Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 16.[1] Synthesis of the Trimetal Compounds $[M_2M'(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (M = Mo or W, M' = W; M = M' = Mo)

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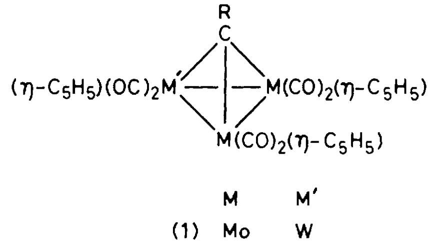
The compounds $[M_2(CO)_n(\eta\text{-}C_5H_5)_2]$ (M = Mo or W, *n* = 4 or 6) react with the alkylidynetungsten compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) in toluene at *ca.* 100 °C to give the trimetal complexes $[M_2W(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)_3]$. In contrast, $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ afford the μ-alkyne-ditungsten compound $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$. This reaction is catalysed by small quantities of the dichromium species, and a possible mechanism is proposed. The compound $[Mo_3(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)_3]$ was obtained in low yield from a complex mixture of products produced in the reaction of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $[W(\equiv CR)Br(CO)_4]$. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. data for the new compounds are reported and discussed.

In a number of recent articles [1-5] we have demonstrated an analogy between the chemistry of diarylalkynes and that of the alkylidynetungsten complex $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4), at least in their reactivity patterns towards low-valent metal compounds. It is well known that the species $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Cr, Mo, or W), which formally contain M≡M bonds,[6] readily add alkynes to give initially the dimetal compounds $[M_2(\mu\text{-}R'C_2R')(CO)_4(\eta\text{-}C_5H_5)_2]$ (R' = alkyl or aryl).[7-10] In view of these observations, reactions between the compounds $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ have been investigated.

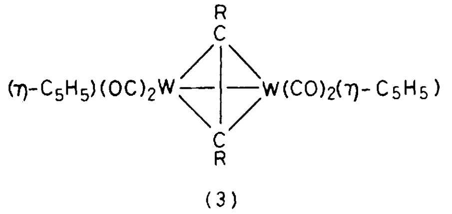
Results and Discussion

Although the compounds $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ did not react with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ at ambient temperatures, it was found that they readily did so when heated in toluene in evacuated vessels. Thus the alkylidynetungsten compound and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ afforded the brown trimetal complex (1) in quantitative yield.

Compound (1) was characterised by microanalysis, by measurement of the molecular ion in the mass spectrum, and by its spectroscopic properties. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (Table) showed the very characteristic resonance for the μ_3-CR group at δ 257.0 p.p.m.[1,2,11] Three signals were observed for the η-C_5H_5 groups, indicating different environments for these ligands. In the room-temperature spectrum only two resonances for the CO groups were observed. However, although (1) is relatively insoluble, it was possible to record a spectrum at −30 °C, at which temperature six peaks for the carbonyls were observed at δ 209.1, 217.3, 213.0, 223.4, 231.6, and 234.6 p.p.m. Those at 209.1 and 217.3 p.p.m. showed $^{187}W\text{-}^{13}C$ coupling [*J*(WC) 132 Hz] and may therefore be assigned to the two tungsten-bonded carbonyl ligands, while the other signals are due to the four carbonyls attached to the molybdenum atoms. Evidently CO site exchange occurs at room temperature, but at low temperatures a structure without mirror symmetry exists. The ^1H n.m.r. spectrum (Table) shows all the expected resonances, including three for the non-equivalent η-C_5H_5 groups.



	M	M'
(1)	Mo	W
(2)	W	W
(4)	Cr	W
(5)	Mo	Mo



(3)

R = C_6H_4Me - 4

The i.r. spectrum of (1) showed six bands in the carbonyl stretching region (see Experimental section). Three of these absorptions at 1 879, 1 853, and 1 817 cm^{-1} are in the range associated with semi-bridging CO groups surrounding the metal triangle. This would be in accord with the dynamic behaviour observed on the n.m.r. time-scale, and providing a mechanism for CO transfer between the metal centres.

