New Investigations in Silanediyl Complex Chemistry: Synthesis, Structure, and Bonding of 1-Metalla-2-sila-1,3-dienes

Markus Weinmann,[†] Gerd Rheinwald, Laszlo Zsolnai,[‡] Olaf Walter,[‡] Michael Büchner,[‡] Berthold Schiemenz,[‡] Gottfried Huttner,[‡] and Heinrich Lang*,§

Technische Universität Chemnitz, Institut für Chemie, Lehrstuhl Anorganische Chemie, Strasse der Nationen 62, D-09107 Chemnitz, Germany

Received January 21, 1998

The synthesis and chemical behavior of the intra- and intermolecular donor-stabilized silanediyl complexes ($C_6H_4CH_2NMe_2$ -2)(Cl)Si=ML_n (**4**, ML_n = Cr(CO)₅ **5**, ML_n = Fe(CO)₄), $(C_6H_5HC=CH)(Cl)Si=ML_n \cdot OP(NMe_2)_3$ (21, $ML_n = Cr(CO)_5$; 22, $ML_n = Fe(CO)_4$), and $(C_6H_5-CH)(Cl)Si=ML_n \cdot OP(NMe_2)_3$ HC=CH)(C₆H₅)Si=Fe(CO)₄·OP(NMe₂)₃ (23) is discussed. Nucleophilic substitution of the chloro atom in compounds 4 and 5 by different nucleophiles leads to a great variety of further functionalized silanediyl complexes of the type $(C_6H_4CH_2NMe_2-2)(R)Si=ML_n (ML_n = Cr (CO)_5$: 7, R = CH₃; 9, R = C₆H₅; 11, R = P(C₆H₅)₂; 13, R = CH=CH₂. ML_n = Fe(CO)₄: 14, $R = CH = CH_2$; 15, $R = CH_3$). Moreover, the 1-metalla-2-sila-1.3-dienes ($C_6H_4CH_2NMe_2$ -2)- $(H_2C=CH)Si=ML_n$ (13, $ML_n = Cr(CO)_5$; 14, $ML_n = Fe(CO)_4$) can be prepared by treatment of the hypervalent dichlorosilane ($C_6H_4CH_2NMe_2$ -2)($H_2C=CH$)SiCl₂ (19) with the carbonylate dianions ML_{p}^{2-} (**2**, $ML_{p} = Cr(CO)_{5}$; **3**, $ML_{p} = Fe(CO)_{4}$). Additionally, compounds of the latter type are accessible by photochemical coupling reactions of the pentavalent silane (C₆H₄-CH₂NMe₂-2)(CH₃)SiH₂ (16) with the transition-metal carbonyls Cr(CO)₆ (17a), Fe(CO)₅ (17b), and $(\eta 5-C_5H_5)Mn(CO)_3$ (**17c**), respectively. The intermolecular donor-stabilized 1-metalla-2-sila-1,3-dienes 21-23 can be prepared by the reaction of tetravalent dichlorosilanes [(R)-(H)C=CH](R')SiCl₂ (**20a**, R = H, R' = Cl; **20b**, R = R' = C₆H₅) with the carbonylmetalates 2 and 3 and in the presence of OP(NMe₂)₃.

Introduction

Recently, we reported about the synthesis and reaction chemistry of the acyclic heterobutadienes (C₆H₄- $CH_2NMe_2-2)(H_2C=CH)Si=S$ (type **A** molecule)¹ and $(C_6H_2O^tBu_3-2,4,6)(RHC=CH)P=M_0(\eta^5-C_5H_5)(CO)_2$ (type) **B** molecule) (R = H, singly bonded organic ligand).^{2,3} The latter compounds show a versatile reaction chemistry, both at the organometallic as well as at the organic π -system.^{3,4}

Molecules of structural type **B** can formally be separated into an electron sextet species, the phosphenium ion fragment $(R)(R')P^+$ (R, R' = singly bonded organic



ligand), and the anionic transition-metal fragment ML_n^{-1} with a total of 16 valence electrons. In terms of the concept of the isolobal rules,⁵ these building blocks are equivalents of e.g. carbenes, silenes, and d⁶ ML₅ or d⁸ ML_4 transition-metal fragments (L = two-electron donor ligands). Replacement of the ionic $(R)(R')P^+$ and $ML_n^$ entities in type **B** molecules by neutral (R)(R')Si and ML_n moieties produces the corresponding acyclic 1-metalla-2-sila-1,3-dienes of structural type C.⁶



In this study, we focus on different possibilities for the preparation of inter- and intramolecular donor-

^{*} E-mail: heinrich.lang@chemie.tu-chemnitz.de.

[†] Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium, Heisenbergstra β e 5, D-70563 Stuttgart, Germany.

E-mail: weinmann@aldix.mpi-stuttgart.mpg.de. [‡] Universität Heidelberg, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany. [§] Dedicated to Prof. Dr. Manfred Weidenbruch on the occasion of

his 60th birthday.

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stabilized heterobutadienes of structural type **C**: (i) reaction of tetra- and pentacoordinated alkenyl-substituted chlorosilanes with carbonylate dianions and (ii) treatment of chloro-functionalized silanediyl complexes with alkenylmagnesium bromides. Likewise, the reaction of $(C_6H_4CH_2NMe_2-2)(Cl)Si=ML_n$ with various organic nucleophiles is described.

Results and Discussion of Reaction Chemistry

1. Synthesis of Intramolecular Donor-Stabilized Silanediyl Complexes. The synthesis of the chloro-functionalized silanediyl compounds ($C_6H_4CH_2NMe_2$ -2)-(Cl) Si=ML_n (**4**, ML_n = Cr(CO)₅;⁸ **5**, ML_n = Fe(CO)₄) proceeds by treatment of ($C_6H_4CH_2NMe_2$ -2)SiCl₃ (**1**)⁷ with the carbonylmetallates K₂[Cr(CO)₅] (**2**) and Na₂-[Fe(CO)₄] (**3**), respectively. The yield of **4** is 53%, and that of **5** is 49%.



While **4** can best be synthesized in tetrahydrofuran solutions at -30 °C, it is of major importance that the preparation of **5** has to be carried out in diethyl ether. Changing the solvent in the synthesis of **5** has a significant influence on the appropriate workup: in tetrahydrofuran only dark-colored oils can be separated, which always contain traces of paramagnetic materials. This can be avoided when diethyl ether is used as solvent; after crystallization from diethyl ether/*n*-pentane, compound **5** can be obtained as a pale red solid.

Compounds **4** and **5** provide the constituents for the preparation of further functionalized silanediyl complexes, as depicted in Scheme 1. The reaction of **4**⁸ with LiR (**6**, R = CH₃; **8**, C₆H₅; **10**, R = P(C₆H₅)₂) or BrMgCH=CH₂ (**12**) produces in tetrahydrofuran at -70

°C the intramolecular donor-stabilized silanediyl complexes ($C_6H_4CH_2NMe_2$ -2)(R)Si=Cr(CO)₅ (**7**, R = CH₃;⁹ **9**, R = C₆H₅;^{9,10} **11**, R = P(C₆H₅)₂; **13**, R = CH=CH₂).

When the same reaction conditions are applied for the preparation of the intramolecular donor-stabilized silanediyl compounds ($C_6H_4CH_2NMe_2-2$)(R)Si=Fe(CO)₄ (**14**, R = CH=CH₂; **15**, R = CH₃), a multitude of different reaction products are formed. However, pure



14 and **15** could not be isolated, by either chromatography or crystallization methods. When the solvent is changed from tetrahydrofuran to diethyl ether, compounds **14** and **15** are easily accessible.

