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# Evidence of Ketenimine Formation during the Multiple C–C Coupling of Isocyanides by Stabilized Group 4 Metallacyclobutanes

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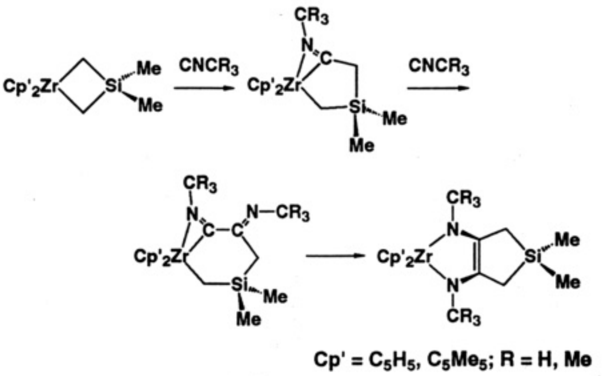
*Summary: Multiple C–C coupling of isocyanides has been demonstrated by the ambient-pressure reactions of CNMe with* $Cp_2M(N(CMe_3)CC({=}NCMe_3)CH_2SiMe_2CH_2)$ *and the high-pressure reactions of* $CNCMe_3$ *with* $Cp_2M(CH_2SiMe_2CH_2)$*, which afford* $Cp_2M(N(Me)C\text{-}C({=}NCMe_3)C({=}NCMe_3)CH_2SiMe_2CH_2)$ *and* $Cp_2M(N\text{-}(CMe_3)C({=}C{=}NCMe_3)C({=}NCMe_3)CH_2SiMe_2CH_2)$ *(M = Zr, Hf), respectively.*

The transition-metal-mediated reductive coupling of $C_1$ units (CO,[1] CNR,[2] and carbynes[3]) represents a C–C bond-forming reaction of fundamental chemical importance and may proceed via several distinct mechanistic pathways. We have shown that the reductive coupling of isocyanides by "stabilized" group 4 metallacyclobutane complexes such as $(C_5R_5)_2Zr(CH_2SiMe_2CH_2)$ (R = H,[4a,b] Me[4a,c]) proceeds via the unusual double-insertion reaction (1), leading to the sequential formation of $\eta^2$-iminoacyl and $\eta^2$-iminoacyl imine intermediates, and involves two different insertion steps. The first insertion is initiated by nucleophilic attack of the isocyanide at the electrophilic metal center followed by migration of the adjacent methylene group of the metallacyclic ring. The second isocyanide insertion, which leads to C–C bond formation, relies on the apparent electrophilic character[5] of the $\eta^2$-iminoacyl carbon to promote nucleophilic attack by the second isocyanide at this position. This remark is supported by nonparameterized Fenske–Hall Hartree–Fock SCF MO calculations,[8] which reveal that the LUMOs of $Cp_2Zr(N(CMe_3)CCH_2\text{-}SiMe_2CH_2)$ and $Cp_2Zr(N(CMe_3)CC({=}NCMe_3)CH_2Si\text{-}Me_2CH_2)$ are comprised of the iminoacyl $\pi^*_{CN}$, which is stabilized by interaction with the Zr $4d_{xz}$ orbital (Figure 1). In view of the similar nature of the LUMOs associated with these $\eta^2$-iminoacyl and $\eta^2$-iminoacyl imine intermediates, the latter species should be capable of promoting the insertion of another equivalent of isocyanide, thereby extending the length of the hydrocarbon chain through



(1)

Cp' = $C_5H_5$, $C_5Me_5$; R = H, Me

**Figure 1.** Molecular orbital representations of the LUMOs with charges in $Cp_2Zr(N(CMe_3)CCH_2SiMe_2CH_2)$ (A) and $Cp_2Zr(N(CMe_3)CC({=}NCMe_3)CH_2SiMe_2CH_2)$ (B).

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[2] (a) Durfee, L. D.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988,** *110,* 1463. (b) Bocarsly, J. R.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *Organometallics* **1986,** *5,* 2380. (c) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989,** *8,* 830. (d) Motz, P. J.; Alexander, J. J.; Ho, D. M. *Organometallics* **1989,** *8,* 2589. (e) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982,** *104,* 1263.

[3] (a) Mayr, A.; Bastos, C. M.; Daubenspeck, N.; McDermott, G. A. *Chem. Ber.* **1992,** *125,* 1583. (b) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993,** *26,* 90.

[4] (a) Berg, F. J.; Petersen, J. L. *Organometallics* **1989,** *8,* 2461. (b) Berg, F. J.; Petersen, J. L. *Organometallics* **1991,** *10,* 1599. (c) Berg, F. J.; Petersen, J. L. *Tetrahedron* **1992,** *48,* 4749.

