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Spectroscopic investigations on the structure and fluxionality of the trihaptocycloheptatrienyl complexes $[MX(CO)_2(L–L)(\eta^3-C_7H_7)]$ (M = Mo, W; X = I, Cl; L–L = bisphosphine or diamine) and synthesis of the tetracyanoethene adducts $[WI(CO)_2\{Ph_2P(CH_2)_nPPh_2\}\{\eta^3-C_9H_7(CN)_4\}]$ (n = 1 or 2)

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Abstract

Spectroscopic investigations, including ^{31}P, ^{1}H and ^{13}C NMR studies, on the formally 6-coordinate bisphosphine complexes $[MX(CO)_2\{Ph_2P(CH_2)_nPPh_2\}(\eta^3-C_7H_7)]$ (M = Mo, W; X = I, Cl; n = 2 (dppe), n = 1 (dppm); C_7H_7 = cycloheptatrienyl) reveal a structure with no molecular plane of symmetry in which inequivalent P-donor atoms are arranged *cis-cis* and *cis-trans* to the two mutually *cis*-carbonyl groups. The dppe complexes exhibit a fluxional process which interconverts inequivalent phosphorus environments. Low temperature ^{1}H and ^{13}C NMR studies on the diamine derivatives $[MCl(CO)_2(H_2NCH_2CH_2NH_2)(\eta^3-R)]$ (M = Mo, W, R = C_7H_7; M = Mo, R = C_3H_5 (allyl)) imply that the non-symmetric structure of the bisphosphine analogues is adopted. The adducts $[WI(CO)_2\{Ph_2P(CH_2)_nPPh_2\}\{\eta^3-C_9H_7(CN)_4\}]$ (n = 1 or 2) are formed by tetracyanoethene addition to the trihapto-bonded cycloheptatrienyl ring of the tungsten complexes $[WI(CO)_2\{Ph_2P(CH_2)_nPPh_2\}(\eta^3-C_7H_7)]$ (n = 1 or 2).

The organometallic chemistry of the cycloheptatrienyl ligand in complexes with Group VI transition metals is dominated by the hepta- and tri-hapto bonding modes. Investigations on trihapto-bonded cycloheptatrienyl complexes of molybdenum and tungsten comprise work on $[M(CO)_2(\eta^3-C_7H_7)Cp]$ (M = Mo, W; Cp = cyclopentadienyl) [1–6]; $[M(CO)_2(\eta^3-C_7H_7)(pyrazolyl)]$ (M = Mo, W; pyrazolyl = $Me_2Ga(N_2C_5H_7)OCH_2CH_2NR_2$ (R = H, Me); M = Mo; pyrazolyl = $H_2B(N_2C_5H_7)_2$ or $PhB(N_2C_3H_3)_3$) [7–10] and a limited number of derivatives of $[MX(CO)_2(L–L)(\eta^3-C_7H_7)]$ (M = Mo, W; X = halide; L–L = chelate phosphine)

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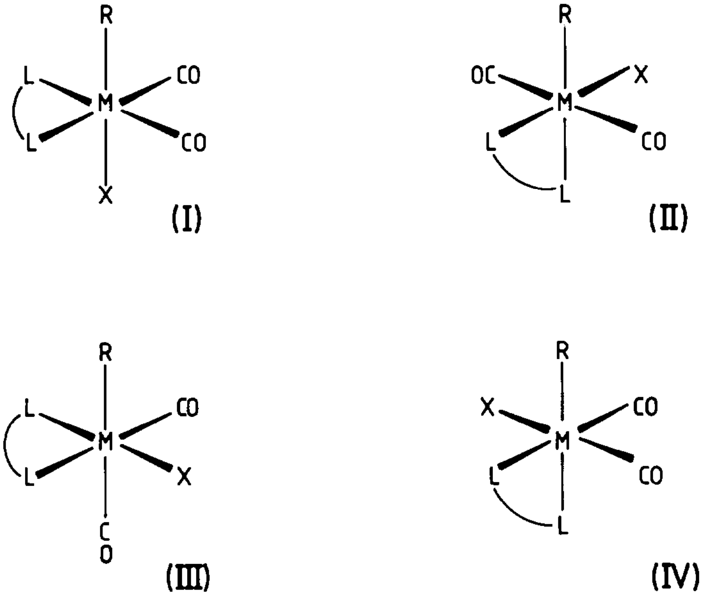

(I) (II) (III) (IV)

Fig. 1. The possible geometric isomers of $[MX(CO)_2(L{-}L)(\eta^3{-}R)]$ (M = Mo, W; X = halide or pseudohalide; R = allyl or cycloheptatrienyl).

[11–13]. In addition we have recently described the synthesis of the cationic complexes $[W(CO)_2(NCMe)L_2(\eta^3{-}C_7H_7)]^+$ (L = NCMe, L_2 = dppe) [14].

Each of these categories of trihapto-cycloheptatrienyl complexes has a counterpart in the chemistry of the allyl ligand (allyl = C_3H_5 or 2-(Me)C_3H_4) bonded trihapto to Mo or W, thus inviting comparative studies of structure and reactivity. Structural studies on $[MoX(CO)_2(L{-}L)(\eta^3{-}C_3H_5)]$ (X = Cl; L–L = dppe [15]; X = NCS; L–L = dipyridyl (dipy) [16]) and $[Mo(CO)_2(\eta^3{-}C_7H_7)\{Me_2Ga(N_2C_5H_7)OCH_2CH_2NH_2\}]$ [8] suggest that all categories of complex discussed are formally 6-coordinate with a pseudo octahedral arrangement of ligands. In the case of $[MX(CO)_2(L{-}L)(\eta^3{-}R)]$ (M = Mo, W; X = halide or pseudohalide; L–L = bisphosphine or diamine; R = C_3H_5 or C_7H_7) four geometric isomers may be proposed as possible structures (Fig. 1); crystallographic studies reveal that $[MoCl(CO)_2(dppe)(\eta^3{-}C_3H_5)]$ adopts structure IV, but the diamine derivative $[Mo(NCS)(CO)_2(dipy)(\eta^3{-}C_3H_5)]$ assumes form I. A number of investigations on trihapto-bonded allyl and cycloheptatrienyl complexes of molybdenum and tungsten have focused on fluxional properties. Of special interest to the work described in this paper are the 1,2-shift of the metal group around the cycloheptatrienyl ring in $[M(CO)_2(\eta^3{-}C_7H_7)Cp]$ (M = Mo, W) [3–6] and the trigonal twist process exhibited by $[MX(CO)_2(P{-}P)(\eta^3{-}C_3H_5)]$ (M = Mo, W; X = halide; P–P = dppe, dppm or *cis*-$Ph_2PCH{=}CHPPh_2$) which interconverts the optical isomers of structure IV (Fig. 2) [15].

