

Supporting Information for

Terminal Hafnium Phosphinidene Complexes and Phosphinidene Ligand Exchange

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General Considerations. All manipulations were performed under an atmosphere of dry nitrogen using Schlenk techniques and/or an M. Braun glovebox. Dry, oxygen-free solvents were employed throughout. Removal of thiophenes from benzene and toluene was accomplished by washing each with H₂SO₄ and saturated NaHCO₃ followed by drying over MgSO₄. Olefin impurities were removed from pentane by treatment with concentrated H₂SO₄, 0.5 N KMnO₄ in 3 M H₂SO₄, saturated NaHCO₃, and then the drying agent MgSO₄. Benzene-*d*₆ was purchased from Cambridge Isotope Laboratory and then degassed and dried over NaK alloy. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. Infrared spectra (Nujol mulls, KBr plates) were recorded using a Mattson FTIR spectrometer at a resolution of 2 cm⁻¹. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker 300, 400, and 500 MHz NMR spectrometers and are reported with reference to solvent resonances (C₆D₆, δ 7.16 and δ 128.0) or external H₂PO₄. X-ray diffraction data were collected on a Bruker Platform goniometer with a Charged Coupled Device (CCD) detector (Smart Apex). Structures were solved using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Complexes CpCp*HfMe(OTf),²⁸ phenylphosphine-*d*₂,²⁹ LiPHdmp•Et₂O¹⁷ from H₂Pdmp,³⁰ (dippe)PtCl₂,²² [(dippe)Pt(μ-H)]₂,²² HN(Np)Ar,²³ were prepared according to the literature protocols. Base-free lithium salts LiPHPh and LiNNp(Ar) were prepared by reaction of the

appropriate precursor with equimolar butyllithium in pentane, and 2-butyne was degassed and vacuum transferred from molecular sieves. All other chemicals were used as received.

CpCp*HfMe(PHPh) (2). A Schlenk flask was charged with CpCp*HfMe(OTf) (530 mg, 0.974 mmol), the solid dissolved in 8 mL Et₂O, and the resulting solution was cooled to -78 °C. A cold 10 mL Et₂O solution of LiPHPh (114 mg, 0.974 mmol) was added via cannula. The resulting orange solution was allowed to warm to ambient temperature with stirring. The volatile materials were removed under reduced pressure, and the orange residue was extracted with Et₂O. The resulting orange solution was filtered, and the volume of the solution was reduced to the point of incipient crystallization. With gentle warming, solids were redissolved and the homogeneous orange solution was cooled to -30 °C to afford yellow crystals of CpCp*HfMe(PHPh) in 2 crops (353 mg, 0.711 mmol, 73%). ¹H (C₆D₆, 400.1 MHz): δ 7.252 (t, C₆H₅, 2 H), 7.147 (m, C₆H₅, 2 H), 6.959 (t, C₆H₅, 1 H), 5.509 (s, C₅H₅, 5 H), 3.446 (dd, PH, 1 H, *J*_{PH} = 198 Hz, *J*_{HH} = 1.5 Hz), 1.755 (s, C₅(CH₃)₅, 15 H), -0.489 (d, CH₃, 3 H, *J*_{HH} = 1.5 Hz). ¹³C (C₆D₆, 100.6 MHz): δ 133.84 (d, Ph, *J*_{PC} = 14 Hz), 130.15 (s, Ph), 128.89 (Ph), 124.78 (Ph), 117.27 (s, C₅Me₅), 111.43 (s, C₅H₅), 44.10 (d, CH₃, *J*_{PC} = 16 Hz), 11.65 (d, C₅Me₅, *J*_{PC} = 6 Hz). ³¹P (C₆D₆, 161.97 MHz): δ -2.81. IR (Nujol, KBr): 2314 m, 1581 s, 1489 s, 1382 s, 1350 m, 1344 m, 1328 s, 1261 m, 1132 m, 1100 m, 1068 m, 1052 m, 1019 s, 898 s, 827 s, 814 s, 738 s, 538 w, 455 w, 404 w cm⁻¹. Anal. Calcd for C₂₂H₂₉HfP: C, 52.54; H, 5.81. Found: C, 53.09; H, 5.49.

CpCp*HfMe(PDPh) (2-d) was prepared by a route analogous to that for CpCp*HfMe(PHPh), using CpCp*HfMe(OTf) (234 mg, 0.430 mmol) and LiPDPh (51 mg, 0.430 mmol), in 75% isolated yield with ca. 95% deuterium incorporation. ¹H (C₆D₆, 400.1 MHz): δ 7.374 (t, C₆H₅, 2 H), 7.186 (m, C₆H₅, 2 H), 6.962 (t, C₆H₅, 1 H), 5.510 (s, C₅H₅, 5 H), 1.755 (s, C₅(CH₃)₅, 15 H), -

0.490 (d, CH_3 , 3 H, $J_{\text{PH}} = 1.3$ Hz). ^{13}C (C_6D_6 , 100.6 MHz): δ 133.84 (d, *Ph*, $J_{\text{PC}} = 14$ Hz), 130.15 (s, *Ph*), 128.89 (*Ph*), 124.78 (*Ph*), 117.27 (s, C_5Me_5), 111.43 (s, C_5H_5), 44.10 (d, CH_3 , $J_{\text{PC}} = 16$ Hz), 11.65 (d, C_5Me_5 , $J_{\text{PC}} = 6$ Hz). ^{31}P (C_6D_6 , 161.97 MHz): δ -2.66 (3-line, *HfPPh*, $J_{\text{PD}} = 30.6$ Hz).

