Heterometallic Carbonyl Cluster Oxide. Formation, Structure and Reactivity of WRe_2 Oxo-acetylide Cluster Compounds

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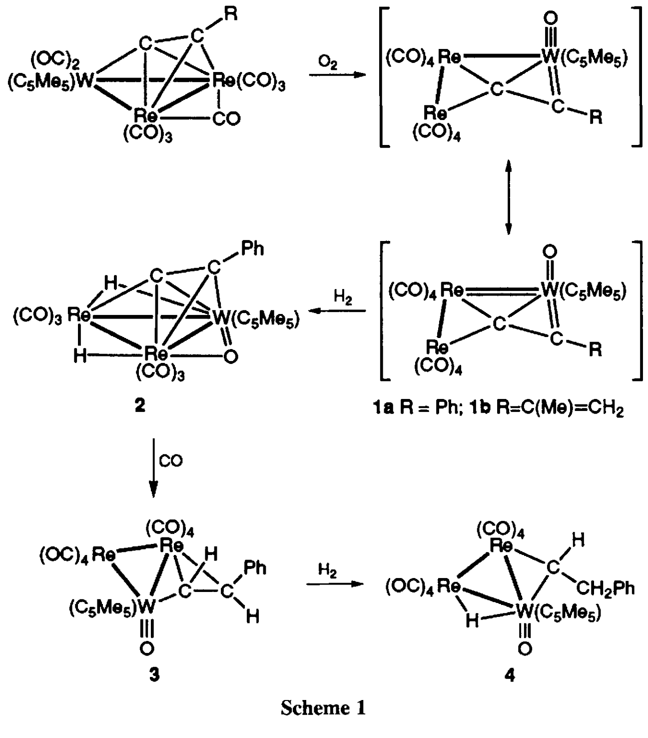
Cluster $[WRe_2(C_5Me_5)(O)(CO)_8(CCPh)]$ **1a** possessing a terminal oxo ligand is prepared by treatment of the acetylide cluster $[WRe_2(C_5Me_5)(CO)_9(CCPh)]$ with O_2 or N_2O; hydrogenation of **1a** affords three isolable clusters, showing an example of oxo-ligand mediated sequential conversion of acetylide to alkenyl and alkylidene.

Organometallic complexes containing both oxygen and hydrocarbon ligands serve as realistic models for metal-mediated oxidations and other homogeneous and heterogeneous reactions with high-valent metal species as catalysts.[1] From the mononuclear and the dinuclear oxo complexes,[2] extension of the preparative work to polynuclear systems[3] is needed because the latter provide insights into the coordination mode common for oxygen atoms bound to surfaces[4] and the enhanced reactivity of cluster-bound hydrocarbon fragments mediated by an oxo ligand.[5] Here, we report preliminary experiments on the structure and reactivity of unique heteropolymetallic clusters, which offer such informative comparisons.

The oxo-acetylide clusters $[WRe_2(C_5Me_5)(O)(CO)_8(CCR)]$, R = Ph **1a**, R = $C(Me)=CH_2$ **1b**,† were obtained initially as minor side products during the preparation of acetylide clusters $[WRe_2(C_5Me_5)(CO)_9(CCR)]$ by combination of $[Re_2(CO)_8(NCMe)_2]$ and $[W(C_5Me_5)(CO)_3(CCR)]$.[6] Later, we found that they were readily and conveniently produced by exposing a solution of $[WRe_2(C_5Me_5)(CO)_9(CCR)]$ to an oxygen or nitrous oxide atmosphere (80 °C, 3 h, 56–68%). An X-ray diffraction study on **1b** confirmed the molecular structure.‡

The molecule consists of an open triangular core arrangement with eight CO ligands, four on each Re atom (Fig. 1). The acetylide ligand adopts a novel $\mu_3,\eta^1,\eta^1,\eta^2$-mode,[7] in which the α-carbon is linked to all three metal atoms, but the β-carbon is bonded only to the W atom, with substantial carbenic character. In accordance with the bonding mode established by X-ray diffraction, the α and β-resonances of acetylide appeared at δ 181.9 and 212.8 (J_{W-C} 72 Hz) in the ^{13}C NMR spectrum. The oxo ligand adopts a terminal mode and the resulting W–O vector is perpendicular to the plane defined by the metal atoms and the acetylide ligand. The W–O(9) distance [1.699(6) Å], similar to that observed in W_2Fe and WCo oxo compounds,[8] cannot be utilized for identifying the nature of the bonding, as the actual mode (double bond *vs* triple bond) is determined by its unsaturation[1] and because the respective W–O interactions show little variation in bond distances.[9] Furthermore, because the W–Re(1) distance [2.7544(8) Å] falls between that in the W=Re double bond (2.672 Å) and W–Re single bond (2.898 Å) in the WRe_2 cluster $[WRe_2(C_5Me_5)(CO)_7(\mu\text{-H})\{CHCHC(Me)CH\}]$,[6] we propose that bonding in the cluster is best illustrated in terms of the resonance forms shown in Scheme 1: one possesses W=Re and W=O double bonds, while the second contains a W–Re single bond and a W≡O triple bond instead.§



