

The Synthesis and X-Ray Crystal Structures of $[\text{MoW}_2(\mu\text{-CR})_2(\mu\text{-CO})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$), $[\text{N}(\text{PPh}_3)_2][\text{W}_2(\mu\text{-CHR})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$, $[\text{AuW}(\mu\text{-CHR})(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$, and $[\text{W}=\text{CHR}(\text{SnPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$

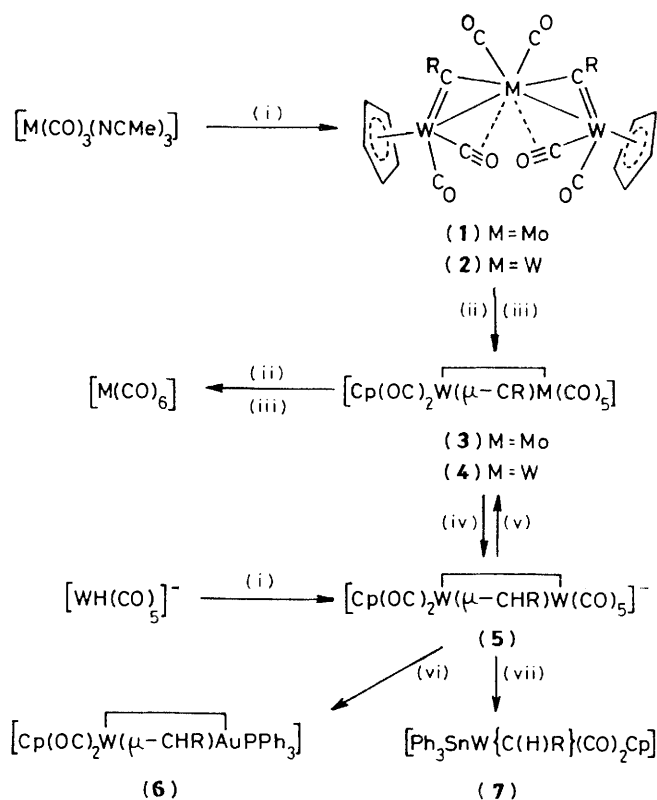
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The structures of the compounds $[\text{MoW}_2(\mu\text{-CR})_2(\mu\text{-CO})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$), $[\text{N}(\text{PPh}_3)_2][\text{W}_2(\mu\text{-CHR})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$, $[\text{AuW}(\mu\text{-CHR})(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$, and $[\text{W}=\text{CHR}(\text{SnPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ have been established by single-crystal X-ray diffraction, following their synthesis from $[\text{W}=\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ and the appropriate reagents.

Compounds in which tolylidene ligands bridge bonds between tungsten and Ni, Pd, Pt,¹ Co, Rh,^{2,3} Ir,⁴ Fe, Os,⁵ Mn, or Re³ are readily obtained from reactions between $[\text{W}=\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) and low-valent complexes of these metals. In contrast, only one dimetal compound of this class with tungsten bonded to one of its congeners in subgroup 6 is known, viz. $[\text{CrW}(\mu\text{-CR})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{Me}_6)]$,³ and none has been reported with W-W bonds.⁶ Herein we describe di- and tri-tungsten species with bridging tolylidene groups which have an extensive derivative chemistry.

Refluxing the compound $[\text{M}(\text{CO})_3(\text{NCMe})_3]$ ($\text{M} = \text{Mo}$ or W) with $[\text{W}=\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ in hexane affords purple crystalline complexes (1) and (2). The spectroscopic proper-



Scheme 1. $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{C} = \eta\text{-C}_5\text{H}_5$, (i) + $[\text{W}=\text{CR}(\text{CO})_2\text{Cp}]$, (ii) + CO , (iii) - $[\text{W}=\text{CR}(\text{CO})_2\text{Cp}]$, (iv) $\text{K}[\text{BH}(\text{CHMeEt})_3]$ in tetrahydrofuran (thf), (v) $[\text{CPh}_3][\text{BF}_4]$ in CH_2Cl_2 , (vi) $[\text{AuCl}(\text{PPh}_3)]$ and TIPF_6 in thf, (vii) SnClPh_3 and TIPF_6 in thf.

