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A New Type of Isomerism in Some Phosphine and Phosphite Derivatives of the Metal Carbonyls

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A new type of isomerism is reported for a wide variety of transition metal carbonyl complexes of the general type (π–Ring)M(CO)(L)X where L is a tertiary phosphine or phosphite ligand. The effects of solvent and temperature upon this isomerism are described, and possible reasons for it are discussed.

Introduction

Infrared and n.m.r. spectroscopy show that derivatives of the general type $\pi-C_5H_5M(CO)(L)X$ exhibit conformational isomerism due to restricted rotation about the M–X bond (*e.g.* in $\pi-C_5H_5Fe(CO)_2SiCl_2Me$,[1] $\pi-C_5H_5Fe(CO)_2(\sigma-C_5H_5)$,[2] and $\pi-C_5H_5Ru(CO)_2(\sigma-C_5H_5)$[2]), optical isomerism due to an asymmetric metal atom (*e.g.* in $\pi-C_5H_5Fe(CO)(PMe_2Ph)COMe$,[3] and $\pi-C_5H_5Mn(NO)(PPh_3)(COY)$ where Y^- is the L-mentholate anion[4]), or both (*e.g.* $\pi-C_5H_5Fe(CO)(PPh_3)(COCH_2SiMe_3)$[5]).

We have previously reported that there are two absorption bands in the infrared spectra of $\pi-C_5H_5Fe(CO)[P(OMe)_3]I$ and related compounds which may be attributed to C–O stretching vibrations.[6] Subsequent work, which is described herein, shows that similar behaviour is exhibited by a wide variety of compounds of the general types (π–Ring)M(CO)[$P(OR)_3$]X or (π–Ring)$M(CO)_2[P(OR)_3]$ (see Tables I and II for a list of these). It is suggested that this type of isomerism is due either to restricted rotation about the M–P bond, or to conformational isomerism within the $P(OR)_3$ ligands. The absence of isomerism in complexes of $P(OCH_2)_3CMe$ alone amongst those of the trialkylphosphites, tends to favour the second of these explanations.

Experimental Section

$[\pi-C_5H_5Fe(CO)_2]_2$, $[\pi-MeC_5H_4Fe(CO)_2]_2$, $\pi-MeC_5H_4Mn(CO)_3$, $Fe(CO)_5$ and $Cr(CO)_6$ were purchased from Strem Chemicals Inc.. Other chemicals were obtained from the usual commercial sources. Published methods were used to prepare $\pi-C_5H_5Fe(CO)_2Br$,[7] $\pi-C_5H_5Fe(CO)_2I$,[8,9] $\pi-CH_3C_5H_4Fe(CO)_2Cl$,[6] $\pi-CH_3C_5H_4Fe(CO)_2Br$,[6] $\pi-CH_3C_5H_4Fe(CO)_2I$,[6] $\pi-C_5H_5Ru(CO)_2I$,[10] $\pi-C_6H_6Cr(CO)_3$,[11] $\pi-C_5H_5Mn(CO)_2(NO)$,[12] and the ligand $P(OCH_2)_3CMe$.[13]

The preparation of $\pi-C_5H_5Fe(CO)[P(OPh)_3]I$ by a thermal reaction between $\pi-C_5H_5Fe(CO)_2I$ and $P(OPh)_3$ has been described.[6] All other compounds given in Table II were prepared similarly except for $\pi-C_5H_5Fe(CO)(SbPh_3)I$, $\pi-CH_3C_5H_4Fe(CO)(AsPh_3)I$, $\pi-CH_3C_5H_4Mn(CO)_2L$ [L = $P(OMe)_3$ and $P(OPh)_3$], $\pi-C_6H_6Cr(CO)_2[P(OMe)_3]$, and $\pi-C_5H_5Mo(CO)(NO)[P(OMe)_3]$. For these a photochemical method similar to that of Strohmeier was used.[14] The products were isolated by removal of the solvents from the filtered reaction mixtures. In some instances, they were purified by chromatography followed by recrystallization from benzene/hexane or methanol/water mixtures. In other cases, recrystallization was sufficient. Melting point and analytical data for most compounds are given in Table I. Some others were very unstable and did not give satisfactory analyses.

Infrared spectra were run on Perkin Elmer 337, 457 and 125 spectrometers in the 1700-2100 cm^{-1} region. They were calibrated with DCl and water vapour[15] so that peak positions are accurate to within ± 1 cm^{-1}. Variable temperature spectra were obtained using a cell manufactured by Research and Industrial Instruments Co.. The spectra are summarised in Table II.

