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Electronic Supplementary Information

Cyclometalated Titanium and Zirconium Complexes Stabilized by a New Silylmethylene-Linked Tetradentate Triamidophosphine

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1) Additional experimental details and additional ORTEP plots

Optimisation studies for the preparation of 1 · 2.5 Et₂O. For the synthesis of P(CH₂SiMe₂NHPh)₃ and its salts, several methods have been examined. Disappointingly, all attempts to directly prepare the free ligand P(CH₂SiMe₂NHPh)₃ (via reaction of PhNHSiMe₂CH₂PH₂ with 2 equiv. of PhNHSiMe₂CH₂Cl in the presence of 2 eq. base) have met with failure. Nevertheless, the free ligand can be obtained via reaction of $1 \cdot 2.5$ Et₂O with excess triethylammonium hydrochloride (*vide infra*). In the preparation of $1 \cdot 2.5$ Et₂O, only moderate yields of 45 % have been obtained after careful optimisation of the amounts of solvents used for the precipitation of $\mathbf{1} \cdot 2.5$ Et₂O. Phosphorus NMR analysis of the filtrate obtained after isolation of $1 \cdot 2.5$ Et₂O revealed that only minor amounts of product remained in solution. Although substantial amounts of the secondary phosphine intermediate PH(CH₂SiMe₂NHPh)₂ have been detected, the overall yield could not be improved by using more than two equivalents of PhNHSiMe₂CH₂Cl (in the presence of additional base). Out of the numerous unidentified products detected in the filtrate, [cyclo-PhN(SiMe₂CH₂)₂P]₂ was identified by single crystal X-ray diffraction (see Figure S1). Despite the fact that the latter crystals have been obtained in a poorly reproducible manner by simply cooling the filtrate to -80 °C, the found unexpected atom connectivity suggested the existence of exceedingly complex side-reactions. Thus, no further attempts were made to clarify the nature of the remaining unidentified by-products. Only traces of **1** were detected when *n*-BuLi was replaced by other bases (*e.g.* NaO^tBu or BnK).

P(CH₂SiMe₂NHPh)₃. Solid **1** · 2.5 Et₂O (0.33 g, 454 μmol, 1.0 eq) was added to a vigorously stirred suspension of Et₃NHCl (0.38 g, 2.76 mmol, 6.1 eq) in toluene (20 mL) and stirring was continued overnight. The resulting reaction mixture was filtered over Celite and the filtrate condensed to dryness to afford the product as a colourless oil (0.23 g, 430 μmol, 95 %). ¹H NMR (Tol-*d*₈, 600 MHz): δ [ppm] = 0.26 (s, 18 H, SiMe₂), 0.87 (s, 6 H, PCH₂), 3.27 (s, 3 H, NH), 6.57 (d, ³*J*_{H,H} = 7.7 Hz, 6 H, *o*-NPh), 6.75 (t, ³*J*_{H,H} = 7.3 Hz, 3 H, *p*-NPh), 7.12 (t, ³*J*_{H,H} = 7.9 Hz, 6 H, *m*-NPh); ³¹P{¹H} NMR (Tol-*d*₈, 162 MHz): δ (ppm) = 44.6 (s) ; ¹³C {¹H} NMR (Tol-*d*₈, 151 MHz): δ [ppm] = 0.4 (d, ³*J*_{C,P} = 4.8 Hz, SiMe₂), 20.8 (d, ¹*J*_{C,P} = 32.5 Hz, PCH₂), 117.1 (s, *o*-NPh), 118.5 (s, *p*-NPh), 137.7 (s, *m*-NPh), 147.6 (s, *ipso*-NPh) ; ²⁹Si DEPT NMR (Tol-*d*₈, 79.5 MHz): δ [ppm] = 0.37 (d, ²*J*_{Si,P} = 16.4 Hz, SiMe₂).



Fig. S1: ORTEP diagram of $[cyclo-PhN(SiMe_2CH_2)_2P]_2$ (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50 % probability). Selected bond lengths (Å) and angles (°):P1–P1' 2.2275(15), Si1–N 1.7382(18), Si2–N 1.7405(18), Si1–N–Si2 129.57(11). Symmetry transformation used to generate equivalent atoms: -x+1, -y+1, -z.



