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Low-Temperature NMR Study of the Reductive C,C-Coupling of CNMe by $(C_5Me_5)_2Zr(CH_2SiMe_2CH_2)$ and Structural Characterization of $(C_5Me_5)_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$‡

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Abstract: Low-temperature NMR measurements within the range -45 to -10°C have provided spectroscopic evidence of the formation and sequential participation of two η^2-iminoacyl intermediates, $Cp^*_2Zr(N(Me)CCH_2SiMe_2CH_2)$ and $Cp^*_2Zr(N(Me)C\text{-}C(=NMe)CH_2SiMe_2CH_2)$, in the reductive coupling of two equivalents of CNMe by $Cp^*_2Zr(CH_2SiMe_2CH_2)$, where $Cp^* = C_5Me_5$. The resultant product, $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$, has been characterized by spectroscopic and structural methods of analysis.

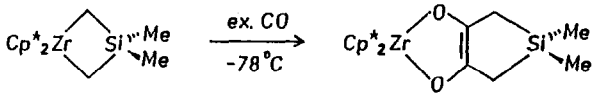
INTRODUCTION

Organozirconocene derivatives are used extensively as stoichiometric reagents for coupling unsaturated substrates in organic synthesis.[1] Zirconocene-based catalysts have also been developed for the regio- and stereoselective reductive cyclization of nonconjugated dienes,[2] diynes, and enynes.[3] The corresponding reductive coupling reaction of carbon monoxide with $Cp^*_2ZrMe_2$ ($Cp^* = C_5Me_5$), as originally reported in 1978 by Bercaw and coworkers,[4] affords the enediolate complex, $Cp^*_2Zr(OC(Me)=C(Me)O)$. Numerous other examples of this important C-C bond forming reaction have since appeared in the literature.[5-11] These reactions are generally initiated by the insertion of carbon monoxide into either electrophilic metal-carbon or metal-hydrogen bonds and can proceed via both intra[5d,9c,10a] and intermolecular[5a,6,7a,8] reaction pathways. Experimental[5d,6,8,10b] and theoretical studies[9b,c] indicate that metal η^2-acyl and η^2-formyl species represent plausible reactive intermediates in this coupling process.

These reactivity studies were performed primarily on acyclic molecular systems. Only a few examples of the migratory insertion of carbon monoxide into the metal-carbon bond(s) of a metallacyclic ring leading to enediolate formation are known.[5d,7c,11b] This situation was due initially to the lack of suitable metallacyclic systems for the purpose of such investigations. Petersen and Egan[11b] reported that the carbonylation of $Cp^*_2Zr(CH_2SiMe_2CH_2)$ ($Cp^* = C_5Me_5$) with excess

‡This paper is dedicated to Professor Gabor Fodor on the occasion of his 75th birthday and in recognition for his lifelong contributions to synthetic organic chemistry.

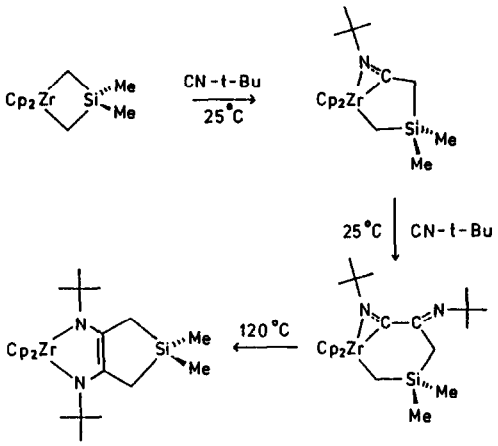
carbon monoxide at -78°C affords exclusively the bicyclic enediolate compound $Cp^*_2Zr(OC(CH_2SiMe_2CH_2)=CO)$ (1). Berg and Petersen[12] subsequently observed that the related reaction of four equivalents of CNMe with $Cp^*_2Zr(CH_2SiMe_2CH_2)$ at -20°C also proceeds with reductive coupling



(1)

to afford the corresponding bicyclic enediamidate complex $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$. By increasing the steric bulk of the alkyl substituent in CNR, they[12] were further able to isolate and identify two intermediate η^2-iminoacyl species, $Cp_2Zr(N(CMe_3)CCH_2SiMe_2CH_2)$ and $Cp_2Zr(N(CMe_3)C\text{-}C(=NCMe_3)CH_2SiMe_2CH_2)$, that participate in the reductive coupling reaction of CN-t-Bu by $Cp_2Zr(CH_2SiMe_2CH_2)$ (Scheme I).[13] On the basis of these results, a low-temperature NMR study was

