Synthesis and characterization of *N*-donor-functionalized enantiomerically pure pentadienyl ligands derived from (1*R*)-(–)-myrtenal

*Ann Christin Fecker, Bogdan-Florin Crăciun,[†] Peter Schweyen, Matthias Freytag, Peter G. Jones and Marc D. Walter**

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

Email: mwalter@tu-bs.de

Table of Content:

1. Tables with crystallographic details

Table S1. Crystallographic data

Compound reference	[K(18-crown-6)][**4b**](C_7H_8)$_{1.5}$	[K(18-crown-6)][**5a**]	**6a**	**7a**	**7c**	[(η^5-**1b**)$_2$Cr]	**8a**
Chemical formula	$C_{44\cdot50}H_{68}KNO_6Si$	$C_{31}H_{58}KNO_6Si$	$C_{34}H_{60}N_2Si_2V$	$C_{38}H_{68}N_2Si_2V$	$C_{36}H_{64}N_2Si_2V$	$C_{36}H_{42}Cr$	$C_{34}H_{60}CrN_2Si_2$
Formula Mass	780.19	607.97	603.96	660.06	632.01	526.70	605.02
Crystal system	triclinic	orthorhombic	trigonal	monoclinic	monoclinic	monoclinic	trigonal
a/Å	12.4737(5)	10.9468(5)	11.1429(5)	20.253(3)	21.1726(4)	18.2976(12)	11.1701(3)
b/Å	13.7720(8)	15.2293(7)	11.1429(5)	9.3776(9)	10.8238(2)	8.4153(4)	11.1701(3)
c/Å	14.5622(6)	21.0704(9)	47.384(4)	11.5863(18)	17.2399(3)	10.3168(6)	47.1697(12)
α/°	75.635(4)	90.00	90.00	90.00	90.00	90.00	90.00
β/°	70.978(4)	90.00	90.00	118.80(2)	112.341(2)	118.956(8)	90.00
γ/°	71.884(5)	90.00	120.00	90.00	90.00	90.00	120.00
Unit cell volume/Å^3	2217.60(18)	3512.7(3)	5095.1(5)	1928.3(5)	3654.27(12)	1389.99(14)	5096.9(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	*P*1	$P2_12_12_1$	$P3_121$	*C*2	*C*2	*C*2	$P3_121$
No. of formula units per unit cell, *Z*	2	4	6	2	4	2	6
Radiation type	Mo Kα	Mo Kα	Cu Kα	Mo Kα	Cu Kα	Cu Kα	Cu Kα
Absorption coefficient, μ/mm^{-1}	0.192	0.224	3.283	0.346	3.072	3.534	3.612
No. of reflections measured	112688	103238	67872	21171	84805	14925	167247
No. of independent reflections	21882	10594	7149	4755	7473	2627	7041
R_{int}	0.0721	0.0757	0.1130	0.0791	0.0434	0.0419	0.0783
Final R_1 values ($I > 2\sigma(I)$)	0.0569	0.0430	0.0521	0.0474	0.0251	0.0227	0.0401
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1029	0.0838	0.1027	0.0871	0.0646	0.0571	0.0858
Final R_1 values (all data)	0.0907	0.0567	0.0555	0.0730	0.0253	0.0232	0.0404
Final $wR(F^2)$ values (all data)	0.1152	0.0904	0.1041	0.0988	0.0648	0.0574	0.0860
Flack parameter	0.04(3)	-0.05(3)	0.014(6)	-0.03(2)	0.003(3)	-0.001(3)	0.012(4)
Goodness of fit on F^2	1.023	1.046	1.098	1.044	1.021	1.059	1.071
Δρ [e Å^{-3}]	0.525/-0.363	0.364/-0.313	0.493/-0.704	0.441/-0.356	0.188/-0.383	0.175/-0.218	0.843/-0.453