We now describe our synthetic and spectroscopic studies on a range of trihapto-cycloheptatrienyl complexes $[MX(CO)_2(L{-}L)(\eta^3{-}C_7H_7)]$ (M = Mo, W; X = I, Cl), with the chelate ligand L–L selected from dppe, dppm or 1,2-diaminoethane, with a view to comparison of the effect of $\eta^3{-}C_7H_7$ vs. $\eta^3{-}C_3H_5$ ligands upon structure

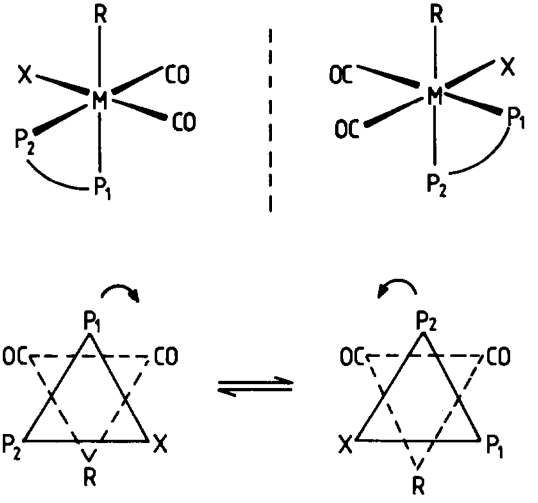

Fig. 2. The proposed trigonal twist rearrangement illustrated for isomer IV.

and fluxional properties. The first confirmed example of cycloaddition to a trihapto-bonded cycloheptatrienyl ring is also described.

Results and discussion

Reaction of $[MX(CO)_2(\eta-C_7H_7)]$ (M = Mo, W; X = I, Cl) with the chelate phosphines dppe or dppm in toluene at 20 °C gives orange to deep red solutions which afford the trihaptocycloheptatrienyl complexes **1–6** (Fig. 3). Details of characterisation by infrared spectroscopy and microanalysis (Table 1), ^{31}P NMR spectroscopy (Table 2) and ^{1}H and ^{13}C NMR spectroscopy (Tables 3 and 4) are presented in the appropriate tables. Complexes **1**, **2** and **6** have been described previously [11,13] and only selected data are included here for ease of comparison.

The low temperature ^{31}P NMR spectra for each of complexes **1–6** exhibit a doublet of doublets pattern, thereby demonstrating inequivalence of the P-donor atoms. This observation, together with the relative intensities of the infrared active carbonyl absorptions (indicative of *cis* carbonyls) and the magnitude of phosphorus–carbon coupling constants to inequivalent carbonyl carbons in the ^{13}C NMR spectra (see later), establishes the structure of **1–6** as one of III or IV (Fig. 1). Although isomer III cannot be eliminated on the basis of spectroscopic data, we prefer structure IV (as illustrated in Fig. 3) from a consideration of the known geometry of $[MoCl(CO)_2(dppe)(\eta^3-C_3H_5)]$ [15] together with comparison of ^{31}P NMR data for corresponding pairs of allyl and cycloheptatrienyl complexes (Table 5).

Variable temperature ^{31}P NMR studies on dppe complexes **1–4** reveal coalescence of the original doublet of doublets spectra to broad singlets at temperatures in the range 8–45 °C. However, the dppm complexes **5** and **6** fail to show any evidence of fluxionality in ^{31}P NMR studies; elevated temperatures, well in excess of 45 °C, lead only to extensive decomposition. By comparison with similar investigations on the analogous allyl complexes $[MX(CO)_2(P–P)(\eta^3-C_3H_5)]$ (M = Mo, W; X = I, Cl;

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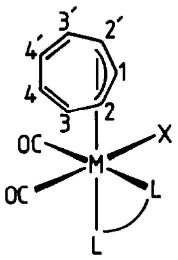
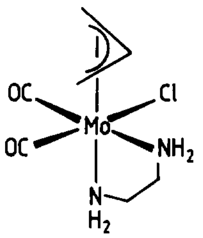
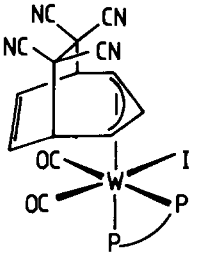


(1) - (8)



(9)

	M	X	L-L
(1)	Mo	I	dppe
(2)	W	I	dppe
(3)	Mo	Cl	dppe
(4)	W	Cl	dppe
(5)	Mo	Cl	dppm
(6)	W	I	dppm
(7)	Mo	Cl	en
(8)	W	Cl	en



(10) P - P = dppe
(11) P - P = dppm

Fig. 3.

Table 1

Infrared and microanalytical data

Complex	Yield (%)	ν(CO) [a] (cm^{-1})	Analysis (Found (calcd.)(%)) C	H	N
[MoCl(CO)$_2$(dppe)(η^3-C$_7$H$_7$)] (**3**)	61	1934 1852	62.6	5.0	
			(62.1)	(4.6)	
[WCl(CO)$_2$(dppe)(η^3-C$_7$H$_7$)] (**4**)	37	1929 1845	54.7	4.1	
			(54.9)	(4.1)	
[MoCl(CO)$_2$(dppm)(η^3-C$_7$H$_7$)] (**5**)	37	1940 1860	61.3	4.5	
			(61.6)	(4.4)	
[MoCl(CO)$_2$(en)(η^3-C$_7$H$_7$)] (**7**)	53	1935 1847	39.3	4.9	8.0
			(39.0)	(4.4)	(8.3) [b]
[WCl(CO)$_2$(en)(η^3-C$_7$H$_7$)] (**8**)	23	1927 1835	31.3	3.8	6.3
			(31.0)	(3.5)	(6.6) [c]
[MoCl(CO)$_2$(en)(η^3-C$_3$H$_5$)] (**9**)	63	1938 1837	29.1	4.8	9.4
			(29.1)	(4.5)	(9.7)
[WI(CO)$_2$(dppe){η^3-C$_9$H$_7$(CN)$_4$}] (**10**)	47	1957 1874	49.5	3.2	5.5
			(50.0)	(3.2)	(5.7)
[WI(CO)$_2$(dppm){η^3-C$_9$H$_7$(CN)$_4$}] (**11**)	60	1964 1884	49.8	3.4	5.7
			(49.5)	(3.0)	(5.8)

[a] In CH$_2$Cl$_2$. [b] Cl Found 10.4, calcd. 10.5%. [c] Cl Found 8.0, calcd. 8.3%.

