# Heterobimetallic Complexes of Copper with Molybdenum and Tungsten, *X*-Ray Crystal and Molecular Structure of Two Isomeric Forms of [CuW(CO)$_3$(PPh$_3$)$_2$($\eta$-C$_5$H$_5$)]

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The new, binuclear complexes [CuM(CO)$_3$(PPh$_3$)$_2$($\eta$-C$_5$H$_5$)] (M = Mo, W) are described and the structures of two isomeric, crystalline forms of [CuW(CO)$_3$(PPh$_3$)$_2$($\eta$-C$_5$H$_5$)], one possessing distinctly bridging CO groups, are established by *X*-ray analysis.

Heteronuclear organometallic complexes with transition metal to copper bonds are uncommon. Although species containing copper and group 6A metals have been reported,[1,2] their molecular structures have not been definitively established. One example of a binuclear complex containing an Mn–Cu bond, *i.e.* [CuMn(CO)$_5$(triars)] [triars = MeAs($o$-C$_6$H$_4$AsMe$_2$)$_2$], has been examined by *X*-ray diffraction;[3] other heteronuclear copper-containing species characterised by *X*-ray analysis are cluster compounds.[4] We now report the new, characterised complexes [CuM(CO)$_3$(PPh$_3$)$_2$($\eta$-C$_5$H$_5$)] [M = Mo(**1**), W(**2**)].

Reaction of [Cu(PPh$_3$)Cl]$_4$ with Na[M(CO)$_3$($\eta$-C$_5$H$_5$)] (M = Mo or W) in tetrahydrofuran at room temperature (up to 2 h) and evaporation to dryness, followed by extraction and crystallisation of the crude product from dichloromethane–hexane gives (**1**) (52%) or (**2**) (28%), repectively. The solid products show considerable stability to air over several weeks but are unstable to air in solution. Complex (**1**)† has been obtained in only one crystalline form. However, (**2**)† crystal-

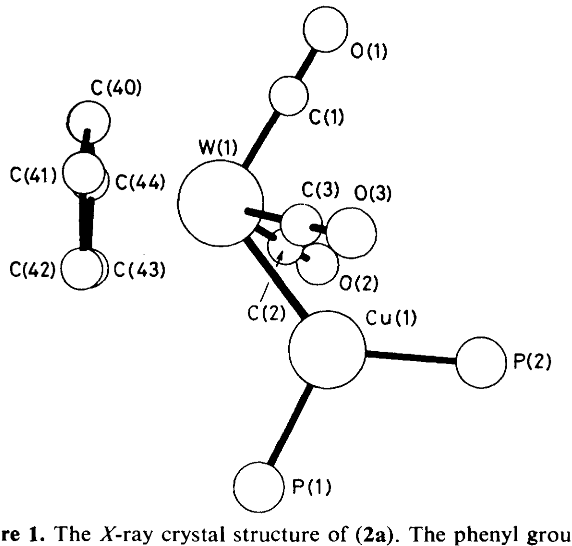

**Figure 1.** The *X*-ray crystal structure of (**2a**). The phenyl groups bonded to P(1) and P(2) have been omitted for clarity. Some important geometrical parameters: W(1)–Cu(1) 2.721(1), Cu(1)–P(1) 2.285(4), Cu(1)–P(2) 2.295(3), W(1)–C(1) 1.922(16), W(1)–C(2) 1.913(15), W(1)–C(3) 1.952(13), Cu(1)–C(2) 2.309(13), Cu(1)–C(3) 2.405(13), C(1)–O(1) 1.192(15), C(2)–O(2) 1.190(16), C(3)–O(3) 1.152(14) Å; W(1)–C(2)–Cu(1) 79.7(5), W(1)–C(3)–Cu(1) 76.5(5), P(1)–Cu(1)–P(2) 126.7(3), W(1)–C(2)–O(2) 172(1), W(1)–C(3)–O(3) 174(1), Cu(1)–C(2)–O(2) 108(1), Cu(1)–C(3)–O(3) 108.6(9), C(2)–W(1)–C(3) 105.0(5), C(2)–Cu(1)–C(3) 81.2(5)°. The cyclopentadienyl ring atoms were found to adopt two possible sites with refined occupancies of 55 and 45%; the major site occupancies [C(40)–C(44)] are indicated above.

