Electronic Supporting Information for

Efficient generation of stable adducts of Si(II) dihydride using a donor-acceptor approach

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Contents

Tables and Figures

Experimental Section

General. All reactions 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 Grubbs-type solvent purification system[1] manufactured by Innovative Technology, Inc., degassed (freeze-pump-thaw method) and stored under atmosphere of nitrogen prior to use. $Li[BH_4]$, $Li[AlH_4]$, $Li[AlD_4]$ and $[Rh(CO)_2Cl]_2$ 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 atmosphere prior to use. IPr•$SiCl_2$,[2] IPr•$SiCl_2$•BH_3[3] were prepared following literature procedures. ^1H, $^2H\{^1H\}$, $^{13}C\{^1H\}$ and ^{29}Si NMR spectra were recorded on a Varian iNova-400 spectrometer and referenced externally to $SiMe_4$ (^1H, $^{13}C\{^1H\}$ and ^{29}Si) and $Si(CD_3)_4$ ($^2H\{^1H\}$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded on a Nicolet IR100 FTIR instrument manufactured by Thermo Electron Corporation. Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and were uncorrected.

X-ray Crystallography. Crystals suitable for X-ray diffraction studies were removed from a vial (in glove box) and immediately coated with thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on glass fiber, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer.[4] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα (**2** and **3**) or Cu Kα (**4**) radiation, with the crystals cooled to -100 °C. The data were corrected for absorption[5] through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using direct (**2**: SHELXS-97; **3**:

SHELXD)[6,7] or Patterson (**4**: DIRDIF 2008)[8] methods, and refined using SHELXS-97.[6] The assignment of hydrogen atoms positions were 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•SiH_2•BH_3 (2) To mixture of IPr•$SiCl_2$•BH_3 (102 mg, 0.204 mmol) and Li[AlH_4] (5.42 mg, 0.143 mmol) was added 8 mL of toluene and the reaction was stirred at room temperature for 1 h to give a cloudy mixture. Afterwards, 3 mL of Et_2O was added and the mixture was stirred for another 30 minutes. The reaction mixture was then filtered through Celite and removal of the volatiles from the pale yellow filtrate afforded **2** as a white powder (47 mg, 55 %). Crystals suitable for X-ray crystallography (colorless blocks) were grown by cooling a saturated Et_2O solution layered with hexanes to -35 °C for 2 days. ^1H NMR (300 MHz, C_6D_6): δ = 0.96 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.38 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 2.63 (septet, $^3J_{HH}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 3.76 (q, $^3J_{HH}$ = 5.6 Hz, 2H, -SiH_2-, assignment made by ^{29}Si-^1H gHSQC experiment), 6.40 (s, 2H, N-C*H*-), 7.05 (d, $^3J_{HH}$ = 7.8 Hz, 4H, Ar*H*) and 7.19 (t, $^3J_{HH}$ = 7.8 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 22.9 ($CH(CH_3)_2$), 25.5 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 124.6 (-N-*C*H-), 124.7 (Ar*C*), 131.4 (Ar*C*), 133.5 (Ar*C*), 145.6 (Ar*C*) and 168.8 (N-*C*-N). $^{11}B\{^1H\}$NMR (128 MHz, C_6D_6): δ = - 46.2 (s). ^{11}B NMR (128 MHz, C_6D_6): δ = - 46.2 (quartet, $^1J_{BH}$ = 93 Hz). $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): δ = - 55.6 (q, $^1J_{SiB}$ = 46 Hz). IR (Nujol/cm^{-1}): 2096 (s, νSi-H), 2238 (w, νB-H), 2304 (m, νB-H) and 2345 (w, νB-H). Mp (°C): 233-235. Anal. Calcd. for: $C_{27}H_{41}BN_2Si$: C, 74.98; H, 9.55; N, 6.48. Found: C, 73.92; H, 9.50; N, 6.16.

Synthesis of IPr•SiD$_2$•BH$_3$ (2D) To mixture of IPr•SiCl$_2$•BH$_3$ (100 mg, 0.204 mmol) and Li[AlD$_4$] (5.9 mg, 0.141 mmol) was added 8 mL of toluene and the reaction was stirred at room temperature for 1 h to give a cloudy mixture. Afterwards, 3 mL of Et$_2$O was added and the reaction was stirred for another 30 minutes. The mixture was then filtered through Celite and removal of the volatiles from the pale yellow filtrate afforded **2D** as a white powder (45 mg, 52 %). ^{1}H NMR (300 MHz, C$_6$D$_6$): All the peaks were identical as for compound **2**, except the -SiH$_2$- resonance was absent. ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): essentially same as for the compound **2**. ^{2}H{^{1}H} NMR (61.4 MHz, C$_6$H$_6$): δ = 3.75 (-SiD_2-). IR (Nujol/cm^{-1}): 1522 (m, νSi-D), 2236 (w, νB-H), 2302 (m, νB-H) and 2344 (w, νB-H).