Moreover, an efficient possibility for the synthesis of intramolecular donor-stabilized silanediyl complexes is given by the photochemically induced dehydrogenative coupling of 16-valence-electron transition-metal fragments, generated from ML_n(CO) (**17a**, ML_n = Cr(CO)₅; **17b**, ML_n = Fe(CO)₄; **17c**, ML_n = Mn(η^{5} -C₅H₅)(CO)₂), with e.g. hypervalent (C₆H₄CH₂NMe₂-2)(CH₃)SiH₂ (**16**). This type of reaction was first described by Corriu and co-workers for (C₁₀H₆CH₂NMe₂-1,8)(C₆H₅)Si=ML_n (ML_n

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= Fe(CO)₄, $(\eta^5$ -C₅H₅)Mn(CO)₂].¹¹ The decisive disadvantage of this reaction is that it cannot be applied to the synthesis of the heterobutadienes **13** and **14**, since in each case polymerization of the alkenylsilanes occurs.

A further synthetic route for the preparation of acyclic 1-metalla-2-sila-1,3-dienes is given by the reaction of $(C_6H_4CH_2NMe_2-2)(H_2C=CH)SiCl_2$ (**19**) with an equimolar amount of $K_2[Cr(CO)_5]$ (**2**) or $Na_2[Fe(CO)_4]$ (**3**). Appropriate workup produces the heterobutadiene **13** or **14** in 43% or 35% yield.



2. Synthesis of Intermolecular Donor-Stabilized Silanediyl Complexes. Acyclic intermolecular donorstabilized heterobutadienes can be synthesized according to a method first described by Zybill and coworkers¹² on treatment of (RHC=CH)(R')SiCl₂ (**20a**, R = H, R' = Cl; **20b**, R = R' = C₆H₅) with the carbonylmetalates **2** and **3** in the presence of $[(CH_3)_2N]_3PO$ (HMPT; =Do) in tetrahydrofuran at -30 °C. After appropriate workup, the 1-metalla-2-sila-1,3-dienes **21**– **23** are obtained in 35–60% yield as yellow (**21**) or red (**22, 23**) solids.



The purification of all synthesized intramolecular as well as intermolecular donor-stabilized silanediyl complexes has to be performed by crystallization from

Table 1.Selected NMR Data for Compounds 4, 7,9, 11, 13–15, and 18

compd	$CH_2(\delta)$	$^{2}J_{\mathrm{HH}}$ (Hz)	$NCH_3(\delta)$	$NCH_3(\delta)$	²⁹ Si (δ)
4 ⁸	3.81, 4.68	13.4	2.66, 2.98	45.8, 46.6	120.4
5	4.45^{a}	15.0	2.50, 2.70	46.9, 48.2	\mathbf{nd}^d
7^{9}	2.61, 3.29	14.2	1.74, 1.97	43.6, 46.4	124.6
$9^{9,10}$	3.77, 3.95	13.9	2.66, 2.83	47.0, 48.8	116.9
11	3.81, 4.90	13.9	2.89, 3.25	45.2^{b}	nd
13	3.90, 4.46	14.7	2.84, 2.96	45.9, 47.9	114.9
14	2.75, 3.36	14.4	1.99, 2.02	45.1, 46.8	116.8
15^{10a}	2.87, 3.31	14.5	1.97, 2.10	44.6, 47.1	127.2
18	3.99 ^c	8.6	2.71, 2.90	39.8, 48.6	nd

^{*a*} One of the CH₂ resonance signals is masked by the resonance signal of the solvent. ^{*b*} Broad resonance signal. ^{*c*} One of the CH₂ resonance signals is masked by the resonance signal of the cyclopentadienyl protons. ^{*d*} nd = not determined.

tetrahydrofuran/*n*-pentane (4, 7, 9, 11, 13, 21–23) or diethyl ether/*n*-pentane (5, 14, 15, 18) solutions at -30°C. When chromatographic methods are applied, an irreversible fixation of the appropriate silanediyl complexes on the surface of most common chromatographic materials is observed. All compounds synthesized are soluble in most common polar organic solvents and are extremely sensitive to oxygen and moisture in the solid state as well as in solution.

3. Structure and Bonding. The most suitable analytical method for the characterization of the synthesized silanediyl compounds is ²⁹Si NMR spectroscopy. In comparison with those of their starting materials, the resonance signals of the silanediyl complexes **4**, **7**, **9**, **13–15**, **18**, and **21–23** are significantly shifted to lower field.^{8–13} The ²⁹Si resonance signals of the intramolecular donor-stabilized silanediyls **4**, **7**, **9**, **13–**15, and **18** are shifted thereby to a lower field (115–127 ppm) than the intermolecular $[(CH_3)_2N]_3PO$ -stabilized molecules **21–23** (75–84 ppm), due to their electron donating capability being lower than that of HMPT. On the other hand, the shifting of the ²⁹Si resonance signal chemical shift seems to be almost independent of the transition-metal moiety (Fe(CO)₄ or Cr(CO)₅) present (Table 1).

The most striking feature of the ¹H NMR spectra of **4**, **7**, **9**, **11**, and **13–15** is the appearance of two resonance signals for the methyl groups of the NMe₂ entity in the region of 2.0–3.3 ppm and an AB resonance pattern between 2.7 and 4.9 ppm with coupling constants of ${}^{2}J_{\text{HH}} = 13-16$ Hz for the methylene protons of the *built-in* arm Me₂NCH₂ (Table 1), indicating that both the methylene protons and the Me groups of the NMe₂ entity as well are diastereotopic. As a typical example, the ¹H NMR spectrum of **13** is depicted in Figure 1.

Neither for the NMe₂ nor for the NCH₂ protons is coalescence observed up to 115 °C. This confirms that the lone pair of electrons at the nitrogen atom of the C₆H₄CH₂NMe₂-2 ligand is strongly bonded to the silicon atom. The appearance of two resonance signals in the range of 44–48 ppm in the ¹³C{¹H} NMR spectra also confirms magnetically inequivalent amino methyl groups (Table 1). In contrast, for the complex (C₆H₄CH₂NMe₂-2)(C₆H₅)Si=Cr(CO)₅ a coalescence temperature of 95 °C was measured, while (C₆H₄CH₂NMe₂-2)₂Si=Cr(CO)₅ is

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Figure 1. ¹H NMR spectrum of $(C_6H_4CH_2NMe_2-2)(H_2C=CH)Si=Cr(CO)_5$ (13).

dynamic at 25 °C.⁷ This behavior is different from that of **13** and can be explained by the fact that the H₂C= CH group in **13** is a weaker π -donor toward the silicon atom.

The IR data in the ν (CO) region for compounds **5**, **14**, **15**, **22**, and **23** are in agreement with the trigonalbipyramidal coordination sphere around the iron center. The appearance of three absorption bands in the region $1880-2030 \text{ cm}^{-1}$ verifies that the silanediyl unit occupies an axial position of the trigonal-bipyramidalcoordinated iron atom. This is in good agreement with theoretical studies, in which ligands with a higher donor to acceptor ratio than that of CO are always bonded in an axial position in LFe(CO)₄ complexes.¹⁴⁻¹⁶

In **4**, **7**, **9**, **11**, **13**, and **21** two very strong ν (CO) absorptions between 1880 and 1960 cm⁻¹ and one medium band in the region of 2020–2070 cm⁻¹ are found. The appearance of two frequencies for the E vibration can be explained by decreasing the local $C_{4\nu}$ symmetry of the Cr(CO)₅ moiety.^{17,18} For **18** two typically very strong vibrations are found at 1818 and 1892 cm⁻¹ for the CO entities.^{18,19}

X-ray structure determinations on selected examples of the synthesized compounds verify the molecular structures of the inter- and intramolecular donorstabilized silanediyl compounds, as already proposed from spectroscopic data. The structures of $(C_6H_4CH_2-NMe_2-2)(Cl)Si=Cr(CO)_5$ (4) and $(C_6H_4CH_2NMe_2-2)-[P(C_6H_5)_2]Si=Cr(CO)_5$ (11) are shown in Figure 2, while the molecular structure of the acyclic heterobutadienes $(C_6H_4CH_2NMe_2-2)(H_2C=CH)Si=Fe(CO)_4$ (14) and $[(C_6H_5)HC=CH](C_6H_5)Si=Fe(CO)_4$ ·OP(NMe₂)₃ (23) are

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Figure 2. ORTEP drawings (drawn at the 50% probability level) of the silanediyl complexes **4** (top) and **11** (bottom) with the atom-numbering schemes.

presented in Figure 3. Crystallographic parameters and selected geometrical details are listed in Tables 2-6.

