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Competitive Pathways Associated with CO Insertion into a 1-Sila-3-zirconacyclobutane Ring. Observation of Intramolecular 1,2-Silyl Shift and Reductive CO Coupling Reactions

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Summary: The insertion of CO into Zr–C bond(s) within the 1-sila-3-zirconacylcobutane ring of $Cp_2Zr(CH_2SiMe_2CH_2)$ and $Cp^*{}_2Zr(CH_2SiMe_2CH_2)$, where Cp = η^5-C_5H_5 and Cp* = η^5-C_5Me_5, has been examined. In the former case, the insertion of 1 equiv of CO is followed by an intramolecular 1,2-silyl shift and the formation of an oligomeric zirconaoxirane species, $Cp_2Zr(OC({=}CH_2)SiMe_2CH_2)_n$. Comparable studies of the carbonylation of $Cp^*{}_2Zr(CH_2SiMe_2CH_2)$ have shown that this reaction can lead to the formation of two entirely different di-insertion products—a cyclic dienolate, $Cp^*{}_2Zr(OC({=}CH_2)SiMe_2(CH_2{=})CO)$, and a bicyclic enediolate, $Cp^*{}_2Zr(OC(CH_2SiMe_2CH_2){=}CO)$.

The migratory insertion of CO into a metal–carbon bond represents one of the most fundamental reactions in organometallic chemistry.[1] Although this reaction has been studied for a wide range of metal–alkyl complexes, it has been examined for only a relatively few metallacyclic compounds.[2,3] Previously, we demonstrated[4] that the electron-deficient Zr center in $Cp_2Zr(CH_2SiMe_2CH_2)$ can induce the lateral insertion of a formaldehyde unit into a Zr–C bond of the 1-sila-3-zirconacyclobutane ring. On the basis of this result, subsequent studies of the reactivity of CO with this and related 1-sila-3-zirconacyclobutane complexes have been undertaken.

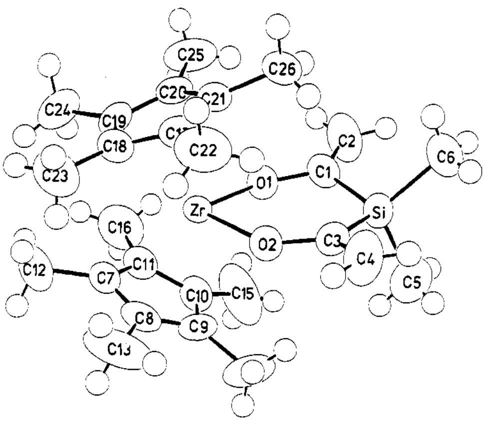
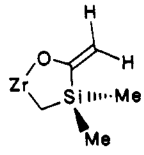


Figure 1. Perspective view of the molecular configuration of $Cp^*{}_2Zr(OC({=}CH_2)SiMe_2(CH_2{=})CO)$. Selected bond distances (Å) and bond angles (deg) for the 1,5-dioxa-3-sila-6-zirconacyclohexane ring: Zr–O1, 1.990 (2); Zr–O2, 1.987 (2); O1–C1, 1.361 (5); O2–C3, 1.363 (4); C1–C2, 1.318 (6); C3–C4, 1.316 (6); O1–Zr–O2, 89.7 (1); Zr–O–C, 139.6 (av); O–C–Si, 118.0 (av).

Quantitative gas measurements using a Toepler pump demonstrate that $Cp_2Zr(CH_2SiMe_2CH_2)$ readily inserts 1 equiv of CO at 25 °C within 30 min. The identity of this metallacyclic product was established by elemental analysis, hydrolysis, and NMR measurements. A combination of GC/MS and ^1H NMR analyses[5] revealed that the sole organic product generated upon hydrolysis is the ketone $CH_3C({=}O)SiMe_3$. The observation of a quartenary carbon resonance at δ 180.7 and a resonance pattern for an exocyclic methylene at δ 93.6 (dd, $J_{^{13}C-H}$ = 152, 157 Hz) in the gated nondecoupled ^{13}C NMR spectrum provided further evidence indicating the presence of the five-membered metallacyclic ring structure I. However, ^1H and ^{13}C NMR spectra[6] of the CO insertion product recorded within the temperature range (−70 to +75 °C) indicated the presence of an equilibrium between two structurally similar species, presumably oligomer A and monomer B, in solution. With the assumption that the oligomer possesses a comparable structure to several dimeric zirconaoxirane species linked by Zr←O–Zr bridges,[7] the oligomer:monomer ratio as determined from the relative intensities of the Cp ring proton resonances is 0.125 at 25 °C. Unfortunately, the low solubility of $[Cp_2Zr(OC({=}CH_2)SiMe_2CH_2)]_n$ has prevented efforts to determine its molecular weight and thus confirm its nuclearity, *n*.



