Synthesis and Structure of the Donor-Stabilized Silylene (Silanediyl) Complexes (*t*-C$_4$H$_9$O)$_2$Si=Cr(CO)$_5$·HMPT and (*t*-C$_4$H$_9$O)$_2$Si=Fe(CO)$_4$·HMPT

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Reactions of di-*tert*-butoxydichlorosilane with Na$_2$Fe(CO)$_4$ and Na$_2$Cr(CO)$_5$ in THF, followed by addition of hexamethylphosphoric triamide (HMPT), afford the donor-stabilized silylene complexes (*t*-C$_4$H$_9$O)$_2$Si=Fe(CO)$_4$·HMPT (1a) and (*t*-C$_4$H$_9$O)$_2$Si=Cr(CO)$_5$·HMPT (7), respectively. In the case of the iron complex the THF adduct (*t*-C$_4$H$_9$O)$_2$Si=Fe(CO)$_4$·C$_4$H$_8$O (1b) could also be isolated. X-ray structure analyses of 1a and 7 show the silylene ligands to be Si-bound to the metal (Fe-Si = 2.289 (2) Å; Cr-Si = 2.431 (1) Å). The HMPT molecules are coordinated via their oxygen atoms to the unsaturated Si atoms, which thereby adopt a distorted tetrahedral geometry. (1a: space group $P2_1/n$, a = 10.069 (1) Å, b = 16.950 (1) Å, c = 15.986 (1) Å, β = 94.17 (1)°, V = 2721.1 Å^3, Z = 4; R_w = 0.044 for 280 refined parameters and 2812 observables with $F_o \geq 4.0\sigma(F_o)$. 7: space group $P2_1/n$, a = 9.912 (1) Å, b = 14.769 (2) Å, c = 19.206 (2) Å, β = 93.86 (1)°, V = 2805.2 Å^3, Z = 4; refinement of 334 parameters on 4926 reflections converged at R_w = 0.046.) The bonding in 1a and 7 is discussed, and a qualitative MO description is presented.

Introduction

Regarding the well-established field of coordination chemistry of carbenes[1] and their heavier analogues, stannylenes and germylenes,[2] the coordination chemistry of silylenes (silanediyls) remained limited. This seems the more surprising, as coordinated silanediyls presumably play an important role as reactive intermediates,[3] e.g., in metal-catalyzed SiSi coupling reactions or in the direct process.[4] The present knowledge about silylene complexes, however, is restricted to bridged μ-silylene species;[5] monomeric silylene complexes remained a virtually unknown class of compounds. Sakurai reported about a stable compound, Me$_2$SiFe(CO)$_4$,[6] and Schmid gave evidence for a donor adduct, Me$_2$Si(Et$_2$NH)Fe(CO)$_4$, which was observed at low temperatures.[7]

Recently cationic complexes containing silylene moieties have been described, like, e.g., the acetonitrile adduct [η^5-C$_5$H$_5$)(Me$_3$P)$_2$RuSi(C$_6$H$_5$)$_2$·CH$_3$CN]$^+$[B(C$_6$H$_5$)$_4$]$^-$.[8]

Finally, evidence for [(η^5-C$_5$H$_5$)(R$_3$P)$_2$FeSiR'$_2$]$^+$ cations (R = CH$_3$, C$_6$H$_5$, H, SiCl$_3$)[9] was obtained in the solvolysis reactions of complexes of several iron chlorosilanes. It should be noted that adduct formation is a well-documented phenomenon for complexes of divalent germanium and tin.[10] In these cases zwitterionic molecules with a characteristic coordination geometry are formed.[2]

We report here synthesis and characterization of the donor adducts (donor = THF, HMPT) of the silylene–iron and –chromium complexes (*t*-C$_4$H$_9$O)$_2$Si=Fe(CO)$_4$·HMPT (1a) and (*t*-C$_4$H$_9$O)$_2$Si=Cr(CO)$_5$·HMPT (7), which to our knowledge are the first fully characterized neutral transition-metal silylene complexes. A preliminary report on the iron complex has appeared.[11]

Experimental Section

All experiments were performed with conventional Schlenk tube techniques in an atmosphere of dry argon. THF and pentane were distilled from NaK alloy prior to use; HMPT was distilled in vacuo from sodium. Chromatography was carried out under argon with a column of 60-cm length and 3-cm diameter, equipped with a cooling jacket. The packing material (silica gel 200 mesh) was dried in vacuo and handled under argon. Na$_2$Cr(CO)$_5$ was prepared according to ref 12. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL FX 270 spectrometer at 270.1704, 67.9385, and 53.5401 MHz, respectively; the IR spectra were recorded on a Nicolet 5DX-FT-IR spectrometer. The mass spectra were recorded on a Varian MAT 311 A spectrometer by EI techniques. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Technischen Universität München.