Compound **4** crystallizes—with tetrahydrofuran as solvent molecule—in the orthorhombic space group *Pnna*

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Figure 3. ORTEP drawings (drawn at the 50% probability level) of the 1-ferra-2-sila-1,3-diene compounds **14** (top) and **23** (bottom) with the atom-numbering schemes.

and compound **11** in the monoclinic space group $P2_1/n$. In these complexes the geometrical environment around the chromium center is fixed by the arrangement of the five carbonyl ligands and the silanediyl moiety (C₆H₄-CH₂NMe₂-2)(R)Si. The latter unit is bonded to the octahedral chromium atom with a short Cr-Si bond length (4, 2.335(2) Å; 11, 2.406(1) Å; Tables 3 and 4), implying a multiple bonding character between these two atoms.⁶⁻¹³ Moreover. *ab initio* calculations for the Cr-Si bond reinforce this observation.²⁰ The difference in the Cr-Si bond lengths in 4 and 11 can best be explained by electronic effects: the $(C_6H_5)_2P$ group in 11 is a stronger donor ligand, as compared with the chlorine atom in **4**. This results in a higher electron density at the silanediyl unit, which finally leads to a weakening of the Cr-Si bond and points to a decreasing back-donation from the chromium center to the silicon atom. This finding is nicely reflected in the differences between the axial $Cr{-}C_{CO}$ distance and the average of

the equatorial Cr-C_{CO} distances (4, Cr-C_{COeq} - Cr- $C_{COax} = 0.011$ Å, **11**, $Cr-C_{COeq} - Cr-C_{COax} = 0.025$ Å; Tables 3 and 4). A further noticeable feature of compounds 4 and 11 is that the Si1-N1 bond lengths at 1.938(5) Å (4) (Table 3) and 1.996(2) (11) Å (Table 4) are shorter than those found in pentacoordinated dichlorosilanes such as $(C_6H_4CH_2NMe_2-2)(R)SiCl_2$ (R = singly bonded organic ligand), in which the CH₂NMe₂ built-in arm is datively bonded to a silicon atom^{1a} and negligibly elongated compared to covalent silicon-nitrogen bonds in hypervalent silane compounds.²¹ The siliconnitrogen distances are additionally clearly affected by the different ligands Cl and $(C_6H_5)_2P$. In comparison with the chlorine atom in 4, the more strongly electrondonating (C₆H₅)₂P group in **11** results in a longer Si-N bond. Due to the dative nitrogen coordination, the silicon atoms in molecules 4 and 11 show a distortedtetrahedral environment.

Compounds 14 and 23 crystallize in the orthorhombic space group $Pna2_1$ (14) and monoclinic space group $P2_1/n$ (23). For 14 and 23 a distorted-tetrahedral arrangement around the silicon atom is found in which the $(C_6H_4CH_2NMe_2-2)(H_2C=CH)Si$ (14) and $(C_6H_5HC=$ CH)(C_6H_5)Si entities (23) occupy an apical position in the coordination sphere of the $Fe(CO)_4(L)$ moiety (L = silanediyl fragment). The bond angles around the silicon atom in both compounds (14, Fe-Si-C11 = 120.5(1)°, Fe-Si-C15 = 117.4(1)°, Fe-Si-N = 118.7-(1)°, N-Si-C15 = 98.9(1)°; **23**, Fe1-Si1-C5 = 117.5-(1)°, Fe1-Si1-C18 = 115.8(1)°, Fe1-Si1-O5 = 109.7-(1)°, O5-Si1-C5 = 102.9(1)°) indicate that the silicon atom shows an almost trigonal-planar environment, which is typical for intra- and intermolecular donorstabilized silanediyl compounds and arises from steric interactions of the ligands at the silicon atom with the metal-bonded carbonyl groups.¹² The atoms Fe1, Si1, C5, and C6 in 23, which form the heterobutadiene framework, are in-plane bonded (maximum deviation 0.026 Å) (Figure 3). The silicon-iron moiety and the carbon-carbon unit are thereby in a cisoid configuration, and the bond lengths observed in these moieties show the typical behavior expected for butadienes and heterobutadienes. However, in compound 14 the heterobutadiene building block H₂C=CH-Si=Fe is not arranged in a cisoid configuration and the atoms which form the 1-ferra-2-sila-1,3-diene are out-of-plane bonded $(Fe-Si-C15/Si-C15-C16 = 135.6^{\circ})$. The Si=Fe bond lengths at 2.265(1) Å in 14 and 2.280(1) Å in 23 are similar to those found in other donor-stabilized silanediyl complexes of type $R_2Si=Fe(CO)_4$ (R = Cl, CH₃, O^tBu, S^tBu).¹² The Si–O distance at 1.726(2) Å in 23 implies a weak interaction between the silicon and oxygen atoms and is significantly elongated as compared to covalent Si-O bonds.²² The Si-N bond distance in 14 at 1.955(3) Å is identical with those observed in 4 and **11** and points to a partially covalent bonding situation between these two atoms.

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	4	11	14	23
formula	C ₁₆ H ₁₆ ClCrNO ₅ ₅ Si	C ₂₆ H ₂₂ CrNO ₅ PSi	C15H15FeNO4Si	C24H30FeN3O5PSi
fw	425.84	539.51	357.22	555.42
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	Pnna	$P2_{1}/n$	$Pna2_1$	$P2_1/n$
a (Å)	11.53(1)	9.637(2)	16.371(4)	11.647(5)
b (Å)	28.219(3)	26.217(6)	10.824(4)	14.911(6)
<i>c</i> (Å)	11.781(4)	10.316(2)	9.320.3	16.131(7)
β (deg)		101.03(2)		100.62(3)
$V(Å^3)$	3883(4)	2558.2(9)	1651(5)	2753(5)
Ζ	8	4	4	4
cryst dimens (mm)	$0.20\times0.20\times0.30$	$0.20\times0.25\times0.25$	$0.20\times0.30\times0.30$	$0.20\times0.20\times0.20$
density (calcd) (g cm^{-3})	1.476	1.401	1.437	1.340
diffraction model	Siemens (Nicolet) R3m/V	Siemens (Nicolet) R3m/V	Siemens (Nicolet) R3m/V	Siemens (Nicolet) R3m/V
radiation (Å)	Mo K α , $\lambda = 0.710~73$	Mo K α , $\lambda = 0.710~73$	Mo K α , $\lambda = 0.710~73$	Mo Kα, $\lambda = 0.710~73$
scan type	ω scan	ω scan	ω scan	ω scan
scan rate (deg min $^{-1}$)	$5 \le 2\dot{\omega} \le 29.3$	$5.3 \le 2\dot{\omega} \le 29.3$	$5 \le 2\dot{\omega} \le 29.3$	$2.3 \le 2\dot{\omega} \le 29.3$
scan range (deg)	0.6	0.65	0.6	0.75
2Θ range (deg)	2.9 - 48.1	4.3-49.1	6.3 - 56.1	3.8 - 52.0
data range (<i>h</i> , <i>k</i> , <i>l</i>)	0-13, 0-32,	-10 to $+10$, -21 to	-9 to $+21$, -7 to	0-12, 0-18, -19 to
-	0-13	+30, -12 to $+11$	+14, -12 to $+12$	+19
total decay	0	0	0	0
temp (K)	200	220	200	205
no. of data collected	3006	4477	2111	4984
no. of data with $I \ge 2\sigma(I)$	2010	3261	1850	3739
no. of params refined	233	318	259	436
min/max residual electron density (e $Å^{-3}$)	+0.646/-0.392	+0.306/-0.199	+0.405/-0.256	+0.343/-0.257
Mo K α linear abs coeff (mm ⁻¹)	0.827	0.593	1.001	0.687
R1 $(I \ge 2\sigma(I)/\text{all})^a$	0.0532/0.0899	0.0383/0.0590	0.0308/0.0396	0.0351/0.0521
wR2 $(I \ge 2\sigma(I)/\text{all})^b$	0.1254/0.1446	0.0843/0.0905	0.0709/0.0743	0.0867/0.0927

Table 2. X-ray Diffraction Data for Compounds 4, 11, 14, and 23

^a R1 = $\sum |F_0 - F_c| / \sum F_c$. ^b wR2 = $[\sum w(F_0^2 - F_c^2)]^2 / [\sum w(F_0^2)]^2$.

