Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 92.[1] Synthesis of Alkynylmethylidyne-molybdenum and -tungsten Complexes and Their Reactions with $[Co_2(CO)_8]$ and $[Mo_2(CO)_6(\eta-C_5H_5)_2]$

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The mononuclear metal–alkylidyne compounds $[M(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2L_2]$ [L_2 = tmen (*N,N,N',N'*-tetramethylethylenediamine), M = Mo (**1a**) or W (**1b**); L_2 = bipy (2,2'-bipyridine), M = Mo (**1c**); L_2 = 2 × py (py = pyridine), M = W (**1d**)] have been prepared by treating the complexes $[M(CO)_6]$ in thf (tetrahydrofuran) successively with $Li(C\equiv CBu^t)$, $(CF_3CO)_2O$, and L_2. The species (**1a**), (**1c**), and (**1d**) have been used as precursors for the synthesis of the compounds $[M(\equiv C{-}C\equiv CBu^t)(CO)_2L]$ {L = η-C_5H_5, M = Mo (**2a**) or W (**2b**); L = $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate], M = Mo (**2c**) or W (**2d**); L = $HB(dmpz)_3$ [tris(3,5-dimethylpyrazol-1-yl)hydroborate], M = Mo (**2e**). Treatment of the complexes (**2a**) and (**2b**), respectively, with $[Co_2(CO)_8]$ in light petroleum gives the trimetallatetrahedrane clusters $[MCo_2(\mu_3\text{-}C{-}C\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$ (M = Mo or W) in quantitative yield. In contrast, (**2d**) and (**2e**) with $[Co_2(CO)_8]$ afford, respectively, the μ-alkyne trimetal compounds $[Co_2\{\mu\text{-}Bu^tC_2C\equiv M(CO)_2L\}(CO)_6]$ [M = W, L = $HB(pz)_3$; M = Mo, L = $HB(dmpz)_3$]. Similarly, whereas (**2b**) reacts with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ to yield a trimetallatetrahedrane cluster $[Mo_2W(\mu_3\text{-}C{-}C\equiv CBu^t)(CO)_6(\eta\text{-}C_5H_5)_3]$, complex (**2d**) with the dimolybdenum reagent gives the μ-alkyne trimetal compound $[Mo_2\{\mu\text{-}Bu^tC_2C\equiv W(CO)_2[HB(pz)_3]\}(CO)_4(\eta\text{-}C_5H_5)_2]$. The n.m.r. data for the new compounds are reported and discussed.

We have studied extensively the metal-ligating properties of the C≡M bonds in the species $[M(\equiv CR)(CO)_2L]$ {M = Cr, Mo, or W; R = alkyl or aryl; L = η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate]}.[1,2] The C≡M groups readily add a variety of low-valent metal–ligand fragments to afford compounds having heteronuclear metal–metal bonds bridged by alkylidyne ligands. We wished to extend these studies to reagents of the type $[M(\equiv C{-}C\equiv CR)(CO)_2L]$. The latter species possess two centres of unsaturation in conjugation, and hence might be expected to show a rich co-ordination chemistry. Fischer and co-workers[3] prepared the first alkynylmethylidyne metal complex $[W(\equiv C{-}C\equiv CPh)Br(CO)_4]$ by treating the alkylidene tungsten complex $[W\{=C(OEt)C\equiv CPh\}(CO)_5]$ with BBr_3. In this paper we report the synthesis of several molybdenum and tungsten compounds in which the metal atoms are ligated by the $C{-}C\equiv CBu^t$ group, and we also report reactions of some of these species with $[Co_2(CO)_8]$ and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$.

Results and Discussion

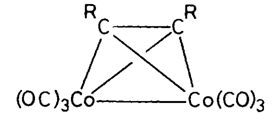
Recently Mayr *et al.*[4] have described a 'one-pot' synthesis of the alkylidyne metal complexes $[M(\equiv CR)X(tmen)(CO)_2]$ (M = Mo or W; R = alkyl or aryl; X = Cl, Br, or O_2CCF_3; tmen = *N,N,N',N'*-tetramethylethylenediamine). We have adapted this procedure to make, directly from the hexacarbonyls $[M(CO)_6]$ (M = Mo or W), in substantial amounts, molybdenum and tungsten complexes containing the alkylidyne group $C{-}C\equiv CBu^t$. Thus treatment of the metal hexacarbonyls in thf (tetrahydrofuran) with 1 equivalent of $Li(C\equiv CBu^t)$ generates the acylate complex $[M\{C(O)C\equiv CBu^t\}(CO)_5]^-$ *in situ*. Cooling the solution to *ca.* −78 °C and adding trifluoroacetic anhydride in slight excess, followed by tmen, affords in high yield the compounds $[M(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2(tmen)]$ [M = Mo (**1a**) or W (**1b**)]. A similar synthesis employing $[Mo(CO)_6]$, and bipy (2,2'-bipyridine) instead of tmen, gives $[Mo(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2(bipy)]$ (**1c**), while the compound $[W(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2(py)_2]$ (**1d**; py = pyridine) was obtained *in situ* in thf from $[W(CO)_6]$, $LiC\equiv CBu^t$, $(CF_3CO)_2O$, and pyridine. The complexes (**1**) were characterised by the data given in Tables 1 and 2.

In their i.r. spectra the compounds show two bands due to the CO ligands, and a band near 1 705 cm^{-1} due to the O_2CCF_3 moiety. In addition, a very weak absorption is observed near 2 130 cm^{-1}, which can be attributed to the $C\equiv CBu^t$ group. The $^{13}C\text{-}\{^1H\}$ n.m.r. data for compounds (**1a**) and (**1b**) are informative (Table 2), but satisfactory measurements on solutions of (**1c**) were not possible due to the insolubility of this product. Complex (**1a**) revealed in its $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum two signals at δ 252.3 and 223.2 p.p.m. which may be assigned, respectively, to the C≡Mo and CO groups. Peaks at δ 90.4 and 75.9 p.p.m. are attributable to the acetylenic-carbon nuclei. Similarly, (**1b**) has resonances at δ 246.8 [C≡W, *J*(WC) 208], 223.2 [CO, *J*(WC) 171 Hz], 96.3 (*C*≡CBu^t), and 81.1 p.p.m. (C≡*C*Bu^t). A fully coupled ^{13}C n.m.r. spectrum of (**1b**) allowed specific assignments to be made. The signal at δ 96.3 shows ^{183}W satellites [*J*(WC) 59 Hz], and more significantly the resonance at δ 81.1 p.p.m. appears as a dectet [*J*(CH) 5 Hz]. The latter coupling is as expected for a three-bond $^1H\text{–}^{13}C$ coupling, while the *C*≡CBu^t nucleus being four bonds remote from the Bu^t protons would be unlikely to show any measurable coupling. The observation that this less deshielded resonance shows ^{183}W satellite peaks is also consistent with the *C*≡CBu^t assignment since this carbon nucleus is only two bonds from the tungsten atom.

