Synthesis and Reactivity of Functionalized Dimethylsilyl Complexes of the Formula (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2X$); New Base-Stabilized Silylene Complexes, Novel Lewis Acid Adducts, and Evidence for Base-Free Silylene Complexes

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Reactions of (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2H$) (**1**) and $CHCl_3$, CBr_4, and CHI_3 give halosilyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2X$) [X = Cl (**2**), Br (**3**), I (**4**); 66–84%]. Addition of Me_3SiOTf to **2** gives triflate (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2OTf$) (**5**; 97%), which in turn reacts with $(Me_2N)_3S^{\oplus}$ $[SiMe_3F_2]^{\ominus}$ to give (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2F$) (**6**; 77%). Reaction of **5** and pyridine gives the base-stabilized silylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{SiMe_2(NC_5H_5)\}]^{\oplus}TfO^{\ominus}$ (**7**; 84%). CH_2Cl_2 solutions of (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**8**) or **2** and Lewis acids are studied by IR and NMR. As assayed by IR, **8**/ECl_3 solutions (E = B, Al) show ReNO – ECl_3 (major) and Re – ECl_3 (minor) adducts. Solutions of **2**/BCl_3 show analogous adducts (–78°C), and in the presence of excess BCl_3 (η^5-C_5H_5)Re(NO – BCl_3)(PPh_3)($SiMe_2Cl$) (**11**) crystallizes. Solutions of **2**/$AlCl_3$ show uncomplexed **2** and Re – $AlCl_3$ (major) and ReNO – $AlCl_3$ (minor) adducts. In contrast to **2** – **7** and **2**/BCl_3, ^{1}H- and ^{13}C-NMR spectra of **2**/$AlCl_3$ suggest an equilibrium with the base-free silylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=SiMe_2)]^{\oplus}X^{\ominus}$.

The synthesis of transition metal silylene complexes $[L_nM=SiR_2]^{n\oplus}$ has been under intensive study in several laboratories[1–6]. To date, only "base-stabilized" adducts $[L_nM\overset{\cdots}{=}Si(\leftarrow:B)R_2]^{n\oplus}$ have proved isolable[2–5,6g]. However, silylene complexes have been proposed as intermediates in many transformations[6,7], some of which are industrially significant[7].

We have recently shown that the triflate-substituted germyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2OTf$) (OTf = OSO_2CF_3) is in facile equilibrium with the germylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=GePh_2)]^{\oplus}TfO^{\ominus}$[8]. Furthermore, the crystal structure of the germyl triflate exhibits several geometric features that are strikingly close to those that would be expected of the germylene complex. Hence, we sought to synthesize and explore the chemical and physical properties of related silyl complexes.

In this paper, we report (1) high-yield syntheses of functionalized silyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2X$), including a cationic base-stabilized silylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{SiMe_2(B)\}]^{\oplus}TfO^{\ominus}$, (2) reactions of the silyl complexes and related compounds with Lewis acids, (3) the isolation and structural characterization of a nitrosyl ligand/Lewis acid adduct, and (4) dynamic NMR behavior that suggests Lewis acid promoted equilibria involving base-free silylene complexes. A portion of this study has been communicated[9].

Results

1. Syntheses of New Functionalized Dimethylsilyl Complexes

Many trialkylsilanes R_3SiH undergo ready free-radical halogenation to trialkylhalosilanes R_3SiX[10]. Accordingly, the hydridosilyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2H$) (**1**) was synthesized from the nucleophilic rhenium "anion" $Li^{\oplus}[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^{\ominus}$ and chlorosilane Me_2SiHCl as described earlier[11]. Complex **1** was dissolved in $CHCl_3$ and kept at 50°C (Scheme 1). Over the course of 4 h, **1** disappeared as a new complex cleanly formed, as assayed by ^{31}P NMR. Workup gave the chlorosilyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2Cl$) (**2**) in 84% yield. Attempts to prepare **2** by silylation of $Li^{\oplus}[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^{\ominus}$ were unsuccessful[11].

Next, **1** was treated with the halogenating agents CBr_4 (0.5 equiv; 3 h) and CHI_3 (1.0 equiv; 8 h) in C_6H_6 at room temperature. Workup gave bromosilyl and iodosilyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2Br$) (**3**; 73%) and (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2I$) (**4**; 66%). Halosilyl complexes **2** – **4** slowly decomposed in CH_2Cl_2 (**4** > **2**) to the known hydride complex (η^5-C_5H_5)Re(NO)(PPh_3)(H)[12].

Complexes **2** – **4**, and all other new compounds isolated below, were characterized by IR and NMR (^{1}H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy (Table 1). General features were similar to those previously reported for other rhenium silyl complexes of the formula (η^5-C_5H_5)Re(NO)(PPh_3)(SiR_2X)[11]. In all cases, the diastereotopic methyl groups gave separate ^{1}H- and ^{13}C-NMR resonances. For some compounds, microanalyses (experimental section) bordered on limits conventionally associated with analytical purity. This was attributed to the air-sensitivity and moderate thermal stability at room temperature of the functionalized silyl complexes, and/or the presence of interfering element combinations.

The chlorogermyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2Cl$) and Me_3SiOTf have been shown to react to give

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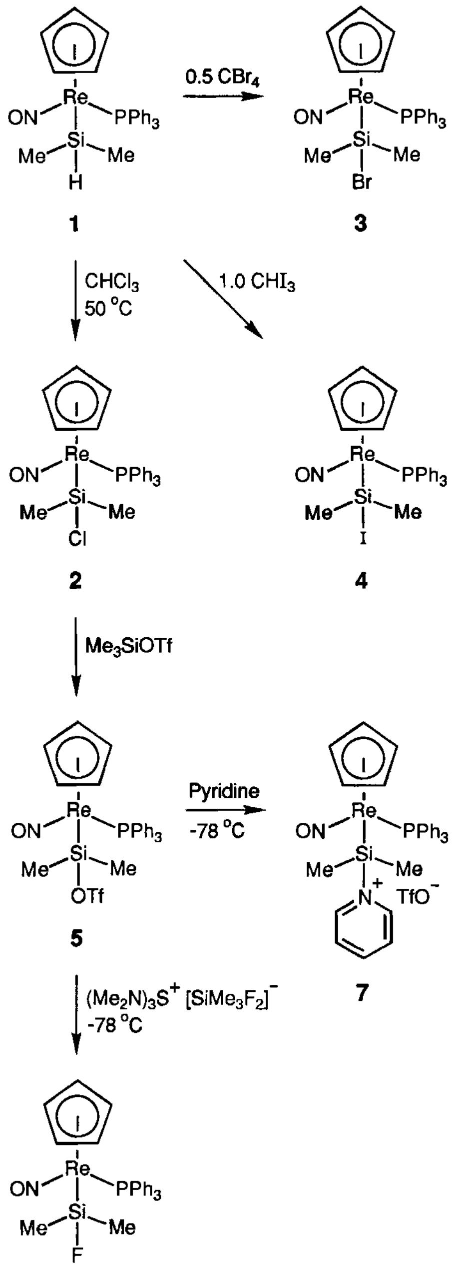
Scheme 1. Preparation of new rhenium silyl complexes



the triflate-substituted germyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2OTf$)[8]. Also, Tilley has found that the ruthenium chlorosilyl complex (η^5-C_5Me_5)Ru(PMe_3)$_2$($SiPh_2Cl$) and Me_3SiOTf react to give triflate (η^5-C_5Me_5)Ru(PMe_3)$_2$($SiPh_2OTf$)[3]. Thus, chlorosilyl complex **2** and Me_3SiOTf were combined in C_6H_6 (25 °C, 2 h; Scheme 1). Workup gave the triflate-substituted silyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2OTf$) (**5**; 97%).

Complex **5** exhibited a $\nu(CF_3SO_3)$ (1366 cm^{-1}) in the IR spectrum that was diagnostic of a covalently bound triflate[13]. The ^1H-NMR spectrum of **5** showed distinct, sharp resonances for the diastereotopic methyl groups, even at 34 °C in CD_2Cl_2 and 83 °C in C_6D_6. This bounds $\Delta G^{\neq}$ for any process capable of equivalencing the methyl groups as greater than 14.8 kcal/mol in CD_2Cl_2 (307 K) and 18.3 kcal/mol in C_6D_6 (356 K)[14]. In contrast, analogous NMR resonances of the triflate-substituted germyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(GeR_2OTf) (R = Ph[8], Me[15]; CD_2Cl_2) coalesce below room temperature.

Substitution of the triflate moiety in **5** was attempted. First, **5** and the fluoride ion source $(Me_2N)_3S^{\oplus}[SiMe_3F_2]^{\ominus}$ (TAS-F)[16] were dissolved in CH_2Cl_2 at −78 °C (Scheme 1). Workup gave the fluorosilyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2F$) (**6**; 77%). The ^1H- and ^{13}C-NMR resonances for the diastereotopic methyl groups of **6** exhibited ^{19}F coupling (Table 1).

Finally, a base-stabilized silylene complex was sought. Thus, the reaction of **5** and pyridine in CH_2Cl_2 was monitored by ^{31}P NMR at −78 °C (Scheme 1). Conversion to the pyridinium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{SiMe_2(NC_5H_5)\}]^{\oplus}$-$TfO^{\ominus}$ (**7**) was complete within 5 min. Workup gave **7** in 84% yield. The IR spectrum of **7** exhibited a $\nu(CF_3SO_3)$ (1275 cm^{-1}) that was diagnostic of an ionic triflate[13], and a symmetric in-plane bending vibration for pyridine C−H at 1617 cm^{-1}. This mode characteristically increases from that of neat pyridine (1578 cm^{-1}) in pyridinium salts and coordination compounds[17].

