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Articles

Rhenium Oxo Complexes of a Chelating Diyne Ligand. Synthesis and Study of the Kinetics of Protonation

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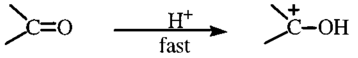
A series of oxo complexes, Re(O)X(diyne) (X = I, Me, Et), have been prepared from 2,7-nonadiyne and Re(O)I_3(PPh_3)$_2$. Addition of B(C_6F_5)$_3$ to Re(O)I(2,7-nonadiyne) (**5**) results in coordination of the oxo ligand to the boron. The protonation of Re(O)(X)(2-butyne)$_2$ and Re(O)(X)(2,7-nonadiyne)$_2$ with a variety of acids has been examined. With **5** and HBF_4/Et_2O, the ultimate product was [Re(CH_3CN)$_3$(I)(2,7-nonadiyne)]$^{2+}$ (**7**). The conversion of **5** to **7** changes the conformation of the diyne ligand from a "chair" to a "boat" and shifts its propargylic protons considerably downfield in the ^1H NMR. The kinetics of the protonation of Re(O)I(2,7-nonadiyne) (**5**) by CF_3SO_3H in CH_3CN have been monitored by visible spectroscopy, in a stopped-flow apparatus, and by low temperature ^1H NMR. Two second-order rate constants, presumably successive protonations, were observed in the stopped-flow, $k_1 = 11.9$ M^{-1} s^{-1} and $k_2 = 3.8$ M^{-1} s^{-1}. Low temperature ^1H NMR spectroscopy indicated that the resulting solution contained a mixture of two doubly protonated intermediates X and Y, each of which slowly formed the product **7** via an acid-independent process.

Introduction

It is generally accepted that "Most proton transfer reactions between electronegative atoms can be characterized as very rapid processes in which equilibrium is established essentially instantaneously."[1] Ketones exchange protons rapidly with their conjugate acids (protonated ketones) on the NMR time scale,[2] and protonation of oxo ligands on transition metals is often assumed to be fast also.[3−5]

However, oxo ligands differ in many regards from the oxygens in organic carbonyl compounds. Reported rate constants for the protonation (with strong acids) and quenching of *excited states* are smaller for oxo complexes (about 10^9 M^{-1} s^{-1} for [ReO_2py_4]$^{+*}$)[6] than for ketones or aldehydes (4×10^{10} M^{-1} s^{-1} for the protonation of methyl 2-naphthyl ketone).[7]



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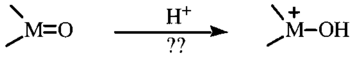

(2)

Depending on the metal and ligands involved, a metal and a terminal oxo ligand can form a single, double, or triple bond;[8] for example, the bond between the Re and the oxo ligand in the series Re(O)X(RC≡CR)$_2$ is believed to have triple bond character.[9] Theoretical study suggests that the bond between the metal (Mo, W, Re) and the oxo ligand in some metathesis catalysts is a triple bond.[10]

Protonation of such an oxo ligand should—and does—change the bonding significantly. The Re−O stretching frequency

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[⊥] Department of Physics, City University of New York (CUNY), 365 5th Ave, New York, NY 10016.

(1) Stewart, R. *The Proton*: *Applications to Organic Chemistry*; Academic: New York, 1985; Chapter 4, p 146.

(2) Bagno, A.; Lucchini, V.; Scorrano, G. *J. Phys. Chem.* **1991**, *95*, 345−352.

(3) A popular test for the intermediacy of oxo complexes in the reactions of metalloproteins has been attempted exchange with external $H_2{}^{18}O$, a reaction that according to Baldwin[4] "apparently requires ... a proton source sufficiently acidic to protonate the oxygen." Valentine[5] has questioned "the assumption that high-valent metal oxo species invariably exchange with labeled water at high rates".

(4) (a) Baldwin, J. E.; Adlington, R. M.; Crouch, N. P.; Pereira, I. A. C.; Aplin, R. T.; Robinson, C. *J. Chem. Soc.*, *Chem. Commun.* **1993**, 105−108. (b) Baldwin, J. E.; Adlington, R. M.; Crouch, N. P.; Pereira, I. A. C. *Tetrahedron* **1993**, *49*, 7499−7518, and references therein. (c) The extent of label incorporation in several products suggested that Fe−OH exchanged much faster with $H_2{}^{18}O$ than did Fe=O.

(5) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* 1993, *115*, 1772−78.

(6) Liu, W.; Thorp, H. H. *Adv. Transition Met. Coord. Chem.* **1996**, *1*, 187−207.

(7) Watkins, A. R. *Z. Phys. Chem.* **1971**, *75*, 327−331.

(8) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*, Wiley-Interscience: New York, 1988.

(9) (a) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc*. **1985**, *107*, 7454. (b) Mayer, J. M.; Tulip, T. H.; Calabrese, J. C.; Valencia, E. *J. Am. Chem. Soc.* **1987**, *109*, 157.

(10) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc*. **1982**, *104*, 448.

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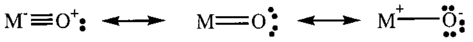


decreases considerably, from 975 to 628 cm^{-1},[11] when Re(O)(Et)(MeC≡CMe)$_2$ (**1**) is protonated, implying a considerable decrease in the Re−O bond order.

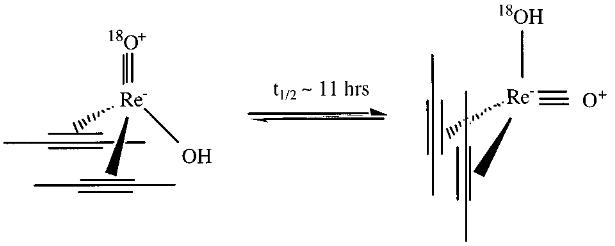
If we compare the X-ray structure of $K_3Na[Mo(O)_2(CN)_4 \cdot 6H_2O]$[12] with those of $[Cr(en)_3][Mo(O)(OH)(CN_4)] \cdot H_2O$[13] and $[Pt(en)_2][Mo(O)(OH_2)(CN)_4] \cdot 2H_2O$,[13] the decrease in Mo−O bond order is shown by an increase in the Mo−O distance, from 1.834(9) Å in the dioxo complex[12] to 2.077(7) Å (Mo−OH) and 2.271(4) Å (Mo−OH_2).[13] Protonation of *trans*-$MoO_2(dppe)_2$ increases the distance between the Mo and the protonated oxygen from 1.818(1) to 1.872(2) Å.[14] Protonation of a dianionic molybdenum oxo complex increases the distance between the Mo and the protonated oxygen from 1.801(4) to 1.872(2) Å.[15] Protonation of $[ReO_2L_4]^+$ to $[Re(O)(OH)L_4]^{2+}$ increases the distance between the Re and the protonated oxygen from an average of 1.76 to 1.896(13) Å.[16] Protonation increases the Zr−O distance from 1.804(4) Å in $(\eta^5\text{-}C_5Me_5)_2Zr(O)(NC_5H_5)$[17] to 1.976(2)−2.028(3) Å in $(\eta^5\text{-}C_5Me_5)_2Zr(OH)_2 \cdot (H_2O)$[17] and 1.950(2) Å in $(\eta^5\text{-}C_5Me_5)_2Zr(OH)Cl$.[18]

It is not yet clear whether this structural rearrangement creates a significant barrier to the protonation of oxo ligands. The rate constant measured by ^{17}O NMR line broadening for $[Re^V(O)_2(CN)_4]^{3-}$ in acidic media, k_{-2a} (eq 3) = 6(1) × 10^{10} M^{-1} s^{-1}, shows that proton transfer to this trianion is quite fast.[19]

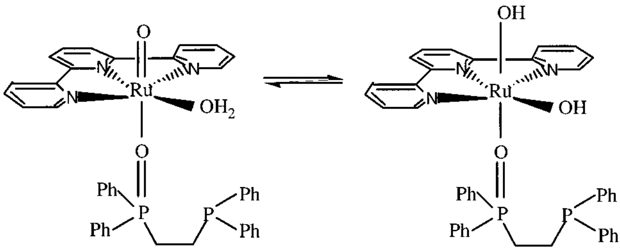
$$[Re(O)(OH)(CN)_4]^{2-} \underset{k_{-2a}}{\overset{k_{2a}}{\rightleftharpoons}} [Re(O)_2(CN)_4]^{3-} + H^+ \quad (3)$$

There is qualitative evidence that proton transfer to terminal oxo ligands can be slow. Erikson and Mayer[20] reported that tautomerization between the oxo and hydroxo ligands in Re(O)(OH)(2-butyne)$_2$ is extremely slow (half-life about 11 h) (eq 4), although a catalytic amount of triflic acid dramatically accelerates it. They suggest that the proton transfers to a rhenium−oxygen π bonding orbital and not to an oxygen lone pair.

Dovletoglou and Meyer[21] reported that the isomerization of *trans*-$[Ru^{II}(tpy)(O)(O{=}P(PPh_2)CH_2CH_2PPh_2)(H_2O)]^{2+}$ (tpy = 2, 2′: 6′, 2″-terpyridine) is achieved by proton transfer from an aqua to an oxo ligand (eq 5). In 1.75 M CH_3CN in H_2O at 20 °C, the rate constant was measured as 6.2(1) × 10^{-2} s^{-1}.



(4)



(5)

In an effort to find a substrate suitable for the direct measurement of the rate of protonation of an oxo ligand, we examined $[Re(O)_2(cyclam)]^+$ [22,23] and Re(O)(Et)(MeC≡CMe)$_2$ (**1**). In preliminary experiments, the protonation of $[Re(O)_2(cyclam)]^+$ proved to be too fast to observe even by stopped-flow methods. Determination of the rate of protonation of **1** from NMR line widths was complicated by the rotation of the coordinated 2-butynes; we were also unable to isolate [Re(OH)(Et)(MeC≡CMe)$_2$]$^+$, although the reversible protonation of the oxo ligand was reported in 1989 by Mayer and co-workers.[11]

It seemed likely that replacement of the pair of 2-butyne ligands in Re(O)(Et)(MeC≡CMe)$_2$ by a chelating diyne[24] would not only stabilize the complex but would simplify exchange rate measurements. We have therefore prepared analogous rhenium oxo complexes from 2,7-nonadiyne,[25] and have examined the rates at which they can be protonated.

