CONSTRAINED PHOSPHITE ESTER COMPLEXES OF π-CYCLOPENTA-DIENYLMOLYBDENUM TRICARBONYL HALIDES*

WILLIAM E. STANCLIFT and DAVID G. HENDRICKER*

Clippinger Laboratories, Department of Chemistry, Ohio University, Athens, Ohio 45701 (U.S.A.)

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SUMMARY

The synthesis of complexes of the type $\pi\text{-}C_5H_5Mo(CO)_2LX$ and $\pi\text{-}C_5H_5Mo(CO)L_2X$, where X = Cl, Br, or I and L = $P(OCH_2)_3CR$ (R = CH_3, C_2H_5, or C_3H_7), is reported. Infrared and conductance data verified that all compounds existed as covalent species in solution. Each of the three $\pi\text{-}C_5H_5Mo(CO)_2LCl$ complexes was isolated as an inseparable mixture of *cis* and *trans* isomeric forms. Only the *trans* forms of the remaining $\pi\text{-}C_5H_5Mo(CO)_2LX$ complexes were observed in solution, as indicated by infrared and PMR spectra. All of the $\pi\text{-}C_5H_5Mo(CO)L_2X$ compounds apparently exist in primarily one isomeric form in solution; their PMR spectra, which exhibited a sharp triplet resonance for the $-OCH_2-$ protons of the phosphite ligands and a single sharp $\pi\text{-}C_5H_5$ proton signal, indicated a predominantly *trans* arrangement of the phosphite ligands at room temperature.

INTRODUCTION

Previous investigations[2-8] of the reaction of $\pi\text{-}C_5H_5Mo(CO)_3X$ (X = halogen) compounds with various ligands have shown that neutral and/or ionic species of varying degrees of substitution may be formed. Although reaction of the related $\pi\text{-}C_5H_5Fe(CO)_2X$ compounds with tertiary alkyl and aryl phosphines results in either carbonyl replacement or halogen displacement and reaction with tertiary alkyl or aryl phosphites usually leads to carbonyl replacement only[9], no such generalizations have yet been made concerning the molybdenum systems. The degree of substitution that can be achieved using a given ligand cannot easily be predicted[8], and the possibility of the formation of isomeric species complicates the process of characterizing reaction products[10].

We examined the nature of the reaction between the bicyclic phosphite esters $P(OCH_2)_3CR$ (R = CH_3, C_2H_5, or C_3H_7) and $\pi\text{-}C_5H_5Mo(CO)_3X$ (X = Cl, Br, or I) compounds to determine whether neutral or ionic, or both, types of products would be formed and to ascertain the degree of substitution that could be achieved using constrained phosphite ligands. The matter of overwhelming interest, however,

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was whether both isomeric forms of mono- and disubstituted neutral species could be prepared and isolated. Because Faller et al.[11], had observed $^{31}P-\pi-C_5H_5$ coupling in the PMR spectra of both cis and trans isomers of some $\pi-C_5H_5Mo(CO)_2LX$ (L=phosphine) complexes, the examination of the PMR spectra of any such phosphite-substituted complexes for similar violations of the "rule of thumb" criterion[7] for assignment of stereochemistry became particularly important. Finally, the assignment of stereochemistry to disubstituted $\pi-C_5H_5Mo(CO)L_2X$ complexes would be of critical interest in order to establish clear criteria to aid in such assignment for other complexes.

RESULTS AND DISCUSSION

The mono- and dicarbonyl derivatives of the type $\pi-C_5H_5Mo(CO)_2LX$ and $\pi-C_5H_5Mo(CO)L_2X$ are solids that exhibit decomposition only after standing in air for several days or longer; however, impurities accelerate decomposition. They readily dissolve in common chlorinated organic solvents, acetone, and benzene at room temperature to give solutions which show decomposition within one or two hours. The solubilities appear to vary according to the nature of the alkyl "tail" of the phosphite ligand, viz., $C_3H_7>C_2H_5>CH_3$. Qualitatively, there appears to be no significant difference in the degree of solubility in a given solvent between related mono- and dicarbonyl compounds. The colors of the solid complexes are dependent on the nature of the halogen group and vary from rust-brown for iodides to deep yellow for chlorides.

