

Synthesis, Reactions, and Electronic Structure of Low-Valent Rhenium-Oxo Compounds. Crystal and Molecular Structure of $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})_2$

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Abstract: Low-valent rhenium-oxo compounds of the form $\text{Re}(\text{O})\text{I}(\text{RC}\equiv\text{CR}')_2$ have been prepared by the reaction of $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ with acetylenes ($\text{RCCR}' = \text{MeCCMe}$ (1), EtCCEt (4), MeCCH (5), Me_3CCCH (6), PhCCMe (7), $\text{MeCC}(\text{CH}_2)_4\text{CCMe}$ (8)). Compound 1 crystallizes in space group $P2_1/c$, $a = 9.749$ (3) Å, $b = 7.307$ (3) Å, $c = 16.106$ (7) Å, $\beta = 106.42$ (3)°, $Z = 4$. The structure was refined to final residuals $R = 0.027$, $R_w = 0.029$. The rhenium adopts a slightly distorted tetrahedral geometry in which the acetylene ligands occupy two vertices. There is a short, multiple rhenium-oxygen bond of 1.697 (3) Å. The chloride and bromide analogues of 1 can be prepared by addition of 2-butyne to solutions of $\text{ReO}(\text{X})_3(\text{EPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{E} = \text{P}, \text{As}$). Reactions of 1, 6, or 7 with Ag^+ in the presence of another ligand form $\text{ReO}(\text{O}_2\text{CMe})(\text{MeCCMe})_2$ or $[\text{ReO}(\text{RCCR}')_2\text{L}]\text{SbF}_6$ ($\text{L} = \text{py}, \text{bpy}, \text{PPh}_3$). A survey of metal complexes with terminal oxo ligands reveals the virtual absence of compounds containing electrons in metal-oxygen antibonding orbitals. In an octahedral coordination geometry, this normally restricts stable oxo complexes to d^0 , d^1 , or d^2 electron counts. Extended Hückel calculations indicate that the rhenium(III), d^4 , oxo compounds reported here are stable because they adopt a pseudotetrahedral structure, in which there is essentially a threefold axis about the Re-O bond. In this geometry, four d electrons can be accommodated without populating rhenium-oxygen antibonding levels.

Metal oxide compounds have for many years been an important area in inorganic chemistry, both because of the enormous number of oxide minerals and because oxo complexes are frequently formed by metal ions in aqueous media.¹ Recently there has been a renewed interest in the area, especially in the reactivity of oxo species. One impetus has been the development of very active and selective oxide catalysts for the production of commodity chemicals, for example, the molybdates that catalyze the amoxidation of propylene to acrylonitrile and the partial oxidation of methanol to formaldehyde.^{2,3} Oxo reagents are also being increasingly used as selective oxidants in the synthesis of natural products and other fine chemicals.⁴ In addition, metal oxo complexes are thought to be important intermediates in a number of biological processes, most notably the oxidations catalyzed by the cytochromes P-450 and related enzymes.⁴⁻⁶ An understanding of these various processes requires a knowledge of the chemistry of oxide compounds.

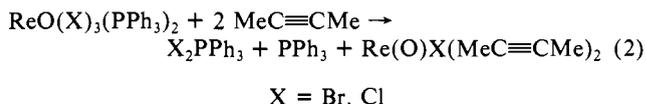
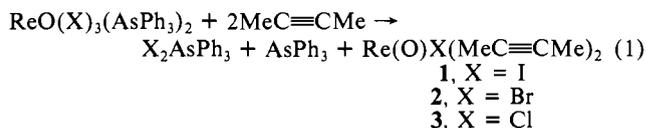
The oxide ion (O^{2-}) can act either as a terminal, multiply bonded ligand or as a bridge between two or more atoms. Stable compounds with a terminal oxo group are known for about half of the elements, and the multiple bond to oxygen is among the shortest and strongest bonds made by these atoms.¹ Transition-metal terminal oxo complexes have been fully characterized only for metals in their highest oxidation states, with d^0 , d^1 , or d^2 electronic configurations.⁷

We wish to report the synthesis, characterization, and reactivity of a family of rhenium(III), d^4 , oxo compounds, the first complexes of a relatively low valent metal with a terminal oxo ligand.⁸ These compounds are stable and fairly unreactive, in contrast to the iron(IV), d^4 oxo species believed to be the active sites of the cytochrome P-450 enzymes and various model systems.⁶ The remarkable stability of the rhenium compounds and their unusual structure have prompted us to undertake a theoretical analysis using extended Hückel molecular orbital calculations, which we report herein.

Results

Addition of excess 2-butyne to benzene solutions of rhenium(V) oxo trihalide bis(triphenylphosphine or triphenylarsine) complexes results in oxidation of a coordinated ligand and the formation of

rhenium(III) oxo compounds (eq 1 and 2). The byproduct I_2AsPh_3 has been identified by comparison with an authentic sample.⁹ The



rhenium products are difficult to separate from AsPh_3 and PPh_3 .

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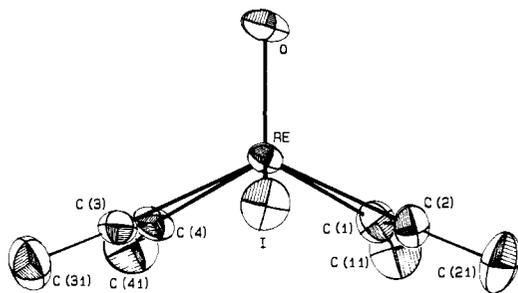
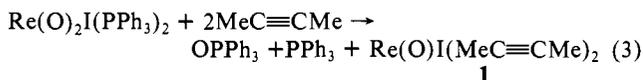


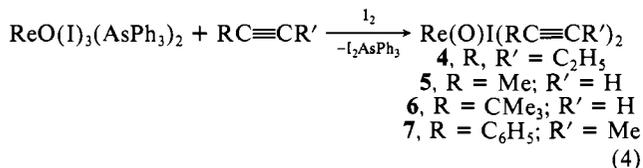
Figure 1. Perspective drawing of $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})_2$ (**1**). Hydrogen atoms have been omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

Our best procedure starts with $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ and gives the iodide derivative **1**: 1 equiv of iodine is added to convert residual triphenylarsine to the arsine diiodide, leaving **1** as the only hexane soluble and sublimable product. $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ has not been obtained in pure form (see Experimental Section), but its infrared spectrum is quite similar to the well-characterized bromide analogue. Paramagnetic products and/or intermediates are apparently also formed in eq 1 and 2 since NMR spectra of the reaction mixtures are often very broad, especially at short reaction times. Sublimation of the product removes these impurities. The overall yield of **1** from potassium perrhenate through $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ is 40% to 50%. Compound **1** is also formed from $\text{ReO}(\text{OC}_2\text{H}_5)_2(\text{EPh}_3)_2$ ($\text{E} = \text{P}, \text{As}$) and 2-butyne, along with a number of other products.

The reaction of $\text{Re}(\text{O})_2\text{I}(\text{PPh}_3)_2$ with 2-butyne stoichiometrically yields **1**, triphenylphosphine, and triphenylphosphine oxide (eq 3). This has not, however, been a useful synthetic route because of the difficulties in isolating **1** free of the phosphorus byproducts.



Rhenium oxo acetylene compounds can be prepared with a number of acetylenes, including terminal ones (eq 4). The 3-



hexyne, *tert*-butylacetylene, and 1-phenylpropyne complexes (**4**, **6**, **7**) are formed in good yields, but the propyne derivative (**5**) is isolated in less than 10% yield (based on KReO_4). Reactions of 4,4-dimethyl-2-pentyne and 2,2,5,5-tetramethylhexyne have not given characterizable products, presumably for steric reasons. Mass spectroscopy indicates that complexes of diphenyl- and di-*p*-tolylacetylenes are formed in low yields. They are, however, difficult to separate from the free acetylene. 2,8-Decadiyne reacts to form a mixture of oligomers but careful sublimation and recrystallization gives the monomeric, chelated product, $\text{Re}(\text{O})\text{I}[\text{MeC}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{CMe}]$ (**8**). Compounds **1**–**8** all sublime readily at 40–80 °C (10^{-3} torr), and their mass spectra contain parent ions.

The crystal structure of **1** consists of discrete molecules with virtual mirror symmetry (Figure 1). Fractional atomic coordinates are listed in Table I, and relevant bond distances and angles appear in Table II. The geometry about rhenium is roughly a pentagonal pyramid with the oxygen atom at the apex. An alternative description of the rhenium coordination is as a slightly distorted tetrahedron in which the acetylene midpoints occupy two vertices. In this description all of the bond angles are within 8° of the tetrahedral angle. The largest deviations occur in the iodine–rhenium–acetylene midpoint angles (av. 102.4°), which appear to be contracted to alleviate steric crowding between C(1) and C(4) ($\text{C}(1)\cdots\text{C}(4) = 2.84 \text{ \AA}$).

