Low-Valent Rhenium–Oxo Alkyl and –Oxo Hydride Complexes. The Stabilizing Influence of the Oxo Ligand[1]

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Abstract: A series of rhenium–oxo alkyl and allyl complexes of the form $Re(O)R'(RC{\equiv}CR)_2$ (R' = Me, Et, ^{i}Pr, η^1-$CH_2CH{=}CH_2$; R = Me, Et) are prepared by the reaction of $Re(O)I(RC{\equiv}CR)_2$ with dialkylzinc reagents. The analogous oxo hydride compounds $Re(O)H(RC{\equiv}CR)_2$ are formed by decarboxylation of the rhenium–oxo formate complexes. The characterization of these compounds is reported, including an X-ray crystal structure determination for $Re(O)Et(MeC{\equiv}CMe)_2$ (**4**). Complex **4** contains a short rhenium–oxygen multiple bond of 1.697 (6) Å, with the oxo, ethyl, and two acetylene ligands arranged in a pseudotetrahedral geometry about the rhenium center. The oxo alkyl compounds are thermally quite stable, decomposing in solution only over a period of weeks at 120 °C; remarkably, there is no evidence for β-hydrogen elimination from the ethyl or isopropyl ligands even on decomposition. Olefin insertion into the Re–H bonds of the oxo hydride complexes is also not observed. Similarly, there is no evidence either for CO insertion into rhenium–alkyl bonds or for decarbonylation of related acyl compounds. Reaction of these compounds with strong acids results in protonation of the oxo ligand, without loss of alkane or H_2 from the alkyl or hydride ligands. The protonated isopropyl complexes have a much lower barrier to β-hydrogen elimination: propene and the protonated rhenium–oxo hydride complex are formed at ambient temperatures. The importance of the terminal oxo group as a stabilizing ligand for alkyl complexes is discussed in light of these results. Crystal data for **4**: monoclinic, $P2_1/m$; a = 7.274 (1), b = 10.248 (1), c = 7.764 (3) Å; β = 105.32 (2)°; Z = 2.

The organometallic chemistry of transition metal–oxo complexes is receiving increasing attention because of the use of oxo compounds in organic synthesis and their involvement in enzymatic and heterogeneous catalytic processes.[3] Oxo alkyl and oxo hydride complexes are of interest both to explore the reactivity of metal–oxygen multiple bonds and to understand the influence of a "spectator" oxo group on the properties of metal–carbon and metal–hydrogen bonds.

Over the last 30 years, many studies have shown the importance of ancillary or supporting ligands on the chemistry of alkyl and hydride ligands. In fact the synthesis of stable transition-metal alkyl compounds normally requires both appropriate ancillary ligands and alkyl groups without β-hydrogen atoms.[4] The classic stabilizing ligands in transition-metal organometallic chemistry are soft, π-accepting groups such as carbon monoxide or phosphines. The terminal oxo ligand is not generally thought of as a good supporting ligand for alkyl complexes, but in fact a number of robust oxo alkyl complexes have been prepared in the last 15 years.[5-9] This report describes our studies of a series of rhenium(III)–oxo alkyl compounds, including methyl, ethyl, and isopropyl derivatives. We also report rare examples of oxo hydride and oxo allyl complexes.[10] Oxo allyl compounds are of interest because they have been discussed as intermediates in olefin oxidation reactions;[11] oxo hydride complexes are (at least formally) related to hydroxides by hydrogen migration.

The rhenium oxo compounds reported here, $Re(O)R'(RC{\equiv}CR)_2$, are a part of our investigation of the chemistry of novel rhenium(III)–oxo bis(acetylene) complexes, beginning with the discovery of $Re(O)I(MeC{\equiv}CMe)_2$ (**1**) in 1984.[12-17] These

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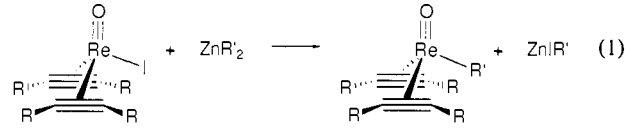
Table I. Crystal Data for $Re(O)Et(MeC{\equiv}CMe)_2$ (4)

formula	$ReOC_{10}H_{17}$
fw	339.45
unit cell	monoclinic
a, Å	7.274 (1)
b, Å	10.248 (1)
c, Å	7.764 (3)
β, deg	105.32 (2)
V, Å^3	558.2 (4)
Z	2
D(calcd), g/cm^3	2.019
space gp	$P2_1/m$
cryst size, mm	0.39 × 0.30 × 0.14
decay, %	15.4
abs coeff μ, cm^{-1}	109.9
transmissn factors	0.999–0.425 (av = 0.784)
reflctns measd	2250
reflctns after averaging	1044
unique obsd reflctns ($I > 3\sigma(I)$)	958
no. of param refined	62
R	0.021
R_w	0.028
goodness of fit	0.948
residual electron density, e/Å^3	±1.2 near Re, ±0.4 elsewhere

compounds are remarkably low valent (Re^{III}, d^4) for complexes with a terminal oxo ligand; the large majority of oxo compounds have high oxidation states and d^0, d^1, or d^2 electronic configurations.[3,13,18-21] The presence of the oxo group in these d^4 rhenium complexes has a profound effect on their chemistry because an unusual electronic structure is adopted.[13] For instance, the molecules are nonfluxional: the acetylene ligands do not rotate,[13] and five-coordinate derivatives do not undergo Berry pseudorotation.[14] Because of the electronic influence of the oxo group, ligand-exchange reactions of the tetrahedral complexes proceed via front-side attack at rhenium, with retention of configuration.[14] The oxo ligand also has a large influence on the chemistry of the alkyl and hydride ligands in the complexes reported here.

Results

Preparation of Oxo Alkyl Complexes. Rhenium(III)–oxo alkyl bis(acetylene) complexes, $Re(O)R'(RC{\equiv}CR)_2$ (**3–8**), are prepared by alkylation of the iodide derivatives (**1** and **2**) using dialkylzinc reagents (eq 1). Compounds **3–8** are stable to air



(1)

R = Me (**1**), Et (**2**)

R = Me, R′ = Me (**3**), Et (**4**), ^{i}Pr (**5**), $CH_2CH{=}CH_2$ (**6**) R = Et, R′ = Et(**7**), ^{i}Pr (**8**)

at ambient temperature for at least several days, both as solids and in solution, and they sublime readily at 40–50 °C (10^{-3} Torr). They are isolated by chromatography, on silica gel, as colorless or pale yellow solids (**3–6**) or oils (**7** and **8**). Yields are 75–90% for the methyl and ethyl complexes but are lower for the isopropyl derivatives (40–50%) because the reactions give another product, the rhenium(II) dimer $[Re(O)(RC{\equiv}CR)_2]_2$[17] (eq 2). Reactions

$$\underset{\textbf{1,2}}{Re(O)I(RC{\equiv}CR)_2} + Zn^iPr_2 \rightarrow \underset{\textbf{5,8}}{Re(O)^iPr(RC{\equiv}CR)_2} + [Re(O)(RC{\equiv}CR)_2]_2 \quad (2)$$

R = Me (**9**), Et (**10**)

with di-*tert*-butylzinc give only reduction to rhenium(II) dimers (>85% isolated yields),[17] without any evidence for the formation of *tert*-butyl complexes. The dimeric products result from electron transfer to rhenium,[17b] which becomes more facile than metathesis of the iodide ligand with increasing steric bulk of the alkyl group. Addition of Grignard or alkyllithium reagents to **1** or **2** results in dark-colored solutions from which only small amounts of alkyl products can be isolated.

Complex **4** has been characterized by an X-ray crystal structure (Figure 1). A summary of crystallographic data is given in Table I, the atomic coordinates are presented in Table II, and selected bond distances and angles are listed in Table III. Molecules of

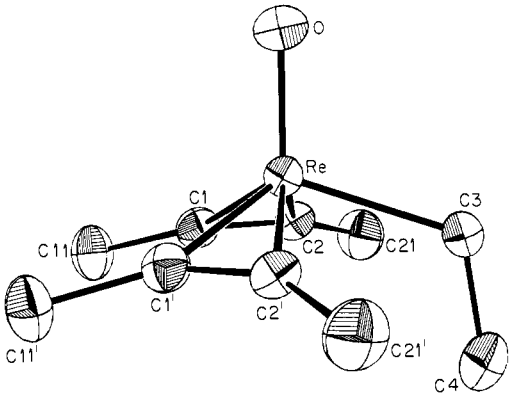


Figure 1. ORTEP drawing of $Re(O)Et(MeC{\equiv}CMe)_2$ (**4**).