The tritungsten compound (2) was similarly prepared from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$ but it was obtained in lower yield (*ca.* 20%) than (1). Compounds (1) and (2) may also be prepared by reacting the hexacarbonyl species $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$. These reactions appear to proceed *via* the tetracarbonyl compounds $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$, since the latter were observed by i.r. in the reaction mixture and among the final products.

Complex (2) was obtained in better yield (*ca.* 60%) by reacting the bridged-alkyne compound (3) with [W(≡CR)-

Table. Hydrogen-1 and ^{13}C n.m.r. data for the complexes[a]

Complex	^1H (δ)	^{13}C (δ)[b]
(1)	2.34 (s, 3 H, Me-4), 4.94 (s, 5 H, C_5H_5), 5.10 (s, 5 H, C_5H_5), 5.29 (s, 5 H, C_5H_5), 7.10 [$(AB)_2$ quartet, 4 H, C_6H_4, J(AB) 9]	257.0 [μ_3-C, J(WC) 102], 230.0 (br, CO), 214.0 (br, CO), 164.9 [C(1) (C_6H_4)], 132.9, 130.6, 127.5 (C_6H_4), 91.4, 89.9, 89.8 (C_5H_5), 20.6 (Me-4)
(2)	2.38 (s, 3 H, Me-4), 5.06 (s, 15 H, C_5H_5), 7.12 [$(AB)_2$ quartet, 4 H, C_6H_4, J(AB) 10]	226.9 [μ_3-C, J(WC) 71], 214.4 [CO, J(WC) 171], 141.2 [C(1) (C_6H_4)], 133.3, 128.1, 127.5 (C_6H_4), 91.0 (C_5H_5), 20.6 (Me-4)
(3)	2.37 (s, 6 H, Me-4), 5.23 (s, 10 H, C_5H_5), 6.96 [$(AB)_2$ quartet, 8 H, C_6H_4, J(AB) 10]	217.5 [CO, J(WC) 173], 142.6 [C(1) (C_6H_4)], 134.6, 130.0, 128.8 (C_6H_4), 90.9 (C_5H_5), 60.0 [μ-C_2, J(WC) 29], 21.0 (Me-4)
(5)	2.32 (s, 3 H, Me-4), 5.72 (s, 5 H, C_5H_5), 7.16 (m, 4 H, C_6H_4)	239.5 (μ_3-C), 222.5 (CO), 167.7 [C(1) (C_6H_4)], 132.4, 131.2, 128.9 (C_6H_4), 95.7 (C_5H_5), 22.8 (Me-4)

[a] Chemical shifts (δ) in p.p.m., relative to $SiMe_4$ with positive values representing shifts to high frequency; coupling constants are in Hz; spectra recorded in [$^2H_1$]chloroform. [b] [$Cr(acac)_3$] (acac = acetylacetonate) added for these measurements.

$(CO)_2(\eta\text{-}C_5H_5)]$ in toluene at 100 °C. In terms of the isolobal relationship between $W(CO)_2(\eta\text{-}C_5H_5)$ and CR groups,[12] this method of synthesis corresponds to the displacement of RC_2R in (3) by the 'alkyne' [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$]. We have previously employed an alkyne displacement route to clusters containing the μ_3-CM_2M' core. Thus [$Ni_2(\mu\text{-}Me_3SiC_2SiMe_3)(\eta\text{-}C_5H_5)_2$] reacts with [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] to afford the dinickeltungsten compound [$Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3$] (R = C_6H_4Me-4) quantitatively.[11]

The analysis and properties of (2) are entirely in accord with the proposed structure. In the ^{13}C n.m.r. spectrum (Table) the resonance for the μ_3-C ligated carbon atom is seen at 226.9 p.p.m. Only one signal is observed for the CO and η-C_5H_5 ligands. The insolubility of (2) prevented n.m.r. studies at low temperatures but the molecule, with three identical metal atoms, would have higher symmetry than (1). The i.r. spectrum of (2) was similar to that of (1), with six bands in the CO stretching region, three at relatively low frequency indicating semi-bridging groups (see Experimental section).