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Di-*tert*-butoxydichlorosilane (3) was prepared by portion-wise addition of 2 equiv of KO-*t*-Bu (33.7 g, 0.3 mol) to 25.5 g (0.15 mol) of SiCl$_4$ in 200 mL of diethyl ether. The mixture was refluxed for 2 h and then filtered. After the solvent was stripped off in vacuo, 3 was purified by distillation: yield 30.2 g (82%); bp 34 °C (5 × 10^{-2} Torr); ^{1}H NMR (C$_6$D$_6$) δ 0.98 (s); ^{13}C NMR (C$_6$D$_6$) δ 31.10, 77.99 (s); ^{29}Si NMR (C$_6$D$_6$) δ -72.2 (s).

Tetracarbonyl(di-*tert*-butoxysilanediyl)iron(0)-hexamethylphosphoric triamide (1a) was prepared by mixing 3.6 g (14.8 mmol) of di-*tert*-butoxydichlorosilane (3) at -40 °C with a suspension of 5.1 g (14.8 mmol) of Na$_2$Fe(CO)$_4$·1,4-C$_4$H$_8$O$_2$ (2) (1,4-C$_4$H$_8$O$_2$ = 1,4-dioxane) in 50 mL of THF. After addition of 1 mL of HMPT and filtration at -30 °C, the brown solution was transferred onto a cooled (-20 °C) chromatography column. 1a was eluted with THF as the fastest running, almost colorless fraction. The solvent was stripped off in vacuo, and 1a was obtained as a white powder: yield 0.91 g (12%); mp 163 °C. 1a can be recrystallized from a saturated THF solution at -15 °C: ^{1}H NMR (C$_6$D$_5$CD$_3$, -48 °C) δ 1.60 (s, CH$_3$), 2.20 (d, ^3J(^{31}P^{1}H) = 10.4 Hz, HMPT); ^{13}C NMR (C$_6$D$_6$, 27 °C) δ 31.90, 72.50 (s, *tert*-butyl), 36.1 (d, ^2J(^{31}P^{13}C) = 5.9 Hz, HMPT), 224.0 (s, CO$_{eq}$), 228.9 (s, CO$_{ap}$); ^{29}Si NMR (C$_6$D$_6$, 27 °C) δ 7.1 (d, ^2J(^{31}P^{29}Si) = 26.4 Hz; IR (cm^{-1}, KBr) 2005 (w), 1920 (vs), 1883 (vs); MS (EI, 70 eV), m/e (relative intensity) 512 (M$^+$, 7.3). Anal. Calcd for C$_{18}$H$_{36}$-FeN$_3$O$_7$PSi (mol wt 512.4): C, 41.46; H, 6.96; Fe, 10.71; N, 8.06; Si, 5.39. Found: C, 41.37; H, 6.95; Fe, 10.58; N, 8.10; Si, 5.35.

1a and 1b from H$_2$Fe(CO)$_4$ and 3. 4 (5.0 g, 14.8 mmol) was dissolved in 80 mL of THF and mixed with 3.6 g (14.8 mmol) of 3 and 2.2 g (29.6 mmol) of Et$_3$N at -40 °C over a period of 30 min. Initially formed 1b was converted into 1a by addition of 5 mL of HMPT. 1a and 1b were purified by column chromatography as described above; yield 0.72 g (12%) of 1b and 0.91 g (12%) of 1a. 1b: ^{1}H NMR (C$_6$D$_5$CD$_3$, -30 °C) δ 1.6 (s, 18 H), 1.8 (m, 4 H), 3.6 (m, 4 H); ^{13}C NMR (C$_6$D$_5$CD$_3$, -31 °C) δ 32.0, 71.9 (s, *tert*-butyl), 223.5 (s, CO$_{eq}$), 229.1 (s, CO$_{ap}$), 25.1, 68.5 (s, THF); ^{29}Si NMR (C$_6$D$_5$CD$_3$, -31 °C) δ -9.4; MS (70 eV), m/e (relative intensity) 414 (M$^+$, 7.3).