Treating a thf suspension of (**1c**), or a solution of (**1d**), with $Na(C_5H_5)\cdot dme$ (dme = 1,2-dimethoxyethane) gives the complexes $[M(\equiv C{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ [M = Mo (**2a**) or W (**2b**)], respectively. These compounds cannot be prepared from the tmen complexes (**1a**) or (**1b**), presumably because the strongly bound chelating tmen ligand is not sufficiently labile. However, treatment of (**1a**) with $K[HB(pz)_3]$ or $K[HB(dmpz)_3]$ [$HB(dmpz)_3$ = tris(3,5-dimethylpyrazol-1-yl)hydroborate] yields the complexes $[Mo(\equiv C{-}C\equiv CBu^t)(CO)_2\{HB(pz)_3\}]$ (**2c**) and $[Mo(\equiv C{-}C\equiv CBu^t)(CO)_2\{HB(dmpz)_3\}]$ (**2e**), respectively. Unfortunately, treating (**1b**) with $K[HB(pz)_3]$

$[M(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2L_2]$

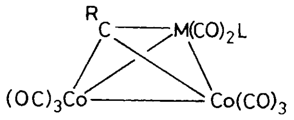
	M	L_2
(1a)	Mo	tmen
(1b)	W	tmen
(1c)	Mo	bipy
(1d)	W	2py



	R
(3)	alkyl or aryl

$[M(\equiv C{-}C\equiv CBu^t)(CO)_2L]$

	M	L
(2a)	Mo	η-C_5H_5
(2b)	W	η-C_5H_5
(2c)	Mo	$HB(pz)_3$
(2d)	W	$HB(pz)_3$
(2e)	Mo	$HB(dmpz)_3$



	M	R	L
(4)	Mo or W	alkyl or aryl	η-C_5H_5, η-C_5Me_5, or $HB(pz)_3$

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

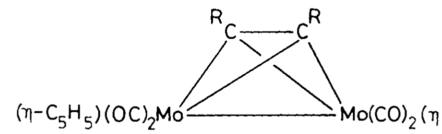
	Compound	Colour	Yield (%)	$\nu_{max.}(CO)$[b]/cm^{-1}	Analysis (%) C	H	N
(1a)	$[Mo(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2(tmen)]$	Yellow	80	2 007s, 1 923vs, 1 705m	42.8 (43.0)	5.6 (5.3)	6.0 (5.9)
(1b)	$[W(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2(tmen)]$	Yellow	83	1 993s, 1 903vs, 1 706m	36.1 (36.3)	4.5 (4.5)	4.9 (5.0)
(1c)	$[Mo(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2(bipy)]$	Orange	70	2 007s, 1 923s, 1 705m	48.5 (49.0)	3.4 (3.3)	5.4 (5.5)
(1d)	$[W(\equiv C{-}C\equiv CBu^t)(O_2CCF_3)(CO)_2(py)_2]$[c]	Orange		[d] 1 995s, 1 908vs, 1 705m			
(2a)	$[Mo(\equiv C{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$	Orange	47	[e] 2 006s, 1 940vs	54.5 (54.2)	4.6 (4.5)	
(2b)	$[W(\equiv C{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$	Orange	70	[e] 1 988s, 1 929vs	42.0 (42.2)	3.6 (3.5)	
(2c)	$[Mo(\equiv C{-}C\equiv CBu^t)(CO)_2\{HB(pz)_3\}]$	Red	87	2 001s, 1 919vs	47.5 (47.2)	4.8 (4.2)	17.5 (18.3)
(2d)	$[W(\equiv C{-}C\equiv CBu^t)(CO)_2\{HB(pz)_3\}]$	Red	85	1 985s, 1 896vs	39.2 (39.6)	3.8 (3.5)	14.7 (15.4)
(2e)	$[Mo(\equiv C{-}C\equiv CBu^t)(CO)_2\{HB(dmpz)_3\}]$	Red	85	1 993s, 1 908vs	52.9 (53.2)	6.0 (5.8)	14.8 (15.5)

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2 unless otherwise stated. [c] Prepared *in situ* and not isolated, see text. [d] In thf. [e] In light petroleum.

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

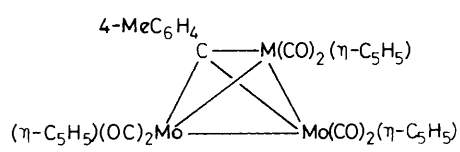
Compound	^1H (δ)[b]	^{13}C (δ)[c]
(1a)	1.20 (s, 9 H, Bu^t), 2.57 (s, 6 H, NMe), 2.79 (m, 4 H, NCH_2), 2.99 (s, 6 H, NMe)	252.3 (C≡Mo), 223.2 (CO), 160.0 [q, $O_2\mathit{C}CF_3$, *J*(CF) 37], 115.9 [q, CF_3, *J*(CF) 290], 90.4 (*C*≡CBu^t), 75.9 (C≡*C*Bu^t), 59.9, 55.8, 50.0 (NCH_2 and NMe), 30.7 ($C\mathit{Me}_3$), 27.6 (*C*Me_3)
(1b)	1.21 (s, 9 H, Bu^t), 2.69 (s, 6 H, NMe), 2.90 (m, 4 H, NCH_2), 3.14 (s, 6 H, NMe)	246.8 [C≡W, *J*(WC) 208], 223.2 [CO, *J*(WC) 171], 160.6 [q, $O_2\mathit{C}CF_3$, *J*(CF) 37], 116.4 [q, CF_3, *J*(CF) 290], 96.3 (*C*≡CBu^t), 81.1 (C≡*C*Bu^t), 61.1, 57.1, 50.8 (NCH_2 and NMe), 30.7 ($C\mathit{Me}_3$), 27.6 (*C*Me_3)
(2a)	[d] 1.22 (s, 9 H, Bu^t), 5.56 (s, 5 H, C_5H_5)	274.9 (C≡Mo), 229.4 (CO), 93.9 (*C*≡CBu^t), 93.1 (C_5H_5), 84.8 (C≡*C*Bu^t), 30.0 ($C\mathit{Me}_3$), 28.0 (*C*Me_3)
(2b)	1.22 (s, 9 H, Bu^t), 5.67 (s, 5 H, C_5H_5)	266.7 [C≡W, *J*(WC) 226], 221.5 [WCO, *J*(WC) 196], 100.1 (*C*≡CBu^t), 92.3 (C_5H_5), 88.9 (C≡*C*Bu^t), 32.4 ($C\mathit{Me}_3$), 29.8 (*C*Me_3)
(2c)	1.21 (s, 9 H, Bu^t), 6.07, 6.18 [t × 2, 3 H, H^4 ($C_3H_3N_2$), *J*(HH) 2], 7.50, 7.55, 7.62, 7.88 [d × 4, 6 H, H^3 and H^5 ($C_3H_3N_2$), *J*(HH) 2]	259.8 (C≡Mo), 226.0 (CO), 143.8—105.0 ($C_3H_3N_2$), 91.7 (*C*≡CBu^t), 78.5 (C≡*C*Bu^t), 30.6 ($C\mathit{Me}_3$), 27.9 (*C*Me_3)
(2d)	[d] 1.26 (s, 9 H, Bu^t), 6.17, 6.28 [t × 2, 3 H, H^4 ($C_3H_3N_2$), *J*(HH) 2], 7.67 [m, 4 H, H^3 and H^5 ($C_3H_3N_2$)], 7.98 [d, 2 H, H^3 or H^5 ($C_3H_3N_2$), *J*(HH) 2]	253.5 [C≡W, *J*(WC) 202], 224.8 [CO, *J*(WC) 168], 144.7—104.9 ($C_3H_3N_2$), 96.9 (*C*≡CBu^t), 82.8 (C≡*C*Bu^t), 30.0 ($C\mathit{Me}_3$), 27.0 (*C*Me_3)
(2e)	1.22 (s, 9 H, Bu^t), 2.30, 2.32 (s × 2, 6 H, Me_2-3,5), 2.34, 2.54 (s × 2, 12 H, Me_2-3,5), 5.69, 5.83 (s × 2, 3 H, $C_3\mathit{H}Me_2N_2$)	256.7 (C≡Mo), 226.6 (CO), 151.0—106.1 ($\mathit{C}_3HMe_2N_2$), 91.8 (*C*≡CBu^t), 78.3 (C≡*C*Bu^t), 30.7 ($C\mathit{Me}_3$), 28.0 (*C*Me_3), 16.0, 14.9, 13.0 (Me_2-3,5)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at ambient temperatures. [b] Measured in $CDCl_3$ unless otherwise stated. [c] Hydrogen-1 decoupled, to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2. [d] In CD_2Cl_2.



