Electronic Supporting Information for

Intercepting low oxidation state main group hydrides with a nucleophilic N-heterocyclic olefin

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Tables and Figures

Experimental Section

General. All the reactions are were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[1] manufactured by Innovative Technology, Inc., then degassed (freeze-pump-thaw method) and stored under atmosphere of nitrogen prior to use. $SnCl_2$, $Li[BH_4]$, $Li[BD_4]$, $Li[AlH_4]$, $Li[AlD_4]$ and $ClSiMe_3$ were purchased from Aldrich and used as received. $W(CO)_6$ was obtained from Aldrich and sublimed under vacuum (0.05 torr) and stored under nitrogen prior to use. Methyl iodide was obtained from Aldrich, degassed and dried over molecular sieves (4 Å) prior to use. 1,3-Bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr),[2a] 1,3-bis-(2,6-diisopropylphenyl)-imidazolium chloride [IPrH]Cl,[2b] $(THF)_2SnCl_2{\bullet}W(CO)_5$[3] and $(THF)GeCl_2{\bullet}W(CO)_5$[4] were prepared following literature procedures. ^1H, $^2H\{^1H\}$, $^{13}C\{^1H\}$ and ^{119}Sn NMR spectra were recorded on a Varian iNova-400 spectrometer and referenced externally to $SiMe_4$ (^1H and $^{13}C\{^1H\}$), $Si(CD_3)_4$ (^2H) and $SnMe_4$ (^{119}Sn). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded Nicolet IR100 FTIR spectrometer as a Nujol mulls between NaCl plates. Mass spectra were obtained on a Agilent 6220 spectrometer. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

X-ray Crystallography. Crystals of suitable quality for X-ray diffraction studies were removed from a vial (in glove box) and immediately covered with thin layer of hydrocarbon oil (Paratone-N). A selected suitable crystal was picked and then mounted on glass fiber, and quickly placed in a low temperature stream of nitrogen on X-ray diffractometer.[5] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα radiation, with the crystals cooled to -100 °C. The data were corrected for absorption[6] through Gaussian integration from the indexing of the crystal faces. Structures were solved using direct methods (SHELXS-97), and refined using SHELXS-97.[7] Hydrogen atoms were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were give thermal parameters 20% greater than those of their parent atoms.

Synthetic Procedures.

Synthesis of IPr=CH_2, 1. To a white slurry of 1,3-bis-(2,6-diisopropylphenyl)-imidazolium chloride, [IPrH]Cl (1.95 g, 4.44 mmol), in 20 mL of THF at -78 °C was added dropwise *n*-BuLi (3.15 mL, 5.04 mmol, 1.6 M solution in hexanes). The reaction was stirred for 10 min and the resulting clear solution was warmed to room temperature and stirred for another 5 min. MeI (0.315 mL, 5.05 mmol) was then added at -78 °C to yield a white precipitate. The resulting 2-methyl-imidazolium salt, [IPrMe]I was then deprotonated *in situ* with *n*-BuLi (3.15 mL, 5.05 mmol, 1.6 M solution in hexanes) at -78 °C to obtain a pale yellow solution. The resulting solution was stirred at ambient temperature for 30 min, and afterwards the volatiles were removed to give a yellow solid. This solid residue was extracted with hexanes (20 mL) and filtered through Celite to obtain yellow filtrate from which the crude product was isolated as a pale yellow solid upon removal of the volatiles. Recrystallization of crude product from hexanes (at *ca*. -35 °C) afforded pure **1** (527 mg, 29 %). Crystals suitable for X-ray crystallography were grown by cooling a saturated hexane solution to -35 °C. ^{1}H NMR (C_6D_6): δ 1.22 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.36 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 2.42 (s, 2H, =CH_2), 3.35 (septet, $^3J_{HH}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 5.85 (s, 2H, N-C*H*-), 7.17 (d, $^3J_{HH}$ = 7.0 Hz, 4H, Ar*H*) and 7.22 (t, $^3J_{HH}$ = 7.0 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 23.8 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 28.8 ($CH(CH_3)_2$), 44.3 (=CH_2), 114.6 (-N-*C*H-), 124.5 (Ar*C*), 129.3 (Ar*C*), 134.9 (Ar*C*), 148.9 (Ar*C*) and 152.46 (N-*C*-N). HR-MS: $[M]^+$; Calcd. 402.30255. Obs. 402.30350 (Δ ppm = 2.4). Mp (°C): 119-121.

Alternate Preparation of IPr=CH$_2$. To a solution of IPr (0.200 g, 0.515 mmol) in 6 mL of toluene, was added methyl iodide (17.7 µL, 0.283 mmol) at ambient temperature. A white precipitate of [IPrH]I was formed immediately and the reaction stirred for 1 h. Filtration of the reaction mixture through Celite gave a pale yellow filtrate and removal of volatiles from the filtrate afforded pure IPr=CH$_2$ (0.93 mg, 90 %) as determined by ^{1}H NMR spectroscopy.

Synthesis of IPr-CH$_2$•SnCl$_2$•W(CO)$_5$ (2). To a mixture of IPr=CH$_2$ (46 mg, 0.11 mmol) and (THF)$_2$SnCl$_2$•W(CO)$_5$ (74 mg, 0.11 mmol) was added 8 mL of toluene. The reaction mixture was stirred at room temperature for 1 h to give a pale yellow slurry. The precipitate was isolated by filtration (83 mg) and identified as **2** by ^{1}H NMR spectroscopy. A further crop of **2** was isolated as colorless crystals (suitable quality for X-ray crystallography) by cooling the filtrate at -35 °C (13 mg, combined yield = 96 mg, 93 %). ^{1}H NMR (C$_6$D$_6$): δ 0.84 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.30 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.69 (s, 2H, -C*H*$_2$-), 2.75 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 6.28 (s, 2H, N-C*H*-), 7.06 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*) and 7.20 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 22.8 (CH(*C*H$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 32.8 (-*C*H$_2$-), 121.9 (-N-*C*H-), 125.7 (Ar*C*), 130.4 (Ar*C*), 132.1 (Ar*C*), 145.5 (Ar*C*) and 155.7 (N-*C*-N), 197.7 (equat. *C*O), 200.9 (ax. *C*O). ^{119}Sn{^{1}H}NMR (C$_6$D$_6$): δ = -96 (s). IR (Nujol, cm^{-1}): 1898 (br, υCO), 1914 (br, υCO), 1970 (br, υCO) and 2063 (s, υCO). Anal. Calcd. for C$_{73}$H$_{84}$Cl$_4$N$_4$O$_{10}$Sn$_2$W$_2$ (**2•0.5toluene**): C, 45.56; H, 4.40; N, 2.91. Found: C, 45.59; H, 4.35; N, 2.92. Mp (°C): 182-186.

