Organometallics 1993, *12*, 3890–3895

Direct Evidence of a Hafnium η^2-Iminoacyl Complex as the Common Intermediate in the Competitive Reductive Coupling and 1,2-Silyl Shift Pathways Associated with the Isocyanide Insertion Chemistry of $Cp_2Hf(CH_2SiMe_2CH_2)$

Frederic J. Berg and Jeffrey L. Petersen*

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

Received April 28, 1993[⊛]

The reaction of 1 equiv of *tert*-butyl isocyanide with $Cp_2Hf(CH_2SiMe_2CH_2)$, 1, affords a 1:1 equilibrium mixture of the η^2-iminoacyl complex $Cp_2Hf(N(CMe_3)CCH_2SiMe_2CH_2)$, **2a**, and the cyclic enamido complex $Cp_2Hf(N(CMe_3)C({=}CH_2)SiMe_2CH_2)$, **3a**. The subsequent addition of a second equivalent of *tert*-butyl isocyanide to this equilibrium mixture proceeds exclusively with the formation of the η^2-iminoacyl imine compound $Cp_2Hf(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)$, 4, which when heated rearranges to the bicyclic enediamido complex $Cp_2Hf(N(CMe_3)C(CH_2SiMe_2CH_2){=}CN(CMe_3))$, **5**. The reversibility associated with **2a** ↔ **3a** enables the overall reductive coupling reaction to proceed with complete consumption of both **2a** and **3a** and provides direct evidence of **2a** as the common intermediate in both the 1,2-silyl shift and the reductive coupling pathways. The enthalpy of activation for the conversion of 4 to 5 is 28.8(11) kcal/mol, which is *ca.* 3 kcal/mol larger than that for the analogous zirconium system. This difference is attributed to a stronger Hf—C(methylene) bond, which was determined by an X-ray crystallographic analysis of 4 to be 0.03 Å shorter than the Zr—C(methylene) bond of $Cp_2Zr(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)$. Crystal data for 4 at 25 °C: monoclinic space group $P2_1/c$ with $a = 8.408(2)$ Å, $b = 18.534(4)$ Å, $c = 16.326(4)$ Å, $\beta = 101.71(2)°$, and $Z = 4$. Full-matrix least-squares refinement (based on F_o^2) of 4384 diffractometry data converged with $R(F_o) = 0.039$.

Introduction

Electrophilic group 4 organometallic complexes have been extensively employed in organic synthesis as stoichiometric reagents for promoting the C,C-coupling of unsaturated substrates.[1] The observation of C—C coupled products from the stoichiometric reduction of CO with various group 4 organometal hydrides and alkyls has also renewed interest in understanding C—C bond forming reactions that may be associated with Fischer–Tropsch chemistry.[2] In our laboratory we have observed that the zirconium-induced insertion reaction of $Cp^*{}_2Zr(CH_2SiMe_2CH_2)$ ($Cp^* = C_5Me_5$) with CO[3] and CNMe[4] can proceed (under kinetic control) with reductive coupling to afford the bicyclic enediolate $Cp^*{}_2Zr(OC(CH_2SiMe_2CH_2){=}CO)$ and the bicyclic enediamidate $Cp^*{}_2Zr(N(Me)C(CH_2SiMe_2CH_2){=}CN(Me))$, respectively, or via an intramolecular 1,2-silyl shift to produce the cyclic enolates $Cp^*{}_2Zr(OC({=}CH_2)SiMe_2CH_2)$ and $Cp^*{}_2Zr(OC({=}CH_2)SiMe_2(CH_2{=})CO)$ and the cyclic enamides $Cp^*{}_2Zr(N(Me)C({=}CH_2)SiMe_2CH_2)$ and $Cp^*{}_2Zr(N(Me)C({=}CH_2)SiMe_2(CH_2{=})CN(Me))$, respectively. Further information about the mechanistic features of the reductive coupling pathway was provided by the sequential addition of 2 equiv of CN-*t*-Bu to $Cp_2Zr(CH_2SiMe_2CH_2)$[4,5] and a low-temperature NMR study of the reaction of excess CNMe with $Cp^*{}_2Zr(CH_2SiMe_2CH_2)$.[6]

Although zirconium(IV) and hafnium(IV) have similar ionic radii[7] (Zr, 0.80 Å; Hf, 0.81 Å) and possess analogous valence electron configurations, organometallic compounds containing third-row transition metals typically are thermodynamically more stable and in some instances may exhibit different reactivities than their first- and second-row congeners.[8] For example, Bickelhaupt and co-workers[9]

[⊛] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

(1) Relevant reviews: (a) Negishi, E.-i. *Acc. Chem. Res.* **1987**, *20*, 65. (b) Buchwald, S. L.; Nielson, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. (d) Erker, G. *Angew. Chem., Int. Ed. Eng.* **1989**, *28*, 397.

(2) Cummins, C. C.; Van Duyne, G. D.; Schaller, C. P.; Wolczanski, P. T. *Organometallics* **1991**, *10*, 164 and references cited therein.

(3) Petersen, J. L.; Egan, J. W., Jr. *Organometallics* **1987**, *6*, 2007.

(4) Berg, F. J.; Petersen, J. L. *Organometallics* **1989**, *8*, 2861.

(5) Berg, F. J.; Petersen, J. L. *Organometallics* **1991**, *10*, 1599.

(6) Berg, F. J.; Petersen, J. L. *Tetrahedron* **1992**, *48*, 4749.

(7) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(8) Cardin, D. J.; Lappert, M. F.; Easton, C. L.; Riley, P. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982.

