Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 70.[1] Tetranuclear Metal Compounds with Rhenium–Molybdenum or –Tungsten Bonds. Crystal Structures of $[Mo_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]\cdot 1.5CH_2Cl_2$ and $[W_2Re_2(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ *

John C. Jeffery, Michael J. Parrott, Ute Pyell, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reactions between the compounds $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) and $[Re_2(\mu\text{-}H)(\mu\text{-}\sigma{:}\eta\text{-}CH{=}CHBu^n)(CO)_8]$ afford the tetranuclear metal complexes $[M_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]$. The corresponding reaction between $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and the dirhenium compound yields a mixture of the cluster compounds $[W_2Re_2(\mu_3\text{-}CMe)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]$, $[W_2Re_2(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$, and $[WRe_2(\mu_3\text{-}CMe)(CO)_{10}(\eta\text{-}C_5H_5)]$. The molecular structures of $[Mo_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]\cdot 1.5CH_2Cl_2$ and $[W_2Re_2(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ have been established by *X*-ray diffraction studies. Crystals of the former contain two very similar crystallographically independent molecules in the asymmetric unit and there are three molecules of CH_2Cl_2 of crystallisation. The structure has a tetrahedral core of metal atoms (mean metal–metal separations 2.914 Å) with two of the faces of the tetrahedron capped by *p*-tolylmethylidyne ligands and two of the Mo–Re edges of the tetrahedron asymmetrically bridged by CO groups [Mo–C–O 155(3) and 157(3)°]. Each rhenium atom carries three orthogonal terminal CO ligands, with the remaining CO group being terminally attached to a molybdenum atom. As expected, the C_5H_5 moieties ligate the Mo atoms. In $[W_2Re_2(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2]$ the four metal atoms adopt a near-planar 'butterfly' arrangement, having a W–Re spine [2.923(1) Å] and with a W and a Re atom at the wing-tip positions. The W_2Re triangle is capped by a CMe group which lies perceptibly closer to the tungsten atoms than the rhenium. On the other side of the W_2Re_2 plane, the WRe_2 triangle is triply bridged by the $C{=}CH_2$ group. The latter is σ bonded to the W and Re atoms which form the spine of the butterfly, and is η^2-co-ordinated to the Re atom at the wing-tip position. A CO ligand asymmetrically bridges [W–C–O 159(2)°] the W–Re edge of the WRe_2 triangle and, although not located by *X*-ray diffraction, the hydrido ligand must bridge the Re–Re edge [3.023(1) Å], since the latter is perceptibly longer than the other metal–metal separations (mean 2.951 Å). Each rhenium atom is ligated by three terminal CO groups, and the tungsten atom is co-ordinated by two such groups. There is a C_5H_5 ligand bonded to each tungsten centre. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the new compounds are reported and discussed.

The complexes $[M(\equiv CR)(CO)_2(\eta\text{-}C_5R'_5)]$ (M = Mo or W, R = C_6H_4Me-4, R′ = H; M = W, R = Me, R′ = H; M = W, R = C_6H_4Me-4, R′ = Me) and $[M(\equiv CR)(CO)_2\{HB(pz)_3\}]$ (M = Mo, R = C_6H_4Me-4; M = W, R = C_6H_4Me-4 or Me; $HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate] have been extensively employed in the synthesis of compounds with heteronuclear metal–metal bonds and bridging alkylidyne groups.[2–6] Two strategies for synthetic work are available. In the first [Scheme 1(i)], alkylidyne–molybdenum or –tungsten species are treated with lightly stabilised mononuclear metal–ligand fragments. The products are usually dimetal complexes, but in some reactions trimetal compounds are obtained. This is because the initially formed dimetal species undergo further reaction with either reactant. In the second preparative method [Scheme 1(ii)], trimetal complexes with capping alkylidyne ligands are obtained from reactions between dimetal compounds and the reagents $[M(\equiv CR)(CO)_2L]$ [L = $C_5R'_5$ or $HB(pz)_3$]. There is some evidence, however, that these syntheses proceed *via* the intermediacy of dimetal species,[7] and not directly as implied in the Scheme. Irrespective of the pathway followed in reactions employing the dimetal complexes as precursors, this method has been used successfully to prepare a variety of cluster compounds. Thus treatment of the dimetal compounds $[Co_2(CO)_8]$, $[Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$, $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, and $[Re_2(CO)_{10}]$ with the appropriate alkylidyne–molybdenum or –tungsten complex affords the following trimetal species: $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5R'_5)]$ (R = C_6H_4Me-4 or Me, R = H or Me),[3,6,8] $[Co_2W(\mu_3\text{-}CR)(CO)_8\{HB(pz)_3\}]$ (R = C_6H_4Me-4 or Me),[5] $[Ni_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5R'_5)]$ (R′ = H or Me),[3,9] $[Rh_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5R'_5)(\eta\text{-}C_5Me_5)_2]$ (R = C_6H_4Me-4 or Me, R′ = H; R = Me, R′ = Me),[6,9] $[Mo_2W(\mu_3\text{-}CR)(CO)_6L(\eta\text{-}C_5H_5)_2]$ [R = C_6H_4Me-4, L = η-C_5H_5; R = Me, L = $HB(pz)_3$],[6,7] and $[Re_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}(\eta\text{-}C_5H_5)]$.[10]

In order to widen the scope of this preparative route, we have

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* 1,3;1,4-Di-μ-carbonyl-1,1,1,2,2,2,3-heptacarbonyl-3,4-di(η-cyclopentadienyl)-1,2,4;2,3,4-di-μ-*p*-tolylmethylidyne-*cyclo*-1,2-dirhenium-3,4-dimolybdenum(*Re–Re*, 4 *Re–Mo*, *Mo–Mo*)–dichloromethane (2/3) and 1,4-μ-carbonyl-1,1,1,2,2,2,3,3-octacarbonyl-3,4-di(η-cyclopentadienyl)-2,3,4-μ_3-ethylidyne-1,2-μ-hydrido-1,2,4-μ_3-[vinylidene-$C^1(Re^{1,2}W^4)C^2(Re^1)$]-*cyclo*-1,2-dirhenium-3,4-ditungsten(*Re–Re*, 3 *Re–W*, *W–W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Analytical[a] and physical data for the complexes

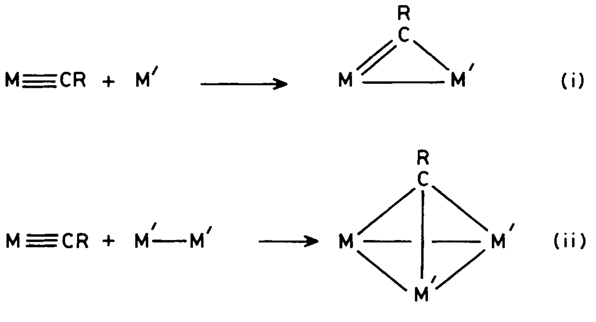
Compound	Colour	Yield (%)	$\tilde{\nu}_{max.}$(CO)[b]/cm^{-1}	Analysis (%)	
				C	H
(3a) $[Mo_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]$[c]	Green	15	2 039s, 2 007vs, 1 951m, 1 832w(br), 1 775w(br)	34.2 (34.2)	2.3 (2.1)
(3b) $[W_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]$[c]	Green	48	2 035m, 2 003s, 1 946m, 1 920 (sh), 1 830w(br), 1 775w(br)	29.9 (30.1)	1.9 (1.9)
(3c) $[W_2Re_2(\mu_3\text{-}CMe)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]$[d]	Brown	41	2 035m, 1 998s, 1 949m, 1 918 (sh), 1 840w(br), 1 735w(br)	22.8 (22.8)	1.5 (1.4)
(4) $[W_2Re_2(\mu\text{-}H)(\mu_3\text{-}\sigma:\sigma':\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8\text{-}(\eta\text{-}C_5H_5)_2]$	Red	35	2 037s, 2 012s, 1 972m, 1 955m, 1 940 (sh), 1 915s, 1 836w	23.2 (23.5)	1.4 (1.4)
(5a) $[WRe_2(\mu_3\text{-}CMe)(CO)_{10}(\eta\text{-}C_5H_5)]$	Violet	5	2 030s, 1 995s, 1 950 (sh), 1 937m		

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] Contains 1.5 CH_2Cl_2 molecules of crystallisation (see *X*-ray data). [d] Contains one CH_2Cl_2 molecule of crystallisation (see ^{1}H n.m.r. data).

