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REACTIONS OF METAL CARBONYL DERIVATIVES
VI*. FURTHER STUDIES OF THE REACTION OF BIS(TRICARBONYL-π-CYCLOPENTADIENYLMOLYBDENUM) WITH TERTIARY PHOSPHITES, PHOSPHONITES AND PHOSPHINITES

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SUMMARY

The ligands L=$P(OC_3H_5)_3$***, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$ react with $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ to yield ionic $[\pi\text{-}C_5H_5Mo(CO)_2L_2][\pi\text{-}C_5H_5Mo(CO)_3]$, neutral $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ or neutral $\pi\text{-}C_5H_5Mo(CO)_2LL'$ [L'=$P(O)(OC_3H_5)_2$, $P(O)(OC_3H_5)(C_6H_5)$ or $P(O)(C_6H_5)_2$] depending on the reaction conditions. The mechanism of the formation of $\pi\text{-}C_5H_5Mo(CO)_2LL'$ via the ionic intermediate $[\pi\text{-}C_5H_5Mo(CO)_2L_2][\pi\text{-}C_5H_5Mo(CO)_3]$ is discussed.

INTRODUCTION

A previous study[1] revealed that the action of the tertiary alkyl phosphites $P(OR)_3$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) on $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in benzene under reflux resulted in the degradation of the phosphorous acid esters and the formation of $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$. No such fission was observed in the corresponding reactions involving tertiary phosphines however[3]. Further neutral compounds of the type $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$, which were shown to exist in solution in two isomeric forms, were produced in the reactions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with the above phosphite ligands in benzene under irradiation with ultraviolet light[1]. In contrast only ionic products could be isolated from the corresponding photochemical reactions involving tertiary phosphines[3].

This study was initiated to establish whether the behaviour of tertiary phosphonites and phosphinites towards $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ parallels that of tertiary phosphites under similar reaction conditions.

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* For Part V, see ref. 1. A preliminary communication of some of this work has been presented, see ref. 2.
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*** C_3H_5=Allyl.

RESULTS AND DISCUSSION

Similar to that found previously for the tertiary phosphines[3] PR_3 ($R=C_2H_5$ and C_6H_5) and the tertiary phosphites[1] $P(OR)_3$ ($R=CH_3, C_2H_5$, i-C_3H_7 and n-C_4H_9), the ligands $L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$ were observed to effect the disproportionation of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in benzene at room temperature to yield the ionic products $[\pi\text{-}C_5H_5Mo(CO)_2L_2][\pi\text{-}C_5H_5Mo(CO)_3]$. These compounds were identified by comparison of their infrared spectra in the C–O stretching region with those of $[\pi\text{-}C_5H_5Mo(CO)_2L_2]B(C_6H_5)_4$ (discussed below) and $[N(C_4H_9)_4][\pi\text{-}C_5H_5Mo(CO)_3]$[4]. They are soluble in benzene indicating a fair degree of association between the cation and anion.

The tetraphenylborate derivatives of the cations $[\pi\text{-}C_5H_5Mo(CO)_2L_2]^+$ [$L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$] were isolated by the addition of $NaB(C_6H_5)_4$ in a little ethanol to solutions of $[\pi\text{-}C_5H_5Mo(CO)_2L_2]$-$[\pi\text{-}C_5H_5Mo(CO)_3]$ in benzene. They were shown to be air stable in the crystalline state and 1/1 electrolytes in acetone. The ratios of the intensities of the two C–O stretching bands observed in the infrared spectra of these derivatives are consistent with them occurring as the "*trans*" isomer (Fig. 1) in solution[1,5,6]. Further the appearance of a single cyclopentadienyl resonance, split into a triplet as a result of coupling between the cyclopentadienyl protons and the phosphorus nuclei, in their NMR spectra is an indication that these compounds exist solely as one isomer in solution.