Table 3.Selected Bond Lengths (Å) and Angles
(deg) of Compound 4^a

		-				
Bond Lengths						
Si1-Cr1	2.335(2)	Cr1-C3	1.880(6)	O4-C4	1.141(6)	
Si1-C6	1.874(5)	Cr1-C4	1.881(6)	O5-C5	1.141(6)	
Si1-N1	1.938(5)	Cr1-C5	1.877(6)	N1-C12	1.511(7)	
Si1-Cl1	2.125(2)	O1-C1	1.131(7)	N1-C13	1.485(7)	
Cr1-C1	1.880(6)	O2-C2	1.134(6)	N1-C14	1.500(7)	
Cr1-C2	1.885(6)	O3-C3	1.143(6)			
		Bond A	Angles			
C1-Cr1	-Si1	172.1(2)	N1-Si1-	-Cr1	122.6(2)	
C5-Cr1	-Si1	83.0(2)	Cl1-Si1	-Cr1	116.5(1)	
C3-Cr1	-Si1	88.8(2)	C14-N1	-C13	110.2(5)	
C4-Cr1	-Si1	86.7(2)	C14-N1	-C12	108.0(4)	
C2-Cr1	-Si1	95.7(2)	C13-N1	-C12	111.0(4)	
C6-Si1-	-N1	87.2(2)	C14-N1	-Si1	107.9(3)	
C6-Si1-	-Cl1	99.4(2)	C13-N1	-Si1	113.5(4)	
N1-Si1-	-Cl1	96.4(2)	C12-N1	-Si1	105.9(3)	
C6-Si1-	-Cr1	127.3(2)				

 a Standard deviations in units of the last significant figure are given in parentheses.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified and dried by distillation. *n*-Pentane, *n*-hexane, and dichloromethane were dried over calcium hydride. Diethyl ether and tetrahydrofuran were refluxed with sodium/benzophenone ketyl, distilled, and saturated with nitrogen. Chlorosilanes were freshly crystallized or distilled from magnesium and stored over magnesium at 0 °C. Na₂-[Fe(CO)₄]and K_2 [Cr(CO)₅] were synthesized according to the literature.^{23,24} Glassware was dried at 300 °C/10⁻³ mbar before

 Table 4.
 Selected Bond Lengths (Å) and Angles (deg) of Compound 11^a

Bond Lengths							
Si1-Cr1	2.406(1)	Cr1-C1	1.870(3)	O4-C4	1.142(3)		
Si1-C6	1.887(3)	Cr1-C2	1.875(3)	O5-C5	1.145(3)		
Si1-N1	1.996(2)	Cr1-C4	1.891(3)	N1-C13	1.496(3)		
Si1-P1	2.294(1)	Cr1-C3	1.904(3)	N1-C14	1.502(3)		
P1-C15	1.837(3)	O1-C1	1.153(3)	N1-C12	1.506(3)		
P1-C21	1.834(3)	O2-C2	1.144(3)				
Cr1–C5	1.860(3)	O3-C3	1.141(3)				
Bond Angles							
C1-Cr1-Si1		87.5(1)	N1-Si1	-P1	96.0(1)		
C2-Cr1	-Si1	86.0(1)	C6-Si1-	-Cr1	121.3(1)		
C3-Cr1	-Si1	96.5(1)	N1-Si1	-Cr1	121.0(1)		
C4-Cr1	-Si1	87.7(1)	P1-Si1-	-Cr1	125.8(1)		
C5-Cr1	-Si1	176.1(1)	C13-N1	-C12	108.9(2)		
C15-P1	-C21	103.6(1)	C13-N1	-C14	107.9(2)		
C15-P1	-Si1	96.4(1)	C14-N1	-C12	108.1(2)		
C21-P1	-Si1	109.3(1)	C12-N1	-Si1	104.9(2)		
C6-Si1-	-N1	85.3(1)	C13-N1	-Si1	116.6(2)		
C6-Si1-	-P1	97.9(1)	C14-N1	-Si1	110.1(2)		

 a Standard deviations in units of the last significant figure are given in parentheses.

use. Infrared spectra were recorded with a Perkin-Elmer 983G spectrometer (KBr pellets or solutions in CaF₂ cells). ¹H NMR spectra were recorded on a Bruker AC 200 spectrometer, operating at 200.132 MHz (internal standard: CDCl₃, δ 7.27; C₆D₆, δ 7.16; (CD₃)₂SO, δ 2.50) in the Fourier transform mode, ¹³C{¹H} NMR spectra (internal standard: CDCl₃, δ 77.0; C₆D₆, δ 126; CD₂Cl₂, δ 53.8) were recorded at 50.323 MHz, ²⁹Si NMR spectra (external standard: SiMe₄, δ = 0, recorded in CDCl₃, C_6D_6 , or tetrahydrofuran/D₂O) at 39.763 MHz, and ³¹P{¹H} NMR spectra (external standard: 85% H₃PO₄ with P(OMe)₃, δ 139, recorded in CDCl₃ or C₆D₆) at 81.015 MHz. Chemical shifts are reported in δ units (parts per million) downfield from the standards used with the solvent as the reference signal. FD and EI mass spectra were recorded on a Finnigan 8400

⁽²³⁾ Collman, J. P.; Finke, R. G.; Cawse, J. N.; Braumann, J. I. J. Am. Chem. Soc. 1977, 99, 2515.

⁽²⁴⁾ Schwindt, M. A.; Lejon, T.; Hegedus, L. S. Organometallics **1990**, *9*, 2814.

 Table 5.
 Selected Bond Lengths (Å) and Angles (deg) of Compound 14^a

		0	-				
Bond Lengths							
Si-Fe	2.265(1)	Fe-C3	1.770(4)	N-C12	1.503(4)		
Si-C15	1.869(3)	Fe-C4	1.781(4)	N-C13	1.494(4)		
Si-C11	1.864(3)	O1-C1	1.140(4)	N-C14	1.493(4)		
Si-N	1.955(3)	O2-C2	1.140(4)	C15-C16	1.305(6)		
Fe-C1	1.784(3)	O3-C3	1.142(5)				
Fe-C2	1.787(4)	O4-C4	1.139(4)				
Bond Angles							
C1-Fe-Si		89.5(1)	C15-S	i–N	98.9(1)		
C2-Fe-	-Si	175.9(1)	C12-N	I–Si	105.0(2)		
C3-Fe-	-Si	83.2(1)	C12-N	I-C13	109.5(3)		
C4–Fe-	-Si	85.0(1)	C12-N	I-C14	108.6(3)		
N-Si-l	Fe	118.7(1)	C13-N	I–Si	114.3(2)		
C11-Si-Fe		120.5(1)	C13-N	I-C14	108.0(3)		
C11-Si-N		88.1(1)	C14-N	I–Si	111.3(2)		
C11-Si-C15		108.0(2)	C16-C	215-Si	124.3(3)		
C15-Si	-Fe	117.4(1)					

^a Standard deviations in units of the last significant figure are given in parentheses.

