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Reversible Intramolecular Base Stabilization in Silylene (Silanediyl) Complexes: Surprising Reactivity for Silylene Coordination Compounds with a Dynamic N···Si···N Bond[§]

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The silane $[2\text{-}(Me_2NCH_2)C_6H_4]_2SiCl_2$ (**7**) shows a new dynamic N···Si···N "flip-flop" coordination mode below $T_c = 233$ K ($\Delta G^{\ddagger} = 46.5\ (\pm 0.5)$ kJ mol^{-1}) with both amine donors displacing each other. **7** is pentacoordinated in the solid state; crystal data: orthorhombic, P_{bca}, $a = 13.802(1)$ Å, $b = 17.908(1)$ Å, $c = 15.544(2)$ Å, $Z = 8$. Reaction of the silanes $C_6H_5[2\text{-}(Me_2NCH_2)C_6H_4]SiCl_2$ (**6**), **7**, and $[2\text{-}(Me_2NCH_2)\text{-}5\text{-}(t\text{-}C_4H_9)C_6H_3]_2SiCl_2$ (**8**) with chromiumpentacarbonylmetallate yields the silanediyl complexes $[2\text{-}(Me_2NCH_2)C_6H_4]C_6H_5Si{=}Cr(CO)_5$ (**11**), $[2\text{-}(Me_2NCH_2)C_6H_4]_2Si{=}Cr(CO)_5$ (**12**), and $[2\text{-}(Me_2NCH_2)\text{-}5\text{-}(t\text{-}C_4H_9)C_6H_3]_2Si{=}Cr(CO)_5$ (**13**); $[2\text{-}(Me_2NCH_2)C_6H_4]HSi{=}Cr(CO)_5$ (**14**) was obtained by photolytic methods. Silanediyl complexes with one chelating donor show a rigid coordination of the donor to silicon which can be lifted at higher temperatures (95 °C for **11**, $\Delta G^{\ddagger} = 80.4\ (\pm 0.5)$ kJ mol^{-1}). A single crystal X-ray structure determination of **11** reveals a CrSi bond distance of 2.409(1) Å and a N→Si bond length of 1.991(2) Å. Crystal data: triclinic, $P\bar{1}$, $a = 9.401(1)$ Å, $b = 10.207(1)$ Å, $c = 11.586(1)$ Å, $Z = 2$. Silanediyl complexes with two intramolecular donor functions feature a dynamic "flip-flop" coordination of the amine groups to silicon. Both (dimethylamino)phenyl groups in **12** and **13** can be detached from silicon under liberation of a three-coordinate silicon atom at $T_c = 58$ °C (VT-^{1}H-NMR), $\Delta G^{\ddagger} = 67.1\ (\pm 0.5)$ kJ mol^{-1} for **12** and $T_c = 61$ °C, $\Delta G^{\ddagger} = 70.1\ (\pm 0.5)$ kJ mol^{-1} for **13**. A single crystal X-ray structure determination of **12** gives 2.408(1) Å for the Si–Cr bond length and 2.046(2) Å for the N1–Si dative bond (the second contact N2–Si has a nonbonding distance of 3.309 Å; the sum of bond angles at silicon amounts to 351.3°). Crystal data: triclinic, $P\bar{1}$, $a = 9.531(1)$ Å, $b = 10.339(1)$ Å, $c = 11.676(1)$ Å, $Z = 2$. The donor in **12** has been functionalized at the nitrogen atom by protonation or complexation with BF_3. Photolysis of **12** and **13** leads to a 1,2-amine shift of one donor from silicon to the metal with loss of CO. The product $[2\text{-}(Me_2NCH_2)C_6H_3][2\text{-}(Me_2\overline{NCH_2)C_6H_3]Si{=}C}r(CO)_4$ (**20**) has been characterized by a single crystal X-ray structure determination and has a bond distance Cr–Si 2.3610(4) Å and N1–Si 1.981(1) Å. Crystal data: monoclinic, $P2_1/c$, $a = 10.344(5)$ Å, $b = 11.761(3)$ Å, $c = 18.96(1)$ Å, $Z = 4$. Furthermore, the silanediyl complex **12** has been immobilized on silica gel. IR and UV spectroscopy and ^{13}C CPMAS NMR provide evidence for the fixation of (silica–O–)$[2\text{-}(HNMe_2CH_2)C_6H_4][2\text{-}(Me_2NCH_2)C_6H_4]Si{=}Cr(CO)_5$ (**22**) to the surface via the silicon atom. Reaction of **13** with H_2O leads to $(HO)[2\text{-}(HNMe_2CH_2)C_6H_4][2\text{-}(Me_2NCH_2)C_6H_4]Si\text{-}Cr(CO)_5$ (**23**) which has a structure similar to **22** with a Cr–Si bond length of 2.469(2) Å. The dimethylamino or dimethylammonium substituent is pointing away from the silicon atom forming hydrogen bridges between N1···HO···HN2; crystal data: monoclinic, $P2_1/n$, $a = 13.198(2)$ Å, $b = 17.017(2)$ Å, $c = 17.066(1)$ Å, $Z = 4$.

Introduction

An increasing variety of coordination compounds with subvalent silicon ligands has recently been introduced[1] including complexes of disilaethenes[2] and silaethenes,[3] silanediyls (silylenes),[4–6] cyclic silylenes[7] and metallasilaallenes,[8] as well as silatrimethylenemethane[9] and cationic μ-silanetriyl complexes.[10] All examples have been characterized by single-crystal X-ray structure determination

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[*] Dr. Christian Zybill: corresponding author.

[†] Dr. Janet Blümel: solid state NMR.

[‡] Dr. Eberhardt Herdtweck, Dr. Pavlo Kiprof, Dr. Andreas Grohmann, and Dr. Peter Bissinger: X-ray structure determination.

[§] In honor of Professor R. West on the occasion of his 65th birthday.

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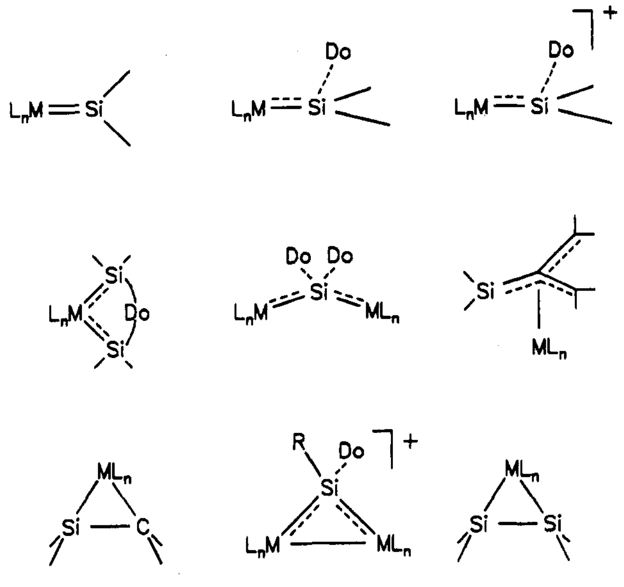
Chart I



and feature a more or less distorted tetrahedral environment at the silicon atom due to the coordination of additional solvent molecules. Examples with a three-coordinated silicon atom either in solution or in the solid state have been obtained only recently.[11,12] (Chart I). Base-free silylene complexes have been proven to play a key role as intermediates of various stoichiometric, and in some cases even catalytic, silanediyl transfer reactions such as the Pannell reaction,[13] the hydrosilation process,[14] silane polymerization,[15] and possibly also in crosslinking reactions of polysilanes with late transition metal catalysts.[16] Recent results from the work of Hengge et al. provide clear evidence for the involvement of highly reactive silanediyl complexes 1 in the dehydrogenative coupling reaction of disilanes.[17]

$$Cp_2Ti{=}SiR_2$$

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Chart II

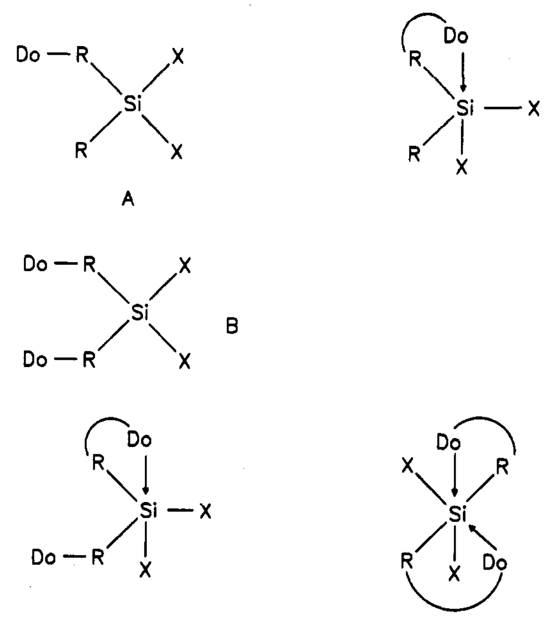
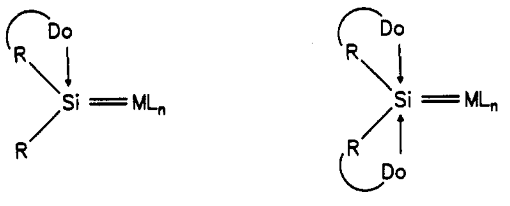


Chart III



C D

However, besides reactions in the homogeneous phase, molecular coordination compounds can also mimick the coordination mode and reactivity of silicon ligands on (metal) surfaces of heterogeneous systems. Surface-bound methylchlorosilanediyl 2 has recently been shown to be a key intermediate in the *direct process* of the selective generation of dichlorodimethylsilane Me_2SiCl_2 (3)[18] by trapping with butadiene (eq 1).

$$\underset{2}{[MeSiCl]_x} \xrightarrow{MeCl} \underset{3}{Me_2SiCl_2}$$

$$[MeSiCl]_x \rightleftharpoons MeSiCl + [\ ]_x$$

$$MeSiCl + C_4H_6 \longrightarrow C_4H_6SiMeCl \qquad (1)$$

Electronic and coordinative saturation of divalent silicon(II) ligands is most effectively accomplished by a reversible coordination of an intramolecular base. Examples so far known include intramolecular base stabilization of tetravalent silicon with monodentate and bidentate donor functions in the silanes A and B (Chart II) and the silanediyl complexes C and D (Chart III).

Related silanediyl complexes of iron and manganese have been introduced by Lanneau and Corriu by photochemical reaction of silyl dihydrides with 16-electron metal complexes and have been studied extensively[19,20] (eq 2).

In this paper a reversible intramolecular base stabilization of tetravalent and divalent silicon is described for the first time for silanes of type B and silanediyl complexes of type D of chromium. The reversible coordination of the donor in D by a "flip-flop" mechanism is investigated

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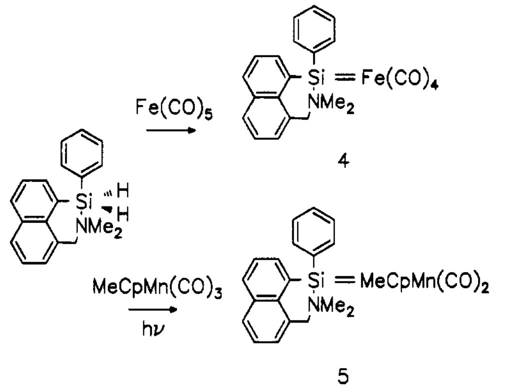
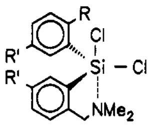


(2)

by VT ^1H and ^{29}Si NMR spectroscopy. The dynamical N···Si···N interaction is the basis for a variety of unexpected reactions at the silicon atom, of which some selected examples are reported, as well as the crystal structures of the silane **7** and the silanediyl complexes **11**, **12**, and **20**. Furthermore, the immobilization of silylene complexes on a silica gel surface is presented as a most efficient method for anchoring transition metal complexes on a solid support. **22** has been characterized by IR and ^{13}C CPMAS NMR spectroscopy. The structure of **22** was also mimicked with the model complex **23** which has been characterized by single crystal X-ray structure determination. A preliminary communication on the structures of **7** and **12** has already appeared.[11]

Results and Discussion

Silanes: Fluxionality and Penta- and Hexacoordination. Silanes with intramolecular donor functions have been investigated extensively by Corriu et al.[21] and related stannanes by van Koten et al.[22] The synthetic procedures given there are straightforward and can readily be applied to synthesize the dichlorosilanes **6–9** in satisfactory yields.



6 R = H, R' = H
7 R = $-CH_2-NMe_2$, R' = H
8 R = $-CH_2-NMe_2$, R' = tBu
9 $2-Me_2NCH_2-C_6H_4SiCl_3$
10 $(2-Me_2HN^+CH_2-C_6H_4)(2-Me_2NCH_2-C_6H_4)SiCl_2\ Cl^-$

An investigation of the molecular dynamics of **6–9** provides insight into the mechanism of intramolecular donor coordination at the silicon atom (Table I). Both silanes **6** and **9** with *one* intramolecular *donor* group show a *rigid pentaccordination* of silicon at low temperatures.[23] However, for silane **7** with *two symmetry equivalent donor groups*, a new *dynamic coordination* mode is observed at lower temperatures involving both dimethylamino substituents simultaneously. For **7**, coalescence of the singlet for both CH_2 groups occurs at 233 K; one well-defined AB pattern (^1H NMR 2.79, 3.38, $^2J(^1H^1H) = 12.0$ Hz, 4 H, 2 × CH_2) and one singlet (1.94, s, 12 H, 4 × NCH_3) for all four methyl groups at the nitrogen atoms is seen at lower temperatures (Figure 1). The signals of the *N*-methyl groups remain singlets because of fast exchange between both methyl substituents at each nitrogen atom by Si–N bond cleavage, rotation around the N–C bond, and inversion at nitrogen.

Table I. Coalescence Temperatures, Gibbs Free Energies of Activation for Detachment of the Amine Donors from Silicon and Selected ^1H and ^{29}Si NMR Data for the Silanes 6 and 7, and the Silanediyl Complexes 11 and 12

Coalescence Temperatures and Gibbs Free Energies

	T_c (°C)	G (kJ mol^{-1})
6	−60.0	40.7[a]
7	−40.3	46.5[b]
11	95.1	80.4[c]
12	58.0	67.1[d]

^1H and ^{29}Si NMR Data

	^1H NMR		
	δ CH_3	δ CH_2	^{29}Si NMR δ
6	(CD_2Cl_2, 22 °C) 1.95 (s)	3.72 (s)	−27.5
	(CD_2Cl_2, −70 °C) 1.25, 2.21 (2 s)	2.82, 3.41 (AB, $^2J(^1H^1H) = 12.2$ Hz)	−51.2
7	($CDCl_3$, 22 °C) 1.94 (s)	3.56 (s)	(23 °C) −30.1
	(d_8-toluene, −75.0 °C) 1.94	2.79, 3.38 (AB, $^2J(^1H^1H) = 12.0$ Hz)	(−70.1 °C) −54.5
11	(d_8-toluene, 22 °C) 1.83, 2.08 (2 s)	2.62, 3.04 (AB, $^2J(^1H^1H) = 14.0$ Hz	121.2
12	(d_8-toluene, −40.0 °C) 2.02, 2.23 (2 s), 2.61 (1 s)	3.81, 4.11 (AB, $^2J(^1H^1H) = 12.2$ Hz) 2.62, 3.04 (AB, $^2J(^1H^1H) = 14.0$ Hz)	120.9
	(22.0 °C) 2.57 (s)	3.80, 4.09 (AB, $^2J(^1H^1H) = 14.0$ Hz)	124.9
	(62 °C) 2.57 (s)	3.90 (s)	138.8

[a] $CDCl_3$, rigid pentacoordination below T_c. [b] d_8-Toluene, dynamic hexacoordination below T_c. [c] d_8-Toluene, rigid tetracoordination below T_c. [d] d_8-Toluene, dynamic pentacoordination below T_c.