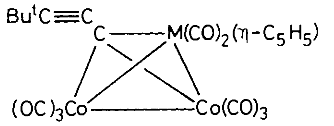
R

(5) alkyl or aryl



M

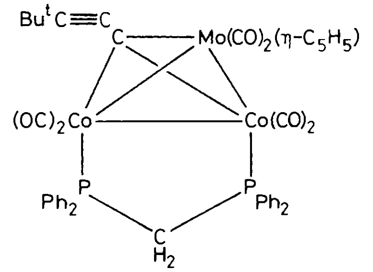
(6) Mo or W



M

(7a) Mo

(7b) W



(8)

does not give $[W(\equiv C\text{-}C\equiv CBu^t)(CO)_2\{HB(pz)_3\}]$ (**2d**). Presumably the tmen ligand is more strongly bound to tungsten than to molybdenum. Nevertheless, (**2d**) may be obtained from the reaction between (**1d**) and $K[HB(pz)_3]$.

The compounds (**2**) were characterised by their microanalytical and spectroscopic properties (Tables 1 and 2). In the i.r. spectra there are, as expected, two CO stretching bands. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra show peaks in agreement with the formulations proposed. A feature of interest is the comparatively shielded resonances observed for the alkylidyne-carbon nuclei. Thus in the spectrum of (**2b**) the resonance occurs at δ 266.7 p.p.m., whereas in the spectrum of the compound $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ the alkylidyne-carbon signal is at 311.4 p.p.m.[5] Similarly, for (**2c**) the alkylidyne-carbon peak in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum is at δ 259.8 p.p.m., to be compared with a chemical shift for the corresponding signal for $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2\{HB(pz)_3\}]$ at 293.1 p.p.m.[2a] Evidently the presence of the $C\equiv CBu^t$ substituent on the alkylidyne-carbon nuclei of the species (**1**) and (**2**) results in a pronounced increase in the shielding of these nuclei in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra, compared with the chemical shifts found for the metal-ligated carbon nuclei in complexes containing $M\equiv CR$ (R = alkyl or aryl) groups.

Dicobalt octacarbonyl and alkynes react readily to give numerous μ-alkyne complexes of formulation $[Co_2(\mu\text{-}C_2R_2)(CO)_6]$ (**3**; R = alkyl or aryl).[6] These species are isolobally mapped[7] with the trimetal compounds $[MCo_2(\mu_3\text{-}CR)(CO)_8L]$ [**4**; M = Mo, L = $\eta\text{-}C_5H_5$, R = $C_6H_4Me\text{-}4$ or $C_6H_3Me_2\text{-}2,6$; M = W, L = $\eta\text{-}C_5H_5$, R = $C_6H_4Me\text{-}4$, $C_6H_3Me_2\text{-}2,6$, or Me; L = $\eta\text{-}C_5Me_5$, R = $C_6H_4Me\text{-}4$ or Me; L = $HB(pz)_3$, R = $C_6H_4Me\text{-}4$ or Me][2a,8] formed in facile reactions between the reagents $[Co_2(CO)_8]$ and $[M(\equiv CR)(CO)_2L]$. A similar isolobal relationship links the two classes of compound $[Mo_2(CO)_4(\mu\text{-}C_2R_2)(\eta\text{-}C_5H_5)_2]$ (R = alkyl or aryl) (**5**)[9,10] and $[MMo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$ (**6**; M = Mo or W).[11] The former complexes are prepared by treating $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with alkynes, and the latter by treating the species $[Mo_2(CO)_n(\eta\text{-}C_5H_5)_2]$ (n = 4 or 6) with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$. These results prompted a study of reactions between $[Co_2(CO)_8]$ or $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and some of the compounds of type (**2**) to determine which of the triple bond sites $C\equiv M$ or $C\equiv C$ in the latter species might react.

Treatment of (**2a**) or (**2b**) with $[Co_2(CO)_8]$ in light petroleum at room temperature affords, respectively, in quantitative yield, the complexes $[MCo_2(\mu_3\text{-}C\text{-}C\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$ [M = Mo (**7a**) or W (**7b**)] (Table 3). These are structurally akin to the compounds (**4**). In the i.r. spectra of (**7**) there are considerably more CO stretching bands than would be expected for complexes having the structure shown. This phenomenon has been observed previously[2a,8] and is explained by the existence in solution of rotameric forms due to different orientations of the $M(CO)_2(\eta\text{-}C_5H_5)$ moiety with respect to the $\mu_3\text{-}CCo_2$ triangle. Neither compound shows a $C\equiv C$ stretching band in the i.r. spectrum; presumably these absorptions are too weak to be observed.

