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Di- and tri-metal compounds prepared from the alkylidyne molybdenum complexes $[\mathrm{Mo}(\equiv\mathrm{CR})(\mathrm{CO})_2(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)]$ ($\mathrm{R} = \mathrm{C}_6\mathrm{H}_4\mathrm{OMe}\text{-}2$, $\mathrm{C}_6\mathrm{H}_4\mathrm{NMe}_2\text{-}4$ or $\mathrm{C}_6\mathrm{H}_3\mathrm{Me}_2\text{-}2,6$) and $[\mathrm{MoFe}(\mu\text{-}\mathrm{CC}_6\mathrm{H}_4\mathrm{Me}\text{-}4)(\mathrm{CO})_6(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)]$

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Abstract

The alkylidynemolybdenum compounds $[\mathrm{Mo}(\equiv\mathrm{CR})(\mathrm{CO})_2(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)]$ ($\mathrm{R} = \mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}4$, $\mathrm{C}_6\mathrm{H}_4\mathrm{OMe}\text{-}2$, $\mathrm{C}_6\mathrm{H}_4\mathrm{NMe}_2\text{-}4$ and $\mathrm{C}_6\mathrm{H}_3\mathrm{Me}_2\text{-}2,6$), and the dimetal species $[\mathrm{MoFe}(\mu\text{-}\mathrm{CC}_6\mathrm{H}_4\mathrm{Me}\text{-}4)(\mathrm{CO})_6(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)]$, have been used to prepare complexes containing bonds between molybdenum and manganese, iron, rhodium, platinum, and copper. Thus the compounds $[\mathrm{MoMn}(\mu\text{-}\mathrm{CR})(\mathrm{CO})_4(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)(\eta\text{-}\mathrm{C}_5\mathrm{H}_4\mathrm{Me})]$ ($\mathrm{R} = \mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}4$, $\mathrm{C}_6\mathrm{H}_4\mathrm{OMe}\text{-}2$, or $\mathrm{C}_6\mathrm{H}_4\mathrm{NMe}_2\text{-}4$), $[\mathrm{MoRh}(\mu\text{-}\mathrm{CC}_6\mathrm{H}_3\mathrm{Me}_2\text{-}2,6)(\mathrm{CO})_3(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)(\eta^5\text{-}\mathrm{C}_9\mathrm{H}_7)]$ ($\mathrm{C}_9\mathrm{H}_7$ = indenyl), and $[\mathrm{MoRh}_2(\mu\text{-}\mathrm{CC}_6\mathrm{H}_3\mathrm{Me}_2\text{-}2,6)(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)(\eta^5\text{-}\mathrm{C}_9\mathrm{H}_7)_2]$ have been synthesised by treating the appropriate mononuclear alkylidynemolybdenum complex with $[\mathrm{Mn}(\mathrm{CO})_2(\mathrm{thf})(\eta\text{-}\mathrm{C}_5\mathrm{H}_4\mathrm{Me})]$ (thf = tetrahydrofuran) and $[\mathrm{Rh}(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C}_9\mathrm{H}_7)]$, respectively. The heterotrinuclear metal compounds $[\mathrm{MoFePt}(\mu_3\text{-}\mathrm{CC}_6\mathrm{H}_4\mathrm{Me}\text{-}4)(\mathrm{CO})_6(\mathrm{PR'}_3)(\mathrm{C}_5\mathrm{H}_5)]$ ($\mathrm{R'} = {}^i\mathrm{Pr}$ or cyclo-$\mathrm{C}_6\mathrm{H}_{11}$), $[\mathrm{MoFeRh}(\mu_3\text{-}\mathrm{CC}_6\mathrm{H}_4\mathrm{Me}\text{-}4)(\mu\text{-}\mathrm{CO})(\mathrm{CO})_5(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)(\eta^5\text{-}\mathrm{C}_9\mathrm{H}_7)]$, and $[\mathrm{MoFeCu}(\mu\text{-}\mathrm{CC}_6\mathrm{H}_4\mathrm{Me}\text{-}4)(\mathrm{CO})_5(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)(\eta\text{-}\mathrm{C}_5\mathrm{Me}_5)]$ have been synthesised by treating the complex $[\mathrm{MoFe}(\mu\text{-}\mathrm{CC}_6\mathrm{H}_4\mathrm{Me}\text{-}4)(\mathrm{CO})_6(\eta\text{-}\mathrm{C}_5\mathrm{H}_5)]$ with the reagents $[\mathrm{Pt}(\mathrm{C}_2\mathrm{H}_4)_2(\mathrm{PR'}_3)]$, $[\mathrm{Rh}(\mathrm{CO})_2(\eta^5\text{-}\mathrm{C}_9\mathrm{H}_7)]$, and $[\mathrm{Cu}(\mathrm{thf})(\eta\text{-}\mathrm{C}_5\mathrm{Me}_5)]$, respectively. The NMR data for the new compounds are reported and discussed.

Introduction

Alkylidyne ligands have shown unparalleled utility in the bridge-assisted synthesis of heteropolymetallic clusters. Successful strategies have included the metal–ligand fragment-substitution procedures developed by Vahrenkamp and coworkers [1], and the more general addition of low-valent metal–ligand fragments to unsaturated metal–carbon linkages [2], guided by the isolobal analogy [3]. We have developed the latter methodology with extensive use of the alkylidynetungsten complexes $[\mathrm{W}(\equiv\mathrm{CR})(\mathrm{CO})_2(\mathrm{L})]$ [R = alkyl or aryl, $\mathrm{L} = \eta\text{-}\mathrm{C}_5\mathrm{H}_5$, $\eta\text{-}\mathrm{C}_5\mathrm{Me}_5$, or $\mathrm{HB(pz)}_3$ {hydrotris(pyrazol-1-yl)borate}] providing synthetic routes to compounds with bonds

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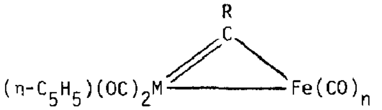
between tungsten and almost all other transition metals [2]. Initial investigations with the related alkylidynemolybdenum compounds $[Mo(\equiv CR)(CO)_2(L)]$ (R = C_6H_4Me-4, L = η-C_5H_5 [4] or $HB(pz)_3$ [5]; R = C_6H_4Me-2, C_6H_4OMe-2, $C_6H_3Me_2$-2,6, or $C_6H_4NMe_2$-4, L = η-C_5H_5 [6]) indicate a similarly rich chemistry for molybdenum, but one which is in many respects distinctly different from that of the tungsten analogues. Furthermore, the properties of the substituents on the alkylidyne carbon, particular its steric requirements, appear to exert a strong influence on the nature of the products obtained. In extending this area of chemistry, we describe herein the synthesis of heteronuclear di- and tri-metallic complexes with bond between molybdenum and the transition elements manganese, iron, rhodium, platinum and copper, employing as precursors the alkylidynemolybdenum compounds $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 (Ia) C_6H_4OMe-2 (Ib), $C_6H_4NMe_2$-4 (Ic) or $C_6H_3Me_2$-2,6 (Id)), and the μ-alkylidynemolybdenum–iron complex $[MoFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ (IIa).

