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Chromium–Silicon Multiple Bonds: The Chemistry of Terminal N-Heterocyclic-Carbene-Stabilized Halosilylidyne Ligands

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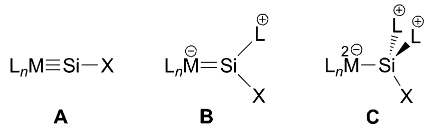
Abstract: An efficient method for the synthesis of the first N-heterocyclic carbene (NHC)-stabilized halosilylidyne complexes is reported that starts from $SiBr_4$. In the first step, $SiBr_4$ was treated with one equivalent of the N-heterocyclic carbene 1,3-bis[2,6-bis(isopropyl)phenyl]imidazolidin-2-ylidene (SIdipp) to give the 4,5-dihydroimidazolium salt $[SiBr_3(SIdipp)]Br$ (**1-Br**), which then was reduced with potassium graphite to afford the silicon(II) dibromide–NHC adduct $SiBr_2(SIdipp)$ (**2-Br**) in good yields. Heating **2-Br** with $Li[CpCr(CO)_3]$ afforded the complex $[Cp(CO)_2Cr{=}SiBr(SIdipp)]$ (**3-Br**) upon elimination of CO. Complex **3-Br** features a trigonal-planar-coordinated silicon center and a very short Cr=Si double bond. Similarly, the reaction of $SiCl_2(SIdipp)$ (**2-Cl**) with $Li[CpCr(CO)_3]$ gave the analogous chloro derivative $[Cp(CO)_2Cr{=}SiCl(SIdipp)]$ (**3-Cl**). Complex **3-Br** undergoes an NHC exchange with 1,3-dihydro-4,5-dimethyl-1,3-bis(isopropyl)-2*H*-imidazol-2-ylidene (IMe_2iPr_2) to give the complex $[Cp(CO)_2CrSiBr(IMe_2iPr_2)_2]$ (**4-Br**). Compound **4-Br** features a distorted-tetrahedral four-coordinate silicon center. Bromide abstraction occurs readily from **4-Br** with $Li[B(C_6F_5)_4]$ to give the putative silylidene complex salt $[Cp(CO)_2Cr{=}Si(IMe_2iPr_2)_2][B(C_6F_5)_4]$, which irreversibly dimerizes by means of an Si-promoted electrophilic activation of one carbonyl oxygen atom to yield the dinuclear siloxycarbyne complex $[Cp(CO)Cr\{(\mu\text{-}CO)Si(IMe_2iPr_2)_2\}_2Cr(CO)Cp][B(C_6F_5)_4]_2$ (**5**). All compounds were fully characterized, and the molecular structures of **2-Br**–**5-Br** were determined by single-crystal X-ray diffraction. DFT calculations of **3-Br** and **3-Cl** and their carbene dissociation products $[Cp(CO)_2Cr{\equiv}Si{-}X]$ ($X=$ Cl, Br) were carried out, and the electronic structures of **3-Br**, **3-Cl** and $[Cp(CO)_2Cr{\equiv}Si{-}X]$ were analyzed by the natural bond orbital method in combination with natural resonance theory.

Keywords: chromium · multiple bonds · nitrogen heterocycles · silicon · silylidynes

Introduction

Halosilylidynes are highly reactive diatomic radicals of the general formula SiX ($X=F$ to I), which have been detected by spectroscopic methods as intermediates during the halogen-based plasma etching of silicon[1] or the plasma-enhanced chemical vapor deposition of amorphous, nanocrystalline, and polycrystalline silicon using halosilanes as process gases.[2] In this context, the thermochemistry and the structures of halosilylidynes were studied by computational and experimental methods.[3] By comparison, the chemistry of these short-lived species remains unexplored. Coordination to a transition-metal center is expected to alter profoundly the reactivity of halosilylidynes and should provide access to mononuclear halosilylidyne complexes, which are promising precursors for new compounds with metal–silicon multiple bonds, given the synthetic utility of the few halocarbyne complexes presently known.[4] Three types of mononuclear halosilylidyne complexes are conceivable (Scheme 1**A**–**C**). However, none of these complexes are presently known due to lack of suitable sources for terminal halosilylidyne ligands. Recent developments in the molecular chemistry of silicon in low oxidation states led to the isolation of stable N-heterocyclic carbene (NHC) adducts of SiX_2 ($X=Cl$, Br).[5] In the present work, the synthetic potential of SiX_2(NHC) is demonstrated by a series of new reactions that provide an entry to first mononuclear chromium complexes that bear carbene-stabilized halosilylidyne ligands (class **B** and **C** complexes).



Scheme 1. Feasible mononuclear halosilylidyne complexes ($ML_n=15VE$ metal fragment; $X=F$–I; L = neutral Lewis base); formal charges are encircled.

The target complexes were obtained by starting from the silicon(II) dibromide–carbene adduct $SiBr_2(SIdipp)$ (**2-Br**)

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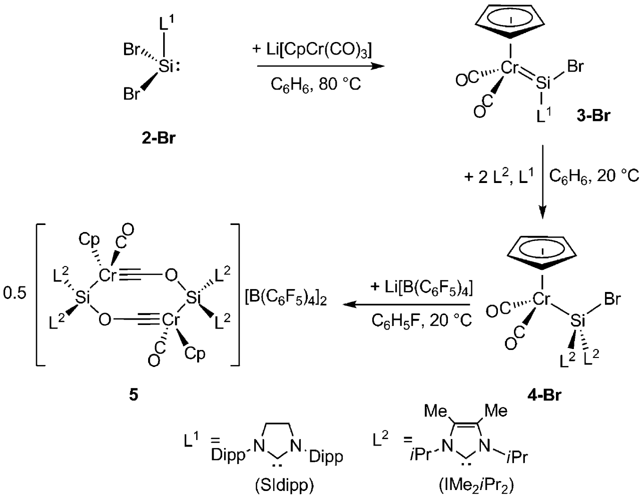
(SIdipp = 1,3-bis[2,6-bis(isopropyl)phenyl]imidazolidin-2-ylidene; Scheme 2). Compound **2-Br** was prepared in overall 75 % yield by following the two-step reaction sequence, which was used for the synthesis of the related adduct $SiBr_2$(Idipp) that contained the unsaturated N-heterocyclic carbene Idipp 1,3-bis[2,6-bis(isopropyl)phenyl)]-1,3-dihydro-2*H*-imidazol-2-ylidene).[5b] In the first step, $SiBr_4$ was treated with one equivalent of SIdipp[6] in petroleum ether to afford the white 2-tribromosilyl-4,5-dihydroimidazolium salt [$SiBr_3$(SIdipp)]Br (**1-Br**) in 97 % yield. The bromide salt **1-Br** was then reduced with potassium graphite (2.35 equiv) in benzene at ambient temperature to give the yellow Si^{II} compound **2-Br** in 77 % yield. Compound **2-Br** is a very air-sensitive solid that decomposes upon heating at 191–192 °C and is stable in benzene at ambient temperature for a prolonged period of time. The most distinctive spectroscopic features of **2-Br** are the low-field shifted ^{29}Si NMR signal (δ = 10.8 ppm in C_6D_6) relative to that of its Si^{IV} precursor **1-Br** (δ = −73.0 ppm in CD_2Cl_2), and the ^{13}C NMR spectroscopic chemical shift of the silicon-bonded carbon atom (δ = 188.7 ppm in C_6D_6), which lies in between those of SIdipp (δ = 244.1 ppm in C_6D_6) and of the 4,5-dihydroimidazolium salts **1-Br** (δ = 161.3 ppm in CD_2Cl_2) and (SIdippH)Br (δ = 160.0 ppm in [D_6]DMSO), thereby reflecting the donor–acceptor character of the Si−C bond in **2-Br**.



Scheme 2. Entry into chromium complexes with NHC-stabilized bromosilylidyne ligands (Cp = η^5-C_5H_5; formal charges are omitted).

The molecular structure of **2-Br** reveals a trigonal-pyramidal-coordinated silicon center (sum of bond angles at Si = 290(1)°) that indicates the presence of a stereochemically active lone pair of electrons at the Si atom (Figure 1).[7] The Si−$C_{carbene}$ bond lengths of **2-Br** (2.007(5) Å),[7] SiX_2(Idipp) (X = Cl 1.985(4) Å, X = Br 1.989(3) Å)[5] and SiCl(C_6H_3-2,6-$Trip_2$)(Im−Me_4) (1.963(2) Å)[8] are similar, thereby indicating a strong $C_{carbene}\rightarrow$Si donor–acceptor single bond. The mean Si−Br bond length of **2-Br** (2.335(6) Å)[7] compares well with that of $SiBr_2$(Idipp) (2.349(11) Å)[5b] but is considerably longer than that of $SiBr_2$ (r_g(Si−Br) = 2.245(3) Å)[9] due to the higher silicon coordination number.

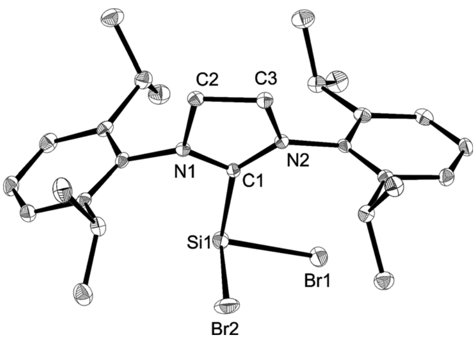


Figure 1. DIAMOND plot of the molecular structure of **2-Br**. Thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] (bond lengths and angles in square brackets are of the second independent molecule of **2-Br** found in the asymmetric unit): Si1−Br1 2.3481(7) [2.3201(7)], Si1−Br2 2.3303(7) [2.3432(7)], Si1−C1 2.012(2) [2.002(2)], C1−N1 1.337(2) [1.343(2)], C1−N2 1.331(2) [1.330(3)], N1−C2 1.478(2) [1.483(2)], N2−C3 1.493(2) [1.482(2)], C2−C3 1.524(3) [1.521(3)]; C1-Si1-Br1 102.53(7) [101.58(7)], C1-Si1-Br2 88.39(6) [91.06(6)], Br1-Si1-Br2 97.68(3) [98.15(3)].