Table S2. Crystallographic data

Compound reference	8c	9a	9c	10a
Chemical formula	$C_{32}H_{56}CrN_2Si_2$	$C_{38}H_{68}CrN_2Si_2$	$C_{36}H_{64}CrN_2Si_2$	$C_{38}H_{68}N_2Si_2Ti$
Formula Mass	576.97	661.12	633.07	657.02
Crystal system	monoclinic	tetragonal	monoclinic	monoclinic
a/Å	12.8435(4)	13.11040(6)	19.0012(12)	20.3829(6)
b/Å	11.4810(4)	13.11040(6)	10.2756(5)	9.3659(2)
c/Å	22.2751(7)	44.8658(4)	10.8293(8)	11.5616(4)
α/°	90.00	90.00	90.00	90.00
β/°	93.430(3)	90.00	119.646(9)	118.629(4)
γ/°	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	3278.72(18)	7711.66(8)	1837.6(2)	1937.30(10)
Temperature/K	100(2)	100(2)	100(2)	100(2)
Space group	$P2_1$	$P4_12_12$	$C2$	$C2$
No. of formula units per unit cell, Z	4	8	2	2
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα
Absorption coefficient, μ/mm^{-1}	3.721	3.221	3.359	2.648
No. of reflections measured	106996	164048	20321	52766
No. of independent reflections	13282	8019	3739	4028
R_{int}	0.0844	0.0454	0.0442	0.0492
Final R_1 values ($I > 2\sigma(I)$)	0.0376	0.0268	0.0285	0.0253
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0843	0.0684	0.0759	0.0675
Final R_1 values (all data)	0.0413	0.0270	0.0293	0.0259
Final $wR(F^2)$ values (all data)	0.0861	0.0686	0.0764	0.0677
Flack parameter	0.004(3)	0.006(3)	-0.004(3)	-0.003(4)
Goodness of fit on F^2	1.035	1.038	1.079	1.080
Δρ [e Å^{-3}]	0.612/-0.441	0.185/-0.366	0.231/-0.375	0.197/-0.272

Table S3. Crystallographic data

Compound reference	**11b**	**11c**	**12b**	**12c**
Chemical formula	$C_{32}H_{48}NPSiZr$	$C_{28}H_{48}NPSiZr$	$C_{34}H_{52}NPSiZr$	$C_{26}H_{44}NPSiZr$
Formula Mass	596.99	548.95	625.05	520.90
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
a/Å	9.0279(4)	9.8671(3)	9.1586(3)	7.92432(10)
b/Å	11.6831(6)	12.8873(4)	11.4856(4)	12.28750(10)
c/Å	29.8354(14)	44.7904(13)	31.2867(10)	27.1770(3)
α/°	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	90.00
γ/°	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	3146.9(3)	5695.6(3)	3291.11(18)	2646.23(5)
Temperature/K	100(2)	100(2)	100(2)	100(2)
Space group	$P2_12_12_1$	$C222_1$	$P2_12_12_1$	$P2_12_12_1$
No. of formula units per unit cell, Z	4	8	4	4
Radiation type	Mo Kα	Mo Kα	Mo Kα	Cu Kα
Absorption coefficient, μ/mm^{-1}	0.459	0.500	0.442	4.488
No. of reflections measured	65376	82038	86435	52804
No. of independent reflections	8747	8086	9027	5564
R_{int}	0.0780	0.0633	0.0651	0.0454
Final R_1 values ($I > 2\sigma(I)$)	0.0467	0.0451	0.0386	0.0229
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0751	0.0755	0.0778	0.0563
Final R_1 values (all data)	0.0615	0.0486	0.0457	0.0234
Final $wR(F^2)$ values (all data)	0.0791	0.0764	0.0804	0.0567
Flack parameter	-0.05(3)	0.01(3)	-0.03(3)	-0.019(7)
Goodness of fit on F^2	1.072	1.265	1.149	1.036
Δρ [e Å^{-3}]	0.491/-0.700	0.576/-1.331	0.947/-0.579	0.339/-0.756

2. Preparation and molecular structure of [(η^5-**1b**)$_2$Cr]

$CrCl_2$ (61.5 mg, 0.5 mmol) was suspended in THF (30 mL) and a solution of the **1b-K** (276 mg, 1 mmol, 2 equiv.) dissolved in THF (5 mL) was added at ambient temperature. The reaction mixture was stirred for 4 h and the solvent was removed under dynamic vacuum. The residue was extracted with hexane (20 mL) to give a deep green solution that was filtered and concentrated to *ca.* 2 mL. The solution was stored at –30 °C to yield deep green crystals. Yield: 122 mg (0.232 mmol, 46%). Mp: 204 °C. Anal. Calc. for $C_{36}H_{42}Cr$ (526.73): C, 82.09; H, 8.04. Found: C, 82.42; H, 8.23. The E.I. mass spectrum (70 eV) showed a molecular ion at m/z = 526 amu with the following isotopic cluster distribution (in %): 524(9), 525(4), 526(100), 527(50), 528(16), 529(3). Simulated distributions (in %) for $C_{36}H_{42}Cr$: 524(5), 525(2), 526(100), 527(52), 528(16), 529(3).

