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Synthesis and characterisation of linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$ bridged tri-, tetra- and pentametallic molybdenum(II) (π-allyl)/tungsten(II) (alkyne) complexes

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Abstract

Equimolar quantities of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ and L, L′ or L″ $\{[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ (L, R = R′ = Me; L′, R = R′ = Ph; L″, R = Me, R′ = Ph} react in CH_2Cl_2 at room temperature to give the tetrametallic linear triphos-bridged, halo-bridged complexes $[\{Mo(\mu\text{-}X)(CO)_2(L, L' \text{ or } L'')(\eta^3\text{-}C_3H_4R'')\}_2]$ (for L, L′ or L″, X = Cl, R″ = H, Me-2 or CH_2Cl-2; X = Br, R″ = H) (**1**–**12**) in high yield. Reaction of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ with two equivalents of L, L′ or L″ in CH_2Cl_2 at room temperature affords the trimetallic complexes $[MoX(CO)_2(L, L' \text{ or } L'')_2(\eta^3\text{-}C_3H_4R'')]$ (for L, L′ or L″, X = Cl, R″ = H, Me-2, CH_2Cl-2; X = Br, R″ = H) also in high yield. Reaction of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$ with three equivalents of L′ afforded the tetrametallic complex *cis*-,*mer*-$[Mo(CO)_2(NCMe)(L')_3]$ (**25**). Treatment of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$ with four equivalents of L or L″ yielded the zero-valent pentametallic complexes *cis*-$[Mo(CO)_2(L \text{ or } L'')_4]$ (**26** and **27**). All the new complexes (**1**–**27**) described in this paper were characterised by elemental analysis, IR, ^1H-NMR and in selected cased by $^{31}P\{^1H\}$-NMR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkyne; Allyl; Molybdenum; Triphos

1. Introduction

The importance of π-allyl complexes of the type $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ has been highlighted by Trost et al. in the use of these complexes as catalysts for allylic alkylations [1–3]. Although a number of such complexes have been prepared where L = phosphine donor ligand [4–13], hitherto, no examples of this type have been reported, where L = an organometallic phosphine donor ligand.

In 1996 [14], we described the synthesis and molecular structures (for R = R′ = Me; R = Me, R′ = Ph) of the bidentately attached linear triphos complexes $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ {R = R′ = Me (L), Ph (L′); R = Me, R′ = Ph (L″)}. In this paper, we describe the reactions of the π-allyl molybdenum(II) complexes $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ (X = Cl, R″ = H, Me-2, CH_2Cl-2; X = Br, R″ = H) with L, L′ or L″ (see above) to give a series of new tri-, tetra- and pentametallic linear triphos-bridged complexes.

2. Results and discussion

Reaction of equimolar quantities of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ and L, L′ or L″ $\{[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ (L, R = R′ = Me; L′, R = R′ = Ph; L″, R = Me, R′ = Ph)} in CH_2Cl_2 at room temperature afforded the tetrametallic linear triphos-bridged and halo-bridged complexes $[\{Mo(\mu\text{-}X)(CO)_2(L, L' \text{ or } L'')(\eta^3\text{-}C_3H_4R'')\}_2]$ (for L, L′ or L″, X = Cl, R″ = H, Me-2 or CH_2Cl-2; X = Br, R″ = H) (**1**–**12**) in high yield, via displacement of the two acetonitrile ligands. The complexes **1**–**12** have been characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^1H- (Table 3) and in selected cases $^{31}P\{^1H\}$-NMR spectroscopy (Table 4). Molecular weight measurements using Rast's method [15] for selected complexes are given in Table 1. Complexes **10**–

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12 were confirmed as CH_2Cl_2 solvates by repeated elemental analyses and ^{1}H-NMR spectroscopy. Complexes **1**–**12** are reasonably stable in the solid state if stored under dinitrogen, however they all rapidly decompose in air in solution. Complexes **1**–**12** are reasonably soluble in chlorinated solvents such as CH_2Cl_2 or $CHCl_3$, but only slightly soluble in diethyl ether.

The IR spectra of complexes **1**–**12** all show two carbonyl bands, with the band at higher wavenumber being stronger and broader than the band at lower wavenumber. For example, complex **1** shows carbonyl bands at 1955 and 1848 cm^{-1}. It is very likely that the two bands at 1955 and 1848 cm^{-1} are due to the *cis*-carbonyl groups on the π-allyl molybdenum moiety, since related $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ have carbonyl bands in this region [4–13]. The band at 1955 cm^{-1} can also be assigned with the carbonyl group on the 2-butyne tungsten part of the molecule $\{\nu(C{\equiv}O)\ (CHCl_3) = 1957\ cm^{-1}$ for $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}MeC_2Me)]\}$ [14]. It should also be noted that in all complexes **1**–**12**, the higher wavenumber band is much more intense than the lower band, which confirms that the band at 1955 cm^{-1} is due to a combination of the higher band of the $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ fragment, and for the monocarbonyl complexes $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ for **1**–**12**. It would not be expected that coordination of the third phosphorus of the linear triphos ligand to another metal would significantly affect the carbonyl ligand. The X–ray crystal structures of a number of π-allyl molybdenum complexes of the type $[MoX(CO)_2L_2(\eta^3\text{-allyl})]$ (L_2 = nitrogen donor ligand) have been determined [16–25], and all have a *cis*-carbonyl geometry with the π-allyl and halide groups *trans* to each other in the axial positions, however, the only monodentate bis(phosphorus) donor ligand complex to be structurally characterised is the bis(trimethylphosphite) molybdenum complex, $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$ [26], which has a distorted pentagonal bipyramidal geometry with a chlorine and a carbonyl ligand in axial positions, and the equatorial girdle having two phosphite groups, one carbonyl ligand, and the π-allyl unit occupying two adjacent sites. In view of the simple IR carbonyl pattern the *pseudo*-octahedral geometry should be favoured for the mono(organotungsten phosphine) ligand complexes **1**–**12**, rather

Table 1
Physical, analytical and molecular weight data for complexes **1**–**27** [a]