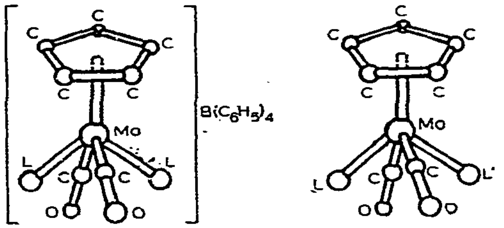
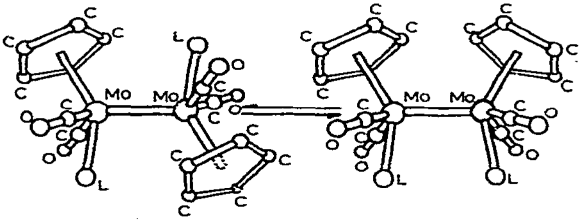


Fig. 1. Proposed structures for the compounds $[\pi\text{-}C_5H_5Mo(CO)_2L_2]B(C_6H_5)_4$ [$L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$] and $\pi\text{-}C_5H_5Mo(CO)_2LL'$ [$L=P(OC_3H_5)_3$, $L'=P(O)(OC_3H_5)_2$; $L=P(OC_3H_5)_2(C_6H_5)$, $L'=P(O)(OC_3H_5)(C_6H_5)$; $L=P(OC_3H_5)(C_6H_5)_2$, $L'=P(O)(C_6H_5)_2$].

Irradiation of benzene solutions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and excess of the ligands $L=P(OC_3H_5)_3$ and $P(OC_3H_5)(C_6H_5)_2$ with ultraviolet light resulted in the formation of the neutral dinuclear compounds $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ in fair yield. The corresponding photochemical reaction involving $P(OC_3H_5)_2(C_6H_5)$ was observed



'*trans*' isomer 'cis' isomer

Fig. 2. Proposed structures of the isomers of $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ [$L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$] existing in solution.

to similarly afford $[\pi\text{-}C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)]_2$ but the yield was exceptionally low, phosphinate derivatives being the major products. It was previously established that the compounds $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ ($R=CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9) are present in solution as a mixture of the "*cis*" and "*trans*" isomers[1] shown in Fig. 2. Further while $[\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-i-}C_3H_7)_3]_2$ was found to occur primarily as the "*cis*" isomer in cyclohexane, $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3\text{-}CCH_3]_2$ was observed to exist solely as the "*trans*" isomer in dichloromethane[1]. Based on a comparison of the infrared spectra in the C–O stretching region of $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ $[L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2]$ with the spectra of the compounds discussed above, it is shown that the dinuclear compounds of the type $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ synthesised in this study occur primarily as the "*trans*" isomer in solution and solely as this isomer in the solid state. The appearance of a single cyclopentadienyl proton resonance, split into a doublet as a result of coupling between the cyclopentadienyl protons and the adjacent phosphorus nucleus, in the NMR spectra of these derivatives is readily explained in terms of a rapid exchange between the two isomers in solution.

The reactions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with excess of the ligands $L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$ in benzene at room temperature were observed to parallel the corresponding reaction[1] involving $P(OCH_3)_3$ and afford neutral products identified as $\pi\text{-}C_5H_5Mo(CO)_3C_3H_5$ and $\pi\text{-}C_5H_5Mo(CO)_2LL'$ $[L=P(OC_3H_5)_3$, $L'=P(O)(C_3H_5)_2$; $L=P(OC_3H_5)_2(C_6H_5)$, $L'=P(O)(OC_3H_5)$-

TABLE 1

COLOURS, CONDUCTIVITY AND ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound[a,b]	Colour	Λ[c]	Analyses found (calcd.)			Mol. wt.[d]
			C(%)	H(%)	P(%)	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_3]_2\}BPh_4$	Yellow	86	62.4 (62.6)	5.8 (5.9)	6.5 (6.6)	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_2Ph]_2\}BPh_4$	Yellow	84	67.2 (67.4)	5.5 (5.7)	6.2 (6.3)	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)Ph_2]_2\}BPh_4$	Yellow	111	71.3 (71.6)	5.3 (5.4)	6.1 (6.1)	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_3]\}_2$	Red	2.0	45.7 (45.8)	4.6 (4.8)	7.3 (7.4)	777 (838)
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)Ph_2]\}_2$	Red	3.1	57.7 (57.5)	4.4 (4.4)	6.6 (6.7)	797[e] (919)
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_3][P(O)(OC_3H_5)_2]$	Yellow	0.1	45.6 (45.5)	5.4 (5.2)		568 (580)
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_2Ph][P(O)(OC_3H_5)Ph]$	Yellow	0.1	53.8 (54.2)	4.9 (4.9)		
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)Ph_2][P(O)Ph_2]$	Yellow	0.4	61.8 (61.8)	4.5 (4.6)	9.1 (9.4)	670 (661)
$\pi\text{-}C_5H_5Mo(CO)_2\text{-}\pi\text{-}C_3H_5$	Yellow	0.5	46.3 (46.5)	4.0 (3.9)		

[a] Compounds in general gave poorly defined melting points. [b] Abbreviations: C_3H_5=Allyl; Ph=C_6H_5. [c] Ohm^{-1} cm^2 mol^{-1} ($1\text{–}10\times10^{-4}$ *M* solutions in acetone). [d] Measured in benzene. [e] Measured in chloroform.