In agreement with the formulations proposed, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of complexes (**7a**) and (**7b**) (Table 4) the resonances observed for the $C\equiv M$ groups in the spectra of the precursors (**2a**) and (**2b**), at δ 274.9 and 266.7 p.p.m., respectively, are no longer seen. However, broad peaks at δ 233.2 (**7a**) and 218.8 p.p.m. (**7b**) may be assigned to the μ_3-C nuclei spanning the metal triangles. Again, as with the mononuclear metal alkylidyne complexes (Tables 1 and 2), the presence of the $C\equiv CBu^t$ substituent on the alkylidyne-carbon nucleus causes substantial shielding of the μ_3-C resonances. Thus in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the related compounds $[MCo_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$ (M = Mo or W), the μ_3-C signals occur at δ 270.7 (M = Mo)[8a] and 257.0 p.p.m. (M = W).[8b] The acetylenic carbon nuclei in the compounds (**7**) resonate at δ 118.7 and 98.4 p.p.m. for the molybdenum species, and at δ 115.9 and 98.2 p.p.m. for the tungsten complex. The assignments were confirmed by a fully coupled ^{13}C n.m.r. spectrum of (**7b**). The signal at 98.4 p.p.m. is a singlet and is therefore attributed to the $\mathit{C}\equiv CBu^t$ carbon nucleus. A much less intense and broad peak at δ 118.4 p.p.m. is assigned to the $C\equiv \mathit{C}Bu^t$ nucleus; poor resolution precluding a measurement for $^3J(HC)$. Interestingly, whereas in the spectrum of (**7b**) the chemical shift for the $\mathit{C}\equiv CBu^t$ nucleus (98.4 p.p.m.) is very similar to that (100.1 p.p.m.) for this nucleus in the spectrum of the precursor (**2b**), the chemical shifts for the signals for the $C\equiv \mathit{C}Bu^t$ nuclei in (**7b**) (118.4 p.p.m.) and (**2b**) (88.9 p.p.m.) are very different. A similar chemical shift pattern is shown for the $\mathit{C}\equiv \mathit{C}Bu^t$ carbons in (**2a**) and (**7a**).

Treatment of (**7a**) with dppm ($Ph_2PCH_2PPh_2$) in CH_2Cl_2 affords in high yield the complex $[MoCo_2(\mu_3\text{-}C\text{-}C\equiv CBu^t)(\mu\text{-}dppm)(CO)_6(\eta\text{-}C_5H_5)]$ (**8**), data for which are given in Tables 3

Table 3. Analytical[a] and physical data for the trimetal complexes

	Compound[b]	Yield (%)	$\nu_{max.}$(CO)[c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(7a)	[MoCo$_2$(μ_3-C–C≡CBu^t)(CO)$_8$(η-C$_5$H$_5$)]	96	[d] 2 083s, 2 074w, 2 046vs, 2 035m, 2 030s, 2 021m, 2 005m, 1 940m, 1 895m	40.6 (40.3)	2.6 (2.4)
(7b)	[WCo$_2$(μ_3-C–C≡CBu^t)(CO)$_8$(η-C$_5$H$_5$)]	96	[d] 2 083s, 2 073w, 2 045vs, 2 036m, 2 029s, 2 021m, 2 003m, 1 989w, 1 939w, 1 889w	35.6 (35.1)	2.2 (2.1)
(8)	[MoCo$_2$(μ_3-C–C≡CBu^t)(μ-dppm)(CO)$_6$(η-C$_5$H$_5$)]	80	2 023s, 1 992vs, 1 967s, 1 942m, 1 894m, 1 845m	55.6 (55.9)	3.7 (3.9)
(9a)	[Co$_2${μ-Bu^{t}C$_2$C≡Mo(CO)$_2$[HB(dmpz)$_3$]}(CO)$_6$]	97	2 090s, 2 055vs, 2 032s (sh), 1 975m, 1 898m	[e] 43.4 (43.5)	3.9 (3.8)
(9b)	[Co$_2${μ-Bu^{t}C$_2$C≡W(CO)$_2$[HB(pz)$_3$]}(CO)$_6$]	96	[d] 2 089s, 2 053vs, 2 035s, 2 029s, 1 978s, 1 902s	[f] 34.3 (34.7)	2.3 (2.3)
(10)	[Co$_2${μ-Bu^{t}C$_2$C≡W(CO)$_2$[HB(pz)$_3$]}(μ-dppm)(CO)$_4$]	74	2 023s, 1 997vs, 1 971vs, 1 955s, 1 873s	[g] 47.8 (48.6)	3.9 (3.6)
(11)	[Mo$_2$W(μ_3-C–C≡CBu^t)(CO)$_6$(η-C$_5$H$_5$)$_3$]	35	1 998m, 1 946s, 1 930vs, 1 869s, 1 801m	40.1 (40.4)	3.0 (2.9)
(12)	[Mo$_2${μ-Bu^{t}C$_2$C≡W(CO)$_2$[HB(pz)$_3$]}(CO)$_4$(η-C$_5$H$_5$)$_2$]	75	2 001s, 1 954s, 1 932vs, 1 874s, 1 840m	[h] 39.5 (39.2)	3.3 (3.0)

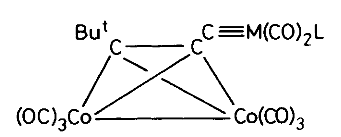
[a] Calculated values are given in parentheses. [b] All complexes are green in colour, except **(11)** which is brown. [c] Measured in CH$_2$Cl$_2$, unless otherwise stated. [d] In light petroleum. [e] N, 9.9 (10.1)%. [f] N, 9.7 (10.1)%. [g] N, 6.8 (7.2)%. [h] N, 8.6 (8.6)%.