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Complex **1**

Atom	x	y	z	B(A**2)
Re	0.30587(2)	0.31165(3)	0.37164(2)	1.395(4)
I	0.10818(5)	0.13110(7)	0.42738(3)	2.716(9)
O	0.4621(5)	0.1936(7)	0.4003(3)	2.4(1)
C(1)	0.2613(7)	0.385(1)	0.2448(4)	2.3(1)
C(2)	0.1760(7)	0.255(1)	0.2492(4)	2.1(1)
C(3)	0.2892(7)	0.511(1)	0.4593(5)	2.2(1)
C(4)	0.3470(7)	0.5802(9)	0.4037(5)	2.1(1)
C(11)	0.3042(9)	0.521(1)	0.1871(5)	3.3(2)
C(21)	0.0547(9)	0.142(1)	0.1983(5)	3.4(2)
C(31)	0.2394(9)	0.553(1)	0.5345(5)	3.5(2)
C(41)	0.4097(9)	0.746(1)	0.3780(6)	3.4(2)

 Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
 $(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab * (\cos \gamma) * B(1,2) + ac * (\cos \beta) * B(1,3) + bc * (\cos \alpha) * B(2,3)]$

Table II. Selected Distances (Å) and Angles (deg) in $\text{Re}(\text{O})\text{I}(\eta^2\text{-MeC}\equiv\text{CMe})_2$

Re–I	2.691 (1)	Re–O	1.697 (3)
Re–C(1)	2.038 (5)	Re–C(3)	2.066 (5)
Re–C(2)	2.061 (5)	Re–C(4)	2.040 (5)
C(1)–C(2)	1.278 (7)	C(3)–C(4)	1.288 (7)
C(1)–C(11)	1.494 (7)	C(3)–C(31)	1.459 (7)
C(2)–C(21)	1.485 (7)	C(4)–C(41)	1.470 (7)
I–Re–O	109.4 (1)	O–Re–C(1)	109.1 (2)
I–Re–C(1)	119.6 (2)	O–Re–C(2)	114.8 (2)
I–Re–C(2)	85.2 (1)	O–Re–C(3)	114.2 (2)
I–Re–C(3)	85.2 (1)	O–Re–C(4)	108.8 (2)
I–Re–C(4)	119.7 (2)	C(1)–Re–C(2)	36.3 (2)
C(2)–Re–C(3)	130.5 (2)	C(1)–Re–C(3)	117.6 (2)
C(2)–Re–C(4)	117.3 (2)	C(1)–Re–C(4)	88.3 (2)
		C(3)–Re–C(4)	36.6 (2)
Re–C(1)–C(2)	72.9 (3)	Re–C(3)–C(4)	70.6 (3)
Re–C(2)–C(1)	70.8 (3)	Re–C(4)–C(3)	72.8 (3)
Re–C(1)–C(11)	141.3 (4)	Re–C(3)–C(31)	145.5 (4)
Re–C(2)–C(21)	144.9 (4)	Re–C(4)–C(41)	142.2 (4)
C(2)–C(1)–C(11)	145.8 (5)	C(4)–C(3)–C(31)	144.0 (5)
C(1)–C(2)–C(21)	144.3 (5)	C(3)–C(4)–C(41)	144.9 (5)

The rhenium–oxygen distance of 1.697 (3) Å is typical of Re–O multiple bond lengths found in high-valent complexes (1.65–1.78 Å).^{10,11} The rhenium–iodine bond length of 2.691 (1) Å is unexceptional.^{11,12} The acetylene ligands are bound in a slightly asymmetric fashion with C(2) and C(3) (the carbon atoms closer to the iodine) slightly farther from rhenium than C(1) and C(4): Re–C(2), C(3) = 2.061, 2.066 (5) Å; Re–C(1), C(4) = 2.038, 2.040 (5) Å. The C≡C bond axes are almost perpendicular to the ReO bond. The acetylenic carbon–carbon distances (1.278, 1.288 (7) Å) and CCC angles (141.3–145.4 (4)°) are within the normal range for acetylene complexes, like those of Pt(O) or

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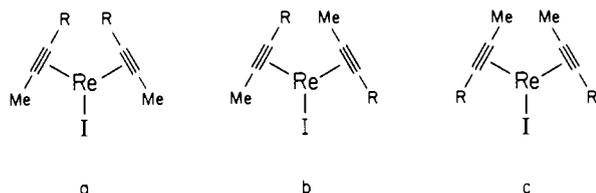


Figure 2. Possible isomers for $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CR})_2$, viewed down the ReO vector (omitted).

$\text{Mo}(\text{II})$.^{13,14} The parameters and overall geometry of **1** are quite similar to the structures of $[\text{CpMo}(\text{MeC}\equiv\text{CMe})_2\text{L}]\text{BF}_4$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$; $\text{L} = \text{CO}$, MeCN), with a cyclopentadienyl molybdenum fragment in place of the ReO group in **1**.¹⁴ In the molybdenum compounds the two acetylene ligands are thought to contribute a total of six electrons to the metal, so that each acetylene is formally a three-electron donor.^{14,15} A four-electron donor acetylene ligand is found in *mer,trans*- $\text{ReCl}_3(\text{MeC}\equiv\text{CMe})\text{-}(\text{PMePh}_2)_2$.¹⁶ This complex, compared with **1**, has a somewhat longer carbon-carbon bond distance (1.330 (7) Å) and substantially shorter rhenium-carbon distances (1.955, 1.958 (5) Å).¹⁶ The structural data are thus consistent with the 2-butyne ligands in **1** acting as three electron donors, as required for an eighteen-electron configuration at rhenium (see Discussion section).

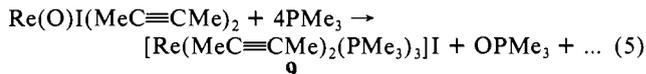
Compounds **1-8** appear to have a geometry in solution similar to that of **1** in the solid state. Proton and carbon-13 NMR spectra (Table III) indicate that the two alkyne ligands are equivalent but that the ends of each acetylene are inequivalent. For example, the ¹H NMR of **1** contains two mutually coupled methyl resonances (⁵ $J_{\text{HH}} = 1$ Hz). The downfield resonance is assigned to the methyl groups next to the iodide by analogy with the 2,8-decadiyne complex (**8**) in which the methyl groups must point toward the halide if the ligand is chelating. The acetylene ligands in **1-7** do not rotate on the NMR time scale: spectra of **1** show only slight broadening at 150 °C, indicating that the barrier to rotation of the 2-butyne groups is greater than 20 kcal/mol. The 1-phenyl-1-propyne derivative (**7**) exists as three isomers (Figure 2, $\text{R} = \text{Ph}$) which do not rapidly interconvert on the NMR time scale. The asymmetric isomer **b** predominates, followed by structure **a** in which both methyl groups point toward the iodide. The ratio of isomers depends on the method of synthesis: a:b:c \cong 1:4:0.15 from eq 4 and 1:2:0.5 from eq 3, thus acetylene rotation is slow even on a chemical time scale. Both mixtures converge to the apparent equilibrium ratio of roughly 1:2:0.2 after heating at 80 °C for a week. The *tert*-butylacetylene complex, **6**, is >98% the asymmetric isomer by NMR. The isomer ratios appear to be dominated by steric interactions. Similar patterns of isomers have been observed in $\text{CpMo}(\text{alkyne})_2\text{X}$ compounds, although acetylene rotation is much more rapid in the molybdenum case.^{14,17}

Templeton and co-workers have suggested that there is a correlation between the electron-donor function of an acetylene ligand and the chemical shifts of the acetylenic carbon and hydrogen atoms.¹⁵ These chemical shift scales, like the structural data, suggest that the alkyne ligands in **1-8** are three-electron donors to rhenium. The ¹³C-¹³C coupling constants in **1** have been measured from the satellites in a high signal-to-noise ¹³C NMR spectrum. The acetylenic coupling of 69 Hz is only slightly larger than the methyl-alkyne carbon coupling of 50 Hz and is more comparable with the value for ethylene (¹ $J_{\text{CC}} = 68$ Hz) than those