[5] Experimental evidence for the "carbenium-type" representation described by Hoffmann *et al.*[6] has been provided by the coordination of phosphorus and nitrogen donors at the C of the $\eta^2$-acyl and the related $\eta^2$-silaacyl ligand.[7]

[6] Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985,** *107,* 4440.

[7] Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. T. *J. Am. Chem. Soc.* **1989,** *111,* 149 and references cited therein.

[8] These calculations were performed on an IBM 3090-300E computer using version 5.1 of the Fenske–Hall program[9] provided to J.L.P. by Professor Dennis L. Lichtenberger at the University of Arizona. The atomic coordinates were idealized from the crystallographic data.[4a] The *z* direction of the local coordinate system at the $\eta^2$-iminoacyl C and N atoms is pointed perpendicular to the plane of the ZrCN ring, and the *xz* plane of the local coordinate system at Zr bisects the N–Zr–C(methylene) bond angle.

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

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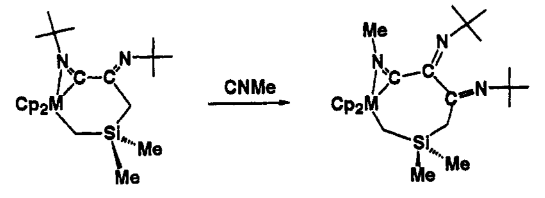
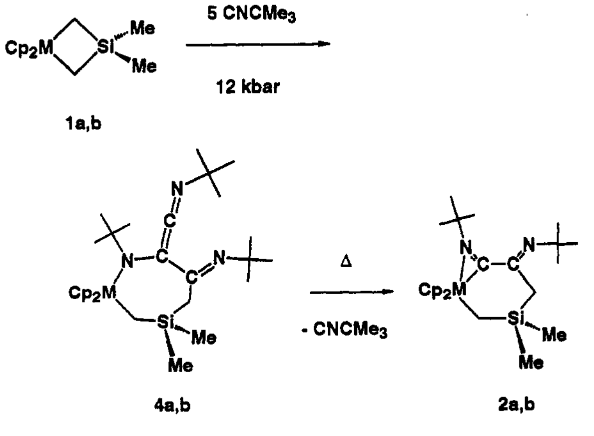
the subsequent formation of a second C–C bond. This premise has been borne out by the ambient-pressure reactions of CNMe with $Cp_2M(N(CMe_3)CC(=NCMe_3)CH_2SiMe_2CH_2)$ (M = Zr (**2a**), Hf (**2b**)) and the high-pressure reactions of $CNCMe_3$ with $Cp_2M(CH_2SiMe_2CH_2)$ (M = Zr (**1a**), Hf (**1b**)).

The NMR-tube reactions of 1 equiv of CNMe with **2a,b** (eq 2) proceed at 25 °C with the formation of $Cp_2M(N(Me)CC(=NCMe_3)C(=NCMe_3)CH_2SiMe_2CH_2)$ (M = Zr (**3a**), Hf (**3b**)).[10] These $\eta^2$-iminoacyl diimine compounds exhibit an upfield $^1H$ NMR resonance at $\delta$ −0.39 (**3a**) and −0.56 (**3b**) for the protons of the metal-bound methylene group. The three $^{13}C$ NMR resonances at $\delta$ 219.2, 170.1, 166.0 (**3a**) and $\delta$ 223.8, 170.1, 168.1 (**3b**) confirm the presence of one $\eta^2$-iminoacyl carbon and two imine carbons. Periodic $^{13}C\{^1H\}$ NMR measurements of the reaction of $^{13}CNMe$ with **2b** indicate that only the intensity of the $\eta^2$-iminoacyl carbon signal of **3b** is enhanced, verifying that reaction 2 proceeds with displacement of the $\eta^2$-iminoacyl group of **2b**. During the C–C coupling reactions that afford the double-insertion products (**2a,b**) and triple-insertion products (**3a,b**), the M–C(methylene) bond remains intact and acts as a tether holding the electrophilic $\eta^2$-iminoacyl moiety in the N-outside orientation needed to facilitate subsequent isocyanide insertions.