Results

Protonation of Re(O)(Et)(MeC≡CMe)$_2$ (1). When **1** was treated with 0.5 equiv of CF_3SO_3H in CD_2Cl_2, low temperature ^1H NMR spectroscopy showed that half of **1** was converted to [Re(OH)(Et)(MeC≡CMe)$_2$]$^+$ (**1H**$^+$) (identified from its published[11] spectrum). At low temperature (−15 °C), the ^1H NMR peaks of the two complexes (**1** + **1H**$^+$) were separate and not much broadened (<1 Hz), indicating that proton exchange between them was slow on the NMR time scale. A 2D EXSY NMR spectrum[26] at −15 °C showed that all four methyl peaks (two apiece from the 2-butyne ligands of each complex) were exchanging with each other, implying that both proton transfer and rotation of the 2-butyne ligands were occurring at similar rates. From the line widths in the ^1H NMR spectrum, a rate constant (k_{obs}) may be extracted for each complex, k_{obs} < 3.14 s^{-1}, and thus the rate constant for proton exchange (k_{ex}) between Re(O)(Et)(MeC≡CMe)$_2$ (**1**) and [Re(OH)(Et)(MeC≡CMe)$_2$]$^+$ may be calculated to be k_{ex} < 120 M^{-1} s^{-1} at −15 °C.

Protonation of Re(O)Me(MeC≡CMe)$_2$ (2). In view of the evidence that β-hydrogen elimination is a significant decom-

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(12) Day, V. W.; Hoard, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 3374.

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(15) Shirin, Z.; Hammes, B. S.; Young, V. G., Jr.; Borovik, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 1836−1837.

(16) Structures have been reported for the dioxo complexes with L = 1-MeImidazole, 2-MeImH, and 5-MeImH, and for the protonated dication with L = 1,2-Me_2ImH. Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1996**, *35*, 7836.

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(21) Dovletoglou, A.; Meyer, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 215.

(22) (Cyclam = 1,4,8,11-tetraazacyclotetradecane) Tsang, B. W.; Reibenspies, J.; Martell, A. E. *Inorg. Chem.* **1993**, *32*, 988.

(23) Blake, A. J.; Greig, J. A.; Schroder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2645.

(24) The low yield preparation of Re(O)I(2,8-decadiyne) had been reported by Mayer and co-workers in ref 9a.

(25) The authors owe to Prof. A. K. Rappé the prediction that three methylene units would permit a diyne to adopt, without strain, the geometry seen in the X-ray structure of Re(O)(I)(MeC≡CMe)$_2$.[9a]

(26) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: New York, 1987.

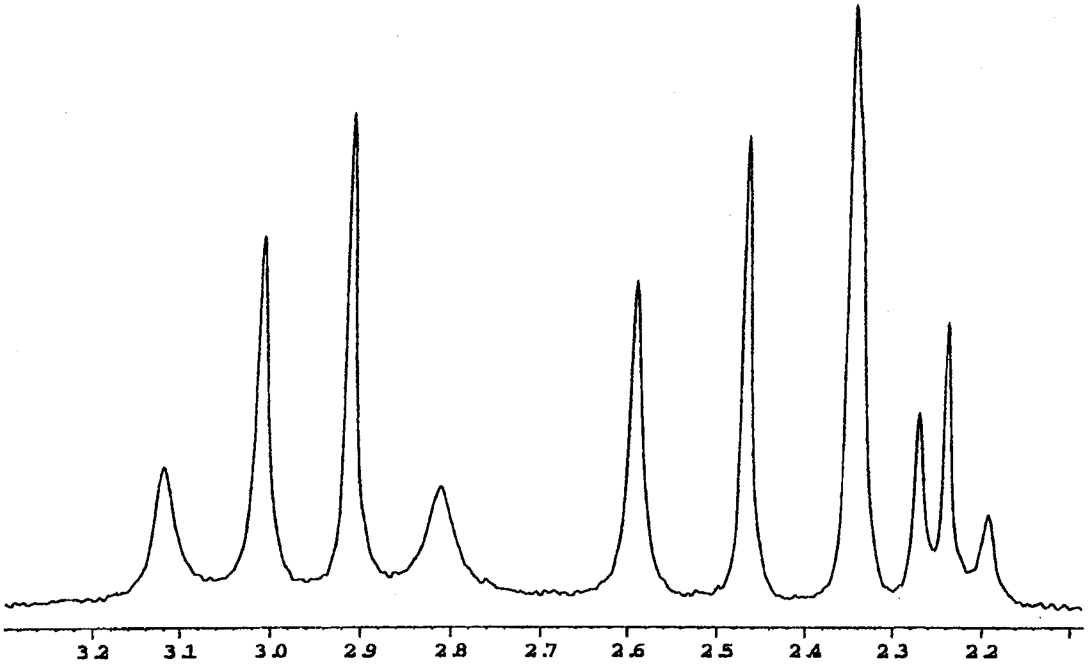


Figure 1. ^{1}H NMR spectrum of the protonation of Re(O)Me(MeC≡MeC)$_2$ (**2**) (0.062 M) with $MeC_6H_4SO_3H$ (0.09 M) in CD_2Cl_2 at −15 °C. **2**: δ 2.24, 2.47, 2.91. **3**: δ 2.27, 2.59, 3.01. **4**: δ 2.19, 2.81, 3.11. The Peak at δ 2.34 is due to $MeC_6H_4SO_3H$.

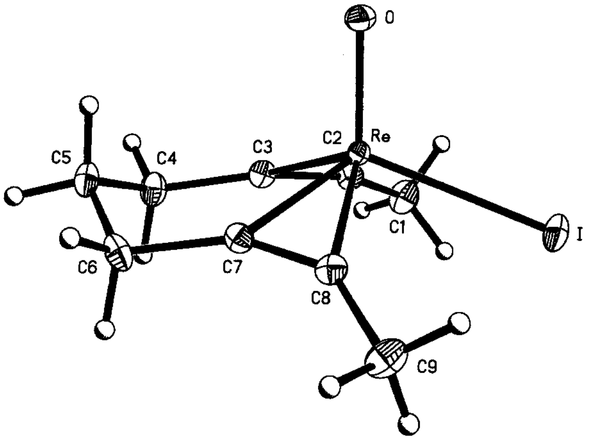


Figure 2. Thermal ellipsoid drawing of **5**. Selected bond distances (Å) and angles (deg): Re−I, 2.6809(5); Re−O, 1.692(4) Re−C(2), 2.064(6); Re−C(8), 2.062(6); Re−C(3), 2.019(6); Re−C(7), 2.016(6); C(2)−C(3), 1.293(9); C(7)−C(8), 1.279(9); I−Re−O 110.64(16).

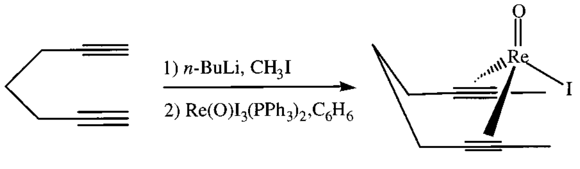
position pathway for protonated Re oxo complexes (Mayer and co-workers[11] observed the formation of propene after Re(O)(isopropyl)(MeC≡CMe)$_2$ was treated with CF_3SO_3H), we examined the protonation of **2**, which is the methyl analogue of **1**; a ^{1}H NMR spectrum attributed to [Re(OH)Me(MeC≡CMe)$_2$]$^+$ had been reported at −20 °C in $CDCl_3$.[11] With CF_3SO_3H or CF_3COOH in CD_2Cl_2 or $CDCl_3$, we obtained broad, complex ^{1}H NMR spectra, although the addition of pyridine cleanly reversed the reaction.

Three sets of broad ^{1}H NMR peaks were observed (Figure 1) when a solution of **2** in CD_3CN was treated with $MeC_6H_4SO_3H$; the reaction again could be reversed by the addition of pyridine. One set of peaks belonged to unreacted **2**; the other sets, which we will call **3** and **4**, grew with the addition of acid, and they were the only peaks present with 2.5 equiv acid. Upon addition of 7.5 equiv acid, all of the rhenium was converted to **4**. It appears that **3** and **4** result from the *sequential* protonation of **2** (eq 6). If **3** is indeed [Re(OH)Me(MeC≡CMe)$_2$]$^+$, it is tempting to assign **4** as the aqua dication, [Re(OH$_2$)Me(MeC≡CMe)$_2$]$^{2+}$, even though the pK_a difference between such structures for **3** and **4** (which we estimate as < 1.2) would be far smaller than that expected from Pauling's rules[27] for two protons on the same oxygen.

$$2 \xrightarrow{H^+} 3 \xrightarrow{H^+} 4 \tag{6}$$

The separate signals in Figure 1 demonstrated that proton exchange among **2**, **3**, and **4** was slow on the NMR time scale. Again, a 2D EXSY NMR spectrum at −15 °C showed that the methyl peaks of all three complexes were exchanging with each other, implying that both proton transfer and rotation of the 2-butyne ligands were occurring at similar rates. The NMR spectra also indicated that a plane of symmetry was present in all three complexes.

Preparation of Re(O)I(2,7-nonadiyne) (5) and Re(O)(Me)(2,7-nonadiyne) (6). The new chelating dialkyne ligand 2,7-nonadiyne was prepared from 1,6-heptadiyne, and its Re(O)I complex **5** was synthesized by modifying the procedure for the preparation of Re(O)(I)(MeC≡CMe)$_2$ (eq 7).[9a] Complex **5**, a crystalline, air- and water-stable solid, is soluble in organic solvents. Its ^{1}H NMR spectrum contains five different C-*H* resonances, indicating that it also has a plane of symmetry. The assignments were confirmed by an HMQC spectrum.