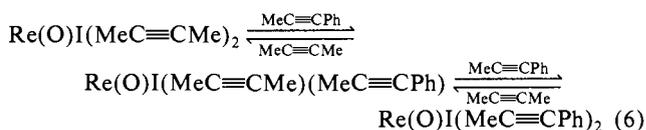
for acetylene or ethane (172, 35 Hz).¹⁸ This coupling constant may prove to be a useful measure of acetylene interactions with a metal center, but the only other reported examples are for μ_2 and μ_4 acetylenes in $\text{Co}_2(\text{CO})_6(\text{HC}\equiv\text{CH})$, $\text{Co}_4(\text{CO})_{10}(\text{HC}\equiv\text{CH})$, and $\text{W}_2(\text{OCMe}_3)_6\text{py}(\text{HC}\equiv\text{CH})$ (¹ $J_{\text{CC}} = 56, 21, \text{ and } 16$ Hz).¹⁹

The IR spectra of **1-8** contain a strong band between 980 and 955 cm^{-1} , assigned to the rhenium-oxygen stretching mode. The assignment has been confirmed for **1** by the expected shift in the oxygen-18 labeled compound ($\nu_{\text{Re}^{18}\text{O}} = 926$ cm^{-1}), prepared by exchange with H_2^{18}O in benzene. These stretching frequencies are characteristic of mono-oxo-rhenium(V) complexes.²⁰ Weak bands in the region 1700 to 1800 cm^{-1} are assigned to acetylenic CC stretching modes, consistent with the absorptions being slightly stronger for complexes of unsymmetrical alkynes **5** and **6**.

Solutions of **1-8** are unreactive with molecular iodine and are stable in air for at least a few hours. This resistance to oxidation is surprising in view of the stability of rhenium(V) oxo complexes²⁰ and tungsten(IV) oxo acetylene species¹⁵ and because in general an oxo ligand is expected to stabilize higher oxidation states.⁷ These compounds also do not undergo an acetylene-acetylene coupling reaction, an intramolecular redox process that would form a rhenium(V) metallacyclopentadiene complex. There is no oxidation wave in the cyclic voltammogram of **1** (THF, *n*-Bu₄NPF₆) to the onset of THF solvent oxidation (1.1 V vs. SCE, referenced to internal ferrocene). The CV does show an irreversible reduction (i_{max} at ca. -1.5 V), followed by a reversible wave ($E_{1/2} = -2.4$ V). The irreversible reduction may explain why the reactions of **1** with Grignard reagents, trimethylaluminum, or borohydride salts form intractable mixtures of products. Compounds **1-8** do not react with triphenylphosphine (cf. eq 2 and 3) but are rapidly reduced by more basic phosphines with formation of phosphine oxides. The rhenium products of the reaction of **1** with trimethylphosphine appear to be $[\text{Re}(\text{MeC}\equiv\text{CMe})_2(\text{PMe}_3)_3]\text{I}$ (**9**, eq 5) and dark green, apparently paramagnetic material(s). Compound **9** has been characterized spectroscopically but has not yet been isolated in pure form.

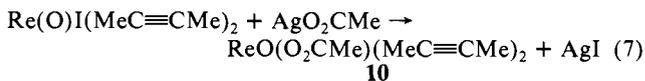


As noted above, the acetylene ligands do not rotate or dissociate on the NMR time scale. However, they do slowly exchange with different acetylenes: reaction 6 reaches equilibrium in a week at 80 °C. The two isomers of $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})(\text{MeC}\equiv\text{CPh})$ have been identified by their NMR spectrum. Compound **1** does



not react with ethylene, 1,5-cyclooctadiene, ethyl vinyl ether, or maleic anhydride during 3 days at 100 °C in benzene solution. It is also inert to carbon monoxide, dihydrogen, and methyl iodide under these conditions. It is stable and soluble in a number of solvents of widely varying polarity, from pentane to methanol.

The iodide ligand is readily removed from the rhenium oxo acetylene complexes by silver ion, leading to a variety of derivatives. Thus **1** reacts with silver acetate to form $\text{ReO}(\text{O}_2\text{CMe})(\text{MeC}\equiv\text{CMe})_2$ (**10**, eq 7) and with AgSbF_6 in the



presence of pyridine, bipyridine, or triphenylphosphine to form

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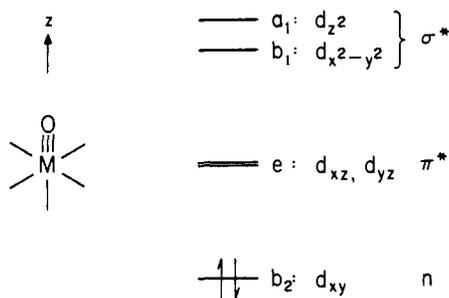
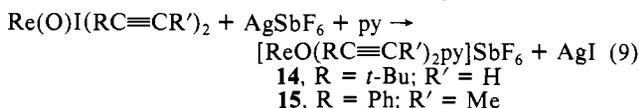
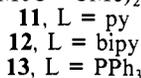
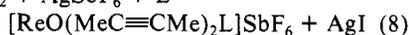
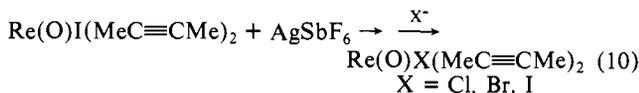


Figure 3. A schematic molecular orbital level diagram for an octahedral d^2 mono-oxo complex.

cationic complexes **11–13** (eq 8). Analogous pyridine complexes have also been prepared from **6** and **7** (eq 9). $[\text{ReO}(\text{t-BuC}\equiv\text{CMe})_2 + \text{AgSbF}_6 + \text{L} \rightarrow$



$\text{CH}_2\text{py}]\text{SbF}_6$ (**14**), like **6**, is entirely the asymmetric isomer. Only two of the three possible isomers of **15** are observed (**15a**:**15b** = 1:3.4). The reaction of **1** with AgSbF_6 in acetonitrile, acetone, or THF generates unstable solvato cations which have not been isolated, but they can be used in cases where an added ligand would react with silver ions, for example, to interconvert the halo compounds **1–3** (eq 10).



Compounds **10–15** appear to have structures analogous to the parent iodo complexes, as evidenced by very similar NMR spectra. The IR spectra of **10–15** all show a strong rhenium–oxygen stretching vibration between 980 and 950 cm^{-1} , e.g., for **11**: $\nu_{\text{ReO}} = 969$; $\nu_{\text{Re}^{18}\text{O}} = 919 \text{ cm}^{-1}$. An X-ray crystal structure of a 4,4'-dimethylbipyridine derivative similar to **12** confirms that the rhenium–oxo–acetylene framework is essentially the same as in **1**.²¹ It also shows that the rhenium binds to both nitrogen atoms of the bipyridine ligand. In contrast, the IR spectrum of **10** indicates that the acetate ligand is bound through only one oxygen atom.²² The coordination chemistry and substitution reactions of these complexes will be the subject of a future publication.²¹

Discussion

The electronic structures of d^0 , d^1 , and d^2 transition-metal terminal oxo compounds have been studied by both theoretical and spectroscopic methods.²³ A brief review of the results is important to an understanding of the d^4 rhenium–oxo complexes

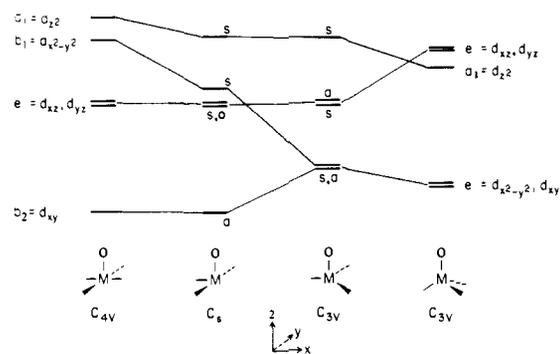


Figure 4. Schematic evolution of the molecular orbital energy levels as a square-pyramidal MO_4 compound is converted to a tetrahedral MO_3 compound. Energy levels are labeled "s, a" for orbitals symmetric or antisymmetric to the xz plane.

reported herein. The molecular orbital description of tetraoxo metalates (MO_4^{n-} , $n = 0, 1, 2, 3$) is relatively simple because of the high tetrahedral symmetry: the metal d orbitals split in the "3 above 2" pattern (t_2 above e).^{23a} The e level is metal–oxygen π antibonding and the t_2 level is both σ and π antibonding. With first-row transition metals, tetraoxo complexes with up to two d electrons can be prepared (hypomanganate, ferrate), although they are very reactive. For second- and third-row metals, however, the ligand field splittings are larger and the e level much more antibonding, so that addition of even one d electron results in loss of the tetrahedral structure, as in oxomolybdenum(V) compounds.^{24a}

Metal–oxo complexes with d^1 or d^2 electron configurations are almost always found in octahedral or square-pyramidal geometries.^{7,20,24} A rough molecular orbital scheme for a C_{4v} mono-oxo complex (Figure 3) is derived from the octahedral MO diagram, in which the d orbitals split into a "2 above 3" pattern (e_g over t_{2g}). The orbitals of the upper (e_g) level in O_h (d_{z^2} and $d_{x^2-y^2}$) are no longer degenerate in C_{4v} symmetry, but they remain σ antibonding. The lower, " t_{2g} " octahedral levels are split substantially by the oxo ligand into an e set (d_{xz} , d_{yz}) that is strongly metal–oxygen π antibonding and a nonbonding b_2 orbital (d_{xy}).^{23b} C_{4v} oxo compounds with two d electrons are invariably diamagnetic with the electrons paired in the b_2 orbital (Figure 3). Note that the two metal–oxygen π levels are degenerate in this symmetry and that the M–O bond is formally a triple bond.