CpCp*Hf(P₃Ph₃) (3). A 25 mL reaction tube was charged with CpCp*HfMe(PHPh) (134 mg, 0.270 mmol), and 7 mL of toluene was introduced via cannula. PH₂Ph (120 mg, 1.078 mmol) was added to the orange solution via syringe under an N₂ counter flow. The vessel was degassed and sealed, then heated to 95 °C for 18 h. The resulting orange solution was cooled to ambient temperature and the volatile material was removed under reduced pressure. The gummy orange residue was extracted with minimal pentane, and the solution was filtered, concentrated to ca 8 mL, and cooled to -30 °C to afford bright orange crystals of CpCp*Hf(η^2 -P₃Ph₃) in 92% yield (174 mg, 0.248 mmol). ^1H (C_6D_6 , 400.1 MHz): δ 8.503 (t, C_6H_5 , 2 H), 7.769 (br., C_6H_5 , 4 H), 7.218 (t, C_6H_5 , 4 H), 7.065-6.988 (m C_6H_5 , 5 H), 5.140 (s, C_5H_5 , 5 H), 1.672 (s, $\text{C}_5(\text{CH}_3)_5$, 15 H). ^{13}C (C_6D_6 , 100.6 MHz): δ 134.8 (m, *Ph*), 130.3 (m, *Ph*), 127.51 (s, *Ph*), 125.98 (s, *Ph*), 116.44 (s, C_5Me_5), 111.21 (s, C_5H_5), 12.28 (t, C_5Me_5 , $J_{\text{PC}} = 8$ Hz). ^{31}P (C_6D_6 , 161.97 MHz): δ 63.62 (d, $J_{\text{PP}} = 305$ Hz), -158.90 (t, $J_{\text{PP}} = 305$ Hz). IR (Nujol, KBr): 1636 m, 1579 s, 1367 s, 1307 m, 1236 w, 1182 w, 1153 w, 1120 m, 1068 m, 1012 m, 836 w, 819 m, 748 m, 734 s, 694 s, 621 w, 593 w, 480 m, 441 w, 414 w cm^{-1} . Anal. Calcd for $\text{C}_{33}\text{H}_{35}\text{HfP}_3$: C, 56.38; H, 5.02. Found: C, 56.49; H, 5.13.

CpCp*Hf[P,C: η^2 -P(Ph)C(Me)=C(Me)] (5). A 25 mL reaction vessel was charged with CpCp*HfMe(PHPh) (80 mg, 0.159 mmol). To the vessel, 8 mL of benzene was introduced via cannula, and 2-butyne (60 μL) was added by syringe under an N₂ counterflow. The vessel was sealed and stirred at 80 °C for 8.5 h. The resulting orange solution was evaporated under reduced

pressure and the residue was extracted into pentane. The pentane extract was filtered, concentrated to ca. 4 mL and cooled to $-30\text{ }^{\circ}\text{C}$ to yield the title compound as yellow crystals (59 mg, 0.109 mmol, 68%). ^1H (C_6D_6 , 400.1 MHz): δ 7.214 (t, C_6H_5 , 2 H), 7.175 (m, C_6H_5 , 2 H), 6.983 (t, C_6H_5 , 1 H), 5.423 (s, C_5H_5 , 5 H), 2.313 (d, CH_3 , 3 H, $J_{\text{PH}} = 6$ Hz), 2.165 (s, CH_3 , 3 H), 1.822 (s, $\text{C}_5(\text{CH}_3)_5$, 15 H). ^{13}C (C_6D_6 , 100.6 MHz): δ 213.79 (d, CMe , $J_{\text{PC}} = 12$ Hz), 151.25 (d, CMe , $J_{\text{PC}} = 49$ Hz), 130.43 (d, Ph , $J_{\text{PC}} = 19$ Hz), 128.16 (Ph), 124.34 (Ph), 117.63 (s, C_5Me_5), 110.75 (s, C_5H_5), 20.79 (d, CH_3 , $J_{\text{PC}} = 4$ Hz), 14.62 (d, CH_3 , $J_{\text{PC}} = 16$ Hz), 11.87 (d, C_5Me_5 , $J_{\text{PC}} = 9$ Hz). ^{31}P (C_6D_6 , 161.97 MHz): δ 53.19 (s, HfPPh). IR (Nujol, KBr): 3063 w, 2278 w, 1641 m ν_{CC} , 1562 m, 1299 w, 1201 w, 1151 w, 1101 m, 1066 m, 1025 s, 1012 m, 996 m, 912 w, 885 m, 738 w, 674 w, 593 w, 489 w, 458 w cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{HfP}_2$: C, 55.51; H, 5.78. Found: C, 55.20; H, 5.92.