Complex	Colour	Yield (%)	Analysis (%) found (calc.)		Molecular weights
			C	H	
1 $[\{Mo(\mu\text{-}Cl)(CO)_2L(\eta^3\text{-}C_3H_5)\}_2]$	Green	79	41.3(41.1)	3.1(3.4)	–
2 $[\{Mo(\mu\text{-}Cl)(CO)_2L'(\eta^3\text{-}C_3H_5)\}_2]$	Green	81	45.4(46.0)	3.3(3.4)	–
3 $[\{Mo(\mu\text{-}Cl)(CO)_2L''(\eta^3\text{-}C_3H_5)\}_2]$	Green	85	43.7(43.7)	3.8(3.5)	–
4 $[\{Mo(\mu\text{-}Cl)(CO)_2L(\eta^3\text{-}C_3H_4(Me\text{-}2))\}_2]$	Green	88	41.9(41.6)	3.3(3.6)	–
5 $[\{Mo(\mu\text{-}Cl)(CO)_2L'(\eta^3\text{-}C_3H_4(Me\text{-}2))\}_2]$	Green	85	47.1(46.4)	3.6(3.5)	–
6 $[\{Mo(\mu\text{-}Cl)(CO)_2L''(\eta^3\text{-}C_3H_4(Me\text{-}2))\}_2]$	Green	80	44.8(44.1)	3.5(3.6)	–
7 $[\{Mo(\mu\text{-}Cl)(CO)_2L(\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2))\}_2]$	Green	83	40.5(40.5)	3.4(3.4)	2699(2664)
8 $[\{Mo(\mu\text{-}Cl)(CO)_2L'(\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2))\}_2]$	Green	75	45.7(45.3)	3.5(3.4)	2961(2912)
9 $[\{Mo(\mu\text{-}Cl)(CO)_2L''(\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2))\}_2]$	Green	86	43.2(43.0)	3.6(3.5)	2956(2791)
10 $[\{Mo(\mu\text{-}Br)(CO)_2L(\eta^3\text{-}C_3H_5)\}_2].CH_2Cl_2$	Green	84	39.6(39.0)	3.6(3.3)	–
11 $[\{Mo(\mu\text{-}Br)(CO)_2L'(\eta^3\text{-}C_3H_5)\}_2].CH_2Cl_2$	Green	63	44.9(44.6)	3.7(3.4)	3412(2988)
12 $[\{Mo(\mu\text{-}Br)(CO)_2L''(\eta^3\text{-}C_3H_5)\}_2].CH_2Cl_2$	Green	76	41.4(41.5)	4.0(3.5)	2490(2866)
13 $[MoCl(CO)_2L_2(\eta^3\text{-}C_3H_5)].CH_2Cl_2$	Green	80	41.9(41.7)	3.4(3.5)	–
14 $[MoCl(CO)_2L'_2(\eta^3\text{-}C_3H_5)]$	Green	84	47.2(47.8)	3.6(3.6)	–
15 $[MoCl(CO)_2L''_2(\eta^3\text{-}C_3H_5)]$	Green	82	45.2(45.3)	3.6(3.6)	2646(2464)
16 $[MoCl(CO)_2L_2\{\eta^3\text{-}C_3H_4(Me\text{-}2)\}]$	Green	89	42.6(42.9)	3.4(3.6)	–
17 $[MoCl(CO)_2L'_2\{\eta^3\text{-}C_3H_4(Me\text{-}2)\}]$	Green	81	49.6(48.6)	3.6(3.6)	–
18 $[MoCl(CO)_2L''_2\{\eta^3\text{-}C_3H_4(Me\text{-}2)\}]$	Green	82	45.3(45.6)	3.8(3.7)	–
19 $[MoCl(CO)_2L_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$	Green	84	42.1(42.3)	3.7(3.6)	–
20 $[MoCl(CO)_2L'_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$	Green	79	47.7(47.4)	3.8(3.5)	–
21 $[MoCl(CO)_2L''_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$	Green	87	45.0(44.9)	4.2(3.6)	–
22 $[MoBr(CO)_2L_2(\eta^3\text{-}C_3H_5)].CH_2Cl_2$	Green	90	40.9(40.9)	4.0(3.4)	2481(2466)
23 $[MoBr(CO)_2L'_2(\eta^3\text{-}C_3H_5)]$	Green	84	47.2(47.0)	3.3(3.5)	2289(2630)
24 $[MoBr(CO)_2L''_2(\eta^3\text{-}C_3H_5)].CH_2Cl_2$	Green	72	44.6(44.5)	3.6(3.6)	2613(2593)
25 *cis,mer*-$[Mo(CO)_2(NCMe)L'_3]$ [b]	Green	83	48.4(48.0)	3.4(3.5)	3726(3729)
26 *cis*-$[Mo(CO)_2L_4]$	Green	86	43.0(43.4)	3.6(3.6)	4315(4369)
27 *cis*-$[Mo(CO)_2L''_4]$	Green	83	46.0(45.2)	4.0(3.6)	4775(4622)

[a] $L = [WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}MeC_2Me)]$, $L' = [WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}PhC_2Ph)]$, $L'' = [WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}MeC_2Ph)]$.

[b] Nitrogen analysis: N(found), 0.4; N(calc.), 1.0.

Table 2
IR data [a] for complexes **1**–**27** [b]

Complex	ν(C≡O) (cm^{-1})	ν(C≡C) (cm^{-1})
1	1955(br, s), 1848(m)	1602(w)
2	1958(br, s), 1879(m)	1588(w)
3	1957(br, s), 1873(m)	1588(w)
4	1958(br, s), 1843(m)	1654(w)
5	1970(br, s), 1850(m)	1588(w)
6	1959(br, s), 1850(m)	1599(w)
7	1957(br, s), 1834(m)	1588(w)
8	1968(br, s), 1833(m)	1588(w)
9	1961(br, s), 1876(m)	1589(w)
10	1955(br, s), 1878(m)	1588(w)
11	1964(br, s), 1878(m)	1620(w)
12	1967(br, s), 1850(m)	1588(w)
13	1940(br, s), 1849(m)	1654(w)
14	1967(br, s), 1836(br, s)	1600(w)
15	1957(br, s), 1878(m)	1589(w)
16	1955(br, s), 1845(m)	1588(w)
17	1967(br, s), 1894(m)	1600(w)
18	1971(br, s), 1890(m)	1598(w)
19	1957(br, s), 1875(m)	1588(w)
20	1961(br, s), 1876(m)	1601(w)
21	1959(br, s), 1878(m)	1558(w)
22	1955(br, s), 1878(m)	1654(w)
23	1964(br, s), 1878(br, s)	1608(w)
24	1966(br, s), 1897(s)	1589(w)
25	1962(br), 1930(sh), 1841(m) [c]	1587(w)
26	1956(br), 1907(s), 1820(m)	1658(w)
27	1969(br), 1896(s), 1819(m)	1672(w)