A third d electron in an octahedral oxo complex would have to occupy the e (π^*) level, destabilizing the metal–oxygen multiple bond. In fact, reductions of d^2 oxo complexes always involve loss of the terminal oxo ligand, commonly by oligomerization (e.g., to manganese or ruthenium dioxides) or by protonation to hydroxide species (as found, for example, for chromium, molybdenum, and manganese trivalent ions in aqueous media).^{1,7,20,24} To our knowledge, the only exception to this rule is the chemistry reported herein, in which reduction of rhenium(V) by a phosphine or arsine ligand does not affect the rhenium–oxygen multiple bond. This is possible because compounds **1–8**, which are d^4 , adopt a pseudotetrahedral geometry. A d^4 terminal oxo complex with C_{4v} symmetry would have two unpaired electrons in the metal–oxygen π^* (e) level (Figure 3). This is thought to be the electronic structure of the active site in cytochrome P-450 enzymes and various model systems, a pseudooctahedral iron(IV)–oxo complex which is an extraordinarily reactive oxidant.^{6,23d} Meyer and co-workers have reported a series of oxo–ruthenium and –osmium(IV) (d^4) polypyridyl compounds that are also very reactive.^{25a,b}

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Table III. ^1H and ^{13}C NMR Data^a

compound	no.	RC=CR		RC=CR and other				
		^{13}C	$m (^1J_{\text{CH}})$	^1H	$m (J_{\text{HH}})$	^{13}C	$m (^1J_{\text{CH}})$	
Re(O)I(MeC=CMe) ₂	1	138.21		2.30	q (1)	14.95	q (130)	
		142.32		2.92	q (1)	17.09	q (130)	
Re(O)Br(MeC=CMe) ₂	2	138.27		2.30	q (1)	11.93	q (130)	
		146.08		2.68	q (1)	15.46	q (130)	
Re(O)Cl(MeC=CMe) ₂	3	138.62		2.31		9.52	q (131)	
		148.34		2.55		15.84	q (130)	
Re(O)I(EtC=CEt) ₂	4	141.99		2.82 dq	{ ² J _{HH} = 16 ³ J _{HH} = 7 }	24.58	t (130)	
		146.34		2.96 dq		CCH'		
Re(O)I(MeC=CH) ₂ a:b:c = 1.3:4.3:1	5 b	143.38		3.51	q (7)	CH ₂	26.35	t (131)
		149.32		1.12	t (7)	CH ₃	13.98	q (128)
		127.94	d (220)	1.16	t (7)	CH ₃	14.77	q (128)
		128.80	d (223)	8.77	q (1)	CH		
		143.52		9.11	q (1)			
		146.86	a, c	2.34	d (1)	CH ₃	15.02	q (131)
		126.78	d (222)	2.95	d (1)		17.53	q (131)
		131.56	d (222)	8.98	q (1)	CH		
		157.34		2.95	d (1)	CH ₃	17.47	q (131)
		164.56		9.19	q (1)	CH		
Re(O)I(Me ₃ CC=CH) ₂ ^b	6b	127.03	d (217)	2.24	d (1)	CH ₃	15.75	q (131)
		128.74	d (223)	9.18		CH	37.50	
		146.30		9.64		C(CH ₃) ₃	38.23	
		146.62		1.20			31.44	q (127)
Re(O)I(PhC=CMe) ₂ ^c	7	138.56		1.50			31.87	q (127)
		139.82		2.17	b	CH ₃	15.14	
		144.33		3.07		CH ₃	18.22	
		145.24		3.10	a	CH ₃	18.22	
		146.30		2.55	c	CH ₃	d	
		146.62		6.9-8.0	m, Ph			
Re(O)I[MeC=C(CH ₂) ₄ C=CMe]	8a	140.90		2.92		CH ₃	17.08	q (130)
		141.60		2.84	m	CHH'	26.43	t (126)
				2.99	m			
				1.15	m	CHH'	33.40	t (127)
[Re(MeC=CMe) ₂ (PMe ₃) ₃]I ^e	9	178.23	MeC=CMe	1.74	m		19.21	
			PMe ₃	2.77			24.78	broad
			(PMe ₃) ₂	1.77	d (J _{PH} = 9)		19.95	broad
				1.06	t (J _{PH} = 3)		10.66	q (130)
				2.37	4Me		16.36	q (130)
[ReO(O ₂ CMe)(MeC=CMe) ₂]	10	140.66		2.24		O ₂ CCH ₃	174.03	
		150.36					22.79	q (128)
				2.33	q (1)		9.88	q (132)
				3.26	q (1)		16.72	q (132)
				8.16	m		α 151.37	d (188)
				7.93	t (7)		β 129.54	d (171)
				8.28	t (8)		γ 142.35	d (191)
				2.08	q (1)		12.34	q (130)
				3.26	q (1)		17.24	q (130)
				6.09	d (5)		2 {148.96 ^h	
				7.38	t (7)		151.77	
				7.79	t (7)		3 {124.12	d (169)
		8.13	t (8)		124.38	d (168)		
		8.48	t		4 {140.77	d (168)		
		8.50	d		143.01	d (170)		
		8.67	d (8)		5 {127.04	d (171)		
		8.89	d (5)		6 {127.96	d (172)		
					146.36	d (184)		
					153.02	d (187)		
[ReO(MeC=CMe) ₂ py]SbF ₆ ^f	11	143.47		2.33	q (1)		9.88	q (132)
		145.77		3.26	q (1)		16.72	q (132)
[ReO(MeC=CMe) ₂ bpy]SbF ₆ ^g	12	139.58 ^h		8.16	m		α 151.37	d (188)
		147.50		7.93	t (7)		β 129.54	d (171)
				8.28	t (8)		γ 142.35	d (191)
				2.08	q (1)		12.34	q (130)
				3.26	q (1)		17.24	q (130)
				6.09	d (5)		2 {148.96 ^h	
				7.38	t (7)		151.77	
				7.79	t (7)		3 {124.12	d (169)
				8.13	t (8)		124.38	d (168)
				8.48	t		4 {140.77	d (168)
		8.50	d		143.01	d (170)		
		8.67	d (8)		5 {127.04	d (171)		
		8.89	d (5)		6 {127.96	d (172)		
					146.36	d (184)		
					153.02	d (187)		

[$\text{Re}(\text{O}(\text{MeC}\equiv\text{CMe})_2\text{PPh}_3)_2\text{SbF}_6$]	13	139.15 148.25	$d(\text{J}_{\text{PC}} = 12^b)$	1.95 3.35 PPH ₃ ⁱ { 7.7-7.6	q (1) q (1) m	CH	12.88 15.74 130.75 133.99 134.67	q (132), d (J _{PC} = 5) q (132) d (165), d (J _{PC} = 11) d (163) d (162), d (J _{PC} = 11)
[$\text{ReO}(\text{PhC}\equiv\text{CMe})_2\text{py})_2\text{SbF}_6$] a:b = 1:3,5	15	143.13 145.72 146.54 146.71 147.30 150.34	d (252) b { 2.52 2.90 a 3.58 8.16 7.7 7.1-7.4	m m m	CH ₃ CH ₃ CH ₃ py:a py:b	10.78 16.61 17.55 α 151.54 γ 142.22 α 150.98 γ 141.53	q (132) q (132) q (132) q (188) d (170) d (187) d (168)	

^a Chemical shifts in ppm downfield from Me₄Si; coupling constants in Hz, m = multiplicity. Spectra of 2, 5, 7, 8, 10 in C₂D₂F₆; 6, 9, 11-15 in CD₂Cl₂; all at ambient temperatures unless otherwise noted. The small letters a, b, c refer to the isomers in Figure 2; assignments made by analogy with 8 which is assumed to have structure a. In C₂D₂F₆ one of the methine carbon atoms appears at 125.87 and the other is obscured by solvent; all other chemical shifts are within 1 ppm of those above, in CD₂Cl₂. Only isomer b is observed. ^c Only a decoupled ¹³C NMR spectrum was obtained. ^d Not observed. ^e ¹H NMR at -40 °C. 9 has not been isolated in pure form; all the resonances are broad. ^f ¹H NMR at 4 °C. ^g For py and bpy assignments, see ref 37. ^h Assignments of acetylenic and 2-bipyridine resonances ambiguous; intensities suggest that δ 139 and 147 are paired. ⁱ The assignments of δ 139 and 148 are ambiguous between acetylenic resonances and the phenyl ipso carbon which was not otherwise observed. The spectrum is essentially identical in THF-d₆, suggesting that δ 139 is not an accidental pairing of two peaks. ^j The ¹³C NMR spectrum contains an additional 14 resonances in the range δ 127-133.