**2a,b** **3a,b** (2)

To investigate the influence of pressure on the insertion chemistry, the reactions of 5 equiv of $CNCMe_3$ with **1a,b** were performed at 12 kbar (eq 3).[11] NMR measurements reveal that the principal product **4a,b** contains three *tert*-butyl groups and two imine carbons. The downfield resonance of the $\eta^2$-iminoacyl carbon of **2a,b** is replaced by a singlet at $\delta$ 75.9 (**4a**) and $\delta$ 81.9 (**4b**), respectively. An X-ray diffraction analysis of **4a**[12] (Figure 2) shows that this compound corresponds structurally to the isocyanide coordination adduct produced upon nucleophilic attack of $CNCMe_3$ at the C $p_z$ orbital of the $\eta^2$-iminoacyl carbon of **2a**. The formation of the C(1)–C(9) bond in **4a** produces several notable structural changes. The Zr–C(iminoacyl) and N–C(iminoacyl) distances of 2.216(4) and 1.266(4) Å in **2a** are lengthened to a nonbonding Zr···C(1) separation of 2.745(5) Å and a N(1)–C(1) distance of 1.422(5) Å in **4a**, respectively. The absence of an $\eta^2$-iminoacyl interaction in **4a** is compensated by the Zr–N(1)[13] and Zr–C(4) bonds, which are *ca.* 0.15 and 0.08 Å shorter than the corre-



**1a,b** **4a,b** **2a,b** (3)

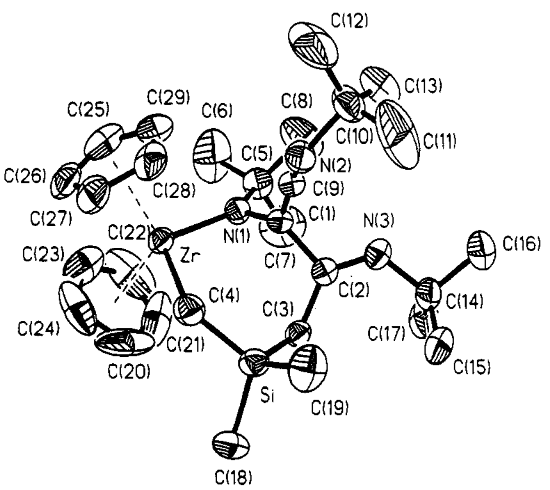


**Figure 2.** Perspective view of the molecular structure of **4a**, $Cp_2Zr(N(CMe_3)C(=C=NCMe_3)C(=NCMe_3)CH_2SiMe_2CH_2)$. Selected bond distances (Å) and angles (deg): Zr–N(1), 2.080(3); Zr–C(4), 2.300(4); N(1)–C(1), 1.422(5); C(1)–C(2), 1.518(5); C(1)–C(9), 1.339(5); C(9)–N(2), 1.206(5); N(1)–Zr–C(4), 105.58(13); Zr–N(1)–C(1), 101.5(2); Zr–C(4)–Si, 120.0(2); N(1)–C(1)–C(2), 122.2(3); N(1)–C(1)–C(9), 125.1(3); C(2)–C(1)–C(9), 112.2(3); C(1)–C(9)–N(2), 168.1(4).

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[10] $^1H$ NMR spectrum of **3a** ($C_6D_6$, 270 MHz): $\delta$ 5.49 ($C_5H_5$), 3.24 ($NCH_3$), 2.14 ($CCH_2Si$), 1.44, 1.35 ($NCMe_3$), 0.35 ($SiMe_2$), −0.39 ($ZrCH_2Si$). $^{13}C\{^1H\}$ NMR data for **3a** ($C_6D_6$, 270 MHz): $\delta$ 219.2 (Zr*C*NMe), 170.1, 166.0 (*C*=$NCMe_3$). $^1H$ NMR spectrum of **3b** ($C_7D_8$, 270 MHz): $\delta$ 5.43 ($C_5H_5$), 3.26 ($NCH_3$), 2.11 ($CCH_2Si$), 1.42, 1.35 ($NCMe_3$), 0.31 ($SiMe_2$), −0.56 ($HfCH_2Si$). $^{13}C\{^1H\}$ NMR data for **3b** ($C_7D_8$, 270 MHz): $\delta$ 223.8 (Hf*C*NMe), 170.1, 168.1 (*C*=$NCMe_3$).

