

SUPPORTING INFORMATION

Activation of CO₂ by a Heterobimetallic Zr/Co Complex.

*Jeremy P. Krogman, Bruce M. Foxman, Christine M. Thomas**

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Experimental Section

General Considerations. All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Benzene, pentane, diethyl ether, tetrahydrofuran, and toluene were degassed and dried by sparging with N₂ gas followed by passage through an activated alumina column. All solvents were stored over 3 Å molecular sieves. Deuterated benzene was purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze-pump-thaw cycles, and dried over 3 Å molecular sieves. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. (THF)Zr(MesNPⁱPr₂)₃CoN₂ was synthesized using literature procedures.¹ All other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded at ambient temperature on a Varian Inova 400 MHz instrument. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent. ³¹P NMR chemical shifts were referenced to 85% H₃PO₄. IR spectra were recorded on a Varian 640-IR spectrometer controlled by Resolutions Pro software. UV-vis spectra were recorded on a Cary 50 UV-vis spectrophotometer using Cary WinUV software. Elemental microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

X-ray Crystallography Procedures. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo K α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.² Preliminary cell constants were obtained from three sets of 12 frames. Fully labeled diagrams and data collection and refinement details are included in Table S1 and on pages S8-S16 of the Supporting Information file. Further crystallographic details may be found in the accompanying CIF files.

Electrochemistry. Cyclic voltammetry measurements were carried out in a glovebox under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments electrochemical analyzer. A glassy carbon electrode and platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was Ag/AgNO₃ in THF. Solutions (THF) of electrolyte (0.40 M [nBu₄N][PF₆]) and analyte (2 mM) were also prepared in the glovebox.

(OC)Co(ⁱPr₂PNMes)₂(μ -O)Zr(ⁱPr₂PNMes) (2). A solution of (THF)Zr(MesNPⁱPr₂)₃CoN₂ (0.1734 g, 0.1734 mmol) in THF (10 mL) was placed in a Schlenk tube equipped with a stir bar and sealed with a Teflon valve. **1** was generated in situ by removing volatiles in vacuo. The color change from red to blue-green indicates the loss of N₂(g). The blue-green solids were then dissolved in argon-sparged THF. The solution was frozen, then the headspace of the flask was evacuated and backfilled with 1 equivalent of CO₂ using a known-volume gas bulb and partial pressure methods. The Schlenk tube was sealed and the solution was allowed to thaw. The reaction was stirred for 10 minutes or until the color of the reaction mixture changed from blue-green to yellow. Solvent was removed from the resulting mixture in vacuo. The remaining solids were washed with pentane to give an analytically pure yellow/green solid (0.1098 g, 67%). Green x-ray quality crystals were grown from concentrated toluene. ¹H NMR (400 MHz, C₆D₆): δ 13.1, 8.5, 7.6, 5.8, 3.9, 3.5, 3.2, 2.9, 2.5, 2.4, 2.0, -5.4. IR (THF): 1926 cm⁻¹. UV-Vis λ (nm) (ϵ , M⁻¹cm⁻¹): 357 (3700), 696 (200), 840 (420). Evans' method (u_{eff} , C₆D₆): 2.99 B.M. Anal. Calcd for C₄₆H₇₅CoN₃O₂P₃Zr: C, 58.45; H, 8.00; N, 4.45. Found: C, 58.32; H, 7.79; N, 4.29.

¹ Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 44-45.

² Apex2, Version 2 User Manual, M86-E01078; Bruker Analytical X-ray Systems: Madison, WI, 2006.

(OC)Co(ⁱPr₂PNMes)₃Zr(O)Na(THF)₃ (3). A 0.5% Na/Hg amalgam was prepared in THF (5 mL) from 0.0027 g Na (0.12 mmol) and 0.540 g Hg. To this vigorously stirred amalgam was added a solution of **2** (0.1009 g, .1067 mmol) in THF (5 mL). After two hours of stirring, the red/orange solution was filtered away from the amalgam and the volatiles were removed in vacuo until concentrated. Pentane was layered onto the concentrated THF solution and crystals were grown at -35 °C. The yellow crystals of the product were separated from the carbonate compound by extracting into benzene. After four such crystallizations the accumulated yield was 0.0303 g (24%). ¹H NMR (400 MHz, C₆D₆): 8.2, 5.5, 3.6, 3.1, 2.3, -2.8. UV-Vis (THF, λ(nm) (ε, M⁻¹cm⁻¹)): 360 (sh), 1064 (216). IR (THF): 1899 cm⁻¹. Evans' method (u_{eff}, C₆D₆): 2.00 B.M. Owing to the high sensitivity of complex **3** to air and moisture, satisfactory combustion analysis data could not be obtained.

(OC)Co(ⁱPr₂PNMes)₃Zr(CO₃)Na₂(THF)₄ (4). A 0.5% Na/Hg amalgam was prepared in THF in a Schlenk tube THF (15 mL) from 0.0072 g Na (0.31 mmol) and 1.440 g Hg. The solution was frozen and a cold solution of **2** (0.1150 g, 0.1217 mmol) in THF (5 mL) was added to the Schlenk tube on top of the frozen Na/Hg amalgam. The solution was frozen, then the headspace of the flask was evacuated and backfilled with 1.1 equivalent of CO₂ using a known-volume gas bulb and partial pressure methods. After four hours of stirring, the red/orange solution was filtered away from the amalgam and the volatiles were removed in vacuo until concentrated. Pentane was layered onto the resulting THF solution and crystals were grown at -35 °C. The product was isolated as red/orange crystals (0.1089 g, 67.4%). ¹H NMR (400 MHz, THF-d₈): δ 6.61 (s, 6H, Mes), 3.62 (THF), 2.47 (m, 6H, CH(CH₃)₂), 2.31 (s, 18 H, Mes-Me), 2.10 (s, 9H, Mes-Me), 1.78(THF) 1.58 (m, 18H, CH(CH₃)₂), 1.31 (m, 18H, CH(CH₃)₂). ³¹P{¹H} NMR (161.8 MHz, THF-d₈): δ 63.56 (br s) ¹³C{¹H} NMR (100.5 MHz, THF-d₈): δ 151.5 (*ipso*-Mes), 130.2 (Mes), 129.1 (Mes), 127.6 (Mes), 68.0(THF), 44.22 (PC(CH₃)₂), 26.2 (THF), overlapping with THF-d₈ (PC(CH₃)₂), 23.7 (PC(CH₃)₂), 23.4 (Mes-Me), 20.8 (Mes-Me). UV-Vis (THF, λ(nm) (ε, M⁻¹cm⁻¹)): 669 (56), 950 (47). IR (THF): 1884 cm⁻¹ (Co-CO), 1684 cm⁻¹ (CO₃), 1645 cm⁻¹ (CO₃). Anal. Calcd for C₆₃H₁₀₇N₃O₈Na₂P₃CoZr: C, 57.17; H, 8.15; N, 3.17. Found: C, 57.12; H, 8.09; N, 2.99.