An interesting reaction occurred between the dichromium compound [$Cr_2(CO)_4(\eta\text{-}C_5H_5)_2$] and [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] yielding the bridged-alkyne ditungsten complex (3) in quantitative yield, rather than the expected product (4). This reaction was subsequently found to be catalytic, small quantities of [$Cr_2(CO)_4(\eta\text{-}C_5H_5)_2$] converting the mononuclear alkylidynetungsten species into (3) quantitatively. In the absence of the dichromium compound, the species [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] does not dimerise. The catalytic formation of (3) is discussed below.

An attempt to prepare compound (4) by displacement of $PhC\equiv CPh$ from [$Cr_2(\mu\text{-}PhC_2Ph)(CO)_4(\eta\text{-}C_5H_5)_2$][10] with [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] in toluene at 60 °C produced only (3) in high yield.

Formation of compounds (1) and (2) by addition of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] to [$M_2(CO)_4(\eta\text{-}C_5H_5)_2$], described above, parallels the reaction of alkynes with the latter to give the bridged species [$M_2(\mu\text{-}R'C_2R')(CO)_4(\eta\text{-}C_5H_5)_2$].[7-9] With alkynes, however, further reactions occur[10,13] to give dimetal compounds in which the metal–metal bonds are bridged by chains of four, six, or eight carbon atoms formed by sequential linking of alkyne fragments. In contrast, we have found no evidence for the trimetal compounds (1) or (2) reacting with further molecules of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] to give tetranuclear or higher polynuclear metal clusters. This observation may well be related to the interesting catalytic dimerisation of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$], mentioned earlier, which occurs when the latter is heated with [$Cr_2(CO)_4(\eta\text{-}C_5H_5)_2$]. Relevant also is the previously described[11] reaction between the mononuclear tungsten alkylidyne complex and the dinickel compound [$Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] which affords (3), as well as the expected trimetal cluster [$Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3$]. A number of experiments have been carried out with [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$], but in the absence of low-valent metal complexes the tungsten compound has never been observed to dimerise to (3), a process which would be formally analogous to two alkyne molecules coupling to give a tetrahedrane structure.

The formation of (3) which accompanied the synthesis of [$Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3$] from [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] and [$Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] has been interpreted in terms of a mechanism elaborated in detail elsewhere,[11] and involving the essential steps (*a*)—(*d*).

