would be expected to attack C5 first, C1 or C2 next, and C9 last, based on substitution patterns[19] and asymmetry in Pt–C bond lengths.[20a,b]

The results at hand suggest that CH_3O^- could attack **4a** first at platinum to form an intermediate analogous to **23** (R′ = CH_3O^-), which then undergoes intramolecular insertion in a manner similar to R′ = aryl or alkyl discussed above. However, we have not yet been able to demonstrate Pt–OCH_3 bonding prior to insertion, nor can we at this time rule out attack at C5 followed by C5→C9 interchange.[21]

Conclusion

The goal of this work was the synthesis of a group of molecules of structure **23**, followed by a thorough mechanistic study of the R′ migration (as in **2**). The need for such a base-line study of this type of reaction has been noted before.[5f,k,q–s] The exocyclic double bond in coordinated 5-methylenecyclooctene is clearly strongly activated toward ligand migration; however, due to the demonstrated extensive dissociation of the exocyclic double bond in the η^2 dimers and to the R′ cis to endocyclic double bond in the η^4 monomers, we must infer structures **23** as reactive intermediates which are undetected prior to R′ migration. We continue our search for "in-plane" olefin–Pt(II) systems in which we can observe the single step analogous to **2**.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work through Grant 15158-AC3. This work also received partial support through the University of California Committee on Research and the Universitywide Energy Research Group.

Registry No. **3**, 38960-31-5; **4a**, 107681-69-6; **4b**, 107681-68-5; **5**, 12080-32-9; **6**, 33010-47-8; **7**, 115826-34-1; **8**, 115826-35-2; **9**, 115795-82-9; **10**, 115795-83-0; **11**, 115795-84-1; **12**, 115795-85-2; **13**, 115826-36-3; **14**, 115795-86-3; **15**, 115795-87-4; **16** (major isomer), 115888-44-3; **16** (minor isomer), 115795-81-8; $[(MCOT)(Br)Pt(Ph)]_2$, 115795-88-5; $[(MCOT)(Cl)Pt(p\text{-}MeOC_6H_4)]_2$, 115795-89-6; $[(MCOT)(Cl)Pt(Et)]_2$, 115795-90-9; $Me_3Sn(p\text{-}ClC_6H_4)$, 14064-15-4; Me_3SnPh, 934-56-5; Me_4Sn, 594-27-4.

Supplementary Material Available: For complexes **12** and **16**, tables of bond distances, bond angles, least-squares planes and dihedral angles between planes, positional parameters, displacement parameters, and torsion angles (15 pages); listings of structure factors (18 pages). Ordering information is given on any current masthead page.

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[19] See: *Nucleophilic Attack on Unsaturated Hydrocarbon Ligands*; pp 409 et. seq. Collman et al. cited in ref 3 above.

[20] (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (b) Wright, L. L.; Wing, R. M.; Rettig, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 610–612.

[21] Preliminary results with $(n\text{-}Bu)_3SnOCH_3$/**4a**/$CDCl_3$ suggest rapid (~1 min) methoxylation at *both* C5 and C9 (~40/60 ratio—variable with conditions). The initial C5/C9 product ratio does not change with time, which suggests that the C5 product tends not to migrate to C9—at least in low polarity conditions. Additional preliminary results indicate that pyridines attack C5 of **4a**, with rapid C5 → C9 migration.

Synthesis and Reactivity of Functionalized Rhenium Silyl Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiR_2X)$. Anionic Rearrangements Leading to the Disilametallacycle $(\eta^5\text{-}C_5H_4\overline{Si(CH_3)_2)Re(NO)(PPh_3)(Si}(CH_3)_2)$

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Received January 25, 1988

Reaction of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (**3**) with silicon electrophiles $(CH_3)_3SiOTf$, $(CH_3)_2SiHCl$, $(CH_3)_2Si(CH{=}CH_2)OTf$, and $Cl(CH_3)_2SiSi(CH_3)_2Cl$ gives functionalized silyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2X)$ (X = CH_3 (**4**), H (**5**), $CH{=}CH_2$ (**6**), and $Si(CH_3)_2Cl$ (**7**)) in 83–21% yields after workup. Reaction of **4** and *n*-BuLi/TMEDA gives, as assayed by ^{31}P NMR, lithiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(Si(CH_3)_3)$ (**8**), which rapidly rearranges at −78 °C to silylcyclopentadienyl complex $Li^+[(\eta^5\text{-}C_5H_4Si(CH_3)_3)Re(NO)(PPh_3)]^-$ (**9**). Addition of CH_3OTf gives methyl complex $(\eta^5\text{-}C_5H_4Si(CH_3)_3)Re(NO)(PPh_3)(CH_3)$ (**10**, 72%). Similar reaction of **7** and *n*-BuLi/TMEDA gives $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(Si(CH_3)_2Si(CH_3)_2Cl)$ (**13**), which rearranges at −24 °C to $Li^+[(\eta^5\text{-}C_5H_4Si(CH_3)_2Si(CH_3)_2Cl)Re(NO)(PPh_3)]^-$ (**14**). Upon warming, **14** cyclizes to disilametallacycle $(\eta^5\text{-}C_5H_4\overline{Si(CH_3)_2)Re(NO)(PPh_3)(Si}(CH_3)_2)$ (**15**, 53%).