Infrared spectral data for the complexes are presented in Table 1. Two bands, a very intense lower-frequency band and a medium-intensity higher-frequency band, were observed for each of the dicarbonyl complexes. Each of the monocarbonyl compounds exhibited only a single, somewhat broad, medium-intensity absorption in the CO stretching region.

Compounds having the general formula $\pi-C_5H_5Mo(CO)_{3-n}L_nX$ may be formally considered to be seven-coordinate complexes of molybdenum with the $\pi-C_5H_5$ ring occupying three coordination positions. Recent crystallographic data[13,14] have established that the idealized lowest-energy configuration of such
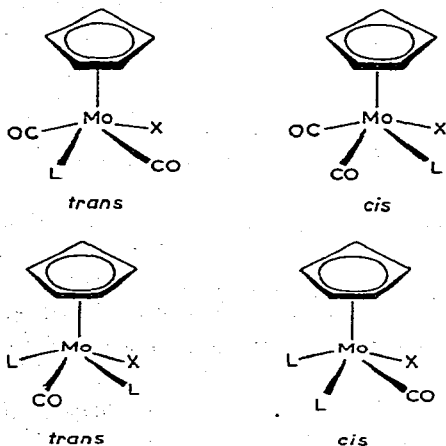
TABLE 1

SPECTRAL DATA FOR STARTING MATERIALS AND PHOSPHITE ESTER COMPLEXES[a]

Compound	Infrared ν(CO) (cm⁻¹)	Proton magnetic resonance						
		π-C$_5$H$_5$[b]	J(PH)	–OCH$_2$–[c]	J(POCH)	H_γ[d]	H_β	H_α
π-C$_5$H$_5$Mo(CO)$_3$Cl[e]	2050, 1991, 1969							
π-C$_5$H$_5$Mo(CO)$_3$Br[e]	2045, 1989, 1968							
π-C$_5$H$_5$Mo(CO)$_3$I[f]	2045, 1978, 1962							
P(OCH$_2$)$_3$CCH$_3$				3.93	1.8	0.73		
P(OCH$_2$)$_3$CC$_2$H$_5$				3.96	1.6	0.81	0.90	
P(OCH$_2$)$_3$CC$_3$H$_7$				3.94	1.9	0.87	0.96	1.08
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CCH$_3$]Cl	2001 m[g], 1918 vs	cis 5.49	0.0	4.30	5.0	0.82		
		trans 5.37	2.0	4.27	5.0	0.82		
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CC$_2$H$_5$]Cl	2001 m, 1918 vs	cis 5.50	0.0	4.34	4.8	0.86	0.98	
		trans 5.37	2.0	4.30	5.0	0.86	0.98	
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CC$_3$H$_7$]Cl	2001 m, 1918 vs	cis 5.49	0.0	4.35	4.9	0.92	1.01	1.17
		trans 5.38	2.2	4.32	5.0	0.92	1.01	1.17
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CCH$_3$]Br	1997 m, 1916 vs	5.38	2.4	4.31	5.0	0.84		
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CC$_2$H$_5$]Br	1997 m, 1916 vs	5.37	2.0	4.33	5.1	0.87	0.98	
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CC$_3$H$_7$]Br	1997 m, 1916 vs	5.39	2.3	4.34	5.0	0.93	1.01	1.17
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CCH$_3$]I	1988 m, 1912 vs	5.37	2.2	4.32	5.2	0.83		
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CC$_2$H$_5$]I	1988 m, 1912 vs	5.34	2.0	4.32	5.2	0.86	0.99	
π-C$_5$H$_5$Mo(CO)$_2$[P(OCH$_2$)$_3$CC$_3$H$_7$]I	1988 m, 1912 vs	5.35	2.0	4.32	5.0	0.92	1.00	1.14
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CCH$_3$]$_2$Cl	1860 m	5.32	0.0	4.27	4.5	0.78		
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_2$H$_5$]$_2$Cl	1862 m	5.33	0.0	4.29	4.6	0.83	0.95	
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_3$H$_7$]$_2$Cl	1861 m	5.32	0.0	4.28	4.8	0.91	0.99	1.15
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CCH$_3$]$_2$Br	1863 m	5.29	0.0	4.27	4.6	0.78		
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_2$H$_5$]$_2$Br	1864 m	5.28	0.0	4.30	4.8	0.84	0.99	
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_3$H$_7$]$_2$Br	1863 m	5.27	0.0	4.28	4.9	0.90	0.98	1.14
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CCH$_3$]$_2$I	1866 m	5.24	0.0	4.25	4.5	0.77		
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_2$H$_5$]$_2$I	1866 m	5.23	0.0	4.26	4.5	0.84	1.00	
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_3$H$_7$]$_2$I	1867 m	5.23	0.0	4.28	4.5	0.91	1.00	1.14

