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Silicon–Oxygen Double Bonds: A Stable Silanone with a Trigonal-Planar Coordinated Silicon Center[**]

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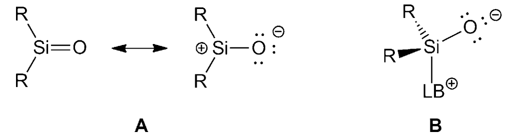
Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

Numerous differences have been discovered over the years between carbon and silicon,[1] with far-reaching consequences especially in the chemistry of multiple-bonded compounds.[2] One of the most impressive examples concerns the chemistry of ketones and their silicon analogues (silanones). Ketones are ubiquitous, valuable building blocks in organic chemistry.[3] In comparison, silanones are highly reactive species[4] that undergo rapid head-to-tail polymerization even at low temperatures to give polysiloxanes $(R_2SiO)_n$ (silicones), one of the most important class of inorganic–organic hybrid polymers.[5] Theoretical studies have shown that the head-to-tail cyclooligomerization of silanones is a highly exothermic process proceeding with no appreciable barrier.[6] These studies provided an explanation for the thermodynamic and kinetic instability of silanones originating from the large difference of the Si−O σ and π bond strengths, and the high polarity of the Si=O bond, in which both the σ and the π bond are strongly polarized towards the oxygen atom (Scheme 1, **A**).[7] Therefore, to date silanones could be only identified in cryogenic argon matrices taking advantage of their diagnostic IR-active ν(Si=O) stretching mode at 1200–1310 cm^{-1}.[8,9] Evidence for the existence of the parent silanone, $H_2Si{=}O$ (silaformaldehyde), was also provided in the gas phase by chemiluminescent emission,[10] neutralization–reionization mass spectrometry,[11] and its structure was determined by rotational spectroscopy.[12] Silanones were mostly generated as reactive intermediates and their formation was inferred either from kinetic studies[13] or from the isolation of trapping products with suitable substrates.[2a–c,4] However, all attempts to isolate silanones in neat or at least in dilute fluid solution, which started with the pioneering work of Kipping 100 years ago,[14] failed to date. Recently, various base-stabilized silanones were isolated featuring a four-coordinate silicon center with a distorted tetrahedral geometry in which the electrophilic silicon center is stabilized by coordination to a Lewis base.[15] These compounds should be better described as zwitterionic silanolates (Scheme 1, **B**). The first stable germanone, $(Eind)_2Ge{=}O$, was also recently isolated using the steric protection of the Eind substituents (Eind = 1,1,3,3,5,5,7,7-Octaethyl-*s*-hydrindacen-4-yl).[16]



Scheme 1. **A**: Resonance forms of a silanone. **B**: Resonance form of zwitterionic silanolates. R = singly bonded substituent; LB = neutral Lewis base.

We envisaged a different approach to tame the high reactivity of silanones by taking advantage of the electronic stabilization provided by transition-metal fragments. This approach has been successfully employed in our group for the stabilization of highly unsaturated silicon fragments.[17] Herein we report the successful implementation of this approach for the isolation of the first room-temperature stable silanone containing a trigonal-planar-coordinated silicon center.

The entry into this chemistry provided the dark-red zwitterionic bromosilylidene complex **1** (Scheme 2), which was prepared from $Li[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]$ and $SiBr_2(SIdipp)$ following a similar procedure with that we used for the synthesis of the cyclopentadienyl analogue $[(\eta^5\text{-}C_5H_5)(CO)_2Cr{=}SiBr(SIdipp)]$ (SIdipp = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene).[18]