(OC)(H)Co(ⁱPr₂PNMes)₃ZrOSiH₂Ph (5). A solution containing 9.8 μL (0.080 mmol) of PhSiH₃ in 2 mL of toluene was added dropwise to a stirring solution of 0.075 g (0.0793 mmol) of **2** in toluene (4 mL) in a scintillation vial. The solution was allowed to stir for 15 minutes. Solvent was removed from the mixture in vacuo. The remaining solids were extracted into Et₂O and concentrated for crystallization at rt. After 24 hours the compound was isolated as yellow crystals (0.0708 g, 84.5%). ¹H NMR (400 MHz, C₆D₆): δ 7.05(t, 3H, Ph), 6.76 (s, 6H, Mes), 6.70 (d, 2H, Ph), 4.32 (s, 2H, Si-H), 2.68 (m, 6H, CH(CH₃)₂), 2.42 (s, 18 H, Mes-Me), 2.16 (s, 9H, Mes-Me), 1.65 (m, 18H, CH(CH₃)₂), 1.35 (m, 18H, CH(CH₃)₂), -14.12 (q, 1H, Co-H). ³¹P{¹H} NMR (161.8 MHz, C₆D₆): δ 66.30 (br s) ¹³C{¹H} NMR (100.5 MHz, C₆D₆): δ 213.7 (Co-CO), 147.5 (*ipso*-Mes), 136.42 (Mes), 134.9 (Ar), 133.6 (Mes), 132.0 (Ar) 129.7 (Mes), 129.4 (Ar), 127.3 (Ar), 43.1 (PC(CH₃)₂), 23.1 (PC(CH₃)₂), 22.2 (PC(CH₃)₂), 22.0 (Mes-Me), 20.7 (Mes-Me). UV-Vis (THF, λ(nm) (ε, M⁻¹cm⁻¹)): 353 (sh). IR(THF): 2129 cm⁻¹ (Si-H), 2085 cm⁻¹ (Co-H?), 1909 cm⁻¹ (Co-CO). Anal. Calcd for C₅₂H₈₃N₃O₂SiP₃CoZr: C, 59.29; H, 7.94; N, 3.99. Found: C, 59.19; H, 7.89; N, 3.88.

Table S1. X-ray Diffraction Experimental Details for (OC)Co(iPr₂PNMes)₂(μ-O)Zr(iPr₂PNMes) (**2**), (THF)₃Na-O-Zr(MesNP^{*i*}Pr₂)₃Co(CO) (**3**), (THF)₄Na₂-(CO)₃-Zr(MesNP^{*i*}Pr₂)₃Co(CO) (**4•THF**), and (OC)(H)Co(iPr₂PNMes)₃Zr(OSiH₂Ph) (**5**)

	2	3	4•THF	5
chemical formula	C ₄₆ H ₇₅ CoN ₃ O ₂ P ₃ Zr	C ₅₈ H ₉₉ CoN ₃ NaO ₅ P ₃ Zr	C ₆₇ H ₁₁₅ CoN ₃ Na ₂ O ₉ P ₃ Zr	C ₅₂ H ₈₃ CoN ₃ O ₂ P ₃ SiZr
fw	945.19	1184.51	1395.72	1053.41
T (K)	120	120	120	120
λ (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	10.7492(5)	12.6585(3)	14.3700(5)	18.5044(9)
b (Å)	11.2308(6)	19.2534(5)	24.6113(8)	12.2107(6)
c (Å)	20.7876(11)	25.0678(15)	20.1119(7)	24.3932(13)
α (°)	93.048(3)	90.0430(10)	90	90
β (°)	103.754(3)	92.5240(10)	90.003(2)	94.917(3)
γ (°)	100.868(3)	91.2040(10)	90	90
V (Å ³)	2381.2(2)	6102.2(2)	7112.9(4)	5491.4(5)
space group	<i>P</i> -1	<i>P</i> -1	P121/n1	P2 ₁ /c
Z	2	4	4	4
D _{calc} (g/cm ³)	1.318	1.289	1.303	1.274
μ (cm ⁻¹)	7.06	5.75	5.14	6.41
R1, wR2 ^a (I > 2σ(I))	0.0482, 0.1063	0.0489, 0.1039	0.0427, 0.0875	0.0270, 0.069
^a R1 = $\frac{\sum F_o - F_c }{\sum F_o }$, wR2 = $\left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$				

Figure S1. ^1H NMR spectrum of $(\text{OC})\text{Co}(\text{iPr}_2\text{PNMes})_2(\mu\text{-O})\text{Zr}(\text{iPr}_2\text{PNMes})$ (**2**) (C_6D_6 , 400 MHz).

