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${}^{t}Bu_2Si{=}Cr(CO)_5 \cdot Na(CF_3SO_3) \cdot 2$ THF: a salt-adduct of a chromium–silicon double bond *

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Abstract

The salt-adduct $({}^{t}Bu)_2Si{=}Cr(CO)_5 \cdot Na(CF_3SO_3) \cdot 2$ THF $[\mathbf{1} \cdot Na(CF_3SO_3)]$ of a chromium–silicon double bond has been investigated in the solid state and in solution. The triflate $Na(CF_3SO_3)$ does not coordinate rigidly to **1** but exchanges rapidly in non-polar solvents (^{29}Si-NMR 150.7 ppm). The X-ray crystal structure of $\mathbf{1} \cdot Na(CF_3SO_3)$ shows a Cr–Si bond distance of 2.475(1) Å and an Si–O6 bond distance of 1.857(3) Å. The sum of bond angles at Si is 349.5°. In the crystal the molecules of $\mathbf{1} \cdot Na(CF_3SO_3)$ are linked by heptacoordinate sodium ions to form a helix along the 2_1 direction of the unit cell ($P2_1/c$). Upon treatment with pyridine or CO, $\mathbf{1} \cdot Na(CF_3SO_3)$ eliminates di(tert-butyl)silylene which trimerizes to give cyclic $[({}^{t}Bu)_2Si]_3$. $\mathbf{1} \cdot Na(CF_3SO_3)$ can be transformed with HPMA (hexamethylphosphorotriamide) into $({}^{t}Bu)_2(HMPA)Si{=}Cr(CO)_5$, **3**. A single crystal X-ray structure determination of **3** shows a Cr–Si bond distance of 2.527(3) Å and an Si–O6 bond distance of 1.777(6) Å. Complex **3** can be described as a σ-donor complex $({}^{t}Bu)_2(HMPA)Si \rightarrow Cr(CO)_5$.

1. Introduction

The investigation of structure and bonding in silanediyl-(silylene) complexes is of great interest [1], since silylene complexes [2] play an essential role as reactive intermediates in a variety of important reactions. Some examples are the dehydrogenative coupling of disilanes to polysilanes [3], the hydrosilylation reaction [4], the direct process of the formation of dimethyldichlorosilane from MeCl and $CuSi_2$ [5], and the MO-Chemical Vapour Deposition (MOCVD) of silicides from volatile unimolecular precursors [6].

2. Results and discussion

The metal–silicon double bonds known for Fischer-carbene complexes so far are highly polar. This polarity is the basis for silylene complexes to form readily adducts with various solvents. The coordination of salt to a silicon–element double bond has only been observed occasionally [7], and is an interesting variant to reduce the electronic and coordinative unsaturation at the silicon atom.

In this paper a 1:1 salt adduct, **1** · NaOTf, of a chromium–silicon double bond is described for the first time. The compound has been obtained by reaction of di-tert-butyl-bis(trifluorosulfonyl)silane with disodium-pentacarbonylchromate. The sodium-trifluorosulfonate co-crystallizes with di-tert-butylsilanediyl-chromiumpentacarbonyl, but does not coordinate rigidly to **1**, not even in non-polar solvents such as benzene or pentane. When toluene is used as solvent, a fast exchange of the trifluorosulfonate in **1** · NaOTf with added NaOTf occurs, as has been proved by ^{13}C- and ^{19}F-NMR spectroscopy (both spectra are identical with NaOTf) and also indirectly by the extreme downfield shift of the ^{29}Si-NMR signal of **1** · NaOTf at 150.7 ppm. Furthermore, the NMR-signals show no significant change upon addition of sodium trifluorosulfonate or upon variation of the temperature.

The salt adduct formation is a typical feature of extremely polar (double) bonds, like those in phosphorus ylides, silaimines or silaethenes. Structural investigations of salt adducts have only been reported for silaimines and silaethenes [7]. **1** · NaOTf has been characterized by a single crystal X-ray structure determina-

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* Dedicated to Professor E.O. Fischer on the occasion of his 75th birthday.

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TABLE 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **1** [a]