Fig. S2. ORTEP plot showing a section of the polymeric structure of $1 \cdot 3$ (O₂C₄H₈) (hydrogen atoms and co-crystallised 1,4-dioxane molecule omitted for clarity, thermal ellipsoids set at 50 % probability). Selected bond lengths (Å) and angles (°): Li1⁻⁻Li2 2.422(7), N1–Li1 2.017(6), N1–Li2 2.129(5), N2–Li1 1.988(5), N2–Li2 2.136(5), Li1–O1 1.871(5), Li2–O2 1.891(5), P–Li2 2.463(5), N3–Li3 1.993(5), N3–Li3' 2.062(5), Li3–O3 1.896(5), O2–Li2–P 124.3(2), Li1–N1–Li2 71.4(2), Li1–N2–Li2 71.8(2), N2–Li1–N1 113.3(3), N1–Li2–N2 103.3(2), O3–Li3–N3 128.5(3).

As mentioned in Note 59 (see main text), $[\kappa^4-N,N,N,P-PN_3]Hf(CH_2SiMe_3)$ (**6-Hf**) was isolated in pure form using the conditions employed for the generation of **6-Ti**. A C₃-symmetric structure in solution was deduced from NMR data (see Fig. S21), but a nearly C_s-symmetric was found for **6-Hf** in the crystal (see Fig. S3). This adds additional evidence to our proposal for the structure of **6-Ti**.

The experimental procedures used for the preparation of $[\kappa^4-N,N,N,P-PN_3]$ HfCl (**4-Hf**) and $[\kappa^4-N,N,N,P-PN_3]$ Hf(CH₂SiMe₃) (**6-Hf**) are provided below.

 $[\kappa^4$ -N,N,N,P-PN₃]HfCl (4-Hf). An intimate mixture of finely ground $1 \cdot 2.5$ Et₂O (500 mg, 688 μ mol, 1.0 eq) and finely ground HfCl₄(THF)₂ (320 mg, 688 μ mol, 1.0 eq) was cooled to -78 °C and pre-cooled (-78 °C) toluene (30 mL) was added via cannula. The reaction mixture was stirred at -78 °C for 1 h and allowed to warm to room temperature over the course of 12 h. The obtained pale yellow suspension was concentrated to approximately 10 mL and filtered over Celite. The clear filtrate was evaporated and the residue triturated with a mixture of *n*-pentane (10 mL) and Et₂O (1 mL). After stirring for 20 min at room temperature, the obtained fine precipitate was filtered off, washed with n-pentane (1 mL) and dried in vacuum to afford the product as a white powder (220 mg, 299 μ mol, 43 %). Elemental analysis calcd. for C₂₇H₃₉ClN₃PSi₃Hf: C 44.13, H 5.35, N 5.72; found: C 44.20, H 5.40, N 5.74. ¹H NMR (600 MHz, C_6D_6): δ [ppm] = 7.18 - 7.10 (m, 12 H, o-NPh and m-NPh), 6.87 (t, ${}^{3}J_{H,H}$ = 6.4 Hz, 3 H, p-NPh), 1.02 (d, $^{2}J_{H,P}$ = 11.7 Hz, 6 H, CH₂), 0.20 (s, 18 H, SiMe₂); $^{1}H\{^{31}P\}$ NMR (600 MHz, C₆D₆, selected peaks only): δ $[ppm] = 1.02 (s, 6 H, CH_2); {}^{13}C{}^{1}H} NMR (151 MHz, C_6D_6): \delta [ppm] = 146.9 (d, {}^{3}J_{C,P} = 7.8 Hz, ipso-NPh),$ 127.9 and 126.5 (s, *o*-NPh and *m*-NPh), 122.5 (s, *p*-NPh), 14.6 (d, ${}^{1}J_{C,P}$ = 9.9 Hz, CH₂), 0.2 (d, ${}^{3}J_{C,P}$ = 3.8 Hz, SiMe₂); ¹³C{¹H} NMR (151 MHz, C₆D₆): δ [ppm] = 150.1 (d, ³J_{C,P} = 7.8 Hz, *ipso*-NPh), 129.5 and 128.7 (s, o-NPh and *m*-NPh), 124.0 (s, *p*-NPh), 16.2 (d, ¹*J*_{C,P} = 7.9 Hz, CH₂), 2.4 (d, ³*J*_{C,P} = 3.7 Hz, SiMe₂); ³¹P{¹H} NMR (162 MHz, C₆D₆): δ [ppm] = -9.7; ²⁹Si DEPT NMR (79 MHz, C₆D₆): δ [ppm] = 9.8 (d, ²J_{Si,P} = 11.7 Hz, SiMe₂); ¹⁵N HMBC NMR (61 MHz, C₆D₆): δ [ppm] = 195.5.