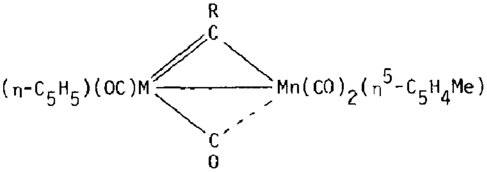
We have recently reported [4a,6] reactions between the compounds I and $[Fe_2(CO)_9]$ which afford the complexes $[MoFe(\mu\text{-}CR)(CO)_{2+n}(\eta\text{-}C_5H_5)]$ ($n = 4$ or 3) (IIa–IIe). Whereas compound IIa is stable and can be employed as a reagent in many further syntheses [4], the tungsten analogue $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ (IIf) has only a fleeting existence [7]. It was therefore of interest to delineate further both the product-determining implications of the alkylidyne substituent (R) and the replacement of tungsten by molybdenum.

Results and discussion

The complex Ia reacts with $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$ (thf = tetrahydrofuran) to afford the red compound $[MoMn(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (IIIa), data for which are given in Tables 1 and 2. Although analytically pure samples of IIIa were not obtained, inspite of repeated attempts, the spectroscopic results leave no doubt as to its constitution. The tungsten analogue $[WMn(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (IIIb) has been prepared previously by a similar method [8]. Both IIIa and IIIb show four CO stretching bands in their IR spectra, and characteristic resonances for the μ-C nuclei in their $^{13}C\ \{^1H\}$ NMR spectra (δ 425.1 (IIIa), and 395.5 ppm (IIIb)). It is noteworthy that signals for μ-C nuclei are more deshielded for molybdenum-containing species than for their



	M	R	n
(IIa)	Mo	C_6H_4Me-4	4
(IIb)	Mo	C_6H_4Me-4	4
(IIc)	Mo	C_6H_4OMe-2	4
(IId)	Mo	$C_6H_4NMe_2$-4	4
(IIe)	Mo	$C_6H_3Me_2$-2,6	3
(IIf)	W	C_6H_4Me-4	4



	M	R
(IIIa)	Mo	C_6H_4Me-4
(IIIb)	W	C_6H_4Me-4
(IIIc)	Mo	C_6H_4OMe-2
(IIId)	Mo	$C_6H_4NMe_2$-4

Table 1

Analytical [a] and physical data for the mixed metal complexes

Compound	Colour	Yield (%)	ν_{max}(CO) [b] (cm^{-1})	Analysis (%) C	Analysis (%) H
$[MoMn(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ [c] (IIIa)	red	24	2017w, 1962m, 1919vs, 1881s		
$[MoMn(\mu\text{-}CC_6H_4OMe\text{-}2)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (IIIc)	purple	58	2019w, 1982m, 1923vs, 1858m	52.7 (52.5)	3.6 (3.7)
$[MoMn(\mu\text{-}CC_6H_4NMe_2\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (IIId)	brown	42	2018vs, 1948m, 1910vs, 1862m	[d]52.7 (53.3)	4.2 (4.1)
$[MoRh(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2$ [c] (IVa)	red-brown	13	1992m, 1936s, 1845 wbr,		
$[MoRh_2(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$ (VI)	black	44	1953m, 1819s, 1783s	52.5 (52.7)	4.6 (3.5)
$[MoFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PPr^i_3)(\eta\text{-}C_5H_5)]$ (VIIa)	black	50	2035m, 2012m, 1998s, 1948s, 1870wbr	39.8 (39.9)	4.2 (3.9)
$[MoFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6\{P(C_6H_{11})_3\}(\eta\text{-}C_5H_5)]$ (VIIb)	black	80	2034m, 2014m, 1995s, 1946s, 1930sh, 1875wbr	46.1 (46.1)	4.9 (4.7)
$[MoFeRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (IXa)	black	90	2031s, 1989s, 1975m 1955m, 1945sh, 1905wbr 1778wbr	47.2 (47.6)	2.8 (2.7)
$[MoFeCu(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (X)	green	30	2038sh, 2027s, 1990sh, 1965s, 1955sh, 1923m, 1860wbr	50.3 (51.0)	4.2 (4.1)

[a] Calculated values are given in parentheses. [b] Measured in dihloromethane. [c] Not obtained in analytically pure form, see text. [d] Found: N, 2.8 (2.6)%.

tungsten analogues. Thus for IIa [5a] and IIf [7a] the μ-C peaks occur at δ 362.3 and 331.3 ppm, respectively, the signal in the molybdenum species being ca. 30 ppm more deshielded than in the tungsten compound. Whilst it would be premature to generalise on the factors determining the chemical shifts of μ-alkylidyne carbon nuclei, given the limited data available, it is clear that a shift to low-field accompanies the replacement of either of the bridged metals by a lighter member of the same triad. Furthermore, inclusion of elements to the left of the transition series in the dimetallacyclopropene unit also appears to induce a positive shift in $\delta(\mu\text{-C})$, as does co-ordinative unsaturation [6,7b,8].

In a similar manner to Ia, the alkylidynemolybdenum complexes Ib and Ic form 1 : 1 adducts with the $Mn(CO)_2(\eta\text{-}C_5H_4Me)$ fragment of composition $[MoMn(\mu\text{-}CR)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ ($R = C_6H_4OMe\text{-}2$ (IIIc) or $C_6H_4NMe_2\text{-}4$ (IIId)). Data for these compounds are summarised in Tables 1 and 2. In the $^{13}C\ \{^1H\}$ NMR spectra the μ-C resonances occur at δ 408.5 (IIIc) and 417.8 (IIId) ppm. For each of the compounds IIIa, IIIc and IIId, four CO resonances are observed, the two to higher field being, in each case, broader and accordingly assignable to manganese-bound carbonyl ligands. For IIIc, the $^{13}C\ \{^1H\}$ NMR spectrum at room temperature showed a broad peak in the carbonyl region, and cooling to −40 °C was necessary to prevent carbonyl site exchange and resolve the four resonances.

