5342 *Organometallics* **1997,** *16,* 5342−5353

Hydroxide-, Amide-, and Sulfhydrylrhenium(I) Tris(alkyne) Complexes. Rearrangements to Rhenium(III) Bis(alkyne) Oxo and Nitrido Compounds[1]

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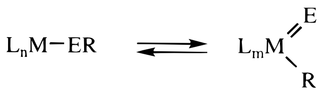
The rhenium hydroxide and amide complexes $Re(OH)(EtC\equiv CEt)_3$ (**3**) and $Re(NH_2)(EtC\equiv CEt)_3$ (**10**) have been prepared by reaction of the related aquo and ammine complexes with KOH and $NaNH_2$, respectively. The sulfhydryl compound $Re(SH)(EtC\equiv CEt)_3$ (**13**) is formed from $Re(OSO_2CF_3)(EtC\equiv CEt)_3$ and NaSH. Compound **3** spontaneously rearranges to the oxo−hydride complex $Re(O)H(EtC\equiv CEt)_2$ (**4**), and $EtC\equiv CEt$ in a first-order process ($k = (5.6 \pm 1.2) \times 10^{-6}\ s^{-1}$ at 294 K). There is a primary isotope effect ($k_{OH}/k_{OD} = 5 \pm 1$), and the rearrangement is unaffected by the presence of 1 M 3-hexyne. These data rule out a mechanism involving initial ligand loss followed by rearrangement. Instead, hydrogen migration from oxygen to rhenium occurs in the coordinatively saturated tris(alkyne) species **3**, either synchronously with or prior to the loss of alkyne. Rearrangement is catalyzed by potassium alkoxides, apparently via deprotonation of **3** and concomitant loss of $EtC\equiv CEt$ to the oxo anion $(EtC\equiv CEt)_2ReO^-$ (**5**), which is reprotonated by ROH. Surprisingly, isolated samples of **5** are not catalysts, apparently due to its slow proton transfer reactions. The amide complex **10** rearranges to the unusual μ-nitrido complex $(EtC\equiv CEt)_3Re{-}N\equiv Re(H)(EtC\equiv CEt)_2$ (**11**), which has been characterized spectroscopically. This reaction is similar to that of the hydroxide **3** in that a hydrogen moves from N or O to the rhenium center, with oxidation of the metal. The mechanism of rearrangement is quite different, however, as added alkynes strongly inhibit conversion of **10** to **11**, indicating initial 3-hexyne dissociation from **10**. No rearrangement has been observed for the sulfhydryl compound **13**, which decomposes at 150 °C.

Introduction

[1,2]- or α-migration of a hydrogen or a hydrocarbyl group between a metal center and a ligand is a fundamental organometallic transformation (eq 1).[2] It inter-



$$L_nM{-}ER \rightleftharpoons L_mM(=E)(R) \qquad (1)$$

converts compounds of quite different structure and reactivity. It is facile and common when E is a Fischer carbene ligand[2] and has been reported in some Schrock alkylidene and alkylidyne complexes.[2,3] There are numerous related [1,2]-migrations in organic chemistry, including Wagner−Meerwein shifts, rearrangements of carbenes, and Wittig, Wolff, and Stevens rearrangements.[4] But [1,2]-migrations involving a metal and an electronegative group E, such as an oxo, a sulfido, or an imido group, are rare despite the large number of known alkoxide, oxo−alkyl, and related compounds.[5−9] In such transformations, the metal undergoes a two-electron change in the formal oxidation state and the group R formally converts from R^+ to R^-.

The most famous invocation of this rearrangement is the redox step in the Sharpless mechanism for oxidation of alkenes by OsO_4 and related oxidants, the transformation of an oxametallacyclobutane to a diolate ligand.[6] There are only two clear examples of an alkoxide/oxo−alkyl interconversion. A $Cp*_2TaOCH_3$ intermediate

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) Low-Valent Rhenium−Oxo Compounds. 16. Part 15: ref 29.

(2) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals,* 2nd ed.; Wiley-Interscience: New York, 1994.

(3) To our knowledge, the only example of alkyl migration to a Schrock carbene is apparently in the rearrangement of $Cp_2Ta(CHMe)CH_3$ to $Cp_2Ta(CH_2{=}CHMe)H$, see: Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43−51.

(4) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992. Harwood, L. M. *Polar Rearrangements*; Oxford: New York, 1992.

(5) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119−12133.

(6) (a) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (b) Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263. (c) Nelson, D. W.; Gypser, A.; Ho, P. T.; Kolb, H. C.; Kondo, T.; Kwong, H.-L.; McGrath, D. V.; Rubin, A. E.; Norrby, P.-O.; Gable, K. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 1840−1858. (d) Norrby, P.-O.; Becker, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1996**, *118*, 35. (e) Gable, K. P.; Juliette, J. J. J. *J. Am. Chem. Soc.* **1996**, *118*, 2625−2633. (f) Jørgensen, K. A.; Schiøtt, B. *Chem. Rev.* **1990**, *90*, 1483−1506.

(7) (a) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347. (b) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (c) Nelson, J. E.; Parkin, G.; Bercaw, J. E. *Organometallics* **1992**, *11*, 2181.

(8) For instance, see references in ref 6 and (a) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759. (b) Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1802−1810. (c) Matsunaga, P. T.; Mauropoulos, J. C.; Hillhouse, G. L. *Organometallics* **1995**, *14*, 175. (d) Gómez, M.; Gómez-Sal, P.; Jiménez, G.; Martín, A.; Royo, P.; Sánchez-Nieves, J. *Organometallics* **1996**, *15*, 3579−3587.

(9) Tahmassebi, S. K.; Conry, R. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 7553.

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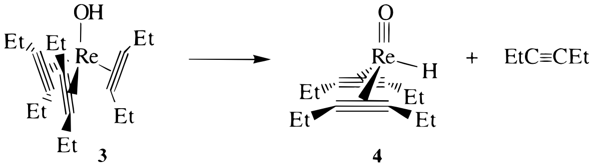
rearranges to the isomeric oxo−methyl complex, $Cp^*_2Ta(O)CH_3$ ($Cp^* = \eta^5$-C_5Me_5).[7] Labeling studies provide strong evidence for the related hydroxide-to-oxo hydride rearrangement, and analogous chemistry with nitrogen and sulfur ligands was described. The cationic rhenium dioxo−phenyl complex $TpReO_2Ph^+OTf^-$ has been found to rearrange below room temperature to a phenoxide complex.[5] Related interconversions have been discussed in a number of systems,[8] but without direct observation of key species. To give two examples, treatment of a chromium *tert*-butylimido complex with diphenylzinc gives $PhNH^tBu$ upon hydrolysis, suggesting an aryl-to-nitrogen migration,[8a] and sulfur insertion into a vanadium−iminoacyl linkage has been suggested to occur via eq 1, with E = S.[8b]

We have communicated the synthesis of the rhenium(I) tris(3-hexyne) hydroxide complex **3** and its rearrangement to the rhenium(III) bis(3-hexyne) oxo−hydride compound (**4**; eq 2).[9] This contrasts with the lack of interconversion of isolated methoxide and oxo−methyl complexes in this system (eq 3).[10] Here we



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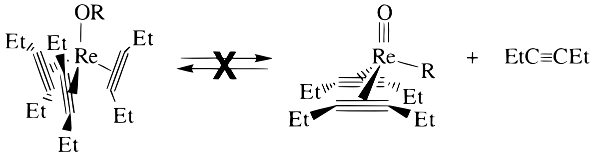
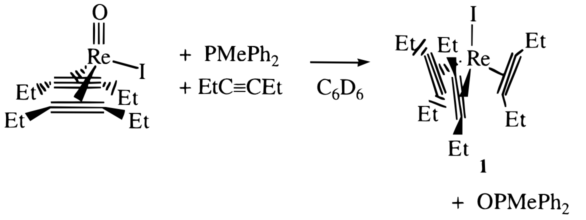


(3)

report a more complete study of the hydroxide rearrangement along with a comparative study of the reactions of analogous tris(alkyne)−amido and −sulfhydryl complexes.

Results

Rhenium(I) Tris(3-hexyne) Hydroxide Complex 3. Rhenium(I) tris(alkyne) complexes such as Re(I)(EtC≡CEt)$_3$ (**1**) are prepared by reduction of rhenium(III) oxo−bis(alkyne) compounds Re(O)I(RC≡CR)$_2$.[10,11] As an improvement over the reported procedure, sodium reduction followed by Me_3SiI, the oxygen atom can, instead, be cleanly removed with $PMePh_2$ in the presence of added alkyne (eq 4). PPh_3 is not a strong enough



(4)

reductant, and reaction with PMe_3 apparently leads to alkyne displacement as well as reduction.[12] AgOTf converts **1** into the triflate complex, Re(OTf)(EtC≡CEt)$_3$ (**2**) (OTf = triflate, O_3SCF_3).[10] The X-ray crystal structure of **2** (Figure 1, Table 1) shows isolated molecules which exhibit disorder in some of the alkyne ethyl groups and in the triflate CF_3 group (see Experimental Section). The bond lengths and angles in **2** are discussed below. The triflate ligand is readily displaced by anionic and neutral ligands.[10]

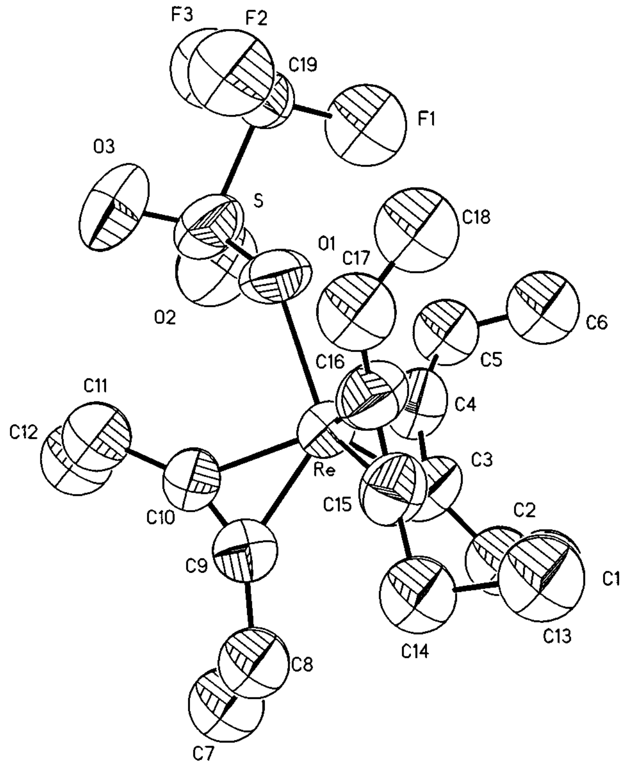


Figure 1. ORTEP diagram of the X-ray crystal structure of Re(OTf)(EtC≡CEt)$_3$ (**2**).

