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Stabilization of Low Valent Silicon Fluorides in the Coordination Sphere of Transition Metals

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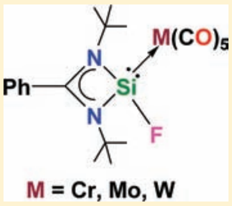
Ⓢ *Supporting Information*



ABSTRACT: Silicon(II) fluoride is unstable; therefore, isolation of the stable species is highly challenging and was not successful during the last 45 years. SiF_2 is generally generated in the gas phase at very high temperatures (~1100−1200 °C) and low pressures and readily disproportionates or polymerizes. We accomplished the syntheses of stable silicon(II) fluoride species by coordination of silicon(II) to transition metal carbonyls. Silicon(II) fluoride compounds $L(F)Si{\cdot}M(CO)_5$ {M = Cr (**4**), Mo (**5**), W(**6**)} (L = $PhC(N\textit{t}Bu)_2$) were prepared by metathesis reaction from the corresponding chloride with Me_3SnF. However, the chloride derivatives $L(Cl)Si{\cdot}M(CO)_5$ {M = Cr (**1**), Mo (**2**), W(**3**)} (L = $PhC(N\textit{t}Bu)_2$) were prepared by the treatment of transition metal carbonyls with L(Cl)Si. Direct fluorination of L(Cl)Si with Me_3SnF resulted in oxidative addition products. Compounds **4**−**6** are stable at ambient temperature under an inert atmosphere of nitrogen. Compounds **4**−**6** were characterized by NMR spectroscopy, EI-MS spectrometry, and elemental analysis. The molecular structures of **4** and **6** were unambiguously established by single-crystal X-ray diffraction. Compounds **4** and **6** are the first structurally characterized fluorides, after the discovery of SiF_2 about four and a half decades ago.

■ INTRODUCTION

Taming of highly reactive species to be isolable at normal laboratory conditions is a challenging task in synthetic chemistry.[1] Carbenes and silylenes R_2E: (where R = alkyl, aryl, H, or halogen and E = C or Si) are highly reactive and play a constantly growing important role in synthetic organic and organosilicon chemistry as well as in material sciences.[2−4] Stable analogues of carbenes and silylenes have been isolated as N-heterocyclic carbenes (NHCs)[5] and N-heterocyclic silylenes (NHSis).[6] The reactivity of NHSis is comparable with that of the NHCs. The latter find many applications in chemistry.[7,8] Gaseous dihalosilylenes X_2Si: (X = F or Cl)[9,10] have been known for many years. However, they are not stable at room temperature; they condense to polymeric $(X_2Si)_x$ or disproportionate to $(SiX)_x$ and perhalosilanes. The properties and reactivity of gaseous X_2Si: and polymeric $(X_2Si)_x$ have been studied, but no stable analogue of halosilylene was known.[11] In 2006,[6e] we reported on a base-stabilized monochlorosilylene L(Cl)Si (L = $PhC(N\textit{t}Bu)_2$), and later developed a facile method to access L(Cl)Si in almost quantitative yield using $LiN(SiMe_3)_2$ as a reducing agent.[6f] Moreover, we isolated NHC stabilized dichlorosilylene $NHC{\bullet}Cl_2Si$ (NHC= 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene or 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene) in high yield without using hazardous reducing agents such as alkali metals or KC_8. $NHC{\bullet}Cl_2Si$ was obtained by a new synthetic procedure comprising the reductive elimination of HCl from trichlorosilane in the presence of NHC under mild reaction conditions.[12] After the report of the chloro-derivatives, we focused our attention on the synthesis of stable silicon(II) fluoride. Due to the high propensity of fluorosilylene toward polymerization or disproportionation, attempts to isolate fluoro-analogues of LSiF were not successful. However, we succeeded in the synthesis of $L(F)Si{\cdot}BH_3$ and $L(H)Si{\cdot}BH_3$ in which each silylene base forms an adduct with the Lewis acid BH_3. $L(F)Si{\cdot}BH_3$ was only characterized by NMR and mass spectrometry.[13] Silylene has a stereoactive lone pair of electrons, which acts as a σ-donor ligand and forms complexes with transition metals by ligand substitution reactions.[14,15] We have reported the properties of silylenes as σ-donor ligands for the synthesis of transition metal complexes,[15] as well as on its oxidative addition reactions with organic substrates[16] and Lewis bases.[17] Stabilization of highly reactive species in the coordination sphere of transition metals is of current interest;[18] however, no fluorosilylene coordinate with a transition metal has been isolated so far. Herein, we report the stable silicon(II) fluoride species {$L(F)Si{\cdot}M(CO)_5$, M = Cr (**4**), Mo (**5**), W(**6**)} (L = $PhC(N\textit{t}Bu)_2$), where **4** and **6** are the first structurally characterized silicon(II) fluoride derivatives.

