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Photochemical Reaction of 16-e Metal Species Generated from $Fe(CO)_5$, $Cr(CO)_6$, or $RCpMn(CO)_3$ (R = H, Me), with Primary and Secondary Arylsilanes in the Presence of Internal or External Electron Donors: Formation of Functionally Stabilized Hydrosilanediyl–Transition Metal Complexes

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Summary: Functional hydrosilanediyl–transition metal complexes, $ArSi(D)H{=}ML_n$ (with D = Lewis base), are obtained, in excellent yield, by the photochemical coupling reaction of $ArSiH_3$ with $Fe(CO)_5$, $Cr(CO)_6$, or $RCpMn(CO)_3$ (R = H, Me), in the presence of either internal (D = [(N,N-dimethylamino)methyl]phenyl group) or external (D = N,N-dimethylimidazolidinone) nucleophiles. Unexpectedly, the Lewis base character of N,N-dimethylimidazolidinone (DMI) is strong enough to quantitatively convert dimeric $[Fe_2(CO)_8(SiPh_2)_2]$ to the more stable $[Ph_2Si(DMI){=}Fe(CO)_4]$.

Transition metal–silanediyl complexes have been proposed as reaction intermediates to account for a number of chemical transformations of organosilicon compounds mediated by metals.[1] Of particular interest are the primary silanes, $RSiH_3$, from which it is possible to generate oligomeric polysilanes.[2] These reactions are rather complex, but in some cases, silanediyl–transition metal species have been isolated.[3] Transition metal carbonyl-induced cross-links are also effective in the case of hydridopolysilanes.[4]

Our current interest in the intramolecular nucleophilic stabilization of low coordinate silicon species[5] led us to investigate the chemical behavior of silanediyl–transition metal complexes stabilized by intramolecular aminoaryl groups.[6] The external Lewis base stabilization of silanediyl–transition metal complexes is well documented,[1a,b,3] but only a few examples have been reported concerning the intramolecular stabilization of such species.[7] Here, we describe new donor-stabilized silanediyl complexes with Si–H functionality,[8] easily obtained through the insertion/coupling reaction[1c,9] of primary silanes with photochemically generated 16-e metal carbonyls.

Addition of pentacoordinated [2-[(N,N-dimethylamino)methyl]phenyl]trihydrosilane, **1**, to $Fe(CO)_5$, $RCpMn(CO)_3$ (R = Me, H), or $Cr(CO)_6$, in degassed pentane under UV irradiation with a 450-W medium-pressure Hg lamp for 5–6 h at room temperature, afforded the transition metal–silanediyl complexes **2**–**5**[10] (Scheme I). The ^1H NMR spectrum of [[2-[(dimethylamino)methyl]phenyl]silanediyl]chromium(0) pentacarbonyl **5**, shows two signals for the diastereotopic NMe_2 and an AB system for the NCH_2 group. No coalescence is observed up to 105 °C, neither for the NMe_2 group nor for the ($N{-}CH_2$) AB system, showing that the NMe_2 substituent is strongly coordinated to the silicon atom ($\Delta G^* > 95$ kJ mol^{-1}).[6,7g] ^{13}C NMR spectra of **2**–**5** also show the presence of two diastereotopic methyl signals for the NMe_2 groups. The ^{29}Si NMR spectra present only doublets by the DEPTC technique. The chemical shifts, measured at 20 °C, respectively 105.2 ppm (**2**), 131.6 ppm (**3**), 131.9 ppm (**4**), and 110.9 ppm (**5**), are in the range expected for such species.[1,6,7,12] The reso-

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nances are shifted slightly downfield, with increasing temperature, for example, varying for the compound **5** from 108.4 ppm at 233 K to 112.6 ppm at 333 K.

Extension of the 16-e transition metal carbonyl complex insertion process to the preparation of external Lewis base-stabilized silanediyl complexes represents a challenge. Ph_2SiH_2, **6**, is known to react with $Fe(CO)_5$ under UV irradiation to afford air-sensitive yellow-orange crystals of a μ-diphenylsilanediyl–iron carbonyl complex, **7**.[13] Liu et al. have described the conversion of such a disiladiferrocycle to a monomeric Fe–silanediyl complex with donor solvent complexation.[14]

We have found that dimer **7** is cleaved in the presence of *N,N*-dimethylimidazolidinone (DMI),[15] affording the Lewis base-stabilized, monomeric silanediyl-iron complex **8**. If the photochemical coupling reaction of **6** with $Fe(CO)_5$ is performed in the presence of DMI, **8** is obtained directly in 93% yield. Only one signal at 91.3 ppm is observed in the ^{29}Si NMR spectrum of the crude mixture, after washing with pentane and dissolving the oil in toluene.[16]