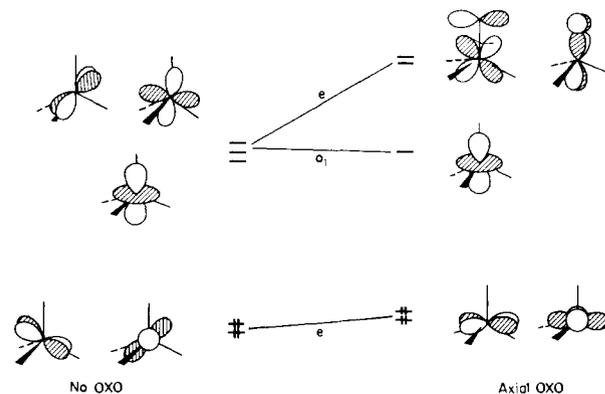


Figure 5. Realignment of the metal d orbitals of a quasitetrahedral complex by the π orbitals of the axial oxo ligand. C_{3v} symmetry is assumed.

together with a recently reported ruthenyl complex of tetraaza-cyclotetradecane,²⁶ they appear to be the only stable terminal oxo compounds with electrons in metal-oxygen π antibonding levels.²⁶

The critical difference between the octahedral and tetrahedral structures is the energy of the $d_{x^2-y^2}$ orbital, which in C_{4v} symmetry is σ antibonding to the ligands in the equatorial plane. This antibonding interaction is greatly reduced in the pseudotetrahedral structure because there is effectively a threefold axis about the metal-oxygen bond and the overlap between the $d_{x^2-y^2}$ and the equatorial ligands is therefore lower (Figure 4). In both structures the z axis is chosen to be coincident with the metal-oxygen bond; note that this is not the normal choice of axes in tetrahedral geometry. In the tetrahedral case there are two roughly non-bonding orbitals, d_{xy} and $d_{x^2-y^2}$, which are degenerate in C_{3v} symmetry. A stable d^4 oxo compound can be prepared because there are no electrons in metal-oxygen antibonding levels.

A more detailed description of the rhenium(III) oxo acetylene complexes has been developed with use of extended Hückel molecular orbital calculations. In tetrahedral symmetry the d orbitals split "3 above 2" so that in principle low-spin (diamagnetic) d^4 tetrahedral complexes are possible. Only one example has been previously reported,²⁷ however, because tetrahedral ligand-field splittings are usually quite small. As described below the particular combination of ligands in the present compounds accentuates the "t₂"-"e" gap and imposes a diamagnetic electronic structure.

The single oxo ligand of the "tetrahedral" compounds lowers the effective symmetry from T_d to C_{3v} and splits the "t₂" d orbitals into orbital sets of a₁ and e symmetry (Figure 5). Thus there are two sets of doubly degenerate e orbitals and they are allowed to mix with each other. Whenever d orbitals mix the effect is simply a reorientation or realignment of the d orbitals with respect to the ligand axes. In this case the axial oxo ligand, a very strong σ and π donor, causes the realignment of the d orbitals shown in Figure 5. In principle both of the e orbital sets have some π interaction with the axial oxo ligand but the canonical molecular orbitals have one e set which is aligned to have maximum π interaction with the oxo ligand and the other e set aligned to have minimal π interaction with the oxo ligand. This phenomenon of d orbital realignment or "tilting" is an inescapable feature of noncubic threefold symmetry, and some of its manifestations have been discussed in the literature.²⁸

The resulting realigned d orbitals, shown on the right of Figure 5, are of course identical with those on the right side of Figure 4, and the orbitals which comprise the Re-O multiple bond are

(26) Che, C.-M.; Tang, T.-W.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1984**, 641-642. Che, C.-M.; Wong, K.-Y.; Mak, T. C. W. *Ibid.* **1985**, 546-548.

(27) $\text{Re}(\text{PR}_2)_4\text{Li}(\text{MeOCH}_2\text{CH}_2\text{OMe})$ (R = cyclohexyl): Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763-5.

(28) See, for example: Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736-7738.

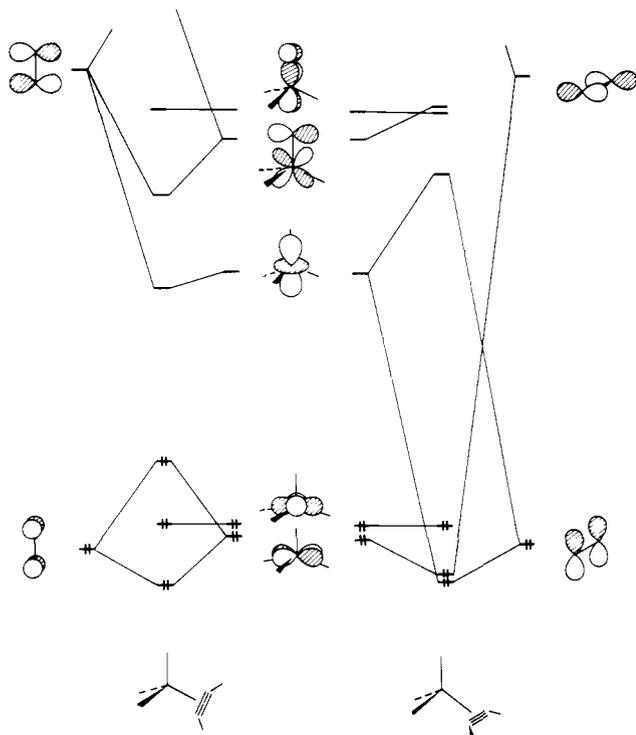


Figure 6. Left: Orbital interaction diagram for a hypothetical monoacetylene complex with "upright" acetylene orientation. Only π interactions are shown. Right: Orbital interaction diagram for a monoacetylene complex with a "planar" acetylene orientation.

equivalent to the $d^2 C_{4v}$ case (Figure 3). Even the d orbital labels are the same when the z axis is defined by the Re–O bond. The equivalence of the theoretical descriptions of the d^2 and d^4 rhenium–oxo bonds is consistent with the similarities in bond distances and stretching frequencies mentioned earlier. The deoxygenation of the d^4 complexes by PMe_3 but not PPh_3 is also typical of Re(V) complexes.

The realigned d orbitals also determine the orientation of the acetylene ligands. An acetylene functions as a σ donor to a metal center through use of a C–C π orbital, in the usual Dewar–Chatt–Duncanson model.¹ This σ donation will be roughly constant in all orientations and any preference comes from the π -donor and π -acceptor functions of the acetylene. In octahedral d^6 compounds, all ligand sites have equal π -bonding opportunities in all alignments. In certain tetrahedral environments this is still true; for instance the single-faced π acceptor in the hypothetical d^4 complex $L_3M(\text{ethylene})$ would rotate freely (barring steric effects), bonding equally well with either component of the filled e level regardless of orientation. But in a quasitetrahedral mono-oxo complex, there is a strong preference for a "planar" disposition of an acetylene ligand (orthogonal to the M–O vector and approximately coplanar with the remaining ligands) over an "upright" orientation (parallel to the M–O vector).

Consider a hypothetical monoacetylene oxo bisligand complex. In the upright orientation the π -donating capability of the acetylene participates in a 4-electron, net destabilizing, interaction with a filled d orbital, and its π -accepting capability is wasted in stabilizing empty d orbitals (Figure 6). An acetylene with a "planar" orientation enjoys more productive π interactions with the metal: the π -donating capability is accommodated by an empty d orbital (d_{z^2}) and its π -accepting capability stabilizes a filled d orbital. Here the acetylene serves as a four-electron donor to the metal and both its π interactions increase the HOMO–LUMO gap.

