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REACTIONS OF METAL CARBONYL DERIVATIVES
V*. REACTION OF BIS(TRICARBONYL-π-CYCLOPENTADIENYLMOLYBDENUM) WITH TERTIARY ALKYL PHOSPHITES**

R. J. HAINES***
Research and Process Development, South African Iron and Steel Industrial Corporation Limited, P.O. Box 450, Pretoria (South Africa)
C. R. NOLTE
Department of Inorganic and Analytical Chemistry, University of Pretoria, Pretoria (South Africa)

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SUMMARY

The tertiary alkyl phosphites $P(OR)_3$ (R = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) and $P(OCH_2)_3CCH_3$ react with $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in benzene at room temperature to give $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}$ $[\pi\text{-}C_5H_5Mo(CO)_3]$ and $\{\pi\text{-}C_5H_5Mo(CO)_2\text{-}[P(OCH_2)_3CCH_3]_2\}$ $[\pi\text{-}C_5H_5Mo(CO)_3]$. Neutral products of the type $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ are obtained by irradiating benzene solutions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and the above ligands with ultraviolet light. Fission of the tertiary phosphites $P(OR)_3$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) is also effected by reaction with $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in benzene. Products of the type $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ and $\pi\text{-}C_5H_5Mo(CO)_3R$ or $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3R$ (depending on the reaction conditions) are formed. It has been shown that the ionic compounds $\{\pi\text{-}C_5H_5Mo(CO)_2\text{-}[P(OR)_3]_2\}$ $[\pi\text{-}C_5H_5Mo(CO)_3]$ are intermediates in the formation of the phosphonate derivatives. The mechanism proposed for the formation of the latter compounds is analogous to the well-established mechanism of the Michaelis–Arbuzov rearrangement involving tertiary phosphites and alkyl halides.

INTRODUCTION

Considerable interest has been focussed recently on the use of phosphorous acid esters as ligands in transition metal chemistry. Their reactions with transition metal carbonyl derivatives in the main parallel those of tertiary phosphines although subtle differences are often observed. For instance they readily replace carbonyl groups in these compounds, as illustrated by the reactions of $M(CO)_6$ (M = Cr, Mo and W) with the ligand L = $P(OCH_2)_3CCH_3$, from which the mono- and di-substituted derivatives $M(CO)_5L$ and $M(CO)_4L_2$ have been isolated[1]. However, tertiary phos-

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[*] For Part IV see ref. 24.
[**] For a preliminary account see ref. 25.
[***] To whom correspondence concerning this publication should be addressed.

TABLE 1

COLOURS, CONDUCTIVITY AND ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound[a]	Colour	Conductivity[b] (ohm^{-1}·cm^2·mol^{-1})	Analyses (%)[c]						Mol. wt.[c,d]	
			Found			Calculated			Found	Calcd.
			C	H	P	C	H	P		
{π-$C_5H_5Mo(CO)_2[P(OCH_3)_3]_2$}$B(C_6H_5)_4$	Yellow	104	56.7	5.6	7.8	56.7	5.6	7.9		
{π-$C_5H_5Mo(CO)_2[P(OC_2H_5)_3]_2$}$B(C_6H_5)_4$	Yellow	102	59.7	6.5	7.0	59.5	6.4	7.1		
{π-$C_5H_5Mo(CO)_2[P(O$-i-$C_3H_7)_3]_2$}$B(C_6H_5)_4$	Yellow	95	62.1	7.2	6.3	61.8	7.1	6.5		
{π-$C_5H_5Mo(CO)_2[P(O$-n-$C_4H_9)_3]_2$}$B(C_6H_5)_4$	Yellow	90	63.7	7.4	5.8	63.7	7.7	6.0		
{π-$C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2$}$B(C_6H_5)_4$	Yellow	84	58.8	5.3	n.d.	59.2	5.2	7.4		
[π-$C_5H_5Mo(CO)_2P(OCH_3)_3$]$_2$	Red	c.m.	35.2	4.2	n.d.	35.2	4.1	9.1	c.m.	682
[π-$C_5H_5Mo(CO)_2P(OC_2H_5)_3$]$_2$	Red	5.1	41.0	5.3	7.9	40.8	5.3	8.1	725	766
[π-$C_5H_5Mo(CO)_2P(O$-i-$C_3H_7)_3$]$_2$	Red	5.0	45.3	6.2	7.2	45.2	6.2	7.3	829	850
[π-$C_5H_5Mo(CO)_2P(O$-n-$C_4H_9)_3$]$_2$	Red	4.7	48.6	6.7	n.d.	48.8	6.9	6.6	953	935
[π-$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3$]$_2$	Red	4.7	39.8	4.1	n.d.	39.5	3.9	8.5	c.m.	730
π-$C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$	Yellow	0.4	37.0	5.0	n.d.	37.1	4.8	8.7	367	356
π-$C_5H_5Mo(CO)_2P(OCH_3)_3P(O)(OCH_3)_2$	Yellow	6.9	32.2	4.6	14.0	32.0	4.5	13.8	470	450
π-$C_5H_5Mo(CO)_2P(OC_2H_5)_3P(O)(OC_2H_5)_2$	Yellow	n.m.	38.9	5.9	11.8	39.2	5.8	11.9	n.m.	520
π-$C_5H_5Mo(CO)_2P(O$-i-$C_3H_7)_3P(O)(O$-i-$C_3H_7)_2$	Yellow	0.3	45.0	6.9	10.5	44.8	6.8	10.5	597	590
π-$C_5H_5Mo(CO)_2P(O$-n-$C_4H_9)_3P(O)(O$-n-$C_4H_9)_2$	Yellow	n.m.	48.7	7.8	9.3	49.1	7.6	9.4	n.m.	660