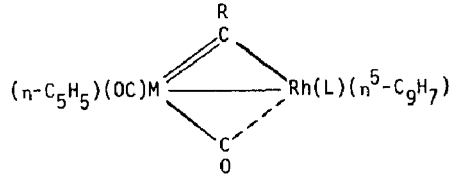
Significantly, the xylylmethylidynemolybdenum complex Id failed to form a stable adduct upon treatment with $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$. This result is consistent with the accumulating evidence that steric properties of the alkylidyne-carbon substituent are of primary importance in determining the structures of alkylidyne-bridged or -capped polymetallic ensembles [6,9]. The observation that $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ forms a stable zirconocene adduct $[WZr(\mu\text{-}CC_6H_3Me\text{-}2,6)(\mu\text{-}\sigma:\eta^2\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ upon treatment with $[Zr(^nC_4H_9)_2(\eta\text{-}C_5H_5)_2]$ [5b] would appear to be at variance. However, the increase in covalent radii for zirconium, as compared with manganese, is presumably important.

In view of the isolobal mapping [3] between the fragments $Mn(CO)_2(\eta\text{-}C_5H_4Me)$ and $Rh(CO)(\eta^5\text{-}C_9H_7)$ (C_9H_7 = indenyl), the reaction between Id and $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ was next investigated. In practice, no reaction occurred at room temperature. However, heating the reagents in thf under reflux for 3 d afforded two products. The minor product (ca. 15%) was unstable, decomposing during chromatography. It was difficult to separate from the major product (ca. 45%), which was identified as a trimetal complex and is discussed further below.

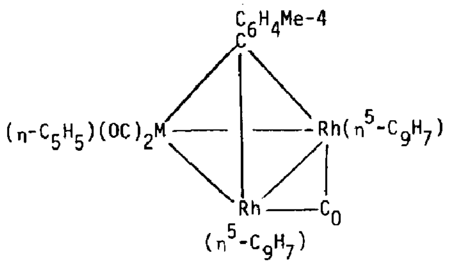
The minor product was partially characterised by $^{13}C\ \{^1H\}$ NMR and IR spectroscopy as the dimetal compound $[MoRh(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (IVa). The $^{13}C\ \{^1H\}$ NMR data were obtained from a mixture containing the major product, and hence only selected peaks for IVa are given in Table 2. However, a low-field resonance at δ 333.2 ppm may be assigned to the μ-C nucleus and may be compared with that (δ 337.3 ppm) observed for this fragment in the spectrum of the related and fully characterised species $[MoRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (IVb). The latter was prepared from the reaction between $[MoW(\equiv CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)]$ and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ [10]. Moreover, the IR spectrum of IVa shows CO stretching bands at 1992m, 1936s, and 1845w(br) cm^{-1}, very similar to those observed in the spectrum of IVb at 1991m, 1938vs, and 1872m(br) cm^{-1}. The bands at 1845 and 1872 cm^{-1}, respectively, are due to one of the CO ligands on molybdenum semibridging the Mo–Rh bond. This is supported by the $^{13}C\ \{^1H\}$ NMR data in the CO region for the two complexes. For IVa there are CO ligand resonances at δ 239.3 [d, J(RhC) 15 Hz], 236.3, and 191.0 ppm [d, J(RhC) 89 Hz]. These may be assigned to Mo(μ-CO)Rh, MoCO, and RhCO groups respectively. In the spectrum of IVb the corresponding signals are at δ 235.0, 233.8 and 189.5 ppm [J(RhC) 89 Hz] [10].

The tungsten–rhodium compounds $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(L)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (L = CO (IVc) or PMe_3 (IVd)), structurally similar to IVa and IVb, have been previously reported. Complex IVc is obtained in a room temperature reaction between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ [8], and a similar reaction between the *p*-tolylmethylidynetungsten complex and $[Rh(CO)(PMe_3)(\eta^5\text{-}C_9H_7)]$ affords VId [11]. The mild conditions required for the preparation of IVc and IVd contrast with the vigorous conditions necessary to obtain IVa, a difference presumably due to the steric demands of the $C_6H_3Me_2\text{-}2,6$ vs. $C_6H_4Me\text{-}4$ groups. An X-ray diffraction study [11] on IVd established the structure, and confirmed the presence of a strongly semi-bridging CO ligand; as implied by the spectroscopic data discussed above for IVa.

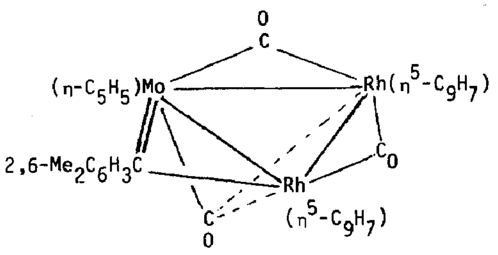
The nature of the trimetal compound formed in the reaction between Id and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ was next addressed. We have previously isolated the trimetal compounds $[MRh_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$ (M = Mo



	M	R	L
(IVa)	Mo	$C_6H_3Me_2$-2,6	CO
(IVb)	Mo	C_6H_4Me-4	CO
(IVc)	W	C_6H_4Me-4	CO
(IVd)	W	C_6H_4Me-4	PMe_3



	M
(Va)	Mo
(Vb)	W



(VI)

(Va) or W (Vb)). Complex Va is obtained, along with IVb, from the reaction between $[MoW(\equiv CC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)]$ and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ [10], while Vb is formed by treating IVc with $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ [12]. From the mode of synthesis of Vb it might have been anticipated, therefore, that the major product isolated from the reaction between Id and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ would have been a species isostructural with Va and Vb. Although microanalysis suggested a similar composition, the spectroscopic data were not in agreement with this expectation.