The same conclusions are valid for bisacetylene compounds, with the following exception: the π -donor orbitals have only one empty d orbital with which they interact strongly (see Figure 7). Thus the acetylenic π -donating orbitals contribute only one pair of electrons to the bonding, the other pair being held in a non-

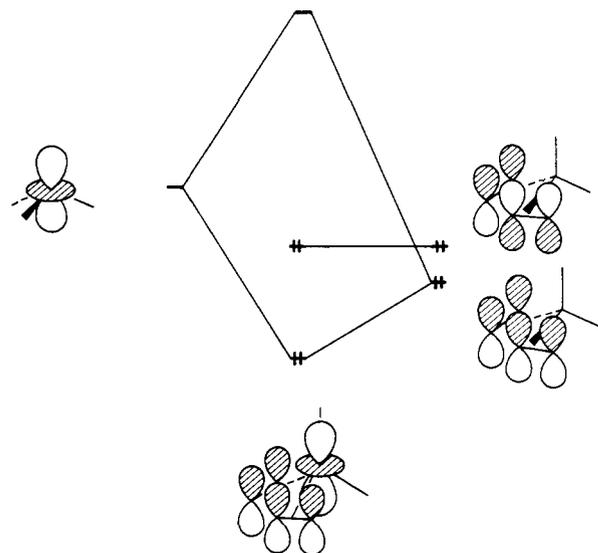


Figure 7. Schematic interaction of acetylene π -donor orbitals with the metal d_{z^2} orbital.

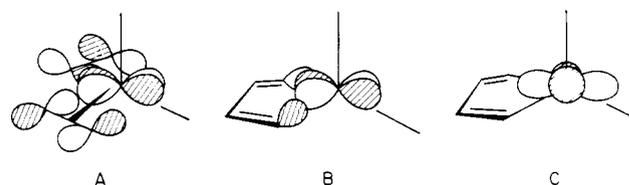


Figure 8. Schematic drawing of the orbitals involved in the hypothetical interconversion of bisacetylene and metallacyclopentadiene complexes.

metal-bonding, acetylene-centered MO. Restated, the two acetylenes contribute approximately 6 electrons, or 3 per acetylene, to the complex. This is consistent with the correlation of NMR chemical shifts discussed above. Thus 1–8 are quite properly viewed as 18-electron complexes: 6 electrons from the oxide (O^{2-}), 6 from the acetylenes, 4 from Re(III), and 2 from the halide. The conclusion that the acetylene π interactions are only stabilizing in the planar form explains not only the structure of **1** but also the very large barriers to acetylene rotation. For our model (see Experimental Section) we compute a preference of 1.1 eV for the planar form, relative to an unrelaxed structure with one upright acetylene.

The theoretical analysis also explains the absence of acetylene–acetylene coupling, since the concerted reaction to form a rhenium(V) metallacyclopentadiene complex is forbidden for a d^4 molecule in C_s symmetry. The orbital correlation diagram for this hypothetical reaction is very similar to that for olefin coupling in trigonal bisolefin nickel(0) compounds.²⁹ In essence the HOMO of the bisacetylene complex, antisymmetric to the mirror plane (A, Figure 8), correlates with an antisymmetric d orbital (B) which would be empty in the ground state of the hypothetical product. This product would have one filled d orbital, but it is symmetric to the mirror plane (C).

The calculations, the structure of **1**, the reaction chemistry, and the spectroscopy all support the formulation of these compounds as rhenium(III), d^4 . The assignment of oxidation states in organometallic compounds is not always meaningful because π -acid ligands can withdraw electron density from a metal center and thereby effectively oxidize it. In this case, back-bonding to the acetylene ligands is clearly important, stabilizing the d_{xy} and $d_{x^2-y^2}$ orbitals, but the electrons in these orbitals are still primarily associated with the rhenium. Acetylene ligands that have been proposed as dianions (as in $Ta(\text{PhC}\equiv\text{CPh})\text{Cl}_4^-$ or $W(\text{RC}\equiv$

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$\text{CR}(\text{Cl})_4$) are hydrolytically very sensitive and, compared with **1**, have significantly longer CC bonds, lower acetylene stretching frequencies, and lower field chemical shifts in the ^{13}C NMR.³⁰

The conclusion that there are four σ nonbonding electrons at rhenium appears to be accurate and is very useful in understanding the stereochemistry and lack of acetylene rotation in these molecules. In addition this description explains why one-electron reduction of **1** is irreversible: an added electron must populate a rhenium–oxygen antibonding level, resulting in loss of the terminal oxo ligand and major structural changes.

Conclusions

Addition of acetylenes to a number of rhenium(V)–oxo complexes results in the oxidation of a coordinated phosphine or arsine ligand and the formation of rhenium(III) oxo acetylene compounds. $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})_2$ has a pseudotetrahedral structure in the solid state, with a short, multiple Re–O bond (1.697 (3) Å). A number of derivatives have been prepared, all with the same basic geometry. The assignment of these compounds as $\text{Re}(\text{III})$, d^4 , is supported by theoretical, crystallographic, spectroscopic, and chemical evidence. They are the first low-valent compounds to have a terminal metal–oxygen linkage. The rhenium–oxygen multiple bond appears unaffected by the low oxidation state. The remarkable stability of the d^4 oxo compounds is apparently due to their pseudotetrahedral structure in which there is effectively a threefold axis about the metal–oxygen bond. In this geometry there are two d orbitals (derived from the e set in T_d symmetry) that are essentially σ nonbonding and nonbonding with respect to the rhenium–oxygen π interactions. These two orbitals are also significantly stabilized by back-bonding with the acetylene π^* levels. Thus four electrons can be incorporated into the molecule without destabilizing the metal–oxygen multiple bond, and a stable structure results.

Experimental Section

Syntheses of **1** and **4–8** were done in a fume hood with commercially available high-purity solvents. The other procedures were performed in a continuous nitrogen flow glovebox or by standard vacuum line techniques. Benzene, toluene, and THF were purified by vacuum transfer from sodium/benzophenone, pentane by transfer from LiAlH_4 , and methylene chloride by transfer from 4 Å molecular sieves. Hexane was filtered through alumina before use. NMR spectra were obtained with Nicolet NT200, NT300, NT360, QE300, Varian FT 80A, and Bruker WM400 spectrometers. IR spectra were obtained on Nujol mulls with Perkin-Elmer 283B and 983G spectrophotometers. Elemental analyses were performed by Galbraith Labs.

$\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ was prepared by the method reported for $\text{ReOBr}_3(\text{AsPh}_3)_2$.³¹ This does not yield pure material for the iodide because ReO_4^- oxidizes I^- to I_2 , forming I_2AsPh_3 which is not easily separated from the product. KReO_4 (Pressure Chemical, 4.0 g, 13.8 mmol) was dissolved in 12 mL of HI (aqueous), and a suspension of 20 g of AsPh_3 (Aldrich, 65.3 mmol) in 200 mL of acetic acid was added. After the mixture was stirred for a day the rust colored product was isolated by filtration and washed with acetic acid and diethyl ether. The solid was suspended in 100 mL of diethyl ether, stirred for 3 h, and isolated. Yield 19.02 g (115% assuming product is $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$). One batch analyzed close to $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2\text{I}_2\text{AsPh}_3$: Anal. Calcd for $\text{C}_{54}\text{H}_{45}\text{As}_3\text{I}_5\text{ORe}$: C, 36.95; H, 2.58; I, 36.15; Re 10.61. Found: C, 37.29, 37.37; H, 2.69, 2.90; I, 36.16, 35.96; Re, 10.07, 9.98. IR: 1574 w (Ph), 1095, 1074, 985 (shoulder), 976 st (ReO), 734 st, 687 cm^{-1} .