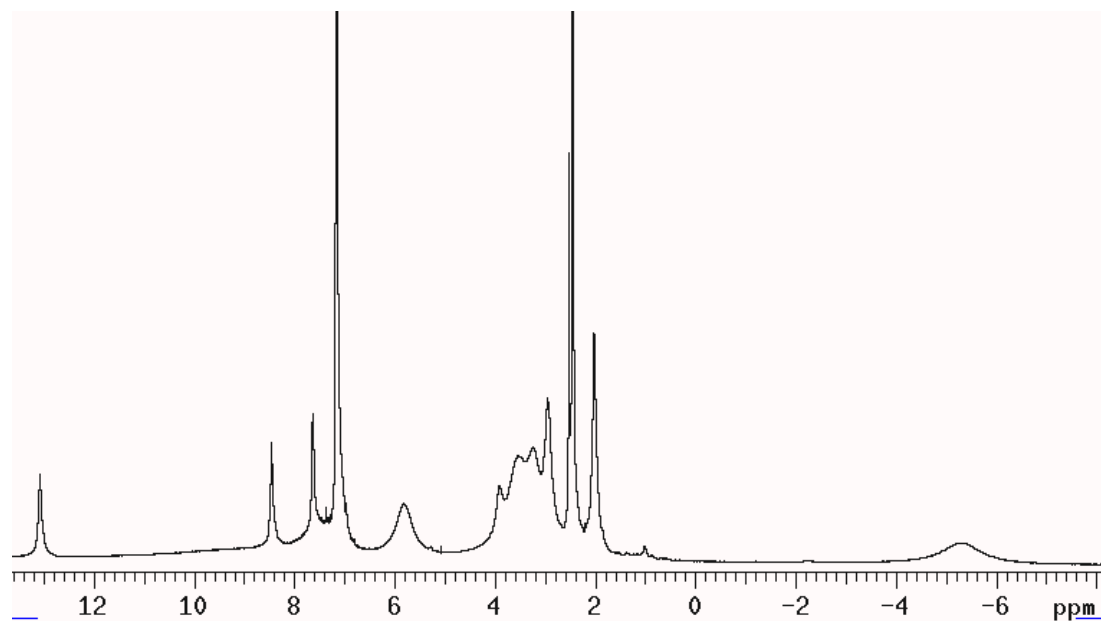


Figure S2. ^1H NMR spectrum of $(\text{OC})\text{Co}(\text{iPr}_2\text{PNMes})_3\text{Zr}(\text{O})\text{Na}(\text{THF})_3$ (**3**) (C_6D_6 , 400 MHz).

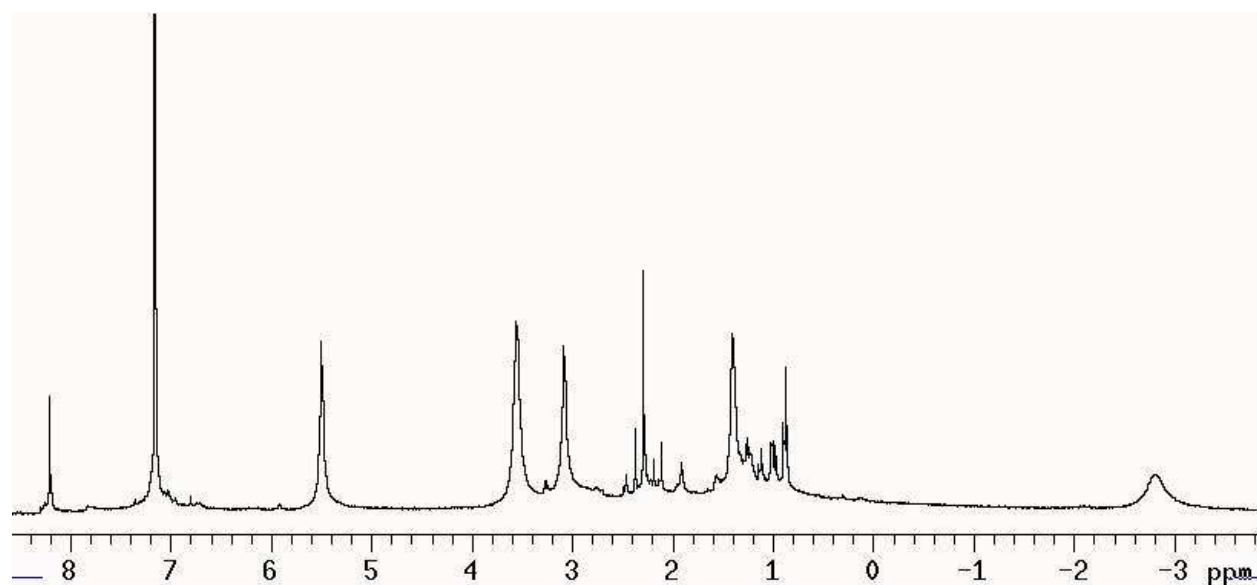


Figure S3. ^1H NMR spectra of $(\text{OC})(\text{H})\text{Co}(\text{iPr}_2\text{PNMes})_3\text{Zr}(\text{OSiH}_2\text{Ph})$ (**5**) and $(\text{OC})(\text{D})\text{Co}(\text{iPr}_2\text{PNMes})_3\text{Zr}(\text{OSiD}_2\text{Ph})$ (**5^D**).

