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

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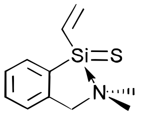
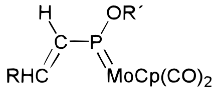
The synthesis and chemical behavior of the intra- and intermolecular donor-stabilized silanediyl complexes $(C_6H_4CH_2NMe_2\text{-}2)(Cl)Si{=}ML_n$ (**4**, $ML_n = Cr(CO)_5$ **5**, $ML_n = Fe(CO)_4$), $(C_6H_5HC{=}CH)(Cl)Si{=}ML_n{\cdot}OP(NMe_2)_3$ (**21**, $ML_n = Cr(CO)_5$; **22**, $ML_n = Fe(CO)_4$), and $(C_6H_5\text{-}HC{=}CH)(C_6H_5)Si{=}Fe(CO)_4{\cdot}OP(NMe_2)_3$ (**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 $(C_6H_4CH_2NMe_2\text{-}2)(R)Si{=}ML_n$ (ML_n = Cr-$(CO)_5$: **7,** R = CH_3; **9**, R = C_6H_5; **11**, R = $P(C_6H_5)_2$; **13**, R = $CH{=}CH_2$. $ML_n = Fe(CO)_4$: **14**, R = $CH{=}CH_2$; **15**, R = CH_3). Moreover, the 1-metalla-2-sila-1,3-dienes $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}ML_n$ (**13**, $ML_n = Cr(CO)_5$; **14**, $ML_n = Fe(CO)_4$) can be prepared by treatment of the hypervalent dichlorosilane $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)SiCl_2$ (**19**) with the carbonylate dianions $ML_n{}^{2-}$ (**2**, $ML_n = Cr(CO)_5$; **3**, $ML_n = Fe(CO)_4$). Additionally, compounds of the latter type are accessible by photochemical coupling reactions of the pentavalent silane $(C_6H_4\text{-}CH_2NMe_2\text{-}2)(CH_3)SiH_2$ (**16**) with the transition-metal carbonyls $Cr(CO)_6$ (**17a**), $Fe(CO)_5$ (**17b**), and $(\eta5\text{-}C_5H_5)Mn(CO)_3$ (**17c**), respectively. The intermolecular donor-stabilized 1-metalla-2-sila-1,3-dienes **21**−**23** can be prepared by the reaction of tetravalent dichlorosilanes $[(R)(H)C{=}CH](R')SiCl_2$ (**20a**, R = H, R′ = Cl; **20b**, R = R′ = C_6H_5) with the carbonylmetalates **2** and **3** and in the presence of $OP(NMe_2)_3$.

Introduction

Recently, we reported about the synthesis and reaction chemistry of the acyclic heterobutadienes $(C_6H_4\text{-}CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}S$ (type **A** molecule)[1] and $(C_6H_2O^tBu_3\text{-}2,4,6)(RHC{=}CH)P{=}Mo(\eta^5\text{-}C_5H_5)(CO)_2$ (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]



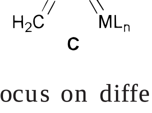
A



B

R′ = 2,4,6-$^tBu_3C_6H_2$

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 $ML_n{}^-$ 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 d^6 ML_5 or d^8 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]



C

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

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[§] Dedicated to Prof. Dr. Manfred Weidenbruch on the occasion of his 60th birthday.

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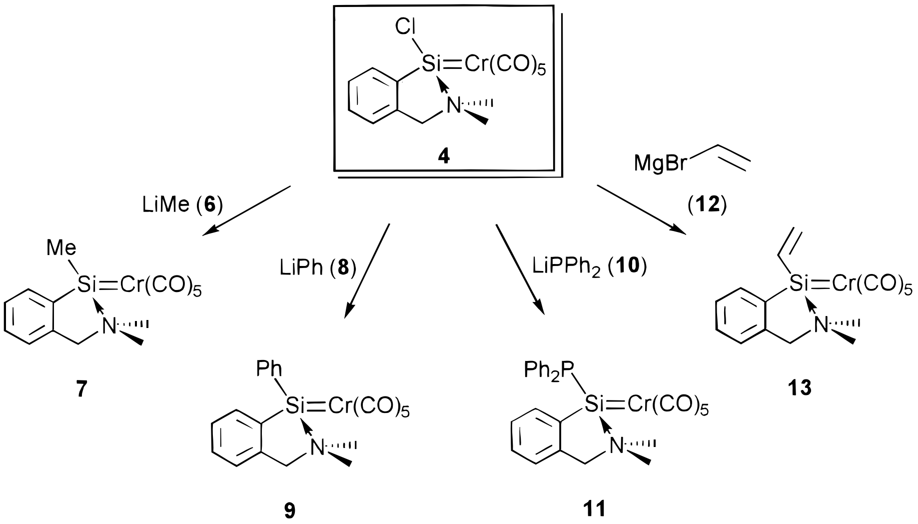
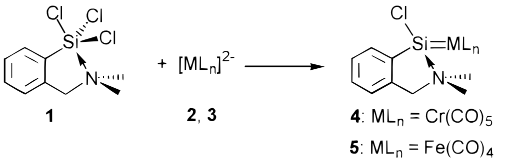
Scheme 1. Reaction Behavior of the Silanediyl Complex 4 with Different Substrates