Bromide abstraction from **1** by $Na[B(Ar^F)_4]$ ($Ar^F = C_6H_3\text{-}3,5\text{-}(CF_3)_2$) in fluorobenzene afforded selectively the chromium silylidyne complex salt $[(\eta^5\text{-}C_5Me_5)(CO)_2Cr{\equiv}Si(SIdipp)][B(Ar^F)_4]$ (**2**), which was isolated in 89% yield as a dark-red, thermally stable solid (m.p. = 158 °C (decomp); Scheme 2).[19] Complex **2** is the first compound containing a Cr−Si triple bond to be reported. It is stable in fluoro- or chlorobenzene solution under vigorous exclusion of oxygen and moisture, but decomposes rapidly in THF or CH_2Cl_2, which reflects the high electrophilic character of the unsaturated silicon center. The crystal structure of **2** was determined by single-crystal X-ray diffraction analysis and shows well-separated cations and anions, thus excluding any bonding contact between the electrophilic silicon center and the counterion.[20] The three-legged piano-stool complex cation

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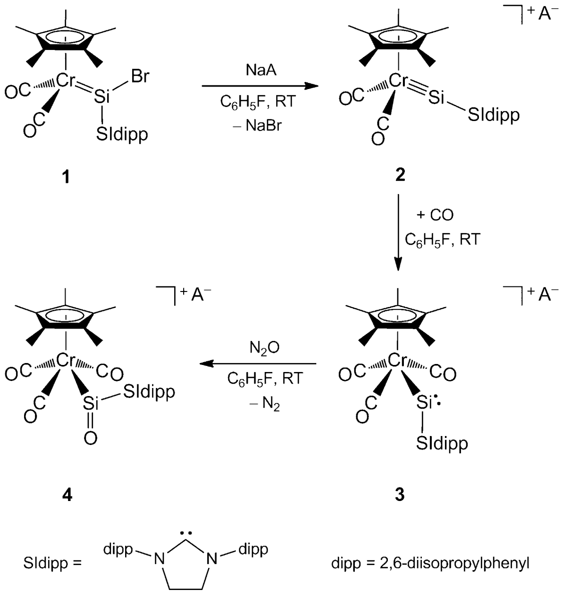


Scheme 2. Syntheses of complexes **2**, **3**, and **4**. $\mathrm{A^-}$ = $[\mathrm{B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4}]^-$ = $[\mathrm{B(Ar^F)_4}]^-$.

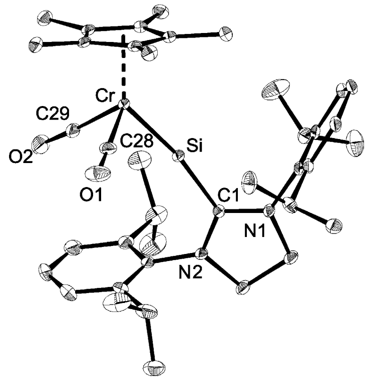


Figure 1. DIAMOND plot of the molecular structure of the complex cation of **2**. Ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr–Si 2.1220(9), Cr–C28 1.844(3), Cr–C29 1.860(3), Si–C1 1.906(3), C1–N1 1.317(4), C1–N2 1.323(4); Cr-Si-C1 169.76(9), Si-Cr-C28 92.28(11), Si-Cr-C29 90.36(10).

features an almost linearly coordinated silicon center (Cr-Si-$\mathrm{C_{SIdipp}}$ = 169.76(9)°) and the shortest Cr–Si bond (2.1220(9) Å) reported to date (Figure 1).

Notably, the Cr≡Si bond of **2** is 5 pm shorter than the Cr=Si bond of **1** (2.1716(7) Å) and 27 pm shorter than Cr–Si single bonds (mean value 2.399 Å).[18] However, the Cr≡Si bond length of **2** compares well with those predicted for the hypothetical silylidyne complexes $[\mathrm{Cp(CO)_2Cr{\equiv}Si{-}X}]$ (X = H, 2.080 Å; X = Me, 2.128 Å; X = Br, 2.100 Å).[18,21,22] Additional evidence for the presence of a Cr–Si triple bond was provided by the calculated Cr≡Si homolytic bond cleavage energy (BCE) of 504.4 kJ mol^{-1}, which is considerably higher than that of the Cr–Si bond of **3** (BCE = 166.2 kJ mol^{-1}) or **4** (BCE = 287.0 kJ mol^{-1}; Supporting Information, Table S8), as well as by a natural resonance theoretical (NRT) analysis of the electron density, which revealed for **2** a combined weight of triply bonded resonance structures of 65.8%, leading to an NRT Cr–Si bond order of 2.60 (Table 1). The Cr–Si triple bond of **2** has considerable covalent character, as evidenced by the higher covalent part of the NRT bond order (1.56) than the ionogenic part (1.04) and the high Wiberg bond index of 1.42. Further insight into the electronic structure of the