An estimation of the Gibbs free energy of activation from the coalescence temperature for this process gives $\Delta G^{\ddagger} = 46.5\ (\pm.5)$ kJ mol^{-1} for **7**. The following conclusions can be drawn from the spectroscopic data:[24]

(a) Both (dimethylamino)methylene units remain magnetically equivalent below the coalescence temperature.[25]

(b) The methyl groups at each nitrogen are interconverted rapidly by a mutual displacement reaction of both amine donors which induces Si–N bond rupture concomitant with rotation around the CH_2–N bond and *inversion at* one *nitrogen* atom. The data from VT ^1H NMR spectra clearly show a dissociative pathway via Si–N bond cleavage and exclude an intramolecular mechanism like Bailar twist, etc.[26]

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(23) According to ^{29}Si NMR data (−58.2 ppm), **9** has a pentacoordinate silicon atom ($CDCl_3$) at 22 °C.

(24) We are indebted to one of the referees for valuable comments.

(25) The lowest measured temperature was 183 K.

(26) Hexacoordination has been established in silicon chemistry by Corriu and co-workers. For hexacoordinated silanes with naphthylaminosilanes, an *intramolecular* rearrangement has been observed: (a) Brelière, C., Carré, F., Corriu, R. J. P., Poirier, M., Royo, G., Zwecker, J. *Organometallics* **1989**, *8*, 1831–1833. (b) Brelière, C., Corriu, R. J. P., Royo, G., Zwecker, J. *Organometallics* **1989**, *8*, 1834. (c) For a summary see: Corriu, R. J. P., *Pure Appl. Chem.* **1988**, *60*, 99.

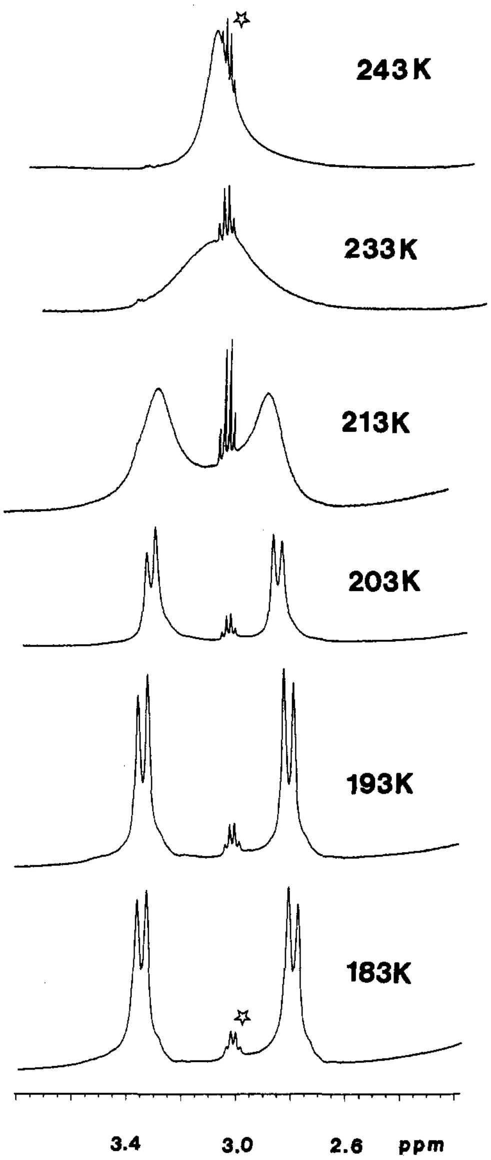


Figure 1. VT ^{1}H NMR spectrum of 7 ($CDCl_3$, 400 MHz). The star denotes an impurity.

(c) This process does not require any hindered rotation, since the protons of the CH_2 groups remain diastereotopic as long as one donor is still coordinated to silicon.

(d) The process proceeds under retention of configuration at silicon.

(e) The exchange involves a *hexacoordinate transition state* with each nitrogen atom in trans position to chlorine (dato-captive interaction) as the energetically favorable most situation; conformational isomers have not been observed.[26]

These results are interpreted in the sense of a dynamic coordination of both dimethylamino substituents at silicon, one displacing the other rapidly through a hexacoordinate C_2-symmetric transition state. This pathway transforms the pentacoordinate isomer A of the silane into A again under retention of configuration (Chart IV). The pentacoordinate ground state of A has been confirmed for the solid state by a single crystal X-ray structure determination.

The exchange mechanism can be described starting from the ground state by attack of the terminal dimethylamino group on silicon (pathway ***a***) through the edge of the trigonal bipyramid to form a C_2-symmetric hexacoordinate transition state and subsequently again A by displacement of the coordinated dimethylamino group from silicon and vice versa. Entrance of the dimethylamino unit through pathway ***b*** also leads to a hexacoordinate transition state with C_2-symmetry which, however, forces both dimethylamino substituents in trans position to each other which apparently is higher in energy. Finally coordination of the amine donor along pathway ***c*** leads to a non C_2-(C_s)-symmetric hexacoordinate transition state, which can be ruled out on the basis of the spectroscopic data.

Chart IV

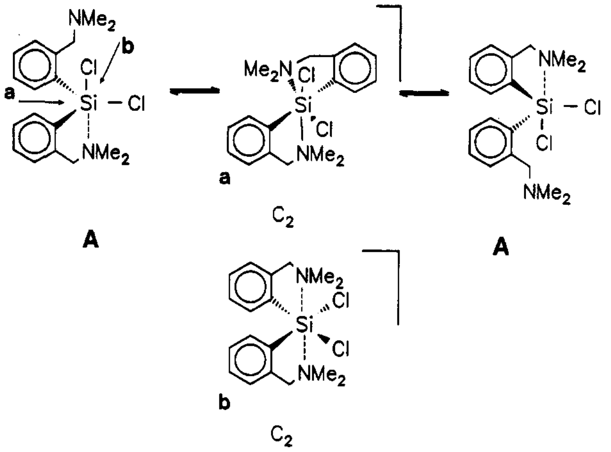


Table II. Selected Interatomic Distances (Å) and Angles (deg) in the Crystal Structure of 7[a]

Si–Cl1	2.081(1)	Si–Cl1	1.869(1)
Si–Cl2	2.181(1)	Si–C21	1.870(1)
Si–N2	2.291(2)	Si–N1	4.493(2)
C11–Si–C21	132.16(6)	Cl1–Si–Cl2	94.46(3)
Cl1–Si–C11	113.22(5)	Cl1–Si–N2	86.72(3)
Cl1–Si–C21	111.53(4)	Cl2–Si–N2	86.72(3)

[a] ESD's in units of the last significant figure in parentheses.

The exchange of both amine and methylene groups has also been proven by a 2D-EXSY exchange spectrum at −52 °C. The ^{29}Si NMR shift of 7 is strongly temperature-dependent, varying from −30.1 ppm at room temperature to −54.5 ppm at −70 °C. A single-crystal X-ray structure determination of 7 shows a trigonal bipyramidal coordination geometry at the silicon atom with one dimethylamino group coordinated to the central silicon atom at an apical position of the polyhedron through N2 (Si–N2 2.291(2) Å) (Figure 2, Table II). The amine donor is located in a trans position to the apical chlorine substituent (Si–Cl2 2.181(1) Å). The second chlorine occupies an equatorial position with a bond length Si–Cl1 of 2.081(1) Å. Owing to the relatively weak N→Si contact, the coordination geometry at silicon is slightly pyramidalized (equatorial sum of bond angles 356.9°). The two Si–C bond lengths are Si–C11 1.869(1) Å and Si–C21 1.870(1) Å. The second dimethylamino unit is directed away from the central silicon atom (Si–N 4.493(2) Å nonbonding distance) and shows no intermolecular bonding interactions. From this ground state conformation A, a direct pathway leads through a hexacoordinated C_2-symmetric transition state to A again by inversion at nitrogen N2, coordination of N2, and displacement of N1 from silicon and vice versa. A related exchange mechanism has been proposed recently for the dynamic donor coordination in hexacoordinated silanes.[27]

Blocking One Nitrogen Donor by Electrophiles. Titration of silane 7 with hydrochloric acid allows the

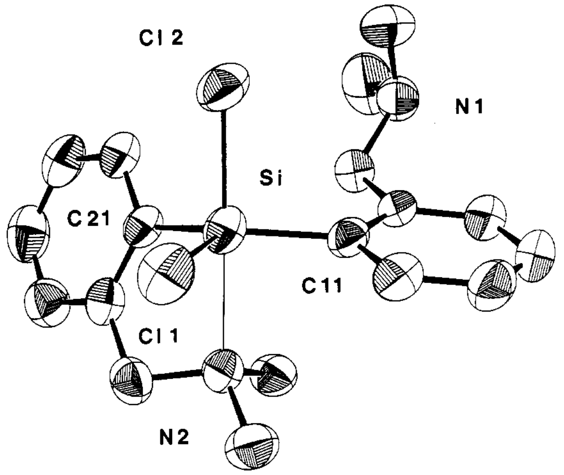
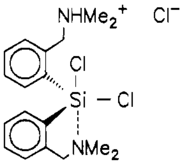


Figure 2. Molecular structure of $[2\text{-}(Me_2NCH_2)C_6H_4]_2SiCl_2$ (**7**) and the crystal numbering scheme used (ORTEP, displacement ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).

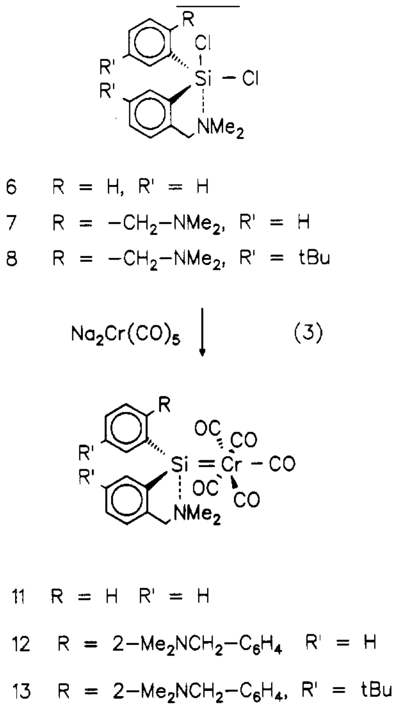
selective functionalization of one amine donor and formation of the hydrochloride **10**. According to spectroscopic data, **10** has a pentacoordinate structure in solution at room temperature. However, ^{1}H-NMR data of **10** in $CDCl_3$ at 22 °C show significant line broadening due to coalescence of the NCH_3 signals (22 °C, $\Delta G^{\ddagger} = 60.2$ (±5) kJ mol^{-1}). Heating of the sample results in line sharpening and observation of distinct signals for the dimethylamino and the protonated dimethylamino group (2.46 ppm, $^3J(^1H^1H) = 16.9$ Hz) indicating the localization of the proton at one nitrogen atom.



10

A single crystal X-ray structure determination of the hydrochloride **10** reveals a TBP pentacoordinate silicon atom in the crystal with one dimethylamine donor coordinated to an apical coordination site of a trigonal bipyramid similar to **7**. Details of this structure determination (see Experimental Section) will be published elsewhere.[28]

Silanediyl Coordination Compounds Stabilized by Intramolecular Interaction with a Base. The silanediyl complexes **11**, **12**, and **13** are available by a straightforward coupling reaction of chlorosilanes with anionic metalates, which has proven to be the most effective one-step access to silanediyl coordination compounds. The discussed complexes **11**, **12**, and **13** have been obtained as described and are air-sensitive, crystalline materials (eq 3).



6 R = H, R' = H

7 R = $-CH_2-NMe_2$, R' = H

8 R = $-CH_2-NMe_2$, R' = tBu

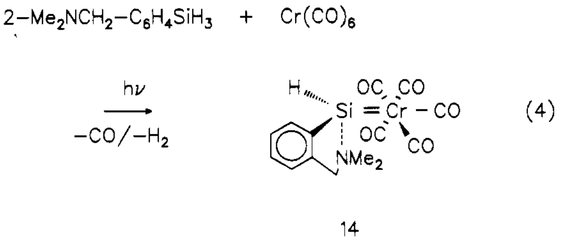
(3)

11 R = H R' = H

12 R = $2\text{-}Me_2NCH_2\text{-}C_6H_4$ R' = H

13 R = $2\text{-}Me_2NCH_2\text{-}C_6H_4$, R' = tBu

A valuable alternative for the generation of formal metal–silicon double bonds is the reaction of intermediate 16-electron metal complexes with dihydrosilanes.[29] This method was originally introduced by Corriu and Colomer and has been applied for the synthesis of **14** (eq 4).[30]



$$2\text{-}Me_2NCH_2\text{-}C_6H_4SiH_3 + Cr(CO)_6 \xrightarrow[-CO/-H_2]{h\nu} \qquad (4)$$

14

The determination of the structures of **11** and **12** in the solid state as well as an investigation into the molecular dynamics of the complexes in solution allows a detailed description of the mechanism of donor interaction between the base and the silicon atom. Depending on the substitution pattern (one or two donor groups) and the temperature range, either a rigid N→Si coordination or a dynamic N···Si···N ("flip-flop") coordination are observed in solution. These features are illustrated with the following examples.

Silanediyl Complexes with One Donor: Rigid Coordination. Silanediyl complexes with one intramolecular donor generally show in solution a rigid coordination of the base to silicon at 22 °C. The Gibbs free energies for the dissociation of the donor are relatively high with coalescence temperatures above rt. For example, **11** shows simultaneous coalescence of both signals of the diastereotopic Me_2N and the AB system of the CH_2 group at 95 °C ($\Delta G^{\ddagger} = 80.4$ (±0.5) kJ mol^{-1}) (a reversible process). However, the N–Si bond can be cleaved by strong donor solvents like THF which leads to a static equilibrium

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(27) Corriu, R. *Münchner Silicontage*, Aug 4,5 1992, plenary lecture no. 1.

(28) (a) Auner, N., manuscript in preparation. (b) For details see; Müller, G., Gamper, S. *Diplomarbeit*, Technische Universität München, 1990.

(29) Corriu, R. J. P., Lanneau, G. F., Chauhan, B. P. *Organometallics*, in press. (We thank Professor Corriu for providing us this information before publication).

(30) (a) Colomer, E., Corriu, R. J. P. *Top. Curr. Chem.* **1981**, 26–55. (b) Colomer, E., Corriu, R. J. P., Lheureux, M. *Chem. Rev.* **1990**, *90*, 265.