2. Model Reactions of BCl_3 and $AlCl_3$

As a prelude to reactions of **2** described below, we sought data on interactions of Lewis acids BCl_3 and $AlCl_3$ with other (η^5-C_5H_5)Re(NO)(PPh_3)(X) complexes. CH_2Cl_2 solutions of methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(Me)[18] (**8**) exhibited a ν_{NO} at 1623 cm^{-1} in the IR spectrum. These were treated with 1 equiv. of BCl_3 or $AlCl_3$ at −78 °C (Scheme 2). Ambient-temperature IR spectra of the **8**/BCl_3 solution showed a ν_{NO} at 1392 cm^{-1} (major) and 1752 cm^{-1} (minor), as summarized in Table 2. IR spectra of **8**/$AlCl_3$ gave a ν_{NO} at 1447 cm^{-1} (major) and 1767 cm^{-1} (minor). In neither case was uncomplexed **8** detected. Also, the major ν_{NO} were much lower than commonly found in terminal, linear nitrosyl complexes[19].

Scheme 2. Reactions of methyl complex **8** withLewis acids ECl_3

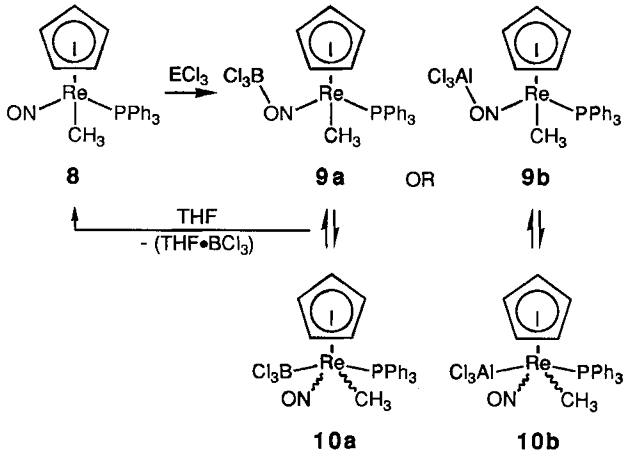
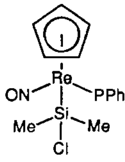
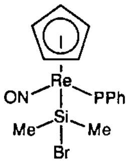
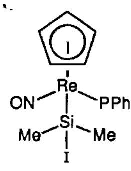
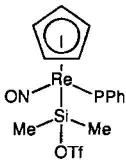
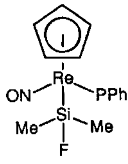
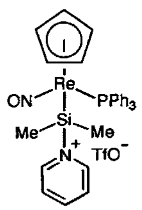


Table 1. Spectroscopic characterization of new rhenium silyl complexes

Complex	IR (KBr) [cm^{-1}]	^1H NMR[a]	$^{13}C\{^1H\}$ NMR[b]	$^{31}P\{^1H\}$ NMR[c]
 **2**	ν_{NO} 1657 (vs)	7.52 (m, 6H of 3 C_6H_5), 6.96 (m, 9H of 3 C_6H_5); 4.63 (s, C_5H_5); 0.94 (s, CH_3), 0.68 (s, $C'H_3$)	PPh_3 at: 138.4 (d, J = 53.0 Hz, *i*), 133.3 (d, J = 11.0 Hz, *o*), 130.2 (s, *p*), 128.4 (d, J = 10.6 Hz, *m*); 89.2 (s, C_5H_5); 13.0 (s, CH_3), 11.6 (s, $C'H_3$)	23.0 (s)
 **3**	ν_{NO} 1660 (vs)	7.49 (m, 6H, 3 C_6H_5), 6.96 (m, 9H, 3 C_6H_5); 4.66 (s, C_5H_5); 1.06 (s, CH_3), 0.85 (s, $C'H_3$)	PPh_3 at: 138.3 (d, J = 53.1 Hz, *i*), 133.8 (d, J = 10.7 Hz, *o*), 130.3 (s, *p*), 128.4 (d, J = 13.9 Hz, *m*); 89.8 (s, C_5H_5); 13.2 (s, CH_3), 12.2 (s, $C'H_3$)	22.8 (s)
 **4**	ν_{NO} 1664 (vs)	7.43 (m, 6H of 3 C_6H_5), 6.92 (m, 9H of 3 C_6H_5); 4.65 (s, C_5H_5); 1.24 (s, CH_3), 1.12 (s, $C'H_3$)	PPh_3 at: 138.1 (d, J = 53.1 Hz, *i*), 133.7 (d, J = 11.0 Hz, *o*), 130.3 (d, J = 2.3 Hz, *p*), 128.5 (d, J = 10.5 Hz, *m*); 90.7 (s, C_5H_5); 13.7 (s, CH_3), 12.7 (s, $C'H_3$)	22.6 (s)
 **5**	ν_{NO} 1675 (vs); $\nu_{CF_3SO_3}$ 1366 (vs), 1198 (s)[d]	7.39 (m, 6H of 3 C_6H_5), 6.95 (m, 9H of 3 C_6H_5); 4.62 (s, C_5H_5); 0.71 (s, CH_3), 0.67 (s, $C'H_3$)	PPh_3 at: 137.6 (d, J = 53.8 Hz, *i*), 133.5 (d, J = 10.8 Hz, *o*), 130.5 (d, J = 2.3 Hz, *p*), 128.6 (d, J = 10.4 Hz, *m*); 119.6 (q, J_{CF} = 318.3 Hz, CF_3); 88.7 (s, C_5H_5); 9.7 (s, CH_3), 8.4 (s, $C'H_3$)	21.6 (s)
 **6**	ν_{NO} 1644 (vs)	7.61 (m, 6H of 3 C_6H_5), 6.99 (m, 9H of 3 C_6H_5); 4.56 (s, C_5H_5); 0.70 (d, J_{HF} = 8.3 Hz, CH_3), 0.62 (d, J_{HF} = 8.2 Hz, $C'H_3$)	PPh_3 at: 138.7 (d, J = 52.6 Hz, *i*), 133.9 (d, J = 11.2 Hz, *o*), 130.0 (d, J = 2.0 Hz, *p*), 128.3 (d, J = 10.1 Hz, *m*); 87.3 (s, C_5H_5); 10.0 (d, J_{CF} = 16.3 Hz, CH_3), 8.3 (d, J_{CF} = 15.5 Hz, $C'H_3$)	24.5 (s)
 **7**	ν_{NO} 1659 (vs); $\nu_{CF_3SO_3}$ 1275 (vs), 1154 (s), 1031 (s); $\delta_{C_5H_5N}$ 1617 (s)	8.73 (d, J = 5.2 Hz, 2H of C_5H_5N)[e], 8.29 (t, J = 7.8 Hz, 1H of C_5H_5N), 7.93 (t, J = 7.1 Hz, 2H of C_5H_5N); 7.42 (m, 15H of 3 C_6H_5); 4.98 (s, C_5H_5); 0.93 (s, CH_3), 0.18 (s, $C'H_3$)	C_5H_5N at[e]: 145.9 (s, *o*), 143.8 (s, *p*), 127.7 (s, *m*); PPh_3 at: 136.6 (d, J = 55.0 Hz, *i*), 133.5 (d, J = 10.8 Hz, *o*), 131.2 (s, *p*), 129.1 (d, J = 10.5 Hz, *m*); 121.3 (q, J_{CF} = 321.5 Hz, CF_3); 89.6 (s, C_5H_5); 8.5 (s, CH_3), 6.0 (s, $C'H_3$)	20.0 (s)[e]

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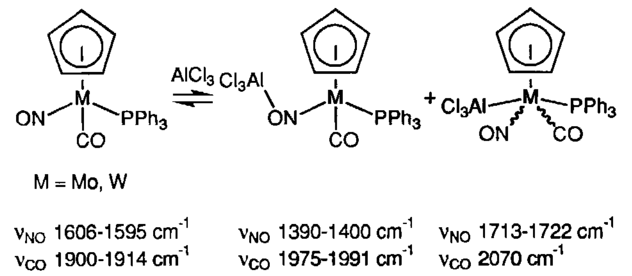
[a] At 300 MHz and ambient probe temperature in C_6D_6 and referenced to residual C_6D_5H (δ = 7.15). — [b] At 75 MHz and ambient probe temperature in C_6D_6 and referenced to solvent (δ = 128.00). All couplings are to ^{31}P unless noted otherwise. Assignments of resonances for phenyl C were made as described in footnote c of Table 1 in: W. E. Buhro, S. Georgiou, J. M. Fernández, A. T. Patton, C. E. Strouse, J. A. Gladysz, *Organometallics* **5** (1986) 956. — [c] At 121 MHz and ambient probe temperature in C_6D_6 and referenced to external 85% H_3PO_4. — [d] IR (CD_2Cl_2) [cm^{-1}]: ν_{NO} 1670 (vs); $\nu_{CF_3SO_3}$ 1364 (vs). — [e] This NMR spectrum was recorded in CD_2Cl_2.

Scheme 3. Some previously reported nitrosyl complex/Lewis acid adducts



Reactions of nitrosyl complexes (η^5-C_5H_5)M(NO)(PPh_3)(CO) (M = Mo, W; ν_{NO} = 1606–1595 cm^{-1}; ν_{CO} = 1900–1914 cm^{-1}) and $AlCl_3$ in CH_2Cl_2 have been investigated previously[20]. Two major products formed (Scheme 3). One exhibited a sharply lower ν_{NO} (1390–1400 cm^{-1}) and a somewhat increased ν_{CO} (1975–1991 cm^{-1}), and was formulated as the nitrosyl ligand/$AlCl_3$ adduct (η^5-C_5H_5)M(NO–$AlCl_3$)(PPh_3)(CO). The other exhibited distinctly higher ν_{NO} (1713–1722 cm^{-1}) and ν_{CO} (2070 cm^{-1}), and was formulated as the metal/$AlCl_3$ adduct (η^5-C_5H_5)M(NO)(PPh_3)(CO)($AlCl_3$). A number of nitrosyl ligand/Lewis acid adducts have also been spectroscopically characterized[21,22], and some have been isolated in pure form[22]. All exhibit lowered ν_{NO}.