Table 2

^{31}P NMR spectral data [a]

Complex	$\delta(^{31}P)$ (ppm)	$\vert {}^{1}J(^{183}W\text{-}P) \vert$	$\delta(^{31}P)$ (ppm)	$\vert {}^{1}J(^{183}W\text{-}P) \vert$	$\vert J(P\text{-}P) \vert$	Coalescence temperature (°C)
$[MoI(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (**1**)	42.8		40.3		12	45
$[WI(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (**2**)	26.8	216	21.8	201	2	41
$[MoCl(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (**3**)	48.3		45.1		12	12
$[WCl(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (**4**)	36.0	216	30.2	194	4	8
$[MoCl(CO)_2(dppm)(\eta^3\text{-}C_7H_7)]$ (**5**)	4.9		−9.4		nr	
$[WI(CO)_2(dppm)(\eta^3\text{-}C_7H_7)]$ (**6**)	−21.6	191	−40.7	173	12	
$[WI(CO)_2(dppe)\{\eta^3\text{-}C_9H_7(CN)_4\}]$ (**10**)	20.7	185	19.3	174	5	38
$[WI(CO)_2(dppm)\{\eta^3\text{-}C_9H_7(CN)_4\}]$ (**11**)	−23.9	159	−39.2	163	15	

[a] In $CDCl_3$, positive chemical shifts to low field of H_3PO_4, J values in Hz. Spectra recorded at the following temperatures: **4** −40 °C; **3** −20 °C; **1**, **2**, **6** −10 °C; **5**, **10** 0 °C; **11** 20 °C.
nr = not clearly resolved.

Table 3

^{1}H NMR spectral data [a]

Complex	
1	7.90–7.30[m,20H,Ph], 5.48[s,7H,C_7H_7], 3.20[br,2H,CH_2], 2.70[br,1H,CH_2], 2.28[br,1H,CH_2]
3	7.98–7.26[m,20H,Ph], 5.34[s,7H,C_7H_7], 3.06[br,2H,CH_2], 2.56[br,1H,CH_2], 2.17[br,1H,CH_2]
4	8.00–7.20[m,20H,Ph], 5.07[s,7H,C_7H_7], 3.08[br,2H,CH_2], 2.58[br,1H,CH_2], 2.11[br,1H,CH_2]
5	7.96–7.04[m,20H,Ph], 5.41[s,7H,C_7H_7], 4.62[m,1H,CH_2], 4.09[m,1H,CH_2]
7 [b]	6.65, 6.48[m,2H,H(3),H(3′)], 5.40[m,2H,H(4),H(4′)], 5.35[br,1H,en], 4.99, 4.63[br,2H,H(2), H(2′)], 4.41[br,1H,en], 3.47[br,1H,en], 3.26[br,1H,en], 3.11[br,1H,en], 2.85[br,1H,en], 2.65[br,2H,en], 2.26[br,1H,H(1)]
8 [b]	6.57[1H,H(3), J(H(3)H(2))11, J(H(3)H(4))8], 6.39[1H,H(3′), J(H(3′)H(2′))11, J(H(3′) H(4′))8], 5.50[d,1H,en], 5.17[m,2H,H(4),H(4′)], 4.72[1H,H(2), J(H(2)H(3)11, J(H(2)H(1)6], 4.55[br,1H,en], 4.37[1H,H(2′), J(H(2′)H(3′))11, J(H(2′)H(1))6], 3.72[br,1H,en], 3.58[br,1H,en], 3.26[br,1H,en], 2.88[br,2H,en], 2.80[br,1H,en], 1.34[t,1H,H(1), J(H(1)H(2)) = J(H(1)H(2′))6]
10	8.00–7.20[m,20H,Ph], 6.64[m,1H,H(4)], 6.52[m,1H,H(4′)], 5.08[m,1H,H(2)], 4.36[m,1H,H(2′)], 4.04[m,1H,H(3)], 3.78[m,1H,H(3′)], 3.54[br,1H,CH_2], 3.32[m,1H,H(1)], 3.18[br,1H,CH_2], 2.78[br,1H,CH_2], 2.24[br,1H,CH_2]
11	7.62–7.06[m,20H,Ph], 6.51[m,2H,H(4),H(4′)], 5.12[m,1H,H(2)], 4.95[m,2H,CH_2], 4.34[m,1H,H(2′)], 3.97[m,1H,H(3)], 3.80[m,1H,H(3′)], 3.41[m,1H,H(1)]

[a] In $CDCl_3$ unless stated otherwise, chemical shifts (δ) downfield from $SiMe_4$, J values in Hz, spectra recorded at the following temperatures: **1** −40 °C, **3** −14 °C, **4** −20 °C, **7** −80 °C, **8** −70 °C, **5**, **10**, **11** ambient. Numbering as in Fig. 3 and 8 but without assignment of ring orientation with respect to the ligand arrangement at the metal centre. [b] In acetone-d_6.