ties† are in accord with the proposed structures (Scheme 1), but that of (1) has been established by an X-ray diffraction study.‡

The molecular structure (Figure 1) reveals a bent W-Mo-W spine $[148.2(1)^\circ]$ with the Mo-W bonds bridged by $\text{C}_6\text{H}_4\text{Me-4}$ groups. The $\text{W}(1)\text{-C}(51)$ and $\text{W}(2)\text{-C}(52)$ separations [mean $1.944(12)$ Å] are close to those found [mean $1.907(13)$

† Selected spectroscopic data (^1H n.m.r. measured in CDCl_3 , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ in $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$; coupling constants in Hz): compound (1), ν_{CO} (max) at 1997w , 1967s , 1936m , 1852w (br), and 1687vw (br) cm^{-1} (CH_2Cl_2), $^{13}\text{C}\{^1\text{H}\}$ n.m.r., δ 360.1 [$\mu\text{-CR}$, $J(\text{WC})$ 144], 233.0 (CO), 228.7 [CO, $J(\text{WC})$ 178], and 218.4 p.p.m. [CO, $J(\text{WC})$ 188]. Compound (2), ν_{CO} (max) at 2002w , 1969s , 1937m (br), 1852w (br) cm^{-1} (CH_2Cl_2), $^{13}\text{C}\{^1\text{H}\}$ n.m.r., δ 376.2 ($\mu\text{-CR}$), 228.1 [CO, $J(\text{WC})$ 171], 226.0 [CO, $J(\text{WC})$ 173], and 214.9 [CO, $J(\text{WC})$ 189]. Compound (4), ν_{CO} (max) at 2072w , 2005m , 1953s , and 1936m cm^{-1} (hexane). Compound (5), ^1H n.m.r., δ 10.15 (s, 1H, $\mu\text{-CHR}$). Compound (6), ν_{CO} (max) at 1896s and 1806m cm^{-1} (thf), n.m.r.: ^1H , δ 13.20 (s, 1H, $\mu\text{-CHR}$); $^{13}\text{C}\{^1\text{H}\}$, δ 246.3 [CO, $J(\text{WC})$ 161], 238.9 [CO, $J(\text{WC})$ 183], and 228.9 p.p.m. [d, $\mu\text{-CH}(\text{R})$, $J(\text{PC})$ 15, $J(\text{WC})$ 103]; $^{31}\text{P}\{^1\text{H}\}$ (to high frequency of H_3PO_4), δ 63.4 p.p.m. Compound (7), ν_{max} at 1948m and 1886s cm^{-1} (thf), n.m.r.: ^1H , δ 14.85 (s, 1H, CHR); $^{13}\text{C}\{^1\text{H}\}$, δ 282.4 (CHR), 214.2 (CO).

‡ 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.

Crystal data for (1): $\text{C}_{22}\text{H}_{24}\text{MoO}_6\text{W}_2$, $M = 968$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.829(1)$, $b = 14.709(2)$, $c = 15.579(2)$ Å, $\alpha = 118.27(1)^\circ$, $\beta = 92.21(1)^\circ$, $\gamma = 105.32(1)^\circ$, $U = 1495(1)$ Å³, $Z = 2$, $D_c = 2.15$ g cm^{-3} , $F(000) = 908$, $\mu(\text{Mo-K}\alpha) = 82.9$ cm^{-1} . Final R 0.038 (R' 0.038) for 3711 unique reflections [$2.9 \leq 2\theta \leq 55^\circ$] measured ($\theta/2\theta$ scan) at 210 K on a Nicolet P3m diffractometer [$I \geq 2.5\sigma(I)$]; blocked-cascade least-squares refinement with all H-atoms isotropic, all other atoms anisotropic.

