was taken up in pentane and filtered. The mother liquor was concentrated and recrystallized at –30 °C to afford yellow crystals (0.25 g, 81% yield). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ (ppm) 3.06 (dq, ^{2}J=14.5 Hz, ^{3}J=7.2 Hz, 1H), 2.98 (dq, ^{2}J=14.5 Hz, ^{3}J=7.2 Hz, 1H), 2.02 (s, 15H), 1.71 (s, 3H), 1.37 (s, 9H), 1.20 (s, 9H), 0.87 (t, ^{3}J=7.2 Hz, 3H) 0.17 (s, 3H).

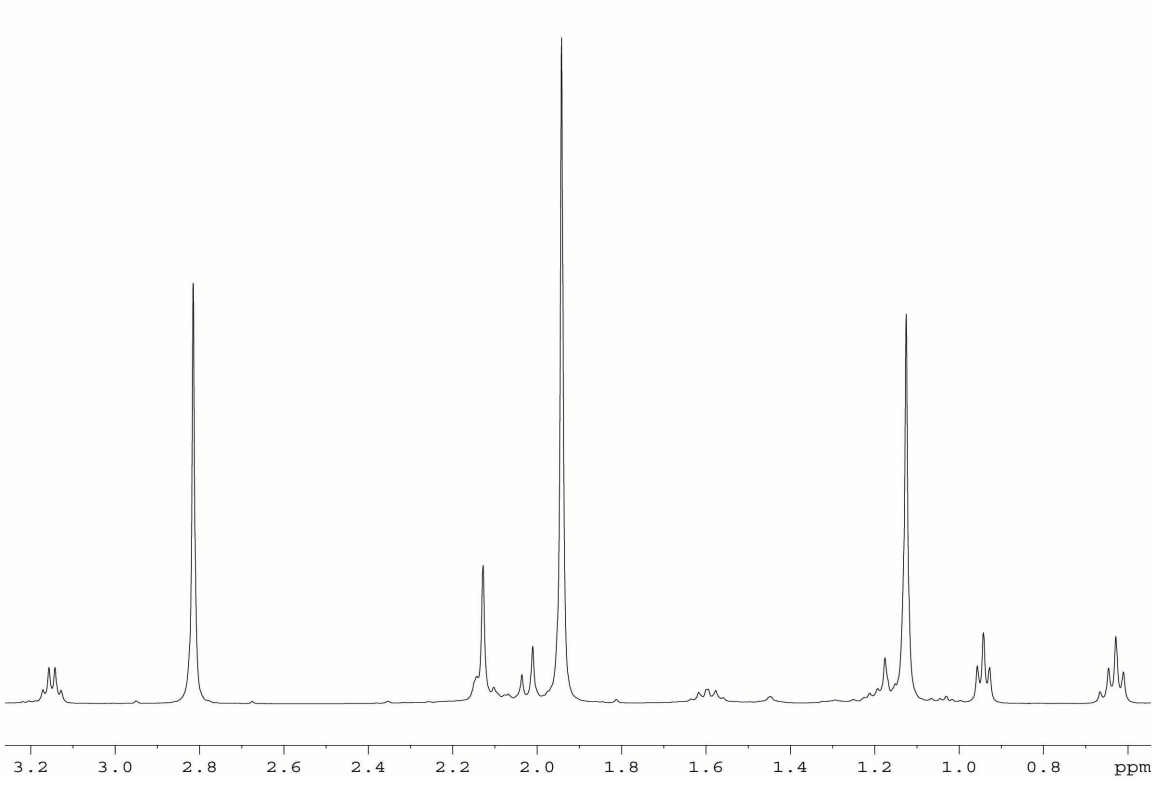


Figure 6: ^{1}H NMR (400 MHz, C_6D_5Cl, 263 K) of {(η^5-C_5Me_5)Zr(Et)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5a.

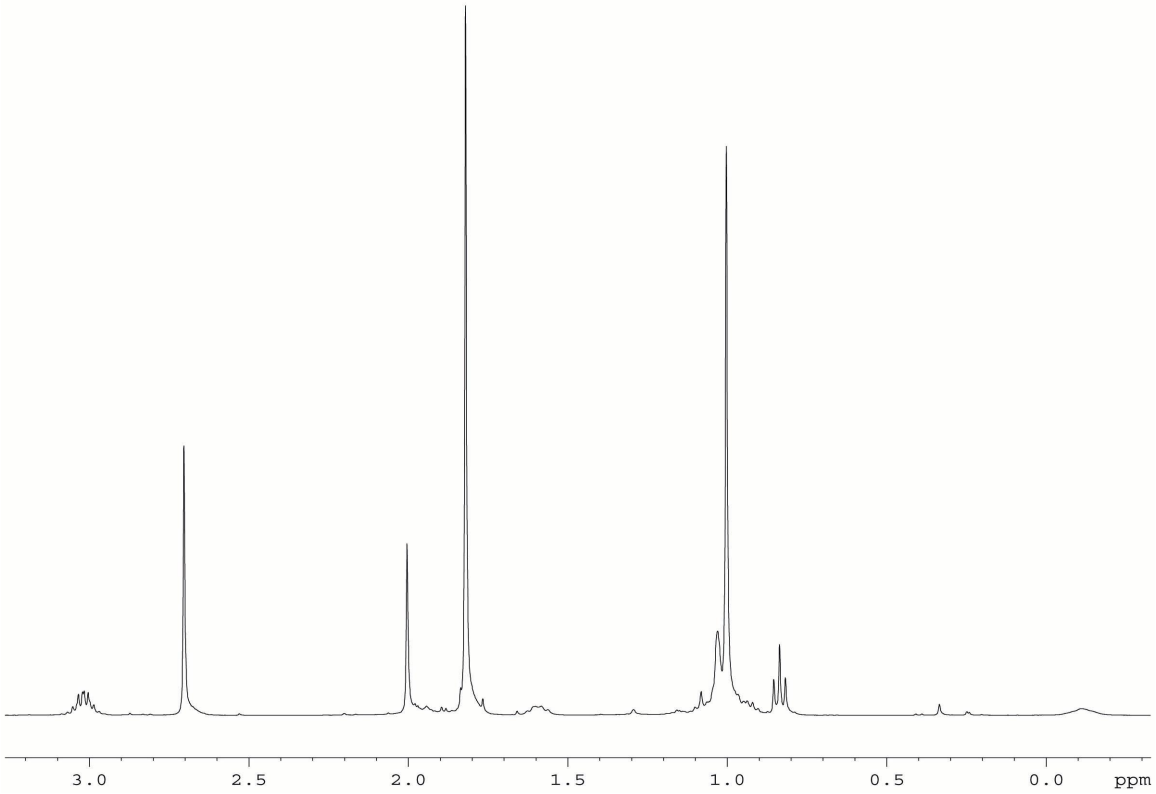


Figure 7: (400 MHz, C_6D_5Cl, 303 K) of {(η^5-C_5Me_5)Zr(nPr)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5b.

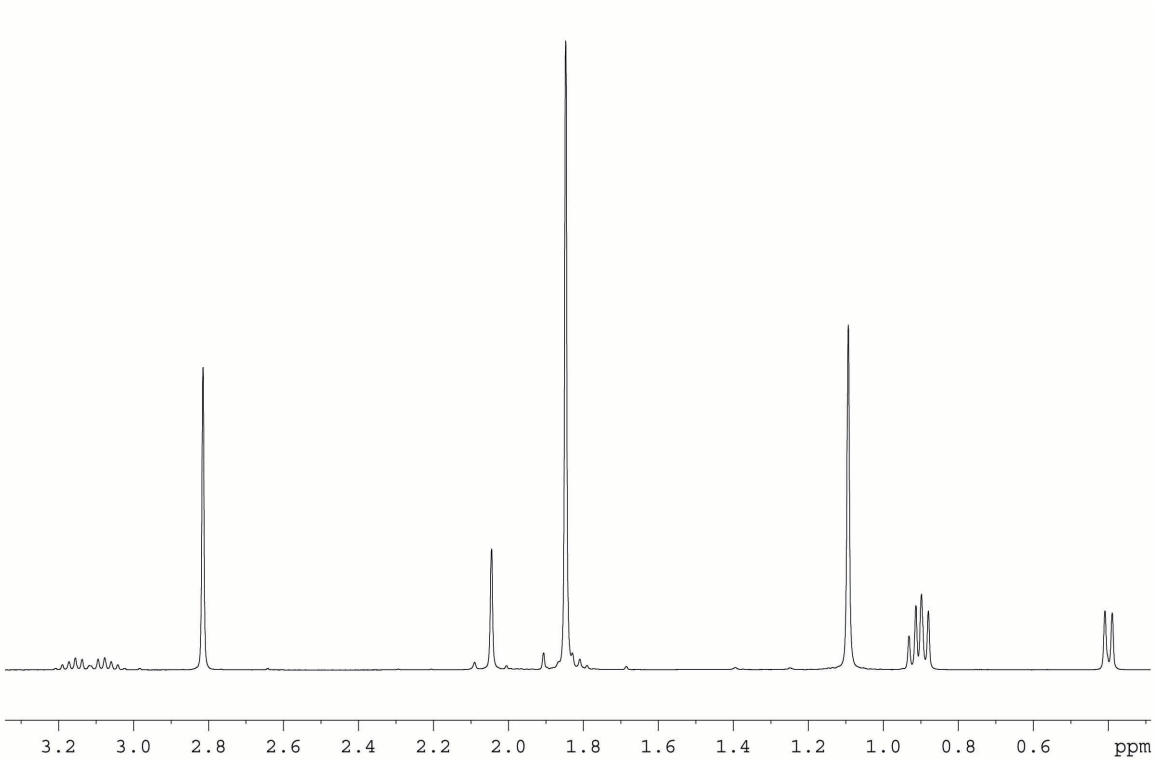


Figure 8: ^{1}H NMR (400 MHz, C_6D_5Cl, 263 K) of {(η^5-C_5Me_5)Zr(iPr)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5c.

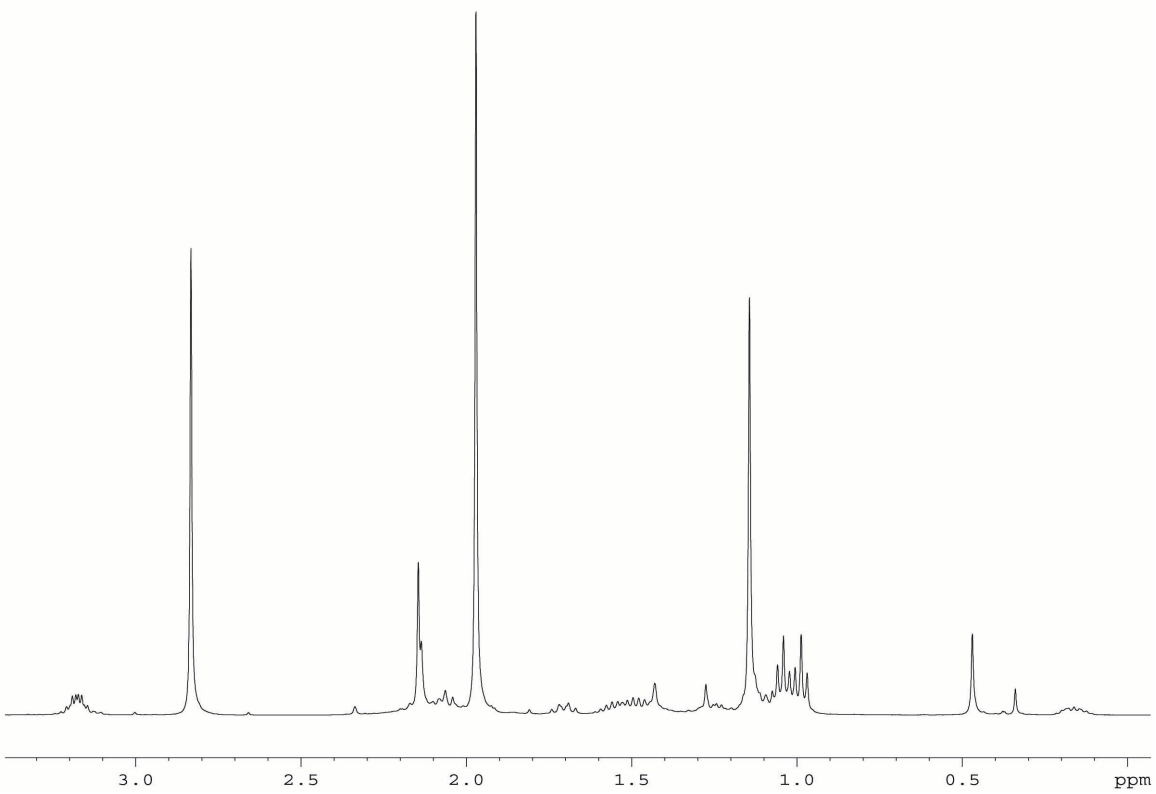


Figure 9: (400 MHz, C_6D_5Cl, 303 K) of {(η^5-C_5Me_5)Zr(nBu)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5d.

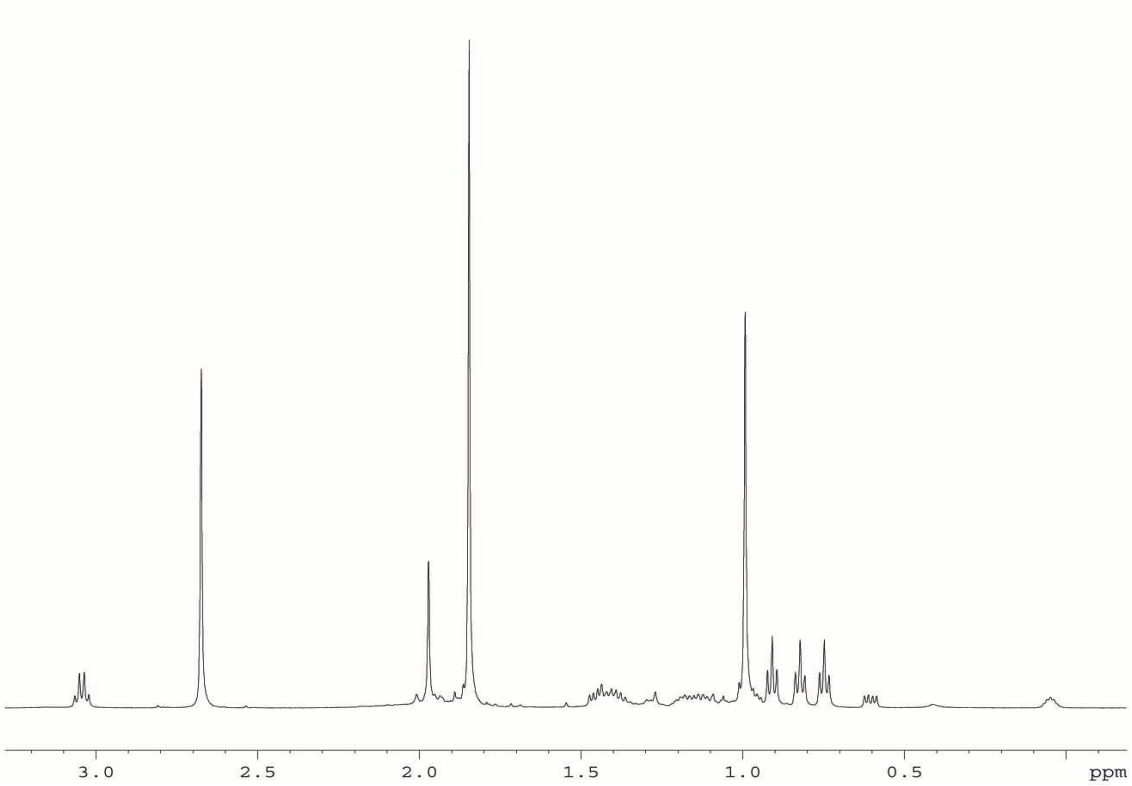


Figure 10: ^{1}H NMR (400 MHz, C_6D_5Cl, 263 K) of {(η^5-C_5Me_5)Zr(2-Et-Bu)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5f.

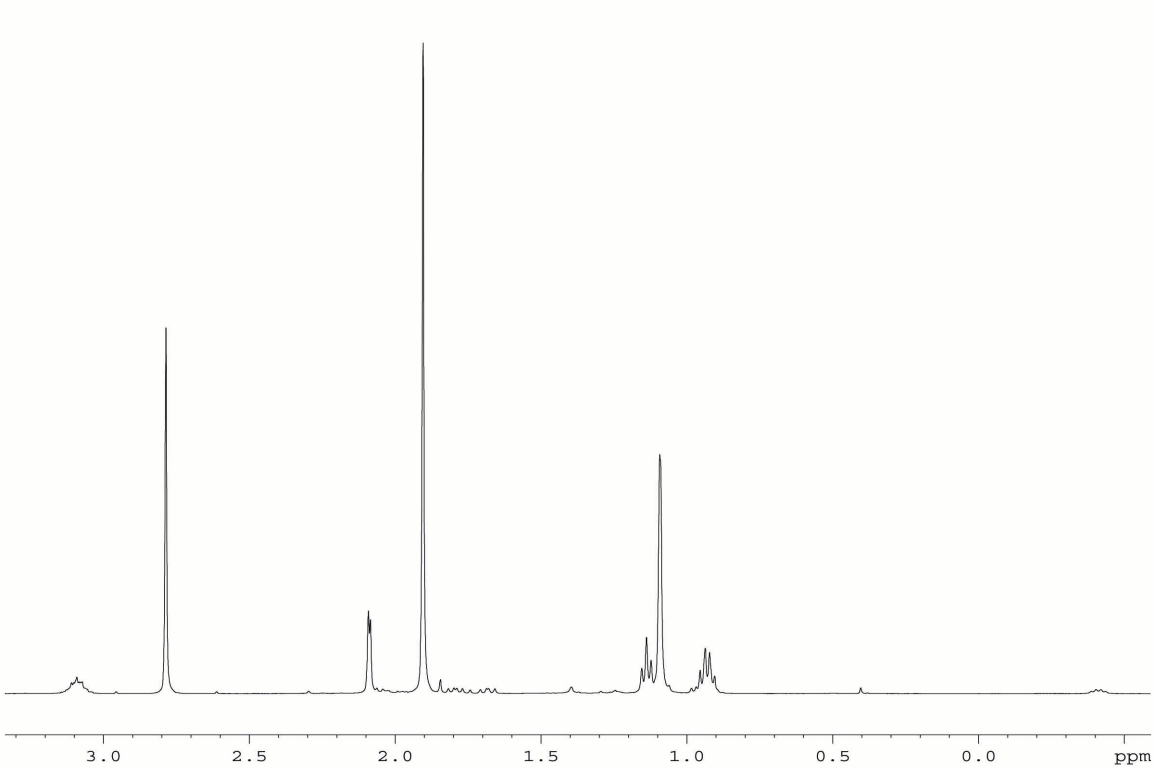


Figure 11: ^{1}H NMR (400 MHz, C_6D_5Cl, 263 K) of {(η^5-C_5Me_5)Zr(2-*d*-nPr)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5b*.

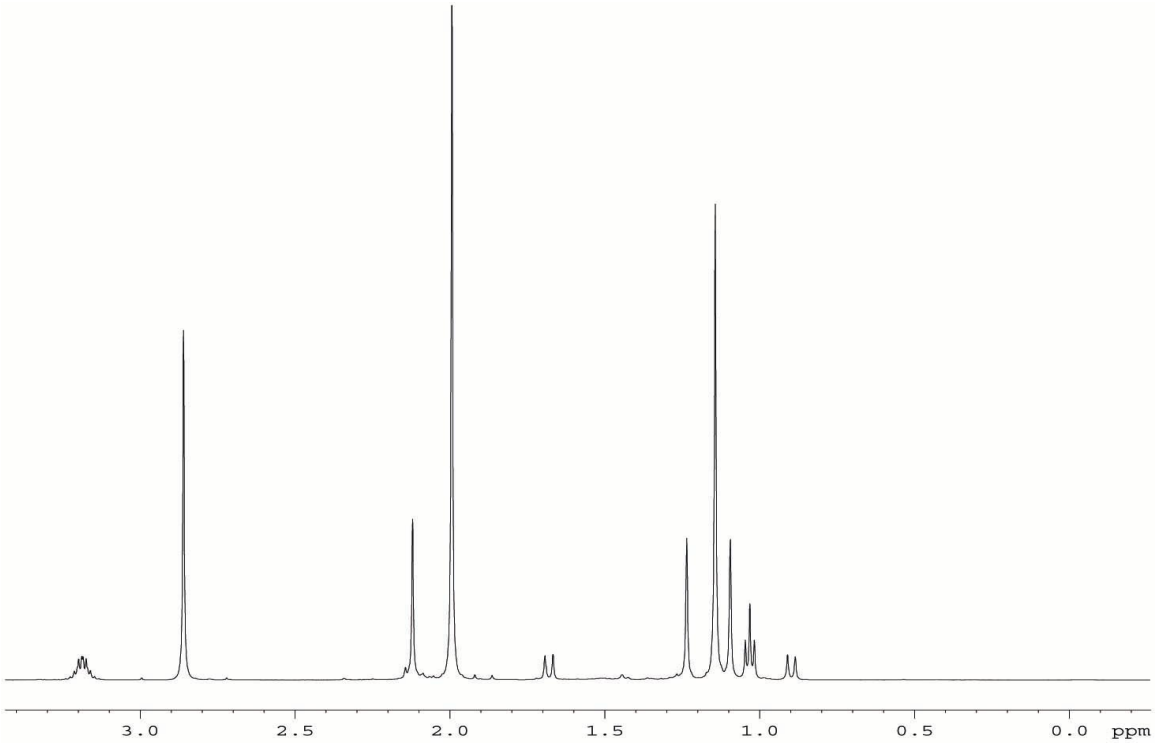


Figure 12: ^{1}H NMR (400 MHz, C_6D_5Cl, 263 K) of {(η^5-C_5Me_5)Zr(2-*d*-iBu)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5e*.

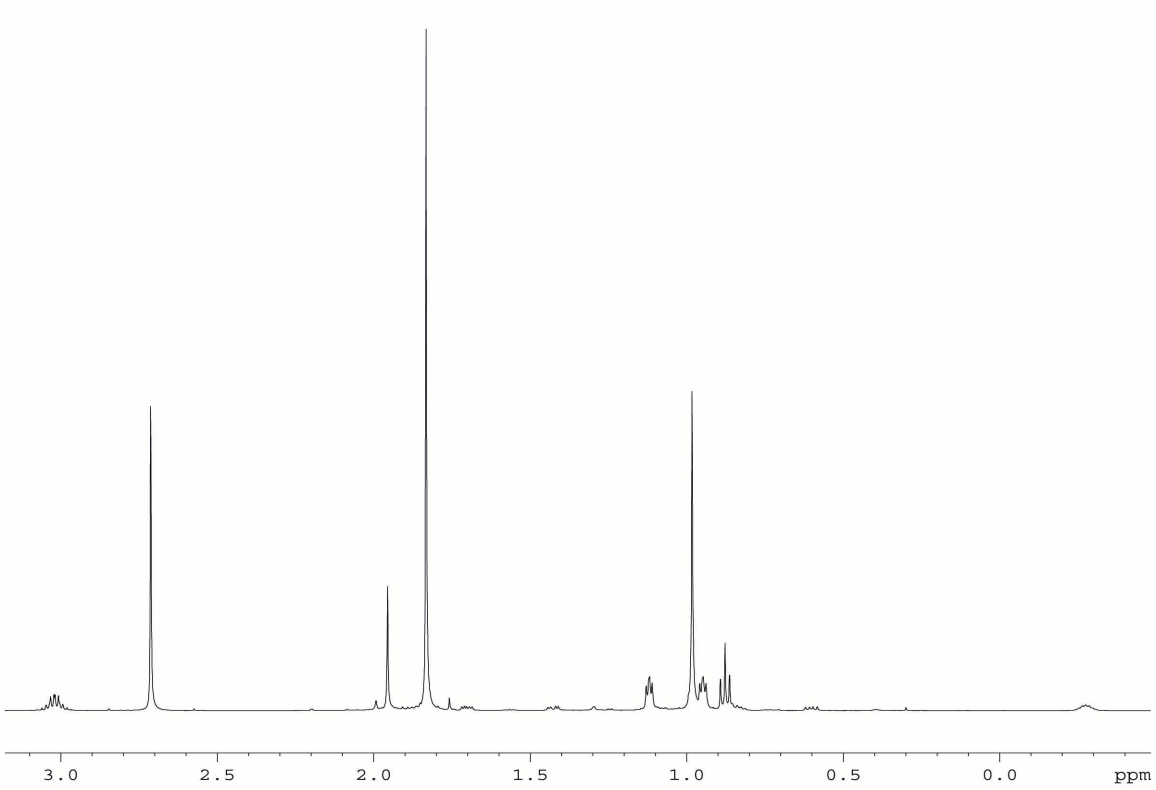


Figure 13: ^{1}H NMR (500 MHz, C_6D_5Cl, 263 K) of {(η^5-C_5Me_5)Zr(1-^{13}C-iBu)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5e.**

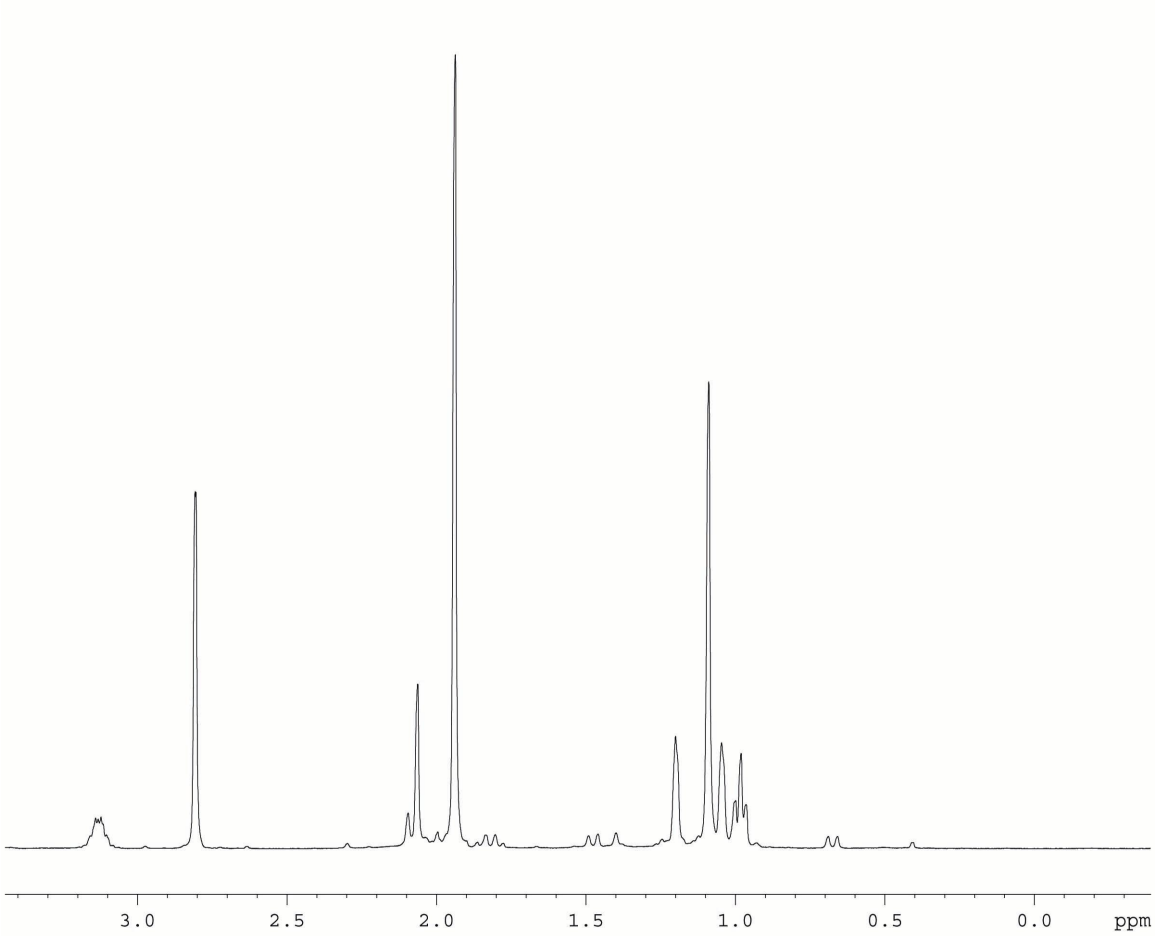


Figure 14: ^{1}H NMR (400 MHz, C_6D_5Cl, 263 K) of {(η^5-C_5Me_5)Zr(1-^{13}C-2-*d*-iBu)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 5e*.**

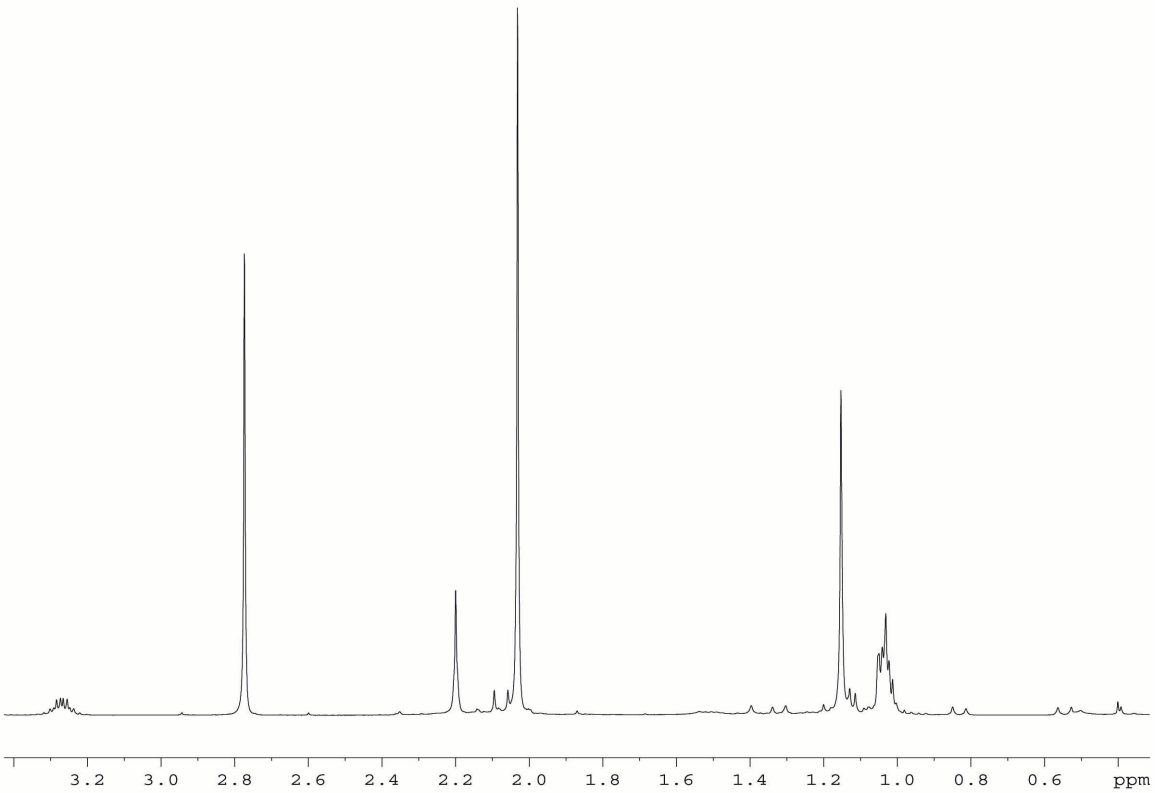


Figure 15: ^{1}H NMR (400 MHz, C_6D_5Cl, 273 K) of {(η^5-C_5Me_5)Hf(1-^{13}C-2-*d*-iBu)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 6.

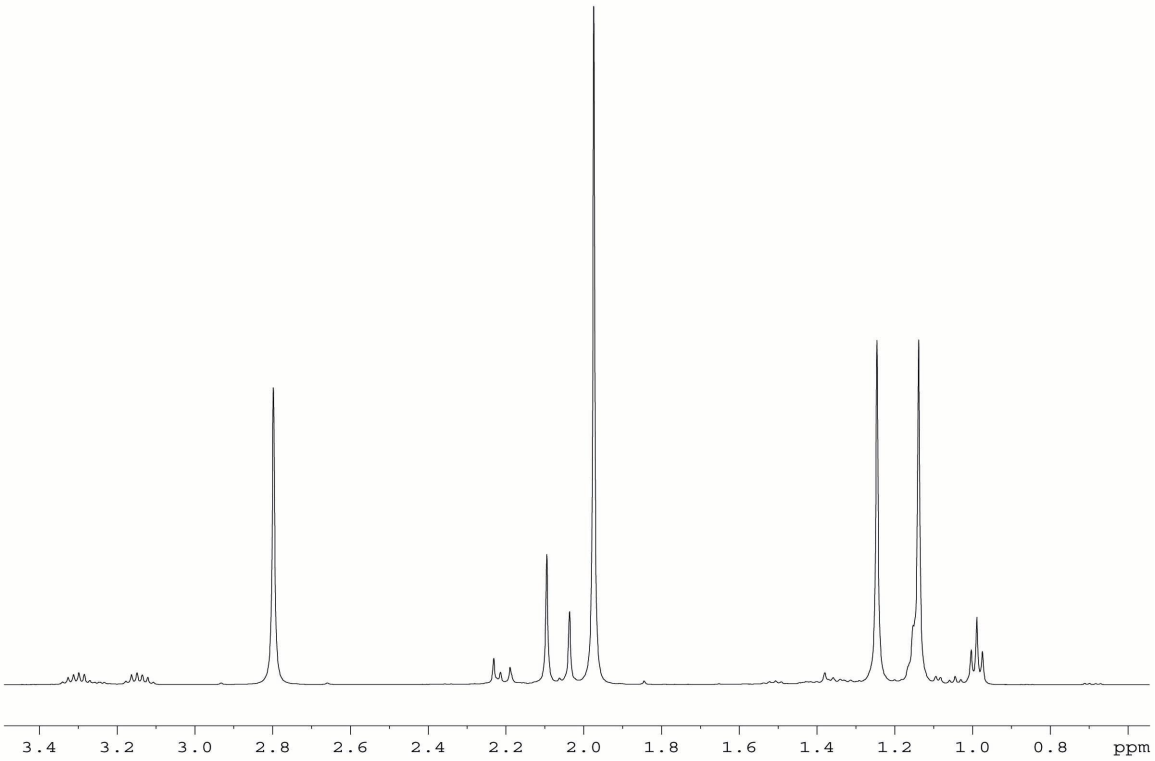
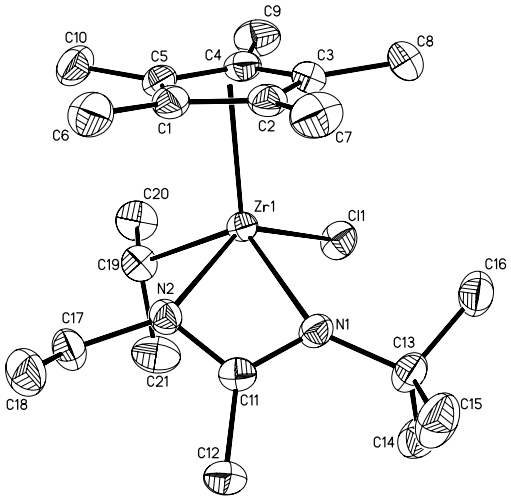


Figure 16: ^{1}H NMR (500 MHz, C_6D_5Cl, 238 K) of {(η^5-C_5Me_5)Hf(tBu)[tBuNC(Me)NEt]}[$B(C_6F_5)_4$], 7.

Crystallographic analysis of compound 3c.