Table 6.Selected Bond Lengths (Å) and Angles
(deg) of Compound 23^a

Bond Lengths							
Si1-Fe1	2.280(1)	Fe-C3	1.782(3)	P1-05	1.535(2)		
Si1-C5	1.871(3)	Fe-C4	1.771(3)	P1-N1	1.619(3)		
Si1-C18	1.884(3)	O1-C1	1.152(3)	P1-N2	1.623(3)		
Si1-05	1.726(2)	O2-C2	1.156(3)	P1-N3	1.619(3)		
Fe-C1	1.772(3)	O3-C3	1.149(3)				
Fe-C2	1.770(3)	O4-C4	1.156(3)				
Rond Angles							
$C1 = C_1 =$					102 6(1)		
		03.3(1)	05-511-	-010	105.0(1)		
C2-FeI-Sil		84.5(1)	C5-S11-	-C18	105.9(1)		
C3-Fe1-Si1		178.3(1)	Si1-05-P1		146.8(1)		
C4-Fe1-Si1		83.4(1)	O5-P1-N1		108.6(1)		
Fe1-Si1-C5		117.5(1)	O5-P1-N2		114.8(1)		
Fe1-Si1-C18		115.8(1)	O5-P1-N3		104.3(1)		
Fe1-Si1-O5		109.7(1)	Si1-C5-C6		126.6(2)		
O5-Si1-C5		102.9(1)	C5-C6-C12 1		127.5(3)		

^{*a*} Standard deviations in units of the last significant figure are given in parentheses.

mass spectrometer, operating in the positive ion mode. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Photochemical reactions were performed with a 400 W medium-pressure mercury lamp in a water-cooled quartz reaction vessel under a steady stream of nitrogen. Microanalyses were performed by the Organisch-Chemisches Institut der Universität Heidelberg.

1. [C₆H₄CH₂N(CH₃)₂-2](Cl)Si=Cr(CO)₅, [[2-((Dimethylamino)methyl)phenyl]chlorosilanediyl]chromium(0) Pentacarbonyl (4).8 A 360 mmol (4.3 g) portion of graphite was heated to 300 °C/10⁻³ mbar for 30 min and then cooled to 25 °C. A 36.36 mmol (1.42 g) amount of K was added, and the mixture was slowly heated to 160 °C and held at this temperature for 10 min. In a strongly exothermic reaction the gold-yellow intercalation compound KC825 was formed, which then was cooled to -70 °C; 20 mL of tetrahydrofuran was added. An 18.18 mmol (4.4 g) amount of Cr(CO)₆ was added in one portion, and the reaction mixture was warmed to 25 °C overnight. The green slurry obtained was cooled to -70 °C, and a solution of 18.18 mmol (4.84 g) of [C₆H₄CH₂N(CH₃)₂-2]- $SiCl_3$ (1)⁷ was added dropwise. The reaction mixure was stirred at this temperature for 6 h and then slowly warmed to 25 °C and filtered through a pad of Celite. The filtrate was concentrated to 30% and treated with *n*-hexane until the precipitation of a yellow solid was observed. Slow cooling to -30 °C afforded **4** as yellow cubes. Yield: 9.6 mmol (3.74 g, 53%, based on **1**). The obtained spectroscopic data of **4** are in agreement with the data published in ref **8**.

2. $[C_6H_4CH_2N(CH_3)_2-2](Cl)Si=Fe(CO)_4$, [[2-((Dimethylamino)methyl)phenyl]chlorosilanediyl]iron(0) Tetra $carbonyl (5). A 9.0 mmol (2.4 g) amount of <math>[C_6H_4CH_2N-(CH_3)_2-2]SiCl_3$ (1)⁷ dissolved in 150 mL of diethyl ether was added dropwise to a suspension of 9.0 mmol (1.93 g) of Na₂- $[Fe(CO)_4]$ (2) in 200 mL of diethyl ether at -70 °C. The reaction mixture was warmed to 25 °C overnight and then filtered through a pad of Celite. The filtrate was concentrated to 30%, 50 mL of *n*-pentane was added, and the resulting deep red solution was slowly cooled to -30 °C. From this solution complex 5 precipitated as a reddish amorphous solid.

Yield: 4.38 mmol (1.60 g, 49% based on 1). Mp: 160 °C dec. Anal. Calcd for $C_{13}H_{12}O_4NCIFeSi$ (365.63): C, 42.70; H, 3.31. Found: C, 42.76; H, 3.51. IR (KBr): ν_{CO} 2032 (s), 1985 (vs, br), 1911 (vs, br) cm⁻¹. ¹H NMR ((CD₃)₂SO): δ 2.50 (br, 3 H, CH₃); 2.70 (br, 3 H, CH₃); 4.45 (d, ²J_{HH} = 15.0 Hz, 1 H, CH₂);²⁶ 7.20-8.05 (m, 4 H, C₆H₄). ¹³C{¹H} NMR (CD₂Cl₂): δ 46.9 (CH₃); 48.2 (CH₃); 67.8 (CH₂); 122.4, 129.3, 131.9, 133.1, 138.0, 139.5 (C₆H₄); 214.8 (CO). EI-MS (m/z (relative intensity)): M⁺, 365 (19); M⁺ - CO, 337 (22); M⁺ - 2 CO, 309 (10); M⁺ - 3 CO, 281 (35); M⁺ - 4 CO, 253 (100); [C₆H₄CH₂N(CH₃)₂]Si⁺, 162 (77); C₆H₄CH₂NCH₃⁺, 119 (30).

3. [C₆H₄CH₂N(CH₃)₂-2](CH₃)Si=Cr(CO)₅, [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl]chromium-(0) Pentacarbonyl (7).⁹ An 8.0 mmol (5 mL) amount of a 1.6 M CH₃Li solution in diethyl ether was diluted with 200 mL of tetrahydrofuran and at -70 °C cautiously added to 8.0 mmol (3.1 g) of $[C_6H_4CH_2N(CH_3)_2-2](Cl)Si=Cr(CO)_5$ (4) dissolved in 250 mL of tetrahydrofuran. The reaction mixture was warmed to 25 °C over 3 h with vigorous stirring. After additional stirring for 3 h at 25 °C all volatile components were evaporated with vacuum and the brown residue was extracted with four 50 mL portions of dichloromethane. The combined phases were concentrated to 30%, and 40 mL of n-pentane was added. From the obtained solution complex 7 crystallized as yellow cubes at -30 °C. Yield: 5.4 mmol (2.0 g, 68%, based on 4). The spectroscopic as well as experimental data of 7 are published in ref 9.

4. [C₆H₄CH₂N(CH₃)₂-2](C₆H₅)Si=Cr(CO)₅, [[2-((Dimethylamino)methyl)phenyl]phenylsilanediyl]chromium(0) Pentacarbonyl (9).^{9,10} To 4.1 mmol (1.6 g) of [C₆H₄CH₂N-(CH₃)₂-2](Cl)Si=Cr(CO)₅ (4) dissolved in 50 mL of tetrahydrofuran was added 4.1 mmol (2.3 mL) of 1.8 M C₆H₅Li (8) diluted with 30 mL of tetrahydrofuran at -50 °C. After the reaction mixture was warmed to 25 °C, all volatile components were removed in vacuo and the residual brownish oil was treated with 100 mL of dichloromethane for 10 min in an ultrasonic bath. The obtained suspension was filtered through a pad of Celite, and the solvent was evaporated at 25 °C/10⁻¹mbar. Crystallization from tetrahydrofuran/*n*-pentane (10:1) at -30°C yielded 9 as yellow cubes. Yield: 2.32 mmol (1.0 g, 57% based on 4). The spectroscopic and analytical data of 9 are published in ref 10.

5. $[C_6H_4CH_2N(CH_3)_2-2][P(C_6H_5)_2]Si=Cr(CO)_5$, [[2-((Dimethylamino)methyl)phenyl](diphenylphosphino)silanediyl]chromium(0) Pentacarbonyl (11). At -30 °C $2.27 mmol (1.4 mL) of 1.6 M CH_3Li was added in one portion$ $to 2.27 mmol (425 mg) of HP(C_6H_5)_2, dissolved in 30 mL of$ diethyl ether. Carefully warming the reaction mixture to 25 $°C yielded a deep red solution of LiP(C_6H_5)_2 (10), which was$ $added dropwise to 2.27 mmol (885 mg) of <math>[C_6H_4CH_2N(CH_3)_2-2](Cl)Si=Cr(CO)_5$ (4) at -70 °C. Warming the reaction mixture to 25 °C led to a change in color at -35 °C from orange to pale green. After the mixture was stirred for 2 h at 25 °C, all

⁽²⁵⁾ Fürstner, A. Angew. Chem. **1993**, 105, 171; Angew. Chem., Int. Ed. Engl. **1993**, 32, 164 and literature cited therein.