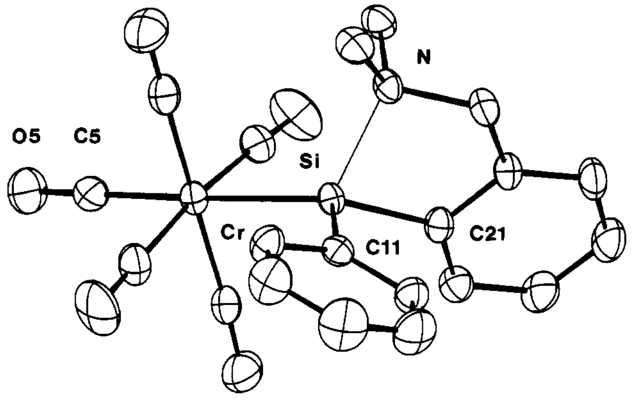

Figure 3. Molecular structure of $[2\text{-}(Me_2NCH_2)C_6H_4]C_6H_5\text{-}Si{=}Cr(CO)_5$ (11) (ORTEP; displacement ellipsoids at 50% probability level).

between 11 and the THF adduct 11a with the equilibrium constant $K_{298} = 1.91 \times 10^{-1}$ L mol^{-1}. From such solutions a five-coordinated donor adduct 11a (with THF and NMe_2 at silicon) can be frozen out below −45 °C.

A single-crystal X-ray structure analysis of 11 shows the silanediyl ligand coordinated to the octahedral $[Cr(CO)_5]$ fragment with a bond distance Cr–Si 2.409(1) Å (Figure 3). This bond length is indicative for a significant degree of multiple bonding for $(t\text{-}BuO)_2(HMPA)Si{=}Cr(CO)_5$ 2.431(1) Å, $Me_2(HMPA)Si{=}Cr(CO)_5$ 2.410(1) Å, and $Cl_2(HMPA)Si{=}Cr(CO)_5$ 2.343(1) Å (cf. 1). Representative Cr–Si single bond lengths are 2.4–2.7 Å.[1b] An *ab initio* calculation by Nakatsuji et al. for $H(HO)Si{=}Cr(CO)_5$ gives 2.40 Å for a Cr=Si double bond;[31] an *ab initio* calculation recently performed by Gordon et al. yields 2.45 Å for the system $[Cr{=}SiH_2]^+$.[32] In agreement with this description a CrSi bond distance of 2.409(1) Å and a N–Si bond distance of 1.991(2) Å are found which is fairly long and out of the range of covalent bonding (1.65–1.85 Å[33]). A further indicator for the magnitude of interaction of the base with the "silanediyl" silicon atom is the sum of bond angles of the three covalently bonded substituents at silicon, which amounts to 347.8°. Both angles Cr–Si–C11 of 120.2(1)° and Cr–Si–C21 of 121.3(1)° are close to 120°, whereas the angle C11–Si–C21 of 106.3(1)° between the phenyl rings is similar to the one calculated for the free silanediyl.[4f,34] A complete list of bond distances and angles is given in Tables III and IV.

Table III. Selected Interatomic Distances (Å) and Angles (deg) in the Crystal Structure of 11[a]

Interatomic Distances (Å)			
Cr–C1	1.878(2)	Cr–C2	1.889(2)
Cr–C3	1.877(2)	Cr–C4	1.884(2)
Cr–C5	1.865(2)	Cr–Si	2.409(1)
C1–O1	1.142(2)	C2–O2	1.141(3)
C3–O3	1.145(2)	C4–O4	1.147(3)
C5–O5	1.144(3)	Si–N	1.991(2)
Si–C11	1.895(2)	Si–C21	1.897(2)
N–C6	1.507(2)	N–C7	1.496(2)
N–C8	1.491(2)	C11–C12	1.394(3)
C11–C16	1.396(3)	C12–C13	1.391(3)
C13–C14	1.375(4)	C14–C15	1.372(4)
C15–C16	1.390(3)	C21–C22	1.390(3)
C21–C26	1.398(3)	C22–C23	1.385(3)
C23–C24	1.387(3)	C24–C25	1.388(3)
C25–C26	1.388(3)	C26–C6	1.502(3)
Bond Angles (deg)			
C1–Cr–C2	85.5(1)	C1–Cr–C3	88.1(1)
C2–Cr–C3	173.6(1)	C1–Cr–C4	175.3(1)
C2–Cr–C4	91.2(1)	C3–Cr–C4	95.0(1)
C1–Cr–C5	92.5(1)	C2–Cr–C5	89.9(1)
C3–Cr–C5	90.9(1)	C4–Cr–C5	90.9(1)
C1–Cr–Si	87.6(1)	C2–Cr–Si	93.4(1)
C3–Cr–Si	85.7(1)	C4–Cr–Si	89.1(1)
C5–Cr–Si	176.7(1)	Cr–C1–O1	177.2(2)
Cr–C2–O2	175.8(2)	Cr–C3–O3	176.8(2)
Cr–C4–O4	179.5(1)	Cr–C5–O5	179.4(2)
Cr–Si–N	119.0(1)	Cr–Si–C11	120.2(1)
N–Si–C11	97.0(1)	Cr–Si–C21	121.3(1)
N–Si–C21	85.7(1)	C11–Si–C21	106.3(1)
Si–N–C6	104.7(1)	Si–N–C7	110.7(1)
C6–N–C7	108.6(1)	Si–N–C8	115.1(1)
C6–N–C8	109.3(1)	C7–N–C8	108.2(2)
Si–C11–C12	120.3(1)	Si–C11–C16	122.6(1)
C12–C11–C16	117.0(2)	C11–C12–C13	122.0(2)
C12–C13–C14	119.5(2)	C13–C14–C15	120.1(2)
C14–C15–C16	120.4(2)	C11–C16–C15	121.1(2)
Si–C21–C22	129.7(1)	Si–C21–C26	112.0(1)
C22–C21–C26	118.2(2)	C21–C22–C23	120.8(2)
C22–C23–C24	120.3(2)	C23–C24–C25	119.9(2)
C24–C25–C26	119.4(2)	C21–C26–C25	121.4(2)
C21–C26–C6	115.5(2)	C25–C26–C6	123.1(2)
N–C6–C26	107.5(1)		

[a] ESD's in units of the last significant figure in parentheses.

Silanediyl Coordination Compounds with Two Nitrogen Donors at Silicon: Dynamic "Flip-Flop" Coordination. Introduction of two dimethylamino donors results in dramatic changes of the coordination mode, coordination geometry, and molecular dynamics of the complexes. Data from VT ^1H NMR spectroscopy in $CDCl_3$ give clear evidence for three different coordination forms in different temperature ranges.[35] Below −21 °C, an asymmetric coordination of one dimethylamino substituent to silicon is observed for 12. Above −21 °C (coalescence) a dynamic coordination of both amine donors to the silicon atom occurs which is indicated in the ^1H-NMR spectra by a singlet for all four methyl substituents at nitrogen and an AB pattern for the methylene CH_2 groups. The dynamic coordination of both nitrogen donors displacing each other rapidly on the ^1H-NMR time scale takes place in a temperature range between −21 °C and 58 °C and proceeds through a pentacoordinate C_2-symmetrical transition state at silicon. The Gibbs free energy of activation for this process is $\Delta G^* = 54.4\ (\pm 0.5)$ kJ mol^{-1}. Inversion at nitrogen and rotation around the C–N bond leads to the chemical equivalence of both methyl groups at N. Also in this case, the assumption of a hindered rotation of the (dimethylamino)phenyl substituents is possible, but *a priori* not necessary, since the protons H_A and H_B of the CH_AH_B groups remain diastereotopic as long as one donor still has contact to the (asymmetric) silicon atom. However, detachment of all donor→silicon contacts is achieved above 58 °C (coalescence of the AB system of the CH_2 groups; ^{29}Si NMR low-field shift to 138.8 ppm) under N→Si bond scission and formation of an essentially three-coordinated silicon atom.[36]

The ^{29}Si-NMR signals for 12 vary strongly with temperature from δ 120.9 ppm at −40.0 °C for the rigidly tetracoordinated form, through δ 124.9 ppm at 22.0 °C for

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

(32) Cundari, T. R., Gordon, M. S., *J. Phys. Chem.* **1992**, *96*, 631.

(33) Covalent bond length N–Si as quoted in ref 11.

(34) Maier, G., Reisenauer, H. P., Schöttler, K., Wessolek-Kraus, U. *J. Organomet. Chem.* **1989**, *366*, 25.

(35) In toluene as solvent 12 has no N→Si donor contact and the silicon atom is three-coordinate at rt (^1H NMR, ^{29}Si NMR δ 138.8 ppm).

(36) A C_2-symmetrical conformer may also be a local minimun (or saddle point) on the energy hypersurface; however, a solution of this problem so far can only be obtained by extended *ab initio* calculations.

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for 11[a]

atom	x/a	y/b	z/c	U_{eq}
Cr	–0.41000(3)	–0.05360(3)	–0.26356(3)	0.021
C1	–0.5662(2)	–0.2080(2)	–0.3788(2)	0.027
C2	–0.5066(3)	–0.1386(2)	–0.1478(2)	0.032
C3	–0.3298(2)	0.0128(2)	–0.3918(2)	0.028
C4	–0.2513(2)	0.0896(2)	–0.1425(2)	0.028
C5	–0.5237(2)	0.0676(2)	–0.2389(2)	0.030
O1	–0.6654(2)	–0.3000(2)	–0.4464(2)	0.040
O2	–0.5732(2)	–0.1919(2)	–0.0820(2)	0.049
O3	–0.2875(2)	0.0498(2)	–0.4732(2)	0.042
O4	–0.1554(2)	0.1773(2)	–0.0684(2)	0.043
O5	–0.5929(2)	0.1423(2)	–0.2228(2)	0.042
Si	–0.25665(5)	–0.20382(5)	–0.30426(4)	0.019
N	–0.0301(2)	–0.1067(2)	–0.2819(1)	0.022
C11	–0.2638(2)	–0.3340(2)	–0.2140(2)	0.022
C12	–0.2797(2)	–0.2949(2)	–0.0911(2)	0.030
C13	–0.2837(3)	–0.3868(3)	–0.0216(2)	0.038
C14	–0.2742(4)	–0.5216(3)	–0.0755(3)	0.043
C15	–0.2585(3)	–0.5635(3)	–0.1963(2)	0.040
C16	–0.2538(2)	–0.4712(2)	–0.2655(2)	0.029
C21	–0.2384(2)	–0.3010(2)	–0.4656(2)	0.022
C22	–0.3473(2)	–0.3683(2)	–0.5690(2)	0.028
C23	–0.3097(3)	–0.4313(2)	–0.6803(2)	0.033
C24	–0.1618(3)	–0.4272(3)	–0.6904(2)	0.035
C25	–0.0507(3)	–0.3592(2)	–0.5888(2)	0.031
C26	–0.0894(2)	–0.2960(2)	–0.4776(2)	0.025
C6	0.0232(2)	–0.2196(2)	–0.3629(2)	0.026
C7	0.0152(2)	0.0251(2)	–0.3248(2)	0.027
C8	0.0475(2)	–0.0609(3)	–0.1550(2)	0.028

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$ where U_1,U_2, and U_3 are the characteristic values of the U_{ij} matrix. ESD's are in parentheses.

the dynamic "flip-flop" coordination, to δ 138.8 ppm above 58.0 °C for the three-coordinate system (Figure 4).

A further example of a silanediyl complex with a dynamical reversible intramolecular base (flip-flop) coordination is provided by the *tert*-butyl compound **13**. The complex shows analogous temperature dependent behavior of the VT ^{1}H-NMR spectrum with a singlet for the dimethylamino substituents at 22 °C and an AB system for the CH_2 bridge at 22 °C, with $^2J(^1H^1H)$ = 12.2 Hz (C_2Cl_2). Coalescence of the AB system is observed at 61 °C, which represents a Gibbs free energy of activation of $\Delta G^{\ddagger}$ = 70.1 (±0.5) kJ mol^{-1}.

A single crystal X-ray structure determination of the silanediyl complex **12** confirms the results obtained spectroscopically and provides information on the molecular structure of **12** in the solid state (Figure 5, Table V). The complex is monomeric and the silanediyl ligand is coordinated to the octahedral chromium fragment with a short Cr–Si bond length of 2.408(1) Å, which is similar to the one observed for **11**, indicating a considerable degree of multiple bonding. An *ab initio* calculation for $(CO)_5Cr{=}Si(OH)H$ gives 2.40 Å for the Cr—Si bond length; an estimation on the grounds of covalent radii leads to 2.30 Å for a Cr(0)=Si double and 2.70 Å for a Cr(0)–Si single bond. The N1–Si bond distance 2.046(2) Å is typical for a partially covalent interaction and somewhat shorter than in the pentacoordinated silane (2.291(2) Å, **7**), but clearly much longer than in any comparable silanediyl complex and out of the range of a full covalent bond.

The partially covalent nature of this bond is confirmed by the relatively small Gibbs free energy of activation for the dissociation of the Si–N1 bond ($\Delta G^{\ddagger}$ = 67.1 (±0.5) kJ mol^{-1}). Furthermore, the UV spectra of **12** also show an unprecedented large bathochromic shift of λ_{max} = 274 nm compared to the absorption of known HMPA adducts of silanediyl complexes. This band is assigned to the $\pi \rightarrow \pi^*$ transition of the Cr=Si double bond.

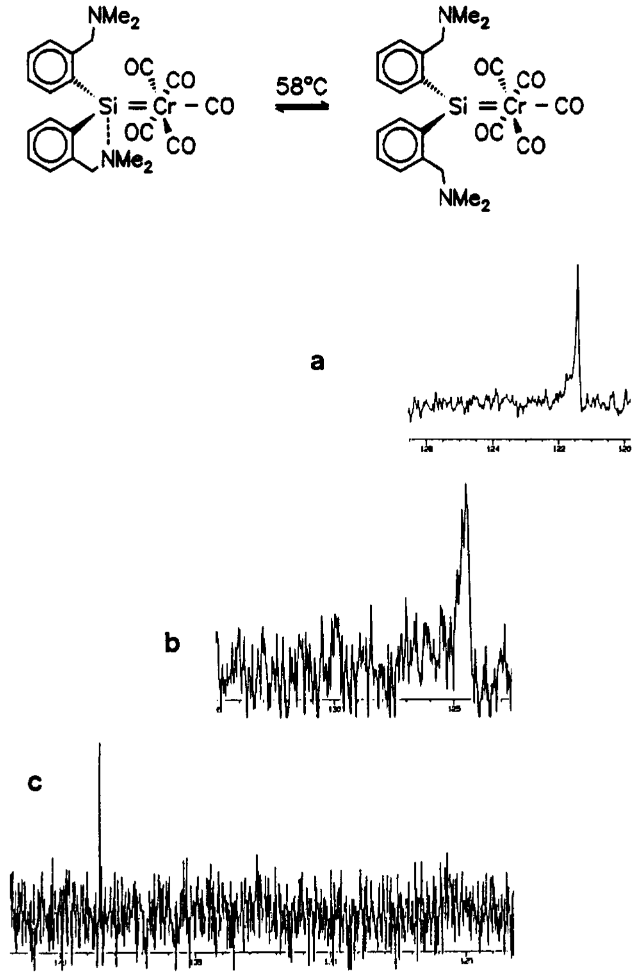


Figure 4. VT ^{29}Si NMR spectra of **12** (d_8-THF, 73.3 MHz): (a) δ 120.9 ppm (–40.0 °C); (b) δ 124.9 ppm (22 °C); (c) δ 138.8 ppm (58 °C).