Results and Discussion

For all compounds in Table II, the distributions of the ligands about the metal atoms are probably similar to those found by X-ray diffraction for $\pi-$

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Table I. Analytical and melting point data for the complexes

Compound	M.p. (°C)[a]	Found % C	Found % H	Found % X	Required % C	Required % H	Required % X
π–$C_5H_5Fe(CO)[P(OCH_3)_3]I$	82-84	27.5	3.4	31.6	27.0	3.5	31.5
π–$C_5H_5Fe(CO)[P(OC_6H_5)_3]I$	136-138	49.4	3.4	—	49.2	3.4	—
π–$CH_3C_5H_4Fe(CO)[P(n–C_4H_9)_3]I$	42-44	46.8	7.1	25.3	46.4	6.9	25.8
π–$CH_3C_5H_4Fe(CO)[P(C_6H_5)_3]I$	114-115	54.0	4.4	23.1	54.2	3.2	22.9
π–$CH_3C_5H_4Fe(CO)[P(OCH_3)_3]I$	44-46	28.5	3.7	30.2	29.0	3.8	30.6
π–$CH_3C_5H_4Fe(CO)[P(O–i–C_3H_7)_3]I$	36-38	38.6	5.8	—	38.6	5.6	—
π–$CH_3C_5H_4Fe(CO)[P(OCH_2)_3C\,.\,CH_3]I$	160-2 (d)	33.7	4.3	—	32.8	3.7	—
π–$CH_3C_5H_4Fe(CO)[P(OC_6H_5)_3]I$	102-103	50.0	3.8	21.4	50.0	3.7	21.2
π–$C_5H_5Fe(CO)[Sb(C_6H_5)_3]I$	128-129	45.4	3.5	20.5	45.8	3.7	21.3
π–$CH_3C_5H_4Fe(CO)[As(C_6H_5)_3]I$	94 (d)	50.2	3.6	21.4	50.3	3.7	21.3
π–$C_5H_5Fe(CO)[P(OCH_3)_3]Br$	84-85 (d)	30.5	4.0	21.6	30.6	4.0	22.6
π–$CH_3C_5H_4Fe(CO)[P(OC_6H_5)_3]Br$	108-112 (d)	54.3	4.1	14.7	53.8	4.0	14.4
π–$CH_3C_5H_4Fe(CO)[P(OCH_3)_3]Cl$			unstable liquid				
π–$CH_3C_5H_4Fe(CO)[P(OC_6H_5)_3]Cl$	102-104	59.3	4.3	—	59.0	4.3	—
π–$C_7H_9Fe(CO)[P(OCH_3)_3]I$	51-53	31.0	4.3	30.0	30.9	4.2	29.7
π–$C_7H_9Fe(CO)[P(OC_2H_5)_3]I$	66-67	36.2	5.2	—	35.8	5.1	—
π–$C_7H_9Fe(CO)[P(O–i–C_3H_7)_3]I$	72-73	39.4	6.1	28.7	39.9	5.9	28.4
π–$C_5H_5Ru(CO)[P(OCH_3)_3]I$	77-78	24.7	3.3	—	24.3	3.2	—
π–$C_5H_5Ru(CO)[P(OC_6H_5)_3]I$	170-172	46.0	3.5	—	45.6	3.2	—
π–$CH_3C_5H_4Mn(CO)_2[P(OCH_3)_3]$			unstable liquid				
π–$CH_3C_5H_4Mn(CO)_2[P(OC_6H_5)_3]$	75-76	62.8	4.4	—	62.4	4.4	—
π–$C_6H_6Cr(CO)_2[P(OCH_3)_3]$	136	46.0	4.9	16.4	46.5	4.9	16.8
π–$C_5H_5Mo(CO)(NO)[P(OCH_3)_3]$							

[a] (d) ≡ melts with decomposition.

Table II. Infrared spectra of the Complexes in the ν(CO) and ν(NO) regions. Peak Positions (cm^{-1}) and relative peak heights in Parentheses. The Solvent is heptane unless it is stated otherwise