Table 1. Crystallographic Data

	Re(OTf)(EtC≡CEt)$_3$ (**2**)	Re(OH)(EtC≡CEt)$_3$ (**3**)
empirical formula	$C_{19}H_{30}F_3O_3ReS$	$C_{18}H_{31}ORe$
fw	581.7	449.6
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/m$
a, Å	8.410(2)	7.734(2)
b, Å	19.450(4)	13.123(4)
c, Å	14.660(3)	9.162(5)
β, deg	102.55(3)	101.65(3)
V, Å^3	2347.4(12)	910.7(6)
D_{calcd}, g/cm^3	1.646	1.640
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
2θ range, deg	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 45$
no. of reflns colld	4684	1257
no. of indep reflns	4108 (R_{int} = 2.53%)	939 (R_{int} = 4.25%)
no. of obsd reflns	2313 ($F > 4\sigma_F$)	889 ($F > 4\sigma_F$)
μ (Mo Kα), cm^{-1}	53.03	66.67
R, %	4.97	8.35
R_w, %	6.76	8.92
GOF	1.39	1.52
data-to-parameter ratio	12.1:1	16.8:1

Addition of water to a benzene solution of **2** generates an equilibrium amount of the aquo complex [Re(H_2O)(EtC≡CEt)$_3$]OTf, which has not been isolated. Treatment of this equilibrium mixture with solid KOH quantitatively gives the hydroxide complex Re(OH)(EtC≡CEt)$_3$ (**3**), as monitored by ^1H NMR (eq 5). Complex **3** is quite soluble in organic solvents and also in the oxo−hydride complex, Re(O)H(EtC≡CEt)$_2$ (**4**), an oil which forms during workup (*vide infra*). Thus,

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(10) Conry, R. R.; Mayer, J. M. *Organometallics* **1993**, *12*, 3179.

(11) Conry, R. R.; Mayer, J. M. *Organometallics* **1991**, *10*, 3160.

(12) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454.

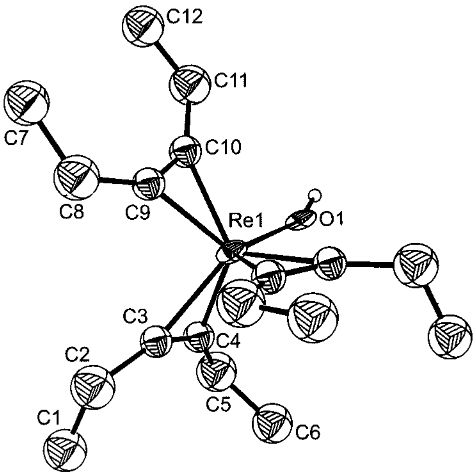
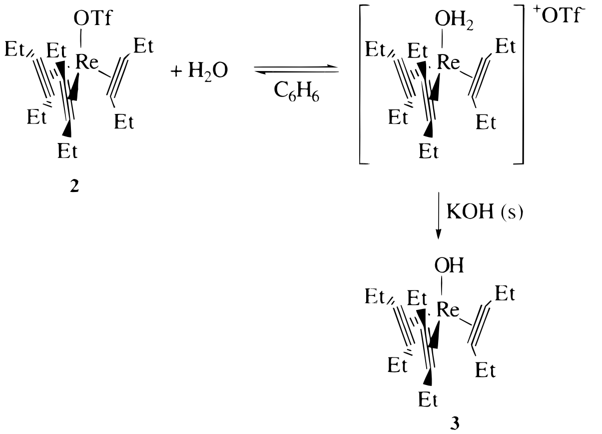


Figure 2. ORTEP diagram of the X-ray crystal structure of $Re(OH)(EtC{\equiv}CEt)_3$ (**3**).

Table 2. Selected Bond Lengths (Å) for $Re(OH)(EtC{\equiv}CEt)_3$ (3), $Re(OTf)(EtC{\equiv}CEt)_3$ (2), and $Re(OSiMe_3)(MeC{\equiv}CMe)_3$

bond[a]	Re(OH)	Re(OTf)	$Re(OSiMe_3)$[c]
Re−O1	2.124(16)	2.201(10)	2.027(8)
Re−C4	2.006(16)	2.009(14)	2.028(11)
Re−C10	1.983(30)	2.002(17)	2.004(10)
Re−C16	NA[b]	1.981(15)	2.023(10)
Re−C3	2.057(16)	1.993(15)	2.005(11)
Re−C9	1.955(21)	1.992(16)	2.066(11)
Re−C15	NA[b]	2.002(14)	2.019(10)
C3−C4	1.312(21)	1.273(21)	1.251(15)
C9−C10	1.282(36)	1.246(26)	1.363(15)
C15−C16	NA[b]	1.251(23)	1.292(14)

[a] The numbering scheme refers to the structure of **2** (Figure 1). [b] Complex **3** has only two unique alkyne ligands due to its site symmetry. [c] Data from ref 10.



(5)

Table 3. Selected Bond Angles (deg) for $Re(OH)(EtC{\equiv}CEt)_3$ (3), $Re(OTf)(EtC{\equiv}CEt)_3$ (2), and $Re(OSiMe_3)(MeC{\equiv}CMe)_3$

angle[a]	Re(OH)	Re(OTf)	$Re(OSiMe_3)$[b]
O−Re−C3	125.6(5)	127.4(5)	124.8(4)
O−Re−C9	122.0(9)	127.7(6)	124.3(4)
O−Re−C15	NA[c]	121.5(5)	125.6(4)
O−Re−C4	88.1(5)	90.4(5)	88.7(5)
O−Re−C10	84.0(9)	91.5(6)	85.3(4)
O−Re−C16	NA[c]	84.9(5)	88.5(4)
C3−Re−C4	37.7(6)	37.1(6)	36.1(4)
C9−Re−C10	38.0(10)	36.4(7)	39.1(4)
C15−Re−C16	NA[c]	36.6(7)	37.3(4)
C3−Re−C9	90.4(7)	89.9(7)	91.2(4)
C9−Re−C15	NA[c]	89.7(7)	88.0(5)
C3−Re−C15	NA[c]	89.0(6)	92.2(4)
C4−Re−C10	119.7(6)	119.7(6)	120.5(4)
C10−Re−C16	NA[c]	122.6(6)	120.3(4)
C4−Re−C16	NA[c]	117.6(6)	118.6(5)
Re−O−X	NA[d]	135.0(6)[e]	167.2(6)[f]

[a] Numbering scheme refers to the structure of **2** (Figure 1). [b] Data from ref 10. [c] Because of a crystallographic mirror plane, **3** has only two unique alkyne ligands and, thus, has no C15 or C16. [d] The hydrogen atom of the hydroxide group in **3** was not located. [e] X = S. [f] X = Si.

isolated yields of **3** are only 35% after recrystallization from pentane. Solid **3** is stable at −11 °C under inert atmosphere for at least a few months.

The X-ray crystal structure of **3** (Figure 2, Table 1) shows that the isolated molecules lie on a crystallographic mirror plane which contains rhenium, oxygen, and one alkyne ligand. The triflate (**2**), hydroxide (**3**), and siloxide $Re(OSiMe_3)(MeC{\equiv}CMe)_3$[10] complexes have nearly identical capped trigonal prism coordination, as is characteristic of $ML(alkyne)_3$ compounds (Tables 2 and 3).[13] The most notable difference between these structures is the Re−O bond length—2.201 (10), 2.124 (16), and 2.027 (8) Å for **2**, **3**, and the siloxide—with the weakly bound triflate having the longest bond. The distance between two neighboring oxygen atoms in solid **3** is about 8 Å, ruling out any hydrogen bonding between hydroxide ligands. Consistent with this conclusion, a sharp O−H stretch is observed at 3630 cm^{-1} in a Nujol mull of **3** (ν_{OD}, 2677; calcd, 2633 cm^{-1}), typical of metal hydroxide complexes.[14] A band at the same frequency is observed in benzene solution, indicating the absence of hydrogen bonding in solution as well.

^1H NMR spectra of **3** at −66 °C in C_7D_8 show two triplets for the methyl groups and two simple quartets for the methylene protons, indicating C_{3v} symmetry. ^1H NMR spectra at 27 °C, however, show a single methyl triplet and a broad peak for the methylene hydrogens. Resonances for 3-hexyne added to a solution of **3** remain sharp at these temperatures, so ligand exchange is not responsible for the coalescence. The fluxional process is most likely rotation of the alkyne ligand(s), as suggested for similar $ReX(RC{\equiv}CR)_3$[10,15] and W(L)-$(RC{\equiv}CR)_3$ compounds.[13] The coalescence temperature is found to be 295 K for the methylene protons, indicating that $\Delta G^{\ddagger}_{rotation} = 14.0 \pm 0.2$ kcal/mol. The ^{13}C NMR chemical shifts of the acetylenic carbons, 167.6 and 179.0 ppm at 240 K, are in the same range as for the other tris(acetylene) complexes and are consistent with the alkynes acting as $3^1/_3$ electron-donor ligands, as predicted by symmetry arguments and the 18-electron rule.[16]

Conversion of **3** to the oxo−hydride $Re(O)H(EtC{\equiv}CEt)_2$ (**4**)[17] and 3-hexyne (eq 2) is complete after 5 days in benzene solution at ambient temperatures and proceeds with a mass balance of nearly 100% by ^1H NMR. This

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(13) Wink, D. J.; Creagan, B. T. *Organometallics* **1990**, *9*, 328 and references therein.

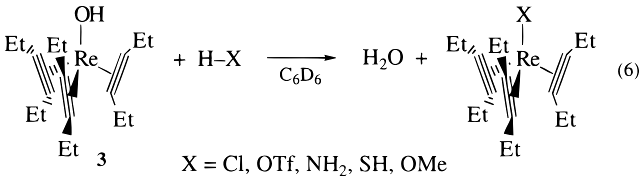
(14) (a) Imadea, M.; Nishihara, H.; Nakano, K.; Ichida, H.; Kobayashi, A.; Saito, T.; Sasaki, Y. *Inorg. Chem.* **1985**, *24*, 1246. (b) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (c) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (d) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.

(15) Manion, A. B.; Erikson, T. K. G.; Spaltenstein, E.; Mayer, J. M. *Organometallics* **1989**, *8*, 1871.

(16) (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1−100. (b) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044.

(17) Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617.

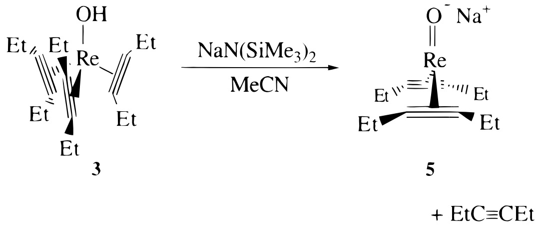
rearrangement occurs in the solid state and in a variety of solvents; its kinetics and mechanism are discussed below. Benzene solutions of **3** react rapidly with triflic acid or HCl gas to give water and **2** or $\mathrm{ReCl(EtC{\equiv}CEt)_3}$[10] (eq 6). Addition of NH_3 or H_2S forms the amide or sulfhydryl complex (**10**, **13**; *vide infra*). Reaction with MeI gives ^{1}H NMR signals attributable to the methanol complex $\mathrm{[Re(MeOH)(EtC{\equiv}CEt)_3]I}$, followed by conversion to methanol and $\mathrm{ReI(EtC{\equiv}CEt)_3}$ (**1**). This presumably occurs through electrophilic attack of MeI on **3** followed by iodide displacement of methanol. Addition of methanol to a benzene solution of **3** immediately changes the ^{1}H NMR to that expected for a nonfluxional tris(3-hexyne) species. In the course of a few days, the solution converts to the methoxide complex Re(OMe)-$\mathrm{(EtC{\equiv}CEt)_3}$ and water. No formation of the oxo−hydride complex **4** is observed in the presence of MeOH. Excess water also causes the 3-hexyne ligands of **3** to become nonfluxional. The changes in the spectrum of **3** are apparently due to the formation of hydrogen bond(s).