CpCp*Hf(PHPh)(OCMePh₂) (6). A 50 mL Schlenk tube was charged with CpCp*HfMe(PHPh) (153 mg, 0.308 mmol) and benzophenone (56 mg, 0.308 mmol), and 6 mL of benzene was introduced via cannula under N_2 . After 8 h of stirring, the solution was filtered and lyophilized to give an orange solid. The solid was extracted with copious amounts of pentane to give an orange solution which was filtered. Cooling the solution to $-35\text{ }^{\circ}\text{C}$ produced orange crystals of CpCp*Hf(OMePh₂)(PHPh) in several crops (194 mg, 0.283 mmol, 92%). Major isomer: ^1H (C_6D_6 , 400.1 MHz): δ 7.576 (d, C_6H_5 , 2 H), 7.201-6.923 (m, C_6H_5 , 12 H), 6.855 (t, C_6H_5 , 1 H), 5.828 (s, C_5H_5 , 5 H), 4.500 (d, PH , 1 H, $J_{\text{PH}} = 214$ Hz), 1.774 (s, $\text{C}_5(\text{CH}_3)_5$, 15 H), 0.374 (s, CH_3 , 3 H). ^{13}C (C_6D_6 , 100.6 MHz): δ 147.0 (s, Ph), 146.2 (s, Ph), 136.0 (s, Ph), 135.8 (s, Ph), 135.7 (s, Ph), 135.2 (s, Ph), 129.4 (s, Ph), 129.3 (s, Ph), 128.5 (s, Ph), 127.7 (s, Ph), 127.2 (s, Ph), 126.4 (s, Ph), 117.20 (s, C_5Me_5), 110.94 (s, C_5H_5), 27.25 (s, CH_3), 14.24 (s, CMePh_2), 11.85 (s, C_5Me_5). ^{31}P (C_6D_6 , 161.97 MHz): δ 4.84 (s, HfPPh). Minor isomer: ^1H

(C₆D₆, 400.1 MHz): δ 7.723 (d, C₆H₅, 2 H), 7.201-6.923 (m, C₆H₅, 12 H), 6.905 (t, C₆H₅, 1 H), 5.725 (s, C₅H₅, 5 H), 4.344 (d, PH, 1 H, $J_{\text{PH}} = 220$ Hz), 1.853 (s, C₅(CH₃)₅, 15 H), 0.269 (s, CH₃, 3 H). ¹³C (C₆D₆, 100.6 MHz): δ 146.6 (s, Ph), 145.9 (s, Ph), 136.1 (s, Ph), 135.9 (s, Ph), 135.5 (s, Ph), 135.4 (s, Ph), 130.2 (s, Ph), 128.7 (s, Ph), 128.6 (s, Ph), 127.5 (s, Ph), 127.2 (s, Ph), 125.9 (s, Ph), 117.11 (s, C₅Me₅), 110.94 (s, C₅H₅), 22.67 (s, CH₃), 14.24 (s, CMePh₂), 11.96 (s, C₅Me₅). ³¹P (C₆D₆, 161.97 MHz): δ 9.66 (s, HfPPh). Anal. Calcd for C₃₅H₃₉HfOP: C, 61.36; H, 5.74. Found: C, 61.28; H, 5.66.

CpCp*Hf(PHPh)[η^2 -C(Me)=N(2,6-Me₂C₆H₃)] (7). A 25 mL reaction vessel was charged with CpCp*HfMe(PHPh) (116 mg, 0.233 mmol) and xylylisocyanide (30 mg, 0.233 mmol). Benzene (5 mL) was added by cannula, and the resulting solution was stirred at ambient temperature for 45 min. The solution was then filtered and lyophilized to give a pure, nearly colorless powder (141 mg, 0.224 mmol, 97%). Analytically pure colorless crystals were obtained by cooling a concentrated Et₂O solution (92%). ¹H (C₆D₆, 400.1 MHz): δ 7.117 (t, Ar, 2 H), 6.989-6.740 (m, Ar, 6 H), 5.293 (s, C₅H₅, 5 H), 3.085 (d, PH, 1 H, $J_{\text{PH}} = 186$ Hz), 2.336 (s, CH₃, 3 H), 2.054 (s, CH₃, 3 H), 1.787 (s, C₅(CH₃)₅, 15 H), 1.589 (s, CH₃, 3 H). ¹³C (C₆D₆, 100.6 MHz): δ 152.9 (d, HfC, $J_{\text{PC}} = 30$ Hz), 145.0 (s, Ar), 132.6 (d, Ar, $J_{\text{PC}} = 15$ Hz), 132.0 (s, Ar), 129.7 (s, Ar), 129.1 (s, Ar), 128.5 (s, Ar), 125.7 (s, Ar), 122.8 (s, Ar), 114.0 (s, C₅Me₅), 107.1 (s, C₅H₅), 23.4 (s, CH₃), 20.5 (d, CH₃, $J_{\text{PC}} = 17$ Hz), 18.4 (s, CH₃), 11.88 (d, C₅Me₅, $J_{\text{PC}} = 7$ Hz). ³¹P (C₆D₆, 161.97 MHz): δ -68.0 (s, HfPPh). IR (Nujol, KBr): 1640 m, 1580 m, 1573 s ν_{CN} , 1356 w, 1276 w, 1258 s, 1210w, 1160 w, 1128 m, 943 w, 897 w, 813 s, 759 w, 735 s, 698 m, 617 w, 593 w, 487 w, 414 w cm⁻¹. Anal. Calcd for C₃₁H₃₈HfNP: C, 58.72; H, 6.04; N, 2.21. Found: C, 58.78; H, 5.93; N, 2.23.