[a] Compounds in general gave poorly defined melting points. [b] 1–10 × 10^{-4} *M* solutions in acetone. [c] Abbreviations: n.d., not determined; c.m., cannot measure; n.m., not measured. [d] Measured in benzene.

phites do not effect disproportionation of metal carbonyl compounds as readily as tertiary phosphines; this is well illustrated by their reactions with $[\pi\text{-}C_5H_5Mo(CO_3]_2$. Whereas the reaction involving excess $P(OC_6H_5)_3$ yields the neutral product $[\pi\text{-}C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$, the corresponding reaction utilising $P(C_6H_5)_3$ affords the ionic derivative[2] $\{\pi\text{-}C_5H_5Mo(CO)_2[P(C_6H_5)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$. Cleavage of bridged halo carbonyl derivatives is also readily effected by tertiary phosphite ligands; for example, the action of $P(OC_6H_5)_3$ on $[Rh(CO)_2Cl]_2$ affords $Rh(CO)[P(OC_6H_5)_3]_2Cl$ in high yield[3]. Phosphite ligands have also been shown to effect halogen displacement in certain metal carbonyl derivatives, but in general they are not as effective in this type of reaction as the harder tertiary phosphines. For instance, whereas the ionic derivative $[\pi\text{-}C_5H_5Fe(CO)_2P(C_6H_5)_3]Cl$ is obtained from the reaction of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with $P(C_6H_5)_3$ in benzene, the corresponding reaction[4] involving $P(OC_6H_5)_3$ yields $\pi\text{-}C_5H_5Fe(CO)P(OC_6H_5)_3Cl$.

The reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with various tertiary alkyl phosphites has now been studied and a new type of product resulting from the fission of the phosphite ligand, has been isolated. The results of this study are reported here.

RESULTS AND DISCUSSION

Previous studies have shown that the action of the tertiary phosphines[2] PR_3 ($R=C_2H_5$ and C_6H_5) and the ditertiary phosphines[2,5] *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ effects disproportionation of the parent dimer to afford the ionic derivatives $[\pi\text{-}C_5H_5Mo(CO)_2(PR_3)_2][\pi\text{-}C_5H_5Mo(CO)_3]$ and $[\pi\text{-}C_5H_5Mo(CO)_2(C_6H_5)_2PC_2H_nP(C_6H_5)_2][\pi\text{-}C_5H_5Mo(CO)_3]$ ($n=2, 4$), respectively. A similar type of reaction has now been observed for tertiary alkyl phosphites. Thus treatment of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with the ligands $P(OR)_3$ ($R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ and $n\text{-}C_4H_9$) and $P(OCH_2)_3CCH_3$ in benzene at room temperature has been shown to yield the compounds $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ and $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ respectively. In view of their extreme air sensitivity these derivatives were identified by comparison of their infrared spectra in the C–O stretching region with the spectra of $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}B(C_6H_5)_4$ ($R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ and $n\text{-}C_4H_9$) or $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}B(C_6H_5)_4$ (discussed below) and $[N(C_4H_9)_4][\pi\text{-}C_5H_5Mo(CO)_3]$[6]. Interestingly the compounds of the type $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ synthesised in this study are soluble in benzene, indicating a fair degree of association between the cation and the anion.

The tetraphenylborate derivatives of the cations $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}^+$ ($R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ and $n\text{-}C_4H_9$) and $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}^+$ were isolated by the addition of $NaB(C_6H_5)_4$ to solutions of the corresponding ionic derivatives $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ and $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$, respectively, in benzene. These compounds are air stable in the crystalline state and 1/1 electrolytes in acetone. Their solution infrared spectra contain two peaks in the C–O stretching region, the frequencies of which are recorded in Table 2. Previous studies have shown that the ratios of the intensities of the two C–O stretching peaks in the spectra of the *cis* and *trans* isomers of the compounds of the type $\pi\text{-}C_5H_5Mo(CO)_2LX$ and $[\pi\text{-}C_5H_5Mo(CO)_2L_2]X'$ (L=ligand, X=halogen, X′=anion) are very different and thus these