Table II. Positional and Equivalent Isotropic Thermal Parameters[a] for $Re(O)Et(MeC{\equiv}CMe)_2$ (**4**)

atom	x	y	z	B_{eq}, Å^2
Re	0.88207 (3)	0.750	0.83604 (3)	3.035 (5)
O	0.8047 (7)	0.750	1.0240 (7)	4.6 (1)
C(11)	1.2862 (7)	0.5790 (6)	0.9009 (8)	5.0 (1)
C(1)	1.0790 (7)	0.6107 (5)	0.8355 (6)	3.66 (9)
C(2)	0.9169 (6)	0.5659 (5)	0.7464 (6)	3.51 (9)
C(21)	0.8216 (9)	0.4514 (6)	0.6435 (8)	5.5 (1)
C(3)	0.6380 (9)	0.750	0.6058 (11)	4.1 (2)
C(4)	0.6740 (13)	0.750	0.4239 (13)	5.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Bond Distances (Å) and Angles (deg) for $Re(O)Et(MeC{\equiv}CMe)_2$ (**4**)

atoms	distance	atoms	distance
Re–O	1.697 (6)	C(11)–C(1)	1.494 (7)
Re–C(1)	2.023 (5)	C(1)–C(2)	1.284 (7)
Re–C(2)	2.050 (5)	C(2)–C(21)	1.484 (8)
Re–C(3)	2.161 (8)	C(3)–C(4)	1.503 (13)
atoms	**angle**	**atoms**	**angle**
O–Re–C(1)	113.4 (2)	C(2)–Re–C(3)	82.4 (2)
O–Re–C(2)	113.0 (1)	Re–C(1)–C(11)	143.5 (4)
O–Re–C(3)	109.0 (3)	Re–C(1)–C(2)	72.8 (3)
C(1)–Re–C(1′)	89.8 (3)	C(11)–C(1)–C(2)	143.7 (5)
C(1)–Re–C(2)	36.7 (2)	Re–C(2)–C(1)	70.5 (3)
C(1)–Re–C(2′)	119.9 (2)	Re–C(2)–C(21)	145.9 (4)
C(1)–Re–C(3)	115.2 (2)	C(1)–C(2)–C(21)	143.6 (6)
C(2)–Re–C(2′)	134.0 (3)	Re–C(3)–C(4)	117.9 (6)

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4 have crystallographically imposed C_s symmetry, with the mirror plane containing the Re–O bond and the ethyl group. The coordination geometry about the rhenium is pseudotetrahedral, taking the acetylene midpoints as two of the vertices. The angles about rhenium are within 10° of the tetrahedral value.

The $Re(O)(MeC{\equiv}CMe)_2$ fragment in the structure of **4** is very similar to that found in the structures of **1**,[13] $[Re(O)L(MeC{\equiv}CMe)_2]SbF_6$ (L = py, bipy),[14] and $[Re(O)(MeC{\equiv}CMe)_2]_2$.[17] For instance, the rhenium–oxo bond distance in **4** of 1.697 (6) Å is typical of these structures and of rhenium–oxo complexes in general.[21] The acetylene ligands are bound to the rhenium in a slightly asymmetric fashion, with the carbon near the ethyl group (C2) having a longer bond to rhenium (Re–C1, 2.023 (5) Å; Re–C2, 2.050 (5) Å).

The ethyl group is bound to the rhenium through a typical rhenium–carbon single bond of 2.161 (8) Å. Compare, for example, the average Re–C distances of 2.145 and 2.123 Å in $Cp^*Re(O)Me_2$[8g] and $Re(O)(PMe_3)(CH_2SiMe_3)_3$.[8j] The ethyl group lies in the mirror plane that bisects the molecule with C4 oriented away from the oxygen atom, as expected on steric grounds.

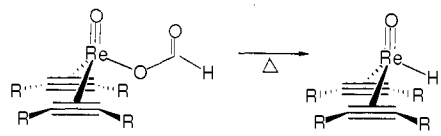
On the basis of their NMR and IR spectra, compounds **3–8** appear to adopt a structure in solution that is similar to the structure of **4** in the solid state. The ^1H NMR spectra of the 2-butyne complexes **3–6** each show two quartets ($^5J_{HH} \simeq 1$ Hz) for the acetylenic methyl groups, consistent with the C_s symmetry of **4**. The acetylene ligands of complexes **3–8** are not fluxional on the NMR time scale at ambient temperatures; the ethyl complex **4** has been shown to be nonfluxional at 80 °C. The IR spectra of compounds **3–8** exhibit a strong characteristic rhenium–oxo stretch in the region 945–975 cm^{-1}.[3,20,22] This assignment has been confirmed for **4** by ^{18}O labelling ($\nu(Re^{16}O)$ = 975 cm^{-1}, $\nu(Re^{18}O)$ = 922 cm^{-1}).

The alkyl protons that are α to the rhenium appear at unusually low field in the ^1H NMR: $\delta(CH_3)$ = 2.35, $\delta(CH_2Me)$ = 3.66, and $\delta(CHMe_2)$ = 5.05. Similar shifts have been reported for other rhenium–oxo methyl complexes ($Cp^*ReO(CH_3)_2$, δ 1.95[8f,g]; $Re_2O_3(CH_3)_6$, δ 2.19, 2.31[8d]), and the trend is similar to that found for $[MoO_3R]^-$ complexes: δ 0.61, 3.61, and 4.08 for R = CH_3, CH_2Me, and $CHMe_2$.[6d] The acetylenic carbons of **3–8** appear in the ^{13}C NMR spectra between δ 144 and 153, consistent with the acetylene ligands acting as three-electron donors to rhenium,[23] as suggested for **1** and **2**.[13]

The ^1H NMR of the allyl ligand in **6** is an $ABCX_2$ pattern and shows no fluxional behavior to 80 °C. This indicates that the allyl is bound to rhenium in a σ fashion with an uncoordinated double bond. This η^1-bonding mode is further supported by the observation of an olefinic stretch at 1615 cm^{-1} in the IR spectrum.

Preparation of Oxo Hydride Complexes. The hydride complexes $Re(O)H(RC{\equiv}CR)_2$ (R = Me, **11**; Et, **12**) are best prepared by thermolysis of the rhenium formate complexes with loss of CO_2. The formate complexes are made by reacting **1** or **2** with thallium formate (eq 3 and 4). Complex **12** is isolated in 49% yield by

$$Re(O)I(RC{\equiv}CR)_2 + TlO_2CH \rightarrow Re(O)[OC(O)H](RC{\equiv}CR)_2 + TlI \quad (3)$$



$$+ \quad CO_2 \quad (4)$$

R = Me (**11**), Et (**12**)

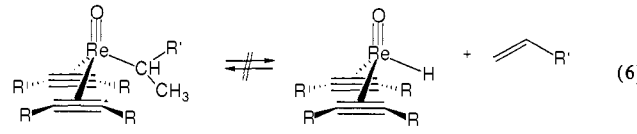
sublimation as a yellow-green oil. Compound **11**, however, has not been isolated in pure form because it does not sublime cleanly and does not crystallize from solution and because it is formed in lower yield (45% by NMR) in a complex mixture that also contains the rhenium dimer (**9**) and hexamethylbenzene. (Complex **11** is stable under the thermolysis conditions, indicating that **9** and C_6Me_6 are produced independently from the formate complex.[24]) Tributyltin hydride converts **1** to **11** in high yield (by NMR, eq 5), but separation from the tin iodide byproduct has proven impossible. The hydride complexes are also formed in low yields on reaction of $Re(O)OEt(RC{\equiv}CR)_2$[15] with $BH_3{\cdot}THF$, Et_3SiH, and Et_2SiH_2.

$$Re(O)I(MeC{\equiv}CMe)_2 + {}^nBu_3SnH \rightarrow Re(O)H(MeC{\equiv}CMe)_2 + {}^nBu_3SnI \quad (5)$$

The hydride complexes **11** and **12** give NMR and IR spectra that are very similar to those of the alkyl derivatives, indicating that they adopt the same pseudotetrahedral structure. For **12**, the hydride ligand appears at δ 6.05 in the ^1H NMR (C_6D_6) and the Re–H stretch is 2015 cm^{-1}; neither is observed for the deuteride $Re(O)D(EtC{\equiv}CEt)_2$. Complex **12** is monomeric in methylene chloride solution.