[κ⁴-N,N,N,P-PN₃]Hf(CH₂SiMe₃) (6-Hf). A solution of LiCH₂SiMe₃ (14.5 mg, 155 μmol, 1.03 eq) in Et₂O (5 mL) was added dropwise to the vigorously stirred solution of 4-Hf (111 mg, 150 μ mol, 1.00 eq) in toluene (15 mL) maintained at -40 °C. The resulting reaction mixture was stirred for 20 min at -40 °C and then allowed to warm to room temperature. After stirring for 4 h at room temperature, all volatiles were removed in vacuum. Pentane (20 mL) was added to the yellowish residue and the resulting suspension filtered over Celite. The filtrate was concentrated to approximately 2 mL and kept at -40 °C overnight. The resulting white precipitate was filtered off and washed quickly with cold (-40 $^{\circ}$ C) npentane (0.5 mL). After drying in vacuum, the product was obtained as an off-white powder (88 mg, 112 μmol, 73 %). Elemental analysis calcd. for C₃₁H₅₀N₃PSi₄Hf: C 47.34, H 6.41, N 5.34; found: C 47.38, H 6.37, N 5.44. ¹H NMR (600 MHz, C₆D₆): δ [ppm] = 7.24 - 7.20 (m, 6 H, *o*-NPh), 7.20 - 7.17 (m, 6 H, *m*-NPh), 6.90 (dd, J_{H,H} = 7.8 and 6.7 Hz, 3 H, *p*-NPh), 0.95 (d, ²J_{H,P} = 11.1 Hz, 6 H, CH₂), 0.23 (s, 18 H, SiMe₂), -0.21 (s, 9 H, SiMe₃), -0.38 (d, ³J_{H,P} = 2.1 Hz, 2 H, CH₂SiMe₃); ¹H{³¹P} NMR (600 MHz, C₆D₆, selected peaks only): δ [ppm] = 0.95 (s, 6 H, CH₂), -0.38 (s, 2 H, CH₂SiMe₃); ¹³C{¹H} NMR (151 MHz, C₆D₆): δ [ppm] = 150.6 (d, ³J_{C,P} = 8.7 Hz, *ipso*-NPh), 129.6 and 128.4 (s, *o*-NPh and *m*-NPh), 123.0 (s, *p*-NPh), 63.8 (d, ${}^{2}J_{C,P}$ = 20.1 Hz, *CH*₂SiMe₃), 15.7 (d, ${}^{1}J_{C,P}$ = 11.2 Hz, CH₂), 3.8 (s, CH₂SiMe₃), 3.1 (d, ${}^{3}J_{C,P}$ = 4.2 Hz, SiMe₂); $^{31}P{^{1}H}$ NMR (162 MHz, C₆D₆): δ [ppm] = -9.2 (s); ²⁹Si DEPT NMR (79 MHz, C₆D₆): δ [ppm] = 8.72 (d, ²J_{Si,P} = 12.0 Hz, SiMe₂), -0.78 (d, ³J_{Si,P} = 3.6 Hz, SiMe₃);¹⁵N HMBC NMR (61 MHz, C₆D₆): δ [ppm] = 192.8.