Table 4. Hydrogen-1 and carbon-13 n.m.r. data[a] for the trimetal complexes

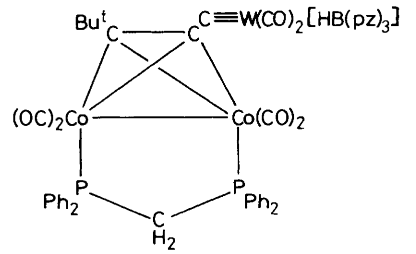
Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
(7a)	1.18 (s, 9 H, Bu^t), 5.42 (s, 5 H, C$_5$H$_5$)	233.2 (br, μ_3-C), 208.2 (br, CO), 118.7 (C≡*C*Bu^t), 98.4 (*C*≡CBu^t), 94.0 (C$_5$H$_5$), 30.1 (C*Me*$_3$), 28.3 (*C*Me$_3$)
(7b)	1.30 (s, 9 H, Bu^t), 5.50 (s, 5 H, C$_5$H$_5$)	[d] 218.8 (br, μ_3-C), 201.3 (br, CO), 115.9 (C≡*C*Bu^t), 98.2 (*C*≡CBu^t), 91.0 (C$_5$H$_5$), 30.1 (C*Me*$_3$), 28.3 (*C*Me$_3$)
(8)	1.17 (s, 9 H, Bu^t), 3.32 [d of t, 1 H, CH$_2$P, *J*(HH) 13, *J*(PH) 10], 4.52 [d of t, 1 H, CH$_2$P, *J*(HH) 13, *J*(PH) 11], 5.37 (s, 5 H, C$_5$H$_5$), 6.95—7.61 (m, 20 H, Ph)	[d] 236.2 (MoCO), 230.8 (μ_3-C), 209.4, 202.4 (CoCO), 137.7—128.0 (Ph), 118.5 (C≡*C*Bu^t), 102.4 (*C*≡CBu^t), 95.4 (C$_5$H$_5$), 31.5 (C*Me*$_3$), 31.4 [t, CH$_2$P, *J*(PH) 21], 30.9 (*C*Me$_3$)
(9a)	1.42 (s, 9 H, Bu^t), 2.32 (s, 3 H, Me$_2$-3,5), 2.36 (s, 9 H, Me$_2$-3,5), 2.49 (s, 6 H, Me$_2$-3,5), 2.74, 2.84 (s × 2, 3 H, C$_3$*H*Me$_2$N$_2$)	[d] 269.1 (C≡Mo), 227.4 (MoCO), 199.1 (br, CoCO), 151.5, 150.9, 144.7, 144.6 (*C*$_3$HMe$_2$N$_2$), 113.0 (C*C*Bu^t), 106.5, 105.8 (*C*$_3$HMe$_2$N$_2$), 92.5 (*C*CBu^t), 37.6 (*C*Me$_3$), 33.3 (C*Me*$_3$), 16.7, 14.8, 12.8, 12.6 (Me$_2$-3,5)
(9b)	[e] 1.39 (s, 9 H, Bu^t), 6.17, 6.24 [t × 2, 3 H, H^4 (C$_3$H$_3$N$_2$), *J*(HH) 2], 7.68 [m, 4 H, H^3 and H^5 (C$_3$H$_3$N$_2$)], 7.85 [d, 2 H, H^3 or H^5 (C$_3$H$_3$N$_2$), *J*(HH) 2]	263.2 [C≡W, *J*(WC) 196], 224.7 [WCO, *J*(WC) 165], 198.9 (br, CoCO), 144.4, 144.2, 135.5, 135.3 (C$_3$H$_3$N$_2$), 113.2 (C*C*Bu^t), 105.9 (C$_3$H$_3$N$_2$), 99.6 (*C*CBu^t), 37.5 (*C*Me$_3$), 31.0 (C*Me*$_3$)
(10)	1.57 (s, 9 H, Bu^t), 3.48 (m, 2 H, CH$_2$P), 5.89, 6.11 [t × 2, 3 H, H^4 (C$_3$H$_3$N$_2$), *J*(HH) 2], 6.95—7.68 [m, 26 H, H^3 and H^5 (C$_3$H$_3$N$_2$) and Ph]	[d] 278.5 (C≡W), 227.4 [WCO, *J*(WC) 169], 206.5, 202.7 (CoCO), 144.9—127.8 (Ph and C$_3$H$_3$N$_2$), 125.0 [t, C*C*Bu^t, *J*(PC) 17], 94.2 [t, *C*CBu^t, *J*(PC) 7], 39.3 (*C*Me$_3$), 37.8 [t, CH$_2$P, *J*(PC) 20], 32.8 (C*Me*$_3$)
(11)	[f] 1.38 (s, 9 H, Bu^t), 1.40 (s × 2, 9 H, Bu^t), 5.10, 5.15, 5.18, 5.20 (s × 4, 20 H, C$_5$H$_5$), 5.21 (s, 10 H, C$_5$H$_5$)	[f] 235.5, 235.2, 234.8, 230.6, 227.4, 224.8, 219.3 (μ_3-C and MoCO), 212.3, 210.4 (WCO), 108.8 (C≡*C*Bu^t), 103.0, 102.5 (*C*≡CBu^t), 95.9, 94.8, 93.7 (MoC$_5$H$_5$), 91.6, 91.5 (WC$_5$H$_5$), 32.8, 32.7 (C*Me*$_3$), 28.4, 28.3 (*C*Me$_3$)
(12)	1.35 (s, 9 H, Bu^t), 5.25 (s, 10 H, C$_5$H$_5$), 6.14, 6.27 [t × 2, 3 H, H^4 (C$_3$H$_3$N$_2$), *J*(HH) 2], 7.60—7.73 [m, 4 H, H^3 and H^5 (C$_3$H$_3$N$_2$)], 7.98 [d, 2 H, H^3 or H^5 (C$_3$H$_3$N$_2$), *J*(HH) 2]	[f] 272.9 (C≡W), 233.1, 232.6, 228.0, 226.6, 226.2, 225.1 (CO), 144.8, 144.3, 143.8, 135.5, 135.3 (C$_3$H$_3$N$_2$), 108.9 (C*C*Bu^t), 105.7, 105.3 (C$_3$H$_3$N$_2$), 92.0, 91.2 (C$_5$H$_5$), 73.2 (*C*CBu^t), 39.5 (*C*Me$_3$), 34.1 (C*Me*$_3$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at ambient temperatures, unless otherwise stated. [b] Measured in CDCl$_3$ unless otherwise stated. [c] Hydrogen-1 decoupled, to high frequency of SiMe$_4$, measurements in CD$_2$Cl$_2$–CH$_2$Cl$_2$. [d] Measured in CDCl$_3$. [e] Measured in CD$_2$Cl$_2$. [f] Measured at −40 °C.

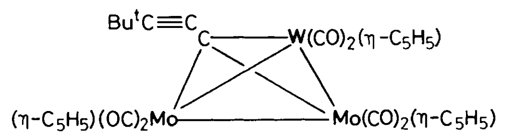
and 4. The dppm ligand bridges the two cobalt atoms, as evidenced by the ^{31}P-{^{1}H} n.m.r. spectrum which shows a single broad peak at δ 43.2 p.p.m. Complex **(8)** is closely related to the previously prepared compound [WCo$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-dppm)(CO)$_6$(η-C$_5$H$_5$)] [8b] in which the dppm ligand also spans the Co–Co bond (^{31}P-{^{1}H} n.m.r.: δ 27.3 p.p.m.). The observed difference in ^{31}P chemical shift, together with differences in the i.r. spectrum in the CO stretching region, suggests that in the tungsten compound the μ-dppm ligand adopts a different position relative to the μ_3-C atom. Since the C–C≡CBu^t group



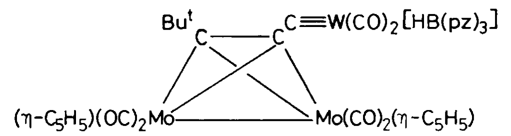
	M	L
(**9a**)	Mo	HB(dmpz)$_3$
(**9b**)	W	HB(pz)$_3$



(**10**)



(**11**)



(**12**)

would be less sterically demanding than the C–C$_6$H$_4$Me-4 fragment it is possible that in (**8**) the dppm ligand lies on the same side of the Co$_2$Mo plane as the alkylidyne group, whereas in the tungsten species it might be located on the opposite side of the metal triangle to the *p*-tolylmethylidyne moiety. There is also an interesting difference in the ^{1}H n.m.r. spectra of the two compounds. The PCH$_2$P protons are diastereomeric in both complexes, but in (**8**) the chemical shifts (Table 4) are appreciably different, whereas in the ^{1}H n.m.r. spectrum of [WCo$_2$(μ_3-CC$_6$H$_4$Me-4)(μ-dppm)(CO)$_6$(η-C$_5$H$_5$)] the two resonances for the CH$_2$ group almost coincide.[8b]

In spite of repeated attempts, and employing forcing conditions such as refluxing thf solutions, neither of the compounds (**2**) would react with [Co$_2$(CO)$_8$] in excess to give MCo$_4$ clusters in which the C≡C as well as the C≡M group ligate two cobalt centres. This is presumably due to steric factors, since once the complexes (**7**) are formed access to the C≡C bond might be difficult.