X = Cl, OTf, NH_2, SH, OMe

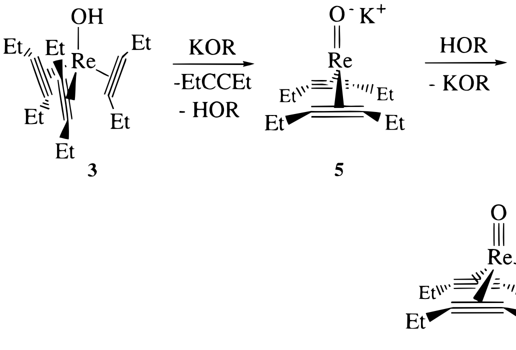
(6)

Deprotonation of **3** by $\mathrm{NaN(SiMe_3)_2}$ in acetonitrile cleanly gives the known deep orange rhenium(I) oxo anion $\mathrm{(EtC{\equiv}CEt)_2Re(O)Na}$ (**5**; eq 7).[18] Addition of KOMe, KO^{t}Bu, or KOPh to an acetonitrile solution of **3** causes an immediate color change from light yellow to the orange color of **5**, which then rapidly changes to dark yellow, and ^{1}H NMR spectra show the formation of **4**. The alkoxide salts are catalysts for the conversion of **3** to **4**, apparently by the mechanism in eq 8.



(7)

The weaker bases triethylamine, pyridine, and potassium *p*-nitrophenoxide do not deprotonate **3**. With the assumption that these kinetic observations reflect its thermodynamic acidity, the pK_a of **3** in acetonitrile is between 20.7 and 27.2, the pK_a's of *p*-nitrophenol and phenol in this solvent.[19] It should be emphasized, however, that deprotonation of **3** is not a simple or reversible process, as removal of the acidic hydrogen is accompanied by loss of an alkyne ligand (eq 7) and reprotonation of **5** gives the rhenium hydride **4**, not **3**.



(8)

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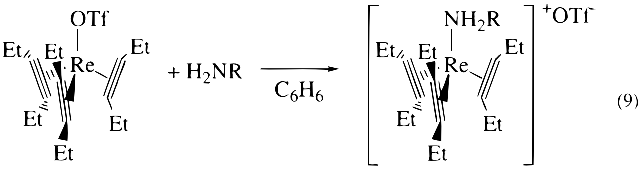
Complex **5** is readily protonated in acetonitrile by water, alcohols, and other proton donors; the pK_a of its conjugate acid **4** is estimated to be 33 ± 3 in MeCN.[20]

Rhenium(I) Tris(3-hexyne) Amine and Amido Complexes. Ammonia, methylamine, and *para*-toluidine displace the triflate ligand from **2** and form amine complexes $\mathrm{[Re(NH_2R)(EtC{\equiv}CEt)_3]OTf}$ (R = H (**6**), Me (**7**), C_6H_4Me (**8**); eq 9). Recrystallization from pentane gives **6**−**8** as analytically pure light gray solids in ca. 85% yield. They are indefinitely stable under inert atmosphere but decompose upon exposure to air. Reaction with aniline gives an equilibrium mixture containing $\mathrm{[Re(NH_2C_6H_5)(EtC{\equiv}CEt)_3]OTf}$ (**9**), **2**, and free aniline. With *p*-nitroaniline, the equilibrium is so unfavorable that no adduct can be seen in the ^{1}H NMR spectrum. The coordinating ability of the amines, thus, correlates with their basicity, consistent with the observation of an equilibrium with water as the ligand (eq 5).



(9)

R = H (**6**), Me (**7**), p-tolyl (**8**)

The ^{1}H and ^{13}C NMR spectra of compounds **6**−**9** are typical of $\mathrm{ML(EtC{\equiv}CEt)_3}$ complexes, with separate resonances for the proximal and distal ethyl groups, nondiastereotopic methylene hydrogens, and acetylenic ^{13}C chemical shifts in the range of 160−180 ppm.[16] The IR spectra of **6**−**8** show bands in the range of 3100−3300 cm^{-1} for NH_2 stretches and ca. 1600 cm^{-1} for NH_2 bends. A strong peak at ∼1270 cm^{-1} is attributed to the triflate counterion, consistent with its formulation as an ionic triflate group.[10,21] The ^{19}F chemical shifts in the vicinity of −2.3 ppm in C_6D_6 (*vs* CF_3COOH) also indicate that the triflate is ionic.[22]

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[18] Cundari, T. R.; Conry, R. R.; Spaltenstein, E.; Critchlow, S. C.; Hall, K. A.; Tahmassebi, S. K.; Mayer, J. M. *Organometallics* **1994**, *13*, 322. The spectroscopic and structural properties of **5** do not vary substantially with the cation, so we do not distinguish the different salts here.

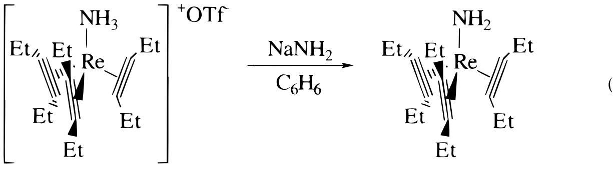
[19] Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

[20] (a) Complex $\mathbf{5}^-Na^+$ is completely protonated by H_2O in MeCN (pK_a ≅ 30[20b]) but $\mathbf{5}^-Na^+$ and $\mathbf{5}^-$[Na(Krypotofix-222)]$^+$ do not react with MeCN solvent.[11,18] Bases stronger than pK_a ≈36 are reported to be unstable in MeCN.[20c] These upper and lower bounds yield the estimated pK_a of 33 ± 3, ignoring counterion and other effects (e.g., Na^+ may stabilize the OH^- or OR^- anions). (b) Barrette, W. C., Jr.; Johnson, H. W., Jr.; Sawyer, D. T. *Anal. Chem.* **1984**, *56*, 1890−1898. (c) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment;* Dedieu, A., Ed.; VCH: New York 1991 (especially ref 25).

[21] Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

[22] In our rhenium systems, ^{19}F chemical shifts for ionic triflates in C_6D_6 are roughly −3 ppm (upfield of CF_3COOH), whereas covalently bound triflates appear closer to −1 ppm.[5,10,21]

The ammonia complex **6** is converted to the neutral amido complex, $Re(NH_2)(EtC{\equiv}CEt)_3$ (**10**), by $NaNH_2$ or NaH (eq 10). NaH must react by deprotonation, but $NaNH_2$ could react either by deprotonation or substitution; reaction of the aquo complex with NaOMe gives both the hydroxide and methoxide complexes. Light yellow crystals of **10** can be stored in a freezer in the drybox for at least 1 month without decomposition, but it is unstable at ambient temperatures (*vide infra*). The ^{1}H NMR spectrum of **10** at 253 K in toluene-d_8 shows two triplets and two quartets for the hexyne ligands, confirming the C_{3v} structure. At higher temperatures, the hexyne signals coalesce into a single triplet and quartet, giving $\Delta G^{\ddagger}_{rot} = 13.8$ kcal/mol at $T_c = 295$ K based on $\Delta\nu = 160$ Hz. This barrier to rotation is essentially the same as that for **3**.

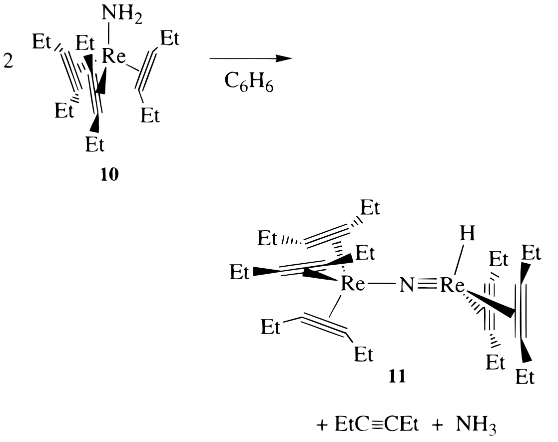


6 **10**

(10)

Deprotonation of **6** with LiN^iPr_2 (lithium diisopropylamide, LDA) gives solutions with ambient-temperature NMR spectra essentially identical to that of **10**. Analytical data for the isolated solid indicate the presence of 1 equiv of LiOTf, and the IR spectra of this material show the presence of ionic triflate. Apparently, the basic amide ligand coordinates the lithium ion and there is hydrogen bonding between the amide and the triflate, as the NH_2 stretching mode in **10** at 3342 cm^{-1} splits into bands at 3321 and 3178 cm^{-1} in **10**·LiOTf.

Complex **10** decays in solution, over 5 days at room temperature or overnight at 50 °C, to a new rhenium product and 0.5 equiv each of 3-hexyne and NH_3. Ammonia is not directly observed in the ^{1}H NMR spectrum of the reaction but can be detected by condensing the vapor from the reaction mixture into a solution of **2**, forming the ammonia complex **6**. The rhenium product is identified from spectroscopic data to be the μ-nitrido complex $(EtC{\equiv}CEt)_3Re{-}N{\equiv}Re(H)(EtC{\equiv}CEt)_2$ (**11**) (eq 11). Compound **11** contains a rhenium(III) nitrido–hydride bis(3-hexyne) fragment, closely related to the oxo–hydride **4**, which serves as a singly bonded ligand to a rhenium(I)–tris(3-hexyne) fragment, very similar to the amine and amide complexes **6**–**10**. The tris(acetylene) unit is identified in the ^{1}H NMR by two clean quartets for the methylene protons, while the bis(acetylene) fragment shows multiplets for the diastereotopic methylene hydrogens (as found for all the rhenium(III) oxo–bis(acetylene) compounds). The quartet and multiplet signals integrate 6:4, and this ratio does not change from one preparation to another nor after sublimation, indicating they all result from a single compound. The hydride ligand is found in the ^{1}H NMR as a singlet at 5.2 ppm (*c.f.*, δ 6.0 for $Re(O)H(EtC{\equiv}CEt)_2$), and the Re–H stretch is assigned to a band in the IR spectrum at 1931 cm^{-1}. Mass spectra show a weak pattern at m/z 797 (M^+) and a stronger pattern at m/z 715 ($M^+ - EtC{\equiv}CEt$), which shows the isotope pattern of a bimetallic rhenium species. ($M^+ - EtC{\equiv}CEt$ is invariably one of the largest peaks in the MS of $ReX(EtC{\equiv}CEt)_3$ compounds.) Initially, the rearrangement of **10** to **11** is clean, exhibiting a mass balance of close to 100% by NMR. But **11** decomposes slowly at room temperature to oily, NMR-silent materials. This is one of the more unusual methods of synthesis of a μ-nitrido bimetallic compound.[23]



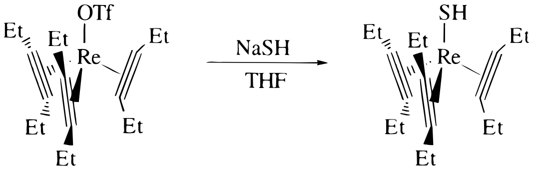
10

11

(11)

The characterization of compound **11** is supported by its reaction chemistry (Scheme 1). Addition of HCl to **11** recovers the tris(hexyne) fragment as the known chloride derivative, $ReCl(EtC{\equiv}CEt)_3$.[10] Passing **11** through a silica gel column converts the bis(hexyne) fragment to the oxo–hydride **4**. Reaction of **11** with CCl_4 gives $CHCl_3$ and the chloride complex $(EtC{\equiv}CEt)_3Re{-}N{\equiv}Re(Cl)(EtC{\equiv}CEt)_2$ (**12**), a classic indication of the presence of a hydride ligand. Complex **12** is characterized by its ^{1}H NMR spectrum, by an [M − hexyne]$^+$ isotope cluster in its mass spectrum (m/z 749), and by an IR absorption at 1085 cm^{-1} ($\nu_{Re{\equiv}N{-}Re}$; compared to 1079 cm^{-1} in **11**). Conversion of **11** to **12** can also be accomplished with *N*-chlorosuccinimide. Complex **12** is unreactive toward water, but slowly decomposes in air. Complexes **11** and **12** have not been isolated in analytically pure form because of their high solubility and thermal instability.