Atom	x	y	z	$U_{eq.}$
Na	0.1564(2)	−0.1837(1)	0.00043(8)	0.064
Cr	0.33239(6)	0.22008(6)	0.01657(3)	0.056
Si	0.3043(1)	0.1637(1)	0.12274(5)	0.052
C1	0.5007(4)	0.1897(3)	0.0192(2)	0.059
C2	0.2894(4)	0.0880(4)	−0.0080(2)	0.060
C3	0.1658(4)	0.2567(4)	0.0094(2)	0.070
C4	0.3759(5)	0.3499(4)	0.0415(3)	0.085
C5	0.3480(5)	0.2556(5)	−0.0638(3)	0.083
O1	0.6064(3)	0.1774(3)	0.0173(2)	0.080
O2	0.2625(3)	0.0097(3)	−0.0255(2)	0.081
O3	0.0651(3)	0.2798(3)	0.0003(2)	0.102
O4	0.4069(5)	0.4311(3)	0.0538(3)	0.136
O5	0.3577(4)	0.2763(4)	−0.1143(2)	0.127
O6	0.1634(2)	0.0850(2)	0.1306(1)	0.059
S	0.0593(1)	0.03228(9)	0.10004(5)	0.051
O7	−0.0178(3)	0.0986(3)	0.0662(2)	0.082
O8	0.0941(4)	−0.0594(3)	0.0730(2)	0.084
C6	−0.0315(5)	−0.0048(5)	0.1655(3)	0.089
F1	0.0348(4)	−0.0501(4)	0.2061(2)	0.141
F2	−0.0793(4)	0.0742(4)	0.1902(2)	0.162
F3	−0.1211(3)	−0.0651(3)	0.1470(2)	0.131
C7	0.4171(4)	0.0636(4)	0.1565(2)	0.067
C71	0.4353(5)	−0.0196(4)	0.1094(3)	0.082
C72	0.5446(5)	0.1120(5)	0.1688(3)	0.096
C73	0.3772(6)	0.0159(6)	0.2152(3)	0.117
C8	0.2560(5)	0.2613(4)	0.1829(2)	0.081
C81	0.1599(6)	0.3312(5)	0.1540(3)	0.104
C82	0.3657(7)	0.3260(5)	0.2030(3)	0.123
C83	0.1976(7)	0.2168(6)	0.2399(3)	0.135
O11	−0.2016(4)	0.2832(3)	−0.0855(2)	0.097
C12	−0.3223(7)	0.3184(7)	−0.1016(4)	0.152
C13	−0.321(1)	0.3466(9)	−0.1652(4)	0.212
C14	−0.200(1)	0.333(1)	−0.1853(5)	0.260
C15	−0.1171(9)	0.3057(8)	−0.1314(5)	0.194
O21	0.8158(4)	0.3229(3)	0.0669(2)	0.104
C22	0.832(1)	0.4290(6)	0.0494(5)	0.184
C23	0.806(1)	0.4860(8)	0.0984(6)	0.264
C24	0.782(1)	0.425(1)	0.1478(5)	0.247
C25	0.7841(9)	0.3153(7)	0.1275(4)	0.164

[a] $U_{eq} = (U_1 U_2 U_3)^{1/3}$ where U_1, U_2 and U_3 are the characteristic values of the U_{ij} matrix. ESDs are in parentheses.

tion; the results are briefly summarized [8] (Table 1, 2): The Cr–Si bond distance of **1** · NaOTf is 2.475 (1) Å, which is in agreement with the Cr–Si bond distance of 2.4 Å obtained by *ab initio* calculations for $(CO)_5Cr{=}Si(OH)H$ [9] and that of 2.45 Å calculated for $[Cr{=}SiH_2]^+$ [10]. The Si–O6 bond distance is 1.857(3) Å and out of the range expected for a covalent Si–O bond [11]; the sum of bond angles between the three covalently bonded substituents at silicon is 349.5°.

The sodium ion in **1** · NaOTf coordinates weakly to the oxygen atom of a carbonyl function [O3–Na 2.861(4) Å] and to the oxygen atom of a sulfonate ion [O7–Na

TABLE 2. Selected interatomic distances (Å) and angles (deg) in the crystal structure of **1** [a]