Accordingly, the ν_{NO} of **8**/BCl_3 and **8**/$AlCl_3$ at 1392–1447 cm^{-1} were attributed to nitrosyl ligand/Lewis acid adducts (η^5-C_5H_5)Re(NO–ECl_3)(PPh_3)(Me) (**9a,b**; Scheme 2). Similarly, the ν_{NO} at 1752–1767 cm^{-1} were attributed to Re/Lewis acid adducts (η^5-C_5H_5)Re(NO)(PPh_3)(Me)(ECl_3) (**10a,b**). The latter bear a close relationship to cationic five-coordinate rhenium complexes of the formula [(η^5-C_5H_5)Re(NO)(PPh_3)(R)(H)]$^{\oplus}$X$^{\ominus}$, which exhibit a ν_{NO} of 1750 to 1769 cm^{-1} in the IR spectrum[8b,23].

Analogous reactions of **8** and Lewis acids ECl_3 were conducted in CD_2Cl_2 at −78°C, and low-temperature NMR spectra were recorded (Table 2). Only one set of resonances was observed in each sample, indicating the rapid equilibration of all adducts on the NMR time scale. The ^{1}H-NMR resonances for the η^5-C_5H_5 ligand of **8**/$AlCl_3$ and **8**/BCl_3 shifted 0.3 ppm downfield from that of **8** (δ = 4.90; −76°C). The ^{31}P-NMR resonances for the PPh_3 ligand were ca. 10 ppm upfield from that of **8** (δ = 25.0). The ^{11}B-NMR resonance of **8**/BCl_3 (δ = 6.8) was upfield of that of BCl_3 (δ = 41.9) and in a range characteristic of Lewis base/BCl_3 adducts[24]. The ^{27}Al-NMR spectrum of **8**/$AlCl_3$ showed a very broad resonance (Table 2), as is normally observed for Lewis base/$AlCl_3$ adducts[25].

An **8**/BCl_3 solution was treated with the Lewis base THF (2 equiv.). The ν_{NO} at 1392 and 1752 cm^{-1} were replaced by ν_{NO} at 1623 cm^{-1} (**8**, major) and 1665 cm^{-1} (minor). The latter absorption slowly increased in intensity while the former decreased, and closely matched that of the known chloride complex (η^5-C_5H_5)Re(NO)(PPh_3)(Cl)[26].

3. Reactions of Chlorosilyl Complex 2 and BCl$_3$

Reactions of functionalized silyl complexes and Lewis acids were probed next. Thus, a CH_2Cl_2 solution of **2** (ν_{NO} = 1656 cm^{-1}; CH_2Cl_2) was treated with 1 equiv. of BCl_3 at −78°C. IR spectra were recorded in a vacuum-jacketed cell at −78°C[27], and showed ν_{NO} at 1395 cm^{-1} (major) and 1759 cm^{-1} (minor). The sample was warmed to −20°C. The ν_{NO} at 1759 cm^{-1} markedly intensified, whereas that at 1395 cm^{-1} nearly vanished. In no case was uncomplexed **2** observed. By analogy to Schemes 2, 3, these data suggest the adduct structures shown in Scheme 4.

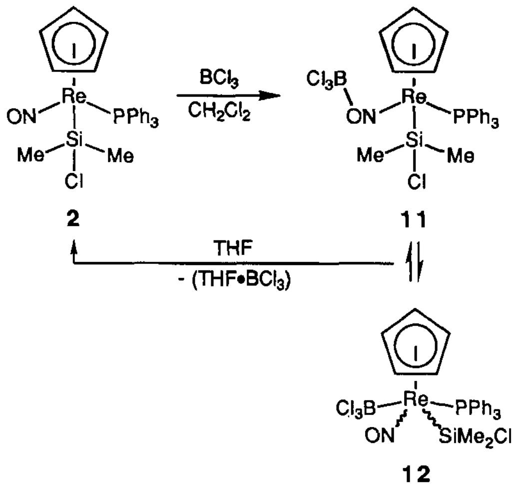
A similar reaction was conducted in CD_2Cl_2 at −78°C, and NMR spectra were recorded (Table 2). Only one set of

Table 2. Spectroscopic characterization of Lewis acid adducts of rhenium complexes

Solution	IR (CH_2Cl_2) [cm^{-1}]	^{11}B or ^{27}Al NMR[a,b]	^{1}H NMR[c]	^{31}P{^{1}H} NMR[d]
8/BCl_3	ν_{NO} 1392 (s), 1752 (w)[e]	6.8 (br. s)	7.36 (m, 15H of 3 C_6H_5); 5.28 (s, C_5H_5); 1.77 (d, J_{HP} = 5.8 Hz, CH_3)	13.8 (s)
8/$AlCl_3$	ν_{NO} 1447 (s), 1767 (w)[e]	93.3 (br. s), $\Delta\nu_{1/2}$ = 349.7 Hz)	7.36 (m, 15H of 3 C_6H_5); 5.28 (s, C_5H_5); 1.66 (d, J_{HP} = 5.8 Hz, CH_3)	14.9 (s)
2/BCl_3	ν_{NO} 1395 (s), 1759 (w)[f]	7.1 (br. s)	7.39 (m, 15H of 3 C_6H_5); 5.21 (s, C_5H_5); 0.54 (s, CH_3), 0.33 (s, C′H_3)[g]	13.8 (s)
2/$(AlCl_3)_{1/x}$	ν_{NO} 1413 (w), 1650 (s), 1764 (w)[f]	102.0 (s, $\Delta\nu_{1/2}$ = 22.3 Hz), 93.3 (br. s, $\Delta\nu_{1/2}$ = 691.8 Hz)	7.38 (m, 15H of 3 C_6H_5); 5.20 (s, C_5H_5); 0.41 (s, CH_3); 0.35 (s, C′H_3)	13.1 (s)
2/$AlCl_3$	ν_{NO} 1413 (w), 1651 (m), 1767 (m)[f]	102.0 (s, $\Delta\nu_{1/2}$ = 23.2 Hz), 94.0 (br. s, $\Delta\nu_{1\%2}$ = 677.2 Hz)	7.51 (m, 15H of 3 C_6H_5); 5.23 (s, C_5H_5); 0.48 (s, br, 2 CH_3)[g]	12.6 (s)
2/$(AlCl_3)_2$	ν_{NO} 1461/1454 (s), 1765/1759 (w)[h]	98.1 (br. s, $\Delta\nu_{1/2}$ = 2318.3 Hz)	7.44 (m, 15H of 3 C_6H_5); 5.46 (s, C_5H_5); 0.76 (s, br, 2 CH_3)[g]	11.3 (s)

[a] At 96 MHz in CD_2Cl_2 (−21°C) and referenced to external Et_2O–BF_3. — [b] At 78 MHz in CD_2Cl_2 (−21°C) and referenced to external $Al(H_2O)_6^{3\oplus}$. — [c] At 300 MHz in CD_2Cl_2 (−76°C) and referenced to residual $CHDCl_2$ at δ = 5.32. — [d] At 121 MHz in CD_2Cl_2 (−76°C) and referenced to external 85% H_3PO_4. — [e] Recorded at ambient temperature. — [f] Recorded at −78°C. — [g] Selected ^{13}C-NMR data (75 MHz, CD_2Cl_2): **2**/BCl_3 (−72°C): δ = 93.3 (s, C_5H_5), 12.9 (s, CH_3), 10.4 (s, C′H_3); **2**/$AlCl_3$ (−76°C): δ = 93.3 (s, C_5H_5), 11.2 (s, 2 CH_3); **2**/$(AlCl_3)_2$ (−21°C): δ = 94.5 (s, C_5H_5), 12.1 (s, 2 CH_3). — [h] Recorded immediately after solution (−78°C) was transferred to cell (ambient temperature).

Scheme 4. Reaction of chlorosilyl complex **2** and BCl_3



resonances was observed, indicating the rapid equilibration of all adducts on the NMR time scale. The ^1H-NMR resonances for the η^5-C_5H_5 and methyl groups of **2**/BCl_3 were downfield of those of **2** (CD_2Cl_2, −72°C: δ = 4.96, 0.47, 0.08), and the ^{31}P-NMR resonance for the PPh_3 ligand was upfield. The diastereotopic methyl groups exhibited separate ^1H- and ^{13}C-NMR resonances.

A second equiv. of BCl_3 was added to a **2**/BCl_3 solution. Extremely air-sensitive, orange microcrystals precipitated. Crystallization was considerably slower if only 1.5 equiv. of BCl_3 was present. In a separate experiment, a CH_2Cl_2 solution of **2** and BCl_3 (2 equiv.) was kept at −25°C. Over the course of several days, orange cubes of **11**[28] formed and were isolated in 72% yield.

Samples of **11** would not dissolve in cold CH_2Cl_2, but did dissolve at room temperature. NMR spectra (CD_2Cl_2, ambient temperature) closely matched those of **2**/BCl_3 above. A fresh solution was cooled to −78°C and transferred to an IR cell (room temperature). A spectrum was immediately recorded, and showed ν_{NO} at 1395 cm^{-1} (major) and 1759 cm^{-1} (minor). An IR spectrum was also acquired in KBr at room temperature, and showed ν_{NO} at 1395 cm^{-1} (major) and 1759 cm^{-1} (minor). The KBr matrix was kept under nitrogen at room temperature for 2 h. The band at 1395 cm^{-1} diminished slightly, and the band at 1759 cm^{-1} intensified slightly.

