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Synthetic and Mechanistic Features of Alcohol Elimination between Gold Alkoxides and Rhenium Polyhydrides. Metal Polyhedron Reconstruction upon Protonation

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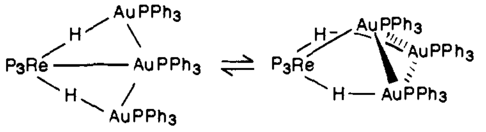
Mixed transition-metal/gold clusters have been attracting wide attention in recent years due to their potential as homogeneous catalysts and precursors to well-defined heterogeneous catalysts.[1] Strategies for the incorporation of gold into metal clusters include the addition of $AuPPh_3^+$[2] and the elimination of CH_4 from R_3PAuMe and a metal hydride[3] (usually at elevated temperature). On the basis of our recent success in forming transition-metal–copper clusters such as $[Os_3Cu_3H_9(PMe_2Ph)_9]$[4] and $[Re_4Cu_2H_{14}(PMe_2Ph)_8]$[5] by dinuclear elimination of alcohol from $[CuO\text{-}t\text{-}Bu]_4$ and H_xML_n, it seemed that a similar route for gold is currently lacking only the appropriate gold alkoxide.

The previously unknown monomeric[6] gold(I) alkoxides, Ph_3PAuOR (R = *t*-Bu (**1**); 2,4,6-*t*-$Bu_3C_6H_2$ (**2**)), can be isolated in over 90% yield as white microcrystalline solids from the reaction of NaOR with Ph_3PAuCl in THF.[7,8] The reaction of 3 equiv of Ph_3PAuO-*t*-Bu with $ReH_5(PMe_2Ph)_3$ proceeds rapidly (<1 min) at 25 °C to quantitatively produce **3**, which analyzes as $(Me_2PhP)_3ReH_2(AuPPh_3)_3$[9] and which shows equivalent $AuPPh_3$ groups and equivalent $RePMe_2Ph$ groups at high temperature (110 °C).[10] While fluxionality causes the ^1H NMR hydride signal to be undetectably broad at 25 °C, the low-temperature limiting $^{31}P\{^1H\}$ and ^1H NMR consist of a complex set of signals diagnostic of **3** existing as a mixture of two interconverting isomers. We propose (eq 1) that these involve a planar and tetrahedral arrangement of the metal atoms; a single crystal which grew from a saturated toluene solution was shown by X-ray diffraction to contain only the planar form (Figure 1).[11]



(1)

The metal-containing product in alcohol elimination is influenced by the acidity of byproduct alcohol: if $ReH_5(PMe_2Ph)_3$ is reacted with 3 equiv of Ph_3PAu(2,4,6-tri-*tert*-butylphenoxide) instead of Ph_3PAuO-*t*-Bu, a new species $[(Me_2PhP)_3ReH_3(AuPPh_3)_3^+][OR^-]$ (**4**) may be isolated as a golden yellow solid. The $^{31}P\{^1H\}$ and ^1H NMR data[12] are consistent with threefold symmetry. Compound **4** converts into **3** with liberation of 1 equiv of ROH over a period of 80 h in benzene at 25 °C but can be isolated as a stable solid with a BF_4^- counterion by the addition of 1 equiv of $HBF_4{\cdot}Et_2O$ to a THF solution of the isomeric mixture **3**. An X-ray diffraction study[13] of the BF_4^- salt, shown in Figure 2, confirms its formulation. The three $AuPPh_3$ units form an

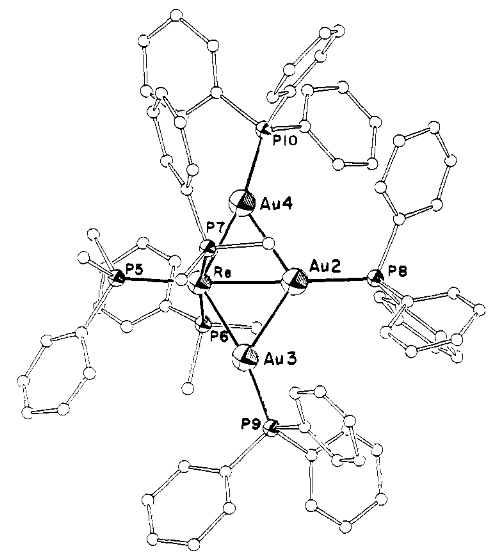


Figure 1. ORTEP drawing of the non-hydrogen atoms of $(PhMe_2P)_3ReH_2(AuPPh_3)_3$. Selected structural parameters: Re–Au(2), 2.7295 (16); Re–Au(3), 2.6881 (19); Re–Au(4), 2.6983 (20); Au(2)–Au(3), 2.8123 (20); Au(2)–Au(4), 2.7868 (19); Au(2)–P(8), 2.320 (4); Au(3)–P(9), 2.275 (4); Au(4)–P(10); 2.273 (4); Re–P(5), 2.361 (4); Re–P(6), 2.358 (4); Re–P(7), 2.374 (4) Å.