Reactivity. Solutions of the alkyl and allyl complexes (**3–8**) are remarkably stable in the absence of air. A C_6D_6 solution of **4** was only 50% decomposed after 21 days at 120 °C, and, surprisingly, **4** remains the only material observed by NMR: no ethylene or ethane (or 2-butyne or hexamethylbenzene) is formed. Indeed, no alkane or alkene products are formed on heating complexes **3–8** for prolonged periods at 120 °C. Attempts to characterize the black insoluble material that precipitates were unsuccessful. The rate of decomposition varies in the order **6** > **3** ≃ **4** ≃ **5** > **7** ≃ **8**; addition of 2-butyne to solutions of **4** appears to inhibit decomposition. The hydride complex **12** decomposes more readily: it is 95% consumed after 12 h at 120 °C, forming a mixture of products.

It is remarkable that the ethyl and isopropyl derivatives do not appear to decompose by β-hydrogen elimination and loss of olefin. In fact, there is little evidence for β-hydrogen elimination or olefin insertion reactions of these compounds. Heating **4** in the presence of *cis*-1,2-dideuterioethylene showed no incorporation of deuterium into the ethyl group, and thermolysis of **5** in the presence of ethylene does not give propylene and **4**. Reactions of the hydride complexes with ethylene form at most a tiny amount of the ethyl complexes (<5% yield after 2 weeks at 70 °C) along with insoluble decomposition products. In sum, there is a sizable kinetic barrier to β-hydride elimination and olefin insertion in this system (eq 6).



$$(6)$$

4,5,7,8 **11,12**

The lack of β-hydrogen elimination is but one example of the inert character of the rhenium–alkyl bonds. Carbon monoxide insertion is not observed: **3** is unchanged after heating at 100 °C for 3 weeks in C_6D_6 solution under 1 atm of CO. Similarly, decomposition of the acyl complex $Re(O)[C(O)Me](MeC{\equiv}CMe)_2$[25] over 4 days at 100 °C does not yield **3**, indicating that there is also a large kinetic barrier to CO insertion/deinsertion (eq 7). The hydride complex **12** reacts with CO only at 70 °C, apparently with the formation of rhenium carbonyl complexes (by IR).

(22) Rouchais, G. *Chem. Rev.* **1974**, *74*, 531–566. Conner, C. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 4, pp 125–213.

(23) Templeton and co-workers have established an empirical relationship between the number of electrons donated by an acetylene and ^{13}C chemical shifts of the acetylene carbon atoms: Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290. Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248–1253.

(24) In addition, the hydride complexes do not appear to react with the starting formates to give **9** or **10**. For instance, thermolysis of $Re(O)[OC(O)H](MeC{\equiv}CMe)_2$ in the presence of **12** yields **9** as the only dimeric product, with no evidence for the formation of a mixed butyne/hexyne dimer.

(25) $Re(O)[C(O)Me](MeC{\equiv}CMe)_2$ has been prepared by reduction of **1** with 2 equiv of sodium naphthalenide followed by treatment with acetic anhydride. It has been characterized by ^1H and ^{13}C NMR, IR, mass spectroscopy, and elemental analysis. Full details will be reported in an upcoming publication.

(7)

Compounds **4** and **12** are unreactive with a variety of small molecules, including hydrogen, water, carbon dioxide, ethylene, and 2-butyne. Addition of $H_2{}^{18}O$ to a solution of **4** does, however, result in ^{18}O exchange with the rhenium oxo group. No reaction of **12** with acetone or acetaldehyde is observed after 3 days at 70 °C. The hydride ligand in **12** can be described as a very weak acid: **12** is stable to triethylamine and to LiO^{t}Bu in benzene for 1 day at 25 °C; reaction with LiMe forms methane and a myriad of rhenium products. The hydride ligand is not exchanged for deuterium on reaction with D_2 (70 °C, C_6D_6) or with D_2O in C_6D_6 or MeCN (25 °C).

Reactions of **4** and **12** are observed with more active reagents. $CDCl_3$, for instance, converts the hydride complexes to the corresponding chlorides over 4 h at 25 °C (eq 8). Reaction of **12**

$$\underset{\textbf{11,12}}{Re(O)H(RC{\equiv}CR)_2} + CDCl_3 \rightarrow \underset{\textbf{13,14}}{Re(O)Cl(RC{\equiv}CR)_2} + CHDCl_2 \quad (8)$$

with methyl iodide slowly (70 °C, 14 days) yields methane and **2** (40% yield by NMR). Complex **4** reacts rapidly with I_2 to give a complex mixture of products. The hydride ligands also undergo ligand exchange at ambient temperatures with other Re(O)X-$(RC{\equiv}CR)_2$ complexes, X = Cl, OEt,[15] OC(O)H (eq 9; K_{eq} = 0.1–0.3).

$$Re(O)H(EtC{\equiv}CEt)_2 + Re(O)X(MeC{\equiv}CMe)_2 \rightleftarrows Re(O)X(EtC{\equiv}CEt)_2 + Re(O)H(MeC{\equiv}CMe)_2 \quad (9)$$

Protonation. Treatment of **3–8** with strong acids such as CF_3SO_3H, $MeC_6H_4SO_3H$, HBF_4, or CF_3COOH results in protonation of the oxo ligand to form a hydroxide complex (eq 10).

$$Re(O)R'(RC{\equiv}CR)_2 \underset{py}{\overset{HX}{\rightleftharpoons}} [Re(OH)R'(RC{\equiv}CR)_2]X \quad (10)$$

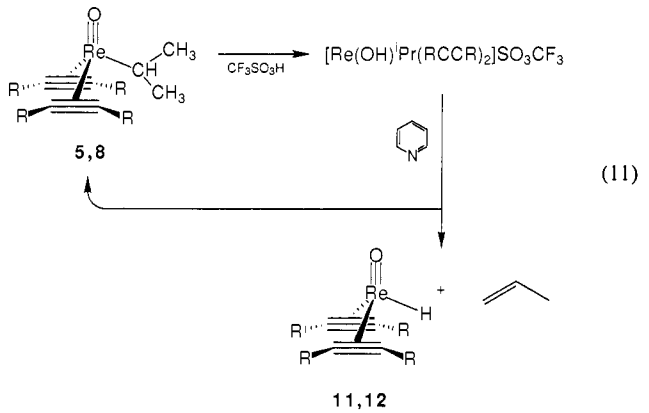
The addition of pyridine rapidly regenerates the starting oxo complexes, along with the pyridinium salt of the acid. Following the reaction by NMR in $CDCl_3$, the two peaks for acetylenic resonances of **3–8** broaden on addition of acid and coalesce into a single broad peak, while the alkyl resonances remain sharp and shift only slightly. Similar behavior is observed for the oxo–halide complexes **1**, **2**, **13**, and **14**. It should be noted that protonation of oxo ligands in monooxo complexes is not a common reaction[26] and, when observed, usually requires a strong acid.[27]

Reaction of a benzene solution of **4** with an equimolar amount of triflic acid precipitates the cationic hydroxide complex $[Re(OH)Et(MeC{\equiv}CMe)_2]^+CF_3SO_3^-$ (**15**) as an extremely air-sensitive white solid. The IR spectrum of **15** exhibits a band at 628 cm^{-1}, which is assigned to the Re–OH stretch ($\nu(Re^{18}OH)$ = 595 cm^{-1}), close to that observed in $Re(O)(OH)(MeC{\equiv}CMe)_2$ [ν(ReOH) = 587 cm^{-1}, $\nu(Re^{18}OH)$ = 558 cm^{-1}].[16] A broad band centered at 3200 cm^{-1} is assigned to the OH group. There are no strong absorptions in the region 800–1000 cm^{-1} characteristic of terminal oxo ligands. The observed triflate stretching modes (1298, 1245, and 1170 cm^{-1}) are similar to the bands exhibited by $NaSO_3CF_3$ (1280, 1240, and 1175 cm^{-1}),[28] suggesting that the anion is at most weakly coordinated to the rhenium center. The acetylenic C–C stretch in **15** appears at 1778 cm^{-1}, slightly lower than the band observed for **4** (1786 cm^{-1}).