Na–O2	2.861(4)	S–O8	1.405(4)
Na–O8	2.411(4)	C6–S	1.830(6)
Na–O1A	2.604(4)	C6–F1	1.278(7)
Na–O3A	2.712(4)	C6–F2	1.292(8)
Na–O7A	2.342(4)	C6–F3	1.311(7)
Na–O11A	2.342(4)	F1–C6	1.278(7)
Na–O21A	2.374(4)	F2–C6	1.292(8)
Cr–Si	2.475(1)	F3–C6	1.311(7)
Cr–C1	1.864(5)	C7–Si	1.934(5)
Cr–C2	1.882(5)	C7–C71	1.525(8)
Cr–C3	1.869(5)	C7–C72	1.538(7)
Cr–C4	1.858(6)	C7–C73	1.509(8)
Cr–C5	1.840(6)	C71–C7	1.525(8)
Si–Cr	2.475(1)	C72–C7	1.538(7)
Si–O6	1.857(3)	C73–C7	1.509(8)
Si–C7	1.934(5)	C8–Si	1.929(6)
Si–C8	1.929(6)	C8–C81	1.517(8)
C1–Cr	1.864(5)	C8–C82	1.519(9)
C1–O1	1.156(6)	C8–C83	1.534(9)
C2–Cr	1.882(5)	C81–C8	1.517(8)
C2–O2	1.138(6)	C82–C8	1.519(9)
C3–Cr	1.869(5)	C83–C8	1.534(9)
C3–O3	1.144(6)	O11–C12	1.422(9)
C4–Cr	1.858(6)	O11–C15	1.41(1)
C4–O4	1.153(7)	O11–NaB	2.342(4)
C5–Cr	1.840(6)	C12–O11	1.422(9)
C5–O5	1.151(7)	C12–C13	1.45(1)
O1–C1	1.156(6)		
O1–NaA	2.604(4)	C13–C14	1.41(2)
O2–Na	2.861(4)		
O2–C2	1.138(6)	C14–C15	1.51(1)
O3–C3	1.144(6)	C15–O11	1.41(1)
O3–NaB	2.712(4)	C15–C14	1.51(1)
O4–C4	1.153(7)	O21–C22	1.465(9)
O5–C5	1.151(7)	O21–C25	1.387(9)
O6–Si	1.857(3)	O21–NaA	2.374(4)
O6–S	1.471(3)	C22–O21	1.465(9)
S–O6	1.471(3)	C22–C23	1.35(2)
S–O7	1.409(4)		
S–O8	1.405(4)	C23–C24	1.38(2)
S–C6	1.830(6)		
S–O7	1.409(4)	C24–C25	1.52(2)
O7–NaB	2.342(4)	C25–O21	1.387(9)
O8–Na	2.411(4)		
O8–Na–O2	69.0(1)	O3–C3–Cr	174.7(5)
O1A–Na–O2	62.8(1)	O4–C4–Cr	175.8(6)
O1A–Na–O8	111.6(1)	O5–C5–Cr	179.0(6)
O3A–Na–O2	141.1(1)	NaA–O1–C1	168.3(3)
O3A–Na–O8	93.2(1)	C2–O2–Na	147.8(3)
O3A–Na–O1A	152.7(1)	NaB–O3–C3	135.4(4)
O7A–Na–O2	72.9(1)	S–O6–Si	147.4(2)
O7A–Na–O8	84.3(1)	O7–S–O6	112.4(2)
O7A–Na–O1A	120.9(1)	O8–S–O6	113.1(2)
O7A–Na–O3A	71.0(1)	O8–S–O7	118.4(2)
O11A–Na–O2	125.5(1)	C6–S–O6	100.9(2)
O11A–Na–O8	84.2(1)	C6–S–O7	105.0(2)
O11A–Na–O1A	87.0(1)	C6–S–O8	104.9(3)
O11A–Na–O3A	84.4(1)	NaB-O7-S	170.0(2)
O11A–Na–O7A	152.1(2)	S–O8–Na	162.4(2)
O21A–Na–O2	121.1(1)	F1–C6–S	111.7(4)

TABLE 2. (*continued*)

O21A–Na–O8	169.2(2)	F2–C6–S	110.1(5)
O21A–Na–O1A	78.2(1)	F2–C6–F1	108.0(5)
O21A–Na–O3A	76.3(1)	F3–C6–S	109.0(4)
O21A–Na–O7A	94.7(1)	F3–C6–F1	109.2(6)
O21A–Na–O11A	91.9(2)	F3–C6–F2	108.7(5)
C1–Cr–Si	92.9(1)	C71–C7–Si	108.9(3)
C2–Cr–Si	87.4(1)	C72–C7–Si	109.7(4)
C2–Cr–C1	92.5(2)	C72–C7–C71	106.8(4)
C3–Cr–Si	90.8(2)	C73–C7–Si	114.9(4)
C3–Cr–C1	176.0(2)	C73–C7–C71	108.9(5)
C3–Cr–C2	89.2(2)	C73–C7–C72	107.4(4)
C4–Cr–Si	92.1(2)	C81–C8–Si	108.4(4)
C4–Cr–C1	87.1(2)	C82–C8–Si	110.6(4)
C4–Cr–C2	179.3(2)	C82–C8–C81	107.5(5)
C4–Cr–C3	91.2(2)	C83–C8–Si	115.3(4)
C5–Cr–Si	176.7(2)	C83–C8–C81	106.4(5)
C5–Cr–C1	88.3(2)	C83–C8–C82	108.3(5)
C5–Cr–C2	89.4(2)	C15–O11–C12	111.2(6)
C5–Cr–C3	88.0(2)	NaB–O11–C12	123.7(4)
C5–Cr–C4	91.1(3)	NaB–O11–C15	124.7(5)
O6–Si–Cr	112.2(1)	C13–C12–O11	107.2(7)
C7–Si–Cr	118.4(1)	C14–C13–C12	107.4(9)
C7–Si–O6	95.3(2)	C15–C14–C13	108.8(9)
C8–Si–Cr	119.1(2)	C14–C15–O11	103.2(8)
C8–Si–O6	94.2(2)	C25–O21–C22	110.8(6)
C8–Si–C7	112.0(2)	NaA–O21–C22	124.2(5)
O1–C1–Cr	174.2(4)	NaA–O21–C25	125.0(4)
O2–C2–Cr	176.8(4)	C23–C22–O21	107.2(8)
		C24–C23–C22	110.4(9)

[a] ESDs in units of the last significant figure in parentheses.