There has been a great deal of interest in the syntheses and reactions of functionalized metal–silyl complexes, L_nMSiR_2X.[1] Such compounds have attracted attention as precursors to complexes of unsaturated organosilicon ligands. At the same time, lithiocyclopentadienyl silyl complexes, $(\eta^5\text{-}C_5H_4Li)MSiR_3$, have been found to undergo unusual metal-to-carbon silatropic shifts, as shown in eq 1.[2–5] This gives metal-centered anions of the general

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[1] See, inter alia: (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Berry, D. H.; Jiang, Q. *Ibid.* **1987**, *109*, 6210. (c) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669. (d) Marinetti-Mignani, A.; West, R. *Organometallics* **1987**, *6*, 141. (e) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Ibid.* **1986**, *5*, 1056. (f) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (g) Bell, L. G.; Gustavson, W. A.; Thanedar, S.; Curtis, M. D. *Organometallics* **1983**, *2*, 740. (h) Pakkanen, T.; Kerber, R. C. *Inorg. Chim. Acta* **1981**, *49*, 47. (i) Malisch, W.; Panster, P. *Chem. Ber.* **1975**, *108*, 2554.

[2] (a) Berryhill, S. R.; Sharenow, B. *J. Organomet. Chem.* **1981**, *221*, 143. (b) Berryhill, S. R.; Clevenger, G. L.; Burdurlu, F. Y. *Organometallics* **1985**, *4*, 1509.

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[4] Pasman, P.; Snel, J. J. M. *J. Organomet. Chem.* **1986**, *301*, 329.

[5] (a) Pannell, K. H.; Vincenti, S. P.; Scott III, R. C. *Organometallics* **1987**, *6*, 1593. (b) Pannell, K. H.; Rozell, J. M.; Tsai, W.-M. *Ibid.* **1987**, *6*, 2085.

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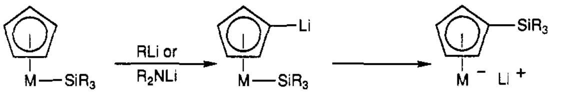
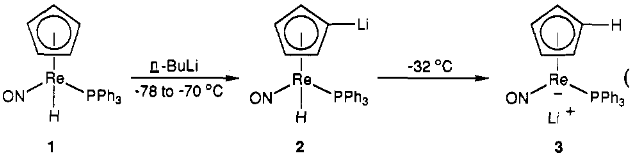
formula $Li^+[(\eta^5\text{-}C_5H_4SiR_3)M]^-$.



(1)

The chiral, electron-rich rhenium fragment $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)^+$ makes stable complexes with a variety of unsaturated organic ligands (e.g., $=CH_2$, $=C=CH_2$, $-CHO$).[6] Hence, we sought to prepare functionalized rhenium-silyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiR_2X)$ for study as precursors to complexes of unsaturated organosilicon ligands. Metal-silyl complexes are frequently synthesized from metal anions and silicon electrophiles.[7] We recently showed that reaction of hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (1) and *n*-BuLi first gives lithiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(H)$ (2; eq 2) and then, by a prototropic shift, rhenium-centered anion $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (3).[8] Hence, we set out to study reactions of anion 3 with functionalized silicon electrophiles. We further sought to deprotonate the target silyl complexes to the corresponding lithiocyclopentadienyl complexes and compare the migratory aptitudes of silyl ligands with that of the hydride ligand in 2.



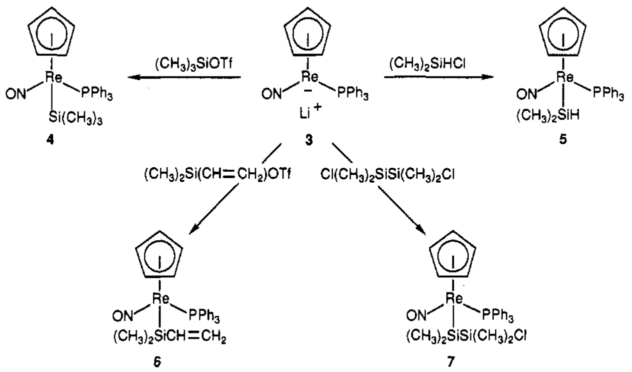
(2)