It was anticipated that the compound (**2e**), with its exceedingly bulky HB(dmpz)$_3$ ligand would be an ideal candidate for attachment of a Co$_2$(CO)$_6$ fragment to the C≡C rather than the C≡Mo bond in a compound of type (**2**). In accord with this premise, treatment of (**2e**) with [Co$_2$(CO)$_8$] in CH$_2$Cl$_2$ gave the 'μ-alkyne-dicobalt' complex [Co$_2${μ-Bu^{t}C$_2$C≡Mo(CO)$_2$[HB(dmpz)$_3$]}(CO)$_6$] (**9a**), characterised by the data given in Tables 3 and 4. As expected, the i.r. spectrum in the CO stretching region (Table 3) does not resemble that of the structurally different species [WCo$_2$(μ_3-CC$_6$H$_4$Me-4)(CO)$_8${HB(pz)$_3$}].[8e]

The ^{13}C-{^{1}H} n.m.r. spectrum of (**9a**) has a resonance at δ 269.1 p.p.m., attributable to the C≡Mo group. The corresponding signal in the spectrum of the precursor (**2e**) is at 256.7 p.p.m., and as expected[8] the C≡Mo peak for (**9a**) is far more deshielded than the μ_3-C resonances in the ^{13}C-{^{1}H} spectra of the compounds (**7**) and (**8**). The bridging μ-C$_2$ nuclei in the ^{13}C-{^{1}H} n.m.r. spectrum of (**9a**) resonate at δ 113.0 and 92.5 p.p.m. These were again distinguished (Table 4) *via* a fully coupled ^{13}C n.m.r. spectrum, which revealed a broad peak for the more deshielded signal and a sharp singlet for the less deshielded signal. Generally the ^{13}C shifts for acetylenic carbons bridging metal–metal bonds lie below δ 100 p.p.m.[9,12] Another interesting feature is that the Bu^t signals occur at δ 37.6 (*C*Me$_3$) and 33.3 p.p.m. (C*Me*$_3$). The former signal is considerably more deshielded than the Bu^t quaternary carbon signals in compounds (**1**), (**2**), (**7**), and (**8**), all of which have unco-ordinated alkyne units.

Somewhat surprisingly, treating the less sterically hindered tungsten alkylidyne species (**2d**) with 1 equivalent of [Co$_2$(CO)$_8$] also yields a μ-alkyne-dicobalt complex [Co$_2${μ-Bu^{t}C$_2$C≡W(CO)$_2$[HB(pz)$_3$]}(CO)$_6$] (**9b**), characterised in the usual manner (Tables 3 and 4). Convincing proof of the structure is found in the ^{13}C-{^{1}H} n.m.r. data. Again the chemical shift for the alkylidyne carbon atom (263.2 p.p.m.) is substantially more deshielded than that of compound (**7b**). Moreover, this signal shows ^{183}W satellite peaks [*J*(WC) 196 Hz] typical for a C≡W rather than a C–W linkage. In the ^{13}C-{^{1}H} n.m.r. spectrum of the complex [WCo$_2$(μ_3-CMe)(CO)$_8${HB(pz)$_3$}] the resonance for the μ_3-C nucleus shows ^{183}W–^{13}C coupling of 83 Hz. Complex (**9b**) did not react with excess of [Co$_2$(CO)$_8$] to yield a cluster of higher nuclearity.

Treatment of (**9b**) with dppm gives [Co$_2${μ-Bu^{t}C$_2$C≡W(CO)$_2$[HB(pz)$_3$]}(μ-dppm)(CO)$_4$] (**10**), identified by the data given in Tables 3 and 4. In the ^{13}C-{^{1}H} n.m.r. spectrum the μ-alkyne carbons of this product resonate at δ 125.0 and 94.2 p.p.m., and both are triplets with *J*(PC) 17 and 7 Hz, respectively. This pattern is in accord with the dppm group bridging the Co–Co bond symmetrically. The ^{31}P-{^{1}H} n.m.r. spectrum shows the expected broad peak (δ 36.2 p.p.m.).

Finally, in view of the isolobal relationship between the species (**5**) and (**6**), and in order to establish whether Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$ fragments would bond preferentially with the C≡C or the C≡M groups in compounds of type (**2**), two reactions employing [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] were studied. Heating the dimolybdenum compound with (**2b**) in toluene gave in moderate yield the complex [Mo$_2$W(μ_3-C–C≡CBu^t)(CO)$_6$(η-C$_5$H$_5$)$_3$] (**11**). The ^{13}C-{^{1}H} n.m.r. spectrum, when measured at ambient temperatures, revealed only a broad peak at δ 95.6 (MoC$_5$H$_5$), a sharp signal at δ 92.9 (WC$_5$H$_5$), and resonances at 33.6 (C*Me*$_3$) and 29.5 p.p.m. (*C*Me$_3$). The absence of signals for the CO and the alkylidyne groups and the broadening of the MoC$_5$H$_5$ peak indicated a fluxional process. At −40 °C the spectrum showed seven resonances assignable to μ_3-C and MoCO groups and two resonances due to carbonyls attached to tungsten (Table 4), thus indicating the presence of two isomers, one symmetrical and the other unsymmetrical. The unsatisfactory signal-to-noise ratio prevented the observation of ^{183}W–^{13}C satellite peaks, and hence definitive assignments for the μ_3-*C*Mo$_2$W nuclei in each isomer could not be made. However, the fact that no resonances were observed above δ 235.5 p.p.m. rules out the presence of a terminal C≡W fragment. In the low-temperature spectrum five C$_5$H$_5$ signals are seen; one peak (δ 95.9 p.p.m.) is significantly more intense than the others indicating the existence of a symmetrical isomer in which two C$_5$H$_5$ ligands are equivalent. There are three signals observed for the acetylenic carbon atoms at δ 108.8, 103.0, and 102.5 p.p.m. The former is assigned to the (C≡*C*Bu^t) carbon of both isomers and the last two to the ($C{\equiv}CBu^t$) carbon, one for each isomer. The ^1H n.m.r. spectrum at −40 °C (Table 4) is also informative. There are two equally intense Bu^t signals, as expected for two isomers, and five C_5H_5 resonances. However, one of these (δ 5.21) is more intense and can probably be assigned to the two chemically equivalent C_5H_5 groups attached to the molybdenum atoms in the symmetrical isomer. The origin of the two isomers may be due to different orientations of the η-C_5H_5 ligands as they can lie *cis* or *trans* to the μ_3-alkylidyne unit.[8b] One isomer would appear to have a plane of symmetry, thus making the two η-C_5H_5 ligands on the molybdenum atoms chemically equivalent. The trimetallatetrahedrane complex $[Mo_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)_3]$, obtained from $[W({\equiv}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, also shows n.m.r. evidence for a dynamic process.[11]