An orange block with approximate orthogonal dimensions 0.505 x 0.318 x 0.304mm^3 was placed and optically centered on the Bruker SMART CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 14 seconds per frame and 606 frames per series. Five complete series were collected at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). Additionally, 200 frames, a repeat of the first series for redundancy and decay purposes, were also collected. The crystal to detector distance was 4.888cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 35921 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 5271 unique [R(int)=0.0216]



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the unique centric monoclinic space group $P2_1/n$ (no. 14). The structure was determined by direct methods with the successful location of all non-hydrogen atoms using the program XS[4]. The structure was refined with XL[5]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located directly from two subsequent difference-Fourier maps and allowed to refine freely. A centroid was calculated for the pentamethylcyclodienyl group. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=2.23%, wR(F^2)=5.44%, GOF=1.085 for all 5271 unique reflections [R(F)=2.08%, wR(F^2)=5.34% for those 4989 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0257*P)^2+0.8984*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also applied to the data in the form $(Fc^2,corr) = k[1 + 0.001 * x * Fc^2 * \lambda^3/\sin(2\theta)]^{(-1/4)}$ where k=0.15162 is the overall scale factor. The value determined for x was 0.0038(3).

Table 1. Crystal data and structure refinement for **3c**.

Identification code	893f	
Empirical formula	C21 H39 Cl N2 Zr	
Formula weight	446.21	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.2180(13) Å	α= 90°.
	b = 16.162(2) Å	β= 92.584(2)°.
	c = 15.474(2) Å	γ = 90°.
Volume	2302.9(5) $Å^3$	
Z	4	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.600 mm^{-1}	
F(000)	944	
Crystal size	0.505 x 0.318 x 0.304 mm^3	
Theta range for data collection	2.52 to 27.50°.	
Index ranges	-11<=h<=11, -20<=k<=20, -20<=l<=20	
Reflections collected	35921	
Independent reflections	5271 [R(int) = 0.0216]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical, SADABS	
Max. and min. transmission	1.00000 and 0.88064	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5271 / 3 / 386	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0208, wR2 = 0.0534 [4989 Data]	
R indices (all data)	R1 = 0.0223, wR2 = 0.0544	
Extinction coefficient	0.0038(3)	
Largest diff. peak and hole	0.350 and -0.360 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	8082(1)	2400(1)	9522(1)	22(1)
Cl(1)	10049(1)	3276(1)	9008(1)	37(1)
N(1)	7705(1)	3231(1)	10659(1)	27(1)
N(2)	7329(1)	1884(1)	10770(1)	26(1)
CNT1	6359(1)	2194(1)	8488(1)	0
C(1)	5728(1)	1739(1)	8960(1)	29(1)
C(2)	5549(2)	2611(1)	8903(1)	30(1)
C(3)	6487(2)	2907(1)	8270(1)	30(1)
C(4)	7253(2)	2219(1)	7938(1)	30(1)
C(5)	6779(1)	1494(1)	8368(1)	29(1)
C(6)	4828(2)	1163(1)	9476(1)	43(1)
C(7)	4457(2)	3103(1)	9385(1)	45(1)
C(8)	6590(2)	3783(1)	7942(1)	46(1)
C(9)	8261(2)	2249(1)	7201(1)	45(1)
C(10)	7151(2)	614(1)	8153(1)	43(1)
C(11)	7652(1)	2584(1)	11199(1)	26(1)
C(12)	7980(2)	2591(1)	12162(1)	38(1)
C(13)	7939(2)	4108(1)	10927(1)	33(1)
C(14)	9516(2)	4262(1)	11241(1)	46(1)
C(15)	6866(2)	4376(1)	11607(1)	50(1)
C(16)	7612(2)	4638(1)	10121(1)	42(1)
C(17)	7361(2)	1076(1)	11198(1)	33(1)
C(18)	6066(2)	904(1)	11749(1)	41(1)
C(19)	9696(1)	1327(1)	9616(1)	32(1)
C(20)	10632(2)	1125(1)	8853(1)	43(1)
C(21)	10713(2)	1563(1)	10395(1)	47(1)

Table 3. Bond lengths [Å] and angles [°] for **3c**.

Zr(1)-CNT1	2.2288(7)
Zr(1)-N(2)	2.2419(11)
Zr(1)-N(1)	2.2528(11)
Zr(1)-C(19)	2.2849(14)
Zr(1)-Cl(1)	2.4606(4)
Zr(1)-C(2)	2.5075(13)
Zr(1)-C(3)	2.5159(13)
Zr(1)-C(1)	2.5373(13)
Zr(1)-C(4)	2.5516(13)
Zr(1)-C(5)	2.5665(13)
N(1)-C(11)	1.3404(17)
N(1)-C(13)	1.4886(16)
N(2)-C(11)	1.3385(16)
N(2)-C(17)	1.4649(16)
C(1)-C(5)	1.4195(19)
C(1)-C(2)	1.4203(18)
C(1)-C(6)	1.501(2)
C(2)-C(3)	1.419(2)
C(2)-C(7)	1.507(2)
C(3)-C(4)	1.425(2)
C(3)-C(8)	1.508(2)
C(4)-C(5)	1.4258(19)
C(4)-C(9)	1.505(2)
C(5)-C(10)	1.5035(19)
C(6)-H(6A)	0.96(2)
C(6)-H(6B)	0.98(2)
C(6)-H(6C)	0.94(2)
C(7)-H(7A)	0.94(2)
C(7)-H(7B)	0.94(3)
C(7)-H(7C)	0.93(3)
C(8)-H(8A)	0.93(3)
C(8)-H(8B)	0.93(3)
C(8)-H(8C)	0.93(3)
C(9)-H(9A)	0.92(3)

C(9)-H(9B)	0.93(3)
C(9)-H(9C)	0.94(3)
C(10)-H(10A)	0.94(2)
C(10)-H(10B)	0.96(3)
C(10)-H(10C)	0.94(2)
C(11)-C(12)	1.5068(19)
C(12)-H(12A)	0.93(2)
C(12)-H(12B)	0.93(2)
C(12)-H(12C)	0.94(2)
C(13)-C(16)	1.532(2)
C(13)-C(14)	1.533(2)
C(13)-C(15)	1.539(2)
C(14)-H(14A)	0.95(2)
C(14)-H(14B)	0.96(2)
C(14)-H(14C)	0.94(2)
C(15)-H(15A)	0.95(2)
C(15)-H(15B)	0.95(2)
C(15)-H(15C)	0.98(2)
C(16)-H(16A)	0.955(19)
C(16)-H(16B)	1.00(2)
C(16)-H(16C)	0.97(2)
C(17)-C(18)	1.524(2)
C(17)-H(17A)	1.005(17)
C(17)-H(17B)	0.964(18)
C(18)-H(18A)	0.92(2)
C(18)-H(18B)	0.98(2)
C(18)-H(18C)	0.92(2)
C(19)-C(20)	1.529(2)
C(19)-C(21)	1.540(2)
C(19)-H(19)	0.933(17)
C(20)-H(20A)	1.02(2)
C(20)-H(20B)	1.01(2)
C(20)-H(20C)	1.04(2)
C(21)-H(21A)	1.09(2)
C(21)-H(21B)	0.93(3)
C(21)-H(21C)	0.93(3)

CNT1-Zr(1)-N(2)	108.93(3)
CNT1-Zr(1)-N(1)	121.33(3)
N(2)-Zr(1)-N(1)	58.97(4)
CNT1-Zr(1)-C(19)	111.90(4)
N(2)-Zr(1)-C(19)	83.60(4)
N(1)-Zr(1)-C(19)	121.70(5)
CNT1-Zr(1)-Cl(1)	111.46(2)
N(2)-Zr(1)-Cl(1)	138.92(3)
N(1)-Zr(1)-Cl(1)	92.96(3)
C(19)-Zr(1)-Cl(1)	88.29(4)
CNT1-Zr(1)-C(2)	28.88(3)
N(2)-Zr(1)-C(2)	93.45(4)
N(1)-Zr(1)-C(2)	92.51(4)
C(19)-Zr(1)-C(2)	136.02(5)
Cl(1)-Zr(1)-C(2)	119.07(4)
CNT1-Zr(1)-C(3)	28.68(3)
N(2)-Zr(1)-C(3)	126.25(4)
N(1)-Zr(1)-C(3)	107.59(4)
C(19)-Zr(1)-C(3)	130.71(5)
Cl(1)-Zr(1)-C(3)	88.72(3)
C(2)-Zr(1)-C(3)	32.81(5)
CNT1-Zr(1)-C(1)	28.33(3)
N(2)-Zr(1)-C(1)	81.10(4)
N(1)-Zr(1)-C(1)	111.04(4)
C(19)-Zr(1)-C(1)	104.27(5)
Cl(1)-Zr(1)-C(1)	139.71(3)
C(2)-Zr(1)-C(1)	32.70(4)
C(3)-Zr(1)-C(1)	53.96(4)
CNT1-Zr(1)-C(4)	28.33(3)
N(2)-Zr(1)-C(4)	133.90(4)
N(1)-Zr(1)-C(4)	140.24(4)
C(19)-Zr(1)-C(4)	98.05(5)
Cl(1)-Zr(1)-C(4)	87.08(3)
C(2)-Zr(1)-C(4)	54.18(5)
C(3)-Zr(1)-C(4)	32.65(4)

C(1)-Zr(1)-C(4)	53.66(4)
CNT1-Zr(1)-C(5)	28.19(3)
N(2)-Zr(1)-C(5)	103.50(4)
N(1)-Zr(1)-C(5)	143.12(4)
C(19)-Zr(1)-C(5)	83.91(5)
Cl(1)-Zr(1)-C(5)	115.61(3)
C(2)-Zr(1)-C(5)	54.04(4)
C(3)-Zr(1)-C(5)	53.90(4)
C(1)-Zr(1)-C(5)	32.29(4)
C(4)-Zr(1)-C(5)	32.35(4)
C(11)-N(1)-C(13)	125.28(11)
C(11)-N(1)-Zr(1)	91.89(8)
C(13)-N(1)-Zr(1)	139.38(8)
C(11)-N(2)-C(17)	122.02(11)
C(11)-N(2)-Zr(1)	92.42(8)
C(17)-N(2)-Zr(1)	136.12(9)
C(5)-C(1)-C(2)	108.56(12)
C(5)-C(1)-C(6)	125.41(14)
C(2)-C(1)-C(6)	125.62(14)
C(5)-C(1)-Zr(1)	74.99(7)
C(2)-C(1)-Zr(1)	72.50(7)
C(6)-C(1)-Zr(1)	124.31(10)
C(3)-C(2)-C(1)	107.71(12)
C(3)-C(2)-C(7)	127.27(14)
C(1)-C(2)-C(7)	124.84(14)
C(3)-C(2)-Zr(1)	73.92(8)
C(1)-C(2)-Zr(1)	74.81(7)
C(7)-C(2)-Zr(1)	120.90(10)
C(2)-C(3)-C(4)	108.24(12)
C(2)-C(3)-C(8)	126.77(14)
C(4)-C(3)-C(8)	124.83(14)
C(2)-C(3)-Zr(1)	73.27(7)
C(4)-C(3)-Zr(1)	75.05(7)
C(8)-C(3)-Zr(1)	121.42(10)
C(3)-C(4)-C(5)	107.83(12)
C(3)-C(4)-C(9)	125.51(14)

C(5)-C(4)-C(9)	126.37(14)
C(3)-C(4)-Zr(1)	72.29(7)
C(5)-C(4)-Zr(1)	74.40(7)
C(9)-C(4)-Zr(1)	123.78(10)
C(1)-C(5)-C(4)	107.65(12)
C(1)-C(5)-C(10)	125.17(13)
C(4)-C(5)-C(10)	126.66(13)
C(1)-C(5)-Zr(1)	72.72(7)
C(4)-C(5)-Zr(1)	73.25(7)
C(10)-C(5)-Zr(1)	126.14(10)
C(1)-C(6)-H(6A)	110.8(13)
C(1)-C(6)-H(6B)	112.5(13)
H(6A)-C(6)-H(6B)	108.2(17)
C(1)-C(6)-H(6C)	113.0(13)
H(6A)-C(6)-H(6C)	108.6(18)
H(6B)-C(6)-H(6C)	103.3(18)
C(2)-C(7)-H(7A)	111.4(15)
C(2)-C(7)-H(7B)	112.9(15)
H(7A)-C(7)-H(7B)	107(2)
C(2)-C(7)-H(7C)	110.8(15)
H(7A)-C(7)-H(7C)	113(2)
H(7B)-C(7)-H(7C)	101(2)
C(3)-C(8)-H(8A)	114.1(17)
C(3)-C(8)-H(8B)	111.1(17)
H(8A)-C(8)-H(8B)	104(2)
C(3)-C(8)-H(8C)	111.4(15)
H(8A)-C(8)-H(8C)	113(2)
H(8B)-C(8)-H(8C)	103(2)
C(4)-C(9)-H(9A)	116(2)
C(4)-C(9)-H(9B)	114.2(16)
H(9A)-C(9)-H(9B)	101(2)
C(4)-C(9)-H(9C)	114.3(18)
H(9A)-C(9)-H(9C)	97(2)
H(9B)-C(9)-H(9C)	112(2)
C(5)-C(10)-H(10A)	114.2(15)
C(5)-C(10)-H(10B)	111.4(15)

H(10A)-C(10)-H(10B)	106(2)
C(5)-C(10)-H(10C)	111.6(13)
H(10A)-C(10)-H(10C)	106.8(19)
H(10B)-C(10)-H(10C)	106.4(19)
N(2)-C(11)-N(1)	111.34(11)
N(2)-C(11)-C(12)	121.78(12)
N(1)-C(11)-C(12)	126.80(12)
C(11)-C(12)-H(12A)	113.5(14)
C(11)-C(12)-H(12B)	111.1(15)
H(12A)-C(12)-H(12B)	113(2)
C(11)-C(12)-H(12C)	109.1(14)
H(12A)-C(12)-H(12C)	109.8(18)
H(12B)-C(12)-H(12C)	99.8(19)
N(1)-C(13)-C(16)	106.54(11)
N(1)-C(13)-C(14)	111.52(12)
C(16)-C(13)-C(14)	108.38(13)
N(1)-C(13)-C(15)	111.69(12)
C(16)-C(13)-C(15)	106.89(14)
C(14)-C(13)-C(15)	111.53(14)
C(13)-C(14)-H(14A)	113.1(13)
C(13)-C(14)-H(14B)	110.1(12)
H(14A)-C(14)-H(14B)	108.4(17)
C(13)-C(14)-H(14C)	109.4(12)
H(14A)-C(14)-H(14C)	109.4(18)
H(14B)-C(14)-H(14C)	106.2(17)
C(13)-C(15)-H(15A)	108.5(14)
C(13)-C(15)-H(15B)	110.2(13)
H(15A)-C(15)-H(15B)	109.2(18)
C(13)-C(15)-H(15C)	111.8(13)
H(15A)-C(15)-H(15C)	108.5(19)
H(15B)-C(15)-H(15C)	108.5(18)
C(13)-C(16)-H(16A)	113.8(12)
C(13)-C(16)-H(16B)	108.5(11)
H(16A)-C(16)-H(16B)	110.1(16)
C(13)-C(16)-H(16C)	110.3(11)
H(16A)-C(16)-H(16C)	107.7(16)

H(16B)-C(16)-H(16C)	106.3(15)
N(2)-C(17)-C(18)	114.52(12)
N(2)-C(17)-H(17A)	110.0(10)
C(18)-C(17)-H(17A)	110.1(10)
N(2)-C(17)-H(17B)	106.8(11)
C(18)-C(17)-H(17B)	106.6(11)
H(17A)-C(17)-H(17B)	108.6(14)
C(17)-C(18)-H(18A)	110.6(13)
C(17)-C(18)-H(18B)	109.5(12)
H(18A)-C(18)-H(18B)	105.9(17)
C(17)-C(18)-H(18C)	109.9(12)
H(18A)-C(18)-H(18C)	111.7(18)
H(18B)-C(18)-H(18C)	109.1(17)
C(20)-C(19)-C(21)	108.17(13)
C(20)-C(19)-Zr(1)	120.08(10)
C(21)-C(19)-Zr(1)	103.53(10)
C(20)-C(19)-H(19)	108.7(10)
C(21)-C(19)-H(19)	108.2(10)
Zr(1)-C(19)-H(19)	107.6(10)
C(19)-C(20)-H(20A)	109.8(11)
C(19)-C(20)-H(20B)	112.5(12)
H(20A)-C(20)-H(20B)	110.7(16)
C(19)-C(20)-H(20C)	111.2(11)
H(20A)-C(20)-H(20C)	107.7(15)
H(20B)-C(20)-H(20C)	104.8(16)
C(19)-C(21)-H(21A)	111.0(10)
C(19)-C(21)-H(21B)	115.9(15)
H(21A)-C(21)-H(21B)	108.5(18)
C(19)-C(21)-H(21C)	110.2(15)
H(21A)-C(21)-H(21C)	102.1(18)
H(21B)-C(21)-H(21C)	108(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	22(1)	24(1)	21(1)	0(1)	2(1)	-2(1)
Cl(1)	35(1)	38(1)	38(1)	1(1)	9(1)	-12(1)
N(1)	32(1)	26(1)	23(1)	-3(1)	4(1)	-4(1)
N(2)	29(1)	24(1)	25(1)	2(1)	4(1)	-1(1)
C(1)	24(1)	32(1)	31(1)	1(1)	-4(1)	-4(1)
C(2)	25(1)	34(1)	30(1)	-2(1)	-6(1)	3(1)
C(3)	35(1)	29(1)	27(1)	2(1)	-6(1)	0(1)
C(4)	32(1)	36(1)	23(1)	-2(1)	-2(1)	-4(1)
C(5)	30(1)	28(1)	30(1)	-4(1)	-4(1)	-2(1)
C(6)	34(1)	49(1)	46(1)	7(1)	-1(1)	-16(1)
C(7)	31(1)	53(1)	50(1)	-12(1)	-2(1)	11(1)
C(8)	65(1)	32(1)	40(1)	10(1)	-11(1)	-2(1)
C(9)	47(1)	62(1)	28(1)	-3(1)	7(1)	-5(1)
C(10)	43(1)	31(1)	54(1)	-11(1)	-7(1)	1(1)
C(11)	23(1)	32(1)	23(1)	-1(1)	3(1)	-1(1)
C(12)	49(1)	41(1)	24(1)	0(1)	-1(1)	-3(1)
C(13)	41(1)	26(1)	32(1)	-6(1)	7(1)	-7(1)
C(14)	49(1)	41(1)	48(1)	-6(1)	-1(1)	-17(1)
C(15)	66(1)	36(1)	50(1)	-12(1)	22(1)	-3(1)
C(16)	57(1)	27(1)	41(1)	0(1)	6(1)	-2(1)
C(17)	41(1)	27(1)	32(1)	6(1)	6(1)	2(1)
C(18)	52(1)	37(1)	36(1)	7(1)	11(1)	-8(1)
C(19)	27(1)	35(1)	34(1)	1(1)	5(1)	3(1)
C(20)	36(1)	51(1)	44(1)	-4(1)	9(1)	8(1)
C(21)	33(1)	67(1)	41(1)	0(1)	-2(1)	5(1)

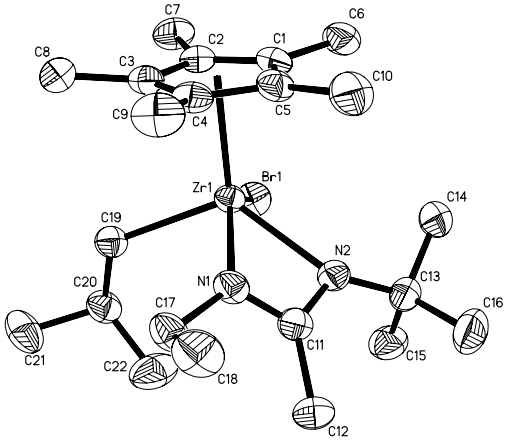
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3c**.

	x	y	z	U(eq)
H(6A)	4520(20)	1429(13)	9989(14)	58(6)
H(6B)	5350(20)	659(14)	9647(14)	64(6)
H(6C)	4000(20)	962(14)	9160(14)	66(6)
H(7A)	3510(30)	3010(15)	9163(15)	76(7)
H(7B)	4620(30)	3677(17)	9359(16)	77(7)
H(7C)	4570(30)	3008(15)	9980(17)	75(7)
H(8A)	7540(30)	3980(17)	7918(17)	89(8)
H(8B)	6160(30)	4152(17)	8311(17)	88(8)
H(8C)	6060(30)	3851(15)	7424(16)	78(7)
H(9A)	7830(30)	2235(19)	6660(20)	106(10)
H(9B)	8900(30)	1801(16)	7181(16)	81(8)
H(9C)	8740(30)	2759(18)	7142(19)	97(9)
H(10A)	7480(20)	296(15)	8632(16)	73(7)
H(10B)	7910(30)	588(15)	7747(16)	79(7)
H(10C)	6350(20)	333(14)	7897(14)	65(6)
H(12A)	8520(20)	3046(15)	12351(15)	69(7)
H(12B)	8390(30)	2094(15)	12346(15)	71(7)
H(12C)	7110(30)	2568(12)	12448(15)	52(6)
H(14A)	9790(20)	3966(14)	11755(14)	61(6)
H(14B)	9670(20)	4842(13)	11348(12)	54(5)
H(14C)	10140(20)	4116(13)	10801(13)	55(6)
H(15A)	5910(30)	4219(14)	11410(14)	65(6)
H(15B)	6900(20)	4960(14)	11683(13)	60(6)
H(15C)	7080(20)	4111(14)	12171(15)	68(6)
H(16A)	8190(20)	4503(13)	9646(12)	49(5)
H(16B)	7750(20)	5230(12)	10282(12)	50(5)
H(16C)	6600(20)	4578(12)	9926(12)	50(5)
H(17A)	8291(18)	1010(10)	11556(11)	37(4)
H(17B)	7336(19)	664(11)	10747(12)	41(4)
H(18A)	6100(20)	1235(13)	12231(13)	54(5)

H(18B)	6120(20)	332(13)	11964(12)	52(5)
H(18C)	5210(20)	974(13)	11423(13)	54(6)
H(19)	9182(18)	854(11)	9761(10)	34(4)
H(20A)	11240(20)	1628(13)	8703(13)	55(5)
H(20B)	10030(20)	927(14)	8327(14)	66(6)
H(20C)	11350(20)	640(13)	9003(13)	59(6)
H(21A)	11430(20)	1053(12)	10578(12)	49(5)
H(21B)	10260(30)	1745(15)	10883(16)	78(7)
H(21C)	11360(30)	1966(16)	10236(15)	72(7)

Crystallographic analysis of compound 3e'.

An orange block with approximate dimensions 0.273 x 0.181 x 0.145mm^3 was placed and optically centered on the Bruker SMART CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans (25 frames/series) that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 10 seconds per frame, 606 frames per series. Three complete series were collected with an additional 200 frames a repeat of the first series for redundancy and decay purposes, with a crystal to detector distance of 4.954cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 10825 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 5501 unique [R(int)=0.0198].



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with dual Pentium 450MHz processors and 384MB of extended memory. The SHELXTL[3] program package was now implemented, XPREP, to determine the probable space group and set up the initial files. System symmetry, lack of systematic absences, and intensity statistics indicated the centrosymmetric space group P-1 (no. 2). The structure was determined by direct methods with the successful location of the heavy atoms and several of the Nitrogen and Carbon atoms as well using the program XS[4]. The structure was refined with XL[5]. After the initial refinement difference-Fourier cycle, the remaining additional non-hydrogen atoms were located and input. Hydrogen atoms were placed initially placed in calculated positions but allowed to refine freely during the final refinement stages. An artificial centroid (Cnt1) for the Cp* ligand was also calculated. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=3.37%, wR(F^2)=7.11%, GOF=1.056 for all 5501 unique reflections [R(F)=2.68%, wR(F^2)=6.85% for those 4789 data with Fo > 4σ(Fo)]. A final difference-Fourier map possessed a single contentious peak that was the correct bonding distance from Zr to be potentially a bromine atom at 2% occupancy; the remainder of this possibly disordered molecule is speculated. Otherwise the difference-Fourier map was featureless indicating the structure is therefore both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0399*P)^2+0.1554*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

Table 6. Crystal data and structure refinement for **3e'**.

Identification code	767afmi	
Empirical formula	C22 H41 Br N2 Zr	
Formula weight	504.70	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9207(11) Å	α= 90.222(2)°.
	b = 9.2385(12) Å	β= 94.385(2)°.
	c = 16.376(2) Å	γ = 115.936(2)°.
Volume	1209.1(3) $Å^3$	
Z	2	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	2.115 mm^{-1}	
F(000)	524	
Crystal size	0.673 x 0.481 x 0.390 mm^3	
Theta range for data collection	2.45 to 27.50°.	
Index ranges	-11<=h<=11, -12<=k<=11, -21<=l<=21	
Reflections collected	10825	
Independent reflections	5501 [R(int) = 0.0198]	
Completeness to theta = 27.50°	99.0 %	
Absorption correction	Empirical, SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5501 / 3 / 402	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0685 [4789 Data]	
R indices (all data)	R1 = 0.0337, wR2 = 0.0711	
Largest diff. peak and hole	0.950 and -0.377 $e.Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3e'**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	9028(1)	1271(1)	2440(1)	27(1)
Br(1)	11619(1)	2881(1)	1577(1)	41(1)
N(1)	7168(2)	1746(2)	3085(1)	33(1)
N(2)	7541(2)	2450(2)	1801(1)	33(1)
CNT1	8290(2)	-1367(2)	2374(1)	0
C(1)	8371(3)	-1295(2)	1641(1)	35(1)
C(2)	9689(2)	-1113(2)	2236(1)	33(1)
C(3)	9072(3)	-1296(2)	3020(1)	33(1)
C(4)	7379(3)	-1569(2)	2911(1)	35(1)
C(5)	6938(2)	-1560(2)	2059(1)	35(1)
C(6)	8442(4)	-1303(3)	726(1)	49(1)
C(7)	11398(3)	-934(3)	2073(2)	45(1)
C(8)	9956(3)	-1414(3)	3813(2)	45(1)
C(9)	6191(4)	-2033(3)	3566(2)	51(1)
C(10)	5227(3)	-1889(4)	1675(2)	54(1)
C(11)	7051(2)	2730(2)	2512(1)	34(1)
C(12)	6512(4)	4025(4)	2692(2)	47(1)
C(13)	7436(3)	3226(3)	1019(1)	39(1)
C(14)	7631(3)	2188(3)	338(1)	44(1)
C(15)	8824(4)	4927(3)	1008(2)	51(1)
C(16)	5706(4)	3208(5)	831(2)	61(1)
C(17)	6831(3)	1902(3)	3935(1)	39(1)
C(18)	4977(3)	1247(4)	4051(2)	53(1)
C(19)	10787(2)	2297(2)	3599(1)	33(1)
C(20)	11916(3)	4111(3)	3704(1)	40(1)
C(21)	12803(4)	4559(4)	4568(2)	55(1)
C(22)	11032(4)	5136(4)	3487(3)	64(1)

Table 8. Bond lengths [Å] and angles [°] for **3e'**.

Zr(1)-N(1)	2.2284(15)
Zr(1)-CNT1	2.2288(13)
Zr(1)-N(2)	2.2587(16)
Zr(1)-C(19)	2.279(2)
Zr(1)-C(5)	2.500(2)
Zr(1)-C(1)	2.5136(19)
Zr(1)-C(4)	2.542(2)
Zr(1)-C(2)	2.5432(19)
Zr(1)-C(3)	2.574(2)
Zr(1)-C(11)	2.6554(19)
Zr(1)-Br(1)	2.6571(4)
N(1)-C(11)	1.339(3)
N(1)-C(17)	1.466(3)
N(2)-C(11)	1.337(3)
N(2)-C(13)	1.486(3)
CNT1-C(4)	1.203(2)
CNT1-C(2)	1.204(2)
CNT1-C(1)	1.207(2)
CNT1-C(3)	1.208(2)
CNT1-C(5)	1.212(2)
C(1)-C(2)	1.417(3)
C(1)-C(5)	1.423(3)
C(1)-C(6)	1.505(3)
C(2)-C(3)	1.417(3)
C(2)-C(7)	1.505(3)
C(3)-C(4)	1.415(3)
C(3)-C(8)	1.497(3)
C(4)-C(5)	1.422(3)
C(4)-C(9)	1.495(3)
C(5)-C(10)	1.504(3)
C(6)-H(6A)	0.98(4)
C(6)-H(6B)	0.96(4)
C(6)-H(6C)	0.96(4)

C(7)-H(7A)	0.88(3)
C(7)-H(7B)	0.88(4)
C(7)-H(7C)	1.00(3)
C(8)-H(8A)	0.93(3)
C(8)-H(8B)	0.93(3)
C(8)-H(8C)	1.04(4)
C(9)-H(9A)	0.86(3)
C(9)-H(9B)	0.95(4)
C(9)-H(9C)	1.02(3)
C(10)-H(10A)	0.98(4)
C(10)-H(10B)	1.01(4)
C(10)-H(10C)	0.92(4)
C(11)-C(12)	1.507(3)
C(12)-H(12A)	1.00(3)
C(12)-H(12B)	0.92(3)
C(12)-H(12C)	0.97(3)
C(13)-C(15)	1.518(4)
C(13)-C(14)	1.536(3)
C(13)-C(16)	1.544(3)
C(14)-H(14A)	1.03(3)
C(14)-H(14B)	1.03(3)
C(14)-H(14C)	1.06(3)
C(15)-H(15A)	0.96(3)
C(15)-H(15B)	0.88(3)
C(15)-H(15C)	0.97(4)
C(16)-H(16A)	1.07(3)
C(16)-H(16B)	0.94(4)
C(16)-H(16C)	1.00(3)
C(17)-C(18)	1.521(3)
C(17)-H(17A)	1.02(3)
C(17)-H(17B)	0.97(2)
C(18)-H(18A)	0.94(3)
C(18)-H(18B)	0.97(3)
C(18)-H(18C)	0.97(3)
C(19)-C(20)	1.532(3)
C(19)-H(19A)	0.94(3)

C(19)-H(19B)	1.02(3)
C(20)-C(22)	1.503(4)
C(20)-C(21)	1.529(3)
C(20)-H(20)	1.08(3)
C(21)-H(21A)	0.99(4)
C(21)-H(21B)	1.00(4)
C(21)-H(21C)	1.03(3)
C(22)-H(22A)	0.95(4)
C(22)-H(22B)	0.92(3)
C(22)-H(22C)	1.05(4)

N(1)-Zr(1)-CNT1	109.81(6)
N(1)-Zr(1)-N(2)	59.01(6)
CNT1-Zr(1)-N(2)	124.33(6)
N(1)-Zr(1)-C(19)	86.48(7)
CNT1-Zr(1)-C(19)	106.91(7)
N(2)-Zr(1)-C(19)	124.55(7)
N(1)-Zr(1)-C(5)	91.73(7)
CNT1-Zr(1)-C(5)	28.97(5)
N(2)-Zr(1)-C(5)	95.80(7)
C(19)-Zr(1)-C(5)	129.90(7)
N(1)-Zr(1)-C(1)	124.39(7)
CNT1-Zr(1)-C(1)	28.70(6)
N(2)-Zr(1)-C(1)	107.59(6)
C(19)-Zr(1)-C(1)	127.86(7)
C(5)-Zr(1)-C(1)	32.97(7)
N(1)-Zr(1)-C(4)	82.80(6)
CNT1-Zr(1)-C(4)	28.25(6)
N(2)-Zr(1)-C(4)	116.80(7)
C(19)-Zr(1)-C(4)	97.77(7)
C(5)-Zr(1)-C(4)	32.75(7)
C(1)-Zr(1)-C(4)	53.96(7)
N(1)-Zr(1)-C(2)	136.17(7)
CNT1-Zr(1)-C(2)	28.26(5)
N(2)-Zr(1)-C(2)	139.74(6)
C(19)-Zr(1)-C(2)	95.53(7)

C(5)-Zr(1)-C(2)	54.20(6)
C(1)-Zr(1)-C(2)	32.55(7)
C(4)-Zr(1)-C(2)	53.49(6)
N(1)-Zr(1)-C(3)	107.29(6)
CNT1-Zr(1)-C(3)	27.98(6)
N(2)-Zr(1)-C(3)	148.15(6)
C(19)-Zr(1)-C(3)	78.97(7)
C(5)-Zr(1)-C(3)	53.92(7)
C(1)-Zr(1)-C(3)	53.66(7)
C(4)-Zr(1)-C(3)	32.10(6)
C(2)-Zr(1)-C(3)	32.15(6)
N(1)-Zr(1)-C(11)	30.25(6)
CNT1-Zr(1)-C(11)	127.87(6)
N(2)-Zr(1)-C(11)	30.21(6)
C(19)-Zr(1)-C(11)	101.72(7)
C(5)-Zr(1)-C(11)	101.20(6)
C(1)-Zr(1)-C(11)	126.40(6)
C(4)-Zr(1)-C(11)	106.29(7)
C(2)-Zr(1)-C(11)	155.39(6)
C(3)-Zr(1)-C(11)	135.59(6)
N(1)-Zr(1)-Br(1)	138.16(5)
CNT1-Zr(1)-Br(1)	111.46(4)
N(2)-Zr(1)-Br(1)	91.46(4)
C(19)-Zr(1)-Br(1)	88.09(6)
C(5)-Zr(1)-Br(1)	122.44(5)
C(1)-Zr(1)-Br(1)	90.79(5)
C(4)-Zr(1)-Br(1)	139.02(4)
C(2)-Zr(1)-Br(1)	85.64(5)
C(3)-Zr(1)-Br(1)	112.27(5)
C(11)-Zr(1)-Br(1)	112.14(5)
C(11)-N(1)-C(17)	121.79(17)
C(11)-N(1)-Zr(1)	92.80(12)
C(17)-N(1)-Zr(1)	137.09(13)
C(11)-N(2)-C(13)	125.47(17)
C(11)-N(2)-Zr(1)	91.54(12)
C(13)-N(2)-Zr(1)	140.10(13)

C(4)-CNT1-C(2)	143.80(17)
C(4)-CNT1-C(1)	144.21(15)
C(2)-CNT1-C(1)	71.99(15)
C(4)-CNT1-C(3)	71.84(16)
C(2)-CNT1-C(3)	71.96(14)
C(1)-CNT1-C(3)	143.95(14)
C(4)-CNT1-C(5)	72.16(14)
C(2)-CNT1-C(5)	144.04(19)
C(1)-CNT1-C(5)	72.06(15)
C(3)-CNT1-C(5)	143.99(17)
C(4)-CNT1-Zr(1)	90.47(11)
C(2)-CNT1-Zr(1)	90.53(10)
C(1)-CNT1-Zr(1)	88.86(11)
C(3)-CNT1-Zr(1)	92.09(10)
C(5)-CNT1-Zr(1)	88.05(11)
CNT1-C(1)-C(2)	53.91(12)
CNT1-C(1)-C(5)	54.11(12)
C(2)-C(1)-C(5)	108.02(18)
CNT1-C(1)-C(6)	176.91(19)
C(2)-C(1)-C(6)	126.1(2)
C(5)-C(1)-C(6)	125.8(2)
CNT1-C(1)-Zr(1)	62.44(9)
C(2)-C(1)-Zr(1)	74.87(11)
C(5)-C(1)-Zr(1)	73.00(11)
C(6)-C(1)-Zr(1)	120.65(15)
CNT1-C(2)-C(3)	54.15(13)
CNT1-C(2)-C(1)	54.10(13)
C(3)-C(2)-C(1)	108.24(17)
CNT1-C(2)-C(7)	175.51(19)
C(3)-C(2)-C(7)	124.9(2)
C(1)-C(2)-C(7)	126.6(2)
CNT1-C(2)-Zr(1)	61.21(9)
C(3)-C(2)-Zr(1)	75.11(11)
C(1)-C(2)-Zr(1)	72.58(11)
C(7)-C(2)-Zr(1)	123.22(15)
CNT1-C(3)-C(4)	53.92(12)