0276-7333/93/2312-3890\$04.00/0

reported that the replacement of Zr by Hf in $Cp_2M(CH_2CMe_2CH_2)$ significantly increases the half-life of the metallacycle in solution. Bercaw and co-workers[10] observed that $Cp^*{}_2M(CO)(\eta^2\text{-}OCH(CH_2CHMe_2))$ (M = Zr, Hf) react quite differently at room temperature in solution. The zirconium compound undergoes decarbonylation and rearranges to the enolate hydride, $Cp^*{}_2Zr(H)(\eta^1\text{-}O\text{-}CH{=}HCHMe_2)$, whereas the hafnium compound rearranges *without* loss of CO to yield the cyclic enediolate, $Cp^*{}_2Hf(OC(H){=}C(CH_2CHMe_2)O)$. Replacement of Zr by Hf can also have a kinetic influence. Rothwell and co-workers[11] found that the intramolecular reductive coupling of the two η^2-iminoacyl ligands of $M(\eta^2\text{-}RCNR')_2(OAr)_2$ is an order of magnitude slower for the hafnium complexes than for the zirconium analogs at a given temperature.

To evaluate the chemical consequences of the replacement of Zr by Hf in the 1-sila-3-metallacyclobutane ring of $Cp_2M(CH_2SiMe_2CH_2)$, the reactions of $Cp_2Hf(CH_2SiMe_2CH_2)$ with *tert*-butyl isocyanide and *tert*-amyl isocyanide have been investigated. Although the corresponding reductive coupling reaction involves the same sequence of chemical steps as demonstrated previously for the Zr system,[5] a dynamic equilibrium involving η^2-iminoacyl and cyclic enamido hafnium species is observed in solution. This result enables us to establish that $Cp_2M(N(R)CCH_2SiMe_2CH_2)$ is the common intermediate in the reductive coupling and 1,2-silyl shift reactions associated with the isocyanide insertion chemistry displayed by these "stabilized" group 4 1-sila-3-metallacyclobutane complexes.

Experimental Section

Reagents. All solvents were purified by standard procedures[12] and vacuum distilled into storage flasks containing either $[Cp_2Ti(\mu\text{-}Cl)_2]_2Zn$[13] (hydrocarbon and ethereal solvents) or P_4O_{10} (chlorinated solvents). Hexamethyldisiloxane was distilled from $LiAlH_4$. Benzene-d_6 and toluene-d_8 (Cambridge Isotope Laboratories) were vacuum distilled from 4-Å molecular sieves. *tert*-Butyl isocyanide (Aldrich) was dried over activated molecular sieves and distilled before use. Pyridine (Aldrich) was dried over BaO and distilled prior to use. *tert*-Amylamine (Aldrich), ethyl formate (Aldrich), $POCl_3$ (Aldrich), and Cp_2HfCl_2 (Boulder Scientific) were used as received. $[MgCH_2SiMe_2CH_2]_n$[14] and *tert*-amylformamide[15] were prepared by literature procedures.

General Considerations. All manipulations and reactions were carried out on a double-manifold, high-vacuum line or in a Vacuum Atmospheres glovebox equipped with a HE-493 Dri-Train. Nitrogen was purified by passage over reduced BTS catalyst and activated 4-Å molecular sieves. All glassware was throughly oven-dried or flame dried under vacuum. NMR sample tubes were sealed under approximately 500 Torr of nitrogen. The addition of a stoichiometric quantity of a volatile isocyanide to a reaction solution was accomplished with a calibrated gas bulb. The instrumentation employed for the measurement of the ^1H and ^{13}C NMR, infrared, and electronic spectra of the hafnium compounds has been described previously.[5] The reaction temperatures for the kinetic experiments were maintained to ±0.1 °C with an Neslab Instruments Exacal high temperature bath. Elemental analyses were carried out either by Oneida Research Services (ORS) of Whitesboro, NY, or by Robertson Microlit Laboratories, Inc. (RM) of Madison, NJ.

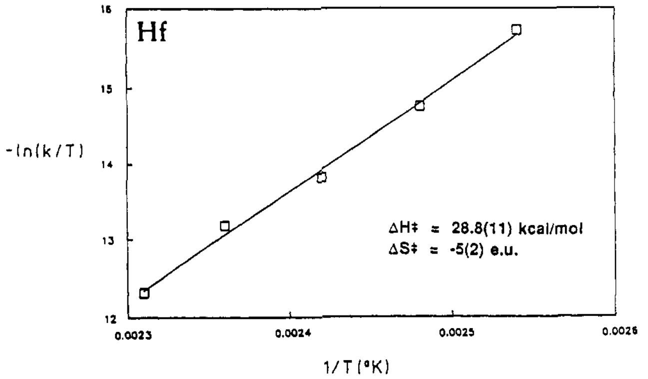


Figure 1. Eyring plot of $-\ln(k/T)$ vs $1/T$ for the intramolecular rearrangement of 4 to 5.

Table I. Rate Constants for the Intramolecular Rearrangement of 4 to 5

T (°C)	k (s^{-1})	$t_{1/2}$ (min)
120.0	$5.81(11) \times 10^{-5}$	199
130.0	$1.56(3) \times 10^{-4}$	74
140.0	$4.11(26) \times 10^{-4}$	28
150.0	$7.97(23) \times 10^{-4}$	14.5
160.0	$1.95(5) \times 10^{-3}$	6.0