[a] Infrared spectra of all phosphite ester complexes recorded in acetonitrile. All PMR measurements made on CDCl$_3$ solutions at ambient temperature; chemical shifts expressed in ppm (δ) downfield with respect to tetramethylsilane as internal standard. J values in Hz. [b] Sharp singlet for mono- and tricarbonyl compounds and for cis-dicarbonyl isomers; sharp doublet for trans-dicarbonyl compounds. [c] Sharp doublet for cis- and trans-dicarbonyl compounds; sharp triplet for monocarbonyl compounds. [d] R group "tail" protons designated as –CH$_\alpha$CH$_\beta$CH$_\gamma$; where R ≠ CH$_3$, centers of main multiplet systems reported. [e] Recorded in cyclohexane; ref. 12. [f] Recorded in hexane; ref. 4. [g] Recorded in hexane; ref. 4.

TABLE 2

PREPARATIVE, ANALYTICAL, AND CONDUCTANCE DATA FOR COMPLEXES

Complex	Preparation		Analysis found (calcd.) (%)		Conductivity	$M \times 10^{-3}$
	$\pi\text{-}C_5H_5Mo(CO)_3X$ [g(mmol)]	L [g(mmol)]	C	H	$\Lambda(cm^2 \cdot \Omega^{-1} \cdot mole^{-1})^a$	
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]Cl^b$	0.20 (0.71)	0.09 (0.61)	36.00 (35.98)	3.63 (3.52)	4.20	0.769
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CC_2H_5]Cl^b$	0.20 (0.71)	0.10 (0.62)	37.48 (37.66)	3.84 (3.89)	4.10	0.680
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CC_3H_7]Cl^b$	0.20 (0.71)	0.12 (0.68)	39.19 (39.23)	4.09 (4.23)	4.44	0.952
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]Br$	0.20 (0.62)	0.09 (0.61)	32.34 (32.39)	2.97 (3.17)	4.26	0.899
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CC_2H_5]Br$	0.20 (0.62)	0.08 (0.49)	33.94 (34.01)	3.52 (3.51)	4.02	0.871
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CC_3H_7]Br$	0.20 (0.62)	0.10 (0.57)	35.30 (35.54)	3.66 (3.84)	3.91	0.761
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CCH_3]I$	0.20 (0.54)	0.06 (0.41)	29.23 (29.29)	2.78 (2.87)	4.15	0.561
$\pi\text{-}C_5H_5Mo(CO)_2[P(OCH_2)_3CC_2H_5]I$	0.20 (0.54)	0.09 (0.56)	30.75 (30.85)	3.16 (3.19)	3.03	0.672
$\pi\text{-}C_5H_5Mo(CO)_1[P(OCH_2)_3CC_3H_7]I$	0.20 (0.54)	0.09 (0.51)	32.03 (32.33)	3.20 (3.49)	4.45	0.669
$\pi\text{-}C_5H_5Mo(CO)[P(OCH_2)_3CCH_3]_2Cl$	0.20 (0.71)	0.21 (1.42)	36.93 (36.91)	4.56 (4.45)	3.74	0.768
$\pi\text{-}C_5H_5Mo(CO)[P(OCH_2)_3CC_2H_5]_2Cl$	0.20 (0.71)	0.23 (1.42)	39.22 (39.40)	4.71 (4.96)	5.14	0.605
$\pi\text{-}C_5H_5Mo(CO)[P(OCH_2)_3CC_3H_7]_2Cl$	0.20 (0.71)	0.26 (1.48)	41.93 (41.65)	5.62 (5.42)	3.98	0.611
$\pi\text{-}C_5H_5Mo(CO)[P(OCH_2)_3CCH_3]_2Br$	0.20 (0.62)	0.19 (1.28)	33.85 (34.00)	3.99 (4.10)	5.51	0.764