CNT1-C(3)-C(2)	53.89(12)
C(4)-C(3)-C(2)	107.81(18)
CNT1-C(3)-C(8)	173.46(19)
C(4)-C(3)-C(8)	125.1(2)
C(2)-C(3)-C(8)	126.55(19)
CNT1-C(3)-Zr(1)	59.93(9)
C(4)-C(3)-Zr(1)	72.70(11)
C(2)-C(3)-Zr(1)	72.74(11)
C(8)-C(3)-Zr(1)	126.57(15)
CNT1-C(4)-C(3)	54.25(12)
CNT1-C(4)-C(5)	54.20(12)
C(3)-C(4)-C(5)	108.44(17)
CNT1-C(4)-C(9)	173.1(2)
C(3)-C(4)-C(9)	125.5(2)
C(5)-C(4)-C(9)	125.5(2)
CNT1-C(4)-Zr(1)	61.27(9)
C(3)-C(4)-Zr(1)	75.20(11)
C(5)-C(4)-Zr(1)	72.03(12)
C(9)-C(4)-Zr(1)	125.63(15)
CNT1-C(5)-C(4)	53.65(13)
CNT1-C(5)-C(1)	53.83(13)
C(4)-C(5)-C(1)	107.48(17)
CNT1-C(5)-C(10)	177.1(2)
C(4)-C(5)-C(10)	125.6(2)
C(1)-C(5)-C(10)	126.8(2)
CNT1-C(5)-Zr(1)	62.99(9)
C(4)-C(5)-Zr(1)	75.22(11)
C(1)-C(5)-Zr(1)	74.03(11)
C(10)-C(5)-Zr(1)	119.83(16)
C(1)-C(6)-H(6A)	115(2)
C(1)-C(6)-H(6B)	119(2)
H(6A)-C(6)-H(6B)	101(3)
C(1)-C(6)-H(6C)	114(2)
H(6A)-C(6)-H(6C)	83(3)
H(6B)-C(6)-H(6C)	118(3)
C(2)-C(7)-H(7A)	112(2)

C(2)-C(7)-H(7B)	111(2)
H(7A)-C(7)-H(7B)	111(3)
C(2)-C(7)-H(7C)	110.6(18)
H(7A)-C(7)-H(7C)	109(3)
H(7B)-C(7)-H(7C)	104(3)
C(3)-C(8)-H(8A)	110.0(18)
C(3)-C(8)-H(8B)	112.0(18)
H(8A)-C(8)-H(8B)	110(3)
C(3)-C(8)-H(8C)	109.4(19)
H(8A)-C(8)-H(8C)	108(3)
H(8B)-C(8)-H(8C)	108(3)
C(4)-C(9)-H(9A)	108(2)
C(4)-C(9)-H(9B)	113(2)
H(9A)-C(9)-H(9B)	106(3)
C(4)-C(9)-H(9C)	108.4(16)
H(9A)-C(9)-H(9C)	114(3)
H(9B)-C(9)-H(9C)	108(3)
C(5)-C(10)-H(10A)	110(2)
C(5)-C(10)-H(10B)	109(2)
H(10A)-C(10)-H(10B)	119(3)
C(5)-C(10)-H(10C)	110(2)
H(10A)-C(10)-H(10C)	115(3)
H(10B)-C(10)-H(10C)	93(3)
N(2)-C(11)-N(1)	111.37(17)
N(2)-C(11)-C(12)	126.3(2)
N(1)-C(11)-C(12)	122.24(19)
N(2)-C(11)-Zr(1)	58.25(10)
N(1)-C(11)-Zr(1)	56.95(9)
C(12)-C(11)-Zr(1)	159.27(16)
C(11)-C(12)-H(12A)	108.5(17)
C(11)-C(12)-H(12B)	110.2(17)
H(12A)-C(12)-H(12B)	114(2)
C(11)-C(12)-H(12C)	107.7(18)
H(12A)-C(12)-H(12C)	106(2)
H(12B)-C(12)-H(12C)	110(2)
N(2)-C(13)-C(15)	111.83(18)

N(2)-C(13)-C(14)	106.24(17)
C(15)-C(13)-C(14)	109.0(2)
N(2)-C(13)-C(16)	112.0(2)
C(15)-C(13)-C(16)	110.8(2)
C(14)-C(13)-C(16)	106.7(2)
C(13)-C(14)-H(14A)	113.4(15)
C(13)-C(14)-H(14B)	107.0(16)
H(14A)-C(14)-H(14B)	108(2)
C(13)-C(14)-H(14C)	109.5(15)
H(14A)-C(14)-H(14C)	106(2)
H(14B)-C(14)-H(14C)	112(2)
C(13)-C(15)-H(15A)	110.7(17)
C(13)-C(15)-H(15B)	108.7(19)
H(15A)-C(15)-H(15B)	112(3)
C(13)-C(15)-H(15C)	113(2)
H(15A)-C(15)-H(15C)	108(3)
H(15B)-C(15)-H(15C)	105(3)
C(13)-C(16)-H(16A)	113.9(16)
C(13)-C(16)-H(16B)	115(2)
H(16A)-C(16)-H(16B)	98(3)
C(13)-C(16)-H(16C)	109.6(17)
H(16A)-C(16)-H(16C)	110(2)
H(16B)-C(16)-H(16C)	110(3)
N(1)-C(17)-C(18)	113.28(19)
N(1)-C(17)-H(17A)	112.8(14)
C(18)-C(17)-H(17A)	109.6(14)
N(1)-C(17)-H(17B)	104.2(14)
C(18)-C(17)-H(17B)	109.5(14)
H(17A)-C(17)-H(17B)	107(2)
C(17)-C(18)-H(18A)	111.7(19)
C(17)-C(18)-H(18B)	112.8(18)
H(18A)-C(18)-H(18B)	108(2)
C(17)-C(18)-H(18C)	116.2(17)
H(18A)-C(18)-H(18C)	103(2)
H(18B)-C(18)-H(18C)	104(2)
C(20)-C(19)-Zr(1)	120.05(14)

C(20)-C(19)-H(19A)	111.9(17)
Zr(1)-C(19)-H(19A)	106.7(16)
C(20)-C(19)-H(19B)	111.5(14)
Zr(1)-C(19)-H(19B)	104.9(14)
H(19A)-C(19)-H(19B)	100(2)
C(22)-C(20)-C(21)	110.9(2)
C(22)-C(20)-C(19)	113.9(2)
C(21)-C(20)-C(19)	111.1(2)
C(22)-C(20)-H(20)	104.4(15)
C(21)-C(20)-H(20)	110.5(15)
C(19)-C(20)-H(20)	105.8(15)
C(20)-C(21)-H(21A)	108.5(19)
C(20)-C(21)-H(21B)	113(2)
H(21A)-C(21)-H(21B)	121(3)
C(20)-C(21)-H(21C)	109.9(18)
H(21A)-C(21)-H(21C)	97(3)
H(21B)-C(21)-H(21C)	106(3)
C(20)-C(22)-H(22A)	113(2)
C(20)-C(22)-H(22B)	109.2(19)
H(22A)-C(22)-H(22B)	108(3)
C(20)-C(22)-H(22C)	110(2)
H(22A)-C(22)-H(22C)	103(3)
H(22B)-C(22)-H(22C)	114(3)

Symmetry transformations used to generate equivalent atoms:

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3e'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	24(1)	26(1)	29(1)	-1(1)	4(1)	11(1)
Br(1)	35(1)	46(1)	43(1)	4(1)	12(1)	17(1)
N(1)	29(1)	40(1)	33(1)	-5(1)	5(1)	18(1)
N(2)	32(1)	34(1)	35(1)	-1(1)	3(1)	18(1)
C(1)	41(1)	28(1)	36(1)	-6(1)	5(1)	14(1)
C(2)	35(1)	26(1)	39(1)	-1(1)	6(1)	15(1)
C(3)	38(1)	25(1)	36(1)	0(1)	7(1)	14(1)
C(4)	36(1)	25(1)	42(1)	1(1)	11(1)	10(1)
C(5)	30(1)	27(1)	43(1)	-5(1)	1(1)	8(1)
C(6)	73(2)	46(1)	35(1)	-5(1)	5(1)	33(1)
C(7)	41(1)	43(1)	60(2)	0(1)	12(1)	24(1)
C(8)	57(2)	38(1)	42(1)	3(1)	0(1)	24(1)
C(9)	49(1)	45(2)	59(2)	10(1)	27(1)	17(1)
C(10)	33(1)	46(2)	74(2)	-8(1)	-10(1)	11(1)
C(11)	25(1)	34(1)	41(1)	-6(1)	0(1)	13(1)
C(12)	55(2)	52(2)	49(1)	-6(1)	5(1)	36(1)
C(13)	44(1)	45(1)	36(1)	2(1)	0(1)	26(1)
C(14)	51(1)	49(1)	35(1)	-1(1)	1(1)	25(1)
C(15)	66(2)	40(1)	51(2)	8(1)	8(1)	28(1)
C(16)	63(2)	90(2)	50(2)	-1(2)	-7(1)	54(2)
C(17)	35(1)	49(1)	34(1)	-6(1)	7(1)	18(1)
C(18)	42(1)	65(2)	54(2)	-3(1)	17(1)	24(1)
C(19)	29(1)	32(1)	38(1)	-2(1)	1(1)	12(1)
C(20)	35(1)	36(1)	43(1)	-5(1)	0(1)	12(1)
C(21)	53(2)	46(2)	44(1)	-9(1)	-2(1)	2(1)
C(22)	54(2)	34(2)	100(3)	-3(1)	-5(2)	18(1)

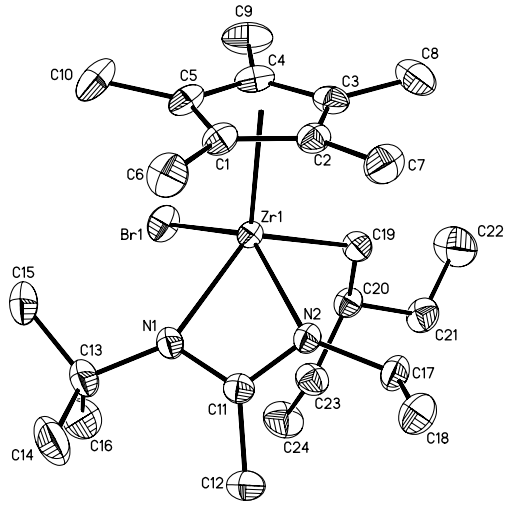
Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3e'**.

	x	y	z	U(eq)
H(6A)	9500(50)	-1200(50)	540(30)	100(13)
H(6B)	8280(50)	-490(50)	420(20)	96(12)
H(6C)	8020(50)	-2360(50)	480(20)	106(13)
H(7A)	12180(40)	-220(40)	2420(20)	70(10)
H(7B)	11600(50)	-680(50)	1560(30)	94(12)
H(7C)	11450(40)	-1980(40)	2117(19)	72(9)
H(8A)	9640(40)	-2490(40)	3925(17)	55(8)
H(8B)	9740(40)	-900(40)	4247(19)	63(8)
H(8C)	11240(50)	-880(40)	3770(20)	89(11)
H(9A)	5420(40)	-1730(40)	3422(19)	65(9)
H(9B)	6690(40)	-1500(40)	4080(20)	79(10)
H(9C)	5750(40)	-3240(40)	3638(18)	61(8)
H(10A)	4480(50)	-3040(50)	1700(20)	86(11)
H(10B)	5340(40)	-1370(40)	1130(20)	85(11)
H(10C)	4860(50)	-1210(50)	1910(20)	102(13)
H(12A)	5280(40)	3570(40)	2575(18)	63(8)
H(12B)	7100(40)	4930(40)	2406(17)	52(8)
H(12C)	6740(40)	4280(40)	3270(20)	66(9)
H(14A)	8740(40)	2100(30)	410(16)	53(7)
H(14B)	7590(40)	2730(40)	-204(18)	62(8)
H(14C)	6670(40)	1000(40)	341(17)	59(8)
H(15A)	8800(30)	5370(30)	484(18)	53(7)
H(15B)	9790(40)	4910(30)	1143(18)	56(8)
H(15C)	8740(40)	5650(40)	1420(20)	79(10)
H(16A)	4680(40)	2060(40)	887(18)	67(9)
H(16B)	5460(40)	3370(40)	280(20)	77(10)
H(16C)	5610(40)	4030(40)	1192(18)	62(8)
H(17A)	7440(30)	3050(30)	4172(15)	39(6)
H(17B)	7290(30)	1270(30)	4236(14)	38(6)
H(18A)	4470(40)	1790(40)	3738(19)	62(9)

H(18B)	4760(40)	1320(40)	4620(20)	68(9)
H(18C)	4290(40)	120(40)	3885(18)	63(9)
H(19A)	10140(30)	1900(30)	4044(17)	55(8)
H(19B)	11470(30)	1650(30)	3647(15)	47(7)
H(20)	12820(40)	4380(30)	3253(17)	60(8)
H(21A)	13410(40)	5750(40)	4630(20)	75(10)
H(21B)	13370(50)	3870(50)	4750(20)	105(13)
H(21C)	11950(40)	4410(40)	4990(20)	75(9)
H(22A)	11730(40)	6260(50)	3580(20)	78(10)
H(22B)	10140(40)	4860(40)	3797(18)	58(9)
H(22C)	10700(50)	5040(50)	2850(30)	103(13)

Crystallographic analysis of compound 3f'.

A pale green block with approximate orthogonal dimensions 0.489 x 0.472 x 0.404mm^3 was placed and optically centered on the Bruker SMART CCD system at –50°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 10 seconds per frame and 606 frames per series. Five complete series were collected at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). Additionally, 200 frames, a repeat of the first series for redundancy and decay purposes, were also collected. The crystal to detector distance was 4.442cm, thus providing a complete sphere of data to $2\theta_{max}$=60.0°. A total of 49021 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 7681 unique [R(int)=0.0201]



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the unique centric monoclinic space group $P2_1/c$ (no. 14). The structure was determined by direct methods with the successful location of nearly all non-hydrogen atoms using the program XS[4]. A single difference-Fourier map was performed to locate the remaining non-hydrogen atoms. The structure was refined with XL[5]. All non-hydrogen atoms were refined anisotropically. Disorder was modeled for Br:Cl atom's site and optimized to be 0.787:0.213. Hydrogen atoms were located from an additional difference-Fourier map but initially placed in calculated positions; then allowed to refine freely. The final structure was refined to convergence [$\Delta/\sigma \leq 0.002$] with R(F)=2.65%, wR(F^2)=5.44%, GOF=1.066 for all 7681 unique reflections [R(F)=2.07%, wR(F^2)=5.14% for those 6851 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0289*P)^2+0.6894*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also applied to the data in the form $(Fc^2,corr) = k[1 + 0.001 * x * Fc^2 * \lambda^3/\sin(2\theta)]^{(-1/4)}$ where k=0.35337 is the overall scale factor. The value determined for x was 0.00014(13).

Table 11. Crystal data and structure refinement for **3f'**.

Identification code	1001ff	
Empirical formula	C24 H45 Br0.79 Cl0.21 N2 Zr	
Formula weight	523.28	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.3325(8) Å	α= 90°.
	b = 9.5577(4) Å	β= 113.4700(10)°.
	c = 17.4875(8) Å	γ = 90°.
Volume	2657.3(2) $Å^3$	
Z	4	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	1.630 mm^{-1}	
F(000)	1097	
Crystal size	0.49 x 0.47 x 0.40 mm^3	
Theta range for data collection	2.34 to 30.03°.	
Index ranges	-24<=h<=24, -13<=k<=13, -23<=l<=24	
Reflections collected	49021	
Independent reflections	7681 [R(int) = 0.0201]	
Completeness to theta = 30.03°	98.8 %	
Absorption correction	Empirical, SADABS (multi-scan)	
Max. and min. transmission	0.5589 and 0.5029	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7681 / 3 / 437	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0514 [6851 Data]	
R indices (all data)	R1 = 0.0265, wR2 = 0.0544	
Extinction coefficient	0.00014(13)	
Largest diff. peak and hole	0.431 and -0.475 $e.Å^{-3}$	

Table 12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3f'**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	2967(1)	8031(1)	547(1)	19(1)
Br(1)	3213(1)	6570(1)	1885(1)	33(1)
Cl(1)	3213(1)	6570(1)	1885(1)	33(1)
N(1)	1980(1)	6463(1)	-243(1)	25(1)
N(2)	1880(1)	8698(1)	-611(1)	24(1)
CNT1	4164(1)	8408(1)	389(1)	0
C(1)	3895(1)	7653(1)	-222(1)	26(1)
C(2)	3801(1)	9139(1)	-213(1)	25(1)
C(3)	4207(1)	9610(1)	625(1)	28(1)
C(4)	4548(1)	8422(2)	1140(1)	30(1)
C(5)	4367(1)	7214(1)	617(1)	28(1)
C(6)	3576(1)	6760(2)	-998(1)	36(1)
C(7)	3447(1)	10071(2)	-964(1)	37(1)
C(8)	4353(1)	11120(2)	891(1)	42(1)
C(9)	5067(1)	8455(2)	2068(1)	46(1)
C(10)	4689(1)	5757(2)	903(1)	44(1)
C(11)	1462(1)	7497(1)	-664(1)	25(1)
C(12)	513(1)	7416(2)	-1110(1)	40(1)
C(13)	1729(1)	4971(1)	-235(1)	36(1)
C(14)	1215(2)	4422(2)	-1120(1)	59(1)
C(15)	2549(1)	4118(2)	115(1)	43(1)
C(16)	1256(1)	4760(2)	342(2)	53(1)
C(17)	1449(1)	10019(1)	-957(1)	30(1)
C(18)	1124(1)	10114(2)	-1907(1)	38(1)
C(20)	2093(1)	9801(1)	1620(1)	27(1)
C(21)	1833(1)	11233(2)	1853(1)	37(1)
C(23)	1307(1)	8932(2)	1110(1)	34(1)
C(19)	2708(1)	9963(1)	1181(1)	26(1)
C(24)	827(1)	8381(2)	1618(1)	50(1)
C(22)	2562(1)	12101(2)	2446(2)	62(1)

Table 13. Bond lengths [Å] and angles [°] for **3f'**.

Zr(1)-CNT1	2.2276(7)	C(9)-H(9B)	0.95(3)
Zr(1)-N(2)	2.2410(10)	C(9)-H(9C)	0.89(3)
Zr(1)-N(1)	2.2806(10)	C(10)-H(10A)	0.97(2)
Zr(1)-C(19)	2.2889(12)	C(10)-H(10B)	0.96(2)
Zr(1)-C(1)	2.4990(11)	C(10)-H(10C)	0.93(3)
Zr(1)-C(5)	2.5058(12)	C(11)-C(12)	1.5155(18)
Zr(1)-C(4)	2.5407(12)	C(12)-H(12A)	0.96(2)
Zr(1)-C(2)	2.5522(11)	C(12)-H(12B)	0.96(2)
Zr(1)-C(3)	2.5848(12)	C(12)-H(12C)	0.92(2)
Zr(1)-Br(1)	2.6083(2)	C(13)-C(15)	1.538(2)
N(1)-C(11)	1.3407(16)	C(13)-C(14)	1.539(2)
N(1)-C(13)	1.4925(16)	C(13)-C(16)	1.545(2)
N(2)-C(11)	1.3407(16)	C(14)-H(14A)	1.00(2)
N(2)-C(17)	1.4686(15)	C(14)-H(14B)	0.94(3)
C(1)-C(5)	1.4285(17)	C(14)-H(14C)	0.97(3)
C(1)-C(2)	1.4305(18)	C(15)-H(15A)	1.00(2)
C(1)-C(6)	1.5095(19)	C(15)-H(15B)	1.00(2)
C(2)-C(3)	1.4233(17)	C(15)-H(15C)	0.946(19)
C(2)-C(7)	1.5002(18)	C(16)-H(16A)	0.97(2)
C(3)-C(4)	1.4231(19)	C(16)-H(16B)	0.94(2)
C(3)-C(8)	1.506(2)	C(16)-H(16C)	0.99(2)
C(4)-C(5)	1.4279(19)	C(17)-C(18)	1.531(2)
C(4)-C(9)	1.5103(19)	C(17)-H(17A)	0.971(17)
C(5)-C(10)	1.510(2)	C(17)-H(17B)	0.972(17)
C(6)-H(6A)	0.96(2)	C(18)-H(18A)	0.941(18)
C(6)-H(6B)	0.99(3)	C(18)-H(18B)	0.95(2)
C(6)-H(6C)	0.97(2)	C(18)-H(18C)	0.97(2)
C(7)-H(7A)	0.96(2)	C(20)-C(23)	1.5403(19)
C(7)-H(7B)	0.96(2)	C(20)-C(21)	1.5456(18)
C(7)-H(7C)	0.96(2)	C(20)-C(19)	1.5495(17)
C(8)-H(8A)	0.94(3)	C(20)-H(20)	1.001(15)
C(8)-H(8B)	0.98(3)	C(21)-C(22)	1.521(3)
C(8)-H(8C)	0.92(3)	C(21)-H(21A)	0.962(19)
C(9)-H(9A)	0.92(3)	C(21)-H(21B)	1.003(18)

C(23)-C(24)	1.533(2)	C(19)-Zr(1)-C(2)	100.28(4)
C(23)-H(23A)	0.984(17)	C(1)-Zr(1)-C(2)	32.88(4)
C(23)-H(23B)	1.003(18)	C(5)-Zr(1)-C(2)	54.26(4)
C(19)-H(19A)	0.980(18)	C(4)-Zr(1)-C(2)	53.77(4)
C(19)-H(19B)	0.959(17)	CNT1-Zr(1)-C(3)	27.96(3)
C(24)-H(24A)	0.96(2)	N(2)-Zr(1)-C(3)	105.27(4)
C(24)-H(24B)	0.94(2)	N(1)-Zr(1)-C(3)	145.40(4)
C(24)-H(24C)	0.99(2)	C(19)-Zr(1)-C(3)	79.76(4)
C(22)-H(22A)	0.95(3)	C(1)-Zr(1)-C(3)	54.08(4)
C(22)-H(22B)	0.97(3)	C(5)-Zr(1)-C(3)	53.89(4)
C(22)-H(22C)	0.99(3)	C(4)-Zr(1)-C(3)	32.22(4)
		C(2)-Zr(1)-C(3)	32.16(4)
CNT1-Zr(1)-N(2)	109.32(3)	CNT1-Zr(1)-Br(1)	111.707(17)
CNT1-Zr(1)-N(1)	122.83(3)	N(2)-Zr(1)-Br(1)	137.84(3)
N(2)-Zr(1)-N(1)	58.74(4)	N(1)-Zr(1)-Br(1)	90.41(3)
CNT1-Zr(1)-C(19)	107.53(4)	C(19)-Zr(1)-Br(1)	89.49(3)
N(2)-Zr(1)-C(19)	87.23(4)	C(1)-Zr(1)-Br(1)	119.65(3)
N(1)-Zr(1)-C(19)	125.39(4)	C(5)-Zr(1)-Br(1)	88.88(3)
CNT1-Zr(1)-C(1)	29.14(3)	C(4)-Zr(1)-Br(1)	87.05(3)
N(2)-Zr(1)-C(1)	92.52(4)	C(2)-Zr(1)-Br(1)	139.92(3)
N(1)-Zr(1)-C(1)	93.86(4)	C(3)-Zr(1)-Br(1)	115.44(3)
C(19)-Zr(1)-C(1)	132.02(4)	C(11)-N(1)-C(13)	125.18(11)
CNT1-Zr(1)-C(5)	28.96(3)	C(11)-N(1)-Zr(1)	91.43(7)
N(2)-Zr(1)-C(5)	125.59(4)	C(13)-N(1)-Zr(1)	140.61(9)
N(1)-Zr(1)-C(5)	107.66(4)	C(11)-N(2)-C(17)	122.34(10)
C(19)-Zr(1)-C(5)	126.93(5)	C(11)-N(2)-Zr(1)	93.16(7)
C(1)-Zr(1)-C(5)	33.17(4)	C(17)-N(2)-Zr(1)	136.34(8)
CNT1-Zr(1)-C(4)	28.49(3)	C(5)-C(1)-C(2)	107.59(11)
N(2)-Zr(1)-C(4)	135.11(4)	C(5)-C(1)-C(6)	127.72(12)
N(1)-Zr(1)-C(4)	140.43(4)	C(2)-C(1)-C(6)	124.63(11)
C(19)-Zr(1)-C(4)	94.09(4)	C(5)-C(1)-Zr(1)	73.67(6)
C(1)-Zr(1)-C(4)	54.58(4)	C(2)-C(1)-Zr(1)	75.60(6)
C(5)-Zr(1)-C(4)	32.86(4)	C(6)-C(1)-Zr(1)	118.82(9)
CNT1-Zr(1)-C(2)	28.32(3)	C(3)-C(2)-C(1)	108.25(11)
N(2)-Zr(1)-C(2)	81.80(4)	C(3)-C(2)-C(7)	125.14(12)
N(1)-Zr(1)-C(2)	113.65(4)	C(1)-C(2)-C(7)	126.09(12)

C(3)-C(2)-Zr(1)	75.18(7)	C(3)-C(8)-H(8C)	111.4(17)
C(1)-C(2)-Zr(1)	71.52(6)	H(8A)-C(8)-H(8C)	105(2)
C(7)-C(2)-Zr(1)	125.67(8)	H(8B)-C(8)-H(8C)	104(2)
C(4)-C(3)-C(2)	108.01(11)	C(4)-C(9)-H(9A)	110.9(15)
C(4)-C(3)-C(8)	126.40(13)	C(4)-C(9)-H(9B)	113.6(16)
C(2)-C(3)-C(8)	125.03(13)	H(9A)-C(9)-H(9B)	107(2)
C(4)-C(3)-Zr(1)	72.18(7)	C(4)-C(9)-H(9C)	115.9(16)
C(2)-C(3)-Zr(1)	72.66(7)	H(9A)-C(9)-H(9C)	109(2)
C(8)-C(3)-Zr(1)	127.59(9)	H(9B)-C(9)-H(9C)	99(2)
C(3)-C(4)-C(5)	108.11(11)	C(5)-C(10)-H(10A)	111.9(14)
C(3)-C(4)-C(9)	125.60(14)	C(5)-C(10)-H(10B)	111.0(14)
C(5)-C(4)-C(9)	126.14(14)	H(10A)-C(10)-H(10B)	103.2(19)
C(3)-C(4)-Zr(1)	75.59(7)	C(5)-C(10)-H(10C)	112.8(16)
C(5)-C(4)-Zr(1)	72.22(7)	H(10A)-C(10)-H(10C)	104(2)
C(9)-C(4)-Zr(1)	121.69(9)	H(10B)-C(10)-H(10C)	113(2)
C(4)-C(5)-C(1)	108.02(11)	N(1)-C(11)-N(2)	111.62(10)
C(4)-C(5)-C(10)	125.18(13)	N(1)-C(11)-C(12)	126.60(12)
C(1)-C(5)-C(10)	126.61(13)	N(2)-C(11)-C(12)	121.68(12)
C(4)-C(5)-Zr(1)	74.91(7)	C(11)-C(12)-H(12A)	112.0(15)
C(1)-C(5)-Zr(1)	73.16(6)	C(11)-C(12)-H(12B)	114.2(13)
C(10)-C(5)-Zr(1)	121.77(10)	H(12A)-C(12)-H(12B)	107.4(19)
C(1)-C(6)-H(6A)	110.4(12)	C(11)-C(12)-H(12C)	108.3(13)
C(1)-C(6)-H(6B)	110.5(14)	H(12A)-C(12)-H(12C)	104.6(19)
H(6A)-C(6)-H(6B)	111.9(18)	H(12B)-C(12)-H(12C)	109.9(18)
C(1)-C(6)-H(6C)	114.7(12)	N(1)-C(13)-C(15)	106.48(11)
H(6A)-C(6)-H(6C)	105.9(16)	N(1)-C(13)-C(14)	111.72(13)
H(6B)-C(6)-H(6C)	103.1(18)	C(15)-C(13)-C(14)	107.02(15)
C(2)-C(7)-H(7A)	113.6(13)	N(1)-C(13)-C(16)	111.30(13)
C(2)-C(7)-H(7B)	112.5(13)	C(15)-C(13)-C(16)	108.51(14)
H(7A)-C(7)-H(7B)	104.0(17)	C(14)-C(13)-C(16)	111.53(16)
C(2)-C(7)-H(7C)	110.7(13)	C(13)-C(14)-H(14A)	114.3(14)
H(7A)-C(7)-H(7C)	110.1(18)	C(13)-C(14)-H(14B)	107.8(16)
H(7B)-C(7)-H(7C)	105.5(17)	H(14A)-C(14)-H(14B)	106(2)
C(3)-C(8)-H(8A)	115.1(17)	C(13)-C(14)-H(14C)	110.2(15)
C(3)-C(8)-H(8B)	114.6(14)	H(14A)-C(14)-H(14C)	110(2)
H(8A)-C(8)-H(8B)	106(2)	H(14B)-C(14)-H(14C)	109(2)

C(13)-C(15)-H(15A)	112.1(12)	C(24)-C(23)-C(20)	114.10(13)
C(13)-C(15)-H(15B)	107.1(12)	C(24)-C(23)-H(23A)	107.0(10)
H(15A)-C(15)-H(15B)	107.8(16)	C(20)-C(23)-H(23A)	110.1(10)
C(13)-C(15)-H(15C)	113.7(12)	C(24)-C(23)-H(23B)	112.4(10)
H(15A)-C(15)-H(15C)	106.9(16)	C(20)-C(23)-H(23B)	109.3(10)
H(15B)-C(15)-H(15C)	109.0(17)	H(23A)-C(23)-H(23B)	103.3(14)
C(13)-C(16)-H(16A)	111.0(12)	C(20)-C(19)-Zr(1)	117.72(8)
C(13)-C(16)-H(16B)	109.2(14)	C(20)-C(19)-H(19A)	106.7(10)
H(16A)-C(16)-H(16B)	108.1(18)	Zr(1)-C(19)-H(19A)	107.8(10)
C(13)-C(16)-H(16C)	112.2(13)	C(20)-C(19)-H(19B)	109.7(10)
H(16A)-C(16)-H(16C)	110.0(18)	Zr(1)-C(19)-H(19B)	107.3(10)
H(16B)-C(16)-H(16C)	106.2(18)	H(19A)-C(19)-H(19B)	107.2(14)
N(2)-C(17)-C(18)	113.88(11)	C(23)-C(24)-H(24A)	112.1(13)
N(2)-C(17)-H(17A)	107.2(10)	C(23)-C(24)-H(24B)	111.8(14)
C(18)-C(17)-H(17A)	109.3(9)	H(24A)-C(24)-H(24B)	105.7(18)
N(2)-C(17)-H(17B)	112.8(10)	C(23)-C(24)-H(24C)	112.6(13)
C(18)-C(17)-H(17B)	108.2(10)	H(24A)-C(24)-H(24C)	104.2(18)
H(17A)-C(17)-H(17B)	105.1(14)	H(24B)-C(24)-H(24C)	110.0(18)
C(17)-C(18)-H(18A)	113.8(11)	C(21)-C(22)-H(22A)	109.5(17)
C(17)-C(18)-H(18B)	111.8(12)	C(21)-C(22)-H(22B)	113.1(16)
H(18A)-C(18)-H(18B)	104.5(16)	H(22A)-C(22)-H(22B)	110(2)
C(17)-C(18)-H(18C)	111.8(11)	C(21)-C(22)-H(22C)	110.2(14)
H(18A)-C(18)-H(18C)	108.6(15)	H(22A)-C(22)-H(22C)	106(2)
H(18B)-C(18)-H(18C)	105.7(16)	H(22B)-C(22)-H(22C)	107(2)
C(23)-C(20)-C(21)	110.30(11)		
C(23)-C(20)-C(19)	113.06(10)		
C(21)-C(20)-C(19)	111.85(11)		
C(23)-C(20)-H(20)	105.8(9)		
C(21)-C(20)-H(20)	108.2(9)		
C(19)-C(20)-H(20)	107.2(9)		
C(22)-C(21)-C(20)	114.38(13)		
C(22)-C(21)-H(21A)	109.3(11)		
C(20)-C(21)-H(21A)	107.4(11)		
C(22)-C(21)-H(21B)	109.2(10)		
C(20)-C(21)-H(21B)	108.8(11)		
H(21A)-C(21)-H(21B)	107.4(15)		

Symmetry transformations used to generate equivalent atoms:

Table 14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3f'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	19(1)	20(1)	19(1)	1(1)	8(1)	2(1)
Br(1)	41(1)	35(1)	25(1)	8(1)	15(1)	8(1)
Cl(1)	41(1)	35(1)	25(1)	8(1)	15(1)	8(1)
N(1)	27(1)	19(1)	28(1)	1(1)	9(1)	-2(1)
N(2)	23(1)	20(1)	25(1)	3(1)	6(1)	2(1)
C(1)	25(1)	32(1)	23(1)	1(1)	13(1)	5(1)
C(2)	23(1)	29(1)	26(1)	3(1)	13(1)	2(1)
C(3)	22(1)	34(1)	32(1)	-4(1)	14(1)	-4(1)
C(4)	19(1)	45(1)	24(1)	0(1)	8(1)	2(1)
C(5)	23(1)	36(1)	27(1)	6(1)	13(1)	10(1)
C(6)	43(1)	39(1)	30(1)	-5(1)	20(1)	3(1)
C(7)	35(1)	41(1)	38(1)	15(1)	19(1)	6(1)
C(8)	41(1)	39(1)	56(1)	-14(1)	28(1)	-14(1)
C(9)	29(1)	78(1)	26(1)	-1(1)	5(1)	-4(1)
C(10)	44(1)	46(1)	45(1)	15(1)	23(1)	25(1)
C(11)	24(1)	25(1)	24(1)	-1(1)	7(1)	-1(1)
C(12)	24(1)	39(1)	47(1)	5(1)	4(1)	-4(1)
C(13)	39(1)	21(1)	45(1)	3(1)	13(1)	-5(1)
C(14)	68(1)	28(1)	60(1)	-9(1)	2(1)	-12(1)
C(15)	50(1)	21(1)	56(1)	3(1)	18(1)	3(1)
C(16)	47(1)	41(1)	75(1)	21(1)	28(1)	-6(1)
C(17)	31(1)	23(1)	31(1)	4(1)	6(1)	6(1)
C(18)	38(1)	36(1)	33(1)	11(1)	7(1)	5(1)
C(20)	29(1)	28(1)	26(1)	0(1)	15(1)	4(1)
C(21)	40(1)	35(1)	42(1)	-5(1)	23(1)	7(1)
C(23)	34(1)	35(1)	39(1)	-2(1)	19(1)	-4(1)
C(19)	28(1)	26(1)	28(1)	-3(1)	15(1)	-1(1)
C(24)	45(1)	55(1)	64(1)	3(1)	35(1)	-8(1)
C(22)	60(1)	53(1)	78(2)	-37(1)	32(1)	-6(1)

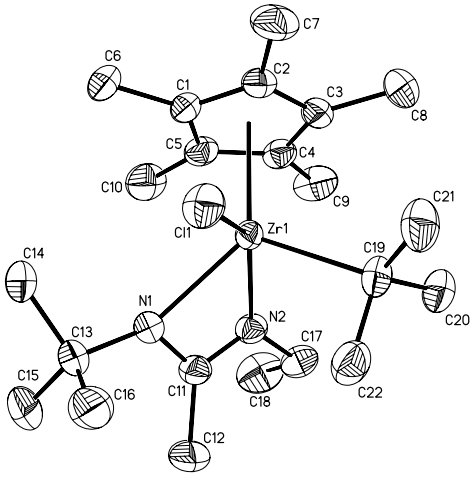
Table 15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3f'**.

	x	y	z	U(eq)
H(6A)	3931(14)	6860(20)	-1295(13)	55(6)
H(6B)	2985(16)	6990(30)	-1349(15)	76(8)
H(6C)	3555(13)	5770(20)	-897(13)	59(6)
H(7A)	3120(13)	10840(20)	-897(13)	61(6)
H(7B)	3065(13)	9590(20)	-1448(13)	55(6)
H(7C)	3885(14)	10420(20)	-1115(13)	64(6)
H(8A)	4633(17)	11260(30)	1465(18)	85(8)
H(8B)	3842(16)	11690(20)	714(15)	74(7)
H(8C)	4682(18)	11570(30)	661(17)	88(8)
H(9A)	5565(16)	8930(30)	2187(15)	80(7)
H(9B)	5206(17)	7550(30)	2313(17)	85(8)
H(9C)	4811(16)	8800(30)	2379(15)	78(8)
H(10A)	5292(15)	5680(20)	1052(14)	67(6)
H(10B)	4455(14)	5090(30)	456(15)	69(7)
H(10C)	4625(16)	5500(30)	1384(17)	83(8)
H(12A)	248(16)	8290(30)	-1089(15)	72(7)
H(12B)	258(13)	6700(20)	-900(13)	57(6)
H(12C)	381(13)	7270(20)	-1670(14)	51(5)
H(14A)	620(15)	4750(20)	-1367(14)	69(7)
H(14B)	1186(16)	3440(30)	-1090(16)	78(7)
H(14C)	1490(16)	4660(30)	-1487(16)	80(8)
H(15A)	2866(12)	4170(20)	-252(13)	53(5)
H(15B)	2389(13)	3120(20)	140(13)	51(5)
H(15C)	2924(12)	4400(20)	653(12)	47(5)
H(16A)	1610(13)	5000(20)	912(13)	54(6)
H(16B)	1105(14)	3810(30)	330(14)	67(6)
H(16C)	726(14)	5300(20)	152(13)	63(6)
H(17A)	1848(10)	10769(18)	-708(10)	32(4)
H(17B)	982(11)	10208(18)	-797(10)	35(4)
H(18A)	1536(11)	9932(19)	-2117(11)	39(5)
H(18B)	925(12)	11030(20)	-2104(12)	52(5)
H(18C)	652(12)	9490(20)	-2180(12)	50(5)

H(20)	2394(9)	9262(16)	2146(9)	26(4)
H(21A)	1552(12)	11745(19)	1344(12)	43(5)
H(21B)	1415(11)	11070(20)	2109(11)	44(5)
H(23A)	1467(11)	8114(18)	863(11)	35(4)
H(23B)	938(11)	9486(19)	610(11)	41(5)
H(19A)	3246(11)	10277(19)	1608(11)	41(5)
H(19B)	2513(10)	10687(19)	769(10)	36(4)
H(24A)	1168(14)	7770(20)	2063(14)	59(6)
H(24B)	355(15)	7840(20)	1288(14)	62(6)
H(24C)	654(14)	9140(30)	1902(14)	65(6)
H(22A)	2855(18)	11580(30)	2940(18)	89(9)
H(22B)	2386(17)	13000(30)	2585(17)	86(8)
H(22C)	2972(16)	12290(30)	2195(15)	74(7)

Crystallographic analysis of compound 3g.