Table 1: Selected results of the natural bond orbital (NBO) and nature resonance theory (NRT) analyses of the compounds **2**, **3** and **4**.

	NPA partial charges[a]	WBI[b]	NBO analysis[c]			NRT analysis[d]	
			occupancy	polarization	hybridization	resonance weight	total/covalent/ionic
2	Cr: −0.93		σ: 1.89	65.2% (Si)	Cr: sd$^{2.1}$; Si: sp$^{0.5}$	Cr–Si: 5.3%	
	Si: +0.91	Cr≡Si: 1.41	π_{ip}: 1.69	78.8% (Cr)	Cr: sd$^{6.3}$; Si: p	Cr=Si: 28.8%	2.60/1.56/1.04
	[SIdipp]: +0.36		π_{oop}: 1.70	67.6% (Cr)	Cr: d; Si: p	Cr≡Si: 65.8%	
	$[\mathrm{Cp^*Cr(CO)_2}]$: −0.27 C:[e] +0.08	Si–$\mathrm{C_{NHC}}$: 0.69	σ: 1.95	77.9% (C)	Si: sp$^{2.4}$; C: sp$^{1.7}$		1.01/0.44/0.57
3	Cr: −1.10	Cr–Si: 0.50	σ: 1.68	88.7% (Cr)	Cr: d; Si: sp$^{12.0}$	Cr–Si: 29.2%	0.29/0.27/0.03
	Si: +0.88 [SIdipp]: +0.26		$\mathrm{LP_{Si}}$: 1.88		Si: sp$^{0.18}$		
	$[\mathrm{Cp^*Cr(CO)_3}]$: −0.15 C:[e] +0.04	Si–$\mathrm{C_{NHC}}$: 0.60	σ: 1.94	83.6% (C)	Si: sp$^{10.6}$; C: sp$^{1.6}$		1.09/0.45/0.65
4	Cr: −1.13 Si: +1.77	Cr–Si: 0.49	$\sigma_{\mathrm{Cr\text{-}Si}}$: 1.74	70.7% (Cr)	Cr: d; Si: sp	Cr–Si: 76.5% Cr=Si: 11.8%	1.00/0.71/0.29
	O: −1.21 [SIdipp]: +0.40	Si=O: 1.12	$\sigma_{\mathrm{Si=O}}$: 1.97 $\pi_{\mathrm{Si=O}}$: 1.98	85.3% (O) 84.7% (O)	Si: sp$^{2.8}$; O: sp$^{1.3}$ Si: p; O: p	Si=O: 85.9% Si–O: 14.1%	1.86/0.56/1.30
	$[\mathrm{Cp^*Cr(CO)_3}]$: +0.04 C:[e] +0.13	Si–$\mathrm{C_{NHC}}$: 0.56	σ: 1.93	79.7% (C)	Si: sp$^{3.2}$; C: sp$^{1.8}$		1.00/0.40/0.60

[a] Partial charges obtained by natural population analysis (NPA). [b] Wiberg bond index (WBI). [c] Occupancy of the corresponding σ or π bonding NBO (ip (in-plane) and oop (out-of-plane) refer to the orientation of the respective Cr–Si π bond in **2** with regard to the plane of the central ring of SIdipp); polarization of the NBO with respect to the atom given in parenthesis; hybridization of the natural atomic orbitals forming the NBO.
[d] Resonance weight: combined resonance weight of all formulas featuring the given bond; total, covalent, and ionic bond order. [e] Denotes the carbene atom of SIdipp.

complex cation in **2** was provided by a natural bond orbital analysis (NBO) of the electron density, which revealed three localized natural bond orbitals corresponding to one σ- and two π-components of the Cr–Si triple bond. The σ-bond is polarized towards the silicon atom and the two π-bonds are strongly polarized towards the chromium atom, as are the M≡C bonds of Fischer-type alkylidyne complexes (Table 1).