Synthesis of IPr-CH$_2$•GeCl$_2$•W(CO)$_5$ (3). To a mixture of IPr=CH$_2$ (100 mg, 0.248 mmol) and (THF)GeCl$_2$•W(CO)$_5$ (134 mg, 0.248 mmol) was added 12 mL of toluene. The reaction mixture was stirred at room temperature for 1 h resulting in the formation of a pale yellow slurry. The precipitate was isolated by filtration and identified as **3** (189 mg) by ^{1}H NMR. A further crop of **3** (colorless crystals suitable for X-ray crystallography) was obtained by cooling the filtrate to -35 °C (17 mg, combined yield = 206 mg, 95 %). ^{1}H NMR (C_6D_6): δ 0.84 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 1.31 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 2.73 (broad, 4H, $CH(CH_3)_2$), 3.18 (s, 2H, -CH_2), 6.33 (s, 2H, N-C*H*-), 7.04 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar*H*) and 7.20 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.6 ($CH(CH_3)_2$), 26.2 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 31.9 (-CH_2-), 122.5 (-N-*C*H-), 125.6 (Ar*C*), 130.6 (Ar*C*), 132.1 (Ar*C*), 145.3 (Ar*C*), 154.6 (N-*C*-N), 198.5 (equat. *C*O, $^1J_{CW}$ = 61.9 Hz) and 202.3 (ax. *C*O). IR (Nujol, cm^{-1}): 1916 (br, υCO), 1978 (br, υCO), and 2063 (s, υCO). Anal. Calcd. for $C_{33}H_{38}Cl_2GeN_2O_5W$: C, 45.56; H, 4.40; N, 3.22. Found: C, 45.53; H, 4.50; N, 3.15. Mp (°C): ~155 (dec.) 184-186 (melts).

Synthesis of IPr-CH_2•SnH_2•W(CO)$_5$ (4). To a mixture of **2** (54 mg, 0.059 mmol) and Li[BH_4] (2.7 mg, 0.12 mmol) was added 8 mL of cold (-35 °C) ether. The reaction mixture was warmed at ambient temperature and stirred for 20 min to obtain a pale yellow solution over precipitate. Filtration of the solution through Celite followed by the removal of the volatiles afforded **4** as a pale brown powder (45 mg, 91%). Crystals suitable for X-ray crystallography were grown by cooling an ether solution of **4** to -35 °C for 3 days. ^{1}H NMR (C_6D_6): δ 0.88 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 2.31 (t, 2H, -CH_2-, $^3J_{HH}$ = 2.0 Hz, satellites: $^3J_{HW}$ = 21 Hz), 2.58 (septet, $^3J_{HH}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 5.48 (t, 2H, SnH_2, $^3J_{HH}$ = 2.0 Hz, satellites: $^2J_{HW}$ = 9.5 Hz, $^1J_{119Sn\text{-}H}$ = 1060 Hz, $^1J_{117Sn\text{-}H}$ = 1013), 6.15 (s, 2H, N-C*H*-), 7.02 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*) and 7.19 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.7 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 31.9 (CH_2), 120.9 (-N-*C*H-), 125.5 (Ar*C*), 130.4 (Ar*C*), 132.7 (Ar*C*), 145.5 (Ar*C*), 160.6 (N-*C*-N), 202.1 (equat. *C*O, $^1J_{CW}$ = 61.3 Hz) and 204.8 (ax. *C*O). $^{119}Sn\{^1H\}$NMR (C_6D_6): δ = -228 (s). ^{119}Sn NMR (C_6D_6): δ -229 (t, $^1J_{SnH}$ = 1066 Hz, $^1J_{SnW}$ = 791 Hz). IR (Nujol, cm^{-1}): 1758 (sh, υSnH), 1889 (br, υCO), 1913 (br, υCO), 1980 (s, υCO) and 2043 (s, υCO). Anal. Calcd. for $C_{33}H_{40}N_2O_5SnW$: C, 46.78; H, 4.76; N, 3.31. Found: C, 48.50; H, 5.03; N, 3.25. Mp (°C): 95-97 (dec., turns black), 117-119 (melts).

Synthesis of IPr-CH$_2$•SnD$_2$•W(CO)$_5$, 4D. To a mixture of **2** (53 mg, 0.058 mmol) and Li[BD_4] (3.1 mg, 0.12 mmol) was added 10 mL of cold (-35 °C) ether. The reaction mixture was warmed to ambient temperature and stirred for 20 min to give a beige colored slurry. The reaction was filtered through Celite and the volatiles were removed to afford **4D** as a pale brown solid (43.6 mg, 88 %). ^{1}H NMR (C_6D_6): essentially same as **4** with the absence of the SnH_2 resonance. ^{2}H{^{1}H} NMR (C_6H_6): δ 5.51 (s, -SnD_2-). ^{119}Sn{^{1}H} NMR (C_6D_6): δ -309 (pentet, $^1J_{\text{Sn-D}}$ = 164.2 Hz). IR (Nujol, cm^{-1}): Similar to **4** except for the absence of υSnH at 1758 cm^{-1}; the Sn-D stretch could not assigned due to the presence of IPrCH$_2$ vibrations in the same region.

Thermolysis of IPr-CH$_2$•SnH$_2$•W(CO)$_5$ (4). A solution of IPr-CH$_2$•SnH$_2$•W(CO)$_5$ (17 mg, 0.020 mmol) in C_6D_6 was heated to 85 °C in a J-Young tube for 30 h to obtain a pale yellow solution over black precipitate. ^{1}H NMR analysis of the soluble fraction revealed the formation of free IPr=CH$_2$ (~96 % by ^{1}H NMR spectroscopy) as the soluble product from the thermal decomposition of **4**.

Synthesis of IPr-CH$_2$•GeH$_2$•W(CO)$_5$, 5. To a mixture of **3** (97 mg, 0.11 mmol) and Li[AlH_4] (2.1 mg, 0.056 mmol) was added 10 mL of toluene. After stirring the reaction mixture for 20 min, 2 mL of Et_2O was added and the reaction was stirred for another 10 min to give a pale yellow solution over brown precipitate. Filtration of the mixture through Celite followed by the removal of solvent from filtrate afforded **5** as a beige powder (81 mg, 90 %). Crystals suitable for X-ray crystallography were grown from a saturated Et_2O/hexanes solution at -35 °C. ^{1}H NMR (C_6D_6): δ 0.86 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 2.41 (t, 2H, -C*H*$_2$-, $^3J_{HH}$ = 4.0 Hz), 2.53 (septet, 4H, C*H*(CH$_3$)$_2$), 4.07 (t, 2H, -Ge*H*$_2$-, $^3J_{HH}$ = 4.0 Hz, satellites: $^3J_{HW}$ = 14.5 Hz), 6.14 (s, 2H, N-C*H*-), 7.04 (d,

$^3J_{HH}$ = 7.8 Hz, 4H, Ar*H*) and 7.13 (t, $^3J_{HH}$ = 7.8 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.9 (-*C*H_2-), 22.6 (CH(*C*$H_3)_2$), 25.8 (CH(*C*$H_3)_2$), 29.3 (*C*H($CH_3)_2$), 121.2 (-N-*C*H-), 125.4 (Ar*C*), 130.3 (Ar*C*), 132.2 (Ar*C*), 145.4 (Ar*C*), 160.1 (N-*C*-N), 202.5 (equat. *C*O) and 205.5 (ax. *C*O). IR (Nujol, cm^{-1}): 1860 (br, υCO), 1901 (br, υCO), 1951 (br, υCO) and 2047 (s, υCO); Ge-H stretch could not conclusively identified due to overlapping W(CO)$_5$ vibrations. Anal. Calcd. for $C_{33}H_{40}GeN_2O_5W$: C, 49.47; H, 5.03; N, 3.50. Found: C, 49.76; H, 4.14; N, 3.52. Mp (°C): ~120 (dec.) 161-163 (melts).

Synthesis of IPr-CH$_2$•GeD$_2$•W(CO)$_5$, 5D. To a mixture of **3** (50 mg, 0.057 mmol) and Li[AlD$_4$] (1.2 mg, 0.029 mmol) was added a mixture of toluene and Et$_2$O (4:1) . The reaction was stirred for 10 min at room temperature to afford a beige slurry. Filtration of the reaction mixture through Celite afforded a pale yellow solution and volatiles were removed to yield **5D** pale yellow powder (43 mg, 91 %). ^{1}H NMR (400 MHz, C_6D_6): essentially same as **5** with the absence of the GeH$_2$ resonance. $^2H\{^1H\}$ NMR (C_6H_6): δ 4.06 (s, -Ge*D*$_2$-). IR (Nujol, cm^{-1}): Similar to **5** except a υGe-D stretching vibration was detected at 1407 cm^{-1}.