An orange block with approximate orthogonal dimensions 0.343 x 0.210 x 0.158mm^3 was placed and optically centered on the Bruker SMART CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans (25 frames/series) that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 30 seconds per frame, 606 frames per series. Five complete series were collected with an additional 200 frames a repeat of the first series for redundancy and decay purposes, with a crystal to detector distance of 4.880cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 37674 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 5616 unique [R(int)=0.0481].



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with dual Pentium 450MHz processors and 384MB of extended memory. The SHELXTL[3] program package was now implemented, XPREP, to determine the probable space group and set up the initial files. System symmetry and systematic absences indicated the unique centrosymmetric monoclinic space group $P2_1/n$ (no.14). The 37674 data collected were merged based upon identical indices yielding 21684 data [R(int)=0.0337] that were further merged during least-squares refinement to 5479 unique data [R(int)=0.0425]. The structure was determined by direct methods with the successful location of nearly the entire molecule using the program XS[4]. The structure was refined with XL[5]. After the initial refinement, a difference-Fourier map revealed the locations of all of the remaining non-hydrogen atoms. Hydrogen atoms were initially placed in calculated positions and later allowed to refine freely (xyzU). After several refinement cycles, all of the atoms were refined isotropically, then anisotropically. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=4.85%, wR(F^2)=9.79%, GOF=1.075 for all 5479 unique reflections [R(F)=3.44%, wR(F^2)=8.98% for those 4416 data with Fo > 4σ(Fo)]. The final difference-Fourier map possessed two large peaks within 1Å of the Zr atom were considered anomalies; the remainder of the map was featureless indicating that the structure is therefore both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0640*P)^2+0.0*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

Table 16. Crystal data and structure refinement for **3g**.

Identification code	782ffmi	
Empirical formula	C22 H41 Cl N2 Zr	
Formula weight	460.24	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.2477(6) Å	α= 90°.
	b = 30.3164(18) Å	β= 110.9500(10)°.
	c = 9.1329(6) Å	γ = 90°.
Volume	2391.2(3) $Å^3$	
Z	4	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	0.580 mm^{-1}	
F(000)	976	
Crystal size	0.343 x 0.210 x 0.158 mm^3	
Theta range for data collection	2.36 to 27.50°.	
Index ranges	-12<=h<=12, -39<=k<=39, -11<=l<=11	
Reflections collected	21421	
Independent reflections	5479 [R(int) = 0.0425]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical, SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5479 / 3 / 402	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0898 [4416 Data]	
R indices (all data)	R1 = 0.0485, wR2 = 0.0979	
Largest diff. peak and hole	1.477 and -0.653 $e.Å^{-3}$	

Table 17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3g**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	2963(1)	1260(1)	6473(1)	25(1)
Cl(1)	3006(1)	1740(1)	8678(1)	43(1)
N(1)	624(2)	1571(1)	5040(2)	34(1)
N(2)	1287(2)	917(1)	4390(2)	32(1)
CT1	5160(2)	1377(1)	6035(2)	0
C(1)	4942(2)	1767(1)	6108(3)	33(1)
C(2)	5796(2)	1492(1)	7378(3)	35(1)
C(3)	5781(2)	1058(1)	6787(3)	35(1)
C(4)	4901(2)	1066(1)	5165(3)	34(1)
C(5)	4379(3)	1504(1)	4735(3)	35(1)
C(6)	4776(3)	2259(1)	6188(4)	48(1)
C(7)	6728(3)	1635(1)	9023(4)	53(1)
C(8)	6801(3)	683(1)	7655(5)	55(1)
C(9)	4731(4)	684(1)	4058(4)	52(1)
C(10)	3473(4)	1663(1)	3109(3)	53(1)
C(11)	125(2)	1187(1)	4339(3)	34(1)
C(12)	-1544(3)	1040(1)	3658(4)	54(1)
C(13)	-391(3)	1944(1)	5111(4)	46(1)
C(14)	633(4)	2355(1)	5470(5)	54(1)
C(15)	-1682(4)	2029(1)	3514(6)	72(1)
C(16)	-1056(4)	1874(1)	6401(5)	62(1)
C(17)	986(3)	490(1)	3583(3)	40(1)
C(18)	453(5)	537(1)	1811(4)	62(1)
C(19)	2983(3)	648(1)	7998(3)	38(1)
C(20)	3204(4)	192(1)	7417(4)	46(1)
C(21)	4030(4)	680(1)	9717(3)	53(1)
C(22)	1292(4)	686(1)	7905(4)	50(1)

Table 18. Bond lengths [Å] and angles [°] for **3g**.

Zr(1)-CT1	2.2349(16)	C(9)-H(9A)	1.00(3)
Zr(1)-N(2)	2.2360(17)	C(9)-H(9B)	1.00(4)
Zr(1)-N(1)	2.2928(18)	C(9)-H(9C)	0.92(4)
Zr(1)-C(19)	2.316(2)	C(10)-H(10A)	0.93(4)
Zr(1)-Cl(1)	2.4732(6)	C(10)-H(10B)	0.89(5)
Zr(1)-C(1)	2.501(2)	C(10)-H(10C)	0.92(4)
Zr(1)-C(5)	2.503(2)	C(11)-C(12)	1.511(3)
Zr(1)-C(2)	2.548(2)	C(12)-H(12A)	0.90(5)
Zr(1)-C(4)	2.554(2)	C(12)-H(12B)	1.05(4)
Zr(1)-C(3)	2.591(2)	C(12)-H(12C)	0.94(3)
Zr(1)-C(11)	2.660(2)	C(13)-C(16)	1.527(5)
N(1)-C(11)	1.328(3)	C(13)-C(14)	1.528(4)
N(1)-C(13)	1.487(3)	C(13)-C(15)	1.540(5)
N(2)-C(11)	1.340(3)	C(14)-H(14A)	0.91(3)
N(2)-C(17)	1.464(3)	C(14)-H(14B)	0.95(4)
C(1)-C(2)	1.417(3)	C(14)-H(14C)	1.03(3)
C(1)-C(5)	1.419(3)	C(15)-H(15A)	1.00(4)
C(1)-C(6)	1.504(3)	C(15)-H(15B)	0.81(4)
C(2)-C(3)	1.420(3)	C(15)-H(15C)	1.01(4)
C(2)-C(7)	1.504(4)	C(16)-H(16A)	1.02(4)
C(3)-C(4)	1.413(3)	C(16)-H(16B)	0.91(4)
C(3)-C(8)	1.508(3)	C(16)-H(16C)	0.99(4)
C(4)-C(5)	1.420(3)	C(17)-C(18)	1.520(4)
C(4)-C(9)	1.506(3)	C(17)-H(17A)	0.99(3)
C(5)-C(10)	1.501(4)	C(17)-H(17B)	1.00(3)
C(6)-H(6A)	0.96(4)	C(18)-H(18A)	1.01(4)
C(6)-H(6B)	0.92(3)	C(18)-H(18B)	0.83(4)
C(6)-H(6C)	0.90(3)	C(18)-H(18C)	0.98(4)
C(7)-H(7A)	0.88(3)	C(19)-C(20)	1.521(3)
C(7)-H(7B)	0.92(4)	C(19)-C(21)	1.524(4)
C(7)-H(7C)	1.01(4)	C(19)-C(22)	1.540(4)
C(8)-H(8A)	0.97(4)	C(20)-H(20A)	1.00(3)
C(8)-H(8B)	0.96(4)	C(20)-H(20B)	0.97(3)
C(8)-H(8C)	0.87(4)	C(20)-H(20C)	1.01(3)

C(21)-H(21A)	1.03(4)	N(2)-Zr(1)-C(4)	83.27(7)
C(21)-H(21B)	0.89(4)	N(1)-Zr(1)-C(4)	120.31(7)
C(21)-H(21C)	0.95(3)	C(19)-Zr(1)-C(4)	103.88(8)
C(22)-H(22A)	0.97(3)	Cl(1)-Zr(1)-C(4)	135.01(5)
C(22)-H(22B)	0.97(3)	C(1)-Zr(1)-C(4)	53.85(7)
C(22)-H(22C)	0.86(4)	C(5)-Zr(1)-C(4)	32.59(8)
		C(2)-Zr(1)-C(4)	53.36(7)
CT1-Zr(1)-N(2)	108.62(7)	CT1-Zr(1)-C(3)	27.72(8)
CT1-Zr(1)-N(1)	124.40(8)	N(2)-Zr(1)-C(3)	110.34(7)
N(2)-Zr(1)-N(1)	58.69(7)	N(1)-Zr(1)-C(3)	150.08(7)
CT1-Zr(1)-C(19)	114.98(10)	C(19)-Zr(1)-C(3)	87.26(8)
N(2)-Zr(1)-C(19)	89.56(8)	Cl(1)-Zr(1)-C(3)	109.03(5)
N(1)-Zr(1)-C(19)	118.41(8)	C(1)-Zr(1)-C(3)	53.50(7)
CT1-Zr(1)-Cl(1)	107.54(6)	C(5)-Zr(1)-C(3)	53.60(8)
N(2)-Zr(1)-Cl(1)	140.51(5)	C(2)-Zr(1)-C(3)	32.07(7)
N(1)-Zr(1)-Cl(1)	87.73(5)	C(4)-Zr(1)-C(3)	31.87(7)
C(19)-Zr(1)-Cl(1)	89.30(6)	CT1-Zr(1)-C(11)	127.13(6)
CT1-Zr(1)-C(1)	28.76(9)	N(2)-Zr(1)-C(11)	30.21(7)
N(2)-Zr(1)-C(1)	119.35(7)	N(1)-Zr(1)-C(11)	29.95(7)
N(1)-Zr(1)-C(1)	104.92(7)	C(19)-Zr(1)-C(11)	99.66(8)
C(19)-Zr(1)-C(1)	136.32(8)	Cl(1)-Zr(1)-C(11)	111.72(6)
Cl(1)-Zr(1)-C(1)	86.99(6)	C(1)-Zr(1)-C(11)	122.03(7)
CT1-Zr(1)-C(5)	28.89(6)	C(5)-Zr(1)-C(11)	99.35(7)
N(2)-Zr(1)-C(5)	87.60(7)	C(2)-Zr(1)-C(11)	153.01(7)
N(1)-Zr(1)-C(5)	96.74(7)	C(4)-Zr(1)-C(11)	108.15(7)
C(19)-Zr(1)-C(5)	136.37(8)	C(3)-Zr(1)-C(11)	138.68(8)
Cl(1)-Zr(1)-C(5)	118.88(6)	C(11)-N(1)-C(13)	124.91(19)
C(1)-Zr(1)-C(5)	32.94(7)	C(11)-N(1)-Zr(1)	90.52(13)
CT1-Zr(1)-C(2)	28.27(6)	C(13)-N(1)-Zr(1)	140.31(16)
N(2)-Zr(1)-C(2)	136.38(7)	C(11)-N(2)-C(17)	121.19(19)
N(1)-Zr(1)-C(2)	136.28(7)	C(11)-N(2)-Zr(1)	92.68(13)
C(19)-Zr(1)-C(2)	103.86(8)	C(17)-N(2)-Zr(1)	142.07(15)
Cl(1)-Zr(1)-C(2)	81.84(6)	C(2)-C(1)-C(5)	108.28(19)
C(1)-Zr(1)-C(2)	32.59(7)	C(2)-C(1)-C(6)	125.4(2)
C(5)-Zr(1)-C(2)	54.13(7)	C(5)-C(1)-C(6)	126.1(2)
CT1-Zr(1)-C(4)	28.08(8)	C(2)-C(1)-Zr(1)	75.54(12)

C(5)-C(1)-Zr(1)	73.59(12)	H(7A)-C(7)-H(7C)	114(3)
C(6)-C(1)-Zr(1)	120.71(16)	H(7B)-C(7)-H(7C)	106(3)
C(1)-C(2)-C(3)	107.9(2)	C(3)-C(8)-H(8A)	112(2)
C(1)-C(2)-C(7)	126.9(2)	C(3)-C(8)-H(8B)	110(2)
C(3)-C(2)-C(7)	124.8(2)	H(8A)-C(8)-H(8B)	110(3)
C(1)-C(2)-Zr(1)	71.88(12)	C(3)-C(8)-H(8C)	106(2)
C(3)-C(2)-Zr(1)	75.65(12)	H(8A)-C(8)-H(8C)	98(3)
C(7)-C(2)-Zr(1)	123.97(19)	H(8B)-C(8)-H(8C)	120(3)
C(4)-C(3)-C(2)	107.9(2)	C(4)-C(9)-H(9A)	112.6(18)
C(4)-C(3)-C(8)	125.5(2)	C(4)-C(9)-H(9B)	110(2)
C(2)-C(3)-C(8)	125.4(2)	H(9A)-C(9)-H(9B)	110(3)
C(4)-C(3)-Zr(1)	72.59(12)	C(4)-C(9)-H(9C)	114(2)
C(2)-C(3)-Zr(1)	72.28(12)	H(9A)-C(9)-H(9C)	93(3)
C(8)-C(3)-Zr(1)	130.66(19)	H(9B)-C(9)-H(9C)	117(3)
C(3)-C(4)-C(5)	108.4(2)	C(5)-C(10)-H(10A)	110(2)
C(3)-C(4)-C(9)	125.0(2)	C(5)-C(10)-H(10B)	114(3)
C(5)-C(4)-C(9)	126.1(2)	H(10A)-C(10)-H(10B)	104(3)
C(3)-C(4)-Zr(1)	75.53(13)	C(5)-C(10)-H(10C)	112(2)
C(5)-C(4)-Zr(1)	71.72(12)	H(10A)-C(10)-H(10C)	112(3)
C(9)-C(4)-Zr(1)	124.68(16)	H(10B)-C(10)-H(10C)	105(4)
C(1)-C(5)-C(4)	107.5(2)	N(1)-C(11)-N(2)	112.61(18)
C(1)-C(5)-C(10)	126.3(2)	N(1)-C(11)-C(12)	125.8(2)
C(4)-C(5)-C(10)	126.1(2)	N(2)-C(11)-C(12)	121.4(2)
C(1)-C(5)-Zr(1)	73.46(12)	N(1)-C(11)-Zr(1)	59.53(11)
C(4)-C(5)-Zr(1)	75.69(12)	N(2)-C(11)-Zr(1)	57.10(11)
C(10)-C(5)-Zr(1)	119.30(17)	C(12)-C(11)-Zr(1)	157.1(2)
C(1)-C(6)-H(6A)	115(2)	C(11)-C(12)-H(12A)	112(3)
C(1)-C(6)-H(6B)	110.8(19)	C(11)-C(12)-H(12B)	108.4(19)
H(6A)-C(6)-H(6B)	113(3)	H(12A)-C(12)-H(12B)	113(3)
C(1)-C(6)-H(6C)	112(2)	C(11)-C(12)-H(12C)	109.1(19)
H(6A)-C(6)-H(6C)	104(3)	H(12A)-C(12)-H(12C)	104(3)
H(6B)-C(6)-H(6C)	101(3)	H(12B)-C(12)-H(12C)	110(3)
C(2)-C(7)-H(7A)	112(2)	N(1)-C(13)-C(16)	111.2(2)
C(2)-C(7)-H(7B)	112(3)	N(1)-C(13)-C(14)	106.1(2)
H(7A)-C(7)-H(7B)	95(3)	C(16)-C(13)-C(14)	109.7(3)
C(2)-C(7)-H(7C)	115(2)	N(1)-C(13)-C(15)	111.9(3)

C(16)-C(13)-C(15)	111.4(3)	C(21)-C(19)-Zr(1)	115.67(18)
C(14)-C(13)-C(15)	106.2(3)	C(22)-C(19)-Zr(1)	96.73(15)
C(13)-C(14)-H(14A)	110.7(17)	C(19)-C(20)-H(20A)	113.4(19)
C(13)-C(14)-H(14B)	108(2)	C(19)-C(20)-H(20B)	118(2)
H(14A)-C(14)-H(14B)	105(3)	H(20A)-C(20)-H(20B)	108(3)
C(13)-C(14)-H(14C)	108.7(17)	C(19)-C(20)-H(20C)	110.5(17)
H(14A)-C(14)-H(14C)	110(2)	H(20A)-C(20)-H(20C)	100(2)
H(14B)-C(14)-H(14C)	114(3)	H(20B)-C(20)-H(20C)	105(3)
C(13)-C(15)-H(15A)	108(2)	C(19)-C(21)-H(21A)	113(2)
C(13)-C(15)-H(15B)	96(3)	C(19)-C(21)-H(21B)	112(2)
H(15A)-C(15)-H(15B)	116(4)	H(21A)-C(21)-H(21B)	107(3)
C(13)-C(15)-H(15C)	113.3(19)	C(19)-C(21)-H(21C)	110.3(16)
H(15A)-C(15)-H(15C)	111(3)	H(21A)-C(21)-H(21C)	106(3)
H(15B)-C(15)-H(15C)	112(4)	H(21B)-C(21)-H(21C)	108(3)
C(13)-C(16)-H(16A)	108(2)	C(19)-C(22)-H(22A)	107.0(18)
C(13)-C(16)-H(16B)	106(3)	C(19)-C(22)-H(22B)	111.0(18)
H(16A)-C(16)-H(16B)	110(3)	H(22A)-C(22)-H(22B)	106(3)
C(13)-C(16)-H(16C)	116(2)	C(19)-C(22)-H(22C)	118(3)
H(16A)-C(16)-H(16C)	108(3)	H(22A)-C(22)-H(22C)	107(3)
H(16B)-C(16)-H(16C)	109(3)	H(22B)-C(22)-H(22C)	107(3)
N(2)-C(17)-C(18)	112.6(2)		
N(2)-C(17)-H(17A)	112.8(15)		
C(18)-C(17)-H(17A)	110.2(14)		
N(2)-C(17)-H(17B)	106.5(17)		
C(18)-C(17)-H(17B)	106.7(17)		
H(17A)-C(17)-H(17B)	108(2)		
C(17)-C(18)-H(18A)	113(2)		
C(17)-C(18)-H(18B)	108(3)		
H(18A)-C(18)-H(18B)	113(3)		
C(17)-C(18)-H(18C)	115(2)		
H(18A)-C(18)-H(18C)	103(3)		
H(18B)-C(18)-H(18C)	105(3)		
C(20)-C(19)-C(21)	107.6(2)		
C(20)-C(19)-C(22)	108.0(2)		
C(21)-C(19)-C(22)	108.1(2)		
C(20)-C(19)-Zr(1)	119.47(18)		

Symmetry transformations used to generate equivalent atoms:

Table 19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3g**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	26(1)	21(1)	27(1)	-1(1)	7(1)	0(1)
Cl(1)	52(1)	36(1)	42(1)	-12(1)	18(1)	-1(1)
N(1)	29(1)	29(1)	41(1)	4(1)	10(1)	2(1)
N(2)	31(1)	31(1)	30(1)	-3(1)	8(1)	-5(1)
C(1)	30(1)	26(1)	43(1)	0(1)	13(1)	-3(1)
C(2)	27(1)	34(1)	41(1)	-3(1)	7(1)	-3(1)
C(3)	26(1)	31(1)	46(1)	0(1)	10(1)	2(1)
C(4)	32(1)	32(1)	43(1)	-6(1)	18(1)	-4(1)
C(5)	32(1)	38(1)	36(1)	2(1)	15(1)	-6(1)
C(6)	42(1)	26(1)	76(2)	2(1)	20(1)	-5(1)
C(7)	40(1)	63(2)	43(2)	-8(1)	0(1)	-10(1)
C(8)	37(1)	46(2)	78(2)	11(2)	16(1)	13(1)
C(9)	51(2)	51(2)	64(2)	-23(1)	33(2)	-9(1)
C(10)	53(2)	63(2)	41(2)	12(1)	15(1)	-9(2)
C(11)	27(1)	36(1)	33(1)	4(1)	6(1)	-4(1)
C(12)	31(1)	50(2)	71(2)	-4(2)	7(1)	-8(1)
C(13)	32(1)	31(1)	72(2)	6(1)	16(1)	7(1)
C(14)	45(1)	27(1)	89(2)	3(1)	21(2)	7(1)
C(15)	44(2)	50(2)	101(3)	17(2)	1(2)	13(1)
C(16)	50(2)	45(2)	102(3)	-9(2)	42(2)	4(1)
C(17)	43(1)	37(1)	39(1)	-11(1)	14(1)	-11(1)
C(18)	71(2)	71(2)	41(2)	-18(2)	15(2)	-19(2)
C(19)	48(1)	29(1)	38(1)	8(1)	15(1)	3(1)
C(20)	57(2)	30(1)	52(2)	4(1)	19(1)	2(1)
C(21)	70(2)	46(2)	38(2)	8(1)	15(1)	6(1)
C(22)	57(2)	43(2)	59(2)	9(1)	32(2)	1(1)

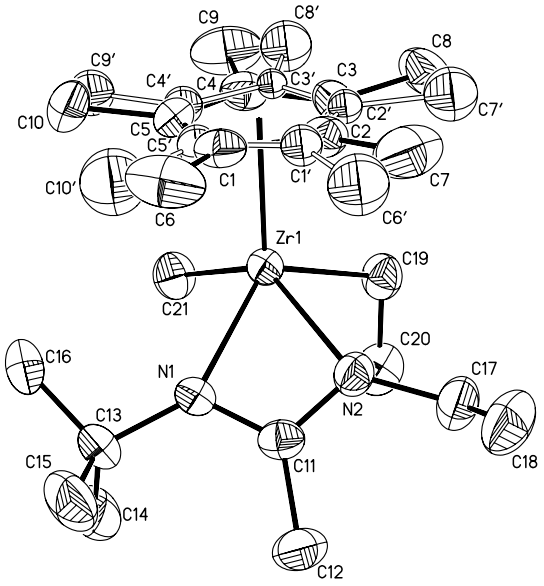
Table 20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3g**.

	x	y	z	U(eq)
H(6A)	4800(40)	2371(11)	7180(40)	66(10)
H(6B)	3940(40)	2359(10)	5350(40)	51(8)
H(6C)	5560(40)	2402(11)	6030(40)	64(9)
H(7A)	6530(40)	1473(11)	9730(40)	55(9)
H(7B)	6360(50)	1893(15)	9290(50)	93(14)
H(7C)	7860(50)	1687(13)	9240(50)	96(13)
H(8A)	6500(40)	406(14)	7110(50)	86(12)
H(8B)	6780(40)	662(13)	8690(50)	83(13)
H(8C)	7670(40)	717(11)	7520(40)	73(11)
H(9A)	3850(40)	724(10)	3040(40)	58(9)
H(9B)	4600(40)	404(13)	4570(50)	83(12)
H(9C)	5450(40)	681(11)	3570(40)	70(10)
H(10A)	4120(50)	1692(12)	2540(50)	82(12)
H(10B)	3070(50)	1932(16)	3070(50)	105(16)
H(10C)	2640(50)	1486(13)	2610(50)	87(12)
H(12A)	-1980(50)	1102(15)	2620(60)	103(15)
H(12B)	-2150(40)	1182(10)	4330(40)	65(10)
H(12C)	-1580(30)	730(11)	3700(40)	53(8)
H(14A)	1420(30)	2327(9)	6410(30)	41(7)
H(14B)	40(40)	2594(12)	5610(40)	70(10)
H(14C)	1060(30)	2400(10)	4590(40)	53(8)
H(15A)	-1220(40)	2001(12)	2680(40)	79(13)
H(15B)	-1880(50)	2277(15)	3710(50)	85(13)
H(15C)	-2600(40)	1824(12)	3300(40)	70(10)
H(16A)	-1760(40)	1605(13)	6110(40)	72(10)
H(16B)	-1620(50)	2121(15)	6400(40)	91(13)
H(16C)	-290(40)	1830(11)	7480(40)	69(10)
H(17A)	240(30)	306(9)	3880(30)	37(7)
H(17B)	2000(30)	331(10)	3920(30)	50(8)
H(18A)	-600(40)	680(12)	1350(40)	76(11)

H(18B)	490(40)	289(14)	1430(50)	81(12)
H(18C)	1110(40)	725(12)	1430(40)	70(10)
H(20A)	4290(40)	132(11)	7490(40)	61(9)
H(20B)	2520(40)	105(11)	6380(40)	66(10)
H(20C)	3090(30)	-44(10)	8150(30)	51(8)
H(21A)	3890(40)	423(13)	10390(50)	90(12)
H(21B)	3870(40)	928(13)	10150(40)	75(11)
H(21C)	5090(30)	671(9)	9810(30)	42(7)
H(22A)	1140(40)	463(10)	8590(40)	55(8)
H(22B)	580(40)	611(10)	6860(40)	52(8)
H(22C)	1000(40)	933(14)	8160(40)	75(11)

Crystallographic analysis of compound 4a.

A colorless rod with approximate orthogonal dimensions 0.382 x 0.184 x 0.170mm^3 was placed and optically centered on the Bruker SMART CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 14 seconds per frame and 606 frames per series. Five complete series were collected at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). Additionally, 200 frames, a repeat of the first series for redundancy and decay purposes, were also collected. The crystal to detector distance was 4.938cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 34520 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 5183 unique [R(int)=0.0311]



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the unique, non-standard setting, centric monoclinic space group $P2_1/n$ (no. 14). The structure was determined by direct methods with the successful location of the entire molecule using the program XS[4]. The structure was refined with XL[5]. The pentamethylcyclopentadienyl (Cp*) ligand was determined to have two orientations in a 0.895:0.105 ratio. Hydrogen atoms were placed in calculated positions and those fully occupied were allowed to have their thermal parameters refine while their positions remained optimized throughout. All non-hydrogen full occupancy atoms were refined anisotropically. A centroid was calculated for the nearly 90% orientation of the Cp* ligand. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=5.66%, wR(F^2)=13.33%, GOF=1.100 for all 5183 unique reflections [R(F)=4.73%, wR(F^2)=12.73% for those 4393 data with Fo > 4σ(Fo)]. The final difference-Fourier map possessed one large peak near the central atom while the remainder of the map was featureless indicating that the structure is both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.050*P)^2+0.3215*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

Table 21. Crystal data and structure refinement for **4a**.

Identification code	912ff	
Empirical formula	C21 H40 N2 Zr	
Formula weight	411.77	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.0417(5) Å	α= 90°.
	b = 16.1399(8) Å	β= 91.8790(10)°.
	c = 15.5233(8) Å	γ = 90°.
Volume	2264.1(2) $Å^3$	
Z	4	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.490 mm^{-1}	
F(000)	880	
Crystal size	0.382 x 0.184 x 0.170 mm^3	
Theta range for data collection	2.52 to 27.50°.	
Index ranges	-11<=h<=11, -20<=k<=20, -20<=l<=20	
Reflections collected	34520	
Independent reflections	5183 [R(int) = 0.0311]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical, SADABS	
Max. and min. transmission	1.00000 and 0.81622	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5183 / 3 / 279	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1273 [4393 Data]	
R indices (all data)	R1 = 0.0566, wR2 = 0.1333	
Largest diff. peak and hole	2.820 and -0.527 $e.Å^{-3}$	

Table 22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	5069(1)	2284(1)	8993(1)	30(1)
N(1)	7130(3)	3007(2)	9379(2)	36(1)
N(2)	7253(3)	1642(2)	9284(2)	37(1)
CNT1	4282(2)	2166(1)	7624(1)	0
C(1)	5398(4)	2511(4)	7413(2)	40(1)
C(2)	5212(5)	1647(3)	7518(2)	45(1)
C(3)	3744(5)	1501(2)	7766(2)	46(1)
C(4)	3022(4)	2274(3)	7825(3)	42(1)
C(5)	4033(7)	2898(3)	7596(3)	38(2)
C(6)	6745(5)	2949(4)	7091(3)	66(1)
C(7)	6340(6)	1012(4)	7289(3)	86(2)
C(8)	3043(7)	653(3)	7866(3)	81(2)
C(9)	1401(5)	2399(4)	7987(4)	76(2)
C(10)	3634(6)	3798(3)	7488(3)	59(1)
C(1')	5638(18)	1845(10)	7388(11)	31(8)
C(2')	4331(18)	1424(9)	7594(9)	23(6)
C(3')	3212(17)	2019(9)	7704(10)	19(6)
C(4')	3828(18)	2807(10)	7565(12)	31(15)
C(5')	5328(19)	2700(11)	7370(14)	29(11)
C(6')	7100(30)	1452(14)	7218(18)	64(10)
C(7')	4160(30)	505(12)	7681(16)	59(9)
C(8')	1640(20)	1843(13)	7928(17)	60(9)
C(9')	3030(30)	3618(14)	7617(19)	44(8)
C(10')	6400(30)	3376(15)	7180(20)	78(15)
C(11)	7865(3)	2322(2)	9629(2)	35(1)
C(12)	9160(4)	2281(2)	10256(3)	53(1)
C(13)	7571(4)	3871(2)	9600(2)	46(1)
C(14)	7418(6)	4062(3)	10558(3)	72(1)
C(15)	9131(4)	4059(3)	9285(3)	71(1)
C(16)	6503(4)	4435(2)	9093(3)	53(1)
C(17)	7729(4)	804(2)	9535(2)	49(1)

C(18)	9057(5)	489(3)	9051(3)	64(1)
C(19)	4141(3)	1227(2)	9777(2)	44(1)
C(20)	4708(5)	1349(3)	10706(3)	60(1)
C(21)	3537(4)	3161(2)	9725(2)	46(1)

Table2 3. Bond lengths [Å] and angles [°] for **4a**.