The composition and structure of **2** was further confirmed by elemental analysis as well as NMR and IR spectroscopy. The ^{1}H and ^{13}C{^{1}H} NMR spectra indicate a rapid rotation of the SIdipp substituent about the Si–C_{SIdipp} bond leading to a time-averaged C_s symmetric structure in solution, and the ^{29}Si{^{1}H} spectrum displays a characteristic downfield-shifted signal at $\delta = 127.8$ ppm in [D$_5$]chlorobenzene, which appears at an even lower field than that of **1** (δ in [D$_6$]benzene = 74.8 ppm). The IR spectrum of **2** in fluorobenzene solution displays two strong vibrational bands of the A′ symmetric (in-phase) and A″ symmetric (out-of-phase) CO stretching modes, which are shifted to considerably higher wavenumbers (1966 and 1912 cm^{-1}) than those of **1** (1882 and 1802 cm^{-1}) and illustrate that the silylidyne ligand Si(SIdipp)$^{2+}$ is a much stronger π-acceptor than the bromosilylidene ligand SiBr(SIdipp)$^+$.

Complex **2** is highly reactive towards nucleophiles. In fact, exposure of a fluorobenzene solution of **2** to CO was accompanied by a rapid color change from red to dark green. IR monitoring of the reaction revealed the selective formation of a tricarbonyl complex, which was isolated in 68 % yield as a very oxygen and moisture-sensitive, dichroic solid and shown by single-crystal X-ray diffraction, elemental analysis, and IR and multinuclear NMR spectroscopy to be the chromiosilylene complex salt [(η^5-C$_5$Me$_5$)(CO)$_3$CrSi(SIdipp)][B(Ar^F)$_4$] (**3**) (Scheme 2).[23] Complex **3** is the first metallosilylene to be reported containing a two-coordinate silicon center.[24] The four-legged piano-stool complex cation of **3** adopts in the solid-state a C_1-symmetric gauche conformation, as seen by the dihedral angle C1-Si-Cr-C29 of 19.1(1)° and displays very different bonding parameters from those of **2** (Figure 2). Thus, the Cr–Si distance (2.393(2) Å)[25] compares well with those of Cr–Si single bonds (mean value 2.399 Å),[18] but is 27 pm longer than the Cr–Si triple bond of **2**. Furthermore, the silicon atom is V-shaped coordinated, with a bonding angle at Si of 116.2(1)° (Figure 2), which compares well with those found in other metalloylenes,[26] and suggests the presence of a non-bonding electron pair at silicon.

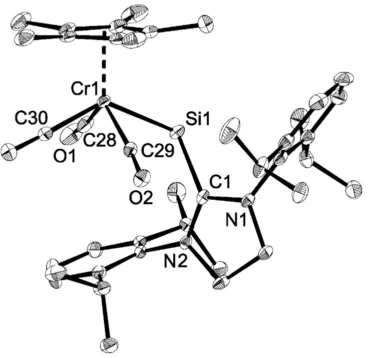


Figure 2. DIAMOND plot of the molecular structure of the complex cation in **3** (one of two independent complex cations in the asymmetric unit is presented). Ellipsoids are set at 30 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–Si1 2.3951(9), Si1–C1 1.966(3), Cr1–C28 1.859(3), Cr1–C29 1.863(3), Cr1–C30 1.858(3), C1–N1 1.325(4), C1–N2 1.340(3); Cr1-Si1-C1 116.33(8), Si1-Cr1-C28 71.95(10), Si1-Cr1-C29 74.55(9), Si1-Cr1-C30 131.45(10).