Thermolysis of IPr-CH$_2$•GeH$_2$•W(CO)$_5$ (5). A solution of IPr-CH$_2$•GeH$_2$•W(CO)$_5$ (32 mg, 0.04 mmol) in toluene was heated at 110 °C for 48 hours to obtain a pale yellow solution over black precipitate. The solution was decanted and volatiles were removed to obtain a pale yellow powder (27 mg). ^{1}H NMR (C_6D_6) analysis of the soluble fraction revealed the presence of starting material, IPr-CH$_2$•GeH$_2$•W(CO)$_5$ (77 %) and IPr=CH$_2$ (23 %) as a decomposition product. When a solution of **5** in C_6D_6 was heated to 85 °C for 30 h (in a J-Young tube), no sign of decomposition could be detected by NMR spectroscopy.

Reaction of IPr-CH$_2$•SnH$_2$•W(CO)$_5$ with IPr. To mixture of IPr-CH$_2$•SnH$_2$•W(CO)$_5$ (0.037 g, 0.043 mmol) and IPr (0.018 g, 0.048 mmol) was added to 6 mL of toluene. The reaction was stirred at ambient temperature overnight to give a pale yellow solution. Removal of the volatiles from the reaction afforded a pale yellow powder (55 mg). ^{1}H NMR analysis (in C_6D_6) of the product revealed the quantitative formation of IPr•SnH$_2$•W(CO)$_5$ and free IPr=CH$_2$ in a 1:1 ratio. Data for IPr•SnH$_2$•W(CO)$_5$:[8] ^{1}H NMR (C_6D_6): δ 0.89 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 2.55 (septet, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 5.55 (s, $^3J_{WH}$ = 8.0 Hz, $^1J_{119Sn\text{-}H}$ = 1159.4 Hz, $^1J_{117Sn\text{-}H}$ = 1108.2 Hz, 2H, Sn*H*$_2$), 6.44 (s, 2H, N-C*H*-), 7.07 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar*H*) and 7.20 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*).

Reaction of IPr-CH$_2$•SnH$_2$•W(CO)$_5$ with excess ClSiMe$_3$. To a solution of IPr-CH$_2$•SnH$_2$•W(CO)$_5$ (28 mg, 0.030 mmol) in 8 mL of Et$_2$O, was added excess trimethylsilyl chloride (ClSiMe$_3$) (34 mg, 0.31 mmol). The reaction mixture was stirred for 18 h at room temperature to give a beige solution. Removal of solvent from the reaction mixture afforded pale yellow powder (22 mg) and ^{1}H NMR (C_6D_6) analysis of the product revealed the presence of IPr-CH$_2$•SnCl$_2$•W(CO)$_5$ (85 % by ^{1}H NMR) along with a minor amount of unidentified carbene-containing products. When the reaction was conducted in a closed system (J-Young NMR tube), a similar product distribution was noted along with the detection of HSiMe$_3$.[9]

Reaction of IPr-CH$_2$•GeH$_2$•W(CO)$_5$ with IPr. To mixture of IPr-CH$_2$•GeH$_2$•W(CO)$_5$ (27 mg, 0.033 mmol) and IPr (13 mg, 0.033 mmol) was added to 5 mL of toluene. The reaction was stirred at roomtemperature overnight to give a pale yellow solution. Removal of the volatiles from the reaction afforded a pale yellow oil (40 mg). ^{1}H NMR analysis (in C_6D_6) of the products revealed that quantitative conversion to IPr•GeH$_2$•W(CO)$_5$ and free IPr=CH$_2$ had occurred. Data for IPr•GeH$_2$•W(CO)$_5$:[8] ^{1}H NMR (C_6D_6): δ 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 2.58 (septet, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.23 (s, $^3J_{WH}$ = 4.2 Hz, 2H, Ge*H*$_2$), 6.46 (s, 2H, N-C*H*-), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar*H*) and 7.21 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*).

Table S1. Crystallographic Experimental Details for IPr=CH_2 (**1**)

A. Crystal Data	
formula	$C_{28}H_{38}N_2$
formula weight	402.60
crystal dimensions (mm)	0.58 × 0.16 × 0.11
crystal system	triclinic
space group	$P\bar{1}$
unit cell parameters[a]	
a (Å)	14.0622(12)
b (Å)	16.6074(15)
c (Å)	22.775(2)
α (deg)	79.6784(11)
β (deg)	81.3389(12)
γ (deg)	78.5042(11)
V (Å^3)	5091.3(8)
Z	8
ρ_{calcd} (g cm^{-3})	1.050
μ (mm^{-1})	0.060
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (25 s exposures)
data collection 2θ limit (deg)	50.50
total data collected	36469 ($-16 \le h \le 16$, $-19 \le k \le 19$, $-27 \le l \le 27$)
independent reflections	18420 ($R_{int} = 0.0670$)
number of observed reflections (*NO*)	9096 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	Gaussian integration (face indexed)
range of transmission factors	0.9931-0.9658
data/restraints/parameters	18420 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 1082
goodness-of-fit (S)[d]	1.006 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[e]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0647
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1921
largest difference peak and hole	0.299 and –0.223 e Å^{-3}

[a] Obtained from least-squares refinement of 5951 reflections with 4.54° < 2θ < 40.78°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction

were those supplied by Bruker.

[c] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0387P)^2 + 2.4077P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$

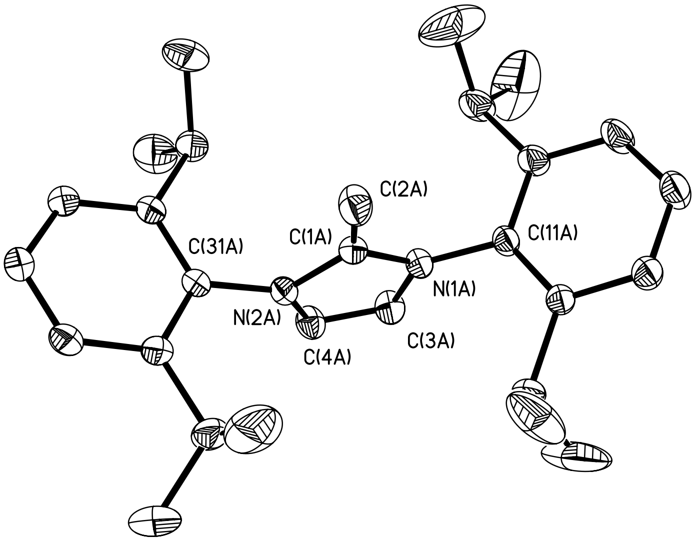


Figure S1. Thermal ellipsoid plot (30 % probability level) of IPr=CH_2 (**1**). Carbon-bound hydrogen atoms have been omitted for clarity. One molecule of the four present in the asymmetric unit is shown. Selected bond lengths (Å) and angles (°): *Molecule A*: C(1)-C(2) 1.332(4), C(1)-N(1) 1.391(3), C(1)-N(2) 1.391(3); N(1)-C(1)-N(2) 104.3(2), N(1)-C(1)-C(2) 127.8(3), N(2)-C(1)-C(2) 128.0(3). *Molecule B*: C(1)-C(2) 1.322(4), C(1)-N(1) 1.388(3), C(1)-N(2) 1.395(3); N(1)-C(1)-N(2) 103.8(2), N(1)-C(1)-C(2) 128.3(3), N(2)-C(1)-C(2) 127.9(3). *Molecule C*: C(1)-C(2) 1.337(4), C(1)-N(1) 1.391(3), C(1)-N(2) 1.396(3); N(1)-C(1)-N(2) 104.3(2), N(1)-C(1)-C(2) 127.6(3), N(2)-C(1)-C(2) 128.0(3). *Molecule D*: C(1)-C(2) 1.334(4), C(1)-N(1) 1.396(3), C(1)-N(2) 1.385(3); N(1)-C(1)-N(2) 104.7(2), N(1)-C(1)-C(2) 126.8(3), N(2)-C(1)-C(2) 128.5(3).