⁽²⁶⁾ One of the resonance signals of the diastereotopic methylene portons is masked by the resonance signal of the solvent d_6 -DMSO and can therefore not be assigned clearly.

volatile materials were removed under vacuum and the yellow oily residue was extracted four times with 30 mL portions of dichloromethane. The obtained yellow solution was filtered through a pad of Celite, and dichloromethane was distilled off at 25 °C. Crystallization of the remaining solid produced complex **11** as yellow crystals.

Yield: 0.62 mmol (335 mg, 27%, based on 4). Mp: 168 °C. Anal. Calcd. for $C_{26}H_{22}O_5NPCrSi$ (539.52): C, 57.88; H; 4.11. Found: C, 57.50; H, 4.58. IR (CH₂Cl₂): ν_{CO} 2067 (s), 1934 (vs, vbr) cm⁻¹. ¹H NMR (CDCl₃): δ 2.89 (s, 3 H, CH₃); 3.25 (s, 3 H, CH₃); 3.81 (d, ²J_{HH} = 13.9 Hz, 1 H, CH₂); 4.90 (d, ²J_{HH} = 13.9 Hz, 1 H, CH₂); 7.16-8.00 (m, 14 H, C₆H₄ and C₆H₅). ¹³C-{¹H} NMR (CDCl₃): δ 45.2 (CH₃); 63.5 (CH₂); 128.2-134.6 (C₆H₄ and C₆H₅); 216.2 (d, ³J_{PC} = 12.0 Hz, CO); 221.1 (d, ³J_{PC} = 5.8 Hz, CO). ³¹P{¹H} NMR (CDCl₃): δ 31.1. EI-MS (m/z (relative intensity)): M⁺, 539 (3); M⁺ - 4 CO, 427 (31); M⁺ -4 CO - HP(C₆H₅)₂, 238; M⁺ - Cr(CO)₅ - P(C₆H₅)₂, 186 (26).

6. $[C_6H_4CH_2N(CH_3)_2-2](H_2C=CH)Si=Cr(CO)_5$, [[2-((Dimethylamino)methyl)phenyl]vinylsilanediyl]chromium- $(0) Pentacarbonyl (13). A 4.0 mmol (4.0 mL) amount of 1.0 M (H_2C=CH)MgBr (12) in tetrahydrofuran was slowly added to 4.0 mmol (1.56 g) of <math>[C_6H_4CH_2N(CH_3)_2-2](CI)Si=Cr(CO)_5$ (4) dissolved in 100 mL of tetrahydrofuran at -50 °C. After the reaction mixture was warmed to 25 °C, all volatiles were removed in vacuo and the oily residue was extracted with four 50 mL portions of dichloromethane. The combined extracts were filtered through a pad of Celite, and dichloromethane was distilled off. Crystallization of the obtained powder from tetrahydrofuran/*n*-pentane (5:1) at -30 °C yielded 13 as yellow cubes.

Yield:1.86 mmol (0.71 g, 47%, based on 4). Mp: 124 °C dec. Anal. Calcd for C₁₆H₁₅O₅NCrSi (381.39): C, 50.39; H, 3.96. Found: C, 49.90; H, 3.99. IR (KBr): v_{CH} 3054 (w), 2997 (w), 2944 (w); ν_{CO} 2036 (m), 1960 (sh), 1899 (vs, vbr); $\nu_{C=C}$ 1580 (w) cm⁻¹. ¹H NMR (CDCl₃): δ 2.84 (s, 3H, CH₃); 2.96 (s, 3H, CH₃); 3.90 (d, ²J_{HH} = 13.7 Hz, 1 H, CH₂); 4.46 (d, ²J_{HH} = 13.7 Hz, 1 H, CH₂); 5.12 (dd, ${}^{2}J_{HH} = 3.4$ Hz, ${}^{3}J_{HH} = 19.8$ Hz, 1 H, C_2H_3 ; 5.85 (dd, ${}^2J_{HH} = 3.4$ Hz, ${}^3J_{HH} = 14.0$ Hz, 1 H, C_2H_3); 6.69 (dd, ${}^{3}J_{HH} = 14.0$ Hz, ${}^{3}J_{HH} = 19.8$ Hz, 1 H, C₂H₃); 7.22-7.27 (m, 1 H, C₆H₄); 7.39-7.43 (m, 2 H, C₆H₄); 7.88-7.92 (m, 1 H, C_6H_4 . ¹³C{¹H} NMR (CDCl₃): δ 45.9 (*C*H₃); 47.9 (*C*H₃); 68.2 (CH2); 123.6, 128.4, 129.7, 131.2, 134.4, 139.4, 141.3, 141.5 $(C_2H_3 \text{ and } C_6H_4)$; 221.3 (CO); 225.5 (CO). ²⁹Si{¹H} NMR (tetrahydrofuran/D₂O): δ 114.9. EI-MS (*m*/*z* (relative intensity)): M^+ , 381 (13); M^+ – CO, 353 (6); M^+ – 3 CO, 297 (11); M^+ – 4 CO, 269 (15); M^+ –5 CO, 241 (100); $C_6H_4CH_2NCH_3^+$, 119 (9)

7. [C₆H₄CH₂N(CH₃)₂-2](H₂C=CH)Si=Fe(CO)₄, [[2-((Dimethylamino)methyl)phenyl]vinylsilanediyl]iron(0) Tetracarbonyl (14). A 6.0 mmol (6.0 mL) amount of 1 M (H₂C= CH)MgBr (12) in tetrahydrofuran was concentrated to 1.0 mL and diluted with 200 mL of diethyl ether. At -30 °C the obtained solution was slowly added to 6.0 mmol (2.2 g) of [C₆H₄-CH₂N(CH₃)₂-2](Cl)Si=Fe(CO)₄ (5), dissolved in 100 mL of diethyl ether. The reaction mixture was warmed to 25 °C over 3 h, filtered through a pad of Celite, and concentrated to 50%. After 100 mL of *n*-pentane was added, [C₆H₄CH₂N(CH₃)₂-2]-(H₂C=CH)Si=Fe(CO)₄ (14) crystallized at -30 °C as reddish cubes.

Yield: 2.3 mmol (0.8 g, 38% based on **5**). Mp: 85 °C dec. Anal. Calcd for $C_{15}H_{15}O_4NFeSi$ (357.23): C, 50.44; H, 4.23; N, 3.92. Found: C, 49.96; H, 4.50; N, 3.92. IR (KBr): ν_{CO} 1996 (vs, br), 1932 (m), 1879 (s) cm⁻¹. ¹H NMR (C₆D₆): δ 1.99 (s, 3 H, CH₃); 2.02 (s, 3 H, CH₃); 2.75 (d, ²J_{HH} = 14.4 Hz, 1 H, CH₂); 3.36 (d, ²J_{HH} = 14.4 Hz, 1 H, CH₂); 5.62 (dd, ²J_{HH} = 3.6 Hz, ³J_{HH} = 19.5 Hz, 1 H, C₂H₃); 5.84 (dd, ²J_{HH} = 3.6 Hz, ³J_{HH} = 13.9 Hz, 1 H, C₂H₃); 6.22 (dd, ³J_{HH} = 13.9 Hz, ³J_{HH} = 19.5 Hz, 1 H, C₂H₃); 6.67-6.72 (m, 1 H, C₆H₄); 7.06-7.16 (m, 2 H, C₆H₄); 7.82-7.86 (m, 1 H, C₆H₄). ¹³C{¹H} NMR (C₆D₆): δ 45.1 (CH₃); 46.8 (CH₃); 66.2 (CH₂); 122.6, 128.0, 129.4, 133.4, 134.5, 136.1, 137.3, 138.2 (C₂H₃ and C₆H₄); 215.4 (CO). ²⁹Si{¹H} NMR (Et₂O/D₂O): δ 116.8. EI-MS (*m*/*z* (relative intensity)): M⁺, 357 (21); M⁺ - CO, 329 (11); M⁺ - 2 CO, 301 (19); M⁺ - 3 CO, 273 (11); M⁺ - 4 CO, 245 (100); M⁺ - 4CO - C₂H₃, 219 (16); C₆H₄CH₂NCH₃⁺, 119 (21).