The silanediyl–iron complex **8** displays a reactivity different from that of **7** (Scheme II). The photochemical degradation of **8** in the presence of a typical trapping agent[17] for diphenylsilanediyl afforded products **9–12**, the spectroscopic properties of which were compared with those of authentic samples.[18-20] Compound **9** is the expected trapping product of the free silanediyl with *tert*-butanol, but compound **10** either could be the direct product of methanolysis of complex **8** or could result from the consecutive methanolysis of $Ph_2SiHOMe$ in the presence of excess methanol. Irradiation of **8** with an excess of 2,3-dimethyl-1,3-butadiene afforded the trapping product **11**, 3,4-dimethyl-1,1-diphenyl-1-silacyclopentene[18,19] (62% yield), and (2,3-dimethylbutadiene)iron tricarbonyl[17e,20] (67%). The silole, **12**, was isolated similarly (37% yield), in the photochemical reaction of **8** with an excess of 3-hexyne.[21]

The external Lewis base activation with DMI has been used to obtain the first external donor-stabilized iron complexes of organohydrosilanediyls, $ArSi(DMI)H{=}Fe(CO)_4$, **15** (Ar = Ph), **16** (Ar = 1-Np). The ^{29}Si NMR spectra (DEPTC, toluene/C_6D_6) show only doublets for the monomeric hydridosilanediyl–iron species ($^1J_{SiH}$ = 199 Hz for **15**, $^1J_{SiH}$ = 218 Hz for **16**).[23] As in the case of intramolecularly coordinated compounds **2–5**, the ^{29}Si