Kinetic Measurements. The rate constants, k, for the intramolecular thermal rearrangement of $Cp_2Hf(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)$, 4, to $Cp_2Hf(N(CMe_3)C(CH_2SiMe_2CH_2){=}CN(CMe_3))$, 5, were determined experimentally within the temperature range 120–160 °C by NMR spectroscopic measurements. A standard solution of 4 and ferrocene (0.108 mM) was prepared in toluene-d_8 and placed in a series of sealed NMR tubes. The concentration of 4 was determined from the ratio of the integrated peak areas for the cyclopentadienyl proton resonances of 4 and ferrocene using the expression [4] = (integrated peak area of 4/integrated peak area of ferrocene)$[Cp_2Fe]$. As the rearrangement proceeds, the decrease in [4] is followed by monitoring the loss of the intensity of its cyclopentadienyl proton resonance at δ 5.52 in toluene-d_8. The rate constant for this first-order process at each temperature was determined from the slope ($-k$) of the corresponding plot of ln [4] vs time. Each NMR tube was submerged in a constant temperature oil bath. During each kinetic run the NMR tube was removed at a predetermined time and cooled immediately in an ice water slush to quench the rearrangement reaction. Every NMR spectrum was measured three times employing a 20-s pulse delay. The integrated intensities were reproducible within 6%, and the averaged integrated intensity was used for the determination of k at each temperature. The rate constants obtained from the first-order plots of ln [4] vs time are tabulated in Table I. The values of the activation parameters, ΔH^* and ΔS^*, were obtained from an Eyring plot (Figure 1) of $-\ln(k/T)$ vs $1/T$, assuming a value of 1 for the transmission coefficient in the Eyring equation $\Delta G^*(T) = RT\ln(\kappa k_B T/kh)$. The enthalpy of activation, ΔH^*, was obtained from the slope, m, of the line, and the entropy of activation, ΔS^*, was calculated from the y-intercept, b, by

---

[9] Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 248.

[10] (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Roddick, D. M.; Bercaw, J. E. *Chem. Ber.* **1989**, *122*, 1579.

[11] Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobringer, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.

[12] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972.

[13] Sekutowski, D. G.; Stucky, G. D. *Inorg. Chem.* **1975**, *14*, 2192.

[14] Tikkanen, W. R.; Liu, J. Z.; Egan, J. W., Jr.; Petersen, J. L. *Organometallics* **1984**, *3*, 825.

[15] Casanova, J., Jr.; Werner, N. D.; Schuster, R. E. *J. Org. Chem.* **1966**, *31*, 3473.

using the expressions $\Delta H^{*} = mR$ and $\Delta S^{*} = -(b + 23.76)R$, where R is the gas constant, 1.987 cal/(mol K). The estimated standard deviations for these activation parameters were calculated by a regression analysis described by Skoog.[16]

Synthesis of Compounds. Preparation of *tert*-Amyl Isocyanide. This isocyanide was prepared by a modification of the procedure of Ugi and co-workers.[17] To a 250-mL three-necked flask, which was equipped with a dropping funnel, condenser, and mechanical stirrer, was added 10.02 g (0.087 mol) of *tert*-amylformamide, 43.0 mL (0.53 mol) of pyridine, and 50 mL of pentane. The flask was immersed in an ice bath, and 5.0 mL (0.054 mol, 8.3 g) of $\mathrm{POCl_3}$ was added from the dropping funnel over a 45-min period. The solution became a thick slurry as the reaction progressed. After the addition was complete, the reaction mixture was refluxed for 15 min. The reaction flask was cooled in an ice bath, and 100 mL of ice water was added slowly with stirring until all of the solids dissolved. The organic phase was separated with a separatory funnel. The aqueous phase was extracted with 3 × 35 mL of pentane, and the extracts were combined with the organic phase, which was then washed with 5 × 40 mL of water. The extracted material was dried over magnesium sulfate and distilled (4.41 g, 52% yield, bp range 112–114 °C at 760 mm). ^{1}H NMR spectrum in benzene-d_6 (mult, $^3J_{\mathrm{X-H}}$ in Hz): δ 1.50 ($\mathrm{CH_2}$, quartet of triplets, $J_{\mathrm{H-H}}$ 7.5, $J_{\mathrm{N-H}}$ 2.0), 1.27 ($\mathrm{CH_3}$, pseudotriplet, $J_{\mathrm{N-H}}$ 2.0), 0.92 ($\mathrm{CH_2C}H_3$, t, 7.4). Gated nondecoupled ^{13}C NMR spectrum (mult, $^1J_{\mathrm{C-H}}$ in Hz): δ 152.9 (CNC, s), 57.6 ($C\mathrm{Me_2Et}$, s), 35.1 ($\mathrm{CH_2}$, t, 127), 28.2 ($\mathrm{C}C\mathrm{H_3}$, q, 128), 8.3 ($\mathrm{CH_2}C\mathrm{H_3}$, q, 126).

Preparation of $\mathrm{Cp_2Hf(CH_2SiMe_2CH_2)}$, 1. In a typical experiment, 0.735 g (1.94 mmol) of $\mathrm{Cp_2HfCl_2}$ and 0.316 g (2.86 mmol) of $\mathrm{[MgCH_2SiMe_2CH_2]_n}$ were added to a 100-mL pear-shaped flask equipped with a 15-mm solv-seal joint. The solv-seal flask was attached to a filter-frit assembly and evacuated. Toluene (40 mL) was added via vacuum distillation, and the reaction mixture was stirred overnight at room temperature. Toluene was removed under vacuo and replaced by an equal volume of pentane. The solution was filtered and slow removal of solvent yielded a light yellow microcrystalline product (0.493 g, 65% yield). Further purification was accomplished by sublimation. ^{1}H NMR spectrum in benzene-d_6: δ 5.59 ($\mathrm{C_5H_5}$, s), 1.34 ($\mathrm{CH_2}$, s), 0.31 ($\mathrm{SiMe_2}$, s). Gated nondecoupled ^{13}C NMR spectrum (mult, $^1J_{\mathrm{C-H}}$ in Hz): δ 108.5 ($\mathrm{C_5H_5}$, d, 172), 47.7 ($\mathrm{CH_2}$, t, 125), 1.21 ($\mathrm{SiMe_2}$, q, 117). Anal. Calcd for $\mathrm{C_{14}H_{20}HfSi}$: C, 42.58; H, 5.10; N, 0.0. Found: (ORS): C, 42.71; H, 4.94; N, 0.0.