A CD_2Cl_2 solution of **2**/$(BCl_3)_{1.5}$ was cooled to −78°C and treated with THF (2 equiv.). A ^1H-NMR spectrum showed the clean formation of precursor **2**. An aliquot was transferred to a IR cell (room temperature), and a spectrum was immediately recorded. The ν_{NO} at 1395 and 1750 cm^{-1} had nearly vanished, and were replaced by that of **2**.

4. Crystal Structure of 11

X-ray data of **11** were collected as described in Table 3. Two crystals were examined, and both underwent considerable decomposition in the X-ray beam. Refinement (Experimental) showed **11** to be a CH_2Cl_2 monosolvate of the nitrosyl ligand/BCl_3 adduct (η^5-C_5H_5)Re(NO−BCl_3)(PPh_3)($SiMe_2Cl$), as shown in Figure 1. An attempt was made to collect a data set at liquid-nitrogen temperature. However, **11** only weakly diffracted upon cooling, suggestive of a phase transition. Microanalytical data (Experimental) suggest that **11** is prone to solvate loss.

The atomic coordinates of **11**, and selected bond lengths, bond angles, and torsion angles are summarized in Tables 3, 4. A complete listing of bond lengths and angles is given elsewhere[15]. The N−O−B linkage was sharply bent (107°), and an oxygen lone-pair position was calculated based upon an idealized trigonal geometry. The B/O/lone pair and Si/Re/N/O planes were found to be essentially coplanar (< 7°). This feature is relevant to geometrical analyses given below.

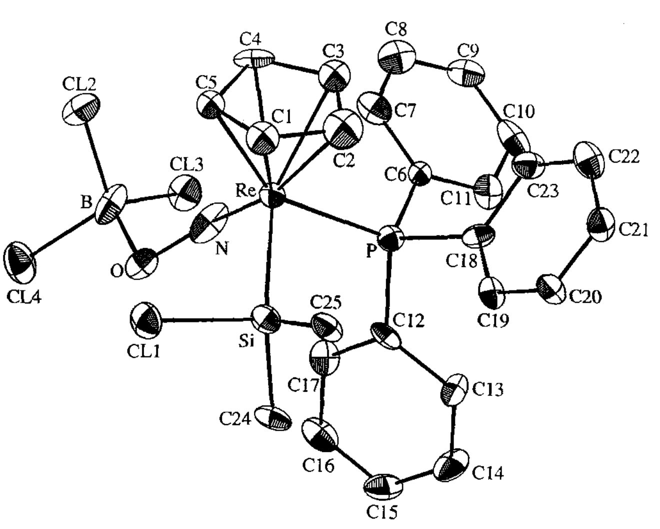


Figure 1. Crystal structure of **11** · CH_2Cl_2*)

Table 3. Summary of Crystallographic Data for **11** · CH_2Cl_2

Molecular formula: $C_{26}H_{28}BCl_6NOPReSi$; molecular mass: 839.308 g/mol; crystal system: monoclinic; space gorup: $P2_1/c$ (no. 14); cell dimensions (16°C): a = 9.498(2), b = 17.021(2), c = 19.794(2) Å; β = 96.44(1)°; V = 3179.63 Å^3; Z = 4.0; d_{found} (25°C) = 1.787 g/cm$^{3\,a)}$; $d_{calcd.}$ (16°C) = 1.753 g/cm^3; crystal dimensions: 0.40 × 0.30 × 0.17 mm; radiation: Mo-K_α (λ = 0.71073 Å); data collection method: Θ-2Θ; scan speed: variable (3.0−8.0°/min); reflections measured: 6018; range $+h$, $+k$, $\pm l$; scan range: $K_{\alpha1} = -1.3$ to $K_{\alpha2} = +1.6$; no. of reflections between standards: 98; total unique data: 5595; observed data [$I > 3\sigma(I)$]: 2498; μ = 44.912 cm^{-1}; min./max. absorption correction: 54.91/99.99; no. of variables: 318; goodness of fit: 5.17; $R = \Sigma \| F_o | - | F_c \| / | F_o | = 0.0604$; $R_w = [w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2} = 0.0756$; Δ/σ (max.) = 0.06; $\Delta\varrho$(max.) = 2.29 e/Å^3, 1.13 Å from Re

[a] Flotation (CCl_4/CH_2I_2).

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Table 4. Atomic coordinates and equivalent isotropic thermal parameters [Å^2] for **11** · CH_2Cl_2[a]

Atom	x	y	z	B
Re	0.1177(1)	0.18855(5)	0.26233(5)	3.45(2)
Cl1	0.4762(7)	0.1183(5)	0.2521(4)	6.3(2)
Cl2	0.2167(8)	0.2771(5)	0.4508(3)	6.5(2)
Cl3	0.1136(7)	0.4144(4)	0.3658(4)	5.8(2)
Cl4	0.4196(8)	0.4074(5)	0.4258(4)	7.3(2)
Cl5	0.2773(9)	0.6939(7)	0.0604(6)	10.9(3)
Cl6	0.511(1)	0.6021(7)	0.0252(7)	13.7(4)
P	-0.0237(6)	0.2645(3)	0.1794(3)	3.5(1)
Si	0.2984(7)	0.1552(4)	0.1860(4)	4.3(2)
O	0.311(2)	0.313(1)	0.3293(7)	4.6(3)
N	0.199(3)	0.259(1)	0.3004(9)	5.8(6)
C1*	0.129(3)	0.056(2)	0.274(1)	5.8(6)
C2*	0.002(4)	0.074(2)	0.233(2)	8.3(9)
C3*	-0.077(3)	0.118(2)	0.279(1)	5.4(6)
C4	0.004(2)	0.125(2)	0.341(1)	5.6(6)
C5*	0.141(2)	0.084(1)	0.332(1)	4.3(5)
C6*	-0.171(2)	0.319(1)	0.2108(9)	2.9(4)
C7	-0.190(2)	0.317(1)	0.277(1)	5.0(6)
C8	-0.306(3)	0.357(2)	0.302(1)	6.0(7)
C9	-0.397(3)	0.397(1)	0.258(1)	5.6(6)
C10	-0.379(2)	0.400(1)	0.190(2)	5.7(7)
C11	-0.259(3)	0.360(2)	0.166(1)	5.3(6)
C12	0.065(2)	0.342(1)	0.140(1)	3.7(5)
C13	0.035(3)	0.358(1)	0.069(1)	4.7(6)
C14	0.103(3)	0.419(1)	0.039(1)	5.8(7)
C15	0.194(3)	0.467(2)	0.078(1)	5.9(6)
C16	0.217(3)	0.456(1)	0.147(1)	5.6(7)
C17	0.145(3)	0.396(1)	0.177(1)	4.6(6)
C18	-0.110(2)	0.203(1)	0.113(1)	4.0(5)
C19	-0.041(2)	0.172(1)	0.065(1)	3.8(5)
C20	-0.096(2)	0.118(1)	0.019(1)	4.6(6)
C21	-0.229(2)	0.092(2)	0.021(1)	5.1(6)
C22	-0.307(3)	0.120(1)	0.072(1)	5.6(6)
C23	-0.250(2)	0.176(1)	0.118(1)	4.9(6)
C24	0.370(2)	0.240(2)	0.140(1)	5.2(6)
C25	0.271(2)	0.071(2)	0.126(1)	4.8(6)
C26	0.459(4)	0.688(2)	0.059(2)	9(1)
B	0.257(4)	0.350(2)	0.392(1)	6.1(8)

[a] Starred atoms were refined isotropically. Atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) $[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 5. Selected bond lengths [Å], bond angles [°], and torsion angles [°] in **11** · CH_2Cl_2

Re-N	1.568(9)	P-C12	1.79(1)
N-O	1.47(1)	P-C18	1.80(1)
O-B	1.53(1)	Re-C1	2.27(1)
B-Cl2	1.78(1)	Re-C2	2.28(2)
B-Cl3	1.77(2)	Re-C3	2.26(1)
B-Cl4	1.88(2)	Re-C4	2.27(1)
Re-Si	2.476(3)	Re-C5	2.25(1)
Si-Cl1	2.113(4)	C1-C2	1.41(2)
Si-C24	1.87(1)	C1-C5	1.25(1)
Si-C25	1.86(1)	C2-C3	1.45(2)
Re-P	2.382(3)	C3-C4	1.37(2)
P-C6	1.849(9)	C4-C5	1.51(1)
P-Re-N	97.4(3)	Re-Si-C25	120.8(3)
Si-Re-P	94.6(1)	Cl1-Si-C24	102.6(4)
Si-Re-N	97.4(4)	Cl1-Si-C25	102.2(4)
Re-N-O	163.7(8)	C24-Si-C25	108.4(6)
N-O-B	106.8(8)	Re-P-C6	115.6(3)
Cl2-B-O	110.5(9)	Re-P-C12	116.2(3)
Cl3-B-O	109.9(8)	Re-P-C18	111.2(3)
Cl4-B-O	100(1)	C2-C1-C5	115(1)
Cl2-B-Cl3	114(1)	C1-C2-C3	103(1)
Cl2-B-Cl4	110.6(7)	C2-C3-C4	109(1)
Cl3-B-Cl4	111.1(8)	C3-C4-C5	105(1)
Re-Si-Cl1	104.5(2)	C1-C5-C4	107(1)
Re-Si-C24	115.6(3)		
P-Re-Si-Cl1	-162.0(3)	N-Re-Si-C25	-178.1(11)
N-Re-Si-Cl1	-63.9(8)	P-Re-Si-C24	-50.0(9)
P-Re-Si-C25	83.8(9)	N-Re-Si-C24	48.1(11)

5. Reactions of Chlorosilyl Complex 2 and $AlCl_3$

A CH_2Cl_2 solution of **2** was treated with 1 equiv. of $AlCl_3$ at −78°C (Scheme 5). Some $AlCl_3$ remained undissolved. An aliquot of this substoichiometric solution [**2**/$(AlCl_3)_{1/x}$] was taken. An IR spectrum was recorded at −78°C and showed ν_{NO} at 1764 (m), 1650 (s, major), and 1409 cm^{-1} (w, minor), as summarized in Table 2. The aliquot was warmed to −20°C for 15 min in the cell. The minor band *shifted* (1413 cm^{-1}) and intensified slightly; the major one (1650 cm^{-1}) was assigned to starting material **2**.