Zr(1)-CNT1	2.2274(19)	C(8)-H(8C)	0.9800
Zr(1)-N(2)	2.263(2)	C(9)-H(9A)	0.9800
Zr(1)-N(1)	2.263(2)	C(9)-H(9B)	0.9800
Zr(1)-C(19)	2.271(3)	C(9)-H(9C)	0.9800
Zr(1)-C(21)	2.306(3)	C(10)-H(10A)	0.9800
Zr(1)-C(1)	2.508(4)	C(10)-H(10B)	0.9800
Zr(1)-C(2)	2.517(3)	C(10)-H(10C)	0.9800
Zr(1)-C(5)	2.535(4)	C(1')-C(5')	1.408(9)
Zr(1)-C(4)	2.548(4)	C(1')-C(2')	1.409(9)
Zr(1)-C(3)	2.551(3)	C(1')-C(6')	1.498(9)
Zr(1)-C(4')	2.592(19)	C(2')-C(3')	1.409(9)
Zr(1)-C(3')	2.605(16)	C(2')-C(7')	1.497(9)
N(1)-C(11)	1.341(4)	C(3')-C(4')	1.409(9)
N(1)-C(13)	1.487(4)	C(3')-C(8')	1.498(9)
N(2)-C(11)	1.332(4)	C(4')-C(5')	1.409(9)
N(2)-C(17)	1.467(4)	C(4')-C(9')	1.497(9)
C(1)-C(2)	1.415(8)	C(5')-C(10')	1.498(9)
C(1)-C(5)	1.420(6)	C(6')-H(6'1)	0.9800
C(1)-C(6)	1.507(6)	C(6')-H(6'2)	0.9800
C(2)-C(3)	1.414(6)	C(6')-H(6'3)	0.9800
C(2)-C(7)	1.497(5)	C(7')-H(7'1)	0.9800
C(3)-C(4)	1.413(6)	C(7')-H(7'2)	0.9800
C(3)-C(8)	1.518(5)	C(7')-H(7'3)	0.9800
C(4)-C(5)	1.413(7)	C(8')-H(8'1)	0.9800
C(4)-C(9)	1.509(6)	C(8')-H(8'2)	0.9800
C(5)-C(10)	1.505(5)	C(8')-H(8'3)	0.9800
C(6)-H(6A)	0.9800	C(9')-H(9'1)	0.9800
C(6)-H(6B)	0.9800	C(9')-H(9'2)	0.9800
C(6)-H(6C)	0.9800	C(9')-H(9'3)	0.9800
C(7)-H(7A)	0.9800	C(10')-H(10D)	0.9800
C(7)-H(7B)	0.9800	C(10')-H(10E)	0.9800
C(7)-H(7C)	0.9800	C(10')-H(10F)	0.9800
C(8)-H(8A)	0.9800	C(11)-C(12)	1.500(4)
C(8)-H(8B)	0.9800	C(12)-H(12A)	0.9800

C(12)-H(12B)	0.9800	CNT1-Zr(1)-C(21)	110.14(10)
C(12)-H(12C)	0.9800	N(2)-Zr(1)-C(21)	135.79(11)
C(13)-C(16)	1.527(5)	N(1)-Zr(1)-C(21)	93.18(11)
C(13)-C(14)	1.530(5)	C(19)-Zr(1)-C(21)	87.65(12)
C(13)-C(15)	1.539(5)	CNT1-Zr(1)-C(1)	28.77(9)
C(14)-H(14A)	0.9800	N(2)-Zr(1)-C(1)	97.58(14)
C(14)-H(14B)	0.9800	N(1)-Zr(1)-C(1)	93.44(11)
C(14)-H(14C)	0.9800	C(19)-Zr(1)-C(1)	133.77(16)
C(15)-H(15A)	0.9800	C(21)-Zr(1)-C(1)	118.97(17)
C(15)-H(15B)	0.9800	CNT1-Zr(1)-C(2)	28.53(8)
C(15)-H(15C)	0.9800	N(2)-Zr(1)-C(2)	85.68(11)
C(16)-H(16A)	0.9800	N(1)-Zr(1)-C(2)	112.63(14)
C(16)-H(16B)	0.9800	C(19)-Zr(1)-C(2)	102.22(15)
C(16)-H(16C)	0.9800	C(21)-Zr(1)-C(2)	138.47(12)
C(17)-C(18)	1.525(5)	C(1)-Zr(1)-C(2)	32.72(18)
C(17)-H(17A)	0.9900	CNT1-Zr(1)-C(5)	28.32(11)
C(17)-H(17B)	0.9900	N(2)-Zr(1)-C(5)	130.20(13)
C(18)-H(18A)	0.9800	N(1)-Zr(1)-C(5)	107.60(18)
C(18)-H(18B)	0.9800	C(19)-Zr(1)-C(5)	128.26(18)
C(18)-H(18C)	0.9800	C(21)-Zr(1)-C(5)	88.30(13)
C(19)-C(20)	1.529(5)	C(1)-Zr(1)-C(5)	32.70(15)
C(19)-H(19A)	0.9900	C(2)-Zr(1)-C(5)	53.85(12)
C(19)-H(19B)	0.9900	CNT1-Zr(1)-C(4)	28.18(9)
C(20)-H(20A)	0.9800	N(2)-Zr(1)-C(4)	138.46(13)
C(20)-H(20B)	0.9800	N(1)-Zr(1)-C(4)	139.81(11)
C(20)-H(20C)	0.9800	C(19)-Zr(1)-C(4)	95.99(12)
C(21)-H(21A)	0.9800	C(21)-Zr(1)-C(4)	85.44(14)
C(21)-H(21B)	0.9800	C(1)-Zr(1)-C(4)	53.95(12)
C(21)-H(21C)	0.9800	C(2)-Zr(1)-C(4)	53.69(14)
		C(5)-Zr(1)-C(4)	32.28(18)
CNT1-Zr(1)-N(2)	113.67(8)	CNT1-Zr(1)-C(3)	28.12(9)
CNT1-Zr(1)-N(1)	122.06(9)	N(2)-Zr(1)-C(3)	107.94(12)
N(2)-Zr(1)-N(1)	58.48(9)	N(1)-Zr(1)-C(3)	144.63(12)
CNT1-Zr(1)-C(19)	109.59(10)	C(19)-Zr(1)-C(3)	81.68(12)
N(2)-Zr(1)-C(19)	83.37(10)	C(21)-Zr(1)-C(3)	113.41(14)
N(1)-Zr(1)-C(19)	124.12(10)	C(1)-Zr(1)-C(3)	53.87(14)

C(2)-Zr(1)-C(3)	32.39(15)	C(3)-C(2)-C(1)	108.2(3)
C(5)-Zr(1)-C(3)	53.43(17)	C(3)-C(2)-C(7)	127.1(5)
C(4)-Zr(1)-C(3)	32.18(13)	C(1)-C(2)-C(7)	124.3(5)
CNT1-Zr(1)-C(4')	25.3(4)	C(3)-C(2)-Zr(1)	75.2(2)
N(2)-Zr(1)-C(4')	132.1(4)	C(1)-C(2)-Zr(1)	73.30(19)
N(1)-Zr(1)-C(4')	112.8(4)	C(7)-C(2)-Zr(1)	123.4(3)
C(19)-Zr(1)-C(4')	123.1(4)	C(4)-C(3)-C(2)	108.0(3)
C(21)-Zr(1)-C(4')	88.3(4)	C(4)-C(3)-C(8)	126.5(4)
C(1)-Zr(1)-C(4')	34.7(4)	C(2)-C(3)-C(8)	125.3(4)
C(2)-Zr(1)-C(4')	52.3(4)	C(4)-C(3)-Zr(1)	73.8(2)
C(5)-Zr(1)-C(4')	5.2(4)	C(2)-C(3)-Zr(1)	72.45(19)
C(4)-Zr(1)-C(4')	27.1(4)	C(8)-C(3)-Zr(1)	123.9(3)
C(3)-Zr(1)-C(4')	49.0(4)	C(5)-C(4)-C(3)	108.0(4)
CNT1-Zr(1)-C(3')	22.4(3)	C(5)-C(4)-C(9)	125.9(4)
N(2)-Zr(1)-C(3')	127.9(4)	C(3)-C(4)-C(9)	125.6(4)
N(1)-Zr(1)-C(3')	142.4(3)	C(5)-C(4)-Zr(1)	73.4(2)
C(19)-Zr(1)-C(3')	92.8(3)	C(3)-C(4)-Zr(1)	74.1(2)
C(21)-Zr(1)-C(3')	95.6(4)	C(9)-C(4)-Zr(1)	124.6(3)
C(1)-Zr(1)-C(3')	50.7(4)	C(4)-C(5)-C(1)	108.1(4)
C(2)-Zr(1)-C(3')	44.4(3)	C(4)-C(5)-C(10)	124.1(5)
C(5)-Zr(1)-C(3')	36.5(4)	C(1)-C(5)-C(10)	127.5(6)
C(4)-Zr(1)-C(3')	10.8(3)	C(4)-C(5)-Zr(1)	74.3(2)
C(3)-Zr(1)-C(3')	21.6(3)	C(1)-C(5)-Zr(1)	72.6(2)
C(4')-Zr(1)-C(3')	31.5(2)	C(10)-C(5)-Zr(1)	123.6(3)
C(11)-N(1)-C(13)	125.4(2)	C(5')-C(1')-C(2')	108.0
C(11)-N(1)-Zr(1)	92.71(17)	C(5')-C(1')-C(6')	126.0
C(13)-N(1)-Zr(1)	139.2(2)	C(2')-C(1')-C(6')	126.0
C(11)-N(2)-C(17)	122.5(3)	C(5')-C(1')-Zr(1)	73.3(6)
C(11)-N(2)-Zr(1)	92.98(17)	C(2')-C(1')-Zr(1)	74.1(6)
C(17)-N(2)-Zr(1)	136.1(2)	C(6')-C(1')-Zr(1)	118.5(5)
C(2)-C(1)-C(5)	107.6(4)	C(3')-C(2')-C(1')	108.0
C(2)-C(1)-C(6)	126.9(5)	C(3')-C(2')-C(7')	126.0
C(5)-C(1)-C(6)	125.3(6)	C(1')-C(2')-C(7')	126.0
C(2)-C(1)-Zr(1)	74.0(2)	C(3')-C(2')-Zr(1)	72.9(5)
C(5)-C(1)-Zr(1)	74.7(2)	C(1')-C(2')-Zr(1)	75.1(6)
C(6)-C(1)-Zr(1)	121.1(3)	C(7')-C(2')-Zr(1)	118.0(6)

C(4')-C(3')-C(2')	108.0	C(4')-C(9')-H(9'1)	109.5
C(4')-C(3')-C(8')	126.0	C(4')-C(9')-H(9'2)	109.5
C(2')-C(3')-C(8')	126.0	H(9'1)-C(9')-H(9'2)	109.5
C(4')-C(3')-Zr(1)	73.8(6)	C(4')-C(9')-H(9'3)	109.5
C(2')-C(3')-Zr(1)	76.0(5)	H(9'1)-C(9')-H(9'3)	109.5
C(8')-C(3')-Zr(1)	116.3(6)	H(9'2)-C(9')-H(9'3)	109.5
C(3')-C(4')-C(5')	108.0	C(5')-C(10')-H(10D)	109.5
C(3')-C(4')-C(9')	126.0	C(5')-C(10')-H(10E)	109.5
C(5')-C(4')-C(9')	126.0	H(10D)-C(10')-H(10E)	109.5
C(3')-C(4')-Zr(1)	74.8(6)	C(5')-C(10')-H(10F)	109.5
C(5')-C(4')-Zr(1)	75.6(6)	H(10D)-C(10')-H(10F)	109.5
C(9')-C(4')-Zr(1)	115.8(5)	H(10E)-C(10')-H(10F)	109.5
C(1')-C(5')-C(4')	108.0	N(2)-C(11)-N(1)	111.6(3)
C(1')-C(5')-C(10')	126.0	N(2)-C(11)-C(12)	122.0(3)
C(4')-C(5')-C(10')	126.0	N(1)-C(11)-C(12)	126.4(3)
C(1')-C(5')-Zr(1)	75.8(5)	C(11)-C(12)-H(12A)	109.5
C(4')-C(5')-Zr(1)	73.1(5)	C(11)-C(12)-H(12B)	109.5
C(10')-C(5')-Zr(1)	117.2(5)	H(12A)-C(12)-H(12B)	109.5
C(1')-C(6')-H(6'1)	109.5	C(11)-C(12)-H(12C)	109.5
C(1')-C(6')-H(6'2)	109.5	H(12A)-C(12)-H(12C)	109.5
H(6'1)-C(6')-H(6'2)	109.5	H(12B)-C(12)-H(12C)	109.5
C(1')-C(6')-H(6'3)	109.5	N(1)-C(13)-C(16)	106.3(2)
H(6'1)-C(6')-H(6'3)	109.5	N(1)-C(13)-C(14)	112.5(3)
H(6'2)-C(6')-H(6'3)	109.5	C(16)-C(13)-C(14)	107.8(3)
C(2')-C(7')-H(7'1)	109.5	N(1)-C(13)-C(15)	110.7(3)
C(2')-C(7')-H(7'2)	109.5	C(16)-C(13)-C(15)	106.8(3)
H(7'1)-C(7')-H(7'2)	109.5	C(14)-C(13)-C(15)	112.5(3)
C(2')-C(7')-H(7'3)	109.5	C(13)-C(14)-H(14A)	109.5
H(7'1)-C(7')-H(7'3)	109.5	C(13)-C(14)-H(14B)	109.5
H(7'2)-C(7')-H(7'3)	109.5	H(14A)-C(14)-H(14B)	109.5
C(3')-C(8')-H(8'1)	109.5	C(13)-C(14)-H(14C)	109.5
C(3')-C(8')-H(8'2)	109.5	H(14A)-C(14)-H(14C)	109.5
H(8'1)-C(8')-H(8'2)	109.5	H(14B)-C(14)-H(14C)	109.5
C(3')-C(8')-H(8'3)	109.5	C(13)-C(15)-H(15A)	109.5
H(8'1)-C(8')-H(8'3)	109.5	C(13)-C(15)-H(15B)	109.5
H(8'2)-C(8')-H(8'3)	109.5	H(15A)-C(15)-H(15B)	109.5

C(13)-C(15)-H(15C)	109.5	Zr(1)-C(21)-H(21C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(21A)-C(21)-H(21C)	109.5
H(15B)-C(15)-H(15C)	109.5	H(21B)-C(21)-H(21C)	109.5
C(13)-C(16)-H(16A)	109.5		
C(13)-C(16)-H(16B)	109.5		
H(16A)-C(16)-H(16B)	109.5		
C(13)-C(16)-H(16C)	109.5		
H(16A)-C(16)-H(16C)	109.5		
H(16B)-C(16)-H(16C)	109.5		
N(2)-C(17)-C(18)	114.0(3)		
N(2)-C(17)-H(17A)	108.8		
C(18)-C(17)-H(17A)	108.8		
N(2)-C(17)-H(17B)	108.8		
C(18)-C(17)-H(17B)	108.8		
H(17A)-C(17)-H(17B)	107.7		
C(17)-C(18)-H(18A)	109.5		
C(17)-C(18)-H(18B)	109.5		
H(18A)-C(18)-H(18B)	109.5		
C(17)-C(18)-H(18C)	109.5		
H(18A)-C(18)-H(18C)	109.5		
H(18B)-C(18)-H(18C)	109.5		
C(20)-C(19)-Zr(1)	106.9(2)		
C(20)-C(19)-H(19A)	110.3		
Zr(1)-C(19)-H(19A)	110.3		
C(20)-C(19)-H(19B)	110.3		
Zr(1)-C(19)-H(19B)	110.3		
H(19A)-C(19)-H(19B)	108.6		
C(19)-C(20)-H(20A)	109.5		
C(19)-C(20)-H(20B)	109.5		
H(20A)-C(20)-H(20B)	109.5		
C(19)-C(20)-H(20C)	109.5		
H(20A)-C(20)-H(20C)	109.5		
H(20B)-C(20)-H(20C)	109.5		
Zr(1)-C(21)-H(21A)	109.5		
Zr(1)-C(21)-H(21B)	109.5		
H(21A)-C(21)-H(21B)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table 24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	30(1)	29(1)	32(1)	0(1)	-1(1)	-1(1)
N(1)	35(1)	33(1)	39(1)	-1(1)	-6(1)	-5(1)
N(2)	33(1)	33(1)	46(1)	2(1)	-1(1)	3(1)
C(1)	38(2)	52(2)	28(2)	1(2)	-3(1)	-5(2)
C(2)	51(2)	46(2)	36(2)	-10(2)	-9(2)	14(2)
C(3)	60(3)	36(2)	42(2)	-3(1)	-9(2)	-11(2)
C(4)	33(2)	50(2)	41(2)	-4(2)	-5(1)	0(2)
C(5)	42(2)	35(2)	37(2)	5(1)	-8(2)	1(2)
C(6)	51(2)	109(4)	40(2)	-5(2)	9(2)	-27(3)
C(7)	101(4)	98(4)	58(3)	-36(3)	-25(3)	59(4)
C(8)	120(5)	49(2)	70(3)	6(2)	-32(3)	-38(3)
C(9)	34(2)	125(5)	69(3)	2(3)	-2(2)	-2(2)
C(10)	80(3)	39(2)	57(3)	8(2)	-12(2)	9(2)
C(11)	31(1)	43(2)	32(1)	2(1)	1(1)	-3(1)
C(12)	45(2)	60(2)	53(2)	8(2)	-14(2)	-2(1)
C(13)	51(2)	35(2)	51(2)	-5(1)	-7(1)	-11(1)
C(14)	103(4)	54(2)	57(2)	-18(2)	-12(2)	-6(2)
C(15)	51(2)	49(2)	113(4)	-1(2)	-7(2)	-21(2)
C(16)	64(2)	29(1)	66(2)	1(1)	-1(2)	-6(1)
C(17)	46(2)	38(2)	63(2)	8(1)	1(2)	6(1)
C(18)	65(2)	60(2)	67(2)	5(2)	4(2)	26(2)
C(19)	44(2)	38(2)	49(2)	7(1)	5(1)	-5(1)
C(20)	62(2)	62(2)	57(2)	5(2)	8(2)	8(2)
C(21)	47(2)	43(2)	50(2)	-5(1)	8(1)	4(1)

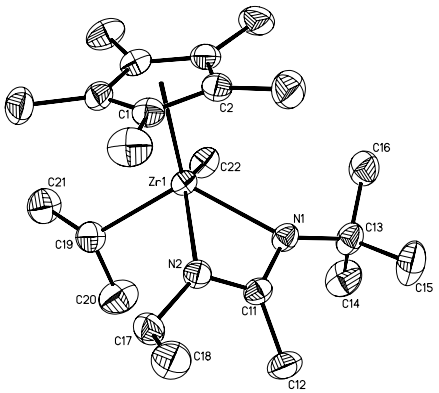
Table 25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4a**.

	x	y	z	U(eq)
H(6A)	6828	2845	6472	100
H(6B)	7631	2740	7400	100
H(6C)	6653	3545	7191	100
H(7A)	6271	536	7677	129
H(7B)	7332	1254	7348	129
H(7C)	6157	830	6693	129
H(8A)	2415	655	8369	121
H(8B)	3822	235	7947	121
H(8C)	2441	521	7348	121
H(9A)	819	2289	7455	114
H(9B)	1236	2972	8171	114
H(9C)	1096	2019	8439	114
H(10A)	2982	3865	6977	88
H(10B)	4537	4124	7420	88
H(10C)	3124	3990	7999	88
H(6'1)	7108	881	7433	96
H(6'2)	7893	1768	7513	96
H(6'3)	7260	1451	6597	96
H(7'1)	3975	367	8283	88
H(7'2)	5069	230	7506	88
H(7'3)	3326	317	7313	88
H(8'1)	1073	1686	7406	90
H(8'2)	1209	2341	8179	90
H(8'3)	1624	1389	8346	90
H(9'1)	3728	4052	7801	67
H(9'2)	2243	3573	8034	67
H(9'3)	2595	3758	7049	67
H(10D)	6451	3447	6553	117
H(10E)	7384	3229	7417	117
H(10F)	6075	3895	7439	117

H(12A)	9045	1805	10640	130(20)
H(12B)	9207	2792	10598	110(20)
H(12C)	10075	2220	9941	72(14)
H(14A)	6401	3949	10724	72(14)
H(14B)	7650	4647	10665	113(19)
H(14C)	8104	3713	10899	95(17)
H(15A)	9866	3764	9648	83(15)
H(15B)	9316	4656	9320	97(17)
H(15C)	9205	3875	8686	74(14)
H(16A)	6621	4349	8474	61(11)
H(16B)	6720	5015	9238	80(14)
H(16C)	5484	4305	9242	88(15)
H(17A)	6891	418	9433	78(14)
H(17B)	7980	801	10160	73(13)
H(18A)	8865	553	8429	80(14)
H(18B)	9221	-98	9186	110(19)
H(18C)	9937	809	9226	120(20)
H(19A)	3046	1237	9746	71(12)
H(19B)	4480	688	9552	51(10)
H(20A)	5750	1184	10758	120(20)
H(20B)	4124	1008	11092	150(30)
H(20C)	4613	1934	10866	130(20)
H(21A)	4018	3319	10276	80(14)
H(21B)	2601	2879	9832	76(14)
H(21C)	3342	3659	9378	107(18)

Crystallographic analysis of compound 4c.

A light yellowish-green cut block with approximate orthogonal dimensions 0.458 x 0.381 x 0.313 mm^3 was placed and optically centered on the Bruker SMART CCD system at –70°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 14 seconds per frame and 606 frames per series. Five complete series were collected at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). Additionally, 200 frames, a repeat of the first series for redundancy and decay purposes, were also collected. The crystal to detector distance was 4.356cm, thus providing a complete sphere of data to $2\theta_{max}$=60.0°. A total of 45880 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1, 2] with 6818 unique [R(int)=0.0222]



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the unique centric monoclinic space group $P2_1/n$ (no. 14). The structure was determined by direct methods with the successful location of all non-hydrogen atoms using the program XS[4]. The structure was refined with XL[5]. A single difference-Fourier map and least square refinement cycle was required to possibly locate any additional non-hydrogen atoms. Hydrogen atoms were located directly from a difference-Fourier map and their positional and thermal parameters were allowed to refine throughout the refinement stages. A centroid, C(x), was calculated for the pentamethylcyclopentadienyl ligand. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=2.70%, wR(F^2)=6.45%, GOF=1.063 for all 6818 unique reflections [R(F)=2.29%, wR(F^2)=6.17% for those 6122 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0352*P)^2+0.5882*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also applied to the data in the form $(Fc^2,corr) = k[1 + 0.001 * x * Fc^2 * \lambda^3/\sin(2\theta)]^{(-1/4)}$ where k=0.41505 is the overall scale factor. The value determined for x was 0.0006(2).

Table 26. Crystal data and structure refinement for **4c**.

Identification code	964ff	
Empirical formula	C22 H42 N2 Zr	
Formula weight	425.80	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.2986(3) Å	α= 90°.
	b = 16.2375(5) Å	β= 92.8320(10)°.
	c = 15.5392(4) Å	γ = 90°.
Volume	2343.34(12) $Å^3$	
Z	4	
Density (calculated)	1.207 Mg/m^3	
Absorption coefficient	0.476 mm^{-1}	
F(000)	912	
Crystal size	0.46 x 0.38 x 0.31 mm^3	
Theta range for data collection	2.50 to 30.00°.	
Index ranges	-12<=h<=13, -22<=k<=22, -21<=l<=21	
Reflections collected	45880	
Independent reflections	6818 [R(int) = 0.0222]	
Completeness to theta = 30.00°	99.7 %	
Absorption correction	Empirical, SADABS	
Max. and min. transmission	0.8653 and 0.8115	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6818 / 3 / 398	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0229, wR2 = 0.0617 [6122 Data]	
R indices (all data)	R1 = 0.0270, wR2 = 0.0645	
Extinction coefficient	0.0006(2)	
Largest diff. peak and hole	0.660 and -0.474 $e.Å^{-3}$	

Table 27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	7996(1)	2379(1)	4498(1)	25(1)
N(1)	7643(1)	3231(1)	5635(1)	30(1)
N(2)	7297(1)	1890(1)	5773(1)	29(1)
C(X)	6294(1)	2187(1)	3447(1)	0
C(1)	5674(1)	1728(1)	3913(1)	32(1)
C(2)	5488(1)	2595(1)	3862(1)	33(1)
C(3)	6411(1)	2897(1)	3235(1)	34(1)
C(4)	7178(1)	2220(1)	2903(1)	34(1)
C(5)	6719(1)	1495(1)	3323(1)	33(1)
C(6)	4811(2)	1148(1)	4432(1)	47(1)
C(7)	4404(2)	3079(1)	4343(1)	49(1)
C(8)	6470(2)	3771(1)	2907(1)	52(1)
C(9)	8177(2)	2254(1)	2169(1)	52(1)
C(10)	7104(2)	622(1)	3105(1)	47(1)
C(11)	7616(1)	2596(1)	6184(1)	28(1)
C(12)	7965(2)	2619(1)	7139(1)	43(1)
C(13)	7847(2)	4104(1)	5894(1)	38(1)
C(14)	9401(2)	4279(1)	6224(1)	56(1)
C(15)	6762(2)	4371(1)	6556(1)	59(1)
C(16)	7525(2)	4621(1)	5086(1)	49(1)
C(17)	7356(2)	1095(1)	6213(1)	38(1)
C(18)	6068(2)	918(1)	6753(1)	48(1)
C(19)	9646(1)	1331(1)	4584(1)	37(1)
C(20)	10670(2)	1578(1)	5350(1)	58(1)
C(21)	10573(2)	1093(1)	3839(1)	52(1)
C(22)	9784(2)	3228(1)	4010(1)	39(1)

Table 28. Bond lengths [Å] and angles [°] for 4c.

Zr(1)-C(X)	2.2387(6)	C(9)-H(9B)	0.92(3)
Zr(1)-N(2)	2.2594(9)	C(9)-H(9C)	0.94(3)
Zr(1)-N(1)	2.2808(9)	C(10)-H(10A)	0.95(2)
Zr(1)-C(19)	2.2896(13)	C(10)-H(10B)	1.00(2)
Zr(1)-C(22)	2.3158(13)	C(10)-H(10C)	0.94(2)
Zr(1)-C(2)	2.5123(12)	C(11)-C(12)	1.5041(18)
Zr(1)-C(1)	2.5318(11)	C(12)-H(12A)	0.90(3)
Zr(1)-C(3)	2.5390(12)	C(12)-H(12B)	0.92(3)
Zr(1)-C(5)	2.5669(11)	C(12)-H(12C)	0.87(3)
Zr(1)-C(4)	2.5688(12)	C(13)-C(16)	1.529(2)
N(1)-C(11)	1.3393(15)	C(13)-C(14)	1.536(2)
N(1)-C(13)	1.4827(15)	C(13)-C(15)	1.538(2)
N(2)-C(11)	1.3386(15)	C(14)-H(14A)	0.97(2)
N(2)-C(17)	1.4606(15)	C(14)-H(14B)	0.94(2)
C(1)-C(5)	1.4191(17)	C(14)-H(14C)	0.93(2)
C(1)-C(2)	1.4203(17)	C(15)-H(15A)	0.96(2)
C(1)-C(6)	1.4989(18)	C(15)-H(15B)	0.96(2)
C(2)-C(3)	1.4181(18)	C(15)-H(15C)	0.94(2)
C(2)-C(7)	1.5045(19)	C(16)-H(16A)	0.97(2)
C(3)-C(4)	1.4205(19)	C(16)-H(16B)	0.97(2)
C(3)-C(8)	1.5101(19)	C(16)-H(16C)	0.98(2)
C(4)-C(5)	1.4224(18)	C(17)-C(18)	1.523(2)
C(4)-C(9)	1.507(2)	C(17)-H(17A)	1.009(16)
C(5)-C(10)	1.5046(18)	C(17)-H(17B)	0.943(19)
C(6)-H(6A)	0.95(2)	C(18)-H(18A)	0.95(2)
C(6)-H(6B)	0.99(2)	C(18)-H(18B)	0.98(2)
C(6)-H(6C)	0.95(2)	C(18)-H(18C)	0.945(19)
C(7)-H(7A)	0.93(3)	C(19)-C(21)	1.5278(19)
C(7)-H(7B)	0.91(3)	C(19)-C(20)	1.539(2)
C(7)-H(7C)	0.91(3)	C(19)-H(19)	0.918(18)
C(8)-H(8A)	0.97(3)	C(20)-H(20A)	1.215(13)
C(8)-H(8B)	0.85(3)	C(20)-H(20B)	0.87(3)
C(8)-H(8C)	0.96(2)	C(20)-H(20C)	0.95(3)
C(9)-H(9A)	0.87(3)	C(21)-H(21A)	1.08(2)

C(21)-H(21B)	1.07(2)	N(1)-Zr(1)-C(5)	144.18(4)
C(21)-H(21C)	1.07(2)	C(19)-Zr(1)-C(5)	84.94(4)
C(22)-H(22A)	0.72(2)	C(22)-Zr(1)-C(5)	114.50(5)
C(22)-H(22B)	0.86(2)	C(2)-Zr(1)-C(5)	53.88(4)
C(22)-H(22C)	0.80(2)	C(1)-Zr(1)-C(5)	32.31(4)
		C(3)-Zr(1)-C(5)	53.49(4)
C(X)-Zr(1)-N(2)	111.52(3)	C(X)-Zr(1)-C(4)	28.07(3)
C(X)-Zr(1)-N(1)	121.70(3)	N(2)-Zr(1)-C(4)	136.57(4)
N(2)-Zr(1)-N(1)	58.36(4)	N(1)-Zr(1)-C(4)	139.53(4)
C(X)-Zr(1)-C(19)	112.78(4)	C(19)-Zr(1)-C(4)	98.51(5)
N(2)-Zr(1)-C(19)	84.75(4)	C(22)-Zr(1)-C(4)	85.82(5)
N(1)-Zr(1)-C(19)	121.79(4)	C(2)-Zr(1)-C(4)	53.83(4)
C(X)-Zr(1)-C(22)	109.71(4)	C(1)-Zr(1)-C(4)	53.50(4)
N(2)-Zr(1)-C(22)	137.60(5)	C(3)-Zr(1)-C(4)	32.29(4)
N(1)-Zr(1)-C(22)	91.45(4)	C(5)-Zr(1)-C(4)	32.16(4)
C(19)-Zr(1)-C(22)	88.38(6)	C(11)-N(1)-C(13)	124.68(10)
C(X)-Zr(1)-C(2)	28.78(3)	C(11)-N(1)-Zr(1)	91.95(7)
N(2)-Zr(1)-C(2)	95.28(4)	C(13)-N(1)-Zr(1)	140.28(8)
N(1)-Zr(1)-C(2)	93.05(4)	C(11)-N(2)-C(17)	122.07(10)
C(19)-Zr(1)-C(2)	137.16(4)	C(11)-N(2)-Zr(1)	92.91(7)
C(22)-Zr(1)-C(2)	117.11(5)	C(17)-N(2)-Zr(1)	135.71(8)
C(X)-Zr(1)-C(1)	28.42(3)	C(5)-C(1)-C(2)	108.31(11)
N(2)-Zr(1)-C(1)	83.74(4)	C(5)-C(1)-C(6)	125.60(13)
N(1)-Zr(1)-C(1)	112.24(4)	C(2)-C(1)-C(6)	125.82(13)
C(19)-Zr(1)-C(1)	105.55(5)	C(5)-C(1)-Zr(1)	75.20(6)
C(22)-Zr(1)-C(1)	138.09(5)	C(2)-C(1)-Zr(1)	72.89(7)
C(2)-Zr(1)-C(1)	32.71(4)	C(6)-C(1)-Zr(1)	122.61(9)
C(X)-Zr(1)-C(3)	28.35(3)	C(3)-C(2)-C(1)	107.72(11)
N(2)-Zr(1)-C(3)	127.81(4)	C(3)-C(2)-C(7)	127.14(13)
N(1)-Zr(1)-C(3)	107.29(4)	C(1)-C(2)-C(7)	124.95(13)
C(19)-Zr(1)-C(3)	130.79(4)	C(3)-C(2)-Zr(1)	74.73(7)
C(22)-Zr(1)-C(3)	87.04(5)	C(1)-C(2)-Zr(1)	74.40(7)
C(2)-Zr(1)-C(3)	32.60(4)	C(7)-C(2)-Zr(1)	120.62(9)
C(1)-Zr(1)-C(3)	53.75(4)	C(2)-C(3)-C(4)	108.28(11)
C(X)-Zr(1)-C(5)	28.12(3)	C(2)-C(3)-C(8)	126.18(14)
N(2)-Zr(1)-C(5)	106.50(4)	C(4)-C(3)-C(8)	125.27(13)

C(2)-C(3)-Zr(1)	72.66(7)	C(4)-C(9)-H(9C)	116.2(17)
C(4)-C(3)-Zr(1)	75.01(7)	H(9A)-C(9)-H(9C)	103(2)
C(8)-C(3)-Zr(1)	122.93(9)	H(9B)-C(9)-H(9C)	104(2)
C(3)-C(4)-C(5)	107.86(11)	C(5)-C(10)-H(10A)	113.7(14)
C(3)-C(4)-C(9)	125.88(14)	C(5)-C(10)-H(10B)	111.3(13)
C(5)-C(4)-C(9)	125.94(14)	H(10A)-C(10)-H(10B)	106.6(18)
C(3)-C(4)-Zr(1)	72.70(7)	C(5)-C(10)-H(10C)	110.4(13)
C(5)-C(4)-Zr(1)	73.85(7)	H(10A)-C(10)-H(10C)	109.1(18)
C(9)-C(4)-Zr(1)	124.19(10)	H(10B)-C(10)-H(10C)	105.3(18)
C(1)-C(5)-C(4)	107.81(11)	N(2)-C(11)-N(1)	111.51(10)
C(1)-C(5)-C(10)	125.10(12)	N(2)-C(11)-C(12)	121.58(11)
C(4)-C(5)-C(10)	126.61(12)	N(1)-C(11)-C(12)	126.83(11)
C(1)-C(5)-Zr(1)	72.48(6)	C(11)-C(12)-H(12A)	106.6(17)
C(4)-C(5)-Zr(1)	74.00(7)	C(11)-C(12)-H(12B)	116.7(16)
C(10)-C(5)-Zr(1)	125.45(9)	H(12A)-C(12)-H(12B)	106(2)
C(1)-C(6)-H(6A)	113.9(13)	C(11)-C(12)-H(12C)	116.2(18)
C(1)-C(6)-H(6B)	111.7(12)	H(12A)-C(12)-H(12C)	95(2)
H(6A)-C(6)-H(6B)	104.5(16)	H(12B)-C(12)-H(12C)	113(3)
C(1)-C(6)-H(6C)	112.0(13)	N(1)-C(13)-C(16)	106.55(11)
H(6A)-C(6)-H(6C)	104.3(18)	N(1)-C(13)-C(14)	111.91(12)
H(6B)-C(6)-H(6C)	109.9(17)	C(16)-C(13)-C(14)	108.38(13)
C(2)-C(7)-H(7A)	111.0(16)	N(1)-C(13)-C(15)	111.84(11)
C(2)-C(7)-H(7B)	111.9(15)	C(16)-C(13)-C(15)	106.62(14)
H(7A)-C(7)-H(7B)	104(2)	C(14)-C(13)-C(15)	111.23(14)
C(2)-C(7)-H(7C)	107.8(17)	C(13)-C(14)-H(14A)	112.4(14)
H(7A)-C(7)-H(7C)	110(2)	C(13)-C(14)-H(14B)	107.7(13)
H(7B)-C(7)-H(7C)	112(2)	H(14A)-C(14)-H(14B)	106.5(19)
C(3)-C(8)-H(8A)	110.3(17)	C(13)-C(14)-H(14C)	106.3(13)
C(3)-C(8)-H(8B)	117.3(19)	H(14A)-C(14)-H(14C)	113.0(19)
H(8A)-C(8)-H(8B)	103(2)	H(14B)-C(14)-H(14C)	110.9(19)
C(3)-C(8)-H(8C)	114.2(15)	C(13)-C(15)-H(15A)	106.9(12)
H(8A)-C(8)-H(8C)	107(2)	C(13)-C(15)-H(15B)	110.6(13)
H(8B)-C(8)-H(8C)	104(2)	H(15A)-C(15)-H(15B)	109.4(17)
C(4)-C(9)-H(9A)	113.0(18)	C(13)-C(15)-H(15C)	112.1(14)
C(4)-C(9)-H(9B)	111.7(15)	H(15A)-C(15)-H(15C)	109.2(18)
H(9A)-C(9)-H(9B)	108(2)	H(15B)-C(15)-H(15C)	108.7(18)

C(13)-C(16)-H(16A)	113.5(13)	Zr(1)-C(22)-H(22A)	106.5(18)
C(13)-C(16)-H(16B)	108.2(12)	Zr(1)-C(22)-H(22B)	115.0(14)
H(16A)-C(16)-H(16B)	113.8(18)	H(22A)-C(22)-H(22B)	117(2)
C(13)-C(16)-H(16C)	112.3(11)	Zr(1)-C(22)-H(22C)	105.5(15)
H(16A)-C(16)-H(16C)	102.4(16)	H(22A)-C(22)-H(22C)	105(2)
H(16B)-C(16)-H(16C)	106.4(16)	H(22B)-C(22)-H(22C)	106.7(19)
N(2)-C(17)-C(18)	114.40(12)		
N(2)-C(17)-H(17A)	110.7(9)		
C(18)-C(17)-H(17A)	109.2(9)		
N(2)-C(17)-H(17B)	109.4(11)		
C(18)-C(17)-H(17B)	106.1(11)		
H(17A)-C(17)-H(17B)	106.7(14)		
C(17)-C(18)-H(18A)	110.2(12)		
C(17)-C(18)-H(18B)	108.4(12)		
H(18A)-C(18)-H(18B)	105.5(16)		
C(17)-C(18)-H(18C)	109.0(11)		
H(18A)-C(18)-H(18C)	112.9(17)		
H(18B)-C(18)-H(18C)	110.7(16)		
C(21)-C(19)-C(20)	107.55(12)		
C(21)-C(19)-Zr(1)	123.02(10)		
C(20)-C(19)-Zr(1)	103.86(10)		
C(21)-C(19)-H(19)	105.8(11)		
C(20)-C(19)-H(19)	108.5(11)		
Zr(1)-C(19)-H(19)	107.5(11)		
C(19)-C(20)-H(20A)	107.9(6)		
C(19)-C(20)-H(20B)	117.2(16)		
H(20A)-C(20)-H(20B)	112.3(18)		
C(19)-C(20)-H(20C)	110.7(15)		
H(20A)-C(20)-H(20C)	97.3(16)		
H(20B)-C(20)-H(20C)	110(2)		
C(19)-C(21)-H(21A)	109.4(12)		
C(19)-C(21)-H(21B)	115.4(12)		
H(21A)-C(21)-H(21B)	110.1(17)		
C(19)-C(21)-H(21C)	111.6(11)		
H(21A)-C(21)-H(21C)	104.0(16)		
H(21B)-C(21)-H(21C)	105.8(16)		

Symmetry transformations used to generate equivalent atoms:

Table 29. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	24(1)	28(1)	23(1)	-1(1)	3(1)	-3(1)
N(1)	35(1)	28(1)	28(1)	-3(1)	4(1)	-5(1)
N(2)	33(1)	28(1)	28(1)	1(1)	5(1)	-2(1)
C(1)	26(1)	35(1)	33(1)	1(1)	-3(1)	-5(1)
C(2)	28(1)	36(1)	33(1)	-2(1)	-4(1)	3(1)
C(3)	39(1)	33(1)	29(1)	3(1)	-5(1)	-1(1)
C(4)	35(1)	41(1)	26(1)	-2(1)	0(1)	-4(1)
C(5)	32(1)	32(1)	34(1)	-5(1)	-4(1)	-2(1)
C(6)	38(1)	53(1)	51(1)	6(1)	-1(1)	-19(1)
C(7)	36(1)	59(1)	53(1)	-13(1)	-1(1)	12(1)
C(8)	74(1)	36(1)	44(1)	11(1)	-12(1)	-2(1)
C(9)	53(1)	73(1)	30(1)	-3(1)	9(1)	-7(1)
C(10)	48(1)	36(1)	58(1)	-15(1)	-8(1)	2(1)
C(11)	26(1)	35(1)	25(1)	-1(1)	3(1)	-1(1)
C(12)	56(1)	47(1)	26(1)	-1(1)	-3(1)	-3(1)
C(13)	49(1)	29(1)	36(1)	-7(1)	7(1)	-8(1)
C(14)	61(1)	48(1)	58(1)	-10(1)	-3(1)	-24(1)
C(15)	81(1)	40(1)	59(1)	-13(1)	29(1)	-2(1)
C(16)	70(1)	29(1)	49(1)	0(1)	7(1)	-4(1)
C(17)	49(1)	31(1)	36(1)	6(1)	8(1)	3(1)
C(18)	61(1)	41(1)	42(1)	7(1)	14(1)	-10(1)
C(19)	31(1)	42(1)	39(1)	-1(1)	6(1)	4(1)
C(20)	37(1)	86(1)	50(1)	-8(1)	-2(1)	6(1)
C(21)	41(1)	64(1)	52(1)	-5(1)	12(1)	11(1)
C(22)	37(1)	42(1)	36(1)	-5(1)	9(1)	-10(1)

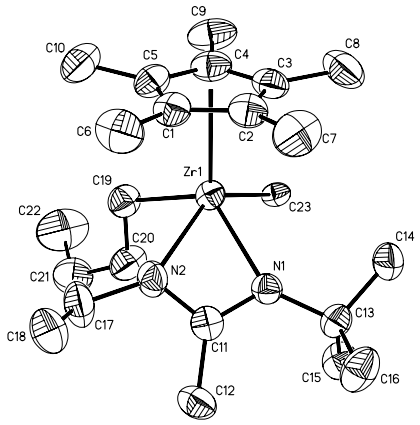
Table 30. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4c**.

	x	y	z	U(eq)
H(6A)	3970(20)	948(13)	4134(13)	71(6)
H(6B)	4460(20)	1418(13)	4952(14)	66(6)
H(6C)	5340(20)	668(14)	4590(14)	75(7)
H(7A)	4570(30)	3640(18)	4296(17)	93(8)
H(7B)	4490(20)	2982(16)	4923(17)	83(7)
H(7C)	3510(30)	2946(18)	4117(17)	100(8)
H(8A)	7440(30)	3907(18)	2752(18)	111(10)
H(8B)	6270(30)	4152(18)	3253(18)	98(9)
H(8C)	5840(30)	3877(15)	2411(16)	83(7)
H(9A)	7740(30)	2174(17)	1669(19)	90(8)
H(9B)	8910(30)	1870(17)	2236(16)	89(8)
H(9C)	8660(30)	2754(17)	2095(18)	90(8)
H(10A)	7450(20)	311(15)	3585(15)	82(7)
H(10B)	7870(20)	604(14)	2674(15)	75(7)
H(10C)	6310(20)	352(13)	2840(13)	66(6)
H(12A)	7120(30)	2611(13)	7396(17)	71(7)
H(12B)	8450(30)	3074(17)	7349(17)	96(8)
H(12C)	8280(30)	2161(17)	7372(18)	91(8)
H(14A)	9660(30)	3985(15)	6750(16)	81(7)
H(14B)	9470(20)	4846(15)	6358(14)	76(6)
H(14C)	9980(20)	4146(13)	5776(14)	66(6)
H(15A)	5820(20)	4213(13)	6326(13)	58(5)
H(15B)	6790(20)	4956(15)	6636(13)	73(6)
H(15C)	6940(20)	4115(14)	7092(15)	75(7)
H(16A)	8070(20)	4457(14)	4602(13)	66(6)
H(16B)	7640(20)	5198(13)	5241(13)	65(6)
H(16C)	6530(20)	4556(12)	4859(12)	58(5)
H(17A)	8269(17)	1045(10)	6589(10)	39(4)
H(17B)	7376(19)	669(12)	5802(12)	50(5)
H(18A)	6090(20)	1268(13)	7246(13)	63(6)

H(18B)	6160(20)	357(13)	6979(13)	61(5)
H(18C)	5210(20)	973(12)	6402(12)	55(5)
H(19)	9166(19)	861(11)	4728(11)	48(5)
H(20A)	11454(14)	995(8)	5519(8)	22(3)
H(20B)	10280(30)	1775(16)	5805(16)	91(8)
H(20C)	11390(30)	1943(16)	5170(15)	82(7)
H(21A)	11260(20)	1606(15)	3684(14)	79(7)
H(21B)	9990(20)	880(15)	3268(15)	82(7)
H(21C)	11320(20)	609(14)	4019(13)	71(6)
H(22A)	10280(20)	3298(15)	4372(15)	74(7)
H(22B)	9480(20)	3651(14)	3725(14)	66(6)
H(22C)	10220(20)	2952(14)	3686(14)	60(6)

Crystallographic analysis of compound 4d.