[11] Preparation of **4a,b**: Because no reaction is observed between **2a,b** and excess $CNCMe_3$ under ambient conditions, the use of higher pressure to promote the insertion of additional equivalent(s) of $CNCMe_3$ was investigated. A solution containing 200 mg of **1a,b** and 5 equiv of $CNCMe_3$ in 5 mL of toluene was added to a 5-mL Teflon cylinder. The reaction vessel was capped under argon, and the solution was pressurized at 12 kbar (Andreas Hofer 14-kbar autoclave). After removal of the solvent, the product residue was washed twice with pentane and dried in vacuo. **4a**: yield 250 mg; IR (KBr) $\nu$ 1956 (C=C=N), 1611 (C=N) cm$^{-1}$; $^1H$ NMR ($C_6D_6$, 200 MHz) $\delta$ 5.94, 5.89 ($C_5H_5$, s), 1.97, 1.90 ($CCH_2Si$, AB system, $^2J_{H-H}$ = 14 Hz), 1.32, 1.27, 1.20 ($NCMe_3$, s), 0.34, 0.32 ($SiMe_2$, s), −0.17, −0.23 ($ZrCH_2$, AB system, $^2J_{H-H} \approx 0$ Hz); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 300 MHz) $\delta$ 182.0, 167.9 (C*C*=N), 108.9, 107.3 ($C_5H_5$), 75.9 (*C*=C=N), 60.2, 59.6, 55.2 (N*C*$Me_3$), 31.9, 31.6, 31.1 (NC*Me*$_3$), 27.0 (C*C*$H_2$Si), 23.1 ($ZrCH_2$), 4.9, 2.3 ($SiMe_2$). **4b**: yield 210 mg; IR (KBr) $\nu$ 1980 (C=C=N), 1616 (C=N) cm$^{-1}$; $^1H$ NMR ($C_6D_6$, 200 MHz) $\delta$ 5.93, 5.92 ($C_5H_5$, s), 2.01, 1.91 ($CCH_2Si$, AB system, $^2J_{H-H}$ = 12 Hz), 1.34, 1.32, 1.18 ($NCMe_3$, s), 0.34, 0.20 ($SiMe_2$, s), −0.50, −0.56 ($HfCH_2$, AB system, $^2J_{H-H} \approx 0$ Hz); $^{13}C\{^1H\}$ NMR ($C_6D_6$, 300 MHz) $\delta$ 186.5, 168.7 (C*C*=N), 110.5, 109.9 ($C_5H_5$), 81.9 (*C*=C=N), 59.77, 59.75, 55.1 (N*C*$Me_3$), 32.1, 31.2, 30.7 (NC*Me*$_3$), 27.9 (C*C*$H_2$Si), 27.0 ($HfCH_2$), 4.9, 1.9 ($SiMe_2$). Anal. Calcd for $C_{29}H_{47}N_3SiHf$ ($M_r$ = 644.288): C, 54.06; H, 7.35; N, 6.52. Found (best of multiple analyses): C, 53.06; H, 7.32; N, 6.80.

[12] Crystallographic data for **4a**: monoclinic, space group $P2_1/n$, $a$ = 9.9260(6) Å, $b$ = 20.881(2) Å, $c$ = 14.843(2) Å, $\beta$ = 101.275(6)°, $V$ = 3017.1(4) Å$^3$, $Z$ = 4. The structure was solved with direct methods. Full-matrix refinement (based on $F_o^2$, SHELXL-93) of the positional and anisotropic thermal parameters for the 34 non-hydrogen atoms converged with $R(F_o)$ = 0.045 and GOF = 1.03 for 3768 unique reflections with $I > 2\sigma(I)$.

[13] The Zr–N(1) distance is comparable to the Zr–N distances for the bridging imido ligands in $[Cp_2Zr{=}N(C_6H_4(4\text{-}t\text{-}Bu))]_2$[14] and reflects $\pi$ donation from the in-plane N 2p orbital into the vacant hybridized Zr $a_1$ orbital.

[14] Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

sponding bonds in **2a**. The C(1)–C(9) and C(9)–N(2) bond distances of 1.339(5) and 1.206(5) Å, respectively, and the nearly linear C(1)–C(9)–N(2) bond angle of 168.1(4)° are consistent with a ketenimine geometry[15] about C(9). The heating of **4a,b** proceeds with slow loss of 1 equiv of $CNCMe_3$ and the complete formation of **2a,b** within 8 h (50 °C) and 74 h (60 °C), respectively. The steric bulk of the *tert*-butyl substituent of the ketenimine fragment presumably inhibits **4a,b** from rearranging to the corresponding $\eta^2$-iminoacyl diimine analogues of **3a,b**. Future studies will be directed at performing high-pressure reactions of **2a,b** with less sterically demanding isocyanides to investigate their ability to promote the construction of larger iminomethylene oligomers $(>C{=}NR)_n$[16] through the sequential C,C-coupling of isocyanide monomers.

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**Supplementary Material Available:** Tables of crystallographic data, positional and temperature parameters, and interatomic distances and bond angles for **4a** (10 pages). Ordering information is given on any current masthead page.

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(15) The dihedral angle for the N(1), C(1), C(2) and C(9), N(2), C(10) planes is 81.1°.

(16) (a) Kramer, P. C. J.; Clej, M. C.; Nolte, R. J. M.; Harada, T.; Hezemans, M. F.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 1581. (b) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7926.