Scheme I

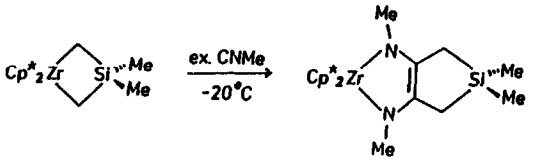


undertaken in an effort to observe the formation and consumption of the corresponding η^2-iminoacyl species during the reductive coupling of CNMe by $Cp^*_2Zr(CH_2SiMe_2CH_2)$. The characteristic upfield location[12] of the proton resonance of the methylene group bound to zirconium in these complexes should provide a specific spectroscopic marker for monitoring the course of this reaction. The outcome of this investigation and a complete description of the structural characterization of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ are discussed herein and indicate that a similar reaction sequence as shown in Scheme I is operative for the reductive coupling of CNMe by $Cp^*_2Zr(CH_2SiMe_2CH_2)$.

DISCUSSION OF RESULTS

Reductive Coupling Reaction of CNMe by $Cp^*_2Zr(CH_2SiMe_2CH_2)$. The reaction of excess CNMe with $Cp^*_2Zr(CH_2SiMe_2CH_2)$ at -20°C readily proceeds with the reductive coupling of two molecules of CNMe and results in the quantitative formation of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ (2). This bicyclic

compound has been characterized by ^1H and ^{13}C NMR, electronic spectroscopy, and an X-ray



(2)

crystallographic analysis. Its proton NMR spectrum contains four distinct singlets at δ 3.31, 1.92, 1.88, and 0.19, which are assigned to the six methyl protons of the two coupled molecules of CNMe, the four methylene protons, the thirty methyl protons of the permethylated cyclopentadienyl rings, and the six methyl protons of the dimethylsilyl group, respectively. The fact that only one proton resonance is observed for the Cp* ligands indicates either the 1,4-diaza-5-zirconacyclopentene ring is planar or the complex is rapidly interconverting, on the NMR time scale, between two folded conformations at 25°C. Cooling a NMR sample of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ in toluene-d_8 to -92°C, however, does not result in significant broadening or separation of any of the proton resonances. Because we were unable to freeze out such a dynamic process, an X-ray structure determination of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ was performed in order to establish the conformational structure of the bicyclic ring. Is it truly planar or is it folded as in $Cp_2Zr(N(CMe_3)C(CH_2SiMe_2CH_2)=CN(R))$, R = CMe_3, 2,6-xylyl,[13] and $Cp_2Zr(N(Ph)C(Ph)=C(Ph)N(Ph))$.[14]

Description of the Molecular Structure of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$. This dark purple compound crystallizes in the noncentrosymmetric space group, $P2_12_12_1$, with four molecules per unit cell. A perspective view of its solid-state structure is illustrated in Figure 1 with the atom numbering scheme. The pseudotetrahedral ligand arrangement about the central zirconium atom consists of two π-bonded permethylated cyclopentadienyl rings and the N-donors of the enediamido ligand. The Zr-N distances of 2.110(6) and 2.112(7) Å indicate the enediamido ligand bonds in a symmetric fashion. Their values are consistent with the Zr-N distances reported for π-donating dialkylamido groups bound to Zr(IV)[15] and are comparable to those in

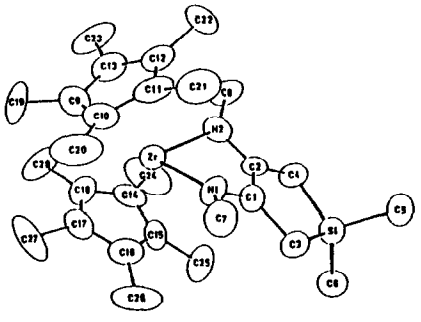


Figure 1. Perspective view of the molecular structure for the non-hydrogen atoms in $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$.