TABLE 2

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA

Compound[a]	Stretching frequencies[b] (cm^{-1})		NMR[c,d]	
	ν(CO)	ν(PO)[e]	$\tau(C_5H_5)$	J(PH)(Hz)
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$	2002 m 1925 s 1891 ms 1772 s (br)[f]		N.m.	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_2Ph]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$	1989 m 1914 s 1888 ms 1773 s (br)[f]		N.m.	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)Ph_2]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$	1985 m 1907 s 1890 ms 1773 s (br)[f]		N.m.	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_3]_2\}BPh_4$	2003 m 1925 s[f]		4.38 t[j]	0.7
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_2Ph]_2\}BPh_4$	1991 m 1915 s[f]		4.64 t[j]	0.7
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)Ph_2]_2\}BPh_4$	1985 m 1907 s[f]		4.57 t[j]	0.7
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_3]\}_2$	1866 m 1844 s[g] 1927 w 1871 m 1855 s 1830 w[h]		5.10 d	1.7
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_2Ph]\}_2$	(*ca.* 1923) 1871 m 1854 s 1815 w[h]		N.m.	
$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)Ph_2]\}_2$	1849 m 1831 s[g] 1918 w 1857 m 1843 s 1815 w[i]		5.28 s (br)	
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_3][P(O)(OC_3H_5)_2]$	1982 m 1906 s[h]	1170	4.51 t	< 1
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)_2Ph][P(O)(OC_3H_5)Ph]$	1972 m 1896 s[h]	1148	4.89 t	< 1
$\pi\text{-}C_5H_5Mo(CO)_2[P(OC_3H_5)Ph_2][P(O)Ph_2]$	1961 m 1875 s[h]	1126	4.95 t	< 1
$\pi\text{-}C_5H_5Mo(CO)_2\text{-}\pi\text{-}C_3H_5$	1960 s 1898 ms 1882 ms[h]		4.74 s[j]	

[a] Abbreviations: C_3H_5=Allyl; Ph=C_6H_5. [b] Abbreviations: s, strong; ms, medium strong; m, medium; w, weak; (br), broad. [c] τ scale measured in $CDCl_3$ at 38° (TMS reference). [d] Abbreviations: s, singlet; d, doublet; t, triplet; (br), broad; N.m., not measured. [e] Measured in CS_2. [f] Measured in CH_2Cl_2. [g] Measured as nujol mull. [h] Measured in C_6H_{12}. [i] Measured in CCl_4. [j] Measured in CD_3COCD_3.

(C_6H_5); L=$P(OC_3H_5)(C_6H_5)_2$, L'=$P(O)(C_6H_5)_2$] as well as the ionic derivatives [π-$C_5H_5Mo(CO)_2L_2$][π-$C_5H_5Mo(CO)_3$]. These neutral compounds were in fact shown to be the major products in the above reactions after prolonged reaction periods. Furthermore their rate of formation was considerably increased by performing the above reactions in refluxing benzene. However, under these latter conditions π-C_5H_5-$Mo(CO)_3C_3H_5$ was observed to react with the ligands to afford a large number of products. For instance six products as well as π-$C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)$-$P(O)(OC_3H_5)(C_6H_5)$ were separated from the reaction involving $P(OC_3H_5)_2(C_6H_5)$. These included π-$C_5H_5Mo(CO)_2$-π-C_3H_5 and two compounds presumed to be π-$C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)COC_3H_5$ and π-$C_5H_5Mo(CO)[P(OC_3H_5)_2(C_6H_5)]_2COC_3H_5$ on the basis of infrared evidence [ν(C–O) 1944 m, 1862 s and 1606 m and 1826 s and 1606 m cm^{-1}, measured in dichloromethane, respectively]. However most products derived from π-$C_5H_5Mo(CO)_3C_3H_5$ were obtained in very low yields and also proved to be very reactive. They were thus not further investigated.