Complex **15** is fluxional on the NMR time scale, the acetylene methyl groups appearing as two singlets at −40 °C, which broaden and coalesce as the temperature is raised to 25 °C. This facile fluxional process ($\Delta G^{\ddagger}$ = 14 kcal/mol) contrasts with observed rigidity of **4** at 80 °C. The resonances for the ethyl and hydroxide ligands are essentially unchanged over the temperature range −40 to +30 °C; the hydroxyl proton is found at δ 9.7 ($CDCl_3$). The fluxional process does not involve acetylene dissociation, since signals for added 2-butyne or 3-hexyne are not affected and acetylene exchange is not observed. The ^{13}C NMR spectrum of **15** at −40 °C shows two peaks for acetylenic carbons at δ 191.0 and 169.4, shifted 23–43 ppm downfield relative to the unprotonated complex. These spectra are consistent with protonation occurring at the oxo group, as concluded from the IR data. Specifically, the spectra do not support the formation of a vinyl group, as observed in the reaction of $Mo(O)(RC{\equiv}CR)(S_2CNMe_2)_2$ with acids.[6c]

Complex **15** reacts with additional triflic acid to form **16**, also observed on reaction of **4** with more than 1 equiv of acid. **15** and **16** have very similar ^1H and ^{13}C NMR spectra: for instance, acetylenic ^{13}C resonances at δ 190.3 and 183.8 for **16** and δ 191.0 and 169.4 for **15**. In the ^1H NMR, coalescence of the acetylene resonances is observed at 5 °C for **16** and at 25 °C for **15**. The only substantial difference between the spectra of **15** and **16** is the hydroxyl proton resonance, sharp for **15** and broad (half-width ~ 100 Hz) for **16**, the latter found in the region δ 6.8–7.2. The exact nature of **16** is not clear; it may be a diprotonated species or possibly **15** and **16** are simply different forms of ion pairs in chloroform solution.[29] The relative concentrations of the two complexes are temperature dependent, with **15** the favored species at low temperature. A second complex such as **16** is not observed on reaction of **4** with excess CF_3COOH or $MeC_6H_4SO_3H$. Species analogous to **16** are observed on treatment of the other oxo alkyl compounds with excess triflic acid.

Protonation of the isopropyl complexes **5** and **8** with triflic acid is reversed by addition of pyridine (eq 10) only after short reaction times (<10 min). When $CDCl_3$ solutions of **5** or **8** and triflic acid remain at ambient temperatures for a few hours, propene and additional broad acetylenic resonances are observed in the ^1H NMR, and quenching with pyridine forms both the starting isopropyl compound and the corresponding hydride complex **11** or **12** (eq 11). The rhenium chloride complex (**13** or **14**) is also



(11)

formed, presumably by reaction of the hydride species with chloroform solvent (eq 8). Protonation of **5** with triflic acid-d_1 in $CDCl_3$ yields predominantly **11**-d_0 after quenching with pyridine, indicating that the hydride ligand derives from the isopropyl group.

These results indicate that β-hydrogen elimination from the isopropyl ligands of **5** and **8** is occurring at ambient temperatures. This is a remarkable contrast with the behavior of **5** and **8** in the

(26) See: Reference 3a, section 6.2. Gamsjager, H.; Murmann, R. K. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 317–380.

(27) See, for instance: Bonadies, J. A.; Butler, W. M.; Pecoraro, V. L.; Carrano, C. J. *Inorg. Chem.* **1987**, *26*, 1218–1222. Dioxo (and oxo alkylidene, oxo imido, etc.) complexes are much easier to protonate because the metal retains one multiply bonded ligand.

(28) Miles, M. G.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta, Part A* **1969**, *25A*, 1515. Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774–6.

(29) The formation of **16** does not seem to require 2 equiv of acid, although the accuracy of the titrations is difficult to assess. Both tight and loose ion pairs have been observed in chloroform solution, and their ratio would be expected to be sensitive to temperature: Szwarc, M., Ed. *Ions and Ion Pairs in Organic Reactions*; Wiley: New York, 1972.

absence of acid for which no propene is observed even on decomposition at 120 °C. The decomposition of the protonated ethyl complex **15** does not form ethylene over a few days at 25 °C or 1 h at 70 °C (by NMR). The isopropyl complexes may undergo more facile β-hydrogen elimination because of increased steric crowding.

The oxo allyl complex **6** is protonated reversibly at low temperatures, but above 0 °C chloroform solutions of **6** and triflic acid rapidly form propene and $Re(O)Cl(MeC{\equiv}CMe)_2$ (eq 12).

$$\underset{\mathbf{6}}{Re(O)(CH_2CH{=}CH_2)(MeC{\equiv}CMe)_2} + CF_3SO_3H/CDCl_3 \rightarrow \underset{\mathbf{13}}{Re(O)Cl(MeC{\equiv}CMe)_2} + CH_3CH{=}CH_2 + \ldots \quad (12)$$

This reaction is believed to occur via protonation of the γ-carbon, a common reaction of neutral η^1-allyl complexes.[30] Complex **13** is the normal decomposition product of the weakly ligated rhenium cation $[Re(O)(MeC{\equiv}CMe)_2]^+$ in chloroform.[31]

The reaction of the oxo–hydride complex **12** with triflic acid also appears to involve protonation of the oxo ligand; in this case, two species with coalesced acetylene resonances are observed by NMR. Again addition of pyridine after short reaction times quantitatively regenerates the starting material (eq 13). Reaction of the deuteride $Re(O)D(EtC{\equiv}CEt)_2$ with triflic acid followed by addition of pyridine does not result in significant H/D exchange.

$$\underset{\mathbf{12}}{Re(O)H(EtC{\equiv}CEt)_2} \underset{py}{\overset{CF_3SO_3H}{\rightleftharpoons}} [Re(OH)H(EtC{\equiv}CEt)_2]^+ \quad (13)$$

Discussion

The rhenium–carbon bonds of the oxo alkyl compounds are remarkably inert. It is uncommon for transition metal–ethyl and –isopropyl complexes to be stable to β-hydrogen elimination at 120 °C and stable to excess triflic acid. Reactions are clearly not inhibited by steric factors, as the oxo alkyls are open and uncrowded molecules (see Figure 1).

The large kinetic barriers to hydride migration/β-hydrogen elimination and to carbon monoxide insertion/deinsertion are probably due to the absence of an available empty orbital on the rhenium.[32] Compounds **1–14** are electronically saturated, with an 18-electron configuration attained via extensive π donation to the rhenium center from both the oxo and acetylene ligands.[13] Apparently, it is difficult for **1–14** to become unsaturated, either by loss of an acetylene ligand or by reduced π donation, suggesting that the π-donor interactions are quite strong.

The influence of rhenium–oxygen π bonding on the reactivity is illustrated by the observation that β-hydrogen elimination occurs on protonation of the isopropyl complexes **5** and **8**. Protonation of the oxo group to form a hydroxide substantially reduces the Re–O π interaction, allowing elimination to occur. The lowering of the rhenium–oxygen bond order on protonation is indicated by the reduction in the Re–O stretching frequency (for **4**, from 975 to 628 cm^{-1}). In addition, because the oxo group dominates the electronic structure of compounds **1–14**,[13] protonation affects much more than just the Re–O bonding. For instance, the acetylene ligands become fluxional on protonation, because they can π-donate to rhenium in any orientation without competition from the oxo ligand.[13] The acetylene ligands also seem to increase their π donation on protonation: the acetylenic ^{13}C signals shift downfield by 23–43 ppm.[23]

The lack of reactivity of the rhenium–carbon and –hydrogen bonds in **3–12** contrasts with the chemistry we have observed for alkoxide ligands in $Re(O)(OR')(RC{\equiv}CR)_2$ complexes.[15] The alkoxide ligands undergo facile exchange with added protic reagents such as water, alcohols, acids, or amines. The ethoxide complex decomposes over weeks at 80 °C to give a number of products including the hydride **11** and acetaldehyde in equimolar amounts, suggesting that β elimination is occurring. In addition, CO readily inserts into the Re–O bond at 80 °C to give carboalkoxy compounds. A similar pattern, that CO insertion and β elimination are more facile for alkoxy than alkyl complexes, has been observed by Bryndza and co-workers in a platinum system.[33]

The results reported here together with the stability of most other oxo alkyl complexes suggest that the oxo group can strongly stabilize metal–carbon single bonds. Oxo–alkyl complexes, even those with β-hydrogens, commonly decompose only at elevated temperatures (cf. **4–8** and $Mo(O)_2R_2(bipy)$[6e]). Only one oxo alkyl complex has been reported to undergo CO insertion.[8j] The alkyl and hydride ligands in **3–12** are particularly inert to electrophiles, another common property of oxo alkyl species.[7k] $[W(O)_3(CH_2CMe_3)]NEt_4$ is stable in water in the range pH 1–13 and melts at 164 °C.[7d,g] Even oxo alkyl compounds with unusual oxidation states, electron counts, or coordination geometries, such as $Re(O)Me_4$, $Re(O)_2Me_3$, $Re(O)_3Me$,[8a-c] and $V(O)(CH_2SiMe_3)_3$,[5a] are hydrolytically, as well as thermally, stable. These molecules are much more robust than analogues without oxo ligands: for instance $Re(O)Me_4$ shows no decomposition below 150 °C[8a] while $ReMe_6$ decomposes at 10 °C.[8b] The oxo hydride complex **12** is also an unusually inert metal hydride compound; it is not yet clear whether this will be a common characteristic of these species.[34]

The remarkable stability of oxo alkyl and oxo hydride complexes seems to be due, at least in part, to the influence of the oxo group. The oxo ligand clearly plays a major role in the chemistry occurring at the metal and is not merely a spectator. The origin of this stabilizing influence has not been established. It is clear that the oxo group as a π donor raises the energy of empty orbitals,[35] which are therefore less available for coordination of another ligand as required for CO insertion or β-hydrogen elimination.