π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_2$H$_5$]$_2$Br	0.20 (0.62)	0.20 (1.23)	36.49 (36.45)	4.47 (4.59)	5.32	0.776
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_3$H$_7$]$_2$Br	0.20 (0.62)	0.22 (1.25)	38.55 (38.67)	4.97 (5.03)	6.30	0.644
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CCH$_3$]$_2$I	0.20 (0.54)	0.16 (1.08)	31.29 (31.39)	3.75 (3.79)	12.11	0.516
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_2$H$_5$]$_2$I	0.20 (0.54)	0.17 (1.05)	33.87 (33.77)	4.04 (4.25)	12.93	0.713
π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CC$_3$H$_7$]$_2$I	0.20 (0.54)	0.19 (1.08)	35.69 (35.95)	4.48 (4.68)	11.70	0.611

[a] All conductances measured in acetone solution at 25.0°. Value for the 1/1 electrolyte tetrabutylammonium bromide: 135 cm² Ω⁻¹ mole⁻¹ in acetone. [b] These three complexes occur as inseparable mixtures of cis–trans isomers. All other π-C$_5$H$_5$Mo(CO)$_2$LX complexes as the trans isomer only. All π-C$_5$H$_5$Mo(CO)I$_2$X complexes were isolated in one form only.

compounds would involve the four remaining ligands located approximately at the corners of a square such that a structure similar to a square pyramid would result. The possibility of the existence of two geometric isomers is suggested by this square-pyramidal geometry.

It is expected that each π-$C_5H_5Mo(CO)_2LX$ isomer would exhibit two infrared-active $\nu(CO)$ vibrations; the higher-frequency band would be the symmetric stretching mode[4]. Although the frequencies of the two CO bands of each isomer are almost always coincident[4], isomers may be distinguished on a qualitative basis by a comparison of the observed intensities of the two bands that appear in the infrared solution spectra. The observance of a very intense lower-frequency band and a medium-intensity high-frequency band for all of the monosubstituted complexes was evidence for the predominance in solution of the *trans* isomeric form (Table 1). The appearance of two bands was also evidence that these compounds are the neutral covalent π-$C_5H_5Mo(CO)_2LX$ species, and not ionic forms, in solution. Verification was provided by conductance measurements (Table 2).

Isomerization in solution may be expected to occur for π-$C_5H_5Mo(CO)L_2X$ complexes. However, only one $\nu(CO)$ mode for either isomer would be expected to arise[3-5,15], and if each isomer were present, the two modes would be most likely coincident. Thus, the appearance of a single CO absorption in the spectra of the disubstituted complexes (Table 1) allowed no inferences concerning isomerism to be drawn but did strongly imply that the complexes are the neutral covalent π-$C_5H_5Mo(CO)L_2X$ species rather than ionic forms. Confirmation of this was provided by conductance measurements (Table 2).