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 $(C_6H_4CH_2NMe_2\text{-}2)(Cl)Si{=}ML_n$ with various organic nucleophiles is described.

Results and Discussion of Reaction Chemistry

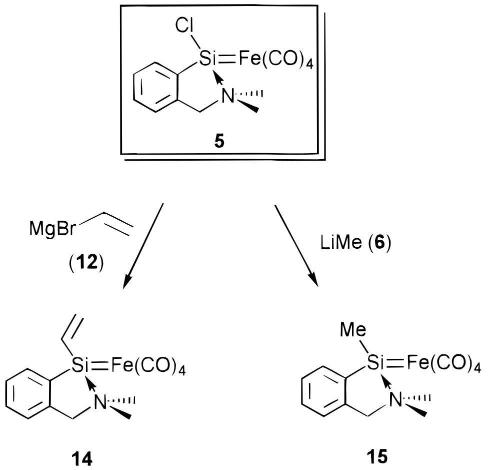
1. Synthesis of Intramolecular Donor-Stabilized Silanediyl Complexes. The synthesis of the chloro-functionalized silanediyl compounds $(C_6H_4CH_2NMe_2\text{-}2)$-(Cl) $Si{=}ML_n$ (**4**, $ML_n = Cr(CO)_5$;[8] **5**, $ML_n = Fe(CO)_4$) proceeds by treatment of $(C_6H_4CH_2NMe_2\text{-}2)SiCl_3$ (**1**)[7] with the carbonylmetallates $K_2[Cr(CO)_5]$ (**2**) and Na_2-$[Fe(CO)_4]$ (**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 = CH_3; **8**, C_6H_5; **10**, R = $P(C_6H_5)_2$) or $BrMgCH{=}CH_2$ (**12**) produces in tetrahydrofuran at −70 °C the intramolecular donor-stabilized silanediyl complexes $(C_6H_4CH_2NMe_2\text{-}2)(R)Si{=}Cr(CO)_5$ (**7**, R = CH_3;[9] **9**, R = C_6H_5;[9,10] **11**, R = $P(C_6H_5)_2$; **13**, R = $CH{=}CH_2$).

When the same reaction conditions are applied for the preparation of the intramolecular donor-stabilized silanediyl compounds $(C_6H_4CH_2NMe_2\text{-}2)(R)Si{=}Fe(CO)_4$ (**14**, R = $CH{=}CH_2$; **15**, R = CH_3), 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**, $ML_n = Mn(\eta^5\text{-}C_5H_5)(CO)_2$), with e.g. hypervalent $(C_6H_4CH_2NMe_2\text{-}2)(CH_3)SiH_2$ (**16**). This type of reaction was first described by Corriu and co-workers for $(C_{10}H_6CH_2NMe_2\text{-}1,8)(C_6H_5)Si{=}ML_n$ (ML_n

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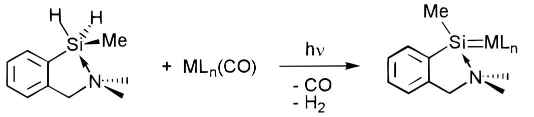


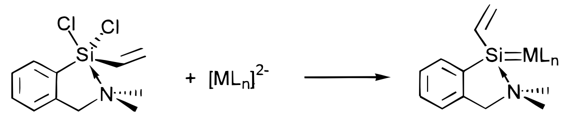
16 **17** **7**: ML$_n$ = Cr(CO)$_5$

15: ML$_n$ = Fe(CO)$_4$

18: ML$_n$ = Mn(η^5-C$_5$H$_5$)(CO)$_2$

= Fe(CO)$_4$, (η^5-C$_5$H$_5$)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.