Rhenium Tris(3-hexyne) Sulfhydryl Complex 13. The rhenium(I) sulfhydryl complex $Re(SH)(EtC{\equiv}CEt)_3$ (**13**) is formed upon addition of sodium hydrosulfide, NaSH, to the triflate complex **2** in THF (eq 12). Recrystallization from pentane gives analytically pure gray solids in 40% yield. Complex **13** is also generated on reaction of H_2S with the hydroxide and amido complexes **3** and **10** (eqs 13 and 14). However, these routes are not synthetically useful since **13** decomposes in the presence of H_2S. Compound **13** is unreactive toward water and ammonia.



2 **13**

(12)

The ^{1}H NMR spectrum of **13** shows the same pattern as the other tris(acetylene) complexes, plus a singlet

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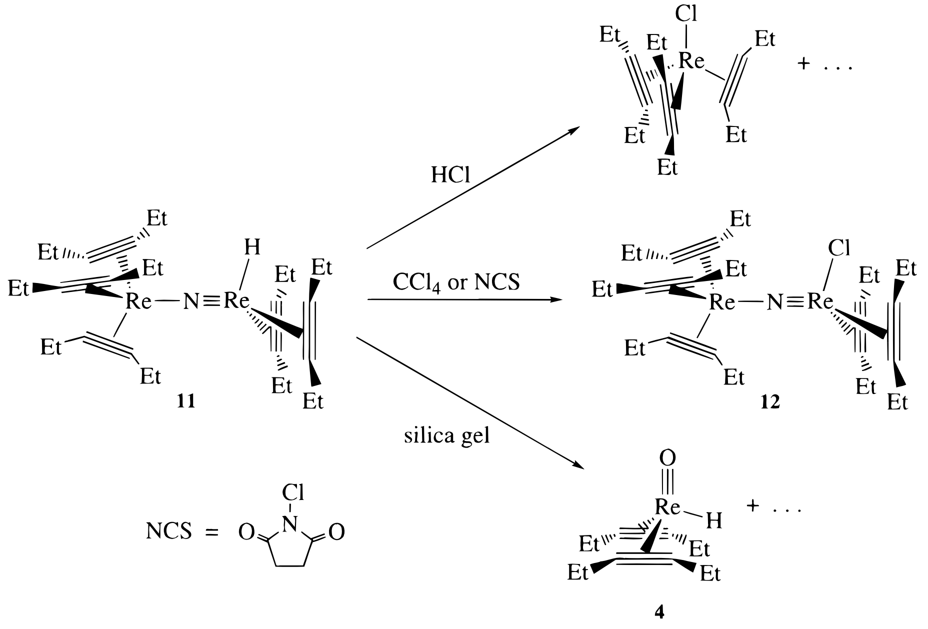
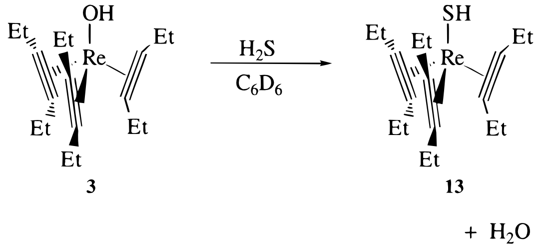
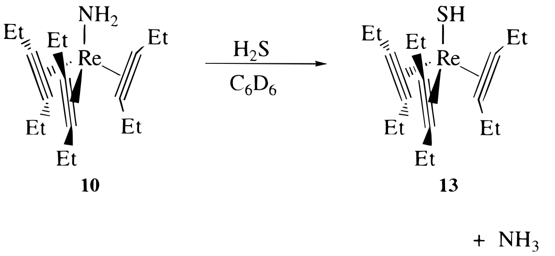
(23) (a) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955–978. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988 (IR studies of M(μ-N)M, pp 121–122; structural studies, pp 179–186).

Scheme 1. Reactions of the μ-Nitrido–Hydride Dimer 11





(13)



(14)

(1H) at 1.15 ppm due to the sulfhydryl proton. The alkyne resonances broaden and coalesce at or above room temperature, with $\Delta G^{\ddagger}_{\mathrm{rot}} = 16.0 \pm 1$ kcal/mol at 314 K based on the coalescence of the methyl resonances ($\Delta\nu = 20$ Hz). The IR spectrum of **13** is very similar to that of the hydroxide complex, with a band at 2555 cm^{-1} assigned as the S–H stretch. This is within the reported range of such frequencies in metal sulfhydryl complexes.[24]

Complex **13** is much more thermally robust than the hydroxide and amido complexes **3** and **10**. Benzene solutions of **13** are indefinitely stable at ambient temperatures and decompose only on heating to 150 °C for 1 week, forming NMR-silent black solids. Heating **13** and 2-butyne in C_6D_6 at 70 °C for 7 days does not result in observable alkyne exchange by ^{1}H NMR. There is no evidence for rearrangement to a sulfido–hydride complex, as free 3-hexyne is not detected by NMR and pyrolysis in the presence of CCl_4 does not yield $CHCl_3$. Photolysis of **13** yields only ca. 0.2 equiv of free 3-hexyne, and photolyses in the presence of CD_2Cl_2 or $CDCl_3$ do not show products that would suggest a rhenium–hydride intermediate.

Kinetic and Mechanistic Studies. The kinetics of the rearrangement of the hydroxide complex **3** to the oxo–hydride complex **4** and free 3-hexyne (eq 2) have been followed by ^{1}H NMR in C_6D_6 solution. Plots of ln[**3**] *vs* time are linear to about three half-lives (Figure 3). The derived first-order rate constant, $k_3 = (5.6 \pm 1.2) \times 10^{-6}\ \mathrm{s}^{-1}$ at 294 ± 1 K, is independent of the initial concentration of **3** over a factor of eight. This rate constant is also independent of the initial purity of **3**, comparing crystalline samples with crude materials. An Eyring plot of five rate constants determined at temperatures between 294 and 327 K yields the activation parameters $\Delta H^{\ddagger} = 17 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -25 \pm 5$ eu. The deuteroxide complex $\mathrm{Re(OD)(EtC{\equiv}CEt)_3}$ (**3**-*d*) rearranges to **4**-*d* more slowly, with $k_{\mathrm{OH}}/k_{\mathrm{OD}} = 5 \pm 1$ at 294 ± 1 K (Figure 3). In C_6D_6 saturated with water, rearrangement of **3** is about 35% slower than in dry solvent.

The rate constant for the rearrangement of **3** is unchanged within experimental error by the presence of added free 3-hexyne, up to 1 M concentration. Likewise, the presence of 1 M 2-butyne at 294 ± 1 K does not affect the rate constant, although in addition to **4**, two minor 2-butyne-containing products are seen, with the total concentration of bound 2-butyne about 10% of the total rhenium concentration. A small amount of the known[17] $\mathrm{Re(O)H(MeC{\equiv}CMe)_2}$ is found and somewhat more of a mixed butyne/hexyne material, most likely $\mathrm{Re(O)H(MeC{\equiv}CMe)(EtC{\equiv}CEt)}$ but the data do not rule out a rhenium(I) hydroxide $\mathrm{Re(OH)(MeC{\equiv}CMe)_{\mathit{x}}(EtC{\equiv}CEt)_{3-\mathit{x}}}$ ($x = 1$ or 2). Compound **4** does not exchange with 2-butyne under these conditions, even when heated to 80 °C for 1 week. Therefore, the formation of butyne-containing products must result from ligand exchange in **3** prior to or during rearrangement. The related methoxide derivative $\mathrm{Re(OMe)(EtC{\equiv}CEt)_3}$ undergoes 2-butyne exchange more rapidly

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[24] Mueting, A. M.; Boyle, P. D.; Wagner, R.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 271.

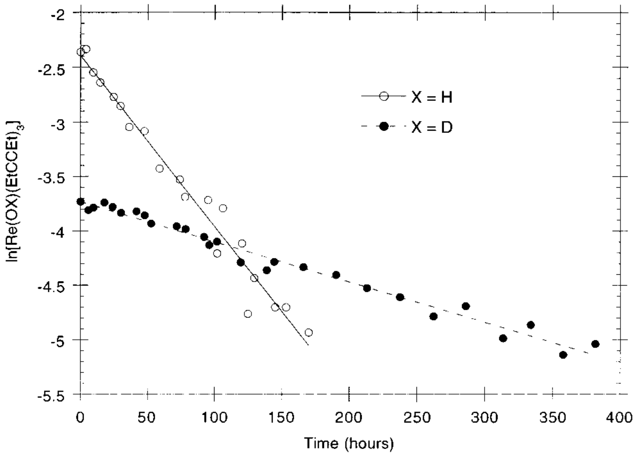

Figure 3. Kinetic data for the rearrangement of Re(OX)-$(EtC{\equiv}CEt)_3$ (X = H, D; *T* = 21 ± 1 °C).

than **3**, with a half-life of only a few hours at ambient temperatures.[10]

The addition of small amounts (~0.08 equiv) of $[(EtC{\equiv}CEt)_2ReO]Na$ (**5**) to a solution of **3** at ambient temperature does not change the rate of rearrangement. Complex **3** decomposes slowly in the presence of larger amounts (~0.8 equiv) of **5**; yet the initial rate of growth of the products in that sample remains roughly the same as that of clean hydroxide samples. To test for the presence of **5** as an intermediate, the rearrangement reaction was run in the presence of *p*-iodotoluene, which reacts rapidly with **5** to form a mixture of Re(O)(*p*-Tol)-$(EtC{\equiv}CEt)_2$ and $Re_2(O)_2(EtC{\equiv}CEt)_4$.[11] Neither of these products were observed, and the rate of rearrangement is unchanged in the presence of *p*-iodotoluene. In a control experiment, **5** was added to a 1:1 mixture of *p*-iodotoluene and phenol, yielding mostly **4** but also small amounts of the trapped products. Since phenol is a more rapid proton donor than **3** (phenol + **5** is fast, while **3** + **5** gives **4** slowly if at all), the lack of any trapped products in the rearrangement of **3** indicates that **5** is not an intermediate. In addition, added **5** is not a catalyst for the rearrangement, although catalysis is observed in acetonitrile solutions with KOMe, KO-^tBu, and KOPh, as noted above (eq 8).

The conversion of the amido complex **10** to the μ-nitrido dimer **11** has also been monitored by ^1H NMR, monitoring the concentrations of all of the reactants and products via their methylene resonances. The reaction was followed over roughly one half-life (12 h at 60 °C), but after this time the thermal decomposition of **11** becomes significant and the data become unreliable. Using data from a solution that was initially 0.1 M **10** in C_6D_6, neither the plot of ln[**10**] *vs* time nor the plot of $[\mathbf{10}]^{-1}$ *vs* time are linear over this time period. The presence of 0.5 M 2-butyne or 0.44 M 3-hexyne dramatically slows the reaction. In 40 h at 60 °C, over which time the reaction of an alkyne-free sample has gone to completion, the samples with added alkyne show less than 5% conversion. Added 2-butyne exchanges with bound 3-hexyne to form a mixture of complexes Re-$(NH_2)(EtC{\equiv}CEt)_x(MeC{\equiv}CMe)_{3-x}$, $x = 0-3$, with a roughly statistical equilibrium reached within 7 h at 60 °C. Assuming that alkyne exchange occurs via a dissociative mechanism, as found for tris(alkyne) alkoxide complexes,[10] the first-order rate constant is 1.9×10^{-4} s^{-1} at 60 °C. Given the inhibition of **10** → **11** by 3-hexyne, which is a product of the rearrangement, it is not surprising that the loss of starting material follows neither simple first-order nor simple second-order kinetics. Surprisingly the time course of the reaction—the fraction of **10** reacted *vs* time—is the same within experimental error for the two reactions whose concentrations of **10** differ by a factor of five (Figure 4).