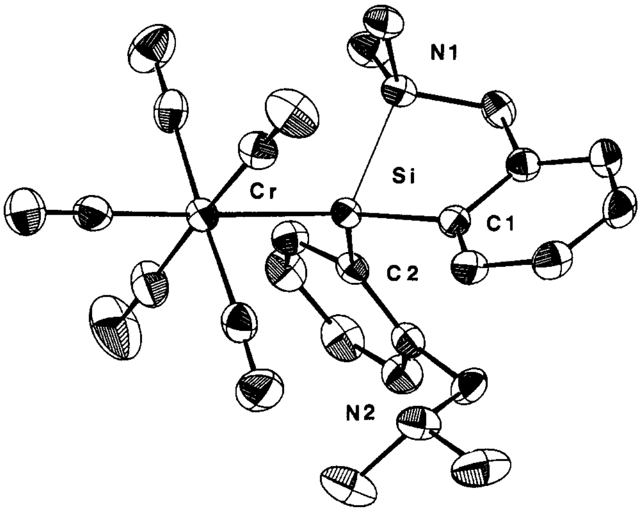


Figure 5. Molecular structure of $[2-(Me_2NCH_2)C_6H_4]_2Si{=}Cr(CO)_5$ (**12**) (ORTEP; displacement ellipsoids at 50% probability level).

The environment around the silicon atom is only slightly pyramidalized, with a sum of bond angles of the three covalently bonded substituents around Si of 351.3° which is close to 360°. This geometry points toward planarization at silicon, particularly considering the fact that similar

Table V. Selected Interatomic Distances (Å) and Angles (deg) in the Crystal Structure of 12

	Interatomic Distances (Å)		
Cr–Si	2.408(1)	Cr–CO1	1.887(2)
Cr–CO2	1.884(2)	Cr–CO3	1.864(2)
Cr–CO4	1.892(2)	Cr–CO5	1.877(2)
Si–N1	2.046(2)	Si–C1	1.898(2)
Si–C2	1.908(2)	N1–C1N1	1.500(2)
N1–C1N2	1.484(2)	N1–C111	1.503(3)
N2–C1N2	1.457(3)	N2–C2N2	1.465(3)
N2–C222	1.465(3)	O1–CO1	1.147(3)
O2–CO2	1.145(2)	O3–CO3	1.146(3)
O4–CO4	1.138(3)	O5–CO5	1.144(3)
C111–C11	1.503(3)	C1–C11	1.396(3)
C1–C15	1.388(3)	C11–C12	1.386(3)
C12–C13	1.377(3)	C13–C14	1.382(3)
C14–C15	1.392(3)	C222–C25	1.502(3)
C2–C21	1.399(3)	C2–C25	1.406(3)
C21–C22	1.385(3)	C22–C23	1.370(3)
C23–C24	1.380(3)	C24–C25	1.399(3)
	Bond Angles (deg)		
Si–Cr–CO1	86.7(1)	Si–Cr–CO2	87.2(1)
CO1–Cr–CO2	89.6(1)	Si–Cr–CO3	177.5(1)
CO1–Cr–CO3	93.5(1)	CO2–Cr–CO3	90.3(1)
Si–Cr–CO4	92.0(1)	CO1–Cr–CO4	87.3(1)
CO2–Cr–CO4	176.8(1)	CO3–Cr–CO4	90.5(1)
Si–Cr–CO5	88.6(1)	CO1–Cr–CO5	173.7(1)
CO2–Cr–CO5	94.4(1)	CO3–Cr–CO5	91.4(1)
CO4–Cr–CO5	88.6(1)	Cr–Si–N1	118.2(1)
Cr–Si–C1	120.3(1)	N1–Si–C1	83.6(1)
Cr–Si–C2	116.9(1)	N1–Si–C2	96.6(1)
C1–Si–C2	114.1(1)	Si–N1–C1N1	109.4(1)
Si–N1–C1N2	119.6(1)	C1N1–N1–C1N2	107.3(2)
Si–N1–C111	102.9(1)	C1N1–N1–C111	108.7(2)
C1N2–N1–C111	108.6(2)	C1N2–N2–C2N2	109.9(2)
C1N2–N2–C222	109.5(2)	C2N2–N2–C222	111.6(2)
Cr–CO1–O1	178.2(2)	Cr–CO2–O2	178.0(2)
Cr–CO3–O3	179.6(1)	Cr–CO4–O4	177.6(2)
Cr–CO5–O5	178.3(2)	N1–C111–C11	107.0(2)
Si–C1–C11	113.2(1)	Si–C1–C15	128.2(1)
C11–C1–C15	118.2(2)	C111–C11–C1	114.6(2)
C111–C11–C12	123.7(2)	C1–C11–C12	121.6(2)
C11–C12–C13	119.1(2)	C12–C13–C14	120.5(2)
C13–C14–C15	120.1(2)	C1–C15–C14	120.4(2)
N2–C222–C25	111.7(2)	Si–C2–C21	115.4(1)
Si–C2–C25	127.5(1)	C21–C2–C25	117.0(2)
C2–C21–C22	122.9(2)	C21–C22–C23	119.0(2)
C22–C23–C24	120.1(2)	C23–C24–C25	121.3(2)
C222–C25–C2	121.2(2)	C222–C25–C24	119.1(2)
C2–C25–C24	119.6(2)		

[a] ESD's in units of the last significant figure in parentheses.

pyramidalization effects are observed for three-coordinated silicon in the crystal structures of various disilaethenes.[37]

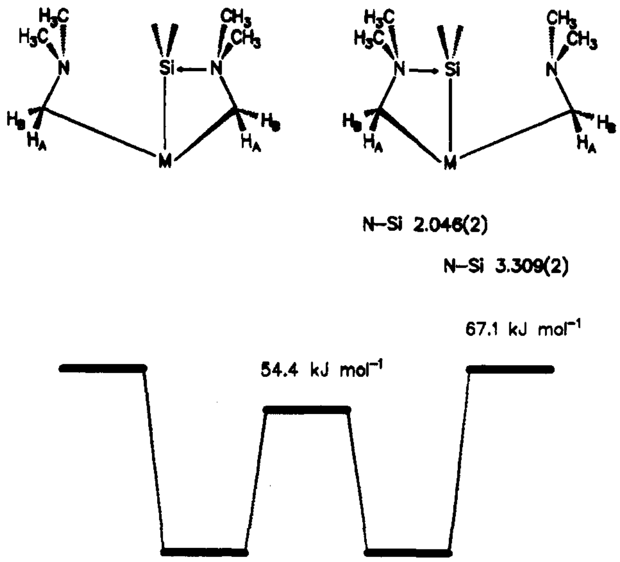
The second dimethylamino unit in 12 is also directed toward the silicon atom, with a bond distance of 3.309 Å being representative of only a weak van der Waals contact. This interaction has no significant structural influence on the coordination geometry at the silicon atom.

A recent *ab initio* CASSCF calculation by Márquez and Sanz provides valuable data on the electronic structure of transition metal complexes $(CO)_5Mo{=}MH_2$, M = C, Si, Ge, and Sn. The bond structure assumed corresponds to the so-called Fischer-type complexes which are 18-electron species and generally feature the metal in a low oxidation state (0). The Mo=M bond can be understood as a singlet carbene (silylene) donating the electron pair to the metal fragment with a corresponding amount of π back-donation from the metal to a vacant p-orbital of methylene of appropriate symmetry. Some selected geometrical data obtained by CASSCF calculations are summarized in Table VI.[38]

Table VI. Selected Structural Parameters for $(CO)_5Mo{=}MH_2$: Bond Distance *R* (Å), Dissociation Energy DE (kcal mol^{-1}), and Force Constant *f* (mdyn $Å^{-1}$)[38]

M	C	Si	Ge	Sn
$R_{Mo=M}$	2.02	2.48	2.56	2.65
$DE_{M=M}$	76.53	47.22	40.64	40.83
$f_{Mo=M}$	3.234	1.270	1.132	0.898

Chart V



The SCF-Mulliken population analysis for $(OC)_5Mo{=}SiH_2$ gives a total of 5.206 valence electrons for Mo and 3.583 for Si (C: 4.222, Ge: 3.557, Sn: 3.271). The calculated electron population justifies a description in the sense of a highly electrophilic silicon atom. Furthermore, a detailed analysis shows a decrease in π-electron density of the Mo=M double bond going from M = C to Sn which is in accordance with a reduced π-backbonding due to the diffuse orbitals of the heavier elements M. The same trend is also found for the bond energies $DE_{Mo=M}$ and the force constants $f_{Mo=M}$. In particular, the small force constant $f_{Mo=Si}$ = 1.270 mdyn $Å^{-1}$ allows the assumption of a predominantly donative interaction $H_2Si{\rightarrow}Mo(CO)_5$ with a highly dipolar contribution which seems to be mainly responsible for the significant bond shortening in silylene complexes.

"Flip-Flop" Coordination. General Comments. "Flip-flop" coordination describes the dynamic coordination mode of two symmetry equivalent donor ligands to an electron deficient central atom. A prerequisite for a dynamic "flip-flop" coordination mode is a geometry of two identical donor ligands which allows mutual displacement reactions. In both cases 7 and 12, the dynamic displacement process proceeds through a C_2-symmetrical transition state transforming two degenerate ground states into each other (Chart V). The Gibbs free energy for the activation of the "flip-flop" process for 12 is 54.4 kJ mol^{-1} (13.0 kcal mol^{-1}). The conformation of the respective ground state is precisely known from the results of the single crystal X-ray structure determinations of 7 and 12.

In the investigated cases, "flip-flop" coordination occurs in a temperature range near rt, which clearly allows inversion at the nitrogen atom. Thus, a mechanism is

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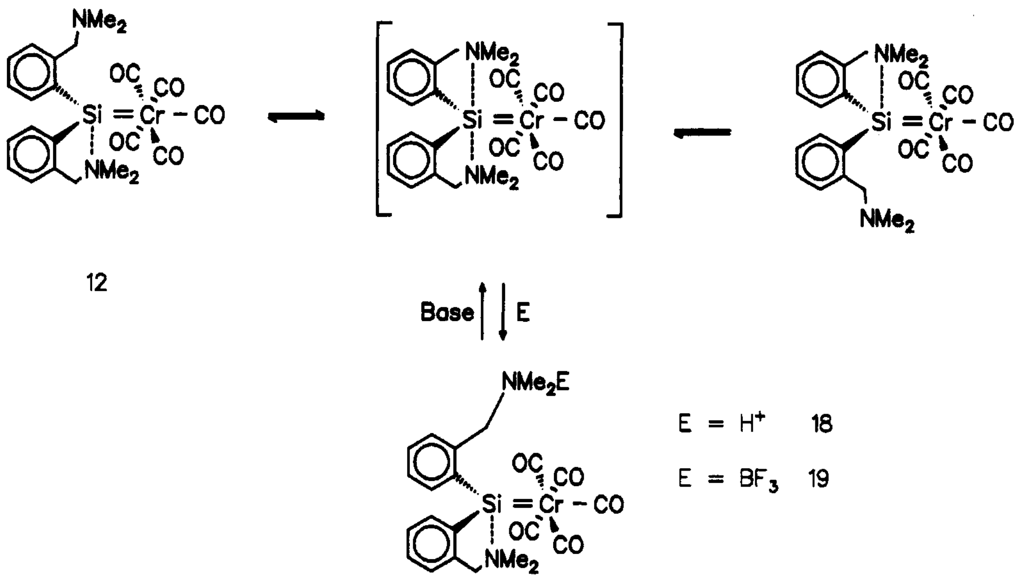
(37) West, R. *Angew. Chem.* **1987**, *99*, 1231. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1201.

(38) Márquez, A., Sanz, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2903.

Chart VI

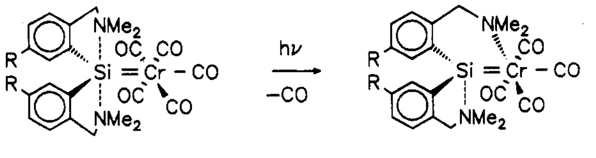


proposed whereby a simultaneous N···Si···N bond formation and rupture process occurs which is coupled with the inversion at nitrogen.[11,39]

A similar observation has been made recently by van Koten and Jastrzebski for the Sn(IV) cation in [2,5-bis-[(dimethylamino)methyl]phenyl]methylphenyltin chloride (15). Also in this case, a separation between the Sn–N bond cleavage process (which leads to inversion of the geometry at Sn) and rotation around the C–C bond was possible. This process of Sn–N bond formation and rupture occurs in the temperature range up to 70 °C and may also be described by a dynamic bond with a "flip-flop" coordination mode.[22] Further cases seem to be present in the systems $[2\text{-}(Me_2NCH_2)C_6H_4]_2Sn{=}W(CO)_5$ (16) and $[2\text{-}(Ph_2PCH_2)C_6H_4]_2Sn{=}W(CO)_5$ (17).[40]

Donor-Functionalization Reactions in Silanediyl Complexes. The derivatization of 12 with electrophiles E (either H^+ or BF_3) allows the selective blocking of one amine unit. Both compounds 18 and 19 have been characterized by spectroscopic methods. Notably the protonation reaction is reversible and allows switching on and off of the dynamic "flip-flop" coordination in 12 (Chart VI).

Photochemical Activation of the Donor: 1,2-Amine Shift. Besides the discussed chemical derivatization reactions, the amine donor in 12 and 13 can also be activated by a highly selective photolysis reaction of the complex 12 at 254 nm which induces loss of CO and a 1,2-shift of one amine donor-substituent from silicon to the metal (eq 5). This process also takes place in a topochemical solid state reaction simply by UV irradiation of crystals of 12 or 13.



(5)

R = H 12

R = tBu 13

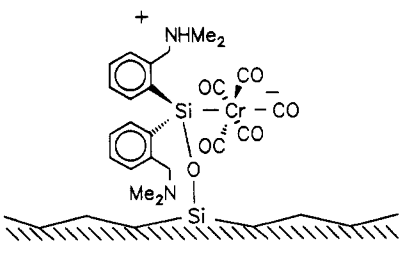
R = H 20

R = tBu 21

Both coordination compounds 20 and 21 have been fully characterized by spectroscopic methods (20, 21 ^1H NMR: two signal sets for the two diastereotopic CH_2NCH_3 substituents). The results from an X-ray structure analysis of 21 are depicted in Figure 6 and in the Tables VII and VIII. A Cr–Si bond length of 2.3610(4) Å is found which is the shortest observed so far for silanediyl complexes of chromium. This effect of bond shortening does not occur, however, for 11 and reflects the increased electron density at chromium due to the amine ligand which leads to a stronger metal–silicon bonding interaction by covalent and dipolar contributions.

The N-donor ligand is slightly stronger coordinated to the silicon atom than in complex 11, which is indicated by a shorter N1–Si bond of 1.981(1) Å (21) compared to 11. The sum of bond angles at silicon amounts to 342.9°. The N–Cr bond length (2.291(1) Å) lies in the expected range for N–Cr bonds in amine complexes as well as the Cr–C (1.815(2)–1.869(2) Å) bonds of the carbonyl ligands. As expected, the Cr–C3 bond of the CO ligand *trans* to nitrogen is shortened (1.815(2) Å) compared to the *cis*-CO's, although, this effect is only marginally above standard deviations.