Refluxing mixtures of (**2d**) and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene affords in high yield the compound $[Mo_2\{\mu\text{-}Bu^tC_2C{\equiv}W(CO)_2[HB(pz)_3]\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (**12**), structurally similar to the complexes (**9**) but with the $C{\equiv}C$ unit transversely bridging a Mo–Mo bond instead of a Co–Co linkage. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at ambient temperatures shows a deshielded peak at δ 273.1 p.p.m., with $^{183}W\text{-}^{13}C$ coupling (199 Hz), unambiguously indicating that the compound possesses a $C{\equiv}W$ group unattached to a metal ligand fragment. The room-temperature spectrum also reveals too broad signals (δ 92.0 and 91.1 p.p.m.) for C_5H_5 groups, indicating first that the molecule does not possess a plane of symmetry, and secondly that it is undergoing dynamic behaviour. This is substantiated by the observation of four broad CO peaks (δ 232.8, 228.0, 226.3, and 225.6 p.p.m.). In the spectrum measured at −40 °C (Table 4) six CO resonances are seen, and the C_5H_5 peaks are sharp. Dynamic behaviour in μ-alkyne-dimolybdenum compounds is well established, and is almost certainly being observed with (**12**).[10,11] In this case, surprisingly, the process also broadens at room temperature the remote WCO groups, which should be inequivalent due to the lack of a plane of symmetry.

In the work described herein we have demonstrated the reactivity of both triple bonds in the compounds (**2**). It is evident that the more bulky hydrotris(pyrazolyl)borato ligands reduce the reactivity of the alkylidyne $M{\equiv}C$ bond, presumably for steric reasons, but the effect must only be marginal since previously these ligands have not substantially altered the reactivity of $M{\equiv}C$ bonds in mononuclear metal aryl- and alkylmethylidyne complexes towards $[Co_2(CO)_8]$ and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$.[2a,8e] It now remains to be seen whether the potential of these alkynylmethylidynemetal reagents extends to the synthesis of larger clusters.

Experimental

All reactions were carried out under oxygen-free nitrogen, using Schlenk-tube techniques. Light petroleum refers to that fraction of b.p. 40—60 °C. The reagents $Na(C_5H_5)\cdot dme$,[13] $K[HB(pz)_3]$ and $K[HB(dmpz)_3]$[14] were prepared by previously described procedures. Aluminium oxide (Brockman, activity II) was used for all separations by column chromatography. The instrumentation used has been described previously.[12] The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were measured in $CDCl_3$, and the chemical shifts are to high frequency of 85% H_3PO_4 (external) taken as positive.

Preparation of the Compounds $[M({\equiv}C\text{–}C{\equiv}CBu^t)(O_2CCF_3)(CO)_2L_2]$.—(*i*) A thf (50 cm³) solution of $HC{\equiv}CBu^t$ (4.0 cm³, 32.5 mmol) at −40 °C was treated dropwise with $LiBu^n$ (20.3 cm³ of a 1.6 mol dm^{-3} solution in hexane). The mixture was stirred and slowly warmed to room temperature, during which time butane was evolved. Stirring was continued for 1 h, and a portion of the resulting solution was titrated against 0.1 mol dm^{-3} HCl to determine the molarity of the $Li(C{\equiv}CBu^t)$.

A suspension of $[Mo(CO)_6]$ (2.64 g, 10 mmol) in thf (*ca.* 50 cm³) was stirred vigorously and cooled to −40 °C. One equivalent of the $Li(C{\equiv}CBu^t)$ solution (*ca.* 22—24 cm³) was added dropwise, and the mixture was warmed to room temperature and stirred for 1 h. The resulting orange solution was cooled to −78 °C, and $(CF_3CO)_2O$ (1.5 cm³, 10.6 mmol) diluted in thf (*ca.* 20 cm³) was added dropwise over 15 min. The solution went red immediately, and CO was evolved. On warming to 0 °C, tmen (2 cm³, excess) was added, and the solution was stirred at room temperature for 2 h, during which period CO was evolved. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 30 cm³) and transferred to the top of a chromatography column (3 × 25 cm). Elution with CH_2Cl_2, removal of solvent from the yellow eluate, followed by crystallisation of the residue from CH_2Cl_2–light petroleum (1:3) gave yellow *microcrystals* of $[Mo({\equiv}C\text{–}C{\equiv}CBu^t)(O_2CCF_3)(CO)_2(tmen)]$ (**1a**) (3.81 g).

(*ii*) In a similar manner, $[W(CO)_6]$ (3.52 g, 10.0 mmol) was treated successively with 1 equivalent of $Li(C{\equiv}CBu^t)$, $(CF_3CO)_2O$ (1.5 cm³, 10.6 mmol), and tmen (2 cm³), yielding yellow *microcrystals* of $[W({\equiv}C\text{–}C{\equiv}CBu^t)(O_2CCF_3)(CO)_2(tmen)]$ (**1b**) (4.70 g).

(*iii*) In a similar fashion, $[Mo(CO)_6]$ (2.64 g, 10.0 mmol) was treated with 1 equivalent of $Li(C{\equiv}CBu^t)$, $(CF_3CO)_2O$ (1.5 cm³, 10.6 mmol), and 2,2′-bipyridine (1.60 g, 10.2 mmol). An orange precipitate was deposited and the suspension allowed to settle overnight. As much of the supernatant as possible was removed with a syringe, and the product was washed with diethyl ether (3 × 100 cm³), yielding orange *microcrystals* of $[Mo({\equiv}C\text{–}C{\equiv}CBu^t)(O_2CCF_3)(CO)_2(bipy)]$ (**1c**) (3.60 g).

Preparation of the Complexes.—$[M({\equiv}C\text{–}C{\equiv}CBu^t)(CO)_2L]$.—(*i*) Compound (**1c**) (5.14 g, 10.0 mmol) was suspended in thf (*ca.* 50 cm³) and treated with $Na(C_5H_5)\cdot dme$ (1.90 g, 10.7 mmol). The mixture was stirred for 2 h during which time all of (**1c**) dissolved. Solvent was removed *in vacuo*, and the dark residue was extracted (6 × 50 cm³) with CH_2Cl_2–light petroleum (1:3). The combined extracts were chromatographed, using the same solvent mixture for elution. After removal of solvent *in vacuo*, the resulting crude product was rechromatographed, eluting with CH_2Cl_2–light petroleum (1:10). Removal of solvent *in vacuo* afforded orange *microcrystals* of $[Mo({\equiv}C\text{–}C{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (**2a**) (1.45 g).

(*ii*) In a similar manner to the preparation of compound (**1b**), $[W(CO)_6]$ (3.52 g, 10.0 mmol) was treated with 1 equivalent of $Li(C{\equiv}CBu^t)$, $(CF_3CO)_2O$ (1.50 cm³, 10.6 mmol), and pyridine (2 cm³, excess) to generate $[W({\equiv}C\text{–}C{\equiv}CBu^t)(O_2CCF_3)(CO)_2(py)_2]$ (**1d**) *in situ*. This solution was treated with $Na(C_5H_5)\cdot dme$ (1.90 g, 10.7 mmol) and stirred for 2 h. Removal of solvent *in vacuo* gave a dark residue which was extracted (3 × 50 cm³) with CH_2Cl_2–light petroleum (1:3) and the combined extracts were chromatographed on alumina (3 × 20 cm), eluting with the same solvent mixture. The solvent was removed from the resulting eluate, and the crude product was rechromatographed using light petroleum–CH_2Cl_2 (1:10). The product $[W({\equiv}C\text{–}C{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (**2b**) (2.80 g) was isolated as orange *microcrystals*.