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One approach that has been employed[8] to inhibit the formation of oligomeric species for early-transition-metal

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[1] The general aspects of CO insertion into a metal–alkyl bond are described in: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

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[5] ^1H NMR spectrum (C_6H_6-d_6): δ 1.97 (CH_3, s), 0.03 ($SiMe_3$, s) (1:3). Parent ion peak: *m/e* 116.

[6] $[Cp_2Zr(OC({=}CH_2)SiMe_2CH_2)]_n$: IR (KBr pellet) ν(C=C) 1640, ν(CO) 1200 cm^{-1}. Anal. Calcd for $C_{15}H_{20}OSiZr$ (empirical formula): C, 53.67; H, 6.02. Found: C, 53.69; H, 6.14. NMR spectra for species A: ^1H NMR spectrum (C_6H_6-d_6) δ 5.89 (C_5H_5, s) 4.73, 4.36 (=CH_2, s) 1.27 ($ZrCH_2$, s), 0.43 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR spectrum (mult, $J_{^{13}C-H}$ in Hz) δ 180.7 (OC=, s) 112.6 (C_5H_5, d qt, 172, 7), 93.6 (=CH_2, dd, 157, 152), 32.9 ($ZrCH_2$, t, 119), 3.0 ($SiCH_3$, q, 119). NMR spectra for species B: ^1H NMR spectrum (C_6H_6-d_6) δ 5.94 (C_5H_5, s), 4.68, 4.50 (=CH_2, s), 1.27 ($ZrCH_2$, s), 0.36 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR spectrum (mult, $J_{^{13}C-H}$ in Hz) δ 181.0 (OC=, s), 111.1 (C_5H_5, d qt, 172, 7), 100.8 (=CH_2, dd, 157, 152), 22.8 ($ZrCH_2$, t, 119), 2.3 ($SiCH_3$, q, 119).

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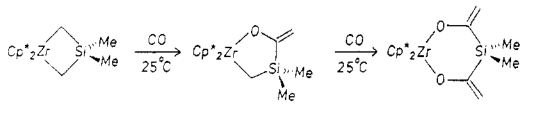
metallocene systems involves the replacement of Cp by Cp*. The synthesis of $Cp^*_2Zr(CH_2SiMe_2CH_2)$[9] was accomplished by the metathetical reaction of $Cp^*_2ZrCl_2$ and $[MgCH_2SiMe_2CH_2]_n$ in refluxing toluene (48 h). Depending on the reaction conditions, the carbonylation of $Cp^*_2Zr(CH_2SiMe_2CH_2)$ as monitored by NMR measurements can follow two entirely different reaction pathways. At room temperature, carbonylation proceeds with the stepwise insertion of 2 equiv of CO (eq 1).[10] The first CO insertion step is complete within several hours whereas the second insertion is substantially slower. During each stage of reaction 1, CO insertion is followed by an intramolecular 1,2-silyl shift, analogous to that observed for the reaction of CO with $Cp_2Zr(CH_2SiMe_2CH_2)$. The added steric bulk of the Cp* ligands apparently ensures the accessibility of a vacant metal orbital in $Cp^*_2Zr(OC({=}CH_2)SiMe_2CH_2)$ for interacting with a second equivalent of CO. The molecular structure of the di-insertion product $Cp^*_2Zr(OC({=}CH_2)SiMe_2(CH_2{=})CO)$ has been established by an X-ray structure determination.[11] A perspective view of this zirconacyclic dienolate (Figure 1) reveals the presence of two exocyclic methylene groups. Alternatively, if the carbonylation of $Cp^*_2Zr(CH_2SiMe_2CH_2)$ is performed at −78 °C, reductive coupling of two carbonyls is observed with the subsequent formation of a bicyclic endiolate, $Cp^*_2Zr(OC(CH_2SiMe_2CH_2){=}CO)$ (eq 2).[12] This dark red compound exhibits a λ_{max} at 492 nm, which is comparable to that reported by Hoffmann et al.[13] for the structurally similar endiolate $Cp^*_2Zr(OC(Me){=}(Me)CO)$, originally prepared by Bercaw and co-workers[2c] from the carbonylation of $Cp^*_2ZrMe_2$.[14] The reaction was repeated at −78 °C with only 1 equiv of CO. Following removal of solvent and unreacted CO, a room-temperature ^1H NMR measurement of the product revealed that the principal insertion adduct is $Cp^*_2Zr(OC({=}CH_2)SiMe_2CH_2)$ rather than the enediolate. This result indicates that the reductive CO coupling pathway will predominate at −78 °C (after the first CO insertion step) only when a reasonably large excess of CO is available. Under these conditions the insertion of a second CO proceeds at a faster rate than the first 1,2-silyl shift.