Fixation of Silylene Complexes on a Silica Surface. A method of particular interest is the anchoring of silylene complexes on a silica gel surface. The fixation of 12 and 13 occurs quantitatively at rt within a few minutes and gives immobilized silylchromium complexes. IR spectroscopy of 22 shows bonding of the complex to the support by a Si–O linkage (ν_{CO} 1082 cm^{-1}) and protonation of the amine function (ν_{NH} 2610 cm^{-1}) as well as an intact $Cr(CO)_5$ unit.



22

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[39] An investigation of the system by molecular dynamics methods will provide further information.

[40] Abicht, H. P., Jurkschat, K., Tzschach, A., Peters, K., Peters, E. M., von Schnering, H. G., *J. Organomet. Chem.* **1987**, *326*, 357.

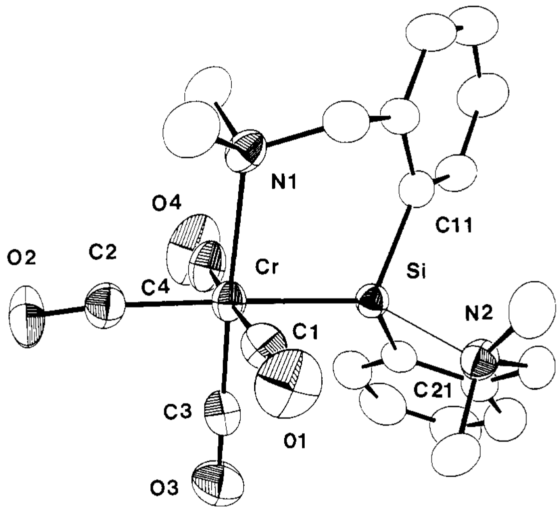
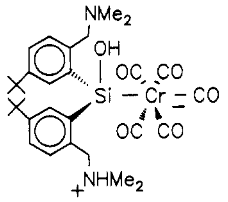


Figure 6. Molecular structure of $[2\text{-}(Me_2NCH_2)C_6H_4][2\text{-}(Me_2NCH_2)C_6H_4]Si{=}Cr(CO)_4$ (**20**) (ORTEP; displacement ellipsoids at 50% probability level).

The ^{13}C CPMAS NMR spectrum of **22** provides further evidence for the binding of **12** to the silica surface (Figure 7). The resonances of the methyl and methylene carbon atoms are clearly visible and their chemical shifts correspond well to the values measured in solution. All signals of the phenyl-C atoms are overlapped and show the typical shift anisotropy observed for aromatic ring systems, whereas the signals of aliphatic C atoms do not possess any side bands. The resonances for the carbonyl substituents cannot be assigned unambiguously due to superimposed rotational sidebands.

Detachment of Both Dimethylamine Groups by Coordination of a Strong Oxygen Donor to Silicon. The silylene complexes **12** and **13** are particularly susceptible to reactions with nucleophiles. Reaction of **13** with 1 equiv of water, for instance, leads to displacement of both nitrogen donors, protonation of one nitrogen atom, and formation of a hydroxysilyl complex (**23**). The spectroscopic parameters of **23** show a close similarity to the surface bound complex **22** (**23** IR: ν_{CO} 2019, 1938, 1892 cm^{-1}, ν_{NH} 2615, $\nu_{SiO\text{-}H}$ 2700 cm^{-1}) which allows the assumption of a strong structural similarity between **22** and **23**.



23

A single crystal structure analysis of **23** gives a Cr–Si bond distance of 2.469(2) Å, which is still short in comparison to bond lengths of base-stabilized silylene complexes (Figure 8, Tables IX and X). This bond shortening is presumably owing to relative strong dipolar effects. The Si–O6 bond distance is clearly in the range of covalent bonding (1.695(3) Å) and the distortion from an ideal tetrahedral geometry at silicon is only slight (sum of bond angles Cr–Si–C101, Cr–Si–C201, C101–Si–C201: 334.4°) compared to the above discussed cases. Both nitrogen atoms of the dimethylamino units are directed toward oxygen O6 by hydrogen bonding (N2–H61···O6 and N1···H62–O6). On the basis of the similarity of spectroscopic data, it can be assumed that the structure of **23** shows a close analogy to the structure of the immobilized complex **22**.

Experimental Section

All experiments have been performed in an atmosphere of dry argon; air-sensitive materials were handled by standard Schlenk techniques. **22** was filled into the rotor in a glove box and dry nitrogen was used as bearing and drive gas for the solid state NMR measurement. All solvents were dried by distillation from NaK alloy or P_4O_{10}. Residual water content was determined by K. Fischer titration and was generally below 3.5 ppm. The preparation of di-*tert*-butyldichlorosilane, disodium pentacarbonyl chromidepentacarbonylate has been described in the literature;[41] all further chemicals were commercially available.

Spectra. IR spectra were recorded on a Nicolet FT 5DX instrument as KBr pellets, a Nujol suspension, or as a solution in 0.1-mm KBr cells. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on the spectrometers JEOL GX 400 at 400.0, 100.4, and 73.3 MHz and on a JEOL FX 270 instrument at 270.1 MHz. The ^{29}Si NMR spectra were partially recorded with DEPT and INEPT pulse programs. ^1H and ^{13}C chemical shifts were measured using the solvent as standard; ^{29}Si chemical shifts were referenced to external Me_4Si in the same solvent. The solid state ^{13}C NMR spectrum was recorded on a Bruker MSL 400 P spectrometer (75.47 MHz). High-power ^1H decoupling, cross polarization (CP), and magic angle spinning (MAS, 4000 Hz) of the 7-mm zirconia rotor were employed for the measurement. The recycle time was 4 s, the contact time 5 ms, and the number of scans 5000. A line broadening of 100 Hz was applied for the processing of the spectrum, and it was referenced to external adamantane (δ of the high-field resonance: 29.472 ppm).[42] UV–VIS spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Mass spectra were measured on a Varian MAT311A instrument by either EI ionization at 70 eV, CI, or FD techniques by Ms. M. Dumitrescu and Professor F. R. Kreissl. GC MS separation was performed on a Hewlett-Packard (5890 A/5970 B) instrument equipped with a CP SIL 5CB column. Microanalyses were done by Mikroanalytisches Laboratorium der Technischen Universität München by Mss. I. Liss, A. Fuss, and M. Barth.

$(C_6H_5)[2\text{-}(Me_2NCH_2)C_6H_4]SiCl_2$ (6), 2-[(Dimethylamino)methyl]phenyl(phenyl)dichlorosilane, and $[2\text{-}(Me_2NCH_2)C_6H_4]_2SiCl_2$ (7), Bis[2-[(dimethylamino)methyl]phenyl]dichlorosilane. To a solution of 22.9 mL (0.2 mol) of $SiCl_4$, distilled from CaH_2 (0.2 mol $C_6H_5SiCl_3$ for **6**) and dissolved in 250 mL of diethyl ether was added 0.4 mol of 2-[(*N,N*-dimethylamino)methyl]phenyllithium (0.2 mol for the formation of **6**)[43] portionwise. The color of the reaction mixture turned yellow during the addition and the solvent started to boil. After completion of the addition of the lithium reagent, the mixture was refluxed for further 2 h and filtered, and all volatile components were removed in the vacuum. The crude product was recrystallized from diethyl ether: yield 50.0 g (68%) (**6**); 82% mp 104 °C (**7**).

6: ^1H NMR (CD_2Cl_2, 22 °C) δ 1.95 (s, 6 H, 2 × NCH_3), 3.72 (s, 2H, NCH_2) 7.48, 7.55, 7.60, 7.73, 8.70 (5 × m, 9 H, C_6H_4, C_6H_5); ^1H NMR (CD_2Cl_2, −70 °C) 1.25, 2.21 (2 × s, NCH_3) 3.41, 2.82 (AB system, $^2J(^1H^1H)$ = 12.2 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 22 °C) δ 45.1 (s, NCH_3) 62.2 (s, CH_2) 126.2, 127.3, 127.6, 128.3, 129.0, 129.7, 130.2, 131.5, 132.7, 137.1, 139.4, 144.7 (s, C_6H_5, C_6H_4); ^{29}Si NMR δ ($CDCl_3$, 22 °C, TMS) −27.5, (−70.0 °C) −51.2; MS (EI, 70 eV;

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[41] Brauer, G. *Handbuch der präparativen Chemie*; Enke Publishers: Stuttgart, 1984; Vol. 3.

[42] Hayashi, S., Hayamizu, K., *Bull. Chem. Soc. Jpn.* **1991**, *64*, 685–687.

[43] Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068.

Table VII. Selected Interatomic Distances (Å) and Angles (deg) in the Crystal Structure of 20[a]

		Interatomic Distances (Å)			
Cr–Si	2.3610(4)	C11–C12	1.402(3)	C21–C22	1.394(2)
Cr–N1	2.291(1)	C11–C16	1.408(2)	C21–C26	1.401(2)
Cr–C1	1.869(2)	C12–C13	1.390(2)	C22–C23	1.389(2)
Cr–C2	1.855(2)	C12–H121	0.95(1)	C22–H221	0.95(1)
Cr–C4	1.860(2)	C13–C14	1.373(3)	C23–C24	1.376(3)
Cr–C3	1.815(2)	C13–H131	0.91(2)	C23–H231	1.00(3)
Si–N2	1.981(1)	C14–C15	1.375(2)	C24–C25	1.380(3)
Si–C11	1.891(1)	C14–H141	1.02(2)	C24–H241	0.98(2)
Si–C21	1.881(2)	C15–C16	1.394(3)	C25–C26	1.373(2)
O1–C1	1.160(2)	C15–H151	1.03(2)	C25–H251	0.89(2)
O2–C2	1.150(2)	C16–C17	1.513(3)	C26–C27	1.495(2)
O4–C4	1.155(2)	C17–H171	1.03(1)	C27–H271	1.05(2)
O3–C3	1.167(2)	C17–H172	1.02(1)	C27–H272	0.90(1)
N1–C17	1.504(2)	C18–H181	0.97(2)	C28–H281	1.05(2)
N1–C18	1.480(3)	C18–H182	1.03(2)	C28–H282	0.95(2)
N1–C19	1.488(2)	C18–H183	0.95(2)	C28–H283	0.98(2)
N2–C27	1.504(2)	C19–H191	0.97(2)	C29–H291	1.00(2)
N2–C28	1.509(3)	C19–H192	0.88(2)	C29–H292	1.08(2)
N2–C29	1.486(2)	C19–H193	1.10(2)	C29–H293	0.94(2)
		Bond Angles (deg)			
Si–Cr–N1	90.71(3)	Cr–N1–C19	109.1(1)	C13–C14–C15	119.6(2)
Si–Cr–C1	93.90(5)	C17–N1–C18	108.7(1)	C13–C14–H141	118(1)
Si–Cr–C2	169.84(5)	C17–N1–C19	105.0(1)	C15–C14–H141	123(1)
Si–Cr–C4	81.86(5)	C18–N1–C19	106.0(2)	C14–C15–C16	121.4(2)
Si–Cr–C3	87.31(5)	Si–N2–C27	105.2(1)	C14–C15–H151	124.3(9)
N1–Cr–C1	89.48(6)	Si–N2–C28	109.6(2)	C16–C15–H151	114.3(9)
N1–Cr–C2	94.42(6)	Si–N2–C29	114.6(2)	C11–C16–C15	119.9(2)
N1–Cr–C4	92.13(6)	C27–N2–C28	108.0(1)	C11–C16–C17	123.0(1)
N1–Cr–C3	176.75(6)	C27–N2–C29	110.5(1)	C15–C16–C17	117.2(1)
C1–Cr–C2	94.92(7)	C28–N2–C29	108.7(1)	N1–C17–C16	115.5(1)
C1–Cr–C4	175.48(7)	Cr–C1–O1	176.3(1)	N1–C17–H171	106.7(7)
C1–Cr–C3	88.07(7)	Cr–C2–O2	171.8(2)	N1–C17–H172	106.8(7)
C2–Cr–C4	89.18(7)	Cr–C4–O4	177.2(2)	C16–C17–H171	112.0(8)
C2–Cr–C3	87.94(8)	Cr–C3–O3	178.5(1)	C16–C17–H172	109.0(8)
C4–Cr–C3	90.15(7)	Si–C11–C12	121.9(1)	H171–C17–H172	106(2)
Cr–Si–N2	123.06(4)	Si–C11–C16	120.2(1)	N1–C18–H181	109(2)
Cr–Si–C11	113.08(5)	C12–C11–C16	117.6(1)	N1–C18–H182	107.7(9)
Cr–Si–C21	125.16(5)	C11–C12–C13	121.5(2)	N1–C18–H183	109(1)
N2–Si–C11	100.00(6)	C11–C12–H121	118.6(9)	H181–C18–H182	110(1)
N2–Si–C21	85.60(6)	C13–C12–H121	120.0(9)	H181–C18–H183	112(1)
C11–Si–C21	104.66(6)	C12–C13–C14	120.1(2)	H182–C18–H183	110(1)
N1–C19–H193	107(1)	C23–C24–H241	119(2)	N2–C28–H281	105.5(9)
H191–C19–H192	105(2)	C25–C24–H241	122(2)	N2–C28–H282	110(1)
H191–C19–H193	114(1)	C24–C25–C26	120.0(2)	N2–C28–H283	108(2)
H192–C19–H193	115(2)	C24–C25–H251	123(2)	H281–C28–H282	120(1)
Si–C21–C22	129.7(1)	C26–C25–H251	118(2)	H281–C28–H283	107(1)
Si–C21–C26	112.8(1)	C21–C26–C25	121.6(2)	H282–C28–H283	107(1)
C22–C21–C26	117.5(2)	C21–C26–C27	114.9(1)	N2–C29–H291	109(1)
C21–C22–C23	120.6(2)	C25–C26–C27	123.6(2)	N2–C29–H292	105(1)
C21–C22–H221	119(2)	N2–C27–C26	108.0(1)	N2–C29–H293	110(2)
C23–C22–H221	121(2)	N2–C27–H271	107.0(8)	H291–C29–H292	111(1)
C22–C23–C24	120.6(2)	N2–C27–H272	105.6(9)	H291–C29–H293	104(1)
C22–C23–H231	122(1)	C26–C27–H271	115.1(9)	H292–C29–H293	117(1)
C24–C23–H231	118(1)	C26–C27–H272	111.1(9)		
C23–C24–C25	119.7(2)	H271–C27–H272	109(1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

m/e (rel inten)) 310 (M^+, 6%, correct isotope distribution). Anal. Calcd $C_{15}H_{19}NSiCl_2$ (M_w = 309.74) C, 58.10; H, 5.48; N, 4.52; Cl, 22.90. Found: C, 57.79; H, 5.86; N, 4.18; Cl, 22.22.

7: ^1H NMR (400 MHz, $CDCl_3$, 22 °C, TMS) δ 1.94 (s, 12 H, 4 × CH_3), 3.56 (s, 4 H, 2 × CH_2), 7.32–7.36, 8.19 (m, 8 H, 2 × C_6H_4); ^1H-NMR (d_8-toluene, −75 °C) δ 1.94 (s, 12 H, 4 × CH_3), 2.79, 3.38 (AB system, $^2J(^1H^1H)$ = 12.0 Hz, 4 H, 2 × CH_2) 7.32–7.36, 8.19 (m, 8 H, 2 × C_6H_4); ^{13}C NMR ($CDCl_3$, 22 °C) δ 45.0 (CH_3), 63.12 (CH_2), 126.60, 127.19, 130.11, 134.72, 134.85, 142.79 (C_6H_4); ^{29}Si NMR ($CDCl_3$, 23 °C) δ −30.1 ($CDCl_3$, −70.1 °C) −54.5; MS (EI, 70 eV; *m/e* (rel inten)) 367 (M + 1, 5%, correct isotope distribution). Anal. Calcd for $C_{18}H_{24}Cl_2N_2Si$ (M_w 367.396): C, 58.85; H, 6.58; N, 7.63; Cl, 19.30. Found: C, 60.16; H, 7.23; N, 7.76; Cl, 20.25.