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates.
[b] br, s = broad, strong; m = medium, sh = shoulder, w = weak.
[c] ν(N≡C) = 2235 cm^{-1}.

than the pentagonal bipyramidal geometry for the bis(phosphite) complex $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$ previously observed [26]. The two halves of the chloro-bridged dimers should also be identical, and hence only one set of *cis*-carbonyl bands will be observed. Also, the molecular structures of $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ (R = R′ = Me; R = Me, R′ = Ph) have been crystallographically characterised [14], and for R = Me, R′ = Ph a single diastereoisomer was crystallised, however, the 2-butyne complex crystallised as a 50:50 mixture of two diastereoisomers. In view of the $^{31}P\{^1H\}$-NMR spectra for complexes **1**, **5**–**12** (Table 4), it is likely that more than one isomer of these tetrametallic complexes exist in solution. The $^{31}P\{^1H\}$-NMR data for selected complexes (Table 4) as expected show no resonances at high field for the uncoordinated phosphorus at $\delta = -13.5$ppm for $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$, which is now attached to the π-allyl molybdenum complex. The spectra are also complex, indicating the presence of several isomers in solution, probably at the tungsten centre of the molecule. Tungsten satellites were not always observed, due to the poor solubility of these complexes in several NMR solvents, but where present they range from $J_{W-P} = 194$–243 Hz. However, the δ values of the two phosphorus atoms attached to the tungsten metal, i.e. W–PPh and W–PPh_2 would not be expected to shift very much from the values in $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ [14]. Therefore, we have assigned resonances identical or near the values of W-PPh and W–PPh_2 in the organotungsten phosphine ligands to these groups in the multimetallic complexes **1**, **5**–**12**. The geometry of one isomer of complexes **1**–**12** is shown in Fig. 1. The ^1H-NMR data for complexes **1**–**12** conforms with the structure proposed in Fig. 1. A number of unsuccessful attempts were made to grow suitable single crystals of the tetrametallic complexes **1**–**12**, only powders or very poor quality crystals were obtained, probably due to the large and unsymmetrical nature of these molecules, and the presence of several isomers in solution.

These chloro-bridged tetrametallic complexes, **1-12**, $[\{Mo(\mu\text{-}X)(CO)_2(L, L' \text{ or } L'')(\eta^3\text{-}C_3H_4R'')\}_2]$ are almost certainly obtained via the mono(acetonitrile) complexes $[MoX(CO)_2(NCMe)(L, L' \text{ or } L'')(\eta^3\text{-}C_3H_4R'')]$ which could not be observed even after short reaction times. The tetrametallic nature of **1**–**12** was confirmed by selected molecular weight studies using Rast's method [15] (see Table 1). A number of attempts were made to obtain FAB mass spectra of these complexes without success. Although fragment peaks were obtained which could be assigned, no parent ion was observed for complexes **1**–**12**.

Treatment of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ with two equivalents of L, L′ or L″ in CH_2Cl_2 at room temperature gives the trimetallic, linear triphos-bridged complexes $[MoX(CO)_2L_2(\eta^3\text{-}C_3H_4R'')]$ (for L, L′ or L″, X = Cl, R″ = H, Me-2 or CH_2Cl-2; X = Br, R″ = H) (**13**–**24**) via displacement of both acetonitrile ligands. Complexes **13**–**24** have been characterised in the normal manner (see Tables 1–4). Complexes **13**, **22** and **24** were confirmed as CH_2Cl_2 solvates by repeated elemental analyses and ^1H-NMR spectroscopy. Molecular weight studies using Rast's method [15] (Table 1) confirmed the trimetallic nature of these complexes. Again as with complexes **1**–**12**, FAB Mass spectrometry was attempted with complexes **13**–**24**, but again no identifiable parent ions were observed. Complexes **13**–**24** are, in general, more stable, and less soluble than their tetrametallic analogues **1**–**12**. However, complexes **13**–**24** must be stored under an inert atmosphere in the solid state to avoid oxidation; in particular, in solution.

The IR spectra of complexes **13**–**24** all show as expected two carbonyl bands in their IR spectra, with a similar intensity pattern as mentioned earlier for complexes **1**–**12**. For example, complex **14** has bands at $\nu(CO) = 1967$ and 1836 cm^{-1} due to the *cis*-carbonyl groups on the π-allyl molybdenum moiety. The very similar carbonyl stretching bands on the tungsten diphenylacetylene $\{\nu(CO) = 1965$ cm^{-1}, for $[WI_2(CO)$-

Table 3
Proton NMR data (δ) for complexes **1**–**27** [a,b]