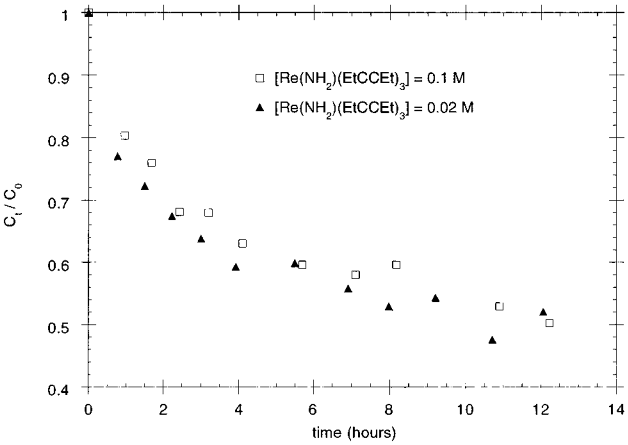

Figure 4. Normalized plot of $[Re(NH_2)(EtC{\equiv}CEt)_3]_t$/[Re-$(NH_2)(EtC{\equiv}CEt)_3]_o$ versus time for two different [Re(NH$_2$)-$(EtC{\equiv}CEt)_3]_o$.

Discussion

The rearrangement of **3** to **4** (eq 2) is the first hydroxide to oxo–hydride rearrangement that can be directly monitored. This transformation also undoubtedly occurs in the reaction of $Cp^*_2Ta({=}CH_2)H$ with water to give $Cp^*_2Ta(O)H$[7] and likely occurs in the formation of $[Re(O)HX\{(Cy_2PCH_2CH_2CH_2)_2PPh\}]SbF_6$ (X = H, F)[25] and in various reactions of the form $L_nM + H_2O \rightarrow L_nM{=}O + H_2$.[26] Amido/imido–hydride interconversion appears to be facile in $Re(NAr)_3H$ (Ar = 2,6-$^iPr_2C_6H_3$) on the basis of NMR studies and reactivity.[27] The amido complex **10** undergoes a similar rearrangement, with hydrogen migration from N to Re and oxidation of a Re(I) center to Re(III). But the product, a μ-nitrido compound, and the mechanism are different from the oxo case. The sulfhydryl complex **13** shows no evidence of rearrangement and decomposes only at 150 °C, while **3** and **10** rearrange at ambient temperatures.

Thermodynamic Considerations. The equilibrium constant for the rearrangement of **3** to **4** can be estimated from the rough pK_a values for **3** and **4**, as shown in Scheme 2: $K_{eq} \cong 10^{9\pm6}$ M or $\Delta G° \cong -12 \pm 8$ kcal/mol. While the pK_a values are crude numbers derived solely from kinetic observations, the derived equilibrium constant is consistent with the complete conversion of **3** to **4** in the presence of 1 M 3-hexyne, which requires that $K_{eq} \geq 10^2$ M ($\Delta G° \leq -2$ kcal/mol). It is also consistent with the observation that **4** does not exchange alkyne ligands over a week at 80 °C, which implies that the reverse reaction (**4** + 3-hexyne → **3**) is very slow, $\Delta G^{\ddagger} > 32$ kcal/mol. Since $\Delta G^{\ddagger}$ for the forward reaction at 80 °C is 26 kcal/mol, the rearrangement

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(25) Kim, Y.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 8600–8602.

(26) See, for instance: Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402–10411.

(27) Williams, D. S.; Schrock, R. R. *Organometallics* **1993**, *12*, 1148.

Scheme 2

$$\begin{array}{ll}
\mathrm{Re(OH)(EtC{\equiv}CEt)_3}\ (\mathbf{3}) \rightleftarrows [\mathrm{ReO(EtC{\equiv}CEt)_2}]^-\ (\mathbf{5}) + \mathrm{EtC{\equiv}CEt} + \mathrm{H^+} & \mathrm{p}K_a = 24 \pm 3 \\
[\mathrm{ReO(EtC{\equiv}CEt)_2}]^-\ (\mathbf{5}) + \mathrm{H^+} \rightleftarrows \mathrm{Re(O)H(EtC{\equiv}CEt)_2}\ (\mathbf{4}) & -\mathrm{p}K_a \cong 33 \pm 3 \\
\hline
\mathrm{Re(OH)(EtC{\equiv}CEt)_3}\ (\mathbf{3}) \rightleftarrows \mathrm{Re(O)H(EtC{\equiv}CEt)_3}\ (\mathbf{4}) + \mathrm{EtC{\equiv}CEt} & K_{eq} \cong 10^{9\pm6}\ \mathrm{M^{-1}}
\end{array}$$

must be favorable by at least 6 kcal/mol at this temperature. The reaction involves loss of an alkyne ligand and conversion of an O−H bond into an Re−H bond, both of which are quite enthalpicaly unfavorable. These processes must be compensated for by the change from an Re−O single bond in **3** to the triple bond in **4**.[28] The rhenium−hexyne bonding does not substantially change on going from **3** to **4**, as the alkynes change from $3^1/_3$- to 3-electron donors. Rearrangement of the amido complex **10** is likely to be similarly driven by the formation of Re−N π bonds, although the more complex nature of this transformation precludes such simple thermochemical analysis. The lack of reaction of the sulfhydryl complex **13** to a sulfido−hydride complex could be due to a reversal in the thermodynamics, due to the presumably weaker Re−S π bonds. Attempts to prepare the sulfido−hydride complex from Re(S)I(EtC≡CEt)$_2$ led to decomposition,[29] so we cannot determine whether the reverse reaction occurs. It is also possible that the lack or reaction of **13** is due to kinetic, rather than thermodynamic, factors. These rearrangements require loss of an alkyne ligand at some stage, which is much less facile for **13** than for **10** or **3** based on their rates of exchange with 2-butyne.

Mechanistic Considerations. The rearrangements discussed here are migratory deinsertion or α-elimination reactions of 18-electron organometallic complexes. The typical mechanism of such processes is initial ligand loss to give an unsaturated intermediate in which migration takes place.[2] A classic example is the reversible α-elimination following loss of a ligand from Cp$_2$W(CH$_3$)L$^+$.[30] In the rhenium compounds, such a pathway would involve initial loss of alkyne to give Re(EH$_x$)(EtC≡CEt)$_2$ (EH$_x$ = OH (**A**), NH$_2$ (**B**), or SH (**C**)), followed by rearrangement or another reaction (eq 15).

$$\mathrm{Re(EH_x)(EtC{\equiv}CEt)_3} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Re(EH_x)(EtC{\equiv}CEt)_2} \xrightarrow{k_2} \qquad (15)$$

$$\mathrm{EH_x} = \mathrm{OH}\ (\mathbf{A}),\ \mathrm{NH_2}\ (\mathbf{B}),\ \mathrm{SH}\ (\mathbf{C})$$

The data for rearrangement of the amido complex **10** are consistent with a pre-equilibrium alkyne loss, as there is inhibition by added 3-hexyne and 2-butyne exchange is faster than conversion to **11**.

In contrast, rearrangement of the hydroxide complex **3** is not inhibited by the presence of 1 M 3-hexyne, and exchange with added 2-butyne is an order of magnitude slower than conversion to **4**. This rules out equilibrium loss of 3-hexyne prior to the rate-limiting step. Alkyne loss, k_1 in eq 15, cannot be rate limiting because there is a primary isotope effect, $k_{\mathrm{OH}}/k_{\mathrm{OD}} = 5 \pm 1$.[31] So, surprisingly, the migratory deinsertion of **3** to **4** does not occur by the mechanism of eq 15. The exchange with 2-butyne likely proceeds through **A** since the analogous methoxide complex exchanges alkynes by a dissociative pathway.[10] The data do not determine whether **A** can rearrange to its isomer **4**, but they indicate that this path can be at most a small fraction of the reaction.

Three other pathways have been considered for the conversion of **3** to **4** (Scheme 3). In path i, hydrogen migration occurs initially to one of the alkyne ligands to give the oxo−3-hexenyl complex Re(O)(CEt=CHEt)(EtC≡CEt)$_2$, which then undergoes β-hydride elimination to form **4** and 3-hexyne.[32] Efforts to independently prepare the hexenyl complex have been unsuccessful. The related vinyl complex Re(O)(CH=CH$_2$)(EtC≡CEt)$_2$[33] decomposes in C$_6$D$_6$ over 2 h to NMR-silent materials, suggesting that the hexenyl derivative would not cleanly eliminate to **4** and, thus, is unlikely to be an intermediate. The analogous oxo−ethyl complex, Re(O)Et(EtC≡CEt)$_2$, does not undergo β-hydrogen elimination at over 100 °C in benzene solution.[17]

Mechanism ii involves deprotonation of **3** to **5** by an external base. This pathway is indicated for the rapid conversion of **3** to **4** in CD$_3$CN when small amounts of KOMe, KO^{t}Bu, and KOPh are added. No catalysis is observed with the weaker base KOC$_6$H$_4$NO$_2$. The flash of dark orange is consistent with the intermediacy of **5** (eq 8). In the absence of added reagents, an adventitious base would be required. This is hard to rationalize with the observation that samples of **3** with varying purity, from impure to crystalline, rearrange at the same rate and that conversion to **4** proceeds at roughly the same rate in the solid state. This also rules out catalysis by adventitious water or another impurity (and small amounts of H$_2$O and MeOH inhibit the reaction). The intermediacy of **5** in the uncatalyzed rearrangement is also ruled out by the experiments with added *p*-iodotoluene (*vide supra*). Surprisingly, small amounts of the sodium salt of **5** (0.08 equiv) do not catalyze the rearrangement. This is because protonation of **5** by **3** is slow, despite being significantly downhill (Scheme 2). Proton transfer to metal centers is typically slower than H$^+$ transfers to oxygen or nitrogen,[34] and there is evidence that proton transfer reactions of metal hydroxides are slow.[35] Proton transfer from **3** to **5** would appear to be sterically encumbered, and deprotonation of **3** is accompanied by loss of an alkyne which should contribute to a kinetic barrier.[34,36] Catalysis by KOMe, KO^{t}Bu, or KOPh is more efficient than by **5** because

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[28] Given the negative $\Delta G°$, conversion of **3** → **4** must have a favorable or near-zero $\Delta H°$.

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

[30] Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

[31] See Supporting Information for the kinetic expressions.