CpCp*(Me₃P)Hf=P(dmp) (8). A 25 mL reaction tube was charged with CpCp*HfMe(OTf) (106 mg, 0.195 mmol) and LiPHdmp•Et₂O (83 mg, 0.195 mmol), and 3 mL toluene was introduced via cannula. PMe₃ (103 μL, 1.18 mmol) was added to the orange solution via syringe under an N₂ counterflow. The solution was degassed, and the vessel was sealed and then heated to 55 °C for 4 h. The dark red solution was cooled to ambient temperature, and the volatile material was removed under reduced pressure. The red solids were extracted with ca. 5 mL Et₂O, and the solution was filtered and then concentrated to ca. 2 mL. Cooling to -30 °C give dark red crystals of the phosphinidene complex in several crops (79 mg, 0.138 mmol, 71%). ¹H (C₆D₆, 400.1 MHz): δ 7.082 (d, C₆H₃Me₃, 2 H), 6.992 (t, C₆H₃Me₃, 1 H), 6.840 (s, C₆H₂Me₃, 2 H), 6.814 (s, C₆H₂Me₃, 2 H), 5.326 (d, C₅H₅, J_{PH} = 2 Hz, 5 H), 2.537 (s, CH₃, 6 H), 2.532 (s, CH₃, 6 H), 2.262 (s, CH₃, 6 H), 1.749 (s, CH₃, 15 H). ¹³C (C₆D₆, 100.6 MHz): δ 141.1 (s, Ar), 139.2 (s, Ar), 136.06 (Ar), 134.8 (d, Ar, J_{PC} = 5.8 Hz), 130.0 (s, Ar), 128.7 (s, Ar), 126.1 (s, Ar), 124.2 (s, Ar), 118.5 (s, C₅Me₅), 109.2 (s, C₅H₅), 23.4 (s, CH₃), 22.6 (s, CH₃), 20.8 (s, CH₃), 12.1 (d, C₅Me₅, J_{PC} = 8 Hz). ³¹P (C₆D₆, 161.97 MHz): δ 626.94 (d, Hf=Pdmp, J_{PP} = 6 Hz), -9.24 (d, PMe₃, J_{PP} = 6 Hz). IR (Nujol, KBr): 1598 s, 1562 m, 1486 s, 1210 w, 1150 w, 1110 s, 1066 m, 1024 s, 1018 m, 998 m, 917 w, 885 m, 746 w, 678 w, 593 m, 492 w, 456 w cm⁻¹. Anal. Calcd for C₄₂H₅₃HfP₂: C, 63.19; H, 6.69. Found: C, 63.19; H, 6.98.

CpCp*HfMe(PHdmp) (9). A Schlenk flask was charged with CpCp*HfMe(OTf) (59 mg, 0.115 mmol) and LiPHdmp•Et₂O (10 mg, 0.115 mmol), and 7 mL of Et₂O was introduced via cannula. The solution was stirred for 2 h, and then the volatile material was removed under reduced pressure. The orange solids were extracted with ca. 8 mL pentane, and the resulting solution was filtered and concentrated to ca. 4 mL then cooled to -30 °C to give orange crystals of the phosphide complex in several crops (68 mg, 0.071 mmol, 62%). ¹H (C₆D₆, 400.1 MHz): δ

7.020 (d, $C_6H_3Mes_2$, 2 H), 6.955 (t, $C_6H_3Mes_2$, 1 H), 6.892 (s, $C_6H_2Me_3$, 2 H), 6.841 (s, $C_6H_2Me_3$, 2 H), 5.625 (d, C_5H_5 , $J_{PH} = 2$ Hz, 5 H), 3.513 (d, PH , 1 H, $J_{PH} = 243.6$ Hz), 2.405 (s, CH_3 , 6 H), 2.350 (s, CH_3 , 6 H), 2.262 (s, CH_3 , 6 H), 1.567 (s, CH_3 , 15 H), -0.931 (d, CH_3 , 3 H, $J_{PH} = 6.4$ Hz). ^{13}C (C_6D_6 , 100.6 MHz): δ 144.7 (s, *Ar*), 141.2 (s, *Ar*), 136.4 (d, *Ar*, $J_{PC} = 5.6$ Hz), 132.4 (s, *Ar*), 129.0 (s, *Ar*), 128.9 (s, *Ar*), 126.1 (s, *Ar*), 125.2 (s, *Ar*), 116.9 (s, C_5Me_5), 110.0 (s, C_5H_5), 39.9 (s, CH_3), 21.8 (s, CH_3), 21.4 (s, CH_3), 21.1 (s, CH_3), 11.6 (d, C_5Me_5 , $J_{PC} = 8$ Hz). ^{31}P (C_6D_6 , 161.97 MHz): δ -6.81 (s). Repeated attempts did not give satisfactory elemental analysis.