Complex	^{1}H-NMR (δ ppm)
1	7.9–7.4 (m, 50H, *Ph*); 3.9 (s, 2H, C*H*-allylic); 3.4 (d, 4H, $J_{H–H}$ = 1.2Hz, CH_b); 3.1 (s, 12H, C_2Me); 2.9–2.6 (m, 16H, CH_2); 0.9 (d, 4H, $J_{H–H}$ = 1.3Hz, CH_a)
2	7.8–7.4 (m, 70H, *Ph*); 4.0 (s, 2H, C*H*-allylic); 3.3 (d, 4H, $J_{H–H}$ = 1.1Hz, CH_b); 2.8–2.6 (m, 16H, CH_2); 1.0 (d, 4H, $J_{H–H}$ = 1.2Hz, CH_a)
3	7.8–7.4 (m, 60H, *Ph*); 3.9 (s, 2H, C*H*-allylic); 3.4 (d, 4H, $J_{H–H}$ = 1.2Hz, CH_b); 3.0 (s, 6H, C_2Me); 2.7–2.4 (m, 16H, CH_2); 0.9 (d, 4H, $J_{H–H}$ = 1.1Hz, CH_a)
4	7.9–7.6 (m, 50H, *Ph*); 3.2 (s, 4H, CH_b); 3.0 (s, 12H, C_2Me); 2.9–2.8 (m, 16H, CH_2); 1.9 (s, 6H, C_3H_4Me); 1.1 (d, 4H, CH_a)
5	7.9–7.6 (m, 70H, *Ph*); 3.1 (s, 4H, CH_b); 2.8–2.6 (m, 16H, CH_2); 2.0 (s, 6H, C_3H_4Me); 1.0 (d, 4H, $J_{H–H}$ = 1.2Hz, CH_a)
6	7.9–7.4 (m, 60H, *Ph*); 3.2 (s, 4H, CH_b); 3.0 (s, 12H, C_2Me); 2.8–2.6 (m, 16H, CH_2); 1.9 (s, 6H, C_3H_4Me); 1.2 (s, 4H, CH_a)
7	7.8–7.4 (m, 50H, *Ph*); 3.9 (s, 4H, CH_2Cl); 3.6 (s, 4H, CH_b); 3.1, 3.05 (s, 12H, C_2Me); 2.9–2.6 (m, 16H, CH_2); 0.9 (s, 4H, CH_a)
8	7.9–7.6 (m, 70H, *Ph*); 4.0 (s, 4H, CH_2Cl); 3.6 (s, 4H, CH_b); 2.8–2.6 (m, 16H, CH_2); 1.0 (s, 4H, CH_a)
9	7.8–7.4 (m, 60H, *Ph*); 3.9 (s, 4H, CH_2Cl); 3.5 (s, 4H, CH_b); 3.1, 3.0 (s, 6H, C_2Me); 2.6–2.4 (m, 16H, CH_2); 1.2 (s, 4H, CH_a)
10	7.8–7.4 (m, 50H, *Ph*); 5.3 (s, 2H, CH_2Cl_2); 4.0 (s, 2H, C*H*-allylic); 3.4 (s, 4H, CH_b); 3.1, 2.9 (s, 12H, C_2Me); 2.8–2.6 (m, 16H, CH_2); 1.2 (s, 4H, CH_a)
11	7.9–7.6 (m, 70H, *Ph*); 5.3 (s, 2H, CH_2Cl_2); 3.9 (s, 2H, C*H*-allylic); 3.4 (s, 4H, CH_b); 2.8 (m, 16H, CH_2); 1.2 (s br, 4H, CH_a)
12	7.9–7.6 (m, 60H, *Ph*); 5.3 (s, 2H, CH_2Cl_2); 4.0 (s, 2H, C*H*-allylic); 3.2 (s, 4H, CH_b); 3.0, 2.9 (s, 6H, C_2Me); 2.8–2.6 (m, 16H, CH_2); 1.05 (d, 4H, CH_a)
13	7.9–7.4 (m, 50H, *Ph*); 5.3 (s, 2H, CH_2Cl_2); 4.0 (s, 1H, C*H*-allylic); 3.3 (s, 2H, CH_b); 3.0 (s, 12H, C_2Me); 2.8–2.6 (m, 16H, CH_2); 1.1 (s, 2H, m CH_b)
14	7.9–7.6 (m, 70H, *Ph*); 3.9 (s, 1H, C*H*-allylic); 3.3 (s, 2H, CH_b); 2.8–2.5 (m, 16H, CH_2); 1.1 (s, 2H, CH_a)
15	7.9–7.4 (m, 60H, *Ph*); 4.0 (s, 1H, C*H*-allylic); 3.2 (s, 2H, CH_b); 3.0, 2.9 (s, 6H, C_2Me); 2.7–2.4 (m, 16H, CH_2); 1.2 (s, 2H, CH_a)
16	7.8–7.6 (m, 50H, *Ph*); 3.0 (s, 12H, C_2Me); 2.9–2.7 (m, 18H, CH_2 and CH_b); 1.8 (s, 3H, C_3H_4Me); 1.1 (s, 2H, CH_a)
17	7.9–7.6 (m, 70H, *Ph*); 2.8–2.6 (m, 18H, CH_2 and CH_b); 1.8 (s, 3H, C_3H_4Me); 1.2 (s, 2H, CH_a)
18	7.9–7.6 (m, 60H, *Ph*); 3.1 (s, 6H, C_2Me); 2.9–2.6 (m, 18H, CH_2 and CH_b); 1.9 (s, 3H, C_3H_4Me); 0.9 (s, 2H, CH_a)
19	7.9–7.4 (m, 50H, *Ph*); 3.7 (s, 2H, CH_2Cl); 3.4 (s, 2H, CH_b); 3.0 (s, 12H, C_2Me); 2.9–2.7 (m, 16H, CH_2); 1.2 (s, 2H, CH_a)
20	7.8–7.6 (m, 70H, *Ph*); 3.9 (s, 2H, CH_2Cl); 3.4 (s, 2H, CH_b); 2.8–2.6 (m, 16H, CH_2); 1.2 (s, 2H, CH_a)
21	7.8–7.6 (m, 60H, *Ph*); 3.9 (s, 2H, CH_2Cl); 3.3 (s, 2H, CH_b); 3.0 (s, 6H, C_2Me); 2.8–2.6 (m, 16H, CH_2); 1.1 (s, 2H, CH_a)
22	7.8–7.4 (m, 50H, *Ph*); 5.3 (s, 2H, CH_2Cl_2); 4.0 (s, 1H, C*H*-allylic); 3.2 (s, 2H, CH_b); 3.0, 2.9 (2s, 12H, C_2Me); 2.8–2.6 (m, 16H, CH_2); 0.95 (s, 2H, CH_a)
23	7.9–7.6 (m, 70H, *Ph*); 4.0 (s, 2H, C*H*-allylic); 3.1 (s, 2H, CH_b); 2.8–2.6 (m, 16H, CH_2); 0.9 (s, 2H, CH_a)
24	7.8–7.6 (m, 60H, *Ph*); 5.3 (s, 2H, CH_2Cl_2); 3.9 (s, 2H, C*H*-allylic); 3.2 (s, 2H, CH_b); 3.0 (s, 6H, C_2Me); 2.8–2.6 (m, 16H, CH_2); 0.9 (s, 2H, CH_a)
25	7.9–7.6 (m, 105H, *Ph*); 2.8–2.6 (m, 24H, CH_2); 2.0 (s, 3H, NC*Me*)
26	7.9–7.6 (m, 100H, *Ph*); 3.1, 3.0 (2s, 24H, C_2Me); 2.8–2.6 (m, 32H, CH_2)
27	7.9–7.6 (m, 120H, *Ph*); 3.1 (s, 12H, C_2Me); 2.8–2.6 (m, 32H, CH_2)

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to $SiMe_4$.
[b] br = broad, d = doublet, m = multiplet, s = singlet.