Fig. S3. ORTEP plot of the molecular structure of [κ^4 -N,N,N,P- PN_3]Hf(CH₂SiMe₃) (**6-Hf**) (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50 % probability). Selected bond lengths (Å) and angles (°): Hf-P 2.6316(9), Hf-N1 2.123(2), Hf-N2 2.126(2), Hf-N3 2.115(2), Hf-C28 2.257(2), Si4-C28 1.869(2), N1-Hf-N2 137.37(7), N1-Hf-P 72.47(6), N2-Hf-P 74.37(6), N3-Hf-P 92.05(5), N3-Hf-C28 121.70(8), C28-Hf-P 146.24(6), Si4-C28-Hf 121.34(11).

As stated in the article text, group 5 and group 6 complexes will be targeted in future studies, which will be directed towards the activation of small molecules. In view of this goal, preliminary experimental work was carried out to probe for the accessibility of tantalum complexes. It was found that the imido complex [κ^4 -N,N,N,P-PN₃]Ta=NSiMe₃ can be prepared and that this complex exhibits a nearly linear P–Ta=N–Si axis (see Fig. S4), which is indicative of a significant triple bond character of the tantalum imido bond. Details on the preparation of this complex and an ORTEP plot of its molecular structure are provided below.

[κ^4 -N,N,P-PN₃]Ta=NSiMe₃. A solution of (py)₂Cl₃Ta=NSiMe₃ (1.50 g, 2.80 mmol, 1.0 eq.) in toluene (25 mL) was added dropwise to stirred solution of $1 \cdot 2.5$ Et₂O (2.00 g, 2.80 mmol, 1.0 eq) in toluene (50 mL) at -78 °C. After 30 min at -78 °C, the mixture was allowed to warm to room temperature and stirred for 4 h. The brown-yellow suspension was filtered over Celite and the filtrate was evaporated subsequently. The beige residue was taken up in Et₂O (10 mL) and filtered once again. The filtrate was layered with *n*-pentane (10 mL) and kept at -40 C. Within 2 days a pale yellow precipitate had formed, which was isolated via filtration. The solid collected on the sinter glass filter was washed with *n*-pentane and dried in vacuum to afford the title compound as pale yellow microcrystals (0.68 g, 0.86 mmol, 30 %). Elemental analysis calcd. for C₃₀H₄₈N₄PSi₄Ta: C 45.67, H 6.13, N 7.10, found: C 44.87, H 5.85, N 6.61. ¹H NMR (600 MHz, C₆D₆): δ [ppm] = 7.24 - 7.17 (m, 12 H, *o*-NPh and *m*-NPh), 6.94 - 6.87 (m, 3 H, *p*-NPh), 0.90 (d, ²J_{H,P} = 11.2 Hz, 6 H, CH₂), 0.15 (s, 18 H, SiMe₂), -0.72 (s, 9 H, SiMe₃); ¹³C{¹H} NMR (151 MHz, C₆D₆): δ [ppm] = 160.6 (d, ³J_{C,P} = 8.4 Hz, *ipso*-NPh), 128.7 and 126.9 (s, *o*-NPh and *m*-NPh), 122.6 (s, *p*-NPh), 15.4 (d, ¹J_{C,P} = 12.3 Hz, CH₂), 2.6 (d, ³J_{C,P} = 5.3 Hz, SiMe₂), 1.48 (s, SiMe₃); ³¹P{¹H} NMR (162 MHz, C₆D₆): δ [ppm] = -10.2 (s); ²⁹Si DEPT NMR (79 MHz, C₆D₆): δ [ppm] = -21.9 (s, SiMe₃), 12.1 (d, ²J_{P,Si} = 13.0 Hz, SiMe₂); ¹⁵N HMBC NMR (61 MHz, C₆D₆): δ [ppm] = 194.1 (NPh), 406.5 (NSiMe₃).