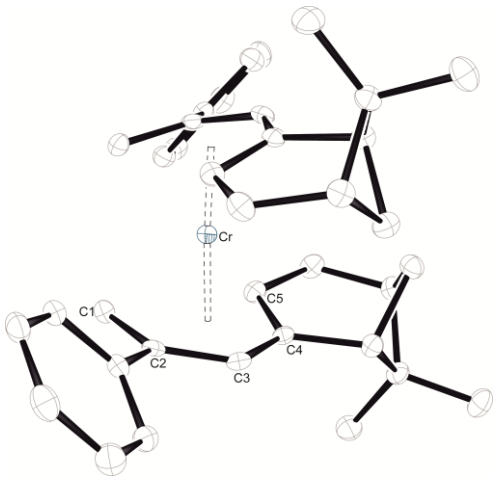

Figure S1. ORTEP of [(η^5-**1b**)$_2$Cr] with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.000, C1–Cr 2.1734(15), C2–Cr 2.1777(14), C3–Cr 2.2113(14), C4–Cr 2.2587(14), C5–Cr 2.2392(14), Pdl_{cent}–Cr 1.632; conformational angle χ 87, α_{planes} 25.3, Pdl_{plane}–Ph_{plane} 37.4, $\alpha_{H1\text{-}exo}$ 7.0, $\alpha_{H1\text{-}endo}$ –42.7,α_{H3} 5.0, α_{H5} –28.1. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

3. ORTEP representations

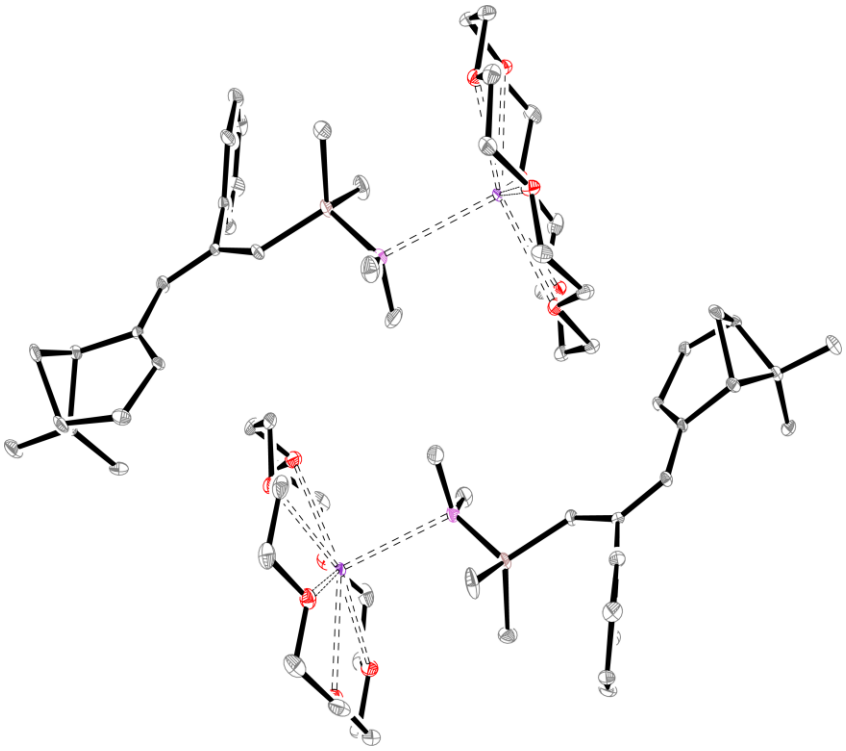

Figure S2. ORTEP of [K(18-crown-6)][**4b**] with thermal displacement parameters drawn at 30% probability. Three toluene molecules co-crystallized, but have been omitted for clarity.

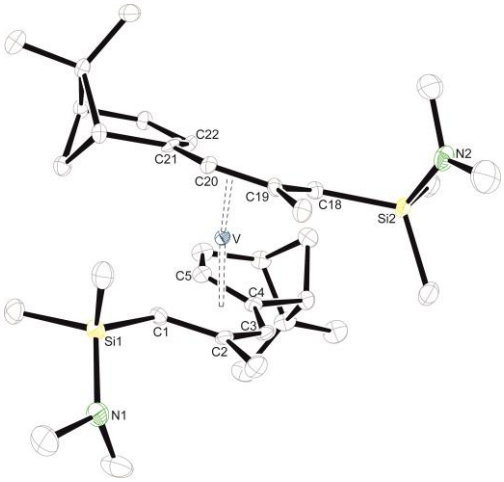

Figure S3. ORTEP of **6a** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.125, C18···C22 3.131, C1–V 2.253(3), C2–V 2.240(3), C3–V 2.237(3), C4–V 2.269(3), C5–V 2.265(3), C18–V 2.237(3), C19–V 2.252(3), C20–V 2.243(3), C21–V 2.273(3), C22–V 2.271(3), C1–C5 3.125, C18–C22 3.131,