Compound	Absorption bands[b]			
π–$C_5H_5Fe(CO)[P(OCH_3)_3]I$	1978 (4.9)			1966 (10)
π–$C_5H_5Fe(CO)[P(OC_6H_5)_3]I$		1988		
π–$CH_3C_5H_4Fe(CO)[P(n–C_4H_9)_3]I$		1950		
π–$CH_3C_5H_4Fe(CO)[P(C_6H_5)_3]I$	1961 (10)			1955 (8.5)
π–$CH_3C_5H_4Fe(CO)[P(OCH_3)_3]I$	1976 (4.3)			1963 (10)
π–$CH_3C_5H_4Fe(CO)[P(O–i–C_3H_7)_3]I$	1972 (5.4)			1955 (10)
π–$CH_3C_5H_4Fe(CO)[P(OCH_2)_3CCH_3]I$[c]		1976		
π–$CH_3C_5H_4Fe(CO)[P(OC_6H_5)_3]I$		1983		
π–$C_5H_5Fe(CO)[Sb(C_6H_5)_3]I$[d]		1954		
π–$CH_3C_5H_4Fe(CO)[As(C_6H_5)_3]I$[d]		1951		
π–$C_5H_5Fe(CO)[P(OCH_3)_3]Br$	1982 (5.1)			1971 (10)
π–$CH_3C_5H_4Fe(CO)[P(OC_6H_5)_3]Br$		1986		
π–$CH_3C_5H_4Fe(CO)[P(OCH_3)_3]Cl$	1977 (5.2)			1965 (10)
π–$CH_3C_5H_4Fe(CO)[P(OC_6H_5)_3]Cl$		1987		
π–$C_7H_9Fe(CO)[P(OCH_3)_3]I$	1984 (3.0)			1970 (10)
π–$C_7H_9Fe(CO)[P(OC_2H_5)_3]I$	1981 (4.1)			1966 (10)
π–$C_7H_9Fe(CO)[P(O–i–C_3H_7)_3]I$	1980 (5.6)			1961 (10)
π–$C_5H_5Ru(CO)[P(OCH_3)_3]I$	1985 (7.9)			1975 (10)
π–$C_5H_5Ru(CO)[P(OC_6H_5)_3]I$		1993		
π–$CH_3C_5H_4Mn(CO)_2[P(OCH_3)_3]$	1955 (3.5)	1949 (8)	1895 (3.7)	1887 (10)
π–$CH_3C_5H_4Mn(CO)_2[P(OC_6H_5)_3]$	1964 (sh)	1960 (9)	1905 (sh)	1901 (10)
π–$C_6H_6Cr(CO)_2[P(OCH_3)_3]$	1922 (sh)	1917 (10)	1876 (3)	1867 (9)
π–$C_5H_5Mo(CO)(NO)[P(OCH_3)_3]$	1932 (10)	1926 (9.0)	1640 (10)	1636 (8.5)

[a] sh = shoulder. [b] carbon disulphide solution. [c] chloroform solution.

$C_6H_6Cr(CO)_3$,[16] π–$C_5H_5Mn(CO)_3$,[17] π–$C_5H_5Fe(CO)_2$-$SnPh_3$,[18] and many related compounds. Those complexes which contain only one CO ligand sometimes show two absorption bands in their infrared spectra which are due to ν(CO) vibrations. Similarly, those which contain two carbonyl groups may show four absorption bands at *ca.* 2000 cm^{-1}. Consequently, it is clear that both types exhibit some form of isomerism.

The ν(CO) absorption band in the infrared spectrum of π–$MeC_5H_4Fe(CO)[P(OMe)_3]I$ is clearly resolved into two components for *n*-heptane solutions. They may be completely separated by a graphical method on the assumption that both are symmetrical about their band centres. Variable temperature studies using solutions of this compound in pentane at −80°C and decalin at *ca.* 150°C show that the relative peak heights of these components vary from 0.285 : 1 to 0.657 : 1 respectively. That at higher frequency is the weaker, and there are no comparable changes in relative band widths. Variable solvent

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studies were less conclusive due to increased absorption band widths in the more polar solvents.[19] These tend to obscure fine detail. The two absorption bands in the spectrum of this compound are well-resolved in heptane and cyclohexane, and less well-separated in xylene, carbon disulphide or carbon tetrachloride solutions. However, only one broad, but symmetrical, absorption band is observed when chloroform is the solvent.

The isomerism is not a consequence of a particular (π–Ring) ligand, a particular group X, or a particular metal atom although variations of each of these do affect the isomer ratio. Furthermore, its occurrence in compounds which possess a plane of symmetry, *e.g.* π–$C_6H_6Cr(CO)_2[P(OMe)_3]$ suggests that it is not due to an asymmetric metal atom in derivatives such as π–$CH_3C_5H_4Fe(CO)[P(OMe)_3]I$. The ligand L is important. Isomerism has been observed in all complexes of the trialkylphoshpites which we have prepared except one. It is also shown by some of the derivatives of $P(OPh)_3$ and PPh_3, but not by those of $AsPh_3$, $SbPh_3$, PMe_3 or PBu_3.

We feel that there are two possible explanations for the observed isomerism, (a) restricted rotation about the M–P bond with the formation of eclipsed and staggered isomers, or (b) restricted rotation within the P–O–C groups of the ligand which allows two conformational isomers of L, and thus two isomers of the complex. Derivatives of $P(OCH_2)_3CMe$ are the only complexes of the trialkylphoshpites which do not exhibit isomerism. As there can be no rotation of the P–O–C groups in this ligand, it suggests that (b) is the more probable. As isomerism is not observed in $(MeO)_3PMo(CO)_5$, the π–bonded hydrocarbon ring ligand must be important. Possibly, its proximity prevents interconversion of the conformational isomers of the coordinated ligand, L.

The presence of isomers among some of the PPh_3 complexes may also be explained on the basis of isomerism within this ligand. For $AsPh_3$ and $SbPh_3$, the larger arsenic or antimony atoms may cause less restriction of the rotation of the phenyl groups, and so conformational isomerism does not occur.

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