Synthesis of IPr•SiH$_2$•W(CO)$_5$ (3) W(CO)$_6$ (49 mg, 0.14 mmol) was suspended in 12 mL of THF and irradiated with a 450 W mercury lamp for 2 h to give a bright yellow solution. A solution of IPr•SiH$_2$•BH$_3$ (60 mg, 0.14 mmol) in 5 mL of THF was then added dropwise *in situ* generated W(CO)$_5$•THF and the reaction was heated overnight at 40 °C, resulting in the formation of a pale orange solution. The volatiles were removed and the resulting solid was washed with 3 mL of hexanes to afford **3** as a yellow solid (83 mg, 66 %). X-ray quality crystals of **3** were grown by cooling a saturated Et$_2$O solution layered with hexanes at - 35 °C for 3 days. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.88 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.62 (septet, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 4.16 (s, 2H, -SiH_2-, satellites: $^1J_{SiH}$ = 164 Hz), 6.40 (s, 2H, N-CH-), 7.08 (d, $^3J_{HH}$ = 7.2 Hz, 4H, ArH) and 7.20 (t, $^3J_{HH}$ = 7.2 Hz, 2H, ArH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ = 22.4 (CH(CH$_3$)$_2$), 25.9 (CH(CH$_3$)$_2$), 29.1 (CH(CH$_3$)$_2$), 124.9 (-N-CH-), 125.2 (ArC), 131.5 (ArC), 133.5 (ArC), 145.1 (ArC), 168.7 (N-C-

N), 201.4 (s, ${}^{1}J_{WC}$ = 122.2 Hz, equatorial *C*O) and 203.1 (axial, *C*O). ^{29}Si NMR (99 MHz, C_6D_6): δ = -71.6 (t, ${}^{1}J_{Si\text{-}H}$ = 164 Hz). IR (Nujol/cm^{-1}): 1876 (s, νCO), 1919 (s, νCO), 1949 (w, νCO), 2044 (s, νCO), 2086 (m, νSi-H) and 2108 (m, νSi-H). Mp (°C): 157-159 (dec., turns gray), 186-188 (melts). Anal. Calcd. for: $C_{32}H_{38}N_2O_5SiW$: C, 51.76; H, 5.16; N, 3.77. Found: C, 52.69; H, 5.99; N, 3.77.

Reaction of IPr•SiCl$_2$ with [Rh(CO)$_2$Cl]$_2$: Synthesis of [*trans*-(IPr•SiCl$_2$)$_2$Rh(CO)$_2$][*cis*-Rh(CO)$_2$Cl$_2$] (4). To a mixture of IPr•SiCl$_2$ (103 mg, 0.211 mmol) and [Rh(CO)$_2$Cl]$_2$ (82 mg, 0.222 mmol) was added 10 mL of toluene. The reaction mixture was stirred at room temperature for 20 min. to give a bright yellow-orange slurry. The reaction was allowed to settle and the precipitate was isolated by filtration. Removal of the volatiles from the precipitate afforded **4** as an orange powder (131 mg, 87 %). Crystals suitable for the X-ray crystallography (orange needles) were grown by cooling a saturated CH_2Cl_2 solution of **4** layered with hexanes at -35 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.11 (d, ${}^{3}J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.32 (d, ${}^{3}J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.47 (septet, ${}^{3}J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 7.30 (d, ${}^{3}J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 7.44 (s, 2H, N-C*H*-), 7.52 (t, ${}^{3}J_{HH}$ = 8.0 Hz, 2H, Ar*H*). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 23.1 (CH(*C*H$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 29.9 (*C*H(CH$_3$)$_2$), 125.2 (-N-*C*H-), 137.6 (Ar*C*), 132.4 (Ar*C*), 132.5 (Ar*C*), 145.8 (Ar*C*), 153.9 (N-*C*-N, ${}^{2}J_{RhC}$ = 4.9 Hz), 182.6 (cis-[Rh(*C*O)$_2$Cl$_2$]$^-$, ${}^{1}J_{RhC}$ = 71.9 Hz) and 191.6 ([(IPr•SiCl$_2$)$_2$Rh(*C*O)$_2$]$^+$, ${}^{1}J_{RhC}$ = 63.4 Hz). ^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2): δ = 27.9 (d, ${}^{1}J_{Si\text{-}Rh}$ = 69 Hz). Mp (°C): 167-170. IR (Nujol/cm^{-1}): 1993 (s, νCO), 2009 (s, νCO), 2066 (s, νCO), 2090 (w, νCO). Anal. Calcd. for $C_{58}H_{72}Cl_6N_4O_4Rh_2Si_2$: C, 51.08; H, 5.32; N, 4.11. Found: C, 51.27; H, 5.60; N, 4.26.