This structure was confirmed by a natural bond orbital analysis of the electron density of the DFT (density functional theory)-optimized structure of the cation of **3**, which revealed a localized lone-pair NBO of high s-character at the silicon center (Table 1). The NBO analysis showed moreover that the silicon atom uses almost pure p-orbitals for the σ-bonding to its substituents, reflecting the reluctance of Si^{II} centers in silylenes for s/p-hybridization. The Cr–Si single bond of **3** is strongly polarized towards the Cr atom (88.7 %) and is rather weak, as seen by the low bond order (0.29) obtained by natural resonance analysis (NRT), as well as the low values of the WBI index (0.50) and the BCE energy (166.2 kJ mol^{-1}), which are roughly one third of the corresponding values of the Cr–Si triple bond in **2**. Further information on the geometric and electronic structure of **3** was obtained from the IR and multinuclear NMR spectra indicating a time-averaged C_s symmetric structure and a rapid rotation of the SIdipp group about the Si–C_{SIdipp} bond in solution. As other four-legged piano-stool tricarbonyl complexes, the IR spectrum of **3** in fluorobenzene displays three intensive absorption bands at 1999, 1938, and 1897 cm^{-1}, which upon comparison with the calculated IR spectrum were assigned to the A′ (all CO in phase), A′ (CO$_{cis}$ in-phase; CO$_{trans}$ out-of-phase), and A″ (CO$_{cis}$ out-of-phase) symmetric CO stretching modes, respectively (Supporting Information, Figure S32). These bands appear at even lower wave numbers than those of [(η^5-C$_5$Me$_5$)Cr(CO)$_3$H] (ν(CO) in *n*-hexane: $\tilde{\nu} = 2001$, 1928 and 1921 cm^{-1}) indicating the absence of a Cr→Si π back-bonding in the metallosilylene, in full agreement with the results of the theoretical calculations. Complex **3** shows an exceptionally high isotropic ^{29}Si NMR chemical shift of $\delta = 828.6$ ppm. In fact, the ^{29}Si NMR signal of **3** is downfield-shifted by 261 ppm than the most deshielded ^{29}Si NMR signal reported to date for a silylene ($\delta = 567.4$ ppm).[27] The ^{29}Si NMR signal of **3** appears also at a much lower field than that of the ferriosilylene [(η^5-C$_5$Me$_5$)(CO)$_2$FeSi(η^3-C$_5$Me$_5$)] ($\delta = 316.7$ ppm) bearing a 8 VE configurated silicon atom,[24] which underlines the electronic unsaturation of the silicon center in **3**. DFT calculations of the eigenvalues of the ^{29}Si NMR shielding tensor revealed a very large chemical shift anisotropy (CSA) of $\delta = 2472$ ppm ($\delta_{11} = 2712$ ppm; $\delta_{22} = 301$ ppm; $\delta_{33} = 178$ ppm; CSA $= \delta_{11} - (\delta_{22} + \delta_{33})/2$), providing a rationale for the exceedingly high isotropic ^{29}Si NMR chemical shift of **3** ($\delta_{iso(calcd)} = \delta_{11} + \delta_{22} + \delta_{33})/3 = 1064$ ppm) (Supporting Information, Table S3). The large positive value of δ_{11} originates from the small energy required to excite an electron from the lone-pair (LP) orbital (HOMO) at Si to the empty 3p orbital at Si (LUMO).[28] Experimental evidence for the small excitation energy was obtained from the UV/Vis spectrum of **3**, which revealed a strongly red-shifted absorption band at $\lambda = 724$ nm ($\varepsilon = 391$ L mol^{-1} cm^{-1}). This band results according to a time-dependent DFT calculation from the LP(Si)→3p(Si) transition.

