Reactions of Metal Carbonyl Derivatives. Part 25.[1] The Bridging Properties of Tetraethyl Diphosphite, $(EtO)_2POP(OEt)_2$ †

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The ditertiary phosphite $(EtO)_2POP(OEt)_2$ (tedip) has been treated with a variety of metal carbonyl complexes such as $[Mo(CO)_6]$, $[Mo(CO)_4(C_7H_8)]$ (C_7H_8 = bicyclo[2.2.1]heptadiene), $[Mo(\eta\text{-}C_5H_5)(CO)_3X]$ (X = Cl, Br, or I), $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, $[\{Fe(CO)_3(SMe)\}_2]$, and $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$, and in all cases products in which the phosphite is bonded unidentate or bridged bidentate have been obtained. These included $[Mo(CO)_4(tedip)_2]$, $[\{Mo(\eta\text{-}C_5H_5)(CO)_2X\}_2(tedip)]$, $[Fe_2(CO)_7(tedip)]$, $[Fe_2(CO)_5(tedip)_2]$, $[\{Fe(CO)_2(SMe)\}_2(tedip)]$, and $[\{Fe(\eta\text{-}C_5H_5)(CO)I\}_2(tedip)]$. The apparent inability of this ligand to afford chelated products is discussed in terms of the tedip bond angle.

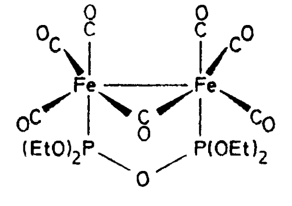
DITERTIARY phosphines have been employed extensively as ligands in transition-metal chemistry.[2] Three modes of co-ordination are possible for them, simple unidentate as found in $[Rh(cp)\{F_2PN(Et)PF_2\}_2]$ (cp = $\eta\text{-}C_5H_5$),[3] bridged bidentate as observed for $[\{Fe(cp)(CO)\}_2(Ph_2PC_2H_4PPh_2)]$,[4] and chelating bidentate as found in $[Mo(CO)_4(Ph_2PC_2H_2PPh_2)]$.[5] The latter mode of bonding is the most widely encountered.

The co-ordination chemistry of tertiary phosphites, $P(OR)_3$ (R = alkyl or aryl group), and related ligands has also been studied in considerable detail[6] but that of ditertiary phosphites of the type $(RO)_2PX'P(OR)_2$ [X' = O, S, NR', $(CH_2)_n$, *etc.*] has received little attention. The reactions of tetraethyl diphosphite, $(EtO)_2POP(OEt)_2$ (tedip), with various metal carbonyl derivatives are reported here.

RESULTS AND DISCUSSION

Treatment of a suspension of $[Fe_2(CO)_9]$ in benzene with a half molar amount of tedip afforded a product, isolated as an oil, whose i.r. spectrum exhibited C–O stretching peaks of frequency and band pattern consistent with the compound being either mononuclear $[Fe(CO)_4(tedip)]$ or dinuclear $[\{Fe(CO)_4\}_2(tedip)]$ {ν(C–O) at 2 060s, 1 987s, and 1 950vs,br cm^{-1}, measured in cyclohexane; *cf.* $[Fe(CO)_4\{P(OMe)_3\}]$: ν(C–O) at 2 062, 1 991, 1 961, and 1 950 cm^{-1}, measured in cetane[7]}. The compound could not be purified chromatographically owing to its ready conversion on the column to $[Fe_2(CO)_7(tedip)]$ (discussed below), but its mass spectral data are best interpreted in terms of it being the dinuclear species; peaks corresponding to $[Fe_2(CO)_n(tedip)]^+$ (n = 0—8) were present in the spectrum whereas peaks corresponding to $[Fe(CO)_n(tedip)]^+$ (n = 0—1), were absent. Octacarbonyl derivatives of this type *viz.* $[\{Fe(CO)_4\}_2\{F_2PN(Me)PF_2\}]$ and $[\{Fe(CO)_4\}_2\{(PhO)_2PN(Et)P(OPh)_2\}]$, have been isolated from the reactions of $[Fe_2(CO)_9]$ with $F_2PN(Me)PF_2$ and $(PhO)_2PN(Et)P(OPh)_2$.[8,9]