X-Ray Structure Determinations. Suitable single crystals were grown from THF solutions. The crystals were sealed into glass capillaries under argon at dry ice temperatures. A summary of the crystal data and important figures pertinent to data collection and structure refinement is given in the experimental part. Exact cell dimensions were obtained by least-squares refinement on the Bragg angles of 15 selected reflections centered on the diffractometer. The integrated intensities were collected on a Syntex-P2$_1$ diffractometer with graphite monochromator for Mo K_α radiation, for details see Experimental Section. Repeated measurement of three standard reflexions did not indicate significant crystal decay nor misalignment during the data collection. Atomic form factors for neutral isolated atoms were those of Cromer and Waber,[44] those for hydrogen based on the bonded spherical model of Stewart, Davidson, and Simpson.[45] The programs used include SHELXS-86[46] (structure solution), SHELX-76[47] (refinement), ORTEP[48] (molecular drawings), Tables II–V and VII–X contain the atomic coordinates and

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(44) Cromer, D. T., Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(45) Stewart, R. F., Davidson, E. R., Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table VIII. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 20

atom	*x*	*y*	*z*	*B* (Å^2)[a]
Cr	0.09517(4)	0.20221(3)	0.16789(2)	2.515(7)
Si	0.23410(6)	0.28211(5)	0.09937(3)	2.31(1)
O1	−0.1026(2)	0.1072(2)	0.0356(1)	5.50(5)
O2	−0.0681(2)	0.1490(2)	0.27381(9)	5.68(5)
O4	0.2910(2)	0.3172(2)	0.2921(1)	7.13(6)
O3	−0.0658(2)	0.4152(2)	0.1401(1)	5.19(5)
N1	0.2156(2)	0.0367(2)	0.1817(1)	2.99(5)
N2	0.1806(2)	0.2948(2)	−0.00821(9)	3.00(4)
C1	−0.0244(2)	0.1402(2)	0.0864(1)	3.23(6)
C2	−0.0040(2)	0.1609(2)	0.2329(1)	3.49(6)
C4	0.2186(3)	0.2717(2)	0.2441(1)	3.94(6)
C3	−0.0013(2)	0.3327(2)	0.1514(1)	3.23(6)
C11	0.3984(2)	0.2045(2)	0.1117(1)	2.74(5)
C12	0.5190(2)	0.2626(2)	0.1174(1)	3.58(6)
C13	0.6400(2)	0.2051(3)	0.1300(2)	5.09(7)
C14	0.6439(3)	0.0890(3)	0.1385(2)	5.22(8)
C15	0.5275(3)	0.0303(2)	0.1347(2)	4.34(7)
C16	0.4050(2)	0.0861(2)	0.1231(1)	2.92(5)
C17	0.2834(2)	0.0139(2)	0.1216(1)	3.20(6)
C18	0.3161(3)	0.0285(3)	0.2525(1)	4.67(7)
C19	0.1233(3)	−0.0610(2)	0.1795(2)	4.82(7)
C21	0.2788(2)	0.4370(2)	0.0984(1)	2.71(5)
C22	0.2982(2)	0.5174(2)	0.1541(1)	3.69(6)
C23	0.3348(3)	0.6281(2)	0.1425(2)	4.81(8)
C24	0.3501(3)	0.6608(2)	0.0754(2)	5.42(8)
C25	0.3293(3)	0.5828(2)	0.0193(2)	4.67(7)
C26	0.2945(2)	0.4730(2)	0.0306(1)	3.19(6)
C27	0.2723(2)	0.3828(2)	−0.0267(1)	3.72(6)
C28	0.0397(3)	0.3394(2)	−0.0322(1)	4.13(7)
C29	0.1894(3)	0.1869(2)	−0.0476(1)	4.44(7)
H121	0.483(2)	0.657(2)	0.887(1)	0.3(5)*
H131	0.284(2)	0.746(2)	0.363(1)	2.5(6)*
H141	0.266(2)	0.550(2)	0.353(1)	2.8(6)*
H151	0.478(2)	0.444(2)	0.360(1)	1.6(6)*
H171	0.212(2)	0.478(2)	0.573(1)	0.4(5)*
H172	0.311(2)	0.570(2)	0.626(1)	0.5(5)*
H181	0.271(2)	0.466(2)	0.791(1)	2.3(6)*
H182	0.362(2)	0.549(2)	0.754(1)	2.0(6)*
H183	0.380(2)	0.413(2)	0.756(1)	1.3(5)*
H191	0.070(2)	0.544(2)	0.713(1)	3.7(7)*
H192	0.066(2)	0.563(2)	0.637(1)	2.8(6)*
H193	0.185(2)	0.638(2)	0.694(1)	3.5(7)*
H221	0.292(2)	0.493(2)	0.201(1)	1.9(6)*
H231	0.352(3)	0.686(3)	0.182(1)	5.2(8)*
H241	0.374(2)	0.760(2)	0.569(1)	3.6(7)*
H251	0.336(2)	0.601(2)	0.975(1)	1.5(6)*
H271	0.228(2)	0.411(2)	0.920(1)	2.0(6)*
H272	0.349(2)	0.346(2)	−1.026(1)	0.3(5)*
H281	0.973(2)	0.635(2)	0.087(1)	3.0(7)*
H282	0.020(2)	0.715(2)	0.020(1)	2.1(6)*
H283	0.034(2)	0.408(2)	−0.004(1)	2.6(6)*
H291	0.283(2)	0.342(2)	0.468(1)	2.3(6)*
H292	0.164(2)	0.290(2)	0.395(1)	3.6(7)*
H293	0.138(2)	0.370(2)	0.467(1)	2.7(6)*

[a] Asterisks designate atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

equivalent isotropic displacement parameters. Figures 2, 3, 5, 6, and 8 show the molecular structures and the crystallographic numbering scheme adopted. Further data of the structure determinations are available as supplementary material (see note at the end of the paper).

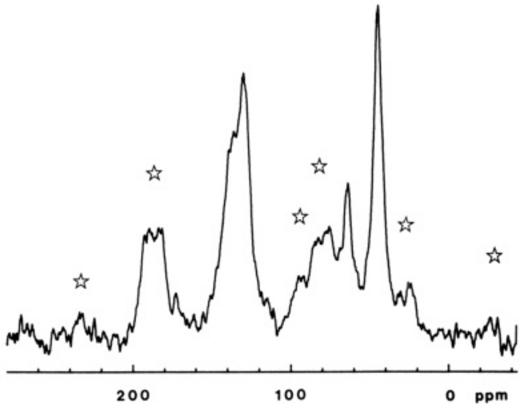

Figure 7. ^{13}C CPMAS NMR spectrum of **22**: 75.47 MHz, 4-s repetition time, 5-ms contact time, 5000 scans. Asterisks denote spinning sidebands.

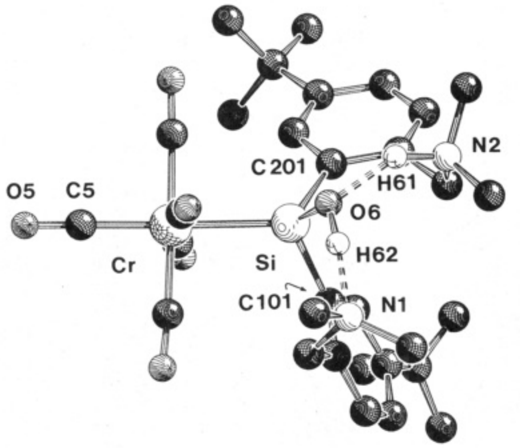

Figure 8. Molecular structure of [2-(Me_2HNCH_2) 5-(t-C_4H_9)-C_6H_3]$_2$(HO)SiCr(CO)$_5$ (**23**) (SCHAKAL).

7: crystal data, $C_{18}H_{24}Cl_2N_2Si$, colorless crystals (0.77 × 0.64 × 0.64 mm); M_r = 367.4, orthorhombic, P_{bca} (No. 61), a = 13.80(1) Å, b = 17.908(2) Å, c = 15.544(2) Å, V = 3842 Å^3, Z = 8, d_{ber} = 1.270 g cm^{-1}, μ[Mo Kα] = 4.0 cm^{-1}, $F(000)$ = 1552. Measurement: Enraf-Nonius CAD4, T = 294 K, 3750 measured reflections ($\theta_{\max}$ = 25°; +h, +k, +l), 422 extinguished reflections and 312 reflections suppressed with negative intensity, 3016 independent reflections ($I > 0.0$) used for refinement. Correction for decay (52.2 h, −14.9%), empirical absorption correction ($0.914 < T < 1.000$), extinction correction [$F_{c(\mathrm{corr})} = F_c/(1 + \epsilon Fc^2 Lp)$; $\epsilon = 0.415 \times 10^{-7}$]. Structure solution: direct methods (MULTAN 11/82, difference Fourier technique), 303 parameters. Refinement: full matrix, least squares (STRUX-III; SDP), R = 0.060, R_w = 0.039; all heavy atoms with anisotropic and all hydrogen atoms with isotropic displacement parameters (hydrogen atoms at C17 and C18 with one collective value). Residual electron density +0.39, −0.42 e$_0$ Å^{-3}.

[2-(Me_2NCH_2)-5-(t-C_4H_9)C_6H_3]$_2$$SiCl_2$ (8), Bis[2-[(dimethylamino)methyl]-5-*tert*-butylphenyl]dichlorosilane. To a solution of 6.52 mL (57.6 mmol) of $SiCl_4$ in 200 mL of diethyl ether was added 22.7 g (115.2 mmol) of [2-[(dimethylamino)-methyl]-5-*tert*-butyl]phenyllithium portionwise at −30 °C and the mixture was stirred for further 12 h at rt. After filtration from precipitated LiCl, **8** was isolated as a white solid in 63% yield: mp 117 °C; ^{1}H NMR ($CDCl_3$, 22 °C) 1.8 (s, 18 H, 2 × t-Bu), 1.95 (s, 12 H, 4 × CH_3), 3.6 (s, 4 H, 2 × CH_2), 7.1–7.7, 8.1–8.3 (m, 4 H + 2 H, 2 × C_6H_3); ^{13}C NMR ($CDCl_3$, 22 °C) 31.37 (s, C(CH_3)), 34.75 (s, C(CH_3)), 45.28 (s, NCH_3), 62.93 (s, NCH_2), 126.88, 127.5, 132.17, 134.22, 140.22, 149.32 (s, C_6H_3); ^{29}Si NMR ($CDCl_3$, 22 °C) −28.5 ppm; MS (CI, 70 eV; m/e (rel inten)) 479 (M$^+$, 5%, correct isotope distribution)). Anal. Calcd for $C_{26}H_{40}Cl_2N_2Si$ (M_w 479.61): C, 65.11; H, 8.41; Cl, 14.78; N, 5.84. Found: C, 65.40; H, 8.40; Cl 14.81; N, 5.80.

[2-(Me_2NCH_2)C_6H_4]$SiCl_3$ (9), [2-[(Dimethylamino)-methyl]phenyl]trichlorosilane. The synthesis of **9** was done in analogy to the reaction described for **7** by reaction of 1 equiv

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Table IX. Selected Interatomic Distances (Å) and Angles (deg) in the Crystal Structure of 23[a]

	Interatomic Distances (Å)		
Cr–C1	1.880(6)	C101–C102	1.423(7)
Cr–C2	1.869(6)	C101–C106	1.406(7)
Cr–C3	1.880(6)	C102–C103	1.369(7)
Cr–C4	1.889(6)	C102–C107	1.513(7)
Cr–C5	1.850(6)	C103–C104	1.382(7)
Cr–Si	2.469(2)	C104–C105	1.383(7)
C1–O1	1.139(6)	C105–C106	1.385(7)
C2–O2	1.156(6)	C105–C110	1.517(7)
C3–O3	1.147(6)	C110–C111	1.40(1)
C4–O4	1.131(6)	C110–C112	1.48(1)
C5–O5	1.159(6)	C110–C113	1.34(1)
Si–C101	1.912(5)	C201–C202	1.412(7)
Si–C201	1.927(5)	C201–C206	1.404(6)
Si–O6	1.695(3)	C202–C203	1.386(7)
N1–C107	1.470(7)	C202–C207	1.509(7)
N1–C108	1.467(7)	C203–C204	1.389(8)
N1–C109	1.471(7)	C204–C205	1.384(7)
N2–C207	1.498(7)	C205–C206	1.392(7)
N2–C208	1.489(7)	C205–C210	1.533(7)
N2–C209	1.487(7)	C210–C211	1.462(9)
		C210–C212	1.480(9)
		C210–C213	1.488(9)
	Bond Angles (deg)		
C1–Cr–C2	168.5(2)	C102–C101–C106	116.9(4)
C1–Cr–C3	88.7(2)	C101–C102–C103	118.7(5)
C2–Cr–C3	87.7(2)	C101–C102–C107	121.4(4)
C1–Cr–C4	88.6(2)	C103–C102–C107	119.9(5)
C2–Cr–C4	95.2(2)	C102–C103–C104	122.7(5)
C3–Cr–C4	177.0(2)	C103–C104–C103	120.7(5)
C1–Cr–C5	95.6(2)	C104–C105–C106	117.0(5)
C2–Cr–C5	95.2(2)	C104–C105–C110	122.4(5)
C3–Cr–C5	88.4(2)	C106–C105–C110	120.6(5)
C4–Cr–C5	90.6(2)	C101–C106–C105	124.0(5)
C1–Cr–Si	85.0(2)	N1–C107–C102	114.3(4)
C2–Cr–Si	84.2(2)	C105–C110–C111	116.3(6)
C3–Cr–Si	92.8(2)	C105–C110–C112	109.2(5)
C4–Cr–Si	88.3(1)	C111–C110–C112	91.9(8)
C5–Cr–Si	178.7(2)	C105–C110–C113	114.9(6)
Cr–C1–O1	178.4(5)	C111–C110–C113	115.3(8)
Cr–C2–O2	176.8(5)	C112–C110–C113	105.9(9)
Cr–C3–O3	176.1(5)	Si–C201–C202	124.9(4)
Cr–C4–O4	177.6(4)	Si–C201–C206	119.3(4)
Cr–C5–O5	178.7(5)	C202–C201–C206	115.7(4)
Cr–Si–C101	114.4(2)	C201–C202–C203	120.3(5)
Cr–Si–C201	117.8(2)	C201–C202–C207	122.5(5)
C101–Si–C201	102.2(2)	C203–C202–C207	117.1(5)
Cr–Si–O6	116.3(1)	C202–C203–C204	121.6(5)
C101–Si–O6	102.8(2)	C203–C204–C205	120.3(5)
C201–Si–O6	101.1(2)	C204–C205–C206	117.2(5)
C107–N1–C108	109.9(4)	C204–C205–C210	122.4(5)
C107–N1–C109	109.1(5)	C206–C205–C210	120.4(5)
C108–N1–C109	109.9(4)	C201–C206–C205	124.8(5)
C207–N2–C208	112.8(4)	N2–C207–C202	113.1(4)
C207–N2–C209	110.2(4)	C205–C210–C211	110.4(5)
C208–N2–C209	110.3(4)	C205–C210–C212	110.7(5)
Si–C101–C102	124.6(4)	C211–C210–C212	107.1(7)
Si–C101–C106	118.5(4)	C205–C210–C213	113.1(5)
		C211–C210–C213	108.4(6)
		C212–C210–C213	107.0(6)

[a] Estimated standard deviations in units of the last significant figure are given in parentheses.