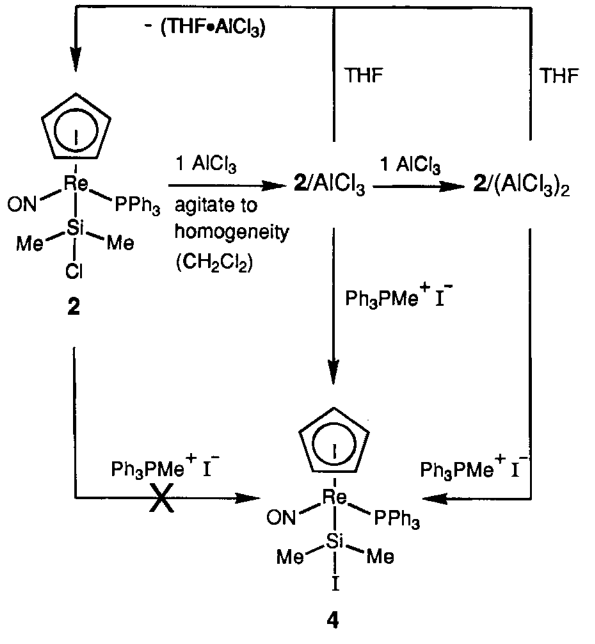
The original sample was vigorously agitated at −78°C, and became homogeneous (**2**/$AlCl_3$)[28]. An aliquot was taken, and an IR spectrum (−78°C) showed ν_{NO} at 1767 (s, major), 1651 (m), and 1413 cm^{-1} (w, minor). The aliquot was warmed to −20°C. No change occurred in the IR spectrum. Based upon the assignments in Schemes 2−4, the ν_{NO} at 1409−1413 cm^{-1} were attributed to the nitrosyl ligand/$AlCl_3$ adduct $(\eta^5\text{-}C_5H_5)Re(NO-AlCl_3)(PPh_3)(SiMe_2Cl)$ (**13**), and the ν_{NO} at 1764−1767 cm^{-1} were attributed to the rhenium/$AlCl_3$ adduct $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiMe_2Cl)(AlCl_3)$ (**14**; Scheme 5). A silyl halide ligand/$AlCl_3$ adduct such as $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiMe_2Cl-AlCl_3)$ (**15**) has precedent[29], but should exhibit a ν_{NO} in the IR spectrum much closer to that of precursor **2**. Alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^{\oplus}X^{\ominus}$, which might be expected to model certain IR features of the silylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=SiMe_2)]^{\oplus}AlCl_4^{\ominus}$ (**16a**), show ν_{NO} in the range of 1704−1730 cm^{-1}[30].

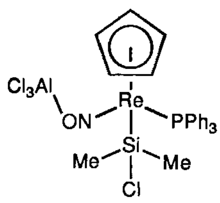
Next, **2**/$(AlCl_3)_{1/x}$ and **2**/$AlCl_3$ were similarly generated in CD_2Cl_2, and NMR spectra were recorded. Data are summarized in Table 2, and ^{1}H-NMR spectra are shown in Figure 2. Only one set of ^{1}H-, ^{13}C-, and ^{31}P-NMR resonances was observed, indicating the rapid equilibrium of **2** and the $AlCl_3$ adducts on the NMR time scale. The ^{27}Al-NMR spectra of both samples showed, in addition to a broad major resonance characteristic of a Lewis base/$AlCl_3$ adduct, a sharp peak due to $AlCl_4^{\ominus}$ (δ = 102.0)[25,31b]. Some minor ^{1}H-NMR resonances found for **2**/$AlCl_3$ (Figure 2; δ = 6.00, 5.79; ca. 7 and 5% of total C_5H_5 area) were attributed to decomposition products.

The ^{1}H-NMR spectrum of **2**/$(AlCl_3)_{1/x}$ exhibited one pair of closely spaced resonances for the diastereotopic methyl groups (Figure 2)[31]. In contrast, ^{1}H- and ^{13}C-NMR spectra of **2**/$AlCl_3$ exhibited a single broad resonance for the methyl groups (δ = 0.48 and 11.2). This coalescence will be interpreted below as evidence for the intermediacy of silylene complex **16a** (Scheme 5).

A CD_2Cl_2 solution of **2**/$AlCl_3$ was treated with 2 equiv. of THF at −78°C. A ^{1}H-NMR spectrum was immediately recorded. The resonances in Table 2 (but not those at δ = 5.76−6.00) were replaced by those of **2** (δ = 4.96; ca. 75%) and a second complex (δ = 5.10; ca. 25%). A **2**/$AlCl_3$ solution was analogously treated with 1 equiv. of $Ph_3PMe^{\oplus}I^{\ominus}$. The resonances in Table 2 were similarly replaced by those of **2** and iodosilyl complex **4** [(57 ± 4):(43 ± 4)]. No reaction occurred when chlorosilyl complex **2** was treated with 1 equiv. of $Ph_3PMe^{\oplus}I^{\ominus}$ at room temperature in CD_2Cl_2.

Scheme 5. Reactions of chlorosilyl complex **2** and $AlCl_3$





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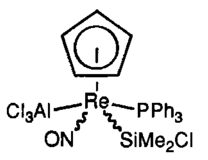

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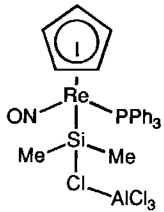

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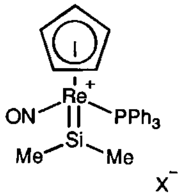


16

$X^- = AlCl_4^-$: **a**
$Al_2Cl_7^-$: **b**

2 equiv. of Lewis acids EX_3 sometimes provide a stronger halide abstracting environment than does 1 equiv.[32]. Thus, a CH_2Cl_2 solution of **2** was treated with 2 equiv. of $AlCl_3$ at $-78\,°C$. Following vigorous agitation, nearly all of the $AlCl_3$ dissolved to give **2**/$(AlCl_3)_2$. This solution was much more sensitive than **2**/$AlCl_3$. An IR spectrum of an aliquot exhibited ν_{NO} at 1765/1759 cm^{-1} (w, minor), 1461/1454 cm^{-1} (m, major), and a number of weaker absorptions in the range of 1600–1700 cm^{-1}.

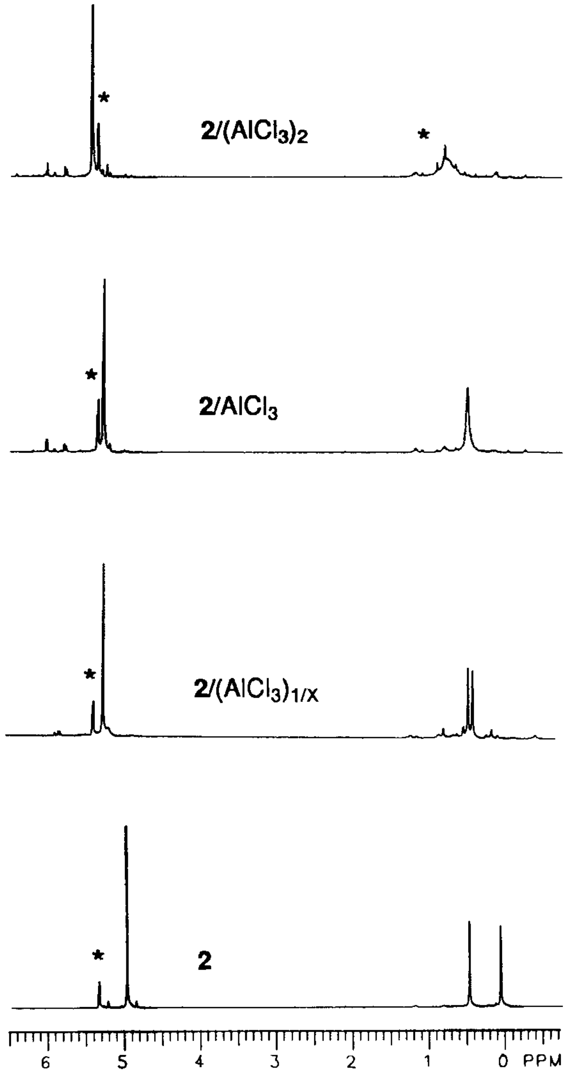


Figure 2. ^1H-NMR spectra of **2** and $AlCl_3$ adducts (CD_2Cl_2, $-76\,°C$); the resonances marked with an asterisk are due to $CDHCl_2$ ($\delta = 5.32$) and hexane ($\delta = 1.13$ and 0.86)

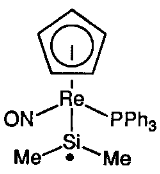
A CD_2Cl_2 solution of **2**/$(AlCl_3)_2$ was generated at $-78\,°C$, and NMR spectra were recorded (Table 2). The ^1H-NMR spectrum (Figure 2) showed one principal broad resonance for the diastereotopic methyl groups at $\delta = 0.76$, and a corresponding resonance for the η^5-C_5H_5 ligand at $\delta = 5.46$. Other peaks were attributed to decomposition products. These included the resonances ($\delta = 5.76-6.00$) noted above, and a large number of resonances for Me ($\delta = 0.98$, 0.78, 0.74, 0.61, 0.43, 0.08, 0.05). When solutions of **2**/$(AlCl_3)_2$ were cooled below $-90\,°C$, the resonance at $\delta = 0.76$ decoalesced into two broad resonances[31b]. Standard two-site exchange treatment[14a] gave a $\Delta G^{\neq}$ (183 K) of 8.3 kcal/mol for the process equivalencing the Me groups.