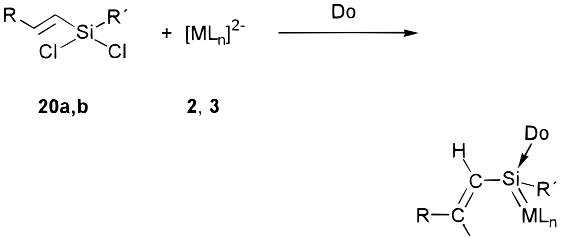
A further synthetic route for the preparation of acyclic 1-metalla-2-sila-1,3-dienes is given by the reaction of ($C_6H_4CH_2NMe_2$-2)($H_2C{=}CH$)$SiCl_2$ (**19**) with an equimolar amount of K_2[Cr(CO)$_5$] (**2**) or Na_2[Fe(CO)$_4$] (**3**). Appropriate workup produces the heterobutadiene **13**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



19 **2**, **3** **13**: ML$_n$ = Cr(CO)$_5$

14: ML$_n$ = Fe(CO)$_4$

2. Synthesis of Intermolecular Donor-Stabilized Silanediyl Complexes. Acyclic intermolecular donor-stabilized heterobutadienes can be synthesized according to a method first described by Zybill and coworkers[12] on treatment of (RHC=CH)(R′)$SiCl_2$ (**20a**, R = H, R′ = Cl; **20b**, R = R′ = C_6H_5) with the carbonylmetalates **2** and **3** in the presence of [$(CH_3)_2N$]$_3$PO (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.



21: R = H, R′ = Cl, ML$_n$ = Cr(CO)$_5$

22: R = H, R′ = Cl, ML$_n$ = Fe(CO)$_4$

23: R = R′ = C$_6$H$_5$, ML$_n$ = Fe(CO)$_4$

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

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

compd	CH_2 (δ)	$^2J_{HH}$ (Hz)	NCH_3 (δ)	NCH$_3$ (δ)	^{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	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 CH$_2$ resonance signals is masked by the resonance signal of the solvent. [b] Broad resonance signal. [c] One of the CH$_2$ resonance signals is masked by the resonance signal of the cyclopentadienyl protons. [d] nd = not determined.

3. Structure and Bonding. The most suitable analytical method for the characterization of the synthesized silanediyl compounds is ^{29}Si 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 ^{29}Si 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 [$(CH_3)_2N$]$_3$PO-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 ^{29}Si 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 ^{1}H NMR spectra of **4**, **7**, **9**, **11**, and **13**−**15** is the appearance of two resonance signals for the methyl groups of the NMe$_2$ 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 $^2J_{HH}$ = 13−16 Hz for the methylene protons of the *built-in* arm Me$_2$NCH$_2$ (Table 1), indicating that both the methylene protons and the Me groups of the NMe$_2$ entity as well are diastereotopic. As a typical example, the ^{1}H NMR spectrum of **13** is depicted in Figure 1.

Neither for the NMe$_2$ nor for the NCH$_2$ protons is coalescence observed up to 115 °C. This confirms that the lone pair of electrons at the nitrogen atom of the $C_6H_4CH_2NMe_2$-2 ligand is strongly bonded to the silicon atom. The appearance of two resonance signals in the range of 44−48 ppm in the ^{13}C{^{1}H} NMR spectra also confirms magnetically inequivalent amino methyl groups (Table 1). In contrast, for the complex ($C_6H_4CH_2NMe_2$-2)(C_6H_5)Si=Cr(CO)$_5$ a coalescence temperature of 95 °C was measured, while ($C_6H_4CH_2NMe_2$-2)$_2$Si=Cr(CO)$_5$ is

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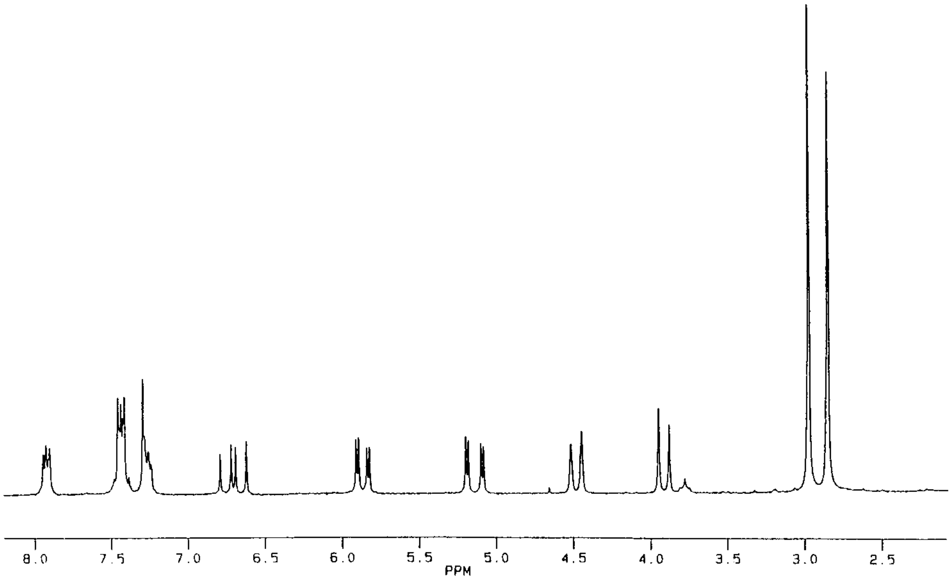

