

Low-valent rhenium-oxo complexes. 13. Rhenium(I) tris(acetylene) complexes: $\text{Re}(\text{OR}')(\text{RC}\equiv\text{CR})_3$ and $[\text{Re}(\text{L})(\text{RC}\equiv\text{CR})_3]\text{OTf}$

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Rhenium(I) Tris(acetylene) Complexes: $\text{Re}(\text{OR}')(\text{RC}\equiv\text{CR})_3$ and $[\text{Re}(\text{L})(\text{RC}\equiv\text{CR})_3]\text{OTf}^1$

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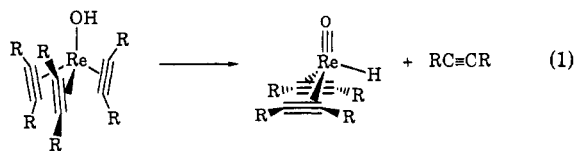
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The syntheses of a number of rhenium(I) tris(acetylene) compounds are presented, including an improved synthesis of $\text{ReI}(\text{RC}\equiv\text{CR})_3$ (1a, R = Me; 1b, R = Et). Reaction of the low-valent oxo anions $\text{NaRe}(\text{O})(\text{RC}\equiv\text{CR})_2$ with Me_3SiCl in the presence of $\text{RC}\equiv\text{CR}$ yields $\text{Re}(\text{OSiMe}_3)(\text{RC}\equiv\text{CR})_3$ (2). Colorless 2a crystallizes in the tetragonal space group $I4_1/a$, with $a = 27.631(3)$ Å, $c = 9.699(1)$ Å, and $Z = 16$. The structure is similar to those of isoelectronic tungsten(0) tris(acetylene) complexes such as $\text{W}(\text{CO})(\text{PhC}\equiv\text{CPh})_3$. Compounds 2 react readily with acids and acidic alcohols to form $\text{Re}(\text{OR})(\text{RC}\equiv\text{CR})_3$ (HOR = acetic acid, *p*-toluenesulfonic acid, phenol, $(\text{CF}_3)_2\text{CHOH}$); reaction with HCl (g) yields $\text{ReCl}(\text{RC}\equiv\text{CR})_3$. In addition, the Lewis acids Me_3SiCl and Me_3SiOTf and 2 form $\text{ReCl}(\text{RC}\equiv\text{CR})_3$ and $\text{Re}(\text{OTf})(\text{RC}\equiv\text{CR})_3$ (3), along with $(\text{Me}_3\text{Si})_2\text{O}$ (OTf = CF_3SO_3 , triflate). Compounds 3 can also be synthesized from 1 and AgOTf or by addition of 2 equiv of Me_3SiOTf to $\text{NaRe}(\text{O})(\text{RC}\equiv\text{CR})_2$. The triflate ligand appears to be covalently coordinated from IR and ^{19}F NMR spectroscopy, but it is readily displaced by better ligands (L = PMe_3 , OPMe_3 , CH_3CN , pyridine, pyridine *N*-oxide) to give $[\text{Re}(\text{L})(\text{RC}\equiv\text{CR})_3]\text{OTf}$ complexes. Weakly coordinating ligands form equilibrium mixtures (e.g., $3 + \text{H}_2\text{O} \rightleftharpoons [\text{Re}(\text{H}_2\text{O})(\text{RC}\equiv\text{CR})_3]\text{OTf}$ (4)). Reactions of 3 with NaOMe in $\text{MeOH}/\text{C}_6\text{H}_6$ yield methoxide complexes, $\text{Re}(\text{OMe})(\text{RC}\equiv\text{CR})_3$ (5). $\text{Re}(\text{OMe})(\text{EtC}\equiv\text{CEt})_3$ (5b) reacts with 2-butyne by acetylene exchange. The reaction occurs within 2 days at 25 °C and appears to be first order in 5b and zero order in 2-butyne, consistent with a dissociative pathway. The rates of acetylene exchange for $\text{Re}(\text{OR}')(\text{RC}\equiv\text{CR})_3$ vary widely in the order $\text{OMe} \approx \text{OSiMe}_3 > \text{OPh} \gg \text{OAc}, \text{OTf}$, paralleling the basicity of the anionic ligands. Unlike the related hydroxide compound,¹⁰ the methoxide, phenoxide, and acetate complexes do not rearrange to the stable oxo-alkyl or oxo-acyl compounds $\text{Re}(\text{O})\text{R}'(\text{RC}\equiv\text{CR})_2$ (R' = Me, Ph, C(O)Me), either thermally or photochemically.

Acetylenes are unique ligands because they can act as both π donors and π acceptors, and because they can donate a variable number of electrons to a metal center without a change in the number of bound atoms.⁴ A consequence of this is the formation of metal complexes with uncommon oxidation states and/or coordination geometries. The classic example is the series of tungsten(0) tris(acetylene) complexes $\text{W}(\text{L})(\text{RC}\equiv\text{CR})_3$,⁵ which adopt a pseudotetrahedral (or capped-trigonal-prismatic) geometry. These tungsten compounds were first prepared in the mid-1960s, but the isoelectronic rhenium(I) tris(acetylene) complexes $\text{ReI}(\text{RC}\equiv\text{CR})_3$ (1a, R = Me; 1b, R = Et) have only recently been reported,⁶ formed as a low-yield side product in the synthesis of $\text{Re}(\text{O})\text{I}(\text{RC}\equiv\text{CR})_2$.

We have been examining the chemistry of rhenium oxo bis(acetylene) compounds, including the unusual anions $\text{NaRe}(\text{O})(\text{RC}\equiv\text{CR})_2$.^{7,8} These highly electron-rich compounds (formally Re(I)) are readily protonated or alkylated to give rhenium(III) oxo-hydride and oxo-alkyl complexes, $\text{Re}(\text{O})\text{R}'(\text{RC}\equiv\text{CR})_2$,⁸ which are also available by direct alkylation of $\text{Re}(\text{O})\text{I}(\text{RC}\equiv\text{CR})_2$.⁹ Described here are the conversion of the anions to rhenium(I) tris(acetylene) compounds using silicon electrophiles and the syntheses of a number of $\text{ReX}(\text{RC}\equiv\text{CR})_3$ and $[\text{Re}(\text{L})(\text{RC}\equiv\text{CR})_3]^+$ derivatives.

Of particular interest have been rhenium(I) alkoxide complexes $\text{Re}(\text{OR}')(\text{RC}\equiv\text{CR})_3$ because they are formally related to the known oxo-alkyl complexes by loss of an acetylene and migration of R' from oxygen to the metal. We have recently reported¹⁰ that the analogous rhenium(I) hydroxide cleanly rearranges to the oxo-hydride complex (eq 1, R = Et). The interconversion of alkoxide



and oxo-alkyl species has been much discussed because it may be involved in the oxidation of organic compounds

(1) Low-Valent Rhenium-Oxo Complexes. 13. Parts 11 and 12: References 8 and 10.

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mediated by metal oxo complexes,¹¹ but the only clear example is in a bis(pentamethylcyclopentadienyl)tantalum system.¹²

Experimental Section

Syntheses were performed using standard Schlenk or vacuum-line techniques and a continuous nitrogen flow glovebox, except as indicated. Solvents and reagents were dried and deoxygenated by standard methods¹³ (unless otherwise mentioned). Reactions were executed at ambient temperatures unless otherwise stated. Column chromatography was performed in the air under slight positive pressure on Merck silica gel 60 (230–400 mesh) using solvents as received. $\text{Re}(\text{O})\text{I}(\text{C}\equiv\text{CR})_2$ were prepared as described in ref 6.

NMR spectra were obtained on Varian VXR-300 or Bruker WM-500 and AC-200 spectrometers. ^1H chemical shifts are reported in ppm downfield from Me_4Si as δ (number of hydrogens, multiplicity, coupling constant, assignment), and ^{13}C chemical shifts were referenced to solvent peaks (CD_3CN , 0.5 ppm; $\text{CD}_2\text{-Cl}_2$, 55.0 ppm; C_6D_6 , 128.7 ppm); CF_3 resonances were not observed under the experimental conditions employed for the ^{13}C NMR spectra. ^{19}F NMR spectra were referenced to CF_3COOH (0.0 ppm) in the same solvent used for the spectrum; ^{31}P NMR spectra were referenced to 85% aqueous H_3PO_4 (0.0 ppm). IR spectra were obtained on NaCl or CsI plates with Perkin-Elmer 283 or FT 1604 spectrometers and are reported in cm^{-1} . Elemental analyses were performed by Canadian Microanalytical (Delta, British Columbia). Mass spectra were obtained, unless otherwise indicated, on a Hewlett-Packard 5985 GC/MS instrument using the direct inlet method with a 70-eV ionizing radiation. For compounds that do not sublime, FAB-MS spectra were acquired using a VG 70 SEQ tandem hybrid instrument of EBQq geometry (VG Analytical, Altrincham, U.K.). The instrument was equipped with a standard unheated VG FAB ion source and a standard saddlefield gun (Ion Tech Ltd., Middlesex, U.K.) producing a beam of xenon atoms at 8 keV and 1 mA. The mass spectrometer was adjusted to a resolving power of 1000, and spectra were obtained at 8 kV and at scan speed of 10 s/decade. 3-Nitrobenzyl alcohol was used as the matrix in the positive ion FAB-MS mode.