[CpCp*(Cl)Hf=P(dmp)][Li(Et₂O)] (10). A Schlenk flask was charged with CpCp*HfMe(OTf) (213 mg, 0.474 mmol) and LiPHdmp•Et₂O (202 mg, 0.474 mmol), and 10 mL of toluene was introduced via cannula. An Et₂O solution of MeLi (295 μ L, 1.6 M) was added to the orange solution via syringe under an N₂ counterflow. After 4 h, the volatile materials were removed under reduced pressure. The dark orange solid was extracted with ca. 12 mL of Et₂O, and the solution was concentrated to ca. 4 mL and then cooled to -30 °C to give bright orange crystals of the title compound in several crops (267 mg, 0.318 mmol, 67%). 1H (C_6D_6 , 400.1 MHz): δ 7.295 (s, $C_6H_2Me_3$, 1 H), 7.090 (t, $C_6H_3Mes_2$, 1 H), 6.923 (d, $C_6H_3Mes_2$, 2 H), 6.912 (s, $C_6H_2Me_3$, 1 H), 6.757 (s, $C_6H_2Me_3$, 1 H), 6.519 (s, $C_6H_2Me_3$, 1 H), 5.662 (s, C_5H_5 , 5 H), 3.264 (q, CH_2CH_3 , 4 H), 2.721 (s, CH_3 , 3 H), 2.602 (s, CH_3 , 3 H), 2.271 (s, CH_3 , 3 H), 2.227 (s, CH_3 , 3 H), 2.157 (s, CH_3 , 3 H), 1.870 (s, CH_3 , 3 H), 1.859 (s, CH_3 , 15 H), 1.116 (q, CH_2CH_3 , 6 H). ^{13}C (C_6D_6 , 100.6 MHz): δ 140.2 (s, *Ar*), 139.8 (s, *Ar*), 138.4 (s, *Ar*), 136.7 (s, *Ar*), 136.1 (s, *Ar*), 135.18 (d, *Ar*, $J_{PC} = 5.8$ Hz), 130.6 (s, *Ar*), 130.0 (s, *Ar*), 128.2 (*Ar*), 125.5 (s, *Ar*), 123.0 (s, *Ar*), 116.55 (s, C_5Me_5), 108.7 (s, C_5H_5), 65.9 (s, CH_2CH_3), 22.8 (s, CH_3), 22.7 (m, CH_3), 21.1 (s, CH_3), 20.9 (s, CH_3), 20.6 (m, CH_3), 20.3 (s, CH_3), 15.5 (s, CH_2CH_3), 12.3 (d, C_5Me_5 , $J_{PC} = 8$

Hz). ^{31}P (C_6D_6 , 161.97 MHz): δ 150.65 (s). IR (Nujol, KBr): 1598 m, 1562 m, 1488 s, 1365 s, 1210 w, 1152 w, 1108 s, 1066 m, 1024 s, 1022 m, 994 m, 918 w, 881 m, 742 w, 694 w, 674 w, 590 m, 495 w, 456 w cm^{-1} . Anal. Calcd for $\text{C}_{43}\text{H}_{55}\text{ClHfLiOP}_2$: C, 61.50; H, 6.60. Found: C, 61.45; H, 6.65.