Figure 1. ^{1}H NMR spectrum of $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}Cr(CO)_5$ (**13**).

dynamic at 25 °C.[7] This behavior is different from that of **13** and can be explained by the fact that the $H_2C{=}CH$ 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 trigonal-bipyramidal coordination sphere around the iron center. The appearance of three absorption bands in the region 1880−2030 cm^{-1} verifies that the silanediyl unit occupies an axial position of the trigonal-bipyramidal-coordinated 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_{4v} 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 donor-stabilized silanediyl compounds, as already proposed from spectroscopic data. The structures of $(C_6H_4CH_2NMe_2\text{-}2)(Cl)Si{=}Cr(CO)_5$ (**4**) and $(C_6H_4CH_2NMe_2\text{-}2)[P(C_6H_5)_2]Si{=}Cr(CO)_5$ (**11**) are shown in Figure 2, while the molecular structure of the acyclic heterobutadienes $(C_6H_4CH_2NMe_2\text{-}2)(H_2C{=}CH)Si{=}Fe(CO)_4$ (**14**) and $[(C_6H_5)HC{=}CH](C_6H_5)Si{=}Fe(CO)_4{\cdot}OP(NMe_2)_3$ (**23**) are presented in Figure 3. Crystallographic parameters and selected geometrical details are listed in Tables 2−6.

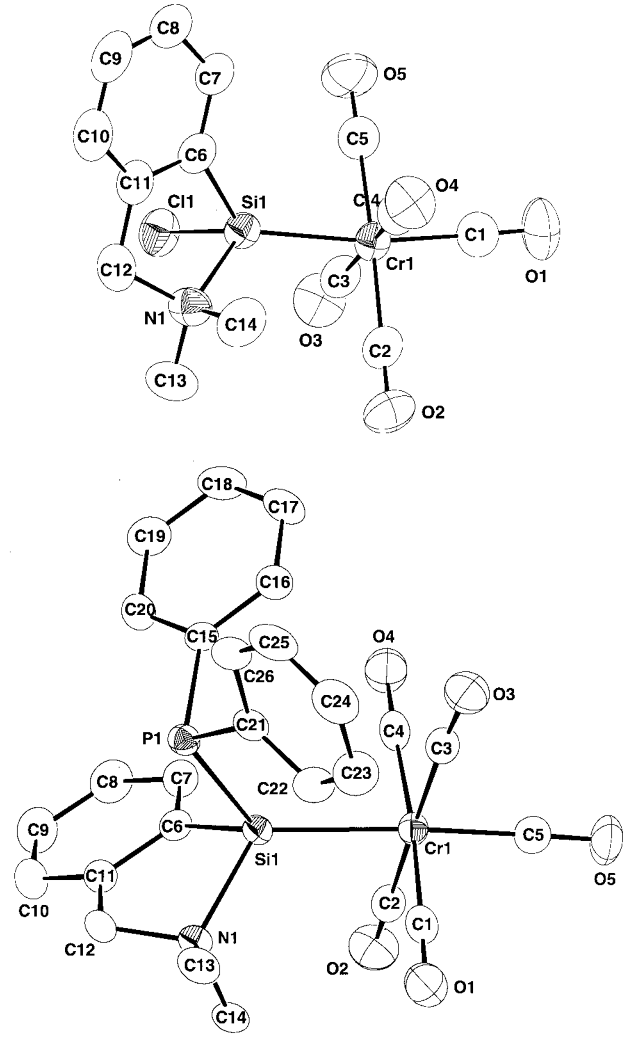

Figure 2. ORTEP drawings (drawn at the 50% probability level) of the silanediyl complexes **4** (top) and **11** (bottom) with the atom-numbering schemes.

