Supporting Information for:

Terminal stibinidene ligands. Generation of CpCp*Hf=Sb(dmp) and trapping reactions with PMe_3 and 2-butyne

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Experimental Section

General Considerations. All manipulations were performed under an atmosphere of dry nitrogen using Schlenk techniques and/or a M. Braun glovebox. Dry, oxygen-free solvents were employed throughout. Removal of thiophenes from benzene and toluene was accomplished by washing each with H_2SO_4 and saturated $NaHCO_3$ followed by drying over $MgSO_4$. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, saturated $NaHCO_3$, and then the drying agent $MgSO_4$. C_6D_6 was purchased form Cambridge Isotope Laboratory then degassed and dried over NaK alloy. Celite, alumina, and 4Å molecular sieves were activated under vacuum overnight at a temperature above 180 ˚C. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. UV-vis spectra were collected on an HP 89531A diode array spectrophotometer and reported as λ_{max} nm (ε $dm^3mol^{-1}cm^{-1}$). Infrared spectra (Nujol mulls, KBr plates) were recorded using a Mattson FTIR spectrometer at a resolution of 2 cm^{-1}. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker 300, 400, and 500 MHz NMR spectrometers and are reported with reference to solvent resonances (C_6D_6, δ 7.16 and δ 128.0) or external H_2PO_4. 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).[1]

CpCp*HfMe(OTf)[2] and $dmpSbH_2$[3] were prepared according to the literature protocols. Butyllithium was crystalized from hexanes solution, and 2-butyne was degassed and vacuum transferred from molecular seives. All other chemicals were used as received.

Observation of CpCp*HfMe[SbH(dmp)]. In a typical experiment, an NMR tube was charged with $dmpSbH_2$ (8 mg, 0.002 mmol), BuLi (1.4 mg, 0.002 mmol), and 500 µL C_6D_6. The resulting yellow solution was aggitated and let to react for 30 minutes. Solid CpCp*HfMe(OTf) (10 mg, 0.002 mmol) was added to the NMR tube and the contents shaken. NMR spectra were aquired within 10 minutes. Attempts to scale this reaction up and isolated CpCp*HfMe[SbH(dmp)] yielded a mixture of products. ^1H (C_6D_6, 400.1 MHz): δ 7.248 (t, $C_6Mes_2H_3$, 1 H), 6.988 (d, $C_6Mes_2H_3$, 2 H), 6.883 (s, $C_6Me_3H_2$, 4 H), 5.727 (s, C_5H_5, 5 H), 2.285 (s, SbH, 1 H), 2.188 (s, CH_3, 6 H), 2.071 (s, CH_3, 12 H), 1.645 (s, $C_5(CH_3)_5$, 15 H) -0.504 (s, CH_3, 3 H). ^{13}C (C_6D_6, 100.6 MHz): δ

148.8 (s, *Ar*), 141.9 (s, *Ar*), 139.4 (d, *Ar*), 136.3 (s, *Ar*), 135.7 (s, *Ar*), 130.6 (s, *Ar*), 128.8 (s, *Ar*), 128.5 (s, *Ar*), 116.2 (s, C_5Me_5), 110.6 (s, C_5H_5), 59.8 (s, Hf*C*H$_3$), 21.4 (s, *C*H$_3$), 21.1 (s, *C*H$_3$), 11.5 (s, C_5Me_5).