$\{PhP(CH_2CH_2PPh_2)_2–P,P'\}(\eta^2\text{-}PhC_2Ph)]\}$ fragment [14], to the higher band (1967 cm^{-1}) of the π-allyl molybdenum part of the molecule, again gives rise to the greater intensity of this band compared to the lower band at 1836 cm^{-1}. Since complexes **13**–**24** have effectively two monodentate phosphorus donor ligands, similar to the only bis(monodentate) phosphorus donor ligand complex $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$, to be crystallographically characterised [26], it is most likely the structure of **13**–**24** will have a similar distorted pentagonal bipyramidal geometry. The structure has chlorine and carbonyl groups in the axial positions, with the equatorial girdle having two organotungsten phosphine groups, one carbonyl ligand, and the π-allyl unit occupying two adjacent sites. Hence, the proposed structure for one possible isomer of the $[MoX(CO)_2L_2(\eta^3\text{-}C_3H_4R'')]$ (**13**–**24**) complexes is very likely to be as shown in Fig. 2, in view of both the previously determined structure of the π-allyl molybdenum complex $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$ [26], and the tungsten linear triphos species $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2–P,P'\}(\eta^2\text{-}RC_2R')]$ (R = R' = Me; R = Me, R' = Ph) [14]. There are, of course, a number of possible isomers of the two tungsten fragments of complexes **13**–**24**, and only one possible isomer is shown in Fig. 2. Both ^{1}H- and $^{31}P\{^1H\}$-NMR data (Tables 3 and 4) for complexes **13**–**24** given in Fig. 2, are complex and indicate the presence of isomers in solution. Again, as for complexes **1**–**12** no high field resonance at $\delta = -13.5$ ppm was observed in the $^{31}P\{^1H\}$-NMR spectra, which indicates that the complexes contain no uncoordinated phosphorus atoms. It should be noted that the low field $^{31}P\{^1H\}$-NMR resonances have been assigned to the terminal phosphine group coordinated to the molybdenum metal centre as the other $^{31}P\{^1H\}$-NMR resonances are similar to those for the two phosphorus atoms attached to the tungsten of the bidentately coordinated linear triphos in the starting complexes, $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2-P,P'\}(\eta^2\text{-}RC_2R')]$ [14]. When observed, the tungsten satellites had values of $J_{W-P} = 194-231$ Hz. Many unsuccessful attempts were made to grow suitable single crystals for X-ray analysis of these complexes probably due to: (i) the large unsymmetrical bulk of the complexes in solution; (ii) their general instability in a wide range of solvents over prolonged periods of time; and (iii) the presence of a number of isomers in solution.

Previous studies by Mawby et al. [4] have shown that reactions of $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (R = H, Me) with three and four equivalents of L (L = PMe_2Ph, $PMePh_2$) gave the zero-valent complexes $[Mo(CO)_2(NCMe)(PMePh_2)_3]$ or $[Mo(CO)_2L_4]$. Kinetic studies [4] showed that the reduction step is first order in both the concentration of the molybdenum complex and L, and most likely involves initial nucleophilic attack on the allyl ligand. In view of these observations, we decided to study the reactions of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ with 3 and 4 equivalents of L, L′ or L″. Treatment of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$ with three equivalents of L′ in CH_2Cl_2 at room temperature gave the complex *cis*-, *mer*-$[Mo(CO)_2(NCMe)(L')_3]$ (**25**). However, no pure products could be isolated from similar attempted reactions of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ with three equivalents of L, L′ and L″. Complex **25** was characterised by elemental analysis (C, H and N), IR (Table 2) and ^{1}H-NMR spectroscopy (Table 3) and molecular weight studies (Table 1). Complex **25** showed carbonyl bands at 1962 (br, s), 1930 (s) and 1841 (m) cm^{-1}, with the band at 1962 cm^{-1} due to the carbonyl groups on the *mer*-group of tungsten units (Fig. 3) and the bands at 1930

Table 4
Phosphorus NMR data (δ) for selected complexes [a,b]