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the rhenium–molybdenum and –tungsten complexes

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(3a)	2.36 (s, 3 H, Me-4), 2.37 (s, 3 H, Me-4), 5.28 (s, 5 H, C_5H_5), 5.42 (s, 5 H, C_5H_5), 7.00 (m, 8 H, C_6H_4)	355.3 (μ-C), 293.0 (μ_3-C), 264.9 (μ-CO), 232.9, 223.5 (MoCO), 197.0, 193.9 (ReCO), 165.9, 163.2 [$C^1(C_6H_4)$], 137.9, 136.1, 129.5, 128.9, 128.7, 128.4, 127.5 (C_6H_4), 101.2, 95.8 (C_5H_5), 21.3, 21.2 (Me-4)
(3b)	2.33 (s, 3 H, Me-4), 2.37 (s, 3 H, Me-4), 5.39 (s, 5 H, C_5H_5), 5.48 (s, 5 H, C_5H_5), 7.14 (s, 8 H, C_6H_4)	337.0 (μ-C), 262.1 (μ_3-C), 253.7 (μ-CO), 222.1, 206.5 (WCO), 198.3, 193.0 (ReCO), 168.4, 165.2 [$C^1(C_6H_4)$], 137.4, 135.7, 129.1, 129.0, 128.8, 128.7, 128.5 (C_6H_4), 99.4, 93.6 (C_5H_5), 21.3, 21.1 (Me-4)
(3c)	3.77 (s, 3 H, Me), 3.92 (s, 3 H, Me), 5.23 (s, 5 H, C_5H_5), 5.30 (s, 2 H, CH_2Cl_2), 5.64 (s, 5 H, C_5H_5)	
(4)	−19.57 (s, 1 H, μ-H), 4.65 (s, 3 H, Me), 5.29 [d, 1 H, CH_2, *J*(HH) 1], 5.34 (s, 5 H, C_5H_5), 5.68 (s, 5 H, C_5H_5), 6.19 [d, 1 H, CH_2, *J*(HH) 1]	238.7, 229.6, 224.7, 224.3, 207.7 (μ_3-*C*Me, μ_3-*C*=CH_2, 3WCO), 194.2, 190.1, 188.5, 188.2, 187.0, 186.5 (ReCO), 98.4, 93.4 (C_5H_5), 78.0 (C=*C*H_2), 52.7 (μ_3-C*Me*)
(5a)	3.76 (s, 3 H, Me), 6.01 (s, 5 H, C_5H_5)	

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in $CDCl_3$ at room temperature. [c] Hydrogen-1 decoupled chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2 at −40 °C.



Scheme 1. M = $M(CO)_2L$ [M = Mo or W, L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$], R = alkyl or aryl. M′ = Transition element in low oxidation state with ligands omitted

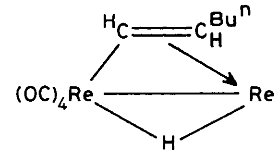
investigated reactions between the dirhenium species $[Re_2(\mu\text{-}H)(\mu\text{-}\sigma:\eta\text{-}CH{=}CHBu^n)(CO)_8]$ (**1**) and the alkylidynemetal complexes $[M({\equiv}CR)(CO)_2(\eta\text{-}C_5H_5)]$ (**2**; M = Mo or W, R = C_6H_4Me-4; M = W, R = Me). The dirhenium compound (**1**) is known to react with nucleophilic substrate molecules with facile loss of $CH_2{=}CHBu^n$ and formation of complexes $[\{Re(CO)_4L\}_2]$ [L = pyridine, $P(OMe)_3$, PPh_3, *etc.*].[11] These products contain the fragment $Re_2(CO)_8$, which is isolobal[12] with alkynes and with the complexes (**2**).[13] It seemed possible, therefore, that reactions between (**1**) and (**2**) would afford the trimetal compounds $[Re_2M(\mu_3\text{-}CR)(CO)_{10}(\eta\text{-}C_5H_5)]$ since, as mentioned above, $[Re_2(CO)_{10}]$ and (**2b**) react to give $[Re_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_{10}(\eta\text{-}C_5H_5)]$. Although reactions readily occur between (**1**) and (**2**), the major products are not trimetal compounds [Scheme 1(ii)] but tetranuclear metal complexes with novel structures.

Results and Discussion

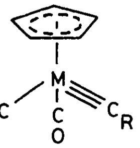
In refluxing thf (tetrahydrofuran), the compounds (**1**) and (**2a**) afford the green crystalline complex $[Mo_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]$ (**3a**), isolated by column chromatography on alumina. Data for this product are given in Table 1, but its formulation was not established until after the *X*-ray diffraction study, described below, had been carried out. The corresponding reaction between (**1**) and (**2b**) in toluene at *ca.* 70 °C affords the ditungstendirhenium compound $[W_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]$ (**3b**) (Table 1). The ^{1}H and ^{13}C-{^{1}H} n.m.r. data for (**3a**) and (**3b**) are similar (Table 2). However, discussion of these results is deferred until after the structure of (**3a**) has been described.

Selected structural parameters for compound (**3a**), obtained from the *X*-ray diffraction data, are listed in Table 3. Crystals of (**3a**) contain two very similar crystallographically independent molecules in the asymmetric unit, and these are designated (a) and (b). There are also three molecules of CH_2Cl_2 in the asymmetric unit. Only data for molecule (a) are discussed and this molecule is shown in Figure 1.

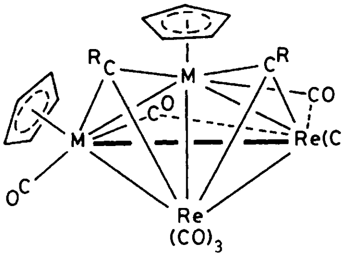
It is immediately apparent that the core of the structure consists of a tetrahedral array of two molybdenum and two



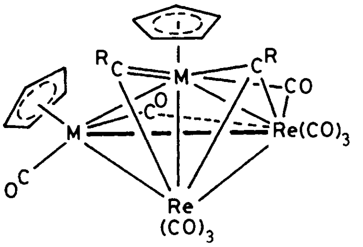
(1)



	M	R
(2a)	Mo	C_6H_4Me-4
(2b)	W	C_6H_4Me-4
(2c)	W	Me

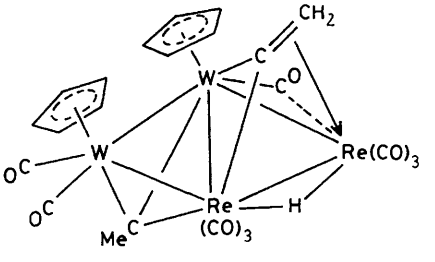


(i)

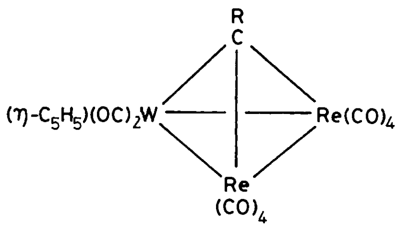


(ii)

	M	R
(3a)	Mo	C_6H_4Me-4
(3b)	W	C_6H_4Me-4
(3c)	W	Me



(4)



	R
(5a)	Me
(5b)	C_6H_4Me-4

rhenium atoms. Two faces of the tetrahedron are capped by *p*-tolylmethylidyne ligands. The metal–metal separations are very similar (mean 2.914 Å). The μ_3-C nuclei are slightly closer to Mo(1a) [2.03(3) Å] than they are to the atoms Mo(2a), Re(1a), and Re(2a) (mean 2.12 Å). The rhenium atoms each carry three terminal CO ligands, and each molybdenum atom is ligated by a cyclopentadienyl group. However, whereas Mo(2a) carries a terminally bonded CO ligand [Mo(2a)–C(8a)–O(8a) 175(3)°], the other two carbonyl groups bonded to the molybdenum atoms strongly semi-bridge the Mo(1a)–Re(2a) [Mo(1a)–C(9a)–O(9a) 155(3)°, Mo(1a)–C(9a) 2.02(4), Re(2a)···C(9a) 2.49(4) Å], and Mo(2a)–Re(2a) [Mo(2a)–C(7a)–O(7a) 157(3)°, Mo(2a)–C(7a) 2.05(4), Re(2a)···C(7a) 2.67(3) Å] edges of the tetrahedron, respectively. The Mo(1a)–C(9a)–O(9a) and Mo(2a)–C(7a)–O(7a) angles are approximately half-way between that expected for a linear bound CO group and that for a symmetrical CO bridge across the metal–metal bond.[14] Hence in this paper the two ligands C(7a)O(7a) and C(9a)O(9a) are delineated in the molecular formula as bridging species (μ-CO).