Tetracarbonyl(di-*tert*-butoxysilanediyl)chromium(0)-Hexamethylphosphoric Triamide (7). To a solution of 0.4 g (1.0 mmol) of Na$_2$Cr(CO)$_5$ in 50 mL of THF was added 1 equiv (0.24 g, 1 mmol) of 3 at -40 °C over a period of 20 min. The yellow mixture was worked up by filtration and column chromatography as described above. The THF adduct was not isolated but transformed to the HMPT adduct 7 by addition of 179 mg (1.0 mmol) of HMPT. 7 crystallizes from a saturated THF solution as colorless rods: yield 0.065 g (12%); mp 144 °C dec; ^{1}H NMR (C$_6$D$_5$CD$_3$, -51 °C) δ 1.60 (s, CH$_3$, *tert*-butyl), 2.30 (d, ^3J(^{31}P^{1}H) = 10.6 Hz, HMPT); ^{13}C NMR (C$_6$D$_5$CD$_3$, -49 °C) δ 36.90, 27.77 (s, *tert*-butyl), 32.33 (d, ^2J(^{31}P^{13}C) = 5.8 Hz, HMPT), 228.1, 224.7 (s, CO); ^{29}Si NMR (C$_6$D$_6$, 27 °C) δ 12.7 (d, ^2J(^{31}P^{29}Si) = 37.2 Hz); IR (cm^{-1}, KBr) 2015 (w), 1991 (vs), 1930 (vs); MS (70 eV, EI), m/e (relative intensity) 545 (M$^+$, 4.3). Anal. Calcd for C$_{19}$H$_{36}$CrN$_3$-O$_8$PSi (mol wt 545.6): C, 41.83; H, 6.65; N, 7.70; Si, 5.15; Cr, 9.53. Found: C, 41.59; H, 6.74; N, 7.95; Si, 5.10; Cr, 9.49.

X-ray Structure Determination of 1a and 7. Suitable single crystals of 1a and 7 (from THF) were sealed into glass capillaries under an atmosphere of dry argon. Crystal data and numbers pertinent to data collection, reduction, and structure refinement are listed in Table I.

The structure of 1a was solved by direct methods (SHELXS-86[13]). Sixteen out of a total of 36 H atoms could be located in difference maps. The remainder was calculated at idealized geometrical positions. Refinement was done by full-matrix least-squares techniques with anisotropic displacement parameters for the non-H atoms (SHELX-76[14]). The hydrogen atoms were included as fixed atom contributions (U_{iso} = 0.10 Å^2). Only the 2812 reflections with $F_o \geq 4.0\sigma(F_o)$ were used in the refinement.

The structure of 7 was solved by conventional Patterson methods. The positions of 30 H atoms could be located; six positions were calculated. Anisotropic displacement parameters

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Table I. Crystallographic Data for 1a and 7

	1a	7
formula	C$_{18}$H$_{36}$FeN$_3$O$_7$PSi	C$_{19}$H$_{36}$CrN$_3$O$_8$PSi
M_r	512.41	545.57
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	10.069 (1)	9.912 (1)
b, Å	16.950 (1)	14.769 (2)
c, Å	15.986 (1)	19.206 (2)
β, deg	94.17 (1)	93.86 (1)
V, Å^3	2721.1	2805.2
Z	4	4
d_{calcd}, g cm^{-3}	1.273	1.292
μ(Mo Kα), cm^{-1}	6.9	5.4
$F(000)$, e	1104	1152
T, °C	23	-35
diffractometer	Enraf-Nonius CAD4	Syntex P2$_1$
radiation	Mo Kα, graphite monochromator	
λ, Å	0.710 69	0.710 69
scan type	θ-2θ	ω
scan width, in ω, deg	0.8 + 0.35 tan θ	0.8
((sin θ)/λ)$_{max}$, Å^{-1}	0.593	0.595
hkl range	+11, +20, ±18	+11, +17, ±22
monitor reflctns	2$\bar{1}$7, $\bar{5}$44, $\bar{2}$72	0$\bar{4}$0, 200, 006
decay, %	2.0	0.0
reflctns measd	5226	5433
reflctns unique	4761	4926
R_{int}	0.01	0.03
absorptn corr	empirical	empirical
rel transmissn	0.94–1.00	0.80–1.00
param ref	280	334
R^a	0.054	0.055
$R_w{}^b$	0.044	0.046
w	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
(shift/error)$_{max}$	0.05	0.2
$\Delta\rho_{fin}$(max/min), e Å^3	+0.50/-0.37	+0.33/-0.40