The chemical composition of the compounds π-$C_5H_5Mo(CO)_2LL'$ [L=$P(OC_3H_5)_3$, L'=$P(O)(C_3H_5)_2$; L=$P(OC_3H_5)_2(C_6H_5)$, L'=$P(O)(OC_3H_5)(C_6H_5)$; L=$P(OC_3H_5)(C_6H_5)_2$, L'=$P(O)(C_6H_5)_2$] was established by elemental analysis and from molecular weight measurements while π-$C_5H_5Mo(CO)_3C_3H_5$ was identified by means of infrared[7] [ν(C–O) 2020 ms and 1923 s (br) cm^{-1}, measured in dichloromethane]. The frequencies of the C–O and P–O stretching peaks observed in the infrared spectra of the former compounds are recorded in Table 2. The relative intensities of the C–O modes are consistent with the compounds occurring primarily as the "*trans*" isomer in solution (Fig. 1) similar to that found previously for the compounds π-$C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9)[1]. A decrease in the P–O stretching frequency is observed along the series π-$C_5H_5Mo(CO)_2$-$P(OC_3H_5)_3P(O)(OC_3H_5)_2$, π-$C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)P(O)(OC_3H_5)(C_6H_5)$ and π-$C_5H_5Mo(CO)_2P(OC_3H_5)(C_6H_5)_2P(O)(C_6H_5)_2$. It is suggested that this decrease is as a result of the replacement of an allyloxy by a less electronegative phenyl group effecting an increase in the electron density on the phosphorus atom which is then redistributed into the P–O anti-bonding orbitals. An alternative possibility that the decrease is due to a mass effect was eliminated on the basis of the observation that the P–O stretching frequencies for the series of compounds π-$C_5H_5Mo(CO)_2P(OR)_3$-$P(O)(OR)_2$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) all occur at *ca.* 1165 cm^{-1}.

The NMR spectra of the complexes π-$C_5H_5Mo(CO)_2LL'$ [L=$P(OC_3H_5)_3$, L'=$P(O)(C_3H_5)_2$; L=$P(OC_3H_5)_2(C_6H_5)$, L'=$P(O)(OC_3H_5)(C_6H_5)$; L=$P(OC_3H_5)(C_6H_5)_2$, L'=$P(O)(C_6H_5)_2$] contain a single cyclopentadienyl resonance split into a triplet as a result of coupling of the cyclopentadienyl protons with the phosphorus nuclei. This splitting pattern contrasts with the 1/1/1/1 pattern observed in the spectra of π-$C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9)[1]. It is thus apparent that for the former compounds the coupling constants *J*(PH) are approximately the same for both phosphorus nuclei.

By monitoring the reactions of [π-$C_5H_5Mo(CO)_3$]$_2$ with the ligands L=$P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$ in benzene at room temperature or under reflux by means of infrared it was observed that the ionic derivatives [π-$C_5H_5Mo(CO)_2L_2$][π-$C_5H_5Mo(CO)_3$] are intermediates in the formation of π-$C_5H_5Mo(CO)_2LL'$. This observation is consistent with the mechanism outlined in eqns. (1) and (2) and which was suggested previously for the formation of π-C_5H_5Mo-

$(CO)_2P(OR)_3P(O)(OR)_2$ from $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and the tertiary phosphites $P(OR)_3$ ($R=CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9)[1]

SCHEME 1

$$[\pi\text{-}C_5H_5Mo(CO)_3]_2+L \rightarrow \pi\text{-}C_5H_5Mo(CO)_3Mo(CO)_2L\text{-}\pi\text{-}C_5H_5 \xrightarrow{L}$$

$$[\pi\text{-}C_5H_5Mo(CO)_2L_2][\pi\text{-}C_5H_5Mo(CO)_3] \rightarrow$$

$$\pi\text{-}C_5H_5Mo(CO)_2LL'+\pi\text{-}C_5H_5Mo(CO)_3C_3H_5 \tag{1}$$

$$\pi\text{-}C_5H_5Mo(CO)_3C_3H_5+L \rightarrow \text{various products} \tag{2}$$

$L=P(OC_3H_5)_3$, $L'=P(O)(OC_3H_5)_2$; $L=P(OC_3H_5)_2(C_6H_5)$, $L'=P(O)$-$(OC_3H_5)(C_6H_5)$; $L=P(OC_3H_5)(C_6H_5)_2$, $L'=P(O)(C_6H_5)_2$

This mechanism is analogous to that for the Michaelis–Arbuzov rearrangement involving tertiary phosphites and alkyl halides[8]. It is thus apparent from the above study that tertiary phosphonites and phosphinites as well as tertiary phosphites are capable of participating in Michaelis–Arbuzov type rearrangements with transition metal complexes.