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(10) A solution of [2-[(*N,N*-dimethylamino)methyl]phenyl]trihydrosilane, **1**[11] (3.30 g, 0.02 mol), in pentane (350 mL) was transferred under argon into a quartz vessel of 500 mL containing 2.63 mL (0.02 mol) of $Fe(CO)_5$. This mixture was irradiated at room temperature for 5–6 h. A dark-red thick oil started precipitating after 15 min. The progress of the reaction was monitored by IR. After complete disappearance of silane **1**, pentane was removed with a cannula, and the dark-red oil, [[2-[(dimethylamino)methyl]phenyl]silanediyl]iron(0) tetracarbonyl, **2**, was washed two/three times with pentane. The same procedure and stoichiometric quantities of reactants were used for the preparation of complexes **3–5**, but in the case of complexes **8**, **15**, and **16**, DMI (2.19 mL, 0.02 mol) was added to **6**, **13**, and **14**, before the transfer into the quartz reactor containing $Fe(CO)_5$. ^1H NMR spectra of compounds **2** and **3**, could not be obtained due to the presence of paramagnetic impurities. Only broad signals were observed at all temperatures. **Compound 1**, [2-[(dimethylamino)methyl]phenyl]trihydrosilane. Anal. Calcd for $C_9H_{15}NSi$: C, 65.46; H, 9.09; N, 8.48; Si, 16.98. Found: C, 65.36; H, 9.12; N, 8.49; Si, 16.96. ^1H NMR ($CDCl_3$): δ 2.13 (N–CH_3), 3.48 (CH_2–N), 4.14 (SiH_3), 6.8–7.2 (m), 7.6–7.8 (m) aromatics. ^{13}C NMR ($CDCl_3$): δ 43.96 (N–CH_3), 63.64 (CH_2–N), 125.69, 129.51, 138.89, 146.17 (aromatics). ^{29}Si NMR ($CDCl_3$): δ −71.62 (INVGATE), −71.48 (DEPTC), $^1J(^{29}Si-^1H)$ = 199.2 Hz. IR ($CDCl_3$): $\nu(SiH_3)$ 2144 (d), 2061 cm^{-1} (s). **Compound 2**, [[2-[(dimethylamino)methyl]phenyl]silanediyl]iron(0) tetracarbonyl. Anal. Calcd for $C_{13}H_{13}NO_4SiFe$: C, 47.14; H, 3.92; N, 4.23. Found: C, 47.18; H, 3.86; N, 4.24. ^{13}C NMR ($CDCl_3$): δ 47.12 (NCH_3), 48.16 (NCH_3), 67.86 (NCH_2) 124.00, 124.08, 131.45, 131.66, (C_6H_4), 214.17, 215.05 (CO, 2s). ^{29}Si NMR (toluene/C_6D_6): δ +105.2 (INVGATE), +105.63 (DEPTC, $^1J(^{29}Si-^1H)$ = 180 Hz). MS (EI, 70 eV): *m/e* (relative intensity, %) 331 (M^+, 0.8), 135 (32), 118 (10), 91 (35), 57 (100) IR (toluene, cm^{-1}): ν(CO, SiH) 1924 (br), 1964 (s), 2040 (s). **Compound 3**, [[2-[(dimethylamino)methyl]phenyl]silanediyl](η^5-methylcyclopentadienyl)manganese dicarbonyl. Anal. Calcd for $C_{17}H_{20}NO_2SiMn$: C, 57.79; H, 5.66; N, 3.96. Found: C, 57.82; H, 5.95; N, 3.98. ^{29}Si NMR (toluene/C_6D_6): δ +131.6 (INVGATE), $^1J(^{29}Si-^1H)$ = 149 Hz (DEPTC). ^{13}C NMR (20 °C, toluene/C_6D_6): δ 14.87 (CP–CH_3), 46.28 (N–CH_3), 47.62 (N–CH_3), 68.91 (N–CH_2), 79.04, 79.12, 80.64, 81.03 (C_5H_4), 93.03 (C–CH_3), 123.96, 134.27, 140.24, 145.59 (aromatics), 233.11, 233.54 (2s, C0). ^{13}C NMR (90 °C, toluene-d_8): no change, except that the two carbonyls give one broad signal at δ 233.08. IR (toluene, cm^{-1}): ν(CO, SiH) 1971, 1904, 1838.5. MS (EI, 70 ev) *m/e* (relative intensity, %) 353 (M^+, 19), 297 (100), 218 (21), 162 (87), 134 (18), 91 (85), 79 (58). **Compound 4**, [[2-[(dimethylamino)methyl]phenyl]silanediyl](η^5-cyclopentadienyl)manganese dicarbonyl. Mp: 136 °C dec. Anal. Calcd for $C_{16}H_{18}NO_2SiMn$: C, 56.63; H, 5.30; N, 4.12. Found: C, 56.72; H, 5.39; N, 4.18. ^{29}Si NMR (toluene/C_6D_6): δ +130.89 (INVGATE), $^1J(^{29}Si-^1H)$ 156.8 Hz (DEPTC). IR (C_6D_6, cm^{-1}): ν(CO, SiH), 1974.4, 1910.3, 1837.6. ^1H NMR (C_6D_6): δ 2.11–1.77 (N–CH_3, 2 br s, 6H), 3.91 (br, N–CH_2), 4.47 (Cp–H), 6.18 (Si–H), 6.84. 7.09, 7.79 (aromatics). ^{13}C NMR (C_6D_6): δ 46.05, 47.50 (2 br s, 2N–CH_3), 68.77 (s, N–CH_2), 80.16 (s, C_5H_5), 123.7–145.4 (C–aromatics), 232.6, 233.7 (CO). **Compound 5**, [[2-[(dimethylamino)methyl]phenyl]silanediyl]chromium(0) pentacarbonyl. Yellow solid. Mp: 163–164 °C. Anal. Calcd for $C_{14}H_{13}NO_5SiCr$: C, 47.32; H, 3.66; N, 3.94. Found: C, 47.53; H, 3.96; N, 4.02. ^1H NMR (C_6D_6): δ 1.85 (N–CH_3), 1.95 (N–CH_3), 2.65–2.73, 3.22–3.30 (N–CH_2) (AB system), 5.68 (s, Si–H), 6.7, 7.08, 8.08 (aromatics). ^{13}C NMR (C_6D_6): δ 45.28 (N–CH_3), 48.43 (N–CH_3), 69.59 (N–CH_2), 123.63, 134.17, 140.19, 142.28 (aromatics) 221.72, 225.51 (CO). ^{29}Si NMR (C_6D_6): δ +110.94 (INVGATE), 110.82 (DEPTC), $^1J(^{29}Si-^1H)$ = 162.35 Hz. IR (toluene, cm^{-1}): ν(CO, SiH) 1914 (br), 1978, 2042.