It is very probable that the molecular structure of (**3b**) is like that of (**3a**), since the spectroscopic properties of the two species are similar. Both metal cluster compounds have 60 valence electrons, and for a tetrahedral arrangement of metal atoms this might imply a closed 18-electron configuration at each metal centre. However, the presence of the two asymmetrically bridging carbonyl ligands makes electron counting at the individual metal atoms unrewarding.

Having established the crystal structure of (**3a**), and by implication that of (**3b**) also, it is possible to discuss the spectroscopic data for these compounds. Interpretation of the ^1H n.m.r. spectra (Table 2) presents no difficulty. In each spectrum the Me-4 and C_5H_5 groups each give rise to two resonances. This is as expected, since the two μ_3-CC_6H_4Me-4 ligands occupy non-equivalent sites, capping Mo_2Re and $MoRe_2$ faces of the tetrahedron.

Interpretation of the ^{13}C-$\{^1H\}$ spectra is more difficult, and strongly suggests that in solution compounds (**3a**) and (**3b**) adopt structures somewhat different from that established by *X*-ray crystallography for (**3a**) in the solid state. The ^{13}C-$\{^1H\}$

Table 3. Selected internuclear distances (Å) and angles (°) for $[Mo_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2]\cdot 1.5CH_2Cl_2$ (**3a**) with estimated standard deviations in parentheses

Molecule a		Molecule b		Molecule a		Molecule b	
Re(1a)–Re(2a)	2.905(2)	Re(1b)–Re(2b)	2.876(2)	Re(1a)–Mo(1a)	2.815(3)	Re(1b)–Mo(1b)	2.821(3)
Re(1a)–Mo(2a)	2.905(3)	Re(1b)–Mo(2b)	2.957(3)	Re(1a)–C(30a)	2.19(3)	Re(1b)–C(30b)	2.14(3)
Re(1a)–C(40a)	2.26(3)	Re(1b)–C(40b)	2.30(3)	Re(1a)–C(1a)	1.82(3)	Re(1b)–C(1b)	1.81(4)
Re(1a)–C(2a)	1.90(4)	Re(1b)–C(2b)	1.87(4)	Re(1a)–C(3a)	1.95(4)	Re(1b)–C(3b)	1.93(2)
Re(2a)–Mo(1a)	2.863(3)	Re(2b)–Mo(1b)	2.909(3)	Re(2a)–Mo(2a)	2.959(3)	Re(2b)–Mo(2b)	2.967(3)
Re(2a)–C(30a)	2.24(2)	Re(2b)–C(30b)	2.22(3)	Re(2a)–C(4a)	1.84(4)	Re(2b)–C(4b)	1.86(4)
Re(2a)–C(5a)	1.80(4)	Re(2b)–C(5b)	1.84(3)	Re(2a)–C(6a)	1.86(4)	Re(2b)–C(6b)	1.92(3)
Re(2a) ··· C(7a)	2.67(3)	Re(2b) ··· C(7b)	2.62(3)	Re(2a) ··· C(9a)	2.49(4)	Re(2b) ··· C(9b)	2.60(4)
Mo(1a)–Mo(2a)	3.037(3)	Mo(1b)–Mo(2b)	3.032(4)	Mo(1a)–C(30a)	2.03(3)	Mo(1b)–C(30b)	1.98(3)
Mo(1a)–C(40a)	2.03(3)	Mo(1b)–C(40b)	2.07(3)	Mo(1a)–C(9a)	2.02(4)	Mo(1b)–C(9b)	2.00(4)
Mo(2a)–C(40a)	2.19(3)	Mo(2b)–C(40b)	2.20(2)	Mo(2a)–C(7a)	2.05(4)	Mo(2b)–C(7b)	1.99(3)
Mo(2a)–C(8a)	1.96(3)	Mo(2b)–C(8b)	2.00(4)	C(1a)–O(1a)	1.27(4)	C(1b)–O(1b)	1.22(5)
C(2a)–O(2a)	1.20(5)	C(2b)–O(2b)	1.21(5)	C(3a)–O(3a)	1.17(4)	C(3b)–O(3b)	1.11(4)
C(4a)–O(4a)	1.25(5)	C(4b)–O(4b)	1.23(5)	C(5a)–O(5a)	1.20(5)	C(5b)–O(5b)	1.21(4)
C(6a)–O(6a)	1.21(5)	C(6b)–O(6b)	1.17(4)	C(7a)–O(7a)	1.20(4)	C(7b)–O(7b)	1.23(4)
C(8a)–O(8a)	1.17(4)	C(8b)–O(8b)	1.11(4)	C(9a)–O(9a)	1.17(4)	C(9b)–O(9b)	1.18(5)
Mo–C(η-C_5H_5) range	2.32—2.39(2)	Mo–C(η-C_5H_5) range	2.32(2)—2.41(2)				

Molecule a		Molecule b	
Re(2a)–Re(1a)–Mo(1a)	60.0(1)	Re(2b)–Re(1b)–Mo(1b)	61.4(1)
Mo(1a)–Re(1a)–Mo(2a)	64.1(1)	Mo(1b)–Re(1b)–Mo(2b)	63.2(1)
Re(1a)–Re(2a)–Mo(2a)	59.4(1)	Re(1b)–Re(2b)–Mo(2b)	60.8(1)
Re(1a)–Mo(1a)–Re(2a)	61.6(1)	Re(1b)–Mo(1b)–Re(2b)	60.2(1)
Re(2a)–Mo(1a)–Mo(2a)	60.1(1)	Re(2b)–Mo(1b)–Mo(2b)	60.6(1)
Re(1a)–Mo(2a)–Mo(1a)	56.5(1)	Re(1b)–Mo(2b)–Mo(1b)	56.2(1)
Re(1a)–C(30a)–Re(2a)	82.0(8)	Re(1b)–C(30b)–Re(2b)	83(1)
Re(2a)–C(30a)–Mo(1a)	84.0(9)	Re(2b)–C(30b)–Mo(1b)	87(1)
Re(2a)–C(30a)–C(31a)	120(2)	Re(2b)–C(30b)–C(31b)	117(2)
Re(1a)–C(40a)–Mo(1a)	82(1)	Re(1b)–C(40b)–Mo(1b)	80.4(8)
Re(2a)–Re(1a)–Mo(2a)	61.2(1)	Re(2b)–Re(1b)–Mo(2b)	61.1(1)
Re(1a)–Re(2a)–Mo(1a)	58.4(1)	Re(1b)–Re(2b)–Mo(1b)	58.4(1)
Mo(1a)–Re(2a)–Mo(2a)	62.9(1)	Mo(1b)–Re(2b)–Mo(2b)	62.1(1)
Re(1a)–Mo(1a)–Mo(2a)	59.4(1)	Re(1b)–Mo(1b)–Mo(2b)	60.6(1)
Re(1a)–Mo(2a)–Re(2a)	59.4(1)	Re(1b)–Mo(2b)–Re(2b)	58.1(1)
Re(2a)–Mo(2a)–Mo(1a)	57.0(1)	Re(2b)–Mo(2b)–Mo(1b)	58.0(1)
Re(1a)–C(30a)–Mo(1a)	83.6(9)	Re(1b)–C(30b)–Mo(1b)	86(1)
Re(1a)–C(30a)–C(31a)	130(2)	Re(1b)–C(30b)–C(31b)	130(2)
Mo(1a)–C(30a)–C(31a)	138(2)	Mo(1b)–C(30b)–C(31b)	136(2)
Re(1a)–C(40a)–Mo(2a)	82(1)	Re(1b)–C(40b)–Mo(2b)	82.2(8)
Mo(1a)–C(40a)–Mo(2a)	92(1)	Mo(1b)–C(40b)–Mo(2b)	90(1)
Mo(1a)–C(40a)–C(41a)	130(2)	Mo(1b)–C(40b)–C(41b)	131(2)
Re(1a)–C(1a)–O(1a)	172(2)	Re(1b)–C(1b)–O(1b)	174(3)
Re(1a)–C(3a)–O(3a)	173(3)	Re(1b)–C(3b)–O(3b)	176(3)
Re(2a)–C(5a)–O(5a)	176(3)	Re(2b)–C(5b)–O(5b)	177(3)
Re(2a)–C(7a)–O(7a)	124(2)	Re(2b)–C(7b)–O(7b)	123(2)
Mo(2a)–C(8a)–O(8a)	175(3)	Mo(2b)–C(8b)–O(8b)	171(3)
Mo(1a)–C(9a)–O(9a)	155(3)	Mo(1b)–C(9b)–O(9b)	158(3)
Re(1a)–C(40a)–C(41a)	128(2)	Re(1b)–C(40b)–C(41b)	125(2)
Mo(2a)–C(40a)–C(41a)	128(2)	Mo(2b)–C(40b)–C(41b)	130(2)
Re(1a)–C(2a)–O(2a)	173(3)	Re(1b)–C(2b)–O(2b)	179(3)
Re(2a)–C(4a)–O(4a)	173(3)	Re(2b)–C(4b)–O(4b)	177(3)
Re(2a)–C(6a)–O(6a)	176(4)	Re(2b)–C(6b)–O(6b)	175(3)
Mo(2a)–C(7a)–O(7a)	157(3)	Mo(2b)–C(7b)–O(7b)	158(3)
Re(2a)–C(9a)–O(9a)	126(3)	Re(2b)–C(9b)–O(9b)	124(3)