EXPERIMENTAL

The ligands $P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$ were synthesised by addition of three moles, two moles and one mole of allyl alcohol to one mole of PCl_3, $P(C_6H_5)Cl_2$ and $P(C_6H_5)_2Cl$ in hexane in the presence of pyridine, respectively. $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ was synthesised according to an established procedure[9]. All reactions and operations were performed under a nitrogen atmosphere. The photochemical reactions employed a low-pressure mercury lamp. The chromatographic separations were effected on an alumina column (50 × 1.5 cm; Merck acid washed alumina, activity III). The infrared and NMR spectra were recorded on a Perkin–Elmer model 21 spectrophotometer and on a Varian A60 respectively. Conductivities were determined using a Metrohm E365B conductoscope. The molecular weights were measured using a Mechrolab vapour pressure osmometer. The elemental analyses (C, H, P) were obtained by the Alfred Bernhardt Microanalytical Laboratory, Elbach–über–Engelskirchen, West Germany and by Mr. G. J. Roberts, National Chemical Research Laboratory, C.S.I.R., Pretoria.

Synthesis of $[\pi\text{-}C_5H_5Mo(CO)_2L_2]$ $[\pi\text{-}C_5H_5Mo(CO)_3]$ $L=P(OC_3H_5)_3$, $P(OC_3H_5)_2$-(C_6H_5) *and* $P(OC_3H_5)(C_6H_5)_2]$

A solution of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (0.5 g, 1.0 mmole) and $P(OC_3H_5)_3$ (1.0 g, 5.0 mmole) or $P(OC_3H_5)_2(C_6H_5)$(1.1 g, 5.0 mmole) or $P(OC_3H_5)(C_6H_5)_2$ (1.2 g, 5.0 mmole) in benzene (*ca.* 80 ml) was stirred until reaction was complete as determined by monitoring with infrared. The solvent was removed under reduced pressure to afford an oily residue which was washed with petroleum ether to remove excess ligand. The oily crystalline solid was identified as $[\pi\text{-}C_5H_5Mo(CO)_2L_2][\pi\text{-}C_5H_5Mo(CO)_3]$ by means of infrared spectroscopy.

Synthesis of $[\pi\text{-}C_5H_5Mo(CO)_2L_2]B(C_6H_5)_4$ [$L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$]

$NaB(C_6H_5)_4$ (0.82 g, 2.4 mmole) in a minimum of ethanol was added to a benzene solution (*ca.* 80 ml) of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (0.5 g, 1.0 mmole) and $P(OC_3H_5)_3$ (1.0 g, 5.0 mmole) or $P(OC_3H_5)_2(C_6H_5)$ (1.1 g, 5.0 mmole) or $P(OC_3H_5)(C_6H_5)_2$ (1.2 g, 5.0 mmole) and the resultant solution stirred until reaction was complete as determined by monitoring with infrared. The solvent was removed under reduced pressure to afford an oil which was dissolved in a minimum of a benzene/dichloromethane mixture and transferred to an alumina column. The column was eluted with benzene to remove neutral products. Elution with dichloromethane afforded a yellow band which was collected. Removal of the solvent under reduced pressure afforded the product which was crystallised from acetone/petroleum ether. Yield 50–60%.

Synthesis of $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ [$L=P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$]

Solutions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (1.0 g, 2.0 mmole) and $P(OC_3H_5)_3$ (2.0 g, 10.0 mmole), $P(OC_3H_5)_2(C_6H_5)$ (1.8 g, 8.0 mmole) and $P(OC_3H_5)(C_6H_5)_2$ (1.9 g, 8.0 mmole) in benzene (*ca.* 150 ml) were irradiated with ultraviolet light for 10, 2 and 70 min respectively. Longer irradiation times for the $P(OC_3H_5)_3$ and $P(OC_3H_5)_2(C_6H_5)$ reactions resulted in the increased formation of phosphonate type products. Removal of the solvent under reduced pressure afforded oils which were dissolved in a minimum of a benzene/petroleum ether mixture and transferred to an alumina column.