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum(|F_i| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 1a^a

atom	x/a	y/b	z/c	U(eq), Å^2
Fe	0.2030 (1)	0.2429 (1)	0.7850 (1)	0.055
P	0.5685 (1)	0.2802 (1)	0.6481 (1)	0.054
Si	0.3579 (1)	0.1710 (1)	0.7199 (1)	0.043
O1	0.3130 (3)	0.0978 (2)	0.6602 (2)	0.056
O2	0.4857 (3)	0.1371 (2)	0.7781 (2)	0.058
O3	0.4458 (3)	0.2284 (2)	0.6535 (2)	0.053
O4	0.0510 (5)	0.0983 (3)	0.7982 (4)	0.109
O5	0.0177 (5)	0.3386 (3)	0.8733 (3)	0.106
O6	0.1631 (6)	0.3340 (3)	0.6302 (3)	0.108
O7	0.4164 (5)	0.2762 (4)	0.9134 (3)	0.108
N1	0.6135 (5)	0.3327 (3)	0.7284 (3)	0.076
N2	0.6923 (4)	0.2240 (3)	0.6333 (3)	0.065
N3	0.5304 (5)	0.3408 (3)	0.5732 (4)	0.082
C1	0.2353 (6)	0.0764 (3)	0.5857 (4)	0.058
C11	0.1429 (11)	0.1332 (6)	0.5571 (6)	0.128
C12	0.1728 (11)	0.0013 (6)	0.6020 (5)	0.136
C13	0.3273 (9)	0.0591 (6)	0.5208 (5)	0.137
C2	0.5102 (6)	0.0676 (4)	0.8282 (4)	0.074
C21	0.3913 (10)	0.0418 (5)	0.8694 (6)	0.128
C22	0.5494 (10)	0.0017 (5)	0.7759 (5)	0.122
C23	0.6218 (10)	0.0882 (5)	0.8896 (6)	0.136
C4	0.1140 (6)	0.1544 (4)	0.7920 (4)	0.074
C5	0.0905 (6)	0.3008 (4)	0.8376 (4)	0.079
C6	0.1797 (6)	0.2977 (4)	0.6909 (4)	0.073
C7	0.3343 (6)	0.2626 (4)	0.8609 (4)	0.077
CO11	0.6948 (9)	0.3017 (6)	0.8002 (5)	0.118
CO12	0.5453 (9)	0.4038 (5)	0.7495 (6)	0.136
CO21	0.8265 (6)	0.2551 (5)	0.6300 (6)	0.123
CO22	0.6816 (6)	0.1460 (4)	0.6029 (5)	0.100
CO31	0.4239 (9)	0.3339 (5)	0.5120 (5)	0.117
CO32	0.6191 (12)	0.4007 (8)	0.5498 (8)	0.183

$^a U_{eq} = (U_1U_2U_3)^{1/2}$ where U_i are the eigenvalues of the U$_{ij}$ matrix.

were used for the refinement of the non-H atoms. The methyl groups were treated as rigid groups (U_{iso}(H) = 0.07 Å^2). All

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 7

atom	x/a	y/b	z/c	U(eq), Å^2
Cr	0.4044 (1)	0.1508 (1)	0.1564 (1)	0.028
P	0.3263 (1)	0.2543 (1)	-0.0753 (1)	0.026
Si	0.2672 (1)	0.2543 (1)	0.0832 (1)	0.024
O1	0.2358 (2)	0.3586 (1)	0.1062 (1)	0.032
O2	0.1172 (2)	0.2179 (1)	0.0539 (1)	0.034
O3	0.3353 (2)	0.2714 (1)	0.0033 (1)	0.027
O4	0.2671 (3)	0.2276 (2)	0.2792 (1)	0.055
O5	0.6270 (2)	0.2908 (2)	0.1710 (1)	0.054
O6	0.5534 (2)	0.0163 (1)	0.2509 (1)	0.048
O7	0.5465 (2)	0.0870 (1)	0.0307 (1)	0.044
O8	0.1828 (2)	0.0137 (2)	0.1209 (1)	0.055
N1	0.2173 (2)	0.1783 (2)	-0.1017 (1)	0.036
N2	0.2917 (2)	0.3514 (1)	-0.1122 (1)	0.033
N3	0.4729 (2)	0.2191 (1)	-0.0956 (1)	0.032
C1	0.3000 (3)	0.4423 (2)	0.1263 (1)	0.033
C11	0.4199 (3)	0.4591 (2)	0.0834 (2)	0.043
C12	0.3418 (4)	0.4397 (2)	0.2044 (1)	0.048
C13	0.1912 (4)	0.5142 (2)	0.1115 (2)	0.048
C2	-0.0175 (3)	0.2303 (2)	0.0778 (2)	0.036
C21	-0.0137 (3)	0.2362 (3)	0.1563 (2)	0.055
C22	-0.0778 (3)	0.3153 (2)	0.0441 (2)	0.048
C23	-0.0968 (3)	0.1475 (2)	0.0516 (2)	0.055
C4	0.3164 (3)	0.1982 (2)	0.2319 (1)	0.036
C5	0.5399 (3)	0.2384 (2)	0.1661 (1)	0.037
C6	0.4974 (3)	0.0682 (2)	0.2145 (1)	0.036
C7	0.4904 (3)	0.1110 (2)	0.0785 (1)	0.033
C8	0.2646 (3)	0.0663 (2)	0.1348 (1)	0.038
CO11	0.0873 (4)	0.1985 (3)	-0.1390 (2)	0.059
CO12	0.2242 (4)	0.0867 (2)	-0.0720 (2)	0.047
CO21	0.3274 (4)	0.3680 (2)	-0.1845 (1)	0.044
CO22	0.1907 (4)	0.4138 (2)	-0.0873 (2)	0.049
CO31	0.5956 (3)	0.2602 (2)	-0.0636 (2)	0.042
CO32	0.4948 (4)	0.1527 (2)	-0.1501 (2)	0.047