The Si^{II} bromide **2-Br** is a very suitable source of low-valent silicon compounds, since it reacts smoothly with nucleophiles. For example, heating **2-Br** with Li[CpCr(CO)$_3$] (Cp = η^5-C_5H_5) in benzene at 80 °C afforded complex **3-Br**, which features an NHC-stabilized bromosilylidyne ligand (Scheme 2). Similarly, treatment of $SiCl_2$(SIdipp) (**2-Cl**) with Li[CpCr(CO)$_3$] in benzene at 70 °C led to the analogous chloro derivative **3-Cl** (Scheme 2). Compounds **3-Br** and **3-Cl** were isolated as dark-brown (**3-Br**) and brown (**3-Cl**) crystalline, very air-sensitive solids, and are the first examples of class **B** base-stabilized halosilylidyne complexes to be reported (Scheme 1).

The molecular structures of **3-Br** and **3-Cl** were determined by single-crystal X-ray diffraction (Figure 2). The three-legged piano-stool complexes are isotypic and display a trigonal-planar-coordinated silicon center (sum of angles at Si: **3-Br** 359.9°, **3-Cl** 360.0°) and the shortest Cr−Si bonds reported to date (**3-Br** 2.1618(9) Å, **3-Cl** 2.1603(7) Å) (Figure 2).[10]

In fact, the Cr−Si bond lengths of **3-Br** and **3-Cl** are 0.17 Å shorter than those of the diaminosilylidene complexes *trans*-[Cr(CO)$_4${Si($\overset{\frown}{NN}$)}$_2$] ($\overset{\frown}{NN}$: *t*BuNCH$_2$CH$_2$N*t*Bu, *d*(Cr−Si) = 2.326 Å; $\overset{\frown}{NN}$: *t*BuNCH=CHN*t*Bu, *d*(Cr−Si) = 2.329 Å),[10a] and also shorter than those of the intra- or intermolecular base-stabilized silylidene complexes [Cr(CO)$_5$(SiR$_2$B)] (*d*(Cr−Si) = 2.335(2)–2.526(3) Å; R = singly-bonded substituent, B = Lewis base).[11] Notably, the Cr−Si distance of **3-Br** and **3-Cl** compares well with that of a Cr−Si double bond (2.18 Å) calculated from the theoretically predicted double-bond radii of Si (1.07 Å) and Cr (1.11 Å).[12] All these geometrical parameters suggest the presence of a strong Cr−Si π bond in **3-Br** and **3-Cl**, but a negligible Cr−Si π bond in *trans*-[Cr(CO)$_4${Si($\overset{\frown}{NN}$)}$_2$] and [Cr(CO)$_5$(SiR$_2$B)] in contrast to previous conclusions.[11] The base-stabilized si-

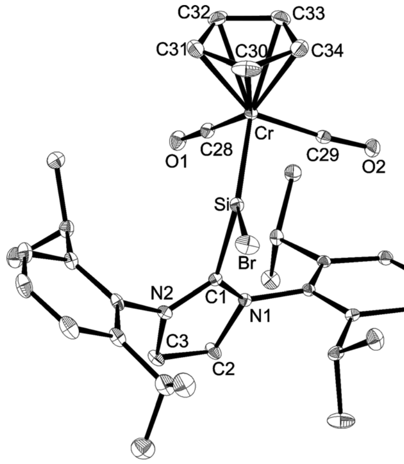


Figure 2. DIAMOND plot of the molecular structure of **3-Br**. Thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] of **3-Br** (bond lengths and angles in square brackets are of **3-Cl**): Cr–Si 2.1618(9) [2.1603(7)], Cr–C28 1.827(3) [1.820(2)], Cr–C29 1.833(3) 1.834(2)], Si–Br 2.2728(8) [Si–Cl 2.1034(9], Si–C1 1.957(3) [1.957(2)], O1–C28 1.165(3) [1.168(3)], O2–C29 1.167(3) [1.164(3)]; Cr-Si-Br 130.51(4) [Cr-Si-Cl 132.78(4)], Cr-Si-C1 131.27(8) [130.55(7)], Br-Si-C1 98.16(8) [Cl-Si-C1 96.66(7)], Si-Cr-C28 89.89(9) [89.55(8], Si-Cr-C29 89.44(9) [89.66(8)], C28-Cr-C29 93.9(1) [94.0(1)].

lylidyne ligand adopts in **3-Br** and **3-Cl** an almost upright conformation with the halogen atom pointing towards the cyclopentadienyl ring.[13] It features a rather acute Br/Cl-Si-$C_{carbene}$ bond angle (**3-Br** 98.16(8)°, **3-Cl** 96.66(7)°), which indicates that the silicon atom uses hybrid orbitals of high p character for the σ bonding to the Br/Cl and carbene substituents in full agreement with the results of the quantum chemical calculations (vide infra). Both the Si–Br and Si–$C_{carbene}$ bonds of **3-Br** (Si–Br 2.2728(8) Å, Si–C 1.957(3) Å) are shorter than those of **2-Br** (Si–Br 2.335(6) Å, Si–C 2.007(5) Å)[7] due to the decreased valence-shell electron-pair repulsion.

The solution IR and NMR spectra of **3-Br** and **3-Cl** corroborate the solid-state structures. The solution IR spectra display in fluorobenzene two very strong ν(CO) absorptions bands of almost equal intensity at rather low wavenumbers (**3-Br** 1894 and 1809 cm^{-1}; **3-Cl** 1890 and 1806 cm^{-1}). The position of these bands suggests the presence of an electron-rich metal center incorporated in a strong metal–carbonyl backbonding.[14] Further evidence for this is provided by the $Cr{-}C_{CO}$ bonds (**3-Br** 1.830(3) Å; **3-Cl** 1.827(7) Å),[15] which are considerably shorter than those of $[Cr(CO)_6]$ (1.915(1) Å).[16] The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra confirm the overall C_s symmetry of the complexes **3-Br** and **3-Cl** in solution. They show, moreover, that rotation of the SIdipp substituent about the Si–$C_{carbene}$ bond is fast on the NMR spectroscopic timescale at ambient temperature and gives rise to a single set of signals of the 2,6- and 3,5-positioned ^{1}H and ^{13}C nuclei of the 2,6-diisopropylphenyl substituents of SIdipp. Complexes **3-Br** and **3-Cl** are characterized by a ^{29}Si NMR singlet signal at $\delta = 95.1$ and 113.6 ppm, respectively, which appears at considerably lower field than that of **2-Br** ($\delta = 10.8$ ppm) or SiX_2(Idipp) (X = Br, $\delta = 10.9$ ppm; X = Cl, $\delta = 19.1$ ppm).[5]

Gradient-corrected density functional theory calculations (DFT) of **3-Br** and **3-Cl** were carried out, and the electronic structures of **3-Br** and **3-Cl** were analyzed using the natural bond orbital (NBO) partitioning scheme in combination with natural resonance theory (NRT). The calculated bond lengths and angles compare well with the experimental values (Table 1).[17]

Table 1. Selected experimental and calculated (B3LYP/I)[a] bond lengths [Å] and angles [°] of **3-Br**, **3-Cl**, and $[Cp(CO)_2Cr{\equiv}Si{-}X]$ (X = Br, Cl).[b]

	3-Br		**3-Cl**		$[Cp(CO)_2Cr{\equiv}Si{-}X]$	
					X = Br	X = Cl
	exptl	calcd	exptl	calcd	calcd	calcd
Cr–Si	2.162(1)	2.177	2.160(1)	2.173	2.100	2.097
Si–X	2.273(1)	2.334	2.103(1)	2.154	2.223	2.060
Si–C1	1.957(3)	1.992	1.957(2)	1.993	–	–
Cr–C28	1.827(3)	1.821	1.820(2)	1.821	1.850	1.849
Cr–C29	1.833(3)	1.842	1.834(2)	1.841	1.850	1.850
Cr-Si-X	130.5(1)	129.3	132.8(1)	131.4	167.6	168.2
Cr-Si-C1	131.3(1)	133.0	130.6(1)	132.0	–	–
C1-Si-X	98.2(1)	97.2	96.7(1)	96.1	–	–
Si-Cr-C28	89.9(1)	92.1	89.6(1)	91.9	89.8	90.1
Si-Cr-C29	89.4(1)	95.7	89.7(1)	95.1	90.2	90.5
C28-Cr-C29	93.9(1)	89.3	94.0(1)	89.3	91.0	91.0

[a] Basis set I: TZVPP basis set for Cr, Si, Br, Cl, and the $C_{carbene}$ atoms; 6-31G* basis set for all other atoms. [b] The same atom numbering was used as for the experimentally determined structures when available.

The NBO/NRT analyses suggest that the base-stabilized halosilylidyne complexes **3-Br** and **3-Cl** have a similar electronic structure (Table 2). The Cr–Si bond can be best described as a polar donor–acceptor double bond. The polarity of this bond is reflected in the NPA partial charges of the Cr (−1.0) and Si atom (≈ +1.0), the Wiberg bond index (1.13), and the covalent (≈1.2) and ionogenic part ≈ 0.6)

Table 2. Selected results of the NBO and NRT analyses of **3-Br** and **3-Cl**.[a]

3-X	NPA	Bond A–B	Occ	(A) [%]	Hyb (A)	(B) [%]	Hyb (B)	WBI	NRT-BO (cov/ion)
X = Br	Cr −1.0 Si +0.9	Cr–Si (σ) Cr–Si (π)	1.78 1.73	36.4 67.7	$sd^{1.63}$ d	63.6 32.3	$sp^{0.82}$ p	1.13	1.75 (1.20/0.54)
	Br −0.4	Si–Br	1.96	23.4	$sp^{4.25}$	76.6	$sp^{3.47}$	0.79	1.00 (0.47/0.53)
	C1 +0.2	Si–C1	1.94	20.7	$sp^{2.74}$	79.3	$sp^{1.43}$	0.61	1.00 (0.41/0.59)
X = Cl	Cr −1.0 Si +1.0	Cr–Si (σ) Cr–Si (π)	1.79 1.73	36.8 68.8	$sd^{1.63}$ d	63.2 31.2	$sp^{0.82}$ p	1.13	1.80 (1.22/0.58)
	Cl −0.5	Si–Cl	1.97	20.3	$sp^{4.04}$	79.7	$sp^{2.58}$	0.74	1.00 (0.40/0.60)
	C1 +0.2	Si–C1	1.94	20.7	$sp^{2.81}$	79.3	$sp^{1.45}$	0.61	1.00 (0.40/0.60)

[a] NPA charges, NBO occupancy (Occ.), bond polarization [%], orbital hybridization, Wiberg bond index (WBI), and NRT bond order divided into covalent and ionogenic parts.

of the NRT bond order (Table 2). The Cr=Si double bond is composed of a σ component that is polarized towards the Si atom (**3-Br** 63.6 %, **3-Cl** 63.2 %) and a π component that is polarized towards the chromium center (**3-Br** 67.7 %, **3-Cl** 68.8 %). Both, the σ and the π NBO orbitals are equally filled with approximately 1.7 to 1.8 electrons that reflect rather localized bonds. The strongly polarized Si–X (X = Cl, Br) and Si–$C_{carbene}$ σ bonds complement the bonding picture of **3-Br** and **3-Cl** (Table 2).