A pale green rod with approximate orthogonal dimensions 0.384 x 0.147 x 0.143mm^3 was placed and optically centered on the Bruker SMART CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.2° wide ω-scans, 10 seconds per frame and 909 frames per series. Five complete series were collected at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). The crystal to detector distance was 4.900cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 62502 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 5934 unique [R(int)=0.0407]



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the acentric hexagonal space groups $P6_1$ (no.169) and $P6_5$ (no.170). Space group $P6_1$ was chosen and the structure was determined by direct methods with the successful location of nearly all non-hydrogen atoms using the program XS[4]. The structure was refined with XL[5]. Additional least-squares difference-Fourier cycles were required to locate the remaining non-hydrogen atoms and to determine the relative occupancies for the disordered pentane molecule that appears as a helix along the c-axis. Due to molecular overlaps the pentane molecule was input at 0.166 occupancy. This molecule was further optimized with DFIX[5] commands. All full occupancy non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. A centroid for the pentamethylcyclopentadienyl ligand was calculated. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=4.41%, wR(F^2)=10.75%, GOF=1.168 for all 5934 unique reflections [R(F)=3.55%, wR(F^2)=9.39% for those 5355 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. The absolute structure parameter, Flack(x)[6], was refined and determined to be –0.07(4) clearly indicating that the correct enantiomorph has been chosen.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0672*P)^2+0.7291*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also applied to the data in the form $(Fc^2,corr) = k[1 + 0.001 * x * Fc^2 * \lambda^3/\sin(2\theta)]^{(-1/4)}$ where k=0.29058 is the overall scale factor. The value determined for x was 0.0007(4).

Table 31. Crystal data and structure refinement for **4d**.

Identification code	906ff	
Empirical formula	C23.83 H46 N2 Zr	
Formula weight	451.85	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P6(1)	
Unit cell dimensions	a = 22.4585(4) Å	α= 90°.
	b = 22.4585(4) Å	β= 90°.
	c = 8.8491(3) Å	γ = 120°.
Volume	3865.37(16) $Å^3$	
Z	6	
Density (calculated)	1.165 Mg/m^3	
Absorption coefficient	0.436 mm^{-1}	
F(000)	1458	
Crystal size	0.384 x 0.147 x 0.143 mm^3	
Theta range for data collection	1.05 to 27.49°.	
Index ranges	-29<=h<=29, -29<=k<=29, -11<=l<=11	
Reflections collected	62502	
Independent reflections	5934 [R(int) = 0.0407]	
Completeness to theta = 27.49°	100.0 %	
Absorption correction	Empirical, SADABS	
Max. and min. transmission	1.00000 and 0.90071	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5934 / 11 / 271	
Goodness-of-fit on F^2	1.168	
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0939 [5355 Data]	
R indices (all data)	R1 = 0.0441, wR2 = 0.1075	
Absolute structure parameter	-0.07(4)	
Extinction coefficient	0.0007(4)	
Largest diff. peak and hole	1.014 and -0.420 $e.Å^{-3}$	

Table 32. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	1496(1)	7258(1)	1743(2)	34(1)
N(1)	994(1)	6666(1)	3887(3)	36(1)
N(2)	1466(2)	7800(1)	3863(4)	44(1)
CNT1	2551(1)	7518(1)	1010	0
C(1)	2785(2)	7929(2)	2009(3)	45(1)
C(2)	2592(2)	7230(2)	2114(3)	45(1)
C(3)	2336(2)	6922(2)	698(4)	47(1)
C(4)	2382(2)	7444(2)	-291(3)	50(1)
C(5)	2658(2)	8062(2)	521(4)	45(1)
C(6)	3129(2)	8459(2)	3244(6)	67(1)
C(7)	2707(2)	6901(2)	3489(6)	68(1)
C(8)	2130(2)	6192(2)	249(7)	74(1)
C(9)	2209(2)	7357(3)	-1958(5)	67(1)
C(10)	2863(2)	8756(2)	-142(6)	66(1)
C(11)	1002(2)	7209(2)	4522(4)	38(1)
C(12)	537(2)	7200(2)	5764(5)	51(1)
C(13)	574(2)	5948(2)	4397(4)	39(1)
C(14)	807(2)	5525(2)	3480(5)	49(1)
C(15)	-196(2)	5655(2)	4078(5)	54(1)
C(16)	681(2)	5857(2)	6068(5)	59(1)
C(17)	1516(3)	8458(2)	4237(5)	63(1)
C(18)	1914(2)	8784(2)	5656(6)	69(1)
C(19)	1217(2)	7987(2)	583(5)	47(1)
C(20)	467(2)	7781(2)	936(6)	60(1)
C(21)	242(2)	8288(3)	441(7)	79(1)
C(22)	285(3)	8423(4)	-1196(8)	108(2)
C(23)	655(1)	6368(1)	203(4)	30(1)
C(31)	1010(30)	10630(30)	6970(60)	130(20)
C(32)	896(18)	10080(30)	5950(50)	105(12)
C(33)	234(19)	9800(30)	5310(40)	134(19)
C(34)	80(20)	9630(20)	3810(40)	130(18)
C(35)	-580(20)	9060(20)	3470(50)	88(10)

Table 33. Bond lengths [Å] and angles [°] for **4d**.

Zr(1)-CNT1	2.2341(15)	C(33)-C(34)	1.37(2)
Zr(1)-N(2)	2.254(3)	C(34)-C(35)	1.42(2)
Zr(1)-N(1)	2.267(3)	C(34)-C(32)#2	2.04(5)
Zr(1)-C(19)	2.269(3)	CNT1-Zr(1)-N(2)	114.48(9)
Zr(1)-C(23)	2.377(2)	CNT1-Zr(1)-N(1)	123.20(8)
Zr(1)-C(2)	2.515(3)	N(2)-Zr(1)-N(1)	58.67(9)
Zr(1)-C(1)	2.520(3)	CNT1-Zr(1)-C(19)	108.62(10)
Zr(1)-C(3)	2.531(3)	N(2)-Zr(1)-C(19)	83.94(12)
Zr(1)-C(5)	2.556(3)	N(1)-Zr(1)-C(19)	124.48(11)
Zr(1)-C(4)	2.558(3)	CNT1-Zr(1)-C(23)	110.24(8)
N(1)-C(11)	1.335(4)	N(2)-Zr(1)-C(23)	134.88(10)
N(1)-C(13)	1.474(4)	N(1)-Zr(1)-C(23)	91.92(9)
N(2)-C(11)	1.342(4)	C(19)-Zr(1)-C(23)	87.54(11)
N(2)-C(17)	1.464(4)	CNT1-Zr(1)-C(2)	28.49(7)
C(1)-C(2)	1.405(5)	N(2)-Zr(1)-C(2)	101.43(11)
C(1)-C(5)	1.411(5)	N(1)-Zr(1)-C(2)	94.72(10)
C(1)-C(6)	1.513(5)	C(19)-Zr(1)-C(2)	134.70(12)
C(2)-C(3)	1.408(5)	C(23)-Zr(1)-C(2)	115.48(10)
C(2)-C(7)	1.511(5)	CNT1-Zr(1)-C(1)	28.27(7)
C(3)-C(4)	1.425(6)	N(2)-Zr(1)-C(1)	86.28(11)
C(3)-C(8)	1.518(5)	N(1)-Zr(1)-C(1)	111.01(10)
C(4)-C(5)	1.403(5)	C(19)-Zr(1)-C(1)	105.09(12)
C(4)-C(9)	1.512(5)	C(23)-Zr(1)-C(1)	138.49(10)
C(5)-C(10)	1.505(5)	C(2)-Zr(1)-C(1)	32.42(11)
C(11)-C(12)	1.510(5)	CNT1-Zr(1)-C(3)	28.42(7)
C(13)-C(16)	1.527(5)	N(2)-Zr(1)-C(3)	133.81(11)
C(13)-C(14)	1.528(5)	N(1)-Zr(1)-C(3)	110.94(11)
C(13)-C(15)	1.539(5)	C(19)-Zr(1)-C(3)	124.39(13)
C(17)-C(18)	1.502(6)	C(23)-Zr(1)-C(3)	86.39(10)
C(19)-C(20)	1.539(5)	C(2)-Zr(1)-C(3)	32.40(11)
C(20)-C(21)	1.524(6)	C(1)-Zr(1)-C(3)	53.63(11)
C(21)-C(22)	1.473(9)	CNT1-Zr(1)-C(5)	28.07(7)
C(31)-C(32)	1.432(19)	N(2)-Zr(1)-C(5)	105.43(11)
C(32)-C(33)	1.41(2)	N(1)-Zr(1)-C(5)	143.27(10)
C(32)-C(34)#1	2.04(5)	C(19)-Zr(1)-C(5)	81.45(12)

C(23)-Zr(1)-C(5)	116.95(10)	C(5)-C(4)-C(3)	108.3(3)
C(2)-Zr(1)-C(5)	53.57(11)	C(5)-C(4)-C(9)	125.8(4)
C(1)-Zr(1)-C(5)	32.27(11)	C(3)-C(4)-C(9)	125.8(4)
C(3)-Zr(1)-C(5)	53.54(11)	C(5)-C(4)-Zr(1)	74.01(19)
CNT1-Zr(1)-C(4)	27.92(7)	C(3)-C(4)-Zr(1)	72.69(18)
N(2)-Zr(1)-C(4)	136.71(11)	C(9)-C(4)-Zr(1)	122.5(3)
N(1)-Zr(1)-C(4)	143.42(11)	C(4)-C(5)-C(1)	107.7(3)
C(19)-Zr(1)-C(4)	92.06(12)	C(4)-C(5)-C(10)	125.4(4)
C(23)-Zr(1)-C(4)	87.70(10)	C(1)-C(5)-C(10)	126.5(3)
C(2)-Zr(1)-C(4)	53.49(11)	C(4)-C(5)-Zr(1)	74.15(19)
C(1)-Zr(1)-C(4)	53.16(10)	C(1)-C(5)-Zr(1)	72.44(18)
C(3)-Zr(1)-C(4)	32.51(13)	C(10)-C(5)-Zr(1)	124.9(2)
C(5)-Zr(1)-C(4)	31.84(11)	N(1)-C(11)-N(2)	111.7(3)
C(11)-N(1)-C(13)	125.5(3)	N(1)-C(11)-C(12)	126.9(3)
C(11)-N(1)-Zr(1)	92.33(18)	N(2)-C(11)-C(12)	121.4(3)
C(13)-N(1)-Zr(1)	139.16(19)	N(1)-C(13)-C(16)	112.7(3)
C(11)-N(2)-C(17)	122.0(3)	N(1)-C(13)-C(14)	106.7(3)
C(11)-N(2)-Zr(1)	92.66(18)	C(16)-C(13)-C(14)	107.8(3)
C(17)-N(2)-Zr(1)	136.4(2)	N(1)-C(13)-C(15)	112.2(3)
C(2)-C(1)-C(5)	108.5(3)	C(16)-C(13)-C(15)	109.8(3)
C(2)-C(1)-C(6)	125.6(3)	C(14)-C(13)-C(15)	107.4(3)
C(5)-C(1)-C(6)	125.8(3)	N(2)-C(17)-C(18)	114.1(4)
C(2)-C(1)-Zr(1)	73.58(17)	C(20)-C(19)-Zr(1)	110.3(2)
C(5)-C(1)-Zr(1)	75.28(17)	C(21)-C(20)-C(19)	116.1(3)
C(6)-C(1)-Zr(1)	121.3(2)	C(22)-C(21)-C(20)	115.1(5)
C(1)-C(2)-C(3)	108.2(3)	C(33)-C(32)-C(31)	110(2)
C(1)-C(2)-C(7)	124.5(3)	C(33)-C(32)-C(34)#1	73.0(19)
C(3)-C(2)-C(7)	127.1(4)	C(31)-C(32)-C(34)#1	39(2)
C(1)-C(2)-Zr(1)	73.99(18)	C(34)-C(33)-C(32)	125(3)
C(3)-C(2)-Zr(1)	74.43(18)	C(33)-C(34)-C(35)	117(3)
C(7)-C(2)-Zr(1)	121.7(2)	C(33)-C(34)-C(32)#2	134(3)
C(2)-C(3)-C(4)	107.4(3)	C(35)-C(34)-C(32)#2	24(2)
C(2)-C(3)-C(8)	126.4(4)		
C(4)-C(3)-C(8)	125.8(4)		
C(2)-C(3)-Zr(1)	73.17(18)		
C(4)-C(3)-Zr(1)	74.80(19)		
C(8)-C(3)-Zr(1)	123.2(2)		

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x-y+2,z+1/3 #2 -x+y-1,-x+1,z-1/3

Table 34. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	32(1)	34(1)	33(1)	-2(1)	-3(1)	14(1)
N(1)	35(1)	35(1)	36(1)	-4(1)	-1(1)	16(1)
N(2)	55(2)	34(1)	39(1)	-6(1)	-3(1)	19(1)
C(1)	31(1)	47(2)	48(2)	-8(1)	-5(1)	14(1)
C(2)	35(2)	55(2)	47(2)	-3(1)	-4(1)	23(1)
C(3)	36(2)	50(2)	53(2)	-10(1)	4(1)	21(1)
C(4)	36(2)	63(2)	43(2)	-7(1)	-1(1)	19(2)
C(5)	33(1)	46(2)	49(2)	4(1)	-1(1)	14(1)
C(6)	45(2)	71(2)	69(3)	-31(2)	-15(2)	18(2)
C(7)	53(2)	85(3)	74(3)	19(2)	-6(2)	40(2)
C(8)	57(2)	62(2)	104(4)	-27(3)	6(2)	31(2)
C(9)	47(2)	97(3)	41(2)	-7(2)	0(1)	23(2)
C(10)	49(2)	58(2)	81(3)	21(2)	8(2)	19(2)
C(11)	39(2)	41(2)	35(1)	-2(1)	-8(1)	21(1)
C(12)	50(2)	55(2)	48(2)	-14(2)	2(2)	27(2)
C(13)	38(2)	36(1)	38(2)	1(1)	-4(1)	14(1)
C(14)	52(2)	35(1)	57(2)	-2(2)	0(2)	20(1)
C(15)	41(2)	46(2)	63(2)	-5(2)	-6(2)	14(2)
C(16)	71(2)	49(2)	42(2)	5(2)	-10(2)	18(2)
C(17)	91(3)	40(2)	60(2)	-8(2)	-6(2)	35(2)
C(18)	79(3)	50(2)	67(3)	-21(2)	0(2)	25(2)
C(19)	45(2)	48(2)	48(2)	5(1)	0(1)	24(2)
C(20)	49(2)	63(2)	66(2)	16(2)	5(2)	26(2)
C(21)	57(2)	79(3)	105(4)	3(3)	13(2)	38(2)
C(22)	102(4)	154(6)	108(5)	56(4)	15(3)	94(4)
C(23)	26(1)	35(1)	23(1)	-3(1)	-1(1)	10(1)

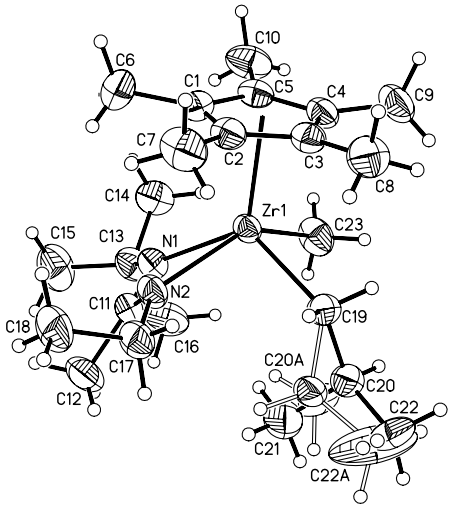
Table 35. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4d**.

	x	y	z	U(eq)
H(6A)	2932	8251	4224	100
H(6B)	3055	8847	3060	100
H(6C)	3624	8621	3247	100
H(7A)	2508	6406	3312	102
H(7B)	2485	6973	4368	102
H(7C)	3201	7109	3677	102
H(8A)	2524	6186	-206	110
H(8B)	1753	6021	-485	110
H(8C)	1978	5897	1146	110
H(9A)	2478	7800	-2472	101
H(9B)	1718	7192	-2091	101
H(9C)	2320	7023	-2391	101
H(10A)	3330	8962	-551	99
H(10B)	2849	9054	647	99
H(10C)	2543	8702	-953	99
H(12A)	118	6748	5794	76
H(12B)	414	7554	5568	76
H(12C)	776	7291	6737	76
H(14A)	750	5579	2400	74
H(14B)	529	5039	3758	74
H(14C)	1292	5685	3692	74
H(15A)	-371	5893	4710	80
H(15B)	-447	5163	4311	80
H(15C)	-261	5724	3010	80
H(16A)	1162	5986	6239	89
H(16B)	381	5375	6357	89
H(16C)	568	6151	6679	89
H(17A)	1046	8386	4348	75
H(17B)	1739	8780	3384	75
H(18A)	1677	8486	6521	103
H(18B)	1947	9232	5803	103
H(18C)	2376	8846	5569	103

H(19A)	1528	8462	935	56
H(19B)	1277	7973	-523	56
H(20A)	162	7333	444	72
H(20B)	397	7712	2040	72
H(21A)	-239	8110	769	95
H(21B)	531	8730	970	95
H(22A)	768	8670	-1508	162
H(22B)	73	8702	-1426	162
H(22C)	42	7985	-1743	162
H(23A)	196	6212	623	45
H(23B)	741	5981	174	45
H(23C)	679	6542	-824	45
H(31A)	1470	10819	7416	195
H(31B)	664	10444	7771	195
H(31C)	978	10987	6416	195
H(32A)	1246	10266	5139	126
H(32B)	939	9723	6500	126
H(33A)	-59	9370	5887	161
H(33B)	67	10118	5552	161
H(34A)	427	9525	3390	155
H(34B)	129	10035	3278	155
H(35A)	-640	9007	2376	133
H(35B)	-937	9147	3895	133
H(35C)	-628	8641	3918	133

Crystallographic analysis of compound 4e.

A colorless block with approximate orthogonal dimensions 0.484 x 0.189 x 0.165mm^3 was placed and optically centered on the Bruker SMART CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans (25 frames/series) that were well distributed in reciprocal space. Data frames were collected [MoKα] with alternating 0.3° wide ω-scans, 20 seconds per frame, 606 frames per series and 0.2° wide ω-scans, 20 seconds per frame, 909 frames per series. Five complete series were collected, three of the former and two of the latter at varying φ angles (φ=0°, 72°, 144°, 216°, 288°) with an additional 200 frames a repeat of the first series for redundancy and decay purposes, with a crystal to detector distance of 4.880cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 19265 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 5616 unique [R(int)=0.0241].



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with dual Pentium 450MHz processors and 384MB of extended memory. The SHELXTL[3] program package was now implemented, XPREP, to determine the probable space group and set up the initial files. System symmetry and lack of systematic absences indicated the unique centrosymmetric triclinic space group P-1 (no.2). The structure was determined by direct methods with the successful location of nearly the entire molecule using the program XS[4]. The structure was refined with XL[5]. After the initial refinement, a difference-Fourier map revealed the locations of all of the remaining non-hydrogen atoms. After several refinement cycles, all of the atoms were refined isotropically, then anisotropically. Disorder was found in the isobutyl ligand and modeled into two components with a final occupancy ratio of 0.61:0.39. Hydrogen atoms were initially placed in calculated positions and later those fully occupied were allowed to refine freely (xyzU). The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=2.73%, wR(F^2)=6.51%, GOF=1.062 for all 5566 unique reflections [R(F)=2.41%, wR(F^2)=6.33% for those 5125 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is therefore both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0640*P)^2+0.0*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

Table 36. Crystal data and structure refinement for **4e**.

Identification code	792f	
Empirical formula	C23 H44 N2 Zr	
Formula weight	439.82	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8883(5) Å	α= 88.7250(10)°.
	b = 9.2527(5) Å	β= 84.7680(10)°.
	c = 16.3360(9) Å	γ= 65.9390(10)°.
Volume	1221.48(12) $Å^3$	
Z	2	
Density (calculated)	1.196 Mg/m^3	
Absorption coefficient	0.459 mm^{-1}	
F(000)	472	
Crystal size	0.165 x 0.189 x 0.484 mm^3	
Theta range for data collection	2.41 to 27.49°.	
Index ranges	-11<=h<=11, -12<=k<=12, -21<=l<=21	
Reflections collected	19265	
Independent reflections	5566 [R(int) = 0.0241]	
Completeness to theta = 27.49°	99.4 %	
Absorption correction	Empirical, SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5566 / 3 / 417	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0241, wR2 = 0.0633 [5125 Data]	
R indices (all data)	R1 = 0.0273, wR2 = 0.0651	
Largest diff. peak and hole	0.673 and -0.457 $e.Å^{-3}$	

Table 37. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	5957(1)	1282(1)	2448(1)	30(1)
N(1)	7464(2)	2532(2)	1797(1)	37(1)
N(2)	7786(2)	1862(2)	3098(1)	37(1)
CNT1	6614(1)	-1326(1)	2393(1)	0
C(1)	7983(2)	-1505(2)	2107(1)	39(1)
C(2)	7458(2)	-1516(2)	2955(1)	37(1)
C(3)	5771(2)	-1263(2)	3027(1)	36(1)
C(4)	5245(2)	-1090(2)	2221(1)	37(1)
C(5)	6614(2)	-1254(2)	1654(1)	38(1)
C(6)	9712(2)	-1809(3)	1755(2)	60(1)
C(7)	8549(3)	-1902(3)	3649(1)	57(1)
C(8)	4803(3)	-1383(3)	3809(1)	54(1)
C(9)	3560(2)	-923(3)	2016(2)	54(1)
C(10)	6638(4)	-1285(3)	730(1)	58(1)
C(11)	7903(2)	2847(2)	2512(1)	38(1)
C(12)	8379(3)	4197(3)	2683(2)	56(1)
C(13)	7603(2)	3307(2)	1005(1)	46(1)
C(14)	7417(3)	2271(2)	335(1)	52(1)
C(15)	9323(3)	3333(4)	819(2)	72(1)
C(16)	6229(3)	4969(2)	965(2)	61(1)
C(17)	8084(2)	2039(2)	3949(1)	46(1)
C(18)	9919(3)	1375(3)	4081(1)	60(1)
C(19)	4168(2)	2313(2)	3588(1)	39(1)
C(20)	3005(4)	4065(3)	3682(2)	41(1)
C(21)	3911(5)	5108(4)	3472(3)	64(1)
C(22)	2120(7)	4488(8)	4533(5)	54(1)
C(20A)	3778(7)	4116(6)	3760(3)	45(1)
C(21A)	3103(9)	5226(6)	3060(4)	67(2)
C(22A)	2400(20)	4751(18)	4500(10)	127(7)
C(23)	3836(2)	2539(3)	1635(1)	51(1)

Table 38. Bond lengths [Å] and angles [°] for **4e**.

Zr(1)-CNT1	2.2415(12)
Zr(1)-N(2)	2.2601(12)
Zr(1)-N(1)	2.2821(12)
Zr(1)-C(19)	2.2824(16)
Zr(1)-C(23)	2.2957(17)
Zr(1)-C(1)	2.5099(15)
Zr(1)-C(5)	2.5328(15)
Zr(1)-C(2)	2.5418(15)
Zr(1)-C(4)	2.5632(15)
Zr(1)-C(3)	2.5804(15)
Zr(1)-C(11)	2.6790(15)
N(1)-C(11)	1.3393(19)
N(1)-C(13)	1.485(2)
N(2)-C(11)	1.334(2)
N(2)-C(17)	1.4627(19)
C(1)-C(5)	1.418(2)
C(1)-C(2)	1.422(2)
C(1)-C(6)	1.505(2)
C(2)-C(3)	1.414(2)
C(2)-C(7)	1.501(2)
C(3)-C(4)	1.421(2)
C(3)-C(8)	1.503(2)
C(4)-C(5)	1.419(2)
C(4)-C(9)	1.510(2)
C(5)-C(10)	1.508(2)
C(6)-H(6A)	1.00(3)
C(6)-H(6B)	0.86(3)
C(6)-H(6C)	0.92(3)
C(7)-H(7A)	0.99(3)
C(7)-H(7B)	0.94(3)
C(7)-H(7C)	1.00(3)
C(8)-H(8A)	0.95(3)
C(8)-H(8B)	0.97(3)
C(8)-H(8C)	0.97(3)

C(9)-H(9A)	0.97(3)
C(9)-H(9B)	0.91(2)
C(9)-H(9C)	0.93(3)
C(10)-H(10A)	0.89(3)
C(10)-H(10B)	0.84(3)
C(10)-H(10C)	0.99(3)
C(11)-C(12)	1.512(2)
C(12)-H(12A)	0.95(3)
C(12)-H(12B)	0.91(3)
C(12)-H(12C)	0.93(3)
C(13)-C(16)	1.529(3)
C(13)-C(14)	1.535(3)
C(13)-C(15)	1.541(3)
C(14)-H(14A)	0.94(2)
C(14)-H(14B)	1.00(2)
C(14)-H(14C)	0.97(2)
C(15)-H(15A)	0.98(3)
C(15)-H(15B)	1.02(3)
C(15)-H(15C)	0.97(3)
C(16)-H(16A)	0.99(3)
C(16)-H(16B)	0.93(2)
C(16)-H(16C)	0.95(3)
C(17)-C(18)	1.525(2)
C(17)-H(17A)	0.962(19)
C(17)-H(17B)	0.98(2)
C(18)-H(18A)	0.99(2)
C(18)-H(18B)	0.92(2)
C(18)-H(18C)	0.97(2)
C(19)-C(20)	1.528(3)
C(19)-C(20A)	1.585(5)
C(19)-H(19A)	0.94(2)
C(19)-H(19B)	0.92(2)
C(20)-C(21)	1.505(5)
C(20)-C(22)	1.509(8)
C(20)-H(20)	1.0000
C(21)-H(21A)	0.9800

C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(20A)-C(21A)	1.515(8)
C(20A)-C(22A)	1.576(16)
C(20A)-H(20A)	1.0000
C(21A)-H(21D)	0.9800
C(21A)-H(21E)	0.9800
C(21A)-H(21F)	0.9800
C(22A)-H(22D)	0.9800
C(22A)-H(22E)	0.9800
C(22A)-H(22F)	0.9800
C(23)-H(23A)	0.99(2)
C(23)-H(23B)	0.96(3)
C(23)-H(23C)	0.91(3)

CNT1-Zr(1)-N(2)	112.38(5)
CNT1-Zr(1)-N(1)	125.45(5)
N(2)-Zr(1)-N(1)	58.30(5)
CNT1-Zr(1)-C(19)	108.19(6)
N(2)-Zr(1)-C(19)	86.04(5)
N(1)-Zr(1)-C(19)	122.91(5)
CNT1-Zr(1)-C(23)	108.59(7)
N(2)-Zr(1)-C(23)	138.07(6)
N(1)-Zr(1)-C(23)	90.67(6)
C(19)-Zr(1)-C(23)	89.56(7)
CNT1-Zr(1)-C(1)	28.77(4)
N(2)-Zr(1)-C(1)	93.44(5)
N(1)-Zr(1)-C(1)	97.36(5)
C(19)-Zr(1)-C(1)	130.51(6)
C(23)-Zr(1)-C(1)	119.98(7)
CNT1-Zr(1)-C(5)	28.47(5)
N(2)-Zr(1)-C(5)	125.49(5)
N(1)-Zr(1)-C(5)	107.62(5)

C(19)-Zr(1)-C(5)	129.45(6)
C(23)-Zr(1)-C(5)	88.40(7)
C(1)-Zr(1)-C(5)	32.65(5)
CNT1-Zr(1)-C(2)	28.26(5)
N(2)-Zr(1)-C(2)	85.67(5)
N(1)-Zr(1)-C(2)	119.10(5)
C(19)-Zr(1)-C(2)	98.27(6)
C(23)-Zr(1)-C(2)	136.15(6)
C(1)-Zr(1)-C(2)	32.70(5)
C(5)-Zr(1)-C(2)	53.74(5)
CNT1-Zr(1)-C(4)	28.03(4)
N(2)-Zr(1)-C(4)	138.93(5)
N(1)-Zr(1)-C(4)	139.20(5)
C(19)-Zr(1)-C(4)	97.40(6)
C(23)-Zr(1)-C(4)	82.99(6)
C(1)-Zr(1)-C(4)	53.77(5)
C(5)-Zr(1)-C(4)	32.32(5)
C(2)-Zr(1)-C(4)	53.29(5)
CNT1-Zr(1)-C(3)	27.94(5)
N(2)-Zr(1)-C(3)	110.54(5)
N(1)-Zr(1)-C(3)	150.05(5)
C(19)-Zr(1)-C(3)	80.26(5)
C(23)-Zr(1)-C(3)	109.71(6)
C(1)-Zr(1)-C(3)	53.70(5)
C(5)-Zr(1)-C(3)	53.45(5)
C(2)-Zr(1)-C(3)	32.03(5)
C(4)-Zr(1)-C(3)	32.08(5)
CNT1-Zr(1)-C(11)	130.11(5)
N(2)-Zr(1)-C(11)	29.82(5)
N(1)-Zr(1)-C(11)	29.98(5)
C(19)-Zr(1)-C(11)	100.37(5)
C(23)-Zr(1)-C(11)	111.71(6)
C(1)-Zr(1)-C(11)	103.15(5)
C(5)-Zr(1)-C(11)	126.97(5)
C(2)-Zr(1)-C(11)	109.14(5)
C(4)-Zr(1)-C(11)	156.87(5)

C(3)-Zr(1)-C(11)	138.58(5)
C(11)-N(1)-C(13)	125.23(13)
C(11)-N(1)-Zr(1)	91.65(9)
C(13)-N(1)-Zr(1)	140.14(10)
C(11)-N(2)-C(17)	122.00(14)
C(11)-N(2)-Zr(1)	92.75(9)
C(17)-N(2)-Zr(1)	136.86(10)
C(5)-C(1)-C(2)	107.74(13)
C(5)-C(1)-C(6)	126.25(17)
C(2)-C(1)-C(6)	125.91(17)
C(5)-C(1)-Zr(1)	74.56(9)
C(2)-C(1)-Zr(1)	74.89(8)
C(6)-C(1)-Zr(1)	119.38(13)
C(3)-C(2)-C(1)	108.38(13)
C(3)-C(2)-C(7)	125.59(16)
C(1)-C(2)-C(7)	125.75(16)
C(3)-C(2)-Zr(1)	75.49(8)
C(1)-C(2)-Zr(1)	72.42(8)
C(7)-C(2)-Zr(1)	122.98(12)
C(2)-C(3)-C(4)	107.72(13)
C(2)-C(3)-C(8)	125.09(15)
C(4)-C(3)-C(8)	126.71(16)
C(2)-C(3)-Zr(1)	72.48(8)
C(4)-C(3)-Zr(1)	73.29(8)
C(8)-C(3)-Zr(1)	126.08(12)
C(5)-C(4)-C(3)	108.17(13)
C(5)-C(4)-C(9)	126.68(16)
C(3)-C(4)-C(9)	124.90(16)
C(5)-C(4)-Zr(1)	72.66(8)
C(3)-C(4)-Zr(1)	74.63(8)
C(9)-C(4)-Zr(1)	123.22(12)
C(1)-C(5)-C(4)	107.99(13)
C(1)-C(5)-C(10)	126.12(17)
C(4)-C(5)-C(10)	125.73(17)
C(1)-C(5)-Zr(1)	72.79(8)
C(4)-C(5)-Zr(1)	75.02(8)