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for 1a^a

Fe-Si	2.289 (2)	Fe-C5	1.758 (6)
Si-O3	1.730 (3)	Fe-C4	1.754 (7)
Si-O1	1.610 (3)	Fe-C6	1.769 (7)
Si-O2	1.636 (4)	Fe-C7	1.761 (7)
P-O3	1.524 (3)	C5-O5	1.156 (6)
P-N1	1.599 (5)	C4-O4	1.152 (7)
P-N2	1.600 (5)	C6-O6	1.150 (7)
P-N3	1.603 (5)	C7-O7	1.158 (7)
Fe-Si-O3	112.1 (1)	C5-Fe-Si	177.1 (2)
Fe-Si-O1	120.5 (1)	C4-Fe-Si	86.7 (2)
Fe-Si-O2	117.6 (1)	C6-Fe-Si	86.9 (2)
O3-Si-O1	101.8 (2)	C7-Fe-Si	84.9 (2)
O3-Si-O2	97.5 (2)	Si-O1-C1	143.7 (3)
O1-Si-O2	104.0 (2)	Si-O2-C2	134.5 (4)
Si-O3-P	144.2 (2)		

^{a} Estimated standard deviation in units of the last significant Figure in parentheses.

measured, unique reflections were used in the refinement, with the exception of 12 reflections which showed abnormally large differences between observed and calculated structure factors, presumably due to mismeasurements.

Tables II and III contain the atomic coordinates and Tables IV and V selected bond distances and angles. Further details of the methods used in data collection and refinement, as well as the sources of the programs and scattering factors, are contained in ref 15. See note at the end of the paper regarding supplementary material.

Results and Discussion

Synthesis. The silylene complexes **1a** and **7** were prepared by reaction of di-*tert*-butoxydichlorosilane (**3**) with the carbonylmetallate dianions[16] of **2** and **6** in THF

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Table V. Selected Interatomic Distances (Å) and Angles (deg) for 7

Cr-Si	2.431 (1)	Cr-C6	1.855 (3)
Si-O3	1.736 (2)	Cr-C4	1.877 (3)
Si-O1	1.639 (2)	Cr-C5	1.866 (3)
Si-O2	1.644 (2)	Cr-C7	1.865 (3)
P-O3	1.527 (2)	Cr-C8	1.890 (3)
P-N1	1.616 (2)	C6-O6	1.154 (3)
P-N2	1.625 (2)	C4-O4	1.146 (3)
P-N3	1.616 (2)	C5-O5	1.158 (3)
		C7-O7	1.160 (3)
		C8-O8	1.142 (3)
Cr-Si-O3	111.5 (1)	C6-Cr-Si	175.8 (1)
Cr-Si-O1	123.0 (1)	C4-Cr-Si	86.6 (1)
Cr-Si-O2	116.7 (1)	C5-Cr-Si	89.6 (1)
O3-Si-O1	101.2 (1)	C7-Cr-Si	90.1 (1)
O3-Si-O2	98.2 (1)	C8-Cr-Si	85.1 (1)
O1-Si-O2	102.5 (1)	Si-O1-C1	142.7 (2)
Si-O3-P	148.2 (1)	Si-O2-C2	132.8 (2)

Scheme I
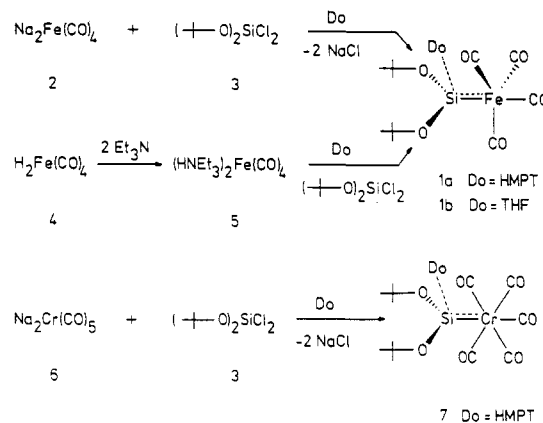
at low temperatures (Scheme I). This method affords the THF adducts, which are converted quantitatively by HMPT into the more stable HMPT adducts. (The THF adduct, however, was not isolated in the case of **7**). An even more convenient route to **1a,b** has been found via the bis(triethylammonium) tetracarbonylferrate(–II) (**5**) in solution by deprotonation of $H_2Fe(CO)_4$ with triethylamine. In all cases the purification of the products is performed by recrystallization or by column chromatography. Pure compounds **1a**, **1b**, and **7** form colorless crystals that are sensitive to air and moisture and can be sublimed in vacuo without decomposition.