Pdl_{cent}(C1–C5)–Cr 1.666, Pdl_{cent}(C18–C22)–Cr 1.669; C2–C1–Si1 124.9(2), C1–Si1–N1 109.6(2), C2–C1–Si1–N1 –46.8(3), C19–C18–Si2 122.6(2), C18–Si2–N2 109.8(2), C19–C18–Si2–N2 –48.8(3), conformational angle χ 76, α_{planes} 9.8. α_{Si1} –4.8, α_{H1} –37.1, α_{C13} 8.2, α_{H3} 7.9, α_{H5} –19.4, α_{Si2} –7.0, α_{H18} –33.8, α_{C30} 3.9, α_{H20} 8.1, α_{H22} –23.9. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

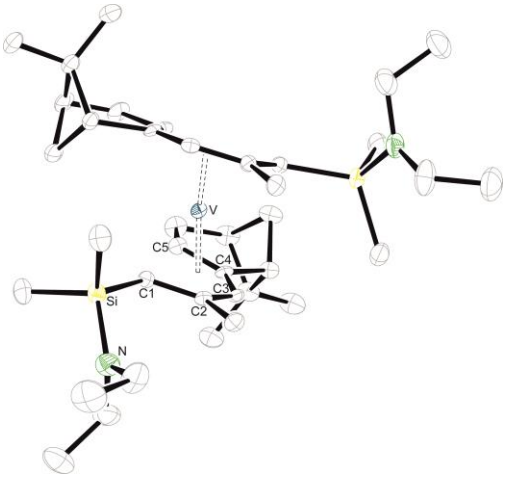

Figure S4. ORTEP of **7a** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.142, C1–V 2.241(3), C2–V 2.239(3), C3–V 2.234(3), C4–V 2.262(2), C5–V 2.253(3), Pdl_{cent}(C1–C5)–V 1.656; C2–C1–Si1 123.0(2), C1–Si1–N1 111.7(1), C2–C1–Si1–N1 –37.4(3), conformational angle χ 80, α_{planes} 11.2. α_{Si1} –6.5, α_{H1} –40.3, α_{C13} 7.8, α_{H3} 7.5, α_{H5} –18.2. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

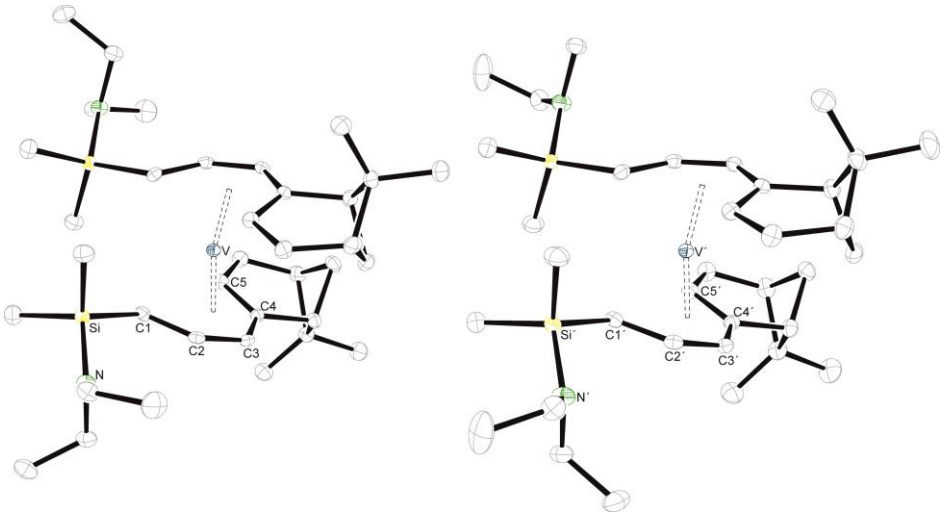

Figure S5. ORTEP of **7c** with thermal displacement parameters drawn at 50% probability. Two independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (deg): C1···C5 3.175 [3.165], C1–V 2.2647(14) [2.2660(14)], C2–V 2.2117(13) [2.2106(13)], C3–V 2.2742(14) [2.2724(13)], C4–V 2.2967(14) [2.3056(13)], C5–V 2.1999(14) [2.2004(14)], Pdl_{cent}(C1–C5)–V 1.660 [1.660]; C2–C1–Si 116.5(1) [117.7(1)], C1–Si–N 107.05(7) [109.28(7)], C2–C1–Si–N –37.6(1) [–35.4(1)], conformational angle χ 79 [78], α_{planes} 18.6 [20.1], α_{Si1} 2.8 [1.4], α_{H1} –37.5 [–39.0,], α_{H2} 18.5 [17.6], α_{H3} 7.0 [5.9], α_{H5} –22.7 [–21.1]. (Values given in brackets [] correspond to the second molecule in the asymmetric unit.). Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

