Unsaturated Heterobinuclear Complexes of Rhodium with Molybdenum, Tungsten, and Manganese. *X*-Ray Crystal Structure of $[MoRh(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5H_5)]$

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The new, related bimetallic complexes $[MRh(\mu\text{-}CO)_2(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo and W) and $[MnRh(\mu\text{-}CO)_2(CO)_2(PPh_3)_3]$ have been characterized and some chemical properties examined; the crystal structure of the molybdenum–rhodium complex, determined by *X*-ray crystallography, reveals a short multiple Mo–Rh bond.

There is currently much interest in the properties of heterobimetallic, binuclear, and cluster transition metal derivatives,[1] particularly in relation to catalytic activity. Second-row transition metals, such as rhodium, are especially active in catalytic reactions so that complexes with M–Rh bonds are of potential interest but relatively uncommon.[2] In continuation of our investigations of reactions of metal–metal-bonded complexes,[3] three new derivatives containing Mo–Rh, W–Rh, and Mn–Rh bonds have now been characterized.

Metathetical reactions of $Na[M(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo and W) or $Na[Mn(CO)_5]$ with $Rh(PPh_3)_3Cl$ (**1**) in tetrahydrofuran at ambient temperatures form the products $[(\eta\text{-}C_5H_5)(OC)M(\mu\text{-}CO)_2Rh(PPh_3)_2]$ [M = Mo (**2**) (65%); M = W (**3**) (85%)] or $[(Ph_3P)(OC)_2Mn(\mu\text{-}CO)_2Rh(PPh_3)_2]$ (48%) (**4**). In these reactions, elimination of NaCl is accompanied by loss or transfer of PPh_3 and products (**2**)—(**4**) do not obey the 18-

$Rh(PPh_3)_3Cl$

(**1**)

$[(\eta\text{-}C_5H_5)(OC)M(\mu\text{-}CO)_2Rh(PPh_3)_2]$

(**2**) M = Mo

(**3**) M = W

$[(Ph_3P)(OC)_2Mn(\mu\text{-}CO)_2Rh(PPh_3)_2]$

(**4**)

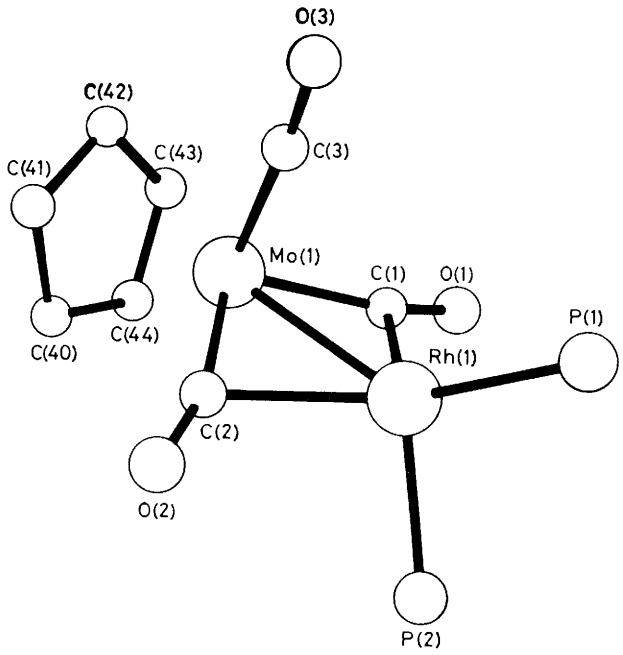
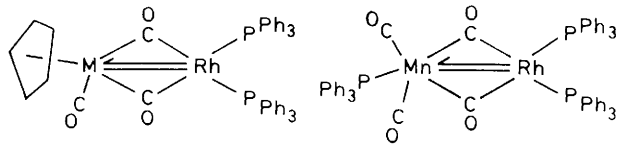