CpCp*Hf(PMe$_3$)=Sb(dmp) (2). A 50 mL Schlenk tube was charged with dmpSbH$_2$ (136 mg, 0.311 mmol), and the solids dissolved in 10 mL Et$_2$O. The resulting solution was cooled to –78 ˚C, and BuLi (0.19 mL, 1.6 *M*) was added via syringe under N$_2$ counter flow. The resulting yellow slurry was stirred for 30 min then warmed slowly to 0 ˚C and maintained at that temperature for 2 h. A solution of CpCp*HfMe(OTf) (154 mg, 0.283 mmol) and PMe$_3$ (0.15 mL, 1.70 mmol) in 5 mL E$_2$O was cooled to –78 ˚C. The stibide solution was trasferred into the hafnium solution via cannula. The resulting brown solution was stirred for 15 min, then slowly warmed to ambient temperature. After 2 h at ambient temperature, the volitile materials were distilled. The residual was dissolved in minimal Et$_2$O, and the solution filtered then cooled to –35 ˚C to give dark amber crystals of CpCp*Hf(PMe$_3$)=Sb(dmp) (174 mg, 0.196 mmol, 63%). ^{1}H (C$_6$D$_6$, 400.1 MHz): δ 7.158 (t, C$_6$Mes$_2$*H*$_3$, 1 H), 7.088 (s, C$_6$Me$_3$*H*$_2$, 4 H), 6.698 (d, C$_6$Mes$_2$*H*$_3$, 2 H), 5.277 (s, C$_5$*H*$_5$, 5 H), 2.463 (s, C*H*$_3$, 6 H), 2.392 (s, C*H*$_3$, 6 H), 2.190 (s, C*H*$_3$, 6 H), 1.711 (s, C$_5$(C*H*$_3$)$_5$, 15 H) 0.429 (d, C*H*$_3$, 9 H). ^{13}C (C$_6$D$_6$, 100.6 MHz): δ 150.3 (s, *Ar*), 144.7 (s, *Ar*), 136.6 (d, *Ar*), 134.7 (s, *Ar*), 129.1 (s, *Ar*), 128.4 (s, *Ar*), 127.5 (s, *Ar*), 125.9 (s, *Ar*), 112.6 (s, C_5Me_5), 100.9 (s, C_5H_5), 23.0 (s, *C*H$_3$), 22.7 (s, *C*H$_3$), 20.8 (s, *C*H$_3$), 20.3 (d, *C*H$_3$, J_{PC} = 24 Hz), 13.4 (s, C_5Me_5). ^{31}P (C$_6$D$_6$, 161.97 MHz): δ 14.0 (s, *P*Me3). IR (KBr, Nujol): 1566 m,1481 s, 1392 s, 1363, w, 1240 s, 1180 s, 1101 s, 1066 s, 1024 s, 971 w, 916 m, 877 w, 858 w, 838 m, 811 w, 746 w, 767 m, 601 w, 588 m, 568 w, 491 w, 470 m cm^{-1}. UV-vis (hexane): 488 nm (4719), 348 (22786). Anal. Calcd for $C_{42}H_{54}HfPSb$: C, 56.67; H, 6.11. Found: C, 56.30; H, 6.14.

CpCp*Hf[*Sb,C*:η^2-Sb(dmp)CMe=C(Me)] (3). A 50 mL Schlenk tube was charged with dmpSbH$_2$ (132 mg, 0.302 mmol), and the solids dissolved in 10 mL Et$_2$O. The resulting solution was cooled to –78 ˚C, and BuLi (0.226 mL, 1.6 *M*) was added via syringe under N$_2$ counter flow. The resulting yellow slurry was stirred for 30 min then warmed slowly to 0 ˚C and maintained at that temperature for 2 h. A 5 mL E$_2$O solution of CpCp*HfMe(OTf) (164 mg, 0.302 mmol) and 2-butyne (0.084 mL) was cooled to –78 ˚C. The stibine solution was trasferred onto the hafnium via cannula. The resulting orange solution was stirred for 15 min, then slowly warmed to ambient temperature. After 1 h at ambient temperature, the volitile materials were distilled. The residual dissolved in minimal pentane, and the solution filtered then cooled to –35 ˚C to give red crystals of the title compound (204 mg, 0.236 mmol, 78%). ^{1}H (C$_6$D$_6$, 400.1 MHz): δ 7.125 (t, C$_6$Mes$_2$*H*$_3$, 1 H), 6.934 (d, C$_6$Mes$_2$*H*$_3$, 2 H), 6.854 (s, C$_6$Me$_3$*H*$_2$, 4 H), 5.475 (s, C$_5$*H*$_5$, 5 H), 2.425 (s, C*H*$_3$, 6 H), 2.381 (s, C*H*$_3$, 6 H), 2.272 (s, C*H*$_3$, 6 H), 1.932 (s, C*H*$_3$, 3 H), 1.670 (s, C*H*$_3$, 3 H), 1.628 (s, C$_5$(C*H*$_3$)$_5$, 15 H). ^{13}C (C$_6$D$_6$, 100.6 MHz): δ 216.2 (s, Hf*C*Me), 147.9 (s, Sb*C*Me), 144.0 (s, *Ar*), 142.2 (s, *Ar*), 136.6 (d, *Ar*), 136.3 (s, *Ar*), 129.0 (s, *Ar*), 128.9 (s, *Ar*), 128.7 (s, *Ar*), 126.4 (s, *Ar*), 116.9 (s, C_5Me_5), 108.6 (s, C_5H_5), 22.3 (s, *C*H$_3$), 21.9 (s, *C*H$_3$), 21.1 (s, *C*H$_3$), 18.7 (s, *C*H$_3$), 18.6 (s, *C*H$_3$), 12.2 (s, C_5Me_5). IR (KBr, Nujol): 1607 s, ν_{CC},1567 m, 1479 s, 1297 m, 1261 m, 1157 w, 1103 m, 1077 m, 1024 s, 960 w, 902 m, 877 w, 850 s, 816 s, 737 w, 767 m, 641 w, 575 m, 547 w, 481 w, 458 m cm^{-1}. Anal. Calcd for $C_{43}H_{51}HfSb$: C, 59.49; H, 5.92. Found: C, 59.15; H, 5.92.