In addition, the zero-point vibrational energy (ZPVE)-corrected bond dissociation energy ($D^0(0)$) for the cleavage of the Si–$C_{carbene}$ bond was calculated (**3-Br** 110.1 kJ mol^{-1}, **3-Cl** 114.9 kJ mol^{-1}) and found to be considerably higher than that of [$Cp(CO)_2Mo{=}Si(Im{-}Me_4)(C_6H_3$-2,6-$Trip_2)$] (62.1 kJ mol^{-1}).[18]

Moreover, both carbene adducts are stable with respect to their dissociation products SIdipp and [$Cp(CO)_2Cr{\equiv}Si{-}X$] at 298 K, as evidenced by the gas-phase Gibbs free dissociation energies (Δ*G*°) of 38.9 (**3-Br**) and 44.4 kJ mol^{-1} (**3-Cl**), respectively. These thermochemical values suggest that the compounds **3-Cl** and **3-Br** may be valuable sources of the halosilylidyne complexes [$Cp(CO)_2Cr{\equiv}Si{-}X$] at rather high temperatures.

Table 3. Selected results of the NBO and NRT analyses of [$Cp(CO)_2Cr{\equiv}Si{-}X$] (X = Br, Cl).

[$Cp(CO)_2Cr{\equiv}Si{-}X$]	NPA	Bond A–B	Occ.	(A) [%]	Hyb (A)	(B) [%]	Hyb (B)	WBI	NRT-BO (cov/ion)
X = Br	Cr −1.0	Cr–Si (σ)	1.85	39.6	$sd^{2.60}$	60.4	$sp^{0.65}$		
	Si +0.9	Cr–Si (π)	1.79	75.7	d	24.3	p	1.36	2.54 (1.41/1.13)
	Br −0.3	Cr–Si (π)	1.62	78.0	$sd^{3.17}$	22.0	$sp^{6.98}$		
		Si–Br	1.97	26.3	$sp^{2.38}$	73.7	$sp^{4.36}$	1.00	0.99 (0.52/0.47)
X = Cl	Cr −1.1	Cr–Si (σ)	1.85	40.0	$sd^{2.59}$	60.1	$sp^{0.65}$		
	Si +1.1	Cr–Si (π)	1.79	76.5	d	23.5	p	1.36	2.72 (1.53/1.19)
	Cl −0.4	Cr–Si (π)	1.62	78.6	$sd^{3.20}$	21.5	$sp^{6.79}$		
		Si–Cl	1.98	22.3	$sp^{2.33}$	77.7	$sp^{3.21}$	0.91	0.99 (0.44/0.55)

[a] NPA charges, NBO occupancy (Occ.), bond polarization [%], orbital hybridization, Wiberg bond index (WBI), and NRT bond order divided into covalent and ionogenic parts.

In this context, the minimum structures of [$Cp(CO)_2Cr{\equiv}Si{-}X$] were calculated at the same level of theory (B3LYP/I) (Table 1, Figure 3). Expectedly, the calculated Cr≡Si triple-bond lengths of [$Cp(CO)_2Cr{\equiv}Si{-}X$] (X = Br 2.100 Å, X = Cl 2.097 Å) are approximately 7 pm shorter than the Cr=Si double-bond lengths of **3-Br** and **3-Cl** (Table 1) but compare well with the Cr≡Si triple-bond length of the cationic silylidyne complex [$(\eta^5$-$C_5Me_5)(CO)_2Cr{\equiv}Si{-}(SIdipp)]^+$ (2.1219(9) Å), the structure of which was recently determined by single-crystal X-ray diffraction in our group.[19] The Cr-Si-X atom array of [$Cp(CO)_2Cr{\equiv}Si{-}X$] deviates slightly from linearity (X = Br 167.6°, X = Cl 168.2°), as is observed in [$(\eta^5$-$C_5Me_5)(CO)_2Cr{\equiv}Si{-}(SIdipp)]^+$ (∢(Cr-Si-C) 169.75(9)°).[19]

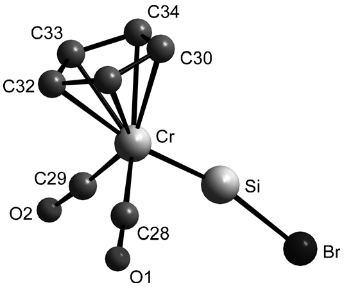


Figure 3. Calculated structure of [$Cp(CO)_2Cr{\equiv}Si{-}Br$] (B3LYP/I). Hydrogen atoms were not depicted. The atom numbering scheme was adjusted to that used for the experimentally determined structures of **3-Br** and **3-Cl**.

The NBO/NRT analyses of [$Cp(CO)_2Cr{\equiv}Si{-}X$] suggest the presence of a polar Cr≡Si donor–acceptor triple bond. The polarity of this bond is reflected in the Wiberg bond index (1.36 in both compounds) and the covalent part (X = Br 1.41; X = Cl, 1.53) and ionogenic part (X = Br 1.13, X = Cl 1.19) of the NRT bond order (Table 3). The Cr≡Si triple bonds of [$Cp(CO)_2Cr{\equiv}Si{-}X$] are composed of a σ component that is polarized towards the Si atom (X = Br 60.4 %, X = Cl 60.1 %) and two non-degenerate π components, which are polarized towards the chromium center (X = Br 75.7 and 78.0 %, X = Cl 76.5 and 78.6 %) (Table 3).

In spite of the large Si–$C_{carbene}$ bond-dissociation energy, treatment of **3-Br** with two equivalents of the NHC 1,3-dihydro-4,5-dimethyl-1,3-bis(isopropyl)-2*H*-imidazol-2-ylidene (IMe_2iPr_2) in benzene at ambient temperature led rapidly to a displacement of SIdipp from **3-Br** to afford complex **4-Br** (Scheme 2). Compound **4-Br** was isolated in 88 % yield as a red-brown, crystalline, air-sensitive solid, which decomposes upon heating at 166–168 °C. It is the first reported example of a class **C** halosilylidyne complex (Scheme 1).

The mild reaction conditions and the large carbene dissociation energy of **3-Br** (vide supra) suggest that the rapid conversion of **3-Br** into **4-Br** does not follow a dissociative pathway through the putative bromosilylidyne complex [$Cp(CO)_2Cr{\equiv}Si{-}Br$]. Instead, an addition–elimination reaction sequence through the intermediates [$Cp(CO)_2Cr{-}SiBr(SIdipp)(IMe_2iPr_2)$] and [$Cp(CO)_2Cr{=}SiBr(IMe_2iPr_2)$] is plausible, which reflects the electrophilic character of the silicon center in **3-Br**. However, no such intermediates were observed by IR spectroscopy during the reaction of **3-Br** with only one equivalent of IMe_2iPr_2, which under the same conditions led rapidly to a 1:1 molar mixture of **4-Br** and unreacted starting material. This suggests that addition of IMe_2iPr_2 to the silicon center of **3-Br** is the slowest step in the whole reaction sequence.

Complex **4-Br** was characterized by IR, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy and its molecular structure was determined by single-crystal X-ray diffraction. The coordination of two NHCs to the silicon center in **4-Br** leads to a considerable shift of the two ν(CO) absorption bonds to lower wavenumbers (1797 and 1733 cm^{-1} in THF), thereby indicating an even stronger Cr−CO backbonding than in **3-Br**. This is confirmed by the shorter $Cr-C_{CO}$ bonds (1.800(2) Å) and longer C−O bonds (1.187(2) Å) of **4-Br** (Figure 4) in comparison to those of **3-Br** ($Cr-C_{CO}$ 1.830(3) Å, C−O 1.166(1) Å).[15] The ^{29}Si NMR spectrum of **4-Br** in $[D_8]THF$ displays a singlet signal at considerably higher field ($\delta = 17.3$ ppm) than that of **3-Br** ($\delta = 95.1$ ppm), thereby indicating the shielding effect exerted by the coordination of an additional N-heterocyclic carbene (NHC). Temperature-dependent ^1H and $^{13}C\{^1H\}$ NMR spectra of **4-Br** reveal that rotation of the NHCs about the $Si-C_{carbene}$ bonds is frozen out at low temperature. This leads to a C_1-symmetric minimum structure, as also observed in the solid-state (Figure 4), in which the two IMe_2iPr_2 ligands become chemically inequivalent.