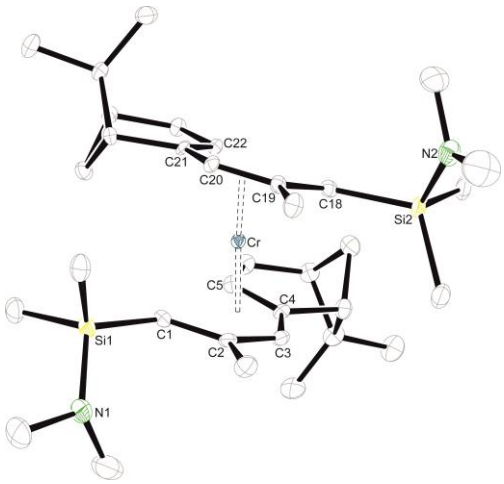

Figure S6. ORTEP of **8a** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.076, C18··· C22 3.076, C1–Cr 2.274(2), C2–Cr 2.206(2), C3–Cr 2.180(2), C4–Cr 2.232(2), C5–Cr 2.299(2), C18–Cr 2.255(2), C19–Cr 2.221(2), C20–Cr 2.187(2), C21–Cr 2.231(2), C22–Cr 2.287(2), Pdl_{cent}(C1–C5)–Cr 1.655, Pdl_{cent}(C18–C22)–Cr 1.654; C2–C1–Si1 124.1(2), C1–Si1–N1 109.3(1), C2–C1–Si1–N1 –48.5(3), C19–C18–Si2 121.9(2), C18–Si2–N2 109.1(2), C19–C18–Si2–N2 –50.3(2), conformational angle χ 79, α_{planes} 8.8. α_{Si1} –4.5, α_{H1} –33.5, α_{C13} 6.2, α_{H3} 5.0, α_{H5} –21.5, α_{Si2} –6.4, α_{H18} –36.6, α_{C30} 7.6, α_{H20} 4.5, α_{H22} –20.6. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

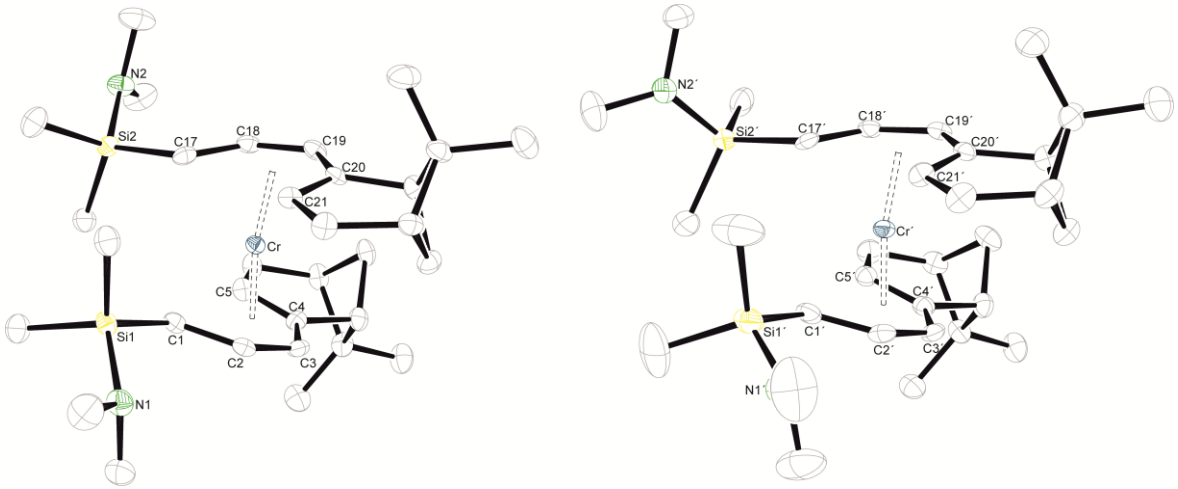

Figure S7. ORTEP of **8c** with thermal displacement parameters drawn at 50% probability. Two independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (deg): C1···C5 3.074 [3.081], C17···C21 3.082 [3.067], C1–Cr 2.240(2) [2.252(2)], C2–Cr 2.138(2) [2.141(2)], C3–Cr 2.193(2) [2.191(2)], C4–Cr 2.276(2) [2.270(3)], C5)–Cr 2.299(2) [2.266(3)], C17–Cr 2.229(2) [2.234(2)], C18–Cr 2.146(2) [2.139(2)], C19)–Cr 2.203(2) [2.190(2)], C20–Cr 2.266(2) [2.276(2),], C21–Cr 2.293(2) [2.292(3)], Pdl_{cent}(C1–C5)–Cr 1.646 [1.640], Pdl_{cent}(C17–C21)–Cr 1.643 [1.644]; C2–C1–Si1 120.0(2) [117.2(2)], C1–Si1–N1 108.1(1) [107.5(1)], C(2)–C(1)–Si(1)–N(1) –36.0(2) [–24.6(2)], C(18)–C(17)–Si(2) 118.1(2) [119.8(2)], C17–Si2–N2 110.6(1) [106.9(1)], C(18)–C(17)–Si(2)–N(2) –34.4(2) [–134.3(2)], conformational angle χ 65 [63], α_{planes} 19.4 [19.5], α_{Si1} 3.2 [2.4], α_{H1} –36.3 [–37.1], α_{H2} 19.5 [17.8], α_{H3} 4.6 [7.6],