Reaction of IPr•SiH_2•BH_3 with Cy_3P: To a mixture of **2** (26 mg, 0.049 mmol) and Cy_3P (14 mg, 0.049 mmol) was added 6 mL of toluene. The reaction mixture was stirred for 24 h. No sign of reaction was observed by NMR spectroscopy. The solution was heated at 35 °C for 48 h at which time the volatiles were removed and ^1H and ^{31}P NMR spectroscopic analysis revealed ~ 15 % decomposition of IPr•SiH_2•BH_3 into IPr•BH_3[9] and $[(HCNAr)_2CH_2]$,[10] while a similar conversion (*ca*. 15 %) of Cy_3P into Cy_3P•BH_3[11] was also noted.

Reaction of IPr•GeH_2•BH_3 with Cy_3P: To a mixture of IPr•GeH_2•BH_3 (19 mg, 0.040 mmol) and Cy_3P (11 mg, 0.030 mmol) was added 4 mL of toluene. After stirring the reaction for 24 h, the volatiles were removed and ^1H, ^{11}B and ^{31}P NMR analysis revealed ~ 25 % decomposition of IPr•GeH_2•BH_3 into IPr•BH_3 and $[(HCNAr)_2CH_2]$, while a similar conversion (*ca*. 20 %) of Cy_3P into Cy_3P•BH_3 was also noted.

Table S1. Crystallographic experimental details for IPr•SiH$_2$•BH$_3$ (**2**).

A. Crystal Data	
formula	$C_{27}H_{41}BN_2Si$
formula weight	432.52
crystal dimensions (mm)	0.43 × 0.14 × 0.08
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	11.2366 (7)
b (Å)	13.7989 (8)
c (Å)	17.9086 (11)
β (deg)	97.2660 (10)
V (Å^3)	2754.5 (3)
Z	4
ρ_{calcd} (g cm^{-3})	1.043
μ (mm^{-1})	0.100
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/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)	52.80
total data collected	21777 ($-14 \le h \le 14$, $-17 \le k \le 17$, $-22 \le l \le 22$)
independent reflections	5649 (R_{int} = 0.0404)
number of observed reflections (*NO*)	4146 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXD*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9918–0.9584
data/restraints/parameters	5649 / 0 / 300
goodness-of-fit (*S*)[E] [all data]	1.026
final *R* indices[F]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0418
wR_2 [all data]	0.1161
largest difference peak and hole	0.296 and –0.258 e Å^{-3}

[a]Obtained from least-squares refinement of 6903 reflections with 4.56° < 2θ < 44.82°.

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

[c] Schneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, *D58*, 1772-1779.

[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; $w = [\sigma^2(F_o^2) + (0.0483P)^2 + 0.8772P]^{-1}$ 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 S2. Crystallographic experimental details for IPr•SiH$_2$•W(CO)$_5$ (**3**).

A. Crystal Data

formula	$C_{35}H_{45}N_2O_5SiW$
formula weight	785.67
crystal dimensions (mm)	0.23 × 0.15 × 0.12
crystal system	orthorhombic
space group	*Pbca* (No. 61)
unit cell parameters[a]	
a (Å)	14.2434 (15)
b (Å)	18.594 (2)
c (Å)	27.175 (3)
V (Å^3)	7196.9 (13)
Z	8
ρ_{calcd} (g cm^{-3})	1.450
μ (mm^{-1})	3.284

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/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)	51.00
total data collected	50262 ($-17 \le h \le 17$, $-22 \le k \le 22$, $-32 \le l \le 32$)
independent reflections	6703 (R_{int} = 0.1106)
number of observed reflections (*NO*)	4839 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*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	0.6901–0.5201
data/restraints/parameters	6703 / 7[e] / 413
goodness-of-fit (S)[f] [all data]	1.162
final R indices[g]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0850
wR_2 [all data]	0.2254
largest difference peak and hole	4.579 and –4.960 e Å^{-3}

[a] Obtained from least-squares refinement of 9403 reflections with 4.38° < 2θ < 47.06°.

[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] (a) The Si–H1 and Si–H2 distances were constrained to be equal (within 0.01 Å) during refinement. (b) The C–C distances within the disordered solvent n-hexane molecule were restrained during refinement: d(C1SA–C1SA') = d(C1SA–C2SA) = d(C2SA–C3SA) = d(C1SB–C1SB') = d(C1SB–C2SB) = d(C2SB–C3SB) = 1.52(1) Å (primed atoms are related to unprimed ones via the crystallographic inversion center ($^1/_2$, 0, $^1/_2$)).

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0781P)^2 + 163.3664P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

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

Table S3. Crystallographic experimental details for *trans*-[(IPr•$SiCl_2$)$_2$Rh(CO)$_2$]*cis*-[Rh(CO)$_2$Cl$_2$] (**4**).