Table S2. Crystallographic Experimental Details for IPrCH$_2$•SnCl$_2$•W(CO)$_5$ (**2**)

A. Crystal Data	
formula	$C_{36.5}H_{42}Cl_2N_2O_5SnW$
formula weight	962.16
crystal dimensions (mm)	0.37 × 0.22 × 0.12
crystal system	monoclinic
space group	$P2_1/c$
unit cell parameters[a]	
a (Å)	18.2204(7)
b (Å)	13.8439(5)
c (Å)	17.6027(7)
β (deg)	118.0937(4)
V (Å^3)	3917.0(3)
Z	4
ρ_{calcd} (g cm^{-3})	1.632
μ (mm^{-1})	3.749
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	54.98
total data collected	34306 ($-23 \le h \le 23$, $-17 \le k \le 17$, $-22 \le l \le 22$)
independent reflections	8962 ($R_{int} = 0.0196$)
number of observed reflections (*NO*)	7764 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6535–0.3415
data/restraints/parameters	8962 [$F_o^2 \ge -3\sigma(F_o^2)$] / 3[d] / 484
goodness-of-fit (S)[e]	1.063 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0300
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0921
largest difference peak and hole	1.629 and –0.863 e Å^{-3}

[a] Obtained from least-squares refinement of 9902 reflections with 4.62° < 2θ < 46.64°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

[d] Distances involving the methyl carbon of the inversion-disordered solvent toluene molecule were restrained during the refinement: d(C1S-C7S) = 1.50(1) Å; d(C2S…C7S) = d(C6S…C7S) = 2.50(1) Å. The phenyl ring of this molecule was modeled as an idealized regular hexagon with d(C-C) = 1.39 Å. All carbon atoms of this molecule were refined with a common isotropic displacement parameter.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0435P)^2 + 0.8599P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

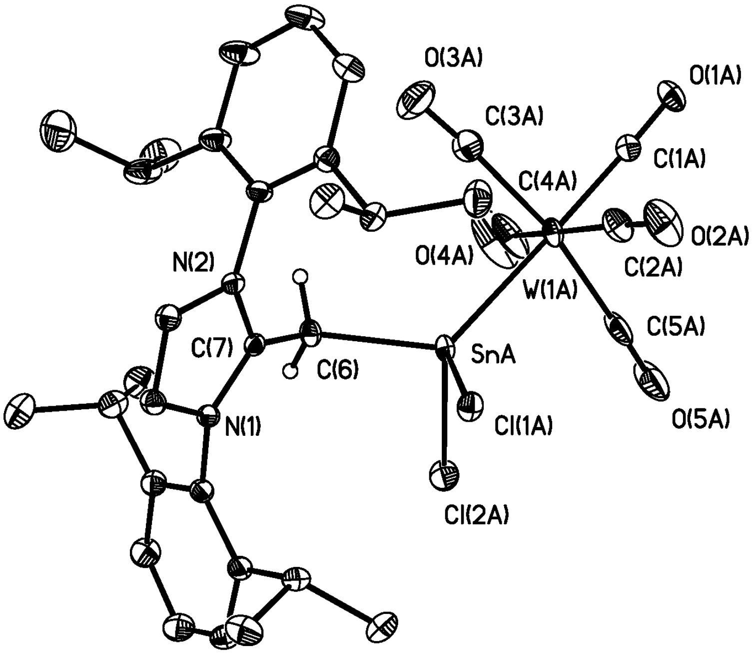


Figure S2. Thermal ellipsoid plot (30 % probability level) of IPrCH$_2$•SnCl$_2$•W(CO)$_5$ (**2**). Carbon-bound hydrogen atoms and toluene solvate have been omitted for clarity. Selected bond lengths (Å) and angles (°) with values belonging to the disordered SnCl$_2$•W(CO)$_5$ residue in parentheses: Sn-W 2.755(2) [2.761(3)], Sn-C(6) 2.178(4) [2.309(5)], C(7)-C(6) 1.452(4), N(1)-C(7) 1.342(4), N(2)-C(7) 1.356(4), Sn-Cl(1) 2.354(17) [2.47(3)], Sn-Cl(2) 2.392(4) [2.397(6)], W-C(1) 1.970(9) [1.973(14)], W-C(2-5) 2.010(8) to 2.045(7); C(6)-Sn-W 124.90(14) [123.96(19)], C(7)-C(6)-Sn 124.0(2) [120.0(2)], Cl(1)-Sn-Cl(2) 96.5(13) [93.5(7)], Sn-W-C(1) 175.0(2) [176.0(4)], Sn-W-C(2-5) 85.2(2) to 90.4(2).

Table S3. Crystallographic Experimental Details for $IPrCH_2{\bullet}GeCl_2{\bullet}W(CO)_5$ (**3**)

A. Crystal Data

formula	$C_{33}H_{38}Cl_2N_2GeO_5W$
formula weight	869.99
crystal dimensions (mm)	0.26 × 0.24 × 0.08
crystal system	orthorhombic
space group	$Pna2_1$
unit cell parameters[a]	
a (Å)	24.2684(11)
b (Å)	11.1671(5)
c (Å)	13.2380(6)
V (Å^3)	3587.6(3)
Z	4
ρ_{calcd} (g cm^{-3})	1.611
μ (mm^{-1})	4.230

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.40
total data collected	31057 ($-31 \leq h \leq 31$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$)
independent reflections	8358 ($R_{int} = 0.0163$)
number of observed reflections (*NO*)	8171 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SIR*97[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7284–0.4059
data/restraints/parameters	8358 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 398
Flack absolute structure parameter[e]	0.442(5)
goodness-of-fit (*S*)[f]	1.150 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0203
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0501
largest difference peak and hole	1.136 and –0.670 e Å^{-3}

[a] Obtained from least-squares refinement of 9918 reflections with $4.56° < 2\theta < 55.30°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giocovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.

[d] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

[e] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876-881; Flack, H. D.; Bernardinelli, G. *Acta. Crystallogr.* **1999**, *A55*, 908-915; Flack, H. D. Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143-1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration, and will refine to a value near one for the inverted configuration. The value observed herein is indicative of racemic twinning, and was accommodated during the refinement (using the *SHELX-93* TWIN instruction [see reference *d*]).