[(dippe)Pt(μ -PPh)]₂ (12). A 25 mL reaction vessel was charged with (dippe)PtCl₂ (240 mg, 0.454 mmol), CpCp*HfMe(PHPh) (225 mg, 0.454 mmol), and 8 mL of benzene. The solution was degassed, and the vessel was sealed and then heated to 76 °C for 8 h. After 8 h, the solution was allowed to cool to ambient temperature and was then filtered, and the crude solid was obtained by lyophilization. In two fractional crystallization steps with Et₂O solvent, the products were separated. From cold (−30 °C), dilute Et₂O, colorless crystals of CpCp*HfCl₂ (147 mg, 0.327 mmol, 72%) were obtained. Orange crystals of [(dippe)Pt(μ -PPh)]₂ (152 mg, 0.134 mmol, 59%) crystallized as the 1:1 Et₂O adduct (Et₂O resonances omitted below). ^1H (C_6D_6 , 400.1 MHz): δ 7.913 (d, C_6H_5 , 4 H), 7.086 (d, C_6H_5 , 4 H), 6.968 (m, C_6H_5 , 2 H), 1.844 (m, CH, 8 H), 1.282 (dd, CH₃, 12 H), 1.036 (m, CH₂, 8 H), 0.780 (dd, CH₃, 12 H), 0.537 (dd, CH₃, 12 H), 0.475 (dd, CH₃, 12 H). ^{13}C (C_6D_6 , 100.6 MHz): δ 134.9 (s, Ph), 129.2 (s, Ph), 127.1 (s, Ph), 125.8 (s, Ph), 25.4 (m, CH₂), 23.2 (m, CH), 19.7 (s, CH₃), 19.2 (s, CH₃), 18.8 (s, CH₃), 17.5 (s, CH₃). ^{31}P (C_6D_6 , 161.97 MHz): δ 82.81 (m, $P^i\text{Pr}_2$, $J_{\text{PP}} = 30$, 35.1 Hz, $J_{\text{PtP}} = 2965$ Hz, 4 P), −51.64 (m, PPh, $J_{\text{PP}} = 30$, 35.1 Hz, $J_{\text{PtP}} = 827$ Hz, 2 P). IR (Nujol, KBr): 1564 s, 1484 s, 1331 m, 1252 s, 1234 s, 1168 m, 1132 m, 1108 s, 1084 s, 1078 s, 1024 s, 958 m, 880 s, 856 w, 752 m, 692 m, 660 m, 631 m, 617 s, 528 w, 414 w cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{47}\text{OP}_3\text{Pt}$: C, 45.07; H, 7.41. Found: C, 44.89; H, 6.94.

[(dippe)Pt]₂(μ -PPh) (13). An NMR tube was charged with [(dippe)Pt(μ -PPh)]₂ (10 mg, 0.009 mmol), [(dippe)Pt(μ -H)]₂ (8.1 mg, 0.009 mmol), and 500 μL benzene-*d*₆. Gas evolution was

observed upon addition of solvent, and a trace amount H_2 was observed in the ^1H NMR spectrum. The reaction proceeded quantitative conversion by ^1H and ^{31}P NMR spectroscopy. Upon standing at ambient temperature X-ray quality crystals precipitated from solution (54%). ^1H (C_6D_6 , 400.1 MHz): δ 7.871 (d, C_6H_5 , 2 H), 7.061 (d, C_6H_5 , 2 H), 6.964 (m, C_6H_5 , 1 H), 1.756 (m, CH, 2 H), 1.543 (m, CH, 2 H), 1.352 (m, CH_2 , 4 H), 1.206 (dd, CH_3 , 6 H), 1.131 (dd, CH_3 , 6 H), 0.827 (dd, CH_3 , 6 H), 0.655 (dd, CH_3 , 6 H). ^{31}P (C_6D_6 , 161.97 MHz): δ 75.22 (m, P^iPr_2 , $J_{\text{PP}} = 5.1, 87.3$ Hz, $J_{\text{PiP}} = 3483$ Hz, 1 P), 71.89 (m, P^iPr_2 , $J_{\text{PP}} = 5.1, 28.4$ Hz, $J_{\text{PiP}} = 1946$ Hz, 1 P), – 38.62 (m, PPh, $J_{\text{PP}} = 28.4, 87.3$ Hz, $J_{\text{PiP}} = 887$ Hz, 1 P).

***trans*-[N(Np)Ar]₃TaCl₂ (14).** Solid LiN(Np)Ar (1.580 g, 7.99 mmol) was added in several portions to a slurry of TaCl₅ (925 mg, 2.58 mmol) in 25 mL of Et₂O at –78 °C, over a period of 30 minutes. The solution was allowed to warm gradually to ambient temperature with stirring over 5 h. The Et₂O was removed under reduced pressure and the resulting solids were washed with ca. 7 mL of cold pentane. The solids were then extracted into Et₂O, and the resulting yellow solution filtered was cooled to –30 °C to give yellow crystals of the dichloride in several crops (1.49 g, 1.75 mmol, 68%). Cooling the pentane wash yielded additional, less pure product. ^1H (C_6D_6 , 400.1 MHz): δ 7.606 (s, $\text{C}_6\text{H}_3\text{Me}_2$, 2 H), 6.585 (s, $\text{C}_6\text{H}_3\text{Me}_2$, 1 H), 3.752 (s, CH_2 , 2 H), 2.113 (s, $\text{C}_6\text{H}_3\text{Me}_2$, 6 H), 0.597 (s, $\text{C}(\text{CH}_3)_3$, 9 H). ^{13}C (C_6D_6 , 100.6 MHz): δ 148.3 (s, Ar), 139.3 (s, Ar), 129.3 (s, Ar), 126.2 (s, Ar), 70.9 (s, CH_2), 35.6 (CMe₃), 28.3 (s, CH_3), 21.2 (s, CH_3). IR (Nujol, KBr): 1602 w, 1566 s, 1395 m, 1376 s, 1302 m, 1288 m, 1261 w, 1201 w, 1153 s, 1060 s, 1029 w, 999 s, 961 m, 928 w, 894 w, 877 m, 852 s, 801 w, 759 m, 728 m, 692 s, 601 w, 548 w, 451 w, 417 w cm^{-1} . Anal. Calcd for $\text{C}_{39}\text{H}_{60}\text{N}_3\text{Cl}_2\text{Ta}$: C, 56.93; H, 7.35; N, 5.11. Found: C, 56.36; H, 7.26; N, 4.99.