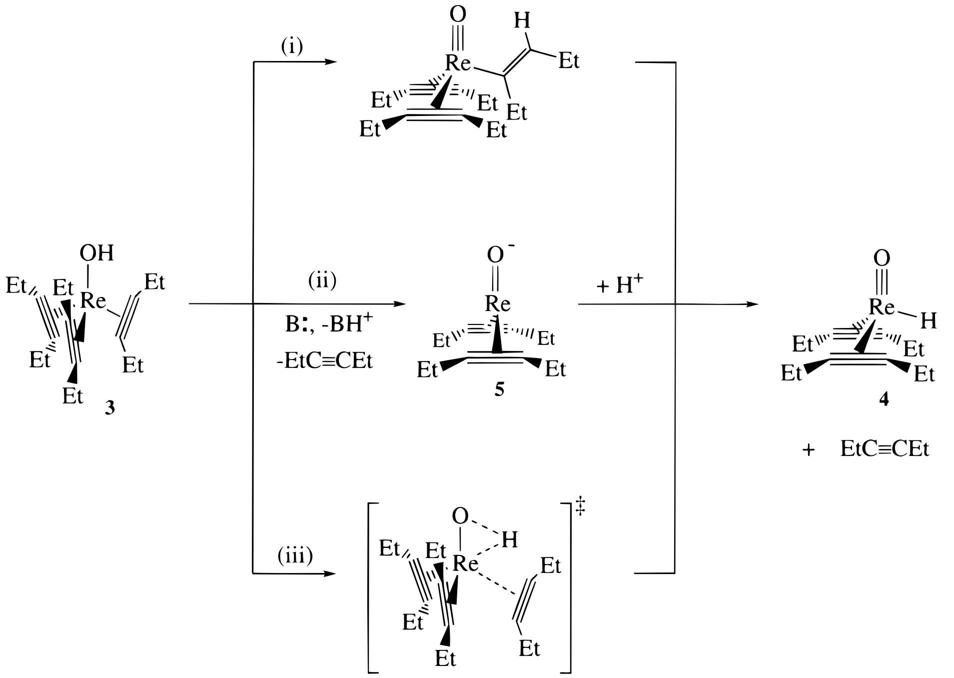
[32] We thank K. G. Caulton for this suggestion, see: Caulton, K. G. *Chemtracts: Inorg. Chem.* **1993**, *5*, 133.

[33] Re(O)(CH=CH$_2$)(EtC≡CEt)$_2$ was formed from Re(O)I(EtC≡CEt)$_2$ and CH$_2$=CHMgBr/ZnCl$_2$ as indicated by its ^{1}H NMR spectrum.

[34] Kramarz, K. W.; Norton, J. R. *Prog. Inorg. Chem.* **1994**, *42*, 1−65.

[35] (a) Carroll, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 8744−5. (b) Erikson, T. K. G.; Mayer, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1527.

Scheme 3. Possible Pathways for Hydroxide to Oxo−Hydride Rearrangement



the alkoxides and resultant alcohols circumvent the kinetic barrier to the reaction of **3** and **5**.

The data, thus, indicate that rearrangement occurs by rate-limiting hydrogen migration synchronously with or prior to loss of ligand. Ligand loss could occur with same-side[37] or back-side displacement; the former is arbitrarily drawn as mechanism iii in Scheme 3. An alternative pathway of pre-equilibrium hydrogen migration followed by rate-limiting ligand loss is ruled out by the k_{OH}/k_{OD} of 5 ± 1. The isotope effect calculated for such a pre-equilibrium, based on ν_{OH} in **3** and using ν_{ReH} in **4** as a model for the intermediate, is only 2.4. Since **3** is an 18-electron species, hydrogen migration preceding alkyne loss would require a reduction in π-donation from the $3^1/_3$-electron donor alkyne ligands. The small $\Delta H^‡$ of 17 kcal/mol is consistent with Re−H σ bond and Re−O π-bond formation accompanying O−H bond cleavage. The negative $\Delta S^‡$ (−25 eu) indicates a transition state that is more ordered than the ground state, suggesting that alkyne dissociation is not well-developed at the transition state.

Rearrangement of the rhenium(I) amido complex **10** to the μ-nitrido dimer **11** is also a formal 1,2-migration, with a hydrogen atom moving from nitrogen onto rhenium. In contrast to the hydroxide case, inhibition by added 3-hexyne indicates that the coordinatively unsaturated intermediate $[Re(NH_2)(EtC{\equiv}CEt)_2]$ (**B**) is on the pathway to rearrangement (eq 15). Even though the inhibitor hexyne is formed in the reaction, the fraction of **10** consumed as a function of time is independent of its starting concentration (Figure 4). This is normally a characteristic of first-order kinetics but it is also consistent with the first steps of the mechanism in Scheme 4, bimolecular reaction of **B** with another molecule of **10**. Alternative pathways involving unimolecular rearrangement of **B** or bimolecular reaction of two molecules of **B** do not have this property.[31] Applying the steady-state approximation to the concentration of **B** in this mechanism gives eq 16. Taking C_o

$$\frac{d[Re(NH_2)(EtC{\equiv}CEt)_3]}{dt} = \frac{-2k_1k_2[Re(NH_2)(EtC{\equiv}CEt)_3]^2}{k_{-1}[EtC{\equiv}CEt] + k_2[Re(NH_2)(EtC{\equiv}CEt)_3]} \quad (16)$$

as the initial concentration of **10** and X as the fraction of starting material remaining, then $[Re(NH_2)(EtC{\equiv}CEt)_3]_t = C_oX$ at time t and $[EtC{\equiv}CEt]_t = {}^1/_2(C_o - C_oX)$ when there is no added 3-hexyne. Substituting this into eq 16 leads to eq 17 from which all the C_o terms cancel (eq 18), indicating that the time course of the reaction is independent of C_o, as observed. The time course

$$\frac{dC_oX}{dt} = \frac{-2k_1k_2C_o^{\,2}X^2}{{}^1/_2k_{-1}(C_o - C_oX) + k_2C_oX} \quad (17)$$

$$\frac{dX}{dt} = \frac{-2k_1k_2X^2}{{}^1/_2k_{-1}(1 - X) + k_2X} \quad (18)$$

of the reaction is reasonably well fit by eq 18, given the scatter in the data, with $k_1 = 1.9 \times 10^{-4}\ s^{-1}$ at 60 °C (from the 2-butyne exchange reaction) and $k_{-1}/k_2 \approx 40$.

Scheme 4 sketches a possible mechanism from **10** to **11**. Nucleophilic attack of the amide lone pair of **10** on the empty coordination site of **B** to form a μ-amido species, as is typical of low-valent metal amido complexes.[38] The amide lone pair is basic and apparently coordinates Li^+ in **10**·LiOTf. Proton transfer from the bridging amide to the terminal one forms a μ-imido dimer with an ammonia coligand. Hydrogen migration

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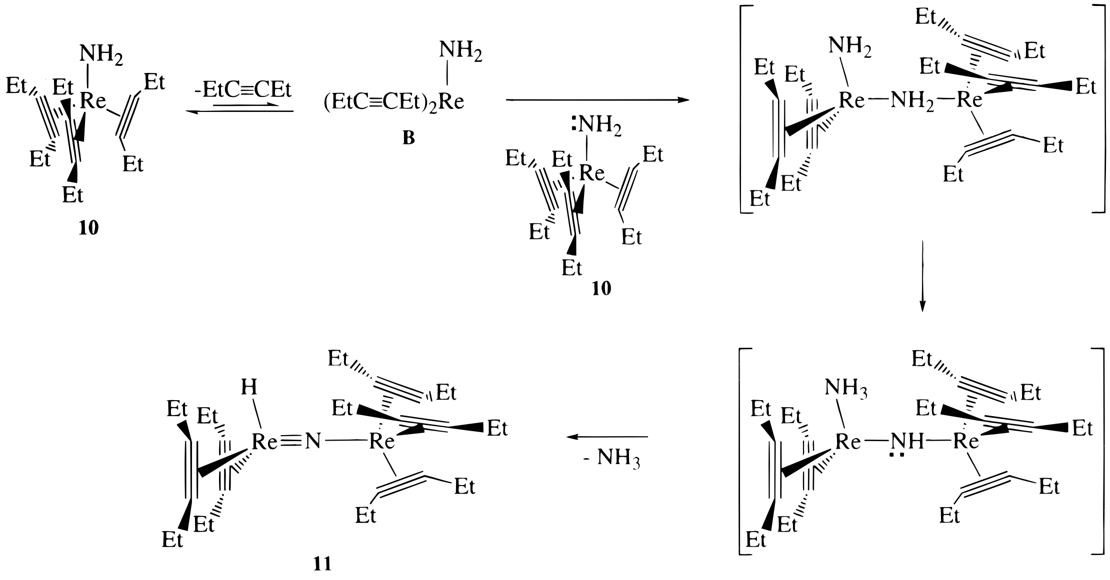
[36] (36) Protonation of **5** at rhenium would appear to occur with only minor rearrangement, based on the structures of $[Re(O)(MeC{\equiv}CMe)_2]$-[Na(crypt)][18] and $Re(O)I(MeC{\equiv}CMe)_2$.[12]

[37] (37) As observed in pyridine exchange reactions in $[Re(O)py(RC{\equiv}CR)_2]^+$, see: Mayer, J. M.; Tulip, T. H.; Calabrese, J. C.; Valencia, E. *J. Am. Chem. Soc.* **1987**, *109*, 157−163.

[38] (38) (a) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley-Interscience: New York, 1980. (b) Fryzuk, M. D.; Mongomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1−40.

Scheme 4. Possible Mechanism for the Rearrangement of 10 to 11



in this complex along with loss of ammonia, similar to the rearrangement of **3**, affords the product. The data are, thus, consistent with a 1,2-hydrogen migration step in the rearrangement of **10** but do not require it. The resistance of the adduct **10**·LiOTf to rearrange may be due to the Lewis acid occupying the nitrogen lone pair and, therefore, preventing the attack on **B**. Alternatively, the presence of the Lewis acid may inhibit alkyne dissociation to give **B**. The migration in **3** is similarly inhibited by the formation of hydrogen bonds to water or methanol, a form of Lewis acid complexation of the lone pair.

Conclusions

The rhenium hydroxide and amide complexes Re(OH)(EtC≡CEt)$_3$ (**3**) and Re(NH$_2$)(EtC≡CEt)$_3$ (**10**) rearrange at ambient temperatures with migration of a hydrogen from oxygen or nitrogen to the rhenium center, a migratory deinsertion or α-elimination reaction. Complex **3** forms the oxo−hydride complex Re(O)H(EtC≡CEt)$_2$ (**4**), while **10** produces the μ-nitrido dimer (EtC≡CEt)$_3$Re−N≡Re(H)(EtC≡CEt)$_2$ (**11**). Neither rearrangement occurs by the typical organometallic mechanism of initial ligand loss followed by deinsertion. The hydroxide complex **3** does appear to lose an alkyne on the time scale of the rearrangement, but this is not on the pathway to the oxo−hydride product. Hydrogen migration is proposed to occur in the coordinatively saturated tris(alkyne) species **3**, either synchronously with or prior to the loss of alkyne. A deprotonation−reprotonation mechanism is not occurring except in the presence of KOMe, KO^{t}Bu, or KOPh, which catalyze the conversion of **3** to **4** via the oxo anion (EtC≡CEt)$_2$ReO$^-$ (**5**). Isolated samples of **5** do not act as catalysts, apparently because of slow proton transfer kinetics. Rearrangement of **10** is suggested to occur by initial alkyne loss to give Re(NH$_2$)(EtC≡CEt)$_2$, which undergoes rate-limiting attack by an amide ligand of another molecule of **10**. The related sulfhydryl complex Re(SH)(EtC≡CEt)$_3$ (**13**) does not rearrange up to its decomposition temperature of 150 °C. The $\Delta G°$ for conversion of **3** to **4** is -12 ± 8 kcal/mol, as derived from estimated pK_a values. The inertness of the sulfhydryl complex may be due to an inversion of the thermochemistry such that the sulfido−hydride complex is uphill.