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0435P)^2 + 0.8599P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

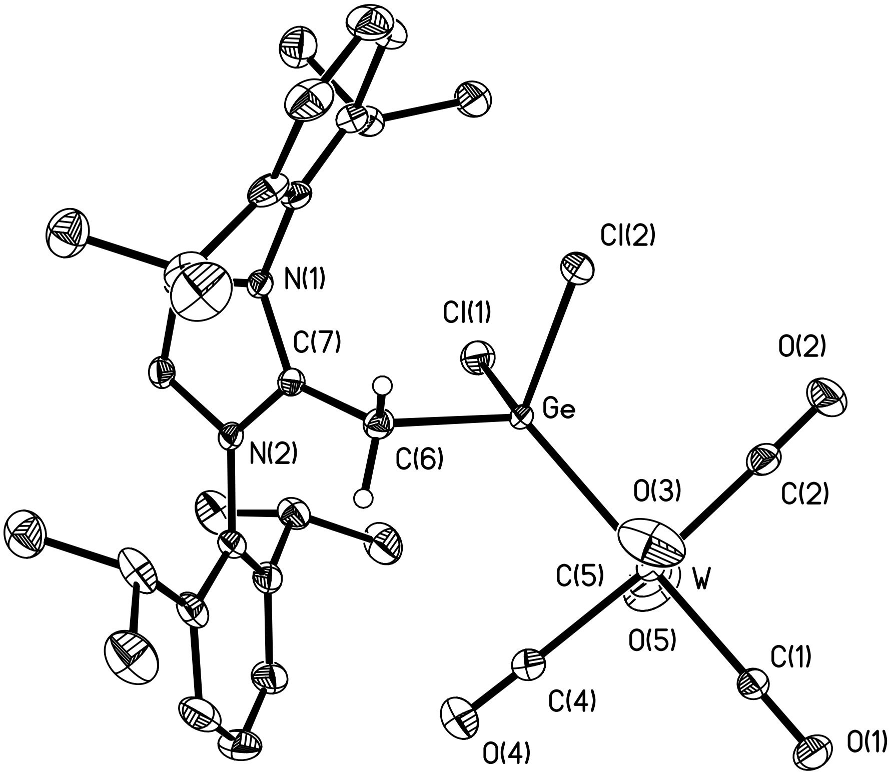


Figure S3. Thermal ellipsoid plot (30 % probability level) of IPrCH$_2$•GeCl$_2$•W(CO)$_5$ (**3**). Carbon-bound hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ge-W 2.5803(3), Ge-C(6) 2.056(3), C(7)-C(6) 1.463(4), N(1)-C(7) 1.350(4), N(2)-C(7) 1.350(4), Ge-Cl(1) 2.2245(10), Ge-Cl(2) 2.2534(9), W-C(1) 2.000(3), W-C(2-5) 2.029(4) to 2.042(4); C(6)-Ge-W 120.37(9), C(7)-C(6)-Ge 118.7(2), Cl(1)-Ge-Cl(2) 99.73(4), Ge-W-C(1) 176.33(10), Ge-W-C(2-5) 86.74(11) to 92.70(13).

Table S4. Crystallographic Experimental Details for $IPrCH_2•SnH_2•W(CO)_5$ (**4**)

A. Crystal Data	
formula	$C_{33}H_{40}N_2O_5SnW$
formula weight	847.21
crystal dimensions (mm)	0.54 × 0.40 × 0.35
crystal system	monoclinic
space group	$P2_1/n$
unit cell parameters[a]	
a (Å)	10.400(2)
b (Å)	22.212(5)
c (Å)	15.597(3)
β (deg)	91.626(3)
V (Å^3)	3601.5(13)
Z	4
ρ_{calcd} (g cm^{-3})	1.562
μ (mm^{-1})	3.922
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	55.18
total data collected	31790 ($-13 \le h \le 13$, $-28 \le k \le 28$, $-20 \le l \le 20$)
independent reflections	8303 ($R_{int} = 0.0150$)
number of observed reflections (*NO*)	7809 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*DIRDIF-2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.3431–0.2259
data/restraints/parameters	8303 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 387
goodness-of-fit (S)[e]	1.045 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0156
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0394
largest difference peak and hole	0.738 and –0.597 e Å^{-3}

[a] Obtained from least-squares refinement of 9978 reflections with $4.32° < 2\theta < 50.64°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O.

(2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

[d] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0435P)^2 + 0.8599P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S5. Crystallographic Experimental Details for IPrCH$_2$•GeH$_2$•W(CO)$_5$ (**5**)

A. Crystal Data	
formula	$C_{35}H_{45}GeN_2O_{5.50}W$
formula weight	838.17
crystal dimensions (mm)	0.19 × 0.18 × 0.11
crystal system	monoclinic
space group	*C*2/*c*
unit cell parameters[a]	
a (Å)	34.3772(15)
b (Å)	10.0524(5)
c (Å)	21.8558(10)
β (deg)	100.6360(10)
V (Å^3)	7423.0(6)
Z	8
ρ_{calcd} (g cm^{-3})	1.500
μ (mm^{-1})	3.948
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ[Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.38
total data collected	32963 ($-44 \le h \le 44$, $-12 \le k \le 13$, $-28 \le l \le 28$)
independent reflections	8636 ($R_{int} = 0.0191$)
number of observed reflections (*NO*)	7859 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SIR*97[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6751–0.5193
data/restraints/parameters	8636 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 410
goodness-of-fit (*S*)[e]	1.038 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0196
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0491
largest difference peak and hole	1.253 and –0.473 e Å^{-3}

[a] Obtained from least-squares refinement of 9217 reflections with 4.54° < 2θ < 55.22°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giocovazzo, C.; Guagliardi, A.;

Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.

[d] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0435P)^2 + 0.8599P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

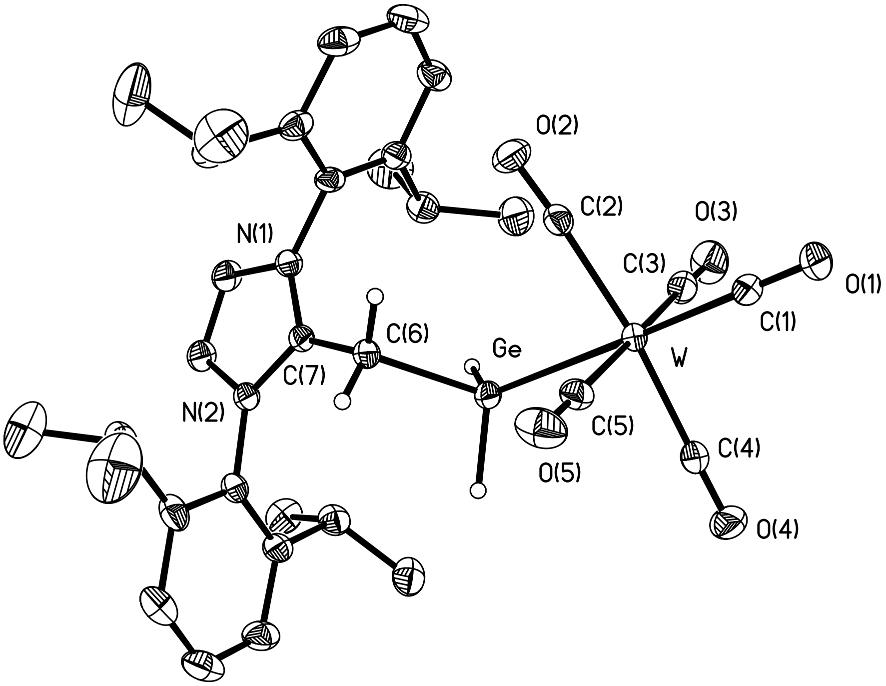


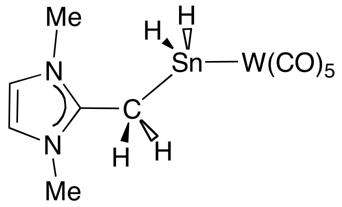
Figure S4. Thermal ellipsoid plot (30 % probability level) of IPrCH$_2$•GeH$_2$•W(CO)$_5$ (**5**). IPr-bound hydrogen atoms and Et$_2$O solvate have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ge-W 2.6503(3), Ge-C(6) 2.057(2), Ge-H 1.46(3) and 1.50(3), C(6)-C(7) 1.463(3), W-C(1) 1.986(3), W-C(2-5) 2.026(3) to 2.037(3); C(6)-Ge-W 113.90(6), Ge-W-C(1) 175.89(7), Ge-W-C(2-5) 64.26(6) to 91.97(7).