The ^{13}C $\{^1H\}$ NMR spectrum of the new trimetal compound VI showed a resonance (δ 315.9 ppm) for the alkylidine-carbon nucleus ca. 13 ppm more deshielded than that observed (δ 302.8 ppm) for this group in the spectrum of Va. This result suggests that the $CC_6H_3Me_2$-2,6 ligand edge-bridges a metal–metal bond rather than capping a metal triangle as does the CC_6H_4Me-4 group in Va [10]. In accord with this inference, the resonance at δ 315.9 ppm appears as a doublet [J(RhC) 33 Hz], indicating coupling with only one rhodium nucleus. Moreover, the ^{13}C $\{^1H\}$ NMR spectrum in the CO region was very informative when compared with that of Va. In the spectrum of the latter the carbonyl ligands of the $Mo(CO)_2$ moiety resonate at δ 231.6 ppm and show no coupling with the ^{103}Rh nuclei, while

Table 2

^1H and ^{13}C NMR data [a] for the mixed metal complexes

Compound	^1H [b]	^{13}C [c]
IIIa	1.82 (s, 3H, $C_5H_3\mathit{Me}$), 2.38 (s, 3H, Me-4), 4.54 (m, 4H, C_5H_4), 5.29 (s, 5H, C_5H_5), 7.51, 7.24 [$(AB)_2$, 4H, C_6H_4, *J*(AB) 8]	[d] 425.1 (μ-C), 239.0, 236.0 (MoCO), 229.0, 224.7 (MnCO), 157.8 [$C^1(C_6H_4)$], 140.0, 128.7, 128.3 (C_6H_4), 105.9 (C_5H_4), 94.7 (C_5H_5), 89.0, 88.8, 87.8, 87.5 (C_5H_4), 21.5 (Me-4), 13.3 ($C_5H_4\mathit{Me}$)
IIIc	[e] 1.97 (s, 3H, $C_5H_4\mathit{Me}$), 3.79 (s, 3H, OMe), 4.21, 4.46 (m×2, 4H, C_5H_4), 5.42 (s, 5H, C_5H_5), 7.06 (m, 4H, C_6H_4)	[f] 408.5 (μ-C), 242.6, 242.4 (MoCO), 230.1, 229.5 (MnCO), 155.4 [$C^1(C_6H_4)$], 146.0, 126.6, 119.1, 118.5, 109.7 (C_6H_4), 102.5 (C_5H_4), 93.5 (C_5H_5), 89.3, 88.5, 87.7, 86.7 (C_6H_4), 54.4 (OMe), 12.9 ($C_5H_4\mathit{Me}$)
IIId	1.81 (s, 3H, $C_5H_4\mathit{Me}$), 3.08 (s, 6H, NMe_2), 4.44, 4.53, 4.60, 4.82 (s×4, 4H, C_5H_4), 5.24 (s, 5H, C_5H_5), 6.72, 7.76 s×2, br, 4H, C_6H_4)	[d] 417.8 (μ-C), 240.8, 239.7 (MoCO), 230.4, 227.6 (MnCO), 151.7 [$C^1(C_6H_4$], 148.9, 135.9, 109.7 (C_6H_4), 105.9 (C_5H_4), 94.5 (C_5H_5), 88.4, 88.1, 87.4, 86.6 (C_5H_4), 40.1 (NMe_2), 13.2 ($C_5H_4\mathit{Me}$).
IVa		[g] 333.2 (μ-C), 239.3 [d, Mo(μ-CO)Rh, *J*(RhC) 15], 236.3 (MoCO), 191.0 [d, RhCO, *J*(RhC) 89], 158.2 [$C^1(C_6H_3)$]
VI	[h] 1.73 (s, 3H, Me), 2.06 (s, 3H, Me), 4.99 5.26, 5.31 (s×3, br, 3H, C_9H_7), 5.33 (s, 5 H, C_5H_5), 5.81–6.09 (m, 3H, C_9H_7), 6.5–7.4 (m, 11H, C_6H_3 and C_9H_7)	315.9 [d, μ-C, *J*(RhC) 33], 260.3 [d, Mo(μ-CO)Rh, *J*(RhC) 29], 244.8 [d of d, MoCO, *J*(RhC) 12, 12], 221.7 [d of d, Rh(μ-CO)Rh, *J*(RhC) 50, 50], 159.2, [$C^1(C_6H_3)$], 132.5, 128.3 (C_6H_3), 128.2, 127.9, 127.3, 126.8 (C_9H_7), 126.3 (C_6H_3), 125.9–98.4 (C_9H_7), 97.2 (C_5H_5), 93.2, 83.7, 80.7 (C_9H_7), 21.5, 21.2 (Me-2,6)
VIIa	1.18, 1.24 [d of d×2, 18H, $CH\mathit{Me}_2$, *J*(PH) 27, *J*(HH) 7], 2.28 (s, 3H, Me-4), 2.75 [d of q, 3H, $C\mathit{H}Me_2$, *J*(PH) 10, *J*(HH) 7], 5.31 (s, 5H, C_5H_5), 6.85, 7.03 [$(AB)_2$, C_6H_4, 4H, *J*(AB) 8]	[i] 341.9 [d, μ_3-C, *J*(PC) 13], 252.4, 243.2, 232.9 227.1 (MoCO), 216.6, 214.8, 214.3, 213.8, 215.5 (FeCO), 189.7, 185.8 (PtCO), 162.1, 160.2, 135.1, 133.9, 127.9, 127.6, 122.7, 119.9 (C_6H_4), 94.7 (C_5H_5), 29.0-27.5 (Pr^i), 21.4 (Me-4), 20.2–18.8 (Pr^i)
VIIb	1.18–1.42 (m, 12H, C_6H_{11}), 1.65–1.97 (m, 18H, C_6H_{11}), 2.28 (s, 3H, Me-4), 2.38–2.52 (m, 3H, $C\mathit{H}Me_2$), 5.28 (s, 5H, C_5H_5), 6.83, 7.00 [$(AB)_2$, 4H, C_6H_4, *J*(AB) 8]	[i] 342.2 [d, μ-C, *J*(PC) 13], 250.6, 241.4, 232.3, 226.8 (MoCO), 217.3, 214.7, 214.5, 213.7, 212.7 (FeCO), 189.0, 186.4 (PtCO), 162.2, 160.2, 135.1, 133.7, 127.8, 127.5, 122.7, 119.7 (C_6H_4), 94.8 (C_5H_5), 41.0–39.0 (C_6H_{11}), 31.0, 25.0 (C_6H_{11}), 21.4 (Me-4)
IXa	2.35 (s, 3H, Me-4), 5.15 (s, 5H, C_5H_5), 5.40, 5.57, 5.84 (s×3, 3H, C_9H_7), 6.42 [d, 1H, C_9H_7, *J*(HH) 8], 6.60 [d of d, 1H, *J*(HH) 8], 6.69, 7.08 [AB)$_2$, 4H, C_6H_4, *J*(AB) 8], 7.01 [d of d, 1H, C_9H_7, *J*(HH) 8, 8], 7.07 [d, 1H, C_9H_7, *J*(HH) 8]	[i] 297.2 [d, μ_3-C, *J*(RhC) 34], 243.7 [d, Fe(μ-CO)Rh, *J*(RhC) 49], 229.1, 227.1 (MoCO), 213.0 (br, FeCO) 155.0 [$C^1(C_6H_4)$], 135.9, 131.0, 130.1, 130.0, 128.0, 126.3, 125.0 (C_6H_4, C_9H_7), 119.2, 117.9, 112.9, 95.0 (C_9H_7), 90.1 (C_5H_5), 85.8, 82.7 (C_9H_7) 21.4 (Me-4)
X	1.69 (s, 15H, C_5Me_5), 2.36 (s, 3H, Me-4) 5.34 (s, 5H, C_5H_5), 7.08, 7.14 [$(AB)_2$, 4H, *J*(AB) 8].	[i] 320.8 (μ-C), 231.3, 229.0 (MoCO), 213.5, 212.9 212.0 (FeCO), 157.5 [$C^1(C_6H_4)$], 136.9, 127.8 126.2 (C_6H_4), 109.0 (C_5Me_5), 94.2 (C_5H_5), 21.5 (Me-4), 10.6 ($C_5\mathit{Me}_5$).