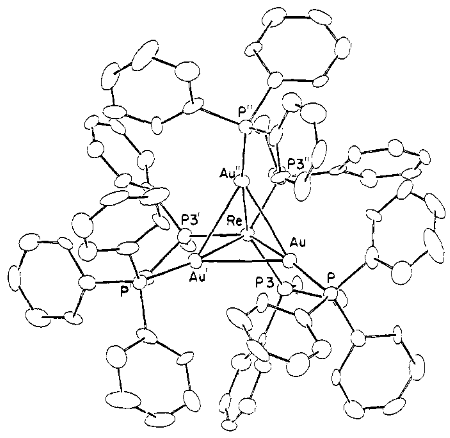


Figure 2. ORTEP drawing of the non-hydrogen atoms of $(PhMe_2P)_3ReH_3(AuPPh_3)_3^+$. A crystallographic C_3 axis passes through Re and the center of the Au_3 triangle. The three hydride ligands bridge the three Au–Re vectors. Selected structural parameters: Re–Au, 2.7231 (15); Au–Au′, 2.9310 (18); Au–P, 2.267 (5); Re–P, 2.391 (5) Å, Au′–Au–Re, 57.440 (23)°; Au′–Au–P, 127.56 (13)°; Re–Au–P, 167.77 (13)°; Au–Re–Au′, 65.12 (5)°; Au–Re–P, 149.41 (13)°; P–Re–P′, 94.55 (17)°.

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[6] Molecular weights were determined by the isopiestic method to be <600 for **1** and <800 for **2**. Exact measurements could not be obtained due to the instability of **1** and **2** in solution over extended periods of time (>24 h).

[7] (a) **1**: 360-MHz ^1H NMR (25 °C, C_6D_6) δ 7.28–6.87 (m, 15 H), 1.82 (s, 9 H); 40.5-MHz $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6) δ 27.0 (s). (b) **2**: 360-MHz ^1H NMR (25 °C, C_6D_6) δ 7.60 (s, 2 H), 7.14–6.84 (m, 15 H), 2.00 (s, 18 H), 1.47 (s, 9 H): 40.5-MHz $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6) δ 25.4 (s).

[8] (a) **1**: Anal. Calcd for $AuPOC_{22}H_{24}$: C, 49.63; H, 4.54%. Found: C, 49.60; H, 4.64. (b) **2**: Anal. Calcd for $AuPOC_{36}H_{44}$: C, 60.00; H, 6.15. Found: C, 59.81; H. 6.39.

[9] Anal. Calcd for $Au_3ReP_6C_{78}H_{80}$: C, 47.21; H, 4.06. Found: C, 47.17; H, 4.33.

[10] 40.5-MHz $^{31}P\{^1H\}$ NMR (110 °C, toluene) δ 55.3 (s, 3 P), −21.6 (s, 3 P).

[11] Crystallographic data (−155 °C) for $(PhMe_2P)_3ReH_2(AuPPh_3)_3$–toluene: $a = 13.686$ (8) Å, $b = 25.157$ (20) Å, $c = 12.558$ (8) Å, $\alpha = 91.22$ (4)°, $\beta = 115.20$ (3)°, $\gamma = 78.75$ (4)°, and $Z = 2$ in space group $P\bar{1}$. $R = 0.0543$ for 10 301 reflections with $F > 3\sigma(F)$, using a model with fixed (d(C–H) = 0.95 Å) hydrogens on carbon and anisotropic thermal parameters on all non-hydrogen atoms. Metal-bound hydrogens were not evident in final difference maps, even after correction for absorption.

[12] 360-MHz ^1H NMR (25 °C, C_6D_6) hydride resonance at δ −5.05 (septet, $J_{P\text{-}H} = 18.4$ Hz); 40.5 MHz $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6) δ 57.3 (quartet, $J_{P\text{-}P} = 11.8$ Hz, 3 P), −29.2 (quartet, $J_{P\text{-}P} = 11.8$ Hz, 3 P).

[13] (a) Crystallographic data for $[(PhMe_2P)_3ReH_3(AuPPh_3)_3]BF_4{\cdot}THF$ at −154 °C: $a = 14.585$ (5) Å, $c = 62.999$ (28) Å in space group $R\bar{3}$ with $z = 6$. $R(F) = 5.86\%$ for 2439 absorption-corrected reflections with $F > 3\sigma(F)$ and anisotropic thermal parameters on all non-hydrogen atoms of the salt. Hydrogens on carbon were included in fixed positions with d(C–H) = 0.95 Å. (b) Molecular mechanics and difference Fourier searches for hydride positions both yielded three μ_2-H sites almost exactly trans to the Re–P vectors.

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equilateral triangle which is symmetrically bound to the Re resulting in a tetrahedral framework. The conversion of **3** to **4** represents the first structural rearrangement of a four-metal core simply upon protonation.[14] Also noteworthy is the fact that protonation converts the meridional arrangement of PMe_2Ph ligands in **3** to a facial array in **4**.