2.411(4) Å], as well as to two THF molecules [Na–O11 2.342(4) Å and Na–O21 2.374(4) Å]. Furthermore, the coordination sphere of Na is completed to a formally sevenfold-coordination *via* interaction of the sodium ion with the CO-groups of two further adjacent molecules of **1** · NaOTf [O2–Na 2.712(4) Å and O1–Na 2.604(4) Å] and the O-atom of a second triflate group [O8–Na 2.342(4) Å]. The linked structure of **1** · NaOTf molecules forms a helix of di-tert-butylsilanediyl-chromiumpentacarbonyl and sodiumtrifluorosulfonate · 2 THF in the crystal, with its repetition vector oriented into the direction of the 2_1-screw-axis (Fig. 2).

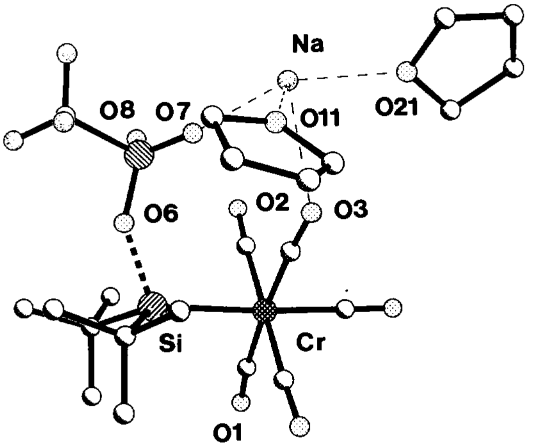


Fig. 1. Crystal structure of the silanediyl complex $(^tBu)_2Si{=}Cr(CO)_5 \cdot NaOTf \cdot 2THF$ [$1 \cdot Na(CF_3SO_3)$]. Selected bond distances (Å) and bond angles (°) are: Cr–Si 2.475(1), Si–O6 1.857(3), Na–O2 2.861(4), Na–O8 2.411(4), Na–O11 2.342(4), Na–O21 2.374(4), Na–O3 2.712(4), Na–O1 2.604(4), Na–O7 2.342(4), C7–Si–Cr 118.4(1), C8–Si–Cr 119.1(2), C8–Si–C7 112.0(2).

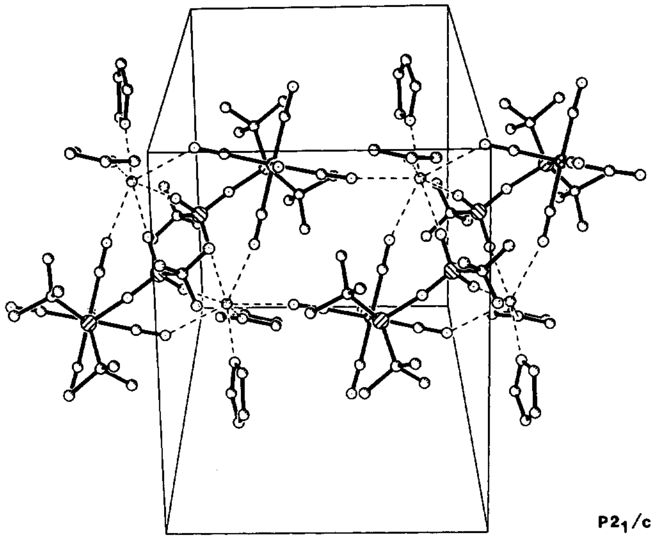
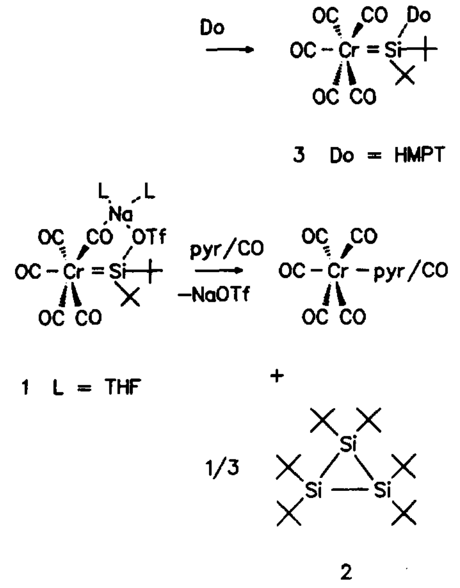


Fig. 2. View of the elemental cell of $1 \cdot NaOTf \cdot 2$ THF showing the helix oriented towards the direction of the 2_1-axis.

A preliminary investigation of the reactivity of **1** · NaOTf shows a high activity towards nucleophilic- and oxygen-containing (O_2) reagents.

By using extreme reaction conditions (an excess of pyridine or CO), di-tert-butylsilanediyl is cleaved from the metal fragment, with formation of hexa-tert-butylcyclotrisilane, **2**. Hexa-tert-butylcyclotrisilane **2** has been shown to undergo a variety of interesting cycloaddition reactions giving rise to either di-tert-butylsilylene or tetra-tert-butyldisilaethene [12]. Thus, **1** · NaOTf has an interesting potential as a silylene- or a disilaethene-transfer reagent [13].