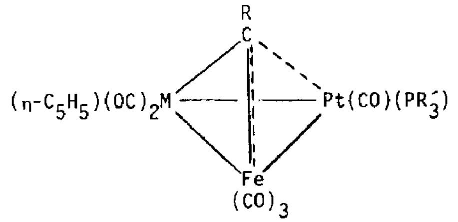
[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measurements at room temperature, unless otherwise stated. [b] Measured in $CDCl_3$ unless otherwise stated. [c] ^1H-decoupled, chemical shifts are positive to high frequency of $SiMe_4$, with measurements in CD_2Cl_2/CH_2Cl_2, unless otherwise stated. [d] In $CDCl_3$. [e] Poorly resolved spectrum. [f] Measured at −40 °C. [g] Peaks interpolated from measurements on a mixture, see text. [h] In CD_2Cl_2/CH_2Cl_2. [i] Measured at −80 °C.

the Rh(μ-CO)Rh group gives a triplet signal at δ 227.0 ppm [J(RhC) 50 Hz] [10]. This pattern is in agreement with the symmetrical structure of Va with two terminal CO ligands attached to molybdenum, and a CO group bridging equivalent rhodium centres. In contrast, the spectrum of the product VI from Id and [$\mathrm{Rh(CO)_2(\eta^5\text{-}C_9H_7)}$] displayed three rather than two CO resonances, and these were at δ 260,3 [d, J(RhC) 29 Hz], 244.8 [d of d, J(RhC) 12 and 12 Hz], and 221.7 ppm [d of d, J(RhC) 50 and 50 Hz]. The latter signal may be attributed to a Rh(μ-CO)Rh group having two non-equivalent rhodium centres. The doublet peak at 260.3 ppm may be assigned to a Mo(μ-CO)Rh group, and the doublet of doublets observed at δ 244.8 ppm, with weak ^{103}Rh–^{13}C coupling, suggests the presence of a CO group asymmetrically bridging a $\mathrm{MoRh_2}$ fragment in which the two rhodium atoms are non-equivalent. The carbonyl-associated IR bands at 1953m, 1819s and 1783s $\mathrm{cm^{-1}}$ also contrast markedly with those of Va at 1983s, 1933s, and 1788 $\mathrm{cm^{-1}}$. All these data are consistent with formulation of the trimetal compound as [$\mathrm{MoRh_2(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2}$] (VI). The preference of the 2,6-xylylmethylidyne ligand for an edge-bridging rather than a triply-bridging site in a polynuclear metal complex appears to be an important factor in determining the structures adopted by products obtained from Id or its tungsten analogue [9].

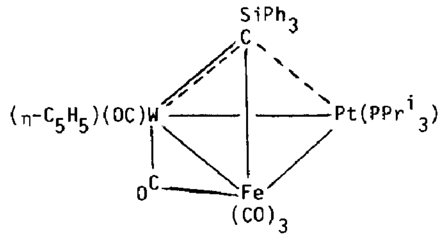
Studies were next directed at employing compound IIa as a precursor for the synthesis of trimetal compounds. Addition of metal–ligand fragments to dimetal compounds in which the metal–metal bonds are bridged by alkylidyne groups such as IIa, and having a dimetallacyclopropene core, provides a systematic route to complexes in which an alkylidyne ligand triply bridges a trimetal fragment [2]. If the metal–ligand moiety added to the dimetal complex is appropriately chosen, the trimetal cluster produced can contain three different metallic elements. Examples of species of the class involving the *p*-tolylmethylidyne group ($\mathrm{R = C_6H_4Me\text{-}4}$), and prepared in this manner, include [$\mathrm{WPtAu(\mu_3\text{-}CR)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)}$][$\mathrm{PF_6}$] [13], [$\mathrm{WPtCu(\mu_3\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)}$] [14], [$\mathrm{WFeCo(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)}$] [12], [$\mathrm{WFeRh(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)}$] [12], [$\mathrm{WFeRh(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(\eta^5\text{-}C_9H_7)\{HB(pz)_3\}}$] [15], [$\mathrm{WRhIr(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2}$] [10], [$\mathrm{WFePt(\mu_3\text{-}CR)(CO)_6(PR'_3)(\eta\text{-}C_5H_5)}$] ($\mathrm{PR'_3 = PMe_3}$, $\mathrm{PEt_3}$, or $\mathrm{PMePh_2}$) [16], [$\mathrm{WFePt(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)}$] [16], and [$\mathrm{ReFeRu(\mu_3\text{-}CR)(\mu\text{-}CO)(\mu\text{-}NO)(CO)_6(\eta^5\text{-}C_9H_7)}$] [17]. In addition, we have recently synthesised the trimetal compounds [$\mathrm{WPtCuCl(\mu_3\text{-}CSiPh_3)(CO)_2(PPr^i_3)(\eta\text{-}C_5H_5)}$], [$\mathrm{WFePt(\mu_3\text{-}CSiPh_3)(CO)_6(PPr^i_3)(\eta\text{-}C_5H_5)}$], [$\mathrm{WFePt(\mu_3\text{-}CSiPh_3)(\mu\text{-}CO)(CO)_4(PPr^i_3)(\eta\text{-}C_5H_5)}$] by treating [$\mathrm{WPt(\mu\text{-}CSiPh_3)(CO)_2(PPr^i_3)(\eta\text{-}C_5H_5)}$] with CuCl and [$\mathrm{Fe_2(CO)_9}$], respectively [18].