Reaction of 1 with *tert*-Butyl Isocyanide. A 0.639-g (1.62-mmol) sample of 1 was added to a 100-mL solv-seal flask, which was then attached to a calibrated gas bulb and evacuated. Pentane (40 mL) was condensed onto the solid and warmed to room temperature. The gas bulb was charged with 1 equiv of *tert*-butyl isocyanide, which was added in small increments over 5 days. Removal of the solvent gave a yellow-orange oil. Solution ^{1}H NMR measurements revealed that the oil contained a 1:1 equilibrium mixture of the η^2-iminoacyl compound $\mathrm{Cp_2Hf(N(CMe_3)CCH_2SiMe_2CH_2)}$, **2a**, and the cyclic enamido complex $\mathrm{Cp_2Hf(N(CMe_3)C({=}CH_2)SiMe_2CH_2)}$, **3a**. This analysis was made by comparing the observed proton NMR resonances with those previously assigned for related zirconacyclic analogs.[4] ^{1}H NMR spectrum of **2a** in benzene-d_6: δ 5.46 ($\mathrm{C_5H_5}$, s), 2.58 ($\mathrm{CCH_2Si}$, s), 1.07 ($\mathrm{NCMe_3}$, s), 0.23 ($\mathrm{SiMe_2}$, s), −0.14 ($\mathrm{HfCH_2}$, s). ^{1}H NMR spectrum of **3a**: δ 5.80 ($\mathrm{C_5H_5}$, s), 4.53, 4.44 ($\mathrm{C{=}CH_2}$, s), 1.39 ($\mathrm{HfCH_2}$, s), 1.25 ($\mathrm{NCMe_3}$, s), 0.34 ($\mathrm{SiMe_2}$, s).

Reaction of 1 with *tert*-Amyl Isocyanide. A 0.393-g (0.995-mmol) sample of 1 was added to a 100-mL solv-seal flask, which was attached to a calibrated gas bulb and evacuated. Pentane (35 mL) was added via vacuum distillation, and the gas bulb was charged with 1 equiv of *tert*-amyl isocyanide. The reaction flask was cooled in liquid nitrogen and the isocyanide was admitted into the flask. The solution was stirred for several days at room temperature. Removal of the pentane gave a red-orange oil, which was determined by ^{1}H NMR measurements to contain a 4:1 equilibrium mixture of $\mathrm{Cp_2Hf(N(CMe_2Et)CCH_2SiMe_2CH_2)}$, **2b**, and $\mathrm{Cp_2Hf(N(CMe_2Et)C({=}CH_2)SiMe_2CH_2)}$, **3b**, respectively. ^{1}H NMR spectrum of **2b** in benzene-d_6 (mult, $^2J_{\mathrm{H-H}}$ in Hz): δ 5.48 ($\mathrm{C_5H_5}$, s), 2.56 ($\mathrm{CCH_2Si}$, s), 1.46 ($\mathrm{C}H_2\mathrm{CH_3}$, q, 7.5), 1.03 ($\mathrm{C}Me_2\mathrm{Et}$, s), 0.68 ($\mathrm{CH_2C}H_3$, t, 7.5), 0.24 ($\mathrm{SiMe_2}$, s), −0.14 ($\mathrm{HfCH_2}$, s). ^{1}H NMR spectrum of **3b**: δ 5.80 ($\mathrm{C_5H_5}$, s), 4.53, 4.48 ($\mathrm{{=}CH_2}$, s), 1.82 ($\mathrm{C}H_2\mathrm{CH_3}$, q, 7.5), 1.39 ($\mathrm{HfCH_2}$, s), 1.14 ($\mathrm{C}Me_2\mathrm{Et}$, s), 0.82 ($\mathrm{CH_2C}H_3$, t, 7.5), 0.37 ($\mathrm{SiMe_2}$, s).

Preparation of $\mathrm{Cp_2Hf(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)}$, 4. A freshly sublimed sample of 1 (0.514 g, 1.30 mmol) was weighed into a 100-mL solv-seal flask. The flask was attached to a calibrated gas bulb and evacuated. Toluene (40 mL) was condensed onto the hafnacycle, and the gas bulb was charged with 2 equiv of *tert*-butyl isocyanide. The isocyanide was added to the reaction solution, which was stirred at room temperature for 5 days. The solvent was removed, and the yellow crystalline product was dried in vacuo. Recrystallization of the product from pentane gave suitable crystals of 4 (overall recrystallized yield of 80%). IR (KBr disks): 1630 cm^{-1}, weak (C=N stretch); 1590 cm^{-1}, medium (C=N stretch). ^{1}H NMR spectrum in benzene-d_6: δ 5.48 ($\mathrm{C_5H_5}$, s), 1.95 ($\mathrm{CCH_2Si}$, s), 1.38, 1.34 ($\mathrm{CMe_3}$, s), 0.36 ($\mathrm{SiMe_2}$, s), −0.51 ($\mathrm{HfCH_2}$, s). Gated nondecoupled ^{13}C NMR spectrum in benzene-d_6 (mult, $^1J_{\mathrm{C-H}}$ in Hz): δ 235.0 ($\mathrm{Hf}C\mathrm{N}$, s), 169.1 ($\mathrm{C\text{-}}C\mathrm{N}$, s), 106.8 ($\mathrm{C_5H_5}$, d, 171), 61.1, 55.7 ($\mathrm{NC}Me_3$, s), 34.6 ($\mathrm{C}C\mathrm{H_2Si}$, t, 122), 31.0, 29.8 ($\mathrm{NC}Me_3$, q, 125, 126), 6.4 ($\mathrm{Hf}C\mathrm{H_2}$, t, 110), 4.4 ($\mathrm{SiMe_2}$, q, 118). Anal. Calcd for $\mathrm{C_{24}H_{38}N_2HfSi}$: C, 51.37; H, 6.83; N, 4.99. Found (ORS): C, 50.82; H, 6.69; N, 4.54.