Table X. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for 23[a]

atom	x/a	y/b	z/c	U_{eq}[a]
Cr	0.02736(6)	0.72671(5)	0.27835(5)	0.031
C1	0.0488(4)	0.7713(3)	0.1796(3)	0.037
C2	0.0205(4)	0.6794(3)	0.3685(3)	0.043
C3	0.0202(4)	0.6274(3)	0.2301(3)	0.036
C4	0.0388(4)	0.8282(3)	0.3225(3)	0.032
C5	0.1628(4)	0.7074(3)	0.3030(3)	0.046
O1	0.0611(3)	0.7967(2)	0.1189(2)	0.056
O2	−0.0513(4)	0.6470(3)	0.4223(3)	0.063
O3	0.0217(3)	0.5666(2)	0.2012(3)	0.051
O4	0.0492(3)	0.8890(2)	0.3484(2)	0.049
O5	0.2478(3)	0.6946(3)	0.3171(3)	0.062
Si	−0.1536(1)	0.75442(8)	0.24810(8)	0.027
N1	−0.2065(4)	0.7016(3)	0.0466(3)	0.043
N2	−0.3569(3)	0.8809(3)	0.1732(3)	0.040
C101	−0.2359(4)	0.6629(3)	0.2322(3)	0.027
C102	−0.2389(4)	0.6164(3)	0.1628(3)	0.031
C103	−0.3030(4)	0.5532(3)	0.1583(3)	0.037
C104	−0.3667(4)	0.5337(3)	0.2176(3)	0.039
C105	−0.3668(4)	0.5772(3)	0.2860(3)	0.035
C106	−0.2997(4)	0.6398(3)	0.2922(3)	0.030
C107	−0.1718(4)	0.6348(3)	0.0953(3)	0.039
C108	−0.3040(5)	0.6828(4)	0.0068(3)	0.050
C109	−0.1302(5)	0.7185(4)	−0.0116(4)	0.062
C110	−0.4374(4)	0.5591(3)	0.3517(4)	0.045
C111	−0.4924(9)	0.4889(7)	0.3448(6)	0.137
C112	−0.3771(8)	0.5291(8)	0.4204(6)	0.154
C113	−0.4893(9)	0.6210(6)	0.3777(8)	0.106
C201	−0.2274(4)	0.8120(3)	0.3246(3)	0.029
C202	−0.3280(4)	0.8393(3)	0.3133(3)	0.037
C203	−0.3770(4)	0.8750(4)	0.3743(4)	0.045
C204	−0.3304(4)	0.8834(3)	0.4482(3)	0.045
C205	−0.2318(4)	0.8579(3)	0.4622(3)	0.032
C206	−0.1830(4)	0.8242(3)	0.3997(3)	0.030
C207	−0.3886(4)	0.8274(3)	0.2375(3)	0.041
C208	−0.3724(5)	0.9654(3)	0.1918(4)	0.053
C209	−0.4115(5)	0.8601(4)	0.0982(4)	0.053
C210	−0.1766(4)	0.8665(3)	0.5424(3)	0.041
C211	−0.0885(7)	0.9179(6)	0.5366(4)	0.093
C212	−0.1388(8)	0.7894(5)	0.5711(4)	0.095
C213	−0.2424(6)	0.8987(7)	0.6036(4)	0.101
O6	−0.1802(2)	0.8079(2)	0.1661(2)	0.033
O7	−0.6411(4)	0.9137(3)	0.1659(3)	0.083

[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. ESD's are in parentheses.

of 2-(Me_2NCH_2)C_6H_4Li with $SiCl_4$, yield 63%: ^{1}H NMR (C_6D_6, 22 °C) 1.84 (s, 6 H, CH_3) 3.06 (s, 2 H, CH_2) 6.68, 7.13, 8.67 (3 × s, 4 H, C_6H_4); ^{13}C NMR (C_6D_6) 45.4 (s, NCH$_3$) 61.6 (s, CH$_2$) 132.1, 133.6, 140.1, 142.7, 125.5, 127.2 (6 s, C_6H$_4$); ^{29}Si NMR ($CDCl_3$) −58.2 ppm.

[[2-(Me_2NHCH_2)C_6H_4][2-(Me_2NCH_2)C_6H_5]$SiCl_2$]$^+$Cl$^-$ (10), [2-[(Dimethylammonio)methyl]phenyl]-2-[(dimethylamino)methyl]phenyldichlorosilane Chloride. To a solution of 367 mg (1 mmol) of 7 in 20 mL of THF, 1 mmol HCl × Et_2O was slowly added. On cooling of the solution to −20 °C, 10 crystallized as colorless needles: 23% yield, mp 173 °C; ^{1}H-NMR ($CDCl_3$, 22 °C) 2.3 (br, 12 H, CH_3) 3.6 (s, 4 H, CH_2), 7.3–8.1 (br, 10 H, C_6H_5); ($CDCl_3$, 42 °C) 2.31 (s, 6 H, CH_3) 2.46 (d, $^3J(^1H^1H)$ = 16.9 Hz, 6 H, CH_3), 5.41 (br, 1 H, NH), 7.35–7.41, 8.52 (m, 2 × C_6H_4). Anal. Calcd for $C_{18}H_{25}Cl_3N_2Si$ (M_w 403.86): C, 53.53; H, 6.24; N, 6.94. Found: C, 53.49; H, 6.21; N, 6.90. Crystal data $C_{18}H_{25}Cl_3N_2Si$ × $CHCl_3$, M_r 523.2, orthorhombic, P_{bca} (No. 61), a = 16.949(2) Å, b = 11.617(2) Å, c = 25.017(3) Å, V = 4925.8 Å^3, Z = 8, d_{calc} = 1.41, μ[Mo Kα] = 7.58, 3879 measured reflections, 3434 independent reflections used for refinement, 309 parameters refined: R = 0.0444, R_w = 0.0349. Residual electron density +0.33 eÅ^{-3}/−0.29 eÅ^{-3}. Si–N1 2.163(2) Å, Si–Cl1 2.086(1) Å, Si–Cl2 2.219(2) Å, equatorial sum of bond angles 358.9°.

[2-(Me_2NCH_2)C_6H_4]C_6H_5Si=Cr(CO)$_5$ (11), [2-[(Dimethylamino)methyl]phenyl]phenylsilanediylchromium(0) Pentacarbonyl, [2-(Me_2NCH_2)C_6H_4]$_2$Si=Cr(CO)$_5$ (12), Bis[2-[(dimethylamino)methyl]phenyl]silanediylchromium(0) Pentacarbonyl, and [2-(Me_2NCH_2)-5-(t-C_4H_9)C_6H_3]$_2$Si=Cr(CO)$_5$ (13), Bis[2-[(dimethylamino)methyl]-5-*tert*-butylphenyl]silanediylchromium(0) Pentacarbonyl. An amount of 2.31 g (9.71 mmol) of $Na_2Cr(CO)_5$ was dissolved in 100 mL of THF by ultrasonification. The yellowish brown solution was cooled to −40 °C and 9.71 mmol of the dichlorosilane (6, 7, or 8) dissolved in 20 mL of THF was added dropwise over a period of ca. 30 min. The reaction mixture was allowed to warm up to rt and was stirred for another 3 h. The mixture was filtered and concentrated to 10 mL in the vacuum (10^{-2} torr). 11, 12, and 13 crystallized at −20 °C as beige yellow crystals: yield (32–63%); mp 170 °C (11), mp 121 °C (12), mp 155 °C (13). 12 and 13 are thermochromic (yellow → red).

11: ^{1}H NMR (d_8-toluene, 22 °C) δ 1.83, 2.08 (s, 6 H, 2 × $\mathrm{NC}H_3$), 2.62, 3.04 (dd, AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 14.0 Hz, 2 H, $\mathrm{NC}H_2$), 6.04, (d, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 10.1 Hz, 1 H), 7.02 (t, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 10.0 Hz, 1 H), 7.04 (d, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 10.1 Hz, 1 H), 8.08 (d, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 10.1 Hz, 1 H; $\mathrm{C_6}H_4\mathrm{CH_2NMe_2}$), 6.97, (s, 2 H), 7.04 (d, $^3J(^1\mathrm{H}^1\mathrm{H})$ = 8.9 Hz, 3 H, $\mathrm{C_6}H_5$); ^{29}Si-NMR (53.5 MHz, d_8-toluene, 22 °C) δ 121.2; MS (EI, 70 eV; *m/e* (rel. inten)) 431 (M$^+$, 9%, correct isotope distribution). IR (cm^{-1}, THF, difference spectrum): 2037 (vs), 2020 (m), 1905 cm^{-1} (vs, br) (ν_{CO}). Anal. Calcd for $\mathrm{C_{20}H_{17}CrO_5NSi}$ (M_w 431.44): C, 55.68; H, 3.97; N, 3.25. Found: C, 55.50; H, 3.21.

11: crystal data $\mathrm{C_{20}H_{17}CrNO_5Si}$, yellow crystals (0.2 × 0.45 × 0.5 mm) M_r = 431.4, triclinic, $P\bar{1}$ (No. 2), A = 9.404(1) Å, b = 10.207(1) Å, c = 11.586(1) Å, α = 106.39(1), β = 91.79(1), τ = 110.04(1)°, V = 992.16 Å^3, Z = 2, d_{calc} = 1.444 g cm^3, μ[Mo Kα] = 6.50 cm^{-1}, $F(000)$ = 404. Measurement: Syntex $P2_1$, T = 223 K, 3489 measured reflections (2° > $\theta \geq$ 25°), 3489 independent reflections of which 3289 with $F_o > 4(F_o)$ were used for refinement (weighing factor: $w = 1/\sigma^2$, l = 2.0716), empirical absorption correction (0.76 < T < 1.00). Structure solution: direct methods (MULTAN 11/82, difference Fourier technique), 321 parameters. Refinement: full matrix, least squares (SHELX-76), R = 0.031, R_w = 0.037, all non-hydrogen atoms with anisotropical and all hydrogen atoms with isotropical displacement parameters refined. Residual electron density +0.31/−0.28 e_0 Å^{-3}.

11a: (^{1}H NMR, CDCl$_3$, 22 °C) 1.72, 3.62 (m, 2 × 4 H, THF), 2.70 (br, 6 H, $\mathrm{C}H_3$), 4.05 (s, 2 H, $\mathrm{C}H_2$) 6.04–8.08 (m, 9 H, $\mathrm{C_6}H_5$, $\mathrm{C_6}H_4$) (^{1}H NMR, CDCl$_3$, −65 °C) 1.71, 6.63 (m, 2 × 4 H, THF), 2.85, 2.97 (2 × s, 2 × 3 H, 2 × $\mathrm{C}H_3$), 4.01, 4.13 (AB, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 7.1 Hz, 2 H, CH$_2$), 6.05–8.01 (m, 9 H, $\mathrm{C_6}H_5$, $\mathrm{C_6}H_4$).

12: ^{1}H NMR (d_8-toluene, 22 °C) δ 2.57 (s, 2 × 6 H, $\mathrm{NC}H_3$), 3.80, 4.09 (dd, AB system, $^2J(^1\mathrm{H},^1\mathrm{H})$ = 12.2 Hz, 2 × 2H, $\mathrm{C}H_2$), 7.18–7.27, 7.61–7.71 (m, 2 × 4 H, $\mathrm{C_6}H_4$); ^{1}H-NMR (d_8-toluene, 62 °C) 3.90 (s, 2 × 2H, $\mathrm{C}H_2$), (−40.0 °C): 2.02, 2.23 (2 s, 6 H, $\mathrm{NC}H_3$), 2.61 (s, 6 H, $\mathrm{NC}H_3$), 3.81, 4.11 (AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 12.2 Hz, 2 H, $\mathrm{C}H_2$, 2.62, 3.04 (AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 14.0 Hz, 2 H, $\mathrm{C}H_2$); ^{13}C-NMR (d_6-acetone, 22 °C) δ 43.44 ($C\mathrm{H_3}$), 64.68 ($C\mathrm{H_2}$), 128.3, 128.6, 132.8, 137.1, 149.3, 150.1 ($C_6\mathrm{H_4}$), 212.8, 227.2 (CO); ^{29}Si-NMR (d_8-THF, 22 °C) δ 124.9; ^{29}Si-NMR (d_8-THF, −40.0 °C) δ 120.9; ^{29}Si-NMR (d_8-THF, 62 °C): 138.8; MS (EI, 70 eV; *m/e* (rel inten)) 488 (M$^+$, 10%, correct isotope distribution); IR (cm^{-1}, Nujol) 2036 (m), 1916 (ss) 1884 (22) (ν_{CO}); UV/vis (cyclohexane) $\lambda_{\max}$ = 274 nm, ϵ = 2700. Anal. Calcd for $\mathrm{C_{23}H_{24}CrN_2O_5Si}$ (M_w 488.536): C, 56.55; H, 4.95; N, 5.73. Found: C, 55.84; H, 5.23; N, 5.40.

12: crystal data: $\mathrm{C_{23}H_{24}CrN_2O_5Si}$, M_r = 488.5, triclinic, $P\bar{1}$ (No. 2), a = 9.531(1) Å, b = 10.339(1) Å, c = 11.676(1) Å, α = 94.47(1), β = 88.09(1), τ = 96.68(1)°, V = 5115 Å^3, Z = 2, d_{calcd} = 1.42 g cm^{-1}, μ[Mo Kα] = 5.7 cm^{-1}, $F(000)$ = 508. Measurement: Syntex $P2_1$, T = 218 K, 4035 measured reflections ($\theta_{\max}$ = 25°; ±h, ±k, ±l), 4035 independent reflections (I > 0.0) used for refinement, empirical absorption correction. Structure solution: Patterson (SHELX 86, difference Fourier technique), 385 parameters. Refinement: full matrix, least squares (SHELX-76), R = 0.040, R_w = 0.032, all heavy atoms anisotropically, all hydrogen atoms with isotropic displacement parameters refined. Residual electron density +0.27; −0.28 e_0 Å^{-3}.