Crystal data for (5): $\{[\text{N}(\text{PPh}_3)_2]^+\text{ salt with } 0.5 \text{ Et}_2\text{O}\}$; $\text{C}_{56}\text{H}_{48}\text{NO}_7\text{P}_2\text{W}_2 \cdot \frac{1}{2} \text{C}_4\text{H}_{10}\text{O}$, $M = 1308$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.326(3)$, $b = 13.856(4)$, $c = 19.114(4)$ Å, $\alpha = 97.62(2)^\circ$, $\beta = 102.72(2)^\circ$, $\gamma = 86.98(2)^\circ$, $U = 2643(2)$ Å³, $Z = 2$, $D_c = 1.70$ g cm^{-3} , D_m (flotation) = 1.68 g cm^{-3} , $F(000) = 1282$, $\mu(\text{Mo-K}\alpha) = 45.6$ cm^{-1} . Final R 0.034 (R' 0.041) for 6361 unique reflections [$2.9 \leq 2\theta \leq 55^\circ$], with $I \geq 2.5\sigma(I)$; otherwise as for (1), but with solvent C atoms isotropic.

Crystal data for (6): $\text{C}_{33}\text{H}_{28}\text{AuO}_2\text{PW} \cdot \text{CH}_2\text{Cl}_2$, $M = 953.3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.176(4)$, $b = 9.837(5)$, $c = 18.319(11)$ Å, $\alpha = 91.17(4)^\circ$, $\beta = 104.29(4)^\circ$, $\gamma = 87.31(4)^\circ$, $U = 1601(1)$ Å³, $Z = 2$, $D_c = 1.98$ g cm^{-3} , $F(000) = 904$, $\mu(\text{Mo-K}\alpha) = 84.0$ cm^{-1} . Final R 0.036 (R' 0.041) for 1812 unique data [$I \geq 1\sigma(I)$], ω scans to $2\theta = 35^\circ$, otherwise as for (1).

Crystal data for (7): $\text{C}_{38}\text{H}_{28}\text{O}_2\text{SnW}$, $M = 759.1$, monoclinic, space group $C2/c$ (No. 15), $a = 19.258(8)$, $b = 8.537(2)$, $c = 34.059(20)$ Å, $\beta = 97.05(4)^\circ$, $U = 5557(4)$ Å³, $Z = 8$, $D_c = 1.78$ g cm^{-3} , $F(000) = 2928$, $\mu(\text{Mo-K}\alpha) = 51.6$ cm^{-1} . Final R 0.038 (R' 0.038) for 3787 corrected data, [$I \geq 2.0\sigma(I)$], ω scans to $2\theta = 50^\circ$, otherwise as for (1). All data were corrected for the effects of X-Ray absorption.

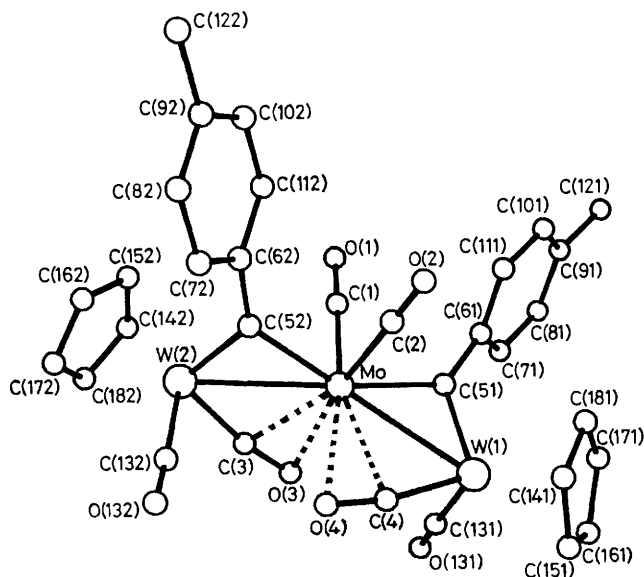


Figure 1. Molecular structure of $[\text{MoW}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (1). Dimensions: Mo-W(1) {W(2)} 2.938(1), Mo-C(51) 2.183(1), Mo-C(52) 2.189(1), W(1)-C(51) 1.940(13), W(2)-C(52) 1.949(11), W(1)-C(4) 1.923(10), Mo-C(4) 2.348(14), Mo-O(4) 2.522(8), C(4)-O(4) 1.20(1), W(2)-C(3) 1.918(15), Mo-C(3) 2.355(12), Mo-O(3) 2.525(10), and C(3)-O(3) 1.19(2) Å. W(1)-C(4)-O(4) 170.3(12), W(2)-C(3)-O(3) 169.7(10), and W(1)-Mo-W(2) 148.2(1)°.