$Cp_2Zr(N(CMe_3)C(CH_2SiMe_2CH_2)=CN(CMe_3))$[13] and $Cp_2Zr(N(Ph)C(Ph)=C(Ph)N(Ph))$.[14] The principal

structural feature of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ is the distinct non-planarity of its 1,4-diaza-5-zirconacyclopentene ring. This five-membered ring is folded along the N1···N2 vector with the dihedral angle between the planes containing atoms Zr, N1, and N2 and atoms N1, N2, C1, and C2 being 35.7°. On the basis of the NMR results, it is apparent that despite the rather pronounced folding of the ZrN_2C_2 ring in the solid state the activation barrier for ring inversion in solution must be relatively low ($\Delta G^{\ddagger}$ (est). << 10 kcal/mol).[14,16]

The unusual purple color displayed by $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ is attributed to an electronic transition from the filled π-orbital of the carbon-carbon double bond to the empty d_{z^2}-like LUMO at zirconium. Hofmann and coworkers[9a] observed for related enediolate complexes, $Cp^*_2Zr(OC(R)=C(R)O)$, where R = Me, CMe_3, that the energy of this transition increases as the folding of the ZrO_2C_2 ring along the O···O vector increases. The corresponding absorption maxima in the electronic spectra of $Cp_2Zr(N(CMe_3)C(CH_2SiMe_2CH_2)=CN(R))$, where R = CMe_3 and 2,6-xylyl, are located at λ_{max} = 352 nm and 366 nm, respectively, and are consistent with the rather large fold angles of 52.1° and 51.3°, found in the solid state for these complexes.[13] However, the location of this absorption band for $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ at λ_{max} = 546 nm is more similar in energy to that of $Cp^*_2Zr(OC(CMe_3)=C(CMe_3)O)$, which possesses a planar structure for its five-membered chelate ring.[9a] One can only speculate then about the conformational structure of the ZrN_2C_2 ring of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ in solution. Does it remain folded as shown in Figure 1 or is it nearly planar? The latter situation would offer an alternative explanation of why our efforts to observe by NMR methods the slow exchange limit in solution for the flipping of the ZrN_2C_2 ring were unsuccessful.

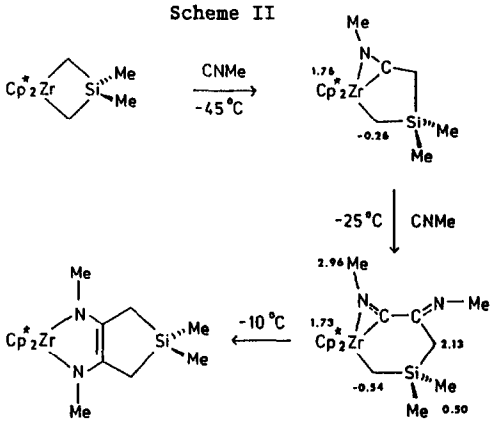
Low-Temperature NMR Study. A low-temperature NMR study was undertaken to observe the formation and monitor the consumption of any η^2-iminoacyl intermediates generated during the reductive coupling of CNMe by $Cp^*_2Zr(CH_2SiMe_2CH_2)$. A sealed NMR tube containing $Cp^*_2Zr(CH_2SiMe_2CH_2)$ and four equivalents of CNMe in toluene-d_8 was kept frozen in liquid nitrogen and then was inserted into the NMR probe precooled to -45°C. Following temperature equilibration of the NMR tube and probe, the ^1H NMR spectrum measured at -45°C contained two distinct singlets at δ -0.26 and -0.54. Upon comparison with the chemical shifts for the protons of the metal-bound methylene groups of $Cp_2M(N(CMe_3)CCH_2SiMe_2CH_2)$ (δ -0.11 (Zr)[12], -0.14 (Hf)[17]) and $Cp_2M(N(CMe_3)C\text{-}C(=NCMe_3)CH_2SiMe_2CH_2)$ (δ -0.44 (Zr)[12], -0.51 (Hf)[17]), the former singlet can be assigned to the methylene proton resonance of $Cp^*_2Zr(N(Me)CCH_2SiMe_2CH_2)$, whereas the latter corresponds to that of $Cp^*_2Zr(N(Me)C\text{-}C(=NMe)CH_2SiMe_2CH_2)$.