Table 4

^{13}C NMR spectral data [a]

Complex	
1	225.0, 223.4 (CO), 136.3–127.7 (Ph), 105.3 (C_7H_7), 28.6, 24.9 (CH_2)
3	226.5, 224.6 (CO), 135.7–128.1 (Ph), 106.3 (C_7H_7), 26.5, 24.5 (CH_2)
6	218.7, 212.2 (CO), 134.3–128.3 (Ph), 101.3 (C_7H_7), 38.8 (CH_2)
7 [b]	230.3, 230.0 (CO), 140.2, 138.8, 121.2, 120.6 (C(3),C(3′),C(4),C(4′)), 73.1, 70.2 (C(2),C(2′)), 52.7 (C(1)), 45.4, 41.6 (CH_2)
8 [b]	223.9, 221.6 (CO), 141.5, 140.1, 120.3, 119.6 (C(3),C(3′),C(4),C(4′)), 64.3, 60.7 (C(2),C(2′)) 45.9, 45.3, 42.4 (C(1) and CH_2)
9 [b]	227.5, 227.4 (CO), 70.1, 59.4, 54.8 (C_3H_5), 44.3, 42.2 (CH_2)
11	217.4, 212.0 (CO), 136.2–127.1 (Ph,C(4),C(4′)), 112.6, 112.5, 112.0 111.7 (CN), 67.0 [*J*(P–C)3], 64.1[*J*(P–C)4] (C(2),C(2′)) 51.8 [*J*(P–C)5] (C(1), 47.5, 46.5, 46.4, 46.0 (C(3),C(3′),C(5),C(5′)) 36.6 (CH_2)

[a] In $CDCl_3$ unless stated otherwise, 75 MHz spectra, chemical shifts in ppm downfield from $SiMe_4$ *J* values in Hz, spectra recorded at following temperatures: **1** 0 °C, **2** −25 °C, **7** −90 °C, **8** −70 °C, **9** −40 °C, **6**, **8** ambient. Numbering as in Fig. 3 and 8 but without assignment of ring orientation with respect to the ligand arrangement at the metal centre. [b] In acetone-d_6.

P–P = bisphosphine) [15], we suggest that the variable temperature behaviour of the ^{31}P NMR spectra of the cycloheptatrienyl complexes can be explained in terms of a trigonal twist process which could operate to interconvert the two discrete phosphorus environments in **1**–**4** irrespective of whether structure III or IV is adopted. Direct numerical comparisons of activation energies for the fluxional process presumed common to [MX(CO)$_2$(P–P)(η^3-R)] (R = allyl, cycloheptatrienyl) are not made, since values reported for the allyl derivatives were determined by line shape analysis methods. However, it is clear from cautious consideration of the coalescence temperatures and chemical shift separations presented in Table 5 that activation energies for the cycloheptatrienyl complexes are higher. This conclusion is supported by observation of the limiting low temperature ^{31}P NMR spectra of the

Table 5

Comparison of ^{31}P NMR data for analogous allyl and cycloheptatrienyl complexes

	R = allyl [a]			R = cycloheptatrienyl		
	Separation of ^{31}P shifts (Hz)	|*J*(W–P)| (Hz) [b]	Coalescence Temperature (°C)	Separation of ^{31}P shifts (Hz)	|*J*(W–P)| (Hz) [b]	Coalescence temperature (°C)
[MoI(CO)$_2$(dppe)(η^3-R)]	68	–	−47	81	–	45
[WI(CO)$_2$(dppe)(η^3-R)]	98	234 177	−33	162	216 201	41
[WI(CO)$_2$(dppm)(η^3-R)]	796	193 153	−1	619	191 173	–

[a] Data from reference 15. [b] Values given in order, low field then high field resonance.

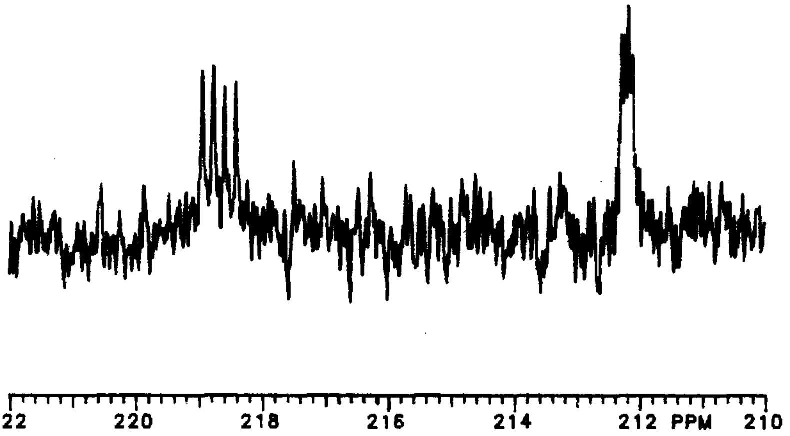


Fig. 4. The 75 MHz ^{13}C NMR spectrum (carbonyl region) of $[WI(CO)_2(dppm)(\eta^3\text{-}C_7H_7)]$.

chloride derivatives **3** and **4**; in the case of the analogous allyl chloride complexes the limiting low temperature spectra are not reached even at −100 °C [15].

The structural inferences drawn from ^{31}P NMR studies on **1–6** are supported by ^{1}H and ^{13}C NMR data (Tables 3 and 4). The ^{13}C NMR data, obtained for selected examples **1**, **3** and **6**, confirm the presence of inequivalent carbonyl carbons each with complex coupling to phosphorus. Figure 4 illustrates the typically observed coupling pattern indicative of the two phosphorus atoms arranged *cis-cis* to one carbonyl group and *cis-trans* to the second [13,17] and thus compatible only with structure types III and IV. For each of complexes **1**, **3** and **6**, the carbonyl signal exhibiting the largest $|^{2}J(^{31}P\text{–}^{13}C)|$ (which may be attributed to the carbonyl located *trans* to one phosphorus [15]) is the low field resonance; this contrasts with low temperature ^{13}C NMR data for $[WI(CO)_2(dppm)(\eta^3\text{-}C_3H_5)]$ [15] but is consistent with assignments for $[Mo(CO)_4(dppe)]$ [17]. The inequivalence of the dppe methylene groups is apparent both from ^{13}C NMR spectra of **1** and **3** and low temperature ^{1}H NMR spectra of complexes **1–4**. Furthermore, on warming from −20 to +30 °C, the ^{1}H NMR spectra of the chloride derivatives **3** and **4** exhibit variable temperature behaviour in the region attributable to dppe methylene protons, ultimately resulting in just two averaged signals for these protons.