Results

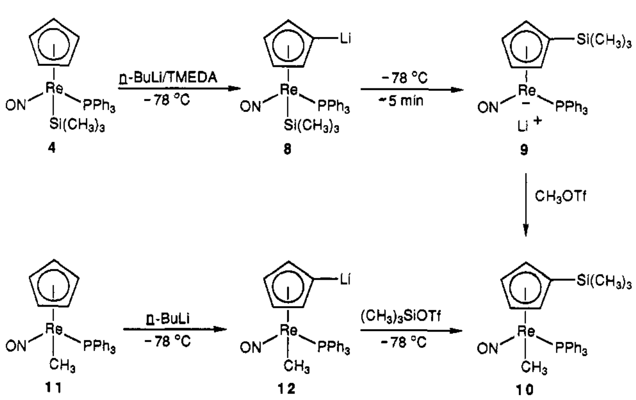
Hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (1) and *n*-BuLi were reacted (THF, −15 °C) to give rhenium-centered anion $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (3; 45.2 ppm, ^{31}P NMR).[8] Subsequent addition of silyl chloride $(CH_3)_3SiCl$ (2–5 equiv, −78 °C) was monitored by ^{31}P NMR. A 38.2 ppm intermediate cleanly and rapidly formed but decomposed to a multitude of products upon warming to room temperature. In contrast, addition of silyl triflate $(CH_3)_3SiOTf$ (2.0 equiv, −78 °C) cleanly gave a 24.8 ppm product. No decomposition occurred upon warming, and workup gave trimethylsilyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_3)$ (4; Scheme I) in 42% yield. The structure of 4 followed readily from its spectroscopic properties, which are summarized in Table I. Satisfactory microanalyses were obtained for all new complexes (Experimental Section).

Reactions of functionalized silicon electrophiles were examined next. Treatment of anion 3 with $(CH_3)_2SiHCl$, $(CH_3)_2Si(CH{=}CH_2)OTf$, and $Cl(CH_3)_2SiSi(CH_3)_2Cl$ (1.1–2.0 equiv, −78 °C) followed by workup gave silyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2H)$ (5, 83%), $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2CH{=}CH_2)$ (6, 21%), and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2Si(CH_3)_2Cl)$ (7, 55%), respectively (Scheme I). These reactions appeared quantitative when monitored by ^{31}P NMR. Treatment of 3 with $(CH_3)_2Si(Cl)OTf$ (1.2–1.4 equiv) also appeared to cleanly give silyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2Cl)$ (^{31}P NMR, 25.8 ppm). However, the product could only be isolated as a viscous oil (26.0 ppm), the mass and appearance of which suggested contamination by a THF polymer.

Scheme I. Syntheses of Silyl Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2X)$



Scheme II. Formation of a Silylcyclopentadienyl Ligand via a Metal-to-Ligand Silatropic Shift



Reactions of silyl complexes with base were studied next. First, complex 4 was treated with 1.2 equiv of *n*-BuLi/TMEDA in THF at −78 °C. After 1.5 h, CH_3OTf (3.8 equiv) was added. This gave silylcyclopentadienyl complex $(\eta^5\text{-}C_5H_4Si(CH_3)_3)Re(NO)(PPh_3)(CH_3)$ (10; Scheme II) in 72% yield upon workup. The structure of 10 followed from its ^1H and ^{13}C NMR spectra, which showed resonances characteristic of a monosubstituted cyclopentadienyl ligand[9] and a $ReCH_3$ moiety (Table I). Complex 10 was independently synthesized in 66% yield by reaction of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (11; Scheme II)[6a] with *n*-BuLi/TMEDA (1.0 equiv, −78 °C) to give lithiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(CH_3)$ (12),[10] followed by addition of $(CH_3)_3SiOTf$.

The reaction sequence leading from silyl complex 4 to methyl complex 10 was monitored by ^{31}P NMR. A spectrum was recorded 15 min after the addition of *n*-BuLi/TMEDA to 4. This showed some starting 4 (24.9 ppm, ca. 55%), a sharp resonance with a chemical shift characteristic of rhenium-centered anions $Li^+[(\eta^5\text{-}C_5H_4X)Re(NO)(PPh_3)]^-$ (44.8 ppm, ca. 40%),[8,10] and a resonance slightly downfield from that of 4 (28.6 ppm, ca. 5%). Small downfield ^{31}P NMR shifts occur upon cyclopentadienyl ligand lithiation in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ complexes.[8,10-12] The 44.8 ppm resonance intensified as the others

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(6) (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* 1982, *104*, 141. (b) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *Ibid.* 1983, *105*, 5811. (c) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *Ibid.* 1988, *110*, 6096.

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(8) (a) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* 1985, 283. (b) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* 1988, *110*, 6110.

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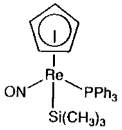
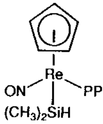
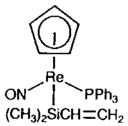
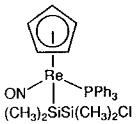
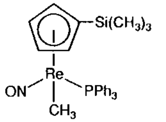
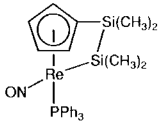
(10) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* 1986, *106*, 1185.

(11) Zwick, B. D.; Arif, A. M.; Patton, A. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 910.

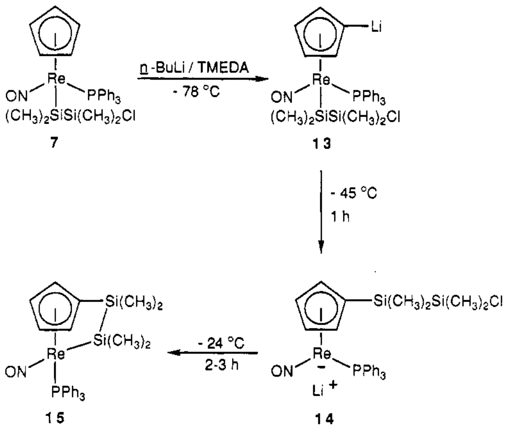
(12) Crocco, G. L.; Gladysz, J. A. *Chem. Ber.* 1988, *121*, 375.