n.m.r. data (Table 2) were obtained at −40 °C, and it is apparent that the spectra observed had not attained the low-temperature limit, since only two ReCO signals are observed. There are five resonances in each spectrum which can be attributed to the ligating carbon atoms of the two *p*-tolylmethylidyne groups, and the three CO ligands associated with the Mo (or W) atoms. Of greatest significance are two signals in the spectrum of (**3a**) at δ 355.3 and 293.0 p.p.m., and correspondingly two in the spectrum of (**3b**) at δ 337.0 and 262.1 p.p.m. The peaks at δ 293.0 (**3a**) and 262.1 (**3b**) have shifts characteristic for the ligating carbon atoms of triply bridging alkylidyne groups. However, the more deshielded resonance in each spectrum [355.3 (**3a**) and 337.0 p.p.m. (**3b**)] is in the chemical shift range expected for an alkylidyne group edge-bridging a metal–metal bond.[15] The non-equivalence of the C_6H_4 fragments in these molecules is further demonstrated by the appearance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (Table 2) of nine peaks due to these moieties. Usually a C_6H_4 group in a bridging $CC_6H_4Me\text{-}4$ ligand shows four resonances, unless there is restricted rotation about the C–C_6H_4 bond, in which case six

Table 4. Selected internuclear distances (Å) and angles (°) for [$W_2Re_2(\mu\text{-}H)(\mu_3\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2$] (**4**) with estimated standard deviations in parentheses

W(1)–Re(1)	2.923(1)	W(1)–W(2)	2.908(1)	W(1)–Re(2)	2.978(1)	W(1)–C(1)	1.96(2)
W(1)–C(31)	2.10(1)	W(1)–C(41)	2.03(2)	Re(1)–W(2)	2.996(1)	Re(1)–Re(2)	3.023(1)
Re(1)–C(4)	1.95(2)	Re(1)–C(5)	1.94(2)	Re(1)–C(6)	1.93(2)	Re(1)–C(31)	2.30(2)
Re(1)–C(41)	2.19(1)	W(2)–C(2)	1.98(2)	W(2)–C(3)	2.02(2)	W(2)–C(31)	2.06(2)
Re(2) ··· C(1)	2.60(2)	Re(2)–C(7)	1.93(2)	Re(2)–C(8)	1.89(2)	Re(2)–C(9)	1.90(2)
Re(2)–C(41)	2.18(2)	Re(2)–C(42)	2.41(2)	C(1)–O(1)	1.20(3)	C(2)–O(2)	1.15(2)
C(3)–O(3)	1.14(3)	C(4)–O(4)	1.13(2)	C(5)–O(5)	1.15(2)	C(6)–O(6)	1.17(2)
C(7)–O(7)	1.13(3)	C(8)–O(8)	1.19(2)	C(9)–O(9)	1.15(2)	C(31)–C(32)	1.56(2)
C(41)–C(42)	1.41(2)	W–C(η-C_5H_5) range	2.30(2)–2.39(2)				
Re(1)–W(1)–W(2)	61.8(1)	Re(1)–W(1)–Re(2)	61.6(1)	W(2)–W(1)–Re(2)	120.5(1)	Re(1)–W(1)–C(1)	98.9(6)
Re(1)–W(1)–C(31)	51.2(4)	W(2)–W(1)–C(31)	45.0(4)	Re(2)–W(1)–C(31)	84.7(4)	Re(1)–W(1)–C(41)	48.5(4)
W(2)–W(1)–C(41)	102.5(4)	Re(2)–W(1)–C(41)	47.0(5)	W(1)–Re(1)–W(2)	58.8(1)	W(1)–Re(1)–Re(2)	60.1(1)
W(2)–Re(1)–Re(2)	116.2(1)	W(1)–Re(1)–C(31)	45.6(4)	W(2)–Re(1)–C(31)	43.3(4)	Re(2)–Re(1)–C(31)	80.6(3)
W(1)–Re(1)–C(41)	44.0(4)	W(2)–Re(1)–C(41)	96.0(4)	Re(2)–Re(1)–C(41)	46.0(4)	C(31)–Re(1)–C(41)	88.4(6)
W(1)–W(2)–Re(1)	59.3(1)	W(1)–W(2)–C(31)	46.3(4)	Re(1)–W(2)–C(31)	49.9(5)	W(1)–Re(2)–Re(1)	58.3(1)
W(1)–Re(2)–C(41)	43.0(4)	Re(1)–Re(2)–C(41)	46.4(4)	W(1)–Re(2)–C(42)	73.6(4)	Re(1)–Re(2)–C(42)	72.6(4)
C(41)–Re(2)–C(42)	35.2(5)	W(1)–C(1)–Re(2)	80.3(7)	W(1)–C(1)–O(1)	159(2)	Re(2)–C(1)–O(1)	120(1)
W(2)–C(2)–O(2)	171(1)	W(2)–C(3)–O(3)	175(2)	Re(1)–C(4)–O(4)	178(1)	Re(1)–C(5)–O(5)	171(2)
Re(1)–C(6)–O(6)	176(2)	Re(2)–C(7)–O(7)	178(2)	Re(2)–C(8)–O(8)	175(2)	Re(2)–C(9)–O(9)	178(2)
W(1)–C(31)–Re(1)	83.2(5)	W(1)–C(31)–W(2)	88.7(6)	Re(1)–C(31)–W(2)	86.8(6)	W(1)–C(31)–C(32)	136(1)
Re(1)–C(31)–C(32)	118(1)	W(2)–C(31)–C(32)	128(1)	W(1)–C(41)–Re(1)	87.5(6)	W(1)–C(41)–Re(2)	90.0(7)
Re(1)–C(41)–Re(2)	87.6(5)	W(1)–C(41)–C(42)	142(1)	Re(1)–C(41)–C(42)	128(1)	Re(2)–C(41)–C(42)	82(1)
Re(2)–C(42)–C(41)	63(1)						

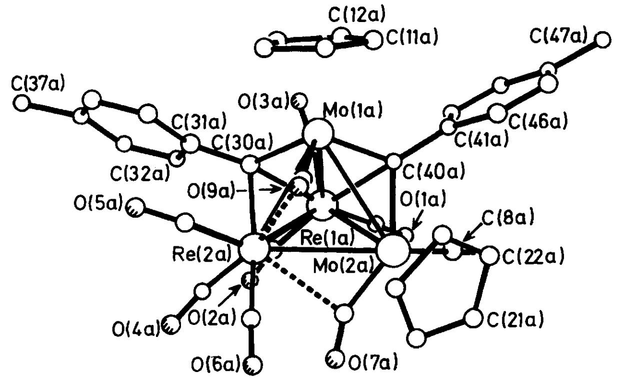


Figure 1. The molecular structure of [$Mo_2Re_2(\mu_3\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2$]·1.5$CH_2Cl_2$ (**3a**) (molecule a) showing the atom-labelling scheme