X-ray Structure of $\text{Re}(\text{OSiMe}_3)(\text{MeC}\equiv\text{CMe})_3$. Crystal data: tetragonal, $I4_1/a$, $a = 27.631(3)$ Å, $c = 9.699(1)$ Å, $V = 7405(3)$ Å³, $Z = 16$, $D_s = 1.57$ g cm^{-3} . One octant of data (3614 reflections to $2\theta = 50^\circ$) was collected at 24 °C on a box-shaped crystal (dimensions $0.8 \times 0.8 \times 0.6$ mm, grown from CH_3CN at -20 °C and mounted in a capillary under N_2) using an Enraf-Nonius CAD4 diffractometer (graphite-monochromatized $\text{Mo K}\alpha$ radiation). The data were corrected for Lorentz and polarization effects, and for absorption using an empirical absorption method ($\mu = 67.07$ cm^{-1} , transmission factors 0.997–0.569), giving 2173 independently observed reflections ($I > 3\sigma_I$). The rhenium was located by direct methods (SHELX¹⁴) and the structure solved by subsequent least-squares refinement and Fourier syntheses. With all 18 non-hydrogen atoms anisotropic and with hydrogen atoms fixed in calculated positions or located from a difference map then regularized (acetylenic methyls), final refinement of

Table I. Positional and Equivalent Isotropic Thermal Parameters for $\text{Re}(\text{OSiMe}_3)(\text{MeC}\equiv\text{CMe})_3$ (2a)

atom	x	y	z	B (Å ²) ^a
Re	0.18655(1)	0.11212(1)	0.87288(4)	3.972(8)
Si	0.08199(13)	0.10938(14)	0.6593(4)	5.51(8)
O	0.1257(3)	0.1172(3)	0.7570(9)	6.5(2)
C1	0.2134(4)	0.0654(4)	0.7317(11)	4.7(2)
C2	0.2463(4)	0.0737(4)	0.8235(11)	4.8(2)
C3	0.1922(4)	0.1837(4)	0.8436(9)	4.1(2)
C4	0.2314(4)	0.1697(4)	0.9189(10)	4.7(2)
C5	0.1457(4)	0.0855(4)	1.0290(12)	5.3(3)
C6	0.1885(4)	0.0894(4)	1.0691(11)	4.8(2)
C7	0.0950(7)	0.1220(7)	0.4743(16)	11.0(5)
C8	0.0331(5)	0.1524(6)	0.7012(17)	8.1(4)
C9	0.0577(8)	0.0470(6)	0.6663(21)	12.3(6)
C11	0.2042(6)	0.0402(5)	0.6029(14)	7.7(4)
C21	0.2968(5)	0.0627(6)	0.8626(14)	7.4(4)
C31	0.1702(5)	0.2258(4)	0.7761(13)	5.9(3)
C41	0.2760(4)	0.1839(4)	0.9849(12)	5.2(3)
C51	0.0961(5)	0.0707(5)	1.0671(15)	6.6(3)
C61	0.2204(5)	0.0832(5)	1.1950(13)	6.5(3)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table II. Bond Distances (Å) for $\text{Re}(\text{OSiMe}_3)(\text{MeC}\equiv\text{CMe})_3$ (2a)

Re–O	2.027(8)	Re–C6	2.005(11)
Re–C1	2.023(10)	Si–O	1.552(8)
Re–C2	2.019(10)	C1–C2	1.292(14)
Re–C3	2.004(10)	C3–C4	1.363(15)
Re–C4	2.066(11)	C5–C6	1.251(15)
Re–C5	2.028(11)		

Table III. Bond Angles (deg) for $\text{Re}(\text{OSiMe}_3)(\text{MeC}\equiv\text{CMe})_3$ (2a)

O–Re–C1	88.5(4)	C3–Re–C5	120.5(4)
O–Re–C2	125.6(4)	C4–Re–C6	91.2(4)
O–Re–C3	85.3(4)		
O–Re–C4	124.3(4)	Re–O–Si	167.2(6)
O–Re–C5	88.7(5)	O–Si–C7	114.4(8)
O–Re–C6	124.8(4)	O–Si–C8	110.2(6)
C1–Re–C2	37.3(4)	O–Si–C9	112.9(9)
C1–Re–C3	120.3(4)	Re–C1–C2	71.2(7)
C1–Re–C4	114.6(5)	Re–C1–C11	145.4(10)
C1–Re–C5	118.6(5)	C2–C1–C11	143.3(12)
C1–Re–C6	115.6(5)	Re–C2–C1	71.5(7)
C2–Re–C4	88.0(5)	Re–C2–C21	145.0(10)
C2–Re–C6	92.2(4)	C1–C2–C21	143.5(12)

163 parameters converged to $R_F = 0.044$, $R_{wF} = 0.060$, and GOF = 1.16. Atomic coordinates and equivalent isotropic thermal parameters are given in Table I; Tables II and III contain selected bond lengths and angles.

$\text{ReI}(\text{MeC}\equiv\text{CMe})_3$ (1a). THF (30 mL) was added to 2.011 g (4.6 mmol) of $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})_2$, 0.394 g (17 mmol) of Na, and 8 mg (62 μmol) of naphthalene. The solution was stirred for 1 h, over which time it turned from bright yellow to green to deep orange. The excess Na was filtered away and the THF distilled off. C_6H_6 (15 mL) was distilled in, and 1.0 mL of 2-butyne (12.8 mmol) and 2–3 equiv of Me_3SiI were added. Stirring for 0.5 h and stripping to dryness *in vacuo* left a dark brown residue, to which 20% EtOAc/80% hexanes was added on the benchtop; this solution was filtered through a short silica column while solvent was continually added until the solution came off nearly colorless. After the resulting brown solution was concentrated, the product was purified on a silica column (made with hexanes: about 1 L of hexanes was run through to wash off the organics, and then the product was eluted with 20% EtOAc/80% hexanes as two overlapping bands, a light yellow one and an orange one). After the solvent was distilled away, a minimum amount of hexane was added to collect the off-white solids and wash away the uncharacterized orange impurity. The yield was 1.113 g (2.3 mmol, 51%). Spectral and analytical data are reported in ref 6.

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ReI(EtC≡CEt)₃ (1b) was prepared by following the procedure for **1a**, using 1.236 g (2.5 mmol) of Re(O)I(EtC≡CEt)₂, 0.273 g (11.9 mmol) of Na, and 7 mg (55 μmol) of naphthalene, except the 20 mL of THF was added to the Re(O)I(EtC≡CEt)₂ before the Na. This solution was stirred 2 h before removing the THF and adding 15 mL of C₆H₆, 1.0 (8.8 mmol) of 3-hexyne, and 1.0 mL (7.0 mmol) of Me₃SiI. The yield was 0.739 g (1.3 mmol, 53%) of off-white solids. Spectral and analytical data are reported in ref 6.

Re(OSiMe₃)(MeC≡CMe)₃ (2a). To Re(O)I(MeC≡CMe)₂ (1.075 g, 2.5 mmol) was added 0.5 g of Na metal (2.2 mmol, 8.8 equiv) and 25 mL of THF at -78 °C. The solution was stirred for 3.5 h at -78 °C; then the excess Na was filtered away. Ten equivalents of 2-butyne and 1 equiv of Me₃SiCl were added, and the resulting solution was stirred 0.5 h. All volatiles were removed *in vacuo*, and **2a** (116 mg, 0.42 mmol, 17%) was sublimed out of the residue at 50–55 °C (10⁻³ Torr) as white solids. ¹H NMR (CD₃CN; δ): 0.22 (s, 9 H, OSi(CH₃)₃); 2.28, 2.87 (q, 1 Hz, 9 H each, CH₃C≡CCH₂); 10.2, 17.8 (CH₃C≡CC¹H₃); 159.9, 176.7 (C≡C). IR (Nujol; cm⁻¹): 1762 w ν(C≡C), 1246, 1233 s, 1170, 1025 vs ν(Si—O), 823 s, 737, 666. Anal. Calcd for C₁₅H₂₇OReSi: C, 41.16; H, 6.22. Found: C, 41.18; H, 6.20.