Preparation of $\mathrm{Cp_2Hf(N(CMe_3)C(CH_2SiMe_2CH_2){=}CN(CMe_3))}$, 5. A 0.257-g sample of 4 was weighed into a 10-mm-diameter cylindrical reaction tube, which was then attached with a 9-mm solv-seal joint to a high-vacuum stopcock adapter. Following evacuation of the tube, ca. 3 mL of hexamethyldisiloxane was added via vacuum distillation. The reaction mixture was heated for 24 h with an oil bath set at 120 °C. Upon cooling, light orange crystals of 5 formed in the reaction mixture. The solvent was removed in vacuo and the product residue was recrystallized from pentane. ^{1}H NMR spectrum in benzene-d_6 (mult, $^2J_{\mathrm{H-H}}$ in Hz): δ 6.02, 5.37 ($\mathrm{C_5H_5}$, s), 2.05, 1.27 ($\mathrm{CH_aH_b}$, d, 16.7), 1.41 (NCMe, s), 0.20, 0.16 ($\mathrm{SiMe_2}$, s). Gated nondecoupled ^{13}C NMR spectrum in benzene-d_6 (mult, $^1J_{\mathrm{C-H}}$ in Hz): 121.8 ($\mathrm{N}C{=}$, s), 107.7, 102.5 ($\mathrm{C_5H_5}$, d, 171, 170), 58.8 ($\mathrm{N}C\mathrm{CH_3}$, s), 34.6 ($\mathrm{NC}C\mathrm{H_3}$, q, 125), 22.8 ($\mathrm{CH_2}$, t, 123), −2.24, −2.93 ($\mathrm{SiMe_2}$, q, 119). Anal. Calcd for $\mathrm{C_{24}H_{38}N_2HfSi}$: C, 51.37; H, 6.83; H, 4.99. Found (RM): C, 50.58; H, 6.44; N, 4.93. $\lambda_{\mathrm{max}} = 332$ nm, $\epsilon_{\mathrm{max}} = 3.3 \times 10^3$ M^{-1} cm^{-1}.

X-ray Structural Analysis of 4. The same general procedures as described previously[4] were followed to determine the crystal structure of 4. The zirconium and hafnium η^2-iminoacyl imine complexes, $\mathrm{Cp_2M(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)}$ (M = Zr, Hf) are isomorphous. Further details regarding the structural analysis of 4 are provided in the supplementary material. Selected interatomic distances and bond angles for these two compounds are compared in Table II.

Results and Discussion

Synthesis and Isocyanide Insertion Chemistry of $\mathrm{Cp_2Hf(CH_2SiMe_2CH_2)}$.

The synthesis of $\mathrm{Cp_2Hf(CH_2SiMe_2CH_2)}$, 1, was accomplished by the metathetical

---

[16] Skoog, D. A. *Principles of Instrumental Analysis*, 3rd ed.; Saunders College Publishing: Philadelphia, 1985.

[17] Ugi, I.; Meyr, R.; Lipinski, M.; Bodeshein, F.; Rosendahl, F. *Org. Synth.* **1973**, *5*, 300.

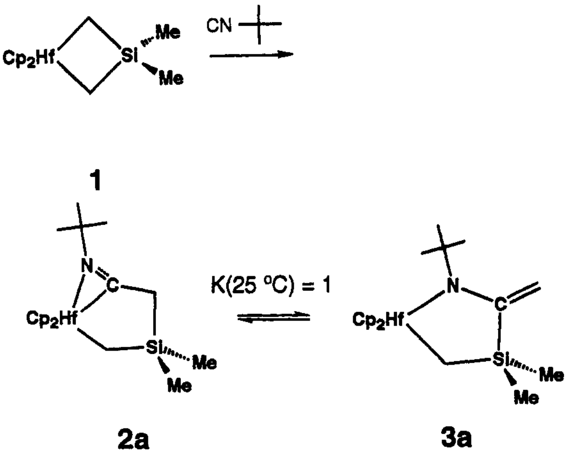
Table II. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp_2M(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)$, M = Zr and Hf[a]

	M = Zr	M = Hf
A. Interatomic Distances		
M–N1	2.231(3)	2.222(5)
M–C1	2.216(4)	2.199(5)
M–C4	2.378(4)	2.347(6)
M–Cp1	2.237(5)	2.221(6)
M–Cp2	2.264(6)	2.244(7)
N1–C1	1.266(4)	1.269(6)
N2–C2	1.259(5)	1.262(7)
C1–C2	1.492(5)	1.500(7)
B. Bond Angles		
N1–M–C1	33.1(1)	33.4(2)
N1–M–C4	115.7(1)	116.7(2)
C1–M–C4	82.9(1)	83.6(2)
Cp1–M–Cp2	129.9(2)	129.1(2)
M–N1–C1	72.8(2)	72.3(3)
M–C1–N1	74.1(2)	74.3(3)
M–N1–C7	154.5(2)	155.4(3)
M–C1–C2	150.2(3)	149.6(4)
C7–N1–C1	132.7(3)	132.3(5)
C2–C1–N1	135.6(3)	136.0(5)
C1–C2–C3	108.1(3)	108.5(4)
M–C4–Si	118.0(2)	118.0(3)

[a] Cpn corresponds to the centroid of a cyclopentadienyl ring. Cp1 and Cp2 contain carbon atoms C15–C19 and C20–C24, respectively.

