Trimethyl Phosphite Complexes of Iron(II): Preparation, Characterisation, and Mössbauer Spectra

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The preparation of a novel series of neutral and cationic low spin iron(II) complexes containing trimethyl phosphite is reported. These complexes are more closely analogous to those of isocyanides than those of other non-chelating tertiary phosphine ligands. Mössbauer spectra show that the unexpected bonding characteristics of $P(OMe)_3$, being both a strong σ-donor and π-acceptor, account for much of this unexpected chemical behaviour. $P(OMe)_3$ preferentially displaces iodide from $Fe(CO)_2I_2\{P(OMe)_3\}_2$ to give the stable intermediate $[Fe(CO)_2I\{P(OMe)_3\}]^+$, from which carbonyl can be displaced subsequently by more phosphite yielding *trans*-$Fe(CO)I\{[P(OMe)_3\}_4]^+$. These species are isoelectronic to known manganese(I) complexes.

In a previous paper,[1] we suggested from Mössbauer parameters that $P(OMe)_3$ had very similar bonding properties to isocyanides, and appreciably stronger σ-donor and π-acceptor properties than other tertiary phosphines and phosphites. Graham [2] suggested that $P(OMe)_3$ was a strong σ-donor and π-acceptor, but comparatively few complexes of this ligand have been characterised compared to the wealth of both isocyanide and trialkyl and triaryl phosphine compounds. In particular, there are no Fe^{II} low spin complexes of $P(OMe)_3$ known at the present time which do not contain the ligands CO or H^-.

The nature of the substitution reactions [3-6] of $M(CO)_6$ ($M = Cr$, Mo, W) and $Mn(CO)_5X$ ($X = Cl$, Br, I, Me) further suggested that $P(OMe)_3$ has chemical properties distinctive from most other tertiary phosphine ligands, since an unusually high degree of carbonyl substitution could be achieved, *viz*: $Cr(CO)\{P(OMe)_3\}_5$, $Mo\{P(OMe)_3\}_6$, and $Mn(CO\{P(OMe)_3\}_4Br$. Mathieu and Poilblanc [3] observed that the ease of substitution in $M(CO)_6$ depended upon the π-acidity and varied inversely as the steric bulk of the entering phosphine ligand. However they were unable to offer a convincing explanation for the variations in substitution by $P(OMe)_3$ across the series, Cr, Mo, W. From the reactions of $Mn(CO)_5X$ ($X = Br$, Me) Treichel *et al.*[4] noted that substitution with $P(OMe)_3$ was more analogous to that with isocyanide [7,8] than other non-chelating tertiary phosphines. Other evidence for the bonding properties of $P(OMe)_3$ is discussed in a recent review [9] while recent papers on complexes of other heavier transition metals have discussed some novel n.m.r. coupling patterns.[10-12]

EXPERIMENTAL

Preparations.—All compounds were prepared under an atmosphere of nitrogen using conventional techniques. Analytical grade solvents were deaerated, but not specially dried, before use. All solids were stored under nitrogen, although all could be handled in the air for short periods without decomposition.

Trimethyl phosphite was obtained from J. T. Baker Chemical Co., and redistilled before use. Anhydrous ferrous chloride was made as in Inorganic Syntheses.[13] Iron pentacarbonyl was obtained from Alfa Inorganics, and the *cis* iron tetracarbonyl dihalides were prepared by the method of Hieber and Bader.[14]

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[1] G. M. Bancroft and E. T. Libbey, *J.C.S. Dalton*, 1973, 2103.

[2] W. A. G. Graham, *Inorg. Chem.*, 1969, **7**, 315.

[3] R. Mathieu and P. Poilblanc, *Inorg. Chem.*, 1972, **11**, 1858.

[4] P. M. Treichel and J. J. Benedict, *J. Organometallic Chem.*, 1969, **17**, 37.

[5] I. S. Butler, N. J. Coville and H. K. Spendjian, *J. Organometallic Chem.*, 1972, **43**, 185.

[6] R. H. Reimann and E. Singleton, *J. Organometallic Chem.*, 1972, **44**, C18.

[7] K. K. Joshi, P. L. Pauson and W. H. Stubbs, *J. Organometallic Chem.*, 1963, **1**, 51.

[8] P. M. Treichel, G. E. Dirreen, and H. J. Mueh, *J. Organometallic Chem.*, 1972, **44**, 339.

[9] J. G. Verkade, *Co-ordination Chem. Rev.*, 1972, **9**, 1, and references therein.

[10] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685; *ibid.*, 1693.

[11] G. M. Bancroft and E. T. Libbey, *Canad. J. Chem.*, 1973, **51**, 1482, and references therein.

[12] D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 4545, and references therein.