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

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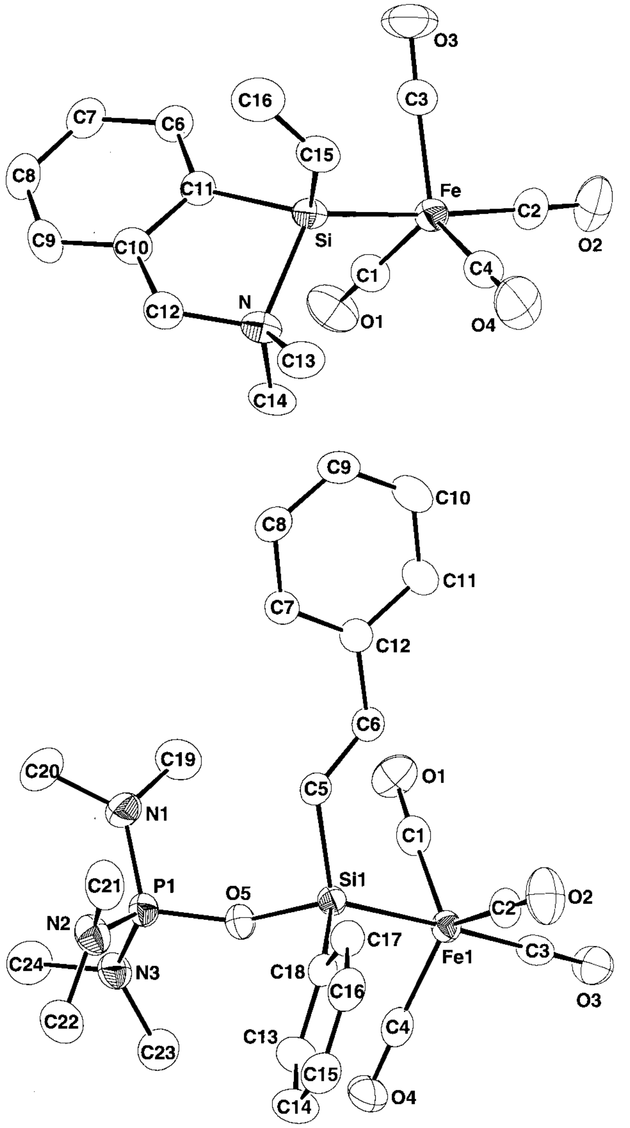

Figure 3. ORTEP drawings (drawn at the 50% probability level) of the 1-ferra-2-sila-1,3-diene compounds **14** (top) and **23** (bottom) with the atom-numbering schemes.

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 (C_6H_4-CH_2NMe_2-2)(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 CH_2NMe_2 *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 silicon−nitrogen 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 electron-donating $(C_6H_5)_2P$ 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 distorted-tetrahedral 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 donor-stabilized 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 H_2C=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°). 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, CH_3, 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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[20] (a) Nakatsuji, H.; Ushio, J.; Yonezawa, T. *J. Organomet. Chem.* **1983**, *258*, C1. (b) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224.

[21] Weinmann, M.; Walter, O.; Huttner, G.; Lang, H. *J. Organomet. Chem.*, in press.

[22] For an overview see: Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, **1989**.

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

	4	**11**	**14**	**23**
formula	$C_{16}H_{16}ClCrNO_{5.5}Si$	$C_{26}H_{22}CrNO_5PSi$	$C_{15}H_{15}FeNO_4Si$	$C_{24}H_{30}FeN_3O_5PSi$
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)
c (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)
Z	8	4	4	4
cryst dimens (mm)	0.20 × 0.20 × 0.30	0.20 × 0.25 × 0.25	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.20
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 Kα, $\lambda = 0.710\ 73$	Mo Kα, $\lambda = 0.710\ 73$	Mo Kα, $\lambda = 0.710\ 73$	Mo Kα, $\lambda = 0.710\ 73$
scan type	ω scan	ω scan	ω scan	ω scan
scan rate (deg min^{-1})	$5 \leq 2\dot{\omega} \leq 29.3$	$5.3 \leq 2\dot{\omega} \leq 29.3$	$5 \leq 2\dot{\omega} \leq 29.3$	$2.3 \leq 2\dot{\omega} \leq 29.3$
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 (h, k, l)	0−13, 0−32, 0−13	−10 to +10, −21 to +30, −12 to +11	−9 to +21, −7 to +14, −12 to +12	0−12, 0−18, −19 to +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 $I \geq 2\sigma(I)$	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 Kα linear abs coeff (mm^{-1})	0.827	0.593	1.001	0.687
R1 ($I \geq 2\sigma(I)$/all)[a]	0.0532/0.0899	0.0383/0.0590	0.0308/0.0396	0.0351/0.0521
wR2 ($I \geq 2\sigma(I)$/all)[b]	0.1254/0.1446	0.0843/0.0905	0.0709/0.0743	0.0867/0.0927

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

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 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.

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.