reaction of Cp_2HfCl_2 and $[MgCH_2SiMe_2CH_2]_n$ in refluxing toluene. This 1-sila-3-hafnacyclobutane compound is a pale yellow solid which is quite soluble in most hydrocarbon solvents and can be sublimed at 60 °C and 10^{-4} Torr without significant decomposition. The ^1H and ^{13}C NMR spectra of 1 exhibit three characteristic resonances with the proton and carbon resonances of the methylene and methyl groups bound to silicon shifted upfield from the corresponding resonances reported by Bickelhaupt and co-workers for $Cp_2Hf(CH_2CMe_2CH_2)$.[9]

The addition of 1 equiv of *tert*-butyl isocyanide to a pentane solution of 1 proceeds with the formation of an equilibrium mixture of the η^2-iminoacyl $Cp_2Hf(N(CMe_3)CCH_2SiMe_2CH_2)$, **2a**, and the cyclic enamide $Cp_2Hf(N(CMe_3)C({=}CH_2)SiMe_2CH_2)$, **3a**, in a 1:1 ratio (1).

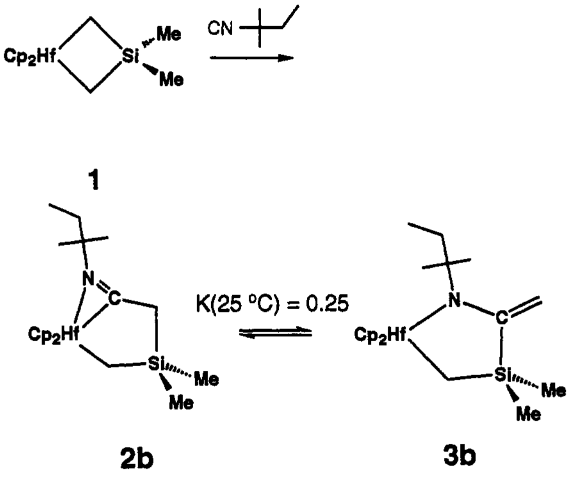


(1)

When the temperature is raised, the intensities of the proton resonances of **2a** were enhanced while those of **3a** diminished. This result is particularly surprising in view of the fact that the corresponding reaction of CN-*t*-Bu with $Cp_2Zr(CH_2SiMe_2CH_2)$ affords exclusively the η^2-iminoacyl species.[4] Initial attempts to convert $Cp_2Zr(N(CMe_3)CCH_2SiMe_2CH_2)$ to the corresponding cyclic enamide by heating at 100 °C led to sample decomposition rather than promotion of the 1,2-silyl shift rearrangement.

Because **2a** and **3a** cannot be separated, their identities were established by solution ^1H NMR measurements. The ^1H NMR assignments are based on the NMR data reported for related zirconium metallacycles with analogous ring structures.[4] The ^1H NMR resonances of the C_5H_5 ring, the *tert*-butyl substituent, and the dimethylsilyl group of **2a** appear as singlets at δ 5.46, 1.07, and 0.23, respectively. Two different resonances are observed for the two methylene groups with the singlet at δ 2.58 assigned to the methylene group bound to the η^2-iminoacyl carbon and the upfield singlet at δ −0.14 assigned to the methylene group attached to hafnium. The corresponding proton resonances for the C_5H_5 rings, the *tert*-butyl group, and the $SiMe_2$ fragment of **3a** appear as singlets at δ 5.80, 1.39, and 0.34, respectively. The two inequivalent protons of the exocyclic methylene group are represented by a pair of singlets at δ 4.53 and 4.44, and the protons of the methylene group that remains bound to hafnium appear as a singlet at δ 1.39.

The corresponding reaction of 1 equiv of *tert*-amyl isocyanide with 1 also affords an equilibrium mixture of the η^2-iminoacyl, **2b**, and the cyclic enamide, **3b** (2). In this case the ratio of **2b**:**3b** is 4:1, thus making it relatively easy to make NMR peak assignments. The characteristic upfield proton resonance of the metal-bound methylene group is found at δ −0.14 for **2b**, whereas the pair of singlets associated with the exocyclic methylene group appear at δ 4.53 and 4.48 for **3b**.



(2)

The reaction of another equivalent of CN-*t*-Bu with the equilibrium mixture of **2a** and **3a** proceeds slowly over a period of 5 days with formation of the η^2-iminoacyl imine $Cp_2Hf(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)$, **4**, as the sole product (3). This compound was characterized by ^1H and ^{13}C NMR measurements, infrared spectroscopy, elemental analysis, and X-ray crystallography. The proton resonance at δ −0.51 confirms that a methylene group is bound to the hafnium. The carbon resonance at δ 235.0

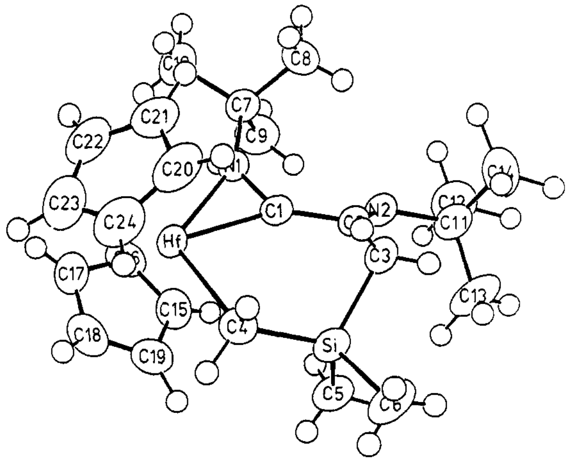
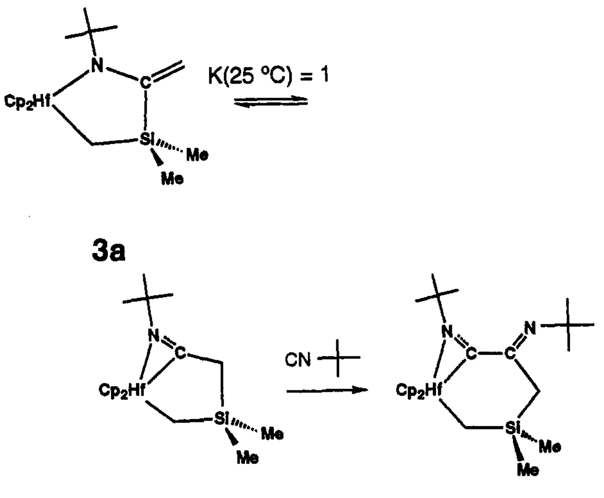