[13] *Inorg. Syntheses*, 1960, Vol. VI, 173.

[14] W. Hieber and G. Bader, *Z. anorg. Chem.*, 1930, **190**, 193.

Tricarbonyldi-iodo(trimethyl phosphite)iron(II), $Fe(CO)_3I_2\{P(OMe)_3\}$. Equimolar quantities of $Fe(CO)_4I_2$ and trimethyl phosphite were allowed to react in diethyl ether. Removal of the ether, under reduced pressure yielded a dark red oil that slowly crystallised when set aside for several days *in vacuo*.

Dicarbonyldi-iodobis(trimethyl phosphite)iron(II), $Fe(CO)_2I_2\{P(OMe)_3\}_2$. $Fe(CO)_4I_2$ (0·42 g, 1 mmol) and $P(OMe)_3$ (0·23 ml, 2 mmol) were added to diethyl ether (25 ml). After *ca.* 1 h of intermittent shaking the ether was removed under reduced pressure and the residual oily solid recrystallised from methanol as dark red plates (yield 0·4 g, *ca.* 60%).

The dibromo- and dichloro-compounds were prepared similarly as orange and yellow crystals, respectively.

trans-*Carbonyliodotetrakis(trimethyl phosphite)iron*(II) *iodide*, $[Fe(CO)I\{P(OMe)_3\}_4]^+I^-$. $Fe(CO)_4I_2$ (0·42 g, 1 mmol) and $P(OMe)_3$ (0·5 ml, 4 mmol) were shaken together in ether. At this stage only two carbonyls had been substituted. The ether was removed under reduced pressure and the oily residue extracted with warm methanol, and filtered. The filtrate was set aside, with occasional shaking and heating, for 2 h when the volume of methanol was reduced to *ca.* 2 ml. Addition of ether, with cooling yielded red needles of the desired product, (yield 0·4 g, *ca.* 50%).

trans-*Carbonyliodotetrakis(trimethyl phosphite)iron*(II) *tetraphenylborate*, $[Fe(CO)I\{P(OMe)_3\}_4]^+BPh_4^-$. This compound was prepared, as above, except that 0·34 g (1 mmol) of sodium tetraphenylborate in methanol was added instead of the volume of methanol being reduced. Orange needles of the product formed which were recrystallised from acetone–ether with cooling (yield 0·7 g, *ca.* 70%).

trans-*Bromocarbonyltetrakis(trimethyl phosphite)iron*(II) *tetraphenylborate*, $[Fe(CO)Br\{P(OMe)_3\}_4]^+BPh_4^-$. This compound was prepared as yellow crystals as for the iodide.

Dicarbonyliodotris(trimethyl phosphite)iron(II) *tetraphenylborate*, $[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$. $Fe(CO)_4I_2$ (0·42 g, 1 mmol) and $P(OMe)_3$ (0·23 ml, 2 mmol) were allowed to react in ether, as above. To the methanol extract $NaBPh_4$ (0·34 g, 1 mmol) and further phosphite (0·1 ml) were added. After *ca.* 10 min of shaking, orange-gold platelets formed, which were washed with methanol and recrystallised from acetone–ether (yield 0·5 g, 65%).

cis-*Chloro(trichlorostannyl)tetrakis(trimethyl phosphite)-iron*(II), $FeCl(SnCl_3)\{P(OMe)_3\}_4$. Anhydrous ferrous chloride (10 mmol, 1·27 g), anhydrous stannous chloride (10 mmol, 1·9 g), and $P(OMe)_3$ (4·5 ml, 37 mmol) were refluxed in benzene (50 ml) for 6 h. An oily phase separated and after the mixture had been cooled to room temperature, the supernatant benzene solution was discarded and the oil extracted with hot methanol. The volume of liquid was reduced to *ca.* 25 ml, after which the solution was filtered, and allowed to cool, when orange-yellow crystals formed. These were separated, washed with a little methanol, and dried *in vacuo* (yield 2·0 g *ca.* 25%). Attempts to increase the yield led to contamination with cationic species.

(Trichlorostannyl)pentakis(trimethyl phosphite)iron(II) *tetraphenylborate*, $[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$. To $FeCl(SnCl_3)[P(OMe)_3]_4$ (0·41 g, 0·5 mmol) in methanol, $NaBPh_4$ (0·17 g, 0·5 mmol) in methanol was *slowly* added. A yellow precipitate immediately formed which was filtered, washed with methanol, and dried *in vacuo* (yield 0·25 g). The compound could similarly be prepared in acetone, and after being filtered to remove sodium chloride was crystallised from ether.