13: ^{1}H-NMR (270 MHz, $\mathrm{CD_2Cl_2}$, 22 °C) δ 1.20 (s, 2 × 9 H, *t*-Bu), 2.46 (s, 12 H; 4 × $\mathrm{C}H_3$), 3.66, 3.87 (dd, 2 × 2 H, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 12.2 Hz; $\mathrm{NC}H_2$), 7.0–7.64 (m, 6 H; 2 × $\mathrm{C_6}H_3$); ^{13}C-{^{1}H}-NMR (67.8 MHz, $\mathrm{CD_2Cl_2}$, 22 °C) δ 31.08 ($\mathrm{C}(C\mathrm{H_3})$), 34.16 ($C(\mathrm{CH_3})_3$), 44.03 ($\mathrm{N}C\mathrm{H_3}$), 64.30 ($\mathrm{N}C\mathrm{H_2}$), 126.26, 130.97, 132.95, 138.41, 139.23, 149.61 ($C_6\mathrm{H_3}$), 211.4, 221.0 (CO); ^{29}Si-NMR (53.5 MHz, $\mathrm{CD_2Cl_2}$, 21 °C) δ 127.1; IR (cm^{-1}, THF, difference spectrum) 2018 (w), 1938 (w), 1893 (vs) (ν_{CO}). Anal. Calcd for $\mathrm{C_{31}H_{40}CrN_2O_5Si}$ (M_r 600.752: C, 61.98; H, 6.71; N, 4.66. Found: C, 61.88; H, 6.70; N, 4.67.

$[2\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_4}]\mathrm{HSi{=}Cr(CO)_5}$ (14), 2-[(Dimethylamino)methyl]phenylsilanediylchromium(0) Pentacarbonyl. An amount of 0.88 g (5.3 mmol) of 2-[(dimethylamino)methyl]phenylsilane and 1.17 g (5.3 mmol) of Cr(CO)$_6$ suspended in 20 mL of pentane were photolyzed at rt with a Hg high pressure immersion lamp. The reaction mixture turned yellow. After 7 h photolysis, **14** was obtained in 63% yield, mp 165 °C: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 2.17 (s, 3 H, $\mathrm{NC}H_3$), 2.28 (s, 3 H, $\mathrm{NC}H_3$), 2.85, 3.52 (AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 13.5 Hz, 2 H, $\mathrm{NC}H_2$) 6.08 (s, 1 H, SiH), 6.8–8.3 (m, 4 H, $\mathrm{C_6}H_4$); ^{13}C NMR ($\mathrm{C_6D_6}$) 45.02 ($\mathrm{N}C\mathrm{H_3}$), 46.19 ($\mathrm{N}C\mathrm{H_3}$), 69.11 ($\mathrm{N}C\mathrm{H_2}$), 123.25, 128.79, 134.73, 134.89, 140.51, 144.76 ($C_6\mathrm{H_4}$); IR (cm^{-1}, THF) 2023.0 (w), 1935.2 (s), 1899.8 (s) (ν_{CO}). Anal. Calcd for $\mathrm{C_{14}H_{13}CrNO_5Si}$ (M_w 355.34): C, 47.32; H, 3.69; N, 3.94. Found: C, 47.21; H, 3.68; N, 3.90.

$[[2\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_4}][2\text{-}(\mathrm{Me_2HN^+CH_2})\mathrm{C_6H_4}]\mathrm{Si{=}Cr(CO)_5}]\mathrm{Cl^-}$ (18), [2-[(Dimethylamino)methyl]phenyl][2-[(dimethylammonio)methyl]phenyl]silanediylchromium(0) Pentacarbonyl Chloride. 488 mg (1 mmol) of **12** dissolved in 20 mL of THF was treated with 1 mmol of anhydrous HCl × Et$_2$O. **18** was formed as a white precipitate: yield 58%, mp 251 °C dec; ^{1}H NMR (CDCl$_3$, 22 °C) 1.82, 2.04 (s, 6 H, 2 × $\mathrm{NC}H_3$, 2.61, 3.05 (dd, AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 14.0 Hz, 2 H, $\mathrm{C}H_2$), 3.52 (s, 6 H, $\mathrm{NC}H_3$), 5.41 (s, 1 H, NH), 6.12–7.95 (m, 2 × 4 H, $\mathrm{C_6}H_4$). Anal. Calcd for $\mathrm{C_{23}H_{25}ClCrN_2O_5Si}$ (525.00): C, 52.62; H, 4.80; N, 5.34; Cl, 6.75. Found: C, 52.55; H, 4.81; N, 5.34; Cl, 6.77.

$[2\text{-}[\mathrm{Me_2N(BF_3)CH_2}]\mathrm{C_6H_4}][2\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_4}]\mathrm{Si{=}Cr(CO)_5}$ (19), [2-[[Dimethyl(trifluoroboranyl)amino]methyl]phenyl][2-[(dimethylamino)methyl]phenyl]silanediylchromium(0) Pentacarbonyl. An amount of 3.61 g (7.4 mmol) of **12** dissolved in 50 mL of Et$_2$O were reacted with 0.9 mL (7.3 mmol) of BF$_3$ × Et$_2$O at −40 °C. The reaction mixture was allowed to warm to rt and stirred for 24 h and concentrated subsequently to 10 mL in the vacuum. **19** was isolated from a THF solution as pale yellow crystals upon cooling: yield 2.0 g (49%); ^{1}H NMR (400 MHz, d_8-toluene, 22 °C) 2.41, 2.60 (s, 6 H, $\mathrm{C}H_3$), 3.10, (m, $^4J(^{19}\mathrm{F}^1\mathrm{H})$ = 2 Hz, 6 H, $\mathrm{C}H_3$), 3.82, 4.11 (dd, AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 12 Hz, 2 H, $\mathrm{C}H_2$), 3.88 (s, 2 H, $\mathrm{C}H_2$), 7.20–7.29, 7.60–7.70 (m, 8 H, 2 × $\mathrm{C_6}H_4$); ^{29}Si NMR (d_8-toluene, 22 °C) 119.7 ppm; ^{11}B NMR (d_8-toluene, 22 °C) 7.9 (s); IR (cm^{-1}, Nujol) 2043 (s), 1958 (s), 1892 (s) (ν_{CO}), 1124 (m) (BF); MS (EI, 70 eV; *m/e* (rel inten)) 488 (M$^+$, 1.6%, correct isotope distribution). Anal. Calcd for $\mathrm{C_{23}H_{24}BCrF_3N_2O_5Si}$ (M_w 556.34): C, 49.66; H, 4.35; N, 5.04; F, 10.24. Found: C, 49.94; H, 4.38; N, 4.99; F, 10.14.

$[2\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_4}][2\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_4}]\mathrm{Si{=}Cr(CO)_4}$ (20), [2-[(dimethylamino)methyl]phenyl][2-[(dimethylamino)methyl]phenyl]silanediylchromium(0) Tetracarbonyl. A suspension of 1.0 g (2.0 mmol) of **12** was photolyzed with a 100-W high-pressure Hg immersion lamp for 12 h during which an orange-colored suspension was formed. After filtration and removal of the THF, **20** was obtained as a pure product: 100% yield, mp 280 °C dec. The reaction can be monitored by IR spectroscopy. **20**: ^{1}H-NMR (400 MHz, $\mathrm{CD_2Cl_2}$, 22 °C) δ 2.05 (s, 3 H), 2.71 (s, 3 H), 2.93 (s, 6 H; $\mathrm{NC}H_3$), 3.14, 4.12 (AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 12.2 Hz, 2 H; $\mathrm{C}H_2\mathrm{NSi}$), 3.85, 4.44 (AB system, $^2J(^1\mathrm{H}^1\mathrm{H})$ = 13.6 Hz, 2 H; $\mathrm{C}H_2\mathrm{NCr}$), 6.7–8.2 (m, 2 × 4 H; $\mathrm{C_6H_4}$); ^{13}C-NMR ($\mathrm{CD_2Cl_2}$, 22 °C) δ 45.35, 47.85, 54.0, 62.44 ($\mathrm{N}C\mathrm{H_3}$), 67.91, 74.52 ($\mathrm{N}C\mathrm{H_2}$), 123.7, 128.58, 129.12, 129.71, 130.13, 131.13, 132.68, 133.3, 134.9, 140.89, 142.9, 144.3 (2 × $C_6\mathrm{H_4}$), 221.6, 228.6, 228.9, 229.1 (CO); ^{29}Si-NMR (53.5 MHz, $\mathrm{CD_2Cl_2}$, 25 °C) δ 143.2; (−35 °C): 124.6; MS (EI, 70 eV; *m/e* (rel. inten) 460 (M$^+$, 5%, correct isotope distribution); IR (cm^{-1}, THF, difference spectrum) 1977 (w), 1851 (s), 1834 (m) (ν_{CO}); UV/vis (cyclohexane) $\lambda_{\max}$ = 310 nm, ϵ_0 = 3200. Anal. Calcd for $\mathrm{C_{22}H_{24}CrN_2O_4Si}$ (M_w 460.53): C, 57.38; H, 5.25; N, 6.08. Found: C, 57.30; H, 5.26; N, 6.10.

20: crystal data $\mathrm{C_{22}H_{24}CrN_2O_4Si}$, orange crystals, (0.21 × 0.42 × 0.22 mm) M_w = 460.5, monoclinic, $P2_1/c$ (No. 14), a = 10.344(5) Å, b = 11.761(3) Å, c = 18.96(1) Å, β = 111.2°, V = 2233 Å^3, Z = 4, d_{calc} = 1.37 g cm^{-3}, μ[Mo Kα] = 1.5418 Å, $F(000)$ = 960. Measurement: Enraf-Nonius CAD4, T = 296 K, 4150 measured reflections (1° < θ < 65°, h(−12/12; k(0/13); l(−22/0), 213 reflections systematically absent and 160 reflections with negative intensity suppressed; 3539 independent reflections with (I > 0.0 $\sigma(I)$) used for refinement. Empirical absorption correction with seven reflections at angles >80°, μ[Cu Kα] = 50.5 cm^{-1}. Structure solution: direct methods (STRUX-III; SDP), R = 0.041; all heavy atoms anisotropically and all hydrogen atoms isotropically refined. Residual electron density +0.62 e_0 Å^{-3}, –0.37 e_0 Å^{-3}.

[2-(Me_2NCH_2)-5-(*t*-C_4H_9)C_6H_3][2-(Me_2NCH_2)-5-(*t*-C_4H_9)-C_6H_3]Si=Cr(CO)$_4$ (21), [2-[(Dimethylamino)methyl]-5-*tert*-butylphenyl][2-[(dimethylamino)methyl]-5-*tert*-butylphenyl]silanediylchromium(0) Pentacarbonyl. The synthesis followed the description given for **20**.

21: ^{1}H-NMR (400 MHz, CD_2Cl_2, 22 °C) δ 0.98 (s, 9 H, *t*-Bu), 1.23 (s, 9 H, *t*-Bu), 1.97 (s, 3 H), 2.17 (s, 3 H), 2.62 (s, 3 H), 2.88 (s, 3 H, NCH_3), 3.01, 3.98 (AB system, $^2J(^1H^1H)$ = 12.5 Hz, 2 H, CH_2NSi), 3.8, 4.23 (AB system, $^2J(^1H^1H)$ = 13.7 Hz, 2 H, CH_2-NCr), 6.5–8.2 (m, 2 × 3 H, C_6H_3); MS (EI, 70 eV; *m/e* (rel. inten) 572 (M^+, 5%, correct isotope distribution); IR (cm^{-1}, THF, difference spectrum) 1976 (w), 1875 (w), 1849 (s), 1834 (m) (ν_{CO}). Anal. Calcd for $C_{30}H_{40}N_2CrO_4Si$ (572.74): C, 62.91; H, 7.04; N, 4.89. Found: C, 62.89; H, 7.01; N, 4.91.

22: Fixation of 13 on Silica Gel. Approximately 500 mg of rigorously dried silica gel (Gilman titration with *n*-BuLi gave one OH group per 7 Å^2) was mixed with a sample of ca. 100 mg of **13** in 20 mL of THF. The THF solution turned colorless within several minutes. The dark yellow silica gel suspension was purified by filtration, washed with THF, and dried in the vacuum (10^{-2} bar): yield 600 mg (100%); ^{13}C CPMAS NMR (75.47 MHz) δ 44.3 (s, CH_3) 63.5 (s, CH_2) 129.0–137.6 (br, C_6H_5, overlapped); IR (cm^{-1}, KBr) 3062 (w), 2961 (w) (ν_{CH}); 2700 (w, br) (ν_{SiO-H}); 2610 (w, br) (ν_{NH}); 2025 (s), 1977 (w), 1940 (s), 1900 (ss) (ν_{CO})); 1082 (ss) (ν_{Si-O}). UV/vis (reflection) λ_{max} 285 nm, ϵ_0 = 3100.

[2-(Me_2NHCH_2)-5-(*t*-C_4H_9)C_6H_3][2-(Me_2NCH_2)-5-(*t*-C_4H_9)-C_6H_3](HO)SiCr(CO)$_5$ (23), [2-[(Dimethylammonio)methyl]-5-*tert*-butylphenyl][2-[(dimethylamino)methyl]-5-*tert*-butylphenyl]hydroxysilylchromium(–2) Pentacarbonyl. An amount of 600 mg (1 mmol) of **13** was mixed with 18 mg (1 mmol) of H_2O in 20 mL of THF. **23** cyrstallized from the crude reaction mixture as colorless cubes, yield 23%: ^{1}H-NMR (200 MHz, d_6-acetone, 22 °C) 1.21 (s, 18 H, *t*-Bu) 2.48 (br, 12 H, NCH_3) 3.69, 3.97 (d, AB system, $^2J(^1H^1H)$ = 12.1 Hz, 4 H, NCH_2) 6.12, (s, 1 H, OH), 6.52 (s, 1 H, NH), 7.10–8.21 (m, 2 × 3) H, C_6H_3); IR (cm^{-1}, THF) 2019 (s), 1938 (ss), 1892 (ss) (ν_{CO}), 2615 (w) (ν_{NH}), 2700 (w) (ν_{OH}); UV/vis (cyclohexane) λ_{max} = 285 nm, ϵ_0 = 3100. Anal. Calcd for $C_{23}H_{26}CrN_2O_6Si$ (M_w 506.55) C, 54.54; H, 5.17; N, 5.53. Found: C, 54.45; H, 5.20; N, 5.40.

23: crystal data $C_{23}H_{26}CrN_2O_6Si \times 2\ C_4H_8O$, colorless cyrstals (0.20 × 0.45 × 0.50 mm) M_w = 650.8, monoclinic, $P2_1/n$ (No. 14), a = 13.198(2) Å, b = 17.017(2) Å, c = 17.066(1) Å, β = 92.23(1)°, V = 3830.0 Å^3, Z = 4, d_{calc} = 1.129 g cm^{-3}, μ[Mo Kα] = 3.64 cm^{-1}, $F(000)$ = 1480. Measurement: Syntex $P2_1$, T = 223 K, 5860 measured reflections, 5332 independent reflections of which 3922 with $F_o > 4(F_o)$ were used for refinement. Structure solution: direct methods (SHELXS-86) 410 parameters. Refinement: disordered Et_2O molecule, C-coordinates refined with split-model in several positions. All non-hydrogen atoms anisotropically and all hydrogen atoms isotropically refined with fixed ($U_{iso/fix}$ = 0.05 Å^2) isotropic displacement parameters. The positions of the hydrogen bridges have been located by difference Fourier analysis. The R factor has been found with R (R_w) = 0.069(0.067) with a residual electron density of +0.88/–0.56 e_0 Å^{-3}. Further data of the structure determination are available as supplementary material.

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Supplementary Material Available: Tables of hydrogen atom coordinates, isotropic displacement parameters, and bond distances and angles for **7**, **11**, **12**, **21**, and **23** (19 pages). Ordering information is given on any current masthead page. The data for the structures of **7** and **11** have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, Germany, under the CSD-number 55494.

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