TABLE 2

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA

Compound	Stretching frequencies[a] (cm^{-1})		Resonances[g,h]	
	ν(C–O)	ν(P–O)[f]	τ(C_5H_5)	τ(CH_3)
{π-$C_5H_5Mo(CO)_2[P(OCH_3)_3]_2$}-[π-$C_5H_5Mo(CO)_3$]	1999(m), 1923(s), 1892(ms), 1770(s, b)[b]		n.m.	n.m.
{π-$C_5H_5Mo(CO)_2[P(OC_2H_5)_3]_2$}-[π-$C_5H_5Mo(CO)_3$]	1996(m), 1918(s), 1894(ms), 1768(s, b)[b]		n.m.	n.m.
{π-$C_5H_5Mo(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$}-[π-$C_5H_5Mo(CO)_3$]	1992(m), 1911(s), 1893(ms), 1772(s, b)[b]		n.m.	n.m.
{π-$C_5H_5Mo(CO)_2[P(O\text{-}n\text{-}C_4H_9)_3]_2$}-[π-$C_5H_5Mo(CO)_3$]	1999(m), 1920(s), 1894(ms), 1774(s, b)[b]		n.m.	n.m.
{π-$C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2$}-[π-$C_5H_5Mo(CO)_3$]	2026(m), 1952(s), 1892(ms), 1773(s, b)[b]		n.m.	n.m.
{π-$C_5H_5Mo(CO)_2[P(OCH_3)_3]_2$}$B(C_6H_5)_4$	1999(m), 1923(s)[b]		4.97 (t; J 0.8 Hz)	6.48 (mt)
{π-$C_5H_5Mo(CO)_2[P(OC_2H_5)_3]_2$}$B(C_6H_5)_4$	1999(m), 1919(s)[b]		4.95 (t; J 0.7 Hz)	8.73 (t; J 7.5 Hz)
{π-$C_5H_5Mo(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$}$B(C_6H_5)_4$	1993(m), 1912(s)[b]		4.88 (t; J 0.7 Hz)	8.70 (d; J 6.5 Hz)
{π-$C_5H_5Mo(CO)_2[P(O\text{-}n\text{-}C_4H_9)_3]_2$}$B(C_6H_5)_4$	1999(m), 1920(s)[b]		4.93 (t; J 0.8 Hz)	n.a.
{π-$C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2$}$B(C_6H_5)_4$	2026(m), 1952(s)[b]		c.m.	c.m.
[π-$C_5H_5Mo(CO)_2P(OCH_3)_3]_2$	1863(ms), 1851 (s), 1837 (s)[c] 1923(w), 1864(sh), 1848 (s)[b]		c.m.	c.m.
[π-$C_5H_5Mo(CO)_2P(OC_2H_5)_3]_2$	1870(m), 1846(s, b)[c] 1929(m), 1875(m), 1857(s), 1847(sh), 1827(w)[d]		4.97 (d; J 1.5 Hz)	8.66 (t; J 7.5 Hz)
[π-$C_5H_5Mo(CO)_2P(O\text{-}i\text{-}C_3H_7)_3]_2$	1881(s), 1830(s)[c]		4.93 (d; J 1.6 Hz)	8.68 (d; J 6.5 Hz)

	1922 (ms), 1868 (sh), 1853 (ms), 1837 (s), 1817 (m)^d			
$[\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}n\text{-}C_4H_9)_3]_2$	1871 (m), 1851 (s, b)^c		4.97 (d; J 1.7 Hz)	n.a.
	1928 (m), 1875 (m), 1856 (s), 1847 (sh), 1826 (w)^d			
$[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$	1870 (ms), 1856 (s), 1844 (sh)^c		c.m.	c.m.
	1875 (sh), 1857 (s)^b			
$\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$	1953 (ms), 1876 (s)^b		4.80 (s)^i	6.47 (d; J 11.5 Hz)^i 10.00 (d; J 10.0 Hz)^i
			4.95 (d; J 1.5 Hz)^j	6.38 (d; J 12.0 Hz)^j 9.70 (d; J 3.2 Hz)^j
$\pi\text{-}C_5H_5Mo(CO)_2P(OC_2H_5)_3C_2H_5$	1936 (ms), 1853 (s)^b		n.m.	n.m.
$\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}n\text{-}C_4H_9)_3\text{-}n\text{-}C_4H_9$	1937 (ms), 1853 (s)^b		n.m.	n.m.
$\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3P(O)(OCH_3)_2$	1979 (m), 1901 (s)^e	1166	4.68 (q; $J_1 < 1$ Hz, $J_2 < 1$ Hz)	6.35 (d; J 11.3 Hz) 6.37 (d; J 12.0 Hz)
$\pi\text{-}C_5H_5Mo(CO)_2P(OC_2H_5)_3P(O)(OC_2H_5)_2$	1976 (m), 1898 (s)^d	1166	4.68 (q; J_1 0.8 Hz, J_2 0.5 Hz)	8.67 (t; J 7.0 Hz) 8.74 (t; J 7.0 Hz)
$\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}i\text{-}C_3H_7)_3\text{-}P(O)(O\text{-}i\text{-}C_3H_7)_2$	1970 (m), 1892 (s)^d	1164	4.72 (q; J_1 0.9 Hz, J_2 0.4 Hz)	8.68 (d; J 6.2 Hz) 8.73 (q; J_1 6.2 Hz, J_2 2.1 Hz)
$\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}n\text{-}C_4H_9)_3\text{-}P(O)(O\text{-}n\text{-}C_4H_9)_2$	1974 (m), 1898 (s)^d	1165	4.67 (q; $J_1 < 1$ Hz, $J_2 < 1$ Hz)	n.a.