■ RESULTS AND DISCUSSION

For the preparation of compounds **4**−**6** {$L(F)Si{\cdot}M(CO)_5$, M = Cr (**4**), Mo (**5**), W(**6**)}, we assembled first the chloride derivatives **1**−**3** {$L(Cl)Si{\cdot}M(CO)_5$ {M = Cr (**1**), Mo (**2**), W(**3**)} and treated these in 1:1 ratio with Me_3SnF as a fluorinating agent.[19]

Compounds **1**−**3** {$L(Cl)Si{\cdot}M(CO)_5$, M = Cr (**1**), Mo (**2**), W(**3**)} were obtained in good yield in one pot reactions of L(Cl)Si with the respective $M(CO)_5(THF)$ in 1:1 ratio (Scheme 1). All compounds are soluble in benzene, toluene, and THF and insoluble in hexane and pentane. They are stable both in solution and solid state for a long period of time without any decomposition under an inert gas atmosphere. Compounds **1**−**3** were fully characterized by

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Scheme 1. Synthesis of 1−6

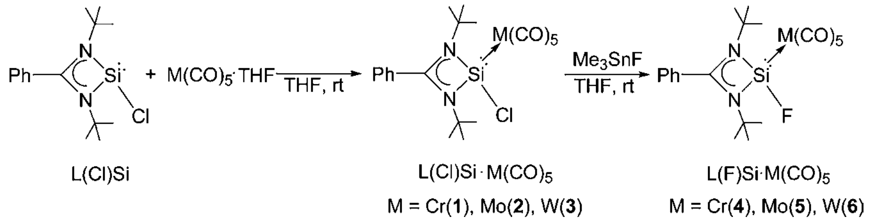


Table 1. Crystal and Structure Refinement Parameters for Compounds 1, 2, 3, 4, and 6