Experimental Section

Reactions were carried out on a vacuum line, by Schlenk methods, or in a glovebox under a nitrogen atmosphere; chromatography was done in the air (see below). Solvents were vacuum transferred from sodium benzophenone (diethyl ether) or calcium hydride (benzene, methylene chloride, and pentane) immediately before use. Deuteriated solvents were dried and transferred from activated 4-Å seives. $ZnEt_2$ was used as received (Aldrich); $ZnMe_2$, Zn^iPr_2, and $Zn(CH_2CH{=}CH_2)_2$ were prepared immediately prior to use according to published procedures[36] based on the alkylation of $ZnCl_2$ with organomagnesium or organolithium compounds (Aldrich and Alfa) in diethyl ether. Anhydrous zinc chloride was prepared by treatment of $ZnCl_2$ (Baker) with thionyl chloride.[37] Pyridine (Baker) was distilled before using while trifluoromethanesulfonic acid (3 M) was used as received. The rhenium complexes $Re(O)I(MeC{\equiv}CMe)_2$ and $Re(O)I(EtC{\equiv}CEt)_2$ have been previously reported.[38]

Microanalyses were performed by Canadian Microanalytical Service, Ltd., Vancouver, or Galbraith Laboratories, Knoxville, TN. NMR spectra were taken in $CDCl_3$ solvent, unless otherwise noted, with Varian CFT-20 and VXR-300 and Bruker CXP-200 and WM-500 spectrometers. Variable-temperature NMR was performed on the VXR-300. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer and are reported in reciprocal centimeters. Mass spectra (MS) were recorded

(30) Candlin, J. P.; Taylor, K. A.; Thompson, D. T. *Reactions of Transition Metal Complexes*; Elsevier: New York, 1968; p 341.

(31) Spaltenstein, E.; Erikson, T. K. G., unpublished results.

(32) An available coordination site is considered to be a prerequisite to migratory insertion and elimination reactions: Reference 4a, Chapter 6.

(33) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686–7. Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805–4813. In the latter paper, the $(DPPE)Pt(OMe)_2$ is reported to undergo β-hydrogen elimination much faster than $(DPPE)PtEt_2$, although in the mixed compound (DPPE)Pt(OMe)Et elimination from the two ligands is suggested to be competitive.

(34) The only other reported oxo hydride, $Cp_2^*Ta(O)H$,[5g] does not react with H_2O or undergo exchange with D_2O: Parkin, G.; Bercaw, J. E., California Institute of Technology, personal communication, 1988.

(35) π bonding from the oxo ligand always has the effect of raising the energy of one or two of the d orbitals (in the ligand field picture). This raising should inhibit β-hydrogen elimination and CO insertion when one of the orbitals involved is the LUMO, as in polyoxo and d^2 monooxo complexes (see ref 3a, Chapter 2, and ref 13).

(36) Boersma, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 2, p 824.

(37) Pray, A. R. *Inorg. Synth.* **1957**, *5*, 153.

(38) See: Reference 13. An improved procedure will be reported in: Manion, A. B.; Erikson, T. K. G.; Spaltenstein, E.; Mayer, J. M., submitted for publication in *Organometallics*.

on a Hewlett-Packard 5985 GC/MS instrument using the direct inlet method with 70-eV ionizing radiation. Molecular weights were determined by the Singer method based on differential vapor pressure osmometry.[39]

Column chromatography was performed on silica gel 60 (Merck, 230–400 mesh). The solvents used in chromatography—methylene chloride, ethyl acetate, and hexanes—were used as received. The workup procedure used in the preparations of the oxo alkyl complexes is as follows: the reaction mixture was stripped to dryness in vacuo, and the residue dissolved in CH_2Cl_2 in the air. This solution was filtered through a short, wide silica gel column to remove zinc salts and then concentrated. If separation was required, the residue was chromatographed on silica gel by elution with CH_2Cl_2 or 10/90 EtOAc/hexanes.

Re(O)Me(MeC≡CMe)$_2$ (3). A stirred solution of anhydrous $ZnCl_2$ (0.31 g, 2.30 mmol) in 15 mL of Et_2O at −78 °C was treated with 2.7 mL (4.6 mmol) of MeLi in Et_2O (Alfa) and slowly warmed to room temperature. After 0.5 h of stirring, the volatile Me_2Zn was vacuum transferred from the reaction mixture into a frozen solution of **1** in 50 mL of benzene at 0 °C. The bath was removed, and the whole was stirred 1 h after reaching ambient temperature, eventually turning golden colored. Column chromatography (CH_2Cl_2) separated **3** from a fast-moving brown band of unidentified material to afford 0.31 g (83%) of colorless crystals following solvent removal under reduced pressure and overnight cooling at −10 °C: ^{1}H NMR δ 2.94, 2.51 (each 6 H, q, 1 Hz, $CH_3C{\equiv}CCH_3'$), 2.35 (3 H, s, $ReCH_3$); $^{13}C\{^1H\}$ NMR δ 145.8, 144.3 (Me*C*≡*C*′Me), 15.6, 8.8 ($CH_3C{\equiv}CC'H_3$), 7.5 ($ReCH_3$). IR (C_6D_6) 2980, 2935, 2865, 1800 [ν(C≡C)], 1448, 1375, 1162, 1050 (br), 965 (s) [ν(ReO)], 808 (w), 745 (w), 620 (w); MS, 324, 326. Anal. Calcd for $ReOC_9H_{15}$: C, 33.22; H, 4.65. Found: C, 33.40; H, 4.66.

Re(O)Et(MeC≡CMe)$_2$ (4). A stirred solution of **1** (1.00 g, 2.30 mmol) in 50 mL of benzene at 10 °C was treated with 1.8 mL (2.8 mmol) of Et_2Zn in toluene (Aldrich) via syringe and slowly warmed to room temperature. After stirring an additional 0.5 h, the rose solution was filtered through silica gel to afford 0.75 g (93%) of **4** following solvent removal in vacuo. Sublimation in vacuo at 40 °C produced pale yellow crystals: ^{1}H NMR δ 3.66 (2 H, q, 8 Hz, $ReCH_2Me$), 2.94, 2.58 (each 6 H, q, 1 Hz, $CH_3C{\equiv}CCH_3'$), 1.41 (3 H, t, 8 Hz, $ReCH_2CH_3$); ^{13}C NMR δ 147.6, 145.6 (both s, Me*C*≡*C*′Me), 22.9 (t, 131 Hz, $ReCH_2Me$), 18.9 (q, 126 Hz, $ReCH_2CH_3$), 15.6, 9.6 (both q, 129 Hz, $CH_3C{\equiv}CC'H_3$); IR (Nujol): 1786 [ν(C≡C)], 1190, 1168, 1055 (br), 975 (s) [ν(ReO)], 636(w); MS, 338, 340. Anal. Calcd for $ReOC_{10}H_{17}$: C, 35.38; H, 5.05. Found: C, 35.31; H, 4.81. **4**-^{18}O was prepared by treating a solution of 0.25 g of **4** (0.74 mmol) in 20 mL of benzene/CH_2Cl_2 (1/1) solvent with 14.7 μL (0.74 mmol) of $^{18}OH_2$ (Cambridge Isotope Laboratories; 97% ^{18}O). After the solution was stirred at room temperature under nitrogen for 24 h, the volatiles were removed and the procedure was repeated with 1 equiv more of $^{18}OH_2$. Isolated **4** showed 70% ^{18}O labeling: ν(Re^{18}O) = 922 cm^{-1}.