Spectroscopic Data. ^{29}Si NMR spectroscopy is the most suitable analytical method for the identification of low-valent silicon compounds.[17] The ^{29}Si signals for **1a** and **7** (**1a**, 7.1 ppm; **1b**, -9.4 ppm; **7**, 12.7 ppm) show a significant low-field shift compared to **3** (**3**, -72.2 ppm).

Deshielded silicon is typically observed in compounds with trivalent Si atoms like in disilaethenes or silaethenes (+49 to +95 ppm (R_2Si=SiR_2); +41.4 ppm for $(Me_3Si)_2Si$=$C(OSiMe_3)CMe_3$).[18] The donor adducts of silaethenes in particular exhibit shift values, which are comparable with our data ($(Me_2Si$=$C(SiMe_3)SiMe$-*t*-Bu_2·THF, δ -7.5; Me_2Si=$C(SiMe_3)SiMe$-*t*-Bu_2·NMe_3 δ 5.83).[19] The IR data of **1a** and **7** are in agreement with trigonal-bipyramidal and octahedral coordination geome-

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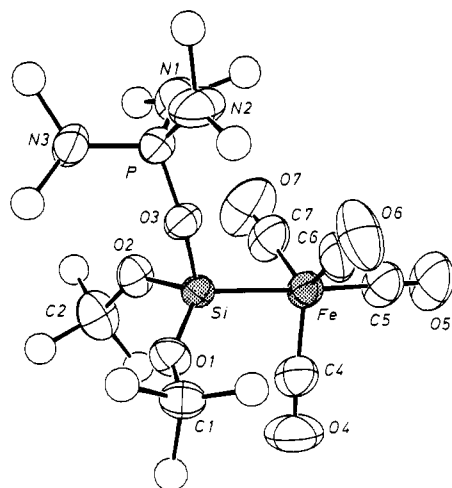
Figure 1. Molecular structure of **1a** and atomic numbering scheme used (ORTEP; thermal ellipsoids at the 50% level; methyl groups with arbitrary radii for clarity).

Figure 2. Molecular structure of **7** (ORTEP; thermal ellipsoids at the 50% level).

tries of the respective metal centers. For the A_1 and E modes of the CO stretching vibrations the following values are obtained: **1a** (local C_{3v} symmetry), 2005 (w), 1920 (vs), 1883 cm^{-1} (vs); **7** (local C_{4v} symmetry) 2015 (w), 1991 (vs), 1930 cm^{-1} (vs). The force constants[20] $k(^{12}CO)$ are lower for **1a** (1623, 1489, 1432 Nm^{-1}) than for **7** (1640, 1601, 1504 Nm^{-1}) and indicate a stronger donor influence of the co-ordinated silylene ligand on the metal-bound CO substituents in **1a** (apical coordination site) as compared to **7**. The ^{13}C NMR shifts of the carbonyl group are similar to those observed for comparable carbene complexes (**1a**, 224.0, 228.9 ppm; **7**, 224.7, 228.1 ppm; $(OC)_5Cr=C(OEt)$-$Si(C_6H_5)_3$ 216.7, 227.6 ppm).[21]