Irradiation of a light petroleum (b.p. 60—80 °C) solution of $[\{Fe(CO)_4\}_2(tedip)]$ with u.v. light, followed by column chromatographic purification of the reaction product, led to the isolation of red-orange crystals characterised by means of elemental and mass spectral analysis as $[Fe_2(CO)_7(tedip)]$. The mass spectrum of this compound contains, as well as the molecular ion at *m/e* 566, peaks corresponding to ions of formula $[Fe_2(CO)_n(tedip)]^+$ (n = 0—6) resulting from the successive loss of seven carbonyl groups. A single methylene multiplet and a single methyl triplet are observed in the ^1H n.m.r. spectrum of the compound while a single resonance at +22.0 p.p.m. relative to trimethyl phosphite is found in its ^{31}P n.m.r. spectrum. The solid-state i.r. spectrum of this species reveals five peaks in the C–O stretching region corresponding to terminal carbonyl groups and one corresponding to a bridging carbonyl. This spectral evidence is interpreted in terms of the structure (1) which is analogous to that established by *X*-ray crystallography for $[Fe_2(CO)_7(Ph_2PCH_2PPh_2)]$[10] and proposed for $[Fe_2(CO)_7\{F_2PN(Me)PF_2\}]$ and $[Fe_2(CO)_7(pydz)]$ (pydz = pyridazine).[8,11] The complex $[Fe_2(CO)_7(tedip)]$ may thus be considered as a substituted derivative of $[Fe_2(CO)_9]$ except that in contrast to the latter only one CO is bridging. In this respect the structure is based more on that of $[Os_2(CO)_9]$.[12] The solution i.r. spectrum of this compound exhibits a band pattern in the C–O stretching



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† Taken in part from the M.Sc. thesis of I. L. Marais presented to the University of Pretoria, December 1970 and the D.Phil. thesis of the late M. Safari presented to the University of Sussex, August 1974.

TABLE 1

Conductivity, analytical, and molecular-weight data

Compound	Colour	Λ[a]/S cm^2 mol^{-1}	Analyses/% Found C	Found H	Found Other	Calc. C	Calc. H	Calc. Other	*M* Found[b]	*M* Calc.
$[\mathrm{Fe_2(CO)_7(tedip)}]$	Red	0.2	32.0	3.6	10.9 (P)	31.8	3.6	10.9 (P)	566[c]	566
$[\mathrm{Fe_2(CO)_5(tedip)_2}]$	Red	0.3	32.8	5.3	16.2 (P)	32.8	5.3	16.2 (P)	768[c]	768
cis-$[\mathrm{Mo(CO)_4(tedip)_2}]$	White	0.1	32.6	5.1		33.1	5.5		720	724
$[\{\mathrm{Fe(CO)_2(SMe)}\}_2\mathrm{(tedip)}]$	Red	0.1	29.2	4.6	10.9 (P)	29.2	4.6	10.8 (P)	555	576
cis,cis-$[\{\mathrm{Mo(cp)(CO)_2Cl}\}_2\mathrm{(tedip)}]$	Orange	1.1	34.5	4.0	9.2 (Cl)	34.6	4.0	9.3 (Cl)	737	763
cis,cis-$[\{\mathrm{Mo(cp)(CO)_2Br}\}_2\mathrm{(tedip)}]$	Orange	0.7	31.3	3.5	17.9 (Br)	31.0	3.6	18.8 (Br)	793	852
cis,cis-$[\{\mathrm{Mo(cp)(CO)_2I}\}_2\mathrm{(tedip)}]$	Orange	0.2	28.2	3.1	26.8 (I)	27.9	3.2	26.8 (I)	927	946
cis,trans-$[\{\mathrm{Mo(cp)(CO)_2I}\}_2\mathrm{(tedip)}]$	Orange	0.6	27.9	3.1	26.8 (I)	27.9	3.2	26.8 (I)		
trans,trans-$[\{\mathrm{Mo(cp)(CO)_2I}\}_2\mathrm{(tedip)}]$	Orange	0.2	27.6	3.1	26.8 (I)	27.9	3.2	26.8 (I)		
$[\{\mathrm{Fe(cp)(CO)I}\}_2\mathrm{(tedip)}]$	Green	2.0	29.7	3.9	7.6 (I)	29.7	3.7	7.7 (I)	745	810
$[\mathrm{Fe(cp)(CO)_2}\{\mathrm{P(O)(OEt)_2}\}]$	Yellow	0.1	41.5	4.8		42.1	4.8		393	314

[a] For *ca.* 10^{-3} mol dm^{-3} solutions in acetone. [b] Measured by vapour-pressure osmometry in benzene, except where stated. [c] *m/e* of parent ion in mass spectrum.