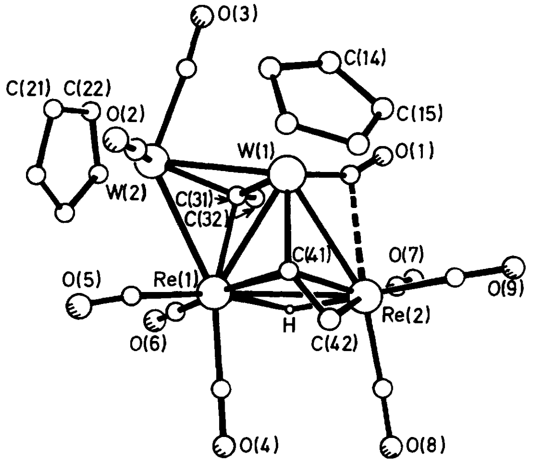


Figure 2. The molecular structure of [$W_2Re_2(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2$] (**4**) showing the atom-labelling scheme. The position of the μ-H ligand was calculated

signals may be observed.[16] However, coincidence of peaks can occur, thereby reducing the number of signals. The number and relative intensities of the peaks indicates that this is the case for (**3a**) and (**3b**), and it is not possible to deduce whether only one or both of the C–C_6H_4Me-4 fragments has restricted rotation.

From their chemical shifts it is probable that the peaks in the spectra of the complexes (**3**) at δ 264.9 (**3a**) and 253.7 p.p.m. (**3b**) are due to the presence of a fully bridging carbonyl group in each molecule. The resonances at δ 232.9 and 223.5 p.p.m. (**3a**), and at 222.1 and 206.5 p.p.m. (**3b**), can then reasonably be assigned to a semi-bridging and a terminal CO ligand, respectively, in each complex.

Thus whereas in the crystal structure of (**3a**), and by inference in that of (**3b**) as well, there are two triply bridging CC_6H_4Me-4 groups and two asymmetrically bridging CO ligands [see (**3**)(i)], the $^{13}C\text{-}\{^1H\}$ n.m.r. data imply structures having both an edge- and a triply-bridging CC_6H_4Me-4 group, together with a fully bridging CO ligand [see (**3**)(ii)]. The i.r. spectra in the carbonyl region, measured in CH_2Cl_2 (Table 1), support this idea showing a band corresponding to a bridging CO group at 1 775 cm^{-1}, with absorptions at 1 832 (**3a**) and 1 830 cm^{-1} (**3b**) corresponding to semi-bridging CO ligands.

The transformation between structures [**3**(i)] and [**3**(ii)] would require minimal rearrangement of the CC_6H_4Me-4 and CO ligands. Interestingly, in the n.m.r. spectra resonances attributable to only a single isomer were observed, indicating the absence of any equilibrium between [**3**(i)] and [**3**(ii)] in solution at −40 °C. In the synthesis of (**3a**) a trace amount of a brown complex was obtained. The latter, unlike (**3a**), is soluble in light petroleum, but has an i.r. spectrum almost identical with (**3a**). However, the appearance of a band at 1 735 cm^{-1} attributable to a bridging CO is evidence that this compound cannot be equivalent to the solid-state structure of (**3a**). The ^{1}H n.m.r. spectrum showed the presence of two Me-4 and two C_5H_5 groups [δ 2.37 and 2.38 (2 × s, 3 H, 4-Me), and 5.51 and 5.65 (2 × s, 5 H, C_5H_5)]. This compound was obtained in insufficient amount for $^{13}C\text{-}\{^1H\}$ n.m.r. studies. It may be an

Table 5. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**3a**), with estimated standard deviations in parentheses

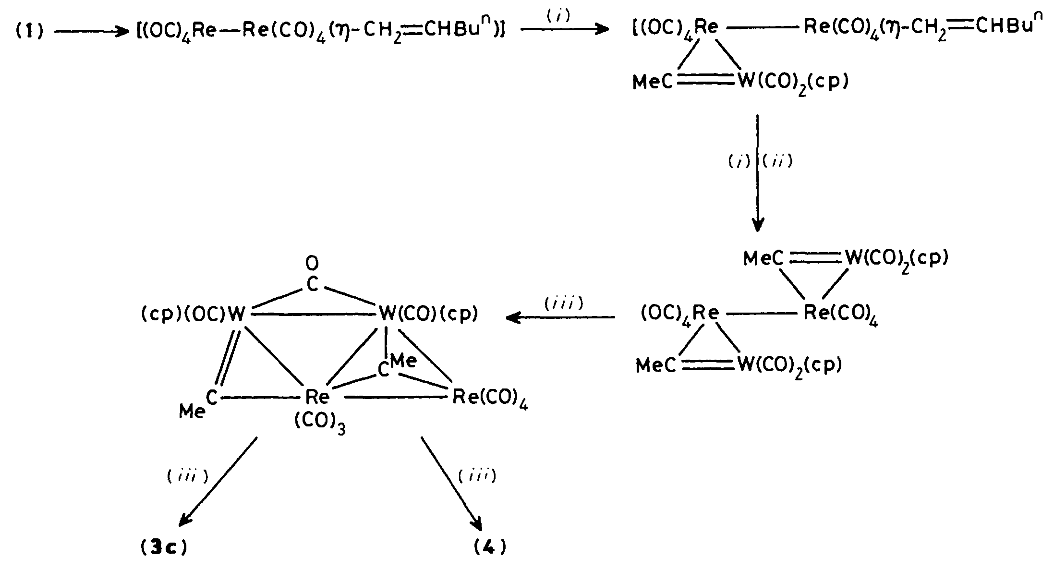
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1a)	4 797(1)	2 920(1)	1 859(1)	C(12b)	−1 729	7 673	5 382
Re(2a)	4 742(1)	1 481(1)	1 461(1)	C(13b)	−1 395	7 074	5 642
Mo(1a)	6 012(1)	2 080(1)	2 003(1)	C(14b)	−1 643	6 492	5 290
Mo(2a)	5 471(1)	2 530(1)	697(1)	C(15b)	−2 130	6 731	4 812
C(11a)	7 214(12)	2 352(11)	2 284(10)	C(21b)	−724(12)	7 936(10)	2 284(11)
C(12a)	6 776	2 607	2 765	C(22b)	−1 387	7 957	2 582
C(13a)	6 436	2 032	3 045	C(23b)	−1 535	7 281	2 808
C(14a)	6 664	1 422	2 737	C(24b)	−962	6 843	2 649
C(15a)	7 145	1 620	2 267	C(25b)	−461	7 248	2 325
C(21a)	5 627(11)	2 706(9)	−389(9)	C(30b)	−34(17)	7 109(16)	5 034(14)
C(22a)	6 305	2 725	−74	C(31b)	295(10)	6 767(10)	5 672(7)
C(23a)	6 444	2 059	186	C(32b)	875	7 069	5 996
C(24a)	5 853	1 628	32	C(33b)	1 187	6 737	6 521
C(25a)	5 348	2 028	−323	C(34b)	920	6 103	6 722
C(30a)	5 047(14)	1 973(13)	2 390(11)	C(35b)	341	5 802	6 399
C(31a)	4 736(9)	1 699(9)	3 007(7)	C(36b)	29	6 134	5 874
C(32a)	4 148	2 022	3 260	C(37b)	1 295(21)	5 724(20)	7 286(16)
C(33a)	3 836	1 744	3 792	C(40b)	−965(14)	8 154(13)	4 215(11)
C(34a)	4 113	1 144	4 071	C(41b)	−1 443(9)	8 764(8)	4 289(9)
C(35a)	4 702	821	3 818	C(42b)	−1 326	9 306	4 715
C(36a)	5 013	1 099	3 286	C(43b)	−1 810	9 851	4 739
C(37a)	3 732(18)	827(17)	4 649(14)	C(44b)	−2 412	9 854	4 336
C(40a)	5 931(15)	3 008(15)	1 558(12)	C(45b)	−2 530	9 312	3 909
C(41a)	6 422(9)	3 651(8)	1 606(9)	C(46b)	−2 045	8 767	3 886
C(42a)	6 244	4 235	1 955	C(47b)	−2 940(19)	10 454(18)	4 347(15)
C(43a)	6 686	4 814	1 964	C(1b)	302(19)	8 992(19)	4 447(16)
C(44a)	7 308	4 809	1 623	O(1b)	436(14)	9 596(14)	4 323(11)
C(45a)	7 486	4 225	1 274	C(2b)	1 172(20)	8 088(19)	4 759(16)
C(46a)	7 044	3 646	1 266	O(2b)	1 809(14)	8 096(13)	4 855(11)
C(47a)	7 805(19)	5 448(18)	1 622(15)	C(3b)	5(18)	8 403(17)	5 440(15)
C(1a)	4 584(17)	3 800(17)	1 616(14)	O(3b)	−113(12)	8 550(12)	5 931(11)
O(1a)	4 385(12)	4 418(12)	1 511(10)	C(4b)	1 314(18)	6 745(17)	4 038(14)
C(2a)	3 805(20)	2 870(18)	1 986(15)	O(4b)	1 964(15)	6 795(14)	4 007(12)
O(2a)	3 170(13)	2 870(12)	2 000(10)	C(5b)	539(18)	5 883(18)	4 550(14)
C(3a)	4 997(20)	3 303(19)	2 698(17)	O(5b)	688(14)	5 339(13)	4 807(11)
O(3a)	5 123(13)	3 465(12)	3 222(11)	C(6b)	322(18)	6 103(18)	3 392(15)
C(4a)	3 788(22)	1 392(20)	1 610(17)	O(6b)	261(14)	5 737(14)	2 953(12)
O(4a)	3 128(17)	1 338(15)	1 641(13)	C(7b)	552(18)	7 688(16)	3 314(14)
C(5a)	4 868(22)	662(21)	1 851(17)	O(7b)	1 146(14)	7 848(13)	3 144(11)
O(5a)	4 937(14)	99(14)	2 082(12)	C(8b)	−414(17)	8 743(18)	3 285(14)
C(6a)	4 553(20)	965(19)	734(17)	O(8b)	−373(14)	9 297(14)	3 157(11)
O(6a)	4 468(15)	644(14)	244(13)	C(9b)	−1 005(20)	6 374(20)	4 030(16)
C(7a)	4 385(20)	2 486(18)	642(15)	O(9b)	−1 232(14)	5 888(13)	3 749(11)
O(7a)	3 799(13)	2 557(12)	410(10)	Cl(1)	3 295(16)	3 531(12)	3 947(15)
C(8a)	5 414(16)	3 536(17)	573(13)	Cl(2)	3 311(15)	4 351(14)	2 939(10)
O(8a)	5 392(12)	4 128(12)	455(10)	C(1)	3 422(35)	4 342(33)	3 703(28)
C(9a)	6 043(19)	1 278(19)	1 390(15)	Cl(3)	1 736(10)	5 152(10)	2 459(10)
O(9a)	6 307(12)	815(12)	1 129(10)	Cl(4)	1 477(13)	6 380(14)	1 711(15)
Re(1b)	188(1)	8 079(1)	4 597(1)	C(2)	1 148(40)	5 523(36)	1 773(31)
Re(2b)	337(1)	6 692(1)	4 124(1)	Cl(5)	2 613(10)	9 734(10)	61(7)
Mo(2b)	−498(1)	7 716(2)	3 363(1)	Cl(6)	3 177(13)	9 381(11)	1 257(7)
Mo(1b)	−993(1)	7 182(1)	4 622(1)	C(3)	2 396(32)	9 469(29)	780(25)
C(11b)	−2 184(11)	7 461(12)	4 869(9)				