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(16) Compound **7**:[13] ^{29}Si (C_6D_6): δ +111.0. IR (Nujol, cm^{-1}): ν(CO) 2040, 2005, 1941. Mass spectrum: parent ion concentrated at *m/e* 700, followed by successive loss of eight carbonyl groups. **Compound 8** (Diphenylsilanediyl)iron(0) tetracarbonyl–DMI. Anal. Calcd for $C_{21}H_{20}N_2O_5SiFe$: C, 54.31; H, 4.31; N, 6.03. Found: C, 54.48; H, 4.49; N, 6.12. ^1H NMR ($CDCl_3$): δ 4.18 (bs, 6H, 2NCH_3), 6.18 (s, 4H, 2NCH_2), 7.01–7.98 (m, 10H, ArH). [For uncoordinated DMI: ^1H NMR ($CDCl_3$) δ 2.70 (s, 2NCH_3), 3.25 (s, 2NCH_2)]. ^{13}C NMR ($CDCl_3$): δ 28.63 (NCH_3), 48.12 (NCH_2), 125.35–143.44 (ArC–), 161.6 (>C═O), 217.59 (CO). MS (EI, 70 ev) *m/e* (relative intensity, %). 437 (M^+ − CO, 100), 396 (0.6), 361 (18), 317 (10), 182 (15), 154 (10), 114 (60). ^{29}Si NMR (toluene/C_6D_6): δ +91.30. IR ($CDCl_3$, cm^{-1}): ν 1688 (>C═O), 2019, 1995 (CO).

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(18) Freshly prepared **8** (4.64 g, 0.01 mol) was dissolved in 350 mL of toluene, and the solution was transferred to a 500-mL quartz vessel. 2,3-Dimethyl-1,3-butadiene (11.4 mL, 0.1 mol) was added, and the mixture was irradiated at 22 °C for 5 h. Toluene was evaporated under vacuum, and the black-red product was chromatographed on a Florisil (33 × 2 cm) column. Product **11**[19] was isolated in pentane/ether (80/20) as the first fraction in 62% yield. The second fraction contained (2,3-dimethylbutadiene)iron tricarbonyl[17e,20] (yield 67%).

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(21) A similar photochemical trapping experiment,[18] with an excess of 3-hexyne afforded 2,3,4,5-tetraethyl-1,1-diphenyl-1-silacyclopenta-2,4-diene, **12**,[22] in 37% yield, following chromatography on Florisil.

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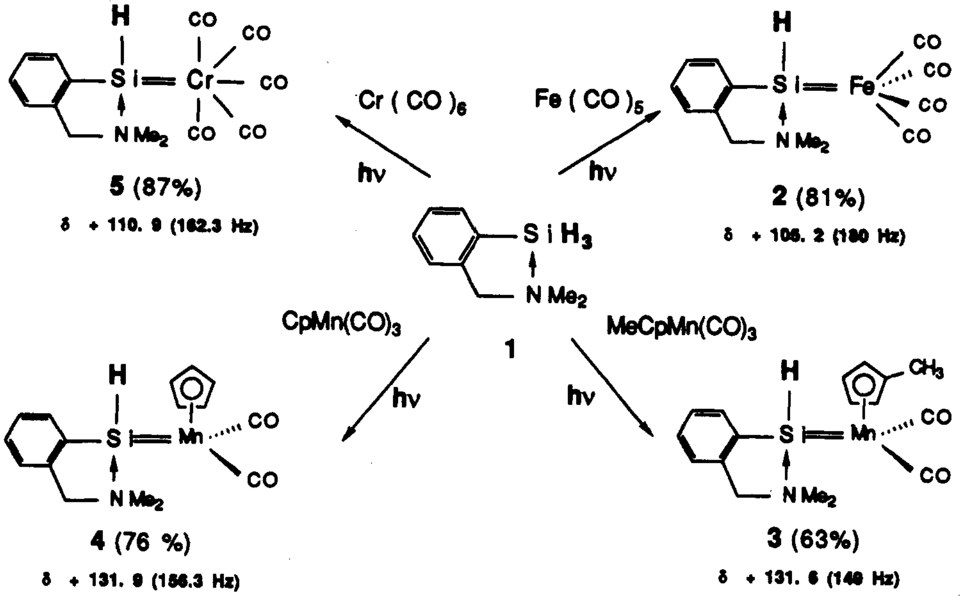
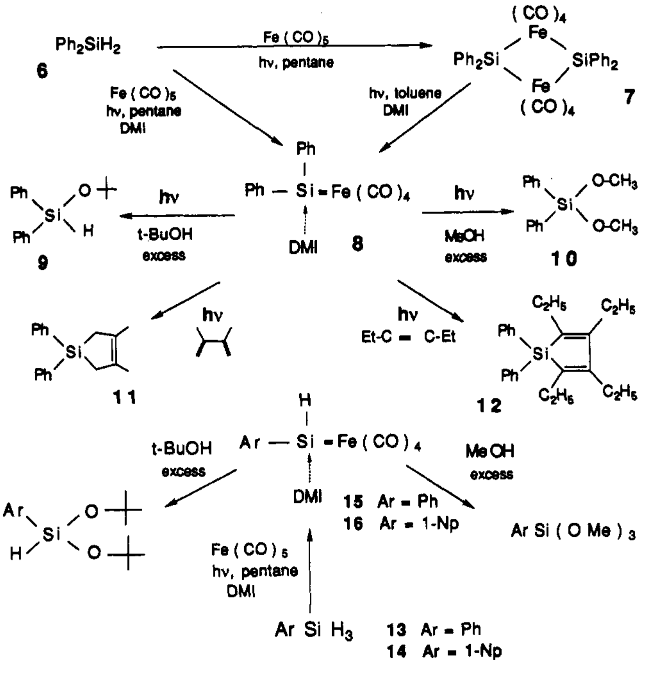
Scheme I. Photolysis of Compound 1 with Transition Metal Carbonyls[a,b]