Complex	$^{31}P\{^1H\}$-NMR (δ ppm)
1	24.4 (d, 1P, $J_{P-P} = 31$ Hz, Mo–PPh$_2$); 23.0 (d, 1P, $J_{P-P} = 31$ Hz, Mo–PPh$_2$); 21.7 (d, 1P, $J_{P-P} = 33$ Hz, W–PPh); 20.0 (m, 1P, W–PPh); 4.5 (s, 1P, $J_{W-P} = 208$ Hz, W–PPh$_2$); –4.3 (s, 1P, $J_{W-P} = 210$ Hz, W–PPh$_2$)
5	30.8 (m, 1P, Mo–PPh$_2$); 25.2 (m, 1P, Mo–PPh$_2$); 20.8 (s, 1P, W–PPh); 20.1 (s, 1P, $J_{W-P} = 209$ Hz, W–PPh$_2$); −4.2 (m, 2P, $J_{W-P} = 214$ Hz, W–PPh$_2$)
6	31.5 (m, 1P, Mo–PPh$_2$); 23.8 (m, 1P, Mo–PPh$_2$); 22.3 (m, 1P, W–PPh); 20.0 (m, 1P, W–PPh); 4.1 (m, 1P, $J_{W-P} = 233$ Hz, W–PPh$_2$); −2.3 (m, 1P, W–PPh$_2$)
7	39.7 (m, 1P, Mo–PPh$_2$); 23.5 (m, 1P, Mo–PPh$_2$); 20.0 (m, 2P, W–PPh); 4.4 (m, 1P, W–PPh$_2$); −3.8 (m, 1P, W–PPh$_2$)
8	31.6 (m, 1P, Mo–PPh$_2$); 24.9 (m, 1P, Mo–PPh$_2$); 20.8 (m, 2P, W–PPh); −4.3 (m, 2P, $J_{W-P} = 213$ Hz, W–PPh$_2$)
9	39.5 (s, br, 1P, Mo–PPh$_2$); 23.4 (m, 1P, Mo–PPh$_2$); 19.8 (m, 2P, $J_{W-P} = 239$ Hz, W–PPh); 7.0 (m, 1P, $J_{W-P} = 194$ Hz, W–PPh$_2$); −3.1 (m, 1P, W–PPh$_2$)
10	25.0 (m, 2P, Mo–PPh$_2$); 20.0 (m, 1P, Mo–PPh); 18.3 (m, 2P, $J_{W-P} = 196$ Hz, W–PPh); 4.5 (m, 1P, $J_{W-P} = 194$ Hz, W–PPh$_2$); −4.4 (m, 1P, $J_{W-P} = 193$ Hz, W–PPh$_2$)
11	28.0 (m, 1P, Mo–PPh$_2$); 24.4 (m, 1P, Mo–PPh$_2$); 20.7 (m, 1P, W–PPh); 20.1 (m, 1P, $J_{W-P} = 208$ Hz, W–PPh); −3.7 (m, 2P, $J_{W-P} = 243$ Hz, W–PPh$_2$)
12	24.3 (m, 1P, Mo–PPh$_2$); 23.4 (m, 1P, Mo–PPh$_2$); 20.3 (m, 1P, $J_{W-P} = 204$ Hz, W–PPh); 17.8 (m, 1P, $J_{W-P} = 205$ Hz, W–PPh); 7.5 (m, 1P, $J_{W-P} = 215$ Hz, W–PPh$_2$); −2.7 (m, 1P, $J_{W-P} = 205$ Hz, W–PPh$_2$)
13	31.2 (m, 1P, Mo–PPh$_2$); 25.5 (m, 1P, Mo–PPh$_2$); 22.4 (m, 1P, $J_{W-P} = 209$ Hz, W–PPh); 20.4 (m, 1P, $J_{W-P} = 209$ Hz, W–PPh); 3.7 (m, 1P, $J_{W-P} = 194$ Hz, W–PPh$_2$); −2.3 (m, 1P, W–PPh$_2$)
14	39.0 (m, 1P, Mo–PPh$_2$); 25.3 (m, 1P, Mo–PPh$_2$); 20.8 (s, br, 2P, $J_{W-P} = 231$ Hz, W–PPh); −3.4 (m, 2P, $J_{W-P} = 231$ Hz, W–PPh$_2$)
15	29.1 (m, 1P, Mo–PPh$_2$); 23.7 (m, 1P, W–PPh$_2$); 21.8 (m, 1P, W–PPh); 20.8 (m, 1P, W–PPh); 3.6 (m, 1P, W–PPh$_2$); −3.2 (m, 1P, W–PPh$_2$)
17	32.1 (brm, 1P, Mo–PPh$_2$); 24.8 (m, 1P, Mo–PPh$_2$); 21.4 (m, 2P, W–PPh); −3.3 (m, 2P, W– PPh$_2$)
18	30.7 (brm, 1P, Mo–PPh$_2$); 24.8 (m, 1P, Mo–PPh$_2$); 22.0 (m, 1P, W–PPh); 19.5 (m, 1P, W–PPh); 6.6 (m, 1P, W–PPh$_2$); −0.4 (m, 1P, W–PPh$_2$)
19	27.0 (m, 1P, Mo–PPh$_2$); 24.7 (m, 1P, Mo–PPh$_2$); 21.4 (m, 2P, W–PPh); −3.3 (m, 2P, W–PPh$_2$)
20	26.0 (brm, 1P, Mo–PPh$_2$); 25.1 (m, 1P, Mo–PPh$_2$); 21.2 (m, 2P, W–PPh); −3.3 (m, 2P, W–PPh$_2$)
22	31.6 (m, 1P, Mo–PPh$_2$); 26.0 (m, 1P, Mo–PPh$_2$); 24.0 (m, 1P, W–PPh); 21.2 (m, 1P, $J_{W-P} = 194$ Hz, W–PPh); −3.3 (m, 2P, W–PPh$_2$)
24	30.9 (m, 1P, Mo–PPh$_2$); 24.4 (m, 1P, Mo–PPh$_2$); 21.9 (m, 1P, W–PPh); 20.0 (m, 1P, W–PPh); 6.9 (m, 1P, W–PPh$_2$); −0.9 (m, 1P, W–PPh$_2$)
26	32.4 (m, 1P, Mo–PPh$_2$); 31.7 (m, 1P, Mo–PPh$_2$); 21.2 (m, 1P, W–PPh); 20.0 (m, 1P, W–PPh); 3.7 (m, 1P, W–PPh$_2$); −2.3 (m, 1P, W–PPh$_2$)
27	31.3 (m, 1P, Mo–PPh$_2$); 30.3 (m, 1P, Mo–PPh$_2$); 25.0 (m, 1P, $J_{W-P} = 217$ Hz, W–PPh); 20.3 (m, 1P, $J_{W-P} = 217$ Hz, W–PPh); −4.3 (m, 2P, $J_{W-P} = 203$ Hz, W–PPh$_2$)

[a] Spectra recorded in CD_2Cl_2 (+25°C) and referenced to 85% H_3PO_4.

[b] br = broad, d = doublet, m = multiplet, s = singlet.

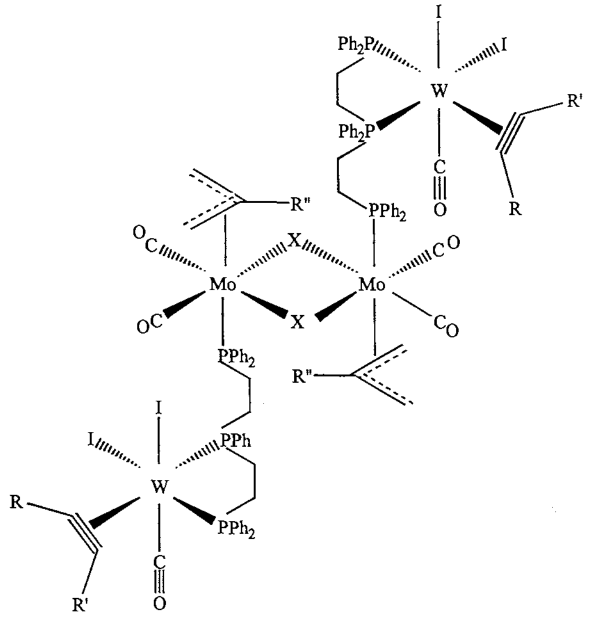

Fig. 1. Proposed structure of one isomer of [{Mo(μ-X)(CO)$_2$(L, L′ or L″)(η^3-C$_3$H$_4$R″)}$_2$] (**1**–**12**).