A. Crystal Data	
formula	$C_{61}H_{78}Cl_{12}N_4O_4Rh_2Si_2$
formula weight	1618.67
crystal dimensions (mm)	0.22 × 0.16 × 0.14
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	13.2122 (2)
b (Å)	21.2410 (3)
c (Å)	13.2241 (2)
β (deg)	97.4269 (6)
V (Å^3)	3680.08 (9)
Z	2
ρ_{calcd} (g cm^{-3})	1.461
μ (mm^{-1})	8.308
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Cu Kα (1.54178)
temperature (°C)	–100
scan type	ω scans (0.8°) (5 s exposures)
data collection 2θ limit (deg)	140.08
total data collected	24802 ($-15 \le h \le 14$, $-25 \le k \le 25$, $-15 \le l \le 15$)
independent reflections	6813 (R_{int} = 0.0170)
number of observed reflections (*NO*)	6390 [$F_o^2 \ge 2\sigma(F_o^2)$]
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	0.3979–0.2682
data/restraints/parameters	6813 / 6[d] / 446
goodness-of-fit (S)[e] [all data]	1.077
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0452
wR_2 [all data]	0.1316
largest difference peak and hole	1.203 and –0.869 e Å^{-3}

[a] Obtained from least-squares refinement of 9846 reflections with 6.74° < 2θ < 139.22°.

[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] Bond distances within the disordered solvent CH_2Cl_2 molecules were restrained during refinement: d(Cl1S–C1S) = d(Cl2S–C1S) = d(Cl3S–C2S) = d(Cl4S–C2S) = d(Cl5S–C3S) = d(Cl6S–C3S) = 1.75(1) Å.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0712P)^2 + 5.0144P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

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

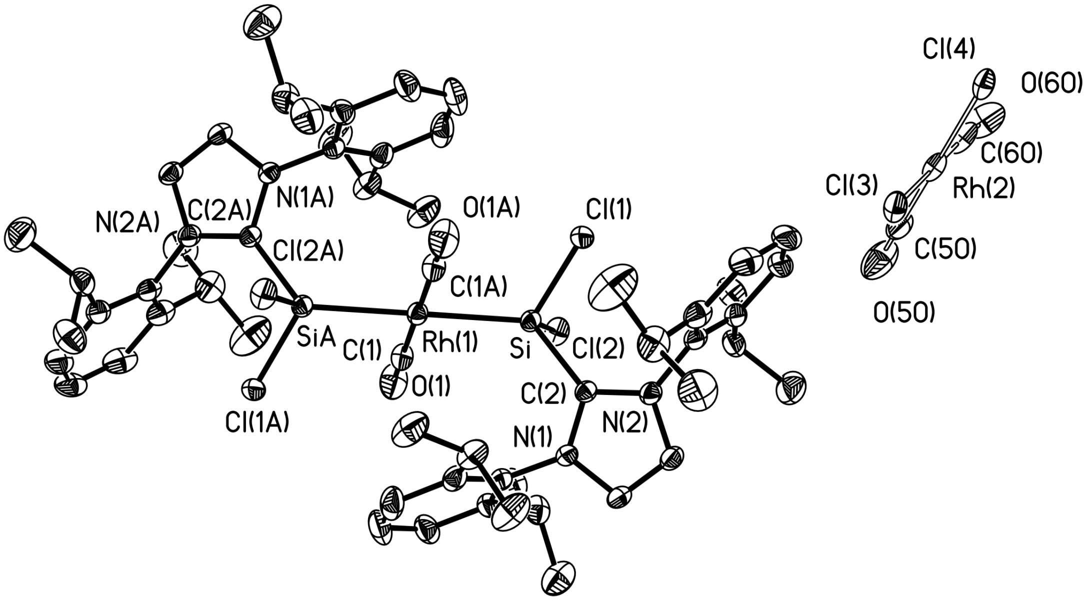


Figure S1. Full structural representation of *trans*-[(IPr•SiCl$_2$)$_2$Rh(CO)$_2$]*cis*-[Rh(CO)$_2$Cl$_2$] (**4**) with hydrogen atoms and CH$_2$Cl$_2$ solvate omitted for clarity. Selected bond lengths [Å] and angles [deg] for the *cis*-[Rh(CO)$_2$Cl$_2$] anion: Rh(2)-Cl(3) 2.357(2), Rh(2)-Cl)4) 2.372(3), Rh(2)-C(50) 1.809(10), Rh(2)-C(60) 1.8457(14), O(50)-C(50) 1.103(13), O(60)-C(60) 1.117(15); C(50)-Rh-C(60) 88.7(6), Cl(3)-Rh-Cl(4) 92.42(8).

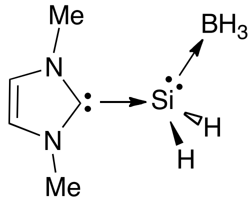
Theoretical Studies

Calculations of geometry optimization, frequency and energy were performed using Gaussian 09, Revision B01 software,[12] 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, while cc-pVDZ was used for all other atoms.[13] 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 2,6-diisopropylphenyl groups with methyl substituents in order to expedite the calculations. Due to the large number of electrons on W, 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 09 and GaussView3. Theoretical IR frequencies for Si-H were obtained using the spectrum generator in Gaussian.

