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Rearrangement of a Rhenium Hydroxide Complex to an Oxo-Hydride Compound[1]

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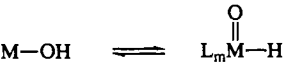
Hydroxide ligands are ubiquitous in aqueous chemistry and are present on most oxide surfaces. They are related to oxo-hydride species through the interconversion in equation 1, formally a 1,2-hydrogen migration or an α-elimination/insertion reaction.


(1)

$$L_nM{-}OH \rightleftharpoons L_m\overset{\overset{\displaystyle O}{\|}}{M}{-}H \qquad (1)$$

This is one of the simplest reactions of a metal–oxo group and is of potential importance because hydroxide and oxo-hydride species should have quite different structures and reactivity. Only four types of oxo-hydride compounds have been synthesized to date: $Re(O)H(RC{\equiv}CR)_2$ (R = Me, Et (**2**), Ph),[4] $Cp^*{}_2Ta(O)H$ ($Cp^* = C_5Me_5$),[5] $[Re(O)HX(Cyttp)]^+$ (X = H, F; Cyttp = $[Cy_2P(CH_2)_3]_2PPh$),[6] and $(HBpz_3)Re(O)(H)Cl$ ($HBpz_3$ = hydridotris(1-pyrazolyl)borate).[7] The formation of the tantalum complex was suggested to involve a reaction similar to that shown in eq. 1.[5] This report describes the synthesis and characterization of the rhenium(I) tris(acetylene) hydroxide complex $Re(OH)(EtC{\equiv}CEt)_3$ (**1**) and a mechanistic study of its rearrangement to the oxo-hydride complex $Re(O)H(EtC{\equiv}CEt)_2$ (**2**). Remarkably, rearrangement occurs by initial hydrogen migration, not via initial alkyne loss from the 18-electron[8] hydroxide complex.

The hydroxide complex **1** is formed upon addition of solid KOH to a benzene solution of the aquotris(acetylene) complex $[Re(OH_2)(EtC{\equiv}CEt)_3]OTf$, which in turn is formed from water and $Re(OTf)(EtC{\equiv}CEt)_3$ (OTf = triflate, O_3SCF_3).[9] Yields are quantitative by NMR, but the high solubility and the instability of **1** reduce the isolated yield to 35% after recrystallization from pentane. The X-ray crystal structure of **1**[10] (Figure 1) is quite similar to those of other tris(acetylene) compounds such as $W(CO)(PhC{\equiv}CPh)_3$[11] and $Re(OSiMe_3)(EtC{\equiv}CEt)_3$,[9] with the bond lengths and angles in **1** nearly identical to those of the latter complex. The spectroscopic data for **1**[12] are consistent with its solid-state structure. A sharp O–H stretch is observed at 3630 cm^{-1} in a Nujol mull of **1**, consistent with the absence of hydrogen bonding in the crystal (ν_{OD}, 2677, calcd, 2633). A band at the same frequency is observed in benzene solution, indicating the absence of hydrogen bonding in solution as well. NMR spectra of **1** at −30 °C show separate resonances for the ethyl groups proximal and distal to the hydroxide ligand. ^1H NMR spectra at 27 °C, however, show a single methyl triplet and a broad peak for the methylene hydrogens, indicating that the 3-hexyne ligands are fluxional, with a barrier to rotation of 14.0 ± 0.2 kcal/mol. The analogous methoxide complex $Re(OMe)(EtC{\equiv}CEt)_3$ (**3**)[9] shows a similar coalescence of the ethyl signals at 50 °C ($\Delta G^{\ddagger} = 16 \pm 1$ kcal/mol).

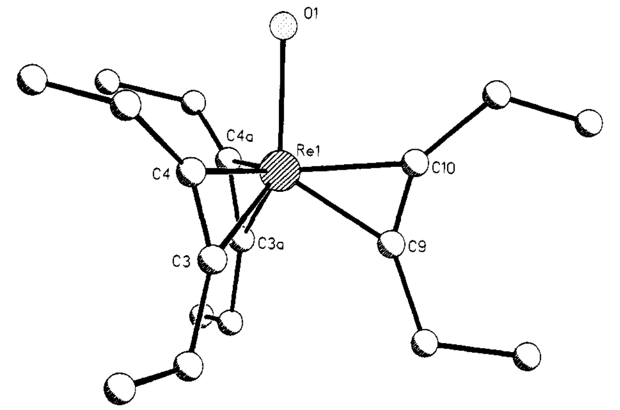


Figure 1. Pluto drawing of the X-ray crystal structure of $Re(OH)(EtC{\equiv}CEt)_3$ (**1**). Selected bond lengths (Å) and angles (deg): Re–O 2.124(16), Re–C3 2.057(16), Re–C4 2.006(16), Re–C9, 1.955(21), Re–C10 1.983(30), O–Re–C3 125.6(5), O–Re–C4 88.1(5), C3–Re–C3A 92.6(9), C4–Re–C4A 119.7(11).