Table I. Characterization of New Rhenium Complexes

complex	IR (cm^{-1}, KBr)	^{1}H NMR (δ)[a]	^{13}C{^{1}H} NMR (ppm)[b]	^{31}P{^{1}H} NMR (ppm)[c]	mass spectrum (m/e, ^{187}Re (rel intensity))
 4	$\nu_{N{\equiv}O}$ 1634 s; ν_{Si-C} 1232 m	7.58–7.51 (m, 6 H of 3 C_6H_5); 7.05–6.95 (m, 9 H of 3 C_6H_5); 4.48 (s, C_5H_5); 0.48 (s, 3 CH_3)[d]	PC_6H_5 at 139.84 (d, J = 51.9 Hz, ipso), 133.83 (d, J = 10.9 Hz), 129.88 (s, p), 128.21;[e] 87.07 (s, C_5H_5); 7.31 (s, CH_3)[d]	24.69 (s)[d]	617 (M^+, 90); 602 ($M^+ - CH_3$, 74); 587 (M^+ − NO, 4); 544 ($M^+ - Si(CH_3)_3$, 5); 355 ($M^+ - PPh_3$, 4); 340 ($M^+ - PPh_3 - CH_3$, 5); 262 (PPh_3^+, 100)[f]
 5	ν_{Si-H} 2037 w; $\nu_{N{\equiv}O}$ 1636 s; ν_{Si-C} 1232 w	7.59–7.52 (m, 6 H of 3 C_6H_5); 7.06–6.96 (m, 9 H of 3 C_6H_5); 4.71 (m, SiH); 4.49 (s, C_5H_5); 0.69 (d, J = 3.8 Hz, CH_3); 0.56 (d, J = 3.9 Hz, CH_3)[d]	PC_6H_5 at 137.30 (d, J = 69.9 Hz, ipso), 133.80 (d, J = 10.9 Hz), 129.92 (s, p), 128.15;[e] 86.88 (s, C_5H_5); 2.83 (s, CH_3); 1.73 (s, CH_3)[d]	24.28 (s)[d]	603 (M^+, 8); 602 (M^+ − H, 33); 544 ($M^+ - Si(CH_3)_2H$, 36); 467 ($M^+ - Si(CH_3)_2H - C_6H_5$, 8); 435 ($M^+ - Si(CH_3)_2H - C_6H_5$ − NO − H_2, 10); 262 (PPh_3^+, 38)[g]
 6	$\nu_{N{\equiv}O}$ 1643 s; $\nu_{C=C}$ 1587 w; ν_{Si-C} 1233 m	7.43 (m, 6 H of 3 C_6H_5); 7.38 (m, 9 H of 3 C_6H_5); 6.28 (dd, $CH{=}CHH'$, J = 18.9, 14.2 Hz); 5.58 (dd, $CH{=}CHH'$, J = 14.4, 4.2 Hz); 5.31 (dd, $CH{=}CHH'$, J = 20.1, 4.2 Hz); 4.78 (s, C_5H_5); 2 CH_3 (s) at 0.13, 0.03[h]	150.1 (s, $CH{=}CH_2$); 138.8 (s, CH=CH); PC_6H_5[i] at 133.5 (d, J = 10.7 Hz), 129.8 (d, J = 2.3 Hz, p), 128.0 (d, J = 10.2 Hz); 87.65 (d, J = 1.2 Hz, C_5H_5); 4.40, 3.17 (s, CH_3)[h]	23.4 (s)[j]	629 (M^+, 9); 614 ($M^+ - CH_3$, 2); 340 ($M^+ - C_2H_3 - PPh_3$, 5); 326 ($M^+ - C_2H_3 - CH_2 - PPh_3$, 5); 262 ($PPh_3^+$, 100)[f]
 7	$\nu_{N{\equiv}O}$ 1633 s; ν_{Si-C} 1238 w; ν_{Si-Cl} 659 m	7.50–7.43 (m, 6 H of 3 C_6H_5); 7.04–6.94 (m, 9 H of 3 C_6H_5); 4.63 (s, C_5H_5); 4 CH_3 (s) at 0.79, 0.72, 0.55, 0.21[d]	PC_6H_5 at 138.60 (d, J = 51.2 Hz, ipso), 133.72 (d, J = 9.6 Hz), 130.09 (s, p), 128.43;[e] 87.65 (s, C_5H_5); 4 CH_3 (s) at 4.15, 4.02, 1.66, 0.73[d]	23.92 (s)[d]	695 (M^+, 1); 602 ($M^+ - Si(CH_3)_2Cl$, 16); 544 ($M^+ - Si(CH_3)_2Si(CH_3)_2Cl$, 4); 467 ($M^+ - Si(CH_3)_2Si(CH_3)_2Cl - C_6H_5$, 18); 262 ($PPh_3^+$, 100)[f]
 10	$\nu_{N{\equiv}O}$ 1624 s; ν_{Si-C} 1250 m	7.62–7.55 (m, 6 H of 3 C_6H_5); 7.06–6.94 (m, 9 H of 3 C_6H_5); C_5H_4 (br m) at 5.07, 5.02, 4.97, 3.39; 1.38 (d, J_{HP} = 6.0 Hz, $ReCH_3$); 0.33 (s, $Si(CH_3)_3$)[d]	PC_6H_5 at 137.50 (d, J = 51.0 Hz, ipso), 133.01 (d, J = 11.3 Hz), 129.91 (s, p), 128.43;[e] C_5H_4 at 105.39 (s, ipso), 96.10 (s), 92.38 (d, J = 4.5 Hz), 88.54 (s), 87.40 (s); −0.19 (s, $Si(CH_3)_3$); −37.05 (d, J = 6.8 Hz, $ReCH_3$)[d]	24.61 (s)[d]	631 (M^+, 100); 616 ($M^+ - CH_3$, 31); 601 (M^+ − NO, 5); 354 ($M^+ - CH_3 - PPh_3$, 9); 262 (PPh_3^+, 42)[f]
 15	$\nu_{N{\equiv}O}$ 1637 s; ν_{Si-C} 1242 w	7.63–7.57 (m, 6 H of 3 C_6H_5); 7.06–6.95 (m, 3 H of 3 C_6H_5); C_5H_4 (br m) at 5.39, 5.13, 4.78, 3.23; 4 CH_3 (s) at 0.99, 0.35, 0.21, 0.15[d]	PC_6H_5 at 139.68 (d, J = 51.6 Hz, ipso), 133.71 (d, J = 11.1 Hz), 129.95 (s, p), 128.56;[e] C_5H_4 at 98.07 (s, ipso), 92.16 (s), 91.33 (s), 87.43 (d, J = 4.6 Hz), 86.47 (s); 4 CH_3 (s) at 0.18, −2.28, −2.83, −3.09[d]	25.80 (s)[d]	659 (M^+, 100), 644 ($M^+ - CH_3$, 24), 629 (M^+ − NO, 9), 614 (M^+ − NO − CH_3, 5), 397 ($M^+ - PPh_3$, 4), 262 (PPh_3^+, 4)[f]