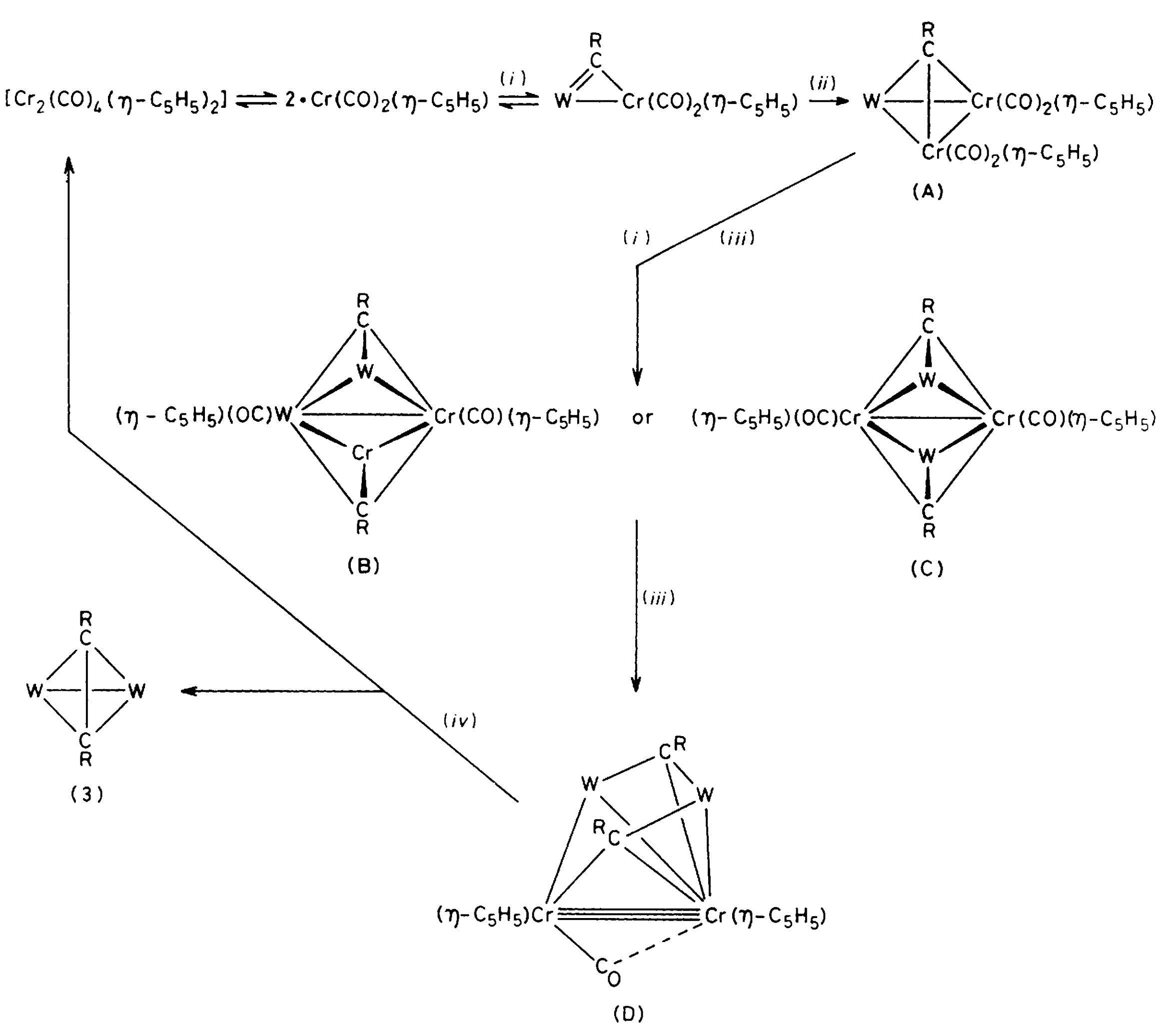
(*a*) Dissociation of [$Ni_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] to give the 17-electron fragment $Ni(CO)(\eta\text{-}C_5H_5)$,[14] which then combines with a molecule of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] to give an intermediate [$Ni\{RC\equiv W(CO)_2(\eta\text{-}C_5H_5)\}(\eta\text{-}C_5H_5)$].

(*b*) Addition of $Ni(\eta\text{-}C_5H_5)$ fragments to the latter would then afford the major product [$Ni_2W(\mu_3\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3$] by a well established route to trimetal compounds with capping CR groups.[11,15]

(*c*) Alternatively, reaction of the dimetal intermediate with a second molecule of [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] might give what could be regarded as a pseudo-bis-alkyne complex of nickel, namely [$Ni\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2(\eta^3\text{-}C_5H_5)$] with perhaps 17 electrons in the valence shell of nickel by slippage of the C_5H_5 ligand.

(*d*) Following analogies based on reactions of alkynes with low-valent complexes of Group 8A metals, the 'bis-alkyne' complex [$Ni\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2(\eta^3\text{-}C_5H_5)$] could collapse to give trimetallacyclopentadiene species (isomers), which by reductive elimination of $Ni(\eta\text{-}C_5H_5)$ would yield (3).