Figure 2. Perspective view of the molecular structure of Cp$_2$Hf(N(CMe$_3$)C—C(=NCMe$_3$)CH$_2$SiMe$_2$CH$_2$), 4, with the atom numbering scheme. The thermal ellipsoids are scaled to enclose 50% probability.

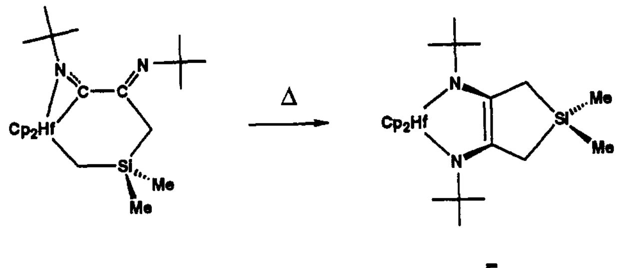


3a

2a 4 (3)

is characteristic of an η^2-iminoacyl fragment.[4] The remaining ^{1}H and ^{13}C NMR resonances of 4 are easily assigned by comparison with the corresponding resonances reported for Cp$_2$Zr(N(CMe$_3$)C—C(=NCMe$_3$)CH$_2$SiMe$_2$CH$_2$).[4] The IR spectrum of 4 displays two different ν_{C-N} stretches, with the main absorption band centered at 1590 cm^{-1} and a shoulder at 1630 cm^{-1}. A perspective view of the molecular structure of 4 is depicted in Figure 2. Although the crystal structures of Cp$_2$M(N(CMe$_3$)C—C(=NCMe$_3$)CH$_2$SiMe$_2$CH$_2$) (M = Zr, Hf) are isomorphous, an examination of the corresponding pairs of M—N, M—C, M—Cp1, and M—Cp2 distances reveals that these distances are consistently shorter by 0.01–0.03 Å for M = Hf than for M = Zr. In view of the slightly larger ionic radius of Hf(IV) relative to Zr(IV), these shorter distances are an indication of stronger metal—ligand bonding interactions within the coordination sphere of 4.

Intramolecular Rearrangement of 4 to 5. Upon thermolysis, the η^2-iminoacyl imine complex, 4, rearranges solely to the bicyclic enediamidate Cp$_2$Hf(N(CMe$_3$)C(CH$_2$SiMe$_2$CH$_2$)=CN(CMe$_3$)), 5 (4). The relative rate of this intramolecular rearrangement is significantly slower for 4 than for the corresponding zirconium system. At 120 °C, $t_{1/2}$ = 2.9 min for Cp$_2$Zr(N(CMe$_3$)C—C(=NCMe$_3$)CH$_2$SiMe$_2$CH$_2$)[5] whereas $t_{1/2}$ = 199 min for 4. The activation parameters for the conversion 4 → 5 have been obtained by examining the temperature dependence of the rate constant, k, within the temperature range 120–160 °C. The first-order rate constants are tabulated in Table I. From the Eyring plot (Figure 1) of $-\ln(k/T)$ vs $1/T$, the values for the enthalpy of activation, $\Delta H^\ddagger$, and the entropy of activation, $\Delta S^\ddagger$, are 28.8(11) kcal/mol and −5(2) eu, respectively. The value of $\Delta H^\ddagger$ for the conversion 4 → 5 is *ca.* 3 kcal/mol higher than that in the zirconium case. This variation in $\Delta H^\ddagger$ probably reflects the difference in the relative strengths of the M—C(methylene) bond that must be broken to initiate[18] the construction of the corresponding chelating enediamido ligand. A comparison of the structural data for Cp$_2$M(N(CMe$_3$)C—C(=NCMe$_3$)CH$_2$SiMe$_2$CH$_2$) (M = Zr, Hf) shows that the Hf—C4(methylene) bond of 4 is 0.03 Å shorter than the corresponding Zr—C4(methylene) bond. While the magnitude of $\Delta H^\ddagger$ is influenced by the replacement of zirconium by hafnium, the value of $\Delta S^\ddagger$ is unaffected, which is consistent with these rearrangements proceeding through analogous transition states.



4 5 (4)

Characterization of Cp$_2$Hf(N(CMe$_3$)C(CH$_2$SiMe$_2$CH$_2$)=CN(CMe$_3$)). The bicyclic enediamido complex, 5, has been characterized by spectroscopic measurements

---

[18] Nonparameterized Hartree–Fock SCF calculations[19] performed on Cp$_2$Zr(N(CMe$_3$)C—C(=NCMe$_3$)CH$_2$SiMe$_2$CH$_2$) indicate that the LUMO is localized primarily on the η^2-iminoacyl fragment. The LUMO consists of nearly equal contributions (with mixing coefficients of opposite sign) from the C(2p$_z$) and N(2p$_z$) atomic orbitals, where the z-direction of the local coordinate system at each of these atoms is pointed perpendicular to the plane of the three-membered ZrCN ring. The presence of significant C(2p$_z$) character in the LUMO provides an orbitally-directed pathway for initiating 1,2-migration of the metal-bound methylene group to the electrophilic η^2-iminoacyl carbon.