α_{H5} –23.5 [–17.2], α_{Si2} 3.5 [4.2], α_{H17} –36.8 [–34.5], α_{H18} 13.9 [14.3], α_{H19} 1.8 [8.1], α_{H21} –24.5 [–20.6]. (Values given in brackets [] correspond to the second molecule in the asymmetric unit.). Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

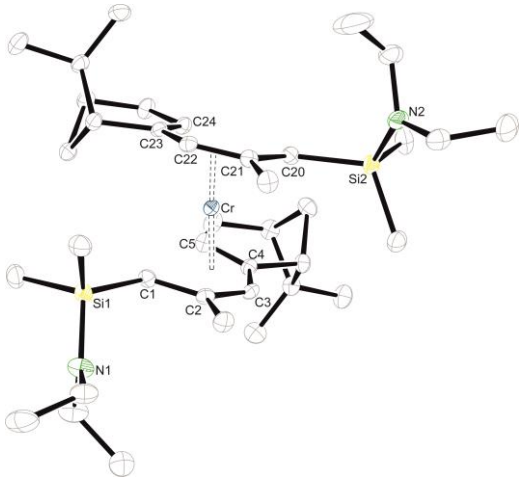

Figure S8. ORTEP of **9a** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.080, C20··· C24 3.061, C1–Cr 2.2826(14), C2–Cr 2.2144(14), C3–Cr 2.1776(14), C4–Cr 2.2255(14), C5–Cr 2.2829(14), C20–Cr 2.2923(14), C21–Cr 2.2210(14), C22–Cr 2.1854(14), C23–Cr 2.2177(14), C24–Cr 2.2643(14), Pdl_{cent}(C1–C5)–Cr 1.653, Pdl_{cent}(C20–C24)–Cr 1.656; C2–C1–Si1 122.5(1), C1–Si1–N1 110.97(6), C2–C1–Si1–N1 –50.0(1), C21–C20–Si2 122.8(1), C20–Si2–N2 109.76(6), C21–C20–Si2–N2 -48.6(1), conformational angle χ 81, α_{planes} 10.2. α_{Si1} –4.5, α_{H1} –33.5, α_{C13} 6.2, α_{H3} 5.0, α_{H5} –21.5, α_{Si2} –6.5, α_{H20} –36.6, α_{C32} 7.6, α_{H22} 4.5, α_{H24} –20.6. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

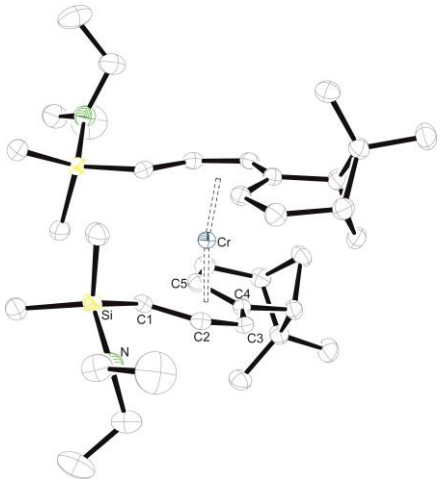

Figure S9. ORTEP of **9c** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.100, C1–Cr 2.2514(16), C2–Cr 2.1397(16), C3–Cr 2.2032(16), C4–Cr 2.2818(15), C5–Cr 2.2785(15), Pdl_{cent}(C1–C5)–Cr 1.645; C2–C1–Si 117.2(1), C1–Si–N 107.47(8), C2–C1–Si1–N –36.2(2), conformational angle χ 70, α_{planes} 20.0. α_{Si1} 2.5, α_{H1} –37.3, α_{H2} 15.4, α_{H3} 6.1, α_{H5} –21.9, α_{Si2} 2.5. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