Results from Theoretical Work

ImMe$_2$•SiH$_2$•BH$_3$

The following compound was used as a model for IPr•SiH$_2$•BH$_3$ (**2**), with the 2,6-^{i}Pr$_2$C$_6$H$_3$ groups replaced by methyl substituents:



IR Spectroscopy

Calculated Si-H stretches for [ImMe$_2$•SiH$_2$•BH$_3$] were 2108.77 cm^{-1} ($\nu_{asym.}$) and 2105.85 cm^{-1} (ν_{sym}). Both bands are calculated to have similar intensities, but due to their close proximity, it is predicted that only one band will be observed in the experimental spectrum; consequently, a single Si-H stretching band for **2** was located at 2096 cm^{-1}.

Table S4: Comparison of experimental and calculated bond lengths and angles for **2** and the model complex [ImMe$_2$•SiH$_2$•BH$_3$] with selected Wiberg bond indices included.

	d. exp (Å)	d. calc. (Å)	θ exp.	θ calc.	Wiberg Bond Index
Si – B	1.992(2)	2.022	-	-	0.989
Si– H	1.409(18)	1.512	-	-	0.914
Si – C	1.9284(15)	1.953	-	-	0.708
B – Si – C	-	-	112.11(8)	105.22	-
H – Si – H	-	-	102.0(10)	103.21	-

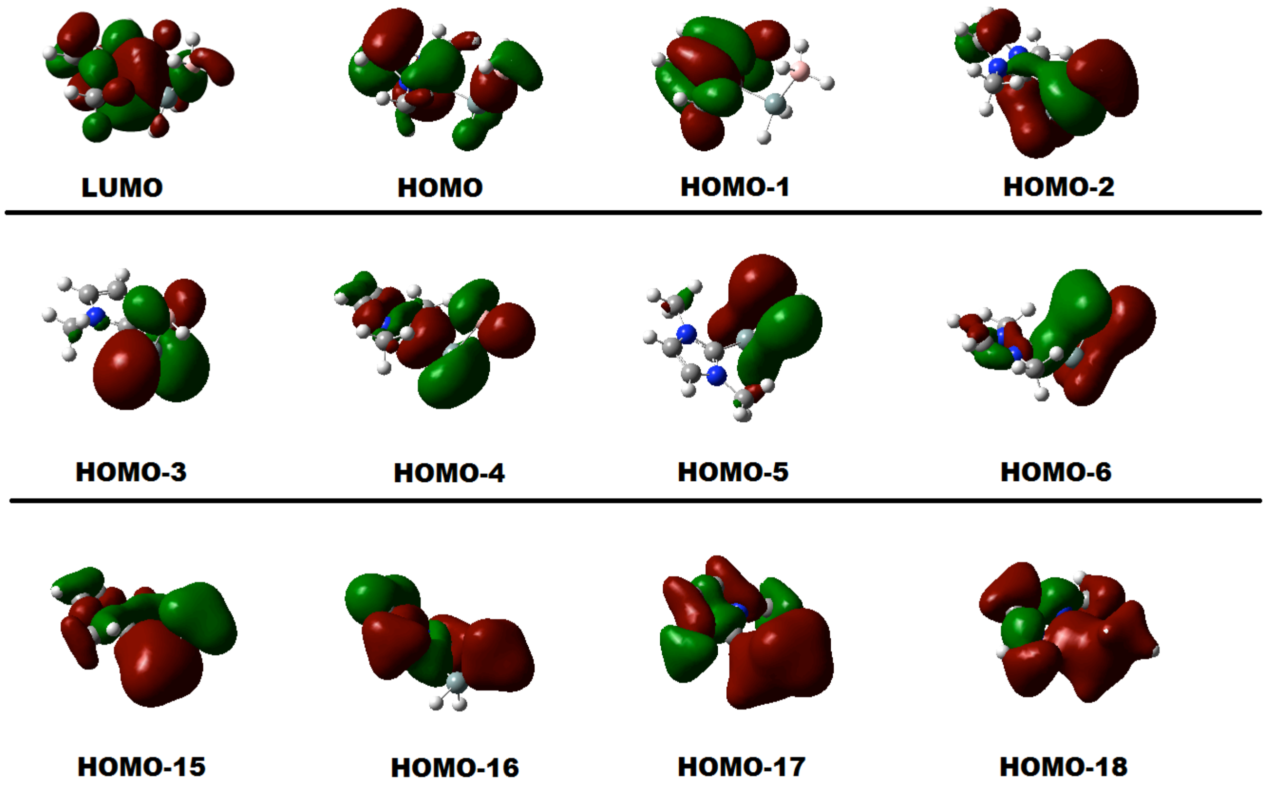


Figure S2: Relevant molecular orbitals for [$ImMe_2•SiH_2•BH_3$].