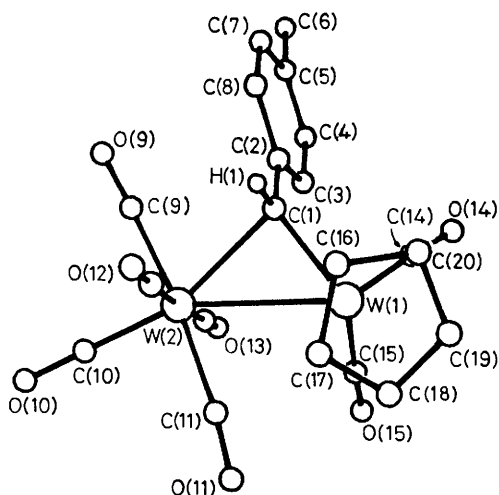


Figure 2. Molecular structure of $[\text{W}_2\{\mu\text{-C(H)C}_6\text{H}_4\text{Me-4}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ (5). Dimensions: W(1)-W(2) 3.111(1), W(1)-C(1) 2.127(7), and W(2)-C(1) 2.436(8) Å. W(1)-C(1)-W(2) 85.7°.

Å] in the compound $[\text{PtW}_2(\mu\text{-CR})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ ¹ to which (1) is related by the isobal mapping: $\text{Mo}(\text{CO})_2 \longleftrightarrow \text{C}^{4+} \longleftrightarrow \text{Pt}^0$. In (1) the molybdenum atom gains an 18-electron configuration by virtue of the two $\mu\text{-}\eta^1, \eta^2$ donor ligands C(3)O(3) and C(4)O(4). The spectroscopic data for (1)[†] are readily interpretable in terms of the structure. Thus

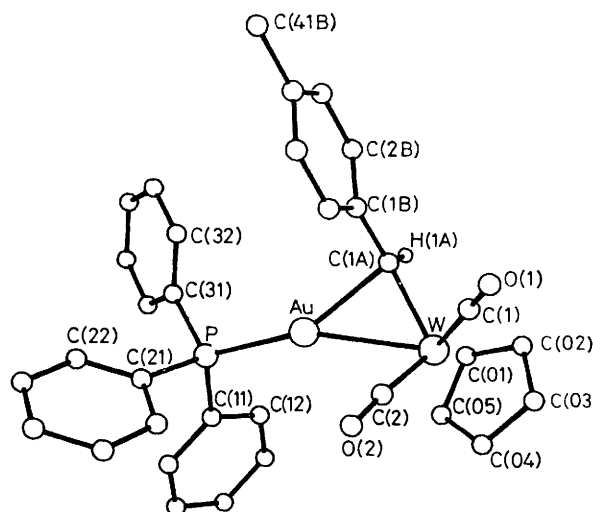


Figure 3. Molecular structure of $[\text{AuW}\{\mu\text{-C(H)C}_6\text{H}_4\text{Me-4}\}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ (6). Dimensions: Au-W 2.729(1), Au-P 2.262(4), Au-C(1A) 2.268(14), and W-C(1A) 2.058(14) Å. W-C(1A)-Au 78.1(5), W-Au-P 159.2, and C(1A)-Au-P 151.8(4)°.

the ¹³C n.m.r. spectrum shows CO ligands in three environments (relative intensity 1:1:1), and the band in the i.r. spectrum at 1 687 cm⁻¹ is due to the four-electron donor CO ligands.