A CD_2Cl_2 solution of **2**/$(AlCl_3)_2$ was treated with 2 equiv. of THF at $-78\,°C$. A ^1H-NMR spectrum was immediately recorded. The reasonances in Table 2 (but not those at $\delta = 5.76-6.00$) were replaced by those of **2** (ca. 80%) and a second complex (δ = 5.10; ca. 20%). Finally, **2**/$(AlCl_3)_2$ was analogously treated with $Ph_3PMe^{\oplus}I^{\ominus}$ (1.3 equiv.). The resonances in Table 2 were similarly replaced by those of **2** and **4** [(32 ± 3):(68 ± 3)].

Discussion

1. Synthesis and Characterization of Functionalized Silyl Complexes

There are several interesting aspects of the reactions and compounds outlined in Scheme 1. First, halogenations of organosilanes R_3SiH commonly proceed via intermediate silyl radicals[10]. Thus, the conversion of **1** into halosilyl complexes **2**–**4** likely involves the silicon-based radical $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\dot{Si}Me_2)$ (**17**). Since **17** contains a divalent silicon ligand, it can be considered a type of silylene complex. Related halogenations of manganese hydridosilyl complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2(H)(SiPh_2H)$ have been reported previously[33].



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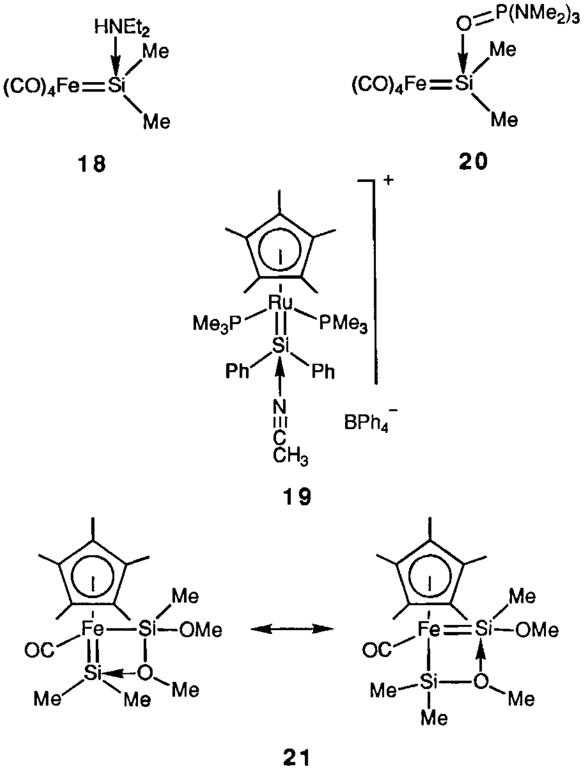
The triflate group in silyl complex **5** is readily displaced by nucleophiles. Analogous behavior is well known for organosilyl triflates[34]. However, substitution reactions of **5** might proceed by a dissociative mechanism involving the silylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=SiR_2)]^{\oplus}TfO^{\ominus}$ (**16c**). We had hoped to acquire rate data and activation parameters that would clarify this point. However, substitution rates were too rapid (CD_2Cl_2, −78°C) to measure by conventional low-temperature NMR techniques.

Triflate-containing compounds exhibit several $\nu(CF_3SO_3)$ in the IR spectrum in the range of 1400–900 cm^{-1}[13]. The highest frequency band is typically at 1395–1365 cm^{-1} in covalent triflates, and at 1280–1270 cm^{-1} in ionic triflates. Accordingly, triflate-substituted silyl complex **5** exhibits a $\nu(CF_3SO_3)$ in the former region (1366 cm^{-1}), and pyridinium salt **7** exhibits a $\nu(CF_3SO_3)$ in the latter region (1275 cm^{-1}). Interestingly, germanium analogs of **5**, $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(GeR_2OTf)$ (R = Ph[8], Me[15]), exhibit $\nu(CF_3SO_3)$ in an intermediate range (1331–1339 cm^{-1}; KBr or CH_2Cl_2). Thus, the silicon-triflate bond in **5** has considerably more covalent character than the germanium–triflate bond in related compounds.

Pyridinium salt 7 constitutes an addition to the series of base-stabilized silylene complexes previously synthesized by the Schmid[2], Tilley[3], Zybill[4], Ogino[5], and Jutzi[6g] groups. Representative compounds are depicted in Scheme 6. Complexes **19**–**21** have been structurally characterized, and bonding features have been analyzed in detail. Tilley has obtained good evidence for a facile equilibrium of **19** and the corresponding base-free silylene complex $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(=SiPh_2)]^{\oplus}BPh_4^{\ominus}$[3].

Scheme 6. Representative previously synthesized base-stabilized silylene complexes



Compounds **6**/**2**/**3**/**4** are one of the few complete series of halosilyl complexes to be characterized[33]. The spectroscopic data in Table 1 show several monotonic trends. For example, the ν_{NO} in the IR spectrum increase in the order **6** < **2** < **3** < **4**, suggesting that the iodosilyl ligand is a stronger π acceptor than the fluorosilyl ligand. Also, the ^1H- and ^{13}C-NMR resonances for the $\eta^5\text{-}C_5H_5$ and methyl groups shift progressively downfield, while the ^{31}P-NMR resonances for the PPh_3 ligands shift progressively upfield. Spectroscopy properties of analogous series of diphenylhalogermyl and dimethylhalogermyl complexes are described elsewhere[8,15].

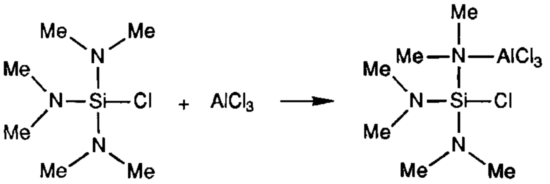
2. Lewis Acidity and Basicity Trends

The IR data given above show that CH_2Cl_2 solutions of **8**/BCl_3 and **8**/$AlCl_3$ contain adducts **9** and **10** (Scheme 2), but no appreciable amount of uncomplexed **8**. Adduct formation is similarly complete for **2**/BCl_3 (Scheme 4). However, some **2** remains in solutions of **2**/$AlCl_3$ (Scheme 5). At first glance, this suggests that $AlCl_3$ is a weaker Lewis acid than BCl_3 towards **2** (and that **2** is a weaker Lewis base than **8** towards $AlCl_3$). However, the detection of some $AlCl_4^{\ominus}$ in **2**/$AlCl_3$ by ^{27}Al-NMR spectroscopy raises the possibility of more complex equilibria.

Also, Lewis acidity orders can be very base-dependent. For example, BCl_3 is a stronger Lewis acid than $AlCl_3$ towards ethyl acetate[35], but a weaker Lewis acid towards pyridine[36]. The Lewis base THF readily cleaves all of the adducts in Schemes 2, 4, 5. Thus, **2** and **8** are weaker Lewis bases than THF towards BCl_3 and $AlCl_3$.

With **8**/ECl_3, nitrosyl ligand/Lewis acid adducts **9** are favored over rhenium/Lewis acid adducts **10** at room temperature. With **2**/$AlCl_3$, the rhenium/$AlCl_3$ adduct **14** is favored over the nitrosyl ligand/$AlCl_3$ adduct **13** at both low and room temperature. With **2**/BCl_3, the nitrosyl ligand/BCl_3 adduct **11** is favored over rhenium/BCl_3 adduct **12** at low temperature, but not at room temperature. Thus, the nitrosyl ligand Lewis basicity of **2** seems to be somewhat diminished relative to that of **8**.

Both **2**/BCl_3 and **2**/$AlCl_3$ do not appear to contain any significant quantity of silyl halide ligand/ECl_3 adducts (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2Cl-ECl_3$) (e.g., **15**; Scheme 5). While silyl halide/$AlCl_3$ adducts are known[29], other functionalities generally show greater Lewis basicity. For example, the amine/$AlCl_3$ adduct $(Me_2N)_2SiCl(Me_2N-AlCl_3)$ (**22**) crystallizes from the reaction of silyl chloride $(Me_2N)_3SiCl$ and $AlCl_3$ [equation (i)], and spectroscopic data suggest an analogous complex in solution[37].



(i)

22

The equilibria in equation (i) and Schemes 4, 5 illustrate a fundamental problem in the utilization of Lewis acid reagents to generate reactive, electron-deficient species by abstraction reactions. In an attempt to stabilize the electron-deficient target, electron-donating groups are often appended. However, these can provide independent binding sites, or enhance the Lewis basicity of alternative binding sites, for the Lewis acid reagents. While such parasitic equilibria do not necessarily compromise the overall thermodynamics of abstraction, abstraction rates are at minimum diminished.