parameter	**1·toluene**	**2**	**3·toluene**	**4**	**6**
empirical formula	$C_{27}H_{31}ClCrN_2O_5Si$	$C_{20}H_{23}ClMoN_2O_5Si$	$C_{27}H_{31}ClN_2O_5SiW$	$C_{20}H_{23}CrFN_2O_5Si$	$C_{20}H_{23}FN_2O_5SiW$
fw	579.08	530.88	710.93	470.49	602.34
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	triclinic
space group	$P2_1/m$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
unit cell dimensions	$a = 9.896(3)$ Å $b = 13.060(5)$ Å $c = 11.577(4)$ Å $\beta = 98.60(2)°$	$a = 9.791(2)$ Å $b = 13.307(2)$ Å $c = 18.432(2)$ Å	$a = 9.873(2)$ Å $b = 11.621(3)$ Å $c = 13.1260(10)$ Å $\alpha = 94.910(10)°$ $\beta = 93.04(2)°$ $\gamma = 97.560(10)°$	$a = 10.538(2)$ Å $b = 18.0290(10)$ Å $c = 12.411(3)$ Å $\beta = 109.130(2)°$	$a = 9.203(3)$Å $b = 10.2800(10)$ Å $c = 13.187(2)$ Å $\alpha = 110.720(10)°$ $\beta = 99.33(2)°$ $\gamma = 91.24(4)°$
volume, Z	1479.4(9) Å^3, 2	2401.5(7) Å^3, 4	1484.4(5) Å^3, 2	2227.7(7) Å^3, 4	1147.2(4) Å^3, 2
density (calcd)	1.300 g/cm^3	1.468 g/cm^3	1.591 g/cm^3	1.403 g/cm^3	1.744 g/cm^3
abs coeff	0.292 mm^{-1}	2.044 mm^{-1}	2.187 mm^{-1}	0.322 mm^{-1}	2.765 mm^{-1}
$F(000)$	604	1080	704	976	588
crystal size/mm^3	0.30 × 0.21 × 0.13	0.20 × 0.20 × 0.15	0.18 × 0.16 × 0.10	0.20 × 0.15 × 0.12	0.20 × 0.20 × 0.15
θ range for data collection	1.40−20.28°	1.74−20.09°	1.23−20.81°	1.63−21.35°	1.32−20.91°
limiting indices	$-12 \leq h \leq 12; -16 \leq k \leq 14; -14 \leq l \leq 10$	$-11 \leq h \leq 11; -16 \leq k \leq 16; -22 \leq l \leq 22$	$-12 \leq h \leq 12; -14 \leq k \leq 14; 0 \leq l \leq 16$	$-12 \leq h \leq 13; -23 \leq k \leq 23; -16 \leq l \leq 16$	$-11 \leq h \leq 11; -13 \leq k \leq 13; -16 \leq l \leq 16$
reflns collected	13 702	17 349	62 539	36 069	68 180
indep reflns	3068 ($R_{int} = 0.0229$)	4609 ($R_{int} = 0.1123$)	6280 ($R_{int} = 0.0303$)	5057 ($R_{int} = 0.0285$)	4949 ($R_{int} = 0.0419$)
completeness to θ	99.9% ($\theta = 20.28°$)	99.8% ($\theta = 20.09°$)	99.2% ($\theta = 20.81°$)	99.1% ($\theta = 21.35°$)	99.6% ($\theta = 20.91°$
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	3068/363/284	4609/0/278	6280/111/353	5057/0/277	4949/0/277
GOFon F^2	1.062	1.042	1.087	1.039	1.065
final R indices [$I > 2\sigma(I)$]	R1 = 0.0313, wR2 = 0.0877	R1 = 0.0472, wR2 = 0.1175	R1 = 0.0205, wR2 = 0.0509	R1 = 0.0253, wR2 = 0.0670	R1 = 0.0139, wR2 = 0.0341
R indices (all data)	R1 = 0.0372, wR2 = 0.0917	R1 = 0.0558, wR2 = 0.1208	R1 = 0.0211, wR2 = 0.0514	R1 = 0.0287, wR2 = 0.0684	R1 = 0.0154, wR2 = 0.0352
largest diff peak and hole	0.306 and −0.363 e Å^{-3}	1.001 and −1.021 e Å^{-3}	1.965 and −1.182 e Å^{-3}	0.352 and −0.370 e Å^{-3}	1.098 and −0.861 e Å^{-3}

NMR spectroscopy, EI-MS spectrometry, elemental analysis, and single crystal X-ray structural analysis (Table 1).

The ^{1}H and ^{13}C NMR spectra of **1−3** show usual resonances expected for the amidinate (**L**) and carbonyl groups. The ^{29}Si NMR spectra of **1−3** exhibit a single resonance each at δ 92.34, 72.75, and 52.99, which is shifted downfield when compared to L(Cl)Si (δ 14.6).[6e] In compounds **1−3**, the silicon atom is deshielded upon coordination to the metal atom. The chemical shifts are pertinent to the reported value of δ 62.69 for L(Cl)Si Ni(CO)$_3$.[15d] Moreover **1−3** show their molecular ions in their mass spectra at m/z 486, 532, and 618, respectively.

The molecular structure of **1** is shown in Figure 1 (for **2** and **3**, see Supporting Information). The selected bond parameters for compounds **1−3** are given in Table 2. The silicon atom is tetracoordinate and features distorted tetrahedral geometry comprising two nitrogen atoms from the supporting amidinato ligand, one chlorine atom, and one metal atom. The metal atom is hexacoordinate with a distorted octahedral geometry derived from one silicon and five carbon atoms of the carbonyl groups. The Si−M bond distances in **1−3** are 2.3458(7), 2.4550(14), and 2.5086(11) Å. The average metal carbonyl bond lengths are 1.884(2), 1.998(6), and 2.038(4) Å, respectively. The Si−Cl bond length each in **1−3** is 2.1006(9), 2.1182(19), and 2.1012(14) Å [Si−Cl of L(Cl)Si, 2.156(1) Å]. The bite angle (N−Si−N) for **1−3** is 71.62(8)°, 71.34(18)°, and 71.41(12)°, respectively [N−Si−N of L(Cl)Si, 71.15(7)°].