Further support for these assignments is provided in the NMR spectra measured as the sample is allowed to warm. At -35°C, further enhancement in the relative intensity of the upfield singlet at δ -0.54 is observed. As the temperature is raised, rapid insertion of CNMe into a Zr-C bond of $Cp^*_2Zr(CH_2SiMe_2CH_2)$ is followed by facile addition of a second equivalent of CNMe to the η^2-iminoacyl precursor. The concentration of the η^2-iminoacyl intermediate remains fairly constant, whereas that for the η^2-iminoacyl imine increases. A comparable variation in the

relative intensities of the methyl proton resonances of the Cp* ligands is also evident. The singlet at δ 1.76 assigned to $Cp^*_2Zr(N(Me)CCH_2SiMe_2CH_2)$ diminishes relative to the peak at δ 1.73 attributed to the Cp* rings of $Cp^*_2Zr(N(Me)C\text{-}C(=NMe)CH_2SiMe_2CH_2)$. Upon raising the temperature to -25°C, the singlet at δ -0.26 decreases dramatically, whereas the resonance at δ -0.54 continues to grow until the resonances for the η^2-iminoacyl imine species dominate the ^1H NMR spectrum. At this point, it is possible to assign the singlets at δ 2.96, 2.13, and 0.50 to the methyl group of the η^2-iminoacyl unit, the methylene group attached to the carbon of the exocyclic imine, and the methyls of the $SiMe_2$ group, respectively. Finally, above -10°C the proton resonances of $(Cp^*_2Zr(N(Me)C\text{-}C(=NMe)CH_2SiMe_2CH_2)$ are completely replaced after two hours by resonances at δ 3.28, 1.88, 1.81, and 0.14 corresponding to $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CH(Me))$. As expected, when the NMR sample was removed from the NMR probe, the color of the solution was dark purple, a further indication of the formation of the bicyclic enediamido product.

Concluding Remarks. *From this low-temperature study it is apparent that the reductive coupling* of CNMe by $Cp^*_2Zr(CH_2SiMe_2CH_2)$ involves the participation of two η^2-iminoacyl species, that are analogous to those isolated during our investigation of the reaction of CN-t-Bu with $Cp_2Zr(CH_2SiMe_2CH_2)$.[12,13] Although the sequence of chemical events for these two reactions is the same, the lower activation barriers associated with the individual insertion and rearrangement steps enable this C,C-coupling process (Scheme II) to occur at significantly lower temperatures. Given that the reductive coupling reactions of CNMe and CO by $Cp^*_2Zr(CH_2SiMe_2CH_2)$ occur under similar reaction conditions, it seems plausible that the latter reaction may involve η^2-acyl intermediates similar to the η^2-iminoacyl species observed during this low temperature NMR study.

Scheme II



EXPERIMENTAL

General Considerations. All chemical manipulations were carried out on a double-manifold high-vacuum line or in a Vacuum Atmospheres glovebox. Glassware was oven-dried or flame-dried under vacuum prior to use. Nitrogen and argon were prepurified by passage over reduced BTS catalyst and activated 4A molecular sieves. All hydrocarbon solvents (reagent grade) were purified by standard techniques and vacuum distilled into storage flasks containing $[Cp_2Ti(\mu\text{-}Cl)_2]_2Zn$[18] prior to use. Toluene-d_8 and benzene-d_6 (Cambridge Isotopic Laboratories) were distilled from 4A molecular sieves. Methyl isocyanide was prepared[19] and stored over 4A molecular sieves. $Cp^*_2ZrCl_2$,[20] $[MgCH_2SiMe_2CH_2]_n$,[21] and $Cp^*_2Zr(CH_2SiMe_2CH_2)$[11b] were prepared using literature procedures.

^1H and ^{13}C NMR measurements were recorded using a JEOL GX-270 FT-NMR spectrometer operating in the FT mode at 270 MHz (^1H) or 67.5 MHz (^{13}C). The ^1H NMR chemical shifts are referenced to the residual proton peak of benzene-d_6 (δ 7.15) or the methyl proton peak of toluene-d_8 (δ 2.09) vs. TMS. The ^{13}C NMR resonances are referenced to the central carbon peak of benzene-d_6 (δ 128.0) vs. TMS. IR spectra were measured on a Perkin-Elmer 1310 infrared spectrometer using KBr discs and calibrated against polystyrene film. Electronic spectra were measured on a Hewlett-Packard 8452A diode array spectrometer using a 1.00 cm quartz cell equipped with a Teflon stopcock. The elemental analysis was performed by Dornis and Kolbe Microanalytical Laboratory, Mulheim, Germany.