Experimental Section

Syntheses were performed using standard vacuum line and glovebox techniques except where noted. Solvents were dried and deoxygenated according to standard methods.[39] KOH (Mallinkrodt), NaN(SiMe$_3$)$_2$ (Aldrich), KO^{t}Bu (Aldrich), NH$_3$ (Aldrich), MeNH$_2$ (Matheson), NaNH$_2$ (Aldrich), and NaSH (Aldrich) were used as received. PhNH$_2$ (Mallinkrodt) was freshly distilled prior to use. *p*-Toluidine and *p*-nitroaniline (Aldrich) were sublimed prior to use. KOPh, K[*p*-OC$_6$H$_4$NO$_2$], and KOMe were made *in situ* by addition of their respective alcohols to potassium metal in toluene. Re(OTf)(EtC≡CEt)$_3$ (**2**)[10] and (EtC≡CEt)$_2$Re(O)Na (**5**)[18] were synthesized as described elsewhere. Some reactions were performed in sealed NMR tubes, and the progress of the reactions was followed by the change in the NMR spectra. Reagents and solvent were added to NMR tubes sealed to a ground glass joint and fitted with a needle valve. The tubes were cooled to 77 K, degassed, sealed with a torch, and thawed under a stream of acetone.

NMR spectra were taken on a Bruker AF300, AC200, or WM500 spectrometer; the Bruker AF300 was used in the variable-temperature studies, in C$_7$D$_8$. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of SiMe$_4$ and are referenced to the solvent peaks: δ (multiplicity, coupling constant, number of protons, assignment). ^{19}F chemical shifts are reported in ppm with CF$_3$COOH used as an external reference. IR spectra were taken on a Perkin-Elmer Series 1600 FT-IR spectrometer and are reported in cm^{-1}. Mass spectra were taken on a Kratos Analytical spectrometer using the direct inlet probe method. FAB-MS spectra were taken on a VG 70 SEQ tandem hybrid instrument of EBqQ geometry. Analytical data were determined by Canadian Microanalytical Service, Inc.

Re(I)(EtC≡CEt)$_3$ (1). Synthesized as described elsewhere[15] or by the following procedure. To a solution of 4.7 g (9.5 mmol) of Re(O)I(EtC≡CEt)$_2$ in 50 mL of benzene, 2.0 mL (10.8 mmol, 1.1 equiv) of PMePh$_2$, and 1.5 mL (13.2 mmol, 1.4 equiv) of 3-hexyne were syringed in. The reaction was stirred under inert atmosphere at room temperature for 10 days. The solvent was removed, and the remaining mixture was eluted

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[39] (a) Perin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988. (b) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley-Interscience: New York, 1967.

down a silica gel column in the air using 5% EtOAc/hexanes. After removal of the solvent, $PMePh_2$ was sublimed away, leaving 2.7 g (50% yield) of **1**.

$Re(OH)(EtC\equiv CEt)_3$ (3). To 0.75 g (1.3 mmol) of $Re(OTf)(EtC\equiv CEt)_3$ (**2**) in 35 mL of benzene was syringed 0.5 mL (28 mmol, 21 equiv) of water, and the suspension was stirred for 1 h under nitrogen. The solution was then transferred via a cannula over 0.78 g of KOH (15 mmol, 12 equiv). The mixture was stirred for another hour, with the solution turning from gray-brown to yellow with formation of green-gray solids. The solvent was removed *in vacuo*, and 30 mL of pentane was transferred in. Filtration, removal of the volatiles, and recrystallization from pentane gave 0.21 g (38% yield) of **3** as a faintly yellow solid. ^1H NMR (C_6D_6, 300 K): 1.10 (t, 7 Hz, 18 H, $CH_3CH_2C\equiv CCH_2CH'_3$), 2.53 (br, 1 H, $Re-OH$), 3.1 (br, 12 H, $MeCH_2C\equiv CCH'_2Me$). ^1H NMR (C_7D_8, 207 K): 1.14, 1.17 (t, 7 Hz, each 9 H, $CH_3CH_2C\equiv CCH_2CH'_3$), 2.49 (br, 1 H, $Re-OH$), 2.92, 3.25 (q, 7 Hz, each 6 H, $MeCH_2C\equiv CCH'_2Me$). $^{13}C\{^1H\}$ NMR (C_7D_8, 240 K): 14.2, 14.7 ($CH_3CH_2C\equiv CCH_2C'H_3$), 19.8, 29.5 ($MeCH_2C\equiv CC'H_2Me$), 167.6, 179.0 ($EtC\equiv C'Et$). MS: 368/366 ($[M - \text{acetylene}]^+$, 100). IR (Nujol, NaCl): 3630 (s, ν(OH)), 1748 ($\nu(C\equiv C)$), 1731 (w, $\nu(C\equiv C)$), 1304, 1253, 1152, 1064, 944, 822, 722. Anal. Calcd for $C_{18}H_{31}ORe$: C, 48.08; H, 6.95. Found: C, 47.57; H, 6.81.

$Re(OD)(EtC\equiv CEt)_3$ (3-*d*). All glassware was flame-dried, washed with D_2O, and flame-dried again. Following the procedure for **3**, 0.281g (0.623 mmol) of **2**, 50 mL of benzene, and 0.11 mL of D_2O were stirred over NaOD, which was synthesized *in situ* from 0.3 g of Na and excess D_2O. Recrystallization yielded 94 mg (43%) of pale yellow solids, which were then washed with 1.0 mL of D_2O in benzene and were recrystallized again. The enrichment was found to be close to 70% based on the integrals of $Re-OH$ and the methylene protons in the ^1H NMR spectrum. IR (Nujol): 2677 (s, ν(OD)); calcd, 2633 cm^{-1}. Other spectral data are similar to that of **3**.

$[Re(NH_3)(EtC\equiv CEt)_3]OTf$ (6). A solution of 0.163 g (0.281 mmol) of **2** in 15 mL of benzene was stirred under 1 atm of NH_3 gas for 30 min. The gas and the solvent were then removed *in vacuo*, and the solids were washed with pentane. Filtration and removal of the volatiles gave 0.144 g (86% yield) of **6** as an off-white solid. ^1H NMR (C_6D_6): 0.94, 1.08 (t, 7 Hz, each 9 H, $CH_3CH_2C\equiv CCH'_2CH'_3$), 2.92, 3.29 (q, 7 Hz, each 6 H, $MeCH_2C\equiv CCH'_2Me$), 6.55 (s, 3 H, $ReNH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 13.5, 14.6 ($CH_3CH_2C\equiv CCH_2C'H_3$), 20.8, 28.2 ($MeCH_2C\equiv CC'H_2Me$), 163.2, 180.2 ($EtC\equiv C'Et$). ^{19}F NMR (C_6D_6): −2.34. FAB-MS: 450/448 ($[M]^+$, 100). IR (Nujol, NaCl): 3319, 3272, 3178 ($\nu(NH_3)$), 1748, 1735 (w, $\nu(C\equiv C)$), 1643 (NH_3 bend), 1267 (ν(OTf)), 1155, 1026, 720, 632. Anal. Calcd for $C_{19}H_{33}F_3NO_3ReS$: C, 38.11; H, 5.56; N, 2.34. Found: C, 37.94; H, 5.36; N, 2.32.

$[Re(NH_2CH_3)(EtC\equiv CEt)_3]OTf$ (7). In a procedure similar to that of **6**, 0.122 g (0.210 mmol) of **2** in 15 mL of benzene was stirred under 1 atm of CH_3NH_2 gas for 30 min. ^1H NMR (C_6D_6): 0.95, 1.07 (t, 7 Hz, each 9 H, $CH_3CH_2C\equiv CCH'_2CH'_3$), 2.98, 3.27 (q, 7 Hz, each 6 H, $MeCH_2C\equiv CCH'_2Me$), 3.77 (t, 6 Hz, 3H, NH_2CH_3), 7.68 (q, 6 Hz, 2 H, NH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): 13.4, 14.6 ($CH_3CH_2C\equiv CCH_2C'H_3$), 21.6, 27.9 ($MeCH_2C\equiv CC'H_2Me$), 36.5 ($NH_2CH_3$), 164.2, 182.1 ($EtC\equiv C'Et$). ^{19}F NMR (C_6D_6): −2.27. FAB-MS: 464/462 ($[M]^+$, 100). IR (Nujol, NaCl): 3260, 3166 ($\nu(NH_2)$), 1749 (w, $\nu(C\equiv C)$), 1607 (NH_2 bend), 1278 (ν(OTf)), 1243, 1155, 1032, 944, 720, 632. Anal. Calcd for $C_{20}H_{35}F_3NO_3ReS$: C, 39.20; H, 5.56; N, 2.29. Found: C, 38.89; H, 5.71; N, 2.28.

$[Re(NH_2C_6H_4\text{-}p\text{-}CH_3)(EtC\equiv CEt)_3]OTf$ (8). A solution of 0.197 g (0.331 mmol) of **2** and 0.037 g (0.35 mmol, 1.02 equiv) of $p\text{-}CH_3C_6H_4NH_2$ in 15 mL of benzene was stirred for 2 h. After the solvent was removed *in vacuo*, the solids were washed with pentane. Filtration and removal of the volatiles gave **8** as an off-white solid. ^1H NMR (C_6D_6): 0.98, 1.04 (t, 7 Hz, each 9 H, $CH_3CH_2C\equiv CCH'_2CH'_3$), 2.13 (s, 3 H, $NH_2C_6H_4\text{-}p\text{-}CH_3$), 3.03, 3.17 (q, 7 Hz, each 6 H, $MeCH_2C\equiv CCH'_2Me$), 7.06, 7.82 (d, each 2 H, $NH_2C_6H_4Me$), 9.59 (s, 2 H, NH_2Tol). $^{13}C\{^1H\}$ NMR (C_6D_6): 13.4, 14.6 ($CH_3CH_2C\equiv CCH_2C'H_3$), 20.8, 28.2 ($MeCH_2C\equiv CC'H_2Me$), 22.1 ($NH_2C_6H_4\text{-}p\text{-}CH_3$), 115.3, 129.9, 136.0, 140.5 ($Re-NH_2C_6H_4Me$), 164.5, 181.4 ($EtC\equiv C'Et$). ^{19}F NMR (C_6D_6): −2.27. FAB-MS: 540/538 ($[M]^+$, 100). IR (Nujol, NaCl): 3190, 3095 ($\nu(NH_2)$), 1614, 1572 (NH_2 bend), 1288 (ν(OTf)), 1222, 1030, 950, 819, 722, 639. Anal. Calcd for $C_{26}H_{39}F_3NO_3ReS$: C, 45.33; H, 5.71; N, 2.03. Found: C, 44.44; H, 5.50; N, 1.93.

$Re(NH_2)(EtC\equiv CEt)_3$ (10). A solution of 0.071 g (0.12 mmol) of **6** and 0.010 g (0.26 mmol, 2.1 equiv) of $NaNH_2$ in 20 mL of THF was stirred for 60 min. The solvent was removed *in vacuo*, and 20 mL of benzene was transferred in. After the mixtue was stirred for 5 min and filtered, the solvent was removed *in vacuo* and the solids were washed with pentane. Recrystallization from pentane gave 0.035 g (65% yield) of **10** as a light yellow solid. ^1H NMR (C_6D_6, 300 K): 1.02 (t, 7 Hz, 18 H, $CH_3CH_2C\equiv CCH_2CH'_3$), 3.11 (q, 7 Hz, 12 H, $MeCH_2C\equiv CCH'_2Me$), 6.47 (s, 2 H, $ReNH_2$). ^1H NMR (C_7D_8, 253 K): 1.12, 1.35 (t, 7 Hz, each 9 H, $CH_3CH_2C\equiv CCH_2CH'_3$), 3.04, 3.57 (q, 7 Hz, each 6 H, $MeCH_2C\equiv CCH'_2Me$), 7.06 (br, 2 H, $ReNH_2$). $^{13}C\{^1H\}$ NMR (C_7D_8, 253 K): 14.0, 15.2 ($CH_3CH_2C\equiv CCH_2C'H_3$), 19.8, 28.3 ($MeCH_2C\equiv CC'H_2Me$), 162.8, 179.8 ($EtC\equiv C'Et$). MS: 449/447 ($[M]^+$, 100). IR (Nujol, NaCl): 3342 ($\nu(NH_2)$), 1155, 1096, 944, 720. The thermal instability of **10** has prevented obtaining suitable analytical data.