Re(O)^{i}Pr(MeC≡CMe)$_2$ (5). A solution of anhydrous $ZnCl_2$ (0.22 g, 1.6 mmol) in 15 mL of Et_2O at −78 °C was treated with 1.1 mL (2.2 mmol) of ^{i}PrMgCl in Et_2O (Aldrich) and warmed to 0 °C. After it was stirred for several hours, the solution was cooled to −78 °C and the supernatant transferred via cannula to a frozen solution of **1** (0.50 g, 1.15 mmol) in 50 mL of benzene at 0 °C. The bath was removed and the reaction stirred for 1 h, eventually turning tan. Column chromatography (CH_2Cl_2) afforded 0.17 g (43%) of **5** as a yellow oil and 0.11 g (31%) of dimer **9**.[17] Sublimation of **5** in vacuo (40 °C) yields bright yellow-green crystals: ^{1}H NMR δ 5.05 (1 H, sept, 7 Hz, $ReCHMe_2$), 2.95, 2.61 (each 6 H, q, 1 Hz, $CH_3C{\equiv}CCH_3'$), 1.73 (6 H, d, 7 Hz, $ReCH(CH_3)_2$); $^{13}C\{^1H\}$ NMR δ 148.3, 147.4 (Me*C*≡*C*′Me), 37.5 ($ReCHMe_2$), 28.5 ($ReCH(CH_3)_2$), 15.5, 10.9 ($CH_3C{\equiv}CC'H_3$); IR (neat) 2942, 2910, 2850, 1790 (w), 1772 [ν(C≡C)], 1450 (br), 1355, 1372, 1190, 1150, 1135, 1022, 949 (s), 940 (sh) [ν(ReO)], 806 (w); MS, 352, 354. Anal. Calcd for $ReOC_{11}H_{19}$: C, 37.38; H, 5.42. Found: C, 37.33; H, 5.36.

Re(O)(η^1-C_3H_5)(MeC≡CMe)$_2$ (6). Following a procedure similar to the synthesis of **5**, 0.25 g of $ZnCl_2$ (1.83 mmol) was treated with 1.8 mL (3.6 mmol) of allyl magnesium chloride in THF (Aldrich). This solution was transferred to a frozen benzene solution of **1** (0.40 g, 0.92 mmol) at 0 °C via cannula, and the solution was warmed to room temperature and stirred for 0.5 h. Silica gel was added to the flask, and the resulting mixture stirred for 10 min before concentration and exposure to air. Column chromatography on silica gel (CH_2Cl_2) separated **6** from unreacted **1** to afford 0.18 g (56%) of **6** as an oil; sublimation of **6** in vacuo (45 °C) yields bright yellow crystals: ^{1}H NMR δ 6.05 (1 H, m, $CH_2CH{=}CH_2$), 5.11 (^{1}H, dd, 2, 17 Hz, $CH_2CH{=}CHH'$), 4.70 (1 H, dd, 2, 10 Hz, $CH_2CH{=}CHH'$), 4.26 (2 H, d, 8 Hz, $ReCH_2CH{=}CH_2$), 2.95, 2.59 (each 6 H, q, 1 Hz, $CH_3C{\equiv}CCH_3'$); ^{13}C NMR (C_6D_6) δ 147.6, 145.6 (both s, Me*C*≡*C*′Me), 143.7 (d, 156 Hz, $CH_2CH{=}CH_2$), 112.4 (t, 155 Hz, $CH_2CH{=}CH_2$), 30.9 (t, 131 Hz, $ReCH_2CH{=}CH_2$), 15.9, 9.7 (both q, 128 Hz, $CH_3C{\equiv}CC'H_3$); IR (C_6H_6) 2938, 2900, 1775 [ν(C≡C)], 1615 [ν(C=C)], 1425, 1350, 1218, 1145, 1115, 1098, 1030, 945 (s) [ν(ReO)], 875, 792 (w). MS, 348, 350. Anal. Calcd for $ReOC_{11}H_{17}$: C, 37.59; H, 4.87. Found: C, 37.67; H, 4.78.

Re(O)Et(EtC≡CEt)$_2$ (7). Following the procedure for **5**, 0.17 g of $ZnCl_2$ (1.21 mmol), 1.4 mL (2.4 mmol) of EtMgBr in THF (Aldrich), and **2** (0.40 g, 0.81 mmol) gave 0.30 g (93%) of **7** as a colorless oil after filtration (silica gel) and concentration: ^{1}H NMR δ 3.69 (2 H, q, 8 Hz, $ReCH_2Me$), 3.38, 3.26 (each 2 H, dq, 8, 16 Hz, $MeCHH'C{\equiv}CCHH'Me$), 3.06 (4 H, m, $MeCHH'C{\equiv}CCHH'Me$), 1.42, 1.31 (each 6 H, t, 8 Hz, $CH_3CH_2C{\equiv}CCH_2CH_3'$), 1.35 (3 H, t, 8 Hz, $ReCH_2CH_3$); $^{13}C\{^1H\}$ NMR δ 151.5, 149.5 (Et*C*≡*C*′Et), 24.6, 19.0 ($MeCH_2C{\equiv}CC'H_2Me$), 21.8 ($ReCH_2Me$), 19.3 ($ReCH_2CH_3$), 14.2, 14.1 ($CH_3CH_2C{\equiv}CCH_2C'H_3$); IR (neat) 1770 [ν(C≡C)], 1452, 1370, 1300, 1250, 1175, 1140 (w), 1015, 955 (s), 930 (sh) [ν(ReO)], 802 (w); MS, 394, 396 ($ReOC_{14}H_{25}$).

Re(O)^{i}Pr(EtC≡CEt)$_2$ (8). Following the procedure for **5**, 0.15 g of $ZnCl_2$ (1.1 mmol), 1 mL of ^{i}PrMgCl (2.0 mmol), and **2** (0.30 g, 0.61 mmol) gave 102 mg of **8** (41%) as a golden oil and 50 mg (23%) of **10**[17] after column chromatography (CH_2Cl_2): ^{1}H NMR δ 5.05 (1 H, sept, 7 Hz, $ReCHMe_2$), 3.42, 3.26 (each 2 H, dq, 8, 16 Hz, $MeCHH'C{\equiv}CCHH'Me$), 3.03 (4 H, m, $MeCHH'C{\equiv}CCHH'Me$), 1.69 (6 H, d, 7 Hz, $ReCH(CH_3)_2$), 1.41, 1.32 (each 6 H, t, 8 Hz, $CH_3CH_2C{\equiv}CCH_2CH_3'$); ^{13}C NMR δ 152.1, 151.9 (both s, Et*C*≡*C*′Et), 36.8 (d, $ReCHMe_2$), 28.9 (q, $ReCH(CH_3)_2$), 24.4, 20.4 (both t, $MeCH_2C{\equiv}CC'H_2Me$), 14.1 (q, $CH_3CH_2C{\equiv}CCH_2C'H_3$); IR (neat) 1790 (w), 1768 [ν(C≡C)], 1452 (br), 1372, 1360, 1302, 1250, 1196, 1140, 1090 (br), 1055 (br), 945 (s) [ν(ReO)], 803 (w), 765 (w); MS, 408, 410 ($ReOC_{15}H_{27}$).

ReO[OC(O)H](MeC≡CMe)$_2$. Method A. Freshly distilled HCOOH (45 μL, 1.2 mmol) was added to 0.39 g (1.09 mmol) of Re(O)OEt(MeC≡CMe)$_2$[15] in 15 mL of CH_2Cl_2. The solution was stirred for 1 h at 25 °C and filtered, and the filtrate was taken to dryness. Recrystallization of the solid residue from pentane at −80 °C gave 0.30 g (78%) of product as a faint green powder.

Method B. A solution of 0.34 g (0.77 mmol) of **1** and 0.20 g (0.78 mmol) of TlOC(O)H (Strem) in 10 mL of methanol was stirred at 40 °C for 1 h unitl the precipitation of yellow-orange TlI was complete. Following filtration, recrystallization from pentane as above gave 0.17 g (63%) of product. ReO[OC(O)H](MeC≡CMe)$_2$ sublimes at 40 °C: ^{1}H NMR (C_6D_6) δ 8.86 (1 H, s, OC(O)*H*), 2.34, 2.32 (each 6 H, q, 1 Hz, $CH_3C{\equiv}CCH'_3$). ^{13}C NMR (C_6D_6) δ 162.3 (d, 209 Hz, O*C*(O)H) 149.7, 141.3 (both s, Me*C*≡*C*′Me), 16.3, 11.1 (both q, 130 Hz, $CH_3C{\equiv}CC'H_3$); IR (Nujol) 1805 (w), 1708 (w), 1642 (s), 1246 (s), 1164, 1045, 965 (s) [ν(ReO)], 764 (s), 626, 447. Anal. Calcd for $C_9H_{13}O_3Re$: C, 30.42; H, 3.69. Found: C, 30.31; H, 3.63.