[a] At 300 MHz and ambient probe temperature; all couplings are to hydrogen, unless noted. [b] At 75 MHz and ambient probe temperature; all couplings are to phosphorus. [c] At 32.2 MHz and ambient probe temperature and referenced to external 85% H_3PO_4. [d] Spectrum taken in C_6D_6 and referenced to solvent at δ 7.15 (^{1}H NMR) and 128.00 ppm (^{13}C NMR). [e] Portion of doublet; other line obscured by solvent. [f] At 17 eV. [g] (+)-FAB (Ar, 7KV, thioglycerol), m/z. [h] Spectrum taken in $CDCl_3$ and referenced to solvent at δ 7.24 (^{1}H NMR) and 77.0 ppm (^{13}C NMR). [i] Ipso carbon not observed. [j] Spectrum taken in CD_2Cl_2.

Scheme III. Formation of a Disilametallacycle via a Metal-to-Ligand Silatropic Shift



diminished. After 1 h, only the 44.8 ppm resonance remained, and addition of CH_3OTf gave methyl complex **10** (25.4 ppm). These data suggest that **4** is slowly deprotonated to lithiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(Si(CH_3)_3)$ (**8**) at −78 °C and that **8** undergoes a rapid subsequent silatropic rearrangement to give anion $Li^+[(\eta^5\text{-}C_5H_4Si(CH_3)_3)Re(NO)(PPh_3)]^-$ (**9**).

The reaction of disilyl complex **7** (25.2 ppm) and n-BuLi/TMEDA was similarly monitored by ^{31}P NMR. A new species with a ^{31}P NMR resonance at 27.9 ppm slowly appeared at −78 °C and was assigned to lithiocyclopentadienyl complex $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(Si(CH_3)_2Si(CH_3)_2Cl)$ (**13**). The reaction was kept at −45 °C for 1 h, after which time resonances of equal intensity were present at 25.7, 28.0, and 45.1 ppm. These were assigned to **7**, **13**, and the rhenium-centered anion $Li^+[(\eta^5\text{-}C_5H_4Si(CH_3)_2Si(CH_3)_2Cl)Re(NO)(PPh_3)]^-$ (**14**), respectively. The reaction was kept at −15 °C for 45 min. A new resonance appeared at 24.3 ppm and intensified with time. After 2–3 h, only the 24.3 ppm resonance remained. The corresponding species was isolated in 53% yield in a preparative experiment and on the basis of ^1H and ^{13}C NMR data (Table I) was assigned the disilametallacycle structure $(\eta^5\text{-}C_5H_4\overline{Si(CH_3)_2)Re(NO)(PPh_3)(Si}(CH_3)_2)$ (**15**). Hence, the sluggish deprotonation of disilyl complex **7** is followed by a slow silatropic shift to give anion **11**, which subsequently cyclizes to disilametallacycle **15** (Scheme III).