TABLE 2

Hydrogen-1 n.m.r. spectroscopic data

Compound	Chemical shift *	Assignment
tedip	5.85 (m)	$\mathrm{CH_2}$
	8.50 (t), ^3J(H–H) 7.3	$\mathrm{CH_3}$
$[\mathrm{Fe_2(CO)_7(tedip)}]$	6.75 (m)	$\mathrm{CH_2}$
	9.60 (t), ^3J(H–H) 7.1	$\mathrm{CH_3}$
$[\mathrm{Fe_2(CO)_5(tedip)_2}]$	6.55 (m)	$\mathrm{CH_2}$
	9.50 (t), ^3J(H–H) 7.0	$\mathrm{CH_3}$
cis-$[\mathrm{Mo(CO)_4(tedip)_2}]$	5.88 (br,m)	$\mathrm{CH_2}$
	8.63 (t), ^3J(H–H) 7.1	$\mathrm{CH_3}$
	8.68 (t), ^3J(H–H) 7.1	$\mathrm{CH_3}$
$[\{\mathrm{Fe(CO)_2(SMe)}\}_2\mathrm{(tedip)}]$	5.87 (br,m)	$\mathrm{CH_2}$
	7.90 (t), ^4J(P–H) 4.1	$\mathrm{CH_3(SMe)}$
	8.33 (t), ^4J(P–H) 1.5	$\mathrm{CH_3(SMe)}$
	8.64 (t), ^3J(H–H) 7.2	$\mathrm{CH_3(OEt)}$
cis,cis-$[\{\mathrm{Mo(cp)(CO)_2Cl}\}_2\mathrm{(tedip)}]$	4.42 (s)	$\mathrm{C_5H_5}$
	4.44 (s)	$\mathrm{C_5H_5}$
	5.81 (br)	$\mathrm{CH_2}$
	8.63 (t), ^3J(H–H) 7.2	$\mathrm{CH_3}$
cis,cis-$[\{\mathrm{Mo(cp)(CO)_2Br}\}_2\mathrm{(tedip)}]$	4.46 (s)	$\mathrm{C_5H_5}$
	4.48 (s)	$\mathrm{C_5H_5}$
	5.84 (m)	$\mathrm{CH_2}$
	8.64 (t), ^3J(H–H) 7.0	$\mathrm{CH_3}$
cis,cis-$[\{\mathrm{Mo(cp)(CO)_2I}\}_2\mathrm{(tedip)}]$	4.45 (s)	$\mathrm{C_5H_5}$
	4.49 (s)	$\mathrm{C_5H_5}$
	5.84 (m)	$\mathrm{CH_2}$
	8.64 (t), ^3J(H–H) 7.2	$\mathrm{CH_3}$
cis,trans-$[\{\mathrm{Mo(cp)(CO)_2I}\}_2\mathrm{(tedip)}]$	4.51 (s)	$\mathrm{C_5H_5}$
	4.56 (d), ^3J(P–H) 0.8	$\mathrm{C_5H_5}$
	5.84 (m)	$\mathrm{CH_2}$
	8.61 (t), ^3J(H–H) 7.0	$\mathrm{CH_3}$
	8.64 (t), ^3J(H–H) 7.2	$\mathrm{CH_3}$
trans,trans-$[\{\mathrm{Mo(cp)(CO)_2I}\}_2\mathrm{(tedip)}]$	4.58 (d), ^3J(P–H) 0.8	$\mathrm{C_5H_5}$
	4.59 (d), ^3J(P–H) 1.0	$\mathrm{C_5H_5}$
	5.84 (m)	$\mathrm{CH_2}$
	8.60 (t), ^3J(H–H) 7.2	$\mathrm{CH_3}$
$[\{\mathrm{Fe(cp)(CO)I}\}_2\mathrm{(tedip)}]$	5.28 (s)	$\mathrm{C_5H_5}$
	5.72 (br)	$\mathrm{CH_2}$
	8.62 (t), ^3J(H–H) 7.0	$\mathrm{CH_3}$
$[\mathrm{Fe(cp)(CO)_2}\{\mathrm{P(O)(OEt)_2}\}]$	4.97 (s)	$\mathrm{C_5H_5}$
	5.96 (m)	$\mathrm{CH_2}$
	8.71 (t), ^3J(H–H) 7.0	$\mathrm{CH_3}$