Molecular Structure of 1a and 7. The X-ray structure determinations of the crystals confirmed the structure assignments derived spectroscopically for the solution state. The Si atoms are bound to the metal in both cases (Figures 1 and 2). In **1a**, the silylene ligand occupies an apical position at the $Fe(CO)_4$ trigonal bipyramide. The Si atoms are further complexed by the oxygen atoms of the HMPT molecules. Together with the two O-*t*-Bu substituents a distorted tetrahedral substituent geometry arises whose bonding parameters (Tables IV and V) show remarkable peculiarities. Most importantly, the O-Si "donor bonds" (O3-Si), resulting from the HMPT complexation, are surprisingly long (**1a**, 1.730 (3) Å; **7**, 1.736 (2) Å) and exceed by far the range normally encountered for Si-O bonds at tetravalent silicon. The bond angles at O3 approach 150° which likewise may be attributed to the donor character of O3. The bond angles at the silicon also deserve some comment. In both compounds, the angles fall into three distinct groups (Tables IV and V). The angles M-Si-O3 are closest to the tetrahedral standard and the M-Si-O1/O2 values are close to 120°, while the remainder angles show only minor deviations from 100°. From an inspection of the molecular geometries (Figures 1 and 2) it is obvious that the deviations in M-Si-O1/O2 are mainly due to steric interactions between the O-*t*-Bu-substituents at Si and the metal-bound carbonyl groups. It should be mentioned that similarly distorted tetrahedral substituent geometries as observed for the Si atoms in **1a** and **7** have been found for the donor adducts of heavier group 14 "diyl" complexes, notably those of
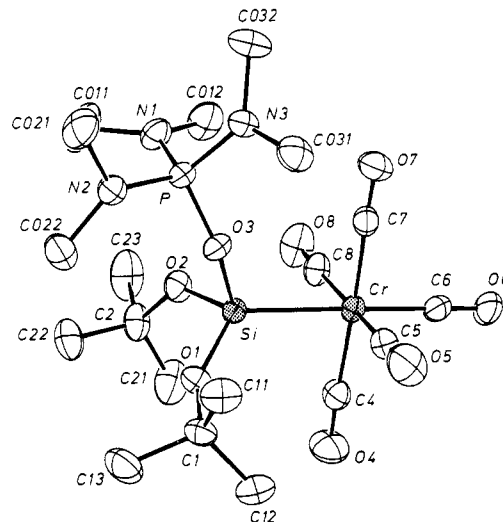
Sn(II).[2,10] Most striking, however, is the similarity to the recently described donor adducts of silicon–carbon[19] and silicon–nitrogen double bonds[22] which likewise have long Si donor bonds (donor = tetrahydrofuran, F$^-$). As discussed in detail in ref[19], a rather loose coordination of the donor molecules was concluded and the bonding was described as a resonance between essentially nonbonding, individual molecules and a strongly bound, zwitterionic adduct. For the donor adducts of Si=C[19] and Si=N[22] double bonds, a comparison with the structures of the uncomplexed silaethenes and silaketimines was possible and proved valuable for a description of the bonding. The metal silicon bonds in **1a** and **7** (Fe–Si = 2.289 (2) Å; Cr–Si = 2.431 (1) Å) have no precedent in the literature and cannot be compared directly with, e.g., other transition-metal silicon single or double bonds. Although data for a variety of silyl complexes are available,[23] they inevitably feature the metal centers in different oxidation states and/or coordination geometries and thus render a direct comparison problematic. Moreover, the work on silaethenes has shown that double bonds involving silicon are particularly susceptible to polarization effects, which are difficult to assess for transition-metal complexes. However, if for a rough comparison 1.11 and 1.21 Å are taken as covalent radii for the zerovalent metal atoms in the Fe(CO)$_4$ and Cr(CO)$_5$ fragments,[24] one arrives with a double-bond radius of 1.07 Å for Si[25] and at 2.18/2.28 Å for uncomplexed $R_2Si=Fe/Cr$ coordinative bonds.[26] That the M–Si bond lengths in donor complexes like **1a** and **7** are slightly longer was also found for the silaethene and silaketimine adducts mentioned above. It therefore appears that even shorter M–Si bonds have to be expected for uncomplexed, neutral silylene transition-metal complexes, with the substituent geometry of the unsaturated

(20) Bratermann, P. *Metal Carbonyl Spectra*; Academic: New York, 1975, p 1.