In polar solvents, such as CH_3CN, THF or HMPA, **1** readily forms adducts with the solvent. The structure of the stable HMPA adduct **3** is depicted in Fig. 3 and allows an interesting comparison with **1** · NaOTf [14] (Table 3, 4). The Cr–Si bond in **3** is lengthened to 2.527(3) Å *via* adduct formation between silicon and HMPA. The bond distances P–O6 and Si–O6 are 1.500(6) and 1.777(6) Å, respectively, the latter clearly beyond the range of covalent bonding (as in **1** · NaOTf). Furthermore, it is interesting to note that the four equatorial CO groups in **3** are bent away from the silicon atom out of the plane normal to the Cr–Si bond by up to 6.2°, which undoubtedly is due to steric



congestion of **3**. An MM2-force field calculation of **3** yields an overall tension energy E_{tot} that is higher (63.2 kcal mol^{-1}) than that for the analogous methyl compound. The total energy of repulsion (E_{tot}) is a result of several (roughly equal) contributions of bond stretching energy E_{str}, angle tension E_{ang} and torsion energy E_{tor}, as well as attractive and repulsive van-der-Waals interactions E_{vdw} [15]. For **3**, no Cr–Si π-bond contributions can be recognized, and **3** can thus be considered as a σ-donor complex of an HMPA-adduct of di-tert-butylsilanediyl, coordinating as a 2e$^-$ donor ligand to the 16e$^-$-complex fragment Cr(CO)$_5$, ^{t}Bu$_2$(HMPT)Si → Cr(CO)$_5$.

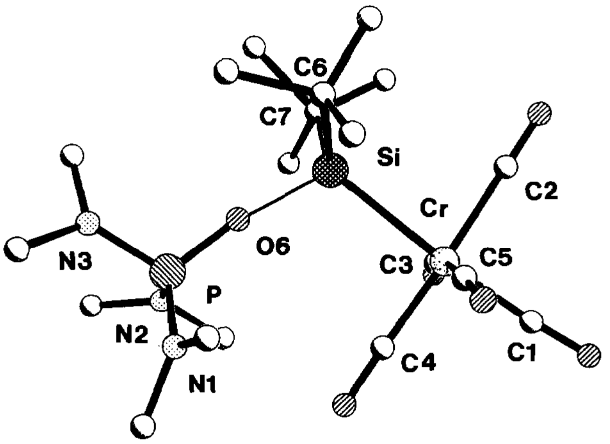


Fig. 3. Crystal structure of the silanediyl complex (^{t}Bu)$_2$(HMPT)Si=Cr(CO)$_5$, **3**. Selected bond distances (Å) and bond angles (°) are: Cr–Si 2.521(1), Si–O6 1.787(1), C6–Si–Cr 116.3(1), C7–Si–Cr 116.4(1), C6–Si–C7 107.6(1), C2–Cr–Si 83.6(1), C3–Cr–Si 92.6(1), C4–Cr–Si 93.4(1), C5–Cr–Si 96.2(1).

TABLE 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for **3** [a]

Atom	x	y	z	U_{eq}
Cr	0.33069(7)	0.3769(1)	0.64144	0.027
Si	0.3938(1)	0.1946(3)	0.7408(2)	0.026
P	0.5541(1)	0.2803(3)	0.7455(2)	0.028
N1	0.5576(3)	0.4506(9)	0.7613(6)	0.032
N2	0.5866(4)	0.2399(8)	0.6471(7)	0.038
N3	0.5983(4)	0.1988(9)	0.8249(7)	0.039
C1	0.2830(5)	0.499(1)	0.5690(6)	0.032
O1	0.2462(4)	0.5719(7)	0.5196(6)	0.050
C2	0.2553(6)	0.2609(9)	0.6731(6)	0.036
O2	0.2089(3)	0.1933(7)	0.6873(7)	0.056
C3	0.3476(5)	0.2803(9)	0.5289(7)	0.036
O3	0.3558(4)	0.2322(8)	0.4522(5)	0.053
C4	0.4081(5)	0.4852(9)	0.6187(5)	0.025
O4	0.4551(4)	0.5560(8)	0.6057(7)	0.063
C5	0.3144(5)	0.510(1)	0.7442(9)	0.044
O5	0.3015(5)	0.6011(8)	0.7933(7)	0.064
C6	0.3663(5)	0.182(1)	0.8759(7)	0.030
C61	0.3473(5)	0.325(1)	0.9155(7)	0.050
C62	0.4316(6)	0.129(1)	0.9357(7)	0.053
C63	0.3092(6)	0.082(1)	0.8907(8)	0.059
C7	0.3994(5)	0.0021(9)	0.6894(8)	0.034
C71	0.3324(7)	−0.0500(9)	0.654(1)	0.068
C72	0.4477(6)	0.000(1)	0.6061(8)	0.045
C73	0.4252(6)	−0.115(1)	0.7614(8)	0.048
O6	0.4817(3)	0.2323(6)	0.7505(6)	0.031
C11	0.6092(7)	0.545(1)	0.720(1)	0.075
C12	0.5120(8)	0.521(1)	0.8331(9)	0.071
C21	0.5557(7)	0.285(1)	0.5551(7)	0.052
C22	0.6568(5)	0.180(1)	0.634(1)	0.067
C31	0.6428(7)	0.272(1)	0.8955(9)	0.068
C32	0.6020(6)	0.045(1)	0.8289(8)	0.053