Hexakis(trimethyl phosphite)iron(II) *bis(tetraphenylborate)*, $[Fe\{P(OMe)_3\}_6]^{2+}(BPh_4^-)_2$. Anhydrous $FeCl_2$ (0·13 g, 1 mmol), $NaBPh_4$ (0·68, 2 mmol), and $P(OMe)_3$ (1·2 ml, *ca.* 10 mmol) were refluxed in methanol for 4 h. The off-white precipitate was filtered, washed with methanol, and dried *in vacuo*. It could be prepared similarly in refluxing benzene. It could not be recrystallised owing to its low solubility in all common solvents (yield 95%).

trans- and *cis*-$Fe(NCS)_2\{P(OMe)_3\}_4$. The preparation of these compounds has been reported elsewhere.[11]

Reaction of $[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$ *with Acetonitrile and γ-Picoline.*—The parent compound was recovered without further loss of carbonyl from hot acetonitrile solution and from an acetone solution containing a several molar excess of γ-picoline.

Reaction of $Fe(SnCl_3)Cl\{P(OMe)_3\}_4$ *with other Neutral Ligands.* The reaction of $Fe(SnCl_3)Cl\{P(OMe)_3\}_4$ with CO and $NaBPh_4$ in acetone, or with $NaBPh_4$ in acetonitrile gave only $[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$. With $p\text{-MeO}{\cdot}C_6H_4{\cdot}NC$ and $NaBPh_4$ in acetone, the i.r. spectrum of the product showed only a very weak band attributable to co-ordinated isocyanide, the major product being $[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$.

Microanalyses (Table 1) were carried out by Chemalytics, Inc., Tempe, Arizona. Satisfactory analyses were obtained for all new compounds, except for *cis*-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$ which showed unexpectedly large fluctuations. (However, the Mössbauer spectra showed no signs of impurity Fe or Sn species.) I.r. spectra were recorded on Perkin-Elmer 621 and Beckmann IR10 instruments, calibrated with polystyrene. Except where otherwise indicated, frequencies are believed accurate to ±3 cm^{-1}, or better (Table 2).

TABLE 1

Analyses (%)

	Found	(Required)	
Compound	C	H	Halide
cis-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$	16·3	3·8	
	(17·7)	(4·4)	
$[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$	38·3	5·2	8·7
	(38·5)	(5·3)	(8·8)
$[Fe\{P(OMe)_3\}_6]^{2+}(BPh_4)_2$	54·8	6·5	
	(55·1)	(6·5)	
$Fe(CO)_3I_2\{P(OMe)_3\}$	13·7	1·7	
	(13·9)	(1·7)	
$Fe(CO)_2I_2\{P(OMe)_3\}_2$	15·6	2·8	
	(15·8)	(2·9)	
trans-$[Fe(CO)I\{P(OMe)_3\}_4]^+I^-$	18·8	4·2	30·5
	(18·7)	(4·3)	(30·6)
trans-$[Fe(CO)I\{P(OMe)_3\}_4]^+BPh_4^-$	43·9	5·6	
	(43·3)	(5·5)	
mer-$[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$	45·3	5·0	
	(45·2)	(5·0)	
trans-$[Fe(CO)Br\{P(OMe)_3\}_4]^+BPh_4^-$	45·3	5·7	
	(45·4)	(5·7)	

Proton n.m.r. spectra were recorded on a Varian T60 Spectrometer, at *ca.* 30 °C (Table 3).

^{57}Fe Mössbauer spectra were recorded at *ca.* 80 K on an Austin Science Associates Spectrometer using a ^{57}Co in Cu source. Spectra were calibrated using an iron foil absorber and centre shifts are quoted relative to sodium nitroprusside at room temp. (Table 4). ^{119}Sn Spectra were obtained with a $BaSnO_3$ source, and centre shifts are quoted relative to this source, using the iron foil calibration. All spectra were fitted without constraints to Lorentzian line shapes using the program of A. J. Stone.[15]

RESULTS AND DISCUSSION

Reactivity.—Mays and Prater,[16] following on the earlier work of Malatesta [17] and his co-workers, prepared and studied a series of iron(II) complexes of *p*-methoxyphenyl isocyanide (ArNC). We have attempted to prepare exactly analogous compounds of trimethyl phosphite. Their parent compound was $FeCl_2(ArNC)_4$: we have been unable to prepare the $P(OMe)_3$ analogue, though we have already reported the preparation of *trans*- and *cis*-$Fe(NCS)_2\{P(OMe)_3\}_4$, the first report of high co-ordination of $P(OMe)_3$ around iron in the absence of such ligands as CO or H. Reaction of anhydrous ferrous chloride and $P(OMe)_3$ in benzene or methanol produces an uncharacterised complex mixture of products, very susceptible to oxidation, the Mössbauer spectra of which shows the probable presence of $[Fe\{P(OMe)_3\}_6]^{2+}$, $FeCl_2\{P(OMe)_3\}_2$ and other ferrous and ferric compounds.