Theoretical Studies

Calculations of geometry optimization, frequency and single point energy were performed using Gaussian 03W, Revision E01 software,[10] using DFT methods and the B3LYP functional with default spin parameters. Two sets of basis sets were used in the calculations: the cc-pVDZ-pp basis set was used for W and Sn, while cc-pVDZ was used for all other atoms.[11] Optimizations were done with tight convergence criteria, and no restrictions or constraints were placed on any of the calculated structures. The NHC fragment was simplified by replacing the 2,5-diisopropylphenyl groups with methyl to expedite the calculations. Due to the large number of electrons on W and Sn, the INT=ULTRAFINE keyword was used to generate the grid for electron density. Default parameters were used for all other options. Molecular orbitals and natural bonding orbital (NBO) analyses were done with the built in MO and NBO suites of Gaussian 03; the CHOOSE command was used to isolate and analyze the W – Sn and W – Ge bonds. Theoretical IR spectra were obtained using the spectrum generator in Gaussian.

Additional Notes/Results from Theoretical Work

The following complex was used as a model for compound **4** [IPr-CH_2•SnH_2•W$(CO)_5$], with the 2,6-$^iPr_2C_6H_3$ groups replaced by methyl substituents:



ImMe$_2$CH$_2$•SnH$_2$•W(CO)$_5$

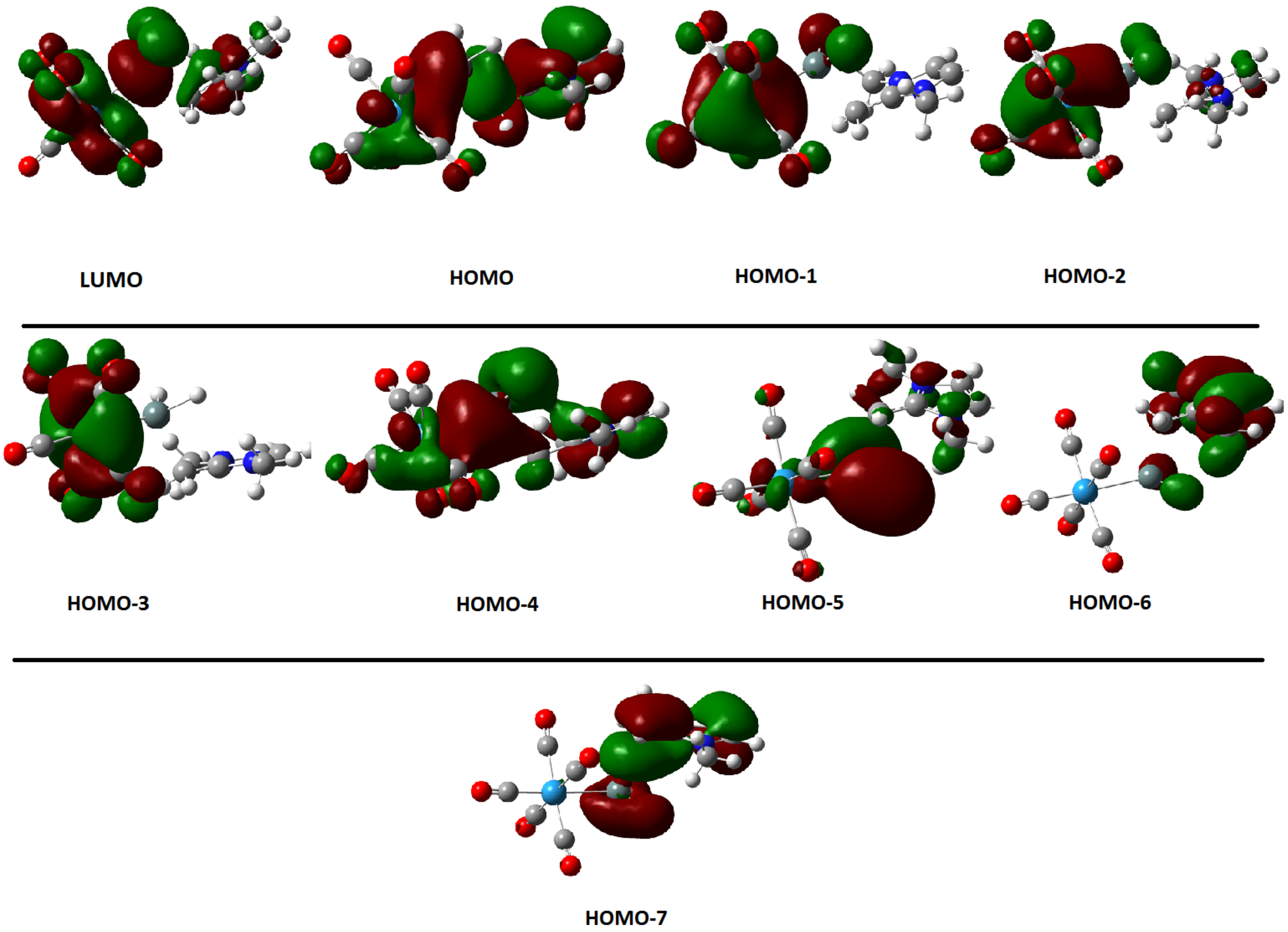
IR Spectroscopy

Calculated Sn-H stretches for [ImMe$_2$-CH$_2$•SnH$_2$•W(CO)$_5$] were 1728.4 cm^{-1} ($\nu_{asym.}$) and 1744.7 cm^{-1} (ν_{sym}). Due to the low oscillator strength of the calculated symmetric stretch, it is predicted that only one Sn-H stretching band would be observed. The experimentally observed Sn-H stretch for **4** was 1758 cm^{-1}.

Table S6: Comparison of experimental and calculated bond lengths and angles for **4** and the model complex [ImMe$_2$-CH$_2$•SnH$_2$•W(CO)$_5$].

	Bond length observed (Å)	Calc. bond length (Å)	Bond angle observed (deg)	Calc. angle (deg)	Wiberg Bond Index
W – Sn	2.7819(5)	2.807	-	-	0.23
Sn – H	1.68(2) 1.66(2)	1.740	-	-	0.90
Sn – C	2.2547(17)	2.317	-	-	0.41
C_{IPr}-CH_2	1.446(2)	1.440	-	-	1.40
W – Sn – C	-	-	109.76(4)	107.67	
H – Sn – H	-	-	98.9(12)	99.39	

Figure S5. Selected Molecular Orbitals for [ImMe$_2$-CH$_2$•SnH$_2$•W(CO)$_5$].