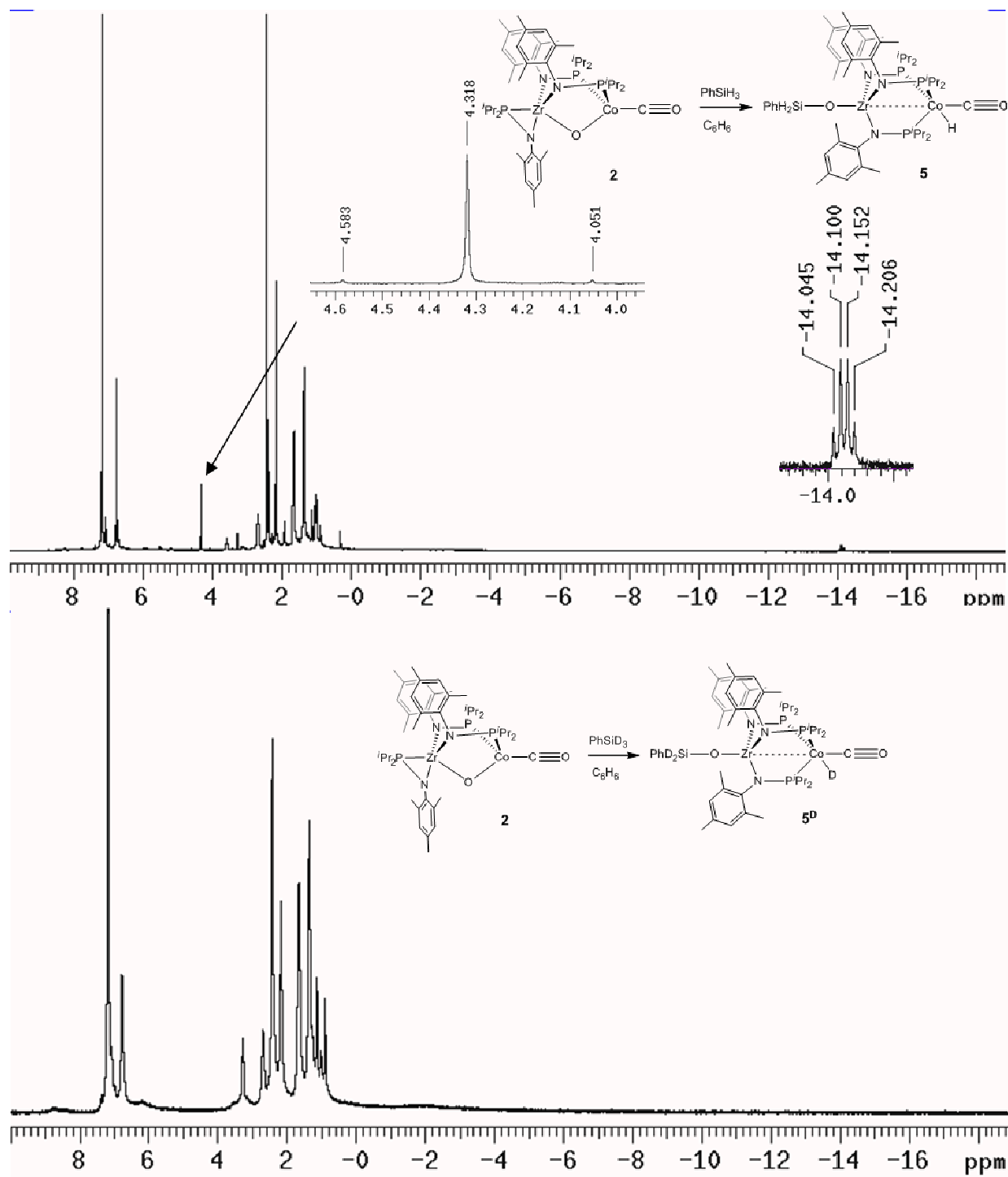


Figure S4. IR spectra of $(OC)(H)Co(iPr_2PNMes)_3Zr(OSiH_2Ph)$ (**5**) and $(OC)(D)Co(iPr_2PNMes)_3Zr(OSiD_2Ph)$ (**5^D**).

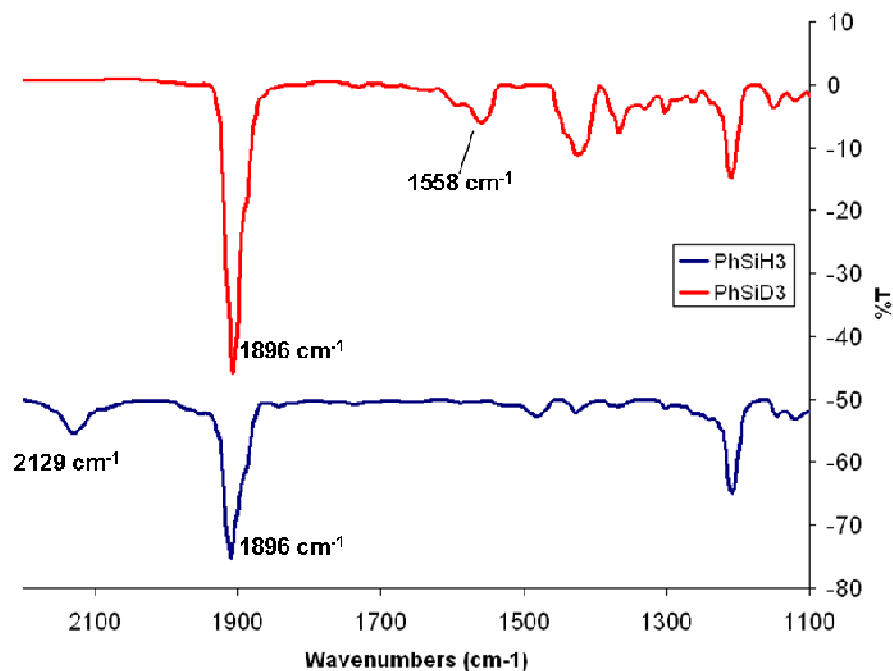


Figure S5. CV of $(OC)Co(iPr_2PNMes)_2(\mu-O)Zr(iPr_2PNMes)$ (**2**) (potentials are references to Fc).