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. $Na_2[Fe(CO)_4]$and $K_2[Cr(CO)_5]$ were synthesized according to the literature.[23,24] Glassware was dried at 300 °C/10^{-3} mbar before use. Infrared spectra were recorded with a Perkin-Elmer 983G spectrometer (KBr pellets or solutions in CaF_2 cells). ^{1}H NMR spectra were recorded on a Bruker AC 200 spectrometer, operating at 200.132 MHz (internal standard: $CDCl_3$, δ 7.27; C_6D_6, δ 7.16; $(CD_3)_2SO$, δ 2.50) in the Fourier transform mode, $^{13}C\{^1H\}$ NMR spectra (internal standard: $CDCl_3$, δ 77.0; C_6D_6, δ 126; CD_2Cl_2, δ 53.8) were recorded at 50.323 MHz, ^{29}Si NMR spectra (external standard: $SiMe_4$, $\delta = 0$, recorded in $CDCl_3$, C_6D_6, or tetrahydrofuran/D_2O) at 39.763 MHz, and $^{31}P\{^1H\}$ NMR spectra (external standard: 85% H_3PO_4 with $P(OMe)_3$, δ 139, recorded in $CDCl_3$ or C_6D_6) 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

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(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]

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−Si−N	98.9(1)
C2−Fe−Si	175.9(1)	C12−N−Si	105.0(2)
C3−Fe−Si	83.2(1)	C12−N−C13	109.5(3)
C4−Fe−Si	85.0(1)	C12−N−C14	108.6(3)
N−Si−Fe	118.7(1)	C13−N−Si	114.3(2)
C11−Si−Fe	120.5(1)	C13−N−C14	108.0(3)
C11−Si−N	88.1(1)	C14−N−Si	111.3(2)
C11−Si−C15	108.0(2)	C16−C15−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−O5	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−O5	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)		

Bond Angles

C1−Fe1−Si1	85.9(1)	O5−Si1−C18	103.6(1)
C2−Fe1−Si1	84.5(1)	C5−Si1−C18	105.9(1)
C3−Fe1−Si1	178.3(1)	Si1−O5−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	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. [$C_6H_4CH_2N(CH_3)_2$-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 KC_8[25] 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 [$C_6H_4CH_2N(CH_3)_2$-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) Tetracarbonyl (5). A 9.0 mmol (2.4 g) amount of [$C_6H_4CH_2N$-$(CH_3)_2$-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 Na_2-[$Fe(CO)_4$] (**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 $C_{13}H_{12}O_4NClFeSi$ (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}. ^{1}H NMR (($CD_3)_2SO$): δ 2.50 (br, 3 H, CH_3); 2.70 (br, 3 H, CH_3); 4.45 (d, $^2J_{HH}$ = 15.0 Hz, 1 H, CH_2);[26] 7.20−8.05 (m, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 46.9 (CH_3); 48.2 (CH_3); 67.8 (CH_2); 122.4, 129.3, 131.9, 133.1, 138.0, 139.5 (C_6H_4); 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); [$C_6H_4CH_2N(CH_3)_2$]Si$^+$, 162 (77); $C_6H_4CH_2NCH_3^+$, 119 (30).

3. [$C_6H_4CH_2N(CH_3)_2$-2](CH_3)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 CH_3Li 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. [$C_6H_4CH_2N(CH_3)_2$-2](C_6H_5)Si=Cr(CO)$_5$, [[2-((Dimethylamino)methyl)phenyl]phenylsilanediyl]chromium(0) Pentacarbonyl (9).[9,10] To 4.1 mmol (1.6 g) of [$C_6H_4CH_2N$-$(CH_3)_2$-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 C_6H_5Li (**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^{-1}mbar. 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 [$C_6H_4CH_2N(CH_3)_2$-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

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[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 (CH_2Cl_2): ν_{CO} 2067 (s), 1934 (vs, vbr) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.89 (s, 3 H, CH_3); 3.25 (s, 3 H, CH_3); 3.81 (d, $^2J_{HH} = 13.9$ Hz, 1 H, CH_2); 4.90 (d, $^2J_{HH} = 13.9$ Hz, 1 H, CH_2); 7.16−8.00 (m, 14 H, C_6H_4 and C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 45.2 (CH_3); 63.5 (CH_2); 128.2−134.6 (C_6H_4 and C_6H_5); 216.2 (d, $^3J_{PC} = 12.0$ Hz, CO); 221.1 (d, $^3J_{PC} = 5.8$ Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.1. EI-MS (*m/z* (relative intensity)): M$^+$, 539 (3); M$^+$ − 4 CO, 427 (31); M$^+$ − 4 CO − HP(C_6H_5)$_2$, 238; M$^+$ − Cr(CO)$_5$ − P(C_6H_5)$_2$, 186 (26).