MO Description:

LUMO	-0.129 a.u.	$ImMe_2$ π^* / Si-H σ^*
HOMO	-0.312 a.u.	Si LP σ donation into a p-orbital of BH_3 / $ImMe_2$ π-bonding
HOMO-1	-0.342 a.u.	$ImMe_2$ π-bonding
HOMO-2	-0.355 a.u.	Si-B/Si-H/B-H σ-bonding
HOMO-3	-0.370 a.u.	Si-H σ-bonding
HOMO-4	-0.393 a.u.	$ImMe_2$ (C)-Si σ-bonding / B-H bonding
HOMO-5	-0.421 a.u.	Si-H/B-H bonding
HOMO-6	-0.426 a.u.	Si-H/B-H bonding
HOMO-15	-0.531 a.u.	SiH_2 symmetric bonding combination
HOMO-16	-0.591 a.u.	BH_3 symmetric bonding combination
HOMO-17	-0.612 a.u.	symmetric bonding combination within SiH_2-BH_3 unit
HOMO-18	-0.651 a.u.	symmetric bonding combination within $ImMe_2$ – SiH_2 – BH_3 array

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

SiH_2 fragment

```
1. (1.97137) BD ( 1) H   1 -Si  18
             ( 59.23%)   0.7696* H   1 s( 99.87%)p 0.00(  0.13%)
             ( 40.77%)   0.6385*Si  18 s( 22.58%)p 3.40( 76.86%)d 0.02(  0.56%)

2. (1.97137) BD ( 1) H   2 -Si  18
             ( 59.23%)   0.7696* H   2 s( 99.87%)p 0.00(  0.13%)
             ( 40.77%)   0.6385*Si  18 s( 22.58%)p 3.40( 76.86%)d 0.02(  0.56%)
```

SiH_2-BH_3 fragment

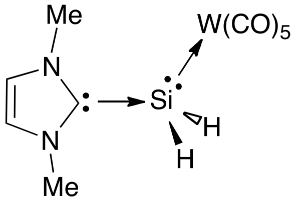
```
21. (1.93097) BD ( 1)Si  18 - B  22
            ( 54.05%)   0.7352*Si  18 s( 39.48%)p 1.53( 60.44%)d 0.00(  0.09%)
            ( 45.95%)   0.6778* B  22 s( 20.78%)p 3.81( 79.15%)d 0.00(  0.07%)
```

$ImMe_2$-SiH_2 fragment

```
20. (1.96115) BD ( 1) C  17 -Si  18
            ( 77.40%)   0.8797* C  17 s( 45.27%)p 1.21( 54.72%)d 0.00(  0.01%)
            ( 22.60%)   0.4754*Si  18 s( 15.38%)p 5.43( 83.54%)d 0.07(  1.07%)
```

$ImMe_2$•SiH_2•$W(CO)_5$

The following compound was used as a model for **3** [IPr•SiH_2•$W(CO)_5$], with the 2,6-${}^iPr_2C_6H_3$ groups replaced by methyl substituents:



