Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 94.[1] Synthesis of Di- and Tri-metal Compounds *via* the Reagents $[M(\equiv C\text{–}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W)

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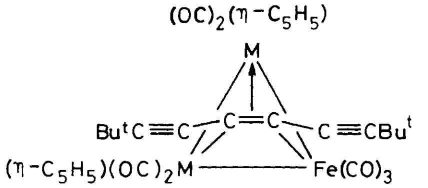
The alkynylmethylidynemetal compounds $[M(\equiv C\text{–}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) react with $[Fe_2(CO)_9]$ in thf (tetrahydrofuran) at ambient temperatures to afford *via* alkylidyne group coupling the trimetal complexes $[M_2Fe\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ in good yield. The reaction between the alkynylmethylidynetungsten reagent and $[Fe_2(CO)_9]$ also gives small quantities of $[Fe_2\{\mu\text{-}Bu^tC_2C\equiv W(CO)_2(\eta\text{-}C_5H_5)\}(CO)_6]$, a product in which a $Fe_2(CO)_6$ fragment is attached to the terminal $C\equiv CBu^t$ group of the $[W(\equiv C\text{–}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ molecule. Treatment of $[Mo(\equiv C\text{–}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ in light petroleum with $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ (C_9H_7 = indenyl) affords a chromatographically separable mixture of the compounds $[MoRh(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$, $[Mo_2Rh\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_4(\eta\text{-}C_5H_5)_2(\eta^5\text{-}C_9H_7)]$, and $[MoRh_2\{\mu_3\text{-}C\text{–}C\equiv C\text{-}Bu^t\}(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$. The corresponding tungsten–rhodium species $[WRh(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ and $[WRh_2\{\mu_3\text{-}C\text{–}C\equiv CBu^t\}(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$ have also been prepared. The dimetal compound $[MoRh(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ reacts with $[W(\equiv C\text{–}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ to give the trimetal complex $[MoWRh\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_4(\eta\text{-}C_5H_5)_2(\eta^5\text{-}C_9H_7)]$, while $[WRh(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ with $[Fe_2(CO)_9]$ and $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$ affords, respectively, the compounds $[WFeRh(\mu_3\text{-}C\text{–}C\equiv CBu^t)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ and $[WCoRh(\mu_3\text{-}C\text{–}C\equiv CBu^t)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]$. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. data for the new compounds are reported and discussed.

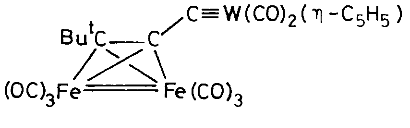
The alkylidyne metal compounds $[M(\equiv CR)(CO)_2L]$ {M = Mo or W, R = alkyl or aryl, L = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]} add metal–ligand fragments to afford numerous di-, tri-, or poly-nuclear metal complexes containing μ-CR or μ_3-CR groups.[2,3] These reactions provide rational procedures for synthesising metal cluster compounds with bonds between dissimilar transition elements. In contrast with the reagents $[M(\equiv CR)(CO)_2L]$, the alkynylmethylidyne compounds $[M(\equiv C\text{–}C\equiv CBu^t)(CO)_2L]$ {M = Mo or W, L = $\eta\text{-}C_5H_5$, $HB(pz)_3$, or $HB(dmpz)_3$ [(3,5-dimethylpyrazol-1-yl)-hydroborate]} contain two potentially active sites ($C\equiv M$ or $C\equiv C$) for combination with metal–ligand fragments.[4] However, on treatment with $[Co_2(CO)_8]$ or $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ reaction occurs exclusively at the $C\equiv M$ group in the cylcopentadienyl species, and at the $C\equiv C$ group in the hydrotris(pyrazol-1-yl)borate complexes, thereby yielding, respectively, the compounds $[MCo_2(\mu_3\text{-}C\text{–}C\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$, $[Mo_2W(\mu_3\text{-}C\text{–}C\equiv CBu^t)(CO)_6(\eta\text{-}C_5H_5)_3]$, and $[Co_2\{\mu\text{-}Bu^tC_2C\equiv M(CO)_2\text{-}L\}(CO)_6]$ [M = W, L = $HB(pz)_3$; M = Mo, L = $HB(dmpz)_3$]. In this paper we describe other reactions of the complexes $[M(\equiv C\text{–}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ [M = Mo (**1a**) or W (**1b**)] which lead to heteronuclear metal clusters, including some containing the novel ligand $\mu_3\text{-}Bu^tC\equiv C\text{–}C\equiv C\text{–}C\equiv CBu^t$.

$[M(\equiv C\text{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$

	M
(**1a**)	Mo
(**1b**)	W



	M
(**2a**)	Mo
(**2b**)	W

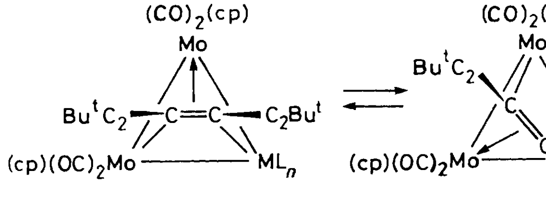


(**3**)

Results and Discussion

Treatment of complex (**1a**) in thf (tetrahydrofuran) at room temperature with 1 equivalent of $[Fe_2(CO)_9]$ gives the trimetal complex $[Mo_2Fe\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**2a**). Similarly, (**1b**) and $[Fe_2(CO)_9]$ afford the tungsten analogue $[W_2Fe\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**2b**). However, the latter reaction also gives very small amounts of a product formulated as $[Fe_2\{\mu\text{-}Bu^tC_2C\equiv W(CO)_2(\eta\text{-}C_5H_5)\}(CO)_6]$ (**3**), as described below. Data for the compounds (**2**) and (**3**) are listed in Tables 1 and 2.

The close similarity in the spectroscopic properties of (**2a**)



Scheme. cp = η-C_5H_5, ML_n = $Fe(CO)_3$ or $Rh(\eta^5$-$C_9H_7)$

and (**2b**) establishes that these species have similar structures. The μ_3-$C_2(C{\equiv}CBu^t)_2$ ligand is derived from the reagents (**1**) by a coupling of two alkynylmethylidyne groups. Linking of alkylidyne fragments is a common feature of reactions involving the compounds $[M({\equiv}CR)(CO)_2L]$ and low-valent metal complexes.[5] The resulting μ-alkyne groups bridge di-, tri-, or tetranuclear metal centres. In products containing three metal atoms *X*-ray diffraction studies have revealed the existence of two different structures, as exemplified by the species $[W_2Fe(\mu_3$-$MeC_2C_6H_4Me$-$4)(CO)_7(\eta$-$C_5H_5)_2]$[5f] and $[Mo_2Fe\{\mu_3$-C_2-$(C_6H_4Me$-$4)_2\}(CO)_6(\eta$-$C_5H_5)_2]$.[5h] In the ditungsten–iron heptacarbonyl complex the alkyne lies on the face of the metal triangle with its C_2 axis parallel to a W–Fe vector [μ_3-(η^2-$\parallel$) bonding mode[6]]. In the electronically unsaturated dimolybdenum–iron hexacarbonyl compound the alkyne also lies on the face of the metal triangle, but the C_2 axis is tilted over a Mo–Fe vector [μ_3(η^2-$\perp$) bonding mode[6]]. The compounds (**2**) are heptacarbonyl species, and accordingly these species are formulated with the μ_3-triyne adopting the η^2-$\parallel$ mode of attachment to the metal triangles, a bonding feature supported by the n.m.r. data discussed below.