Benzene solutions of **1** spontaneously rearrange to equimolar amounts of the known[4a] oxo-hydride complex **2** and free 3-hexyne over 5 days at ambient temperatures (Scheme I). The growth of the hydride peak of **2** in the ^1H NMR is found to follow first-order kinetics, with $k_{obs} = (5.6 \pm 1.2) \times 10^{-6}\ s^{-1}$ at 294 ± 1 K, independent of the initial concentration of **1** over a factor of 8. An Eyring plot of five rate constants determined at temperatures between 294 and 327 K yields $\Delta H^{\ddagger} = 17 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -25 \pm 5$ eu. The deuteroxide complex $Re(OD)(EtC{\equiv}CEt)_3$ (**1**-*d*) rearranges to the oxo–deuteride **2**-*d* more slowly, with a kinetic isotope effect $k_H/k_D = 5 \pm 1$. The presence of 1 M 3-hexyne in the benzene solution of **1** does not affect the rate of rearrangement within experimental error. Likewise, addition of 1 M 2-butyne does not appear to affect the half-life for rearrangement. Complex **2** is still the predominant product in the presence of 2-butyne, as only ca. 10% of the alkyne ligands in the oxo-hydride products have exchanged with 2-butyne to give $Re(O)H(MeC{\equiv}CMe)(EtC{\equiv}CEt)$ and $Re(O)H(MeC{\equiv}CMe)_2$. Since **2** does not exchange with 2-butyne under these conditions, the formation of butyne-containing products most likely results from ligand exchange in **1** prior to rearrangement.[13] The methoxide derivative **3** undergoes exchange with added 2-butyne with a half-life of only a few hours at ambient temperatures, and kinetic studies indicate a dissociative mechanism.[9] The methoxide complex thus undergoes ligand exchange much more rapidly than **1**.

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[1] Low-Valent Rhenium-Oxo Compounds 12. For part 11, see ref 4b; for part 13, see ref 9.

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[4] (a) $Re(O)H(MeC{\equiv}CMe)_2$, $Re(O)H(EtC{\equiv}CEt)_2$: Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617. (b) $Re(O)H(PhC{\equiv}CPh)_2$: Conry, R. R.; Mayer, J. M. *Organometallics* **1991**, *10*, 3160.

[5] (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.

[6] Kim, Y.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 8600.

[7] Brown, S. N.; Mayer, J. M., unpublished results.

[8] King, R. B. *Inorg. Chem.* **1968**, *7*. 1044–1046. Wink, D. J.; Creagan, B. T. *Organometallics* **1990**, *9*, 328–334. Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1–100.

[9] Conry, R. R.; Mayer, J. M. *Organometallics*, in press.

[10] Crystal data for **1**: $P2_1/m$, $a = 7.734(2)$ Å, $b = 13.123(4)$ Å, $c = 9.162(5)$ Å, $\beta = 101.65(3)°$, $V = 910.7(6)$ Å^3, $Z = 2$. Data were collected at 213 K using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation: 939 independent, 889 observed reflections ($2.0° < 2\theta$, 45.0°, $F > 4\sigma(F)$). Refinement of 53 parameters using Siemens SHELX (Re anisotropic, C, O isotropic) converged to $R = 8.4$, $R_w = 8.9$, GOF = 1.52.

[11] Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Ross, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261.

[12] ^1H NMR (C_6D_6, 300 K): δ 1.10 (t, 7 Hz, 18 H, $CH_3CH_2C{\equiv}CCH'_2CH'_3$); 2.53 (br, 1 H, ReO*H*); 3.1 (br, 12 H, $CH_3CH_2C{\equiv}CCH'_2CH'_3$). $^{13}C\{^1H\}$ NMR (C_7D_8, 270 K): δ 14.2, 14.7 ($CH_3CH_2C{\equiv}CCH_2C'H_3$); 19.8, 29.5 ($CH_3CH_2C{\equiv}CC'H_2CH_3$); 167.6, 179.0 ($CH_3CH_2C{\equiv}C'CH_2CH_3$). MS: *m/z* 368/366 [M − acetylene]$^+$ (100). IR (Nujol): 3630 s, ν(OH); 1748, 1731 w, $\nu(C{\equiv}C)$; 1304, 1253, 1152, 1064, 944, 822, 722. Anal. Calcd for $C_{18}H_{31}ORe$: C, 48.00; H, 6.89. Found: C, 47.57; H, 6.81.