Re(OSiMe₃)(EtC≡CEt)₃ (2b). To a flask containing NaRe(O)(EtC≡CEt)₂ (0.232 g, 0.60 mmol), several equivalents of 3-hexyne, and 20 mL of THF was added Me₃SiCl (0.60 mmol, 1.01 equiv) at -78 °C. The reaction mixture was stirred at -78 °C for 10 min; then all volatiles were removed *in vacuo*. Sublimation of the residue at 80 °C under static vacuum (10⁻³ Torr) yielded 116 mg (0.22 mmol, 37%) of white solids. ¹H NMR (CD₃CN; δ): 0.22 (s, 9 H, OSi(CH₃)₃); 0.95, 1.24 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 2.96, 3.25 (q, 7 Hz, 6 H each, CH₃-CH₂C≡CCH₂CH₃). ¹³C{¹H} NMR (CD₃CN; δ): 4.1 (OSi(CH₃)₃); 13.2, 13.9 (CH₃CH₂C≡CCH₂CH₃); 19.7, 28.1 (CH₃CH₂C≡CCH₂CH₃); 165.2, 178.7 (C≡C). IR (neat; cm⁻¹): 2965, 2931, 1750 w ν(C≡C), 1457, 1414, 1330 w, 1278, 1163 w, 1027 s ν(Si—O), 967, 930 w, 907, 820. MS (*m/e*): 440/438 (M - EtC≡CEt)⁺. Anal. Calcd for C₂₁H₃₉OReSi: C, 48.34; H, 7.53. Found: C, 48.26; H, 7.16.

ReCl(EtC≡CEt)₃. To 0.136 g (0.35 mmol) NaRe(O)(EtC≡CEt)₂ was added 10 mL of CH₃CN, 1.4 mL (11.8 mmol, 34 equiv) of EtC≡CEt, and then 0.5 mL (3.9 mmol, 11.3 equiv) of Me₃SiCl. The solution was stirred 20 min at ambient temperature; then the volatiles were removed *in vacuo*. The brown residue was loaded onto a silica column made with hexanes. Hexanes was run through; then the product was eluted with 1:1 EtOAc/hexanes. The solvent was removed to yield 0.103 g (0.22 mmol, 63%) of ReCl(EtC≡CEt)₃ as off-white solids. Further purification can be accomplished by sublimation at 90 °C (10⁻³ Torr). ¹H NMR (CD₃CN; δ): 0.95, 1.25 (t, 7 Hz, 9 H each, CH₃-CH₂C≡CCH₂CH₃); 3.05, 3.33 (q, 7 Hz, 6 H each, CH₃-CH₂C≡CCH₂CH₃). ¹³C{¹H} NMR (CD₃CN; δ): 13.0, 13.5 (CH₃-CH₂C≡CCH₂CH₃); 20.0, 27.4 (CH₃CH₂C≡CC¹H₃); 162.9, 174.8 (C≡C). MS (*m/e*): 468/466 M⁺; 386/384 [M - EtC≡CEt]⁺; 433/431 [M - Cl]⁺.

Re(OTf)(MeC≡CMe)₃ (3a). To ReI(MeC≡CMe)₃ (0.510 g, 1.07 mmol) and AgOTf (0.278 g, 1.08 mmol) was added CH₂Cl₂ (20 mL), and the resulting solution was stirred for 1 h. Within 15 min flocculent green-yellow solids had appeared. The solids were filtered away, and the solvent was removed *in vacuo*. The minimum amount of pentane (~5 mL) was added to collect the white solids, yield 0.389 g (0.78 mmol, 73%). ¹H NMR (C₆D₆; δ): 2.18, 2.48 (q, 1 Hz, 9 H each, CH₃C≡CCH₂); 12.2, 18.3 (CH₃C≡CC¹H₃); 160.5, 175.3 (C≡C). ¹⁹F NMR (C₆D₆; δ): -0.8. IR (Nujol, cm⁻¹): 1769 w ν(C≡C), 1317 s ν(OTf), 1232 s ν(OTf), 1201 s ν(OTf), 1181 s, ν(OTf), 1044, 1019, 1019 s, 761 w. Anal. Calcd for C₁₃H₁₃F₃O₃ReS: C, 31.38; H, 3.65. Found: C, 31.24; H, 3.57.

Re(OTf)(EtC≡CEt)₃ (3b). **Method A: ReI(EtC≡CEt)₃ plus AgOTf**. The preparation was analogous to that of Re(OTf)(MeC≡CMe)₃ given, using 0.500 g (0.89 mmol) of ReI-

(EtC≡CEt)₃ and 0.233 g (0.91 mmol) of AgOTf. The isolated yield was 0.445 g (0.77 mmol, 86%) of white solids.

Method B: Re(OSiMe₃)(EtC≡CEt)₃ plus Me₃SiOTf. To Re(OSiMe₃)(EtC≡CEt)₃ (53 mg, 0.10 mmol) and C₆H₆ was added Me₃SiOTf (20 μL, 0.10 mmol). The solution was stirred 0.5 h; then the solvent and (Me₃Si)₂O were distilled away to give a quantitative yield of Re(OTf)(EtC≡CEt)₃. ¹H NMR (C₆D₆; δ): 0.93, 0.95 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 2.77, 3.26 (q, 7 Hz, 6 H each, CH₃CH₂C≡CCH₂CH₃). ¹³C{¹H} NMR (C₆D₆; δ): 14.5, 15.7 (CH₃CH₂C≡CCH₂CH₃); 22.0, 28.9 (CH₃-CH₂C≡CC¹H₃); 165.8, 178.2 (C≡C). ¹⁹F NMR (C₆D₆; δ): -0.9. IR (Nujol, Csl; cm⁻¹): 1759 w ν(C≡C), 1321 ν(OTf), 1230 s ν(OTf), 1205 vs ν(OTf), 1180 s ν(OTf), 1108 s ν(OTf), 1077 w, 1051 w, 1012 w, 950 w, 633 s, 583 w, 513. Anal. Calcd for C₁₉H₃₀F₃O₃ReS: C, 39.23; H, 5.20. Found: C, 39.14; H, 5.18.

Re(OMe)(MeC≡CMe)₃ (5a). Re(OTf)(MeC≡CMe)₃ (0.159 g, 0.32 mmol), NaOMe (39 mg, 0.72 mmol), ~100 equiv of MeOH, and C₆H₆ (15 mL) were combined and then stirred for 5 days. The solvent was removed *in vacuo*, and pentane (15 mL) was distilled in and stirred 0.5 h. White solids were filtered off, and the solvent was distilled away to yield light yellow solids (82 mg, 0.22 mmol, 68%). Sublimation at 40–45 °C (10⁻³ Torr) yields analytically pure material. ¹H NMR (C₆D₆; δ): 2.48, 2.53 (q, 1 Hz, 9 H each, CH₃C≡CCH₂); 5.48 (s, 3 H, OCH₃). ¹³C{¹H} NMR (C₆D₆; δ): 12.4, 19.5 (CH₃C≡CC¹H₃); 66.2 (OCH₃); 163.5, 178.6 (C≡C). IR (Nujol; cm⁻¹): 2754 s, 1765 w ν(C≡C), 1171 s, 1066 s ν(C—O). Anal. Calcd for C₁₃H₂₁ORe: C, 41.14; H, 5.58. Found: C, 41.15; H, 5.54.

Re(OMe)(EtC≡CEt)₃ (5b). The preparation is similar to that of the 2-butyne analog above using Re(OTf)(EtC≡CEt)₃ (0.252 g, 0.43 mmol), NaOMe (57 mg, 1.06 mmol), and MeOH (5 mL, 124 mmol). The yield was 0.151 g (0.33 mmol, 75%) of light yellow gummy solids. Sublimation at 45 °C (10⁻³ Torr) gives analytically pure material. This compound stores best at -20 °C under a N₂ atmosphere (at room temperature it darkens significantly). ¹H NMR (C₆D₆; δ): 1.10, 1.13 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 3.05, 3.21 (q, 7 Hz, 6 H each, CH₃CH₂C≡CCH₂CH₃); 5.44 (s, 3 H, OCH₃). ¹³C{¹H} NMR (C₆D₆; δ): 14.9, 15.5 (CH₃CH₂C≡CCH₂CH₃); 22.0, 30.1 (CH₃-CH₂C≡CC¹H₃); 66.4 (OCH₃); 168.8, 181.2 (C≡C). IR (Nujol, Csl; cm⁻¹): 2758, 1730 w ν(C≡C), 1301, 1252 w, 1158, 1069 s ν(C—O), 945, 452 ν(Re—O). Anal. Calcd for C₁₉H₃₃ORe: C, 49.22; H, 7.17. Found: C, 49.20; H, 7.01.

Re(OPh)(MeC≡CMe)₃. To Re(OSiMe₃)(MeC≡CMe)₃ (50 mg, 0.11 mmol) and phenol (11 mg, 0.12 mmol) was added C₆H₆ (~3 mL), and the solution was stirred for 4.5 h, at which time the solvent was removed *in vacuo*. A ¹H NMR spectrum showed the reaction was only 50% complete; therefore, 8 mg of phenol and 2 mL of C₆H₆ were added, and the mixture was stirred an additional 20 h. The solvent was distilled away to yield 43 mg (0.10 mmol, 85%) of off-white solids. ¹H NMR (C₆D₆; δ): 2.30, 2.51 (q, 1 Hz, 9 H each, CH₃C≡CCH₂); 6.92 (m, 1 H, H_{para}); 7.12, 7.47 (each m, 2 H, H_{ortho} and H_{meta}). ¹³C{¹H} NMR (C₆D₆; δ): 12.4, 19.3 (CH₃C≡CC¹H₃); 115.5 (C_{para}); 121.7, 130.0 (C_{ortho} and C_{meta}); 170.6 (C_{ipso}); 161.8, 177.2 (C≡C). IR (Nujol; cm⁻¹): 3016 w, 1763 w ν(C≡C), 1587 s, 1560 w, 1319, 1284 s, 1265, 1173, 1060, 1066 w, 987, 838, 768, 699. Anal. Calcd for C₁₈H₂₃O₂Re: C, 48.96; H, 5.25. Found: C, 48.84; H, 4.95.