The contrasting structures of $[MoCl(CO)_2(dppe)(\eta^3\text{-}C_3H_5)]$ and $[Mo(NCS)(CO)_2(dipy)(\eta^3\text{-}C_3H_5)]$ prompted us to investigate further the factors determining the molecular geometry of analogous η^3-allyl and η^3-cycloheptatrienyl complexes $[MX(CO)_2(L\text{–}L)(\eta^3\text{-}R)]$. Important considerations include steric constraints of the allyl or cycloheptatrienyl ligand together with properties associated with the chelate ligand such as flexibility, the identity of Group V donor atoms and the substituents attached to these donor atoms. For example low temperature ^{1}H and ^{13}C NMR studies on $[Mo(O_2CR)(CO)_2(dipy)(\eta^3\text{-}2R'C_3H_4)]$ ($R = CF_3$, C_2F_5, C_3F_7; $R' = H$ or Me) indicate that, whereas the methallyl complexes adopt only structure type I (Fig. 1) in solution, the allyl derivatives exist as a mixture of two isomers [8]. As a further example, $[WCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$, reacts with $Ph_2AsCH_2AsPh_2$ to give a binuclear product [19], in contrast to the corresponding reaction with dppm.

The cycloheptatrienyl dipyridyl complexes $[MX(CO)_2(dipy)(\eta^3\text{-}C_7H_7)]$ ($M = Mo$, W; X = halide) are not accessible by direct addition of dipyridyl to $[MX(CO)_2(\eta$-

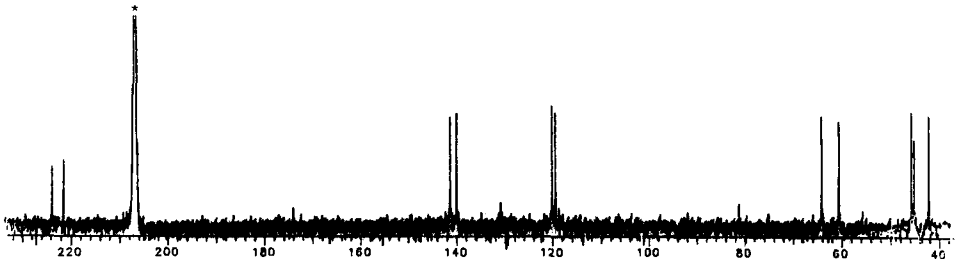


Fig. 5. The 75 MHz ^{13}C NMR spectrum of [WCl(CO)$_2$(en)(η^3-C$_7$H$_7$)] at −70 °C. * = solvent.

C$_7$H$_7$)]; this reaction, which proceeds only at high temperatures, affords carbonyl substituted products [MX(dipy)(η-C$_7$H$_7$)] [11,20]. (A different approach to [WX(CO)$_2$(dipy)(η^3-C$_7$H$_7$)] (X = halide) starting from [W(CO)$_2$(NCMe)$_3$(η^3-C$_7$H$_7$)]$^+$ [14] may prove feasible and our findings will be reported in a subsequent paper). However, for the purpose of the current investigation the more flexible, N-donor chelate ligand 1,2-diaminoethane (en) was employed as an alternative to dipy. Reaction of [MCl(CO)$_2$(η-C$_7$H$_7$)] (M = Mo, W) with 1,2-diaminoethane in toluene at 0 °C gives moderate yields of the orange trihaptocycloheptatrienyl complexes **7** and **8** (Fig. 3); characterisation details supporting this formulation are given in Tables 1, 3 and 4.

At ambient temperature the ^{13}C NMR spectrum of [MoCl(CO)$_2$(en)(η^3-C$_7$H$_7$)] (**7**) exhibits a total of five signals; two carbonyl carbons, two methylene carbons of 1,2-diaminoethane, and a very broad resonance assigned to the cycloheptatrienyl ring. Cooling to −90 °C effects complete resolution to eleven distinct signals, thus establishing all seven cycloheptatrienyl carbons as inequivalent. A parallel result was obtained with the tungsten analogue **8** for which the limiting low temperature spectrum (Fig. 5) was reached at −70 °C. Additional support for a low temperature structure of **7** and **8** in which all seven positions of the cycloheptatrienyl ring are inequivalent, is obtained from ^{1}H NMR studies. Thus at −70 °C the ^{1}H NMR spectrum of **8** (Fig. 6) exhibits seven inequivalent C$_7$H$_7$ ring protons (assigned by double irradiation methods) and a further eight inequivalent protons attributed to 1,2-diaminoethane. A similar ^{1}H NMR spectrum of **7** was recorded at −80 °C, albeit with much poorer resolution of proton–proton couplings. The temperature dependence of the NMR spectra of the trihapto-bonded cycloheptatrienyl ligand may be explained in terms of a 1,2 shift of the metal group around the ring and is proven in the case of [Mo(CO)$_2$(η^3-C$_7$H$_7$)Cp] [3]. One salient point from the current study is the relatively high temperature at which the 1,2 shift process is 'frozen out' in **7** and **8**; we note that the pyrazolylethanolaminegallate complex [W(CO)$_2$(η^3-C$_7$H$_7$){Ga(N$_2$C$_3$H$_3$)(OCH$_2$CH$_2$NMe$_2$)}], also with two *N*-donor atoms attached to tungsten, exhibits a limiting low temperature ^{1}H NMR spectrum at −75 °C [7], and confirm that, by contrast, the ^{1}H NMR spectrum of dppe complex **1** at −50 °C exhibits a slightly broadened but nevertheless distinct singlet signal for the C$_7$H$_7$ ring [11].