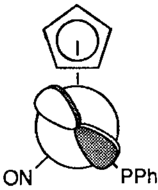
3. Crystal Structure of 11

Several curious features attend the isolation of the nitrosyl ligand/BCl_3 adduct **11**. First, IR data indicate that **11** is not the major species in solution under the crystallization conditions commonly utilized. Second, excess BCl_3 is required for crystallization to be rapid. Thus, unusual dynamics are clearly associated with the mechanism of lattice growth.

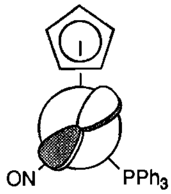
Crystals of **11** are extremely air-sensitive, decompose in the X-ray beam, and do not diffract upon cooling. Thus, there are practical limits on the quality of structural data. Accordingly, the esd's associated with the bond lengths and angles, and final R and R_w values, are somewhat greater than normal for structures in this series of compounds[8,38]. In particular, the nonpositive definite behavior of several atoms (Experimental) suggests approximations in the refinement model. Significantly, when IR spectra of crystalline **11** are recorded in KBr, some rhenium/BCl_3 adduct **12** is always present.

Regardless, the structure of **11** (Figure 1) shows several interesting features. First, the Re–N bond (1.57 Å) is distinctly shorter than that in the germyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2OTf$) [1.759(4) Å][8], or those in neutral alkyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(R) (1.78–1.74 Å, average 1.75 Å)[38e]. Conversely, the N–O bond (1.47 Å) is much longer than that in (η^5-C_5H_5)Re(NO)(PPh_3)($GePh_2OTf$) [1.205(5) Å] and neutral alkyl complexes (1.22–1.19 Å, average 1.21 Å).

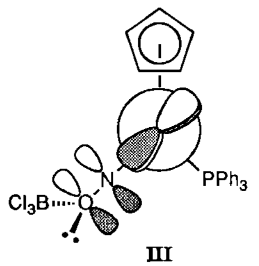
Analogous structural trends have been noted in carbonyl ligand/Lewis acid adducts, and have been attributed to an increase in metal/ligand backbonding upon Lewis acid coordination[39]. The highest occupied molecular orbitals of the rhenium fragment [(η^5-C_5H_5)Re(NO)(PPh_3)]$^{\oplus}$ have been shown to be **I** (HOMO) and **II** (SHOMO)[38a,40]. The HOMO (**I**) is orthogonal to the π^* acceptor orbitals of the NO ligand, but the SHOMO (**II**) is of appropriate symmetry for backbonding.



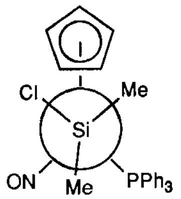
I



II



III

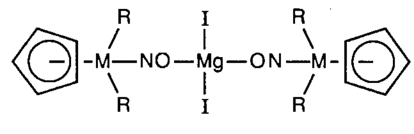


IV

The Re–N–O linkage in **11** is slightly bent (164°) relative to those in other (η^5-C_5H_5)Re(NO)(PPh_3)(X) complexes, but still in the range of linear nitrosyl ligands[19]. However, the N–O–B linkage is sharply bent (107°), suggestive of sp^2 hybridization at the oxygen atom. Such a bonding model would predict that the boron atom, oxygen atom, and oxygen lone pair would lie in the plane of the SHOMO (**II**), as shown in **III**. The plane of the SHOMO (**II**) can be approximated by the Si/Re/N/O least squares plane. Accordingly, the Si/Re/N/O and B/O/lone pair planes are nearly coincident ($\measuredangle$ 7°).

The Si–Cl bond in **11** lies approximately in the plane of the HOMO (**I**), as shown in the Newman projection **IV**. Since the Re–P bond lies in the plane of the HOMO (**I**), this feature is conveniently quantified by the P–Re–Si–Cl1 torsion angle [162.0(3)°].

Scant structural data on nitrosyl ligand/Lewis acid adducts are available. Notably, Legzdins has reported the crystallization of 2:1 NO ligand/MgI_2 adducts [(η^5-C_5H_5)M(NO)(CH_2SiMe_3)$_2$]$_2$$MgI_2 \cdot OEt_2$ [**23**; M = W(**a**), Mo (**b**)][22]. The ν_{NO} in the IR spectra of **23a, b** (1505, 1520 cm^{-1}; nujol) decreased only moderately from those of uncomplexed analogs (η^5-C_5H_5)M(NO)(CH_2SiMe_3)$_2$ (**24a,b**; 1541, 1587 cm^{-1}). In contrast, the ν_{NO} of **2** and **11** differ by 261 to 263 cm^{-1} (CH_2Cl_2, KBr). The smaller $\Delta\nu_{NO}$ for **23**/**24** probably reflects the lower Lewis acidity of MgI_2. Crystal disorder prevented an accurate structural characterization of adducts **23**. However, the W−N and N−O bond lengths in **23a** (1.77, 1.20 Å) were not significantly different from those in **24a** [1.757(8), 1.226(10) Å].



23

M = W, Mo
R = CH_2SiMe_3

4. Equilibria Involving Silylene Complexes

Solutions of **2**/$AlCl_3$ and **2**/($AlCl_3$)$_2$ (Scheme 5) contain two principal types of Lewis acid adducts, **13** and **14**. However, equilibria involving silyl halide ligand/$AlCl_3$ adduct **15** and base-free silylene complex **16** are also readily envisioned. Both chemical and spectroscopic data strongly suggest the accessibility of **15** and/or **16**.

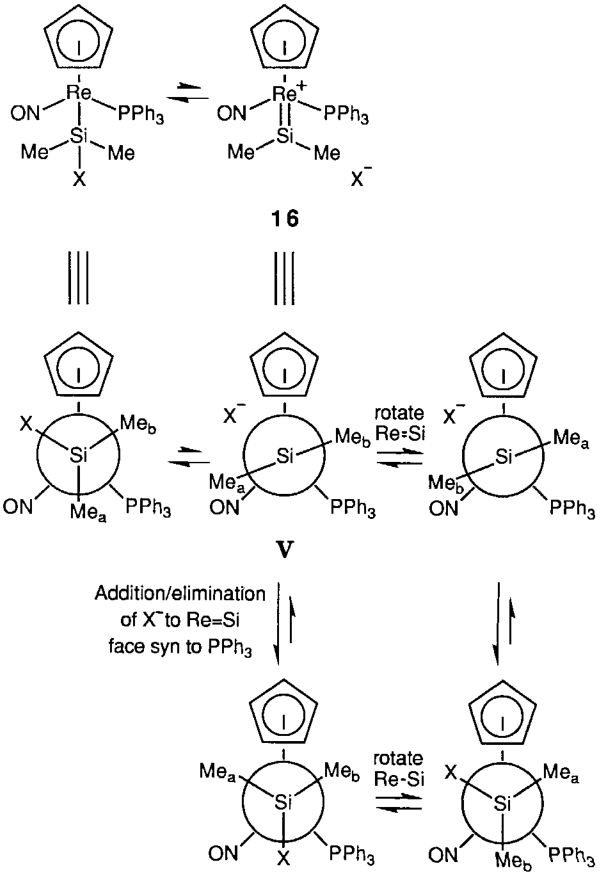
First, note that the methyl groups bound to the silicon atom in adducts **13**−**15** are diastereotopic, and thus should exhibit separate ^{1}H- and ^{13}C-NMR resonances. Even when the equilibration of **13**−**15** is rapid on the NMR time scale, two resonances for the methyl groups should be observed. The methyl groups can only become equivalent by a formal inversion of configuration at the silicon or rhenium atom[41].

However, the ^{1}H-NMR spectra of **2**/$AlCl_3$ and **2**/($AlCl_3$)$_2$ show only one resonance for the methyl groups (Figure 2). This requires a low energy pathway for the exchange of the diastereotopic methyl groups. Scheme 7 shows that this is easily accomplished through the intermediacy of silylene complex **16**. The silylene ligand is depicted in a conformation **V** analogous to that found for alkylidene ligands in the corresponding complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(=CHR)]$^{\oplus}$X$^{\ominus}$ [38a]. Exchange may be consumated by either of two routes: (1) Re=Si bond rotation in **V**, followed by reattachment of the chlorine-containing moiety, or (2) reattachment of the chlorine-containing moiety to the Re=Si face opposite from which dissociation occurred, followed by a Re−Si bond rotation.

Significantly, chlorosilyl complex **2** is inert towards iodide ions in CH_2Cl_2 at room temperature. However, **2**/$AlCl_3$ and **2**/($AlCl_3$)$_2$ rapidly react with iodide ions at −78°C to give varying amounts of **2** and iodosilyl complex **4**. Both silyl chloride ligand/$AlCl_3$ adduct **15** and silylene complex **16** constitute plausible precursors to **4** under these conditions. The formation of **2** can be rationalized by iodide ion attack upon free $AlCl_3$, or the $AlCl_3$ moieties in adducts **13**−**15**.

Similar dynamic NMR data have established the facile equilibration of triflate-substituted germyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(GeR_2OTf) and germylene complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(=GeR_2)]$^{\oplus}$TfO$^{\ominus}$ [8,15]. However, in these cases no Lewis acid is required. The barriers (CD_2Cl_2) for equivalencing the diastereotopic substituents in the germyl complexes [R = Me: $\Delta G^{\neq}$(211 K) = 9.6 kcal/mol; R = Ph: $\Delta G^{\neq}$(268 K) = 12.6 kcal/mol] are higher than that of **2**/($AlCl_3$)$_2$ [$\Delta G^{\neq}$(183 K) = 8.3 kcal/mol], but lower than that of triflate-substituted silyl complex **5** [$\Delta G^{\neq}$(307 K) > 14.8 kcal/mol]. Thus, base-free silylene complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(=SiR_2)]$^{\oplus}$X$^{\ominus}$ are clearly much less accessible than either germanium or carbon analogs.