The ^1H n.m.r. spectrum of complex (**2a**), measured at room temperature, shows three resonances at δ 1.27, 1.31, and 5.11 (relative intensity 9:9:10), indicating the presence of two Bu^t and two C_5H_5 groups, the former being non-equivalent. The room-temperature ^{13}C-$\{^1H\}$ n.m.r. spectrum is similar to the ^1H spectrum in showing two distinct Bu^t signals and only one C_5H_5 peak. However, when the ^{13}C-$\{^1H\}$ n.m.r. spectrum is measured at −40 °C, two C_5H_5 resonances (δ 97.8 and 97.1 p.p.m.) are observed. The ^1H n.m.r. spectrum of complex (**2b**), measured at −40 °C, shows two Bu^t signals and a resonance at δ 5.22 ascribed to the C_5H_5 ligands. However, the latter peak is very broad, suggesting two overlapping singlets. The ^{13}C-$\{^1H\}$ n.m.r. spectrum, also measured at −40 °C, shows two C_5H_5 resonances (δ 95.3 and 94.9 p.p.m.), but as with (**2a**) the chemical shifts are so close that the two C_5H_5 environments must be very similar. It was thus evident that the compounds (**2**) undergo dynamic behaviour in solution, a common property of species wherein the alkyne adopts the μ_3-(η^2-$\parallel$) bonding mode,[5] and this feature is discussed further below.

In the room-temperature ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**2a**) no resonance is observed for CO groups ligating molybdenum, and there is only a broad signal for the $Fe(CO)_3$ group at δ 209.8 p.p.m. In contrast, the spectrum measured at −40 °C has seven peaks (Table 2) in accordance with the structure shown. The ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**2b**) at −40 °C displays four WCO resonances, as expected, but there are only two peaks for the $Fe(CO)_3$ fragment. For the latter group, either two signals are coincident or more likely site exchange of CO groups at the iron centre has not ceased at the temperature of the measurement.

Resonances at δ 151.0 and 137.7 p.p.m. in the ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**2a**) are ascribed, by virtue of their deshielded nature, to the metal-ligated $C_2(C{\equiv}CBu^t)_2$ nuclei of the triyne. For the structurally related compound $[Mo_2Fe\{\mu_3$-$C_2(C_6H_4$-Me-$4)_2\}(CO)_7(\eta$-$C_5H_5)_2]$ the μ_3-C_2 resonances are more deshielded, being observed at δ 184.8 and 170.4 p.p.m.[5h] However, the $C{\equiv}CBu^t$ and C_6H_4Me-4 substituents on the ligated carbon atoms in the two species have very different electronic properties, and this would account for the large difference in chemical shifts of the μ_3-C_2R_2 nuclei. In the spectrum of (**2a**) the less deshielded pairs of peaks at δ 108.4 and 106.3, and 86.9 and 86.8 p.p.m., are assigned to the $C{\equiv}\mathit{C}Bu^t$ and $\mathit{C}{\equiv}CBu^t$ carbons, respectively. The proximity of the resonances within each pair rules out the possibility that (**2a**) should be formulated as $[Mo_2Fe(\mu_3$-$Bu^tC_2C{\equiv}C$–$C{\equiv}CBu^t)(CO)_7(\eta$-$C_5H_5)_2]$, with a terminal $C{\equiv}CBu^t$ bond bridging the Mo_2Fe triangle. Such a structure should give rise to a spectrum in which the six alkyne-carbon nuclei show a spread of ^{13}C chemical shifts, rather than occur in discrete pairs. The observation of six alkyne-carbon resonances in the spectra of (**2a**) and (**2b**) does, however, indicate that the triyne is attached to the metal cluster in an asymmetric manner, *i.e.* with the C–C axis of the ligated carbon atoms lying parallel to the M–Fe (M = Mo or W) rather than the M–M edge of the triangle. The dynamic behaviour of the complexes in solution can then be explained by their existing as one isomer which undergoes the 'windscreen-wiper' motion indicated in the Scheme [ML_n = $Fe(CO)_3$] for (**2a**). This process renders the $Mo(CO)_2(\eta$-$C_5H_5)$ moieties equivalent but not the Bu^t groups, one enantiomer exchanging with another. The structurally related compounds $[W_2M\{\mu_3$-$C_2(C_6H_4Me$-$4)_2\}(CO)_7(\eta$-$C_5H_5)_2]$ (M = Ru or Os) also show dynamic behaviour.[5d] However, two isomers exist for each of these species. In one the C_2 axis of the alkyne lies parallel to the W–W bond, and in the other it lies parallel to the W–M bond. Three dynamic processes are observed. These depend on whether, *via* a 'windscreen-wiper' motion, the alkyne traverses an $M(CO)_3$ or a $W(CO)_2(\eta$-$C_5H_5)$ vertex of the metal triangle, or whether it rotates so as to traverse all three vertices. The process of lowest activation energy is that in which the alkyne traverses the $M(CO)_3$ vertex,[5d] the pathway envisaged as occurring with the compounds (**2**). It is interesting that we obtained no spectroscopic evidence for the existence of isomers of (**2a**) or (**2b**) in which the C≡C axis of the ligand $Bu^tC_2C{\equiv}CC_2Bu^t$ lies parallel to the Mo–Mo or W–W bonds of the metal triangles.