[19] These calculations were performed on an IBM 3090-300E computer using version 5.1 of the Fenske–Hall program[20] provided to J.L.P. by Professor Dennis Lichtenberger of the Chemistry Department at the University of Arizona. The atomic coordinates were idealized from the crystallographic data,[4] and the basis set of Slater-type atomic orbitals was generated by the numerical Xα atomic orbital program of Herman and Skillman[21] used in conjunction with the Xα-to-Slater basis program of Bursten and Fenske.[22]

[20] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

[21] Herman, F.; Skillman, S. *Atomic Structure Calculations*; Prentice-Hall: Englewood Cliffs, NJ, 1963.

[22] Bursten, B. E.; Jensen, R. J.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320 and references cited therein.

and elemental analysis. The ^{1}H and ^{13}C NMR data are consistent with the 1,4-diaza-5-hafnacyclopentene ring being folded significantly along the N···N vector. The resultant inequivalence of the two cyclopentadienyl rings and the two methyl substituents of $SiMe_2$ leads to the appearance of two distinct pairs of resonances for these groups in the ^{1}H and ^{13}C NMR spectra. In addition, the methylene protons are represented by an AB quartet at δ 2.05 and 1.27 with a geminal coupling constant of 16.7 Hz. The corresponding carbon resonance in the gated nondecoupled ^{13}C NMR spectrum appears as a "pseudo" triplet at δ 22.8, indicating that $^1J_{C-Ha} \approx {}^1J_{C-Hb}$.

The nonplanarity of the HfN_2C_2 ring in **5** is further indicated by the location of the electronic absorption band, which has been tentatively assigned to a $\pi(NC{=}CN) \rightarrow a_1(d_{z^2})$ transition.[23] The λ_{max} value of 332 nm for this transition is comparable to the that observed for $Cp_2Zr(N(CMe_3)C(CH_2SiMe_2CH_2){=}CN(CMe_3))$[5] in which the ZrN_2C_2 ring is folded along the N···N vector by 52.1°.

The folded enediamido ligand of **5** also exhibits dynamic behavior in solution arising from the interconversion between two folded conformations of the five-membered HfN_2C_2 ring. Variable temperature NMR measurements indicate that the two cyclopentadienyl proton resonances observed at room temperature for **5** coalesce upon heating at 85 ± 1 °C. The free energy of activation associated with the inversion barrier was calculated from the expression $\Delta G^\ddagger = 4.576T_c\,(10.319 + \log T_c - \log k_c)$,[24] where T_c is the coalescence temperature, $k_c = 2.22\Delta\nu_{AB}$, and $\Delta\nu_{AB}$ is the difference in the corresponding cyclopentadienyl proton frequencies in the slow-exchange limit.[25] This analysis led to a calculated barrier of 16.9(5) kcal/mol, which is notably lower than the inversion barrier of 19.5(5) kcal/mol associated with $Cp_2Zr(N(CMe_3)C(CH_2SiMe_2CH_2){=}CN(CMe_3))$.[5] Assuming that the 1,4-diaza-5-metallacyclopentene rings are bent to the same extent in these two compounds, the lower inversion barrier observed for **5** probably reflects a greater stabilization of the "planar" transition state. An analogous decrease in $\Delta G^\ddagger$ was reported by Rothwell and co-workers[11] during their evaluation of this dynamic interconversion in $M(N(Ph)C(Me){=}C(Me)NPh)(OAr)_2$, with $\Delta G^\ddagger$ = 15.5 kcal/mol for M = Zr and 14.2 kcal/mol for M = Hf.

Concluding Remarks. The replacement of zirconium with hafnium has two notable effects on the reductive coupling reaction of CN-*t*-Bu with $Cp_2M(CH_2SiMe_2CH_2)$. The most prominent difference is that the first insertion step results in an equilibrium mixture of the η^2-iminoacyl complex, **2a**, and the cyclic enamido complex, **3a**. Addition of another equivalent of CN-*t*-Bu to this equilibrium mixture proceeds exclusively with the formation of the η^2-iminoacyl imine compound, **4**. The reversibility associated with **2a** ↔ **3a** enables the reductive coupling pathway to occur with complete consumption of **3a** as well as **2a** and provides direct evidence that $Cp_2Hf(N(CMe_3)CCH_2SiMe_2CH_2)$ is the common intermediate in both the 1,2-silyl shift pathway that leads to the cyclic enamide **3a** and the alternative reductive coupling pathway that ultimately affords the bicyclic enediamidate **5**. The results of our kinetic study indicate that $\Delta H^\ddagger$ for the conversion of **4** to **5** is *ca.* 3 kcal/mol higher than determined for the analogous zirconium system. This higher enthalpy of activation is attributed to a stronger Hf—C(methylene) bond, which must be broken to initiate this intramolecular rearrangement. This statement is consistent with our crystallographic analysis of **4** which shows that the Hf—C(methylene) bond is 0.03 Å shorter than the corresponding Zr—C(methylene) bond in $Cp_2Zr(N(CMe_3)C{-}C({=}NCMe_3)CH_2SiMe_2CH_2)$.

Acknowledgment. Financial support for this research was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-9113097). Computer time for the X-ray structural analysis of **4** and the MO calculations described in ref 18 was provided by the West Virginia Network for Educational Telecomputing.

Supplementary Material Available: Textual presentation of further details regarding the crystallographic analysis of **4** and tables of crystal data, positional and thermal parameters, and interatomic distances and bond angles (9 pages). Ordering information is given on any current masthead page.

OM930277Q

---

[23] Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712.

[24] Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

[25] In the slow exchange ^{1}H NMR spectrum of **5** in toluene-d_8, the two cyclopentadienyl resonances (δ 5.965 and 5.340) are separated by 168.7 Hz.