Like **1−3**, the respective fluorine derivatives **4−6** are soluble in benzene, toluene, and THF and insoluble in hexane and pentane. Furthermore, they are stable both in solution and the solid state for a long period of time without any decomposition provided they are stored in an inert gas atmosphere. Compounds **4−6** were characterized by NMR spectroscopy, EI-MS spectrometry, and elemental analysis. The molecular structures of **4** and **6** were unequivocally established by single crystal X-ray diffraction studies (Table 1).

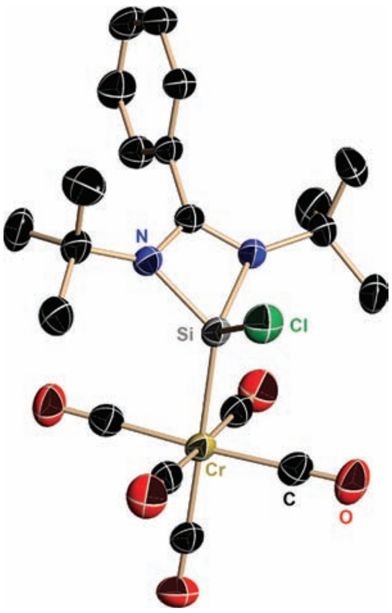


Figure 1. Molecular structure of **1**. Anisotropic displacement parameters are depicted at the 50% probability level.

Formation of the silicon(II) fluorides **4**–**6** was readily observed in their related ^{19}F NMR spectrum. Compounds **4**–**6** exhibit a single ^{19}F NMR resonance at δ −89.95, −90.33, and −93.20, respectively. They show satellite signals due to the coupling to the silicon atom with $J_{\text{Si–F}}$ of 440, 442, and 428 Hz (Table 3). The ^{29}Si NMR spectra of **4**–**6** exhibit a doublet centered at δ 73.98 ($J_{\text{Si–F}}$ = 440 Hz), 56.65 ($J_{\text{Si–F}}$ = 442 Hz), and 41.79 ($J_{\text{Si–F}}$ = 428 Hz) each, which is shifted upfield compared to those of the silicon(II) chlorides **1**–**3**. It is interesting to set side by side the above NMR data with those of $LSiF_3$[19d] {^{19}F NMR, δ −132.38 ($J_{\text{Si–F}}$ = 219 Hz); ^{29}Si NMR, δ −124.91 ($J_{\text{Si–F}}$ = 219 Hz)}. In $LSiF_3$ both the ^{19}F and ^{29}Si NMR resonances are shifted to higher field as expected when compared with those of **4**–**6**. The reason might be due to the higher coordinate silicon in $LSiF_3$ which is unmatched to those of **4**–**6**. The EI-MS spectra of compounds **4**–**6** exhibit their molecular ions at *m*/*z* 470, 516, and 602, respectively. In **4**–**6** the silicon atom is tetracoordinate with a distorted tetrahedral geometry comprising two nitrogen atoms from the amidinate ligand, one fluorine atom, and one metal atom. The metal atom each in **4**, **5**, and **6** features distorted octahedral geometry derived from one silicon atom and five carbon atoms of the carbonyl groups.

Table 3. NMR and EI-MS Data for Compounds 4–6

compound	^{29}Si (δ/ppm), $J_{\text{Si–F}}$ /Hz	^{19}F (δ / ppm), $J_{\text{Si–F}}$ / Hz	$[M^+]$/ amu
4	73.98, 440	−89.95, 440	470
5	56.65, 442	−90.33, 442	516
6	41.79, 428	−93.20, 428	602

The molecular structure of **4** is shown in Figure 2 (for **6**, see Supporting Information), and the selected bond parameters for compounds **4** and **6** are given in Table 2. There is a small variation in the Si–M bond distances in **4** and **6** after the replacement of the chlorine by the fluorine atom. The average metal carbonyl bond lengths in **4** and **6** are 1.8893(14) and 2.039(2) Å, respectively. These values are quite comparable to the chloro analogues of **1** and **3**. The Si–F bond lengths in **4** and **6** are 1.6168(8) and 1.6245(14) Å and are close to those found in $LSiF_3$.[19d] The bite angle (N–Si–N) for **4** and **6** is 71.62(5)° and 70.93(8)°. A comparison of gaseous SiF_2 with its