As mentioned above, the reaction between (**1b**) and $[Fe_2$-$(CO)_9]$ gave in low yield a red crystalline complex (**3**). Both an electron impact and a fast atom bombardment (f.a.b.) mass spectrum of (**3**) gave at highest mass an envelope of peaks centred at *m/z* 678. This corresponds to an $Fe_2(CO)_6$ adduct of (**1b**). Given the effectiveness of f.a.b. mass spectra in detecting molecular ions, it seems unlikely that the peak at *m/z* 678 represents the molecular ion minus one CO group. The i.r. spectrum in the CO region (Table 1) showed no band corresponding to a bridging carbonyl group, which if present would have allowed each iron centre to attain an 18-electron configuration. However, formulation of (**3**) with an Fe=Fe double bond would not be unusual, since $Bu^tC{\equiv}CBu^t$ reacts with $[Fe_2(CO)_9]$ to give the isolobal complex $[Fe_2(\mu$-$C_2Bu^t{}_2)(CO)_6]$. The latter has an Fe=Fe bond, and has been structurally characterised by *X*-ray crystallography.[7]

The n.m.r. data support the structure shown for complex (**3**). The ^{13}C-$\{^1H\}$ n.m.r. spectrum shows resonances due to CO ligands at δ 212.5 and 208.1 p.p.m. of approximate relative intensity 3:1, and these peaks are assigned to the $Fe(CO)_3$ and $W(CO)_2$ groups, respectively. The observation of one sharp signal for the carbonyl groups ligating the iron implies equivalent $Fe(CO)_3$ units. However, it is well established that these fragments have a very low barrier to rotation. If $Fe_2(CO)_7$ were present, a unique μ-CO signal would be expected in the spectrum. A resonance at δ 327.8 p.p.m. is attributed the C≡W nucleus, but the signal-to-noise ratio was not of sufficient quality to make an unambiguous assignment. Peaks at δ 125.6 and 108.3 p.p.m. are assigned to the $\mathit{C}{\equiv}\mathit{C}Bu^t$ nuclei. The Bu^t

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

	Compound	Colour	Yield (%)	$\nu_{max.}(CO)^b/cm^{-1}$	Analysis (%) C	H
(2a)	$[Mo_2Fe\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$	Brown	62	2 044vs, 1 994s, 1 978s, 1 887m, 1 846m, 1 816m	48.6 (48.9)	3.7 (3.7)
(2b)	$[W_2Fe\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$	Brown	60	2 041vs, 1 988s, 1 971s, 1 887m, 1 845m, 1 824m	39.6 (39.8)	3.2 (3.0)
(3)	$[Fe_2(\mu\text{-}Bu^tC_2C\equiv W(CO)_2(\eta\text{-}C_5H_5)\}(CO)_6]$	Red	3	2 053m, 2 003vs, 1 973m, 1 930 (sh)	34.4 (35.4)	2.7 (2.1)
(4a)	$[MoRh(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$	Brown	45	2 003s, 1 931vs, 1 849m	52.0 (51.8)	4.2 (3.8)
(4b)	$[WRh(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$	Brown	48	1 998s, 1 924vs, 1 840m	44.5 (44.7)	3.4 (3.3)
(5)	$[Mo_2Rh\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_4(\eta\text{-}C_5H_5)_2(\eta^5\text{-}C_9H_7)]$	Green	14	[c] 1 968s, 1 853s(sh), 1 814vs	52.8 (53.0)	4.5 (4.2)
(6a)	$[MoRh_2(\mu_3\text{-}C\text{–}C\equiv CBu^t)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$	Green	90	1 884vs, 1 813s	51.0 (51.2)	3.7 (3.7)
(6b)	$[WRh_2(\mu_3\text{-}C\text{–}C\equiv CBu^t)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$	Green	86	1 881vs, 1 808s	46.0 (46.0)	3.5 (3.3)
(7)	$[MoWRh\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_4(\eta\text{-}C_5H_5)_2(\eta^5\text{-}C_9H_7)]$	Green	15	[c] 1 956s, 1 846vs(sh), 1 808s	47.2 (48.0)	3.6 (3.8)
(8)	$[WFeRh(\mu_3\text{-}C\text{–}C\equiv CBu^t)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$	Green	69	2 048vs, 1 989s, 1 901s, 1 833m	41.8 (41.4)	2.6 (2.7)
(9)	$[WCoRh(\mu_3\text{-}C\text{–}C\equiv CBu^t)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]$	Green	49	1 876vs, 1 806s	47.0 (47.7)	4.0 (4.3)

[a] Calculated values are given in parentheses. [b] Measured in CH_2Cl_2, unless otherwise stated. [c] Measured in light petroleum.

group gives rise to two signals at δ 33.4 (*C*Me$_3$) and 29.4 p.p.m. (C*Me*$_3$). These assignments are based on previous results,[4] which showed that the ^{13}C chemical shifts of the two carbon nuclei of the Bu^t group can be used to determine whether it is the C≡M or the C≡C unit of the alkynylmethylidyne group which is involved in bridging a dimetal centre. Thus the compounds $[M(\equiv C\text{–}C\equiv Bu^t)(CO)_2L]$ [M = Mo, L = $HB(dmpz)_3$; M = W, L = $HB(pz)_3$] react to give products in which the C≡C unit bridges the metal–metal bond and in these products the *C*Me$_3$ signal is more deshielded than the C*Me*$_3$.[4] In contrast, when the compounds (**1**) react to give products in which the C≡M fragment bridges the metal–metal bond the *C*Me$_3$ nucleus is more shielded than the C*Me*$_3$, as found in the spectrum of $[WCo_2(\mu_3\text{-}C\text{–}C\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$ [δ 30.1 (C*Me*$_3$) and 28.3 p.p.m. (*C*Me$_3$)].[4] The ^1H n.m.r. spectrum of complex (**3**) shows the expected resonances for the Bu^t and C_5H_5 groups (Table 2).

There was no evidence for the formation of a molybdenum analogue of (**3**) in the reaction between (**1a**) and $[Fe_2(CO)_9]$. Moreover, (**3**) is the minor product of the reaction between (**1b**) and $[Fe_2(CO)_9]$. These observations are in accord with the earlier work[4] which demonstrated that addition of metal–ligand fragments to the complexes (**1**) occurs preferentially at the C≡M groups. Moreover, with the exception of (**3**), the compounds (**2**) were the only products of the reactions between (**1**) and $[Fe_2(CO)_9]$, irrespective of the proportions of the reactants used. This is surprising in view of previous results employing the compounds $[M(\equiv CR)(CO)_2L]$ (M = Mo or W, R = C_6H_4Me-4, L = η-C_5H_5;[5b,h] M = W, R = C_6H_4Me-4, L = η-C_5Me_5[8]). These species react with $[Fe_2(CO)_9]$ to produce, depending on the stoicheiometry, either di- or tri-metal compounds. The dimetal compounds $[MFe(\mu\text{-}CR)(CO)_nL]$ (n = 5 or 6) contain $Fe(CO)_3$ or $Fe(CO)_4$ groups, while the trimetal complexes are of three types, *viz*. $[MFe_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8L]$ or $[M_2Fe(\mu\text{-}RC_2R)(CO)_n(\eta\text{-}C_5H_5)_2]$ (n = 6 or 7), the last two corresponding to the previously discussed μ_3-(η^2-⊥) and μ_3-(η^2-∥) bonding modes of the alkyne, respectively. The trimetal compounds are formed *via* addition of iron carbonyl or $RC\equiv M(CO)_2L$ groups to the dimetal species. It is likely, therefore, that the compounds (**2**) form *via* addition of a second molecule of (**1a**) or (**1b**) to an intermediate dimetal complex $[MFe(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_n(\eta\text{-}C_5H_5)]$ (n = 5 or 6).[9]