8. [C₆H₄CH₂N(CH₃)₂-2](CH₃)Si=Fe(CO)₄, [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl]iron(0) Tetracarbonyl (15).^{10a} A 4.8 mmol (3.0 mL) amount of a 1.6 M CH₃Li solution in diethyl ether was diluted with 100 mL of diethyl ether, and at -30 °C this mixture was slowly added to a solution of 4.8 mmol (1.8 g) of [C₆H₄CH₂N(CH₃)₂-2](Cl)-Si=Fe(CO)₄ (5) in 100 mL of diethyl ether. The pale red reaction mixture was slowly warmed to 25 °C, filtered through a pad of Celite, and concentrated to 30%. A 30 mL portion of *n*-pentane was added, and the solution was cooled to -30 °C. [C₆H₄CH₂N(CH₃)₂-2](CH₃)Si=Fe(CO)₄ (15) was obtained as a pale red solid. Yield: 3.8 mmol (1.3 g, 80%, based on 5). The spectroscopic and analytical data of 15 are published in ref 10a.

9. $[C_6H_4CH_2N(CH_3)_2-2](CH_3)Si=Cr(CO)_5$, [[2-((Dimeth-ylamino)methyl)phenyl]methylsilanediyl]chromium- $(0) Pentacarbonyl (7), by Photochemical Reaction of <math>[C_6H_4CH_2N(CH_3)_2-2](CH_3)SiH_2$ (16) with $Cr(CO)_6$ (17a). A 1.5 mmol (330 mg) amount of $Cr(CO)_6$ was dissolved in 200 mL of diethyl ether and transferred to a photochemical reactor. A 1.5 mmol (270 mg) amount of $[C_6H_4CH_2N(CH_3)_2-2](CH_3)-SiH_2$ (16)²¹ was added in one portion, and the mixture was irradiated for 3 h at 5 °C. Afterward the reaction mixture was cooled to 0 °C and held there for 3 days to crystallize unreacted $Cr(CO)_6$. Thereafter the reaction mixture was filtered through a pad of Celite. A 20 mL portion of *n*-pentane was added, and 7 was obtained at -30 °C as yellow crystals. Yield: 0.66 mmol (240 mg, 44%, based on 7). The spectroscopic and analytical data of 7 are published in ref 9.

10. [C₆H₄CH₂N(CH₃)₂-2](CH₃)Si=Fe(CO)₄, [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl]iron(0) Tetracarbonyl (15), by Photochemical Reaction of [C₆H₄-CH₂N(CH₃)₂-2](CH₃)SiH₂ (16) with Fe(CO)₅ (17b). A 1.5 mmol (290 mg) amount of Fe(CO)5 and 1.5 mmol (270 mg) of [C₆H₄CH₂N(CH₃)₂-2](CH₃)SiH₂ (17) were dissolved in 200 mL of diethyl ether and irradiated in a guartz vessel for 3 h at 0 °C under a steady flow of nitrogen. During irradiation the color of the reaction mixture changed from yellow to dark brown. After filtration through a pad of Celite, all volatiles were removed under vacuum and the red oily residue was dissolved in 40 mL of dichloromethane/n-pentane (10:1). Crystallization at −30 °C gave **15** as a red-brown microcrystalline solid. Yield: 1.0 mmol (350 mg, 66%, based on 17). The spectroscopic and analytical data of 15 are published in ref 10a.

11. $[C_6H_4CH_2N(CH_3)_2-2](CH_3)Si=Mn(\eta^5-C_5H_5)(CO)_2,$ [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl]-(η^5 -cyclopentadienyl)manganese(I) Dicarbonyl (18). A 1.95 mmol (350 mg) amount of $[C_6H_4CH_2N(CH_3)_2-2](CH_3)SiH_2$ (16) and 1.95 mmol (400 mg) of ($\eta^5-C_5H_5$)Mn(CO)₃ (17c) were dissolved in 300 mL of diethyl ether and irradiated in a quartz vessel for 3 h at 0 °C. The brown solution was filtered through a pad of Celite, and the filtrate was concentrated to 50 mL. After 10 mL of *n*-pentane was added at -30 °C, $[C_6H_4CH_2N-(CH_3)_2-2](CH_3)Si=Mn(\eta^5-C_5H_5)(CO)_2$ (19) was obtained as an amorphous solid, which is extremely sensitive to air.

Yield: 0.7 mmol (250 mg, 36%, based on **17**). Anal. Calcd. for $C_{17}H_{20}NO_2MnSi$ (353.38): C, 57.78; H, 5.70. Found: C, 55.35; H, 5.68 (due to the high instability of **18**, only poor elemental analyses could be obtained). IR (CHCl₃): ν_{CO} 1892 (vs), 1818 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ 0.65 (s, 3 H, SiC*H*₃); 2.71 (s, 3 H; NC*H*₃); 2.90 (s, 3 H, NC*H*₃); 3.99 (d, ²*J*_{HH} = 8.6 Hz, 1 H, C*H*₂);²⁷ 4.47 (s, C₅*H*₅, 5 H); 7.19–7.33 (m, 3 H, C₆*H*₄);

 $[\]left(27\right)$ One of the resonance signals of the methylene protons is presumably masked by the resonance signal of the cyclopentadienyl protons.

7.64–7.67 (m, 1 H, C_6H_4). ¹³C{¹H} NMR (CDCl₃): δ 6.5 (Si*C*H₃); 39.8 (N*C*H₃); 48.6 (N*C*H₃); 67.2 (*C*H₂); 79.4 (*C*₅H₅); 122.9, 127.5, 128.1, 132.4, 137.1, 146.2 (*C*₆H₄) 233.2 (*C*O); 233.4 (*C*O). EI-MS (*m*/*z* (relative intensity)): M⁺, 353 (25); M⁺ – 2 CO, 297 (100); [C₆H₄CH₂N(CH₃)₂](CH₃)Si⁺, 176 (41); [C₆H₄-CH₂N(CH₃)₂]Si⁺, 162 (20).

12. $[C_6H_4CH_2N(CH_3)_2\cdot 2](H_2C=CH)Si=Cr(CO)_5$, [[2-((Dimethylamino)methyl)phenyl]vinylsilanediyl]chromium(0) Pentacarbonyl (13), from $[C_6H_4CH_2N-(CH_3)_2\cdot 2](H_2C=CH)SiCl_2$ (19) and $K_2[Cr(CO)_5]$ (2). The synthesis of complex 13 was carried out in a manner similar to the synthesis of 4. Used quantities of the reactants: 18.2 mmol of $K_2[Cr(CO)_5]$ (2) and 18.2 mmol (4.73) g of $[C_6H_4CH_2N-(CH_3)_2\cdot 2](H_2C=CH)SiCl_2$ (19).

Yield: 7.8 mmol (2.96 g, 43%, based on **16**). Spectroscopic and analytical data: see synthesis of complex **13**, reaction of **4** with **12** (section 6)).

13. $[C_6H_4CH_2N(CH_3)_2-2](H_2C=CH)Si=Fe(CO)_4$, [[2-((Dimethylamino)methyl)phenyl]vinylsilanediyl]iron(0) Tet $racarbonyl (14), from <math>[C_6H_4CH_2N(CH_3)_2-2](H_2C=CH)SiCl_2$ (19) and $Na_2[Fe(CO)_5]$ (3). The synthesis of compound 14 was carried out in a manner similar to the procedure described for the synthesis of 5. Used quantities of the reactants: 9.0 mmol (1.93 g) of $Na_2[Fe(CO)_4]$ (2) and 9.0 mmol (2.34) g of $[C_6H_4CH_2N(CH_3)_2-2](H_2C=CH)SiCl_2$ (16).

Yield: 3.1 mmol (1.11 g, 35%, based on **16**). Analytical and spectroscopic data: see synthesis of **14**, reaction of **5** with **12** (Section 7)).