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† Satisfactory elemental analyses have been obtained for complexes (**1**), (**2a**), and (**2b**) (C, H, P, Cu, Mo). Spectral data: (**1**) i.r. (CH$_2$Cl$_2$) ν(CO): 1914, 1808, and 1776 cm$^{-1}$; (Nujol) 1896, 1795, and 1778 cm$^{-1}$; $^1$H n.m.r. (C$_6$D$_6$): δ 7.5(m), 7.0(m), and 4.87(s); $^{31}$P {$^1$H} n.m.r. (C$_6$D$_6$): δ −3.0(s) p.p.m. (**2**) I.r. (CH$_2$Cl$_2$) ν(CO): 1908, 1803, and 1769 cm$^{-1}$; $^1$H n.m.r. (CDCl$_3$): δ 7.36(m) and 5.27(s); $^{31}$P{$^1$H} n.m.r. (CDCl$_3$): δ −1.5 p.p.m.; $^{13}$C{$^1$H} n.m.r. (toluene–10% C$_6$D$_6$): δ 220.8 (s, CO) and 86.2 p.p.m. (s, C$_5$H$_5$) (31.5 °C), δ 223.4 (br., CO) and 87.4 p.p.m. (s, C$_5$H$_5$) (−71 °C). (**2a**) I.r. (Nujol) ν(CO): 1890, 1790, and 1769 cm$^{-1}$; (**2b**) i.r. (Nujol) ν(CO): 1890, 1786, and 1731 cm$^{-1}$.

$[CuM(CO)_3(PPh_3)_2(\eta\text{-}C_5H_5)]$

**(1)**; M = Mo
**(2)**; M = W

lises in two distinct forms, often obtained in admixture but, by varying the conditions of crystallisation, either form may predominate; the yellow form **(2a)**† has an i.r. spectrum analogous to **(1)** whereas the red-orange isomer **(2b)**† has two ν(CO) bands shifted to lower frequencies. In solution **(2a)** and **(2b)** show identical i.r. and n.m.r. spectra. Crystals of **(2a)** and **(2b)** have been subjected to *X*-ray analysis.‡§

The *X*-ray crystal structures of **(2a)** (Figure 1) and **(2b)** (Figure 2) show normal co-ordination of $PPh_3$ groups to Cu,[5] and typical W–($\eta$-$C_5H_5$) interactions. The Cu–W separations are both rather long and, although the CO groups resemble typical terminal, tungsten-bonded carbonyl ligands, two CO groups approach the Cu atoms.¶ More interestingly, the Cu–W distance of **(2b)** is longer and the Cu–C(2) and Cu–C(3) separations are significantly shorter than in **(2a)**. Also, in **(2b)** the Cu atom is almost in the plane W–C(2)–C(3) whereas in **(2a)** the $Cu(PPh_3)_2$ group occupies a position more appropriate for a ligand in a 'four-legged piano stool' configuration about W [interplanar angles W–Cu–C(2)/W–Cu–C(3) 170.9° **(2b)**, and 139.8° **(2a)**].

The isomeric structures can be rationalised in terms of heteropolar $\overset{\delta-}{W}$–$\overset{\delta+}{Cu}$ bonds and interactions of bridging CO groups, as indicaed in (A). A greater ionicity in **(2b)** will favour the reduction of the electron deficiency of formal $\overset{+}{Cu}(PPh_3)_2$ (14 valence electrons) by donation of two electrons