Re[OC(O)CH₃](EtC≡CEt)₃. To **1b** (0.149 g, 0.27 mmol) and AgO₂CCH₃ (91 mg, 0.55 mmol, 2 equiv) was added 5 mL of CH₂-Cl₂. After the solution was stirred for 2 days, the green-gray solids were filtered away and the solvent was removed to yield 113 mg (0.23 mmol, 85%) of gummy yellow solids. Sublimation at 60–65 °C gave analytically pure material. ¹H NMR (C₆D₆; δ): 1.08, 1.97 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 2.81 (s, 3 H, C(O)CH₃); 2.99, 3.17 (q, 7 Hz, 6 H each, CH₃CH₂C≡CCH₂-CH₃). ¹³C{¹H} NMR (C₆D₆; δ): 14.8, 15.3 (CH₃CH₂C≡CCH₂CH₃); 22.7, 29.6 (CH₃CH₂C≡CC¹H₃); 25.9 (C(O)CH₃); 167.0, 177.8 (C≡C); 176.3 (C(O)CH₃). IR (Nujol; cm⁻¹): 1737 w ν(C=O), 1637, s ν(C=O), 1309 s, 1158, 1101 w, 1064, 1010 w, 945, 814 w, 667. Anal. Calcd for C₂₀H₃₃O₂Re: C, 48.86; H, 6.76. Found: C, 48.95; H, 6.65.

[Re(py-O)(EtC≡CEt)₂]OTf. To 0.199 g (0.34 mmol) of **3b** was added 33 mg (0.35 mmol, 1.03 equiv) of pyridine *N*-oxide and 10 mL of CH₂Cl₂. The solution was stirred for 3 days, and then the solvent was distilled away, yielding 0.174 g (75%) of off-white solids slightly contaminated with a decomposition product (see text). ¹H NMR (CD₂Cl₂; δ): 0.97, 1.34 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 2.78, 3.41 (q, 7 Hz, 6 H each, CH₃CH₂C≡CCH₂CH₃); 7.92 (m, 2 H, H_{3-py}); 8.06 (m, 1 H, H_{4-py}); 8.69 (m, 2 H, H_{2-py}). ¹³C{¹H} NMR (CD₂Cl₂; δ): 14.8, 15.6 (CH₃-CH₂C≡CCH₂CH₃); 22.2, 29.7 (CH₃CH₂C≡CCH₂CH₃); 129.4, 140.8 (C_{2,3-py}); 136.1 (C_{4-py}); 164.5, 183.5 (C≡C'). ¹⁹F NMR (C₆D₆; δ): -1.9. IR (Nujol, CsI; cm⁻¹): 3110, 3078, 1732 w ν(C≡C), 1270 s ν(OTf), 1222 s ν(OTf), 1197 ν(N-O), 1155 s ν(OTf), 1029 s ν(OTf), 946, 831, 780 s, 636 s, 585, 571, 517. FAB-MS (*m/e*): 528/526, M⁺ (65%); 433/431, [M - (py-O)]⁺ (100%).

[Re(PMe₃)(EtC≡CEt)₂]OTf. To 99 mg (0.17 mmol) of **3b** and 5 mL of C₆H₆ was added 0.77 mL (7.4 mmol, 44 equiv) of PMe₃. The solution was stirred a couple of hours at ambient temperature; then it was stripped to dryness *in vacuo* to yield 95 mg (0.14 mmol, 85%) of off-white solids. ¹H NMR (CD₂Cl₂; δ): 1.05, 12.9 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 2.22 (d, 7 Hz, 9 H, P(CH₃)₃); 2.96 (q, 7 Hz, 6 H, CH₃CH₂C≡CCH₂CH₃); 3.74 (d of q, 7 Hz (³J_{HH}), 2 Hz (⁴J_{PH}), 6 H, CH₃CH₂C≡CCH₂CH₃). ¹³C{¹H} NMR (CD₂Cl₂; δ): 14.6, 15.6 (CH₃CH₂C≡CCH₂CH₃); 19.4 (d, 32 Hz, P(CH₃)₃); 26.3 (d, 9 Hz, CH₃-CH₂C≡CCH₂CH₃); 28.9 (CH₃CH₂C≡CCH₂CH₃); 160.2 (d, 14 Hz, C≡C'); 186.9 (C≡C'). ¹⁹F NMR (CD₂Cl₂; δ): -2.8. ³¹P{¹H} NMR (CD₂Cl₂; δ): -7.3. IR (Nujol; cm⁻¹): 1741 w ν(C≡C), 1269 s ν(OTf), 1221 ν(OTf), 1146 s ν(OTf), 1097, 1031 s ν(OTf), 951 s, 736, 636 s. FAB-MS (*m/e*) 509/507 M⁺. Anal. Calcd for C₂₂H₃₈F₃O₃PrReS: C, 40.17; H, 5.98. Found: C, 40.20; H, 5.83.

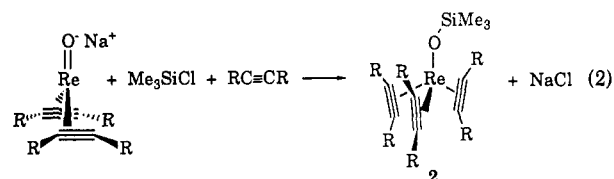
[Re(OPMe₃)(EtC≡CEt)₂]OTf was observed upon addition of 2–3 equiv of OPMe₃ to **3b** in an NMR tube in CD₂Cl₂; the reaction was complete and quantitative (by NMR) in ca. 2 h. ¹H NMR (CD₂Cl₂; δ): 1.04, 1.30 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 2.04 (d, 13 Hz, 9 H, OP(CH₃)₃); 2.94, 3.31 (q, 7 Hz, 6 H each, CH₃CH₂C≡CCH₂CH₃). ¹³C{¹H} NMR (CD₂Cl₂; δ): 20.0, 21.1 (CH₃CH₂C≡CCH₂CH₃); 24.2 (d, 72 Hz, OP(CH₃)₃); 27.4, 34.4 (CH₃CH₂C≡CCH₂CH₃); 169.9, 186.4 (C≡C'). ¹⁹F NMR (CD₂Cl₂; δ): -2.8. ³¹P{¹H} NMR (CD₂Cl₂; δ): 37.2. FAB-MS (*m/e*): 525/523, M⁺ (73%); 433/431, [M - (OPMe₃)]⁺ (100%).

[Re(CH₃CN)(EtC≡CEt)₂]OTf. To 103 mg (0.18 mmol) of **3b** and 10 mL of CH₂Cl₂ was added 0.5 mL (9.6 mmol, 54 equiv) of CH₃CN. The solution was stirred 2 h at ambient temperature and then stripped to dryness *in vacuo*. The isolated yield was 70 mg (0.11 mmol, 64%) of off-white solids. ¹H NMR (CD₂Cl₂; δ): 1.07, 1.32 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 3.13 (s, 3 H, CH₃CN); 3.10, 3.41 (q, 7 Hz, 6 H each, CH₃CH₂C≡CCH₂CH₃). ¹³C{¹H} NMR (CD₂Cl₂; δ): 6.2 (CH₃CN); 14.9, 15.7 (CH₃-CH₂C≡CCH₂CH₃); 23.1, 29.5 (CH₃CH₂C≡CCH₂CH₃); 138.3 (CH₃CN); 162.2, 179.6 (C≡C'). ¹⁹F NMR (CD₂Cl₂; δ): -2.9. IR (Nujol; cm⁻¹): 2293 w ν(C≡N), 1760 w ν(C≡C), 1269 s ν(OTf), 1223 ν(OTf), 1149 s ν(OTf), 1031 s ν(OTf), 950, 638 s. FAB-MS (*m/e*): 474/472 M⁺ (57%); 433/431, [M - (CH₃CN)]⁺ (100%). Anal. Calcd for C₂₁H₃₈NF₃O₃ReS: C, 40.50; H, 5.34; N, 2.25. Found: C, 40.52; H, 5.22; N, 2.29.