$\text{Re}(\text{O})\text{I}(\text{Me}\equiv\text{CMe})_2$ (**1**). " $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ " (8.0 g, product from 1.81 g of KReO_4 or 6.25 mmol) and 2-butyne (Farchan, 3 g, 55 mmol) were stirred in 40 mL of benzene for 16 h. The solution was filtered, 1.6 g of I_2 (6.30 mmol) was added, and stirring was continued for 1 h. After filtration an additional 0.1 g of I_2 (0.39 mmol) was added and stirring continued for another hour. After filtration the benzene and excess 2-butyne were removed by distillation and the residue extracted into hexane. The hexane solubles were sublimed at 60 °C for 4 h (10^{-3} torr), yielding 1.47 g of yellow **1** (3.35 mmol, 54% based on KReO_4). Compound **1** is soluble in hexane, benzene, methylene chloride, diethyl ether, THF, acetonitrile, acetone, and methanol; it does not survive chromatography on alumina. Anal. Calcd for $\text{C}_8\text{H}_{12}\text{IORe}$: C, 21.97; H, 2.77. Found: C, 22.22, 21.94; H, 2.76, 2.88. Mass spectrum: calcd 437.9496,

found 437.9506. IR: 1803 w, 1795 w (C≡C), 1153, 1039, 975 st (ReO), 808, 625 cm^{-1} . The IR spectra of **1**- ^{18}O has a band at 926 instead of 975; calculated for $\nu(\text{Re}^{18}\text{O})$ by reduced mass: 924. $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})_2$ was prepared by adding 5 μL of H_2^{18}O (Monsanto, 95–99% labeled) to a solution of **1** in 0.5 mL of C_6D_6 . After 4 days removal of the volatiles yielded a roughly equal mixture of **1** and **1**- ^{18}O (by IR and mass spectrum).

$\text{Re}(\text{O})\text{Br}(\text{MeC}\equiv\text{CMe})_2$ (**2**). A solution of AgSbF_6 (0.25 g, 0.73 mmol) in 5 mL of acetone was added dropwise to a stirred –30 °C solution of **1** (0.25 g, 0.57 mmol). After 10 min of stirring and filtering, NMe_4Br (0.13 g, 0.84 mmole) in 10 mL of acetone was added. After the mixture was stirred for 20 min, filtration, removal of the volatiles, and recrystallization from hexane gave 0.10 g (45%) of yellow **2**. Anal. Calcd for $\text{C}_8\text{H}_{12}\text{BrORe}$: C, 24.62; H, 3.10. Found: C, 24.72, 24.79; H, 3.38, 3.21. Mass spectrum: calcd 389.9632, found 389.9622. IR: 1810 w, 1800 w, 1158, 1043, 980 cm^{-1} st (ReO).

$\text{Re}(\text{O})\text{Cl}(\text{MeC}\equiv\text{CMe})_2$ (**3**) was prepared by the method used for **2**: 0.25 g of **1**, 0.25 g of AgSbF_6 , and 0.13 g of NEt_4Cl gave 98 mg of pale yellow **3** (50%). Anal. Calcd for $\text{C}_8\text{H}_{12}\text{ClORe}$: C, 27.78; H, 3.50. Found: C, 28.00, 28.01; H, 3.48, 3.67. Mass spectrum: calcd 346.0137, found 346.0138. IR: 1806 w, 1797 w, (C≡C), 1157, 1041, 980 st (ReO), 723 cm^{-1} .

$\text{Re}(\text{O})\text{I}(\text{EtC}\equiv\text{CEt})_2$ (**4**). Following the procedure used for **1**, 2.0 g of $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ and 1.5 g of 3-hexyne (Farchan) were stirred for 2 h in 15 mL of benzene before adding 0.46 g + 0.10 g of I_2 . Compound **4** sublimed as a yellow oil. Mass spectrum: calcd 494.0121; found 494.0121. IR: 1783 (C≡C), 1305, 1252, 1142, 1093, 1063, 971 st (ReO), 941, 808 cm^{-1} .

$\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CH})_2$ (**5**). Propyne was bubbled through a solution of 2.0 g of $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ in 30 mL of benzene for 2 h. The solution was filtered, 0.42 g of I_2 added, and stirring continued for 2.5 h. After filtration and removal of the volatiles, recrystallization from hexane gave 74 mg of yellow-brown **5** (13%). Mass spectrum: calcd 409.9182, found, 409.9182. IR: 3092 (C≡CH), 1716 (C≡C), 1073, 980 (s, ReO), 901, 772 cm^{-1} .

$\text{Re}(\text{O})\text{I}(\text{Me}_3\text{CC}\equiv\text{CH})_2$ (**6**). A solution of 1.0 g of $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ and 0.4 g of 3,3-dimethyl-1-butyne in 20 mL of benzene was stirred for 3 h, then 0.23 g of I_2 in 40 mL of benzene was added dropwise. After the mixture was filtered and the volatiles removed, the residue was recrystallized from hexane, yielding 0.19 g (43%) of yellow-brown **6**. Analytically pure bright yellow **6** is obtained by sublimation at 60 °C (10^{-3} torr). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{IORe}$: C, 29.21; H, 4.09. Found: C, 29.43, 29.26; H, 4.13, 4.24. Mass spectrum: calcd 494.0121, found 494.0123. IR: 3091 (CH), 1705 w, 1689, 1677, 1232, 1211, 1035, 974 st (ReO), 944, 906, 899, 795, 781 cm^{-1} .

$\text{Re}(\text{O})\text{I}(\text{PhC}\equiv\text{CMe})_2$ (**7**). Following the procedure for **6**, 1.0 g of $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ and 0.8 g of 1-phenyl-1-propyne, in 10 mL of benzene, plus 0.23 g of I_2 in 40 mL benzene gave 0.20 g of **7** (40%). Sublimation yields bright yellow pure **7**. This preparation is difficult to scale up. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{IORe}$: C, 38.51; H, 2.87. Found: C, 38.66; H, 3.00. Mass spectrum: calcd 561.9808, found, 561.9816. IR: 1594 w, 1573 (Ph), 1250, 1073, 956 st (ReO), 758, 693, 682 cm^{-1} .

$\text{Re}(\text{O})\text{I}[\text{MeC}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{CMe}]$ (**8**). A solution of 2.0 g of $\text{ReO}(\text{I})_3(\text{AsPh}_3)_2$ and 0.30 g of 2,8-decadiene in 100 mL of benzene was stirred for 3 h and filtered. I_2 (0.46 g) was added, and the solution was stirred for 1 h and filtered again. After extraction into hexane and removal of the volatiles, the residue was sublimed, giving a yellow oil containing **8b**, oligomers of **8**, and decadiene. Recrystallization from hexane gave 50 mg (7%) of predominantly **8b** with 10–15% of the diyne. Mass spectrum: calcd 463.9651, found 463.9647. IR: 1788 vw, 1734w, 1155, 1048, 972 st (ReO), 904, 741 cm^{-1} .

$[\text{Re}(\text{MeC}\equiv\text{CMe})_2(\text{PMe}_3)_3]\text{I}$ (**9**). A solution of 0.2 g of PMe_3 in 5 mL of toluene was added dropwise to a –30 °C solution of 0.14 g of **1** in 4 mL of toluene. The resulting dark green solids were filtered off and washed with hexane, 0.175 g (84%). This material appears to be a mixture of **9** and a paramagnetic compound. Fast atom bombardment mass spectrum shows essentially only 447/445 = $[\text{Re}(\text{MeC}\equiv\text{CMe})_2(\text{PMe}_3)_2]^+$. IR: 1610 w, 1285, 940, 722 cm^{-1} . $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2): δ –35.7, –37.2; both broad singlets, integral 1:1.96.

$\text{Re}(\text{O}_2\text{CMe})(\text{MeC}\equiv\text{CMe})_2$ (**10**). $\text{Ag}(\text{O}_2\text{CMe})$ (132 mg, 0.79 mmol) and **1** (140 mg, 0.32 mmol) were stirred in 7 mL of CH_2Cl_2 for 16 h. After the mixture was filtered and the volatiles removed, the residue was recrystallized from hexane, giving 85 mg (72%) of white **10**. Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{O}_3\text{Re}$: C, 32.51; H, 4.09. Found: C, 32.49, 32.53; H, 4.20, 4.10. Mass spectrum: calcd 370.0581, found 370.0571. IR: 1796 w, 1650 st, 1293 st (O_2CMe), 1160, 1040, 1022, 962 st (ReO), 670, 628 cm^{-1} .