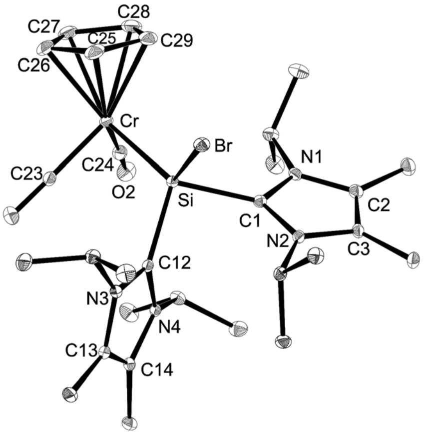


Figure 4. DIAMOND plot of the molecular structure of **4-Br**. Thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cr−Si 2.2515(7), Cr−C23 1.796(2), Cr−C24 1.803(3), Si−Br 2.4340(6), Si−C1 2.007(2), Si−C12 1.964(2), O1−C23 1.185(3), O2−C24 1.189(3); Cr-Si-Br 114.45(3), Cr-Si-C1 132.56(7), Cr-Si-C12 116.86(7), Br-Si-C1 87.47(6), Br-Si-C12 104.67(7), C1-Si-C12 94.92(9).

The molecular structure of **4-Br** reveals several peculiarities (Figure 4). The Cr−Si distance (2.2515(7) Å) is considerably shorter than that calculated for a Cr−Si single bond (2.38 Å)[20] or the Cr−Si bond lengths of chromium silyl and silane complexes (2.361(2)–2.6603(8) Å).[10b,21] In addition, the Si−Br bond of **4-Br** (2.4340(6) Å) is considerably longer than those of metal bromosilyl complexes (2.314 Å) and of bromosilanes (2.243 Å).[22] All these bonding parameters suggest a strong M(dπ)–σ*(Si−Br) hyperconjugation that leads to a strong polarization of the Si−Br bond in **4-Br** as expressed by the ionic canonical formula $[CpCr(CO)_2{=}Si(IMe_2iPr_2)_2]^+[Br]^-$. This bond polarization let us assume that bromide abstraction from **4-Br** might easily proceed with electrophilic agents. In fact, the addition of one equivalent of $LiB(C_6F_5)_4$ to a fluorobenzene solution of **4-Br** at ambient temperature led to a rapid precipitation of LiBr and a color change from dark brown to green. IR monitoring of the reaction revealed the formation of a new dicarbonyl complex that displayed two characteristic ν(CO) absorption bands of almost equal intensity at considerably higher wavenumbers (1895 and 1821 cm^{-1}) than those of the starting material **4-Br** (1794 and 1726 cm^{-1} in fluorobenzene). The position of the ν(CO) bands, which compare well with those of **3-Br** and **3-Cl**, support the formulation of this product as the silylidene complex salt $[Cp(CO)_2Cr{=}Si(IMe_2iPr_2)_2][B(C_6F_5)_4]$.[23] All attempts to isolate this complex were hampered by its irreversible rapid dimerization upon concentration of the reaction solution or crystallization at −16 °C to afford the insoluble, yellow dinuclear siloxycarbyne complex salt **5** (Scheme 2). Apparently, the steric shielding of the electrophilic Si center by the two carbenes in $[Cp(CO)_2Cr{=}Si(IMe_2iPr_2)_2][B(C_6F_5)_4]$ is not sufficient to prevent an interionic nucleophilic attack of one carbonyl oxygen atom at silicon to lead to the dimer **5**. Compound **5** is the first chromium siloxycarbyne complex to be reported.[24] Its IR spectrum displays as a result of the carbonyl–oxygen coordination of one of the two CO ligands to silicon and the centrosymmetric structure of the complex dication (Figure 5) only one ν(CO) band in the expected region for terminal CO ligands (1860 cm^{-1}).

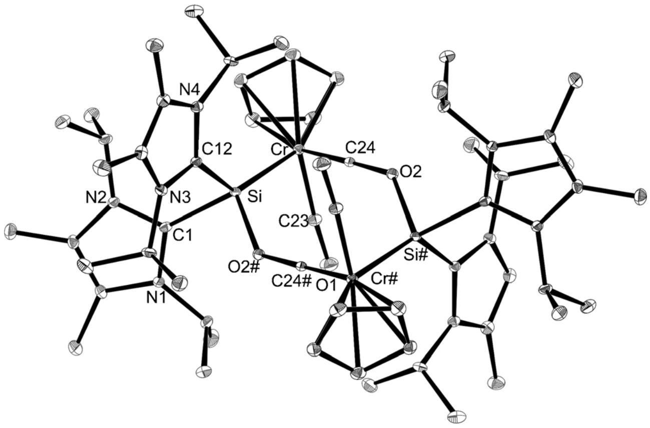


Figure 5. DIAMOND plot of the molecular structure of the complex cation of **5**. Thermal ellipsoids are set at 30 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cr−Si 2.2847(6), Cr−C23 1.803(2), Cr−C24 1.717(2), Si−C1 1.965(2), Si−C12 1.993(2), Si−O2# 1.749(1), O1−C23 1.178(2), O2−C24 1.291(2); Cr-Si-C1 119.76(6), Cr-Si-C12 130.53(6), Cr-Si-O2# 115.94(5), C1-Si-C12 93.84(8), C1-Si-O2# 94.37(7), C12-Si-O2# 94.33(7), C1-Si-C12 93.84(8), Cr-C23-O1 175.2(2), Cr-C24-O2 172.4(2), C24-O2-Si# 133.8(1).

The dication resides on a crystallographic inversion center at the midpoint of the eight-membered metallacycle (Figure 5). The Cr−C24 bond (1.717(2) Å) is considerably shorter than the Cr−C23 bond of the terminal carbonyl ligand (1.803(2) Å), and compares very well with the Cr≡C triple bonds of carbyne complexes (e.g., 1.705(2) Å in $[Cp(CO)_2Cr{\equiv}CPh]$ and 1.728(8) Å in $[Cp(CO)_2Cr{\equiv}CNiPr_2]$.[25] Furthermore, the O2−C24 bond (1.291(2) Å) is considerably longer than that of the terminal carbonyl ligand (O1–C23 1.178(2) Å) and close in length to the C_{sp}–O single bonds of alkoxyalkynes (e.g., 1.303(1) Å in *t*BuO–(C≡C)$_2$–O*t*Bu).[26] The elongated Si–O bond of **5** (1.749(1) Å) relative to those of alkoxysilanes (1.642 Å),[27] complements the bonding picture of a siloxycarbyne complex with some μ-isocarbonyl character. This is further confirmed by the short Cr–Si distance (2.2847(6) Å) lying between those of Cr=Si double bonds (e.g., 2.161 Å in **3-Cl** and **3-Br**) and Cr–Si single bonds (2.399 Å).[21]

Conclusion

In summary, the isolation of the first NHC-stabilized halosilylidyne complexes highlights the synthetic potential of the NHC adducts of silicon(II) dihalides in low-valent silicon chemistry, and opens a new avenue of chemical exploration that takes advantage of the multifaceted functionalization of the metal-bonded Si–X moiety.

Experimental Section

General: All experiments were carried out under an atmosphere of argon using Schlenk or glovebox techniques. The glassware was dried in the oven at approximately 110 °C and baked under vacuum prior to use. The solvents were heated to reflux over the corresponding drying agent (petroleum ether 40/60: CaH_2, hexane: sodium wire/benzophenone/tetraglyme; benzene: sodium wire/benzophenone; toluene: sodium wire), purged several times during reflux with argon, and distilled under argon. Fluorobenzene was trap-to-trap condensed from CaH_2. All solvents were stored in the glovebox.

1,3-Bis[2,6-bis(isopropyl)phenyl]imidazolidin-2-ylidene (SIdipp) was prepared from (SIdippH)Br using two methods. The first method involved the reaction of (SIdippH)Br with KH in the presence of a catalytic amount of dibenzo[18]crown-6 as reported by Arduengo et al.[6] The advantage of this method is the high selectivity of the reaction, its drawback the rather long reaction time. For example, workup of the reaction mixture after 5 days of stirring afforded the carbene SIdipp in only 64 % yield due to incomplete conversion of (SIdippH)Br. The second method employed deprotonation of (SIdippH)Br by $NaN(SiMe_3)_2$ in diethyl ether using a similar approach to that reported recently by Cavell, Dervisi, and Fallis et al. for a series of N-heterocyclic carbenes.[28] In this case, conversion of (SIdippH)Br was complete within 3 h, but the reaction was less selective and led to a 4:1 mixture of SIdipp and a second product, which was shown by X-ray crystallography and ^{1}H NMR spectroscopy to be the imine CH_2=CH–N(dipp)–CH=N–dipp.[29] Fractional crystallization of the product mixture from diethyl ether at −30 °C afforded the pure carbene in 48 % yield.[30] The 4,5-dihydroimidazolium salt (SIdippH)Br[31] was prepared from *N*,*N*′-[2,6-bis(isopropyl)phenyl]formamidine and 1,2-dibromoethane in the presence of *N*,*N*-diisopropylethylamine using a similar method to that described by Nechaev et al. for the synthesis of 3,4,5,6-tetrahydropyrimidinium salts[32] and was characterized by NMR spectroscopy.[33] 1,3-Dihydro-4,5-dimethyl-1,3-bis(isopropyl)-2*H*-imidazol-2-ylidene (IMe_2iPr_2)[34] and $LiB(C_6F_5)_4\cdot 2.5\,Et_2O$[35] were prepared as described previously. Li[CpCr(CO)$_3$] was obtained as a cream-colored solid in almost quantitative yield by treating [CpCr(CO)$_3$H][36] with one equivalent of *n*-butyllithium in hexane at ambient temperature and was characterized by ^{1}H NMR and IR spectroscopy.[37]