[Re(H₂O)(EtC≡CEt)₂]OTf (4b). This compound has not been isolated cleanly, because it is formed as an equilibrium mixture with **3b** on addition of H₂O to **3b** in an NMR tube. ¹H NMR (C₆D₆; δ): 0.96, 1.14 (t, 7 Hz, 9 H each, CH₃CH₂C≡CCH₂CH₃); 2.79, 3.41 (q, 7 Hz, 6 H each, CH₃CH₂C≡CCH₂CH₃); 9.7 (s, 2 H, H₂O). ¹³C{¹H} NMR (C₆D₆; δ): 14.4, 15.6 (CH₃-CH₂C≡CCH₂CH₃); 20.9, 29.1 (CH₃CH₂C≡CCH₂CH₃); 165.3, 179.5 (C≡C'). ¹⁹F NMR (C₆D₆; δ): -2.0. FAB-MS (*m/e*): 433/431, [M - (H₂O)]⁺ (100%); no molecular ion was seen. IR (Nujol, not OTf but SbF₆⁻ salt, prepared by addition of 1 equiv of AgSbF₆ to **1b** in CH₂Cl₂, analogous to the synthesis of **3b**; cm⁻¹): 3433 br s ν(OH), 1755 w ν(C≡C), 1642 (HOH bend), 1305, 1252 w, 1161, 1104, 1064, 1052, 949, 676 s ν(SbF₆), 658 s ν(SbF₆), 639 s ν(SbF₆). IR (Nujol, SbF₆⁻ D₂O derivative, prepared by addition of 0.6 equiv of D₂O in the synthesis, followed by distillation of the CH₂Cl₂ away at 0 °C; cm⁻¹): 2553 ν(OD), 1212 (DOD bend).

Results and Discussion

Synthesis, Characterization, and Reactivity of Re-(OSiMe₃)(RC≡CR)₃ (2). Reaction of the Re(I) anions NaRe(O)(RC≡CR)₂ with 1 equiv of Me₃SiCl at -78 °C in the presence of excess acetylene yields Re(OSiMe₃)(RC≡CR)₃ (**2a**, R = Me; **2b**, R = Et; eq 2).⁷ With excess



Me₃SiCl at higher temperatures, this reaction also forms the chloride derivative ReCl(RC≡CR)₃ and (Me₃Si)₂O. Compounds **2** are best isolated by sublimation out of the brown residue left after the volatiles are removed *in vacuo*, although the isolated yields of off-white solids (15–40%) represent only about half of the compound formed on the basis of ¹H NMR spectra of the crude residue. Heating may cause some decomposition. Compounds **2** do not survive silica gel; they appear to be stable to oxygen, but they are slightly sensitive to H₂O in solution (see below).

The ¹H and ¹³C NMR spectra of **2** are similar to those of ReI(RC≡CR)₃ (**1**)⁶ and all of the other tris(acetylene) compounds reported here, with two sets of resonances for the R groups, for those proximal and distal to the siloxide. For R = Et, the methylene protons are not diastereotopic. These data are consistent with C_{3v} molecular symmetry. The nondiastereotopic methylene resonances distinguish the tris(acetylene) compounds from the oxo-bis(acetylene) complexes derived from Re(O)I(RC≡CR)₂; to take advantage of this spectroscopic "handle", much of the chemistry has been pursued with 3-hexyne supporting ligands (R = Et, b series). The ¹³C chemical shifts of the acetylenic carbons (δ 160–180) are consistent with each acetylene acting as a 3^{1/3}-electron donor ligand, as in other ML(RC≡CR)₃ compounds.¹⁵ The base peak in the mass spectrum of **2b** is [M - EtC≡CEt]⁺; the molecular ion is not observed.

The structure of **2a**, as established by single-crystal X-ray diffraction (Figure 1; Table I), is similar to that of isoelectronic tungsten tris(acetylene) complexes such as W(CO)(PhC≡CPh)₃.^{5d} It has essentially C_{3v} symmetry and can be viewed as either a distorted tetrahedron or a tapered monocapped trigonal prism, depending on whether each acetylene is considered to occupy one or two coordination sites. The acetylenes are nearly parallel with each other and with the vector containing the metal and the first atom of the siloxide ligand. This is most clearly seen by looking down the Re-O vector (Figure 1b). The acetylenes have slid down and away from the siloxide (as is also seen in the tungsten structures), and the acetylenes and the siloxide methyls are staggered, reminiscent of the structure of ethane.

The Re-O distance of 2.027(8) Å is consistent with a Re-O single bond—compare Re₂Cl₅(OEt)(dppm)₂ at 2.085-(14) Å¹⁶ and Re(O)(OPh)(MeC≡CMe)₂ at 1.966(14) Å¹⁷—and is significantly longer than that seen for rhenium-

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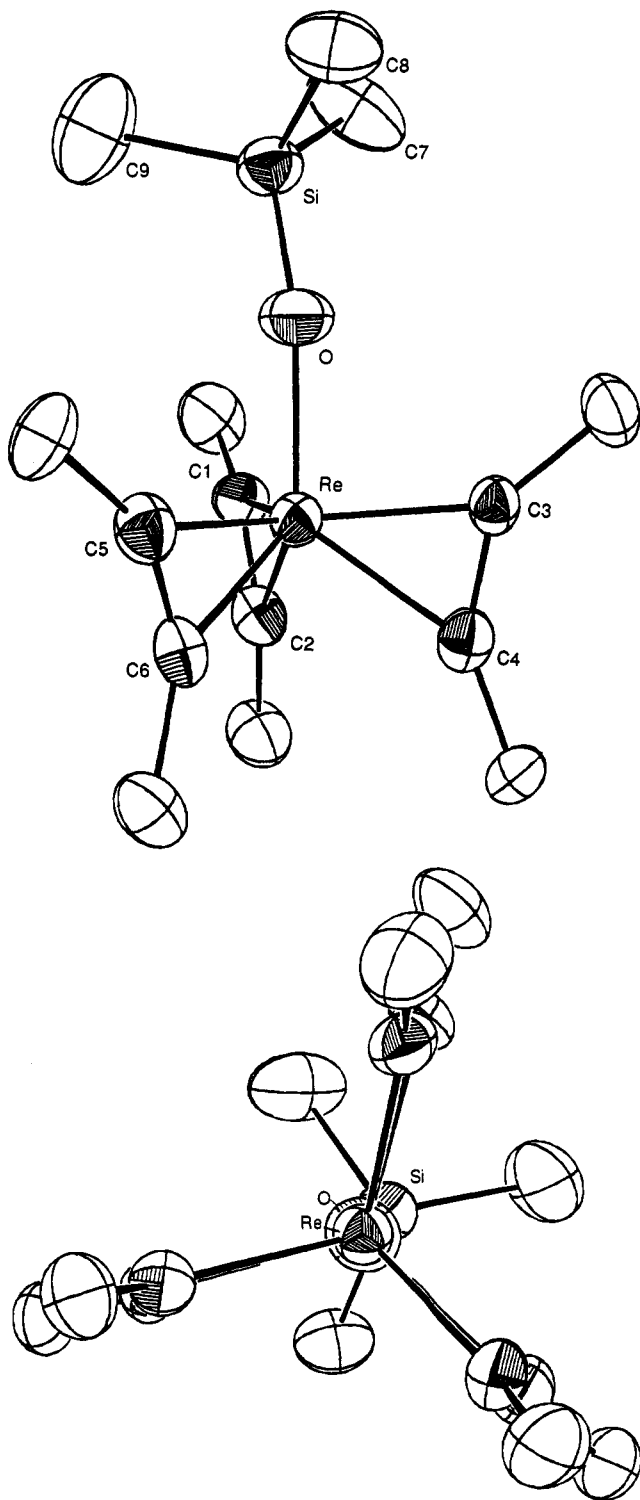
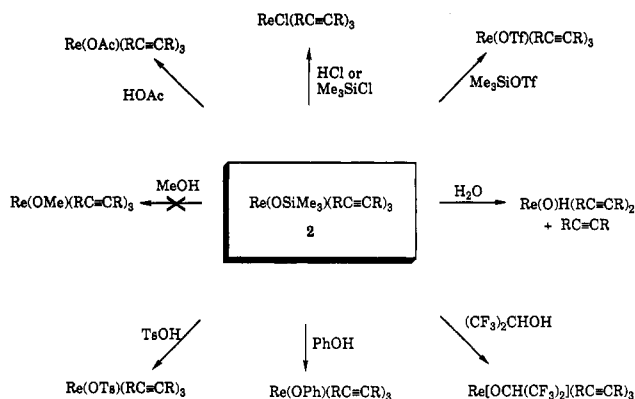


Figure 1. (a, top) ORTEP drawing of $\text{Re}(\text{OSiMe}_3)(\text{MeC}\equiv\text{CMe})_3$ (**2a**) with 30% probability ellipsoids showing the atom-numbering scheme. (b, bottom) ORTEP view of **2a** down the $\text{Re}-\text{O}$ vector. The oxygen and silicon atoms are partially obscured by the rhenium.