TABLE 2

Infrared carbonyl stretching frequencies (cm^{-1} ±3 cm^{-1})

	CHCl$_3$ soln.			Nujol mull		
$Fe(CO)_3I_2\{P(OMe)_3\}$	2103m	2056	2043sh (±5)			
$Fe(CO)_2I_2\{P(OMe)_3\}_2$		2055	2007	2046	1998	1968w
trans-$[Fe(CO)I\{P(OMe)_3\}_4]^+I^-$		2062w	2006	2056w	1995	
trans-$[Fe(CO)I\{P(OMe)_3\}_4]^+BPh_4^-$		2077vw	2001	2069w	1988	
mer-$[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$		2079	2031	2074	2032br	
trans-$[Fe(CO)Br\{P(OMe)_3\}_4]^+BPh_4^-$			2030	2078vw	2019	
$Fe(CO)_2Br_2\{P(OMe)_3\}_2$		2062	2013			
$Fe(CO)_2Cl_2\{P(OMe)_3\}_2$				2060br (±5)	2010br (±5)	

All bands strong and sharp unless otherwise indicated.

TABLE 3

^1H N.m.r. spectra, in $CHCl_3$, of the methoxy-resonance

	τ, Chemical shift, ±0·03	Apparent coupling constant $^3J(P–H) + {}^5J(P–H)$ (Hz ±0·3)	
$Fe(CO)_2I_2\{P(OMe)_3\}_2$	6·05	Triplet	10·8
$Fe(CO)_2Br_2\{P(OMe)_3\}_2$	6·03 ± 0·05	Triplet	10·2 ±0·5
$[Fe(CO)I\{P(OMe)_3\}_4]^+I^-$	6·14	Quintet	10·6
$[Fe(CO)I\{P(OMe)_3\}_4]^+BPh_4^-$	6·15	Quintet	10·4
$[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$	6·10 ± 0·05	Multiplet	*ca.* 10·5
$[Fe(CO)Br\{P(OMe)_3\}_4]^+BPh_4^-$	6·10	Quintet	10·8
	in CH_3CN		
	τ ± 0·05	Width at half-height (±0·5 Hz)	
cis-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$	6·20	20	
$[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$	6·18	12	
$[Fe\{P(OMe)_3\}_6]^{2+}$ $(BPh_4^-)_2$	6·24	6	

However ferrous chloride, stannous chloride, and $P(OMe)_3$ react in stoicheiometric quantities to give *cis*-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$. In view of the reaction of this compound with sodium tetraphenylborate to give $[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$, we attempted to co-ordinate other neutral ligands L, to produce species of the type $[Fe(SnCl_3)\{P(OMe)_3\}_4L]^+$. This was largely unsuccessful, since $P(OMe)_3$ appears to compete effectively with other neutral ligands, including CO. Even *p*-MeO·C_6H_4·NC, in excess, showed no great readiness to co-ordinate. Attempts to prepare other (trichlorostannyliron)–trimethyl phosphite complexes were unsuccessful.

Although Mathieu and Poilblanc [3] were unable to prepare $Cr\{P(OMe)_3\}_6$ by photochemical substitution of $Cr(CO)_6$, our preparation of $[Fe\{P(OMe)_3\}_6]^{2+}$, and the existence [18] of $[Co\{P(OMe)_3\}_6]^{3+}$, suggest that there is probably no steric reason for not anticipating its preparation (and that of $[Mn\{P(OMe)_3\}_6]^+$) by some other route.

TABLE 4

^{57}Fe Mössbauer spectra

mm s^{-1} (±0·01 mm s^{-1}) at 77K

Compound	C.S.	Q.S.	Predicted Q.S.
cis-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$	0·34	0·44	−0·58 (η = 0·66)
$[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$	0·34	0·36	+0·44
$[Fe\{P(OMe)_3\}_6]^{2+}(BPh_4^-)_2$	0·30	<0·10	0·0
fac-$Fe(CO)_3I_2\{P(OMe)_3\}$	0·29	0·36	−0·72
$Fe(CO)_2I_2\{P(OMe)_3\}_2$	0·29	0·73	−0·92
trans-$[Fe(CO)I\{P(OMe)_3\}_4]^+I^-$	0·27	0·83	+0·92
trans-$[Fe(CO)I\{P(OMe)_3\}_4{}^+BPh_4^-$	0·26	0·77	+0·92
mer-$[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$	0·22	0·67	+0·84 (η = 0·37)
trans-$[Fe(CO)Br\{P(OMe)_3\}_4]^+BPh_4^-$	0·28	0·68	+0·94
$Fe(CO)_2Br_2\{P(OMe)_3\}_2$	0·29	0·93	−0·94
$Fe(CO)_2Cl_2\{P(OMe)_3\}_2$	0·27	0·89	−0·90
trans-$Fe(NCS)_2\{P(OMe)_3\}_4$	0·46	0·56	
cis-$Fe(NCS)_2\{P(OMe)_3\}_4$	0·41	0·30	−0·28

Centre shift given with respect to sodium nitroprusside at room temp. Predicted η = 0, unless otherwise shown.