Reactions between the complexes (**1**) and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ (C_9H_7 = indenyl), the latter generated *in situ* from $[Rh(\eta\text{-}C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ and CO in light petroleum, were next investigated. The rhodium dicarbonyl species acts as a source of the $Rh(CO)(\eta^5\text{-}C_9H_7)$ fragment which readily adds to C≡M (M = Mo or W) bonds.[10] Treatment of $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ with (**1a**) gave three compounds $[MoRh(\mu\text{-}C\text{–}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (**4a**), $[Mo_2Rh\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_4(\eta\text{-}C_5H_5)_2(\eta^5\text{-}C_9H_7)]$ (**5**), and $[MoRh_2(\mu_3\text{-}C\text{–}C\equiv CBu^t)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$ (**6a**) in varying proportions. In general, (**4a**) can be isolated in reasonable yield as brown crystals from the reaction (*ca*. 3 h) between (**1a**) and $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ in 1:1 ratio. Using an excess of (**1a**) favours the formation of (**5**), but only to a limited degree, since it is a minor product. Treating (**1a**) with 2 equivalents of $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ for *ca*. 24 h affords (**6a**) in high yield.

Compound (**4a**) was characterised (Tables 1 and 2) as the μ-C–C≡CBu^t analogue of the μ-CC_6H_4Me-4 compound $[MoRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$.[11] However, whereas the latter complex is stable, compound (**4a**) decomposes in solution within a few hours, and also decomposes slowly in the solid state. The chief decomposition product of (**4a**) is the trimetal compound (**6a**). Complex (**5**) is not produced by this pathway. The ^1H n.m.r. spectrum of (**4a**) (Table 2) shows characteristic peaks for the Bu^t and η^5-C_9H_7 groups. However, some of the signals for the indenyl ligand are broadened by a fluxional process which probably involves site exchange of the terminal and semi-bridging CO ligands attached to the molybdenum *via* a rocking motion of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ group. Evidence for this process comes from the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum since not only are the η^5-C_9H_7 resonances broad, but only one signal is seen for the $Mo(CO)_2$ group. As expected, the i.r. spectrum of (**4a**) in the carbonyl region shows three bands (2 003, 1 931, and 1 849 cm^{-1}), that at lowest frequency being due to the semi-bridging CO ligand. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum the μ-*C*–C≡CBu^t resonance occurs as a doublet at δ 292.8 p.p.m. [J(RhC) 32 Hz]. This signal is considerably less deshielded than that observed (δ 337.3 p.p.m.) for the μ-C nucleus in the spectrum of the dimetal complex $[MoRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$.[11] Earlier it was found[4] that the ^{13}C n.m.r. chemical shifts of μ_3-*C*–C≡CBu^t nuclei in trimetal compounds are also less deshielded than those