$[\pi\text{-}C_5H_5Mo(CO)_2P(OC_3H_5)_3]_2$. The column was eluted with petroleum ether and then with benzene to afford a red band which was collected. The solvent was removed under reduced pressure to give a residue of the titled compound which was crystallised from benzene/petroleum ether. Yield *ca.* 40%.

$[\pi\text{-}C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)]_2$. The column was eluted with petroleum ether and then with benzene/petroleum ether (1/1) to afford a red band which was collected. Removal of the solvent under reduced pressure afforded $[\pi\text{-}C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)]_2$ as a red solid. The compound was identified by means of infrared spectroscopy only. Yield *ca.* 1%.

$[\pi\text{-}C_5H_5Mo(CO)_2P(OC_3H_5)(C_6H_5)_2]_2$. The column was eluted with petroleum ether and benzene/petroleum ether (1/1) to remove other products. Elution with benzene/petroleum ether (2/1) afforded a red band which was collected. The solvent was removed under reduced pressure to afford a red residue of the titled compound which was crystallised from benzene/petroleum ether. Yield *ca.* 40%.

Synthesis of $\pi\text{-}C_5H_5Mo(CO)_2LL'$ through reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with the ligands L [$L=P(OC_3H_5)_3$, $L'=P(O)(OC_3H_5)_2$; $L=P(OC_3H_5)_2(C_6H_5)$, $L'=P(O)(OC_3H_5)(C_6H_5)$; $L=P(OC_3H_5)(C_6H_5)_2$; $L'=P(O)(C_6H_5)_2$]

A solution of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (1.0 g, 2.0 mmole) and $P(OC_3H_5)_3$ (2.4 g, 12 mmole) or $P(OC_3H_5)_2(C_6H_5)$ (2.7 g, 12 mmole) or $P(OC_3H_5)(C_6H_5)_2$ (2.9 g, 12 mmole) in benzene (*ca.* 100 ml) was refluxed for 2 h. The solvent was removed under reduced pressure to afford a brown oil which was dissolved in a minimum of a benzene/petroleum ether mixture and transferred to an alumina column. Elution in turn with petroleum ether, benzene/petroleum ether (1/4), benzene and dichloromethane/benzene (1/2) afforded at least five bands which were collected and monitored but in general not further investigated. Elution of the column with chloroform afforded a yellow band which was collected. The solvent was removed under reduced pressure to afford π-$C_5H_5Mo(CO)_2P(OC_3H_5)(C_6H_5)_2P(O)(C_6H_5)_2$ as an oily crystalline solid and π-$C_5H_5Mo(CO)_2P(OC_3H_5)_3P(O)(OC_3H_5)_2$ and π-$C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)P(O)(OC_3H_5)(C_6H_5)$ as yellow oils. π-$C_5H_5Mo(CO)_2P(OC_3H_5)(C_6H_5)_2P(O)(C_6H_5)_2$ was crystallised from benzene/petroleum ether while the other two derivatives, which were characterised as oils, were dried thoroughly. Yield >60%.

Removal of the solvent from the first band eluted from the column involved in the separation of the products from the $P(OC_3H_5)_2(C_6H_5)$ reaction afforded a yellow crystalline residue. This was recrystallised from petroleum ether at −78° and characterised as π-$C_5H_5Mo(CO)_2$-π-C_3H_5. The compound isolated from the second band of this separation was crystallised from petroleum ether and identified as π-$C_5H_5Mo(CO)[P(OC_3H_5)_2(C_6H_5)]_2COC_3H_5$ by means of infrared spectroscopy as discussed in the text [ν(C–O) 1826 s and 1606 m cm^{-1}, measured in dichloromethane]. Removal of the solvent from the fifth band of the separation afforded an orange residue which was shown by means of infrared to be a mixture of two compounds. The major component π-$C_5H_5Mo(CO)_2P(OC_3H_5)_2(C_6H_5)COC_3H_5$ was isolated by fractional crystallisation from benzene/petroleum ether.

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