[13] Ligand exchange could also occur in an intermediate on the pathway to **2**, but such a pathway is hard to imagine given the primary isotope effect and the absence of ligand inhibition.

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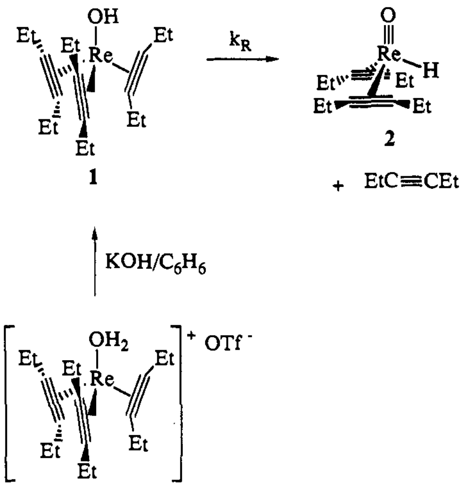
Scheme I. Synthesis and Rearrangement of $\mathrm{Re(OH)(EtC{\equiv}CEt)_3}$ (**1**)



The kinetic and mechanistic data rule out the standard organometallic mechanism of initial ligand loss and rearrangement occurring in the coordinatively unsaturated rhenium(I) bis(acetylene) hydroxide intermediate, $\mathrm{[Re(OH)(EtC{\equiv}CEt)_2]}$ (eq 2).' Initial ligand loss (k_1) cannot be rate limiting, because a

$$\underset{\mathbf{1}}{\mathrm{Re(OH)(EtC{\equiv}CEt)_3}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{EtC{\equiv}CEt}}{\underset{+}{\mathrm{[Re(OH)(EtC{\equiv}CEt)_2]}}} \cancel{\xleftarrow{k_2}} \underset{\mathbf{2}}{\mathrm{Re(O)H(EtC{\equiv}CEt)_2}} \qquad (2)$$

primary kinetic isotope effect is observed ($k_H/k_D = 5$). Similarly, preequilibrium loss of acetylene is inconsistent with a lack of ligand inhibition and inconsistent with rearrangement being faster than ligand exchange with added 2-butyne. It is also very unlikely that rearrangement occurs by deprotonation to the oxo anion $\mathrm{[Re(O)(EtC{\equiv}CEt)_2]^-}$ (**4**),[14] catalyzed by trace base. Deprotonation of **1** gives **4** but not cleanly, and the rate of rearrangement is reproducible and unaffected by the presence of *p*-iodotoluene, which reacts rapidly with **4**.[14]

We propose that rearrangement takes place intramolecularly in the coordinatively saturated tris(acetylene) species **1**, so that k_{obs} corresponds directly to the rate of rearrangement (k_R in Scheme I). Hydrogen migration must take place either synchronously with or prior to the loss of ligand.[15] The small ΔH^* of 17 kcal/mol is consistent with Re–H bond formation accompanying O–H bond cleavage, and the negative ΔS^* (−25 eu) suggests a transition state that is more ordered than the ground state. The small amount of 2-butyne exchange observed during the rearrangement likely occurs via 3-hexyne dissociation from **1** (k_1, k_{-1} in eq 2), by analogy with the reactivity of the methoxide **3**. Thus the unsaturated intermediate $\mathrm{[Re(OH)(EtC{\equiv}CEt)_2]}$ appears to be accessible, but—remarkably—it is not on the pathway to rearrangement.

Conversion of a hydroxide to an oxo-hydride is a facile process in this system. In contrast, the analogous methoxide, phenoxide, and acetate complexes do not readily rearrange to the known oxo–methyl, –phenyl, and –acyl complexes.[9] Hydrogen appears to have a much higher migratory aptitude[16] than other groups, as has been found in the related tantalum migrations[5b] and in other organometallic rearrangements.[17] We are currently exploring this rearrangement with other organic groups and with amide and thiolate ligands in place of alkoxide or hydroxide.

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Supplementary Material Available: Experimental procedures, spectral data, and crystallographic tables for **1** (11 pages); observed and calculated sturcture factors (3 pages). Ordering information is given on any current masthead page.

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[14] Spaltenstein, E.; Conry, R. R.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8741–8742. Cundari, T. R.; Conry, R. R.; Spaltenstein, E.; Hall, K. A.; Tahmassebi, S. K.; Mayer, J. M., manuscript in preparation. Protonation of **4** gives **2**.

[15] The primary isotope effect rules out preequilibrium hydrogen migration followed by rate-limiting ligand loss (the equilibrium isotope effect for hydrogen migration is estimated to be $K_H/K_D = 2.4$ based on stretching frequencies in **1** and **2**).

[16] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 949–951.

[17] For a recent example, see: Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394–10401.