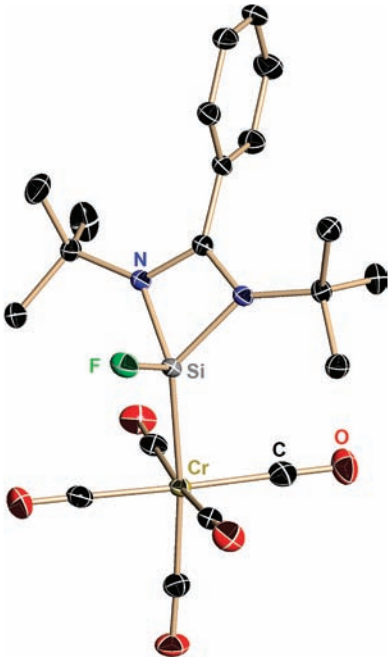
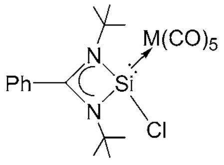
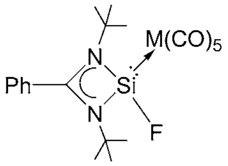


Figure 2. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level.

Table 2. Selected Bond Parameters for Compounds 1–4 and 6

Metal ion **M**						
	Si–Cl / Å	**Si–M / Å**	**N–Si–N / °**	**Si–F / Å**	**Si–M / Å**	**N–Si–N / °**
Cr	2.1006(9)	2.3458(7)	71.62(8)	1.6168(8)	2.3398(4)	71.62(5)
Mo	2.1182(19)	2.4550(14)	71.34(18)	------	------	------
W	2.1012(14)	2.5086(11)	71.41(12)	1.6245(14)	2.4990(8)	70.93(8)

Si−F bond length of 1.59 Å[20] indicates an increase in the bond length of only 0.03 Å. In contrast to that are the physical properties. SiF_2 is a gas at 25 °C and has a half-life of 150 s at <1 mmHg,[10a] whereas the complexes **4**−**6** can be stored at room temperature in an inert atmosphere for a long period of time without decomposition.

■ CONCLUSION

Four and a half decades ago, Margrave, Timms, and co-workers generated the silicon(II) fluoride in the gas phase at high temperatures (∼1100−1200 °C) and low pressures. They published their results in this journal. However, SiF_2 is unstable and readily disproportionates or polymerizes. Herein, we report on the first structurally characterized stable silicon(II) fluoride compounds that have been accomplished by utilizing the coordination sphere of transition metals. The compound $L(F)Si{\cdot}M(CO)_5$ {M = Cr (**4**), Mo (**5**), W(**6**)} (L = PhC(N*t*Bu)$_2$) contains the fluorosilylene moiety LSiF which coordinates to a transition metal carbonyl $M(CO)_5$ fragment. These compounds were prepared for the first time by metathesis reaction from the corresponding chloride with Me_3SnF. This approach marked a route to an easy access of low valent silicon fluorides.

■ EXPERIMENTAL SECTION

Syntheses were carried out under an inert gas atmosphere of dinitrogen in oven-dried glassware using standard Schlenk techniques, and other manipulations were accomplished in a dinitrogen filled glovebox. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. L(Cl)Si was prepared as reported in the literature.[6e,f] ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded with a Bruker Avance DPX 300, or a Bruker Avance DRX 500 spectrometer, using C_6D_6 as solvent. Chemical shifts δ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in sealed glass capillaries on a Büchi B-540 melting point apparatus.

General Procedure for the Synthesis of LSi(Cl)·M(CO)$_5$ {M = Cr (1), Mo (2), W(3)}. The respective $M(CO)_5(THF)$ complex was prepared by UV irradiation of the corresponding $M(CO)_6$ in THF as described in the literature.[21] The prepared $M(CO)_5(THF)$ solution was added to the flask containing L(Cl)Si. The mixture was stirred for 14 h at room temperature. Finally the solvent was removed *in vacuo* and extracted with toluene to obtain the corresponding $L(Cl)Si{\cdot}M(CO)_5$.