Figure 1. Molecular structure of complex (**2**). Some important bond lengths and angles: Rh(1)–Mo(1) 2.588(1), Rh(1)–P(1) 2.321(1), Rh(1)–P(2) 2.242(1), Rh(1)–C(1) 2.185(5), Rh(1)–C(2) 2.095(5), Rh(1)–C(3) 2.92(1), Mo(1)–C(1) 1.980(6), Mo(1)–C(2) 2.026(5), Mo(1)–C(3) 1.943(6) Å; Rh(1)–C(1)–Mo(1) 76.7(2), Rh(1)–C(2)–Mo(1) 77.9(2), C(1)–Mo(1)–C(2) 105.2(2), C(1)–Rh(1)–C(2) 96.2(2), P(1)–Rh(1)–P(2) 103.3(1), Mo(1)–C(1)–O(1) 164.7(5), Mo(1)–C(2)–O(2) 122.7(4), Rh(1)–C(1)–O(1) 118.6(5), Rh(1)–C(2)–O(2) 159.4(4)°. The cyclopentadienyl ring atoms were found to adopt two possible sites with refined occupancies of 74 and 26%, respectively; the major site occupancies [C(40)—C(44)] are indicated above. The phenyl groups bonded to P(1) and P(2) have been omitted for clarity.

electron rule unless multiple M–Rh bonds are present. Complexes (**2**)† and (**3**)† are obtained from CH_2Cl_2 as black crystals, stable in air over several weeks but unstable to air in solution at room temp. Complex (**4**)† crystallizes as an air-sensitive green solid which decomposes readily in solution unless air is rigorously excluded. A crystal of (**2**) has been subjected to *X*-ray structural analysis.

Crystal data: $C_{44}H_{35}MoO_3P_2Rh$, $M = 872.56$, monoclinic, space group $P2_1/c$, $a = 18.102(2)$, $b = 10.407(1)$, $c = 20.736(2)$ Å, $\beta = 104.99(1)°$, $U = 3773.4$ Å^3, $D_c = 1.53$ g cm^{-3}, $D_o = 1.55$ g cm^{-3}, $Z = 4$, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 7.97 cm^{-1}. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-K_α radiation and the ω—2θ scanning technique, corrected for Lorentz and polarisation effects but not for absorption, and averaged to give 5233 intensities [$F > 2\sigma(F)$]. The structure was solved by a combination of Patterson and Fourier-difference techniques, and refined by full-matrix least-squares methods (all non-hydrogen atoms except cyclopentadienyl ring atoms were anisotropic).‡ At convergence, the conventional and weighted *R*-factors were $R = 0.0361$ and $R_w = 0.0743$ $\{W = 1.115/[\sigma^2(F) + 0.03069(F^2)]\}$, respectively.



The crystal structure of complex (**2**) is shown in Figure 1 with some important geometrical parameters.

The binuclear complex (**2**) contains typical (η-C_5H_5)–Mo and Rh–PPh_3 interactions and the two μ-CO groups appear to be normal bridging ligands. The Rh(μ-CO)$_2$Mo framework possesses a 'butterfly' configuration with an Rh–C–Mo interplanar dihedral angle of 161°; this is related to the geometry of homonuclear complexes [$Rh_2(\mu\text{-}CO)_2(PR_3)_4$] although significantly smaller dihedral angles are found in these complexes: 132.8(5)° (R = Ph),[4] 140.8(6)° (R = OPr^i).[5] The unique CO group is essentially terminally bound to Mo and, although slightly bent [174.7(5)°], the long Rh–C(3) distance [2.919(10) Å] suggests little bridging character.§

A single Mo–Rh bond places Mo and Rh atoms in 16-electron environments which is very unusual for Mo^I, although both Mo and Rh can obtain 18-electron environments by formation of a triple bond Mo≡Rh (*cf.* Mo≡Mo, ref. 7). However, in light of the Rh–Mo bond length¶ [2.588(1) Å] and the tendency for Rh to acquire 16-electron configurations, the bonding can be rationalized in terms of a double bond involving a co-ordinate link from Rh, as depicted in (I) [(**2**) and (**3**)] or (II) (**4**).[10] Rh^I complexes can act as Lewis bases[11] and such dative M→M bonding has been invoked to explain structures of homobinuclear complexes.[12] It is notable that the isoelectronic complex [(η-C_5H_5)$WIr(CO)_5$]$_2$ forms a saturated tetranuclear cluster[13] and that the heteronuclear complexes [(η-C_5H_5)(CO)Fe(μ-CO)(μ-PPh_2)RhL_2]$^+$,[14] [(η-C_5H_5)$(CO)_3$Mo–PtH$(PPh_3)_2$],[15] or [$(CO)_4$Co–Rh$(CO)(PEt_3)_2$][2] possess single M–M bonds with 18-electron environments for atoms Fe, Mo, or Co, respectively.