5

(7)

The X-ray structure of **5** (Figure 2) is very like that of Re(O)(I)(MeC≡CMe)$_2$.[9a] The coordination sphere of the rhenium is approximately tetrahedral, with the midpoints of the two triple bonds occupying two vertices. An approximate mirror

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[27] Shriver, D. F.; Atkins, P.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; Freeman: New York, 1994.

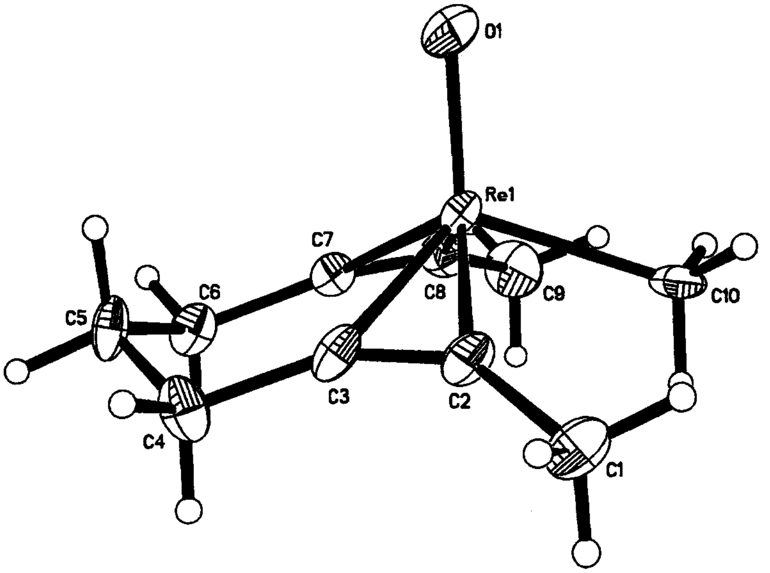
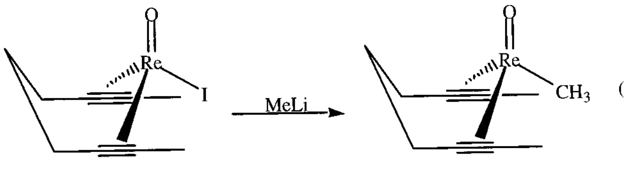


Figure 3. Thermal ellipsoid drawing of **6**. Selected bond distances (Å) and angles (deg): Re−O, 1.716(8); Re−C(10), 2.210(10); Re−C(2), 2.066(9); Re−C(8), 2.062(10); Re−C(3), 2.032(11); Re−C(7), 2.008(10); C(2)−C(3), 1.290(14); C(7)−C(8),1.287(14); O−Re−C(10) 111.6(4).

plane contains the Re, the oxo and iodide ligands, and the central methylene of the dialkyne ligand; the Re−C(2) distance, 2.064(6) Å, is the same as the Re−C(8) distance, 2.062(6) Å, while the Re−C(3) distance, 2.019(6) Å, is the same as the Re−C(7) distance, 2.016(6) Å. The Re−O bond length in **5**, 1.692(4) Å, is the same as the Re−O bond length in Re(O)(I)(MeC≡CMe)$_2$, 1.697(3) Å.[9a] The C≡C bond distances (1.293(9), 1.279(9) Å) in **5** are close to those reported for Re(O)(I)(MeC≡CMe)$_2$ (1.288(7), 1.278(7) Å). The central methylene (C5) of **5** points toward the Re═O bond in a "chair" structure.

Templeton and co-workers[28] have suggested that there is a correlation between the ^{13}C chemical shifts of acetylene ligands and the number of the electrons that they donate to the metal center. On this basis, as already noted by Mayer and co-workers for earlier oxo Re(III) diyne complexes,[9a] the ^{13}C chemical shifts, δ 138.5 and 143.4, of the coordinated carbons of the dialkyne ligand of **5** suggest that it acts as a six-electron donor to the rhenium.

The methyl derivative **6** of the chelating diyne ligand was synthesized by addition of MeLi to **5** (eq 8).

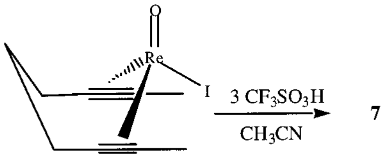


5 **6** (8)

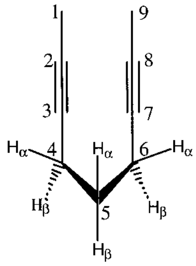
The X-ray structure of **6** (Figure 3) was similar to that of **5**.

Protonation of 5 and 6. When a solution of **5** was treated with excess CF$_3$SO$_3$H in acetonitrile, we obtained a product, **7** (eq 9), that was stable at room temperature under N$_2$ up to eight h.

As with **1-6**, the ^{1}H NMR spectrum of **7** shows that it has a plane of symmetry in solution; the spectrum contains five chemical shifts (H on C(1,9), Hα on C(4,6), Hβ on C(4,6), Hα on C5, and Hβ on C5) with the relative intensities 6:2:2:1:1 (the stereochemical descriptors α and β are, of course, arbitrary).



5 (9)



The chemical shifts (δ 6.00, 5.05) of the propargylic protons in **7** (i.e., those on C4 and C6) are far downfield of those in **5** (δ 3.50, 2.59), whereas the chemical shift of one of the C5 protons (α) of **7** is far upfield (δ 0.64) of that in **5** (δ 2.05, 2.46); the final proton (β on C5) resides at 2.31 ppm. However, both of the C−H coupling constants within the central methylene in **7** are high enough (119 Hz) to argue against coordination of a C−H bond to the Re. The geminal $^2J_{\mathrm{HH}}$ between the α and β protons on C5 is 12.4 Hz, while it is 15.4 Hz between the α and β protons on C4 and C6. The solution IR spectrum of **7** contains no Re−O stretch, suggesting that the terminal oxo ligand has been lost.

The reaction of **5** with CF$_3$SO$_3$H is a *protonation* reaction, as evidenced by the complete and clean reversal of the reaction upon the addition of a slight excess of pyridine to a solution of **7**. Titration experiments showed that 3 equiv of CF$_3$SO$_3$H were needed to convert **5** to **7** completely. As confirmed by a ^{1}H NMR spectrum, complex **5** was reformed when a solution of **7** was treated with excess H$_2$^{18}O. A solution IR spectrum showed one Re−^{18}O stretching band at 916 cm^{-1}, approximately the expected frequency (it is difficult to calculate the expected ν(Re−^{18}O) because there are two strong peaks (974 and 956 cm^{-1}) in the Re−O stretching region of the IR spectrum of unlabeled **5**, perhaps as a result of Fermi resonance with an overtone or combination band). As **7** does not contain a terminal

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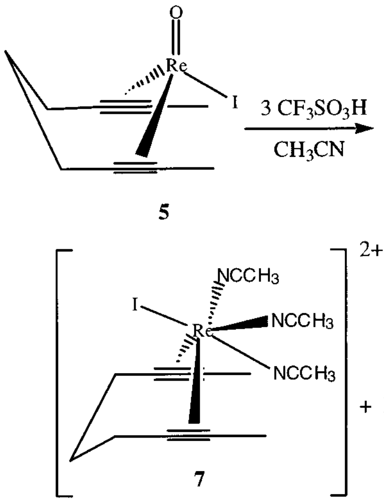
[28] (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288. (b) Templeton, J. L.; Ward, B. C.; Chen, G., J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248.

oxo ligand, and the addition of water to **7** regenerates **5**, the protonation of **5** (eq 9) is likely to involve two consecutive protonations on the terminal oxo ligand and the replacement of an aqua ligand by acetonitrile (having acetonitrile as a solvent proved to be essential). We can thus rewrite eq 9 in balanced form.



5

7

$$+\ H_3O^+\ +\ 3CF_3SO_3^- \qquad (9b)$$

Both HBF$_4$·(CH$_3$)$_2$O and (C$_6$Me$_3$H$_4$)B(C$_6$F$_5$)$_4$[29] converted **5** into **7**. There was no observable reaction between **5** and *p*-TsOH (pK_a = 8.7 in CH$_3$CN[30]) in CH$_3$CN.

There are four possible protonation sites for **5**: the terminal oxo, the coordinated triple bonds, the iodide, and the metal itself. In view of the ^{1}H chemical shifts of the diyne ligand in **7**, we considered the possibility that the acid might have catalyzed the tautomerization of that ligand to **7′** or **7″** (eq 10).[31] However, treatment of **5** with CF$_3$SO$_3$D gave **7** with no deuterium incorporation, so the diyne is not the site of protonation. Furthermore, the absence of an obvious Re−H resonance in the ^{1}H NMR suggested that the metal is not one of the sites of protonation. The possibility of protonation at the iodide ligand will be discussed later.

5 7' 7'' (10)

Crystals of **7** suitable for X-ray diffraction were obtained from the reaction of **5** with excess HBF$_4$·(CH$_3$)$_2$O in CH$_2$Cl$_2$/CH$_3$CN overnight at −35 °C. The resulting structure (Figure 4), with a crystallographic mirror plane, confirms that **7** contains no oxygen ligand. Three CH$_3$CN molecules are linearly coordinated to the Re, with the CH$_3$CN trans to iodide having a Re−N distance of 2.085(11) Å, and the two cis CH$_3$CN ligands have Re−N distances of 2.185(8) Å, which is typical of such coordination.[32] As the ^{13}C chemical shifts (δ 175.5 and 188.3) of its chelating dialkyne ligand imply[28] that that ligand is still a six-electron donor, **7** is an 18-electron complex.