isomer of (**3a**), but the two species could not be interconverted.

The reaction between compound (**1**) and the ethylidyne-tungsten complex (**3c**) was also studied. After refluxing the reactants in thf, column chromatography of the mixture of products obtained afforded the three complexes [$W_2Re_2(\mu_3\text{-}CMe)_2(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)_2$] (**3c**), [$W_2Re_2(\mu\text{-}H)(\mu_3\text{-}\sigma{:}\sigma'{:}\eta^2\text{-}C{=}CH_2)(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)_2$] (**4**), and [$WRe_2(\mu_3\text{-}CMe)(CO)_{10}(\eta\text{-}C_5H_5)$] (**5a**). The latter was a very minor product, and was characterised only by its i.r. and ^1H n.m.r. spectra (Tables 1 and 2). The i.r. spectrum is very similar to that of (**5b**), the product of the reaction between (**2b**) and [$Re_2(CO)_{10}$], mentioned in the Introduction.

Compound (**3c**) was fully characterised by the data given in Tables 1 and 2, which showed it to be of similar formulation to that of (**3a**) and (**3b**). However, (**3c**) was very insoluble, and no $^{13}C\text{-}\{^1H\}$ n.m.r. data could be obtained.

The nature of compound (**4**) was established by a single-crystal *X*-ray diffraction study. Selected data are given in Table 4, and the structure is shown in Figure 2. The four metal atoms form two triangles sharing a common edge [W(1)–Re(1) 2.923(1) Å]. The metal core thus has a nearly flat butterfly arrangement with the dihedral angle between the planes defined by W(1)Re(1)W(2) and W(1)Re(1)Re(2) being only 19.4°. The W(1)Re(1)W(2) triangle is capped by an ethylidyne ligand [W(1)–C(31) 2.10(1), W(2)–C(31) 2.06(2), Re(1)–C(31) 2.30(2) Å] lying somewhat further from the rhenium than from the tungsten atoms. The W(1)Re(1)Re(2) triangle is bridged by a vinylidene ligand such that the latter is σ bonded to W(1) and



Scheme 2. cp = η-C_5H_5. (*i*) + [W(≡CMe)(CO)$_2$(cp)]; (*ii*) −CH$_2$=CHBu^n; (*iii*) −CO

Re(1) [W(1)–C(41) 2.03(2), Re(1)–C(41) 2.19(1) Å] and η-co-ordinated to Re(2) [Re(2)–C(41) 2.18(2), Re(2)–C(42) 2.41(2) Å]. The μ_3-CMe and μ_3-σ:σ′:η^2-C=CH$_2$ ligands lie on opposite sides of the W_2Re_2 array.

Table 6. Atomic positional parameters (fractional co-ordinates × 10^4) for compound (**4**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W(1)	2 569(1)	3 627(1)	389(1)
Re(1)	2 855(1)	6 207(1)	−544(1)
W(2)	1 540(1)	3 752(1)	−1 158(1)
Re(2)	3 428(1)	6 449(1)	1 148(1)
C(1)	2 057(13)	4 756(23)	1 098(10)
O(1)	1 588(9)	5 026(15)	1 505(8)
C(2)	2 468(11)	2 225(20)	−1 164(8)
O(2)	2 951(10)	1 311(15)	−1 269(8)
C(3)	882(14)	2 202(24)	−692(11)
O(3)	454(11)	1 351(17)	−471(9)
C(4)	3 854(12)	7 545(19)	−521(10)
O(4)	4 419(9)	8 351(15)	−519(7)
C(5)	3 155(11)	5 237(18)	−1 397(9)
O(5)	3 422(9)	4 790(16)	−1 884(7)
C(6)	2 076(11)	7 730(20)	−1 113(9)
O(6)	1 574(9)	8 649(15)	−1 429(7)
C(7)	2 643(14)	7 665(19)	1 565(9)
O(7)	2 175(11)	8 347(15)	1 813(8)
C(8)	4 267(11)	8 039(18)	1 269(8)
O(8)	4 829(10)	8 986(16)	1 321(7)
C(9)	3 940(12)	5 696(24)	2 130(11)
O(9)	4 256(10)	5 289(17)	2 730(8)
C(31)	1 648(10)	5 167(18)	−243(8)
C(32)	945(11)	6 297(19)	−83(11)
C(41)	3 674(10)	4 782(16)	340(9)
C(42)	4 544(11)	5 036(21)	740(10)
C(11)	3 591(15)	1 933(21)	1 160(11)
C(12)	3 382(14)	1 292(18)	453(11)
C(13)	2 492(13)	887(19)	315(10)
C(14)	2 192(16)	1 400(20)	934(12)
C(15)	2 892(18)	2 041(22)	1 459(11)
C(21)	682(14)	2 748(27)	−2 250(10)
C(22)	129(11)	3 649(26)	−1 946(10)
C(23)	428(15)	5 183(26)	−1 961(11)
C(24)	1 176(13)	5 148(29)	−2 292(10)
C(25)	1 350(12)	3 674(22)	−2 455(9)