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

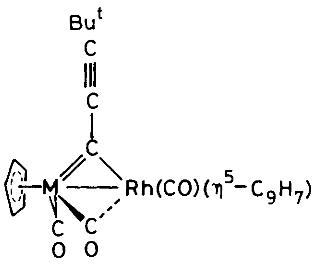
Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
(2a)	1.27, 1.31 (s × 2, 18 H, Bu^t), 5.11 (s, 10 H, C_5H_5)	[d] 242.7, 235.4, 233.7, 225.9 (MoCO), 212.3, 208.7, 208.0 (FeCO), 151.0, 137.7 [*C*$_2$(C≡CBu^t)$_2$], 108.4, 106.3 (C≡*C*Bu^t), 97.8, 97.1 (C_5H_5), 86.9, 86.8 (*C*≡CBu^t), 31.9, 31.4 (C*Me*$_3$), 28.4 (*C*Me$_3$)
(2b)	[d] 1.24, 1.31 (s × 2, 18 H, Bu^t), 5.22 (br. 2 × s,[e] 10 H, C_5H_5)	[d] 231.5, 219.8, 217.3, 213.2 (WCO), 212.3, 208.8 (FeCO), 141.8, 131.1 [*C*$_2$(C≡CBu^t)$_2$], 106.7, 101.6 (C≡*C*Bu^t), 95.3, 94.9 (C_5H_5), 88.6, 87.8 (*C*≡CBu^t), 32.1, 31.6 (C*Me*$_3$), 28.3, 28.1 (*C*Me$_3$)
(3)	1.16 (s, 9 H, Bu^t), 5.58 (s, 5 H, C_5H_5)	327.8 (C≡W),[f] 212.5 (FeCO), 208.1 (WCO), 125.6, 108.3 (*C*≡*C*Bu^t), 87.5 (C_5H_5), 33.4 (*C*Me$_3$), 29.4 (C*Me*$_3$)
(4a)	1.28 (s, 9 H, Bu^t), 5.29 (s, 5 H, C_5H_5), 5.82 (br, 2 H, C_9H_7), 5.86 [d of t, 1 H, C_9H_7, *J*(HH) 5, *J*(RhH) 2], 7.22 (br m, 4 H, C_9H_7)	292.8 [d, μ-C, *J*(RhC) 32], 237.2 (br, MoCO), 188.4 [d, RhCO, *J*(RhC) 88], 127.4 (C≡*C*Bu^t), 125.5, 119.3, 114.4 (br), 101.5 (C_9H_7), 101.4 (*C*≡CBu^t), 93.4 (C_5H_5), 81.7 (br, C_9H_7), 30.5 (C*Me*$_3$), 28.9 (*C*Me$_3$)
(4b)	[g] 1.22 (s, 9 H, Bu^t), 5.43 (s, 5 H, C_5H_5), 5.60, 5.81, 5.95 (m × 3, 3 H, C_9H_7), 7.16, 7.20 (m × 2, 4 H, C_9H_7)	269.7 [d, μ-C, *J*(RhC) 25], 229.5 [WCO, *J*(WC) 186], 227.6 (WCO), 190.0 [d, RhCO, *J*(RhC) 89], 126.3, 126.1 (C_9H_7), 123.0 (C≡*C*Bu^t), 120.1, 119.4, 117.8, 116.3 (C_9H_7), 102.5 (*C*≡CBu^t), 102.3 (C_9H_7), 92.6 (C_5H_5), 82.8, 82.4 (C_9H_7), 30.3 (C*Me*$_3$), 29.8 (*C*Me$_3$)
(5)	1.26, 1.39 (s × 2, 18 H, Bu^t), 4.95 (s, 10 H, C_5H_5), 5.31 [d, 2 H, C_9H_7, *J*(HH) 3], 5.67 [d of t, 1 H, C_9H_7, *J*(HH) 3, *J*(RhH) 1], 7.13, 7.20 (m × 2, 4 H, C_9H_7)	238.2, 238.0 (CO), 143.9 [d, *C*$_2$(C≡CBu^t)$_2$, *J*(RhC) 28], 136.3 [d, *C*$_2$(C≡CBu^t)$_2$, *J*(RhC) 9], 127.6, 121.5, 119.6 (br, C_9H_7), 113.3 (C≡*C*Bu^t), 108.3 [d, C_9H_7, *J*(RhC) 5], 105.8 (C≡*C*Bu^t), 96.5 (C_5H_5), 88.6 (*C*≡CBu^t), 86.7 (br, C_9H_7), 85.7 (*C*≡CBu^t), 32.2, 31.9 (C*Me*$_3$), 29.1, 28.6 (*C*Me$_3$)
(6a)	[g] 1.51 (s, 9 H, Bu^t), 5.18 (s, 5 H, C_5H_5), 5.28 (m, 2 H, C_9H_7), 5.39 [t, 2 H, C_9H_7, *J*(HH) 3], 6.07 (m, 2 H, C_9H_7), 6.51, 6.73 [d × 2, 4 H, C_9H_7, *J*(HH) 8], 6.92, 7.28 [t × 2, 4 H, C_9H_7, *J*(HH) 8]	274.3 [t, μ_3-C, *J*(RhC) 34], 236.4 (MoCO), 219.0 [t, μ-CO, *J*(RhC) 49], 130.3 (C≡*C*Bu^t), 123.8, 123.6, 118.6, 118.1, 113.3, 111.8, 100.6 (C_9H_7), 93.7 (C_5H_5), 91.7 (*C*≡CBu^t), 86.7, 81.0 (C_9H_7), 33.7 (C*Me*$_3$), 29.3 (*C*Me$_3$)
(6b)	1.51 (s, 9 H, Bu^t), 5.21 (m, 2 H, C_9H_7), 5.27 (s, 5 H, C_5H_5), 5.39 [t, 2 H, C_9H_7, *J*(HH) 3], 6.07 (m, 2 H, C_9H_7), 6.52, 6.75 [d × 2, 4 H, C_9H_7, *J*(HH) 8], 6.95, 7.25 [t × 2, 4 H, C_9H_7, *J*(HH) 8]	[h] 262.9 [t, μ_3-C, *J*(RhC) 31], 227.1 [WCO, *J*(WC) 174], 219.4 [t, μ-CO, *J*(RhC) 49], 130.3 (C≡*C*Bu^t), 125.2, 124.6, 120.2, 119.2, 115.0, 112.6, 102.1 (C_9H_7), 95.4 (*C*≡CBu^t), 93.4 (C_5H_5), 88.2, 81.6 (C_9H_7), 33.8 (C*Me*$_3$), 29.7 (*C*Me$_3$)
(7)	1.26, 1.38 (s × 2, 18 H, Bu^t), 4.88 (s, 5 H, C_5H_5), 5.04 (m, 1 H, C_9H_7), 5.09 (s, 5 H, C_5H_5), 5.50 (m, 1 H, C_9H_7), 5.64 [d of t, 1 H, C_9H_7, *J*(HH) 3, *J*(RhH) 1], 7.10—7.30 (m, 4 H, C_9H_7)	242.5, 240.8 (MoCO), 222.2, 212.6 (WCO), 138.4 [d, *C*$_2$(C≡CBu^t)$_2$, *J*(RhH) 29], 130.1, 128.3 (C_9H_7), 122.1 [d, *C*$_2$(C=CBu^t)$_2$, *J*(RhH) 7], 121.9, 121.1, 120.5, 116.7 (C_9H_7), 112.9 (C=*C*Bu^t), 111.0 [d, C_9H_7, *J*(RhC) 3], 103.1 (C≡*C*Bu^t), 96.7, 94.4 (C_5H_5), 89.3 (C_9H_7), 88.7, 85.7 (*C*≡CBu^t), 84.6 (C_9H_7), 32.1, 31.7 (C*Me*$_3$), 29.0, 28.3 (*C*Me$_3$)
(8)	1.45 (s, 9 H, Bu^t), 5.35 (s, 5 H, C_5H_5), 5.41 (m, 1 H, C_9H_7), 5.56 [t, 1 H, C_9H_7, *J*(HH) 3], 6.21 (m, 1 H, C_9H_7), 6.75 [d, 1 H, C_9H_7, *J*(HH) 8], 7.05 [d, 1 H, C_9H_7, *J*(HH) 8], 7.19 [t, 1 H, C_9H_7, *J*(HH) 8], 7.55 [t, 1 H, C_9H_7, *J*(HH) 8]	255.1 [d, μ_3-C, *J*(RhC) 31], 227.8 [d, μ-CO, *J*(RhC) 52], 225.0, 222.1 (WCO), 210.7 (FeCO), 128.7 (C≡*C*Bu^t), 126.3, 126.0, 120.0, 119.7, 116.2, 115.3 (C_9H_7), 101.1 [d, C_9H_7, *J*(RhC) 7], 96.6 (*C*≡CBu^t), 93.2 (C_5H_5), 81.7, 81.6 (C_9H_7), 32.5 (C*Me*$_3$), 29.6 (*C*Me$_3$)
(9)	1.48 (s, 30 H, C_5Me_5), 1.55, 1.61 (s × 2, 18 H, Bu^t), 5.13, 5.20 (s × 2, 10 H, C_5H_5), 5.25, 5.35, 5.78, 6.02 (m × 4, 6 H, C_9H_7), 6.44—7.35 (m, 8 H, C_9H_7)	270.7 [d, μ_3-C, *J*(RhC) 29], 262.3 [d, μ_3-C, *J*(RhC) 30], 235.0 (br, μ-CO), 233.0, 226.6 (WCO), 130.0, 129.6 (C≡*C*Bu^t), 124.7, 124.3, 124.2, 124.1, 119.8, 119.4, 119.3, 118.8, 115.1, 114.7, 112.3, 112.2 (C_9H_7), 102.4 [d, C_9H_7, *J*(RhC) 6], 101.9 (C_9H_7), 100.0 (*C*≡CBu^t), 96.2 (*C*$_5$Me$_5$), 95.0 (*C*≡CBu^t), 92.9, 92.5 (C_5H_5), 88.0, 86.9, 84.2, 81.3 (C_9H_7), 33.7, 32.8 (C*Me*$_3$), 29.8, 29.3 (*C*Me$_3$), 8.0 (C$_5$*Me*$_5$)

[a] Chemical shifts (δ), coupling constants in Hz, measurements at ambient temperatures unless otherwise stated. [b] Measured in $CDCl_3$ unless otherwise stated. [c] Hydrogen-1 decoupled with chemical shifts (p.p.m.) to high frequency of $SiMe_4$. Measured in $CDCl_3$ unless otherwise stated. [d] Measured at −40 °C. [e] Overlapping singlets. [f] Tentative assignment. [g] Spectra measured in CD_2Cl_2. [h] Measured in CD_2Cl_2–CH_2Cl_2.