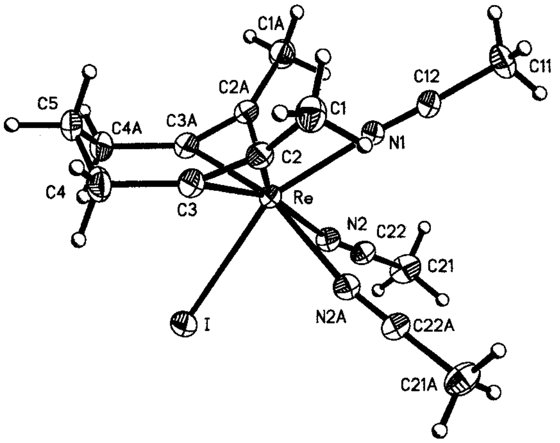
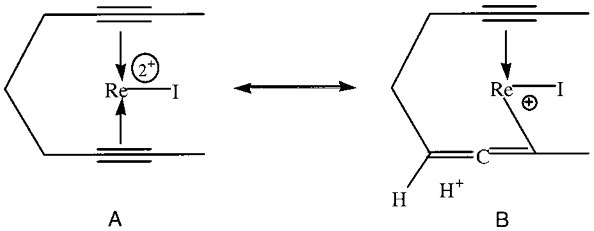


Figure 4. Thermal ellipsoid drawing of the dication in **7**; the two [BF$_4$]$^-$ counterions have been omitted for clarity. Selected bond distances (Å) and angles (deg): Re−N(1), 2.085(11); Re−N(2), 2.185(8); Re−I, 2.7540(11); Re−C(2), 2.023(10); Re−C(3), 2.030(10); C(2)−C(3),1.277(13).

The structure of **7** gives insight into the unusual ^{1}H chemical shifts observed. The conversion of **5** to **7** changes the conformation of the diyne ligand from a "chair" to a "boat" (Figure 5), and brings one proton on the central methylene (C5) directly under the coordinated triple bonds; presumably that proton is the one shifted upfield (to δ 0.64) (the propargylic protons ^{1}H chemical shifts are harder to explain on the basis of the structure). The conversion of **5** to **7** also brings the iodide ligand close to the diyne ligand, which may contribute to the downfield shifts observed for the propargylic protons of **7**.

To assess the importance of the iodide/diyne interaction, we examined the protonation of the methyl analogue of **5**, Re(O)-(Me)(2,7-nonadiyne) (**6**), with triflic acid. No significant intermediates were observed; the addition of acid cleanly converted the ^{1}H resonances of **6** to those of a product, **8**, that appeared (similar relative intensities, multiplet patterns, and coupling constants) to have a structure analogous to **7**. However, the propargyl protons are not as far downfield in **8** as in **7**: δ 4.04 and 5.21 for **8** versus δ 5.05 and 6.00 for **7**. Interaction with the iodide ligand probably contributes to the downfield ^{1}H NMR shift of the propargyl protons in **7**, but this interaction cannot provide the entire explanation. Perhaps the double positive charge leads to some contribution from the hyperconjugative resonance structure B.



The Reaction of 5 with Other Electrophiles. In an effort to model the addition of the first proton to **5**, we treated **5** with a solution of B(C$_6$F$_5$)$_3$.[33] The ^{1}H NMR spectrum of Re(O)(I)-(2,7-nonadiyne)·B(C$_6$F$_5$)$_3$ (**9**) indicated a plane of symmetry in solution. The X-ray structure of **9** (Figure 6) is similar to that of **5**, with B(C$_6$F$_5$)$_3$ attached to the terminal oxo ligand along

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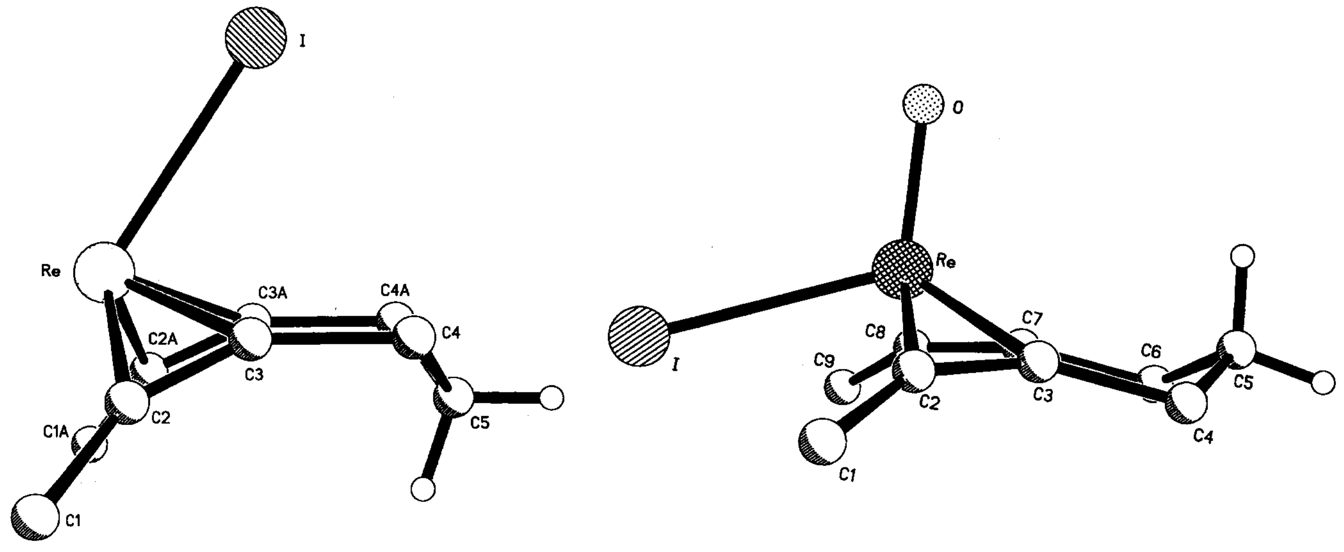
(29) Reed, C. A.; Fackler, N. L. P.; Kim, K.-C.; Stasko, D.; Evans, D. R.; Boyd, P. D.; Rickard, C. E. F. *J. Am. Chem. Soc.* **1999**, *121*, 6314.

(30) Jasinski, T.; El-Harakany, A. A.; Halaka, F. G.; Sadek, H. *Croat. Chem. Acta* **1978**, *51*, 1.

(31) (a) Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500−12511. (b) Casey, C. P.; Brady, J. T. *Organometallics* **1998**, *17*, 4620−4629.

(32) (a) Bernstein, S. N.; Dunbar, K. R.; *Angew Chem., Int. Ed. Engl.* **1992**, *31*, 1360. (b) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1. (c) Wadepohl, H.; Arnold, U.; Pritzkow, H.; Calhorda, M. J.; Veiros, L. F. *J. Organomet. Chem.* **1999**, *587*, 233.

(33) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345−354.

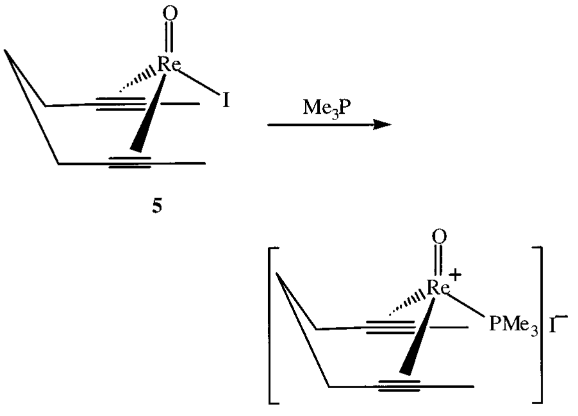


7 **5**

Figure 5. Ball and stick representations of **5** and the dication from **7**, showing the structural differences between the compounds. The three acetonitriles of **7**, counterions, and some of the hydrogen atoms have been omitted for clarity.

the Re−O axis with an Re−O−B angle of 169.1(3)°. As expected, the Re−O distance has increased, to 1.742(3) Å from 1.692(4) Å in **5**. Upon coordination of the boron to the oxygen, some small but significant conformational changes occur in **9** relative to **5**. The Re−I distance decreases from 2.6809(5) to 2.6388(5) Å, presumably due to an increase in the π donation of the iodide to the rhenium center. The distances from the metal to the C=C (C(2,3) and C(7,8)) also decrease by approximately 0.02 Å due to a decrease in the electron density at the metal upon coordination of the boron to the oxygen.

The Reaction of 5 with P(CH$_3$)$_3$. Oxo Re(III) diyne complexes sometimes transfer their oxygen atom to tertiary phosphines.[34] However, a different reaction occurred when **5** was treated with PMe$_3$; the iodide ligand was displaced, forming [Re(O)(PMe$_3$)(2,7-nonadiyne)]I (**10**) (eq 11). A conductivity measurement showed negligible dissociation of I$^-$ from **5**.



(11)

The X-ray structure of **10** (Figure 7) is again close to that of **5**, with an approximate mirror plane. A summary of the structural features of the five complexes, characterized by X-ray crystallography, is presented in Tables 1 and 2.

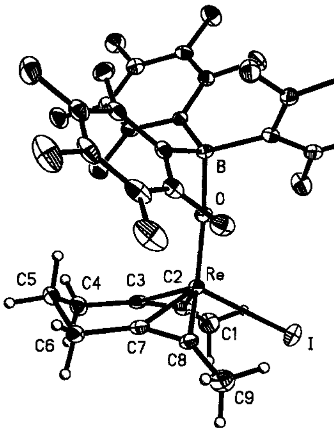


Figure 6. Thermal ellipsoid drawing of **9**. Selected bond distances (Å) and angles (deg): Re−I, 2.6388(5); Re−O, 1.742(3); Re−C(2), 2.038(5); Re−C(8), 2.043(5); Re−C(3), 2.010(5); Re−C(7), 1.993(5); Re−O−B 169.1(3).