The W(1)–Re(2) edge is strongly semi-bridged by a CO group [W(1)–C(1)–O(1) 159(2)°, W(1)–C(1) 1.96(2), Re(2)···C(1) 2.60(2) Å]. There is unequivocal n.m.r. evidence (see below) for the presence of a μ-H ligand in (**4**). It is likely that the hydrido group bridges the Re(1)–Re(2) edge [3.023(1) Å], since this metal–metal separation is somewhat longer than the other metal–metal distances (mean 2.951 Å). Moreover, although the hydrido ligand was not detected from the *X*-ray diffraction data, its location along the Re(1)–Re(2) vector is in accord with calculations based on the potential-energy minimisation technique.[17]

The two rhenium atoms in (**4**) carry three essentially orthogonal CO groups. The tungsten atoms are both ligated by a C_5H_5 group, and in addition W(2) is co-ordinated by two terminally bound CO ligands. The C_5H_5 fragment attached to W(1) lies on the same side of the W_2Re_2 cluster as the μ_3-C=CH$_2$ group, whereas the C_5H_5 ligand attached to W(2) lies on the other side of the metal array.

Compound (**4**) has 62 cluster valence electrons, and the metal atom core is nearly flat. This configuration is relatively rare,[18] but is found[19] also in the tetrarhenium anion $[Re_4(CO)_{16}]^{2-}$. The μ_3-σ:σ′:η^2-C=CH$_2$ group present in (**4**) is well established in metal cluster chemistry, and is commonly formed *via* degradation of a μ_3-CMe ligand.[20,21] Thus recently we have reported[22] that the reaction between (**2c**) and [Fe$_2$W(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_8$(η-C_5H_5)] affords a mixture of trimetal compounds, including [FeW$_2$(μ_3-σ:σ′:η^2-C=CH$_2$)(CO)$_7$(η-C_5H_5)$_2$].

Having established the molecular structure of (**4**) by *X*-ray diffraction, the spectroscopic data are readily interpretable. The asymmetrically bridging carbonyl group C(1)O(1) reveals itself by a band in the i.r. spectrum at 1 836 cm^{-1} (Table 1). The ^{1}H n.m.r. spectrum (Table 2) shows a characteristic resonance for the μ-H ligand at δ −19.57, and doublet signals for the μ-C=CH$_2$ group at δ 5.29 and 6.19 [*J*(HH) 1 Hz]. The absence of ^{183}W satellite peaks on the peak at δ −19.57 is in accord with the hydrido ligand bridging the Re–Re bond. As expected, the ^{1}H n.m.r. spectrum shows resonances for the two non-equivalent C_5H_5 groups, and a characteristic peak for the μ_3-CMe ligand.

The ^{13}C-{^{1}H} n.m.r. spectrum of (**4**) (Table 2) indicates that at the temperature of the measurement (−40 °C) site exchange of CO ligands does not occur. The two Re(CO)$_3$ groups give rise to six resonances. The μ_3-*C*Me, μ_3-*C*=CH$_2$, and WCO groups would be expected to show five distinct signals, and these are seen at δ 238.7, 229.6, 224.7, 224.3, and 207.7 p.p.m. Unfortunately, a definitive assignment of these resonances to specific groups cannot be made. However, based on data reported in previous papers in this series, the following assignment might be reasonable: 238.7 (μ_3-*C*=CH$_2$), 229.6 (μ-CO), 224.7, 224.3 (CO), and 207.7 p.p.m. (μ_3-*C*Me). The ^{13}C-$\{^1$H$\}$ n.m.r. spectrum of (**4**) shows a resonance for the μ_3-C=*C*H$_2$ nucleus at δ 78.0 p.p.m. In the spectrum of [FeW$_2$(μ_3-σ:σ':η^2-C=CH$_2$)(CO)$_7$(η-C$_5$H$_5$)$_2$] the corresponding signal occurs at δ 80.7 p.p.m.[22]

Compounds (**3c**) and (**4**) are isomers. When the former was refluxed in thf only unidentified decomposition products were observed. However, when (**4**) is heated under similar conditions it is partially converted into (**3c**), but the reaction is not clean. Moreover, since (**4**) has a μ_3-C=CH$_2$ ligand derived from a μ_3-CMe group, compounds similar to (**4**) cannot be intermediates in the formation of (**3a**) and (**3b**).

The pathways by which the new compounds described herein are formed are of interest. As mentioned in the Introduction, it had seemed likely that the products would have had structures like that of (**5b**),[10] since decomposition of (**1**) might release Re$_2$(CO)$_8$ fragments which could be captured by the alkylidyne metal complexes (**2**). However, only in the formation of (**5a**) does this process appear to occur, and then only to a very minor extent. An explanation for the formation of the tetranuclear metal compounds (**4**) and (**5**) can be based on Nubel's and Brown's[11] kinetic studies on reactions between pyridine (py) and either of the two complexes (**1**) and [Re$_2$(μ-H)(μ-σ:η-CH=CH$_2$)(CO)$_8$] which afford [$\{$Re(CO)$_4$(py)$\}_2$]. The first step in these reactions is an intramolecular C–H reductive elimination to produce an intermediate [(OC)$_4$Re–Re(CO)$_4$(η-CH$_2$=CHR)] (R = H or Bu^n) with a vacant site at one rhenium centre and with a co-ordinated alkene at the other. This species can add a molecule of py. Displacement of the alkene by a second molecule of pyridine yields the end product [$\{$Re(CO)$_4$(py)$\}_2$]. If similar steps are involved in the reactions between (**1**) and (**2**) formation of the complexes (**3**) and (**4**) would proceed according to the pathways shown in Scheme 2 for (**3c**) and (**4**). As mentioned above, in the reactions involving (**2a**) and (**2b**), leading to (**3a**) and (**3b**), respectively, a μ_3-C=CH$_2$ tetranuclear metal complex could not form.

The synthesis reported in this paper provides the first examples wherein alkylidyne metal compounds react with low-valent dimetal complexes to afford tetranuclear rather than trinuclear metal cluster species. Other tetranuclear metal cluster compounds obtained directly from an alkylidynetungsten complex include: (*i*) [Os$_3$W(μ_3-CC$_6$H$_4$Me-4)(CO)$_{11}$(η-C$_5$H$_5$)] from (**2b**) and [Os$_3$(CO)$_{10}$(η^2-C$_8$H$_{14}$)$_2$];[23] (*ii*) [RuW$_3$(μ-CR)$_2$(μ_3-CR)(μ-CO)(μ_3-η-CO)(CO)$_2$(η-C$_5$H$_5$)$_3$] (R = C$_6$H$_4$Me-4 or Ph) from (**2b**) or [W($\equiv$CPh)(CO)$_2$(η-C$_5$H$_5$)] and [Ru(η^6-C$_8$H$_{10}$)(cod)] (cod = cyclo-octa-1,5-diene), respectively;[24] and (*iii*) [Co$_2$RuW(μ_3-CC$_6$H$_4$Me-4)(μ-CO)$_2$(CO)$_8$(η-C$_5$H$_5$)] from (**2b**) and [Co$_2$Ru(CO)$_{11}$].[25]

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. Light petroleum refers to that fraction of b.p. 40—60 °C. Brockman activity II alumina was used for chromatography. Analytical and other data for the new compounds are given in Table 1. The i.r. spectra were measured with Nicolet MX 10 or MX 5 spectrophotometers, and n.m.r. spectra were recorded with JNM FX 90Q, GX 270, and GX 400 instruments. The compounds [Re$_2$(μ-H)(μ-σ:η-CH=CHBu^n)(CO)$_8$][11] and [M($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] (M = Mo or W, R = C$_6$H$_4$Me-4; M = W, R = Me)[26] were prepared as described elsewhere.