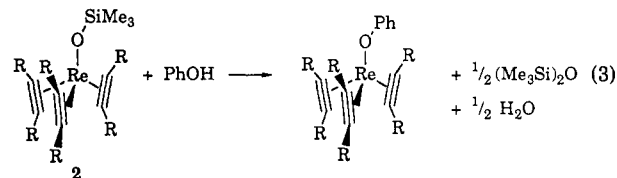
oxygen double bonds (ca. 1.76 Å in d^2 *trans*- ReO_2 structures).¹⁸ The $\text{Re}-\text{O}-\text{Si}$ angle of $167.2(6)^\circ$ is large, but this is typical for silicon-containing species.¹⁹ Rothwell and co-workers have found no correlation between $\text{M}-\text{O}-\text{X}$ angle and the metal-oxygen distance (or the metal-oxygen bond order).²⁰ In **2a**, the opening of the $\text{Re}-\text{O}-\text{Si}$ bond

Scheme I. Reactions of $\text{Re}(\text{OSiMe}_3)(\text{RC}\equiv\text{CR})_3$ (Silicon Products Not Shown)



may in part be due to steric interactions between the SiMe_3 group and the acetylenes, as suggested also by the staggered structure and the tilt of the acetylenes. The $\text{Re}-\text{C}$ distances (average 2.024(11) Å) are approximately equal for the carbons proximal and distal to the siloxide and are comparable to those in $\text{W}(\text{CO})(\text{PhC}\equiv\text{CPh})_3$ (average 2.06(3) Å^{5d}).

Compounds **2** react readily with phenol to form hexamethyldisiloxane and the phenoxide complexes $\text{Re}(\text{OPh})(\text{RC}\equiv\text{CR})_3$ (eq 3, Scheme I). $\text{Re}(\text{OPh})(\text{MeC}\equiv\text{CMe})_3$ has



been isolated as an off-white solid in 85% yield. Conversion of **2b** to the phenoxide complex is complete within 1 day in C_6D_6 but requires roughly 5 days in CD_3CN .

Reactions of **2** in C_6D_6 or CD_3CN with aliphatic alcohols, such as methanol or allyl alcohol, give a few percent of new compounds by ^1H NMR but do not go to completion even over 2 months at ambient temperatures. Similar results were obtained with alkali-metal alkoxides and with alcohols in the presence of base; no reaction was observed with *tert*-butyl alcohol. This lack of reaction is due to the low acidity of the alcohols, as the more acidic hexafluoro-2-propanol, $(\text{CF}_3)_2\text{CHOH}$, reacts completely with **2b** within 2 h to give a species whose NMR spectra are consistent with the formulation $\text{Re}[\text{OCH}(\text{CF}_3)_2](\text{EtC}\equiv\text{CEt})_3$ (Scheme I). Rapid reactions occur between **2a** and acetic acid (HOAc), *p*-toluenesulfonic acid (HOTs), and hydrogen chloride (gas), yielding $\text{Re}(\text{OAc})(\text{RC}\equiv\text{CR})_3$, $\text{Re}(\text{OTs})(\text{RC}\equiv\text{CR})_3$, and $\text{ReCl}(\text{RC}\equiv\text{CR})_3$, respectively (Scheme I). $\text{Re}(\eta^1\text{-OAc})(\text{EtC}\equiv\text{CEt})_3$ has been previously prepared by reacting **1b** and AgOAc .⁶ The Lewis acidic reagents Me_3SiCl and Me_3SiOTf convert **2** to $\text{ReCl}(\text{RC}\equiv\text{CR})_3$ and $\text{Re}(\text{OTf})(\text{RC}\equiv\text{CR})_3$, along with $(\text{Me}_3\text{Si})_2\text{O}$ (Scheme I).

Synthesis, Characterization, and Reactivity of $\text{Re}(\text{OTf})(\text{RC}\equiv\text{CR})_3$ (3**).** As the alkoxide compounds $\text{Re}(\text{OR}')(\text{RC}\equiv\text{CR})_3$ are not accessible from **2**, a synthetic route has been developed starting from the triflate derivatives $\text{Re}(\text{OTf})(\text{RC}\equiv\text{CR})_3$ (**3**). Triflate and tosylate groups are commonly used as leaving groups in organic

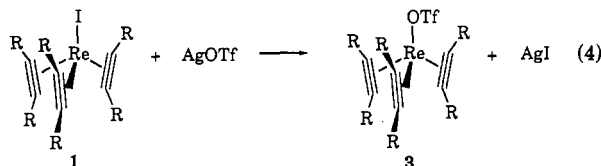
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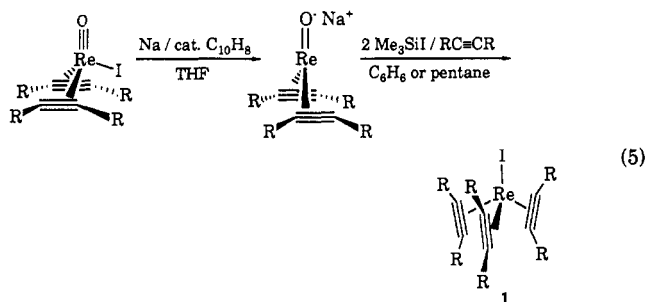
(20) Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* 1990, 29, 3221–3226 and references therein.

synthesis²¹ and to a lesser extent in inorganic synthesis;²² the former was chosen because of its higher reactivity.²³

The triflate complexes $\text{Re}(\text{OTf})(\text{RC}\equiv\text{CR})_3$ (**3a**, $\text{R} = \text{Me}$; **3b**, $\text{R} = \text{Et}$) are formed in quantitative yield from **2** and Me_3SiOTf , but the difficulty in preparing **2** in quantity (maximum yield 37% for **2b**) makes this a poor route to a starting material. Thus, compounds **3** were also found to be accessible in good yields from the iodide complex **1**, on treatment with AgOTf in CH_2Cl_2 (eq 4); with 1 equiv



of AgOTf , the AgI is simply filtered away and the solvent removed to isolate **3** cleanly. The iodide **1** is best prepared directly from $\text{Re}(\text{O})\text{I}(\text{RC}\equiv\text{CR})_2$, $\text{RC}\equiv\text{CR}$, and Me_3SiI , without isolation of the anion or siloxide compounds (eq 5). Generation of anion is best done in THF, but THF is



incompatible with Me_3SiI ,²⁴ necessitating its removal and subsequent addition of a different solvent prior to Me_3SiI addition. Purification of **1** is then carried out by column chromatography on silica gel. Alternatively, **3** can be obtained directly by adding 2 equiv of Me_3SiOTf to the anion, which gives higher yields (~50%) and eliminates a step (eq 4), but skipping the chromatographic purification of **1** leads to less pure product.

The triflates **3** are off-white solids, soluble in CH_2Cl_2 , Et_2O , and benzene and slightly soluble in pentane. IR spectra of solid **3** (Nujol mulls) suggest a covalent $\text{Re}-\text{OTf}$ interaction, based on key bands at 1317 cm^{-1} in **3a** and 1321 cm^{-1} in **3b**. Ionic triflates typically show a strong band at 1270 cm^{-1} , which shifts to higher wavenumber upon coordination,^{22,25} for example to 1350 cm^{-1} in $[\text{Co}(\text{NH}_3)_5(\text{OTf})^{2+}]$;^{25c} no bands are observed in IR spectra of **3** at ca. 1270 cm^{-1} . NMR spectra of **3** support the presence of coordinated triflate. The ^{19}F chemical shifts²⁶ at -0.8 and -0.9 ppm (in C_6D_6 , versus CF_3COOH) are similar to that of triflic acid in this solvent (-0.8 ppm), while ionic

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(24) Me_3SiI reacts with THF to form $\text{Me}_3\text{SiO}(\text{CH}_2)_4\text{I}$: Reference 21, p 385.

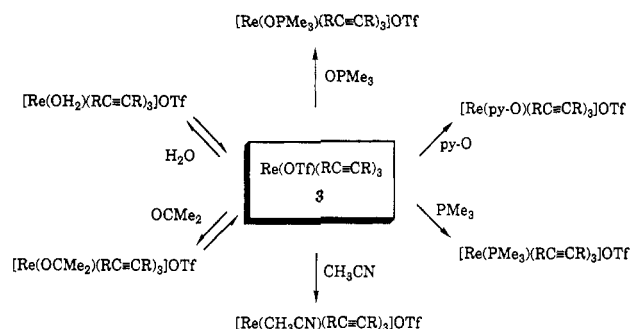
(25) (a) Brown, S. D.; Gard, G. L. *Inorg. Chem.* **1975**, *14*, 2273-2274.

(b) Batchelor, R. J.; Ruddick, J. N. R.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1977**, *16*, 1414-1417. (c) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrence, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470-476.

(d) Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2274-2276.

(26) A review on coordinated triflate and fluorosulfate groups²² describes ^{19}F NMR spectroscopy as "clearly a technique of potential value" for studying these groups.