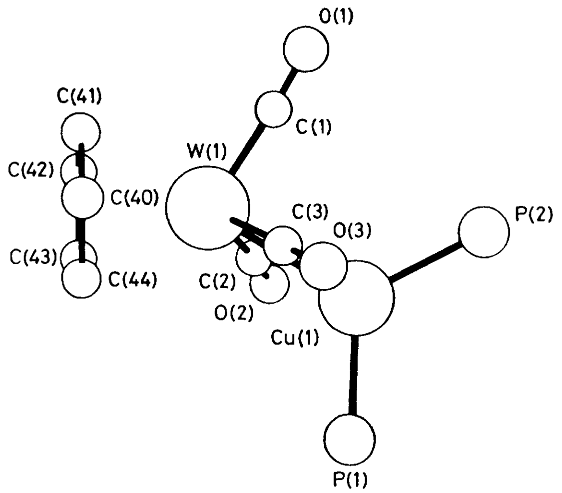
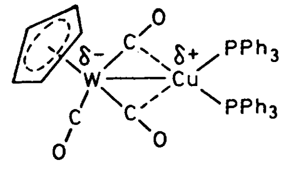


**Figure 2.** The *X*-ray crystal structure of **(2b)**. The phenyl groups bonded to P(1) and P(2) have been omitted for clarity. Some important bond lengths and angles: W(1)–Cu(1) 2.771(1), Cu(1)–P(1) 2.307(2), Cu(1)–P(2) 2.309(2), W(1)–C(1) 1.945(7), W(1)–C(2) 1.960(7), W(1)–C(3) 1.952(7), Cu(1)–C(2) 2.260(6), Cu(1)–C(3) 2.197(6), C(1)–O(1) 1.153(8), C(2)–O(2) 1.166(8), C(3)–O(3) 1.168(7) Å; W(1)–C(2)–Cu(1) 81.7(2), W(1)–C(3)–Cu(1) 83.6(2), P(1)–Cu(1)–P(2) 119.0(1), W(1)–C(2)–O(2) 170.9(5), W(1)–C(3)–O(3) 171.4(5), Cu(1)–C(2)–O(2) 107.1(5), Cu(1)–C(3)–O(3) 104.9(4), C(2)–W(1)–C(3) 105.4(2), C(2)–Cu(1)–C(3) 88.6(3)°. The cyclopentadienyl ring atoms were disordered; the atomic positions [C(40)–C(44)] represent the major site occupancies (78.5%)



(A)

from each of two terminal CO groups;** such interactions are analogous to those observed in bridging acetylides of polynuclear compounds containing copper.[4a,5,10] The carbonyl bridging interactions are weaker in isomer **(2a)** for which the polarity of the W–Cu bond is probably less. These two bonding arrangements, apparently of comparable energies, illustrate the structural variations that may occur in heterobimetallic complexes, even in simple binuclear systems. It is interesting that in $[Fe(CO)_3(\eta^3\text{-}C_3H_5)X]$ when X = $Au(PPh_3)$ the Au atom is located between two CO groups [*cf.* **(2b)**] and not in a ligand position in contrast to X = Br when pseudo-octahedral co-ordination about Fe is found [*cf.* **(2a)**].[11]

In solution only one form of **(2)** is observed spectroscopically. In the $^{13}C\{^1H\}$ n.m.r. spectrum all the CO groups appear equivalent at temperatures > −71 °C in non-polar solvents† indicating that the molecule is not rigid; although some intramolecular process may be occurring this non-rigidity could alternatively arise from ionic dissociation of the W–Cu bond, as found in $[(PEt_3)_2(CO)RhCo(CO)_4]$,[12] albeit in more co-ordinating solvents.

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‡ The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-$K_\alpha$ radiation ($\omega$–$2\theta$ scan), and corrected for Lorentz-polarisation effects and absorption. The structures of **(2a)** and **(2b)** were solved by a combination of Patterson and Fourier-difference methods, and refined by full-matrix least-squares techniques (all non-hydrogen atoms except the cyclopentadienyl-ring atoms were anisotropic). The phenyl and cyclopentadienyl groups were treated as rigid bodies and their associated hydrogen atoms placed in calculated positions ($d_{C-H}$ 1.08 Å). All crystallographic calculations were carried out using the SHELX programs: G. Sheldrick, 'SHELX, a System of Programs for Crystal Structure Determinations,' Cambridge, 1976.