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[a] Abbreviations: s, strong; ms, medium strong; m, medium; w, weak; sh, shoulder; b, broad. [b] Measured in CH_2Cl_2 [c] Measured in nujol. [d] Measured in C_6H_{12}. [e] Measured in CCl_4. [f] Measured in CS_2. [g] τ scale measured in $CDCl_3$ at 38° (TMS reference). [h] Abbreviations: s, singlet; d, doublet; t, triplet; q, quadruplet; mt, multiplet; n.m., not measured; n.a., not assigned; c.m., cannot measure. [i] *cis* Isomer. [j] *trans* Isomer.

ratios may be used to distinguish the isomers[7,8]. As shown, the higher energy peak in the solution spectra of $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}B(C_6H_5)_4$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) and $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}B(C_6H_5)_4$ is considerably weaker in intensity than the peak of lower energy indicating that these compounds occur as the *trans* isomer in solution. The NMR spectra of these latter ionic compounds are summarised in Table 2. The single cyclopentadienyl resonance, which is split into a triplet as a result of coupling of the cyclopentadienyl protons with the two phosphorus atoms, confirms the presence of a single isomer in solution.

Irradiation of benzene solutions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and excess of the ligands $P(OR)_3$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) and $P(OCH_2)_3CCH_3$ with ultraviolet light led to the formation of the di-substituted derivatives $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ and $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$ respectively. The compounds $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3]_2$ and $[\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}n\text{-}C_4H_9)_3]_2$ have been synthesised previously, the former by irradiating a solution of $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3]_2Hg$ in benzene with ultraviolet light[8] and the latter by direct substitution[2] of the carbonyl groups in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. The chemical composition of the bis-substituted compounds was established by elemental analysis and from a comparison of the integrated intensities of the cyclopentadienyl and ligand proton peaks. The diamagnetism of these compounds was demonstrated by the sharpness of the NMR spectral peaks. Conductance measurements showed the complexes to be neutral in solution while their dimeric nature in solution was established from molecular weight measurements. The solubilities of these compounds vary considerably; for example, whereas $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$ is virtually insoluble in benzene, $[\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}n\text{-}C_4H_9)_3]_2$ is extremely soluble in petroleum ether.

The infrared and NMR spectra of $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ (R=CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) and $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$ are summarised in Table 2. The solution infrared spectra in the C–O stretching region can only be explained in terms of the existence of more than one isomer in solution. For instance the spectra of $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ (R=C_2H_5, i-C_3H_7 and n-C_4H_9) measured in cyclohexane contain five terminal carbonyl stretching peaks whose relative intensities are observed to vary with compound. It is also observed that the relative intensities of these C–O stretching peaks are solvent dependent, and that an increase in intensity of three of the peaks is always accompanied by a decrease in intensity of the other two and *vice versa*. The two most likely structures of these di-substituted derivatives of the type $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ are illustrated in Fig. 2. The structure of isomer (A) is based on the known structure of the parent compound $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with the carbonyl groups in the plane of symmetry replaced by the tertiary phosphite ligands[9] while isomer (B) is the *cis* analogue of isomer (A). Isomers (A) and (B) belong to the molecular point groups C_{2h} and C_{2v} respectively for which two (A_u+B_u) and three $(A_1+B_1+B_2)$ infrared-active carbonyl stretching modes are predicted respectively. Based on the infrared data discussed above, it is proposed that these di-substituted derivatives exist as a mixture of isomers (A) (*trans*) and (B) (*cis*) in solution. The infrared data are also consistent with the ratio of the "*trans*" to the "*cis*" isomer increasing along the solvent series $C_6H_{12} < THF \sim C_6H_6 < CH_2Cl_2$. It is also noted that while $[\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}i\text{-}C_3H_7)_3]_2$ is shown to occur primarily as the "*cis*" isomer in cyclohexane, $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$ is shown to exist solely as the "*trans*" isomer in dichloromethane. Based on