(21) Schubert, U. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983, p 73.
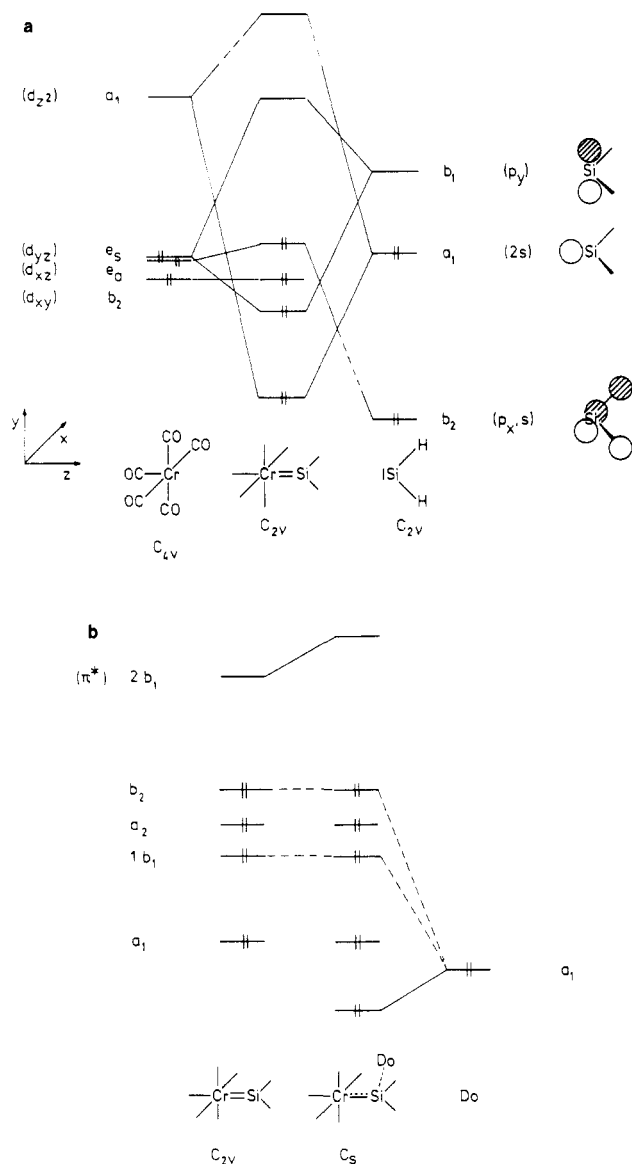
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(24) Obtained by subtraction of a presumed C atom radius of 0.7 Å from the M–CO bond lengths in Fe(CO)$_5$[24a] and Cr(CO)$_6$.[24b] (a) Fe–C-(axial) = 1.810 (3) Å: Beagley, B.; Schmidling, D. G. *J. Mol. Struct.* **1974**, *22*, 466. (b) Cr–C(ar) = 1.914 Å: Rees, B.; Mitschler, A. *J. Am. Chem. Soc.* **1976**, *98*, 7918.

(25) One-half of the Si=Si bond lengths in West's or Masamunes's (symmetrical) Disilaethenes. Cf., e.g.: Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793.

(26) This argumentation largeley neglects dipolar contributions to the bond lengths in question.

Figure 3. a. Qualitative correlation diagram (energies arbitrary) for a Cr=Si double bond according to ref 28. b. Qualitative correlation diagram for the interaction between the lone pair of a donor molecule and the π*-orbital of the Cr=Si bond, which leads to an increased gap between the π*- and the π-orbital of the donor adduct compared to the uncomplexed molecule.

Si atom close to trigonal planar.

Discussion of the M-Si Bond in 1a and 7. The bonding in a "donor-free" silylene complex can basically be described in a way analogous to that for the a M=C bond in metal carbene complexes. However, the degree of π-back-bonding is different in the discussed compounds. In a trigonal-bipyramidal d^8 system, the degree of π-

back-bonding betweeen the central metal atom and a π-acidic ligand is lower for an apical coordination site than for an equatorial one. For a octahedral d^6 system, all coordination sites for a ligand L in $LM(CO)_5$ are equivalent. In both cases the "π-back-bond" is formed by an interaction of a set of degenerate e orbitals (d_{xz}, d_{yz}; in ref 27d, however, also 4p orbitals at Fe are used) with the empty b_1 orbital of the silanediyl ligand.[27] The degenerate e orbitals are orthogonal to each other. As a consequence, any rotational barrier of the M=Si bond should be negligible.[28] This could be confirmed by variable temperature NMR investigations.[11] According to an ab initio SCF calculation for $(OC)_5Cr=Si(OH)H$, the LUMO is π-antibonding between Cr and Si and is basically located at the silicon atom with a maximum coefficient at Si of 0.85 and an orbital energy of 2.12 eV.[28] This means that the silylene–metal bond is rather polar and that, in analogy to Fischer-type metal carbene complexes, the metal-substituted Si atom is electron-deficient. The additional bonding of a donor molecule to the unsaturated Si atoms leads to a stabilizing interaction between the lone pair of the HMPT-O atom and the LUMO of the silylene complex (Figure 3a,b). The coordination of a donor molecule to the positively polarized silicon atom gives rise, depending on the donor strength of the ligand, to a simultaneous reduction of the Cr–Si π-bond and to a pyramidalization at the silicon atom.

Summary. The synthesis of stable donor adducts of neutral transition-metal silylene complexes affords a first full spectroscopic and structural characterization of examples of this long sought for class of compounds. The structural data obtained yield reference values for future work and allow a first tentative assignment of the mode of bonding in donor adducts of coordinated silylenes. It remains to be seen, if the adducts described here also provide the basis for the preparation of sufficiently stable "donor-free" silylene transition-metal complexes.

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(28) Nakatsuji, H.; Ushio, J.; Yonezawa, T. *J. Organomet. Chem.* **1983**, *258*, C1.