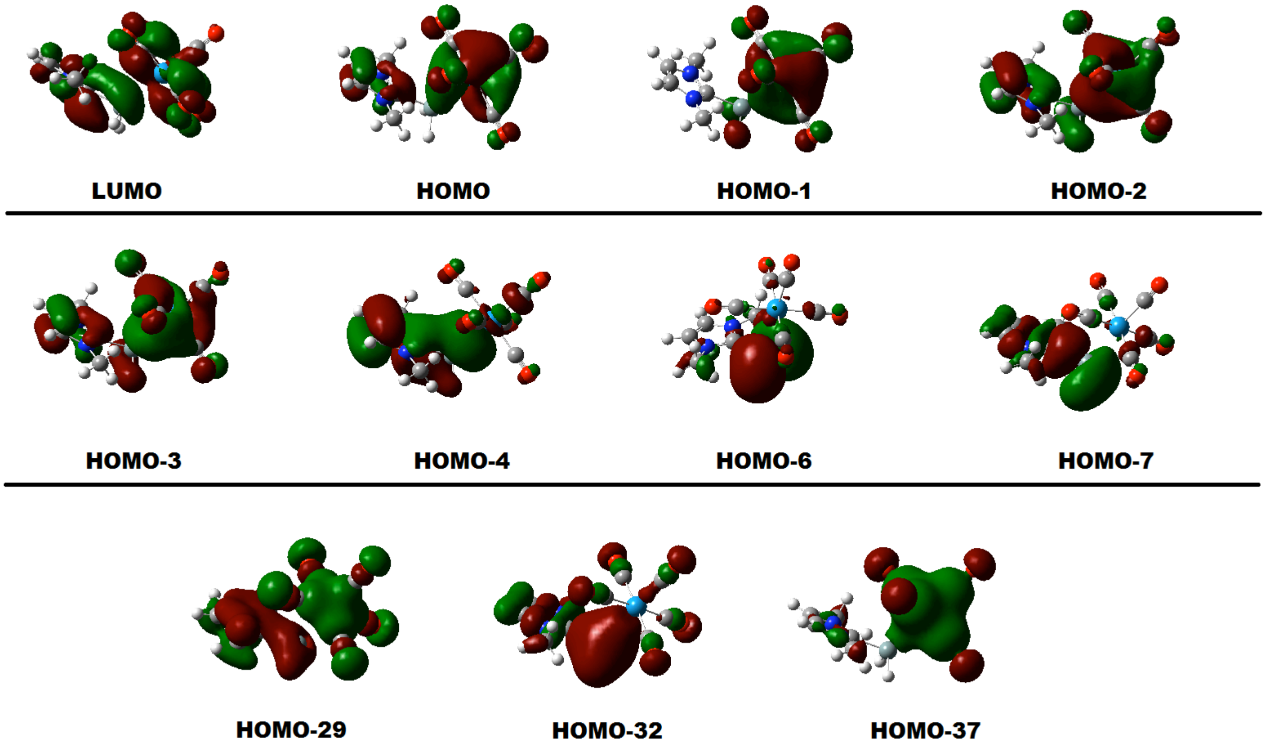
IR Spectroscopy

Calculated Si-H stretches for [$ImMe_2$•SiH_2•$W(CO)_5$] were 2086.08 cm^{-1} ($\nu_{asym.}$) and 2093.13 cm^{-1} (ν_{sym}). Two Si-H stretching bands for **3** were observed in the IR spectrum at 2086 cm^{-1} and 2107 cm^{-1}.

Table S5: Comparison of experimental and calculated bond lengths and angles for **3** and the model complex [$ImMe_2$•SiH_2•$W(CO)_5$], with selected Wiberg bond indices included.

	d. exp (Å)	d. calc. (Å)	θ exp.	θ calc.	Wiberg Bond Index
Si – W	2.573(4)	2.628	-	-	0.791
Si– H	1.32(9)*	1.513	-	-	0.915
Si – C	1.928(13)	1.966	-	-	0.725
W – Si – C	-	-	121.4(4)	113.59	-
H – Si – H	-	-	88(8)*	101.82	-

* = Si-H bond lengths constrained to be equal during the refinement.



LUMO HOMO HOMO-1 HOMO-2

HOMO-3 HOMO-4 HOMO-6 HOMO-7

HOMO-29 HOMO-32 HOMO-37

Figure S3: Relevant molecular orbitals for [$ImMe_2{\bullet}SiH_2{\bullet}W(CO)_5$].

MO Descriptions:

LUMO	-0.139 a.u.	$ImMe_2$-Si slipped π-interaction / C-O σ^*
HOMO	-0.292 a.u.	$ImMe_2$ π-bonding/ W($d_{xz/yz}$)-CO π-backbonding
HOMO-1	-0.293 a.u.	W($d_{yz/xz}$)-CO π-backbonding
HOMO-2	-0.300 a.u.	Si(p) – W(d_{z2}) σ-bonding / $ImMe_4$ π-bonding
HOMO-3	-0.300 a.u.	W(d_{x2-y2})-CO π-backbonding
HOMO-4	-0.330 a.u.	Si(p) donation into W(d_{z2})-C σ^* orbital
HOMO-6	-0.373 a.u.	Si– H σ-bonding
HOMO-7	-0.397 a.u.	$ImMe_2$ LP → Si (p) σ-bonding
HOMO-29	-0.522 a.u.	$ImMe_2$ π-system mixed with SiH_2 bonding interaction / W(s)-C(p) σ-bonding
HOMO-32	-0.543 a.u.	symmetric bonding combination in SiH_2
HOMO-37	-0.614 a.u.	symmetric combination W(s)-C(s) bonding

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

SiH_2 fragment

```
22. (1.96546) BD ( 1) H  12 -Si  29
           ( 58.79%)   0.7668* H  12 s( 99.88%)p 0.00(  0.12%)
           ( 41.21%)   0.6419*Si  29 s( 22.59%)p 3.40( 76.91%)d 0.02(  0.50%)

23. (1.96546) BD ( 1) H  13 -Si  29
           ( 58.79%)   0.7668* H  13 s( 99.88%)p 0.00(  0.12%)
           ( 41.21%)   0.6419*Si  29 s( 22.59%)p 3.40( 76.91%)d 0.02(  0.50%)
```

SiH_2-W(CO)$_5$ fragment

```
6. (1.79876) BD ( 1) W   1 -Si  29
           ( 39.02%)   0.6247* W   1 s( 15.31%)p 3.61( 55.20%)d 1.93( 29.47%)
                                               f 0.00(  0.02%)
           ( 60.98%)   0.7809*Si  29 s( 37.90%)p 1.64( 62.07%)d 0.00(  0.03%)
```

$ImMe_2$-SiH_2 fragment

```
41. (1.96162) BD ( 1) C  28 -Si  29
            ( 76.67%)   0.8756* C  28 s( 44.97%)p 1.22( 55.03%)d 0.00(  0.01%)
            ( 23.33%)   0.4830*Si  29 s( 16.96%)p 4.84( 82.11%)d 0.05(  0.93%)
```

Calculation Summary (Optimized Geometry and Frequencies)