C(10)-C(5)-Zr(1)	121.72(12)
C(1)-C(6)-H(6A)	112.2(16)
C(1)-C(6)-H(6B)	107.1(18)
H(6A)-C(6)-H(6B)	111(2)
C(1)-C(6)-H(6C)	116(2)
H(6A)-C(6)-H(6C)	112(3)
H(6B)-C(6)-H(6C)	97(3)
C(2)-C(7)-H(7A)	113.8(14)
C(2)-C(7)-H(7B)	110.8(16)
H(7A)-C(7)-H(7B)	108(2)
C(2)-C(7)-H(7C)	109.0(16)
H(7A)-C(7)-H(7C)	104(2)
H(7B)-C(7)-H(7C)	111(2)
C(3)-C(8)-H(8A)	109.9(14)
C(3)-C(8)-H(8B)	110.3(16)
H(8A)-C(8)-H(8B)	107(2)
C(3)-C(8)-H(8C)	111.7(17)
H(8A)-C(8)-H(8C)	103(2)
H(8B)-C(8)-H(8C)	114(2)
C(4)-C(9)-H(9A)	109.7(15)
C(4)-C(9)-H(9B)	110.6(15)
H(9A)-C(9)-H(9B)	108(2)
C(4)-C(9)-H(9C)	112.3(15)
H(9A)-C(9)-H(9C)	107(2)
H(9B)-C(9)-H(9C)	110(2)
C(5)-C(10)-H(10A)	113.4(19)
C(5)-C(10)-H(10B)	112(2)
H(10A)-C(10)-H(10B)	104(3)
C(5)-C(10)-H(10C)	109.3(17)
H(10A)-C(10)-H(10C)	109(2)
H(10B)-C(10)-H(10C)	109(3)
N(2)-C(11)-N(1)	111.71(13)
N(2)-C(11)-C(12)	122.04(15)
N(1)-C(11)-C(12)	126.15(16)
N(2)-C(11)-Zr(1)	57.42(7)
N(1)-C(11)-Zr(1)	58.37(8)

C(12)-C(11)-Zr(1)	158.18(13)
C(11)-C(12)-H(12A)	108.8(17)
C(11)-C(12)-H(12B)	109.6(18)
H(12A)-C(12)-H(12B)	106(2)
C(11)-C(12)-H(12C)	113.8(16)
H(12A)-C(12)-H(12C)	111(2)
H(12B)-C(12)-H(12C)	107(2)
N(1)-C(13)-C(16)	112.12(15)
N(1)-C(13)-C(14)	106.02(13)
C(16)-C(13)-C(14)	108.36(17)
N(1)-C(13)-C(15)	112.06(16)
C(16)-C(13)-C(15)	111.11(19)
C(14)-C(13)-C(15)	106.82(18)
C(13)-C(14)-H(14A)	109.9(12)
C(13)-C(14)-H(14B)	110.9(13)
H(14A)-C(14)-H(14B)	108.1(18)
C(13)-C(14)-H(14C)	109.5(13)
H(14A)-C(14)-H(14C)	109.1(18)
H(14B)-C(14)-H(14C)	109.4(17)
C(13)-C(15)-H(15A)	109.5(16)
C(13)-C(15)-H(15B)	108.8(15)
H(15A)-C(15)-H(15B)	109(2)
C(13)-C(15)-H(15C)	114.8(15)
H(15A)-C(15)-H(15C)	107(2)
H(15B)-C(15)-H(15C)	108(2)
C(13)-C(16)-H(16A)	109.2(15)
C(13)-C(16)-H(16B)	107.1(15)
H(16A)-C(16)-H(16B)	112(2)
C(13)-C(16)-H(16C)	112.0(15)
H(16A)-C(16)-H(16C)	108(2)
H(16B)-C(16)-H(16C)	109(2)
N(2)-C(17)-C(18)	112.85(15)
N(2)-C(17)-H(17A)	108.3(11)
C(18)-C(17)-H(17A)	105.7(11)
N(2)-C(17)-H(17B)	112.7(11)
C(18)-C(17)-H(17B)	109.1(12)

H(17A)-C(17)-H(17B)	108.0(16)
C(17)-C(18)-H(18A)	113.8(13)
C(17)-C(18)-H(18B)	111.8(15)
H(18A)-C(18)-H(18B)	106(2)
C(17)-C(18)-H(18C)	108.6(14)
H(18A)-C(18)-H(18C)	109.2(19)
H(18B)-C(18)-H(18C)	107(2)
C(20)-C(19)-C(20A)	27.03(17)
C(20)-C(19)-Zr(1)	122.90(15)
C(20A)-C(19)-Zr(1)	113.2(2)
C(20)-C(19)-H(19A)	98.0(14)
C(20A)-C(19)-H(19A)	124.0(14)
Zr(1)-C(19)-H(19A)	109.0(14)
C(20)-C(19)-H(19B)	113.9(13)
C(20A)-C(19)-H(19B)	97.9(13)
Zr(1)-C(19)-H(19B)	108.1(12)
H(19A)-C(19)-H(19B)	102.3(19)
C(21)-C(20)-C(22)	109.6(4)
C(21)-C(20)-C(19)	111.4(3)
C(22)-C(20)-C(19)	112.6(3)
C(21)-C(20)-H(20)	107.7
C(22)-C(20)-H(20)	107.7
C(19)-C(20)-H(20)	107.7
C(21A)-C(20A)-C(22A)	105.2(7)
C(21A)-C(20A)-C(19)	115.5(4)
C(22A)-C(20A)-C(19)	108.8(7)
C(21A)-C(20A)-H(20A)	109.0
C(22A)-C(20A)-H(20A)	109.0
C(19)-C(20A)-H(20A)	109.0
C(20A)-C(21A)-H(21D)	109.5
C(20A)-C(21A)-H(21E)	109.5
H(21D)-C(21A)-H(21E)	109.5
C(20A)-C(21A)-H(21F)	109.5
H(21D)-C(21A)-H(21F)	109.5
H(21E)-C(21A)-H(21F)	109.5
C(20A)-C(22A)-H(22D)	109.5

C(20A)-C(22A)-H(22E)	109.5
H(22D)-C(22A)-H(22E)	109.5
C(20A)-C(22A)-H(22F)	109.5
H(22D)-C(22A)-H(22F)	109.5
H(22E)-C(22A)-H(22F)	109.5
Zr(1)-C(23)-H(23A)	104.3(13)
Zr(1)-C(23)-H(23B)	115.2(17)
H(23A)-C(23)-H(23B)	108(2)
Zr(1)-C(23)-H(23C)	113.8(18)
H(23A)-C(23)-H(23C)	108(2)
H(23B)-C(23)-H(23C)	107(2)

Symmetry transformations used to generate equivalent atoms:

Table 39. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	30(1)	31(1)	33(1)	0(1)	-8(1)	-14(1)
N(1)	39(1)	38(1)	38(1)	1(1)	-4(1)	-20(1)
N(2)	35(1)	47(1)	37(1)	-3(1)	-9(1)	-21(1)
C(1)	34(1)	33(1)	47(1)	-4(1)	-3(1)	-11(1)
C(2)	39(1)	31(1)	41(1)	3(1)	-13(1)	-12(1)
C(3)	40(1)	30(1)	39(1)	1(1)	-6(1)	-15(1)
C(4)	37(1)	33(1)	45(1)	0(1)	-12(1)	-17(1)
C(5)	47(1)	33(1)	36(1)	-4(1)	-8(1)	-18(1)
C(6)	39(1)	58(1)	78(1)	-7(1)	7(1)	-15(1)
C(7)	62(1)	51(1)	61(1)	13(1)	-35(1)	-20(1)
C(8)	65(1)	50(1)	50(1)	6(1)	4(1)	-28(1)
C(9)	48(1)	51(1)	75(1)	3(1)	-23(1)	-29(1)
C(10)	89(2)	55(1)	37(1)	-4(1)	-8(1)	-37(1)
C(11)	31(1)	39(1)	46(1)	-6(1)	-3(1)	-18(1)
C(12)	65(1)	56(1)	63(1)	-7(1)	-8(1)	-40(1)
C(13)	57(1)	47(1)	42(1)	5(1)	-3(1)	-30(1)
C(14)	68(1)	53(1)	39(1)	3(1)	-2(1)	-30(1)
C(15)	76(2)	98(2)	61(1)	10(1)	4(1)	-59(2)
C(16)	87(2)	42(1)	59(1)	10(1)	-14(1)	-30(1)
C(17)	42(1)	60(1)	41(1)	-7(1)	-12(1)	-24(1)
C(18)	48(1)	77(2)	62(1)	-1(1)	-24(1)	-30(1)
C(19)	37(1)	37(1)	42(1)	-5(1)	-5(1)	-12(1)
C(20)	37(2)	39(2)	47(2)	-3(1)	-6(1)	-13(1)
C(21)	54(2)	39(2)	99(3)	1(2)	-4(2)	-18(2)
C(22)	51(2)	40(2)	49(3)	-11(2)	-1(2)	3(2)
C(20A)	33(2)	38(3)	62(3)	-12(2)	-12(2)	-12(2)
C(21A)	81(4)	39(3)	66(3)	-7(2)	10(3)	-13(3)
C(22A)	226(17)	59(6)	44(5)	-7(4)	1(8)	-7(8)
C(23)	48(1)	51(1)	59(1)	13(1)	-25(1)	-22(1)

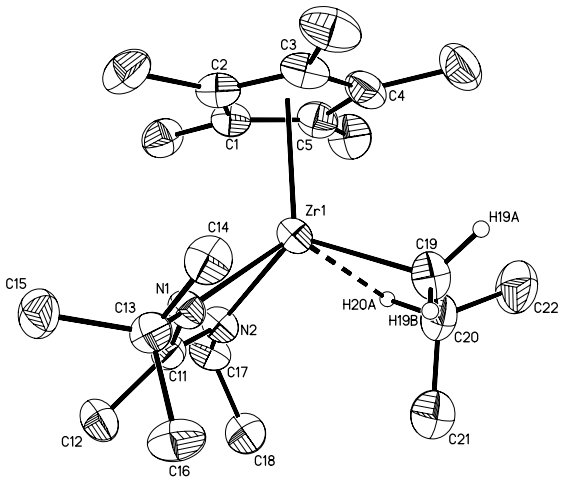
Table 40. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4e**.

	x	y	z	U(eq)
H(6A)	10460(40)	-2960(40)	1742(17)	93(8)
H(6B)	10060(30)	-1270(30)	2050(17)	83(9)
H(6C)	9800(40)	-1330(40)	1270(20)	110(11)
H(7A)	7970(30)	-1390(30)	4177(16)	73(7)
H(7B)	9440(30)	-1610(30)	3522(15)	80(8)
H(7C)	8950(30)	-3060(40)	3766(17)	98(9)
H(8A)	5080(30)	-2470(30)	3936(14)	70(7)
H(8B)	3620(40)	-890(30)	3745(16)	91(9)
H(8C)	5120(40)	-990(40)	4277(18)	97(9)
H(9A)	3510(30)	-1950(30)	2028(15)	76(7)
H(9B)	3360(30)	-530(30)	1500(15)	65(7)
H(9C)	2720(30)	-280(30)	2395(15)	74(7)
H(10A)	7160(40)	-730(40)	479(18)	98(9)
H(10B)	5680(40)	-870(40)	580(20)	109(12)
H(10C)	7190(40)	-2390(40)	527(18)	103(9)
H(12A)	9560(40)	3820(30)	2607(17)	93(9)
H(12B)	8080(30)	4510(30)	3217(18)	85(8)
H(12C)	7880(30)	5080(30)	2367(15)	76(7)
H(14A)	6390(30)	2190(20)	434(12)	52(5)
H(14B)	8310(30)	1180(30)	330(13)	63(6)
H(14C)	7460(30)	2740(30)	-198(14)	61(6)
H(15A)	9460(30)	3610(30)	245(18)	90(8)
H(15B)	10210(30)	2230(30)	916(15)	80(8)
H(15C)	9530(30)	4080(30)	1151(15)	77(7)
H(16A)	5140(30)	4910(30)	1074(15)	78(7)
H(16B)	6360(30)	5350(30)	444(15)	70(7)
H(16C)	6300(30)	5670(30)	1361(15)	74(7)
H(17A)	7630(20)	1430(20)	4293(11)	45(5)
H(17B)	7560(20)	3140(20)	4146(11)	47(5)
H(18A)	10530(30)	250(30)	3912(14)	64(6)

H(18B)	10080(30)	1440(30)	4623(15)	70(7)
H(18C)	10410(30)	2010(30)	3773(14)	68(7)
H(19A)	3360(30)	1900(30)	3620(14)	69(7)
H(19B)	4730(30)	1900(20)	4047(13)	53(5)
H(20)	2148	4293	3284	50
H(21A)	4776	4895	3846	96
H(21B)	3131	6221	3528	96
H(21C)	4417	4886	2904	96
H(22A)	1438	5629	4571	81
H(22B)	2935	4199	4940	81
H(22C)	1413	3911	4640	81
H(20A)	4804	4199	3913	54
H(21D)	2165	5070	2869	100
H(21E)	3972	5003	2606	100
H(21F)	2736	6324	3251	100
H(22D)	2267	5810	4666	190
H(22E)	2722	4034	4965	190
H(22F)	1349	4802	4330	190
H(23A)	2860(30)	2460(30)	1942(14)	69(7)
H(23B)	3980(30)	2070(40)	1102(18)	98(9)
H(23C)	3600(30)	3580(40)	1564(17)	90(9)

Crystallographic analysis of compound 5e.

An orange block with approximate orthogonal dimensions 0.27 x 0.24 x 0.13mm^3 was placed and optically centered on the Bruker SMART CCD system at –100°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 45 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.2° wide ω-scans, 20 seconds per frame and 909 frames per series. Six data series were collected, five at varying φ angles (φ=0°, 72°, 144°, 216°, 288°), a sixth composed of 909 0.2° wide φ-scans with fixed ω=0° and finally a partial repeat of the first series, 300 frames, for decay purposes. The crystal to detector distance was 4.442cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 43220 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 10611 unique [R(int)=0.0280]



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, lack of systematic absences and intensity statistics indicated the centrosymmetric triclinic space group P-1 (no. 2). The structure was determined by direct methods with the successful location of nearly the entire ensemble using the program XS[4]. The structure was refined with XL[5]. A single least-squares difference-Fourier cycle was required to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Nearly all of the hydrogen atoms were placed initially in calculated positions, however those attached to C(19) and C(20) were located directly from an additional difference-Fourier map and allowed to refine freely. All of the hydrogen atoms were allowed to refine freely during the final stages of refinement with soft restraints applied to those hydrogen atoms attached to C(7), C(8) and C(9). The final structure was refined to convergence [$\Delta/\sigma \leq 0.002$] with R(F)=6.00%, wR(F^2)=13.23%, GOF=1.079 for all 10584 unique reflections [R(F)=4.60%, wR(F^2)=12.34% for those 8573 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0904*P)^2+0.1078*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

Table 46. Crystal data and structure refinement for **5e**.

Identification code	1005ffmi	
Empirical formula	C46 H41 B F20 N2 Zr	
Formula weight	1103.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.2046(8) Å	α= 70.9290(10)°.
	b = 13.3258(9) Å	β= 72.1160(10)°.
	c = 17.3270(12) Å	γ = 77.0170(10)°.
Volume	2304.6(3) $Å^3$	
Z	2	
Density (calculated)	1.591 Mg/m^3	
Absorption coefficient	0.356 mm^{-1}	
F(000)	1112	
Crystal size	0.27 x 0.24 x 0.13 mm^3	
Theta range for data collection	1.78 to 27.50°.	
Index ranges	-14<=h<=14, -17<=k<=17, -22<=l<=22	
Reflections collected	21038	
Independent reflections	10584 [R(int) = 0.0203]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical, SADABS (multi-scan)	
Max. and min. transmission	0.9539 and 0.9110	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10584 / 21 / 798	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1234 [8573 Data]	
R indices (all data)	R1 = 0.0600, wR2 = 0.1323	
Largest diff. peak and hole	1.164 and -0.956 $e.Å^{-3}$	

Table 47. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	7059(1)	1748(1)	7526(1)	30(1)
N(1)	6776(2)	1102(1)	6627(1)	31(1)
N(2)	6125(2)	2832(2)	6562(1)	32(1)
CNT1	5942(1)	1474(1)	8839(1)	0
C(1)	5019(2)	1938(2)	8590(1)	35(1)
C(2)	5461(2)	818(2)	8727(1)	36(1)
C(3)	6569(2)	610(2)	9019(2)	40(1)
C(4)	6810(2)	1588(2)	9066(2)	41(1)
C(5)	5853(2)	2416(2)	8792(2)	37(1)
C(6)	3805(3)	2475(2)	8341(2)	44(1)
C(7)	4789(3)	0(2)	8664(2)	48(1)
C(8)	7344(3)	-473(2)	9271(2)	53(1)
C(9)	7784(3)	1678(3)	9456(2)	56(1)
C(10)	5662(3)	3565(2)	8804(2)	51(1)
C(11)	6232(2)	2064(2)	6201(1)	30(1)
C(12)	5795(3)	2254(2)	5429(2)	39(1)
C(13)	7256(2)	108(2)	6361(1)	32(1)
C(14)	7893(3)	-638(2)	7047(2)	39(1)
C(15)	6197(3)	-425(2)	6331(2)	42(1)
C(16)	8252(3)	315(2)	5514(2)	46(1)
C(17)	5499(2)	3925(2)	6261(2)	38(1)
C(18)	6313(3)	4614(2)	5496(2)	44(1)
C(19)	9075(3)	1770(2)	7381(2)	45(1)
C(20)	8833(3)	2987(2)	7054(2)	49(1)
C(21)	9342(3)	3375(3)	6112(2)	64(1)
C(22)	9280(4)	3581(3)	7518(3)	64(1)
B(31)	2664(2)	7424(2)	7790(2)	28(1)
C(31)	2130(2)	6957(2)	7204(1)	29(1)
C(32)	1315(2)	7515(2)	6691(1)	29(1)
C(33)	820(2)	7053(2)	6267(1)	33(1)
C(34)	1132(2)	5970(2)	6346(2)	34(1)

C(35)	1926(2)	5368(2)	6853(2)	33(1)
C(36)	2384(2)	5868(2)	7265(1)	31(1)
C(37)	1818(2)	6878(2)	8754(1)	32(1)
C(38)	510(2)	7172(2)	8960(2)	35(1)
C(39)	-298(2)	6749(2)	9726(2)	41(1)
C(40)	192(3)	5978(2)	10348(2)	44(1)
C(41)	1472(3)	5635(2)	10175(2)	41(1)
C(42)	2252(2)	6065(2)	9393(2)	36(1)
C(43)	4215(2)	7113(2)	7682(1)	30(1)
C(44)	4749(2)	7308(2)	8237(1)	32(1)
C(45)	6022(2)	7095(2)	8207(2)	35(1)
C(46)	6861(2)	6688(2)	7571(2)	36(1)
C(47)	6396(2)	6509(2)	6990(2)	37(1)
C(48)	5104(2)	6729(2)	7048(1)	32(1)
C(49)	2481(2)	8753(2)	7530(1)	30(1)
C(50)	2993(2)	9321(2)	6702(2)	33(1)
C(51)	2973(2)	10416(2)	6418(2)	38(1)
C(52)	2463(2)	11016(2)	6984(2)	41(1)
C(53)	1960(2)	10504(2)	7814(2)	38(1)
C(54)	1956(2)	9400(2)	8065(2)	33(1)
F(32)	935(1)	8582(1)	6578(1)	35(1)
F(33)	32(1)	7645(1)	5789(1)	42(1)
F(34)	675(2)	5512(1)	5935(1)	46(1)
F(35)	2242(1)	4312(1)	6938(1)	44(1)
F(36)	3139(1)	5224(1)	7766(1)	37(1)
F(38)	-34(1)	7933(1)	8384(1)	41(1)
F(39)	-1552(2)	7087(1)	9874(1)	55(1)
F(40)	-571(2)	5562(1)	11101(1)	61(1)
F(41)	1971(2)	4871(1)	10766(1)	59(1)
F(42)	3483(1)	5642(1)	9286(1)	43(1)
F(44)	3993(1)	7714(1)	8868(1)	39(1)
F(45)	6459(1)	7294(1)	8777(1)	45(1)
F(46)	8109(1)	6493(1)	7514(1)	47(1)
F(47)	7202(1)	6138(1)	6357(1)	50(1)
F(48)	4755(1)	6543(1)	6429(1)	39(1)
F(50)	3558(1)	8779(1)	6114(1)	37(1)

F(51)	3466(2)	10901(1)	5597(1)	50(1)
F(52)	2467(2)	12088(1)	6726(1)	59(1)
F(53)	1468(2)	11077(1)	8381(1)	49(1)
F(54)	1408(1)	8996(1)	8889(1)	42(1)

Table 48. Bond lengths [Å] and angles [°] for **5e**.

Zr(1)-N(1)	2.1376(18)	C(9)-H(9B)	0.989(16)
Zr(1)-N(2)	2.1882(18)	C(9)-H(9C)	0.955(17)
Zr(1)-CNT1	2.1884(11)	C(10)-H(10A)	0.99(4)
Zr(1)-C(19)	2.202(3)	C(10)-H(10B)	0.95(4)
Zr(1)-C(2)	2.469(2)	C(10)-H(10C)	1.00(5)
Zr(1)-C(1)	2.479(2)	C(11)-C(12)	1.490(3)
Zr(1)-C(3)	2.497(2)	C(12)-H(12A)	0.98(4)
Zr(1)-C(5)	2.519(2)	C(12)-H(12B)	0.85(4)
Zr(1)-C(4)	2.538(2)	C(12)-H(12C)	0.92(4)
Zr(1)-H(20A)	2.25(3)	C(13)-C(14)	1.528(3)
N(1)-C(11)	1.366(3)	C(13)-C(16)	1.531(3)
N(1)-C(13)	1.477(3)	C(13)-C(15)	1.535(3)
N(2)-C(11)	1.331(3)	C(14)-H(14A)	1.00(3)
N(2)-C(17)	1.468(3)	C(14)-H(14B)	0.96(3)
C(1)-C(5)	1.421(4)	C(14)-H(14C)	0.96(3)
C(1)-C(2)	1.428(3)	C(15)-H(15A)	0.95(3)
C(1)-C(6)	1.506(3)	C(15)-H(15B)	0.92(3)
C(2)-C(3)	1.419(4)	C(15)-H(15C)	0.98(3)
C(2)-C(7)	1.505(4)	C(16)-H(16A)	0.88(3)
C(3)-C(4)	1.421(4)	C(16)-H(16B)	0.91(4)
C(3)-C(8)	1.512(3)	C(16)-H(16C)	0.98(4)
C(4)-C(5)	1.425(3)	C(17)-C(18)	1.507(4)
C(4)-C(9)	1.493(4)	C(17)-H(17A)	0.90(3)
C(5)-C(10)	1.504(4)	C(17)-H(17B)	1.02(3)
C(6)-H(6A)	0.99(4)	C(18)-H(18A)	0.98(4)
C(6)-H(6B)	1.05(4)	C(18)-H(18B)	1.04(3)
C(6)-H(6C)	1.00(3)	C(18)-H(18C)	0.97(3)
C(7)-H(7A)	0.952(17)	C(19)-C(20)	1.524(4)
C(7)-H(7B)	0.956(17)	C(19)-H(19A)	1.02(4)
C(7)-H(7C)	0.958(16)	C(19)-H(19B)	0.96(3)
C(8)-H(8A)	0.946(18)	C(20)-C(21)	1.505(5)
C(8)-H(8B)	0.969(17)	C(20)-C(22)	1.538(4)
C(8)-H(8C)	1.013(17)	C(20)-H(20A)	1.09(3)
C(9)-H(9A)	0.970(16)	C(21)-H(21A)	1.16(3)

C(21)-H(21B)	1.14(4)	C(45)-C(46)	1.385(3)
C(21)-H(21C)	0.99(4)	C(46)-F(46)	1.343(3)
C(22)-H(22A)	1.15(4)	C(46)-C(47)	1.369(4)
C(22)-H(22B)	1.23(3)	C(47)-F(47)	1.345(3)
C(22)-H(22C)	1.04(4)	C(47)-C(48)	1.389(3)
B(31)-C(31)	1.651(3)	C(48)-F(48)	1.357(3)
B(31)-C(43)	1.659(3)	C(49)-C(54)	1.382(3)
B(31)-C(49)	1.659(3)	C(49)-C(50)	1.393(3)
B(31)-C(37)	1.662(3)	C(50)-F(50)	1.355(3)
C(31)-C(36)	1.389(3)	C(50)-C(51)	1.377(3)
C(31)-C(32)	1.393(3)	C(51)-F(51)	1.352(3)
C(32)-F(32)	1.356(2)	C(51)-C(52)	1.375(4)
C(32)-C(33)	1.387(3)	C(52)-F(52)	1.351(3)
C(33)-F(33)	1.341(3)	C(52)-C(53)	1.372(4)
C(33)-C(34)	1.378(3)	C(53)-F(53)	1.350(3)
C(34)-F(34)	1.338(3)	C(53)-C(54)	1.393(3)
C(34)-C(35)	1.380(3)	C(54)-F(54)	1.345(3)
C(35)-F(35)	1.341(2)		
C(35)-C(36)	1.381(3)	N(1)-Zr(1)-N(2)	62.13(7)
C(36)-F(36)	1.358(3)	N(1)-Zr(1)-CNT1	124.38(6)
C(37)-C(38)	1.393(3)	N(2)-Zr(1)-CNT1	116.75(6)
C(37)-C(42)	1.395(3)	N(1)-Zr(1)-C(19)	112.39(9)
C(38)-F(38)	1.353(3)	N(2)-Zr(1)-C(19)	119.75(9)
C(38)-C(39)	1.379(3)	CNT1-Zr(1)-C(19)	112.88(8)
C(39)-F(39)	1.346(3)	N(1)-Zr(1)-C(2)	95.15(8)
C(39)-C(40)	1.380(4)	N(2)-Zr(1)-C(2)	109.21(8)
C(40)-F(40)	1.339(3)	CNT1-Zr(1)-C(2)	29.49(5)
C(40)-C(41)	1.373(4)	C(19)-Zr(1)-C(2)	130.61(10)
C(41)-F(41)	1.345(3)	N(1)-Zr(1)-C(1)	108.40(8)
C(41)-C(42)	1.386(3)	N(2)-Zr(1)-C(1)	88.02(7)
C(42)-F(42)	1.347(3)	CNT1-Zr(1)-C(1)	29.08(5)
C(43)-C(48)	1.387(3)	C(19)-Zr(1)-C(1)	137.97(10)
C(43)-C(44)	1.392(3)	C(2)-Zr(1)-C(1)	33.54(7)
C(44)-F(44)	1.349(3)	N(1)-Zr(1)-C(3)	115.31(8)
C(44)-C(45)	1.378(3)	N(2)-Zr(1)-C(3)	141.26(8)
C(45)-F(45)	1.347(3)	CNT1-Zr(1)-C(3)	28.86(5)

C(19)-Zr(1)-C(3)	97.50(10)	C(5)-C(1)-Zr(1)	75.05(13)
C(2)-Zr(1)-C(3)	33.19(9)	C(2)-C(1)-Zr(1)	72.86(13)
C(1)-Zr(1)-C(3)	54.86(8)	C(6)-C(1)-Zr(1)	122.00(17)
N(1)-Zr(1)-C(5)	141.16(8)	C(3)-C(2)-C(1)	107.3(2)
N(2)-Zr(1)-C(5)	101.24(7)	C(3)-C(2)-C(7)	126.6(2)
CNT1-Zr(1)-C(5)	28.83(5)	C(1)-C(2)-C(7)	125.7(2)
C(19)-Zr(1)-C(5)	106.31(10)	C(3)-C(2)-Zr(1)	74.50(14)
C(2)-Zr(1)-C(5)	55.24(8)	C(1)-C(2)-Zr(1)	73.61(13)
C(1)-Zr(1)-C(5)	33.02(8)	C(7)-C(2)-Zr(1)	122.60(17)
C(3)-Zr(1)-C(5)	54.64(8)	C(2)-C(3)-C(4)	108.6(2)
N(1)-Zr(1)-C(4)	147.65(8)	C(2)-C(3)-C(8)	126.1(3)
N(2)-Zr(1)-C(4)	133.91(8)	C(4)-C(3)-C(8)	125.3(3)
CNT1-Zr(1)-C(4)	28.44(6)	C(2)-C(3)-Zr(1)	72.31(13)
C(19)-Zr(1)-C(4)	84.84(10)	C(4)-C(3)-Zr(1)	75.18(14)
C(2)-Zr(1)-C(4)	54.81(9)	C(8)-C(3)-Zr(1)	120.26(17)
C(1)-Zr(1)-C(4)	54.45(8)	C(3)-C(4)-C(5)	108.0(2)
C(3)-Zr(1)-C(4)	32.77(9)	C(3)-C(4)-C(9)	124.7(3)
C(5)-Zr(1)-C(4)	32.73(8)	C(5)-C(4)-C(9)	126.7(3)
N(1)-Zr(1)-H(20A)	122.4(7)	C(3)-C(4)-Zr(1)	72.05(13)
N(2)-Zr(1)-H(20A)	74.6(7)	C(5)-C(4)-Zr(1)	72.92(13)
CNT1-Zr(1)-H(20A)	107.8(7)	C(9)-C(4)-Zr(1)	127.52(19)
C(19)-Zr(1)-H(20A)	59.2(7)	C(1)-C(5)-C(4)	107.5(2)
C(2)-Zr(1)-H(20A)	135.6(7)	C(1)-C(5)-C(10)	125.4(2)
C(1)-Zr(1)-H(20A)	105.9(7)	C(4)-C(5)-C(10)	126.7(2)
C(3)-Zr(1)-H(20A)	122.2(7)	C(1)-C(5)-Zr(1)	71.93(13)
C(5)-Zr(1)-H(20A)	80.4(7)	C(4)-C(5)-Zr(1)	74.35(13)
C(4)-Zr(1)-H(20A)	89.8(7)	C(10)-C(5)-Zr(1)	124.46(19)
C(11)-N(1)-C(13)	128.62(19)	C(1)-C(6)-H(6A)	108(2)
C(11)-N(1)-Zr(1)	93.63(13)	C(1)-C(6)-H(6B)	110(2)
C(13)-N(1)-Zr(1)	135.87(14)	H(6A)-C(6)-H(6B)	110(3)
C(11)-N(2)-C(17)	122.77(19)	C(1)-C(6)-H(6C)	110.5(18)
C(11)-N(2)-Zr(1)	92.40(13)	H(6A)-C(6)-H(6C)	108(3)
C(17)-N(2)-Zr(1)	144.79(16)	H(6B)-C(6)-H(6C)	111(3)
C(5)-C(1)-C(2)	108.6(2)	C(2)-C(7)-H(7A)	109(2)
C(5)-C(1)-C(6)	127.0(2)	C(2)-C(7)-H(7B)	97(3)
C(2)-C(1)-C(6)	124.2(2)	H(7A)-C(7)-H(7B)	108(2)

C(2)-C(7)-H(7C)	117(2)	C(13)-C(14)-H(14A)	114.0(17)
H(7A)-C(7)-H(7C)	114(2)	C(13)-C(14)-H(14B)	109.7(18)
H(7B)-C(7)-H(7C)	111(2)	H(14A)-C(14)-H(14B)	105(2)
C(3)-C(8)-H(8A)	124(3)	C(13)-C(14)-H(14C)	105.7(16)
C(3)-C(8)-H(8B)	112(3)	H(14A)-C(14)-H(14C)	107(2)
H(8A)-C(8)-H(8B)	110(2)	H(14B)-C(14)-H(14C)	115(2)
C(3)-C(8)-H(8C)	99(2)	C(13)-C(15)-H(15A)	108.3(19)
H(8A)-C(8)-H(8C)	106(2)	C(13)-C(15)-H(15B)	108.9(19)
H(8B)-C(8)-H(8C)	102(2)	H(15A)-C(15)-H(15B)	112(3)
C(4)-C(9)-H(9A)	113.5(18)	C(13)-C(15)-H(15C)	113.2(18)
C(4)-C(9)-H(9B)	110(2)	H(15A)-C(15)-H(15C)	106(3)
H(9A)-C(9)-H(9B)	102.1(19)	H(15B)-C(15)-H(15C)	109(3)
C(4)-C(9)-H(9C)	111(2)	C(13)-C(16)-H(16A)	106(2)
H(9A)-C(9)-H(9C)	114(2)	C(13)-C(16)-H(16B)	105(2)
H(9B)-C(9)-H(9C)	106(2)	H(16A)-C(16)-H(16B)	118(3)
C(5)-C(10)-H(10A)	107(2)	C(13)-C(16)-H(16C)	111(2)
C(5)-C(10)-H(10B)	112(2)	H(16A)-C(16)-H(16C)	103(3)
H(10A)-C(10)-H(10B)	113(3)	H(16B)-C(16)-H(16C)	113(3)
C(5)-C(10)-H(10C)	113(2)	N(2)-C(17)-C(18)	113.8(2)
H(10A)-C(10)-H(10C)	106(3)	N(2)-C(17)-H(17A)	109.2(18)
H(10B)-C(10)-H(10C)	106(3)	C(18)-C(17)-H(17A)	116.2(19)
N(2)-C(11)-N(1)	111.77(19)	N(2)-C(17)-H(17B)	109.2(17)
N(2)-C(11)-C(12)	122.9(2)	C(18)-C(17)-H(17B)	114.2(16)
N(1)-C(11)-C(12)	125.3(2)	H(17A)-C(17)-H(17B)	92(2)
C(11)-C(12)-H(12A)	108(2)	C(17)-C(18)-H(18A)	114(2)
C(11)-C(12)-H(12B)	110(3)	C(17)-C(18)-H(18B)	111.1(18)
H(12A)-C(12)-H(12B)	108(3)	H(18A)-C(18)-H(18B)	107(3)
C(11)-C(12)-H(12C)	108(2)	C(17)-C(18)-H(18C)	113(2)
H(12A)-C(12)-H(12C)	103(3)	H(18A)-C(18)-H(18C)	107(3)
H(12B)-C(12)-H(12C)	120(3)	H(18B)-C(18)-H(18C)	103(3)
N(1)-C(13)-C(14)	104.20(18)	C(20)-C(19)-Zr(1)	88.06(16)
N(1)-C(13)-C(16)	110.84(19)	C(20)-C(19)-H(19A)	116(2)
C(14)-C(13)-C(16)	108.9(2)	Zr(1)-C(19)-H(19A)	122(2)
N(1)-C(13)-C(15)	112.88(19)	C(20)-C(19)-H(19B)	124(2)
C(14)-C(13)-C(15)	108.8(2)	Zr(1)-C(19)-H(19B)	110(2)
C(16)-C(13)-C(15)	110.9(2)	H(19A)-C(19)-H(19B)	98(3)

C(21)-C(20)-C(19)	112.1(3)	F(35)-C(35)-C(34)	119.8(2)
C(21)-C(20)-C(22)	111.6(3)	F(35)-C(35)-C(36)	121.1(2)
C(19)-C(20)-C(22)	114.0(3)	C(34)-C(35)-C(36)	119.1(2)
C(21)-C(20)-H(20A)	102.9(14)	F(36)-C(36)-C(35)	115.95(19)
C(19)-C(20)-H(20A)	113.6(14)	F(36)-C(36)-C(31)	118.8(2)
C(22)-C(20)-H(20A)	101.8(14)	C(35)-C(36)-C(31)	125.3(2)
C(20)-C(21)-H(21A)	114.7(13)	C(38)-C(37)-C(42)	113.4(2)
C(20)-C(21)-H(21B)	110(2)	C(38)-C(37)-B(31)	119.26(19)
H(21A)-C(21)-H(21B)	114(2)	C(42)-C(37)-B(31)	127.1(2)
C(20)-C(21)-H(21C)	107(2)	F(38)-C(38)-C(39)	116.1(2)
H(21A)-C(21)-H(21C)	97(3)	F(38)-C(38)-C(37)	119.2(2)
H(21B)-C(21)-H(21C)	113(3)	C(39)-C(38)-C(37)	124.7(2)
C(20)-C(22)-H(22A)	109.0(19)	F(39)-C(39)-C(38)	120.8(2)
C(20)-C(22)-H(22B)	115.4(16)	F(39)-C(39)-C(40)	119.9(2)
H(22A)-C(22)-H(22B)	109(2)	C(38)-C(39)-C(40)	119.3(2)
C(20)-C(22)-H(22C)	110(2)	F(40)-C(40)-C(41)	120.8(2)
H(22A)-C(22)-H(22C)	108(3)	F(40)-C(40)-C(39)	120.5(2)
H(22B)-C(22)-H(22C)	105(3)	C(41)-C(40)-C(39)	118.7(2)
C(31)-B(31)-C(43)	113.88(17)	F(41)-C(41)-C(40)	119.9(2)
C(31)-B(31)-C(49)	113.25(17)	F(41)-C(41)-C(42)	119.8(2)
C(43)-B(31)-C(49)	102.00(17)	C(40)-C(41)-C(42)	120.3(2)
C(31)-B(31)-C(37)	101.66(17)	F(42)-C(42)-C(41)	115.1(2)
C(43)-B(31)-C(37)	113.29(18)	F(42)-C(42)-C(37)	121.5(2)
C(49)-B(31)-C(37)	113.27(17)	C(41)-C(42)-C(37)	123.4(2)
C(36)-C(31)-C(32)	112.7(2)	C(48)-C(43)-C(44)	113.3(2)
C(36)-C(31)-B(31)	119.63(19)	C(48)-C(43)-B(31)	127.2(2)
C(32)-C(31)-B(31)	127.37(19)	C(44)-C(43)-B(31)	119.31(19)
F(32)-C(32)-C(33)	114.69(19)	F(44)-C(44)-C(45)	115.8(2)
F(32)-C(32)-C(31)	120.82(19)	F(44)-C(44)-C(43)	119.4(2)
C(33)-C(32)-C(31)	124.5(2)	C(45)-C(44)-C(43)	124.8(2)
F(33)-C(33)-C(34)	119.5(2)	F(45)-C(45)-C(44)	121.0(2)
F(33)-C(33)-C(32)	120.9(2)	F(45)-C(45)-C(46)	119.8(2)
C(34)-C(33)-C(32)	119.5(2)	C(44)-C(45)-C(46)	119.2(2)
F(34)-C(34)-C(33)	120.4(2)	F(46)-C(46)-C(47)	120.6(2)
F(34)-C(34)-C(35)	120.7(2)	F(46)-C(46)-C(45)	120.6(2)
C(33)-C(34)-C(35)	118.9(2)	C(47)-C(46)-C(45)	118.7(2)