ReO[OC(O)H](EtC≡CEt)$_2$. Following method A above, 60 μL (1.59 mmol) of HCOOH and 0.63 g (1.52 mmol) of Re(O)OEt(EtC≡CEt)$_2$ gave 0.47 g (99%); mp 5–10 °C. Following method B above, 0.71 g (1.44 mmol) of **2** and excess TlOC(O)H (0.97 g, 3.90 mmol) gave 0.48 g (82%): ^{1}H NMR δ 8.79 (1 H, s, OC(O)*H*), 3.44, 3.19, 3.01, 2.85 (each 2 H, m, $MeCHH'C{\equiv}CCHH'Me$), 1.44, 1.28 (each 6 H, t, 7 Hz, $CH_3CH_2C{\equiv}CCH_2CH_3'$). ^{13}C NMR ($C_6D_6$) δ 164.3 (d, 209 Hz, O*C*(O)H), 153.3, 144.9 (both s, Et*C*≡*C*′Et), 26.1, 20.8 (both t, 130 Hz, $MeCH_2C{\equiv}CC'H_2Me$), 14.3, 14.1 (both q, 128 Hz, $CH_3CH_2C{\equiv}CCH_2C'H_3$); IR (Nujol) 1787, 1657 (s), 1252 (s), 1143, 1059, 976 (s) [ν(ReO)], 940, 761, 448. MS, 412, 282. Complex **17a**-d_1 was prepared via method A above using DCOOD (Cambridge Isotope Laboratories). The IR spectrum of **17a**-d_1 shows a new band at 2134 cm^{-1}, and the ^{1}H NMR spectrum is identical with that of **17a** except that the resonance at δ 8.79 is missing.

Re(O)H(MeC≡CMe)$_2$ (11). A solution of 0.50 g (1.42 mmol) of ReO[OC(O)H](MeC≡CMe)$_2$ in 10 mL of benzene was refluxed under nitrogen for 40 h. Filtration of the dark solution and solvent removal gave a dark brown oily residue, which contained **11** as the major product (~20% yield) along with **9** and C_6Me_6. The products could not be separated by crystallization or sublimation, and **11** does not survive treatment with silica gel. **11** is also formed on reaction of **1** (30 mg, 0.07 mmol) with ^{n}Bu$_3$SnH (19 μL, 0.07 mmol) (or with Ph_3SnH) in 0.5 mL of C_6D_6 at 25 °C: the yield of **11** after 2 h was 90% (by NMR): ^{1}H NMR (C_6D_6) δ 6.18 (s, Re*H*), 2.59, 2.50 (both 6 H, q, 1 Hz, $CH_3C{\equiv}CCH_3'$). ^{13}C NMR (C_6D_6) δ 145.5, 140.5 (s, Me*C*≡*C*′Me), 18.7, 15.2 (both q, 129 Hz, $CH_3C{\equiv}CC'H_3$); IR (C_6D_6) 2011 (w) [ν(ReH)], 962 (s) [ν(ReO)]; MS, 312, 254.

Re(O)H(EtC≡CEt)$_2$ (12). A solution containing 0.59 g (1.44 mmol) of ReO[OC(O)H](MeC≡CMe)$_2$ in 20 mL of C_6H_6 was refluxed for 40 h. The resulting dark solution was filtered, and the benzene was distilled off (the volatiles contained CO_2 by gas-phase IR). The oily residue was then distilled at 40 °C to give 0.26 g (49%) of **12** as a pale yellow-green

(39) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

oil (pure by NMR): ^{1}H NMR (C_6D_6) δ 6.05 (1 H, s, Re*H*), 3.03 (4 H, m, MeC*HH'*C≡CCHH'Me), 2.94, 2.88 (each 2 H, m, MeCHH'C≡CC*HH'*Me), 1.22, 1.18 (each 6 H, t, 7 Hz, $CH_3CH_2C{\equiv}CCH_2CH_3'$). ^{13}C NMR δ 149.0, 146.6 (both s, EtC≡*C'*Et), 25.5, 25.0 (both t, 128 Hz, $MeCH_2C{\equiv}CC'H_2Me$), 15.7, 14.4 (both q, 127 Hz, $CH_3CH_2C{\equiv}CCH_2C'H_3$); IR ($C_6H_6$) 2015 [$\nu$(ReH)], 1778, 1147, 1063, 959 (s), 940, 803, 779, 720 (w); MS, 368, 282. MW (in CH_2Cl_2): calcd, 368; found, 355. Complex **12**-d_1 was prepared similarly from ReO[OC(O)D]-(MeC≡CMe)$_2$. The Re-D band in the IR is obscured by other bands in the region 1450–1420 cm^{-1}; the weak band at 720 cm^{-1} moves to 521 cm^{-1} on deuterium substitution.

[Re(OH)Et(MeC≡CMe)$_2$]SO$_3$CF$_3$ (15). Addition of 27 μL of CF_3SO_3H (0.30 mmol) to a solution of 0.10 g of **4** (0.295 mmol) in 15 mL of benzene under N_2 at 5 °C caused an immediate change from pale green to bright yellow-green, and solids deposited on the flask walls. The volume was then reduced to <5 mL, and CH_2Cl_2 was added to bring the total volume to 10 mL. Cooling the solution with a −78 °C bath while it was stirred and the flask walls were scraped produced a white precipitate, which was collected by filtration, washed with cold CH_2Cl_2, and vacuum dried to give 73 mg (51%) of **15**: ^{1}H NMR (−15 °C) δ 9.69 (1 H, s, ReO*H*); 3.69 (2 H, q, 8 Hz, $ReCH_2Me$), 3.09, 2.79 (each 6 H, s, $CH_3C{\equiv}CCH_3'$), 1.44 (3 H, t, 7 Hz, $ReCH_2CH_3$); ^{13}C{^{1}H} NMR (0 °C) δ 191.0, 169.4 (MeC≡*C'*Me) [alkyl group resonances were tentatively assigned at 23.0 ($ReCH_2CH_3$), 16.2 ($ReCH_2CH_3$), and 15.5, 12.8 ($CH_3C{\equiv}CC'H_3$)]; IR (Nujol) 3200 (br) [ν(OH)], 1778 [ν(C≡C)], 1298 (s), 1245 (s), 1230, 1195, 1170, 1150, 1030 (s), 911 (w), 815 (w), 758, 688, 635 (s), 628 [ν(ReO)], 595 [ν(Re^{18}O)], 578, 510. In situ, generation of **15** with 1.5 equiv of triflic acid gives **16**: ^{1}H NMR (−15 °C) δ 7.00 (2 H, br s, ReO*H*; this chemical shift and integration varies in different runs), 3.79 (2 H, q, 8 Hz, $ReCH_2Me$), 3.22, 3.00 (each 6 H, s, $CH_3C{\equiv}CCH_3'$), 1.44 (3 H, t, 7 Hz, $ReCH_2CH_3$); ^{13}C{^{1}H} NMR (−40 °C) δ 190.3, 183.8 (MeC≡*C'*Me). Alkyl group resonances were tentatively assigned at 23.0 ($ReCH_2CH_3$), 16.8 ($ReCH_2CH_3$), and 16.0, 14.5 ($CH_3C{\equiv}CC'H_3$).

General Procedure for the Protonation Reactions of Rhenium-Oxo Alkyl and Hydride Compounds with CF_3SO_3H. The reactions of **3**, **5–8**, and **12** with triflic acid were studied by ^{1}H and ^{13}C NMR using the following experimental procedure: In a drybox, an NMR tube was charged with 0.037 mmol of rhenium compound and 0.50 mL of $CDCl_3$ and capped with a rubber septa. The tube was cooled to −78 °C, and 1 equiv of CF_3SO_3H (3.30 μL, 0.037 mmol) was added. Immediately prior to obtaining a spectrum, the tube was warmed to room temperature and shaken, the solution turning from colorless to bright yellow-green. The room-temperature spectrum was recorded, followed by variable-temperature NMR studies to −40 °C. All systems were tested for reversibility. The [Re(OH)R(RC≡CR)$_2$]$^+$ complexes were identified by the similarities of their NMR spectra to the spectra of **15**. Excess triflic acid produced, except for **6**, a second rhenium product. ^{1}H NMR data ($CDCl_3$) are reported below. Low solubility at low temperatures in many cases prevented our obtaining ^{13}C NMR data; assignments of ^{13}C resonances in the alkyl region should be considered tentative. Quenching reactions involved adding 1 equiv (3.0 μL) of pyridine to the tube at ambient temperature.