Fig. S4. ORTEP plot of the molecular structure of $[\kappa^4-N,N,N,P-PN_3]$ Ta=NSiMe₃) (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50 % probability). Selected bond lengths (Å) and angles (°): Ta–P 2.7109(5), Ta–N1 2.0473(16), Ta–N2 2.0551(15), Ta–N3 2.0453(16), Ta–N4 1.7999(16), N4–Si4 1.7284(17), N1–Ta–N2 118.29(6), N2–Ta–N3 115.54(6), N3–Ta–N1 115.89(6), N4–Ta–P 179.04(6), Si4–N4–Ta 178.71(10).

2) Selected NMR spectra

¹H NMR spectra and ³¹P{¹H} NMR spectra of compounds **2**, **1** · 2.5 Et₂O, **4**-**M**, **5**-**M** and **7**-**M** (M = Ti, Zr) are provided on the following pages.



Fig. S6: ¹H NMR (600MHz, C₆D₆) of **2** (residual proton signal of C₆D₆ is labeled with *)



Fig. S8: ¹H NMR (400 MHz, THF- d_8) of **1** · 2.5Et₂O (residual proton signals of THF- d_8 are labeled with *).



Fig. S10: ¹H NMR (400 MHz, C_6D_6) of **4-Ti** (residual toluene signals are labeled with §, residual proton signal of C_6D_6 is labeled with *) and ¹H{³¹P} NMR (400 MHz, C_6D_6) of **4-Ti** (insets).



Fig. S12: ¹H NMR (600 MHz, C_6D_6) of **4-Zr** (residual proton signal of C_6D_6 is labeled with *).



Fig. S14: ¹H NMR (600 MHz, C_6D_6) of **5-Ti** (a silicon grease impurity is labeled with §, residual proton signal of C_6D_6 is labeled with *). ¹H and ¹H{³¹P} NMR (600 MHz, C_6D_6) of the aliphatic region is shown in the inset.



Fig. S16: ¹H NMR (600 MHz, C_6D_6) of **5-Zr** (residual toluene signals are labeled with \$, a silicon grease impurity is labeled with \$, residual proton signal of C_6D_6 is labeled with *).



Fig. S18: ¹H NMR (600 MHz, Tol- d_8) of **7-Ti** (residual proton signal of C₆D₆ is labeled with *); aromatic and aliphatic region of the ¹H and ¹H{³¹P} NMR spectrum shown in the insets.



Fig. S20: ¹H NMR (600 MHz, C₆D₆) of **7-Zr** (residual proton signal of C₆D₆ is labeled with *).



Fig. S22: ³¹P{¹H} NMR (243 MHz, C_6D_6) of the attempted dehydrocoupling reaction of PhPH₂ using **5-Zr** (10 mol-%). The decomposition products of **5-Zr** are found as several peaks in the range 0 ppm to -65 ppm and sum up to less than 10% as minor amounts of unidentified species precipitated from the mixture. The ¹H-coupled ³¹P NMR signals of the substrate and the product are shown in the insets.

3) Crystallographic data

compound	[cyclo-PhN(SiMe ₂ CH ₂) ₂ P] ₂	1 · 3 dioxane
formula	$C_{24}H_{42}N_2P_2Si_4$	$C_{39}H_{63}Li_3N_3O_6PSi_3$
Mr	532.89	805.98
crystal system	triclinic	triclinic
space group	P -1	P -1
a /Å	7.1947(2)	12.4277(2)
b /Å	8.3354(2)	13.1483(2)
c /Å	13.4789(3)	14.8044(3)
α /°	86.273(2)	106.9639(16)
β /°	78.908(2)	92.2955(16)
γ /°	73.161(3)	98.2181(15)
V /Å ³	759.19(4)	2281.50(7)
Z	1	2
F ₀₀₀	286	864
d _c /Mg⋅m ⁻³	1.166	1.173
X-radiation, λ /Å	Cu- <i>K</i> _α , 1.5418	Cu- <i>K</i> _α , 1.5418
μ /mm ⁻¹	2.920	1.639
max., min. transmission factors	1.0000, 0.7220	1.0000, 0.5658
data collect. temperature /K	110(1)	110(1)
heta range /°	3.3 - 70.9	3.6 - 71.1
index ranges (indep. set) h,k,l	±8, ±10, ±16	±15, ±16, ±17
reflections measured	22999	67698
unique [<i>R</i> _{int}]	2845 [0.0325]	9598 [0.059]
observed [/≥2♂(/)]	2583	7720
parameters refined [restraints]	177 [0]	503 [7]
GooF on <i>F</i> ²	1.045	1.024
<i>R</i> indices [<i>F</i> >4 σ (<i>F</i>)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0446, 0.1089	0.0598, 0.1485
R indices (all data) R(F), wR(F ²)	0.0488, 0.1112	0.0773, 0.1576
difference density: max, min /e·Å-3	1.082, -0.312	1.104, -0.626