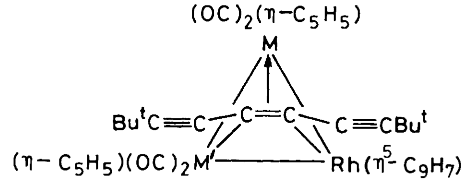
of μ_3-*C*C$_6$H$_4$Me-4 nuclei. Peaks at δ 127.4 and 101.4 p.p.m. in the ^{13}C-{^{1}H} n.m.r. spectrum of (**4a**) are assigned to the alkyne-carbon nuclei C≡*C*Bu^t and *C*≡CBu^t, respectively. These assignments were made by recording a fully coupled ^{13}C n.m.r. spectrum which showed a broadening of the C≡*C*Bu^t resonance due to unresolved ^{1}H–^{13}C coupling, while the peak for the *C*≡CBu^t nucleus, more remote from the Bu^t group, remained sharp.

Compound (**6a**) is structurally similar to [MoRh$_2$(μ_3-CC$_6$H$_4$-Me-4)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)$_2$].[11] As expected the μ_3-*C*–C≡CBu^t resonance in the ^{13}C-{^{1}H} n.m.r. spectrum of (**6a**) (δ 274.3 p.p.m.) is less deshielded than the corresponding μ_3-C signal (δ 302.8 p.p.m.) in the spectrum of [MoRh$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)$_2$].[11]

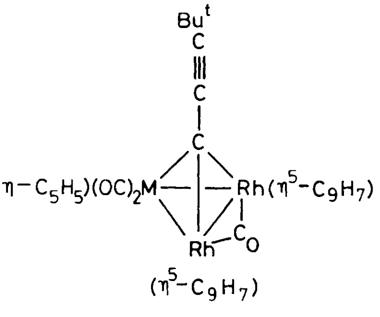
Compound (**5**) is isolated in variable yield, but never exceeding 15%. Its spectroscopic properties have much in common with those of (**2a**). The i.r. spectrum in the CO stretching region shows bands at 1 968, 1 853, and 1 814 cm^{-1}, with that at 1 853 cm^{-1} having a shoulder to high frequency. This suggests that the complex has four carbonyls, and indeed the observation of an envelope of peaks centred at *m/z* 838 in the f.a.b. mass spectrum indicates that this is so. The ^{1}H n.m.r. spectrum shows two peaks for inequivalent Bu^t groups but only one C$_5$H$_5$ resonance. This observation, and the ^{13}C-{^{1}H} n.m.r. data discussed below, can be accounted for by the dynamic process shown in the Scheme [ML$_n$ = Rh(η^5-C$_9$H$_7$)]. Thus the Bu^{t}C$_2$C≡CC$_2$Bu^t ligand displays resonances indicating that the two ends of the triyne are not equivalent. There are thus ten resonances for this group which may be assigned as follows: δ 143.9 [d, *J*(RhC) 28, *C*$_2$(C≡CBu^t)$_2$], 136.3 [d, *J*(RhC) 9 Hz, *C*$_2$(C≡CBu^t)$_2$], 113.3, 105.8 (C=*C*Bu^t), 88.6, 85.7 (*C*≡CBu^t), 32.2, 31.9 (C*Me*$_3$), and 29.1, 28.6 p.p.m. (*C*Me$_3$). The signal at δ 143.9 p.p.m., with the larger of the two ^{108}Rh–^{13}C couplings, is presumably due to the carbon atom directly bonded to rhodium. This carbon remains σ bonded to the rhodium in the fluxional process, during which the triyne traverses the Rh(η^5-C$_9$H$_7$) vertex. There is one C$_5$H$_5$



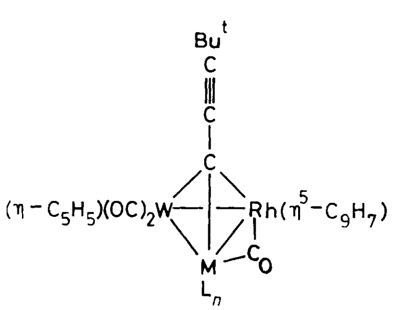
	M
(**4a**)	Mo
(**4b**)	W



	M	M′
(**5**)	Mo	Mo
(**7a**)	W	Mo
(**7b**)	Mo	W



	M
(**6a**)	Mo
(**6b**)	W



	ML$_n$
(**8**)	Fe(CO)$_3$
(**9**)	Co(η-C$_5$Me$_5$)

peak (δ 96.5 p.p.m.), and the C_9H_7 ligand shows five resonances. These occur as two sharp peaks at δ 127.6 and 121.5 p.p.m., a doublet at δ 108.3 p.p.m. [J(RhC) 5 Hz] and two broad signals at δ 119.6 and 86.7 p.p.m. The broad peak at δ 119.6 p.p.m. may be ascribed to an averaging on the n.m.r. time-scale of the resonances due to the two carbons common to the five- and six-membered rings. Similarly, the peak at δ 86.7 p.p.m. is ascribed to averaging of the signals of the C^1 and C^3 nuclei of the five-membered ring, and the peaks at 127.6 and 121.5 p.p.m. to averaging of the signals for the four CH nuclei (two pairs) in the six-membered ring. Thus in the dynamic process the Bu^t groups remain distinct, whereas the C_5H_5 ligands and the 'opposite halves' of the C_9H_7 group effectively exchange sites. In a limiting low-temperature ^{13}C-{^1H} n.m.r. spectrum four CO, two C_5H_5, and nine C_9H_7 resonances should be observed. However, at −40 °C the spectrum of (**5**) is essentially no different from that observed at ambient temperatures. Thus we conclude that the fluxional behaviour of (**5**) proceeds with a lower activation energy than that of the compounds (**2**).