Several other conclusions may be drawn from the infrared data for these complexes. For all compounds, the recorded frequencies were lower than for the respective starting tricarbonyl halide compound. Moreover, the $\nu(CO)$ absorption energy was lowered upon going from the dicarbonyl to the monocarbonyl complexes. This behavior is typical for the replacement of CO groups with phosphites in numerous carbonyl complexes and may be rationalized in the accepted manner as a combination of π and σ effects[16,17]. The $\nu(CO)$ absorption(s) of these compounds occur(s) at higher frequency (frequencies) than for analogous complexes wherein the ligand is one of several alkyl or aryl phosphines or $P(OCH_3)_3$[3-5,10,11,13-15]. It was found for the π-$C_5H_5Mo(CO)_2LX$ complexes that the order in the position of the $\nu(CO)$ frequencies varied as expected $(Cl > Br > I)$ from electronegativity considerations. For the π-$C_5H_5Mo(CO)L_2X$ complexes, the reverse order $(I > Br > Cl)$ in the position of the $\nu(CO)$ absorptions was noted. This result is similar to that observed for the complexes where $L = P(C_2H_5)_3$[3] and $P(OCH_3)_3$[3]. The magnitudes of difference in the $\nu(CO)$ frequencies between the I and Cl complexes are 20 cm^{-1} for $P(C_2H_5)_3$, 8 cm^{-1} for $P(OCH_3)_3$, and 5 ± 1 cm^{-1} for the three constrained phosphites. This suggests that the unexpected order may partly result from steric considerations. The coordination properties of the bridgehead phosphorus were unaffected by the nature of the alkyl "tail" group as indicated by the similarity in $\nu(CO)$ positions for a series of mono- or dicarbonyl complexes of each of the three ligands.

The PMR spectra (Table 1) of both the mono- and dicarbonyl complexes are of especial interest. For the complexes π-$C_5H_5Mo(CO)_2LX$, where X = Br or I, a sharp doublet for the π-C_5H_5 protons and a sharp doublet for the $-OCH_2-$ protons of the ligand were observed. For the π-$C_5H_5Mo(CO)_2LCl$ compounds, a sharp

doublet and a separate sharp singlet for the π-C$_5$H$_5$ protons were observed; a doublet of doublets appeared for the $-$OCH$_2-$ protons of the ligand. The PMR spectra of all the π-C$_5$H$_5$Mo(CO)L$_2$X compounds were similar and showed a sharp singlet for the π-C$_5$H$_5$ protons and a sharp triplet for the $-$OCH$_2-$ protons of the two phosphite ligands.

It was tentatively concluded from the infrared spectra of the π-C$_5$H$_5$Mo-(CO)$_2$LX complexes that all of them existed in solution predominantly as the *trans* isomer. The observation of only a doublet π-C$_5$H$_5$ resonance in the PMR spectra of the bromo and iodo dicarbonyl derivatives confirms this conclusion. The appearance of both a singlet and doublet π-C$_5$H$_5$ resonance in the solution spectra of the π-C$_5$H$_5$Mo(CO)$_2$LCl compounds indicates the presence of both *cis* and *trans* isomeric forms. A comparison of the signal intensities indicates that the ratio of the amount of *trans* isomer present to that of *cis* is approximately 3/1. Thus, it is not surprising that the intensities of the two ν(CO) bands were unequal (with the lower-energy band having the greatest intensity) and that the infrared spectra failed to unequivocally indicate the presence of the *cis* form. The lack of a singlet π-C$_5$H$_5$ signal in the PMR spectra of the bromo and iodo compounds, even after long standing, suggested the absence of significant amounts of *cis* isomer. These observations are in agreement with the conclusion reached by Faller and Anderson[10], who, from a consideration of thermodynamic data for *cis-* and *trans*-π-C$_5$H$_5$Mo(CO)$_2$LX complexes, found that the *trans* configuration is favored for the iodo compounds more than for the chloro derivatives.