To explain the formation of (3) from [$Cr_2(CO)_4(\eta\text{-}C_5H_5)_2$] and [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] a modified version of the earlier mechanism is proposed, based on the intermediates established in the sequential reaction of alkynes with the dichromium compound.[10] As discussed previously,[11] it is assumed that the dimetal reactant dissociates to a mononuclear species in the first step (Scheme). This is in accord with the work of Madach and Vahrenkamp[14] who have established that the paramagnetic moiety $Cr(CO)_3(\eta\text{-}C_5H_5)$ is readily accessible from [$Cr_2(CO)_6(\eta\text{-}C_5H_5)_2$], and also the experiments of Curtis and Klingler[7] who have shown that [$Mo_2(CO)_4(\eta\text{-}C_5H_5)_2$] forms from its hexacarbonyl precursor *via* dimerisation of $Mo(CO)_2(\eta\text{-}C_5H_5)$, a dicarbonyl mononuclear molybdenum fragment.



Scheme. For clarity W and Cr represent the groups M(CO)$_2$(η-C$_5$H$_5$) (M = W or Cr, respectively), isolobal with CR: (*i*) + RC≡W(CO)$_2$(η-C$_5$H$_5$); (*ii*) + Cr(CO)$_2$(η-C$_5$H$_5$); (*iii*) − CO; (*iv*) + CO

Thus a reasonable route to the intermediate (A) is shown (Scheme). It is proposed that compound (4) [intermediate (A)] is highly reactive in the presence of [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)], as evidenced by its non-isolation in the reaction of the mononuclear tungsten compound with [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$], and in the displacement of PhC≡CPh from [Cr$_2$(μ-PhC$_2$Ph)(CO)$_4$(η-C$_5$H$_5$)$_2$] with [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)]; both these reactions give (3) only in high yield.

Rapid addition of the alkylidynetungsten compound to (A) could afford the intermediates (B) and (C), depending on whether the [RC≡W(CO)$_2$(η-C$_5$H$_5$)] molecules add to the Cr–W or Cr–Cr edges of the trimetallatetrahedrane structure (A). The intermediates (B) and (C) are similar to those invoked in the reaction of alkynes with [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$].[10] In (B) the W(≡CR)(CO)$_2$(η-C$_5$H$_5$) fragment, isolobal with RC≡CR,[12] bridges the Cr–W bond of the trimetal core μ$_3$-CCr$_2$W in a similar manner to the way the alkyne Me$_3$SiC$_2$SiMe$_3$ bridges the Fe–W bond in the compound [Fe$_2$W(μ$_3$-CR)(μ-Me$_3$SiC$_2$SiMe$_3$)(CO)$_7$(η-C$_5$H$_5$)].[16] Rearrangement of (B) or (C) could give (D), a transformation perhaps easier for the former. Isomers of (D) are possible with C–C or W–W bonds in the bridge system, but we prefer that depicted for steric reasons, and because reaction of PhC≡CH with the dichromium compound forms predominantly (>70%) the complex [Cr$_2$(CO)(μ-C$_4$H$_2$Ph$_2$)(η-C$_5$H$_5$)$_2$] having a bridge system with a C(Ph)C(H)C(Ph)C(H) 'head-to-tail' arrangement.[10] Reaction of (D) with CO could result in reductive elimination of the C$_2$W$_2$ bridging fragment, thereby giving (3) with concomitant regeneration of the 'catalyst' [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$].