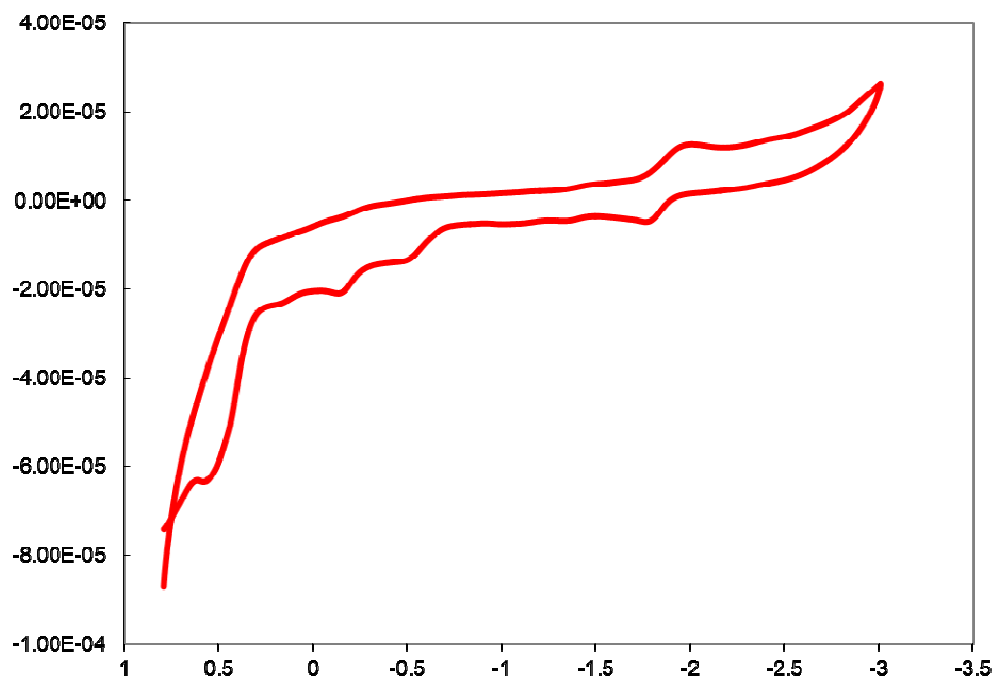
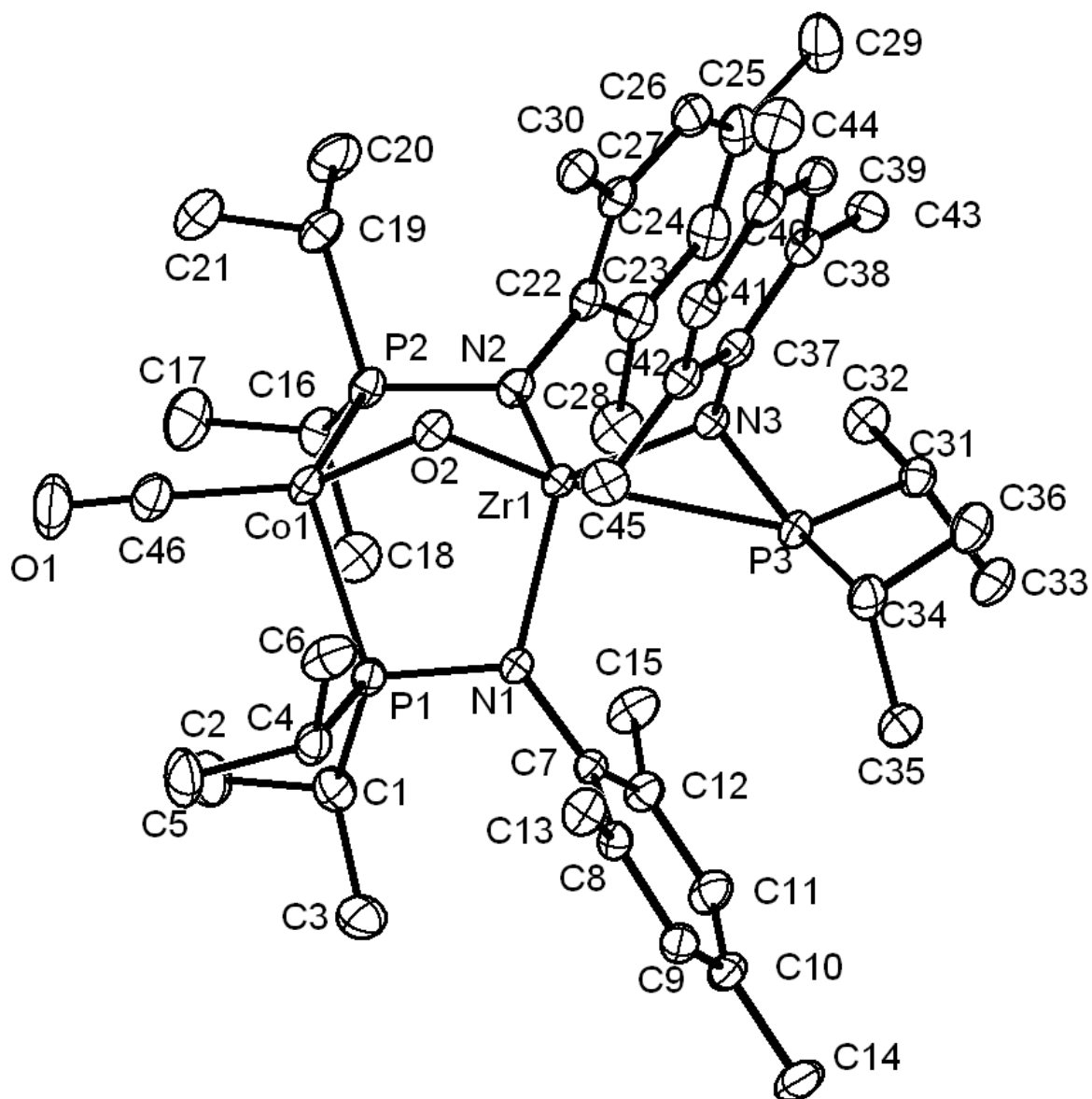


Figure S6. Fully labeled ellipsoid representation of (OC)Co(ⁱPr₂PNMes)₂(μ-O)Zr(ⁱPr₂PNMes)
(2).