Table S1: Details of the crystal structure determinations of $[cyclo-PhN(SiMe_2CH_2)_2P]_2$ and $1 \cdot 3$ dioxane.

compound	4-Ti ·0.5 toluene	4-Zr
formula	C _{30.5} H ₄₃ CIN ₃ PSi ₃ Ti	$C_{27}H_{39}CIN_3PSi_3Zr$
Mr	650.27	647.52
crystal system	monoclinic	monoclinic
space group	P 21/c	P 21/c
a /Å	10.90658(10)	8.92072(7)
b /Å	18.00949(16)	17.53308(17)
c /Å	17.67069(16)	21.06985(16)
β /°	101.8442(9)	101.8664(7)
V /Å ³	3397.01(5)	3225.06(5)
Z	4	4
F ₀₀₀	1372	1344
d _c /Mg⋅m ⁻³	1.271	1.334
X-radiation, λ /Å	Μο- <i>Κ</i> _α , 0.71073	Cu- <i>K</i> _α , 1.5418
μ /mm ⁻¹	0.508	5.247
max., min. transmission factors	1.0000, 0.9353	0.758, 0.686
data collect. temperature /K	110(1)	110(1)
heta range /°	3.3 - 29.0	4.3 - 72.0
index ranges (indep. set) h,k,l	-13 14, -23 24, -23 22	-11 10, -21 20, -25 26
reflections measured	49411	73372
unique [<i>R</i> _{int}]	8403 [0.0360]	6318 [0.0531]
observed [/≥2♂(/)]	7135	5848
parameters refined [restraints]	383 [23]	331 [0]
GooF on F ²	1.028	1.140
<i>R</i> indices [<i>F</i> >4 σ (<i>F</i>)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0380, 0.0914	0.0489, 0.1120
R indices (all data) R(F), wR(F ²)	0.0481, 0.0973	0.0528, 0.1141
difference density: max, min /e·Å⁻³	2.073, -0.999	2.481, -0.700

Table S2: Details of the crystal structure determinations of **4-Ti**·0.5 toluene and **4-Zr**.

compound	5-Zr	7-Ti
formula	$C_{31}H_{46}N_3OPSi_3Zr$	$C_{30}H_{47}N_3P_2Si_3Ti$
Mr	683.17	643.81
crystal system	monoclinic	monoclinic
space group	P 21/c	P 21/c
a /Å	10.51494(10)	11.600(5)
b /Å	15.79043(15)	17.549(7)
<i>c</i> /Å	20.4802(2)	17.579(7)
β /°	104.1509(10)	109.041(13)
V /Å ³	3297.26(6)	3383(2)
Ζ	4	4
F ₀₀₀	1432	1368
d _c /Mg⋅m ⁻³	1.376	1.264
X-radiation, λ /Å	Cu- <i>K</i> _α , 1.5418	Μο- <i>K</i> _α , 0.71073
μ /mm ⁻¹	4.456	0.478
max., min. transmission factors	0.820, 0.597	0.7464, 0.7098
data collect. temperature /K	110(1)	100(1)
heta range /°	3.6 - 70.8	1.7 - 32.5
index ranges (indep. set) h,k,l	±12, ±19, -24 23	±17, ±26, ±26
reflections measured	146326	86850
unique [<i>R</i> _{int}]	6306 [0.0933]	11765 [0.0324]
observed [/≥2♂(/)]	5815	10028
parameters refined [restraints]	367 [0]	437 [0]
GooF on <i>F</i> ²	1.092	1.049
<i>R</i> indices [<i>F</i> >4 σ (<i>F</i>)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0323, 0.0704	0.0295, 0.0743
R indices (all data) R(F), wR(F ²)	0.0374, 0.0723	0.0388, 0.0811
difference density: max, min /e·Å⁻³	0.633, -0.822	0.620, -0.250