1a R = Ph; **1b** R=C(Me)=CH$_2$

Scheme 1

Compound **1a** reacts with hydrogen in refluxing heptane (1 atm, 90 °C, 40 min) to afford three products of formula $[WRe_2(C_5Me_5)(CO)_6(\mu\text{-O})(\mu\text{-H})_2(CCPh)]$ **2** (dark red, 50%), $[WRe_2(C_5Me_5)(CO)_8(O)(\mu\text{-CHCHPh})]$ **3** (orange, 28%) and $[WRe_2(C_5Me_5)(CO)_8(O)(\mu\text{-H})(\mu\text{-CHCH_2Ph})]$ **4** (yellow, 5%).¶ For cluster **2**, X-ray diffraction studies|| confirm that it possesses a triangular WRe_2 core, on which the C–C bond of acetylide is perpendicular to one W–Re edge supporting a bridging oxo ligand (Fig. 2), whilst the two bridging hydrides, derived from H_2 gas, span the second W–Re edge and the unique Re–Re edge, respectively. Here, the oxo ligand alters to a W=O→Re mode, which is identical to that in the trinuclear cluster $[W_2Re(C_5H_5)(CO)_3(\mu\text{-Br})(\mu\text{-O})(\mu\text{-CTol})_2]$[10] and is also related to the W=O→Os mode of

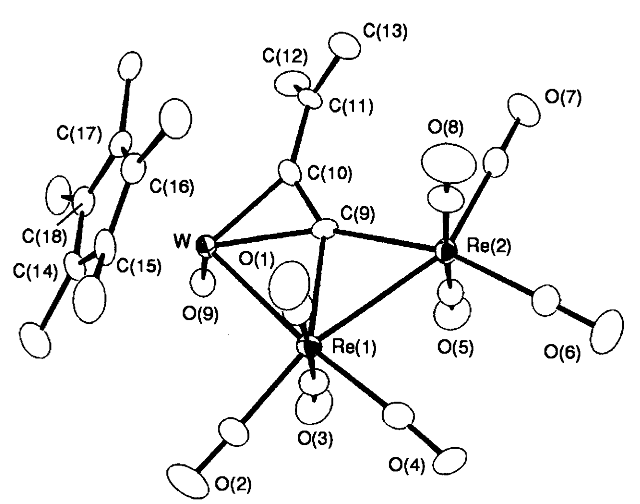


Fig. 1 Molecular structure of **1b** and selected bond lengths (Å): W–Re(1) 2.7544(8), Re(1)–Re(2) 2.9167(9), W–O(9) 1.699(6), W–C(9) 2.182(9), Re(1)–C(9) 2.160(7), Re(2)–C(9) 2.215(9), W–C(10) 2.012(9), C(9)–C(10) 1.31(1)

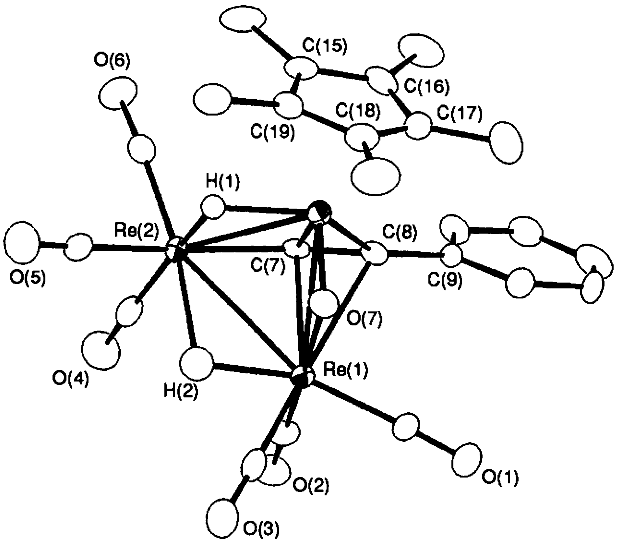


Fig. 2 Molecular structure of **2** and selected bond lengths (Å): Re(1)–Re(2) 3.0412(5), Re(1)–W 2.8652(6), Re(2)–W 2.9918(6), W–O(7) 1.765(6), Re(1)–O(7) 2.286(5), W–C(7) 2.189(8), Re(1)–C(7) 2.370(8), Re(2)–C(7) 2.028(7), W–C(8) 2.118(8), Re(1)–C(8) 2.496(8), C(7)–C(8) 1.34(1)

cluster compounds having the $WOs_3(\mu\text{-}O)$ core arrangement.[11]

Compounds **3** and **4** were also fully characterized. As depicted in Scheme 1, **3** contains eight CO ligands and is generated by formal addition of one H_2 molecule, of which both hydrogens migrated to the acetylide moiety to give a *trans*, edge-bridging vinyl fragment. Consistent with this assignment were the ^1H NMR data of two olefinic doublets at δ 5.93 and 4.72 with large coupling (^3J 13.6 Hz), and signals at δ 161.3 (J_{W-C} 115 Hz) and 76.8 in its ^{13}C NMR spectrum. For alkylidene complex **4**, the structural evidence comprises of the ^{13}C NMR signals at δ 141.6 (J_{W-C} 104 Hz) due to the alkylidene α-carbon, the proton signals at δ 7.15, 4.65 and 4.13 with an expected ABX splitting pattern and the hydride signal at δ −10.93 (J_{W-C} 97.2 Hz) in the ^1H NMR spectrum.