6. $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si{=}Cr(CO)_5$, [[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 $[C_6H_4CH_2N(CH_3)_2\text{-}2](Cl)Si{=}Cr(CO)_5$ (**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 $C_{16}H_{15}O_5NCrSi$ (381.39): C, 50.39; H, 3.96. Found: C, 49.90; H, 3.99. IR (KBr): ν_{CH} 3054 (w), 2997 (w), 2944 (w); ν_{CO} 2036 (m), 1960 (sh), 1899 (vs, vbr); $\nu_{C=C}$ 1580 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.84 (s, 3H, CH_3); 2.96 (s, 3H, CH_3); 3.90 (d, $^2J_{HH} = 13.7$ Hz, 1 H, CH_2); 4.46 (d, $^2J_{HH} = 13.7$ Hz, 1 H, CH_2); 5.12 (dd, $^2J_{HH} = 3.4$ Hz, $^3J_{HH} = 19.8$ 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, $^3J_{HH} = 14.0$ Hz, $^3J_{HH} = 19.8$ Hz, 1 H, C_2H_3); 7.22−7.27 (m, 1 H, C_6H_4); 7.39−7.43 (m, 2 H, C_6H_4); 7.88−7.92 (m, 1 H, C_6H_4. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 45.9 (CH_3); 47.9 (CH_3); 68.2 (CH_2); 123.6, 128.4, 129.7, 131.2, 134.4, 139.4, 141.3, 141.5 (C_2H_3 and C_6H_4); 221.3 (CO); 225.5 (CO). ^{29}Si{^{1}H} NMR (tetrahydrofuran/D_2O): 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. $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si{=}Fe(CO)_4$, [[2-((Dimethylamino)methyl)phenyl]vinylsilanediyl]iron(0) Tetracarbonyl (14). A 6.0 mmol (6.0 mL) amount of 1 M ($H_2C{=}CH$)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 $[C_6H_4CH_2N(CH_3)_2\text{-}2](Cl)Si{=}Fe(CO)_4$ (**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, $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si{=}Fe(CO)_4$ (**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}. ^{1}H NMR (C_6D_6): δ 1.99 (s, 3 H, CH_3); 2.02 (s, 3 H, CH_3); 2.75 (d, $^2J_{HH} = 14.4$ Hz, 1 H, CH_2); 3.36 (d, $^2J_{HH} = 14.4$ Hz, 1 H, CH_2); 5.62 (dd, $^2J_{HH} = 3.6$ Hz, $^3J_{HH} = 19.5$ Hz, 1 H, C_2H_3); 5.84 (dd, $^2J_{HH} = 3.6$ Hz, $^3J_{HH} = 13.9$ Hz, 1 H, C_2H_3); 6.22 (dd, $^3J_{HH} = 13.9$ Hz, $^3J_{HH} = 19.5$ Hz, 1 H, C_2H_3); 6.67−6.72 (m, 1 H, C_6H_4); 7.06−7.16 (m, 2 H, C_6H_4); 7.82−7.86 (m, 1 H, C_6H_4). ^{13}C{^{1}H} NMR (C_6D_6): δ 45.1 (CH_3); 46.8 (CH_3); 66.2 (CH_2); 122.6, 128.0, 129.4, 133.4, 134.5, 136.1, 137.3, 138.2 (C_2H_3 and C_6H_4); 215.4 (CO). ^{29}Si{^{1}H} NMR (Et_2O/D_2O): 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 − C_2H_3, 219 (16); $C_6H_4CH_2NCH_3^+$, 119 (21).

8. $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)Si{=}Fe(CO)_4$, [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl]iron(0) Tetracarbonyl (15).[10a] A 4.8 mmol (3.0 mL) amount of a 1.6 M CH_3Li 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 $[C_6H_4CH_2N(CH_3)_2\text{-}2](Cl)Si{=}Fe(CO)_4$ (**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. $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)Si{=}Fe(CO)_4$ (**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. $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)Si{=}Cr(CO)_5$, [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl]chromium(0) Pentacarbonyl (7), by Photochemical Reaction of $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)SiH_2$ (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 $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)SiH_2$ (**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. $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)Si{=}Fe(CO)_4$, [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl]iron(0) Tetracarbonyl (15), by Photochemical Reaction of $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)SiH_2$ (16) with $Fe(CO)_5$ (17b). A 1.5 mmol (290 mg) amount of $Fe(CO)_5$ and 1.5 mmol (270 mg) of $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)SiH_2$ (**17**) were dissolved in 200 mL of diethyl ether and irradiated in a quartz 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. $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)Si{=}Mn(\eta^5\text{-}C_5H_5)(CO)_2$, [[2-((Dimethylamino)methyl)phenyl]methylsilanediyl](η^5-cyclopentadienyl)manganese(I) Dicarbonyl (18). A 1.95 mmol (350 mg) amount of $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)SiH_2$ (**16**) and 1.95 mmol (400 mg) of (η^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, $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)Si{=}Mn(\eta^5\text{-}C_5H_5)(CO)_2$ (**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 ($CHCl_3$): ν_{CO} 1892 (vs), 1818 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.65 (s, 3 H, SiCH_3); 2.71 (s, 3 H; NCH_3); 2.90 (s, 3 H, NCH_3); 3.99 (d, $^2J_{HH} = 8.6$ Hz, 1 H, CH_2);[27] 4.47 (s, C_5H_5, 5 H); 7.19−7.33 (m, 3 H, C_6H_4);