[a] $U_{eq} = (U_1 U_2 U_3)^{1/3}$ where U_1, U_2 and U_3 are the characteristic values of the U_{ij} matrix. ESDs are in parentheses.

3. Experimental details

3.1. *Di(tert-butyl)silanediyl-chromium(0)-pentacarbonyl, 1*

2.62 g (11.0 mmol) of Na$_2$[Cr(CO)$_5$] were dissolved in 250 ml of THF and 5.0 g (11.0 mmol) of Di-tert-butylbis(trifluorosulfonyl)silane were slowly added to the solution at −40°C. The solvent was removed at −20°C under vacuum and the residue was redissolved in ether. After separation from a residue of NaOTf, **1** · NaOTf was crystallized at −20°C.

^{1}H-NMR (toluene-d_8): $\delta = 1.23$, s, 18 H (CH$_3$); ^{13}C-NMR (toluene-d^8): $\delta = 29.9$ (q, $^1J(^{13}C^1H) = 124$ Hz, CH$_3$), 30.6 (m, CCH$_3$), 118.7 (q, $^1J(^{19}F^{13}C) = 317$, CF$_3$), 225.1 (s, CO$_{eq}$), 228.5 (s, CO$_{ax}$); ^{29}Si-NMR (toluene-d^8): $\delta = 150.7$. IR (THF): ν(CO) 2044, 1987, 1936. Mp. 212°C. Analysis $C_{22}H_{34}CrF_3NaO_{10}SSi$

TABLE 4. Selected interatomic distances (Å) and angles (deg) in the crystal structure of **3** [a]

Cr–Si	2.527(3)	C3–O3	1.18(1)
Cr–C1	1.795(9)	O3–C3	1.18(1)
Cr–C2	1.89(1)	C4–Cr	1.860(9)
Cr–C3	1.85(1)	C4–O4	1.15(1)
Cr–C4	1.860(9)	O4–C4	1.15(1)
Cr–C5	1.93(1)	C5–Cr	1.93(1)
Si–Cr	2.527(3)	C5–O5	1.13(1)
Si–C6	1.98(1)	O5–C5	1.13(1)
Si–C7	1.935(9)	C6–Si	1.98(1)
Si–O6	1.777(6)	C6–C61	1.49(1)
P–N1	1.602(8)	C6–C62	1.62(1)
P–N2	1.57(1)	C6–C63	1.48(1)
P–N3	1.606(9)	C61–C6	1.49(1)
P–O6	1.500(6)	C62–C6	1.62(1)
N1–P	1.602(8)	C63–C6	1.48(1)
N1–C11	1.47(1)	C7–Si	1.935(9)
N1–C12	1.50(2)	C7–C71	1.49(2)
N2–P	1.57(1)	C7–C72	1.51(1)
N2–C21	1.49(1)	C7–C73	1.57(1)
N2–C22	1.51(1)	C71–C7	1.49(2)
N3–P	1.606(9)	C72–C7	1.51(1)
N3–C31	1.49(2)	C73–C7	1.57(1)
N3–C32	1.43(1)	O6–Si	1.777(6)
C1–Cr	1.795(9)	O6–P	1.500(6)
C1–O1	1.21(1)	C11–N1	1.47(1)
O1–C1	1.21(1)	C12–N1	1.50(2)
C2–Cr	1.89(1)	C21–N2	1.49(1)
C2–O2	1.13(1)	C22–N2	1.51(1)
O2–C2	1.13(1)	C31–N3	1.49(2)
C3–Cr	1.85(1)	C32–N3	1.43(1)
C1–Cr–Si	177.1(3)	C11–N1–P	124.7(7)
C2–Cr–Si	82.8(3)	C12–N1–P	119.9(7)
C2–Cr–Cl	94.7(4)	C12–N1–C11	114.8(8)
C3–Cr–Si	93.2(3)	C21–N2–P	122.0(7)
C3–Cr–C1	85.4(4)	C22–N2–P	124.9(9)
C3–Cr–C2	93.7(4)	C22–N2–C21	112(1)
C4–Cr–Si	93.1(3)	C31–N3–P	124.5(7)
C4–Cr–Cl	89.4(4)	C32–N3–P	121.8(7)
C4–Cr–C2	175.6(4)	C32–N3–C31	113.5(9)
C4–Cr–C3	88.2(4)	O1–C1–Cr	173.8(8)
C5–Cr–Si	95.7(3)	O2–C2–Cr	176.2(9)
C5–Cr–Cl	85.9(4)	O3–C3–Cr	172.6(8)
C5–Cr–C2	93.3(4)	O4–C4–Cr	177.9(8)
C5–Cr–C3	169.2(4)	O5–C5–Cr	169(1)
C5–Cr–C4	85.4(4)	C61–C6–Si	111.8(7)
C6–Si–Cr	115.8(3)	C62–C6–Si	107.3(6)
C7–Si–Cr	116.4(3)	C62–C6–C61	106.2(8)
C7–Si–C6	108.5(4)	C63–C6–Si	112.5(7)
O6–Si–Cr	113.1(2)	C63–C6–C61	108.7(8)
O6–Si–C6	101.9(4)	C63–C6–C62	110.1(8)
O6–Si–C7	99.0(4)	C71–C7–Si	111.9(7)
N2–P–N1	110.0(4)	C72–C7–Si	109.8(6)
N3–P–N1	110.4(4)	C72–C7–C71	107.5(9)
N3–P–N2	106.0(5)	C73–C7–Si	114.9(7)
O6–P–N1	109.2(3)	C73–C7–C71	105.8(8)
O6–P–N2	111.1(5)	C73–C7–C72	106.5(8)
O6–P–N3	110.1(4)	P–O6–Si	170.7(5)