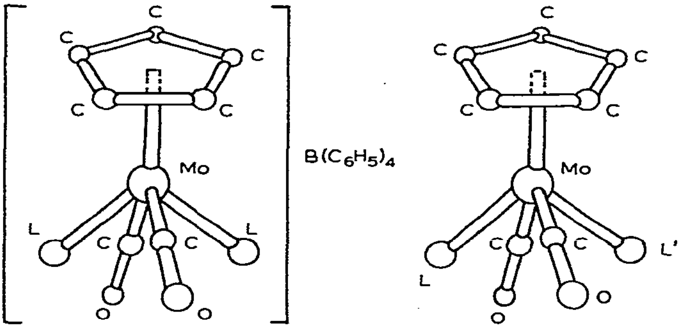

Fig. 1. Proposed structures for the compounds $[\pi\text{-}C_5H_5Mo(CO)_2L_2]B(C_6H_5)_4$ [L = $P(OR)_3$ (R = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) and $P(OCH_2)_3CCH_3$] and $\pi\text{-}C_5H_5Mo(CO)_2LL'$ [L = $P(OR)_3$ (R = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9); L' = $P(O)(OR')_2$ (R' = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9)].

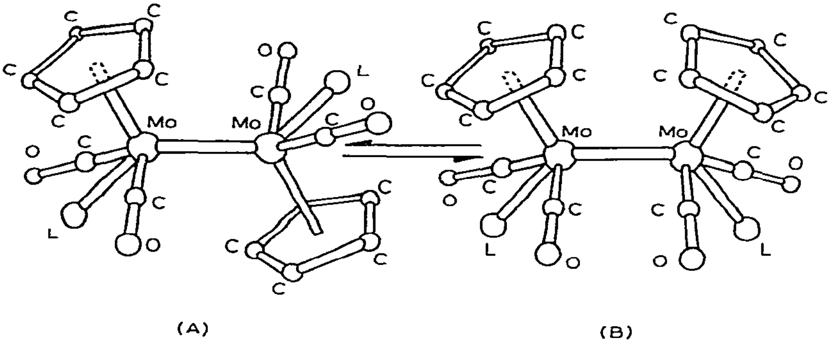

Fig. 2. Proposed structures of the isomers of $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ [L = $P(OR)_3$ (R = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) and $P(OCH_2)_3CCH_3$] existing in solution.

a study of the influence of solvents on the intensities of the C–O and Fe–C stretching modes and on the Fe–C–O bending modes, compounds of the type $[(\pi\text{-Dienyl})Fe(CO)_2]_2$ have also been shown to exist as a mixture of the *cis* and *trans* isomers in solution[10,11], while the unexpected number of peaks in the infrared spectra of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3L$ (L = phosphorus donor ligand) has been explained in terms of a similar *cis–trans* equilibrium in solution[12]. The infrared spectra of $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ (R = CH_3, C_2H_5 and n-C_4H_9) and $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$ in the solid state contain two peaks in the terminal carbonyl stretching region, which is consistent with these compounds occurring as the "*trans*" isomer (A) in the crystalline state. These peaks are split in the $P(OCH_3)_3$ substituted derivative due to lowering of the site symmetry. The solid state spectrum of $[\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-i-}C_3H_7)_3]_2$ is very different to the corresponding spectra of the other derivatives and cannot be readily explained.

The proton NMR spectra of these compounds contain a single cyclopentadienyl resonance split into a doublet as a result of coupling of the cyclopentadienyl protons with the phosphorus atom bonded to the same metal atom. To account for this single resonance in terms of the *cis–trans* isomeric equilibria proposed above, a rapid exchange between the isomers is proposed. A similar explanation has been offered to account for the single cyclopentadienyl peak[10,13] in the NMR spectra of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and $[\pi\text{-}C_5H_5Ru(CO)_2]_2$ and for the presence of only two resonances[12] in the spectra of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(OR)_3$ ($R = CH_3$, C_2H_5, i-C_3H_7, n-C_4H_9 and C_6H_5).

The reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with excess $P(OCH_3)_3$ in benzene at room temperature was observed to afford two other products, *viz.* $\pi\text{-}C_5H_5Mo(CO)_3CH_3$ and $\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3P(O)(OCH_3)_2$, as well as the ionic derivative $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_3)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ discussed above. In fact, after prolonged reaction the former two compounds were found to be the major products and to be formed in equimolar amounts. The corresponding reaction in refluxing benzene is considerably faster. Substitution of a carbonyl group in $\pi\text{-}C_5H_5Mo(CO)_3CH_3$ by trimethyl phosphite than occurs, however, so that $\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$ as well as $\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3P(O)(OCH_3)_2$ are formed. Although the formation of the phosphonate derivatives $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ ($R = C_2H_5$, i-C_3H_7 and n-C_4H_9) could not be detected in the reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with the appropriate tertiary phosphite in benzene at room temperature, the corresponding reaction under reflux conditions readily yielded $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ and $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3R$. $\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-i-}C_3H_7)_3\text{-i-}C_3H_7$ is unstable under these reaction conditions however and decomposed on formation. Further there was no evidence for the formation of any phosphonate derivative in the reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with $P(OCH_2)_3CCH_3$ in benzene under reflux.