A single resonance for the π-C$_5$H$_5$ protons in π-C$_5$H$_5$Mo(CO)L$_2$X complexes has been reported in may cases[3−5]. However, King *et al.*, have reported the presence of two separate singlets as evidence for both *cis* (L groups *cis*) and *trans* forms of π-C$_5$H$_5$Mo(CO)[(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$]Cl in solution[18], while a multiplet and a singlet have been observed for a *cis* and *trans* mixture of π-C$_5$H$_5$Mo(CO)[P-(C$_6$H$_5$)$_3$]$_2$NCO[13]. Wright and Mawby observed two separate sharp singlets at low temperature for the π-C$_5$H$_5$ protons of π-C$_5$H$_5$Mo(CO)[P(C$_6$H$_5$)$_2$CH$_3$]$_2$Cl which they suggested arose from the presence of both *cis* and *trans* isomeric forms[19]. Their studies showed that a temperature-dependent equilibrium between isomers existed and that as the temperature was raised, the two π-C$_5$H$_5$ proton signals broadened and then collapsed to a singlet indicative of the predominance of one isomer (*trans*) at ambient temperature[19]. Broad, temperature-dependent π-C$_5$H$_5$ resonances observed when L $=$ P(C$_6$H$_5$)$_3$, P(C$_2$H$_5$)$_3$, or (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ and X $=$ Cl or I are proposed to arise from restricted rotation of the π-C$_5$H$_5$ moiety[3]. Thus, it is apparent that the "rule of thumb"[7] applied to dicarbonyl compounds is not applicable when considering monocarbonyl systems. The observation of a single sharp π-C$_5$H$_5$ resonance for the complexes where L $=$ P(OCH$_2$)$_3$CR (R $=$ CH$_3$, C$_2$H$_5$, C$_3$H$_7$) and X $=$ Cl, Br, or I is tentatively taken as evidence of the presence in solution of only a single isomer. The absence of broadening suggests a lack of restricted rotation of the π-C$_5$H$_5$ ring[3].

For the $-$OCH$_2-$ protons of the phosphite ligands, a well-defined 1/2/1 triplet resonance was observed in every case. In a *cis* arrangement, the phosphite ligands would be non-equivalent and would be expected to yield two separate doublets (J(POCH)) or multiplets (J(POCH) and J(PP)), while the *trans* form would give rise to a single doublet or multiplet for the equivalent ligands. Verification that the observed

triplet results only from coupling and not from the overlap of two separate resonances was obtained from a comparison of the 60 and 100 MHz spectra. P–P spin coupling for *trans*-P(OCH$_2$)$_3$CR–Mo systems is much stronger than for *cis* arrangements and typically yields an apparent triplet −OCH$_2$− resonance[20]. If *cis–trans* isomerism were occurring at a rapid rate, an averaging effect would yield a resonance signal typical of "intermediate" P–P coupling rather than a 1/2/1 triplet for strong coupling. Therefore, if isomerism is occurring at room temperature, the equilibrium for the π-C$_5$H$_5$Mo(CO)[P(OCH$_2$)$_3$CR]$_2$X complexes most likely lies far towards the *trans*-phosphite arrangement.

The chemical shift of the π-C$_5$H$_5$ signal varies with the degree of CO substitution (δ tricarbonyl > dicarbonyl > monocarbonyl) in agreement with the explanation offered for the change in ν(CO); varies within a tricarbonyl or monocarbonyl series (δ Cl > Br > I) as expected from a consideration of the electronegativity of the halogen groups; and is independent of the nature of the alkyl "tail" of the phosphite. Unlike previously reported dicarbonyl series[3,7,10,11], the π-C$_5$H$_5$ δ values for the bicyclic phosphite complexes are independent of the nature of the halogen. The −OCH$_2$− resonance positions for the monocarbonyl complexes are slightly less deshielded with respect to the free ligand than are those of the dicarbonyl compounds. This suggests a greater degree of π-backbonding or lesser σ-donation of the ligand in the monocarbonyl complexes.

As noted for other metal carbonyl complexes[21], the J(POCH) values for the ligands increase upon coordination. This increase is more likely to result from a change in the effective nuclear charge of the phosphorus induced by an increase in coordination number rather than from a change in the O–P–O bond angles of the constrained phosphite. The decrease in J(POCH) value in the monocarbonyl complexes compared to the dicarbonyl compounds indicates a decrease in net charge donation (σ–π) from the ligand to the metal. The J(PH) values for the dicarbonyl complexes are similar in magnitude (0.9–2.3 Hz) to those reported for other π-C$_5$H$_5$Mo(CO)$_2$LX compounds exhibiting a *trans*-L-X arrangement[10].