Preparation of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$. This bicyclic enediamidate complex was prepared by a modification of a literature procedure.[12] A 1.293 g (2.78 mmol) sample of $Cp^*_2Zr(CH_2SiMe_2CH_2)$ was added to a Solv-seal flask. The flask was attached to a calibrated gas bulb and evacuated. Approximately 40 mL of pentane was condensed into the flask and four equivalents of CNMe were added to the calibrated gas bulb. The solution was then frozen in liquid nitrogen and the isocyanide was admitted into the flask. The reaction mixture was slowly warmed to room temperature and then stirred for several hours to ensure complete reaction. Following removal of the solvent, the reaction flask was attached to a pressure equalizing filter frit and evacuated. The product residue was dissolved in ca. 20 mL of pentane. Decantation through the frit and slow removal of the solvent gave a dark purple crystalline solid (isolated yield 97%). Crystals suitable for X-ray diffraction studies were obtained by the slow removal of octane from a saturated solution. IR (KBr): 1550 cm^{-1} (C=C stretch, weak). ^1H NMR spectrum in benzene-d_6: δ 3.31 (NCH_3, s), 1.92 ($C=CH_2$, s), 1.88 (C_5Me_5, s), 0.19 ($SiMe_2$, s); gated nondecoupled ^{13}C NMR spectrum in benzene-d_6 (mult., $^1J_{C-H}$ in Hz): δ 116.2 ($\underline{C}CH_3$, s), 40.4 (NCH_3, q, 132), 18.9 ($=\underline{C}CH_2$, t, 123), 11.9 ($\underline{C}CH_3$, q, 126), -0.55 ($Si\underline{C}H_3$, q, 121). Anal. Calcd. for $C_{28}H_{46}N_2SiZr$: C, 63.46; H, 8.75. Found: C, 62.71; H, 8.69. λ_{max} = 546 nm, ϵ_{max} = 1.10 x 10^3 L mol^{-1} cm^{-1}.

Sample for Low-Temperature NMR Study. In a typical experiment, 0.0302 g (0.0674 mmol) of $Cp^*_2Zr(CH_2SiMe_2CH_2)$ was added to a NMR tube equipped with a 14/20 ground glass joint. Toluene-d_8 (0.4 mL) was added and the NMR tube was connected to a calibrated gas bulb. The apparatus was attached to a vacuum line and the solution was freeze-pump-thawed twice. Four equivalents of methyl isocyanide were added to the calibrated gas bulb and then condensed into the NMR tube. The tube was then sealed under 500 mm N_2 with a torch and kept frozen in liquid nitrogen until placed in the precooled probe of the NMR spectrometer.

X-Ray Data Collection. A dark purple crystal of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$ was sealed in a glass capillary tube under a prepurified N_2 atmosphere and then was transferred to a Picker goniostat operated by a Krisel Control diffractometer automation system. Procedures analogous to those described elsewhere[22] were used to determine the lattice parameters and collect the single-crystal diffraction data. The intensity data were corrected for Lorentz-polarization effects. The standard deviation of each square of each structure factor was calculated from $\sigma(F_o^2) = [\sigma_c(F_o^2)^2 + (0.03\ F_o^2)^2]^{1/2}$. Crystal data: crystal system, orthorhombic; space group, $P2_12_12_1$; cell dimensions, a = 9.285(3) Å, b = 16.138(4) Å, c = 18.691(4) Å; cell volume, 2800(1) $Å^3$; calculated density, 1.257 g/cm^3 for Z = 4; linear absorption coefficient, 4.47 cm^{-1}; crystal dimensions, 0.125 x 0.175 x 0.475. Data collection information: radiation, Zr-filtered Mo K_α at takeoff angle of 2°; temperature, 22 ± 1°C; sampled reflections, $h\ k\ l$ with $5° < 2\theta < 45°$; scan rate, 2 deg/min; scan width, 1.1 + 0.9 tanθ; standard reflections, 3 measured every 90 minutes and showed no evidence of crystal decay; total number of unique reflections, 2109 with $F_o^2 > 0$.

Structural Analysis and Refinement of $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$. The initial coordinates for the Zr atom was determined by an analysis of the three strongest Harker peaks on the corresponding unsharpened Patterson map. Approximate positions for the remaining non-hydrogen atoms were obtained by Fourier methods and then refined with anisotropic thermal parameters. The coordinates of most hydrogen atoms were obtained from a difference Fourier summation utilizing only low-angle data ($\sin\theta/\lambda < 0.40\ Å^{-1}$) with the remainder calculated with the aid of MIRAGE.[23] Full-matrix refinement[22] (based on F_o^2) of the positional and anisotropic thermal parameters for the 32 non-hydrogen atoms with fixed isotropic contributions for the 46 hydrogen atoms converged with final discrepancy indices of $R(F_o) = 0.056$, $R(F_o^2) = 0.063$, $R_w(F_o^2) = 0.084$ with $\sigma_1 = 1.50$ for the 1828 reflections with $F_o^2 > \sigma(F_o^2)$. The values of these R-factors were slightly higher for the other enantiomorph. A final difference Fourier synthesis verified the completeness of the structural analysis. The positional parameters for the refined non-hydrogen atoms are provided in Table 1 for $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$. Selected interatomic distances and bond angles and their esd's are listed in Table 2.