The small HOMO–LUMO gap of the metallosilylene **3** suggests that this compound should be highly reactive. In fact, complex **3** cleaves rapidly the σ bonds of H_2, NH_3, H_2O, or HCl to give selectively the corresponding silyl complexes $[(\eta^5\text{-}C_5Me_5)(CO)_3CrSi(H)X(SIdipp)][B(Ar^F)_4]$ (X = H, NH_2, OH, Cl). Remarkably, exposure of **3** to an atmosphere of N_2O was accompanied by a rapid color change from green to yellow and afforded the metallosilanone **4** (Scheme 2).[29] Complex **4** was isolated as bright yellow, thermally stable crystals (m.p. = 154 °C (decomp)) in 40% yield. Single-crystal X-ray diffraction analysis of **4** proved unambiguously the presence of a trigonal-planar coordinated silicon center (sum of bonding angles at Si: 359.9°) and a Si=O bond (Figure 3).

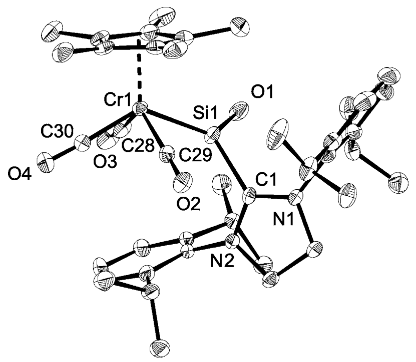


Figure 3. DIAMOND plot of the molecular structure of the complex cation of **4** (only one of two independent molecules in the asymmetric unit is presented). Ellipsoids are set at 30% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–Si1 2.314(1), Si1–C1 1.947(4), Si1–O1 1.523(3), Cr1–C28 1.863(3), Cr1–C29 1.865(4), Cr1–C30 1.861(4), C1–N1 1.332(4), C1–N2 1.333(4); Cr1-Si1-C1 125.1(1), Cr1-Si1-O1 129.0(1), C1-Si1-O1, 105.8(2), Si1-Cr1-C28 71.0(1), Si1-Cr1-C29 77.0(1), Si1-Cr1-C30 132.4(1).

The Si=O bond length (1.526(3) Å) is slightly longer than that found by rotational spectroscopy for $H_2Si{=}O$ (1.515(2) Å),[12] but shorter than those of the base-stabilized silanones (1.531–1.579 Å) (Scheme 1, **B**)[15] and considerably shorter than the Si–O single bonds of **5** (1.631(2) and 1.640(2) Å). The Cr–Si bond of **4** (2.317(3) Å) is slightly shorter than a typical Cr–Si single bond (2.399 Å). This shortened bond can be explained according to a NBO analysis by the increased s-character of the silicon hybrid orbital used for the Cr–Si bond and by the small weight (11.8%) of Cr=Si double bonded resonance structures obtained by NRT analysis (Table 1).

Furthermore, the σ and π NBO orbital of the Si=O bond is strongly polarized towards the oxygen atom (85% of the NBO density resides on the O atom), indicating a strong contribution of a zwitterionic resonance structure ($Si^+{-}O^-$) as suggested earlier for silanones (Scheme 1, **A**).[7] Additional evidence for the high polarity of the Si=O bond is indicated by the high opposite NPA charges at silicon (+1.77 e) and oxygen (−1.21 e), and the high ionic contribution (1.30) versus the covalent contribution (0.56) of the total NRT bond order (1.86).

The complex cation in **4** can be viewed as a N-heterocyclic carbene (NHC) donor adduct of the silicon monoxide complex $[(\eta^5\text{-}C_5Me_5)(CO)_3CrSiO]^+$, featuring (according to quantum chemical calculations) a linear coordinated silicon atom with a short Cr–Si (2.248 Å) and Si–O bond (1.512 Å). This view would imply the presence of a C→Si donor–acceptor bond in **4**. However, the calculated cleavage energies for the $Si{-}C_{SIdpp}$ bond homolysis (408.9 kJ mol^{-1}) and heterolysis (392.8 kJ mol^{-1}) have very similar values and are less supportive of this view. They suggest instead a typical $Si{-}C_{SIdipp}$ covalent bond in **4**, which is further supported by the calculated zero-point vibrational energy corrected bond dissociation enthalpy (BDE) of 269 kJ mol^{-1}. The latter is much larger than the BDE values of the Si–C dative bonds in $SiX_2(NHC)$ (X = Cl, Br, I: 121–124 kJ mol^{-1}).[30]