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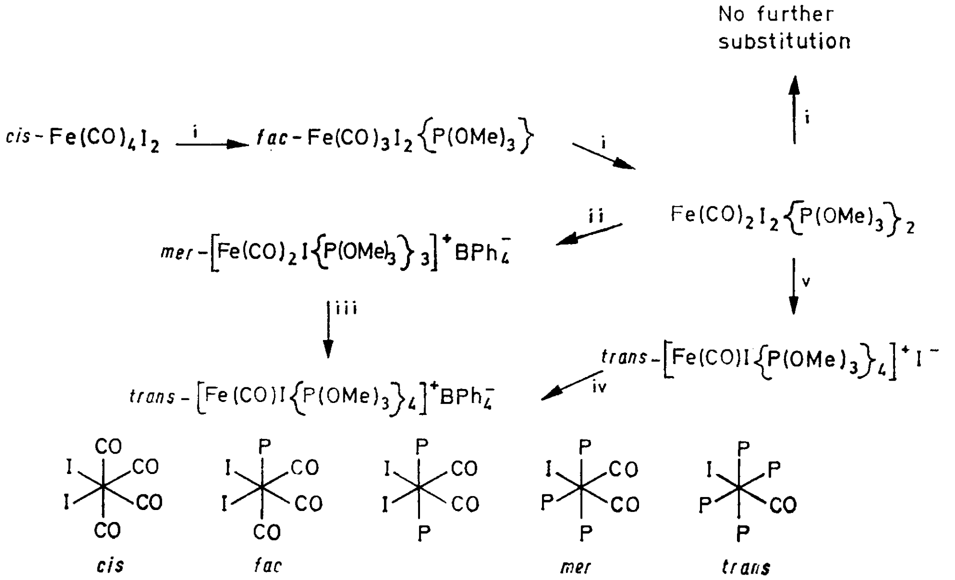
[15] A. J. Stone, appendix to G. M. Bancroft, W. K. Ong, A. G. Maddock, and R. H. Price, *J. Chem. Soc.* (*A*), 1967, 1966.

[16] M. J. Mays and B. E. Prater, *J. Chem. Soc.* (*A*), 1969, 2525.

[17] L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley-Interscience, New York, 1969 and references therein.

[18] K. J. Coskran, T. J. Huttemann, and J. G. Verkade, *Adv. Chem. Ser.*, 1966, **62**, 590.

The substitution reactions of $Fe(CO)_4X_2$ (X = halogen) have been studied extensively, both quantitatively and qualitatively.[19-21] With most neutral ligands, L, $Fe(CO)_3LX_2$, and $Fe(CO)_2X_2L_2$ are successively formed, although in many cases the monosubstituted intermediates have not been isolated. With *p*-tolyl isocyanide[22] the third substituted derivative, $Fe(CO)L_3X_2$, was formed, while with trimethylphosphine[23] two isomers at each stage of substitution [up to $Fe(CO)I_2(PMe_3)_3$] have been characterised in the solid state. In view of the high degree of substitution that has been achieved in the above cases, it might be anticipated that similar reactions would be observed for $Fe(CO)_4I_2$ with $P(OMe)_3$. However the actual sequence of reactions is shown in the Scheme. After the initial substitution to $Fe(CO)_2I_2\{P(OMe)_3\}_2$, iodide is now preferentially displaced over carbonyl, which is displaced subsequently, both reactions occurring under mild conditions. Such halide substitution reactions are usually only observed in the presence of silver ions or strong halide acceptors,[21] *e.g.* $AlCl_3$. The intermediate ion, $[Fe(CO)_2I\{P(OMe)_3\}_3]^+$, is extremely stable, since carbonyl is not displaced in boiling acetonitrile or by γ-picoline, the latter being able to replace weakly bound CO in, for example, $Fe(CO)_4I_2$. The role of the solvent in these substitution reactions is important, but not the only controlling factor: $Fe(CO)_2I_2\{P(OMe)_3\}_2$ can be recrystallised from hot methanol without decomposition.