During the course of our work we also studied the reaction between [W(≡CR)Br(CO)$_4$] and [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$]. Reaction occurred well below room temperature in diethyl ether to give a complex mixture of products, including [W(CO)$_6$], [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$], [Mo$_2$(μ-RC$_2$R)(CO)$_4$(η-C$_5$H$_5$)$_2$], RC$_2$R, and RCH=CHR. Among the products separated by chromatography was the trimolybdenum compound (5). The latter, like the related compounds (1) and (2), showed in its i.r. spectrum six bands in the carbonyl stretching region. The ^{13}C-{^{1}H} n.m.r. spectrum of (5) (Table) showed the characteristic resonance for the μ$_3$-C group at δ 239.5 p.p.m. There is only one signal for the C$_5$H$_5$ groups in the ^{13}C-{^{1}H} and the ^{1}H spectra.

Because of the complicated nature of the products, and the formation of (5) in low yield (*ca.* 22%), the mechanism of the reaction is not understood. Earlier, Fischer and Däweritz[17] had observed transfer of CR ligands in reactions of the compounds [Cr(≡CR)Br(CO)$_4$] (R = Me or Ph) with [Co$_2$(CO)$_8$] and [Ni(η-C$_5$H$_5$)$_2$] to give the trimetal species [Co$_3$(μ$_3$-CR)(CO)$_9$] (R = Me or Ph) and [Ni$_3$(μ$_3$-CPh)(η-C$_5$H$_5$)$_3$], respectively.

Experimental

The techniques used, and instrumentation employed, have been previously described.[2,4,11] The compounds $[W(\equiv CC_6H_4\text{-}Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ were prepared by methods described in the literature.[18,19] The complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [7,9] was obtained by decarbonylating $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene at 100 °C in an evacuated Schlenk tube fitted with a Young's high-pressure stopcock. The species $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Cr or W) were prepared as described elsewhere.[20] Light petroleum refers to that fraction having b.p. 40—60 °C. N.m.r. spectra (Table) were measured in $[^2H_1]$chloroform.

Synthesis of the Compounds $[M_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (M = Mo *or* W).—(*a*) The compounds $[Mo_2(\mu\text{-}CO)_4(\eta\text{-}C_5H_5)_2]$ (0.21 g, 0.5 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.5 mmol) were dissolved in toluene (10 cm^3), and heated at 100 °C for 24 h in an evacuated Schlenk tube (Young's high-pressure stopcock). On cooling to room temperature, brown microcrystals appeared which were filtered off, washed with light petroleum (20 cm^3), and recrystallised from hot toluene or diethyl ether to give brown *needles* of $[Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (1) (0.40 g, 98%), m.p. 242—245 °C (decomp.) {Found: C, 41.4; H, 2.6%; *M* [field desorption (f.d.) mass spectrum] 842 ± 2. $C_{29}H_{22}Mo_2O_6W$ requires C, 41.4; H, 2.6%; *M* 842}; $\nu_{max.}$(CO) 1 973m, 1 943vs, 1 909s, 1 879m, 1 853s, and 1 817m cm^{-1} (CH_2Cl_2).

(*b*) The compound $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$ was generated by refluxing $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.68 g, 1 mmol) in the dark in xylene (200 cm^3) for 24 h with an argon purge to remove CO. Solvent was removed *in vacuo*, the residue dissolved in toluene (5 cm^3), and the solution chromatographed on Florisil (2 cm × 10 cm column). Elution with toluene gave first a trace of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ followed by a brown solution of $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$, collected in a Schlenk tube (Young's stopcock). The volume was reduced *in vacuo* to *ca.* 5 cm^3 and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.40 g, 1 mmol) was added. The mixture was heated at 110 °C for 24 h, after the reaction vessel had been evacuated. Toluene was removed *in vacuo*, the residue dissolved in dichloromethane–light petroleum (1 : 1, 5 cm^3) and chromatographed on an alumina column (2 cm × 10 cm). Elution with dichloromethane–light petroleum (1 : 1) afforded a brown solution. Solvent was removed *in vacuo* and the residue crystallised from pentane to give brown *crystals* of $[W_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (2) (0.20 g, 20%) [Found: C, 34.3; H, 2.2%; *M* (f.d. mass spectrum) 1 016 ± 4. $C_{29}H_{22}O_6W_3$ requires C, 34.2; H, 2.2%; *M* 1 018]; $\nu_{max.}$(CO) 1 974 (sh), 1 942vs, 1 908s, 1 876m, 1 852s, and 1 812m cm^{-1} (CH_2Cl_2).