§ *Crystal data:* **(2a)**, yellow needles, $CuC_{44}H_{35}O_3P_2W$, $M = 921.1$, triclinic, space group $P\bar{1}$(No. 2), $a = 12.404(4)$, $b = 11.756(3)$, $c = 14.208(3)$ Å, $\alpha = 101.4(2)$, $\beta = 79.5(2)$, $\gamma = 110.3(2)$°, $U = 1890.3$ Å$^3$, $D_c = 1.62$ g cm$^{-3}$, $D_o = 1.63$ g cm$^{-3}$, $Z = 2$, Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0.71069$ Å, $\mu$(Mo-$K_{\bar{\alpha}}$) = 35.58 cm$^{-1}$, $2 \leqslant 2\theta \leqslant 50$°. Final $R$ 0.058 {$R_w$ 0.076, w = 0.9707/[$\sigma^2(F)$ + 0.00568 $F^2$]} for 3997 unique reflections [with $F > 2\sigma(F)$].

*Crystal data:* **(2b)**, orange-red plates, $CuC_{44}H_{35}O_3P_2W$, $M = 921.1$, monoclinic, space group $P2_1/c$ (No. 14), $a = 17.991(3)$, $b = 10.098(2)$, $c = 21.608(2)$ Å, $\beta = 105.66(1)$°, $U = 3779.7$ Å$^3$, $D_c = 1.62$ g cm$^{-3}$, $D_o = 1.63$ g cm$^{-3}$, $Z = 4$, Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0.71069$ Å, $\mu$(Mo-$K_{\bar{\alpha}}$) = 17.80 cm$^{-1}$, $2 \leqslant 2\theta \leqslant 44$°. Final $R$ 0.034 {$R_w$ 0.049, w = 2.0612/[$\sigma^2$ ($F$) + 0.00139 $F^2$]} for 4009 unique reflections [with $F > 2\sigma(F)$].

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

¶ In the compounds $[Ga\{W(CO)_3(\eta\text{-}C_5H_5)\}_3]$,[6] $[Me_2GaW(CO)_3(\eta\text{-}C_5H_5)]$,[7] $[Zn\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[8] $[ZnCl(OEt_2)Mo(CO)_3(\eta\text{-}C_5H_5)]$,[8] and $[Ph_3PAuW(CO)_3(\eta\text{-}C_5H_5)]$[9] the Ga–C, Zn–C, or Au–C distances are considerably greater (>2.5 Å) and metal-metal bonds are <2.74 Å [*e.g.* Au–W, 2.698(3) Å[9]].

** A bridging CO group has recently been identified in a binuclear copper complex: M. Pasquali, C. Floriani, G. Venturi, A. Gaetani-Manfredotti, and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 1982, **104**, 4092.

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## References

1 P. Hackett and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1975, 1606.
2 R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 1968, 46.
3 B. T. Kilbourn, T. L. Blundell, and H. M. Powell, *Chem. Commun.*, 1965, 444.
4 *Cf.* (a) M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1974, **13**, 1418; (b) V. G. Albano, D. Braga, S. Martinengo, P. Chini, M. Sansoni, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 1980, 52.
5 F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, 1975, **15**, 115, and references therein.
6 A. J. Conway, P. B. Hitchcock, and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1975, 1945.
7 J. N. St. Denis, W. Butler, M. D. Glick, and J. P. Oliver, *J. Organomet. Chem.*, 1977, **129**, 1.
8 J. N. St. Denis, W. Butler, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, 1974, **96**, 5427.
9 J. B. Wilford and H. M. Powell, *J. Chem. Soc. A.*, 1969, 8.
10 P. Clark, J. Howard, and P. Woodward, *J. Chem. Soc. Dalton Trans.*, 1974, 2027; P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 1966, **21**, 957.
11 F. E. Simon and J. W. Lauher, *Inorg. Chem.*, 1980, **19**, 2338.
12 D. A. Roberts, W. C. Mercer, S. M. Zahurak, G. L. Geoffroy, C. W. DeBroose, M. E. Cass, and C. G. Pierpont, *J. Am. Chem. Soc.*, 1982, **104**, 910.