SCHEME

Reagents: i, $P(OMe)_3$ in Et_2O or $CHCl_3$; ii, $P(OMe)_3$ (1 mol), $NaBPh_4$ (1 mol), MeOH; iii, $P(OMe)_3$ in MeOH or Me_2CO; iv, $NaBPh_4$ in MeOH or Me_2CO; v, $P(OMe)_3$ (2 mol) in MeOH

Again, the substitution reactions of $P(OMe)_3$ show the striking change between this phosphite and other phosphorus ligands. Using $P(OEt)_3$ and PEt_3, the substitution stops[23] at $Fe(CO)_2I_2(PR_3)_2$: the similarity between the Mössbauer parameters of analogous $P(OEt)_3$ and $P(OMe)_3$ compounds suggest that this is a steric factor, but that PEt_3, like PMe_3 is a weaker σ-donor and π-acceptor than $P(OMe)_3$.[1]

N.m.r. and Structural Assignment.—The carbonyl i.r. spectra (Table 2), do not lead to unambiguous structural geometries for these compounds, though the fairly symmetric doublet for $[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$ shows the presence of *cis* carbonyls. However this assignment can be achieved in conjunctiion with ^1H n.m.r. spectra, (Table 3 and Figure), which lead to both stoicheiometry and stereochemistry. Integration gives the ratio of phenyl to methoxy in the cationic complexes, although for $[Fe\{P(OMe)_3\}_6]^{2+}(BPh_4^-)_2$, the low solubility, even in $[^2H_6]$-acetone, permitted an approximate value only to be obtained.

The ^1H n.m.r. spectra of *cis*- and *trans*-$Fe(NCS)_2\{P(OMe)_3\}_4$ have been discussed in detail elsewhere: the *cis* showing a well resolved pair of chemically inequivalent identical triplets, and the *trans*, a quintet of approximately 1 : 1 : 2 : 1 : 1 intensity ratio.[11] This is the characteristic pattern of a square planar environment of four trimethyl phosphite molecules[10,11] and this pattern for the $[Fe(CO)X\{P(OMe)_3\}_4]^+$ ion, uniquely confirms the *trans*-configuration of these species. The 1 : 2 : 1 triplet pattern for $Fe(CO)_2I_2\{P(OMe)_3\}_2$ probably

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[19] I. A. Cohen and F. Basolo, *J. Inorg. Nuclear Chem.*, 1966, **28**, 511.

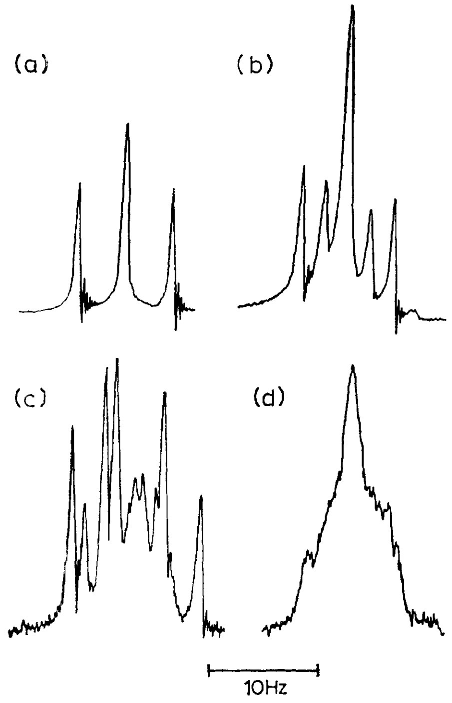
[20] W. Hieber and A. Thalhofer, *Agnew. Chem.*, 1956, **68**, 679.

[21] W. Hieber, V. Frey, and P. John, *Chem. Ber.*, 1967, **100**, 1961.

[22] R. C. Taylor and W. D. Horrocks, Jr., *Inorg. Chem.*, 1964, **3**, 584.

[23] M. Pankowski and M. Bigorgne, Compt rendue, 1966, *C*, **263**, 239.

defines a *trans*-arrangement of phosphite ligands (with *cis* carbonyls), but in view of our work [11] on *cis*-$Fe(NCS)_2\{P(OMe)_3\}_4$, this conclusion should be treated, perhaps with caution. Unfortunately the assignment of geometry to $[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$ is less straightforward and certain. Integration yields the expected phenyl/methoxy ratio confirming the stoicheiometry (and purity) of the sample. One cannot eliminate the possibility of two isomers in solution, although the i.r. spectrum is hardly consistent with this interpretation, and the Mössbauer spectrum of the solid shows evidence for only one species. The n.m.r. spectrum is not readily interpreted as a sum of simple triplet–doublet patterns, but we feel that the consistent stereochemistry for the sequence of substitutions is shown in the Scheme. These stereochemistries are the same as those assigned [4,6] to the isolectronic species, $Mn(CO)_2Br\{P(OMe)_3\}_3$ and $Mn(CO)Br\{P(OMe)_3\}_4$.