F(47)-C(47)-C(46)	119.4(2)
F(47)-C(47)-C(48)	120.5(2)
C(46)-C(47)-C(48)	120.1(2)
F(48)-C(48)-C(43)	121.2(2)
F(48)-C(48)-C(47)	114.9(2)
C(43)-C(48)-C(47)	123.9(2)
C(54)-C(49)-C(50)	113.2(2)
C(54)-C(49)-B(31)	127.3(2)
C(50)-C(49)-B(31)	119.28(19)
F(50)-C(50)-C(51)	115.9(2)
F(50)-C(50)-C(49)	119.20(19)
C(51)-C(50)-C(49)	124.9(2)
F(51)-C(51)-C(52)	120.0(2)
F(51)-C(51)-C(50)	120.7(2)
C(52)-C(51)-C(50)	119.3(2)
F(52)-C(52)-C(53)	120.9(2)
F(52)-C(52)-C(51)	120.3(2)
C(53)-C(52)-C(51)	118.7(2)
F(53)-C(53)-C(52)	119.7(2)
F(53)-C(53)-C(54)	120.3(2)
C(52)-C(53)-C(54)	120.0(2)
F(54)-C(54)-C(49)	121.8(2)
F(54)-C(54)-C(53)	114.4(2)
C(49)-C(54)-C(53)	123.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 49. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	34(1)	30(1)	28(1)	-9(1)	-12(1)	-2(1)
N(1)	37(1)	26(1)	31(1)	-9(1)	-13(1)	-2(1)
N(2)	38(1)	28(1)	32(1)	-10(1)	-13(1)	0(1)
C(1)	38(1)	33(1)	30(1)	-9(1)	-6(1)	-3(1)
C(2)	42(1)	31(1)	29(1)	-7(1)	-4(1)	-4(1)
C(3)	50(1)	35(1)	28(1)	-7(1)	-9(1)	2(1)
C(4)	46(1)	50(1)	29(1)	-14(1)	-13(1)	-3(1)
C(5)	44(1)	36(1)	33(1)	-16(1)	-8(1)	-2(1)
C(6)	36(1)	42(1)	47(2)	-7(1)	-8(1)	-2(1)
C(7)	50(2)	41(1)	49(2)	-15(1)	3(1)	-17(1)
C(8)	65(2)	43(2)	41(2)	-7(1)	-18(1)	12(1)
C(9)	57(2)	77(2)	44(2)	-24(2)	-22(1)	-7(2)
C(10)	59(2)	40(1)	58(2)	-24(1)	-14(2)	-3(1)
C(11)	28(1)	29(1)	31(1)	-6(1)	-7(1)	-6(1)
C(12)	51(2)	34(1)	40(1)	-10(1)	-21(1)	-6(1)
C(13)	35(1)	28(1)	34(1)	-12(1)	-4(1)	-5(1)
C(14)	39(1)	31(1)	45(1)	-9(1)	-12(1)	-1(1)
C(15)	50(2)	34(1)	48(2)	-10(1)	-17(1)	-14(1)
C(16)	51(2)	38(1)	38(1)	-11(1)	3(1)	-5(1)
C(17)	46(1)	30(1)	35(1)	-9(1)	-14(1)	5(1)
C(18)	54(2)	29(1)	48(2)	-6(1)	-17(1)	-5(1)
C(19)	43(1)	48(2)	50(2)	-17(1)	-18(1)	-7(1)
C(20)	43(1)	54(2)	57(2)	-15(1)	-15(1)	-17(1)
C(21)	61(2)	77(2)	59(2)	-14(2)	-17(2)	-24(2)
C(22)	64(2)	67(2)	75(2)	-24(2)	-18(2)	-28(2)
B(31)	31(1)	26(1)	29(1)	-9(1)	-10(1)	-2(1)
C(31)	30(1)	27(1)	29(1)	-8(1)	-4(1)	-7(1)

C(32)	29(1)	26(1)	31(1)	-9(1)	-5(1)	-5(1)
C(33)	33(1)	35(1)	31(1)	-6(1)	-9(1)	-10(1)
C(34)	34(1)	37(1)	36(1)	-14(1)	-7(1)	-14(1)
C(35)	33(1)	27(1)	41(1)	-11(1)	-5(1)	-9(1)
C(36)	29(1)	30(1)	34(1)	-8(1)	-8(1)	-5(1)
C(37)	37(1)	28(1)	31(1)	-9(1)	-9(1)	-4(1)
C(38)	40(1)	31(1)	33(1)	-9(1)	-9(1)	-2(1)
C(39)	39(1)	39(1)	41(1)	-14(1)	-1(1)	-6(1)
C(40)	56(2)	40(1)	32(1)	-8(1)	-1(1)	-14(1)
C(41)	59(2)	32(1)	32(1)	-3(1)	-14(1)	-8(1)
C(42)	42(1)	30(1)	35(1)	-9(1)	-12(1)	-3(1)
C(43)	32(1)	24(1)	35(1)	-7(1)	-11(1)	-5(1)
C(44)	37(1)	25(1)	35(1)	-8(1)	-10(1)	-5(1)
C(45)	39(1)	29(1)	42(1)	-7(1)	-19(1)	-6(1)
C(46)	31(1)	28(1)	48(1)	-6(1)	-13(1)	-4(1)
C(47)	33(1)	32(1)	42(1)	-12(1)	-5(1)	-4(1)
C(48)	35(1)	27(1)	36(1)	-10(1)	-10(1)	-5(1)
C(49)	32(1)	26(1)	35(1)	-10(1)	-14(1)	-2(1)
C(50)	33(1)	32(1)	38(1)	-13(1)	-13(1)	-4(1)
C(51)	42(1)	32(1)	44(1)	-7(1)	-16(1)	-9(1)
C(52)	44(1)	25(1)	61(2)	-13(1)	-21(1)	-3(1)
C(53)	38(1)	33(1)	55(2)	-24(1)	-22(1)	3(1)
C(54)	34(1)	34(1)	35(1)	-12(1)	-15(1)	-1(1)
F(32)	39(1)	26(1)	41(1)	-7(1)	-16(1)	-1(1)
F(33)	46(1)	41(1)	44(1)	-5(1)	-24(1)	-9(1)
F(34)	55(1)	46(1)	52(1)	-16(1)	-20(1)	-20(1)
F(35)	45(1)	28(1)	67(1)	-18(1)	-18(1)	-6(1)
F(36)	39(1)	26(1)	49(1)	-10(1)	-19(1)	-1(1)
F(38)	34(1)	44(1)	38(1)	-8(1)	-9(1)	2(1)
F(39)	39(1)	57(1)	54(1)	-13(1)	4(1)	-5(1)
F(40)	69(1)	59(1)	38(1)	-2(1)	6(1)	-19(1)
F(41)	75(1)	48(1)	40(1)	8(1)	-19(1)	-7(1)
F(42)	43(1)	35(1)	45(1)	-3(1)	-17(1)	1(1)
F(44)	42(1)	40(1)	40(1)	-20(1)	-14(1)	-1(1)
F(45)	48(1)	44(1)	52(1)	-15(1)	-27(1)	-4(1)
F(46)	30(1)	49(1)	61(1)	-11(1)	-15(1)	-3(1)

F(47)	36(1)	60(1)	57(1)	-31(1)	-2(1)	-2(1)
F(48)	37(1)	47(1)	38(1)	-20(1)	-8(1)	-7(1)
F(50)	46(1)	33(1)	34(1)	-12(1)	-5(1)	-11(1)
F(51)	64(1)	37(1)	47(1)	1(1)	-14(1)	-19(1)
F(52)	74(1)	27(1)	80(1)	-14(1)	-27(1)	-9(1)
F(53)	54(1)	42(1)	65(1)	-33(1)	-24(1)	5(1)
F(54)	53(1)	41(1)	36(1)	-17(1)	-13(1)	1(1)

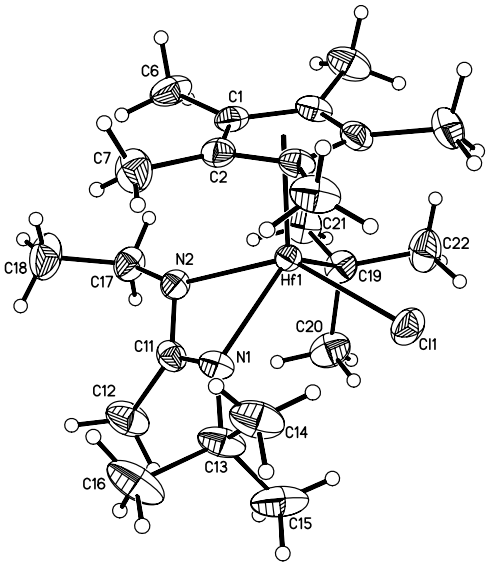
Table 50. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5e**.

	x	y	z	U(eq)
H(6A)	3790(40)	2240(30)	7860(30)	82(12)
H(6B)	3760(40)	3310(30)	8160(20)	78(11)
H(6C)	3060(30)	2240(20)	8810(20)	55(9)
H(7A)	4050(20)	-90(30)	9118(15)	86(12)
H(7B)	5410(30)	-610(30)	8790(20)	110(16)
H(7C)	4640(30)	100(30)	8125(13)	79(12)
H(8A)	7360(50)	-1060(30)	9070(30)	160(20)
H(8B)	7300(40)	-710(30)	9869(11)	110(16)
H(8C)	8220(20)	-250(30)	9020(20)	84(12)
H(9A)	8020(30)	2394(14)	9276(17)	52(9)
H(9B)	8600(20)	1250(20)	9254(19)	69(10)
H(9C)	7550(30)	1390(20)	10054(11)	97(14)
H(10A)	5110(40)	3600(30)	9370(30)	81(12)
H(10B)	5340(40)	4040(30)	8350(20)	76(12)
H(10C)	6470(40)	3820(30)	8750(30)	96(14)
H(12A)	6420(40)	2620(30)	4940(20)	68(10)
H(12B)	5090(40)	2660(30)	5460(20)	74(12)
H(12C)	5870(30)	1600(30)	5330(20)	66(10)
H(14A)	8590(30)	-340(20)	7118(19)	50(8)
H(14B)	8290(30)	-1290(20)	6902(18)	46(8)
H(14C)	7240(30)	-720(20)	7568(17)	36(7)
H(15A)	5540(30)	-440(20)	6830(20)	53(9)
H(15B)	6530(30)	-1100(30)	6275(19)	46(8)
H(15C)	5800(30)	-20(20)	5860(20)	51(8)
H(16A)	7890(30)	830(30)	5160(20)	53(9)
H(16B)	8520(30)	-340(30)	5410(20)	60(9)
H(16C)	8940(30)	640(30)	5530(20)	66(10)
H(17A)	5140(30)	4200(20)	6701(19)	45(8)
H(17B)	4640(30)	3890(20)	6192(18)	47(8)
H(18A)	7130(40)	4670(30)	5570(20)	75(11)

H(18B)	5850(30)	5390(30)	5320(20)	60(9)
H(18C)	6500(30)	4380(30)	4990(20)	56(9)
H(19A)	9480(30)	1470(30)	7880(20)	74(11)
H(19B)	9590(30)	1310(30)	7040(20)	61(9)
H(20A)	7830(30)	3310(20)	7147(17)	38(7)
H(21A)	10400(20)	3080(20)	5865(16)	32(6)
H(21B)	9080(40)	4280(30)	5880(30)	87(12)
H(21C)	9000(40)	2970(30)	5860(20)	73(11)
H(22A)	8930(40)	3210(30)	8240(20)	75(11)
H(22B)	8950(30)	4560(30)	7340(20)	66(10)
H(22C)	10260(40)	3490(30)	7360(30)	83(12)

Crystallographic analysis of compound 14.

A faint yellowish-green block with approximate orthogonal dimensions 0.335 x 0.263 x 0.219mm^3 was placed and optically centered on the Bruker SMART CCD system at –100°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 14 seconds per frame and 606 frames per series. Five data series were collected at varying φ angles (φ=0°, 72°, 144°, 216°, 288°), including a partial repeat of the first series, 200 frames, for decay purposes. The crystal to detector distance was 4.831cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 37412 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1, 2] with 5576 unique.



Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the centrosymmetric monoclinic non-standard space group $P2_1/c$ (no. 14). The structure was determined by direct methods with the successful location of nearly the entire molecule using the program XS[4]. The structure was refined with XL[5]. A single least-squares difference-Fourier cycle was required to locate the remaining, full occupancy, non-hydrogen atoms. The 37412 data collected were truncated to $2\theta_{max}$=55.00° yielding 36946 reflections that were then merged during least-squares refinement to 5443 unique data [R(int)=0.0257]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were initially calculated and placed in idealized positions, then allowed to refine freely during the final refinement cycles. A centroid was calculated for the pentamethylcyclopentadienyl ligand. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=2.22%, wR(F^2)=4.15%, GOF=1.215 for all 5443 unique reflections [R(F)=2.04%, wR(F^2)=4.10% for those 5135 data with Fo > 4σ(Fo)]. The final difference-Fourier was featureless indicating that the structure is both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.0692*P)^2+0.2665*P]$ and $P=(\max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

Table 51. Crystal data and structure refinement for **14**.

Identification code	1103ff	
Empirical formula	C22 H41 Cl Hf N2	
Formula weight	547.51	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.2282(4) Å	α= 90°.
	b = 30.2290(12) Å	β= 111.4190(10)°.
	c = 9.1425(4) Å	γ = 90°.
Volume	2374.24(17) $Å^3$	
Z	4	
Density (calculated)	1.532 Mg/m^3	
Absorption coefficient	4.514 mm^{-1}	
F(000)	1104	
Crystal size	0.34 x 0.26 x 0.22 mm^3	
Theta range for data collection	2.37 to 27.50°.	
Index ranges	-11<=h<=11, -39<=k<=39, -11<=l<=11	
Reflections collected	36946	
Independent reflections	5443 [R(int) = 0.0257]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Empirical, SADABS (multi-scan)	
Max. and min. transmission	0.4380 and 0.3131	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5443 / 3 / 402	
Goodness-of-fit on F^2	1.215	
Final R indices [I>2sigma(I)]	R1 = 0.0204, wR2 = 0.0410 [5135 Data]	
R indices (all data)	R1 = 0.0222, wR2 = 0.0415	
Largest diff. peak and hole	1.476 and -0.723 $e.Å^{-3}$	

Table 52. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Hf(1)	3012(1)	1261(1)	1443(1)	21(1)
Cl(1)	3061(1)	1737(1)	3613(1)	38(1)
N(1)	681(3)	1564(1)	58(3)	29(1)
N(2)	1332(3)	910(1)	-597(3)	27(1)
CNT1	5191(1)	1379(1)	1009(2)	0
C(1)	4923(3)	1065(1)	138(3)	29(1)
C(2)	4402(3)	1504(1)	-289(3)	28(1)
C(3)	4974(3)	1770(1)	1075(3)	28(1)
C(4)	5836(3)	1495(1)	2356(3)	30(1)
C(5)	5820(3)	1058(1)	1765(4)	30(1)
C(6)	4756(4)	684(1)	-965(5)	43(1)
C(7)	3480(5)	1660(1)	-1923(4)	45(1)
C(8)	4811(4)	2263(1)	1144(5)	41(1)
C(9)	6773(4)	1642(1)	3994(4)	45(1)
C(10)	6838(4)	683(1)	2640(5)	47(1)
C(11)	166(3)	1181(1)	-660(3)	29(1)
C(12)	-1521(4)	1038(1)	-1374(5)	48(1)
C(13)	-332(3)	1942(1)	106(4)	41(1)
C(14)	701(4)	2354(1)	471(6)	49(1)
C(15)	-1007(5)	1878(1)	1386(6)	56(1)
C(16)	-1634(5)	2028(2)	-1495(7)	65(1)
C(17)	1025(4)	485(1)	-1415(4)	35(1)
C(18)	466(6)	531(2)	-3193(4)	55(1)
C(19)	2989(4)	663(1)	2987(3)	33(1)
C(20)	1291(4)	688(1)	2936(5)	45(1)
C(21)	3207(4)	202(1)	2406(4)	41(1)
C(22)	4075(5)	696(1)	4716(4)	48(1)

Table 53. Bond lengths [Å] and angles [°] for **14**.

Hf(1)-N(2)	2.211(2)	C(9)-H(9B)	0.95(4)
Hf(1)-CNT1	2.2157(12)	C(9)-H(9C)	0.95(5)
Hf(1)-N(1)	2.254(2)	C(10)-H(10A)	0.95(5)
Hf(1)-C(19)	2.298(3)	C(10)-H(10B)	0.98(4)
Hf(1)-Cl(1)	2.4389(7)	C(10)-H(10C)	0.95(4)
Hf(1)-C(2)	2.485(3)	C(11)-C(12)	1.515(4)
Hf(1)-C(3)	2.492(3)	C(12)-H(12A)	1.01(4)
Hf(1)-C(4)	2.530(3)	C(12)-H(12B)	0.95(4)
Hf(1)-C(1)	2.534(3)	C(12)-H(12C)	1.02(5)
Hf(1)-C(5)	2.573(3)	C(13)-C(15)	1.525(5)
N(1)-C(11)	1.328(3)	C(13)-C(14)	1.529(4)
N(1)-C(13)	1.488(3)	C(13)-C(16)	1.540(5)
N(2)-C(11)	1.337(3)	C(14)-H(14A)	0.94(3)
N(2)-C(17)	1.463(3)	C(14)-H(14B)	0.96(3)
C(1)-C(5)	1.414(4)	C(14)-H(14C)	0.95(4)
C(1)-C(2)	1.417(4)	C(15)-H(15A)	0.96(4)
C(1)-C(6)	1.502(4)	C(15)-H(15B)	0.99(4)
C(2)-C(3)	1.414(4)	C(15)-H(15C)	0.95(4)
C(2)-C(7)	1.500(4)	C(16)-H(16A)	0.98(4)
C(3)-C(4)	1.420(4)	C(16)-H(16B)	0.95(5)
C(3)-C(8)	1.499(4)	C(16)-H(16C)	0.99(4)
C(4)-C(5)	1.426(4)	C(17)-C(18)	1.521(5)
C(4)-C(9)	1.498(4)	C(17)-H(17A)	1.00(3)
C(5)-C(10)	1.503(4)	C(17)-H(17B)	0.97(3)
C(6)-H(6A)	0.98(4)	C(18)-H(18A)	0.96(4)
C(6)-H(6B)	0.98(4)	C(18)-H(18B)	0.93(5)
C(6)-H(6C)	0.95(5)	C(18)-H(18C)	0.95(4)
C(7)-H(7A)	0.95(5)	C(19)-C(21)	1.530(4)
C(7)-H(7B)	0.92(5)	C(19)-C(22)	1.535(4)
C(7)-H(7C)	0.89(5)	C(19)-C(20)	1.553(4)
C(8)-H(8A)	0.98(4)	C(20)-H(20A)	1.01(4)
C(8)-H(8B)	0.93(4)	C(20)-H(20B)	1.00(3)
C(8)-H(8C)	0.94(4)	C(20)-H(20C)	1.01(4)
C(9)-H(9A)	0.99(5)	C(21)-H(21A)	0.94(4)

C(21)-H(21B)	0.97(4)	N(1)-Hf(1)-C(1)	121.06(9)
C(21)-H(21C)	1.01(4)	C(19)-Hf(1)-C(1)	105.67(10)
C(22)-H(22A)	1.03(4)	Cl(1)-Hf(1)-C(1)	135.36(6)
C(22)-H(22B)	1.03(4)	C(2)-Hf(1)-C(1)	32.78(9)
C(22)-H(22C)	0.99(4)	C(3)-Hf(1)-C(1)	54.24(9)
		C(4)-Hf(1)-C(1)	53.87(9)
N(2)-Hf(1)-CNT1	109.18(7)	N(2)-Hf(1)-C(5)	110.42(9)
N(2)-Hf(1)-N(1)	59.30(8)	CNT1-Hf(1)-C(5)	28.00(6)
CNT1-Hf(1)-N(1)	125.21(7)	N(1)-Hf(1)-C(5)	151.16(9)
N(2)-Hf(1)-C(19)	88.89(10)	C(19)-Hf(1)-C(5)	88.68(10)
CNT1-Hf(1)-C(19)	116.68(8)	Cl(1)-Hf(1)-C(5)	109.22(7)
N(1)-Hf(1)-C(19)	116.33(9)	C(2)-Hf(1)-C(5)	53.93(9)
N(2)-Hf(1)-Cl(1)	140.14(6)	C(3)-Hf(1)-C(5)	53.98(9)
CNT1-Hf(1)-Cl(1)	107.60(4)	C(4)-Hf(1)-C(5)	32.44(9)
N(1)-Hf(1)-Cl(1)	86.97(6)	C(1)-Hf(1)-C(5)	32.14(9)
C(19)-Hf(1)-Cl(1)	88.08(8)	C(11)-N(1)-C(13)	124.6(2)
N(2)-Hf(1)-C(2)	88.32(9)	C(11)-N(1)-Hf(1)	91.15(16)
CNT1-Hf(1)-C(2)	28.98(6)	C(13)-N(1)-Hf(1)	140.98(19)
N(1)-Hf(1)-C(2)	97.50(9)	C(11)-N(2)-C(17)	120.9(2)
C(19)-Hf(1)-C(2)	138.33(10)	C(11)-N(2)-Hf(1)	92.78(16)
Cl(1)-Hf(1)-C(2)	118.85(7)	C(17)-N(2)-Hf(1)	142.90(19)
N(2)-Hf(1)-C(3)	120.16(9)	C(5)-C(1)-C(2)	108.3(2)
CNT1-Hf(1)-C(3)	28.94(6)	C(5)-C(1)-C(6)	124.8(3)
N(1)-Hf(1)-C(3)	105.34(8)	C(2)-C(1)-C(6)	126.4(3)
C(19)-Hf(1)-C(3)	137.67(10)	C(5)-C(1)-Hf(1)	75.45(15)
Cl(1)-Hf(1)-C(3)	86.91(7)	C(2)-C(1)-Hf(1)	71.74(15)
C(2)-Hf(1)-C(3)	33.00(9)	C(6)-C(1)-Hf(1)	125.19(19)
N(2)-Hf(1)-C(4)	137.11(9)	C(3)-C(2)-C(1)	108.1(2)
CNT1-Hf(1)-C(4)	28.52(6)	C(3)-C(2)-C(7)	126.4(3)
N(1)-Hf(1)-C(4)	136.75(9)	C(1)-C(2)-C(7)	125.5(3)
C(19)-Hf(1)-C(4)	104.89(10)	C(3)-C(2)-Hf(1)	73.75(15)
Cl(1)-Hf(1)-C(4)	81.70(7)	C(1)-C(2)-Hf(1)	75.48(15)
C(2)-Hf(1)-C(4)	54.42(9)	C(7)-C(2)-Hf(1)	119.4(2)
C(3)-Hf(1)-C(4)	32.83(9)	C(2)-C(3)-C(4)	108.1(2)
N(2)-Hf(1)-C(1)	83.43(8)	C(2)-C(3)-C(8)	126.2(3)
CNT1-Hf(1)-C(1)	28.35(6)	C(4)-C(3)-C(8)	125.6(3)

C(2)-C(3)-Hf(1)	73.25(14)	C(4)-C(9)-H(9C)	115(3)
C(4)-C(3)-Hf(1)	75.04(15)	H(9A)-C(9)-H(9C)	105(4)
C(8)-C(3)-Hf(1)	121.27(19)	H(9B)-C(9)-H(9C)	97(3)
C(3)-C(4)-C(5)	107.8(2)	C(5)-C(10)-H(10A)	114(3)
C(3)-C(4)-C(9)	126.6(3)	C(5)-C(10)-H(10B)	112(3)
C(5)-C(4)-C(9)	125.2(3)	H(10A)-C(10)-H(10B)	109(4)
C(3)-C(4)-Hf(1)	72.12(14)	C(5)-C(10)-H(10C)	109(2)
C(5)-C(4)-Hf(1)	75.44(15)	H(10A)-C(10)-H(10C)	109(4)
C(9)-C(4)-Hf(1)	124.2(2)	H(10B)-C(10)-H(10C)	104(3)
C(1)-C(5)-C(4)	107.7(2)	N(1)-C(11)-N(2)	112.0(2)
C(1)-C(5)-C(10)	125.7(3)	N(1)-C(11)-C(12)	126.0(3)
C(4)-C(5)-C(10)	125.4(3)	N(2)-C(11)-C(12)	121.9(3)
C(1)-C(5)-Hf(1)	72.41(15)	C(11)-C(12)-H(12A)	110(2)
C(4)-C(5)-Hf(1)	72.12(15)	C(11)-C(12)-H(12B)	110(2)
C(10)-C(5)-Hf(1)	130.4(2)	H(12A)-C(12)-H(12B)	109(3)
C(1)-C(6)-H(6A)	112(2)	C(11)-C(12)-H(12C)	112(2)
C(1)-C(6)-H(6B)	112(2)	H(12A)-C(12)-H(12C)	111(3)
H(6A)-C(6)-H(6B)	109(3)	H(12B)-C(12)-H(12C)	105(3)
C(1)-C(6)-H(6C)	111(3)	N(1)-C(13)-C(15)	111.2(3)
H(6A)-C(6)-H(6C)	105(3)	N(1)-C(13)-C(14)	106.5(2)
H(6B)-C(6)-H(6C)	108(3)	C(15)-C(13)-C(14)	109.5(3)
C(2)-C(7)-H(7A)	114(3)	N(1)-C(13)-C(16)	112.5(3)
C(2)-C(7)-H(7B)	112(3)	C(15)-C(13)-C(16)	110.8(3)
H(7A)-C(7)-H(7B)	100(4)	C(14)-C(13)-C(16)	106.1(3)
C(2)-C(7)-H(7C)	119(3)	C(13)-C(14)-H(14A)	113(2)
H(7A)-C(7)-H(7C)	103(4)	C(13)-C(14)-H(14B)	110(2)
H(7B)-C(7)-H(7C)	108(4)	H(14A)-C(14)-H(14B)	105(3)
C(3)-C(8)-H(8A)	113(2)	C(13)-C(14)-H(14C)	111(2)
C(3)-C(8)-H(8B)	112(2)	H(14A)-C(14)-H(14C)	111(3)
H(8A)-C(8)-H(8B)	111(3)	H(14B)-C(14)-H(14C)	106(3)
C(3)-C(8)-H(8C)	111(2)	C(13)-C(15)-H(15A)	111(2)
H(8A)-C(8)-H(8C)	105(3)	C(13)-C(15)-H(15B)	109(2)
H(8B)-C(8)-H(8C)	104(3)	H(15A)-C(15)-H(15B)	108(3)
C(4)-C(9)-H(9A)	111(3)	C(13)-C(15)-H(15C)	111(2)
C(4)-C(9)-H(9B)	114(3)	H(15A)-C(15)-H(15C)	110(3)
H(9A)-C(9)-H(9B)	113(4)	H(15B)-C(15)-H(15C)	108(3)

C(13)-C(16)-H(16A)	108(2)	C(19)-C(22)-H(22A)	110(2)
C(13)-C(16)-H(16B)	106(3)	C(19)-C(22)-H(22B)	112(2)
H(16A)-C(16)-H(16B)	113(4)	H(22A)-C(22)-H(22B)	110(3)
C(13)-C(16)-H(16C)	111(2)	C(19)-C(22)-H(22C)	112(2)
H(16A)-C(16)-H(16C)	110(3)	H(22A)-C(22)-H(22C)	107(3)
H(16B)-C(16)-H(16C)	108(4)	H(22B)-C(22)-H(22C)	105(3)
N(2)-C(17)-C(18)	113.2(3)		
N(2)-C(17)-H(17A)	113.1(18)		
C(18)-C(17)-H(17A)	108.8(17)		
N(2)-C(17)-H(17B)	108.2(18)		
C(18)-C(17)-H(17B)	110.0(18)		
H(17A)-C(17)-H(17B)	103(2)		
C(17)-C(18)-H(18A)	113(3)		
C(17)-C(18)-H(18B)	111(3)		
H(18A)-C(18)-H(18B)	106(4)		
C(17)-C(18)-H(18C)	110(2)		
H(18A)-C(18)-H(18C)	110(3)		
H(18B)-C(18)-H(18C)	107(3)		
C(21)-C(19)-C(22)	107.3(3)		
C(21)-C(19)-C(20)	107.1(3)		
C(22)-C(19)-C(20)	107.4(3)		
C(21)-C(19)-Hf(1)	118.1(2)		
C(22)-C(19)-Hf(1)	115.6(2)		
C(20)-C(19)-Hf(1)	100.28(19)		
C(19)-C(20)-H(20A)	110(2)		
C(19)-C(20)-H(20B)	108.4(19)		
H(20A)-C(20)-H(20B)	112(3)		
C(19)-C(20)-H(20C)	108(2)		
H(20A)-C(20)-H(20C)	105(3)		
H(20B)-C(20)-H(20C)	113(3)		
C(19)-C(21)-H(21A)	112(2)		
C(19)-C(21)-H(21B)	111(2)		
H(21A)-C(21)-H(21B)	109(3)		
C(19)-C(21)-H(21C)	109(2)		
H(21A)-C(21)-H(21C)	108(3)		
H(21B)-C(21)-H(21C)	108(3)		

Symmetry transformations used to generate equivalent atoms:

Table 54. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Hf(1)	22(1)	20(1)	22(1)	-1(1)	8(1)	0(1)
Cl(1)	46(1)	34(1)	36(1)	-12(1)	18(1)	-1(1)
N(1)	23(1)	27(1)	37(1)	3(1)	10(1)	2(1)
N(2)	28(1)	28(1)	27(1)	-2(1)	11(1)	-5(1)
C(1)	25(1)	31(1)	36(2)	-7(1)	18(1)	-3(1)
C(2)	26(1)	32(1)	31(1)	2(1)	15(1)	-4(1)
C(3)	22(1)	25(1)	37(2)	-1(1)	12(1)	-4(1)
C(4)	21(1)	32(1)	33(2)	-3(1)	8(1)	-4(1)
C(5)	21(1)	28(1)	43(2)	0(1)	12(1)	2(1)
C(6)	43(2)	42(2)	57(2)	-20(2)	32(2)	-9(2)
C(7)	47(2)	50(2)	35(2)	11(2)	14(2)	-5(2)
C(8)	35(2)	24(1)	66(2)	0(2)	21(2)	-5(1)
C(9)	35(2)	54(2)	37(2)	-11(2)	2(1)	-9(2)
C(10)	33(2)	39(2)	63(3)	8(2)	12(2)	11(1)
C(11)	24(1)	33(1)	27(1)	5(1)	7(1)	-3(1)
C(12)	27(2)	48(2)	61(2)	-5(2)	9(2)	-8(1)
C(13)	28(1)	30(2)	65(2)	5(1)	15(2)	7(1)
C(14)	38(2)	27(2)	80(3)	5(2)	19(2)	6(1)
C(15)	43(2)	40(2)	97(4)	-10(2)	41(2)	3(2)
C(16)	36(2)	47(2)	93(4)	18(2)	3(2)	11(2)
C(17)	39(2)	34(2)	34(2)	-10(1)	15(1)	-12(1)
C(18)	64(3)	64(3)	34(2)	-16(2)	14(2)	-20(2)
C(19)	40(2)	29(1)	32(2)	5(1)	16(1)	3(1)
C(20)	54(2)	42(2)	50(2)	9(2)	32(2)	0(2)
C(21)	49(2)	29(2)	45(2)	3(1)	17(2)	2(1)
C(22)	64(2)	46(2)	30(2)	7(2)	13(2)	5(2)

Table 55. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for **14**.

	x	y	z	U(eq)
H(6A)	3870(40)	722(11)	-1950(40)	48(10)
H(6B)	4660(40)	403(12)	-480(40)	48(10)
H(6C)	5630(50)	666(15)	-1270(50)	82(14)
H(7A)	4090(50)	1714(15)	-2550(50)	82(15)
H(7B)	3080(50)	1940(16)	-1920(50)	76(14)
H(7C)	2720(60)	1490(17)	-2540(60)	95(17)
H(8A)	4770(50)	2366(13)	2140(50)	61(12)
H(8B)	3970(50)	2370(13)	290(50)	62(12)
H(8C)	5680(50)	2408(12)	1050(40)	56(11)
H(9A)	7890(60)	1676(15)	4140(50)	83(14)
H(9B)	6620(50)	1469(14)	4790(50)	67(13)
H(9C)	6480(50)	1918(16)	4290(50)	76(14)
H(10A)	6510(50)	402(16)	2180(50)	83(15)
H(10B)	6920(50)	672(14)	3740(50)	72(14)
H(10C)	7870(50)	736(13)	2700(50)	67(12)
H(12A)	-2140(50)	1167(13)	-770(50)	62(12)
H(12B)	-1580(40)	723(14)	-1340(50)	62(12)
H(12C)	-2010(50)	1116(14)	-2540(50)	71(13)
H(14A)	1550(40)	2333(11)	1430(40)	38(9)
H(14B)	120(40)	2607(11)	580(40)	41(9)
H(14C)	1040(40)	2421(12)	-370(40)	52(11)
H(15A)	-1670(40)	1622(13)	1180(40)	57(11)
H(15B)	-1640(50)	2139(15)	1410(50)	72(13)
H(15C)	-200(50)	1850(13)	2390(50)	59(12)
H(16A)	-1200(50)	1995(14)	-2320(50)	64(13)
H(16B)	-2000(50)	2319(16)	-1440(50)	86(15)
H(16C)	-2510(50)	1820(13)	-1680(40)	58(11)
H(17A)	270(40)	299(10)	-1140(40)	32(8)
H(17B)	1970(40)	311(10)	-1030(40)	33(8)
H(18A)	-540(50)	666(14)	-3630(50)	74(14)

H(18B)	370(50)	256(16)	-3670(50)	83(15)
H(18C)	1200(40)	695(12)	-3480(40)	48(10)
H(20A)	530(50)	615(13)	1850(50)	61(12)
H(20B)	1110(40)	991(11)	3280(40)	38(9)
H(20C)	1150(40)	448(12)	3630(40)	53(10)
H(21A)	4200(40)	163(11)	2370(40)	47(10)
H(21B)	2440(40)	145(11)	1370(40)	45(10)
H(21C)	3070(40)	-26(12)	3150(40)	52(10)
H(22A)	3890(50)	433(14)	5350(50)	69(12)
H(22B)	3940(40)	989(13)	5220(40)	51(10)
H(22C)	5180(40)	686(11)	4840(40)	46(10)

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