The structural inferences drawn from spectroscopic studies on **7** and **8** are less definitive than those from the work on **1**–**6**, which was aided by the availability of ^{31}P data. Molecular geometry II, with *trans* carbonyls, is excluded by IR data, but structure I in which the C$_7$H$_7$ ring adopts an unsymmetrical low temperature

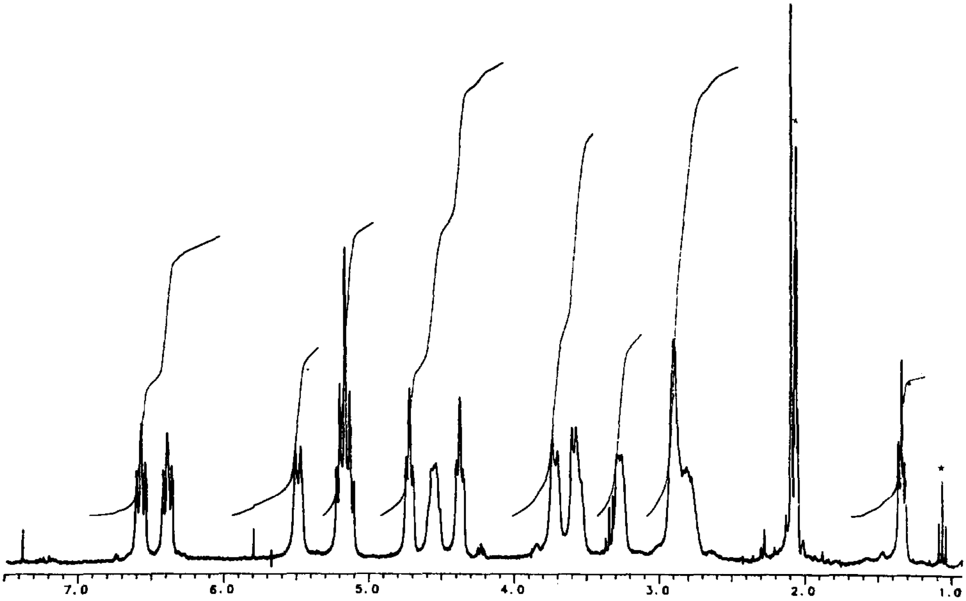


Fig. 6. The 300 MHz ^{1}H NMR spectrum of [WCl(CO)$_2$(en)(η^3-C_7H_7)] at −70 ° C. * = solvent impurity.

alignment with respect to the symmetry plane bisecting the MCl(CO)$_2$(en) group (Fig. 7) should be considered. However, the activation energy for reorientation of the C_7H_7 ring relative to the metal group is likely to be small and therefore this form of structure I seems inconsistent with ambient temperature ^{13}C NMR spectra of **7** and **8** which still exhibit sharp, discrete signals for two inequivalent carbonyls and two inequivalent 1,2-diaminoethane methylene carbons. We therefore, suggest a molecular geometry for **7** and **8** analogous to that of bisphosphine complexes **1–6**. This supposition may appear to be at variance with the results of X-ray diffraction studies on a number of complexes [MoX(CO)$_2$(diamine)(η^3-allyl)]^z (X = NCS, $z = 0$; X = pyridine, $z = +1$) [16,21,22], which have, in all cases, revealed structure type I; however, in each of these examples the diamine chelate was dipyridyl or σ-phenanthroline. Therefore, to provide a valid comparison, it became necessary to synthesise [MoCl(CO)$_2$(en)(η^3-C_3H_5)] (**9**); the methallyl derivative [MoCl(CO)$_2$(en){η^3-2(Me)C_3H_4}] has been reported previously [23], but no consideration was given to its structure.

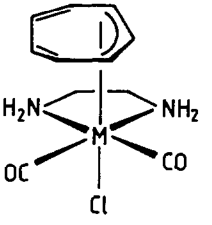


Fig. 7. Unsymmetrical orientation of the cycloheptatrienyl ring in geometric isomer I.

Yellow $[MoCl(CO)_2(en)(\eta^3\text{-}C_3H_5)]$ (**9**) was prepared by reaction of $[MoCl(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_5)]$ with 1,2-diaminoethane in acetonitrile and characterised as detailed in Tables 1 and 4. Ambient temperature ^{13}C NMR studies on **9** reveal equivalent carbonyl carbons, equivalent 1,2-diaminoethane methylene carbons and equivalent terminal allyl carbons (although the signal assigned to the latter is very broad). The limiting low temperature spectrum, obtained at −40 °C, exhibits seven inequivalent carbons consistent with a single low temperature geometry which lacks a molecular plane of symmetry. Again an unsymmetrical low temperature orientation of the allyl ligand with respect to the mirror plane of the $MoCl(CO)_2(en)$ group in structure type I must be considered, but such an arrangement is inconsistent with the results of a molecular orbital analysis of the preferred conformation of the η^3-allyl ligand in $Mo^{II}(CO)_2(\eta^3\text{-allyl})$ complexes [24]. Therefore, our investigations point towards a low temperature structure for **9** analogous to that of the cycloheptatrienyl complexes **7** and **8** rather than $[Mo(NCS)(CO)_2(dipy)(\eta^3\text{-}C_3H_5)]$ and the conclusion that, for the chelate ligands investigated, interchange of $\eta^3\text{-}C_7H_7$ and $\eta^3\text{-}C_3H_5$ does not significantly affect the preferred molecular geometry of $[MX(CO)_2(L\text{–}L)(\eta^3\text{-R})]$ ($R = C_7H_7$ or C_3H_5). A trigonal twist process analogous to that described for $[MX(CO)_2(P\text{–}P)(\eta^3\text{-}C_3H_5)]$ (M = Mo, W; X = halide; P–P = bisphosphine) [15], is one possible explanation for signal averaging of the two 1,2-diaminoethane methylene carbons and the two carbonyl carbons of **9** at ambient temperature.

An alternative approach to constraint of the 1,2 shift of the metal group around the trihapto-bonded cycloheptatrienyl ring involves addition to the momentarily uncoordinated 1,3-diene unit. This method has been investigated for tetracyanoethene (tcne) addition to $[Mo(CO)_2(\eta^3\text{-}C_7H_7)Cp]$ [1] and coordination of an $Fe(CO)_3$ group to $[Mo(CO)_2(\eta^3\text{-}C_7H_7)\{Me_2Ga(N_2C_5H_7)OCH_2CH_2NMe_2\}]$ or $[Mo(CO)_2(\eta^3\text{-}C_7H_7)Cp]$ [6,7], but only in the last example was a fully characterisable product obtained.