$[\text{ReO}(\text{MeC}\equiv\text{CMe})_2\text{py}]\text{SbF}_6$ (**11**). A cold (ca. –10 °C) solution of AgSbF_6 (308 mg, 0.90 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a stirred, –40 °C solution of **1** (392 mg, 0.90 mmol) and pyridine (72

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Table IV. Summary of X-ray Diffraction Data

complex	Re(O)I(CH ₃ C≡CCH ₃) ₂ (1)
formula	C ₈ H ₁₂ ORe
fw	437.29
space group	C ₂ ^h -P2 ₁ /c (no. 14)
a, Å	9.749 (3)
b, Å	7.307 (3)
c, Å	16.106 (7)
β, deg	106.42 (3)
V, Å ³	1111 (2)
Z	4
ρ(calcd), g cm ⁻³	2.639
crystal dimensions, mm	0.19 × 0.25 × 0.30
temp., °C	-100
radiation	Mo Kα (0.71069 Å) from graphite monochromator
μ, cm ⁻¹	139.23
2θ limits, deg	4.0-55.0
transmission factors	0.376-0.995 (av 0.665)
total no. of unique observations	2821
data, F _o ² > 3σ(R _o ²)	2087
final no. of variables	100
R	0.027
R _w	0.029
error in observation of unit wt	2.05 electrons

μL, 0.89 mmol) in 4 mL of CH₂Cl₂. The solution was stirred for 5 min and filtered, and **11** was isolated as pale green crystals by evaporation and cooling of the solution: yield 476 mg (76%). Anal. Calcd for C₁₃H₁₇O(15N)SbF₆Re: C, 24.97; H, 2.74; N, 2.24. Found: C, 24.83; H, 2.78; N, 2.27. IR: 1606 (py), 1147, 969 st (ReO), 752, 653 cm⁻¹ st (SbF₆). The IR spectrum of [Re¹⁸O(MeC≡CMe)₂py]SbF₆ contains a band at 919 cm⁻¹ instead of 969 cm⁻¹; calculated by reduced mass ν_{Re¹⁸O} = 920. The oxygen-18 labeled material was prepared by stirring a 2-mL THF solution of 45 mg of **11** and 20 μL of H₂¹⁸O (Monsanto, 95-99% ¹⁸O) for 2 h, stripping to dryness, and repeating the procedure.

[ReO(MeC≡CMe)₂bpy]SbF₆ (**12**). A cold (ca. -10 °C) solution of AgSbF₆ (312 mg, 0.91 mmol) in 6 mL of CH₂Cl₂ was added dropwise to a stirred, -40 °C solution of **1** (400 mg, 0.91 mmol) and bipyridine (144 mg, 0.92 mmol) in 6 mL of CH₂Cl₂. After being stirred in the dark for 1 h, the solution was filtered and reduced to 3 mL; addition of hexane yielded 488 mg pale green **12** (76%). IR: 1604, 1497 (bpy), 1318, 1152, 1038, 1015, 950 st (ReO), 773 st, 731, 661 cm⁻¹ st (SbF₆).

[ReO(MeC≡CMe)₂PPh₃]SbF₆ (**13**). Following the procedure for **12**, 115 mg of **1** (0.26 mmol), 70 mg of PPh₃ (0.27 mmol), and 96 mg of AgSbF₆ (0.28 mmol) gave 167 mg of light yellow **13** (78%). Anal. Calcd for C₂₆H₂₇OPReSbF₆: C, 38.63; H, 3.37. Found: C, 38.78, 38.51; H, 3.53, 3.29. IR: 1150, 1102, 1091, 1001, 966 st (ReO), 754, 693, 658 cm⁻¹ st (SbF₆). ³¹P{¹H} NMR (CD₂Cl₂): δ 39.8.

[ReO(Me₃CC≡CH)₂py]SbF₆ (**14**). Following the procedure for **12**, 100 mg of **6**, 16.5 μL of pyridine, and 70 mg of AgSbF₆ (all 0.20 mmol) gave 90 mg of cream colored **14** (51%). Diethyl ether was used instead of hexane to precipitate the product. IR: 3117 (CH), 1715 w, 1694, 1612 (py), 1233, 1224, 1204, 1073, 992 st, 961, 933, 901, 807, 762 st, 696, 657 cm⁻¹ st (SbF₆).

[ReO(PhC≡CMe)₂py]SbF₆ (**15**). Following the procedure for **12** (except that diethyl ether was used to precipitate solids), 50 mg of **7** (0.089 mmol), 7 μL of pyridine (0.087 mmol), and 35 mg of AgSbF₆ (0.10 mmol) gave 48 mg (72%) of cream colored **15**. IR: 1611, 1572, 1240, 1178, 1162, 1074, 965 (st, ReO), 755, 693, 657 cm⁻¹.

Re(O)I(MeC≡CMe)(MeC≡CPh). A sealed tube containing **1**, 1-phenylpropyne, and C₆D₆ was heated at 80 °C for a week. The resonances for **1**, 7, 2-butyne, and 1-phenylpropyne were observed in a ratio of 1:5:20:100. In addition, peaks assigned to Re(O)I(MeC≡CMe)-(MeC≡CPh) were observed: isomer a, δ 3.05 (CH₃C≡CPh), 2.94 q, 1.97 q, ⁵J_{HH} = 1 Hz, (CH₃C≡CCH₃); isomer c, δ 2.48 (CH₃C≡CPh), 2.37 q, ⁵J_{HH} = 1 Hz (CH₃C≡CCH₃), the other methyl quartet was not observed; ratio a:c:1 = 8:1:1.

The reaction of **1** with AgSbF₆ in acetonitrile gives a purple solution which on addition of iodide ion reforms **1**. Spectroscopically the major species in solution appears to be [ReO(MeC≡CMe)₂(MeCN)₂]SbF₆ which decomposes over a period of hours. ¹H NMR (CD₃CN): δ 2.85, 3.17 (CH₃C≡CCH₃). ¹³C NMR (CD₃CN): δ 140.81, 142.86 (MeC≡CMe), 11.52, 16.58 (CH₃C≡CCH₃).

X-ray Data Collection and Structure Solution and Refinement. Crystals of complex **1** were grown from a hexane solution by cooling to -40

°C. A suitable crystal was sealed in a glass capillary under a nitrogen atmosphere. The crystal was then placed on a Syntex P3 diffractometer and cooled to -100 °C. Preliminary photographs revealed the space group and approximate cell dimensions. The cell parameters were then accurately defined on the basis of 41 computer-centered reflections chosen from diverse regions of reciprocal space. Crystallographic data are compiled in Table IV.

Intensity data were collected with use of the ω-scan techniques (variable scan range, 4.0-10.0 deg min⁻¹; total background counting time = scan time). The intensities of three reflections were monitored at intervals of 200 reflections; no significant variations in these standard intensities were observed. The intensities of several reflections were measured at 10° increments about the diffraction vector and the curve derived was used in the subsequent application of an empirical correction for absorption. The data were processed by using counting statistics and standard deviations were derived by using a *p* factor of 0.02.³²

The solution and refinement of the structure were carried out on a PDP-11 computer with use of local modifications of the SDP-Plus program series supplied by the Enraf-Nonius Corp. The Re atom was located from an origin-removed Patterson synthesis, and the positions of the remaining non-hydrogen atoms were established by using the usual combination of structure factor, Fourier synthesis, and full-matrix least-squares refinement. In these refinements the function minimized was Σ_w(|F_o| - |F_c|)², where |F_o| and |F_c| are respectively the observed and calculated structure amplitudes and where w = 1/σ²(F_o). The atomic scattering factors and anomalous dispersion terms were taken from the standard compilations.³³ Hydrogen atoms were located, placed in idealized positions, and included as fixed contributions in the final cycles of refinement. Tables of anisotropic thermal parameters and hydrogen atom positions (Tables V and VI) are available as Supplementary Material, as are observed and calculated structure factor amplitudes (Table VII). Final values for the agreement indices are in Table IV.

Calculations

Calculations were performed on the model compound Re(O)Cl(HCCCH)₂ with use of the Du Pont implementation of the Extended Hückel method,³⁴ including two-body repulsions introduced by Anderson.³⁵ Parameters were taken from the literature.³⁶ Idealized tetrahedral angular geometries were used with distances Re-Cl = 2.34 Å, Re-C = 2.05 Å, Re-O = 1.70 Å, C-C = 1.29 Å, C-H = 1.1 Å.

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Registry No. 1, 90623-35-1; 2, 98778-22-4; 3, 98778-23-5; 4, 98778-24-6; 5, 98778-25-7; 6, 98778-26-8; 7, 90623-37-3; 8, 98778-27-9; 9, 98799-30-5; 10, 98778-28-0; 11, 98799-32-7; 12, 98778-30-4; 13, 98778-32-6; 14, 98778-34-8; 15, 98778-36-0; ReO(I)₃(AsPh₃)₂, 90623-36-2; KReO₄, 10466-65-6; Re(¹⁸O)I(MeC≡CMe)₂, 98778-37-1; Ag-(O₂CMe), 563-63-3; [Re¹⁸O(MeC≡CMe)₂py]SbF₆, 98778-39-3; Re(O)I(MeC≡CMe)(MeC≡CPh), 90641-16-0; H₂¹⁸O, 14314-42-2.

Supplementary Material Available: Tables V, VI, and VII giving anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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