Addition of compound IIa to either of the reagents [$\mathrm{Pt(C_2H_4)_2(PR'_3)}$] ($\mathrm{R' = Pr^i}$ or cyclo-$\mathrm{C_6H_{11}}$), suspended in toluene, affords the cluster compounds [$\mathrm{MoFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PR'_3)(\eta\text{-}C_5H_5)}$] ($\mathrm{R' = Pr^i}$ (VIIa) or cyclo-$\mathrm{C_6H_{11}}$ (VIIb)), data for which are summarised in Tables 1 and 2. In these reactions a CO ligand migrates from Fe to Pt, as occurs also in the formation of the above mentioned compounds [$\mathrm{WFePt(\mu_3\text{-}CR)(CO)_6(PR'_3)(\eta\text{-}C_5H_5)}$] ($\mathrm{R = C_6H_4Me\text{-}4}$, $\mathrm{R' = Me}$ (VIIc) or Et (VIId); $\mathrm{R = SiPh_3}$, $\mathrm{R' = Pr^i}$ (VIIe)) [16,18]. The clusters VII have 46 valence electrons and *closo*-structures. They are thus formally electronically unsaturated, a typical property for a trimetallatetrahedrane structure containing a platinum atom.

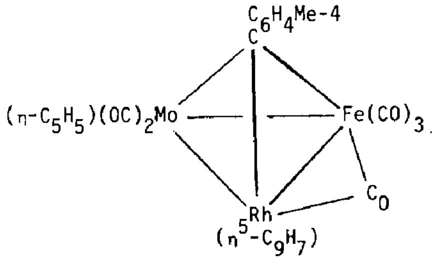
An X-ray diffraction study [16] on VIId revealed that the *p*-tolylmethylidyne ligand asymmetrically bridges the WFePt triangle, being only weakly bound to the



	M	R	R′
(VIIa)	Mo	$C_6H_4Me\text{-}4$	Pr^i
(VIIb)	Mo	$C_6H_4Me\text{-}4$	cyclo-C_6H_{11}
(VIIc)	W	$C_6H_4Me\text{-}4$	Me
(VIId)	W	$C_6H_4Me\text{-}4$	Et
(VIIe)	W	$SiPh_3$	Pr^i



(VIII)



	M
(IXa)	Mo
(IXb)	W

platinum atom. In accord with this property [10], the μ-C resonance at δ 323.1 ppm is relatively deshielded in the ^{13}C $\{^1H\}$ NMR spectrum. It is noteworthy that in the spectra of VIIa and VIIb the peaks for the alkylidyne-carbon nuclei are even more deshielded at δ 341.9 and 342.2 ppm, respectively. In part the greater shift to low field can be attributed to substitution of molybdenum for tungsten, a property referred to earlier. However, the degree of deshielding when compared, for example, with the corresponding resonance at δ 302.8 ppm for Va [10], must reflect the presence of asymmetrically capping alkylidyne ligands in VIIa and VIIb. Interestingly, the alkylidyne-carbon signals in VIIa and VIIb (Table 2) are doublets due to ^{31}P–^{13}C coupling (ca. 13 Hz). Weak ^{31}P–^{13}C coupling (9 Hz) also occurs on the μ-C resonance at 323.1 ppm in the ^{13}C $\{^1H\}$ NMR spectrum of VIId.

Examination of the NMR spectra (^{13}C $\{^1H\}$, ^{31}P $\{^1H\}$, and ^{195}Pt $\{^1H\}$) of compounds VIIa and VIIb at variable temperatures revealed an equilibrium between two isomers which was rapid on the NMR time-scale at room temperature, but which was sufficiently slow at −80 °C to observe peaks for both species. Thus in the ^{13}C $\{^1H\}$ NMR spectra of both complexes, measured at −80 °C there are two MoCO, five FeCO, and two PtCO resonances (Table 2). Evidently the expected sixth FeCO peak lies under the other five signals. The ^{31}P $\{^1H\}$ and ^{195}Pt $\{^1H\}$ NMR spectra (measured in CD_2Cl_2) also indicate a dynamic system. Thus room temperature ^{31}P $\{^1H\}$ NMR spectra show one resonance [(VIIa), δ 61.5 $\{J(PtP)$

3655 Hz}; (VIIb), δ 47.4 ppm {J(PtP) 3664 Hz}] whereas measurements at −80 °C reveal two resonances for each species [(VIIa), δ 56.2 {J(PtP) 3621 Hz} and 62.5 {J(PtP) 3591 Hz}; (VIIb), 45.4 {J(PtP) 3603 Hz} and 49.6 ppm {J(PtP) 3564 Hz}]. Relative peak intensities in the low temperature spectra indicate that the isomers are present in ca. 1/1 ratio. The ^{195}Pt {^{1}H} NMR spectra when measured at −80 °C also show two signals, one for each isomer: VIIa, δ 230.4 [J(PPt) 3621 Hz] and −232.7 ppm [J(PPt) 3591 Hz]; and for VIIb, δ 285.6 [J(PPt) 3603 Hz] and −201.5 ppm [J(PPt) 3564 Hz].

A likely explanation of the isomerism is that it relates to alternative orientations for the $Pt(CO)(PR'_3)$ fragment with respect to the remainder of the molecule. We referred earlier to the X-ray diffraction study on VIId which revealed the asymmetrically bridging CC_6H_4Me-4 group. This study also showed that if the bond between platinum and the bridging carbon atom is neglected, the platinum atom is in an approximately square planar environment with respect to the CO, PEt_3, Fe, and W groups. In contrast with this result, in the closely related compound $[WFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ the X-ray structural study [16], while again revealing an asymetrically bridging *p*-tolylmethylidyne ligand, showed that the platinum atom, neglecting the W–Pt bond, was in a coplanar environment with respect to the μ-C and Fe atoms, and the two P atoms of the ligating $PMePh_2$ groups. It is possible that two conformers of VIIa or VIIb correspond with the two different orientations of the $Pt(CO)(PEt_3)$ and $Pt(PMePh_2)_2$ groups found in VIId and in $[WPtFe(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$, respectively. Alternatively, in a structure analogous to VIId the PR'_3 groups in VIIa or VIIb can be either *cisoid* or *transoid* with respect to the Fe or Mo atoms.