The time sequence of formation of **2**, **3** and **4** was established. The experimental evidence suggested that **2** was the initial product. Then, it coupled with free CO in solution to afford **3**, followed by addition of another H_2 molecule to produce **4**. This proposed reaction sequence is supported by the observation that, when **2** was treated with CO in refluxing dichloromethane, it slowly gave **3** in addition to the regeneration of **1a** by loss of a H_2 molecule. Treatment of **3** with D_2 afforded the labeled derivative **4** $[WRe_2(C_5Me_5)(CO)_8(O)(\mu\text{-}D)(\mu\text{-}CHCHDPh)]$ in which the deuterium atoms selectively replaced the hydride and the methylene proton that exhibits a signal at δ 4.13 in the ^1H NMR spectrum.

The precise role of the oxo ligand in the conversion **2** → **3** → **4** remains in doubt, although we have demonstrated that such reactivity was inhibited in the absence of the oxo ligand, because carbonylation of the acetylide cluster $[WRe_2(C_5Me_5)(CO)_8(\mu\text{-}H)_2(CCPh)]$, which is related to **2** by formally replacing two CO ligands with an oxo ligand, produced only elimination of H_2.[12] The contribution of the oxo ligand *via* its high electronegativity and its capabilty to serve as both a four- and six-electron donor[13] and to adopt various bonding modes[4] may be key factors which have allowed the transfer of hydrides.

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Footnotes

† *Selected data* for **1a**: IR(C_6H_{12}): ν (CO)/cm^{-1} 2093m, 2060m, 2004vs, 1986s, 1979s, 1964w, 1958w, 1940vw; ^1H NMR ($CDCl_3$): δ 7.43 (t, 2H, *J* 7.6 Hz), 7.37 (d, 1H, *J* 8.0 Hz), 7.30 (t, 2H, *J* 7.2 Hz), 2.00 (s, 15H). For **1b**: ^1H NMR ($CDCl_3$): δ 5.22 (s, 1H), 5.12 (s, 1H), 2.12 (s, 15H), 2.00 (s, 3h).

‡ *Crystal data* for **1b**: $C_{23}H_{20}O_9Re_2W_1$, triclinic, $P\bar{1}$, a = 10.482(6), b = 10.700(2), c = 12.026(3) Å, α = 93.63(2), β = 105.13(3), γ = 96.13(3)°, $F(000)$ = 920, μ(Mo-Kα) = 14.1 mm^{-1}, 3732 reflections with $I > 2\sigma(I)$, R = 0.029, R_w = 0.025, GOF = 1.99.

§ Sometimes a different notation $M^{-}{\equiv}O^{+}$ is selected to indicate that lone-pair donation from oxygen to the metal contre imparts the triple bond character.

¶ *Selected data* for **2**: IR(C_6H_{12}): ν(CO)/cm^{-1} 2052vs, 2017vs, 1971vs, 1954vs, 1938m, 1932s; ^1H NMR ($CDCl_3$): δ 7.92 (d, 2H, *J* 8 Hz), 7.53 (t, 2H, *J* 7.2 Hz), 7.38 (t, 1H, *J* 7.2 Hz), 2.09 (s, 15H), −7.44 (s, 1H, *J* 135 Hz), −14.08 (s, 1H). For **3**: IR(C_6H_{12}): ν(CO)/cm^{-1} 2088m, 2043s, 2008vs, 1992vs, 1981s, 1961vw, 1942w, 1919s; ^1H NMR ($CDCl_3$): δ 7.42–7.21 (m, 5H), 5.93 (d, 1H, ^3J 13.6 Hz), 4.72 (d, 1H, ^3J 13.6 Hz), 2.22 (s, 15H). For **4**: IR(C_6H_{12}): ν(CO)/cm^{-1}, 2087s, 2041s, 2000vs, 1987vs, 1974w, 1963w, 1943w, br; ^1H NMR ($CDCl_3$): δ 7.42–7.30 (m, 5H), 7.15 (dd, 1H, ^3J 9.8, 5.5 Hz), 4.65 (dd, 1H, ^2J 14, ^3J 5.5 Hz), 4.13 (d, 1H, ^2J 14, ^3J 9.8 Hz), 2.08 (s, 15H), −10.93 (s, 1H, J_{W-H} 97.2 Hz).

‖ *Crystal data* for **2**: $C_{24}H_{22}O_7Re_2W_1\cdot 1/2CHCl_3$, triclinic, $P\bar{1}$, a = 9.740(1), b = 10.533(1), c = 15.357(1) Å, α = 102.50(1), β = 93.50(1), γ = 114.76(1)°, $F(000)$ = 904, μ(Mo-Kα) = 132.0 cm^{-1}, 3223 reflections with $I > 2\sigma(I)$, R = 0.023, R_w = 0.022, GOF = 2.26. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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