The C, H, N analyses were carried out in triplicate for each sample using an Elementar Vario Micro elemental analyser. The individual C, H, N values did not differ by more than ±0.3. The mean C, H, N values are given below for each compound. The melting points were determined in duplicate for each sample using a Büchi melting-point apparatus. The samples were sealed in capillary tubes under vacuum and rapidly heated to a temperature approximately 20 K lower than that at which melting or decomposition started. Heating was then continued with a rate of approximately 3 K min^{-1} until the sample melted or decomposed. IR spectra of solutions were recorded using a Nicolet 380 FTIR spectrometer in the range of 2200–1500 cm^{-1} with a cell of NaCl windows. IR spectra of the solids (4000–400 cm^{-1}) were recorded using a Bruker Alpha FTIR spectrometer in the glovebox with the platinum single-reflection diamond ATR module. The following abbreviations are used for the intensities of the IR absorption bands: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak, (sh) shoulder. NMR spectra were recorded using a Bruker Avance DMX-300 or DPX-400 NMR spectrometer in dry deoxygenated [D$_6$]benzene, [D$_8$]THF, [D$_3$]acetonitrile, and [D$_6$]dimethyl sulfoxide. [D$_6$]Benzene and [D$_8$]THF were trap-to-trap condensed from sodium powder and [D$_3$]acetonitrile from CaH_2. [D$_6$]Dimethyl sulfoxide was used as purchased. The ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent relative to tetramethylsilane ([D$_6$]benzene, δ_H = 7.15 ppm and δ_C = 128.0 ppm; [D$_8$]tetrahydrofurane, δ_H = 1.73 ppm and δ_C = 25.3 ppm; [D$_3$]acetonitrile δ_H = 1.93 ppm and δ_C = 1.3 ppm; [D$_6$]dimethyl sulfoxide, δ_H = 2.49 ppm and δ_C = 39.5 ppm). The ^{29}Si NMR spectra were calibrated against external pure $SiMe_4$. The standard was filled in a capillary, which was sealed-off and introduced into a 5 mm NMR spectroscopy tube that contained the corresponding deuterated solvent. The NMR spectroscopy tube was finally vacuum-sealed and used for the calibration. The following abbreviations were used for the forms and multiplicities of the NMR spectroscopic signals: (s) singlet, (d) doublet, (t) triplet, (sept) septet, (m) multiplet, (br) broad. The ^{1}H and ^{13}C NMR spectroscopic signals of SIdipp, (SIdippH)Br, and **1-Br**–**4-Br** were assigned by a combination of H,H-COSY, HMQC, HMBC, and DEPT experiments. This allowed an unequivocal assignment of all proton and carbon resonances including those of the diastereotopic methyl groups of the isopropyl substituents, which were labeled with the subscript letters A and B, respectively. The chemically different carbene substituents in the low-temperature NMR spectra of **4-Br** were designated with the superscript letters X and Y, respectively.

Synthesis of 1-Br: $SiBr_4$ (1.25 mL, 3.48 g, 10.0 mmol) was added to a stirred suspension of ISdipp (3.91 g, 10.0 mmol) in petroleum ether (80 mL) at ambient temperature within 5 min. Formation of a voluminous, white precipitate was observed. The reaction mixture was stirred for 20 min, the precipitate was filtered off and then dried under vacuum to give **1-Br** as a white powder. Yield: 7.16 g (9.70 mmol, 97 %). The compound decomposes at 171–172 °C and turns into a yellow liquid with gas evolution. ^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K):[38] δ = 1.38 (d, ^3J(H,H) = 6.8 Hz, 12 H; $2\times C^{2,6}$-CH$\mathit{Me_A}$Me$_B$, dipp), 1.43 (d, ^3J(H,H) = 6.8 Hz, 12 H; $2\times C^{2,6}$-CHMe$_A$$\mathit{Me_B}$, dipp), 3.16 (sept, ^3J(H,H) = 6.8 Hz, 4 H; $2\times C^{2,6}$-CHMe$_A$Me$_B$, dipp), 4.83 (s, 4 H; $2\times NC\mathit{H_2}$), 7.34 (d, ^3J(H,H) = 7.8 Hz, 4 H; $2\times C^{3,5}$-H, dipp), 7.54 ppm (t, ^3J(H,H) = 7.8 Hz, 2 H; $2\times C^4$-H, dipp); ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 298 K): δ = 23.7 (s, 4 C; $2\times C^{2,6}$-CHMe$_A$$\mathit{Me_B}$, dipp), 26.8 (s, 4 C; $2\times C^{2,6}$-CH$\mathit{Me_A}$Me$_B$, dipp), 29.7 (s, 4 C; $2\times C^{2,6}$-CHMe$_A$Me$_B$, dipp), 57.0 (s, 2 C; $2\times N\mathit{C}H_2$), 125.9 (s, 4 C; $2\times \mathit{C}^{3,5}$-H, dipp), 131.2 (s, 2 C; $2\times \mathit{C}^1$, dipp), 132.5 (s, 2 C; $2\times \mathit{C}^4$-H, dipp), 147.1 (s, 4 C; $2\times \mathit{C}^{2,6}$, dipp), 161.3 ppm (s, 1 C; NCN); ^{29}Si NMR (59.63 MHz, CD_2Cl_2, 298 K): δ = −73.0 ppm (s); elemental analysis calcd (%) for $C_{27}H_{38}Br_4N_2Si$ (738.31): C 43.92, H 5.19, N 3.79; found: C 44.09, H 5.23, N 3.70.

Synthesis of 2-Br: A mixture of **1** (7.16 g, 9.70 mmol) and KC_8 (3.08 g, 22.8 mmol, 2.35 equiv) was treated with benzene (100 mL) and the suspension was stirred at ambient temperature for 16 h. The suspension was filtered, and the red-brown filtrate was concentrated under vacuum to approximately 20 mL. A part of the product precipitated out as a yellow solid. Hexane (30 mL) was added and the suspension was stirred at 0 °C for 10 min to complete precipitation of the product. The yellow precipitate was filtered off, washed first with a benzene/hexane mixture (2 × 12 mL, 1:5) then with hexane (10 mL) and finally dried under vacuum (10 min, 40 °C, 0.05 mbar) to afford **2-Br** as a fine yellow powder. Yield: 4.30 g (7.43 mmol, 77 %). The compound decomposes at 191–192 °C and turns into a brown liquid. ^{1}H NMR (300.1 MHz, C_6D_6, 298 K): δ = 1.10 (d, ^3J(H,H) = 6.8 Hz, 12 H; $2\times C^{2,6}$-CH$\mathit{Me_A}$Me$_B$, dipp), 1.51 (d, ^3J(H,H) =

6.8 Hz, 12 H; 2×C^{2,6}-CHMe$_A$*Me*$_B$, dipp), 3.29 (sept, ^3J(H,H)=6.8 Hz, 4 H; 2×C^{2,6}-C*H*Me$_A$Me$_B$, dipp), 3.47 (s, 4 H; 2×NC*H*$_2$), 7.03 (d, ^3J(H,H)=7.7 Hz, 4 H; 2×C^{3,5}-*H*, dipp), 7.17 ppm (t, ^3J(H,H)=7.7 Hz, 2 H; 2×C^4-*H*, dipp); ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$, 298 K): δ=23.8 (s, 4 C; 2×C^{2,6}-CHMe$_A$*Me*$_B$, dipp), 26.1 (s, 4 C; 2×C^{2,6}-CH*Me*$_A$Me$_B$, dipp), 29.4 (s, 4 C; 2×C^{2,6}-*C*HMe$_A$Me$_B$, dipp), 54.1 (s, 2 C; 2×N*C*H$_2$), 124.9 (s, 4 C; 2×*C*^{3,5}-H, dipp), 130.5 (s, 2 C; 2×*C*^{4}-H, dipp), 133.7 (s, 2 C; 2×*C*^{1}, dipp), 146.6 (s, 4 C; 2×*C*^{2,6}, dipp), 188.7 ppm (s, 1 C; N*C*N); ^{29}Si NMR (59.63 MHz, C$_6$D$_6$, 298 K): δ=10.8 ppm (s); IR (solid): $\tilde{\nu}$=3065 (vw), 2961 (s), 2926 (m), 2867 (m), 1589 (w), 1488 (s), 1476 (s), 1453 (s), 1446 (s), 1419 (m), 1384 (m), 1363 (m), 1344 (vw), 1321 (m), 1302 (w), 1269 (s), 1245 (m), 1182 (m), 1163 (vw), 1150 (vw), 1102 (m), 1056 (m), 1047 (m), 1018 (w), 987 (vw), 956 (vw), 933 (w), 916 (m), 801 (s), 754 (s), 709 (vw), 677 (vw), 633 (vw), 619 (m), 611 (w, sh), 581 (vw), 572 (vw), 546 (w), 530 (vw), 457 (m), 423 cm^{-1} (m); elemental analysis calcd (%) for C$_{27}$H$_{38}$Br$_2$N$_2$Si (578.50): C 56.06, H 6.62, N 4.84; found: C 56.27, H 6.47, N 4.78.