Scheme 7. Possible mechanism for equivalencing of the diastereotopic Me groups in **2**/$AlCl_3$ and **2**/($AlCl_3$)$_2$



In summary, this study has provided a high-yield entry into functionalized dimethylsilyl complexes of the formula (η^5-C_5H_5)Re(NO)(PPh_3)($SiMe_2X$). The complex with X = triflate (**5**) can serve as a precursor to cationic, base-stabilized silylene complexes, but the triflate moiety is somewhat more covalently bound than in germanium analogs. Reactions of the complex with X = Cl (**2**) and Lewis acids ECl_3 (E = B, Al) give principally nitrosyl ligand/ECl_3 and rhenium/ECl_3 adducts. However, NMR data suggest rapid equilibria involving the base-free silylene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=$SiMe_2$)]$^{\oplus}$ $Al_xCl_y^{\ominus}$.

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Experimental

General Data: General procedures (instrumentation, dynamic NMR, analytical data) were identical to those described in a recent paper[8b,15]. NMR spectra were recorded with Varian XL-300 spectrometers as described in Tables 1 and 2. Solvents were distilled [CH_2Cl_2 and $CHCl_3$ from P_2O_5; benzene and THF from sodium/benzophenone; hexane from sodium; pentane and petroleum ether (boiling range 35–60°C) from $LiAlH_4$] and freeze-pump-thaw-degassed (3 ×) before use. Deuterated solvents were trap-to-trap-distilled as follows: CD_2Cl_2 from P_2O_5; C_6D_6 from CaH_2. Reagents were obtained as follows: CHI_3 (Eastman); CBr_4, $(Me_2N)_3S^{\oplus}[SiMe_3F_2]^{\ominus}$, and 1.0 M BCl_3 in CH_2Cl_2 (Aldrich), used as purchased; $Ph_3PMe^{\oplus}I^{\ominus}$ (Aldrich), used as purchased; $(CH_3)_3SiOTf$ (Petrarch), distilled from CaH_2; pyridine (Baker), distilled from BaO; $AlCl_3$ (EM Science), twice sublimed.

(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(SiMe$_2$Cl) (**2**): A 5-mm NMR tube was charged with **1** (0.200 g, 0.332 mmol)[11] and $CHCl_3$ (1 ml), and was capped with a septum. The tube was kept at 50°C for 4 h and was then transferred to a glove box. The solvent was removed in vacuo, and the resulting orange residue was crystallized from CH_2Cl_2/hexane. Orange needles, plates, and prisms formed, which were collected by filtration, washed with hexane, and suction-dried (1 min)[42] to give **2** (0.178 g, 84%), mp 180–183°C. – $^{29}Si\{^1H\}$ NMR (59.6 MHz, −21°C, CD_2Cl_2/TMS): δ = 48.09 (d, J_{SiP} = 11 Hz).

$C_{25}H_{26}ClNOPReSi$ (637.2) Calcd. C 47.12 H 4.11
Found C 47.61 H 4.08

(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(SiMe$_2$Br) (**3**): Complex **1** (0.050 g, 0.083 mmol), C_6H_6 (1 ml), and CBr_4 (0.014 g, 0.042 mmol) were combined in a procedure analogous to that given for **2**. The tube was kept at 25°C for 3 h and was then transferred to a glove box. An identical workup gave (via a dark yellow residue) dark orange needles of **3** (0.043 g, 76%), mp 188–190°C.

$C_{25}H_{26}BrNOPReSi$ (681.7) Calcd. C 44.05 H 3.84
Found C 43.86 H 3.86

(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(SiMe$_2$I) (**4**): Complex **1** (0.050 g, 0.083 mmol), C_6H_6 (1 ml), and CHI_3 (0.036 g, 0.091 mmol) were combined in a procedure analogous to that given for **2**. The tube was kept at 25°C for 8 h and was then transferred to a glove box. The mixture was filtered through micro-fibre filter paper, and solvent was removed from the filtrate in vacuo. The resulting dark orange residue was crystallized from CH_2Cl_2/pentane. Dark brown needles formed, which were collected by filtration and suction-dried (1 min)[42] to give **4** (0.040 g, 66%), mp 190–192°C.

$C_{25}H_{26}INOPReSi$ (728.7) Calcd. C 41.21 H 3.60
Found C 41.04 H 3.58

(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(SiMe$_2$OTf) (**5**): Complex **2** (0.163 g, 0.256 mmol), C_6H_6 (1 ml), and Me_3SiOTf (0.074 ml, 0.085 g, 0.384 mmol) were combined in a procedure analogous to that given for **2**. An identical workup gave (via a dark yellow residue) yellow cubes of **5** (0.187 g, 97%), mp 154–156°C.

$C_{26}H_{26}F_3NO_4PReSSi$ (750.8) Calcd. C 41.59 H 3.49
Found C 41.32 H 3.66

(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(SiMe$_2$F) (**6**): A 5-mm NMR tube was charged with **5** (0.025 g, 0.033 mmol) and CH_2Cl_2 (0.5 ml), and was capped with a septum. The yellow solution was cooled to −78°C and was transferred, by a nitrogen-purged cannula, to a second NMR tube (−78°C) containing $(Me_2N)_3S^{\oplus}[SiMe_3F_2]^{\ominus}$ (0.010 g, 0.037 mmol). After 5 min, the tube was brought to room temperature and transferred to a glove box. The solvent was removed in vacuo, and the resulting yellow residue was extracted with a minimum of C_6H_6. The extract was filtered through a fritted funnel that had been layered with dry cellulose (1 cm). The solvent was removed from the filtrate in vacuo, and the resulting yellow residue was crystallized from CH_2Cl_2/petroleum ether. Yellow needles formed, which were collected by filtration and suction-dried (1 min)[42] to give **6** (0.020 g, 78%), mp 167–170°C.

$C_{25}H_{26}FNOPReSi$ (620.8) Calcd. C 48.37 H 4.22
Found C 47.77 H 4.31

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$){SiMe$_2$(NC$_5$H$_5$)}]$^{\oplus}$ TfO$^{\ominus}$ (**7**): A 5-mm NMR tube was charged with **5** (0.118 g, 0.157 mmol) and CH_2Cl_2 (1.0 ml), and was capped with a septum. The yellow solution was cooled to −78°C, and pyridine (0.012 ml, 0.012 g, 0.157 mmol) was added by syringe. After 5 min, the tube was brought to room temperature and transferred to a glove box. The solvent was removed in vacuo. The resulting dark yellow residue was crystallized from CH_2Cl_2/hexane. A yellow powder formed, which was collected by filtration and suction-dried (1 min)[42] to give **7** (0.110 g, 84%), mp 85–87°C (dec.).

$C_{31}H_{31}F_3N_2O_4PReSSi$ (829.9) Calcd. C 44.86 H 3.77
Found C 45.31 H 4.19

(η^5-C$_5$H$_5$)Re(NO−BCl$_3$)(PPh$_3$)(SiMe$_2$Cl) · CH$_2$Cl$_2$ (**11**): A 5-mm NMR tube was charged with **2** (0.019 g, 0.030 mmol) and CH_2Cl_2 (0.5 ml), and was capped with a septum. The yellow solution was cooled to −78°C, and BCl_3 (0.065 ml, 1.0 M in CH_2Cl_2, 0.065 mmol), was added by syringe. The solution became light orange, and was kept at −25°C for 5 d. Orange cubes formed. The tube was transferred to a glove box. The cubes were collected by filtration, washed with hexane, and suction-dried (1 min) to give **11** (0.018 g, 72%), mp 96–100°C (dec.).

$C_{25}H_{26}BCl_4NOPReSi \cdot CH_2Cl_2$ (839.3)
Calcd. C 37.21 H 3.36 Cl 25.34
$C_{25}H_{26}BCl_4NOPReSi$ (754.4)
Calcd. C 39.80 H 3.47 Cl 18.80
Found C 38.41 H 3.47 Cl 18.61

Crystal Structure of **11** *· CH$_2$Cl$_2$*: An orange cube was sealed in a glass capillary and mounted for data collection on an automated Syntex PI diffractometer. Cell constants (Table 3) were determined from 25 centered reflections with 22° < 2Θ < 30°. The space group was determined from systematic absences ($h0l$, $l = 2n$; $0k0$, $k = 2n$) and subsequent least squares refinement. The intensities of standard reflections decayed 23.6% during collection. A decay correction, Lorentz and polarization corrections, and an empirical absorption correction based upon a series of Ψ scans were applied. The structure was solved by standard heavy-atom techniques with the SDP/VAX package[43]. Non hydrogen atoms were refined with anisotropic thermal parameters, except for C1, C2, C3, C5, C6 (which exhibited nonpositive definite behavior). Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined. Anomalous dispersion corrections were applied throughout the refinement. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature[44]. Additional details are provided elsewhere[15,45].

CAS Registry Numbers

1: 115827-21-9 / **2**: 128803-74-7 / **3**: 130670-90-5 / **4**: 130670-91-6 / **5**: 130698-82-7 / **6**: 130670-92-7 / **7**: 130670-94-9 / **8**: 71763-18-3 / **9a**: 130670-96-1 / **9b**: 130670-95-0 / **10a**: 130670-99-4 / **10b**: 130698-83-8 / **11**: 128803-73-6 / **11** · CH_2Cl_2: 128803-76-9 / **12**: 128803-75-8 / **13**: 130670-97-2 / **14**: 130670-98-3 / **16a**: 130671-01-1 / **16b**: 130671-02-2

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