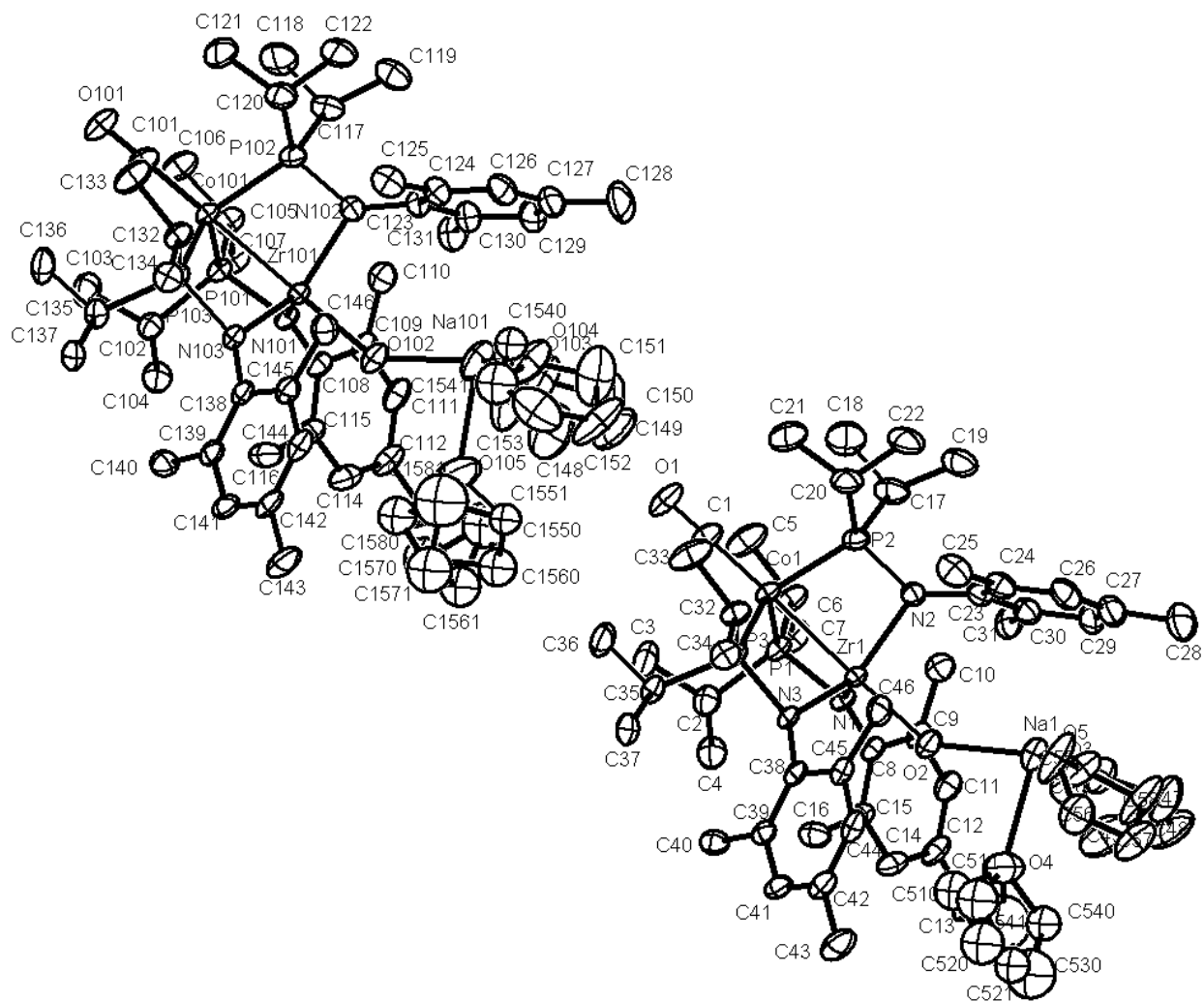
X-Ray data collection, solution, and refinement for 2. Data collection carried out at 120K, using a frame time of 20 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of five phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 98.2%. A total of 3324 frames were collected. Final cell constants were obtained from the xyz centroids of 9903 reflections after integration.

From the systematic absences and the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using direct methods (*SIR92*).³ Refinement (full-matrix-least squares) was carried out using the Oxford University *Crystals for Windows* program.⁴ All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps (including H atoms attached to metal bound –CH₃ moieties), the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. The final least-squares refinement converged to $R_1 = 0.0482$ ($I > 2\sigma(I)$, 10724 data) and $wR_2 = 0.1147$ (F^2 , 13843 data, 505 parameters). The final CIF is available as supporting material.

³ Altomare, A; Cascarano, G; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, 27, 435.

⁴ Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, 36, 1487.

Figure S7. Fully labeled ellipsoid representation of (THF)₃Na-O-Zr(MesNP^{*i*}Pr₂)₃Co(CO) (**3**).