Crystallographic Experimental Section

Data Collection

Red crystals of the hafnium metallacycle CpCp*Hf [*Sb,C*:η^2-Sb(dmp)C(Me)=C(Me)] were obtained by cooling a concentrated hexane solution to –30 ˚C. A crystal of 0.20 x 0.18 x 0.16 mm was cut from a larger block under Paratone-N oil to minimize reaction with air. The crystal was removed from the oil using a platic 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 123 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.

Structure solution and refinement

The space group was determined as $P2_1/n$ based on systematic absences and intensity statistics. A Patterson search was used to locate the hafium and antimony atoms. 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. Integration of the data at 0.80 Å resolution provided a high quality data set and solution despite the relatively low value of $2\theta = 24.73°$.

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$

$wR_2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

$GoF = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

$R_1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

where: $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$;

n = number of independent reflections;

p = number of parameters refined.

All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Table 1. Crystal and structure refinement for CpCp*Hf [*Sb,C*:η^2-Sb(dmp)C(Me)=C(Me)].

Identification Code	rw1017m	
Empirical formula	$C_{43}H_{51}HfSb$	
Formula weight	868.08	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space Group	$P2_1/n$	
Unit cell dimensions	a = 12.046(1) Å	α = 90°
	b = 16.500(1) Å	β = 93.404(1)°
	c = 18.075(1) Å	γ = 90°
Volume	3586.2(5) $Å^3$	
Z	4	
Density (calculated)	1.608 mg/mm^3	
Absorption coefficient	3.675 mm^{-1}	
F(000)	1728	
Crystal size, color, habit	0.20 x 0.18 x 0.16 mm, red block	
Theta range for data collection	3.15 to 24.73°	
Index ranges	$-7 \leq h \leq 14$, $-17 \leq k \leq 19$, $-21 \leq l \leq 18$	
Completeness to theta = 24.73°	99.1 %	
Reflections collected	15986	
Independent reflections	6075 (R_{int} = 0.0331)	
Absorption correction	semi empirical from psi-scans	
Max. and min. transmission	0.5554 and 0.4953	
Refinement method	Full-matrix least squares on F^2	
Weighting scheme	$w = q [\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2 F_c^2)/3$, a =, b =, q =1	
Data / restraints / parameters	6075 / 0 / 406	
Goodness-of-fit on F^2	1.236	
Final R indices [I > 2 sigma(I)]	R1 = 0.0347, wR2 = 0.0613	
R indices (all data)	R1 = 0.0401, wR2 = 0.0626	
Largest diff. peak and hole	0.957 and -1.279 $eÅ^{-3}$	

References

1 All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library; G. Sheldrick, Bruker Analytical Systems, Madison, WI.
2 Sadow, A. D.; Tilley, T. D. *Organometallics* **2003,** *22,* 3577-3585.
3 Waterman, R.; Tilley, T. D. *Angew. Chem. Int. Ed.* **2006**, *45*, 2926-2929.