[a] Reactions performed at 25 °C, for 5 h, in pentane. Isolated yields of the products are given in parentheses.[b] ^{29}Si NMR chemical shifts, with ^{1}J(Si–H) coupling constants in brackets.

Scheme II. Synthesis and Reactivity of Compounds 8, 15, and 16, Obtained upon Photolysis of 6, 13, and 14 in the Presence of *N,N*-Dimethylimidazolidinone, $CH_3N(CO)N(CH_3)CH_2CH_2$ (DMI)



NMR chemical shifts of 15 and 16 move linearly downfield with increasing temperature, but Δδ is even less significant, for example, the δ value changing in the case of compound 15 from +83.19 ppm at 233 K to +84.53 ppm at 313 K. Reaction of 15 and 16 with methanol or *tert*-butanol in excess at room temperature for 1 h caused the cleavage of the Si–Fe bonds to give quantitatively aryltrimethoxy- and aryldi-*tert*-butoxysilanes.

The intramolecular nucleophilic stabilization of hydridosilanediyl complexes 2–5 was expected, in view of the results obtained in the cases of zwitterionic silanethione[5b] and silaphosphene,[6a] both of which were stabilized by intramolecular coordination of an aminoaryl group. Extension of the 16-e transition metal carbonyl insertion reaction to primary organosilanes, leading directly to Lewis base-stabilized silanediyl complexes with a Si–H bond functionality, represents a significant advance, and we expect a wide variety of applications.

We are currently examining the influence of Lewis bases upon the stability of the silanediyl–transition metal carbonyl complexes through a study of the physical properties of the Si–H bond, as well as the reactivity of these complexes with electrophiles and nucleophiles.

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(23) **Compound 15,** (phenylsilanediyl)iron(0) tetracarbonyl (DMI). Yield of isolated product: 61%. Anal. Calcd for $C_{15}H_{16}FeN_2O_5Si$: C, 46.39; H, 4.12; N, 7.21. Found: C, 46.40; H, 4.08; N, 7.16. ^{13}C NMR ($CDCl_3$): δ 29.87 (NCH_3), 46.97 (NCH_2), 127–142 (ArC–), 159.28 (>C=O), 215.62, 216.34 (CO). ^{29}Si NMR (toluene/C_6D_6): δ +83.52 (INVGATE), 84.02 (DEPTC), $^{1}J(^{29}Si–^{1}H)$ = 199 Hz. IR (toluene, cm^{-1}): ν 1708 (>C=O), 1889, 1904, 1998, 2032 (CO, SiH). **Compound 16,** (1-naphthylsilanediyl)iron(0) tetracarbonyl (DMI). Yield: 58%. Anal. Calcd for $C_{19}H_{18}FeN_2O_5Si$: C, 52.05; H, 4.10; N, 6.39. Found: C, 52.13; H, 4.12; N, 6.42. ^{29}Si NMR (toluene/C_6D_6): δ +81.51 (INVGATE), +82.20 (DEPTC), $^{1}J(^{29}Si–^{1}H)$ = 218.6 Hz. IR (toluene, cm^{-1}): ν 1711 (>C=O, br), 1890, 1997, 2025 (CO, SiH). MS (EI, 70 ev): *m/e* (relative intensity, %). 439 (M^+, 1) 411 (M^+ – CO, 0.5), 359 (0.5), 331 (0.4), 290 (0.8), 239 (0.8), 114 (100).