[N(Np)Ar]₃Ta=PPh (15). A reaction tube was charged with [N(Np)Ar]₃TaCl₂ (210 mg, 0.255 mmol), CpCp*HfMe(PHPh) (127 mg, 0.255 mmol), and 6 mL of benzene. The tube was degassed and sealed, then heated to 76 °C. After 8 h, the solution was allowed to cool to ambient temperature was then filtered, and the crude solid was obtained by lyophilization. In two fractional crystallization steps involving the cooling of a dilute pentane solution to -30 °C, colorless crystals of CpCp*HfCl₂ (90 mg, 0.199 mmol, 78%) precipitated, followed by orange crystals of [N(Np)Ar]₃Ta=PPh (184 mg, 0.214 mmol, 84%). ¹H (C₆D₆, 400.1 MHz): δ 7.579 (s, C₆H₃Me₂, 2 H), 7.042 (t, C₆H₅, 4 H), 6.982 (d, C₆H₅, 4 H), 6.865 (t, C₆H₅, 2 H), 6.474 (s, C₆H₃Me₂, 1 H), 2.733 (s, CH₂, 2 H), 2.186 (s, C₆H₃Me₂, 6 H), 0.833 (s, C(CH₃)₃, 9 H). ¹³C (C₆D₆, 100.6 MHz): δ 144.9 (s, Ar), 142.5 (d, Ar, J_{PC} = 14 Hz), 138.7 (s, Ar), 133.4 (s, Ar), 131.6 (s, Ar), 129.1 (s, Ar), 128.9 (s, Ar), 125.4 (s, Ar), 76.2 (s, CH₂), 36.1 (CMe₃), 28.4 (s, CH₃), 20.6 (s, CH₃). ³¹P (C₆D₆, 161.97 MHz): δ 415.63 (s). IR (Nujol, KBr): 1608 s, 1566 s, 1395 m, 1376 s, 1304 m, 1286 m, 1263 w, 1208 w, 1154 s, 1066 s, 1024 w, 994 s, 961 m, 928 w, 894 w, 877 m, 852 s, 801 w, 759 m, 728 m, 690 s, 610 w, 544 w, 450 w, 414 w cm⁻¹. Anal. Calcd for C₄₅H₆₅N₃PTa: C, 62.85; H, 7.62; N, 4.89. Found: C, 62.85; H, 8.04; N, 5.34.

Thermal decomposition of 2 and 2-d: An NMR tube was charged with either **2** or **2-d** (4–20 mg; 0.0206 M for Eyring analysis), and the solid was dissolved in benzene-*d*₆ containing a known concentration of an internal standard, Cp₂Fe or C₆Me₆ (0.015 M). The contents of the tube were frozen in liquid N₂, and the tube was flame-sealed under vacuum. The tube was defrosted and equilibrated to the appropriate temperature. At appropriate intervals, the sample was transferred to a pre-shimmed NMR spectrometer and data was collected. The data was not corrected for sample cooling during NMR acquisition. The decomposition was followed for at least five half-lives. Concentration was monitored by integration of the C₅H₅ resonances in single

scan experiments. Products of the reaction were triphosphanato complex **3**, precipitate, and a myriad of minor hafnium products. Methane or methane-*d* was observed during the thermolysis.

X-ray Crystallography. Crystals of the appropriate complex were typically cut from a larger block under Paratone-*N* oil to minimize reaction with air. The crystal was removed from the oil using a loop that also served to hold the crystal for data collection. The crystal was then mounted and centered on a Bruker SMART system. Rotation and still images showed diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "hemisphere" data set was obtained of reciprocal space to a resolution of 0.85 Å using 0.3° steps in ω using integration times of 10 sec for each frame. Data was collected at 148 K. Integration of intensities and refinement of cell parameters were done using SAINT. Absorption corrections were applied using psi-scans and were small due to low absorption and equidimensional shape. Observation of the crystal after data collection showed no signs of decomposition.

CpCp*HfMe(PHPh) (2). An orange crystal (0.11 x 0.12 x 0.15 mm) of the hafnium methyl phosphide complex **2** was obtained by cooling a concentrated Et₂O solution to -30 °C. The space group was determined as P2₁/c based on systematic absences and intensity statistics. The highest residual electron density peak and hole in the difference map were located near the Hf atom and were 1.238 and -1.880 eÅ⁻³, respectively. Maximum and minimum transmissions were equal to 0.5558 and 0.4402, respectively. Crystal data for C₂₂H₂₈HfP, *M* = 501.9, monoclinic, P2₁/c, *a* = 8.4351(9), *b* = 28.233(3), *c* = 8.7547(9) Å, β = 107.590(2)°, *Z* = 4, *V* = 1987.4(4) Å³, *T* = 148(2) K, μ(Mo-Kα) = 5.330 mm⁻¹, *D*_{calc} = 1.677 mg/mm³, *F*(000) = 988, Of 8965 total reflections (2.53 = θ = 25.25°), 3377 were independent (*R*_{int} = 5.71%). A semi-empirical absorption correction was

performed using psi-scans. A Patterson search was used to locate the Hf atom. All non-hydrogen atoms were converted to and refined anisotropically. Hydrogen atoms were refined isotropically and fixed at calculated positions. No anomalous bond lengths or angles were observed. $R(F) = 3.40\%$, $R(wF) = 8.19\%$, $GoF = 1.042$.