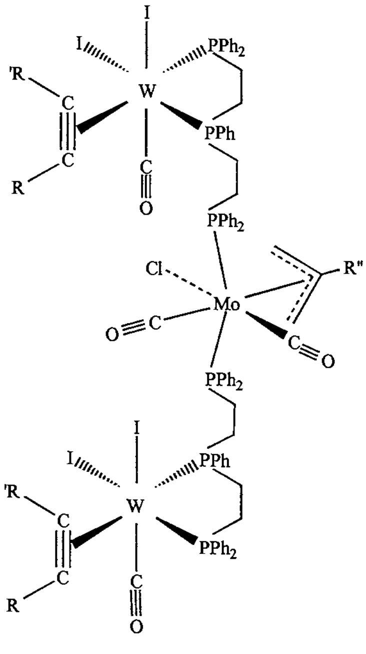

Fig. 2. Proposed structure of one isomer of [MoX(CO)$_2$(L, L′ or L″)$_2$(η^3-C$_3$H$_4$R″)] (**13**–**24**).

and 1841 due to *cis*-carbonyl groups in the zero-valent molybdenum centre. The nitrile band at ν(N≡C) = 2235 cm^{-1}, is typical for a coordinated acetonitrile group. In order to release steric crowding, it is more likely that the three tungsten diphenylacetylene units are *mer* to each other as shown in Fig. 3.

Reaction of [MoCl(CO)$_2$(NCMe)$_2${η^3-C$_3$H$_4$(CH$_2$Cl-2)}] with four equivalents of L or L″ in CH$_2$Cl$_2$ at room temperature gave the fully characterised (Tables 1–4) pentametallic complexes *cis*-[Mo(CO)$_2$(L or L″)$_4$] (**26** and **27**) which have calculated molecular weights of 4369 and 4622 for the 2-butyne and 1-phenylpropyne analogues respectively, which is approximately confirmed by the Rast's method [15] for molecular weight determinations (see Table 1). The IR spectra of complexes **26** and **27** have strong broad bands at 1956 and 1969 cm^{-1} respectively, which are due to the carbonyl groups in L and L″, respectively. Two other carbonyl bands at, for example, 1907 and 1820 cm^{-1} for **26**, strongly suggest that the carbonyl groups in the zero-valent molybdenum fragment are *cis to* each other. The ^{31}P{^{1}H}-NMR spectra of **26** and **27** both have six and five resonances respectively, and no resonance at $\delta = -13.5$ ppm, which suggests the presence of isomers, and that the uncoordinated phosphorus atoms on L and L″ are attached to the zero-valent molybdenum centres in **26** and **27**. One possible isomer of complexes **26** and **27** is shown in Fig. 4. A number of unsuccessful attempts to explore the reactions of the bis(L, L′ or L″) complexes **13**–**24** with two equivalents of PPh$_3$ to give [Mo(CO)$_2$(PPh$_3$)$_2$(L, L′ or L″)$_2$] were made. Also several reactions of [MoX(CO)$_2$(L, L′ or L″)$_2$(η^3-C$_3$H$_4$R″)] (**13**–**24**) with Ag[BF$_4$] in acetonitrile were attempted, without any positive results being obtained. It should be noted, however, that reaction of [{Mo(μ-Cl)(CO)$_2$L(η^3-C$_3$H$_5$)}$_2$] (**1**) with two equivalents of L gave the expected trimetallic complex [MoCl(CO)$_2$L$_2$(η^3-C$_3$H$_5$)] (**13**) in 75% yield (see Section 3).

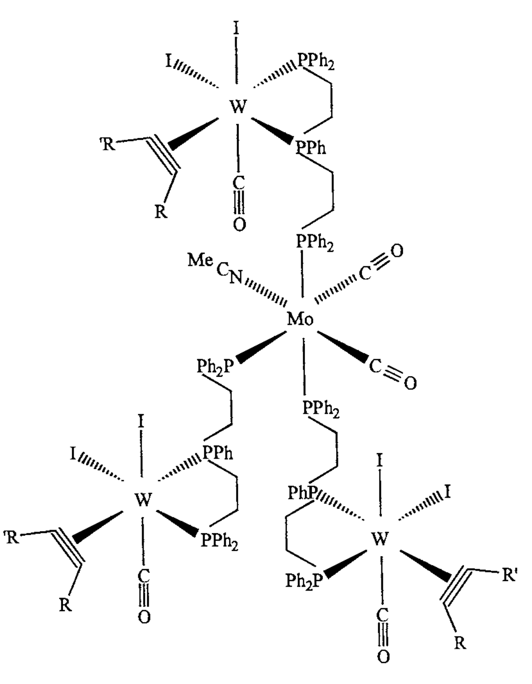

Fig. 3. Proposed structure of one isomer of *cis,mer*-[Mo(CO)$_2$(NCMe)L′$_3$] (**25**).

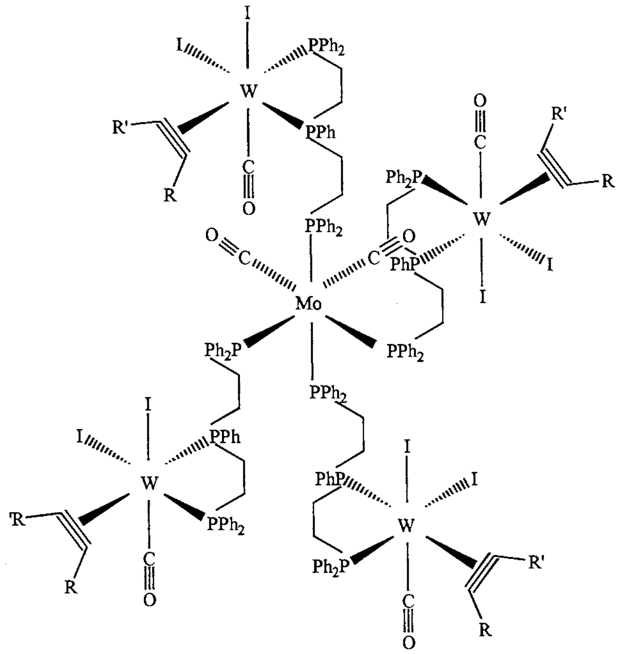

Fig. 4. Proposed structure of one isomer of *cis*-$[Mo(CO)_2(L \text{ or } L'')_4]$ (**26** and **27**).