The chemical reactivity of the new unsaturated complexes (**2**)—(**4**) should prove interesting. Initial studies show that (**2**) in toluene is a catalyst for hydrogenation of cyclohexene by H_2 (>200 catalytic cycles followed) although at room temp. its activity is significantly less than that of (**1**). Cleavage of M–Rh bonds occurs in some reactions. Thus, photolysis of (**2**) (−70 °C) or (**4**) (−40 °C) in the presence of nitrosodurene

† Satisfactory elemental analyses have been obtained for complexes (**2**), (**3**), and (**4**). Spectroscopic data: (**2**) i.r. (Nujol) 1873(s), 1778(s), and 1749(s) cm^{-1}, (CH_2Cl_2) 1890(s) and 1760(s) cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ *ca.* 7.3 (m, rel. int. 6.5) and 5.20 (s, rel. int. 1); ^{31}P{^{1}H} n.m.r. (C_6D_6) δ 37.1 p.p.m. [d, ^1J (Rh–P) 170 Hz]. (**3**) i.r (Nujol) 1871(s), 1770(s), and 1738(s) cm^{-1}, (CH_2Cl_2) 1886(s) and 1748(s) cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ *ca.* 7.3 (m, rel. int. *ca.* 6) and 5.24 (s, rel. int. 1); ^{31}P{^{1}H} n.m.r. (C_6D_6) δ 30.2 p.p.m. [d, ^1J(Rh–P) 174 Hz]. (**4**) i.r. (Nujol) 1947(s), 1874(s), 1776(m), 1771(m), and 1750(s) cm^{-1}, (CH_2Cl_2) 1955(s), 1882(s), and 1751(s) cm^{-1}; ^{31}P{^{1}H} n.m.r. (C_6D_6) δ 88.7(s) and 41.3 p.p.m. [d, ^1J (Rh–P) 256 Hz].

‡ The phenyl and cyclopentadienyl rings were treated as rigid bodies and their associated hydrogen atoms placed on calculated positions ($d_{C-H} = 1.08$ Å).

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Note that semi-bridging CO groups in homobinuclear complexes [$Mo_2(\mu\text{-}C_2R_2)(CO)_4(\eta\text{-}C_5H_5)_2$] (R = H, Et, Ph) have bridging Mo–C separations in the region 2.826—2.902 Å [see ref. 6(b)].

¶ *Cf.* 2.98—3.23 Å for Mo–Mo (ref. 6) and 2.44—2.50 Å for Mo≡Mo (ref. 7) in Mo^I organometallics, 2.63—2.78 Å for Rh–Rh in Rh^0 derivatives (refs. 4, 5, 8), and 2.9212(7) Å for Rh–Mo in [(η-Me_5C_5)Rh(μ-PMe_2)$_2$Mo$(CO)_4$] (ref. 9). From these and related values we estimate 2.8—3.0 Å for Rh^0–Mo^I which supports a bond order of *ca.* 2 for (**2**).

produces the paramagnetic derivatives $[Mo(CO)_n(\dot{N}OC_6Me_4H)(\eta\text{-}C_5H_5)]$** or $[Mn(CO)_n(PPh_3)(\dot{N}OC_6Me_4H)]$ in CH_2Cl_2 (identified by e.s.r. spectroscopy).[16,3] Photolysis of (**4**) in the presence of O_2 in CH_2Cl_2 forms the unstable dioxygen species $[Mn(CO)_n(PPh_3)(O_2)]$ in CH_2Cl_2, identical to that obtained from $[Mn_2(CO)_8(PPh_3)_2]$[17] [in CH_2Cl_2, e.s.r. parameters: $g = 2.020$; A (^{55}Mn) = 1.53 mT; A (^{31}P) *ca.* 0.76 mT].

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** In this case a second multiplet signal is also observed, which has not been unambiguously identified, but is probably assignable to a rhodium–(aminyl oxide) derivative.