Synthesis of 3-Br: A suspension of **2-Br** (517 mg, 0.894 mmol) and Li[CpCr(CO)$_3$] (217 mg, 1.04 mmol, 1.12 equiv) in benzene (10 mL) was immersed in an ultrasonic bath for 5 min and heated at 80 °C for 30 min. Pressure release was allowed for through a mercury bubbler. Evolution of CO was observed and the color of the reaction mixture changed from yellow to dark red-brown. The mixture was cooled to room temperature, filtered to a schlenk-tube that contained a new portion of Li[CpCr(CO)$_3$] (50 mg, 0.24 mmol, 0.27 equiv), and heating was repeated as described above to complete the conversion of **2-Br**.[39] Then the reaction mixture was cooled to ambient temperature, concentrated to approximately 7 mL under vacuum, and diluted with hexane (7 mL). After storage at ambient temperature for 10 min, the reaction mixture was filtered. The brown filtrate was treated with hexane (10 mL) to precipitate a brown less soluble component, and the mixture was filtered as fast as possible before the product started to crystallize. The filtrate was stored at −5 °C for 16 h to give dark brown (almost black) crystals of **3-Br**·0.5 C$_6$H$_6$ and some brownish powder of a contaminant. The supernatant solution was decanted, and the crystals were washed with hexane (2×3 mL) and dried under vacuum (15 min, RT, 0.05 mbar). The crystals of **3-Br**·0.5 C$_6$H$_6$ were easily separated from the contaminant upon shaking into another Schlenk tube. Yield: 340 mg (0.478 mmol, 53 %). The compound starts to decompose above 140 °C and turns until 160 °C into a brown liquid with gas evolution. ^{1}H NMR (300.1 MHz, C$_6$D$_6$, 298 K): δ=1.13 (d, ^3J(H,H)=6.8 Hz, 12 H; 2×C^{2,6}-CH*Me*$_A$Me$_B$, dipp), 1.59 (d, ^3J(H,H)=6.8 Hz, 12 H; 2×C^{2,6}-CHMe$_A$*Me*$_B$, dipp), 3.51 (s, 4 H; 2×NC*H*$_2$), 3.52 (sept, ^3J(H,H)=6.8 Hz, 4 H; 2×C^{2,6}-C*H*Me$_A$Me$_B$, dipp), 4.64 (s, 5 H; C$_5$*H*$_5$), 7.10–7.14 (m, 4 H; 2×C^{3,5}-*H*, dipp), 7.17–7.22 ppm (m, 2 H; 2×C^4-*H*, dipp); ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$, 298 K): δ=23.8 (s, 4 C; 2×C^{2,6}-CHMe$_A$*Me*$_B$, dipp), 26.9 (s, 4 C; 2×C^{2,6}-CH*Me*$_A$Me$_B$, dipp), 29.1 (s, 4 C; 2×C^{2,6}-*C*HMe$_A$Me$_B$, dipp), 53.9 (s, 2 C; 2×N*C*H$_2$), 85.9 (s, 5 C; *C*$_5$H$_5$), 125.5 (s, 4 C; 2×*C*^{3,5}-H, dipp), 130.7 (s, 2 C; 2×*C*^{4}-H, dipp), 133.5 (s, 2 C; 2×*C*^{1}, dipp), 146.6 (s, 4 C; 2×*C*^{2,6}-CHMe$_A$Me$_B$, dipp), 177.4 (s, 1 C; N*C*N), 251.7 ppm (s, 2 C; 2×*C*O); ^{29}Si NMR (59.63 MHz, C$_6$D$_6$, 298 K): δ=95.1 ppm (s); IR (toluene): $\tilde{\nu}$=1898 (vs), 1809 cm^{-1} (vs) [ν(CO)]; IR (fluorobenzene):$\tilde{\nu}$=1894 (vs), 1809 cm^{-1} (vs) (ν(CO)); IR (solid): $\tilde{\nu}$=3066 (vw), 3034 (vw), 3015 (vw), 2963 (m), 2927 (w), 2868 (w), 1893 (vs) (ν(CO)), 1867 (m, sh), 1805 (vs) (ν(CO)), 1776 (s, sh), 1630 (vw), 1588 (w), 1478 (s), 1465 (m), 1453 (s), 1445 (s), 1421 (m), 1386 (m), 1366 (w), 1345 (vw), 1323 (m), 1314 (w), 1302 (m), 1288 (vw), 1272 (s), 1242 (m), 1231 (w, sh), 1217 (vw, sh), 1190 (w, sh), 1180 (m), 1150 (vw), 1111 (w, sh), 1106 (w), 1097 (w, sh), 1055 (w), 1037 (vw), 1017 (vw), 1007 (w), 990 (vw), 963 (vw), 934 (w), 924 (m), 894 (vw), 886 (vw), 840 (vw), 822 (w), 801 (s), 754 (m), 725 (vw), 702 (vw), 680 (s), 651 (s), 623 (m), 602 (s), 567 (s), 547 (m), 523 (m), 505 (s), 488 (m), 464 (m), 445 (m), 429 (m), 416 (vw), 408 (vw), 378 cm^{-1} (s); elemental analysis calcd (%) for C$_{34}$H$_{43}$BrCrN$_2$O$_2$Si·0.5C$_6$H$_6$ (710.76): C 62.52, H 6.52, N 3.94; found: C 62.34, H 6.65, N 3.75.

Synthesis of 3-Cl: Using a similar procedure to that described for **3-Br**, a suspension of Li[CpCr(CO)$_3$] (approx. 3 equiv) in benzene was heated at 70 °C with **2-Cl**[40] until conversion of **2-Cl** was complete. The resulting reaction mixture was worked up as described above for the isolation of **3-Br** to afford after crystallization from a toluene/hexane mixture complex **3-Cl** as a brown, crystalline solid in around 45 % yield. ^{1}H NMR (300.1 MHz, C$_6$D$_6$, 298 K): δ=1.13 (d, ^3J(H,H)=6.7 Hz, 12 H; 2×C^{2,6}-CH*Me*$_A$Me$_B$, dipp), 1.58 (d, ^3J(H,H)=6.8 Hz, 12 H; 2×C^{2,6}-CHMe$_A$*Me*$_B$, dipp), 3.50 (sept, ^3J(H,H)=6.8 Hz, 4 H; 2×C^{2,6}-C*H*Me$_A$Me$_B$, dipp), 3.52 (s, 4 H; 2×NC*H*$_2$), 4.59 (s, 5 H; C$_5$*H*$_5$), 7.10–7.13 (m, 4 H; 2×C^{3,5}-*H*, dipp), 7.17–7.22 ppm (m, 2 H; 2×C^4-*H*, dipp); ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$, 298 K): δ=23.7 (s, 4 C; 2×C^{2,6}-CHMe$_A$*Me*$_B$, dipp), 26.9 (s, 4 C; 2×C^{2,6}-CH*Me*$_A$Me$_B$, dipp), 29.1 (s, 4 C; 2×C^{2,6}-*C*HMe$_A$Me$_B$, dipp), 53.9 (s, 2 C; 2×N*C*H$_2$), 85.0 (s, 5 C; *C*$_5$H$_5$), 125.5 (s, 4 C; 2×*C*^{3,5}-H, dipp), 130.7 (s, 2 C; 2×*C*^{4}-H, dipp), 133.3 (s, 2 C; 2×*C*^{1}, dipp), 146.6 (s, 4 C; 2×*C*^{2,6}-CHMe$_A$Me$_B$, dipp), 178.7 (s, 1 C; N*C*N), 251.3 ppm (s, 2 C; 2×*C*O); ^{29}Si NMR (59.63 MHz, C$_6$D$_6$, 298 K): δ=113.6 ppm (s); IR (toluene): $\tilde{\nu}$=1894 (vs), 1806 cm^{-1} (vs) (ν(CO)); IR (fluorobenzene): $\tilde{\nu}$=1890 (vs), 1806 cm^{-1} (vs) (ν(CO)); IR (THF, cm^{-1}): $\tilde{\nu}$=1894 (vs), 1809 cm^{-1} (vs) (ν(CO)).