Table S3: Details of the crystal structure determinations of **5-Zr** and **7-Ti**.

compound	6-Hf	$[\kappa^4-N,N,N,P-PN_3]$ Ta=NSiMe ₃
formula	$C_{31}H_{50}N_3PSi_4Hf$	$C_{30}H_{48}N_4PSi_4Ta$
Mr	786.56	789.00
crystal system	monoclinic	orthorhombic
space group	P 21/n	P bca
a /Å	13.187(6)	18.2029(17)
b /Å	17.538(7)	19.8978(17)
c /Å	15.841(6)	20.392(9)
β /°	106.018(7)	90
V /Å ³	3521(2)	7386.0(12)
Ζ	4	8
F ₀₀₀	1600	3200
d _c /Mg⋅m ⁻³	1.484	1.419
X-radiation, λ /Å	Μο- <i>Κ</i> _α , 0.71073	Μο- <i>Κ</i> _α , 0.71073
μ /mm ⁻¹	3.169	3.174
max., min. transmission factors	0.5655, 0.4844	0.5655, 0.4365
data collect. temperature /K	100(1)	100(2)
heta range /°	2.1 - 32.4	1.8 - 32.5
index ranges (indep. set) h,k,l	±19, ±25, ±23	-2627, -2930, -3029
reflections measured	89103	180196
unique [<i>R</i> _{int}]	12131 [0.0349]	12952 [0.0477]
observed [/≥2♂(/)]	9442	10407
parameters refined [restraints]	370 [0]	370 [0]
GooF on F ²	1.083	1.074
<i>R</i> indices [<i>F</i> >4 σ (<i>F</i>)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0252, 0.0542	0.0234, 0.0448
R indices (all data) R(F), wR(F ²)	0.0409, 0.0624	0.0382, 0.0509
difference density: max, min /e·Å ⁻³	1.766, -1.028	1.959, -1.052

Table S4: Details of the crystal structure determinations of **6-Hf** and $[\kappa^4-N,N,N,P-PN_3]$ Ta=NSiMe₃.

Crystal data and details of the structure determinations are compiled in Tables S1-S4. Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo- K_{α} radiation, sealed X-ray tube, graphite monochromator; compound **6-Hf**, **7-Ti** and [κ^4 -N,N,N,P-PN₃]Ta=NSiMe₃) or an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu- K_{α} radiation, microfocus X-ray tube, multilayer mirror optics; all other compounds). Data were corrected for air and detector absorption, Lorentz and polarization effects;^{1,2} absorption by the crystal was treated numerically (Gaussian grid; compounds 4-Zr and 5-Zr)^{2,3} or with a semiempirical multiscan method.⁴⁻⁶ The structures were solved by intrinsic phasing (compound 1.3 dioxane)⁷ or by the charge flip procedure (all other compounds),⁸ and refined by full-matrix least squares methods based on F^2 against all unique reflections.⁹ All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data the positions of most hydrogen atoms were taken from difference Fourier syntheses and refined. When found necessary, disordered groups and/or solvent molecules were subjected to suitable geometry and adp restraints. Crystals of $[cyclo-PhN(SiMe_2CH_2)_2P]_2$ and 1.3 dioxane were twinned; after de-twinning refinement for [cyclo-PhN(SiMe₂CH₂)₂P]₂ (twin fractions 0.78 and 0.22) was carried out against all singles involving the major domain whilst 1.3 dioxane (twin fractions 0.60 and 0.40) was refined against all singles and composites involving the major domain.

CCDC 1437764 - 1437769 and 1442399 - 1442400 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4) References

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