Compound 1. Quantity used: $Cr(CO)_6$, 1.00 g (4.54 mmol), L(Cl)Si, 1.34 g (4.54 mmol); yield (2.02 g, 91.4%). Mp 147−150 °C (d). Elemental analysis (%) calcd for $C_{20}H_{23}ClCrN_2O_5Si$ (486.94): C, 49.33; H, 4.76; N, 5.75. Found: C, 49.22; H, 4.62; N, 5.78. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.09 (s, 18H, $C(CH_3)_3$), 6.79−6.93 (m, 5H, C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 30.52 $C(CH_3)_3$, 55.15 ($C(CH_3)_3$), 127.91, 128.19, 128.29, 128.35, 129.68, 130.77 (C_6H_5), 174.22 (NCN), 217.61 (CO), 219.76 (CO), 222.95 (CO) ppm. $^{29}Si\{^{1}H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 92.34 ppm. EI-MS: *m/z*: 486 [M^+], 458 [M^+ − CO], 430 [M^+ − 2CO], 402 [M^+ − 3CO], 374 [M^+ − 4CO], 346 [M^+ − 5CO].

Compound 2. Quantity used: $Mo(CO)_6$, 1.00 g (3.79 mmol), L(Cl)Si, 1.12 (3.80 mmol); yield (1.70 g, 84.2%). Mp 140−143 °C (d). Elemental analysis (%) calcd for $C_{20}H_{23}ClMoN_2O_5Si$ (530.89): C, 45.25; H, 4.37; N, 5.28. Found: C, 45.16; H, 4.32; N, 5.12. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.09 (s, 18H, $C(CH_3)_3$), 6.79−6.94 (m, 5H, C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 30.72 $C(CH_3)_3$, 54.94 ($C(CH_3)_3$), 127.91, 128.25, 128.40, 128.56, 130.16, 130.77 (C_6H_5), 173.48 (NCN), 208.65 (CO), 210.50 (CO) ppm. $^{29}Si\{^{1}H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 72.75 ppm. EI-MS: *m/z*: 532 [M^+], 504 [M^+ − CO], 476 [M^+ − 2CO], 448 [M^+ − 3CO], 420 [M^+ − 4CO], 392 [M^+ −5CO].

Compound 3. Quantity used: $W(CO)_6$, 1.00 g (2.84 mmol), L(Cl)Si, 0.84 g (2.85 mmol); yield (1.50 g, 85.2%). Mp 142−145 °C (d). Elemental analysis (%) calcd for $C_{20}H_{23}ClN_2O_5SiW$ (618.79): C, 38.82; H, 3.75; N, 4.53. Found: C, 38.72; H, 3.72; N, 4.51. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.09 (s, 18H, $C(CH_3)_3$), 6.81−6.93 (m, 5H, C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 30.71 $C(CH_3)_3$, 54.98 ($C(CH_3)_3$), 128.29, 128.40, 128.47, 129.53, 130.05, 130.88 (C_6H_5), 174.47 (NCN), 199.06 (CO), 200.07 (CO) ppm. $^{29}Si\{^{1}H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 52.99 ppm. EI-MS: *m/z*: 618 [M^+], 590 [M^+ − CO], 562 [M^+ − 2CO], 534 [M^+ − 3CO], 506 [M^+ − 4CO], 478 [M^+ − 5CO].

General Procedure for the Synthesis of L(F)Si·M(CO)$_5$ {M = Cr (4), Mo (5), W(6)}. THF (60 mL) was added to a 100 mL Schlenk flask containing corresponding $L(Cl)Si{\cdot}M(CO)_5$ and Me_3SnF. The reaction mixture was stirred at room temperature for 36 h. After the completion of reaction, the solvent was removed *in vacuo* and the remaining substrate extracted with toluene (60 mL) to yield $L(F)Si{\cdot}M(CO)_5$.