LUMO

HOMO

HOMO-1

HOMO-2

HOMO-3

HOMO-4

HOMO-5

HOMO-6

HOMO-7

LUMO	-0.147 a.u. = -3.999 eV	CO π^* / W – Sn, Sn-H and Sn – C σ^*
HOMO	-0.288 a.u. = -7.836 eV	W(d)-CO π-bonding, C-CH_2 π^* with donation into Sn (p) orbital (partial Sn-W and Sn-C bonding)
HOMO – 1	-0.293 a.u. = -7.972 eV	W(d)-CO π-bonding with SnH_2 non-bonding
HOMO – 2	-0.294 a.u. = -7.999 eV	W(d)-CO π-bonding with Sn(p) mixing
HOMO – 3	-0.301 a.u. = -8.190 eV	W(d_{xy})-CO π-bonding
HOMO – 4	-0.309 a.u. = -8.408 eV	Sn lone pair donation into W (d_{z2})/Sn-H σ
HOMO – 5	-0.336 a.u. = -9.142 eV	Sn-H σ bonding
HOMO – 6	-0.342 a.u. = -9.306 eV	N=C π (heterocycle)
HOMO – 7	-0.371 a.u. = -10.095 eV	C=C π donation into Sn (p)/ C=C π (heterocycle)

** z-direction along Sn-W-CO_{ax} axis

NBO Output/Analysis using the cc-pVDZ-pp/cc-pVDZ basis sets

SnH_2 and CH_2 Fragments:

```
(1.92618) BD ( 1) H   1 -Sn   2
           ( 51.94%)   0.7207* H   1 s( 99.99%)p 0.00(  0.01%)
           ( 48.06%)   0.6932*Sn   2 s( 19.06%)p 4.25( 80.94%)

(1.96914) BD ( 1) H   4 - C   5
           ( 30.96%)   0.5565* H   4 s( 99.92%)p 0.00(  0.08%)
           ( 69.04%)   0.8309* C   5 s( 28.32%)p 2.53( 71.63%)d 0.00(  0.05%)
```

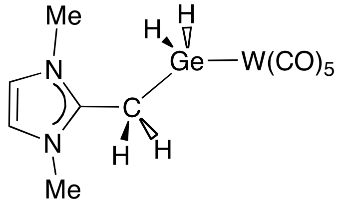
Sn-W interaction:

```
 (1.68403) BD ( 1)Sn   2 - W  22
           ( 82.44%)   0.9080*Sn   2 s( 60.57%)p 0.65( 39.43%)
           ( 17.56%)   0.4191* W  22 s(  1.78%)p10.02( 17.81%)d45.21( 80.41%)
```

IPrCH_2-Sn interaction:

```
 (1.51101) BD ( 1)Sn   2 - C   5
           ( 18.97%)   0.4355*Sn   2 s(  0.78%)p99.99( 99.22%)
           ( 81.03%)   0.9002* C   5 s(  9.96%)p 9.04( 90.02%)d 0.00(  0.02%)
```

The following complex was used as a model for compound **5** [IPr-CH_2•GeH_2•$W(CO)_5$], with the 2,6-$^iPr_2C_6H_3$ groups replaced by methyl substituents:



$ImMe_2CH_2$•GeH_2•$W(CO)_5$

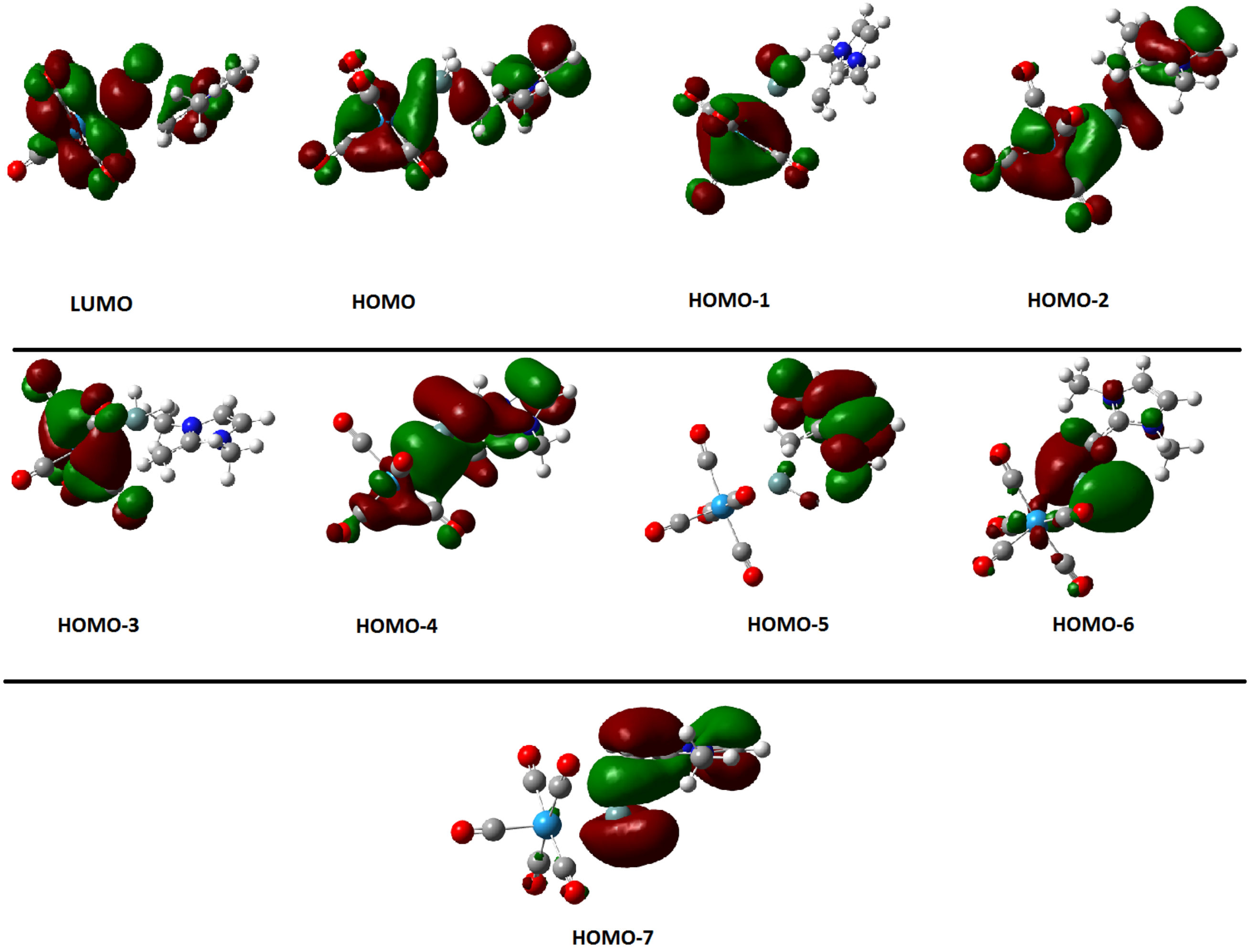
IR Spectroscopy

Calculated Ge-H stretches for [$ImMe_2$-CH_2•GeH_2•$W(CO)_5$] were 1932.5 cm^{-1} ($\nu_{asym.}$) and 1937.5 cm^{-1} (ν_{sym}). Due to the low oscillator strength of the calculated symmetric stretch, it is predicted that only one Ge-H stretching band would be observed. Due to the overlap with the CO stretching bands, a Ge-H stretch in **5** could not be directly identified using IR spectroscopy; the related deuterium analogue, $IPrCH_2$•GeD_2•$W(CO)_5$, gave a Ge-D band at 1407 cm^{-1}.

Table S7: Comparison of experimental and calculated bond lengths and angles for **5** and the model complex [$ImMe_2$-CH_2•GeH_2•$W(CO)_5$].