[a] ESDs in units of the least significant figure in parentheses.

(650.64) Calcd.: C, 40.61; H, 5.27. Found: C, 39.81; H, 5.10.

3.2. *Di(tert-butyl)silanediyl-chromium(0)-pentacarbonyl · HMPT*, **3**

To a solution of 2.62 g (11.0 mmol) of $Na_2[Cr(CO)_5]$ and 1.97 g (11.0 mmol) of HMPA in 250 ml of THF at −40°C, 5.0 g (11.0 mmol) $(^tBu)_2Si(OTf)_2$ are added slowly. After warming to room temperature the mixture is stirred for a further 5 h, then filtered and the filtrate concentrated to 5 ml. The solution is layered with pentane allowing **3** to crystallize.

^{1}H-NMR (400 MHz, toluene-d^8, 25°C, TMS): δ = 1.27 (s, 18 H, CCH_3), 2.09 (d, $^3J(^{31}P^1H)$ = 10.4, NCH_3); ^{13}C-NMR (toluene-d^8): δ = 30.6 (m, CCH_3), 31.8 (q, $^1J(^1H^{13}C)$ = 125), 37.1 (qd, $^1J(^1H^{13}C)$ = 138, $^2J(^{31}P^{13}C)$ = 4.6), 226.0 (s, CO_{eq}), 227.3 (*s*, CO_{ax}); ^{29}Si-NMR (toluene-d^8): δ = 133.1 (dm, $^1J(^{31}P^{29}Si)$ = 37.2, $^3J(^1H^{29}Si)$ = 5.5); IR (THF): ν(CO) 2024 (s), 1940 (w), 1897 (ss). Mp: 148°C. Analysis $C_{19}H_{36}N_3CrO_6PSi$ (513.57) Calcd.: C, 44.44; H, 7.07; N, 8.18. Found: C, 44.14; H, 7.01; N, 8.20.

3.3. *Di(tert-butyl)silanediyl-chromium(0)-pentacarbonyl · THF*, **4**

^{1}H-NMR (toluene-d^8): δ = 1.23 (s, 18 H, ^{t}Bu), 1.55, 3.55 (s, 2 × 4 H, THF); ^{13}C-NMR (toluene-d^8): δ = 29.9 (q, $^1J(^1H^{13}C)$ = 124, CH_3), 30.6 (m, CCH_3), 27.3 (t, $^1J(^1H^{13}C)$ = 145), 70.9 (t, $^1J(^1H^{13}C)$ = 124, THF), 225.1 (s, CO_{eq}), 228.5 (s, CO_{ax}); ^{29}Si-NMR (toluene-d^8): δ = 149.7. Mp: 121°C (dec.).

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References and notes

1 (a) C. Zybill, H. Handwerker and H.B. Friedrich, *Adv. Organomet. Chem.*, in press; (b) C. Zybill, *Top. Curr. Chem.*, *160* (1991) 1; (c) C. Leis, D.L. Wilkinson, H. Handwerker, C. Zybill and G. Müller, *Organometallics*, *12* (1992) 514; (d) R. Probst, C. Leis, S. Gamper, E. Herdtweck, C. Zybill and N. Auner, *Angew. Chem.*, *103* (1991) 1155; *Angew. Chem., Int. Ed. Engl.*, *30* (1991) 1132.