$(EtC\equiv CEt)_3Re-N\equiv Re(H)(EtC\equiv CEt)_2$ (11). A benzene solution of **10** was stirred at 50 °C for 12 h, followed by the removal of the solvent *in vacuo.* Attempts to purify **11** by recrystallization, sublimation, or chromatography were unsuccessful. ^1H NMR (C_6D_6): 1.02, 1.05 (t, 7 Hz, each 6 H, $Re(CH_3CH_2C\equiv CCH_2CH'_3)_2$), 1.61, 1.62 (t, 7 Hz, each 9 H, $Re(CH_3CH_2C\equiv CCH_2CH'_3)_3$), 2.91, 3.32 (q, 7 Hz, each 6 H, $Re(MeCH_2C\equiv CCH'_2Me)_3$), 3.43, 3.60 (m, each 4 H, $Re(MeCHH'C\equiv CCH''H'''Me)_2$), 5.3 (s, 1 H, ReH). DIP-MS: 797 ($[M]^+$), 715 ($[M - \text{acetylene}]^+$, 100). IR (Nujol, NaCl): 1930 ($\nu(Re-H)$), 1742 ($\nu(C\equiv C)$), 1642, 1584, 1449, 1367, 1302, 1255, 1079 ($\nu(Re\equiv N-Re)$), 797, 714.

$(EtC\equiv CEt)_3Re\text{-}N\equiv Re(Cl)(EtC\equiv CEt)_2$ (12). A few drops of CCl_4 were added to a C_6D_6 solution of **11**. Overnight, ^1H NMR resonances for **11** disappear and new resonances grow in. Solvent removal *in vacuo* gives **12**. Attempts to purify **12** from larger scale reactions were unsuccessful. ^1H NMR (C_6D_6): 1.08, 1.10 (t, 7 Hz, each 6 H, $Re(CH_3CH_2C\equiv CCH_2CH'_3)_2$), 1.47, 1.51 (t, 7 Hz, each 9 H, $Re(CH_3CH_2C\equiv CCH_2CH'_3)_3$), 2.87, 3.32 (q, 7 Hz, each 6 H, $Re(MeCH_2C\equiv CCH'_2Me)_3$), 3.6, 3.8 (m, each 4 H, $Re-(MeCHH'C\equiv CCH''H'''Me)_2$). DIP-MS: 749 ($[M - \text{acetylene}]^+$, 100). IR (Nujol, NaCl): 1155, 1085 ($\nu(Re\equiv N-Re)$), 973, 938, 890, 726.

$Re(SH)(EtC\equiv CEt)_3$ (13). To a mixture of 0.21 g (0.36 mmol) of **2** and 0.023 g (0.41 mmol, 1.1 equiv) of NaSH, about 15 mL of dry THF was added. The mixture was stirred for 1.5 h. The solvent was removed *in vacuo*, and about 20 mL of benzene was transferred in. The solution was stirred for 5 min and filtered. Benzene was removed *in vacuo.* The resulting solid was recrystallized from pentane to afford 40% yield (0.067 g) of gray **13**. ^1H NMR (C_6D_6): 1.01, 1.08 (t, 7 Hz, each 9 H, $CH_3CH_2C\equiv CCH_2CH'_3$), 1.15 (s, 1 H, $ReSH$), 3.12, 3.24 (q, 7 Hz, each 6 H, $MeCH_2C\equiv CCH'_2Me$). $^{13}C\{^1H\}$ NMR (C_6D_6): 13.8, 14.2 ($CH_3CH_2C\equiv CCH_2C'H_3$), 22.2, 28.2 ($MeCH_2C\equiv CC'H_2Me$), 164.5, 174.7 ($EtC\equiv C'Et$). MS: 466/464 ($[M]^+$, 100). IR (Nujol, NaCl): 2555 (w, ν(SH)), 1304, 1255, 1150, 1063, 944, 822, 722. Anal. Calcd for $C_{18}H_{31}SRe$: C, 46.42; H, 6.71. Found: C, 46.55; H, 6.67.

$Re(O)(CH{=}CH_2)(EtC\equiv CEt)_2$ (14). Vinylmagnesium bromide in THF (0.6 mL, 1 M, 0.6 mmol) was added slowly to 0.13 g (0.98 mmol, 1.6 equiv) of $ZnCl_2$ in 10 mL of THF at −78 °C. White solids formed, and the yellow mixture was slowly warmed to room temperature and stirred for 1 h. The suspension was then slowly added via a syringe to a −78 °C solution of 0.113 g (0.23 mmol, 0.4 equiv) of $Re(O)I(EtC\equiv CEt)_2$ in 25 mL of THF. It was stirred for 3 h, after which time the solvent was removed *in vacuo.* Benzene (30 mL) was transferred in, and the solution was stirred for 5 min and filtered. Benzene was removed *in vacuo* to give **14** as an oil. Complex **14** is thermally unstable and decomposes to an NMR-silent material within 2 h. ^1H NMR (C_6D_6): 1.15, 1.21 (t, 7 Hz, each 6 H, $CH_3CH_2C{\equiv}CCH_2CH'_3$), 2.9 (m, 8 H, $MeCHH'C{\equiv}CCH''H'''Me$), 5.4 (d of d, $J_{gem} = 1$ Hz, $J_{trans} = 18$ Hz, $ReCH{=}CH_{cis}H_{trans}$), 6.1 (d of d, $J_{gem} = 1$ Hz, $J_{cis} = 13$ Hz, $Re{-}CH{=}CH_{cis}H_{trans}$); the peak for $ReCH{=}CH_2$ was not identified.

Kinetics. C_6D_6 (Cambridge Isotope), 3-hexyne, and 2-butyne were dried over sodium overnight and were vacuum transferred prior to use. Ferrocene was either weighed on an analytical balance on the bench top and degassed at −77 °C prior to entering the glovebox or sublimed *in vacuo* and weighed in the glovebox. In the glovebox, stock solutions (C_6D_6) of Cp_2Fe and **3** or **10** were prepared, and appropriate quantities of these solutions, 3-hexyne, and C_6D_6 were syringed into NMR tubes to attain a volume of 400 μL. For the sample with 2-butyne, the alkyne was vacuum transferred into the NMR tube. The NMR tubes were cooled in liquid nitrogen, sealed with a torch, and thawed immediately prior to use.

In the ambient-temperature kinetic studies of **3** → **4**, the tubes were kept in an insulated, room-temperature (21 ± 1 °C) water bath. For the high-temperature experiments, the tubes were placed in the NMR probe at room temperature. After completing the lock and shim processes, the temperature control unit was set to the desired temperature and the automated acquisition program was activated. The shims were later adjusted as the sample temperature rose to the designated temperature. The actual temperature was calculated using a methanol sample.[40] Concentrations were calculated by integrating the hydride resonance of **4** (δ 6.02) and the methylene resonances (δ 2.0) of free 3-hexyne *vs* a ferrocene standard (δ 4.00). The concentration of $Re(O)D(EtC{\equiv}CEt)_2$ (**4-*d***) was found by subtracting the concentration of **4** from the concentration of the free 3-hexyne. In the kinetic studies of **10** → **11**, the tubes were kept in an oil bath at 59.7 ± 0.4 °C. At appropriate times, the tubes were removed and NMR spectra obtained at room temperature. The concentrations of **11**, **12**, and free alkyne were calculated by integrating the methylene resonances *vs* Cp_2Fe.

X-ray Crystallographic Structure Determination of $Re(OTf)(EtC{\equiv}CEt)_3$ (2). Clear crystals were grown by the slow evaporation of a saturated pentane solution in the glovebox. A fragment was encased in epoxy on a glass fiber and transferred to an Enraf-Nonius CAD4 diffractometer. A unit cell was obtained from 25 reflections in the range $2\theta = 24{-}30°$ (Table 1). A high-χ (88°) reflection was scanned to provide for an absorption correction. The intensity of standard reflections decayed substantially (75%) during data collection, without loss of orientation. Reduction of data was carried out using XCAD4, and all further work was carried out using the PC version of Siemens SHELX. The Laue merging *R* factor was 1.6% for 345 reflections, indicating that the decay factors were applied well. The structure was solved from direct methods, and full refinement showed a large amount of disorder, though not involving any of the atoms in the rhenium coordination sphere. Disorder in the ethyl groups was modeled with two equal occupancy sites for C(1), C(2), C(6), C(7), C(11), C(12), C(13), C(14), C(17), and C(18). Figure 1 shows the set of ligand carbons that best fit on the planes containing Re, O(1), and the acetylenic carbons for each ligand. The smeared electron density of the CF_3 group was modeled with seven fluorine atoms around the carbon (F1, F1A, F2, and F2A at 50% occupancy and F3, F3A, and F3B at 33% occupancy).

X-ray Crystallographic Structure Determination of $Re(OH)(EtC{\equiv}CEt)_3$ (3). Clear crystals were grown by the slow evaporation of a saturated pentane solution of **3** in the glovebox freezer. A crystal was mounted with stopcock grease in a cold nitrogen stream (−60 °C) on an Enraf-Nonius CAD4 diffractometer. A unit cell was obtained from 25 reflections in the range $2\theta = 26{-}34°$, and data were collected with minimal decay (Table 1). A spherical absorption correction was applied, as it gave a better *R* of averaging (2.7%) than an empirical correction (3.4%). The cell errors, the soft and oily nature of the crystal, and the broad diffraction peaks suggested less than optimal crystal quality. The data was refined in $P2_1/m$ using Siemens SHELXTL PLUS (PC Version), initially with anisotropic thermal parameters for all non-hydrogen atoms, to $R = 7.9\%$, $R_w = 7.9\%$, and goodness of fit = 1.50. In this space group, the rhenium, oxygen, and one of the hexyne ligands lie in a mirror plane. Anisotropic thermal parameters for three of the atoms, O(1), C(1), and C(9) (two of which lie on the mirror plane), were nonpositive definite. This may reflect a disorder problem, possibly involving the mirror plane, but alternative refinements in the acentric space group $P2_1$ were no better, and statistical tests did not provide strong guidance (presumably because the scattering is dominated by the rhenium atom). No attempts were made to model any disorder because of the data quality and the lack of any indication of disorder in the difference maps. Because of the nonpositive definite thermal parameters, final refinement in $P2_1/m$ was done with all carbon and oxygen atoms refined isotropically. The hydroxide hydrogen was placed on a reasonable peak in the electron-density map.

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Supporting Information Available: Text giving the derivations of the kinetic equations for alternative pathways for the rearrangements of **3** and **10** and tables of atom positional and thermal parameters and bond distances and angles for **2** (8 pages). Crystallographic details for **3** are available as Supporting Information for ref 9. Ordering information is given on any current masthead page.

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[40] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972.