Compound 4. Quantity used: $L(Cl)Si{\cdot}Cr(CO)_5$, 0.30 g (0.62 mmol), Me_3SnF, 0.12 g (0.66 mmol); yield (0.24 g, 82.7%). Mp 107−110 °C (d). Elemental analysis (%) calcd for $C_{20}H_{23}FCrN_2O_5Si$ (470.49): C, 51.06; H, 4.93; N, 5.95. Found: C, 50.96; H, 4.88; N, 5.86. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.05 (s, 18H, $C(CH_3)_3$), 6.82−6.91 (m, 5H, C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 30.91 $C(CH_3)_3$, 54.39 ($C(CH_3)_3$), 127.85, 128.20, 128.50, 128.62, 129.64, 130.75 (C_6H_5), 175.51 (NCN), 211.51 (CO), 220.34 (CO), 222.92 (CO) ppm. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, C_6D_6, 25 °C): δ 73.98 (d) ppm (J_{SiF} = 440 Hz). $^{19}F\{^{1}H\}$ NMR (282.40 MHz, C_6D_6, 25 °C): δ −89.95 ppm (J_{FSi} = 440 Hz). EI-MS: *m/z*: 470 [M^+], 442 [M^+ − CO], 414 [M^+ − 2CO], 386 [M^+ − 3CO], 358 [M^+ − 4CO], 330 [M^+ − 5CO].

Compound 5. Quantity used: $L(Cl)Si{\cdot}Mo(CO)_5$, 0.35 g (0.66 mmol), Me_3SnF, 0.12 g (0. 66 mmol); yield (0.26 g, 76.5%). Mp 100−103 °C (d). Elemental analysis (%) calcd for $C_{20}H_{23}FMoN_2O_5Si$ (514.43): C, 46.70; H, 4.51; N, 5.45. Found: C, 46.66; H, 4.42; N, 5.38. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.06 (s, 18H, $C(CH_3)_3$), 6.80−6.93 (m, 5H, C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 30.87 $C(CH_3)_3$, 54.16 ($C(CH_3)_3$), 127.90, 128.20, 128.53, 128.70, 130.22, 130.65 (C_6H_5), 174.59 (NCN), 208.66 (CO), 209.13 (CO) ppm. $^{29}Si\{^{1}H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 56.65 (d) ppm (J_{SiF} = 442 Hz). $^{19}F\{^{1}H\}$ NMR (282.40 MHz, C_6D_6, 25 °C): δ −90.33 ppm (J_{FSi} = 442 Hz). EI-MS: *m/z*: 516 [M^+], 488 [M^+ − CO], 460 [M^+ − 2CO], 432 [M^+ − 3CO], 404 [M^+ − 4CO], 376 [M^+ − 5CO].

Compound 6. Quantity used: $L(Cl)Si{\cdot}W(CO)_5$, 0.49 g (0.79 mmol), Me_3SnF, 0.15 g (0.82 mmol); yield (0.42 g, 87.5%). Mp 110−113 °C (d). Elemental analysis (%) calcd for $C_{20}H_{23}FN_2O_5SiW$ (602.33): C, 39.88; H, 3.85; N, 4.65. Found: C, 39.83; H, 3.81; N, 4.62. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.07 (s, 18H, $C(CH_3)_3$), 6.80−6.91 (m, 5H, C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 30.86 $C(CH_3)_3$, 54.19 ($C(CH_3)_3$), 127.81, 128.30, 128.62, 128.64, 130.17, 130.75 (C_6H_5), 175.53 (NCN), 199.18 (CO), 200.48 (CO) ppm. $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, C_6D_6, 25 °C): δ 41.79 (d) ppm (J_{SiF} = 428 Hz). $^{19}F\{^{1}H\}$ NMR (282.40 MHz, C_6D_6, 25 °C): δ −93.20 ppm (J_{FSi} = 428 Hz). EI-MS: *m/z*: 602 [M^+], 574 [M^+ − CO], 546 [M^+ − 2CO], 518 [M^+ − 3CO], 490 [M^+ − 4CO], 462 [M^+ − 5CO].

Crystal Structure Determination. Suitable single crystals for X-ray structural analysis of **1**−**4** and **6** were obtained by slow evaporation of their corresponding toluene solutions, and the crystals were mounted at low temperature in inert oil under argon atmosphere by applying the X-Temp2 device.[22] The diffraction data were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Ag microsource with INCOATEC Quazar mirror optics (λ = 0.5608 Å). The data were integrated with SAINT,[23] and an empirical absorption correction with SADABS[24] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-97).[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structures of **2**, **3**, and **6**. CIF files for **1**, **2**, **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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