Discussion

The above data show that the rhenium anion $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (**3**) reacts with a variety of silicon electrophiles to give functionalized silyl complexes. However, as noted in the reaction of **3** and $(CH_3)_3SiCl$, a product with a ^{31}P NMR resonance in the 34–38 ppm region sometimes cleanly forms instead. This appears to happen less with silyl triflates than silyl chlorides.[13] We speculate that these may be nitrosyl ligand silylation products, $(\eta^5\text{-}C_5H_5)Re(\equiv NOSiR_3)(PPh_3)$. However, in all cases a multitude of decomposition products are generated upon warming.

Reactions involving migrations of silyl ligands to lithiocyclopentadienyl ligands were first observed by Berryhill.[2a] He found that addition of n-BuLi or $LiNR_2$ to iron silane complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2(Si(CH_3)_3)$ at −78 °C gave anion $Li^+[(\eta^5\text{-}C_5H_4Si(CH_3)_3)Fe(CO)_2]^-$, which was characterized spectroscopically and by alkylation reactions. Earlier, Graham had reported an analogous reaction of germyl complex $(\eta^5\text{-}C_5H_5)Mo(CO)_3(GePh_3)$.[14] Subsequent studies by Berryhill,[2b] Malisch,[3] Pasman and Snel,[4] and Pannell[5] have extended the scope of this rearrangement to several other systems. However, only with complexes **4** and **7** has it proved possible to spectroscopically observe the lithiocyclopentadienyl intermediate prior to silyl ligand migration.

Comparison of Schemes II and III with eq 2 indicates that silyl ligands have better migratory aptitudes than hydride ligands. This is in agreement with observations of Pasman and Snel, who reacted the rhenium silyl hydride complex $(\eta^5\text{-}C_5H_5)Re(CO)_2(SiPh_3)(H)$ and $t\text{-}BuCH_2Li$ at −78 °C.[4] Only the *silyl* ligand migration product $Li^+[(\eta^5\text{-}C_5H_4SiPh_3)Re(CO)_2(H)]^-$ formed, as assayed spectroscopically and by protonation reactions. Our data further show that the trimethylsilyl ligand, $-Si(CH_3)_3$, migrates faster than the disilyl ligand $-Si(CH_3)_2Si(CH_3)_2Cl$.

In other studies, we have shown that acyl ligands have slightly better migratory aptitudes than silyl ligands.[10] In contrast, halide and alkyl ligands in lithiocyclopentadienyl complexes $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(X)$ and $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(R)$ show no tendency to migrate.[10,12] This gives the following order of ligand migratory aptitudes: acyl > silyl > hydride ≫ halide $\gtrsim$ alkyl. Berryhill has proposed that vacant silicon d orbitals play a key role in these reactions.[2b] Accordingly, acyl ligands, which have low-lying π^*-acceptor orbitals, also migrate readily.

The disilametallacycle **15** is to our knowledge a new type of ring system, and the reactivity of the silicon linkage is under investigation. Carbocyclic analogues of **15**, $(\eta^5\text{-}C_5H_4\overline{CH_2)M(L)_n(CH_2})$, have been prepared and undergo a variety of bridge reactions.[15] Interestingly, lithiocyclopentadienyl complex **13** (Scheme III) can in principle directly cyclize to **15**. However, we see no evidence by NMR for this reaction pathway.

In summary, we have shown that functionalized silyl complexes can be prepared from anion **3** and that the corresponding lithiocyclopentadienyl complexes undergo facile metal-to-ligand silatropic shifts. Additional reactions of these functionalized silyl complexes will be described in future reports.[16]

Experimental Section

General Data. All reactions were conducted under a dry N_2 atmosphere. IR spectra were recorded on a Perkin-Elmer 1500 (FT) spectrometer. NMR spectra were recorded on Varian XL-300 (^1H, ^{13}C) and FT-80A (^{31}P) spectrometers as outlined in Table I. Mass spectra were obtained on a VG 770 spectrometer. Microanalyses were conducted by Galbraith Laboratories.

Solvents were purified as follows: THF, ether, and benzene, distilled from Na/benzophenone; hexane, heptane, and toluene, distilled from Na; CH_2Cl_2, distilled from P_2O_5; ethyl acetate, used as received; C_6D_6, vacuum transferred from CaH_2; CD_2Cl_2 and $CDCl_3$, vacuum transferred from P_2O_5.

Base n-BuLi (Aldrich) was standardized[17] before use. Reagents were purified as follows: CH_3OTf (Aldrich), $(CH_3)_3SiOTf$ (Petrarch), $(CH_3)_2SiHCl$ (Petrarch), $(CH_3)_2Si(CH{=}CH_2)Cl$ (Petrarch), and TMEDA (Aldrich), distilled from CaH_2; $Cl(CH_3)_2SiSi(CH_3)_2Cl$, prepared by a literature procedure (16-h reaction time)[18] and purified by preparative GLC; AgOTf (Aldrich), used as received.