Synthesis of 4-Br: 1,3-Dihydro-4,5-dimethyl-1,3-bis(isopropyl)-2*H*-imidazol-2-ylidene (90 mg, 0.50 mmol, 2.64 equiv) was added in portions to a stirred solution of **3-Br**·0.5 C$_6$H$_6$ (134 mg, 0.189 mmol) in benzene (5 mL). The reaction mixture was stirred for 15 min, filtered from a tiny amount of a brown insoluble material, and stored overnight at ambient temperature. The supernatant solution was removed with a syringe, and the dark red-brown crystals of **4-Br**·C$_6$H$_6$ were washed with benzene (2×1 mL), then hexane (2 mL), and dried for 1 h at ambient temperature in the glovebox in an open vial. Yield: 120 mg (0.167 mmol, 88 %). The compound **4-Br**·C$_6$H$_6$ desolvates upon heating and then decomposes at 166–168 °C to give a black liquid. ^{1}H NMR (300.1 MHz, [D$_8$]THF, 298 K): δ=1.31 and 1.47 (br each, 12 H each; 2×N^{1,3}-CH*Me*$_A$*Me*$_B$, IMe$_2$*i*Pr$_2$), 2.31 (s, 12 H; 2×C^{4,5}-*Me*, IMe$_2$*i*Pr$_2$), 4.30 (s, 5 H; C$_5$*H*$_5$), 6.1 (br, $\Delta\nu_{1/2}\approx$300 Hz, 4 H; 2×N^{1,3}-C*H*Me$_A$Me$_B$, IMe$_2$*i*Pr$_2$), 7.30 ppm (s, 6 H; C$_6$H$_6$); ^{1}H NMR (300.1 MHz, [D$_8$]THF, 213 K): δ=0.76 (d, ^3J(H,H)=6.7 Hz, 3 H; N^1-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 0.90 (d, ^3J(H,H)=6.7 Hz, 3 H; N^1-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y), 1.37 (d, ^3J(H,H)=6.7 Hz, 3 H; N^1-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^X), 1.42 (d, ^3J(H,H)=6.7 Hz, 3 H; N^3-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y), 1.48 (d, ^3J(H,H)=6.7 Hz, 3 H; N^1-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^Y), 1.56 (d, ^3J(H,H)=6.7 Hz, 3 H; N^3-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 1.66 (d, ^3J(H,H)=6.7 Hz, 3 H; N^3-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^Y), 1.68 (d, ^3J(H,H)=6.7 Hz, 3 H; N^3-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^X), 2.26 (s, 3 H; C^4-*Me*, (IMe$_2$*i*Pr$_2$)^X), 2.34 (s, 3 H; C^4-*Me*, (IMe$_2$*i*Pr$_2$)^Y), 2.37 (s, 3 H; C^5-*Me*, (IMe$_2$*i*Pr$_2$)^X), 2.38 (s, 3 H; C^5-*Me*, (IMe$_2$*i*Pr$_2$)^Y), 4.27 (s, 5 H; C$_5$*H*$_5$), 4.94 (sept, ^3J(H,H)=6.7 Hz, 1 H; N^1-C*H*Me$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 5.12 (sept, ^3J(H,H)=6.7 Hz, 1 H; N^1-C*H*Me$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y), 6.19 (sept, ^3J(H,H)=6.7 Hz, 1 H; N^3-C*H*Me$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 7.34 (s, 6 H; C$_6$H$_6$), 9.54 ppm (sept, ^3J(H,H)=6.7 Hz, 1 H; N^3-C*H*Me$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y); ^{13}C{H} NMR (75.47 MHz, [D$_8$]THF, 298 K): δ=10.6 (s, 4 C; 2×C^{4,5}-*Me*, IMe$_2$*i*Pr$_2$), 21.1 and 22.4 (br s each, 4 C each; 2×N^{1,3}-CH*Me*$_A$*Me*$_B$, IMe$_2$*i*Pr$_2$), 52.4 (br s, 4 C; 2×N^{1,3}-*C*HMe$_A$Me$_B$, IMe$_2$*i*Pr$_2$), 81.5 (s, 5 C; *C*$_5$H$_5$), 127.0 (s, 4 C; 2×*C*^{4,5}-Me, IMe$_2$*i*Pr$_2$), 129.0 (s, 6 C; *C*$_6$H$_6$), 157.4 (s, 2 C; 2×*C*^{2}, IMe$_2$*i*Pr$_2$), 250.6 ppm (s, 2 C; 2×*C*O); ^{13}C{^{1}H} NMR (75.47 MHz, [D$_8$]THF, 213 K): δ=10.36 (s, 1 C; C^4-*Me*, (IMe$_2$*i*Pr$_2$)^Y), 10.42 (s, 1 C; C^4-*Me*, (IMe$_2$*i*Pr$_2$)^X), 10.54 (s, 2 C; C^5-*Me*, (IMe$_2$Pr$_2$)^X and (IMe$_2$*i*Pr$_2$)^Y), 19.0 (s, 1 C; N^1-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y), 19.3 (s, 1 C; N^1-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 20.9 (s, 1 C; N^3-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^X), 21.7 (s, 1 C; N^3-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 22.0 (s, 1 C; N^1-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^Y), 22.37 (s, 1 C; N^3-CH*Me*$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y), 22.43 (s, 1 C; N^3-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^Y), 23.9 (s, 1 C; N^1-CHMe$_A$*Me*$_B$, (IMe$_2$*i*Pr$_2$)^X), 50.3 (s, 1 C; N^3-*C*HMe$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y), 52.2 (s, 1 C; N^3-*C*HMe$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 53.3 (s, 1 C; N^1-*C*HMe$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^Y), 54.1 (s, 1 C; N^1-*C*HMe$_A$Me$_B$, (IMe$_2$*i*Pr$_2$)^X), 81.3 (s, 5 C; *C*$_5$H$_5$), 126.6 (s, 1 C; *C*^{5}-Me, (IMe$_2$*i*Pr$_2$)^Y), 126.8 (s, 1 C; *C*^{5}-Me, (IMe$_2$*i*Pr$_2$)^X), 127.4 (s, 1 C; *C*^{4}-Me, (IMe$_2$*i*Pr$_2$)^X), 127.9 (s, 1 C; *C*^{4}-Me, (IMe$_2$*i*Pr$_2$)^Y), 129.1 (s, 6 C; *C*$_6$H$_6$), 156.2 (s, 1 C; *C*^{2}, (IMe$_2$*i*Pr$_2$)^X or (IMe$_2$*i*Pr$_2$)^Y), 156.3 (s, 1 C; *C*^{2}, (IMe$_2$*i*Pr$_2$)^X or (IMe$_2$*i*Pr$_2$)^Y), 248.9 (s, 1 C; *C*O), 251.8 ppm (s, 1 C; *C*O); ^{29}Si NMR (59.63 MHz, [D$_8$]THF, 298 K): δ=17.3 ppm (s); IR (THF): $\tilde{\nu}$=1797 (vs), 1733 cm^{-1} (vs) (ν(CO)); IR (fluorobenzene): $\tilde{\nu}$=1794 (vs), 1726 cm^{-1} (vs) (ν(CO)); IR (solid): $\tilde{\nu}$=3088 (vw), 3032 (vw), 2991 (vw, sh), 2975 (w), 2937 (w), 2874 (vw), 2654 (vw), 1889 (vw), 1776 (vs) (ν(CO)), 1707 (vs) (ν(CO)), 1632 (m), 1476 (w), 1463 (w), 1441 (m), 1402 (vw), 1384 (m), 1369 (s), 1346 (m), 1336 (w), 1313 (vw), 1209 (m), 1183 (vw), 1168 (vw), 1148 (vw), 1134 (w), 1109 (m), 1078 (w), 1058 (vw), 1033 (w), 1006 (vw), 997 (w), 932 (vw), 903 (w), 883 (vw), 837 (vw), 794 (m), 779 (m), 767 (m), 754 (m), 691 (s), 671 (s), 652 (w), 623 (s), 604 (s), 547 (s), 531 (s), 490 (m), 474 (s), 458 (s), 437 (s), 412 cm^{-1} (m); elemental analysis calcd (%) for $C_{29}H_{45}BrCrN_4O_2Si{\cdot}C_6H_6$ (719.79): C 58.40, H 7.14, N 7.78; found: C 59.25, H 7.16, N 7.56.

Synthesis of 5: A solution of $Li[B(C_6F_5)_4]{\cdot}2.5\,Et_2O$ (87 mg, 0.10 mmol) in fluorobenzene (2 mL) was added to a stirred solution of **4-Br**·C_6H_6 (72 mg, 0.10 mmol) in fluorobenzene (5 mL). The color of the reaction solution changed rapidly from dark brown to green. The reaction mixture was stirred for 3 min and then filtered from some insoluble yellow solid. An IR spectrum of an aliquot of the green filtrate was recorded, which revealed that the starting material had been consumed and that a new dicarbonyl complex had formed and displayed two ν(CO) absorption bands of almost equal intensity at $\tilde{\nu} = 1895$ and 1821 cm^{-1}. This intermediate is suggested to be the silylidene complex $[Cp(CO)_2Cr{=}Si(IMe_2iPr_2)_2][B(C_6F_5)_4]$. The green filtrate was stored at −16 °C for 2 days. The resulting yellow crystals of **5** were separated from the yellow mother liquor by decantation, washed with fluorobenzene (2×1 mL) and hexane (2 mL), and then dried for 15 min at ambient temperature under vacuum (0.05 mbar). Yield: 70 mg (0.028 mmol, 56 %). Elemental analysis calcd (%) for $C_{106}H_{90}B_2Cr_2F_{40}N_8O_4Si_2$ (2481.62): C 51.30, H 3.66, N 4.52; found: C 51.49, H 3.77, N 4.36 %. Complex **5** is insoluble in common organic solvents including fluorobenzene, MeCN, and CH_2Cl_2. It turns brown upon heating above 170 °C, and then liquefies at 191–192 °C. IR (solid): $\tilde{\nu} = 2985$ (w), 2945 (vw), 1860 (s) (ν(CO)), 1642 (m), 1630 (w,sh), 1596 (w), 1513 (s), 1497 (w), 1458 (vs), 1385 (m, sh), 1373 (s), 1318 (w), 1273 (m), 1214 (m), 1183 (vw), 1170 (vw), 1153 (vw), 1137 (vw), 1085 (s), 1034 (vw), 976 (vs), 933 (vw), 903 (m), 883 (vw), 843 (vw), 824 (vw), 806 (m), 773 (m), 754 (s), 719 (m), 684 (m), 661 (s), 609 (m), 572 (m), 564 (m), 547 (w), 520 (m), 501 (m), 477 (m), 468 (m ,sh), 449 (m), 436 (sh), 410 (w), 388 cm^{-1} (m).

Crystal structure determination of 2, 3-Br·0.5 (hexane), 3-Cl·0.5 (hexane), 4-Br·C_6H_6, and 5·C_6H_5F: Yellow single crystals of **2** were obtained upon slow cooling of a warm benzene solution to room temperature. Cooling of a hexane/toluene solution of **3** to −30 °C afforded brown needles of **3-Br**·0.5(hexane). Orange plates of **3-Cl**·0.5 (hexane) were obtained upon diffusion of hexane into a benzene solution of **3-Cl** at 5 °C. Red-brown crystals of **4-Br**·C_6H_6 were obtained upon storage of a benzene solution at ambient temperature. Yellow plates of **5**·C_6H_5F were grown from a dilute fluorobenzene solution at ambient temperature. The data collection of **2** was performed using a Nonius KappaCCD diffractometer (area detector), and the data collection of **3-Br**·0.5(hexane), **3-Cl**·0.5(hexane), **4-Br**·C_6H_6, and **5**·C_6H_5F using a Bruker X8-KappaApexII diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Both diffractometers were equipped with a low-temperature device (Nonius KappaCCD diffractometer: Cryostream 600er series, Oxford Cryosystems, 123 K; Bruker X8-KappaApexII diffractometer: Kryoflex, Bruker AXS GmbH, 100 K). Intensities were measured by fine-slicing ω and ϕ scans and corrected for background, polarization, and Lorentz effects. An empirical absorption correction was applied to all data sets.[41] The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system.[42] Hydrogen atoms were included isotropically using the riding model on the bound carbon atoms. The crystals of **5**·C_6H_5F turned out to be non-merohedral twins. The diffraction pattern could be indexed using the least-squares procedure.[43] Subsequent multidomain integration of the data set led to a refined twin law of (0.99161, 0.00069, 0.04000, 0.00148, 1.00051, −0.01542, −0.06138, 0.02687, 1.00506). Rotation of 2.7° about the reciprocal axis (0.467, 1.000, 0.340) converted the HKLs from one to the other twin domain.[44] The data reduction and empirical absorption correction with TWINABS[45] gave an HKLF 5 file suitable for the twin refinement in SHELX.

CCDC-836569 (**2-Br**), 836570 (**3-Cl**·0.5 (hexane)), 836571 (**3-Br**·0.5 (hexane)), 836572 (**4-Br**·C_6H_6), and 836573 (**5**·C_6H_5F) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electronic-structure calculations: All calculations were carried out at the non-local density functional level of theory (DFT) using the hybrid three-parameter functional of Becke and the correlation functional of Lee, Yang, and Parr (B3LYP).[46] The TZVPP basis set[47] was used for the chromium, silicon, bromine, chlorine, and the carbene carbon atoms, and the 6-31G* basis set[48] for all other atoms (basis set "I"). All geometry optimizations were carried out without symmetry restraints with the program package Gaussian 03 using its standard convergence criteria.[49] The optimized geometries were verified as minima on the potential-energy surface by evaluation of their harmonic vibrational frequencies, which were used to calculate the zero-point vibrational energies (ZPE) of **3-Br**, **3-Cl**, and their fragments SIdipp and $[Cp(CO)_2Cr{\equiv}Si{-}X]$ (X = Cl, Br) after carbene dissociation.