Proton n.m.r. spectra of methoxy resonance. (a) $Fe(CO)_2I_2\{P(OMe)_3\}_2$, (b) *trans*-$[Fe(CO)I\{P(OMe)_3\}_4]^+I^-$, (c) *mer*-$[Fe(CO)_2I\{P(OMe)_3\}_3]^+BPh_4^-$, and (d) $[Fe\{P(OMe)_3\}_6]^{2+}(BPh_4)_2$

The stereochemistry of $[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$ is unambiguous, though the n.m.r. of the methoxy-resonance shows a broad peak, width *ca.* 12 Hz, with no clearly resolved fine structure. The geometry of $Fe(SnCl_3)Cl\{P(OMe)_3\}_4$ could not be obtained from the n.m.r. spectrum owing to the lack of any resolved coupling pattern.

Mössbauer Spectra.—The ^{57}Fe Mössbauer spectra (Table 4) give a valuable insight into underlying electronic and bonding characteristics of $P(OMe)_3$. By use of the well-established partial quadrupole splitting (p.q.s) and partial centre shift (p.c.s.) treatment for the ^{57}Fe spectra [24] we have shown [1] that $P(OMe)_3$ is unlike any other common tertiary non-chelating phosphorus ligand (with the possible exception [25] of PF_3), but very similar to an isocyanide (in particular, in our study, to *p*-methoxyphenyl isocyanide, ArNC). Derived p.q.s. and p.c.s. values (mm s^{-1}) for $P(OMe)_3$ (—0·65, 0·03), PMe_3 (—0·66, 0·06), ArNC (—0·70, 0·00), and PPh_3 (—0·53, 0·07) showed that only in CO, ArNC, and $P(OMe)_3$ did the Mössbauer experiment detect substantial π-contributions in the bonding of a wide range of neutral ligands. Even without such semi-quantitative treatment, it is apparent from Table 5 that the Mössbauer parameters for $(POMe)_3$ and analogous ArNC complexes are remarkably similar. (We have used this methodology to assign the *cis*-configuration to $Fe(SnCl_3)Cl\{P(OMe)_3\}_4$.)

TABLE 5

Comparison of ^{57}Fe Mössbauer parameters for trimethyl phosphite and *p*-methoxyphenyl isocyanide complexes

mm s^{-1} (± 0·01) at 77 K

Compound†	C.S.	Q.S.	Ref.
cis-$Fe(NCS)_2\{P(OMe)_3\}_4$	0·41	(—) 0·30	
cis-$Fe(NCS)_2\{ArNC\}_4$	0·38	(—) 0·42	1
cis-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$	0·34	(—) 0·44	
cis-$Fe(SnCl_3)Cl(ArNC)_4$	0·33	(—) 0·67	16
$[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$	0·34	+0·36	*a*
$[Fe(SnCl_3)(ArNC)_5]^+ClO_4^-$	0·22	(+) 0·33	16
$Fe(CO)_3I_2\{P(OMe)_3\}$	0·29	0·36	
$Fe(CO)_3I_2(ArNC)$	0·29	0·58	1
$Fe(CO)_2I_2\{P(OMe)_3\}_2$	0·29	(—) 0·73	
$Fe(CO)_2I_2(ArNC)_2$	0·29	(—) 0·79	1

† ArNC = *p*-$MeO{\cdot}C_6H_4{\cdot}NC$.

Centre shift given with respect to sodium nitroprusside at room temperature.

[a] Sign determination, E. T. Libbey and G. M. Bancroft, *Chem. Comm.*, 1973, 50.

Table 4 also shows our calculated quadrupole splittings obtained from the p.q.s. treatment, along with the observed values. While the geometry of the *trans*-$[Fe(CO)I\{P(OMe)_3\}_4]^+$ and *mer*-$[Fe(CO)_2I\{P(OMe)_3\}_3]^+$ ions can be assigned with reasonable confidence from the n.m.r. and i.r. data, the predicted quadrupole splittings also differ from isomer to isomer. *cis*- and *fac*-Isomers are also possible for these two species respectively (eliminating the *trans*-CO isomer of $[Fe(CO)_2I\{P(OMe)_3\}_3]^+$ on i.r. evidence). These have predicted quadrupole splittings of +0·64 mm s^{-1} (η = 0·48) and 0·52 mm s^{-1} (η = 0). Hence it is not possible on Mössbauer predictions alone to define the co-ordination stereochemistry. However it is worth noting that the predictions for *cis*- and *trans*-$[Fe(CO)I\{P(OMe)_3\}_4]^+$ are +0·64 mm s^{-1} (η = 0·48) and +0·92 mm s^{-1} (η = 0) respectively. Although these are a distinct *cis–trans* pair, the expected signs of the splittings are both positive, which, of course, is not in general true for *cis–trans* FeA_2B_4 pairs.[24] We have discussed previously the expected variations in the quadrupole splittings of a

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[24] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.