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Preparation of $(CH_3)_2Si(CH{=}CH_2)OTf$. A Schlenk flask was charged with AgOTf (3.85 g, 15 mmol), ether (50 mL), and a stir bar. The solution was cooled to 0 °C and stirred. Then $(CH_3)_2Si(CH{=}CH_2)Cl$ (1.53 g, 2.04 mL, 15 mmol) was added dropwise by syringe. The mixture was stirred for 6 h and allowed to slowly warm to room temperature. The flask was transferred to a N_2 atmosphere glovebox. The reaction mixture was filtered, and solvent was removed from the filtrate by rotary evaporation. The remaining liquid was vacuum distilled (40 °C, 0.1 mmHg) into a N_2-cooled receiving flask to give $(CH_3)_2Si(CH{=}CH_2)OTf$ (3.2 g, 14 mmol, 95%). ^1H NMR (δ, 500 MHz, C_6D_6): 5.79 (dd, J = 20, 14 Hz, 1 H), 5.71 (dd, J = 14, 4 Hz, 1 H), 5.55 (dd, J = 20, 4 Hz, 1 H), 0.04 (s, $2CH_3$).

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_3)$ (4). A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (1, 0.35 g, 0.63 mmol), THF (15 mL), and a stir bar. The yellow solution was cooled to −15 °C and stirred. Then *n*-BuLi (0.36 mL, 2.5 M in hexane) was added, and the solution turned dark red. After 0.5 h, the solution was cooled to −98 °C, and $(CH_3)_3SiOTf$ (0.29 g, 1.3 mmol) was added. After 0.5 h, the yellow solution was warmed to room temperature, and solvents were removed in vacuo. The flask was transferred to a N_2 atmosphere glovebox, and the residue was extracted with hexane. The extract was filtered, and the filtrate was kept at −40 °C for 3 days. Light orange crystals formed, which were collected by filtration and dried in vacuo to give 4 (0.17 g, 0.27 mmol, 42%), mp 155–157 °C dec. Anal. Calcd for $C_{26}H_{29}NOPReSi$: C, 50.63; H, 4.74. Found: C, 50.63; H, 4.87.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2H)$ (5). Complex 1 (0.064 g, 0.12 mmol), THF (4 mL), and *n*-BuLi (0.064 mL, 2.4 M in hexane) were combined as described in the preparation of 4. After 0.5 h, the solution was cooled to −78 °C, and $(CH_3)_2SiHCl$ (0.036 g, 0.39 mmol) was added. After 0.5 h, the dark yellow solution was warmed to room temperature, and solvents were removed in vacuo. The flask was transferred to a N_2 atmosphere glovebox, and the residue was extracted with benzene. The extract was filtered through a 2-cm plug of silica gel, and the filtrate was concentrated to an orange oil by rotary evaporation. The resulting oil was dissolved in CH_2Cl_2 (5 mL), heptane was added (20 mL), and the solvents were removed by rotary evaporation. The resulting yellow powder was collected and dried in vacuo to give 5 (0.054 g, 0.96 mmol, 83%), mp 124–125 °C. Anal. Calcd for $C_{25}H_{27}NOPReSi$: C, 49.82; H, 4.52. Found: C, 50.10; H, 4.46.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2CH{=}CH_2)$ (6). Complex 1 (0.74 g, 1.4 mmol), THF (5 mL), and *n*-BuLi (0.72 mL, 2.0 M in hexane) were combined as described in the preparation of 4. Then $(CH_3)_2Si(CH{=}CH_2)OTf$ (0.35 g, 1.5 mmol) was added (−78 °C). After 15 min, the solution was warmed to room temperature and solvents were removed in vacuo. The flask was transferred to a N_2 atmosphere glovebag. The dark residue was extracted with a minimum of CH_2Cl_2. The extract was loaded on a preparative TLC plate (silica gel G) and eluted with 50:50 (v/v) CH_2Cl_2/hexane. A leading yellow-orange band was collected and transferred to a N_2 atmosphere glovebox. The product was washed from the silica gel with benzene. The benzene was removed by rotary evaporation, and the resulting orange residue was dissolved in ether. Slow evaporation gave small waxy orange plates. These were collected and vacuum dried to give 6 (0.19 g, 0.30 mmol, 21%). Anal. Calcd for $C_{27}H_{29}NOPReSi$: C, 52.93; H, 4.77; Si, 5.23. Found: C, 52.59; H, 4.81; Si, 5.06.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Si(CH_3)_2Si(CH_3)_2Cl)$ (7). Complex 1 (0.53 g, 0.98 mmol), THF (25 mL), and *n*-BuLi (0.50 mL, 2.4 M in hexane) were combined as described in the preparation of 4. Then $Cl(CH_3)_2SiSi(CH_3)_2Cl$ (0.30 g, 1.6 mmol) was added (−78 °C). After 1 h, the dark yellow solution was warmed to room temperature and solvents were removed in vacuo. The flask was transferred to a N_2 atmosphere glovebox and the residue was extracted with benzene. The extract was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting dark residue was washed with cold toluene (2 × 10 mL) and filtered. The resulting yellow powder was dried in vacuo to give 7 (0.37 g, 0.54 mmol, 55%). The powder was dissolved in CH_2Cl_2 (10 mL), layered with hexane, and kept at −40 °C for 2 days to give yellow crystals of 7, mp 151–154 °C. Anal. Calcd for $C_{27}H_{32}ClNOPReSi_2$: C, 46.64; H, 4.64. Found: C, 46.32; H, 4.56.