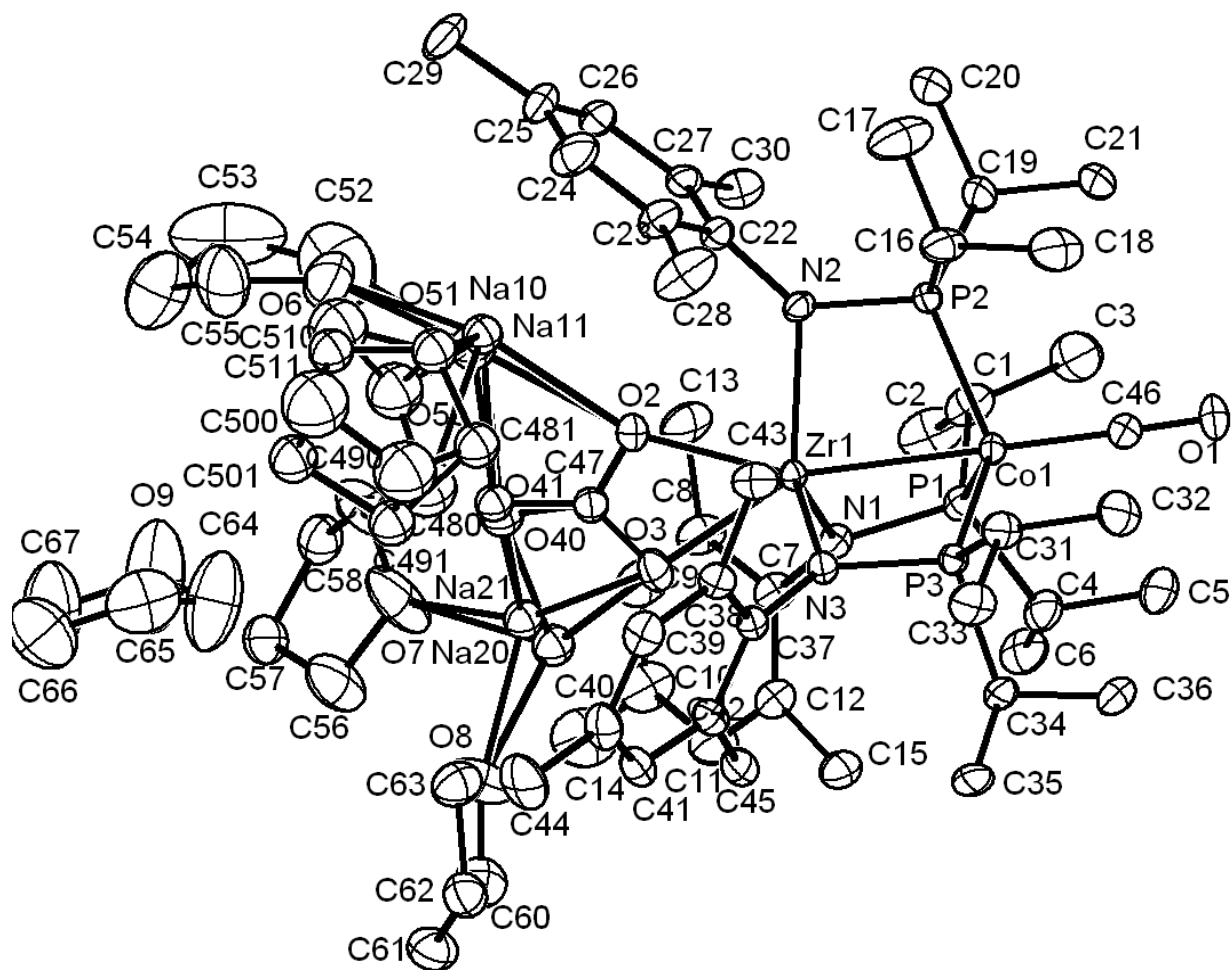
X-Ray data collection, solution, and refinement for 3. Data collection was carried out at 120K, using a frame time of 40 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of three phi and one omega scan sets, with 0.5° steps in phi or omega; completeness was 99.5%. A total of 2300 frames were collected. Final cell constants were obtained from the xyz centroids of 9960 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*.³ The structure was refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁴ All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. There are two molecules of each heterobimetallic complex in the asymmetric unit; the second molecule has a numbering scheme 100 greater than the first molecule. The two molecules are pseudo-B-centered; the B-centering is inexact, as strongly evidenced by the presence of *many* reflections with $h+l$ odd; these have about 30% of the $\langle F^2 \rangle$ of other reflection classes. Three of the six THF molecules bonded to Na(1) and Na(101) were significantly disordered. The THF molecules have O atoms labeled O(3) through O(5), and O(103) through O(105). Resolvable disorder was modeled, in whole or part, for the carbon atoms of the THF molecules attached to O(4), O(104) and O(105). Occupancies of the disordered atoms were fixed at 0.5 and the atoms were refined by using isotropic displacement parameters. For the molecule containing atom O(4), the disordered pairs were: C(510)/C(511), C(520)/C(521), C(530)/C(531) and C(540)/C(541); for the molecule containing O(104): C(1540)/C(1541); and for the molecule containing O(105): C(1550)/C(1551), C(1560)/C(1561), C(1570)/C(1571), C(1580)/C(1581). After location of H atoms on electron-density difference maps, the H atoms attached to ordered atoms were initially

refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.⁵ The remaining H atoms on disordered THF carbon atoms were placed at geometric positions and refined with riding constraints. The final least-squares refinement converged to $R_1 = 0.0489$ ($I > 2\sigma(I)$, 16601 data) and $wR_2 = 0.1221$ (F^2 , 29526 data, 1288 parameters). The final CIF is available as supporting material; we note that the CheckCIF routine produced six alert B items, related to pseudosymmetry and the solvate disorder. Accordingly, the CIF file contains validation reply form items which explain these issues in detail.

⁵ Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Cryst.* **2010**, *43*, 1100–1107.

Figure S8. Fully labeled ellipsoid representation of $(\text{THF})_4\text{Na}_2(\text{CO}_3)\text{-Zr}(\text{MesNP}^i\text{Pr}_2)_3\text{Co}(\text{CO})$ ($4\cdot\text{THF}$).



X-Ray data collection, solution, and refinement for 4•THF. Data collection was carried out at 120K, using a frame time of 10 sec and a detector distance of 65 mm. The optimized strategy used for data collection consisted of four phi and six omega scan sets, with 0.5° steps in phi or omega; completeness was 97.5%. A total of 1286 frames were collected. Final cell constants were obtained from the xyz centroids of 9955 reflections after integration.