Scheme II. Formation of Cationic Tris(acetylene) Complexes by Addition of Neutral Ligands to $\text{Re}(\text{OTf})(\text{RC}\equiv\text{CR})_3$ (**3**)



triflates show peaks farther upfield, between ca. -2 and -3 ppm in C_6D_6 , as observed for $\text{NEt}_3\text{H}^+\text{OTf}^-$ and the $[\text{Re}(\text{L})(\text{EtC}\equiv\text{CEt})_3]^+\text{OTf}^-$ complexes discussed below. The ^1H and ^{13}C NMR spectra of **3** are similar to those of **1** and **2**, with two sets of resonances for the R groups, consistent with the C_{3v} $\text{ReX}(\text{RC}\equiv\text{CR})_3$ structure. This suggests that the triflate ligand is not rapidly dissociating on the NMR time scale at ambient temperatures in C_6D_6 or CD_2Cl_2 , as dissociation should form a symmetrical $[\text{Re}(\text{RC}\equiv\text{CR})_3]^+$ species.

The triflate ligand in **3**, though coordinated, is easily replaced with better ligands. Thus, PMe_3 , OPMe_3 , CH_3CN , pyridine (py), and pyridine *N*-oxide (py-O) react with **3** to give $[\text{Re}(\text{PMe}_3)(\text{RC}\equiv\text{CR})_3]\text{OTf}$, $[\text{Re}(\text{OPMe}_3)(\text{RC}\equiv\text{CR})_3]\text{OTf}$, $[\text{Re}(\text{CH}_3\text{CN})(\text{RC}\equiv\text{CR})_3]\text{OTf}$, $[\text{Re}(\text{py})(\text{EtC}\equiv\text{CEt})_3]\text{OTf}$,²⁷ and $[\text{Re}(\text{py-O})(\text{RC}\equiv\text{CR})_3]\text{OTf}$ complexes (Scheme II). No reaction was seen, however, between **3b** and O_2 , CO , or PPh_3 . The cationic compounds are white to off-white solids that are soluble in C_6H_6 and CH_2Cl_2 but insoluble in pentane. Their NMR spectra show ^{19}F NMR signals upfield of compounds **3**. IR spectra also indicate the presence of ionic triflate, as a strong band occurs in each case at 1270 cm^{-1} . The N—O stretching mode of pyridine *N*-oxide at 1265 cm^{-1} shifts on coordination to 1197 cm^{-1} , as expected.^{28a}

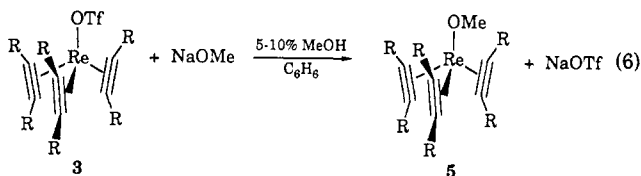
It is interesting that the $\text{Re}(\text{I})$ fragment $\text{Re}(\text{RC}\equiv\text{CR})_3^+$ will bind such a variety of ligands apparently without strong preferences. It binds strongly to OPMe_3 and py-O, which are "hard" ligands, as well as PMe_3 , a "soft" ligand. With the more weakly coordinating ligands water and acetone, an equilibrium is established between **3** and $[\text{Re}(\text{L})(\text{RC}\equiv\text{CR})_3]\text{OTf}$ ($\text{L} = \text{H}_2\text{O}$ (4), Me_2CO (5); Scheme II). The ^1H NMR spectrum of **3b** in acetone- d_6 solvent shows both **3b** and $[\text{Re}(d_6\text{-Me}_2\text{CO})(\text{RC}\equiv\text{CR})_3]\text{OTf}$, but after removal of the acetone *in vacuo*, a spectrum in CD_2Cl_2 shows only **3b**. Upon addition of water to a solution of **3b** in C_6D_6 , both the aquo cation **4b** and **3b** are observed. The ratios of the two products do not change (within experimental error) from a few hours to 6 days, but addition of more H_2O causes the resonances attributable to **4b** to increase relative to those due to **3b**. Attempts to isolate **4b** also yielded mixtures of **3b** and **4b** (usually less than one-third **4b**); presumably removal of the solvent *in vacuo*, even at 0°C , also removes most of the water. **4b** can also be generated as the SbF_6^- salt by reaction of **1b** with AgSbF_6 and water in CH_2Cl_2 ; the equilibrium appears to

(27) $[\text{Re}(\text{py})(\text{EtC}\equiv\text{CEt})_3]\text{SbF}_6$ has been prepared previously from py, AgSbF_6 , and **1b**.⁶

(28) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 208. (b) *Ibid.*, p 231 ($600\text{--}300\text{ cm}^{-1}$).

favor the aquo complex more with this counterion. NMR spectra of **4b** are consistent with its formulation as an aquo complex, including a resonance for bound water at δ 9.7 in the ^1H NMR and ionic triflate at -2.0 ppm in the ^{19}F NMR (see above). IR spectra of $[\text{Re}(\text{H}_2\text{O})(\text{EtC}\equiv\text{CEt})_3]\text{SbF}_6^-$ (in a mixture with $[\text{Re}(\text{SbF}_6)(\text{EtC}\equiv\text{CEt})_3]$) show a broad O-H stretch at 3433 cm^{-1} and an H—O—H bending mode at 1642 cm^{-1} , which would not be present in a hydroxide complex. When D_2O is used in the synthesis, additional bands appear at 2553 and 1212 cm^{-1} (calculated for ν_{OD} , 2503 cm^{-1}). The FAB mass spectrum of $[\text{Re}(\text{H}_2\text{O})(\text{RC}\equiv\text{CR})_3]\text{OTf}$ (**4b**) does not show a parent ion but has a base peak for $[\text{M} - (\text{H}_2\text{O})]^+$ ($[\text{Re}(\text{RC}\equiv\text{CR})_3]^+$, m/e 433/431), not surprising in light of the weak binding of water observed in solution.

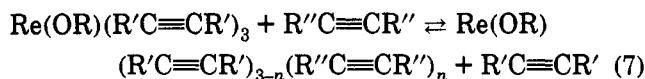
Synthesis and Characterization of $\text{Re}(\text{OR}')(\text{RC}\equiv\text{CR})_3$ Complexes. Reaction of the triflate complexes **3** with NaOMe in methanol/benzene gives the methoxide complexes $\text{Re}(\text{OMe})(\text{RC}\equiv\text{CR})_3$ (**5a**, $\text{R} = \text{Me}$; **5b**, $\text{R} = \text{Et}$; eq 6). The excess base is filtered off, the solvent removed,



and the residue sublimed to give analytically pure materials. This procedure appears to be applicable to a number of alcohols. Treatment of **3** with MeOH in the absence of base (or MeOH and Et_3N) forms a small, equilibrium amount of a new product, probably the alcohol complexes $[\text{Re}(\text{MeOH})(\text{RC}\equiv\text{CR})_3]\text{OTf}$ by analogy to the equilibrium observed on adding water to **3**.

Compounds **5** are light yellow solids that are soluble in organic solvents such as benzene and acetonitrile. Like most alkoxide complexes, they are sensitive to water and do not survive silica gel. They are best kept in the freezer under N_2 , as they appear to melt and turn brown within days at ambient temperatures. ^1H NMR spectra of **5** are similar to those of the other tris(acetylene) complexes, with two sets of acetylene resonances. Warming **5b** to 50°C , however, causes coalescence of the ethyl resonances, corresponding to a barrier to acetylene rotation of 16 ± 1 kcal/mol. The methoxide resonance appears at 5.5 ppm in C_6D_6 , similar to the methoxide in $\text{Re}(\text{O})\text{OMe}(\text{RC}\equiv\text{CR})_2$ (5.0 ppm)¹⁷ but much different from the rhenium-bound methyl groups in $\text{ReMe}(\text{RC}\equiv\text{CR})_3$ and $\text{Re}(\text{O})\text{Me}(\text{RC}\equiv\text{CR})_2$ ($2.2, 2.4$ ppm^{6,9}). Strong IR bands at 1066 and 1069 cm^{-1} in **5a** and **5b** can be assigned as $\nu(\text{C}-\text{O})$ and a medium band at 452 cm^{-1} in the spectrum of **5b** as $\nu(\text{Re}-\text{O})$.²⁹ The latter value is about 50 cm^{-1} lower than that seen in $\text{Re}(\text{O})\text{OR}'(\text{RC}\equiv\text{CR})_2$ compounds²⁹ (although still well within the range for $\nu(\text{M}-\text{OR})$ ^{28b}), presumably reflecting the absence of alkoxide π donation in these Re(I) compounds. Compounds **5** also display an band at ca. 2755 cm^{-1} in the IR whose origin has not been determined.³⁰

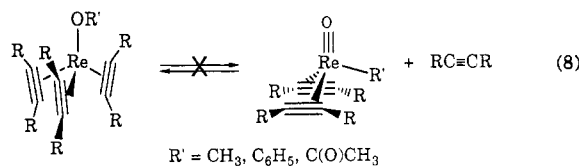
Acetylene Lability. The lability of the acetylene ligands has been probed by adding 2-butyne to the tris-(3-hexyne) complexes and vice versa (eq 7). The siloxide



and methoxide complexes **2** and **5** give what appear to be statistical distributions of all possible tris(acetylene) products $\text{Re}(\text{OR})(\text{MeC}\equiv\text{CMe})_n(\text{EtC}\equiv\text{CEt})_{3-n}$ ($n = 0-3$) within 2 days at ambient temperatures. For **5**, the reaction is slightly faster in C_6D_6 than in CD_3CN . The kinetics of the reaction of **5b** and 2-butyne has been followed in C_6D_6 under pseudo-first-order conditions ($[\text{MeC}\equiv\text{CMe}] \gg [\text{5b}]$), at two different rhenium concentrations and three alkyne concentrations. First-order behavior is observed over the first half-life, but once there is a substantial amount of $\text{Re}(\text{OMe})(\text{EtC}\equiv\text{CEt})_2(\text{MeC}\equiv\text{CMe})$ present, the NMR spectra and the kinetic interpretation become more complex, which has precluded obtaining reliable rate constants. It is clear, however, that the rate is first order in **5b** and does not depend on the concentration of 2-butyne. The exchange reaction thus appears to proceed via a dissociative pathway, which is reasonable for an 18-electron compound.