The first confirmed example of tcne addition to a trihaptocycloheptatrienyl ring is provided by reaction with the tungsten bisphosphine complexes **2** and **6**. Thus treatment of red, dichloromethane solutions of **2** or **6** with tcne at 0 °C affords brown solutions, the infrared spectra of which reveal a shift of carbonyl stretching frequencies to higher wavenumber by approximately 20 cm^{-1}. Subsequent work-up yields the adducts **10** and **11**, which were characterised as detailed in Tables 1, 2, 3 and 4. Identical reactions with the molybdenum analogues **1** and **5** were unsuccessful in forming simple adducts; full characterisation of the deep purple solids resulting from these latter reactions proved impossible but infrared spectra exhibited only very broad and weak absorptions in the carbonyl stretching region. A possible rationalisation for this contrasting reactivity of the trihapto-bonded cycloheptatrienyl tungsten or molybdenum complexes concerns the relative strengths of the metal carbonyl bonds. Thus, although **1** rapidly forms $[Mo(CO)(dppe)(\eta\text{-}C_7H_7)]^+$ in refluxing benzene [11], the tungsten analogue **2** appears stable towards loss of CO and reversion to a heptahapto-bonded cycloheptatrienyl ligand [12].

There are two major considerations in examining the structure of adducts **10** and **11**, firstly the geometrical arrangement of ligands around the tungsten centre and secondly the mode of tcne addition to the cycloheptatrienyl ring. The ^{13}C NMR spectrum of **11** exhibits two inequivalent carbonyl signals each split by phosphorus coupling. The coupling pattern is similar to that observed for **6** with coupling

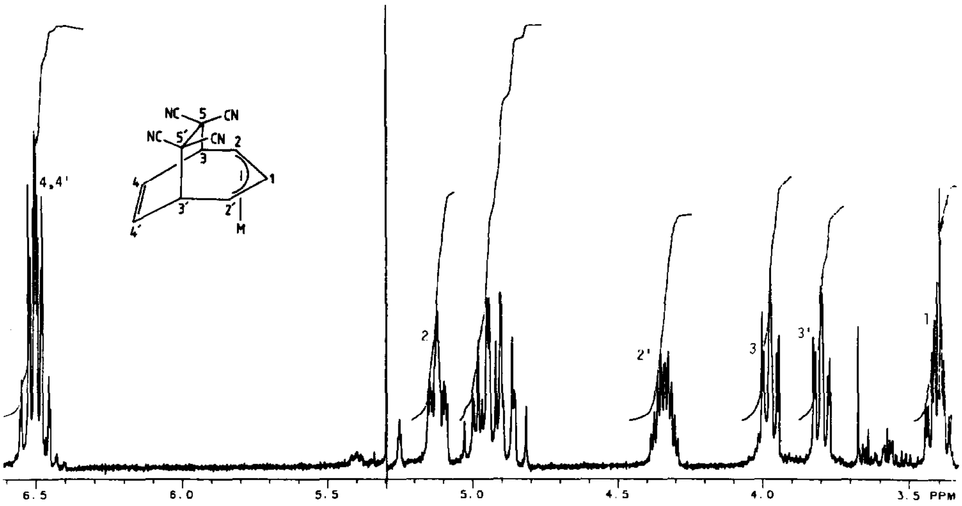


Fig. 8. The 300 MHz ^{1}H NMR spectrum of $[WI(CO)_2(dppm)\{\eta^3\text{-}C_9H_7(CN)_4\}]$ (Ph protons omitted), $M = WI(CO)_2(dppm)$.

constants attributable to one carbonyl arranged *cis-cis*, the second *cis-trans* to the two phosphorus atoms. Interestingly however, for **11** the *cis-cis* coupled carbonyl is the low field resonance. This data together with the low temperature ^{31}P NMR studies described later suggest that **11**, and indeed **10**, retain the ligand arrangement of their precursors **6** and **2**.

Addition of tcne at the cycloheptatrienyl ring is confirmed by ambient temperature ^{1}H NMR spectra of **10** and **11** which each exhibit seven inequivalent protons arising from the statically bonded η^3-$C_9H_7(CN)_4$ ligand. Proton–Proton decoupling experiments were employed to establish connectivity; the assignments and structural conclusions drawn for **11** are illustrated in Fig. 8. Other modes of tcne addition to the cycloheptatrienyl ring, including those accommodated by σ,η^2-bonding to tungsten, have been considered, but the spectroscopic data are most consistent with symmetric 1,4-addition; inequivalence of all seven protons of the $C_9H_7(CN)_4$ ligand is introduced by the asymmetry of the metal centre. Our data do not however permit comment on the *exo* vs. *endo* stereochemistry of tcne addition with respect to the metal centre. Further support for η^3-allyl bonding of the $C_9H_7(CN)_4$ ligand in adducts **10** and **11** is provided by the ^{13}C NMR spectrum of **11**. Resonances at 51.8, 64.1 and 67.0 ppm, which each exhibit a small splitting attributable to $^2J(^{31}P\text{–}^{13}C)$ coupling, are closely comparable to the chemical shifts assigned to the allyl carbons in the limiting low temperature ^{13}C NMR spectrum of 1,2-diaminoethane complex **8**.

The limiting low temperature ^{31}P NMR spectra of **10** and **11** again demonstrate inequivalence of the P-donor atoms; in both cases distinct doublet of doublet patterns are observed but the dppe complex **10**, like its precursor **2**, exhibits variable temperature behaviour. Thus on warming, the ^{31}P NMR spectrum of **10** collapses to a broad singlet with coalescence temperature 38 °C; the activation energy to the proposed trigonal twist process is therefore not drastically altered by tcne addition to the cycloheptatrienyl ring.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, and distilled and deoxygenated before use. The complexes [MoCl(CO)$_2$(η-C_7H_7)] [25], [WCl(CO)$_2$(η-C_7H_7)] [26], [MoCl(CO)$_2$(NCMe)$_2$(η^3-C_3H_5)] [27], [MoI(CO)$_2$(dppe)(η^3-C_7H_7)] [1] and [WI(CO)$_2$(P–P)(η^3-C_7H_7)] (P–P = dppe, dppm) [13] were prepared by published procedures. Aldrich Chemical Co. supplied dppe, dppm, 1,2-diaminoethane and tcne.