The NBO analyses were performed with the NBO 5.0 program.[50] Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the NBO approach. The NBO method interprets a many-electron molecular wave function in terms of localized electron-pair bonding units and leads to a natural Lewis structure, which best describes the system.

All thermodynamic energies were calculated using standard procedures. Details can be found in ref. [51]. The Gibbs free bond dissociation energy of **3-Br** and **3-Cl** was calculated at the B3LYP/I level of theory and corrected for the difference in the zero-point vibrational energies (B3LYP/I). Thermal corrections were carried out at standard conditions ($T = 298.15$ K, and $P = 1$ atmosphere).

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[23] An alternative view of the 18VE complex $[Cp(CO)_2Cr{=}Si(IMe_2iPr_2)_2]^+$ is that of na IMe_2iPr_2 adduct of the cationic 18VE silylidyne complex $[Cp(CO)_2Cr{\equiv}Si(IMe_2iPr_2)]^+$ or a bis-IMe_2iPr_2 adduct of the cationic complex $[Cp(CO)_2CrSi]^+$ that features an end-on bonded Si atom. Attempts to isolate such elusive species are currently underway.

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[30] NMR spectroscopic data of SIdipp are as follows: ^1H NMR (300.1 MHz, C_6D_6, 298 K): $\delta = 1.28$ (d, $^3J(H,H) = 6.8$ Hz, 12H; $2\times C^{2,6}{-}CH\mathit{Me_A}Me_B$, dipp), 1.33 (d, $^3J(H,H) = 6.8$ Hz, 12H; $2\times C^{2,6}{-}CHMe_A\mathit{Me_B}$, dipp), 3.28 (sept, $^3J(H,H) = 6.9$ Hz, 4H; $2\times C^{2,6}{-}C\mathit{H}Me_AMe_B$, dipp), 3.37 (s, 4H; $2\times NC\mathit{H_2}$), 7.16–7.20 (m, 4H; $2\times C^{3,5}{-}\mathit{H}$, dipp), 7.24–7.29 (m, 2H; $2\times C^4{-}\mathit{H}$, dipp). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 298 K, ppm): $\delta = 23.6$ (s, 4C; $2\times C^{2,6}{-}CH\mathit{Me_A}Me_B$, dipp), 25.4 (s, 4C; $2\times C^{2,6}{-}CHMe_A\mathit{Me_B}$, dipp), 28.9 (s, 4C; $2\times C^{2,6}{-}\mathit{C}HMe_AMe_B$, dipp), 53.7 (s, 4C; $2\times N\mathit{C}H_2$), 124.0 (s, 4C; $2\times \mathit{C}^{3,5}{-}H$, dipp), 128.3* (s, 2C; $2\times \mathit{C}^4{-}H$, dipp), 139.4 (s, 2C; $2\times \mathit{C}^1$, dipp), 147.4* (s, 4C; $2\times \mathit{C}^{2,6}$, dipp), 244.1 ppm (s, 1C; $N\mathit{C}N$). The signals marked with an asterisk were incorrectly assigned in reference [6].

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[33] NMR spectroscopic data of (SIdippH)Br are as follows: ^1H NMR (300.1 MHz, $[D_6]DMSO$, 298 K, ppm): $\delta = 1.19$ (d, $^3J(H,H) = 6.8$ Hz, 12H; $2\times C^{2,6}{-}CH\mathit{Me_A}Me_B$, dipp), 1.35 (d, $^3J(H,H) = 6.8$ Hz, 12H; $2\times C^{2,6}{-}CHMe_A\mathit{Me_B}$, dipp), 3.09 (sept, $^3J(H,H) = 6.8$ Hz, 4H; $2\times C^{2,6}{-}C\mathit{H}Me_AMe_B$, dipp), 4.56 (s, 4H; $2\times NC\mathit{H_2}$), 7.42 (d, $^3J(H,H) =$

7.7 Hz, 4H; $2\times C^{3,5}$-*H*, dipp), 7.55 (t, ^3J(H,H) = 7.7 Hz, 2H; $2\times C^4$-*H*, dipp), 9.49 (s, 1H; NC*H*N). $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_6$]DMSO, 298 K, ppm): $\delta = 23.3$ (s, 4C; $2\times C^{2,6}$-CHMe$_A$*Me*$_B$, dipp), 24.9 (s, 4C; $2\times C^{2,6}$-CH*Me*$_A$Me$_B$, dipp), 28.2 (s, 4C; $2\times C^{2,6}$-*C*HMe$_A$Me$_B$, dipp), 53.7 (s, 2C; $2\times$N*C*H$_2$), 124.8* (s, 4C; $2\times C^{3,5}$-H, dipp), 129.8* (s, 2C; $2\times C^1$, dipp), 131.0* (s, 2C; $2\times C^4$-H, dipp), 146.1* (s, 4C; $2\times C^{2,6}$, dipp), 160.0 ppm (s, 1C; N*C*HN). The signals marked with an asterisk were either not or incorrectly assigned in reference [28].

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[37] Li[CpCr(CO)$_3$]: ^{1}H NMR (400.1 MHz, CD$_3$CN, 298 K): $\delta = 4.41$ ppm (s, 5H; C$_5$*H*$_5$); IR (THF): 1902 (s), 1804 (vs), 1779 (m), 1717 cm^{-1} (s) (ν(CO)).

[38] ^{1}H NMR spectroscopy revealed that compound **1-Br** decomposes slowly in CD$_2$Cl$_2$. Therefore, the $^{13}C\{^1H\}$ NMR spectrum of **1-Br** also displayed the signals of the decomposition products, which could be easily distinguished from those of **1-Br** due to their lower intensity and by using correlation spectroscopy.

[39] The reaction of **2-Br** with Li[CpCr(CO)$_3$] was carried out several times. In all cases, addition of a fresh portion of Li[CpCr(CO)$_3$] and repeated heating was necessary to complete the conversion of **2-Br** despite the presence of an excess amount of Li[CpCr(CO)$_3$] during the first heating. This observation can be explained by the concomitant formation of (SIdippH)[CpCr(CO)$_3$], which was found by NMR spectroscopy to be the major byproduct of this reaction. In addition, lithium bromide precipitates out during the reaction, which may cover the surface of Li[CpCr(CO)$_3$] and decrease its activity. (SIdippH)[CpCr(CO)$_3$] could be easily separated from **3-Br** by taking advantage of its low solubility in toluene/hexane (1:1) mixtures and isolated as a pale-brown solid, which was characterized by IR and NMR spectroscopy. IR and NMR spectroscopic data of (SIdippH)[CpCr(CO)$_3$] are as follows: ^{1}H NMR (300.1 MHz, [D$_8$]THF, 298 K): $\delta = 1.24$ (d, ^3J(H,H) = 6.5 Hz, 12H; $4\times$ CH*Me*$_A$Me$_B$), 1.42 (d, ^3J(H,H) = 6.5 Hz, 12H; $4\times$CHMe$_A$*Me*$_B$), 3.19 (br sept, 4H; $4\times$C*H*Me$_A$Me$_B$), 4.29 (s, 5H; C$_5$*H*$_5$), 4.73 (br s, 4H; $2\times$ NC*H*$_2$), 7.38 (d, ^3J(H,H) = 7.7 Hz, 4H; $2\times C^{3,5}$-*H*, Dipp), 7.51 ppm (t, ^3J(H,H) = 7.7 Hz, 2H; $2\times C^4$-*H*, Dipp); $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_8$]THF, 298 K): $\delta = 24.1$ (s, 4C; $2\times C^{2,6}$-CHMe$_A$*Me*$_B$, dipp), 25.5 (s, 4C; $2\times C^{2,6}$-CH*Me*$_A$Me$_B$, dipp), 29.7 (s, 4C; $2\times C^{2,6}$-*C*HMe$_A$Me$_B$, dipp), 55.6 (s, 2C; $2\times$N*C*H$_2$), 82.1 (s, 5C; *C*$_5$H$_5$), 125.7 (s, 4C; $2\times$ *C*^{3,5}-H, Dipp), 130.9 (s, 2C; $2\times$*C*^{1}, dipp), 132.1 (s, 2C; $2\times$*C*^{4}-H, dipp), 147.7 (s, 4C; $2\times$*C*^{2,6}, dipp), 161.0 (s, 1C; N*C*HN), 246.9 ppm (s, 3C; $3\times$*C*O); IR (THF): $\tilde{\nu} = 1892$ (vs), 1782 (vs), 1759 cm^{-1} (vs) [ν(CO)]; IR (toluene): $\tilde{\nu} = 1887$ (vs), 1778 (vs), 1753 cm^{-1} (vs) (ν(CO)).

[40] [SiCl$_2$(SIdipp)] (**2-Cl**) was generated upon treatment of SiHCl$_3$ with two equivalents of SIdipp in toluene at −60 °C and isolated after filtration of (SIdippH)Cl and evaporation of the solvent at ambient temperature as a yellow solid, which was found by NMR spectroscopy to contain some impurities. Attempts to purify **2-Cl** by crystallization were not successful so far due to the low stability of **2-Cl** in solution, and so the crude product was used for the synthesis of **3-Cl**. ^{1}H NMR (300.1 MHz, C$_6$D$_6$, 298 K): $\delta = 1.12$ (d, ^3J(H,H) = 6.7 Hz, 12H; $2\times C^{2,6}$-CH*Me*$_A$Me$_B$, dipp), 1.50 (d, ^3J(H,H) = 6.8 Hz, 12H; $2\times C^{2,6}$-CHMe$_A$*Me*$_B$, dipp), 3.25 (sept, ^3J(H,H) = 6.8 Hz, 4H; $2\times C^{2,6}$-C*H*Me$_A$Me$_B$, dipp), 3.42 (s, 4H; $2\times$NC*H*$_2$), 7.04 (d, ^3J(H,H) = 7.7 Hz, 4H; $2\times C^{3,5}$-*H*, dipp), 7.17 ppm (t, ^3J(H,H) = 7.7 Hz, 2H; $2\times C^4$-*H*, dipp).

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