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[27] 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 6.5 ($SiCH_3$); 39.8 (NCH_3); 48.6 (NCH_3); 67.2 (CH_2); 79.4 (C_5H_5); 122.9, 127.5, 128.1, 132.4, 137.1, 146.2 (C_6H_4) 233.2 (*C*O); 233.4 (*C*O). EI-MS (*m*/*z* (relative intensity)): M^+, 353 (25); $M^+ - 2$ CO, 297 (100); $[C_6H_4CH_2N(CH_3)_2](CH_3)Si^+$, 176 (41); $[C_6H_4CH_2N(CH_3)_2]Si^+$, 162 (20).

12. $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si{=}Cr(CO)_5$, [[2-((Dimethylamino)methyl)phenyl]vinylsilanediyl]chromium(0) Pentacarbonyl (13), from $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiCl_2$ (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 $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiCl_2$ (**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. $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si{=}Fe(CO)_4$, [[2-((Dimethylamino)methyl)phenyl]vinylsilanediyl]iron(0) Tetracarbonyl (14), from $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiCl_2$ (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 $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiCl_2$ (**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. $(H_2C{=}CH)(Cl)Si{=}Cr(CO)_5{\cdot}OP[N(CH_3)_2]_3$ (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 KC_8[25] 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 $(H_2C{=}CH)SiCl_3$ (**20a**) dissolved in 100 mL of tetrahydrofuran. The reaction mixture was warmed to 0 °C, and 18.2 mmol (3.25 g) of $[(CH_3)_2N]_3P{=}O$ 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 ($CDCl_3$): δ 2.76 (d, $^3J_{PH} = 10.4$ Hz, 18 H, NCH_3); 5.82 (dd, $^2J_{HH} = 3.6$ Hz, $^3J_{HH} = 20.2$ Hz, 1 H, C_2H_3); 5.91 (dd, $^2J_{HH} = 3.6$ Hz, $^3J_{HH} = 13.9$ Hz, 1 H, C_2H_3); 6.45 (dd, $^3J_{HH} = 13.9$ Hz, $^3J_{HH} = 20.2$ Hz, 1H, C_2H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.8 (d, $^2J_{PC} = 5.9$ Hz, NCH_3); 128.1 (C_2H_3); 144.8 (C_2H_3); 221.1 (*C*O); 225.9 (*C*O). $^{29}Si\{^1H\}$ NMR (tetrahydrofuran/D_2O): δ 83.3 (d, $^2J_{P-Si} = 35.4$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 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. $(H_2C{=}CH)(Cl)Si{=}Fe(CO)_4{\cdot}OP[N(CH_3)_2]_3$ (22), [Vinylchlorosilanediyl]iron(0) Tetracarbonyl Hexamethylphosphoric Triamide. At −40 °C 13.16 mmol (2.12 g) of $(H_2C{=}CH)SiCl_3$ dissolved in 50 mL of tetrahydrofuran were added dropwise to a suspension of 13.16 mmol (2.81 g) of $Na_2[Fe(CO)_4]$ (**3**) and 13.16 mmol (2.36 g) of $[(CH_3)_2N]_3P{=}O$ 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 $(H_2C{=}CH)SiCl_3$)). Mp: 113 °C dec. Anal. Calcd for $C_{12}H_{21}O_5N_3PClFeSi$ (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, $^3J_{PH} = 10.5$ Hz, 18H, CH_3); 5.98−6.58 (m, 3H, C_2H_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 37.3 (d, $^2J_{PC} = 4.6$ Hz, CH_3); 132.3 (C_2H_3); 143.1 (C_2H_3); 217.1 (*C*O). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 75.8 (d, $^2J_{PSi} = 30.3$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 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), [ω-Styrylphenylsilanediyliron(0) Tetracarbonyl Hexamethylphosphoric Triamide. As in the preparation of compound **22**, 7.06 mmol (1.51 g) of $Na_2[Fe(CO)_4]$ (**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, $^3J_{PH} = 10.2$ Hz, 18H, CH_3); 7.10−8.10 (m, 12H, C_2H_2 and C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 36.8 (br, CH_3); 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 (*C*O). $^{29}Si\{^1H\}$ NMR (tetrahydrofuran/D_2O): δ 83.6 (d, $^2J_{PSi} = 29.7$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 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).

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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.

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