Compound (**1b**) reacts with [Rh(CO)$_2$(η^5-C$_9$H$_7$)] to give a chromatographically separable mixture of [WRh(μ-C–C≡CBu^t)(CO)$_3$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)] (**4b**) and [WRh$_2$(μ$_3$-C–C≡CBu^t)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)$_2$] (**6b**), characterised by the data given in Tables 1 and 2. No tungsten analogue of (**5**) was observed in this reaction. Compound (**4b**) decomposes in solution, unlike its p-tolylmethylidyne analogue [WRh(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_9$H$_7$)].[12] Although (**4b**) does not appear to add a molecule of (**1b**) to give a ditungstenrhodium species analogous to (**5**), compound (**4a**) reacts with (**1b**) to give the trimetal complex [MoWRh{μ$_3$-C$_2$(C≡CBu^t)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$(η^5-C$_9$H$_7$)] (**7**) in low yield (Table 1). The n.m.r. data (Table 2) are in essence similar to those of (**5**), given that (**7**) possesses three different transition elements instead of two. Thus the CO region of the ^{13}C-{^1H} n.m.r. spectrum shows four resonances due to the Mo(CO)$_2$ and W(CO)$_2$ groups. There is no indication that the complex undergoes dynamic behaviour. Of the two possible isomers (**7a**) or (**7b**) one must be favoured over the other, and on the basis of the data available a distinction between the two possibilities cannot be made.

Complex (**4b**) reacts with [Fe$_2$(CO)$_9$] to yield the trimetallic compound [WFeRh(μ$_3$-C–C≡CBu^t)(μ-CO)(CO)$_5$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)] (**8**). The spectroscopic data (Tables 1 and 2) are in accord with the structure proposed. Diagnostic resonances in the ^{13}C-{^1H} n.m.r. spectrum at δ 255.1 [d, J(RhC) 31], 227.8 [d, J(RhC) 52 Hz], 128.7, and 96.6 p.p.m. may be assigned to the μ$_3$-C, μ-CO, C≡CBu^t, and C≡CBu^t nuclei, respectively. Formation of compound (**8**) from (**4b**) and [Fe$_2$(CO)$_9$] parallels the synthesis of [WFeRh(μ$_3$-CC$_6$H$_4$Me-4)(μ-CO)(CO)$_5$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)] from [WRh(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η^5-C$_9$H$_7$)] and [Fe$_2$(CO)$_9$].[5a]

Compound (**4b**) also reacts with [Co(η-C$_2$H$_4$)$_2$(η-C$_5$Me$_5$)]. The product [WCoRh(μ$_3$-C–C≡CBu^t)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)(η^5-C$_9$H$_7$)] (**9**) was characterised in the usual manner (Tables 1 and 2). Not surprisingly the i.r. spectrum of (**9**) in the carbonyl region is very similar to that of (**6b**) since they have similar μ$_3$-CWRhM (M = Co or Rh) core structures with one bridging CO ligand and a W(CO)$_2$ unit. The ^1H and ^{13}C-{^1H} n.m.r. spectra indicate that the compound is formed as a mixture of two isomers in the ratio *ca.* 55:45, based on peak intensities. Assuming, as seems reasonable, the η-C$_5$Me$_5$ and η^5-C$_9$H$_7$ rings are free to rotate, the isomers very probably arise due to two slightly different orientations of the W(CO)$_2$(η-C$_5$H$_5$) group. This type of rotomeric isomerism has been observed in several other systems containing M(CO)$_2$(η-C$_5$H$_5$) (M = Mo or W) fragments.[5b,h,8,13] Thus in the ^{13}C-{^1H} n.m.r. spectrum of (**9**) there are eighteen signals due to the η^5-C$_9$H$_7$ ligand and two for the C_5H_5 group. Surprisingly, there are also two pairs of signals due to the much more remote Bu^t groups. The alkyne-type carbons resonate at δ 130.0 and 129.6 (C≡CBu^t) and 100.0 and 95.0 p.p.m. (C≡CBu^t). The μ$_3$-C nuclei of the isomers give rise to doublets at δ 270.7 and 262.3 p.p.m. A very broad peak at δ 235.0 p.p.m. is tentatively assigned to the μ-CO groups. The observation of only two peaks for the $W(CO)_2$ fragment rather than four is probably due to a degeneracy of signals. It was noted that the WCO resonance at δ 233.0 p.p.m. was broad, suggesting an overlap of peaks.

The results described in this and an earlier paper[4] show that the compounds (**1**) can be used to prepare a variety of di- and tri-metal compounds having bonds between dissimilar transition elements. Moreover, the synthesis of the complexes (**2**), (**5**), and (**7**) allows an opportunity to study the behaviour of a triyne group bound to a transition metal centre.

Experimental

The experimental techniques used, and the instrumentation employed for the spectroscopic measurements, have been described earlier,[3] as has the synthesis of the compounds (**1**),[4] $[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]$,[14] and $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$.[15] Light petroleum refers to that fraction of b.p. 40—60 °C. Alumina (BDH aluminium oxide, Brockman Activity II) was used for all chromatography columns. Analytical and other data for the new compounds are given in Table 1.

Reactions of the Compounds $[M(\equiv C{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo *or* W) *with* $[Fe_2(CO)_9]$.—(*i*) Compound (**1a**) (0.62 g, 2.0 mmol) in thf (20 cm^3) was treated with $[Fe_2(CO)_9]$ (0.73 g, 2.0 mmol), and the mixture was stirred for 12 h. Solvent was removed *in vacuo* and the residue, after being dissolved in CH_2Cl_2 (*ca.* 5 cm^3), was chromatographed on a 3 × 15 cm column. Elution with CH_2Cl_2–light petroleum (1:1) removed initially traces of unidentified products, followed by a broad brown fraction. Solvent was removed *in vacuo* from the latter, and the residue was dissolved in CH_2Cl_2 (*ca.* 5 cm^3), and light petroleum (20 cm^3) was added. Reduction in volume to *ca.* 15 cm^3, cooling to −78 °C, and removal of supernatant liquid with a syringe afforded brown *microcrystals* of $[Mo_2Fe\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**2a**) (0.47 g).

(*ii*) Similarly, compound (**1b**) (0.80 g, 2.0 mmol) with $[Fe_2(CO)_9]$ (0.73 g, 2.0 mmol) gave, after elution of the chromatography column with CH_2Cl_2–light petroleum (1:2), a red eluate. Solvent was removed from the latter *in vacuo*, and the residue was dissolved in light petroleum (*ca.* 15 cm^3). Cooling to −78 °C, and removal of supernatant liquid with a syringe, afforded red *microcrystals* of $[Fe_2\{\mu\text{-}Bu^tC_2C\equiv W(CO)_2(\eta\text{-}C_5H_5)\}(CO)_6]$ (**3**) (0.04 g). Continued elution of the column with CH_2Cl_2–light petroleum (1:1), with work-up procedures as for (**2a**), gave brown *microcrystals* of $[W_2Fe\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_7(\eta\text{-}C_5H_5)_2]$ (**2b**) (0.56 g).