Reactions of [Re$_2$(μ-H)(μ-σ:η-CH=CHBu^n)(CO)$_8$].—(*i*) *With* [Mo($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)]. A sample of [Re$_2$(μ-H)(μ-σ:η-CH=CHBu^n)(CO)$_8$] (0.44 mmol) was prepared from [Re$_2$(CO)$_{10}$] (0.29 g, 0.44 mmol) and hex-1-ene (5 cm^3) in toluene (15 cm^3). Volatile material was removed *in vacuo* affording a yellow oil. The latter was dissolved in thf (20 cm^3) and [Mo($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.30 g, 0.94 mmol) was added. The mixture was refluxed for 12 h, after which volatile material was removed *in vacuo*. The residue was extracted with CH$_2$Cl$_2$ (2 × 10 cm^3), and the extracts were added to alumina (*ca.* 2.5 g). After pumping to dryness, the alumina was placed on top of a chromatography column (*ca.* 3 × 20 cm). Elution with CH$_2$Cl$_2$–light petroleum (1:4) removed traces of unreacted [Mo($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] and [Mo$_2$$\{\mu$-C$_2$(C$_6H_4$Me-4)$_2\}(CO)_4$($\eta$-C$_5H_5$)$_2$] (identified by i.r. spectroscopy). Further elution gave two unidentified inseparable orange eluates which yielded $<$30 mg of material. Continued elution with CH$_2$Cl$_2$–light petroleum (1:1) gave a green eluate from which solvent was removed *in vacuo*. The residue was washed with light petroleum (20 cm^3) yielding green *microcrystals* of [Mo$_2$Re$_2$(μ_3-CC$_6$H$_4$Me-4)$_2$(μ-CO)$_2$(CO)$_7$(η-C$_5$H$_5$)$_2$] (**3a**) (0.084 g). Evaporation of the light petroleum washings afforded a trace of a brown compound, possibly an isomer of (**3a**) (see Discussion section).

(*ii*) *With* [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)]. A sample (0.44 mmol) of [Re$_2$(μ-H)(μ-σ:η-CH=CHBu^n)(CO)$_8$] in toluene (20 cm^3) was treated with [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.34 g, 0.88 mmol) in a Schlenk tube fitted with a high-pressure stopcock. The reaction vessel was heated in an oven at 70 °C for 20 h, after which volatile material was removed *in vacuo*. The green residue was dissolved in CH$_2$Cl$_2$–light petroleum (5 cm^3, 1:1) and chromatographed (2 × 15 cm column). Elution with the same solvent mixture removed a trace of unreacted [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)]. Continued elution with CH$_2$Cl$_2$–light petroleum (7:3) gave a green eluate. Removal of solvent *in vacuo* followed by crystallisation of the residue from CH$_2$Cl$_2$–light petroleum (5 cm^3, 1:4) gave green *microcrystals* of [W$_2$Re$_2$(μ_3-CC$_6$H$_4$Me-4)$_2$(μ-CO)$_2$(CO)$_7$(η-C$_5$H$_5$)$_2$] (**3b**) (0.28 g).

(*iii*) *With* [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)]. A mixture of [Re$_2$(μ-H)(μ-σ:η-CH=CHBu^n)(CO)$_8$] (0.46 mmol) and [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)] (0.31 g, 0.92 mmol) in thf (20 cm^3) was refluxed for 18 h. Solvent was removed *in vacuo*, the residue was dissolved in CH$_2$Cl$_2$–light petroleum (7 cm^3, 1:2), and chromatographed (3 × 15 cm column). Elution with the same solvent mixture removed traces of unreacted [W($\equiv$CMe)(CO)$_2$(η-C$_5$H$_5$)], contaminated with [Re$_2$(CO)$_{10}$] (identified by i.r. spectroscopy). Elution with CH$_2$Cl$_2$–light petroleum (2:1) gave a red eluate, which after removal of solvent *in vacuo* and crystallisation of the residue from a mixture of the same solvents (10 cm^3, 1:1) afforded red *microcrystals* of [W$_2$Re$_2$(μ-H)(μ_3-σ:σ':η^2-C=CH$_2$)(μ_3-CMe)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)$_2$] (**4**) (0.19 g). Elution of the column with neat CH$_2$Cl$_2$ gave a brown eluate which after removal of solvent *in vacuo* gave brown *microcrystals* of [W$_2$Re$_2$(μ_3-CMe)$_2$(μ-CO)$_2$(CO)$_7$(η-C$_5$H$_5$)$_2$] (**3c**) (0.22 g). Finally, further elution with CH$_2$Cl$_2$ gave a blue band which yielded, after removal of solvent *in vacuo*, violet *microcrystals* of [WRe$_2$(μ_3-CMe)(CO)$_{10}$(η-C$_5$H$_5$)] (**5a**) (0.02 g).

Crystal Structure Determination and Refinements.—(*i*) Black poorly diffracting crystals of complex (**3a**) were eventually obtained from CH$_2$Cl$_2$–light petroleum (1:10). A crystal of dimensions *ca.* 0.45 × 0.25 × 0.20 mm was used for data collection at room temperature on a Nicolet *P*3 automated diffractometer. Of the 7 181 unique data collected (Wyckoff ω scans, $2\theta \leqslant 40°$), 4 416 met the criteria $I \geqslant 2.5\sigma(I)$ and only these were used in the structure solution and refinement. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[27]

Crystal data for complex (**3a**). $C_{35}H_{24}Mo_2O_9Re_2$ (1.5 CH_2Cl_2), $M = 2\,560.5$, monoclinic, $a = 18.841(5)$, $b = 19.317(10)$, $c = 21.148(7)$ Å, $\beta = 91.96(2)°$, $U = 7\,693(5)$ Å^3, $Z = 8$, $D_c = 2.21$ g cm^{-3}, $F(000) = 4\,824$, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 72.5 cm^{-1}.

The asymmetric unit contains two, very similar, crystallographically independent molecules of the complex (a and b) and three molecules of dichloromethane. Due to the limited data obtained from the poor quality crystal, only the metal atoms were given anisotropic thermal parameters, and hydrogen atoms were not included in the refinement. The structure was solved by conventional heavy-atom methods and difference Fourier syntheses were used to locate all non-hydrogen atoms. The aromatic ring systems were treated as rigid groups [C–C 1.395 (phenyl) and 1.420 Å (cyclopentadienyl)] and refinement by blocked-cascade least squares converged at $R = 0.061$ ($R' = 0.059$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005|F|^2]$. The final electron-density difference map showed no peaks $\geqslant 1.1$ e Å^{-3}.

(*ii*) Red crystals of (**4**) were grown from CH_2Cl_2–light petroleum (1:10). Diffracted intensities were collected, as described for (**3a**), from a crystal of dimensions *ca.* 0.60 × 0.20 × 0.21 mm. Of the 4 293 unique data collected (ω scans, $2\theta \leqslant 50°$), 3 133 had $I \geqslant 2.5\sigma(I)$. The data were corrected for Lorentz, polarisation, and *X*-ray absorption effects.[27]

Crystal data for complex (**4**). $C_{23}H_{16}O_9Re_2W_2$, $M = 1\,176.5$, monoclinic, $a = 15.774(4)$, $b = 8.690(3)$, $c = 18.370(12)$ Å, $\beta = 104.22(4)°$, $U = 2\,441(2)$ Å^3, $Z = 4$, $D_c = 3.20$ g cm^{-3}, $F(000) = 2\,096$, space group $P2_1/n$, μ(Mo-K_α) = 196.8 cm^{-1}.

The structure was solved as for (**3a**), except that all the non-hydrogen atoms were refined with anisotropic thermal parameters. Moreover, cyclopentadienyl and methyl hydrogen atoms were included in calculated positions [C–H 0.96 Å, refined U_{iso}(Me), fixed $U_{iso}(\eta\text{-}C_5H_5)$]. The vinylidene [$C(42)H_2$] and μ-H hydrogen atoms were not located, but a reasonable position for the latter ligand (fractional co-ordinates 0.279, 0.739, 0.028) was calculated using the potential-energy minimisation program HYDEX.[17] Refinement by blocked-cascade least squares, with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0030|F|^2]$, led to $R = 0.045$ ($R' = 0.046$). The final electron-density difference synthesis showed no peaks $\geqslant 1.2$ e Å^{-3}. The data required substantial correction for *X*-ray absorption and should therefore be treated with due caution.

For both structures scattering factors and corrections for anomalous dispersion were from ref. 28, and all calculations were carried out on a Data General 'Eclipse' computer with the SHELXTL system of programs.[24] Atomic co-ordinates for complexes (**3a**) and (**4**) are listed in Tables 5 and 6, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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