Complex **4** is distinguished by a characteristic ν(Si=O) absorption band at 1157 cm^{-1} in the Raman spectrum,[31] which appears at slightly lower wavenumbers than that of $Me_2Si{=}O$ (1204 cm^{-1} in argon matrix).[8a] Furthermore, complex **4** features a distinctive ^{29}Si NMR signal in solution at δ = 169.6 ppm. Owing to the lower coordination number and altered electronic distribution at silicon, the ^{29}Si NMR signal of **4** is observed considerably downfield shifted from those of the base-stabilized silanones (Scheme 1, **B**) (δ = −61 to −86 ppm).[15]

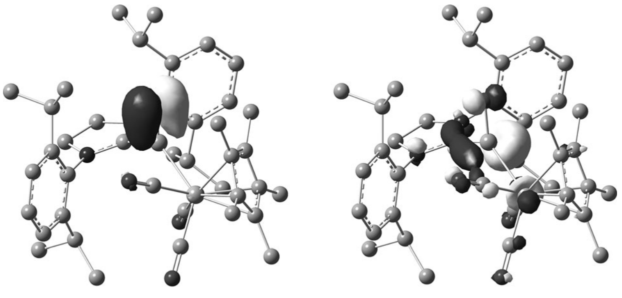
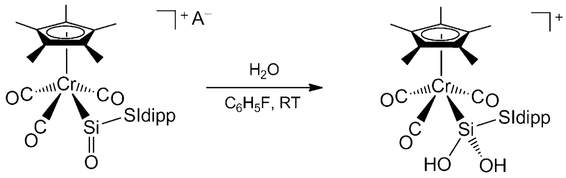

HOMO-10 (-10.65 eV) LUMO (-4.48 eV)

Figure 4. Kohn–Sham orbitals of the Si=O π bond of **4** (π orbital (left), π* orbital (right), isosurface value 0.065 e Bohr^{-3}).

The analysis of the frontier orbitals of silanone **4** shows that the LUMO is the Si=O π*-orbital with a large contribution of silicon, which indicates the high polarity of the Si=O bond (Figure 4). Therefore, it is not surprising that complex **4** reacts instantaneously with water to give the yellow dihydroxysilyl complex $[(\eta^5\text{-}C_5Me_5)(CO)_3CrSi(OH)_2(SIdipp)][B(Ar^F)_4]$ (**5**; Scheme 3). Formation of **5** occurs rapidly even in the argon atmosphere of a glove box containing 1 ppm of H_2O and is indicated by a huge upfield shift of the ^{29}Si NMR signal to δ = 39.6 ppm, the appearance of two distinctive ν(O–H) stretching bands in the solid-state IR spectrum at 3684 and 3599 cm^{-1}, and a shift of the ν(CO) absorption bands to lower wavenumbers (2001, 1939, and 1902 cm^{-1} in fluorobenzene). The molecular structure of **5** reveals a distorted tetrahedral coordinated silicon atom, a Cr–Si single bond (2.4128(7) Å), and two silicon–oxygen bonds (1.631(2) and 1.640(2) Å),



4 **5**

Scheme 3. Reaction of silanone **4** with water. $A^- = [B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]^-$.

which are much longer than that of **4**. The Si–O distances in **5** compare well with those of typical Si–O single bonds (Supporting Information, Figure S24).

In conclusion, the isolation and full characterization of silanone **4** can be regarded as a major achievement in organosilicon chemistry in view of the numerous unsuccessful attempts that have been undertaken to isolate silanones in neat form for more than 100 years. It confirms the potential of our approach to use transition-metal fragments for the stabilization of unsaturated silicon-based functional groups. The high reactivity of silanone **4** originating from the high polarity of the Si=O bond offers many perspectives, which are currently being investigated.

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Keywords: chromium · silanones · silicon · silylenes · silylidynes

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