Table 1. Positional Parameters for $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$.

Atom	x	y	z
Zr	0.07637(9)	0.03667(5)	0.11577(4)
Si	0.4419(3)	0.1656(1)	0.2952(1)
N1	0.2293(7)	0.1330(3)	0.1083(3)
N2	0.2388(7)	-0.0124(4)	0.1825(3)
C1	0.2946(8)	0.1307(5)	0.1744(4)
C2	0.3013(9)	0.0560(5)	0.2115(5)
C3	0.3627(9)	0.2075(5)	0.2104(4)
C4	0.3766(9)	0.0554(5)	0.2848(4)
C5	0.6384(10)	0.1695(6)	0.2952(6)
C6	0.3733(9)	0.2172(5)	0.3769(4)
C7	0.2572(11)	0.2051(5)	0.0647(4)
C8	0.2724(10)	-0.0913(5)	0.2148(5)
C9	-0.0355(9)	-0.0373(8)	0.0078(5)
C10	0.0512(12)	0.0251(6)	-0.0210(4)
C11	0.1948(12)	0.0043(6)	-0.0077(5)
C12	0.1976(10)	-0.0692(6)	0.0299(5)
C13	0.0578(12)	-0.0957(5)	0.0412(5)
C14	-0.0896(11)	0.0255(6)	0.2250(4)
C15	-0.0366(8)	0.1062(6)	0.2263(5)
C16	-0.0912(12)	0.1478(6)	0.1670(6)
C17	-0.1830(10)	0.0961(7)	0.1314(5)
C18	-0.1847(10)	0.0209(6)	0.1680(6)
C19	-0.1871(12)	-0.0501(9)	-0.0148(6)
C20	0.0079(13)	0.0696(7)	-0.0676(5)
C21	0.3307(11)	0.0448(7)	-0.0351(5)
C22	0.3338(11)	-0.1195(6)	0.0480(5)
C23	0.0119(12)	-0.1765(5)	0.0709(5)
C24	-0.0731(13)	-0.0359(7)	0.2836(5)
C25	0.0355(10)	0.1490(7)	0.2887(6)
C26	-0.0752(16)	0.2390(6)	0.1516(7)
C27	-0.2875(12)	0.1246(9)	0.0757(6)
C28	-0.2888(12)	-0.0494(8)	0.1593(6)

Table 2. Selected Structural Parameters in $Cp^*_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$.[a]

A. Interatomic Distances (Å)

Zr-N1	2.110(6)	Zr-N2	2.112(7)
Zr-Cp1	2.29(1)	Zr-Cp2	2.30(1)
N1-C1	1.377(10)	N2-C2	1.360(10)
N1-C7	1.444(10)	N2-C8	1.444(11)
C1-C3	1.546(12)	C2-C4	1.538(12)
C1-C2	1.391(11)		

B. Bond Angles (deg)

N1-Zr-N2	80.5(2)	Cp1-Zr-Cp2	132.6(3)
Zr-N1-C1	102.6(5)	Zr-N2-C2	103.6(5)
Zr-N2-C7	138.7(5)	Zr-N2-C8	137.2(6)
C7-N1-C1	116.7(6)	C8-N2-C2	117.2(7)
N1-C1-C2	119.3(7)	N2-C2-C1	119.1(7)
N1-C1-C3	123.3(7)	N2-C2-C4	122.9(7)
C2-C1-C3	117.3(7)	C1-C2-C4	118.0(7)
C1-C3-Si	103.9(5)	C2-C4-Si	103.4(5)
C3-Si-C4	97.2(4)	C5-Si-C6	109.2(4)

[a]Cpn denotes the centroid of a cyclopentadienyl ring. The rings containing the centroids designated by Cp1 and Cp2 contain carbon atoms C9-C13 and C14-C18, respectively.

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