EXPERIMENTAL

π-C$_5$H$_5$Mo(CO)$_3$Cl and π-C$_5$H$_5$Mo(CO)$_3$I were prepared according to procedures previously described[22,23]. The dimer [π-C$_5$H$_5$Mo(CO)$_3$]$_2$, required for the preparation of these tricarbonyl halides, was purchased from the Pressure Chemical Company and was used as received. π-C$_5$H$_5$Mo(CO)$_3$Br was prepared in the following manner. A mixture of 2.00 g (4.08 mmol) [π-C$_5$H$_5$Mo(CO)$_3$]$_2$, 100 ml CHCl$_3$, and 20 ml 48% HBr was stirred magnetically under a helium flush while being irradiated for 3 to 4 h using two General Electric 60-watt light bulbs. Upon cooling, distilled water was added to the mixture, which was then shaken in a separatory funnel. The CHCl$_3$ layer was withdrawn and was reduced to near dryness by vacuum evaporation. The residue was dissolved in approximately 30 ml CH$_2$Cl$_2$, and the resulting solution was passed through a small column of Woelm neutral alumina. The CH$_2$Cl$_2$ eluate was reduced to a small volume by vacuum evaporation; addition of n-pentane precipitated the product, which was collected on the suction filter and washed with n-pentane. The orange crystals were dried and stored under vacuum. A PMR spectrum of the product in CDCl$_3$ solution showed a sharp singlet at δ 5.25 ppm for the π-C$_5$H$_5$ protons.

A Hanovia 200-watt, Model 654A-10, ultraviolet light (maximum intensity in a range from 3130 to 5780 Å) was used for all photochemical preparations. The light source was placed parallel to the quartz reaction tube (24 cm in height with an inside diameter of 2.5 cm) at a distance of approximately 6 cm.

The chromatography column used to purify the complexes was 10 cm in height with an inside diameter of 1 cm. Woelm neutral alumina was loaded on the column from a CHCl$_3$ slurry until a column approximately 4 cm high was obtained.

Carbon and hydrogen contents were ascertained by combustion using an F and M Carbon–Hydrogen–Nitrogen Analyzer, Model 185. Conductivities were determined for 10^{-3} M acetone solutions using an Industrial Instruments RC16B2 conductivity bridge and a Sargent Model S-29885 conductivity cell with a cell constant of 0.679138 cm^{-1}. All conductivities were measured at a temperature of 25.0°.

The infrared spectra in the region of 4000 to 600 cm^{-1} were obtained with a Perkin–Elmer Model 621 double-beam grating spectrophotometer using sodium chloride optics. Spectra were recorded for acetonitrile solutions contained in a 0.2–0.3 mm sodium chloride cell. All spectra were recorded *versus* air in the reference beam with the exception of certain spectra which were recorded *versus* pure acetonitrile in the reference beam. All spectra were calibrated with polystyrene film.

The PMR spectra of all complexes were obtained using a Varian Associates Model A-60 spectrometer. Spectra of selected complexes were also recorded using a Varian Associates HA-100 spectrometer. Spectra were recorded for approximately 15 to 20% CDCl$_3$ solutions at normal probe temperature; tetramethylsilane was employed as an internal reference for all spectra.

Preparation of phosphite ester complexes

One general method was employed to prepare all the π-C$_5$H$_5$Mo(CO)$_2$LX and π-C$_5$H$_5$Mo(CO)L$_2$X (L = phosphite ester; X = Cl, Br, or I) complexes. A mixture of the appropriate phosphite ester and π-C$_5$H$_5$Mo(CO)$_3$X compound in 30 ml benzene was placed in a quartz tube under a flush of nitrogen. The solution was magnetically stirred and was irradiated with ultraviolet light for the appropriate time [2 h for π-C$_5$H$_5$Mo(CO)$_2$LX complexes and 6 h for π-C$_5$H$_5$Mo(CO)L$_2$X complexes]. Upon completion of the reaction, the volume of the solution was reduced to a few ml by vacuum evaporation, and then a small amount of CHCl$_3$ was added. The CHCl$_3$ solution was passed through a column of Woelm neutral alumina, and the eluate was reduced to a volume of a few ml by vacuum evaporation. One or two ml of CCl$_4$ were added, and then n-pentane was slowly added, in portions while continuously swirling the contents of the flask, until crystallization was complete. The product was collected on the suction filter, washed with n-pentane and was dried and stored under vacuum. Preparative data for each of the complexes are summarized in Table 2, along with conductance data and results for the carbon–hydrogen analyses.

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