The chemical composition of the compounds $\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$ and $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ ($R = CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9) was established by elemental analysis and molecular weight determination. Characterisation of $\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$ was further achieved by comparison of its infrared and NMR spectra with the spectra of the previously reported $\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$, obtained[8] by reacting methyl iodide with $Na[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3]$. The products $\pi\text{-}C_5H_5Mo(CO)_2P(OC_2H_5)_3C_2H_5$ and $\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-n-}C_4H_9)_3\text{-n-}C_4H_9$ were isolated as oils and were identified by means of infrared spectroscopy. $\pi\text{-}C_5H_5Mo(CO)_3CH_3$, previously synthesised by other workers[14], was identified similarly. The phosphonate derivatives $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ ($R = C_2H_5$ and n-C_4H_9) were isolated as analytically pure oils while $\pi\text{-}C_5H_5Mo(CO)_2P(OR')_3P(O)(OR')_2$ ($R' = CH_3$ and i-C_3H_7) were obtained in crystalline form. These compounds are stable under a nitrogen atmosphere but decompose rapidly in air. They are shown to be diamagnetic, neutral in acetone and soluble in all common organic solvents apart form petroleum ether. Phosphonate derivatives of Pd and Pt have been previously synthesised using $P(OR)_2(OH)$ or $P(O)(OR)_2^-$ (R = alkyl or aryl) as reagents[15,16] but metal carbonyl derivatives containing the ligand $P(O)(OR)_2^-$ are not known.

The infrared and NMR spectra of the phosphonate compounds synthesised in this study are summarised in Table 2. As has been observed for the compounds $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}B(C_6H_5)_4$ discussed above, the intensity of the symmetric C–O stretching band in the spectra of these compounds is considerably lower than the intensity of the peak corresponding to the asymmetric mode. In fact the ratio of the intensities of these two peaks corresponds to an angle of approximately 120° between the C–O bonds if the relationship $\tan^2\theta = I_a/I_s$ is applied. This is consistent with these compounds occurring predominantly as the *trans* isomer in solution. The infrared spectra of π-$C_5H_5Mo(CO)_2P(OR)_3R$, $[\pi$-$C_5H_5Mo(CO)_2P(OR)_3]_2$ and π-$C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$, measured in CS_2, are identical in the 1200–1000 cm^{-1} region for any one of the ligands $P(OR)_3$ ($R = CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9) apart from an extra peak at ~ 1165 cm^{-1} in the spectra of the phosphonate derivatives. This peak is assigned to ν(P–O). The corresponding mode has been assigned to the peak at 1103 cm^{-1} in the spectrum[17] of $[PtP(C_2H_5)_3P(O)(C_2H_5)_2SC_2H_5]_2$ and to a peak in the region 1170–1190 cm^{-1} in the spectra[18] of $XHgP(O)(OR)_2$ ($X = Cl$ and Br; $R = C_2H_5$, i-C_3H_7 and n-C_4H_9).

The NMR 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) readily show the presence of two types of phosphorus ligands in these compounds. Thus they contain a single cyclopentadienyl resonance which exhibits a 1/1/1/1 pattern as a result of coupling of the cyclopentadienyl protons with the two nonequivalent phosphorus atoms, *i.e.* an AXY system. Further two resonances assigned to methyl protons are observed in the spectra of π-$C_5H_5Mo(CO)_2P(OR)_3$-$P(O)(OR)_2$ ($R = CH_3$, C_2H_5 and i-C_3H_7); the spectrum of π-$C_5H_5Mo(CO)_2P(O$-n-$C_4H_9)_3P(O)(O$-n-$C_4H_9)_2$ is too complex for the ligand proton resonances to be assigned. The methyl resonances in the spectra of the $P(OCH_3)_3$ and $P(O$-i-$C_3H_7)_3$ substituted derivatives occur as doublets but their chemical shifts are insufficiently different for their relative intensities to be obtained. The corresponding peaks in the spectrum of π-$C_5H_5Mo(CO)_2P(OC_2H_5)_3P(O)(OC_2H_5)_2$ occur as triplets of relative intensity 3/2.