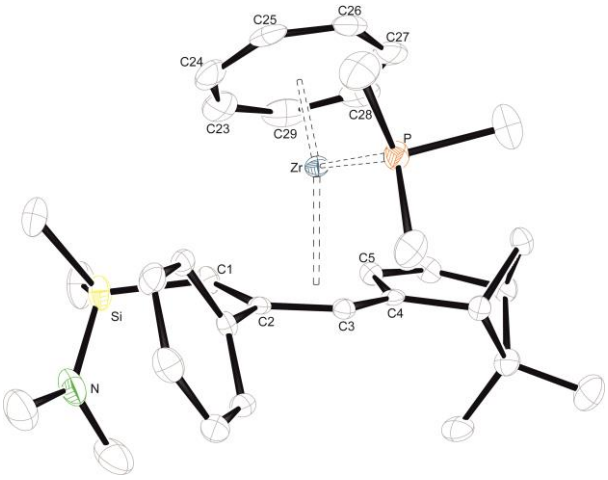

Figure S10. ORTEP of **11b** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.25, Zr–C1 2.683(3), Zr–C2 2.592(3), Zr–C3 2.472(3), Zr–C4 2.622(3), Zr–C5 2.755(3), Zr–C(av.) 2.6248±0.1058, Zr–P 2.8477(8), Pdl_{cent}(C1-C5)–Zr 2.13, CHT_{cent}(C25–C31)–Zr 1.77; Pdl_{plane}(C1-C5)-Ph_{plane} 59, α_{planes} 40, β 98, γ 112, δ 150, C2–C1–Si 126.1(2), C1–Si–N 110.4(1), C2–C1–Si–N –41.3(3), α_{Si} –11.3, α_{H1} –7.2,

α_{Ph} 1.1, α_{H3} 0.5, α_{H5} –14.1. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

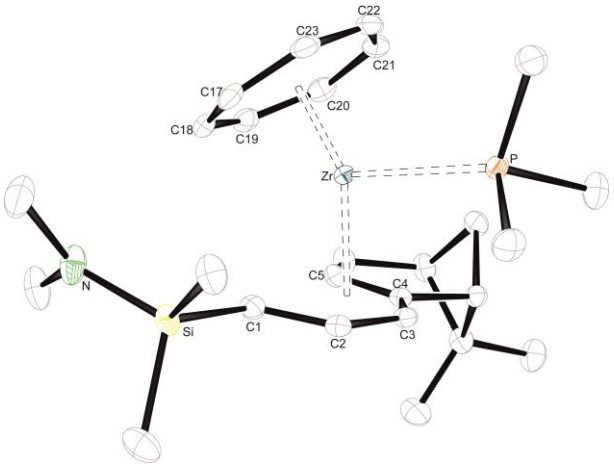

Figure S11. ORTEP of **11c** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.21, Zr–C1 2.655(2), Zr–C2 2.557(2), Zr–C3 2.492(2), Zr–C4 2.6310(19), Zr–C5 2.7235(19), Zr–C(av.) 2.6117±0.0895, Zr–P 2.8291(5), Pdl_{cent}(C1–C5)–Zr 2.13, CHT_{cent}(C19–C25)–Zr 1.78; α_{planes} 42, β 96, γ 116, δ 148, C2–C1–Si 121.29(15), C1–Si–N 109.9(1), C2–C1–Si–N 164.5(2), α_{Si} 0.3, α_{H1} –14.8, α_{H2} 4.1, α_{H3} 1.1, α_{H5} –14.5. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

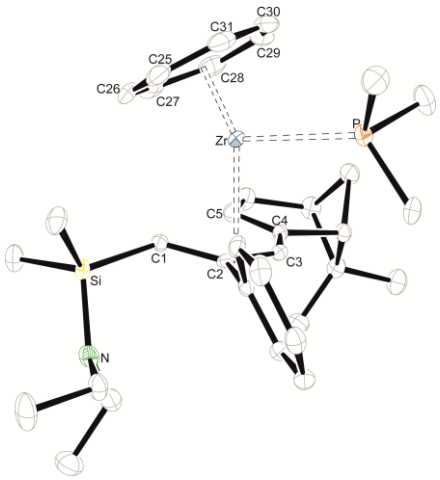

Figure S12. ORTEP of **12b** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.24, Zr–C1 2.665(2), Zr–C2 2.590(2), Zr–C3 2.480(2), Zr–C4 2.626(2), Zr–C5 2.777(3), Zr–C(av.) 2.6276±0.1083, Zr–P 2.8513(7), Pdl_{cent}(C1-C5)–Zr 2.14, CHT_{cent}(C25–C31)–Zr 1.77; Pdl_{plane}(C1–C5)–Ph_{plane} 59, α_{planes} 39, β 98, γ 112, δ 150, C2–C1–Si 125.4(2), C1–Si–N 109.4(1), C2–C1–Si–N –41.9, α_{Si} –12.3, α_{H1} –7.6, α_{Ph} 0.3, α_{H3} –1.6, α_{H5} –12.4. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