Phosphorus-31 NMR spectra were recorded at 32.4 MHz on a Bruker WP80 spectrometer and ^{13}C NMR spectra at 75 MHz on a Varian Associates XL300 spectrometer. Hydrogen-1 NMR spectra were recorded on Varian Associates SC300 or XL300 instruments. Infrared spectra were obtained with a Perkin–Elmer FT1710 spectrometer and microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparation of [MoCl(CO)$_2$(dppe)(η^3-C_7H_7)] (3)

A stirred solution of [MoCl(CO)$_2$(η-C_7H_7)] (0.95 g, 3.41 mmol) in toluene (70 cm^3) was treated with dppe (1.36 g, 3.42 mmol). After 24 h the red solution was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (50 cm^3). The solution was filtered and n-hexane was added, and the volume of the solution was reduced to give the product as a red-purple solid; yield 1.41 g (61%). [WCl(CO)$_2$(dppe)(η^3-C_7H_7)] (**4**) and [MoCl(CO)$_2$(dppm)(η^3-C_7H_7)] (**5**) were prepared similarly, but several recrystallisations from CH_2Cl_2 n-hexane were required to obtain a pure sample of **5**.

Preparation of [MoCl(CO)$_2$(en)(η^3-C_7H_7)] (7)

A stirred solution of [MoCl(CO)$_2$(η-C_7H_7)] (0.62 g, 2.23 mmol) in toluene (60 cm^3) was cooled to 0 °C and a solution of 1,2-diaminoethane (0.27 g, 4.50 mmol) in toluene (10 cm^3) added dropwise during 10 minutes. Stirring was continued for a total of 3 h, to yield the crude product as an orange-brown precipitate, and decantation of the toluene mother liquors followed by recrystallisation of the precipitate from acetone diethyl ether afforded **7** as a bright orange solid; yield 0.40 g (53%). An identical procedure was employed in the preparation of [WCl(CO)$_2$(en)(η^3-C_7H_7)] (**8**) from [WCl(CO)$_2$(η-C_7H_7)] (0.70 g, 1.91 mmol) and 1,2-diaminoethane (0.23 g, 3.83 mmol). Both **7** and **8** have only limited solubility in CH_2Cl_2 or acetone.

Preparation of [MoCl(CO)$_2$(en)(η^3-C_3H_5)] (9)

A solution of 1,2-diaminoethane (0.10 g, 1.67 mmol) in acetonitrile (6 cm^3) was added dropwise to a stirred acetonitrile solution of [MoCl(CO)$_2$(NCMe)$_2$(η^3-C_3H_5)] (0.51 g, 1.64 mmol). After 1 h the pale yellow solution was evaporated to dryness and the residue recrystallised from acetone diethyl ether to give the product as a bright yellow powder; yield 0.30 g (63%).

Preparation of [WI(CO)$_2$(dppm){η^3-$C_9H_7(CN)_4$}] (11)

A solution of [WI(CO)$_2$(dppm)(η^3-C_7H_7)] (**6**) (0.61 g, 0.72 mmol) in CH_2Cl_2 (30 cm^3), cooled in an ice bath, was treated with tcne (0.092 g, 0.72 mmol), and the mixture was stirred for 20 min at 0 °C then 40 min at room temperature. The solution was filtered and n-hexane added to give the crude product as a light brown solid, which was recrystallised from CH_2Cl_2/n-hexane; yield 0.42 g (60%). An analogous reaction of $[WI(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$ (**2**) (0.52 g, 0.61 mmol) with tcne (0.078 g, 0.61 mmol) afforded brown $[WI(CO)_2(dppe)\{\eta^3\text{-}C_9H_7(CN)_4\}]$ (**10**); yield 0.28 g (47%).

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References

1 R.B. King and M.B. Bisnette, Inorg. Chem., 3 (1964) 785.
2 R.B. King and A. Fronzaglia, Inorg. Chem., 5 (1966) 1837.
3 J.W. Faller, Inorg. Chem., 8 (1969) 767.
4 R.B. King, J. Organomet. Chem., 8 (1967) 129.
5 M.A. Bennett, R. Bramley, and R. Watt, J. Am. Chem. Soc., 91 (1969) 3089.
6 F.A. Cotton and C.R. Reich, J. Am. Chem. Soc., 91 (1969) 847.
7 K.S. Chong and A. Storr, Can. J. Chem., 58 (1980) 2278.
8 K.S. Chong, S.J. Rettig, A. Storr, and J. Trotter, Can. J. Chem., 59 (1981) 1665.
9 F.A. Cotton, M. Jeremic, and A. Shaver, Inorg. Chim. Acta, 6 (1972) 543.
10 F.A. Cotton, C.A. Murillo, and B.R. Stults, Inorg. Chim. Acta, 22 (1977) 75.
11 T.W. Beall and L.W. Houk, Inorg. Chem., 12 (1973) 1979.
12 R. Panter and M.L. Ziegler, Z. Anorg. Allg. Chem., 453 (1979) 14.
13 R. Breeze, S. Endud, and M.W. Whiteley, J. Organomet. Chem., 302 (1986) 371.
14 R. Breeze, A. Ricalton, and M.W. Whiteley, J. Organomet. Chem., 327 (1987) C29.
15 J.W. Faller, D.A. Haitko, R.D. Adams, and D.F. Chodosh, J. Am. Chem. Soc., 101 (1979) 865.
16 A.J. Graham and R.H. Fenn, J. Organomet. Chem., 17 (1969) 405.
17 P.S. Braterman, D.W. Milne, E.W. Randall, and E. Rosenberg, J. Chem. Soc., Dalton Trans., 1973, 1027.
18 B.J. Brisdon and A. Day, J. Organomet. Chem., 221 (1981) 279.
19 B.J. Brisdon, M. Cartwright, D.A. Edwards, and K.E. Paddick, Inorg. Chim. Acta, 40 (1980) 191.
20 S. Endud, M. Sc. Thesis, University of Manchester, 1985.
21 A.J. Graham and R.H. Fenn, J. Organomet. Chem., 25 (1970) 173.
22 P. Powell, J. Organomet. Chem., 129 (1977) 175.
23 H.D. Murdoch and R. Henzi, J. Organomet. Chem., 5 (1966) 552.
24 M.D. Curtis and O. Eisenstein, Organometallics, 3 (1984) 887.
25 E.E. Isaacs and W.A.G. Graham, Can. J. Chem., 53 (1975) 975.
26 G. Hoch, R. Panter, and M.L. Ziegler, Z. Naturforsch B, 31B (1976) 294.
27 R.G. Hayter, J. Organomet. Chem., 13 (1968) P1.