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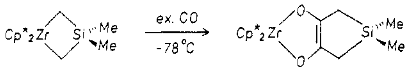
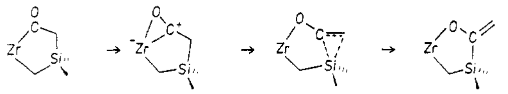


(2)

This intramolecular 1,2-silyl shift has been observed in both cyclic[3] and acyclic[15] organometallic systems with a Si atom located in a β-position relative to an electron-deficient metal center. It is well-known in organosilicon chemistry that a Si atom can stabilize a positive charge at a β-carbon via hyperconjugation.[16] In light of recent calculations by Hoffmann and co-workers,[17] who suggest that it may be more appropriate to describe the reactivity of an η^2-acyl (formed upon migratory insertion of CO into a metal–alkyl bond) in terms of a "carbenium-type" rather than "oxycarbene" interaction, one could envision each 1,2-silyl shift in these silazirconacyclic complexes as proceeding according to pathway 3. Studies are in progress to investigate the mechanistic aspects of this intramolecular 1,2-silyl shift.



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Supplementary Material Available: Summary of crystal data and data collection parameters and tables of positional and thermal parameters and interatomic distances and bond angles for the X-ray structural analysis of $Cp^*_2Zr(OC({=}CH_2)SiMe_2(CH_2{=})CO)$ (11 pages), a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[9] $Cp^*_2Zr(CH_2SiMe_2CH_2)$: ^1H NMR spectrum (C_6H_6-d_6) δ 1.78 (CCH_3, s), 0.74 ($ZrCH_2$, s), 0.34 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR spectrum (mult, $J_{^{13}C-H}$ in Hz) δ 116.8 (CCH_3, s), 48.1 ($ZrCH_2$, t, 123), 12.6 (CCH_3, q, 125), 2.78 ($SiCH_3$, q, 118).

[10] (a) $Cp^*_2Zr(OC({=}CH_2)SiMe_2CH_2)$: ^1H NMR spectrum (C_6H_6-d_6) δ 4.72, 4.26 (${=}CH_2$, s), 1.85 (CCH_3, s), 0.68 ($ZrCH_2$, s), 0.51 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR spectrum (mult, $J_{^{13}C-H}$ in Hz) δ 179.2 (OC=, s), 119.8 (CCH_3, s), 97.2 (${=}CH_2$, dd, 151, 156), 38.5 ($ZrCH_2$, t, 115), 12.1 (CCH_3, q, 125), 5.80 ($SiCH_3$, q, 118). (b) $Cp^*_2Zr(OC({=}CH_2)SiMe_2(CH_2{=})CO)$: ^1H NMR spectrum (C_7H_8-d_8) δ 4.97, 4.53 (${=}CH_2$, s), 1.88 (CCH_3, s), 0.44 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR spectrum (mult, $J_{^{13}C-H}$ in Hz) δ 171.5 (OC=, s), 120.9 (CCH_3, s), 101.5 (${=}CH_2$, dd, 151, 156), 11.1 (CCH_3, q, 126), 1.15 ($SiCH_3$, q, 117). Anal. Calcd for $C_{26}H_{40}O_2SiZr$: C, 61.97; H, 8.00. Found: C, 61.89; H, 8.04.

[11] (a) crystal data for $Cp^*Zr(OC({=}CH_2)SiMe_2(CH_2{=})CO)$: space group $P2_1/c$, $a = 8.681$ (2) Å, $b = 20.933$ (6) Å, $c = 14.717$ (5) Å, $\beta = 92.91$ (3)°, $V = 2671$ (2) Å^3, $Z = 4$, $d_{calcd} = 1.253$ g/cm^3. Of the 4372 unique diffraction data collected within a detector range $5° < 2\theta < 48°$ ($\pm h,k,l$) with Zr-filtered Mo $K\alpha$ radiation, the 3501 data having $F_o^2 > \sigma(F_o^2)$ were used in the structural analysis. Data collection, reduction, and refinement procedures have been described elsewhere.[11b] Full-matrix least-squares refinement (based on F_o^2) with anisotropic temperature factors for the 30 non-hydrogen atoms and fixed isotropic temperature factors for the 40 hydrogen atoms converged with final discrepancy indices of $R(F_o) = 0.047$, $R(F_o^2) = 0.049$, and $R_w(F_o^2) = 0.075$ with $\sigma_1 = 1.30$. (b) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

[12] $Cp^*_2Zr(OC(CH_2SiMe_2CH_2){=}CO)$: ^1H NMR spectrum (C_6H_6-d_6) δ 1.87 (CH_3, s), 1.74 (${=}CCH_2$, s), 0.22 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR spectrum (mult, $J_{^{13}C-H}$ in Hz): δ 141.2 (OC=, s), 120.5 (CCH_3, s), 22.0 (${=}CCH_2$, t, 124), 11.4 (CCH_3, q, 126), 0.03 ($SiCH_3$, q, 118). Anal. Calcd for $C_{26}H_{40}O_2SiZr$: C, 61.97; H, 8.00. Found: C, 61.94; H, 8.03.

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