[Re(OH)Me(MeC≡CMe)$_2$]$^+$: ^{1}H NMR (−20 °C) δ 7.42 (1 H, s, ReO*H*), 3.21, 3.05 (each 6 H, s, $CH_3C{\equiv}CCH_3'$), 2.61 (3 H, s, $ReCH_3$).

[Re(OH)^{i}Pr(MeC≡CMe)$_2$]$^+$: ^{1}H NMR (−15 °C) δ 8.61 (1 H, s, ReO*H*), 4.90 (1 H, m, $ReCHMe_2$), 3.18, 2.89 (each 6 H, s, $CH_3C{\equiv}CCH_3'$), 1.68 (6 H, d, 7 Hz, $ReCH(CH_3)_2$. Quenching the reaction (room temperature) of **5** and triflic acid with pyridine after 3 h at 0 °C gives 90% **5**, 10% **11**, and propene, while quenching after 2 h at 25 °C yields 25% **5**, 25% **11**, 10% **13**, and propene along with dark solids.

[Re(OH)(η^1-C$_3$H$_5$)(MeC≡CMe)$_2$]$^+$: ^{1}H NMR (−15 °C) δ 7.60 (1 H, s, ReO*H*), 6.47 (1 H, m, $ReCH_2CH{=}CH_2$), 5.70 (1 H, dd, 2, 17 Hz, $ReCH_2CH{=}CHH'$), 5.45 (1 H, dd, 2, 10 Hz, $ReCH_2CH{=}CHH'$), 4.25 (2 H, d, 8 Hz, $ReCH_2CH{=}CH_2$), 2.93, 2.78 (each 6 H, s, $CH_3C{\equiv}CCH_3'$). ^{13}C{^{1}H} NMR (−15 °C) δ 206.2, 179.7 (MeC≡*C'*Me), 143.0 ($ReCH_2CH{=}CH_2$), 118.8 ($ReCH_2CH{=}CH_2$), 40.1 ($ReCH_2CH{=}CH_2$), 16.6, 15.6 ($CH_3C{\equiv}CC'H_3$).

[Re(OH)Et(EtC≡CEt)$_2$]$^+$: ^{1}H NMR (−15 °C) δ 9.39 (1 H, s, ReO*H*), 3.72 (2 H, m, $ReCH_2CH_3$), 3.0–3.7 (8 H, m, $MeCH_2C{\equiv}CCH'_2Me$), 1.42, 1.18 (each 6 H, s, $CH_3CH_2C{\equiv}CCH_2CH_3'$; the $ReCH_2CH_3$ signal is obscured by the resonance at 1.42); ^{13}C{^{1}H} NMR (−15 °C) δ 192.9, 172.6 (EtC≡*C'*Et), 25.3 ($ReCH_2CH_3$) 24.6, 21.6 ($MeCH_2C{\equiv}CC'H_2Me$), 17.2 ($ReCH_2CH_3$), 14.1, 13.8 ($CH_3CH_2C{\equiv}CCH_2C'H_3$).

[Re(OH)^{i}Pr(EtC≡CEt)$_2$]$^+$: ^{1}H NMR (−15 °C) δ 8.50 (1 H, s, ReO*H*), 4.91 (1 H, m, $ReCHMe_2$), 3.0–3.5 (8 H, m, $MeCH_2C{\equiv}CCH'_2Me$), 1.46, 1.19 (6 H, s, $CH_3CH_2C{\equiv}CCH_2CH_3'$), 1.63 (6 H, d, 7 Hz, $ReCH_3$); ^{13}C{^{1}H} NMR (−40 °C) δ 196.6, 174.3 (EtC≡*C'*Et), 28.8 ($ReCH(CH_3)_2$) 25.5, 21.6 ($MeCH_2C{\equiv}CC'H_2Me$), 14.4 ($CH_3CH_2C{\equiv}CCH_2C'H_3$). The methyne carbon could not be assigned with certainty.

[Re(OH)H(EtC≡CEt)$_2$]$^+$: (species I) ^{1}H NMR (−50 °C) δ 6.78 (1 H, s, ReO*H*), 6.22 (1 H, s, Re*H*), 3.10–3.90 (8 H, m, $MeCH_2C{\equiv}CCH'_2Me$), 1.29, 1.26 (each 6 H, t, 7 Hz, $CH_3CH_2C{\equiv}CCH_2CH_3'$); (species II) ^{1}H NMR (−50 °C) δ 6.01 (1 H, s, Re*H*), 3.10–3.90 (8 H, m, $MeCH_2C{\equiv}CCH'_2Me$), 2.35 (1 H, s, Re*H*) 1.16, 1.12 (each 6 H, t, 7 Hz, $CH_3CH_2C{\equiv}CCH_2CH_3'$).

Thermolyses were performed in NMR tubes containing 25 mg of complex and 0.6 mL of C_6D_6 sealed under vacuum. For the oxo alkyl complexes, the tubes were heated at 120 °C for 21 days; thermolysis of **12** at 120 °C was stopped after 12 h. Final solutions were dark, and black solids were present. Thermolysis of **12** resulted in a mixture of products, which, although not fully characterized, did not contain hexaethylbenzene, 3-hexyne, or the rhenium oxo dimer **10** or its asymmetric isomer.[17]

X-ray Structure of Re(O)Et(MeC≡CMe)$_2$ (4). A yellow crystal of **4**, grown by slow evaporation of a pentane solution, was mounted in the air on a glass fiber and examined at 25 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation monochromatized with graphite (λ = 0.71037 Å). Table I summarizes the crystal data and structure refinement results. A total of 2250 reflections in four octants (hkl, $h\bar{k}l$, $hk\bar{l}$, $h\bar{k}\bar{l}$) with $2\theta < 50°$ were collected with a θ–2θ scan, with a scan range $\Delta\theta = 0.90° + 0.347 \tan\theta$ and a scan rate of 2.7°/min. The systematic extinction observed ($0K0$, $K = 2n + 1$) restricted the choice of space group to either $P2_1$ or $P2_1/m$, with the latter requiring the molecule to have mirror symmetry, which indeed proved to be the case. Three standard reflections with $2\theta \simeq 33°$ measured roughly every 140 reflections showed a 15.4% decay in intensity during data collection. An empirical absorption correction with a set of ψ scans was applied (μ = 109.9 cm^{-1}, transmission factors ranged from 0.999 to 0.425). After corrections for absorption, decay (linear), and Lorentz and polarization effects, 1044 independent reflections were obtained on averaging in $P2_1/m$, with the final data set consisting of 958 unique observed reflections ($I > 3\sigma(I)$, $R_{av} = 0.020$ on F_o). Precise monoclinic unit cell dimensions were obtained from a least-squares fit of the setting angles of 25 reflections with $32° < 2\theta < 37°$.

The rhenium atom was located on a Patterson map, and the structure, solved in the centric space group $P2_1/m$ by subsequent least-squares refinements and Fourier syntheses. Hydrogen atoms were located on a difference map, regularized, and fixed during refinement. The secondary extinction coefficient (9.4 (4) × 10^{-7}) was allowed to vary on observing that F_o was less than F_c for most low-angle intense reflections. Final full-matrix least-squares refinement with all eight non-hydrogen atoms anisotropic converged at $R = 0.021 = \sum||F_o| - |F_c||$ and $R_w = 0.028 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 1/(\sigma_F)^2$ using a p value of 0.04 to downweight intense reflections.[40] Attempts were made to refine the structure in both enantiomorphs in the acentric space group $P2_1$ using an appropriately averaged data set; strong coupling between the acetylene carbons resulted in poor convergence, unreasonable bond distances, and significantly higher residuals than for the centric model. All calculations used the SDP/VAX package of programs supplied by the Enraf-Nonius Corp., with scattering factors and anomalous dispersion terms taken from the standard compilations.[41] The final positional and thermal parameters for **4** are given in Table II, and bond distances and angles are listed in Table III.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positions, torsional angles, and miscellaneous calculations for Re(O)Et(MeC≡CMe)$_2$ (**4**) (3 pages); observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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