2 T.D. Tilley, in S. Patai and Z. Rappoport (eds.), *The Silicon–Heteroatom Bond*, Wiley, New York, 1991.

3 (a) E. Hengge and M. Weinberger, *J. Organomet. Chem.*, *443* (1993) 167; (b) T.D. Tilley, *Acc. Chem. Res.*, *26* (1993) 22.

4 (a) K.A. Brown-Wensley, *Organometallics, 6* (1987) 1590; (b) H. Yamashita, M. Tanaka and M. Goto, *Organometallics, 11* (1992) 3227.

5 M.P. Clarke and I.M.T. Davidson, *J. Organomet. Chem., 408* (1991) 149.

6 I.P. Hermann, *Chem. Rev., 89* (1989) 1323.

7 (a) For structures of salt adducts of silaimines see: S. Walter, U. Klingebiel and M. Noltemeyer, *Chem. Ber., 125* (1992) 783; (b) For salt adducts of silaethenes see: N. Wiberg, G. Wagner, G. Reber, J. Riede and G. Müller, *Organometallics, 6* (1987) 35.

8 **1**·NaOTf·2 THF. Crystal data: $C_{22}H_{34}CrF_3NaO_{10}SSi$ ($0.2\times0.35\times0.4$ mm) $M_r = 650.63$, monoclinic, $P2_1/c$ (Nr. 14), $a = 10.817(1)$, $b = 13.216(1)$, $c = 21.972(1)$ Å, $\beta = 91.51(1)°$, $V = 3140.0$ Å^3, $Z = 4$, $\rho_{calc} = 1.376$ g cm^{-3}, μ(Mo-K$_\alpha$) = 5.5 cm^{-1}, $F(000) = 1352$ e. Measurement: Enraf-Nonius CAD4-Turbo, $T = 23$°C, 7296 measured reflections, 1816 extinguished reflections, 1865 reflections not used. 3615 unique reflections with $F_0 > 4\ \sigma\ (F_0)$ used for refinement. Correction for decay (58 h, −14.8%). Structure solution: direct methods ($R_{int} = 0.014$), 353 parameters. Refinement: full-matrix, least-squares ($R = \Sigma\| F_0| - |F_c\|/\Sigma|F_0|$, $R_w = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^{-2}\}^{1/2}$, $w = 1/[\sigma^2(F_o) - kF_0^2]$), $R = 0.057$, $R_w = 0.057$, all heavy atoms with anisotropic and all hydrogen atoms with isotropic displacement parameters refined. Residual electron density +0.33/-0.33e Å^{-3}.

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

10 T.R. Cundari and M.S. Gordon, *Organometallics, 11* (1992) 3122.

11 Si–O covalent bonds are 1.6–1.65 Å long, see also [2].

12 For a summary see: M. Weidenbruch, B. Brand-Roth, S. Pohl and W. Saak, *Polyhedron 10* (1991) 1147.

13 H. Handwerker, M. Paul, J. Blümel and C. Zybill, *Angew. Chem., 105* (1993) in press.

14 **3**. Crystal data: $C_{19}H_{36}CrN_3O_6PSi$ ($0.1\times0.25\times0.5$ mm) $M_r = 513.57$, orthorhombic, $Pca2_1$ (Nr.29), $a = 9.312(1)$, $b = 14.045(1)$, $c = 19.752(4)$ Å, $V = 2583.3$ Å^3, $Z = 4$, $\rho_{calc} = 1.320$ g cm^{-3}, μ(Mo-K$_\alpha$) = 5.9 cm^{-1}, $F(000) = 1088$ e. Measurement: Enraf-Nonius CAD4, $T = -65$°C, 5216 measured reflections (+11, +16, +23, *hkl*), 908 extinguished resp. with negative intensity suppressed, after deduction of the Friedl-pairs (652), 3656 unique reflections remained ($F_o > 4\sigma\ (F_o)$). Correction for decay (58 h, −34.0%), empirical absorption correction. Structure solution: direct methods (SHELXTL) 280 parameters. Refinement: full-matrix, least-squares, $R = 0.087$, $R_w = 0.087$, all heavy atoms were refined anisotropically and all hydrogen atoms were calculated in idealized geometry. Residual electron density +3.26/−1.55 A^{-3} (localized at the Cr-atom).

Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, on quoting the CSD-57367 number, the authors and the literature reference.

15 The total energy is obtained as $E_{tot} = E_{str} + E_{ang} + E_{tot} + E_{vdW}$. $E_{str} = \Sigma_i k_i^d/2(d_i - d_i^0)^2$; $E_{ang} = \Sigma_i k_i^\theta/2(\Theta_i - \Theta_i^0)^2$; $E_{tor} = \Sigma_i k_i/2(1 + \text{sign}\ (\text{per}_i) \cos(\text{per}_i(\omega_i))$; $E_{vdW} = \Sigma_i(\Sigma_j\Sigma_i[1.0/a_{ij}^{12} - 2.0a_{ij}^6])$: V. Burkert and N.L. Allinger, *Molecular Mechanics*, ACS Monography 177, Washington, 1982.