	Bond length observed (Å)	Calc. bond length (Å)	Bond angle observed (deg)	Calc. angle (deg)	Wiberg Bond Index
W – Ge	2.6503(3)	2.672	-	-	0.46
Ge – H	1.46(3) 1.50(3)	1.580	-	-	0.89
Ge – C	2.057(2)	2.129	-	-	0.55
C_{IPr}-CH_2	1.463(3)	1.446	-	-	1.29
W – Ge – C	-	-	113.90(6)	109.75	
H – Ge – H	-	-	101.8(17)	99.63	

Figure S6. Selected Molecular Orbitals for [ImMe$_2$-CH$_2$•GeH$_2$•W(CO)$_5$].



LUMO	-0.140 a.u. = -3.809 eV	CO π* / W – Ge, Ge-H and Ge – C σ*
HOMO	-0.289 a.u. = -7.863 eV	W(d)-CO π-bonding, C-CH_2 π* with donation into Ge (p) orbital (partial Ge-W and Ge-C bonding)
HOMO – 1	-0.292 a.u. = -7.945 eV	W(d)-CO π-bonding with GeH_2 non-bonding
HOMO – 2	-0.295 a.u. = -8.027 eV	W(d)-CO π-bonding with Ge(p) mixing
HOMO – 3	-0.300 a.u. = -8.163 eV	W(d$_{xy}$)-CO π-bonding
HOMO – 4	-0.314 a.u. = -8.544 eV	Ge lone pair donation into W (d$_{z2}$)/Ge-H σ
HOMO – 5	-0.341 a.u. = -9.278 eV	N=C π (heterocycle)
HOMO – 6	-0.351 a.u. = -9.550 eV	Ge-H σ bonding
HOMO – 7	-0.378 a.u. = -10.285 eV	C=C π donation into Ge (p)/ C=C π (heterocycle)

** z-direction along Ge-W-CO$_{ax}$ axis

NBO Output/Analysis using the cc-pVDZ-pp/cc-pVDZ basis sets

GeH_2 and CH_2 Fragments:

```
(1.96092) BD ( 1) H   1 -Ge  32
                ( 59.71%)   0.7728* H   1 s( 99.89%)p 0.00(  0.11%)
                ( 40.29%)   0.6347*Ge  32 s( 24.11%)p 3.14( 75.62%)d 0.01(  0.26%)

(1.97172) BD ( 1) H   3 - C   4
                ( 31.51%)   0.5613* H   3 s( 99.86%)p 0.00(  0.14%)
                ( 68.49%)   0.8276* C   4 s( 24.69%)p 3.05( 75.29%)d 0.00(  0.02%)
```

Ge-W interaction:

```
(1.76784) BD ( 1) W  21 -Ge  32
                ( 47.04%)   0.6859* W  21 s( 32.00%)p 0.03(  0.89%)d 2.10( 67.11%)
                                         f 0.00(  0.01%)
                ( 52.96%)   0.7277*Ge  32 s( 32.30%)p 2.09( 67.63%)d 0.00(  0.07%)
```

IPrCH$_2$-Ge interaction:

```
(1.89467) BD ( 1) C   4 -Ge  32
                ( 79.27%)   0.8903* C   4 s( 19.95%)p 4.01( 80.05%)d 0.00(  0.00%)
                ( 20.73%)   0.4553*Ge  32 s( 19.59%)p 4.08( 80.01%)d 0.02(  0.40%)
```

Calculation Summary (Optimized Geometry and Frequencies)

Gaussian 03 Input Parameters and Coordinates

[ImMe$_2$CH$_2$•SnH$_2$•W(CO)$_5$]

opt=(calcall,tight) freq b3lyp geom=connectivity pseudo=read gen int=ultrafine

Input orientation:

```
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          1          0        0.000000    0.000000    0.000000
    2         50          0        0.000000    0.000000    1.746055
    3          1          0        1.722635    0.000000    2.031077
    4          1          0       -0.130745   -2.488647    3.024897
    5          6          0       -0.251019   -2.294506    1.958956
    6          1          0       -1.283039   -2.488642    1.666321
    7          6          0        1.719290   -3.982025   -0.600454
    8          6          0        2.595639   -3.982029    0.432777
    9          1          0        1.817071   -4.346594   -1.609808
   10          1          0        3.607417   -4.346602    0.501041
   11          6          0        0.698841   -3.018504    1.153316
   12          7          0        1.955921   -3.388645    1.514443
   13          7          0        0.547722   -3.388638   -0.145849
   14          6          0       -0.654138   -3.145114   -0.938107
   15          1          0       -0.853393   -2.071864   -0.989402
   16          1          0       -0.489233   -3.531696   -1.943778
   17          1          0       -1.512790   -3.656674   -0.495520
   18          6          0        2.541402   -3.145128    2.829493
   19          1          0        3.560503   -3.531708    2.830931
   20          1          0        2.559486   -2.071880    3.034456
   21          1          0        1.964612   -3.656696    3.604394
   22         74          0       -1.927229    1.223769    3.380607
   23          6          0       -1.372376   -0.136877    4.800104
   24          8          0       -1.032771   -0.937273    5.570707
   25          6          0       -3.237091   -0.136924    2.601524
   26          8          0       -3.941905   -0.937348    2.140706
   27          6          0       -3.332475    2.032105    4.572442
   28          8          0       -4.145396    2.491084    5.261908
   29          6          0       -2.369193    2.521963    1.848860
   30          8          0       -2.610721    3.243630    0.976968
   31          6          0       -0.488195    2.522009    4.066638
   32          8          0        0.332565    3.243703    4.447226
```

```
 ---------------------------------------------------------------------
```

For [$ImMe_2CH_2$•GeH_2•$W(CO)_5$]

```
# opt=(calcall,tight) freq b3lyp geom=connectivity pseudo=read gen int=ultrafine
```

Input Orientation

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number      Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1           1           0        1.436502    1.204122    1.586744
    2           1           0        1.436500   -1.204136    1.586739
    3           1           0        1.866186   -0.889315   -1.415245
    4           6           0        2.118261   -0.000003   -0.837487
    5           1           0        1.866182    0.889308   -1.415246
    6           6           0        5.500591    0.677834    0.347757
    7           6           0        5.500594   -0.677826    0.347757
    8           1           0        6.261107    1.384288    0.637342
    9           1           0        6.261112   -1.384278    0.637342
   10           6           0        3.500243    0.000000   -0.408505
   11           7           0        4.260914   -1.087803   -0.125420
   12           7           0        4.260909    1.087806   -0.125421
   13           6           0        3.806427    2.470040   -0.257798
   14           1           0        2.921744    2.628202    0.363081
   15           1           0        4.607484    3.130129    0.074526
   16           1           0        3.566994    2.694653   -1.300225
   17           6           0        3.806437   -2.470040   -0.257799
   18           1           0        4.607495   -3.130125    0.074528
   19           1           0        2.921752   -2.628204    0.363076
   20           1           0        3.567009   -2.694654   -1.300227
   21          74           0       -1.707096    0.000000   -0.055769
   22           6           0       -1.092502   -1.441474   -1.361676
   23           8           0       -0.672348   -2.249264   -2.084549
   24           6           0       -1.092480    1.441426   -1.361719
   25           8           0       -0.672311    2.249189   -2.084613
   26           6           0       -3.600204    0.000004   -0.756687
   27           8           0       -4.685984    0.000006   -1.167700
   28           6           0       -2.121627    1.451042    1.338623
   29           8           0       -2.325951    2.270625    2.129964
   30           6           0       -2.121650   -1.450993    1.338668
   31           8           0       -2.325988   -2.270547    2.130033
   32          32           0        0.799638   -0.000005    0.806827
 ---------------------------------------------------------------------
```

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