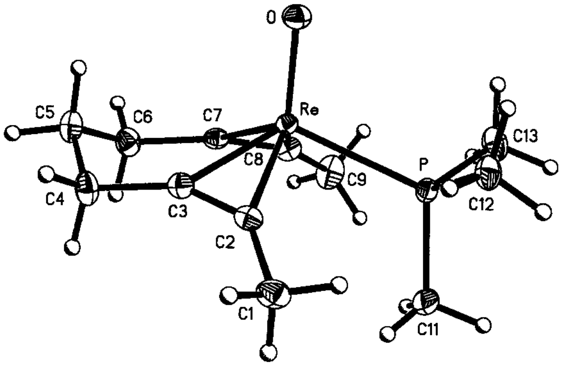


Figure 7. Thermal ellipsoid drawing of the cation in **10**. The iodide counterion has been omitted for clarity. Selected bond distances (Å) and angles (deg): Re−O, 1.702(2); Re−P, 2.4148(10); Re−C(2), 2.078(4); Re−C(8), 2.074(4); Re−C(3), 2.016(4); Re−C(7), 2.019(4); C(2)−C(3), 1.285(5); C(7)−C(8), 1.278(5); O−Re−P 108.41(10).

Kinetics of the Protonation of 5 by CF$_3$SO$_3$H in CH$_3$CN. UV-vis Observation in a Stopped-flow Apparatus. The visible spectra of **5** and **7** in CH$_3$CN are shown in Figure 8. The extinction coefficient of **5** at 439 nm is 184 cm^{-1} M^{-1}, and that of **7** at 450 nm is 1514 cm^{-1} M^{-1}. Solutions of **5** and CF$_3$SO$_3$H in CH$_3$CN were cooled to −40 °C and mixed in a

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[34] Tahmassebi, S. K.; Mayer, J. M. *Organometallics* **1995**, *14*, 1039.

Table 1. Selected Bond Distances (Å) and Angles (Deg) for Complexes **5**, **6**, **7**, **9**, and **10**

	5	**6**	**7**[a]	**9**	**10**
Re−O	1.692(4)	1.716(8)	–	1.742(3)	1.702(2)
Re−X	2.6809(5)[b]	2.210(10)[c]	2.7540(11)[b]	2.6388(5)[b]	2.4148(10)[d]
Re−C(2)	2.064(6)	2.066(9)	2.030(10)	2.038(5)	2.078(4)
Re−C(3)	2.019(6)	2.032(11)	2.023(10)	2.010(5)	2.016(4)
Re−C(7)	2.016(6)	2.008(10)	2.023(10)	1.993(5)	2.019(4)
Re−C(8)	2.062(6)	2.062(10)	2.030(10)	2.043(5)	2.074(4)
O−Re−X	111.64(16)[b]	116.6(4)[c]	–	112.29(11)[b]	108.41(10)[d]
C(2)−C(3)	1.293(9)	1.290(14)	1.277(13)	1.284(7)	1.285(5)
C(7)−C(8)	1.279(9)	1.287(14)	1.277(13)	1.275(7)	1.278(5)

[a] Due to a crystallographic mirror plane the labeling for **7** is C(2), C(3), C(2a), and C(3a). [b] X = Iodide. [c] X = Methyl. [d] X = $P(CH_3)_3$.

Table 2. Crystallographic Data for Complexes **5**, **6**, **7**, **9**, and **10**

	5	**6**	**7**	**9**	**10**
empirical formula	$C_9H_{12}IORe$	$C_{10}H_{15}ORe$	$C_{15}H_{21}B_2F_8IN_3Re$	$C_{33}H_{18}BF_{15}IORe$	$C_{12}H_{21}IOPRe$
fw	449.29	337.42	730.07	1039.38	525.36
T, K	228(2)	163(2)	228(2)	228(2)	228(2)
crystal system	monoclinic	tetragonal	tetragonal	monoclinic	monoclinic
Space Group	$P2_1/n$	$P42_1c$	$I4/m$	$P2_1/n$	$P2_1/n$
a (Å)	10.0184(15)	16.56890(10)	23.889(2)	10.6281(6)	8.9812(16)
b (Å)	7.1551(10)	16.56890(10)	23.889(2)	10.6867(6)	18.417(3)
c (Å)	15.790(2)	7.45200(10)	9.7525(11)	29.8237(15)	9.7160(17)
α, deg	90	90	90	90	90
β, deg	108.326(2)	90	90	95.7890(10)	94.068(3)
γ, deg	90	90	90	90	90
V (Å^3), Z	1074.5(3), 4	2045.79(3), 8	5565.6(9), 8	3370.1(3), 4	1603.0(5), 4
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
reflections collected	7028	9010	18516	23579	11017
independent reflections	2381	1460	3438	7805	3638
data/restraints/parameters	2381/0/112	1460/0/110	3438/0/158	7805/0/472	3638/0/151
μ(Mo Kα), mm^{-1}	14.137	11.832	5.534	4.633	9.588
GOF on F^2	1.109	1.133	1.073	1.008	1.083
$R1$, w$R2$ [$I>2\sigma(I)$]	0.0293, 0.0772	0.0351, 0.0645	0.0588, 0.1696	0.0379, 0.0614	0.0219, 0.0415
$R1$, w$R2$ (all data)	0.0304, 0.0780	0.0511, 0.0681	0.0810, 0.1932	0.0798, 0.0684	0.0301, 0.0428

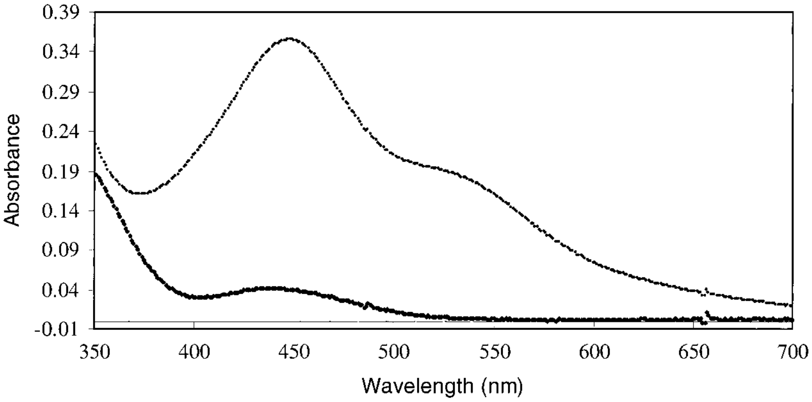

Figure 8. Visible Spectra of **5** (◆) and **7** (●) in CH_3CN.

rapid-scan stopped-flow apparatus. Early spectra (e.g., at 128 ms after mixing) matched that of **5**, but a broad peak centered at 422 nm appeared soon after mixing (Figure 9) and continued to increase for the first 8 s of reaction. Eventually, at longer times, the spectrum matched that of **7**.

Clearly two rate constants were involved, both depended linearly upon [acid], implying that both steps were *protonations*; the second-order rate constants were $k_1 = 11.9$ M^{-1} s^{-1} and $k_2 = 3.8$ M^{-1} s^{-1}. Global fits gave calculated spectra (Figure 10) for the starting material, the intermediate, and the product in an A→B→C sequence. The spectrum calculated for A matched the spectrum of **5**, the spectrum calculated for C was close to the spectrum of **7**, and the spectrum calculated for B, which had a peak at 422 nm, agreed with that observed for the intermediate. (Reversal of the order of the rate constants[35] gave unreasonably large extinction coefficients for B.) As the oxo ligand is eventually lost, it is reasonable to propose that both protonations occur at oxygen; an indeterminate number of solvent molecules may become coordinated as protonation occurs. The third equivalent of CF_3SO_3H is presumably needed to protonate the water that has been formed.

^{1}H NMR Observation. Three complexes with similar, but different, spectra were observed by ^{1}H NMR when a solution of **5** was treated with an excess of CF_3SO_3H in CD_3CN at 233 K. One was the final product, **7**, the other two, designated as X (the more abundant of the two) and Y, changed into **7** when the temperature was raised to room temperature, and were thus

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[35] Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995.

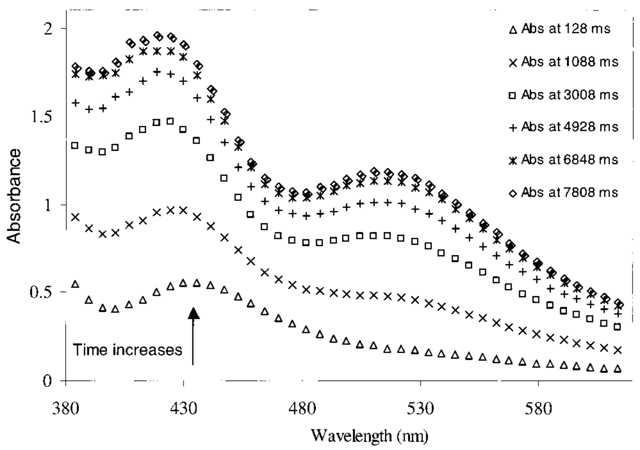
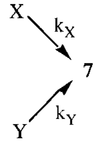


Figure 9. Stopped-flow traces of the reaction of **5** (0.0032 M) with CF_3SO_3H (0.08 M) in CH_3CN at −40 °C.

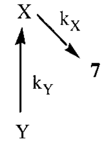
intermediates in the conversion of **5** into **7**. The ^1H NMR spectra of X and Y, which were very similar to that of **7**, showed chelating diyne ligands, as in complexes **5** and **7**, again with a mirror plane.

The observed rate constant (k_X) for the conversion of X to **7** proved to be 3×10^{-3} s^{-1} at 243 K, while the observed rate constant (k_Y) for the conversion of Y to **7** was 8×10^{-5} s^{-1} at 243 K. It is possible that X and Y convert to **7** independently (Scheme 1), or that k_Y is the rate constant for Y→X (Scheme 2). Kinetic simulations confirm that, as $k_X > k_Y$, both schemes can fit the observed data.