14. (H₂C=CH)(Cl)Si=Cr(CO)₅·OP[N(CH₃)₂]₃ (21), [Vinylchlorosilanediyl]chromium(0) Pentacarbonyl Hexamethylphosphoric Triamide. A 360 mmol (4.3 g) amount of graphite and 36.36 mmol (1.42 g) of K were heated for 10 min to 160 °C. The obtained golden yellow KC825 was cooled to -70 °C and suspended in 20 mL of tetrahydrofuran. Cr-(CO)₆ was added slowly, and the reaction mixture was warmed to 25 °C overnight. The green slurry was cooled to -50 °C and treated with 20 mmol (3.22 g) of (H₂C=CH)SiCl₃ (20a) dissolved in 100 mL of tetrahydrofuran. The reaction mixture was warmed to 0 °C, and 18.2 mmol (3.25 g) of [(CH₃)₂N]₃P= O was added in one portion. After it was stirred for 1 h at 25 °C, the dark suspension was filtered through a pad of Celite and the filtrate was concentrated to 30%. A 30 mL portion of *n*-hexane was added. Complex **21** crystallized at -30 °C as yellow needles.

Yield: 10.4 mmol (4.8 g, 57%, based on **20a**). Mp: 119 °C dec. Anal. Calcd for $C_{13}H_{21}O_6N_3PClCrSi$ (461.82): C, 33.81; H, 4.58. Found: C, 34.00; H, 4.81. IR (KBr): ν_{CH} 3053 (w), 3000 (m), 2945 (s), 2908 (m), 2858 (m), 2823 (w); ν_{CO} 2035 (vs), 1891 (vs, vbr); $\nu_{C=C}$ 1586 (vw); $\nu_{P=O}$ 1184 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 2.76 (d, ${}^{3}J_{PH}$ = 10.4 Hz, 18 H, NCH₃); 5.82 (dd, ${}^{2}J_{HH}$ = 3.6 Hz, ${}^{3}J_{HH}$ = 20.2 Hz, 1 H, C_2H_3); 5.91 (dd, ${}^{2}J_{HH}$ = 3.6 Hz, ${}^{3}J_{HH}$ = 13.9 Hz, 1 H, C_2H_3); 6.45 (dd, ${}^{3}J_{HH}$ = 13.9 Hz, ${}^{3}J_{HH}$ = 20.2 Hz, 1H, C_2H_3); 13C{¹H} NMR (CDCl₃): δ 36.8 (d, ${}^{2}J_{PC}$ = 5.9 Hz, NCH₃); 128.1 (C_2H_3); 144.8 (C_2H_3); 221.1 (CO); 225.9 (CO). ${}^{29}Si{}^{1}H$ } NMR (tetrahydrofuran/D₂O): δ 83.3 (d, ${}^{2}J_{P-Si}$ = 35.4 Hz). ${}^{31}P{}^{1}H$ NMR (CDCl₃): 22.58 (s). EI-MS (m/e (relative intensity)): M⁺, 461 (22); M⁺ - CO, 433 (8); M⁺ - 2 CO, 405 (6); M⁺ - 3 CO, 377 (7); M⁺ - 4 CO, 349 (37); M⁺ - 5 CO, 321 (100).

15. (H₂C=CH)(Cl)Si=Fe(CO)₄·OP[N(CH₃)₂]₃ (22), [Vinylchlorosilanediyl]iron(0) Tetracarbonyl Hexamethylphosphoric Triamide. At -40 °C 13.16 mmol (2.12 g) of (H₂C=CH)SiCl₃ dissolved in 50 mL of tetrahydrofuran were added dropwise to a suspension of 13.16 mmol (2.81 g) of Na₂-[Fe(CO)₄] (3) and 13.16 mmol (2.36 g) of [(CH₃)₂N]₃P=O in 40 mL of tetrahydrofuran. The reaction mixture was slowly warmed to 25 °C and after stirring for 3 h filtered through a pad of Celite. After removal of all volatile components in vacuo, the red residue was crystallized from 30 mL of tetrahydrofuran/*n*-hexane at -30 °C. Complex 22 was obtained as red-brown crystals.

Yield: 4.8 mmol (2.1 g, 36%, based on (H₂C=CH)SiCl₃)). Mp: 113 °C dec. Anal. Calcd for $C_{12}H_{21}O_5N_3PCIFeSi$ (437.66): C, 32.93; H, 4.84. Found: C, 32.54; H, 4.99. IR (tetrahydrofuran): ν_{CO} 2020 (vs), 1935 (vs), 1906 (vs, br); $\nu_{C=C}$ 1600 (w) cm⁻¹. ¹H NMR (C_6D_6): δ 2.22 (d, ³ J_{PH} = 10.5 Hz, 18H, CH₃); 5.98-6.58 (m, 3H, C_2H_3). ¹³C{¹H} NMR (C₆D₆): δ 37.3 (d, ² J_{PC} = 4.6 Hz, CH₃); 132.3 (C_2H_3); 143.1 (C_2H_3); 217.1 (CO). ²⁹Si{¹H} NMR (C₆D₆): δ 75.8 (d, ² J_{PSi} = 30.3 Hz). ³¹P-{¹H} NMR (CDCl₃): δ 22.23 (s).

16. $[(C_6H_5)CH=CH](C_6H_5)Si=Fe(CO)_4 \cdot OP[N(CH_3)_2]_3$ (23), $[\omega$ -Styrylphenylsilanediyliron(0) Tetracarbonyl Hexamethylphosphoric Triamide. As in the preparation of compound 22, 7.06 mmol (1.51 g) of Na₂[Fe(CO)₄] (3), 7.06 mmol (1.97 g) of $[(C_6H_5)HC=CH](C_6H_5)SiCl_2$ (8a), and 7.06 mmol (1.27 g) of $[(CH_3)_2N]_3P=O$ were reacted in 90 mL of tetrahydrofuran at -40 °C. Crystallization from tetrahydrofuran/*n*-hexane (10:1) produced 23 as red cubes.

Yield: 0.34 mmol (190 mg, 5%, based on **8a**). Anal. Calcd for $C_{24}H_{30}O_5N_3PFeSi$ (555.41): C, 51.90; H, 5.44. Found: C, 51.65; H, 5.72. IR (tetrahydrofuran): ν_{CO} 2008 (s), 1924 (vs), 1891 (vs, br); $\nu_{C=C}$ 1600 (w) cm⁻¹. ¹H NMR (C_6D_6): δ 1.94 (d, ${}^{3}J_{PH} = 10.2$ Hz, 18H, CH₃); 7.10–8.10 (m, 12H, C_2H_2 and C_6H_5). ¹³C{¹H} NMR (C_6D_6): δ 36.8 (br, CH₃); 126.7, 127.5, 128.0, 128.4, 128.8, 131.4, 134.1, 138.2, 142.6, 145.5 (C_2H_2 and C_6H_5); 217.2 (CO). ²⁹Si{¹H} NMR (tetrahydrofuran/D₂O): δ 83.6 (d, ${}^{2}J_{PSi} = 29.7$ Hz). ³¹P{¹H} NMR (CDCl₃): δ 22.13 (s). EI-MS (m/z (relative intensity)): M⁺, 555 (19); M⁺ – CO, 527 (15); M⁺ – 2 CO, 499 (16); M⁺ – 3 CO, 471 (44); M⁺ – 4 CO, 443 (100); M⁺ – Fe – 4 CO, 386 (14).

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich SFB 247) and the Fonds der Chemischen Industrie for financial support. Moreover, we thank Miss Anja Gehrig for her assistance in laboratory, Mr. Thomas Jannack for carrying out the MS measurements, and Miss Sabine Ahrens and Miss Karin Dörr for assistance in drawing up the manuscript.

Supporting Information Available: Tables giving nonhydrogen atomic coordinates and equivalent isotropic parameters, anisotropic displacement parameters, all bond distances and angles, hydrogen coordinates and isotropic displacement parameters, and torsion angles for **4**, **11**, **14**, and **23** (32 pages). Ordering information is given on any current masthead page.

OM980032J