The results above suggest that the ionic derivatives $\{\pi$-$C_5H_5Mo(CO)_2[P$-$(OR)_3]_2\}[\pi$-$C_5H_5Mo(CO)_3]$ ($R = CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9) are intermediates in the formation of the phosphonate compounds π-$C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$. Confirmation that they are indeed intermediates was achieved by studying the decomposition of $\{\pi$-$C_5H_5Mo(CO)_2[P(OCH_3)_3]_2\}[\pi$-$C_5H_5Mo(CO)_3]$ in benzene under reflux. The compounds π-$C_5H_5Mo(CO)_2P(OCH_3)_3P(O)(OCH_3)_2$ and π-$C_5H_5Mo(CO)_3CH_3$ were shown to be the products of this decomposition. If the decomposition is performed in the presence of excess of the ligand $P(OCH_3)_3$, π-$C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$ and not π-$C_5H_5Mo(CO)_3CH_3$ is formed. A further observation pertinent to the elucidation of the mechanism of formation of the phosphonate compounds is that if $[\pi$-$C_5H_5Mo(CO)_3]_2$ is treated with excess $P(OR)_3$ in benzene in the presence of $NaB(C_6H_5)_4$, the di-substituted derivative $\{\pi$-C_5H_5Mo-$(CO)_2[P(OR)_3]_2\}B(C_6H_5)_4$ and not the mono-substituted compound $[\pi$-C_5H_5Mo-$(CO)_3P(OR)_3]B(C_6H_5)_4$ precipitates from solution.

The mechanism outlined in the scheme is thus proposed for the formation of π-$C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ from $[\pi$-$C_5H_5Mo(CO)_3]_2$ and $P(OR)_3$.

$$[\pi\text{-}C_5H_5Mo(CO)_3]_2 + P(OR)_3 \xrightarrow{(1)}$$

$$\pi\text{-}C_5H_5Mo(CO)_3Mo(CO)_2P(OR)_3\text{-}\pi\text{-}C_5H_5 \xrightarrow[P(OR)_3]{(2)}$$

$$\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3] \xrightarrow{(3)}$$

$$\pi\text{-}C_5H_5Mo(CO)_3R + \pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$$

$$[\pi\text{-}C_5H_5Mo(CO)_3R + P(OR)_3 \rightarrow \pi\text{-}C_5H_5Mo(CO)_2P(OR)_3R + CO]$$

Although mono-substituted derivatives of the type π-$C_5H_5Mo(CO)_3Mo(CO)_2P(OR)_3$-$\pi$-$C_5H_5$ [the products of step (1)] have not been isolated in this study, the tertiary phosphine analogues π-$C_5H_5Mo(CO)_3Mo(CO)_2PR_3$-$\pi$-$C_5H_5$ have been prepared previously[2]. It is proposed that step (3) involves the nucleophilic attack of the anion $[\pi\text{-}C_5H_5Mo(CO)_3]^-$ on the cation $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}^+$. Consistent with this proposal is the observation that $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}B(C_6H_5)_4$ is stable in benzene under reflux or unreactive towards $P(OR)_3$ under the same reaction conditions. Clearly the mechanism proposed is analogous to that for the Michaelis–Arbuzov rearrangement involving tertiary phosphites and alkyl halides, *viz.*:

$$P(OR)_3 + R'X \rightarrow [R'P(OR)_3]X \rightarrow R'P(O)(OR)_2 + RX$$

with the ionic derivative $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ corresponding to the phosphonium intermediate[19] $[R'P(OR)_3]X$.

The results of this study suggest that any ionic derivative of the type $\{M[P(OR)_3]_xL_y\}^+X'^-$ (M = metal, R = alkyl) might decompose to $M[P(OR)_3]_{x-1}\,P(O)(OR)_2L_y$ under the appropriate experimental conditions. Recent studies[20] in these laboratories have in fact shown that the reaction of π-$C_5H_5Fe(CO)_2Cl$ with $P(OR)_3$ yields the ionic derivative $[\pi\text{-}C_5H_5Fe(CO)_2P(OR)_3]Cl$ which decomposes further to π-$C_5H_5Fe(CO)_2P(O)(OR)_2$ (R = CH_3, C_2H_5 and C_3H_5). Further a recent communication[21] reports the formation of $RCOMn(CO)_3[P(OR)_3]_2$ and $OP[OSi(C_6H_5)_3]_3$ through reaction of $Mn(CO)_5Si(C_6H_5)_3$ with $P(OR)_3$ (R = alkyl or aryl) and proposes that the reaction involves a Michaelis–Arbuzov type rearrangement although no intermediates or an expected product $(C_6H_5)_3SiP(O)(OR)_2$ could be isolated.

EXPERIMENTAL

The ligand $P(OCH_2)_3CCH_3$ and the parent compound $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ were synthesised according to established methods[22,23] while the ligands $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(O\text{-}n\text{-}C_4H_9)_3$ were obtained commercially (B.D.H. and Eastman–Kodak). The photochemical reactions employed a Hanovia medium pressure arc photochemical reactor. 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 621 grating spectrophotometer and the Varian A60 and 100 MHz instruments respectively. Conductivities were determined using a Philips PW 9501 conductivity meter. The molecular weights were measured using a Mechrolab vapour pressure osmometer. The elemental analyses (C, H, P) were obtained by the 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 $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ *(R =* CH_3, C_2H_5, $i\text{-}C_3H_7$ *and* $n\text{-}C_4H_9$*) and* $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$

A solution of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (0.5 g, 1.0 mmole) and $P(OCH_3)_3$ (1.2 g, 10.3 mmole) or $P(OC_2H_5)_3$ (1.5 g, 9.0 mmole) or $P(O\text{-}i\text{-}C_3H_7)_3$ (1.5 g, 7.2 mmole) or $P(O\text{-}n\text{-}C_4H_9)_3$ (1.5 g, 6.0 mmole) or $P(OCH_2)_3CCH_3$ (1.5 g, 10.0 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 crystalline solid which was identified as $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ ($R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ and $n\text{-}C_4H_9$) or $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}$-$[\pi\text{-}C_5H_5Mo(CO)_3]$ by means of infrared spectroscopy.