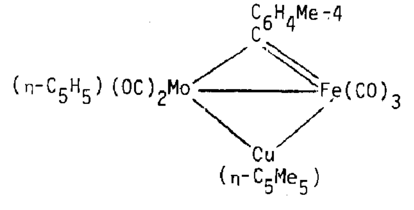
Theoretical studies [19] have shown that rotation of the $Pt(CO)(PH_3)$ moiety in the hypothetical molecule $[PtFe_3(CO)_{10}(PH_3)]^{2-}$ involves a low activation energy (ca. 25 kJ mol^{-1}). Based on a coalescence temperature of ca. 218 K, the barrier to activation in VIIa with respect to rotation of the $Pt(CO)(PPr^i_3)$ moiety about an axis through the platinum and the mid-point of the μ-CMoFe triangle is ca. 42 kJ mol^{-1}. Evidently at room temperature the $Pt(CO)(PR'_3)$ fragments in VIIa and VIIb undergo rapid rotation on the NMR time-scale, but at −80 °C the process is sufficiently slow for NMR resonances of both isomers to be observed.

An interesting property of VIIe is reversible loss of a molecule of CO in solution to give $[WFePt(\mu_3\text{-}CSiPh_3)(\mu\text{-}CO)(CO)_4(PPr^i_3)(\eta\text{-}C_5H_5)]$ (VIII) [ν_{max}(CO bridging) at 1764 cm^{-1}] [18]. It is possible that in solution compounds VIIa and VIIb also reversibly release CO to give species related to VIII, as evidenced by the occasional appearance of a very weak band at 1746 cm^{-1} in their IR spectra. However, the concentration of such species, if formed, is small. The IR spectrum of VIId [16] in the CO region [ν_{max}(CO) at 2035, 2013, 1985, 1954, 1933 and 1872 cm^{-1}] is very similar to those of VIIa and VIIb (Table 1).

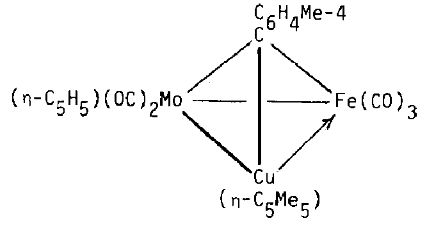
The complex $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ reacted cleanly with IIa in dichloromethane under reflux affording the trimetal compound $[FeMoRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (IXa) in essentially quantitative yield. Infrared data for IXa (Table 1) indicate that more than one isomer forms. These are presumably rotamers of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ unit [10,20]. In the ^{13}C {^{1}H} NMR spectrum of IXa (Table 2) the resonance for the μ_3-C nucleus occurs at δ 297.2 ppm as a doublet [J(RhC) 34 Hz]. The corresponding signal in the spectrum of the tungsten analogue IXb occurs at δ 287.3 ppm [J(RhC) 34 Hz] [12]. Compound IXb was prepared by treating $[WRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ with $[Fe_2(CO)_9]$.

The thf complex [Cu(thf)(η-C_5Me_5)] is a convenient source of the Cu(η-C_5Me_5) fragment [14,21], isolobal with Rh(CO)(η^5-C_9H_7) [3]. Hence the reaction between IIa and [Cu(thf)(η-C_5Me_5)] was investigated. The product was the green complex [MoFeCu(μ_3-CC_6H_4Me-4)$(CO)_5$(η-C_5H_5)(η-C_5Me_5)] (X), data for which are summarised in Tables 1 and 2. Again the observation of several CO bands in the IR spectra indicates the presence of diastereoisomers in solution corresponding to different orientations of the $Mo(CO)_2$(η-C_5H_5) group; a feature observed in several other trimetal compounds containing the groups $M(CO)_2$(η-C_5H_5) [10,20].

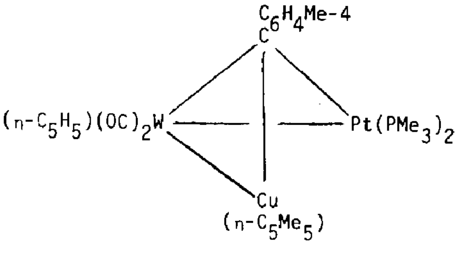
The ^{13}C $\{^1H\}$ NMR spectrum of X, measured at −80 °C, shows a resonance at δ 320.8 ppm, attributable to the CC_6H_4Me-4 nucleus. The chemical shift is in the range expected for an alkylidyne group edge-bridging a metal–metal bond, suggesting that the structure of this product is Xa, with a 'butterfly' arrangement of the core atoms, as established by X-ray diffraction in [WPtCu(μ_3-CC_6H_4Me-4)$(CO)_2(PMe_3)_2$(η-C_5H_5)(η-C_5Me_5)] (XI) [14]. In the latter complex, however, the alkylidyne-carbon triply bridges the metal atoms and resonates in the ^{13}C $\{^1H\}$ NMR spectrum at δ 266.5 ppm, a shift typical for a μ_3-C moiety. However, the alternative *closo*-structure Xb cannot be neglected, since in the compound [W_2Cu(μ_3-CC_6H_4Me-4)$(CO)_4(PPh_3)$(η-$C_5H_5)_2$] (XII), the structure of which is also based on X-ray diffraction [21], the μ_3-C ^{13}C $\{^1H\}$ NMR resonance is at δ 339.6 ppm, close to that observed for X. In the room temperature ^{13}C $\{^1H\}$ NMR spectrum of X resonances due to the CO ligands occur at δ 230.7, 229.3 (MoCO) and 212.7 ppm (FeCO), indicating site-exchange of the CO groups attached to the iron. However, in the spectrum measured at −80 °C resonances are seen at δ 231.3,



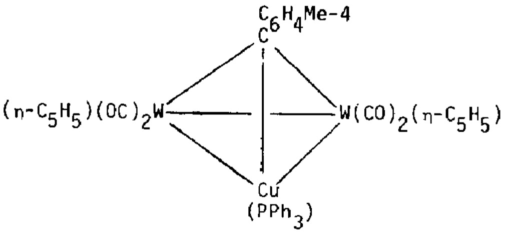
(Xa)



(Xb)



(XI)



(XII)

229.0 (MoCO), 213.5, 212.9 and 212.0 ppm (FeCO), showing that three carbonyl groups ligate the iron atoms and that on the NMR time-scale they do not undergo dynamic behaviour at the lower temperature. Without an X-ray diffraction study, however, the molecular structure of X cannot be assigned with certainty.

The results described in this paper significantly extend the range of known di- and tri-metal compounds in which molybdenum is bonded to another metallic element. Of special interest are compound VIIa, VIIb, IXa and X since they add to the number of complexes containing three dissimilar metals bridged by an alkylidyne group.