In summary, the reaction of Ph_3PAuOR with transition-metal hydrides proceeds smoothly and rapidly at room temperature to give one product in essentially quantitative yield. The number of hydrides can also be increased by simple addition of H^+ and such protonation, which does not change the total valence electron count, can nevertheless cause reconstruction of the metal polyhedron. One feature of dinuclear reductive elimination (eq 2)

$$\text{M-X} + R_3PAuY \rightarrow R_3PAuM + \text{X-Y} \qquad (2)$$

as a synthetic procedure for Au/other metal(M) compounds is that it occurs without change in charge on the species containing M; it is thus particularly suitable for (but not limited to) the synthesis of uncharged molecules. This sets the methodology apart from procedures which *add* $AuPR_3^+$. Finally, the observation that proton transfer within $[(PhMe_2P)_3ReH_3(AuPPh_3)_3]OR$ completes what is stoichiometrically a dinuclear reductive elimination (even in a nonpolar solvent) emphasizes the Brønsted acidity of certain transition-metal polyhydrides.[15] Consequently, reductive elimination is not a concerted extrusion of the molecule X–Y in certain of the reactions reported here.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for $(PhMe_2P)_3ReH_2(AuPPh_3)_3$ and $[(PhMe_2P)_3ReH_3(AuPPh_3)_3]BF_4$ (3 pages). Ordering information is given on any current masthead page.

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[14] Note that metal framework rearrangement has been observed when protonation causes a CO ligand to take up a π-CO function. See: Horwitz, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8147.

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New Dimeric Quadruply Metal-Metal Bonded Molybdenum(II) Derivative with a Dibenzotetraaza[14]annulene Ligand: Access to New Mixed Valence Complexes and Structural Characterization of the Mo^{II}/Mo^{III} Dimer

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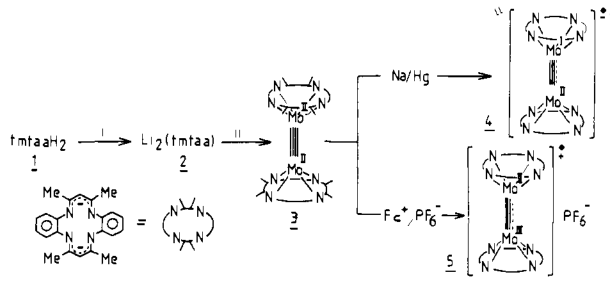
Scheme I[a]



[a] (i) 2 equiv of BuLi; (ii) 0.5 equiv of $Mo_2(OAc)_4$.

Coordination of small macrocycles such as tetraazaannulenes to transition metals is of current interest due to the complementaries of these ligands with other well-known N_4 macrocyclic derivatives such as porphyrins and phtalocyanines. The dibenzotetramethyltetraaza[14]annulene dianionic ligand[1,2] ($tmtaa^{2-} = C_{22}H_{22}N_4^{2-}$; see Scheme I), although resembling porphyrins, shows important differences relative to electronic delocalization, core size, and framework flexibility.[3]

With hopes that some of them would be used as catalysts in redox processes, or would mimic naturally occurring systems, many "$[M^{II}(tmtaa)]$-type" complexes have been synthesized.[4] However, facing the wide field of the metalloporphyrin chemistry — especially the new class of dinuclear $[ML_4]_2$ metal complexes recently reported[5-8] —chemistry of $[M^{II}(tmtaa)]_2$ dimers with nonbridging macrocycles remains still undeveloped in spite of the promising reactivity of dimeric Ru-Ru bonded complexes.[9] This lack may be attributed to the difficulties encountered in the synthesis of such nonbridged dimers.

The in situ formation of an organic dianionic species by abstraction of two protons from the neutral macrocycle $tmtaaH_2$ may be involved in complexation processes leading to $[M^{II}(tmtaa)]$-type complexes, but so far, isolation of such an intermediate has not been reported.[10] Furthermore, with M = Mo and W, tetradentate coordination of $tmtaa^{2-}$ is not observed, the only known species being the M^0 carbonyl monomers $M(CO)_4(\eta^2\text{-}tmtaaH_2)$ obtained from $M(CO)_6$ and $tmtaaH_2$.[11]

Thus to obtain $[Mo^{II}(tmtaa)]$-type complexes, a new synthetic approach was necessary. We report a convenient and high-yield synthesis of complex **3**, $[Mo(tmtaa)]_2$, involving (i) the isolation of the lithium salt Li_2tmtaa **2** and (ii) the reaction of **2** with $Mo_2(OAc)_4$.[12] We also describe some of the redox properties of **3** and the first X-ray crystal structure of a mixed-valence Mo^{II}/Mo^{III} macrocyclic complex, compound **5**, obtained by chemical oxidation of **3** (see Scheme I).

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