It is interesting to relate (1) and (2) to the long known compound $[\text{W}(\text{CO})(\text{PhC}_2\text{Ph})_3]$,⁷ formed by treating $[\text{W}(\text{CO})_5(\text{NCMe})_3]$ with PhC_2Ph . The formation of (1) and (2) rather than the species $[\text{M}(\text{CO})\{\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_3]$ is probably due to steric reasons. Compounds (1) and (2) react with CO with step-wise displacement of $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (Scheme 1), but the dimetal complexes (3) and (4) are very unstable. However, treatment of (4)[†] with H⁻ affords the ditungsten anionic species (5), which is much better prepared (80%) as its $[\text{N}(\text{PPh}_3)_2]^+$ salt from the reaction between $[\text{W}\equiv\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ and $[\text{N}(\text{PPh}_3)_2][\text{WH}(\text{CO})_5]$.⁸

The anion (5) is apparently the first member of its class, and is synthetically useful. Thus with $[\text{AuCl}(\text{PPh}_3)]$ and SnClPh_3 it affords purple (6) and yellow (7), respectively (Scheme 1). These transformations correspond to the replacement of the $\text{W}(\text{CO})_5$ group by the isolobal fragments AuPPh_3^+ and SnPh_3^+ , respectively. Complexes (5), (6), and (7)[†] have been structurally identified by X-ray diffraction studies.[‡]

The molecular structure of the anion (5) is shown in Figure 2, from which it is seen that it corresponds to an essentially octahedral $\text{W}(\text{CO})_5$ fragment co-ordinated to a $(\eta\text{-C}_5\text{H}_5)\text{-}(\text{OC})_2\text{W}=\text{C(H)C}_6\text{H}_4\text{Me-4}$ moiety. The W(1)-C(1) separation [2.127(7) Å] is very similar to the tungsten-carbene carbon bond length [2.14(2) Å] in $[\text{W}=\text{CPh}_2(\text{CO})_5]$.⁹ The structure of

(6) (Figure 3) reveals the novel $\text{Au}(\mu\text{-CHR})\text{W}$ bridge system, while that of (7) (Figure 4) establishes this species as a mononuclear tungsten complex with an SnPh_3 group in a *transoid* configuration to an alkylidene ligand. The W-C(01) separation [2.032(7) Å] is significantly shorter than that in $[\text{W}=\text{CPh}_2(\text{CO})_5]$, mentioned above, probably owing to the higher formal oxidation state of tungsten in (7). Compounds $[\text{W}(\text{SnPh}_3)\{\text{C}(\text{OR})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (R = Me or Et), with tungsten bonded to an alkoxyphenyl carbene ligand, have been reported.¹⁰

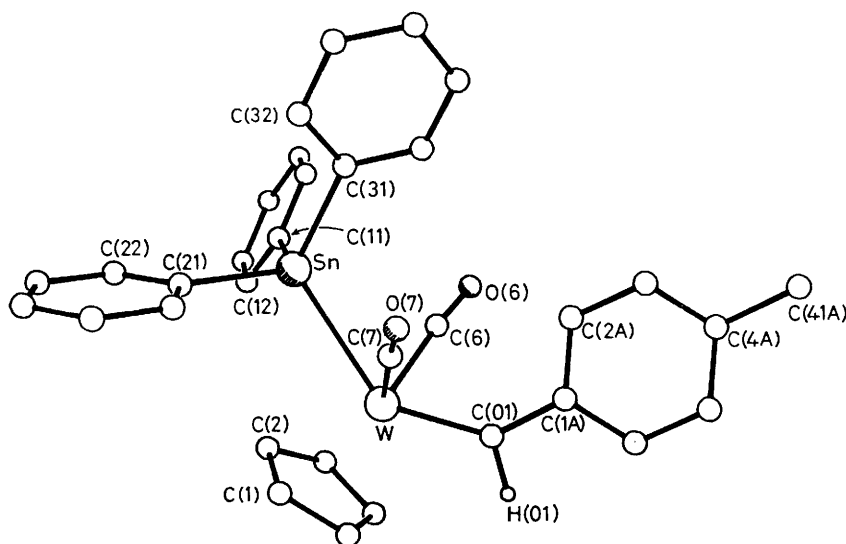


Figure 4. Molecular structure of $[W=C(H)C_6H_4Me-4(SnPh_3)(CO)_2(\eta-C_6H_5)]$ (7). Dimensions: W–Sn 2.837(1) and W–C(01) 2.032(7) Å. W–C(01)–C(1A) 137.8(5) and Sn–W–C(01) 137.8(2)°.

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