Experimental

All reactions were carried out under oxygen-free nitrogen by Schlenk-tube techniques. Light petroleum refers to that fraction of b.p. 40–60 ° C. The complexes $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$, $C_6H_4OMe\text{-}2$, $C_6H_4NMe_2\text{-}4$, $C_6H_3Me_2\text{-}2,6$) [6], $[FeMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ [4a], $[Pt(C_2H_4)_2(PR_3)]$ ($R = Pr^i$ or cyclo-C_6H_{11}) [22], and $[Cu(thf)(\eta\text{-}C_5Me_5)]$ [14] were prepared by published procedures. The reagent $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ was generally prepared in situ by passing CO through a light petroleum solution of $[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ [10,23]. Analytical and other data for the new compounds are given Tables 1 and 2. Spectra were recorded with instrumentation previously described [4]. Phosphorus-31 chemical shifts are to high frequency of 85% H_3PO_4 (external) and the $^{195}Pt\{^1H\}$ chemical shifts are to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz.

Synthesis of the complexes $[MoMn(\mu\text{-}CR)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ *(*$R = C_6H_4Me\text{-}4$, $C_6H_4OMe\text{-}2$, *or* $C_6H_4NMe_2\text{-}4$*)*

A thf (150 cm^3) solution of $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$ (0.87 g, 4.0 mmol) in a water-cooled Schlenk tube was irradiated with UV light (500 W medium-pressure Hanovia mercury vapour lamp), the reaction being monitored by infrared spectroscopy. After ca. 3 h the lamp was turned off, and solid $[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (I) (2.0 mmol) was added to the burgundy solution of in situ generated $[Mn(CO)_2(thf)(\eta\text{-}C_5H_4Me)]$. The mixture was stirred overnight. Solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2/light petroleum (20 cm^3), and chromatographed on a column (5 × 40 cm^3) packed with silica gel, eluting with the same solvent mixture. The initially eluting yellow band containing unreacted $[Mn(CO)_3(\eta\text{-}C_5H_4Me)]$ was discarded, and the following red-purple eluate was collected. Solvent was removed in vacuo and the residue was crystallised from light petroleum (10 cm^3) to give $[MnMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (IIIa) (0.26 g), $[MnMo(\mu\text{-}CC_6H_4OMe\text{-}2)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (IIIc) (0.61 g) or $[MnMo(\mu\text{-}CC_6H_4NMe_2\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)]$ (IIId) (0.45 g). The complexes III all give molecular ions $[M]^+$ in their mass spectra as well as ions due to the fragments $[M - 2(CO)]^+$, $[M - 4(CO)]^+$ and $[M - 4(CO) - Mn]^+$.

Reaction of $[Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ *with* $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$

The reagent $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ was prepared in situ by bubbling CO gas for 10 min through a solution of $[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.17 g, 0.62 mmol) in thf (20 cm^3). Then Id (0.25 g, 0.75 mmol) was added, and the mixture was heated under reflux for 3 d. Solvent was removed in vacuo from the dark red solution, and the residue was dissolved in a mixture of CH_2Cl_2 (5 cm^3) and light petroleum (25 cm^3), and chromatographed on a water-cooled Kieselgel column (2 × 10 cm), eluting with the same solvent mixture. The first eluate afforded unreacted Id. Continued elution with CH_2Cl_2/light petroleum (1/3) gave a brown solution. Removal of solvent from the latter afforded dark brown microcrystals of $[MoRh(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (IVa) (0.05 g). This compound was not stable in solution. Elution with pure dichloromethane gave a dark red third eluate. Removal of solvent in vacuo yielded brown microcrystals of $[MoRh_2(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$ (VI) (0.11 g).

Preparation of the complexes $[MoFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PR'_3)(\eta\text{-}C_5H_5)]$ *(*$R' = Pr^i$ *or cyclo-*C_6H_{11}*),* $[MoFeRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$*, and* $[MoFeCu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$

(*i*) The compound $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) (0.16 g, 0.41 mmol) was added to ethylene-saturated toluene (100 cm^3), and the mixture was stirred for 10 min. The tertiary phosphine [0.41 mmol of PPr^i_3 or $P(cyclo\text{-}C_6H_{11})_3$ as appropriate] was then added, and the mixture was stirred for a further 30 min, and then treated with solid IIa (0.20 g, 0.41 mmol). After stirring the solution for 1 h at room temperature, solvent was removed in vacuo, and the black residue was dissolved in a mixture of CH_2Cl_2 (4 cm^3) and light petroleum (8 cm^3). The solution was chromatographed on a water-cooled Kieselgel column (2 × 20 cm). Elution with CH_2Cl_2/light petroleum (1/2), increasing to 1/1 afforded a dark brown eluate containing the trimetal compound. Removal of solvent in vacuo afforded, respectively, black microcrystals of $[MoFePt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PR'_3)(\eta\text{-}C_5H_5)]$ [$R' = Pr^i$ (VIIa) (0.17 g) or R' = cyclo-C_6H_{11} (VIIb) (0.32 g)].

(*ii*) The complex $[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.13 g, 0.47 mmol) was dissolved in CH_2Cl_2 (50 cm^3) and CO gas was bubbled through the solution for 30 min. Solid IIa (0.22 g, 0.45 mmol) was added, and the mixture was stirred and heated gently under reflux for 2 h. Solvent was removed in vacuo, and the black residue was dissolved in CH_2Cl_2/light petroleum (10 cm^3, 1/1). The solution was chromatographed on a water-cooled Kieselgel column (3 × 40 cm), eluting with the same solvent mixture. Solvent was removed in vacuo from a dark brown eluate affording black microcrystals of $[MoFeRh(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (IXa) (0.24 g).

(*iii*) The copper reagent $[Cu(thf)(\eta\text{-}C_5Me_5)]$ was prepared in situ by dissolving pentamethylcyclopentadiene (0.05 g, 0.55 mmol) in thf (50 cm^3) at −80 °C, and adding $LiBu^n$ (0.50 mmol, in hexane solution) and stirring for 10 min, followed by addition of CuCl (0.05 g, 0.50 mmol). After a further 30 min, solid IIa (0.15 g, 0.31 mmol) was added, and the mixture was warmed to ca. −10 °C and stirred for 10 h. Solvent was removed in vacuo, and the dark residue was dissolved in CH_2Cl_2 (5 cm^3) and light petroleum (10 cm^3). The solution was chromatographed on an alumina column (2 × 20 cm). Elution with CH_2Cl_2/light petroleum (1/2) removed a dark green-brown eluate. Removal of solvent in vacuo gave green microcrystals of $[MoFeCu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (X) (0.06 g).

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