In conclusion, we have prepared a wide range of new tri-, tetra- and pentametallic complexes which have linear triphos bridges, all having large molecular weights. By using the large organometallic phosphine ligands, L, L′ and L″, we can coordinate the unattached phosphine to a wide range of metal centres. We are currently studying the catalytic chemistry of these multimetallic complexes.

3. Experimental

3.1. Reagents and general techniques

All reactions described in this research were carried out using standard vacuum/Schlenk line techniques. The starting materials used, namely $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ (X = Cl, Br, R″ = H; X = Cl, R″ = CH_3-2) [27], $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$ [28] and $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ (R = R′ = Me, Ph; R = Me, R′ = Ph) [14] were prepared by published methods. The solvent, CH_2Cl_2 was dried and distilled over calcium hydride. All chemicals were purchased from commercial sources.

Elemental analyses were determined using a Carlo Erba Elemental Analyser MOD 1108 (using helium as the carrier gas). IR spectra were obtained using a Perkin–Elmer FT 1600 series IR spectrophotometer. ^1H- and $^{31}P\{^1H\}$-NMR spectra were recorded using a Bruker AC 250 MHz NMR spectrometer, and spectra were referenced to $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P). Molecular weight measurements were made by Rast's method [15], using camphor as the standard.

3.2. *Preparation of* $[\{Mo(\mu\text{-}Cl)(CO)_2L(\eta^3\text{-}C_3H_5)\}_2]$ *(**1**)*

To a solution of $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (0.07 g, 0.22 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature, was added $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}MeC_2Me)]$ (L) (0.23 g, 0.22 mmol), and the reaction was stirred for 15 min. The resulting green solution was filtered, and the solvent removed in vacuo giving a green crystalline powder of $[\{Mo(\mu\text{-}Cl)(CO)L(\eta^3\text{-}C_3H_5)\}_2]$ (**1**), which was recrystallised by cooling a CH_2Cl_2/diethyl ether solution of the complex at −17°C. (Yield of pure product = 0.23 g, 79%).

Similar reactions of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ {X = Cl; R″ = H, Me-2 or CH_2Cl-2; X = Br; R″ = H) with one equivalent of L, L′ or L″ $\{[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ (L, R = R′ = Me; L′, R = R′ = Ph; L″, R = Me, R′ = Ph)} in CH_2Cl_2 followed by recrystallisation gave the analogous complexes $[\{Mo(\mu\text{-}X)(CO)_2(L, L' \text{ or } L'')(\eta^3\text{-}C_3H_4R'')\}_2]$ (**2**–**12**). See Table 1 for physical and analytical data.

3.3. *Preparation of* $[MoCl(CO)_2L_2(\eta^3\text{-}C_3H_5)]$ *(**13**)*

To a solution of $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ (0.04 g, 0.12 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature, was added $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}MeC_2Me)]$(L) (0.25 g, 0.24 mmol) and the reaction was stirred for 24 h. The resulting green solution was filtered, and the solvent removed in vacuo giving a green crystalline powder of $[MoCl(CO)_2L_2(\eta^3\text{-}C_3H_5)]$ (**13**), which was recrystallised by cooling a CH_2Cl_2/diethyl ether solution of the complex at −17°C. Yield of pure product was 0.24 g or 80%.

Similar reactions of $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R'')]$ {X = Cl; R″ = H, 2-Me or 2-CH_2Cl; X = Br, R″ = H) with two equivalents of L, L′ or L″ $\{[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}RC_2R')]$ (L, R = R′ = Me; L′, R = R′ = Ph; L″, R = Me, R′ = Ph)} in CH_2Cl_2 followed by recrystallisation gave the analogous complexes $[MoX(CO)_2(L, L' \text{ or } L'')_2(\eta^3\text{-}C_3H_4R'')]$ (**14**–**24**). See Table 1 for physical and analytical data.

3.4. *Reaction of* $[\{Mo(\mu\text{-}Cl)(CO)_2L(\eta^3\text{-}C_3H_5)\}_2]$ *(**1**) with two equivalents of L*

To $[\{Mo(\mu\text{-}Cl)(CO)_2L(\eta^3\text{-}C_3H_5)\}_2]$ (0.22 g, 0.08 mmol) was added $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}MeC_2Me)]$ (L) (0.16 g, 0.16 mmol) in CH_2Cl_2 (30 cm^3). The solution was stirred for 24 h, followed by filtration through cellite and removal of the solvent in vacuo gave the green crystalline product, [Mo-

$Cl(CO)_2L_2(\eta^3\text{-}C_3H_5)]\cdot CH_2Cl_2$, which was recrystallised from CH_2Cl_2. Yield of pure product = 0.3 g, 75%. $C_{84}H_{85}Cl_3I_4MoO_4P_6W_2$ requires: C, 41.7; H, 3.5. Found: C, 41.6; H, 3.7. IR and NMR data are identical to complex **13**, prepared as described above by reacting $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ with two equivalents of L.

3.5. Preparation of *cis*-, *mer*-$[Mo(CO)_2(NCMe)(L')_3]$ (**25**)

To a solution of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$ (0.36 g, 0.10 mmol) dissolved in NCMe (30 cm^3) at room temperature, was added $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{–}P,P'\}(\eta^2\text{-}PhC_2Ph)]$ (0.36 g, 0.30 mmol), and the reaction was stirred for 24 h. The resulting green solution was filtered and the solvent removed in vacuo giving a green crystalline powder of *cis*-,*mer*-$[Mo(CO)_2(NCMe)(L')_3]$ (**25**) which was recrystallised by cooling a CH_2Cl_2/diethyl ether solution of the complex at −17°C. The yield of pure product was 0.7 g or 83%.

3.6. Preparation of *cis*-$[Mo(CO)_2L_4]$ (**26**)

To a solution of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$ (0.03 g, 0.08 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature, was added $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2 - P,P'\}(\eta^2 - MeC_2Me)]$ (0.34 g, 0.32 mmol), and the reaction was stirred for 24 h. The resulting green solution was filtered and the solvent removed in vacuo giving a green crystalline powder of *cis*-$[Mo(CO)_2L_4]$ (**26**), which was recrystallised by cooling a CH_2Cl_2/diethyl ether solution of the complex at −17°C. The yield of pure product was 0.31 g or 86%.

A similar reaction of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(CH_2Cl\text{-}2)\}]$ with four equivalents of L″ gives the complex *cis*-$[Mo(CO)_2L''_4]$ (**27**). See Table 1 for physical and analytical data.

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