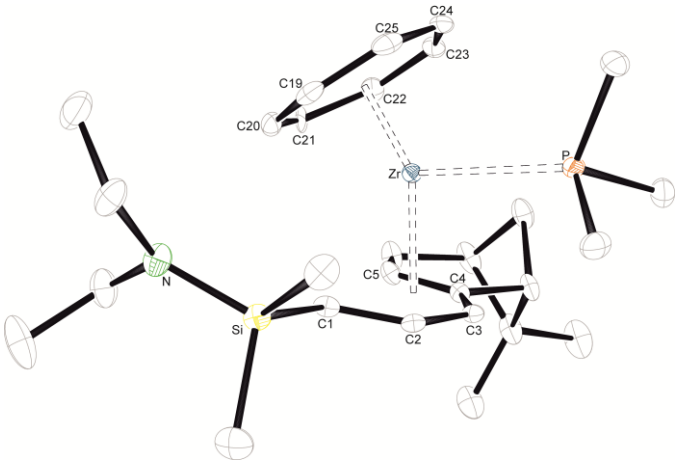

Figure S13. ORTEP of **12c** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1···C5 3.24, Zr–C1 2.669(3), Zr–C2 2.549(3), Zr–C3 2.484(3), Zr–C4 2.622(3), Zr–C5 2.729(3), Zr–C(av.) 2.6106±0.0967, Zr–P 2.8361(8), Pdl_{cent}(C1–C5)–Zr 2.12, CHT_{cent}(C19–C25)–Zr 1.77; α_{planes} 41, β 95, γ 116, δ 149, C2–C1–Si

119.9(2), C1–Si–N 111.0(1), C2–C1–Si–N 161.3(2), α_{Si} 2.8, α_{H1} –13.3, α_{H2} 4.4, α_{H3} –1.2, α_{H5} –17.5. Angles associated with a negative sign indicate that the group/atom is orientated away from the metal atom, whereas a positive sign specifies that the group/atom points towards the metal.

3. EPR Studies on **7a**

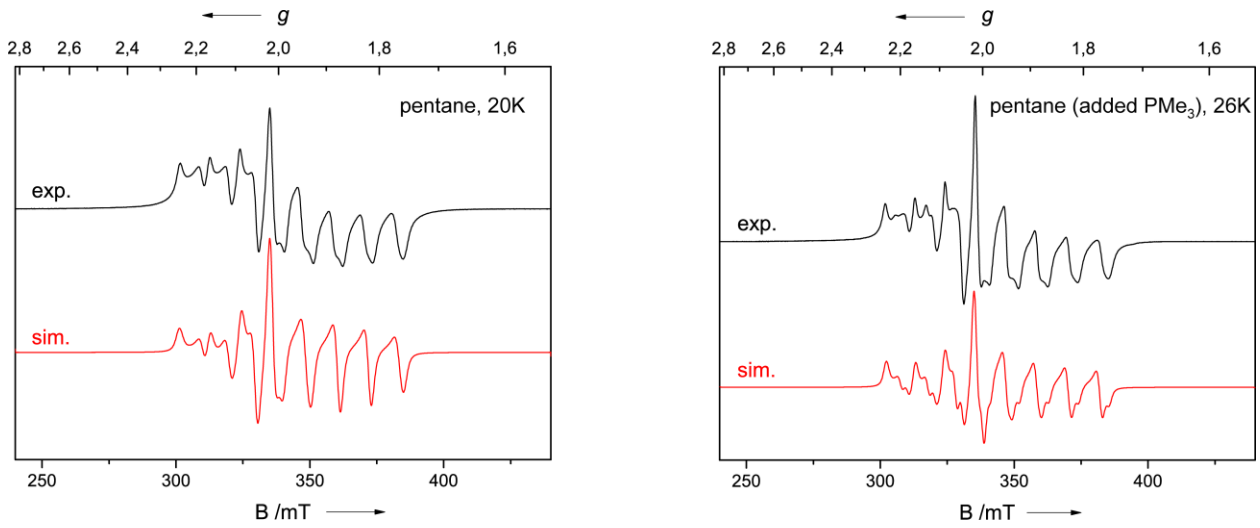

Figure S14. X-Band EPR spectra of **7a** recorded in pentane solution at 20K and 26K. Simulated parameters are listed in Table S3.

Table S3. Simulated EPR parameters for **7a** in the presence and absence of PMe_3.

Compound / host	**g_1, g_2, g_3**	**$A_{V,1}$, $A_{V,2}$, $A_{V,3}$ / cm^{-1}**	**$A_{P,1}$, $A_{P,2}$, $A_{P,3}$ / cm^{-1}**
7a / pentane [20K]	1.95, 1.97, 2.00	0.011, 0.0095, 0.001	
7a + PMe_3 / pentane [26K]	1.95, 1.975, 1.99	0.0098, 0.0105, 0.001	0.0024, 0.0005, 0.002