Reactions of the Compounds $[M(\equiv C{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo *or* W) *with* $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$.—(*i*) The compound $[Rh(\eta\text{-}C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) in light petroleum (20 cm^3) was treated with a stream of CO for 10 min to generate $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ *in situ.* Compound (**1a**) (0.31 g, 1.0 mmol) was then added, and the mixture was stirred for 3 h. Solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (*ca.* 4 cm^3), and the resulting solution was chromatographed (3 × 20 cm column). Elution with CH_2Cl_2–light petroleum (1:2) removed a brown band, which was collected and the solvent was removed *in vacuo*. The residue was dissolved in light petroleum (*ca.* 20 cm^3). Cooling to −78 °C, and removal of supernatant liquid with a syringe, gave brown air-sensitive *microcrystals* of $[MoRh(\mu\text{-}C{-}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (**4a**) (0.25 g). Continued elution with the same solvent mixture gave a small amount of $[Mo_2Rh\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_4(\eta\text{-}C_5H_5)_2(\eta^5\text{-}C_9H_7)]$ (**5**), and elution with CH_2Cl_2 gave a trace of $[MoRh_2(\mu_3\text{-}C{-}C\equiv CBu^t)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$ (**6a**). Yields of (**5**) and (**6a**) were optimised as follows.

The compound $[Rh(\eta\text{-}C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) was treated with CO and with (**1a**) (0.62 g, 2.0 mmol), and the mixture was stirred for 24 h. Using the same work-up procedure as above for (**4a**), elution with CH_2Cl_2–light petroleum (1:2) gave some unreacted (**1a**), a trace of (**4a**), and a green eluate. Solvent was removed from the latter *in vacuo*, and the residue was dissolved in light petroleum (*ca.* 10 cm^3). Cooling to −78 °C, and removal of solvent with a syringe, gave green *microcrystals* of (**5**) (0.14 g). Elution of the column with CH_2Cl_2 afforded a second green fraction. Reduction in volume *in vacuo* to *ca.* 3 cm^3, and addition of light petroleum (15 cm^3), gave green *microcrystals* of (**6a**) (0.25 g).

Using similar procedures, $[Rh(\eta\text{-}C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.54 g, 2.0 mmol) with CO and (**1a**) (0.31 g, 1.0 mmol) gave after 24 h compound (**6a**) (0.70 g) and a trace of (**5**).

(*ii*) In a similar procedure to that used to obtain (**4a**), treating the compound $[Rh(\eta\text{-}C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) with CO and (**1b**) (0.40 g, 1.0 mmol) gave brown *microcrystals* of $[WRh(\mu\text{-}C{-}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (**4b**) (0.31 g), and a trace of $[WRh_2(\mu_3\text{-}C{-}C\equiv CBu^t)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)_2]$ (**6b**). Preparation of the latter was optimized by treating $[Rh(\eta\text{-}C_2H_4)_2(\eta^5\text{-}C_9H_7)]$ (0.27 g, 1.0 mmol) with CO, and adding (**1b**) (0.20 g, 0.50 mmol). After 24 h, work-up in the usual manner gave green *microcrystals* of (**6b**) (0.37 g).

Reaction of $[MoRh(\mu\text{-}C{-}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (**4a**) *with* $[W(\equiv C{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (**1b**).—Compound (**1b**) (0.30 g, 0.75 mmol) and (**4a**) (0.28 g, 0.50 mmol) were dissolved in light petroleum (30 cm^3), and the mixture was stirred for 24 h. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 (*ca.* 2 cm^3), and the solution was chromatographed (3 × 25 cm column). Elution with CH_2Cl_2–light petroleum (1:8) gave some unreacted (**1b**), and two green bands which could only be separated with difficulty. A second chromatography process was usually necessary to achieve full separation. The first green eluate contained compound (**5**) (0.05 g). The second eluate afforded, after removal of solvent *in vacuo*, dissolving the residue in light petroleum (*ca.* 5 cm^3), and cooling to −78 °C, green *microcrystals* of $[MoWRh\{\mu_3\text{-}C_2(C\equiv CBu^t)_2\}(CO)_4(\eta\text{-}C_5H_5)_2(\eta^5\text{-}C_9H_7)]$ (**7**) (0.07 g). Continued elution of the column with CH_2Cl_2 gave (**6a**) (0.10 g).

Reactions of $[WRh(\mu\text{-}C{-}C\equiv CBu^t)(CO)_3(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (**4b**) *with* $[Fe_2(CO)_9]$ *and* $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$.—(*i*) Compound (**4b**) (0.32 g, 0.50 mmol) was dissolved in Et_2O (10 cm^3), and an excess of $[Fe_2(CO)_9]$ (0.40 g, 1.1 mmol) was added. The resulting suspension was stirred for 12 h, during which period all the $[Fe_2(CO)_9]$ dissolved. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 5 cm^3) and chromatographed (3 × 15 cm column). Elution with CH_2Cl_2–light petroleum (1:1) gave two green bands. The first fraction was collected, and its volume reduced to *ca.* 5 cm^3. Addition of light petroleum (15 cm^3), followed by removal of the supernatant liquid, gave green *microcrystals* of $[WFeRh(\mu_3\text{-}C{-}C\equiv CBu^t)(\mu\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ (**8**) (0.27 g). The second band removed from the column contained a trace of (**6b**).

(*ii*) Complex (**4b**) (0.32 g, 0.50 mmol) and $[Co(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5Me_5)]$ (0.25 g, 1.0 mmol) were dissolved in CH_2Cl_2 (20 cm^3), and the mixture was stirred for 3 d. Solvent was reduced to *ca.* 5 cm^3 *in vacuo*, and the mixture was chromatographed (3 × 15 cm column). Elution with CH_2Cl_2–light petroleum (4:1) removed a green fraction which was collected. Solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 (*ca.* 3 cm^3), and light petroleum (30 cm^3) was added. Reduction in the volume of solvent to *ca.* 10 cm^3 *in vacuo* and cooling to −78 °C gave green *microcrystals* of

$[\mathrm{WCoRh}(\mu_3\text{-C–C}\equiv\mathrm{CBu^t})(\mu\text{-CO})(\mathrm{CO})_2(\eta\text{-C}_5\mathrm{H}_5)(\eta\text{-C}_5\mathrm{Me}_5)(\eta^5\text{-C}_9\mathrm{H}_7)]$ (**9**) (0.20 g).

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