Scheme I



Scheme II

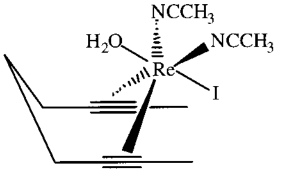


Repeated experiments in CD_3CN at 233 K with different $[CF_3SO_3H]$ showed that the rate constants k_X and k_Y, and the resulting ratio X:Y, are independent of $[CF_3SO_3H]$. Thus *neither reaction is a protonation*. The two acid-independent processes k_X and k_Y observed in the ^1H NMR experiments can hardly be the same as the two acid-dependent processes $k_1[H^+]$ and $k_2[H^+]$ observed in the stopped-flow experiments. In addition to the change in order in acid, their time scales are quite different. From k_1 and k_2, the half-lives of **5** and the stopped-flow intermediate B, under the conditions of the ^1H NMR experiments, can be calculated as 0.2 and 0.6 s, respectively, whereas the half-life observed for X in those experiments was about 200 s, and that of Y was even longer.

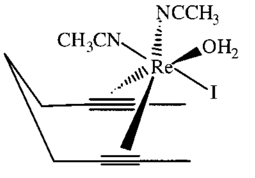
UV-Vis Observation of the Protonation of 5 by CF_3SO_3H Under the Same Conditions as the ^1H NMR Experiments. To compare the transformations observed by stopped-flow with those observed by NMR, we obtained low-temperature UV-vis spectra of a solution of **5** with CF_3SO_3H prepared in the same manner as in the NMR experiments. The spectrum taken just after mixing (Figure 11) was similar to the spectrum of C in the stopped-flow experiments. The spectrum did not change after the reaction had been followed for 1 h at −40 °C, 1 h at −15 °C, and 1 h at 25 °C.

Discussion

Identity of the Intermediates X and Y. Because two acid-dependent steps have preceded their formation, it seems likely that X and Y still carry the two added protons[36] but are structural isomers. Like B, X and Y may also contain one or more coordinated molecules of the solvent, CH_3CN. The symmetry of X and Y and the absence of D^+ incorporation into the diyne of **7** rule out protonation of that ligand. Thus, the two protons must be attached to the oxo ligand, the iodide ligand, or the Re, and the fact that the oxo ligand is eventually lost makes it the most likely protonation site. The absence of any obvious hydride resonance in the ^1H NMR of Y argues against protonation at Re. If both protons are attached to the oxo ligand in X, Y may be a coordination isomer of X (a possibility suggested by a referee) or a tautomer of X with its iodide protonated.[37] If X and Y are coordination isomers and have the structures shown, the reaction occurs according to Scheme 1. Alternatively, if Y contains protonated iodide, tautomerization of Y to X (Scheme 2) is necessary before water can be lost and **7** formed. The fact that the protonation of **6** gives **8** without significant observable intermediates has implications for the structures of X and Y; loss of H_2O from $[Re(OH_2)(CH_3CN)_?Me(2,7\text{-nonadiyne})]^{2+}$ may be faster than from $[Re(OH_2)(CH_3CN)_?I(2,7\text{-nonadiyne})]^{2+}$.

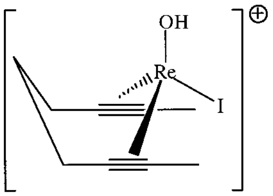


X



Y

Proposed Overall Mechanism for the Conversion of 5 to 7. The overall proposal is shown as Scheme 3 below, where X and Y are the isomers just discussed, and the stopped flow intermediate B is surely the hydroxo complex. The first step, $k_1[H^+]$, is thus the initial protonation of the oxo ligand; the second step, $k_2[H^+]$,[38] is the second protonation, giving X and Y. If X and Y have the structures shown, k_X is the rate constant for the dissociation of water from X and k_Y is the rate constant for the dissociation of water from Y. If Y contains a protonated iodide, k_X is the rate constant for the dissociation of water from X and k_Y is the rate constant for the tautomerization of Y to X. The magnitude of the difference between k_X and k_Y offers some support for the second possibility.



B

A mixture of X, Y, and **7** must be C in the stopped-flow experiments (the scanned spectra showed no significant changes

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[36] If water has left before the formation of X and Y, there is no plausible reason their transformation into **7** should be slow.

[37] Examples of HX complexes: (a) Aullón, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *J. Chem. Soc.*; *Chem. Commun.* **1998**, 653. (b) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428. (c) Peris, E.; Lee, J. C., Jr.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2573. (d) Murphy, V. J.; Rabinovich, D.; Hascall, T.; Klooster, W. T.; Koetzle, T. F.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 4372.

[38] The sum of the first-order rate constant for the formation of X and the first-order rate constant for the formation of Y is thus equal to $k_2[H^+]$.

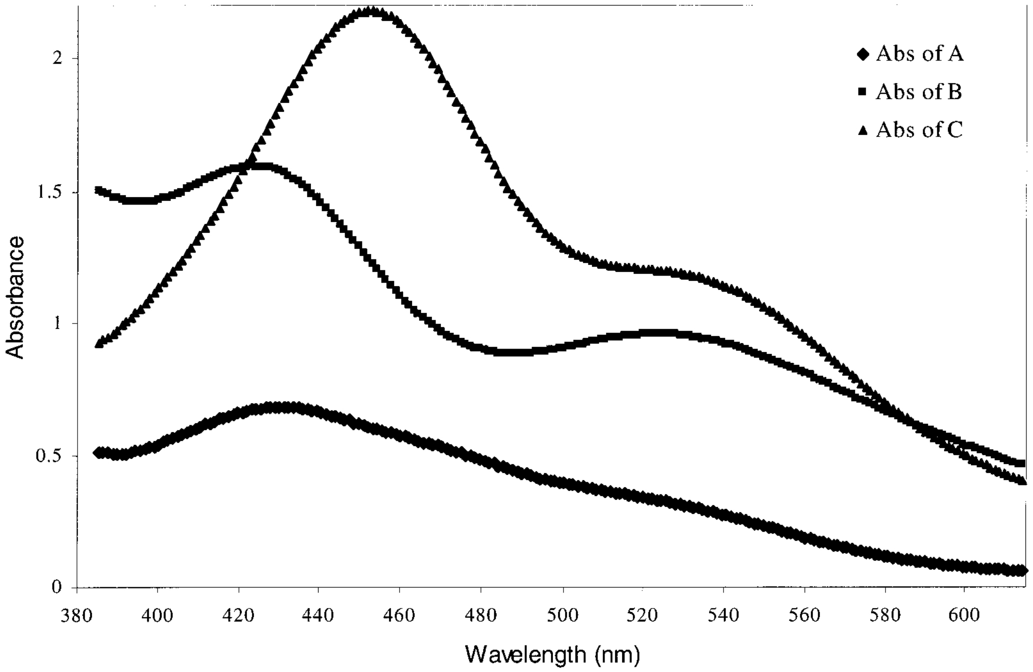


Figure 10. Calculated spectra of the starting material (A), the intermediate (B), and the product (C) that best fits the observed stopped-flow traces for the reaction of **5** (0.003 M) with CF_3SO_3H (0.09 M).

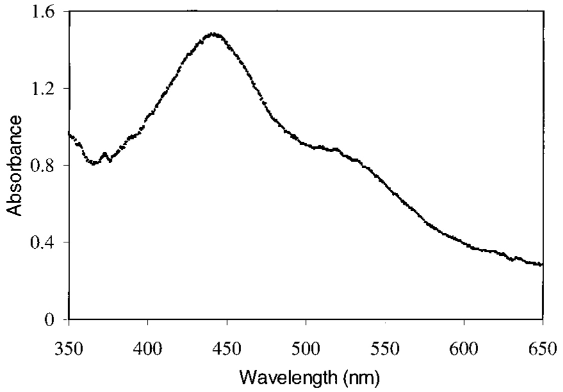
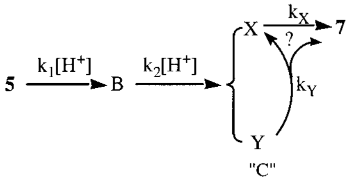


Figure 11. UV-vis spectrum of **5** (0.0012 M) with CF_3SO_3H (0.01 M) in CD_3CN at −40 °C just after mixing.

Scheme III



after the formation of C), so X, Y, and **7** must have similar visible spectra. This hypothesis is confirmed by the low-temperature visible spectrum of an NMR reaction mixture (the spectrum did not change while X and Y were converting to **7**). Such similar spectra are plausible if X and Y are coordination isomers and have the structures shown.

We have been unable to quantify the thermodynamic driving force involved in the $k_1[H^+]$ step, because B is only an intermediate. However, the second-order rate constant for the protonation of **5** by TfOH ($k_1 = 11.9$ M^{-1} s^{-1} at −40 °C in CH_3CN) is remarkably slow for a proton transfer between two oxygens, surely much slower than the rate constants for the protonation of $[Re^V(O)_2(CN)_4]^{3-}$ and $[Re(O)_2(cyclam)]^+$ (see Introduction). With the Re(V) trianion[19] one factor is charge, which is likely to be sufficiently localized on the oxo ligands to minimize the need for reorganization during protonation. It is also possible that the electronic and structural reorganization when a single oxo ligand is protonated exceeds that when a proton is added to one of a trans pair of oxo ligands (both of which can serve as π donors into the same metal orbital).

Experimental Section

Materials. Manipulations were performed under an atmosphere of N_2 purified by passage through BTS catalyst (BASF) and molecular sieves (3 Å), using either standard Schlenk techniques or an inert atmosphere box. $Re(O)(I)_3(PPh_3)_2$,[39] $[Re(O)_2(cyclam)](ClO_4)$,[22] Re(O)(I)(MeC≡CMe)$_2$,[11] Re(O)(Et)(MeC≡CMe)$_2$,[11] Re(O)(Me)(MeC≡CMe)$_2$,[11] $Et_3SiB(C_6F_5)_4$,[40] and $(C_6Me_3H_4)B(C_6F_5)_4$[29] were prepared according to published procedures. C_6H_6, C_6D_6, and THF were distilled from Na/Ph$_2$CO; hexanes and pentane were distilled from Na/Ph$_2$CO in the presence of tetraglyme; toluene was distilled from Na. CH_2Cl_2, CD_2Cl_2, $CDCl_3$, and CD_3CN were distilled from P_4O_{10}. CH_3CN was stirred with anhydrous $CuSO_4$, filtered, and distilled first from P_4O_{10} and then CaH_2;[41] however, if CH_3CN (DriSolv, water, 50 ppm max) purchased from EM Science was used as received, no difference was found. CF_3SO_3H(D) was purified by three freeze/pump/thaw cycles at −196 °C and transferred under vacuum into flame-dried bulbs (it discolored upon lengthy storage). $B(C_6F_5)_3$ (Boulder Scientific) was purified via recrystallization from hexane or by sublimation at 60 °C. *p*-TsOH was dried by heating it at 50 °C under vacuum overnight or by azeotropic distillation with benzene.