Preparation of $(\eta^5\text{-}C_5H_4Si(CH_3)_3)Re(NO)(PPh_3)(CH_3)$ (10). A. A Schlenk tube was charged with 4 (0.085 g, 0.14 mmol), THF (4 mL), and a stir bar. The solution was cooled to −78 °C, and TMEDA (0.021 g, 0.18 mmol) and *n*-BuLi (0.075 mL, 2.5 M in hexane) were added with stirring. After 2 h, CH_3OTf (0.087 g, 0.53 mmol) was added to the dark red solution. After 5 min, the resulting orange solution was transferred to a round-bottom flask, and solvents were removed by rotary evaporation. The residue was extracted with benzene. The extract was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting red oil was chromatographed on a 12 × 2.5 cm silica gel column with 10:90 (v/v) ethyl acetate/hexane. The yellow band was collected and concentrated to an oil. The oil was dissolved in ca. 10 mL of hexane and kept at −24 °C for 3 days. Orange crystals formed, which were collected by filtration and dried in vacuo to give **10** (0.061 g, 0.10 mmol, 72%), mp 173–175 °C. Anal. Calcd for $C_{27}H_{31}NOPReSi$: C, 51.41; H, 4.95. Found: C, 51.65; H, 4.91. **B.** A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$[6a] (0.31 g, 0.58 mmol), THF (15 mL), and a stir bar. The solution was cooled to −78 °C, and *n*-BuLi (0.42 mL, 1.4 M in hexane) was added with stirring. After 0.5 h, $(CH_3)_3SiOTf$ (0.14 mL, 0.77 mmol) was added, and the solution was stirred for 1 h. The solution was warmed to room temperature, and solvents were removed in vacuo. The flask was transferred to a N_2 atmosphere glovebox, and the orange oil was extracted with CH_2Cl_2. The extract was loaded on a preparative TLC plate (silica gel G) and eluted with 50:50 (v/v) CH_2Cl_2/hexane. A leading orange band was collected, and the product was washed from the silica gel with benzene. The benzene was removed by rotary evaporation. The resulting oil was dissolved in hexane and kept at −24 °C for 2 days. Orange crystals of **10** formed and were collected by filtration and dried in vacuo (0.23 g, 0.38 mmol, 66%).

Preparation of $(\eta^5\text{-}C_5H_4\overline{Si(CH_3)_2)Re(NO)(PPh_3)(Si}(CH_3)_2)$ (15). A Schlenk tube was charged with 7 (0.22 g, 0.31 mmol), THF (15 mL), and a stir bar. The solution was cooled to −78 °C, and TMEDA (0.42 g, 0.36 mmol) and *n*-BuLi (0.23 mL, 1.5 M in hexane) were added with stirring. The solution was warmed to room temperature over 1 h and then stirred an additional hour. The solvents were removed in vacuo, and the flask was transferred to a N_2 atmosphere glovebox. The residue was extracted with benzene. The extract was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting orange oil was dissolved in pentane (25 mL). Slow evaporation of the pentane gave small orange crystals. The crystals were collected by filtration and vacuum dried at 78 °C to give **15** (0.11 g, 0.16 mmol, 53%), mp 155–157 °C. Anal. Calcd for $C_{27}H_{31}NOPReSi_2$: C, 49.22; H, 4.74. Found: C, 49.35; H, 4.53.

Monitoring of Reactions by ^{31}P NMR. The following experiment is representative. A 5-mm NMR tube was charged with 4 (0.032 g, 0.052 mmol) and THF (0.5 mL) and capped with a septum. A ^{31}P NMR spectrum was recorded at −78 °C (24.9 ppm). The tube was immersed in a −78 °C bath. Then TMEDA (0.007 g, 0.63 mmol) and *n*-BuLi (0.028 mL, 2.0 M in hexane) were added. The sample was shaken and immediately transferred back to the −78 °C NMR probe. Sharp singlets were observed at 44.8, 28.6, and 24.9 ppm (55:5:40). After 30 min, a spectrum was recorded, and a sharp singlet was observed at 44.8 ppm. The tube was immersed in a −78 °C bath. Then CH_3OTf (0.012 g, 0.073 mmol) was added, and the sample was shaken. A ^{31}P NMR was immediately recorded (−78 °C), and a sharp singlet was observed at 25.4 ppm.

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Registry No. 1, 79919-58-7; 4, 97396-46-8; 5, 115827-21-9; 6, 115827-22-0; 7, 115827-23-1; 10, 115827-24-2; 11, 71763-18-3; 15, 115827-25-3; $(CH_3)_2Si(CH{=}CH_2)OTf$, 115827-19-5; $(CH_3)_2Si(CH{=}CH_2)Cl$, 1719-58-0; $Cl(CH_3)_2SiSi(CH_3)_2Cl$, 4342-61-4.