[25] T. Kruck and R. Kobelt, *Chem. Ber.*, 1972, **105**, 3772.

wide series of carbonyl complexes, and found that owing to the variable bonding properties of CO, predicted quadrupole splittings are less likely to be as reliable in such compounds.[1] As expected, agreement for the cationic complexes, where there might be significant contributions to the electric field gradient from the counter ion, is sometimes poorer. Despite these limitations, agreement in all but two cases is better than 0·20 mm s^{-1}, which we consider good, allowing for the inherent errors and assumptions in the treatment.

The ^{119}Sn Mössbauer spectra (Table 6) show centre shift and quadrupole splittings typical of Fe–$SnCl_3$ moieties.[26-28] Although this tin system is not amenable to quantitative interpretation by the point charge methodology, variations in parameter values can be discussed qualitatively. ^{119}Sn Mössbauer parameters for *cis*-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$, *cis*-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$, and *cis*-$Fe(SnCl_3)Cl(CO)_4$ are also shown in Table 6. It is noticeable that the carbonyl compound has parameters both of which are smaller than those of the isocyanide or trimethyl phosphite complexes. The lone pair in the $Sn^{II}Cl_3^-$ entity has a high *s*-character,[26-31] and donation of this lone pair to iron will decrease $[\psi(0)_s]_{\mathrm{Sn}}^2$ and hence the observed ^{119}Sn centre shift. This enhanced σ-donation from the $SnCl_3$-moiety to the iron carbonyl species, over the iron isocyanide and trimethyl phosphite species, is probably a measure of the greater electron acceptor ability of iron arising from the increasing π-acceptor ability, CO > ArNC > $P(OMe)_3$. Since the ^{119}Sn quadrupole splitting is almost certainly positive,[31,32] and, hence, the e.f.g., negative, the isocyanide and trimethyl phosphite derivatives must have a more negative e.f.g., and hence larger, in magnitude, quadrupole splitting. *If* the loss of *s*-electron density from the Sn lone pair, results in decreased *s*-character in the Sn–Cl bonds, to more nearly p^3 hybridisation, one would anticipate from point charge considerations a simultaneous decrease in the quadrupole splitting. However it must be pointed out that in general, correlations between quadrupole splitting and centre shift in $SnCl_3$–M derivatives are poor, and often contrary, depending both on the nature of M and the substituents around it.[28]

TABLE 6

^{119}Sn Mössbauer spectra

mm s^{-1} at 77 K

Compound	C.S.	Q.S.	Ref.
$[Fe(SnCl_3)\{P(OMe)_3\}_5]^+BPh_4^-$	1·98 ± 0·02	2·05 ± 0·02	
cis-$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$	1·93 ± 0·02	2·00 ± 0·02	
cis-$Fe(SnCl_3)Cl(ArNC)_4$	1·77 ± 0·05	2·02 ± 0·05	26
cis-$Fe(SnCl_3)Cl(CO)_4$	1·55 ± 0·03	1·40 ± 0·03	27

Centre shift given with respect to barium stannate at room temp.

Conclusion.—In the light of this and other studies, and the wealth of co-ordination chemistry of isocyanides, it is surprising that more chemistry of trimethyl phosphite complexes has not been reported. In view of its low steric requirements, and strong σ-donor and π-acceptor properties (and the undoubted advantage of its easy availability), we feel that $P(OMe)_3$ offers a scope in co-ordination and organometallic chemistry that has not been appreciated fully hitherto. This is not for reasons of its chemical or physical properties, nor its ease of solvolysis as was recently suggested,[33] but more likely the ligand has been overlooked.

[3/765 *Received, 10th April,* 1973]

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[26] G. M. Bancroft and K. D. Butler, *J.C.S. Dalton*, 1972, 1209.

[27] N. Dominelli, E. Wood, P. Vasudev, and C. H. W. Jones, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1077.

[28] R. V. Parish and P. J. Rowbotham, *J.C.S. Dalton*, 1973, 37.

[29] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc. (A)*, 1971, 1311.

[30] D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 6226.

[31] R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 101, and refs. therein.

[32] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59, and references therein.

[33] D. A. Couch and S. D. Robinson, *Chem. Comm.*, 1971, 1508.