Instruments and Techniques. HMQC, COSY, NOESY, and EXSY experiments were performed on 400 or 500 MHz Bruker spectrometers; HMQC results are reported as δ $^{13}C/\delta$ ^1H. Residual ^1H shifts and solvent ^{13}C shifts were used as internal standards. ^{19}F shifts are relative to $CFCl_3$.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN. Conductivity measurements were performed on a Yellow Springs Instrument Co. model 31 bridge with a YSI model 3402 cell, $K = 0.1$/cm. Mass spectra were obtained on a VG 7070 EQ-HF or a VG Autospec.

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Chromatography with less than 1 g material was done on a Chromatotron (Harrison Research Inc.) with silica gel (Merck, TLC grade 7749) as the adsorbent. Otherwise, flash chromatography was done on silica gel 60 (Merck, 230−400 mesh).

The rapid scan stopped-flow system was a Hi-Tech Canterbury SF-41, with temperature control ±0.1 °C, fitted to an On-Line Instrument Systems RSM-1000 rapid scanning device capable of scanning 1000 spectra/s. OLIS system version 6.2.4 was used to control the apparatus and to collect and analyze the data.

Low-Temperature UV-Vis Spectra. The measuring beam was provided by a xenon flash lamp (IBH Model 500XeF). The flashes had a typical t_{hwfm} of about 460 ns and power of 50 mJ. The use of this flash lamp as the light source enabled the investigation of kinetics with much faster time scale (∼μs) than a normal lamp and shutter apparatus. The temperature of the sample was controlled by a closed-cycle helium cryostat system (APD Cryogenics Inc., Model CSW202A) with a programmable temperature controller. The temperature resolution was 0.1 K and controllability was ± 0.4 K. During sample change, helium gas was blown through the sample chamber to maintain the temperature and to prevent frost from being formed inside the chamber or on the quartz window where the probe light was transmitted. The transmitted light was sent through an optical fiber to a spectrometer (Instrument SA HR460). A liquid nitrogen cooled CCD detector (Princeton Instruments, LN/CCD-1024-EHRB/1) operating at −80 °C was used to collect the spectrum. The CCD detector contained 1024 by 256 pixels; each pixel converted the light it observed to a charge, which was subsequently read. The 256 pixels in the *Y* dimension were binned together in this measurement. The detector and the flash lamp were controlled by a delay generator (Stanford research DG535) for synchronization.

Kinetic Simulations and the Optimization of Rate Constants. MacKinetics[42] was used to calculate [X] and [Y] as a function of time for Schemes 1 and 2.

Protonation of Re(O)(Et)(MeC≡CMe)$_2$ (1). (a) An NMR tube was charged with **1** (0.0212 g, 0.062 mmol), and CD_2Cl_2 and CF_3SO_3H (3 μL, 0.034 mmol) were transferred into the NMR tube on a high-vacuum line. ^{1}H NMR spectra were recorded from −70 to 0 °C. (b) An NMR tube was charged with **1** (0.0101 g, 0.03 mmol) and [Re(OH)(Et)(MeC≡CMe)$_2$](CF_3SO_3)[11] (0.0144 g, 0.029 mmol) in CD_2Cl_2. ^{1}H NMR spectra were recorded from −15 to 20 °C.

Reversible Protonation of Re(O)Me(MeC≡CMe)$_2$ (2). A solution of **2** (0.012 g, 0.037 mmol) in $CDCl_3$ (0.6 mL) was treated with a solution of CF_3SO_3H (0.37 M) in $CDCl_3$ (0.1 mL) at −20 °C. The ^{1}H NMR spectrum showed peaks at δ 6.92 (smaller), 6.73 (larger), 3.15 (smaller), 3.09 (larger), 2.96 (smaller), 2.91 (larger), 2.74 (larger), and 2.69 (smaller), suggesting at least two protonation products. The solution was then treated with a solution of pyridine (0.19 M) in $CDCl_3$ (0.2 mL), and a ^{1}H NMR spectrum showed only **2** again. Similar results were obtained with CF_3COOH and $MeC_6H_4SO_3H$, in $CDCl_3$ and CD_3CN, respectively.

^{1}H NMR Studies of the Protonation of 2. An NMR tube was charged with Re(O)Me(MeC≡CMe)$_2$ (**2**) (0.012 g, 0.037 mmol) and $MeC_6H_4SO_3H$ (0.0112 g, 0.060 mmol); CD_3CN (0.6 mL) was then added. The ^{1}H NMR spectrum in Figure 3 (new peaks at δ 3.12, 3.01, 2.81, and 2.59, suggesting two protonation products) was obtained at −20 °C.

2,7-Nonadiyne. 1,6-Heptadiyne (4.61 g, 0.05 mol) and THF (40 mL) were added via syringe to a 500 mL three-neck round-bottom flask sealed with a septum, an additional funnel, and a nitrogen/vacuum inlet. At −40 °C, *n*-BuLi (1.6 M, 68.75 mL) was added dropwise. At −30 °C, MeI (15.6 g, 0.11 mol) in THF (15 mL) was added dropwise, more THF (25 mL) was added, and the mixture stirred overnight. After addition of the reaction mixture to a 1 L separatory funnel with an ice/water mixture (150 mL) and extraction with hexane (3 × 50 mL), the combined hexane layers were washed with water (3 × 50 mL) and dried by $MgSO_4$ overnight. Yield: 3.9 g (65%). ^{1}H NMR ($CDCl_3$): δ 1.61 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, qn, $J = 7.0$ Hz, 2 H), 1.75 ($\mathrm{C}H_3$, t, $J = 2.5$ Hz, 6 H), 2.21 ($\mathrm{C}H_2\mathrm{CH_2}$, tq, 4 H). ^{13}C NMR ($CDCl_3$): δ 3.67 ($C\mathrm{H_3}$), 18.1 ($C\mathrm{H_2}$), 28.7 ($C\mathrm{H_2}$), 76.1, 78.6.

Re(O)(I)(2,7-nonadiyne) (5). Re(O)I$_3$(PPh$_3$)$_2$ (4.0 g, 3.61 mmol) in benzene (40 mL) was treated with 2,7-nonadiyne (1.3 g, 10.8 mmol), and the mixture was stirred overnight then filtered through silica gel. The silica gel was washed with benzene (3 × 20 mL), and the filtrate was evaporated. The resulting dark red solution was loaded on the chromatotron and eluted with ethyl acetate/hexane (10:90). The yellow portion was collected, and the solvent was evaporated. After drying overnight under vacuum, the yield was 0.43 g (27%). The product can be further purified by recrystallization from ether/pentane or by sublimation at 60 °C under dynamic vacuum. Crystals suitable for X-ray diffraction were obtained via diffusion of hexane into THF solution. The conductivity of a solution of **5** (0.0171 g, 0.038 mmol) in CH_3CN (10 mL) was measured with the conductivity bridge; the readout was only 0.45 cm^2 ohm^{-1} mol^{-1}. ^{1}H NMR (CD_3CN): δ 2.05 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 2.46 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 2.59 ($\mathrm{C}H_2\mathrm{CH_2}$, m, 2 H), 3.08 ($\mathrm{C}H_3$, t, 6H), 3.50 ($\mathrm{C}H_2\mathrm{CH_2}$, m, 2 H). ^{13}C NMR ($CD_3CN$): δ 16.57 ($C\mathrm{H_3}$), 22.80 ($C\mathrm{H_2}$), 31.49 ($C\mathrm{H_2}$), 138.5, 143.4. IR (Nujol, cm^{-1}): 2925, 1456, 1360, 1313, 1240, 1140, 1055, 974, 956, 864, 768, 633. Its mass spectrum showed a parent peak at *m*/*e* 450 (^{187}Re) with the appropriate isotopic distribution.

Re(O)Me(2,7-nonadiyne) (6). A solution of **5** (0.5 g, 1.11 mmol) in benzene (40 mL) was cooled to 10 °C and treated with $CH_3Li \cdot LiBr$ (1.5 M, 0.9 mL). The solution was stirred overnight then filtered through silica gel. After the silica gel was washed with benzene (3 × 20 mL), the concentrated solution was loaded on the chromatotron and eluted ($R_f = 0.32$) with ethyl acetate/hexane (15:85). After evaporation, the resulting solid **6** was dried overnight under vacuum. Yield: 0.15 g (40%). For further purification it was sublimed at 10^{-3} Torr under dynamic vacuum at 45 °C. Crystals suitable for X-ray diffraction were obtained via diffusion of hexane into ether solution. ^{1}H NMR (CD_3CN): δ 2.04 ($\mathrm{ReC}H_3$, s, 3 H), 2.09 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 2.38 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 2.42 ($\mathrm{C}H_2\mathrm{CH_2}$, m, 2 H), 2.50 ($\mathrm{C}H_3$, t, 6 H), 3.38 ($\mathrm{C}H_2\mathrm{CH_2}$, m, 2 H). ^{13}C NMR ($CD_3CN$): δ 5.6 ($\mathrm{Re}C\mathrm{H_3}$), 9.30 ($C\mathrm{H_3}$), 22.90 ($C\mathrm{H_2}$), 32.4 ($C\mathrm{H_2}$), 141.6, 148.5. Anal. Calcd for $C_{10}H_{15}ORe$ (337.4): C, 35.6; H, 4.48; N, 0.00. Found: C, 35.1; H, 4.21; N, −0.08. Its mass spectrum showed a parent peak at *m*/*e* 339 (^{187}Re) with the appropriate isotopic distribution.