Synthesis of $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}B(C_6H_5)_4$ *(*$R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ *and* $n\text{-}C_4H_9$*) and* $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}B(C_6H_5)_4$

$NaB(C_6H_5)_4$ (0.41 g, 1.2 mmole) in a minimum of ethanol was added to a benzene solution of $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ ($R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ or $n\text{-}C_4H_9$) or $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ (1.0 mmole) prepared as above. The product which separated from solution was crystallised from acetone/petroleum ether. Yield >60%.

Synthesis of $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$ *(*$R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ *and* $n\text{-}C_4H_9$*) and* $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$

A solution of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (0.5 g, 1.0 mmole) and $P(OCH_3)_3$ (0.3 g, 2.4 mmole) or $P(OC_2H_5)_3$ (1.5 g, 9.0 mmole) or $P(O\text{-}i\text{-}C_3H_7)_3$ (1.5 g, 7.2 mmole) or $P(O\text{-}n\text{-}C_4H_9)_3$ (1.5 g, 6.0 mmole) in benzene (ca. 100 ml) was irradiated with ultraviolet light until reaction was complete as determined by monitoring with infrared (5–15 h). The solvent was removed under reduced pressure and the oily residue washed with methanol to remove excess ligand. $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3]_2$ was obtained pure by crystallising from CH_2Cl_2/petroleum ether while the other three derivatives were crystallised from petroleum ether. $[\pi\text{-}C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2$ was synthesised similarly except that THF was employed as solvent. The product which separated from solution was washed thoroughly with methanol and benzene to remove any traces of $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]_2\}$ $[\pi\text{-}C_5H_5Mo(CO)_3]$ or the starting compounds.

Synthesis of $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3R$ *and* $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ *through reaction of* $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ *with* $P(OR)_3$ *(*$R=CH_3$, C_2H_5, $i\text{-}C_3H_7$ and $n\text{-}C_4H_9$*)*

A solution of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (0.5 g, 1.0 mmole) and $P(OCH_3)_3$ (1.2 g, 10.3 mmole) or $P(OC_2H_5)_3$ (1.5 g, 9.0 mmole) or $P(O\text{-}i\text{-}C_3H_7)_3$ (1.5 g, 7.2 mmole) or $P(O\text{-}n\text{-}C_4H_9)_3$ (1.5 g, 6.0 mmole) in benzene (ca. 80 ml) was refluxed until reaction was complete as determined by monitoring with infrared (10–20 h). The solution was filtered, concentrated to a small volume and transferred to an alumina column. Elution with benzene : petroleum ether (1/2) afforded a yellow band which was collected. The solvent was removed under reduced pressure to afford the product $\pi\text{-}C_5H_5$-$Mo(CO)_2P(OR)_3R$ as a yellow solid for $R=CH_3$ and as yellow oils for $R=C_2H_5$ and $n\text{-}C_4H_9$ (Yield >50%). $\pi\text{-}C_5H_5Mo(CO)_2P(OCH_3)_3CH_3$ was crystallised from methanol while $\pi\text{-}C_5H_5Mo(CO)_2P(OC_2H_5)_3C_2H_5$ and $\pi\text{-}C_5H_5Mo(CO)_2P(O\text{-}n\text{-}C_4H_9)_3\text{-}n\text{-}C_4H_9$ which could not be obtained in crystalline form, were identified by means of infrared spectroscopy. Elution of the column with chloroform afforded a second yellow band which was collected. The solvent was removed to afford $\pi\text{-}C_5H_5$-$Mo(CO)_2P(OR)_3P(O)(OR)_2$ as oily crystalline solids for $R=CH_3$ and $i\text{-}C_3H_7$ and as yellow oils for $R=C_2H_5$ and $n\text{-}C_4H_9$ (Yield >50%). $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3$-

$P(O)(OR)_2$ ($R=CH_3$ and $i\text{-}C_3H_7$) were crystallised from benzene/petroleum ether and petroleum ether respectively while $\pi\text{-}C_5H_5Mo(CO)_2P(OR')_3P(O)(OR')_2$ ($R'=C_2H_5$ and $n\text{-}C_4H_9$), which were characterised as oils, were dried thoroughly.

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