Gaussian 09 Input Parameters and Coordinates for [ImMe$_2$•SiH$_2$•BH$_3$]:

opt=(calcall,tight) freq b3lyp geom=connectivity 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          1           0        0.000000    0.000000    2.694809
      3          6           0        4.761297    0.000000    2.028062
      4          6           0        4.761298    0.000000    0.666750
      5          1           0        5.566780   -0.152782    2.738713
      6          1           0        5.566780   -0.152783   -0.043902
      7          7           0        3.455434    0.236036    0.269090
      8          7           0        3.455432    0.236037    2.425721
      9          6           0        3.034939    0.364705   -1.126734
     10          1           0        3.103946    1.413668   -1.448811
     11          1           0        3.684344   -0.261132   -1.753002
     12          1           0        1.998014    0.020166   -1.222734
     13          6           0        3.034936    0.364707    3.821545
     14          1           0        1.998014    0.020161    3.917545
     15          1           0        3.684345   -0.261125    4.447814
     16          1           0        3.103937    1.413670    4.143619
     17          6           0        2.643287    0.385873    1.347404
     18         14           0        0.425197    1.035715    1.347404
     19          1           0        0.827118    3.352515    2.221054
     20          1           0        0.827120    3.352513    0.473751
     21          1           0       -0.684597    3.285321    1.347401
     22          5           0        0.339052    2.973802    1.347402
 ---------------------------------------------------------------------
```

Gaussian 09 Input Parameters and Coordinates for [ImMe$_2$•SiH$_2$•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         74           0        0.000000    0.000000    0.000000
      2          6           0        0.000000    0.000000    2.064733
      3          8           0        0.004912    0.000000    3.218871
      4          6           0        0.231002   -1.994720   -0.049942
      5          8           0        0.370408   -3.144421   -0.084974
      6          6           0       -0.015507    0.104981   -2.040033
      7          8           0       -0.021310    0.189153   -3.198217
      8          6           0       -2.056287   -0.186514    0.003110
      9          8           0       -3.205674   -0.291215   -0.000043
     10          6           0        2.022130    0.289802    0.002890
     11          8           0        3.167955    0.478430   -0.000677
     12          1           0        0.214336    3.884751    1.341723
     13          1           0       -1.684808    3.712495   -0.562372
     14          6           0        2.100447    4.367065   -3.453373
     15          6           0        3.059821    4.454081   -2.491500
     16          1           0        2.139722    4.576364   -4.517244
     17          1           0        4.100746    4.754233   -2.551108
     18          7           0        2.462862    4.078071   -1.299281
     19          7           0        0.942994    3.940216   -2.823110
     20          6           0        3.171253    3.985912   -0.022024
     21          1           0        3.588892    2.977269    0.108496
     22          1           0        3.979719    4.728765   -0.009252
     23          1           0        2.470040    4.199747    0.793887
     24          6           0       -0.316007    3.669611   -3.518370
     25          1           0       -1.152529    3.871181   -2.838124
     26          1           0       -0.390252    4.332396   -4.390617
     27          1           0       -0.352331    2.619791   -3.842989
     28          6           0        1.157789    3.756477   -1.494614
     29         14           0       -0.298357    2.828282    0.041716
 ---------------------------------------------------------------------
```

References:

(1) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

(2) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn and D. Stalke, *Angew. Chem. Int. Ed.*, 2009, **48**, 5683.

(3) R. Azhakar, G. Tavcar, H. W. Roesky, J. Hey and D. Stalke, *Eur. J. Inorg. Chem.*, 2011, 475.

(4) H. Hope, *Prog. Inorg. Chem.*, 1995, **43**, 1.

(5) R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33.

(6) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

(7) T. R. Schneider, and Sheldrick, G. M. *Acta Crystallogr.* 2002, **D58**, 1772.

(8) P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda and R. O. Gould, The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

(9) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.* 2007, **129**, 12412.

(10) S. M. I. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, R. McDonald and E. Rivard, *J. Am. Chem. Soc.*, 2011, **133**, 777.

(11) A. Blumenthal, P. Bissinger and H. Schmidbaur, *J. Organomet. Chem.* 1993, **462**, 107.

(12) Gaussian 09, Revision **B.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O.

Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

(13) (*a*) K.A. Peterson, *J. Chem. Phys.* 2003, **119**, 1109; (*b*) K.A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, *J. Chem. Phys*. 2003, **119**, 11113; (*c*) K.A. Peterson and C. Puzzarini, *Theor. Chem. Acc.* 2005, **114**, 283; (*d*) K.A. Peterson, D. Figgen, M. Dolg, H. Stoll, *J. Chem. Phys.* 2007, **126**, 124101; (*e*) K. A. Peterson, B. C. Shepler, D. Figgen, H. Stoll, *J. Phys. Chem. A* 2006, **110**, 13877; (*f*) D. Figgen, K.A. Peterson, M. Dolg, and H. Stoll, *J. Chem. Phys.* 2009, **130**, 164108.