[Re(I)(CH$_3$CN)$_3$(2,7-nonadiyne)][BF$_4$]$_2$ (7). A solution of **5** (0.012 g, 0.027 mmol) in CH_2Cl_2 (0.4 mL) and CH_3CN (0.2 mL) was treated with $HBF_4 \cdot (CH_3)_2O$ (24 mmol, 30 μL). Toluene (ca. 1 mL) was added and the solution was cooled to −35 °C overnight, yielding red needles. Yield: 0.0071 g (36%). ^{1}H NMR (CD_3CN, −15 °C): δ 0.64 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 2.31 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 3.39 ($\mathrm{C}H_3$, s, 6 H), 5.05 ($\mathrm{C}H_2\mathrm{CH_2C}H_2$, m, 2 H), 6.00 ($\mathrm{C}H_2\mathrm{CH_2C}H_2$, m, 2 H). ^{13}C NMR ($CD_3CN$, −15 °C): δ 17.0 ($C\mathrm{H_3}$, $J_{\mathrm{CH}} = 134$ Hz), 20.9 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$, $J_{\mathrm{CH}} = 119$ Hz), 35.9 ($C\mathrm{H_2CH_2}C\mathrm{H_2}$, $J_{\mathrm{CH}} = 136$ Hz), 175.5, 188.3. ^{19}F (CD_3CN, −15 °C): δ −150. IR (KBr, cm^{-1}): 2937, 2297, 1809, 1052, 522.

[Re(Me)(CH$_3$CN)$_3$(2,7-nonadiyne)][OTf]$_2$ (8). A solution of **6** (0.012 g, 0.035 mmol) in CD_3CN (0.75 mL) was frozen and treated with triflic acid (35 mmol). The tube was immediately placed in a precooled (240 K) NMR probe, and the reaction followed by ^{1}H NMR. Immediately all of the starting material **6** had reacted, and only **8** remained. Although its instability precluded isolation, ^{1}H NMR (CD_3CN) showed a dication analogous to **7**. ^{1}H NMR (CD_3CN): δ 0.54 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 2.68 ($\mathrm{CH_2C}H_2\mathrm{CH_2}$, m, 1 H), 2.87 ($\mathrm{C}H_3$, s, 6 H), 2.91 ($\mathrm{Re{-}C}H_3$, s, 3H), 4.04 ($\mathrm{C}H_2\mathrm{CH_2C}H_2$, m, 2 H), 5.21 ($\mathrm{C}H_2\mathrm{CH_2C}H_2$, m, 2 H).

Re(O)(I)(2,7-nonadiyne)·B(C$_6$F$_5$)$_3$ (9). A solution of **5** (0.057 g, 0.13 mmol) in C_6D_6 (0.2 mL) was treated with a solution of $B(C_6F_5)_3$ (0.072 g, 0.14 mmol) in C_6D_6 (0.3 mL), forming a dark red solution. Hexane (1.5 mL) was added and the solution was cooled to −20 °C overnight, giving large red blocks. Yield: 93 mg (74%). ^{1}H NMR (CD_2Cl_2): δ 2.21 (m, 1 H), 2.55 (m, 1 H), 2.69 (m, 2 H), 3.40 (s, 6 H) 3.68 (m, 2 H). ^{13}C NMR (CD_2Cl_2): δ 18.1, 24.3, 29.3, 154.8, 162.2. Anal. Calcd for $C_{27}H_{12}BF_{15}IORe$ (961.3): C, 33.74; H, 1.26; N, 0.00. Found: C, 33.87; H, 0.64; N, 0.00.

[Re(O)(P(CH$_3$)$_3$)(2,7-nonadiyne)]I (10). A solution of **5** (0.052 g, 0.12 mmol) in $CD_3C_6D_5$ (0.4 mL) and CD_2Cl_2 (0.2 mL) was treated with two drops of PMe_3, causing an immediate change from orange to

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pale yellow. A pale yellow powder precipitate formed, which was washed with C_6H_6 (1.0 mL) and dried under vacuum. Yield: 20 mg (32%). Crystals suitable for X-ray diffraction were obtained via cooling of the supernatant (−20 °C). ^{1}H NMR (CD_2Cl_2, −45 °C): δ 2.19 (m, 1 H), 2.39 (d, 9 H), 2.59 (m, 1 H), 2.82 (s, 3 H), 2.87 (m, 2 H), 3.60 (m, 2 H). ^{13}C NMR (CD_2Cl_2, −45 °C): δ 14.1, 16.2(d), 22.1, 29.7, 130.8, 148.3. Anal. Calcd for $C_{12}H_{21}IOPRe$ (525.4): C, 27.43; H, 4.03; N, 0.00. Found: C, 27.65; H, 4.09; N, −0.04.

Re(^{18}O)(I)(2,7-nonadiyne)(5-^{18}O). A solution of **7** (0.0086 g, 0.012 mmol) in CD_3CN (0.6 mL) was treated with $H_2$18O (98% enriched, 5 μL, 0.28 mmol). ^{1}H NMR (CD_3CN): the same as unlabeled **5**. IR (CD_3CN, cm^{-1}): 916 (s) [ν(Re^{18}O)].

General Procedures for the Protonation of 5 Under Various Conditions. The protonation of **5** was examined using a variety of acids, $CF_3SO_3H(D)$, *p*-$CH_3C_6H_4SO_3H$, $HBF_4{\cdot}(CH_3)_2O$, and $(C_6Me_3H_4)B(C_6F_5)_4$, and a variety of solvents, CD_3CN, CD_2Cl_2, CD_2Cl_2/CD_3CN, and CD_2Cl_2/THF-d_8. In a typical reaction, a 5 mm NMR tube was charged with **5** (0.008 g, 0.018 mmol) in CD_3CN (0.6 mL) and treated with CF_3SO_3H (8 μL, 0.09 mmol). A ^{1}H NMR spectrum at 233 K showed not only **7** but two intermediates, X and Y, in an initial ratio of 3:1:0.8 (**7**:X:Y). ^{1}H NMR of X: δ 5.98 (CH_2CH$_2$CH_2, m, 2H), 4.84 (CH_2CH$_2$CH_2, m, 2H), 3.21 (CH$_3$, s, 6H), 2.29 (CH$_2$CH_2CH$_2$, m, 1 H), 0.62 (CH$_2$CH_2CH$_2$, m, 1 H). ^{1}H NMR of Y: 5.58 (CH_2CH$_2$CH_2, m, 2H), 3.94 (CH_2CH$_2$CH_2, m, 2H), 3.61 (CH$_3$, s, 6H), 2.63 (CH$_2$CH_2CH$_2$, m, 1H), 0.60), 0.62 (CH$_2$CH_2CH$_2$, m, 1H). Protonation with CF_3SO_3D, in a manner analogous to that used with CF_3SO_3H resulted in the same product (i.e., no deuterium incorporation into the product (**7**) was observed).

Reversible Protonation of 5. A 5 mm NMR tube was charged with **5** (0.008 g, 0.018 mmol) in CD_3CN (0.6 mL) and was treated with CF_3SO_3H (8 μL, 0.09 mmol); ^{1}H NMR showed the spectrum of **7**. A solution of pyridine (8.1 μL, 0.1 mmol) was then added, and ^{1}H NMR showed the spectrum of **5** again.

Titration of 5 with CF_3SO_3H. A 5 mm NMR tube was charged with **5** (0.012 g, 0.027 mmol) in CD_3CN (0.6 mL) and was treated with CF_3SO_3H (1.2 μL, 0.014 mmol) at −15 °C; a ^{1}H NMR spectrum at that temperature showed a mixture of **5** and **7**. CF_3SO_3H (1.2 μL, 0.014 mmol) was added to the solution seven more times at the same temperature, and the ^{1}H NMR spectrum was recorded after each addition. The spectra ceased changing after three equivalents of acid had been added.

General Procedure for the Rapid-Scan Stopped-Flow Study of the Kinetics of Protonation of 5 by CF_3SO_3H. The solution in one reservoir in the stopped-flow apparatus contained **5** (0.0355 g, 0.079 mmol) in CH_3CN (25 mL), the other contained CF_3SO_3H (0.145 mL, 1.64 mmol) in CH_3CN (10 mL). Rapid-scan spectra, like those in Figure 9, were observed when these solutions were mixed at −40 °C. The data were best fit as two consecutive first-order reactions, A→B→C. The pseudo-first-order rate constants, and thus the second-order rate constants k_1 and k_2, were obtained from a single wavelength fit at 422 nm; the same results were obtained at 517 nm. The spectra calculated for A, B, and C from a global fit are shown in Figure 10.

General Procedure for the NMR Study of the Kinetics of Protonation of 5 by CF_3SO_3H. A 5 mm NMR tube was charged with **5** (0.008 g, 0.018 mmol) in CD_3CN (0.6 mL) and was treated with CF_3SO_3H (8 μL, 0.09 mmol) at 233 K. ^{1}H NMR spectra were recorded every minute for two hours at 233 K, using the Bruker macro program "kineticzg". The integrals of individual species were plotted against time. The rate constants for the decay of X and Y were obtained by nonlinear least-squares fitting.

Low-Temperature UV-Vis Studies of the Protonation of 5 with CF_3SO_3H in CD_3CN. A shortened NMR tube was charged with **5** (0.0006 g, 0.0013 mmol) in CD_3CN (1.1 mL), frozen at −78 °C, and treated with CF_3SO_3H (1 μL, 0.011 mmol). The solid was melted quickly, mixed with the acid, and placed in the precooled probe. The UV-vis spectra were recorded at −40 °C.

General Procedure for X-ray Structure Determinations. Data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques, and refined by full matrix least-squares procedures using SHELXTL.[43] Hydrogen atoms on carbon were included in calculated positions.

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Supporting Information Available: Complete details of the crystallographic study (PDF and CIF) are available free of charge via the Internet at http://pubs.acs.org.

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