The phenoxide complex $\text{Re}(\text{OPh})(\text{MeC}\equiv\text{CMe})_3$ exchanges alkyne ligands more slowly than the methoxide, with only 20% reaction after 1 week at room temperature and 10 days at 40°C . No discernible bound 2-butyne was observed for $\text{Re}(\text{OAc})(\text{EtC}\equiv\text{CEt})_3$ after 9 days at 100°C and for the triflate **3b** after more than 3 months at 20°C . The hydroxide complex $\text{Re}(\text{OH})(\text{EtC}\equiv\text{CEt})_3$ undergoes exchange with 2-butyne more slowly than its rearrangement (5 days at 21°C), giving only 10% 2-butyne in the oxo-hydride product (which is inert to acetylene exchange under these conditions).¹⁰ The large differences in acetylene substitution rates— $\text{OMe} \approx \text{OSiMe}_3 > \text{OH} > \text{OPh} \gg \text{OAc}, \text{OTf}$ —parallel the donor ability of the oxygen ligand. Probably the more strongly donating ligands better stabilize the unsaturated bis(acetylene) complexes formed on loss of an acetylene, by increased σ and/or π donation.

Possible Rearrangements to Oxo Compounds. Rearrangements analogous to the hydroxide-to-oxo-hydride reaction (eq 1) would convert the rhenium(I) methoxide, phenoxide, or acetate complexes to the known⁷⁻⁹ oxo-methyl, oxo-phenyl, and oxo-acetyl complexes. However, thermolysis of these complexes does not cause any rearrangement to oxo species (eq 8). The methoxide



complex **5** decomposes very slowly at ambient temperatures and is completely decomposed after 2.5 days at 90°C in C_6D_6 , without formation of $\text{Re}(\text{O})\text{Me}(\text{RC}\equiv\text{CR})_2$ in either case ($<5\%$ by NMR). $\text{Re}(\text{OPh})(\text{MeC}\equiv\text{CMe})_3$ is slightly decomposed after 10 days at 40°C , spectra showing only a small amount of free 2-butyne and $[\text{Re}(\text{O})(\text{MeC}\equiv\text{CMe})_2]_2$ dimers.³¹ The acetate derivative is remarkably robust, exhibiting only a slight darkening of a toluene solution with no change in the NMR after 1 month at 150°C . It is also inert to photolysis. The siloxide complex **2b** is stable at ambient temperatures but reacts

(29) (a) Reference 17. (b) Erikson, T. K. G.; Mayer, J. M. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1527-1529.

(30) Bands in the range $2800-2900\text{ cm}^{-1}$ have been reported for other rhenium methoxide complexes: Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* 1968, 489-496. Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* 1980, 2467-2475.

(31) Spaltenstein, E.; Mayer, J. M. *J. Am. Chem. Soc.* 1991, 113, 7744-7753.

very slowly with 1 equiv of H₂O in C₆D₆ to form some of the oxo-hydride **6b** and EtC≡CEt (Scheme I), via hydrolysis to the hydroxide which is observed as an intermediate.

[Re(py-O)(EtC≡CEt)₃]OTf is similarly related to the known³² [Re(O)py(EtC≡CEt)₂]OTf. In an NMR tube in C₆D₆ or CD₂Cl₂ at ambient temperatures, the pyridine *N*-oxide complex disappears slowly as a new set of resonances grow in over 1-2 weeks at ambient temperature, but the resonances are not those for free 3-hexyne, free pyridine, or [Re(O)py(EtC≡CEt)₂]OTf; the new compound has not been characterized. Pyridine *N*-oxide is thermodynamically a quite good oxidant ($D(\text{O-py}) = 72 \text{ kcal/mol}^{33}$), yet it does not readily oxidize the formally low-valent Re center.

In the reverse of eq 8, the rhenium(III) oxo-methyl, oxo-phenyl, oxo-acyl, and oxo-pyridine complexes do not react with excess alkyne to give tris(acetylene) compounds. There is thus a significant kinetic barrier to the rearrangement in eq 8 for R ≠ H. The oxo-hydride also does not go back to the hydroxide, as no exchange of the hydride with D₂O is observed even in the presence of excess acetylene. This suggests that the rhenium(III) oxo compounds are significantly thermodynamically favored over the rhenium(I) tris(acetylene) compounds.

The methoxide and hydroxide complexes are very similar compounds, for instance in their barriers to acetylene rotation and dissociation.¹⁰ The lack of rearrangement in the methoxide complex is therefore most likely due to an inherently lower migratory aptitude of methyl versus hydrogen. A similar conclusion was reached in the classic study by Bercaw and co-workers¹² on α -migratory deinsertion reactions of kinetically implied [Cp*₂Ta(ER)] intermediates (E = CH₂, NH, O, S; R = H, Me). Rearrangement of the putative hydroxide complex occurs at ambient temperatures, while the methoxide intermediate forms the oxo complex only at 140 °C. For migrations between tantalum and carbon in [Cp*₂Ta(CH₂R)] (R = H, CH₃), migration of hydrogen is 10⁶–10¹⁰ faster than methyl migration. A similar rate difference has been found in β -migratory insertion reactions.³⁴ If this large rate difference applied to the rearrangements discussed here, methyl migration in Re(OMe)(EtC≡CEt)₃ (**5**) would be much slower than the observed decomposition of **5** by a different pathway.

The mechanism of the hydroxide rearrangement (eq 1) does not involve initial acetylene dissociation but rather initial hydrogen migration, either concerted with or followed by acetylene loss.¹⁰ If concerted, the rearrangement would resemble an intramolecular interchange or

S_N2 reaction. The rates of acetylene dissociation discussed above are therefore not directly relevant to the lack of migration. However, any factors that make acetylene loss a slow process are likely to add to the barrier for a concerted process, just as poor leaving groups resist both S_N1 and S_N2 reactions in organic chemistry. Thus, the fact that acetylene loss in the acetate complex is much slower than in the hydroxide prevents any conclusion concerning the relative migratory aptitudes of hydrogen and acyl groups. Acetylene loss from the phenoxide complex is only slightly slower than in the hydroxide, so phenyl migration appears to be less facile than hydrogen movement. While the ease of migration in this system is H ≫ Me, Ph, it should be noted that there is no general order of migratory aptitudes, which depend on the nature of the specific reaction.³⁵ Further work is in progress in this system to understand the nature of the migrations and to observe rearrangements of alkoxide and related species.

Conclusions

Rhenium(I) tris(acetylene) compounds are readily accessible by reduction and then silylation of Re(O)-I(RC≡CR)₂. The [Re(RC≡CR)₃]⁺ fragment forms stable compounds with a wide range of ligands, including alkoxide, halide, carboxylate, triflate, pyridine, acetonitrile, and trimethylphosphine ligands. While the hydroxide complex rearranges to an oxo-hydride compound,¹⁰ the methoxide, phenoxide, acetate, and pyridine *N*-oxide complexes do not rearrange to the known rhenium(III) oxo species Re(O)R(RC≡CR)₂ or [Re(O)py(RC≡CR)₂]⁺. This is likely due to the lower migratory aptitudes of methyl and phenyl groups versus that of hydrogen in this rearrangement.

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Supplementary Material Available: Tables giving crystal data and data collection parameters, anisotropic thermal parameters for non-hydrogen atoms, positional parameters for hydrogen atoms, additional bond distances and angles, and torsion angles and a figure showing the atom labeling in Re(OSiMe₃)-(MeC≡CMe)₃ (**2a**) (6 pages). Ordering information is given on any current masthead page.

OM9301997

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(33) Shaofeng, L.; Pilcher, G. *J. Chem. Thermodyn.* **1988**, *20*, 463.

(34) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10 394–10 401.

(35) Reference 21, Chapter 18, especially pp 949–951. Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum: New York, 1990; pp 313–319.