(*iii*) Complex (**1a**) (2.30 g, 5.0 mmol) was dissolved in CH_2Cl_2 (*ca.* 25 cm³) and $K[HB(pz)_3]$ (1.26 g, 5.0 mmol) was added. The solution was stirred for 12 h, during which time the mixture became red. Solvent was removed *in vacuo* and the residue was extracted (4 × 50 cm³) with CH_2Cl_2–light petroleum (2:3). The combined extracts were chromatographed on alumina (3 × 20 cm), eluting with the same solvent mixture. Reduction of the eluate solvent volume *in vacuo* to *ca.* 25 cm³ and cooling to *ca.* −78 °C gave red *microcrystals* of $[Mo({\equiv}C\text{–}C{\equiv}CBu^t)(CO)_2\{HB(pz)_3\}]$ (**2c**) (2.00 g).

(*iv*) In a similar manner, the alkylidyne molybdenum complex

(**1a**) (2.37 g, 5.0 mmol) was treated with $K[HB(dmpz)_3]$ (1.68 g, 5.0 mmol) yielding red *microcrystals* of $[Mo(\equiv C{-}C\equiv CBu^t)(CO)_2\{HB(dmpz)_3\}]$ (**2e**) (2.30 g).

(*v*) In a similar procedure to the preparation of (**2b**), $[W(CO)_6]$ (3.52 g, 10.0 mmol) was converted into (**1d**) and treated with $K[HB(pz)_3]$ (2.52 g, 10.0 mmol), the mixture being stirred for 2 h. Similar work-up as in the preparation of (**2c**) yielded red *microcrystals* of $[W(\equiv C{-}C\equiv CBu^t)(CO)_2\{HB(pz)_3\}]$ (**2d**) (4.65 g).

Reactions between the Compounds $[M(\equiv C{-}C\equiv CBu^t)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo *or* W) *and* $[Co_2(CO)_8]$.—(*i*) The compounds (**2a**) (0.31 g, 1.0 mmol) and $[Co_2(CO)_8]$ (0.34 g, 1.0 mmol) were stirred together in light petroleum (*ca.* 25 cm^3) for 1 h, during which period CO evolution was observed, and the mixture turned green. Cooling to −78 °C, and removal of the supernatant liquid with a syringe, gave green *microcrystals* of $[MoCo_2(\mu_3\text{-}C{-}C\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$ (**7a**) (0.57 g).

(*ii*) Similarly, the complexes (**2b**) (0.40 g, 1.0 mmol) and $[Co_2(CO)_8]$ (0.34 g, 1.0 mmol) gave green *microcrystals* of $[WCo_2(\mu_3\text{-}C{-}C\equiv CBu^t)(CO)_8(\eta\text{-}C_5H_5)]$ (**7b**) (0.66 g).

Reactions of the Complexes $[M(\equiv C{-}C\equiv CBu^t)(CO)_2L]$ [M = Mo, L = $HB(dmpz)_3$; M = W, L = $HB(pz)_3$] *with* $[Co_2(CO)_8]$.—(*i*) In a similar manner to the synthesis of (**7a**), complex (**2e**) (0.27 g, 0.50 mmol) was treated with $[Co_2(CO)_8]$ (0.17 g, 0.50 mmol) to afford green *microcrystals* of $[Co_2\{\mu\text{-}Bu^tC_2C\equiv Mo(CO)_2[HB(dmpz)_3]\}(CO)_6]$ (**9a**) (0.40 g).

(*ii*) In a similar manner to the preparation of (**7b**), complex (**2d**) (0.28 g, 0.51 mmol) was treated with $[Co_2(CO)_8]$ (0.17 g, 0.50 mmol) yielding green *microcrystals* of $[Co_2\{\mu\text{-}Bu^tC_2C\equiv W(CO)_2[HB(pz)_3]\}(CO)_6]$ (**9b**) (0.40 g).

Reactions with dppm.—(*i*) Compound (**7a**) (0.30 g, 0.5 mmol) and dppm (0.20 g, 0.52 mmol) were dissolved in CH_2Cl_2 (*ca.* 20 cm^3) and heated under reflux for 30 min. The solvent volume was reduced to *ca.* 7 cm^3 and transferred to the top of an alumina column (2 × 15 cm). Elution with CH_2Cl_2, followed by removal of solvent *in vacuo* from the green eluate and crystallisation from CH_2Cl_2–light petroleum (1:10), gave green *microcrystals* of $[MoCo_2(\mu_3\text{-}C{-}C\equiv CBu^t)(\mu\text{-}dppm)(CO)_6(\eta\text{-}C_5H_5)]$ (**8**) (0.37 g).

(*ii*) As in the preparation of (**8**), complex (**9b**) (0.42 g, 0.50 mmol) was treated with dppm (0.20 g, 0.52 mmol), yielding green *microcrystals* of $[Co_2\{\mu\text{-}Bu^tC_2C\equiv W(CO)_2[HB(pz)_3]\}(\mu\text{-}dppm)(CO)_4]$ (**10**) (0.40 g).

Reactions of $[W(\equiv C{-}C\equiv CBu^t)(CO)_2L]$ [L = $\eta\text{-}C_5H_5$ *or* $HB(pz)_3$] *with* $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$.—(*i*) Compound (**2b**) (0.40 g, 1.0 mmol) and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.47 g, 1.0 mmol) were dissolved in toluene (*ca.* 25 cm^3), and heated under reflux for 2 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (*ca.* 10 cm^3) and transferred to the top of an alumina column (3 × 20 cm). Elution with CH_2Cl_2–light petroleum (1:1) removed some unreacted $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$, followed by a brown band. The latter was collected and the solvent was removed *in vacuo*. Crystallisation of the residue from CH_2Cl_2–light petroleum (1:10) gave brown *microcrystals* of $[Mo_2W(\mu_3\text{-}C{-}C\equiv CBu^t)(CO)_6(\eta\text{-}C_5H_5)_3]$ (**11**) (0.29 g).

(*ii*) Compound (**2d**) (0.55 g, 1.0 mmol) and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.47 g, 1.0 mmol) were refluxed in toluene (*ca.* 25 cm^3) for 12 h, and the mixture was worked up in the same way as for compound (**11**) to give green *microcrystals* of $[Mo_2\{\mu\text{-}Bu^tC_2C\equiv W(CO)_2[HB(pz)_3]\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (**12**) (0.74 g).

Acknowledgements

We thank the S.E.R.C. for support and for a research studentship (to I. J. H.).

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Received 28*th November* 1988; *Paper* 8/04700F