(*c*) The compounds $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.40 g, 0.5 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.5 mmol) in toluene (10 cm^3) were heated at 100 °C for 12 h in an evacuated Schlenk tube (Young's stopcock). Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane–light petroleum (1 : 9, 5 cm^3) and chromatographed on alumina. Elution with the same solvents (1 : 1) gave first a red solution, which afforded unreacted $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.25 g), and second a brown solution. The latter was evaporated *in vacuo* giving brown microcrystals of $[W_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (2) (0.20 g, 39%), identified as described above.

Reaction of $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ *with* $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.—The compounds $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.35 g, 1 mmol) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.40 g, 1 mmol) were heated at 100 °C in toluene (5 cm^3) for 24 h. Removal of solvent *in vacuo* gave a solid residue which was dissolved in dichloromethane–light petroleum (1 : 1, 5 cm^3), and chromatographed on alumina. Elution with the same solvent mixture gave a dark green solution which afforded, on cooling to −20 °C, crystals of $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (*ca.* 0.35 g, *ca.* 95—100% recovered). A second eluant fraction on cooling gave red *crystals* of $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (3) (0.40 g, 100%), m.p. 210—212 °C [Found: C, 44.0; H, 3.0%; *M* (f.d. mass spectrum) 816. $C_{22}H_{17}O_4W_2$ requires C, 44.1; H, 3.0%; *M* 816]; $\nu_{max.}$(CO) 1 969s, 1 911vs, and 1 813m cm^{-1} (CH_2Cl_2).

It was subsequently observed that the compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ could be quantitatively converted to (3) by heating the former with $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in a 10 : 1 mol ratio.

Reaction of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ *with* $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$.—The compound $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$ was prepared *in situ* by treating the alkylidene complex $[W\{=C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ (0.5 g, 0.86 mmol) in diethyl ether (50 cm^3) at −40 °C with BBr_3 (0.3 cm^3 in 10 cm^3 of diethyl ether). After stirring at −40 °C for 2 h, solvent was decanted from the precipitate, and the latter washed with light petroleum (3 × 10 cm^3) at −80 °C. The buff coloured precipitate was dried *in vacuo* below −30 °C. A solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.48 g, 1.1 mmol) in diethyl ether (20 cm^3) was added at −30 °C, and the mixture allowed to warm to room temperature over a period of 4 h. Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane–light petroleum (1 : 4, 5 cm^3) and chromatographed on Florisil. The same solvent mixture eluted a pale yellow solution which afforded a residue shown by mass spectroscopy to be a mixture of $[W(CO)_6]$, $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$, $C_2(C_6H_4Me\text{-}4)_2$, and $4\text{-}MeC_6H_4(H)C{=}C(H)C_6H_4Me\text{-}4$. Continued elution with the same solvent gave $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.038 g, 6%). Further chromatography with dichloromethane–light petroleum (1 : 2) afforded $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.18 g, 38%). Elution with pure CH_2Cl_2 yielded first $[Mo_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.208 g, 29%), and subsequently air sensitive brown *microcrystals* (on concentration and cooling to −78 °C) of $[Mo_3(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (5) (0.12 g, 22%) (Found: C, 45.8; H, 3.0. $C_{29}H_{22}Mo_3O_6$ requires C, 46.2; H, 2.9%); $\nu_{max.}$(CO) 2 045m, 2 016vw, 1 997vw, 1 977s, 1 957m, and 1 905vw cm^{-1} (hexane). Yields of products are based on $Mo(CO)_2(\eta\text{-}C_5H_5)$ groups consumed.

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