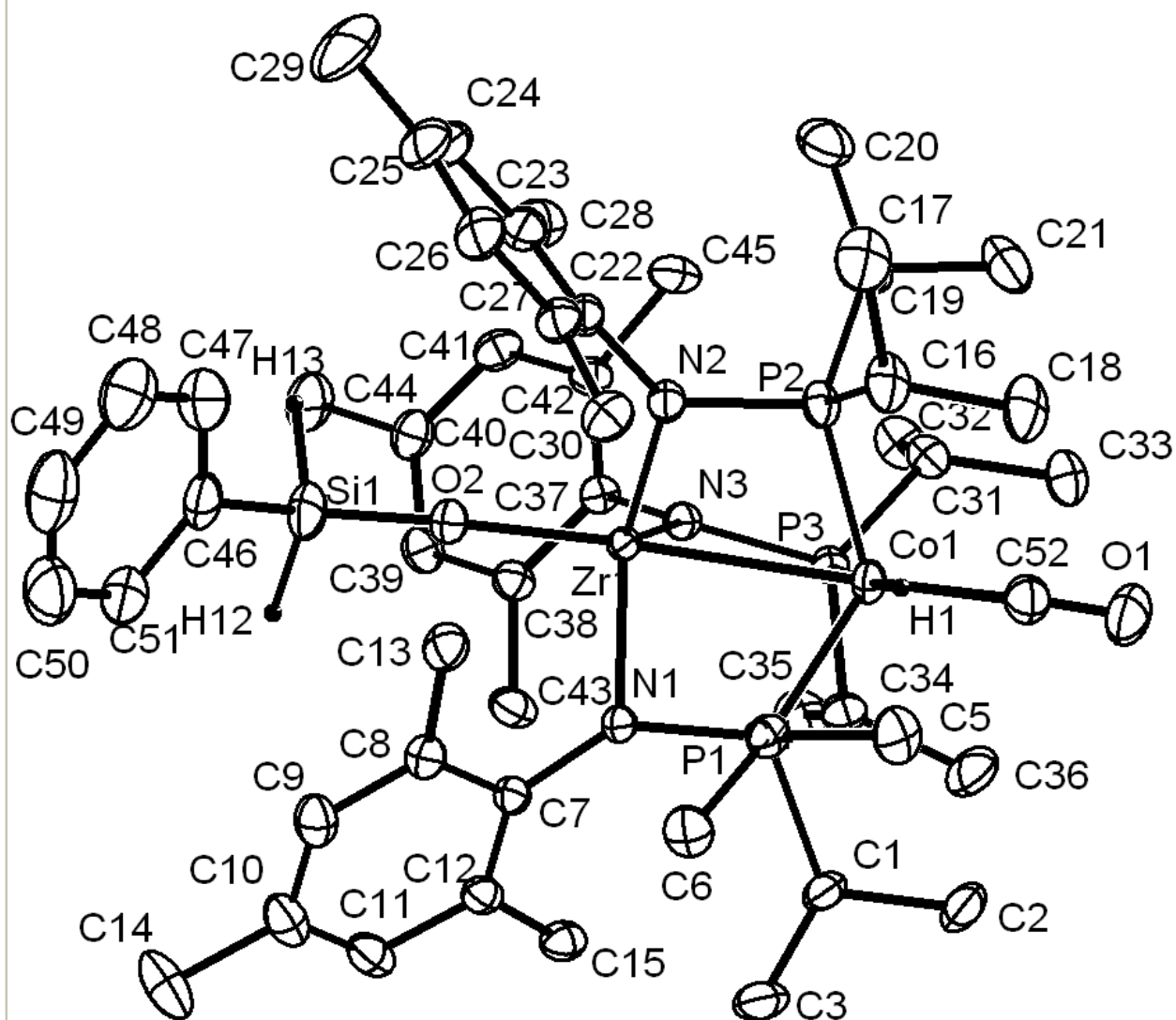
Initial examination of the data showed it to have metric orthorhombic symmetry, with additional *mmm* diffraction symmetry; however, the structure could not be solved successfully in the orthorhombic system. Reconsideration of the data, including use of the ROTAX procedure in the Oxford *CRYSTALS* software,⁶ suggested a monoclinic TLS twin,⁷ with a rotation about the *a* axis, and twin law (1 0 0 / 0 -1 0 / 0 0 1). The component ratio was accordingly fixed at 1:1 and was not refined (later refinement tests showed this to be a valid assumption). For the monoclinic analysis, space group *P2₁/n* was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*.³ The structure was refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁴ All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. A disordered carbonate ion is bound to the Zr atom, and also to two Na ions. The Na ions are each disordered as well, and each bound to two THF molecules. Additionally, there is a THF solvate molecule not associated with a metal atom. The disorder was resolved, in part, for one O atom of the carbonate, the Na ions, and one of the three THF molecules. The THF molecules have O atoms labeled O(50), O(51) and O(6) through O(9). Resolvable disorder was modeled, in whole or part, for the major component (carbonate O(40), Na(10), Na(20) and THF

⁶ Cooper, R. I.; Gould, R. O.; Parsons, S.; Watkin, D. J. *J. Appl. Cryst.* **2002**, 35, 168-174.

⁷ Donnay, G.; Donnay, J. D. H. *Canadian Mineralogist*, **1974**, 12, 422-425.

O(50), C(480)/(490)/(500)/(510)) and the minor component ((carbonate O(41), Na(11), Na(21) and THF O(51), C(481)/(491)/(501)/(511)). Occupancies of the disordered atoms were refined and constrained to sum to 1.0; the major component occupancy refined to a value of 0.605(4). Disordered component atoms were refined by using isotropic displacement parameters. After location of most H atoms on electron-density difference maps, the H atoms attached to ordered atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.⁵ The remaining H atoms on disordered THF carbon atoms were placed at geometric positions and refined with riding constraints. The final least-squares refinement converged to $R_1 = 0.0427$ ($I > 2\sigma(I)$, 17163 data) and $wR_2 = 0.0911$ (F^2 , 20407 data, 768 parameters). The final CIF is available as supporting material; we note that the CheckCIF routine produced four alert B items, related to the solvate disorder. Accordingly, the CIF file contains validation reply form items which explain these issues in detail.

Figure S9. Fully labeled ellipsoid representation of (OC)Co(ⁱPr₂PNMes)₃Zr(OSiH₂Ph) (**5**).



X-Ray data collection, solution, and refinement for 5. Data collection was carried out at 120K, using a frame time of 5 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and six omega scan sets, with 0.5° steps in phi or omega; completeness was 99.8%. A total of 2446 frames were collected. Final cell constants were obtained from the xyz centroids of 9838 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P2_1/c$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using SIR-92,³ and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.⁴ All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, most of the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.⁵ Positional and isotropic displacement parameters were refined for the hydride H atom (H(1)) attached to Co(1) and the H atoms (H(12) and H(13)) attached to Si(1). The final least-squares refinement converged to $R_1 = 0.0270$ ($I > 2\sigma(I)$, 13182 data) and $wR_2 = 0.0761$ (F^2 , 15935 data, 580 parameters). The final CIF is available as supporting material; we note that the CheckCIF routine produced three alert B items, related to Hirshfeld test issues. Accordingly, the CIF file contains a validation reply form item which explains this issue in detail.