[(dippe)Pt]₂(μ -PPh) (13). A yellow crystal (0.12 x 0.11 x 0.07 mm) of the platinum μ -phosphinidene dimer **12** was obtained by cooling a concentrated Et₂O solution to -30 °C. The space group was determined as *Pbca* based on systematic absences and intensity statistics. The largest peak and hole in the difference map were 1.167 and -0.0965 eÅ⁻³, respectively. Maximum and minimum transmissions were equal to 0.6112 and 0.4639, respectively. Crystal data for C₃₄H₆₉P₅Pt₂, $M = 1022.92$, orthorhombic, *Pbca*, $a = 11.699(3)$, $b = 15.370(4)$, $c = 45.23(1)$ Å, $Z = 8$, $V = 8133(3)$ Å³, $T = 139(2)$ K, $\mu(\text{Mo-K}\alpha) = 7.091$ mm⁻¹, $D_{\text{calc}} = 1.671$ mg/mm³, $F(000) = 4032$, Of 35685 total reflections ($1.96 = \theta = 25.25^\circ$), 7118 were independent ($R_{\text{int}} = 14.34\%$). A semi-empirical absorption correction was performed using psi-scans. A Patterson search was used to locate the platinum atoms. All non-hydrogen atoms were converted to and refined anisotropically. Hydrogen atoms were refined isotropically and fixed at calculated positions. No anomalous bond length or angles were observed, despite the relatively large R_{int} . $R(F) = 4.82\%$, $R(wF) = 7.99\%$, $GoF = 0.884$.

Figure S-1. Representative first-order plot of $\ln([\text{CpCp}^*\text{HfMe(PHPh)}]_i / [\text{CpCp}^*\text{HfMe(PHPh)}])$ and $\ln([\text{CpCp}^*\text{HfMe(PDPh)}]_i / [\text{CpCp}^*\text{HfMe(PDPh)}])$ vs. time for the termolysis of $\text{CpCp}^*\text{HfMe(PHPh)}$ (**2**) and of $\text{CpCp}^*\text{HfMe(PDPh)}$ (**2-d**) at 77.9 °C.

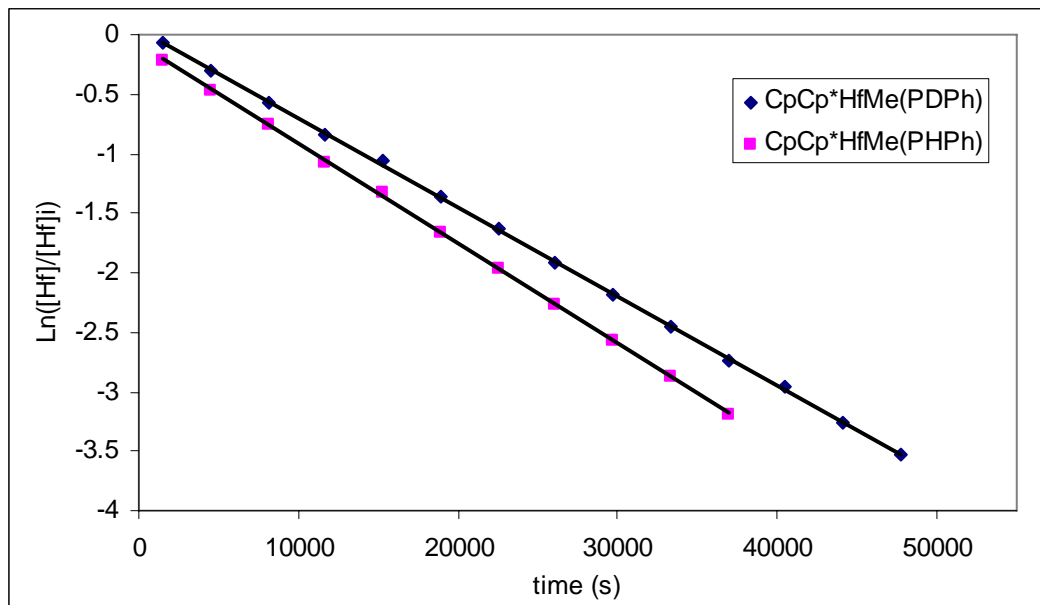


Figure S-2. Eyring plot of $\ln(1/kT)$ vs. $1/T$ used to calculate activation parameters ΔH^\ddagger and ΔS^\ddagger .