* τ scale ($\mathrm{SiMe_4}$ reference); measured at 38 °C in $\mathrm{CDCl_3}$. *J* values in Hz.

region very similar to that of the solid-state spectrum, apart from the presence of a shoulder on the bridging carbonyl peak, indicating that the solid-state structure is retained in solution. The low-temperature (−149 °C) limiting ^{13}C-{^{1}H} n.m.r. spectrum reveals a poorly resolved triplet at 260.3 p.p.m. (relative to $\mathrm{SiMe_4}$) and an irregular multiplet at 214.3 p.p.m. which is also consistent with the structure illustrated in (1).[13] In contrast the room-temperature ^{13}C spectrum contains a closely spaced triplet at 220.8 p.p.m. which can be assigned to carbonyl carbons, indicative of a fluxional process occurring. The fluxional behaviour of this compound, as well as that of $[\mathrm{Fe_2(CO)_5(tedip)_2}]$, is described in a separate paper.[13] The presence of two bridging carbonyl stretching modes in the solution i.r. spectrum is readily explained in terms of more than one

TABLE 3

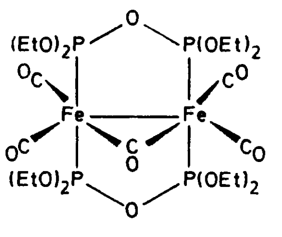
Infrared spectroscopic data (cm^{-1})

Compound	C–O Stretching frequencies *
$[\{Fe(CO)_4\}_2(tedip)]$	2 060s, 1 987s, 1 950vs, br
$[Fe_2(CO)_7(tedip)]$	2 063s, 2 010vs, 1 975m, 1 962s, 1 950s, 1 772m, 1 762s
$[Fe_2(CO)_5(tedip)_2]$	2 010s, 1 955vs, 1 929s, 1 910s, 1 720 (sh), 1 710s, 1 700 (sh)
cis-$[Mo(CO)_4(tedip)_2]$	2 039w, 1 949s, 1 923vs
$[\{Fe(CO)_2(SMe)\}_2(tedip)]$	2 011m, 1 978s, 1 941s, 1 936m
cis,cis-$[\{Mo(cp)(CO)_2Cl\}_2(tedip)]$	1 986vs, 1 898s
cis,cis-$[\{Mo(cp)(CO)_2Br\}_2(tedip)]$	1 982vs, 1 896s
cis,cis-$[\{Mo(cp)(CO)_2I\}_2(tedip)]$	1 978vs, 1 896s
cis,trans-$[\{Mo(cp)(CO)_2I\}_2(tedip)]$	1 979s, 1 898s
trans,trans-$[\{Mo(cp)(CO)_2I\}_2(tedip)]$	1 979s, 1 899vs
$[\{Fe(cp)(CO)I\}_2(tedip)]$	1 971
$[Fe(cp)(CO)_2\{P(O)(OEt)_2\}]$	2 045s, 1 993s

* Measured in cyclohexane.

conformer existing in solution resulting from different relative orientations of the tedip ligand, as has been proposed to explain the presence of more than one C–O stretching peak in the solution spectra of $[Fe(cp)(CO)\{P(OR)_3\}I]$ (R = Me or Et).[14,15]

Irradiation of a light petroleum solution of $[Fe_2(CO)_7(tedip)]$ and an excess of tedip {or $[Fe_2(CO)_9]$ and an excess of tedip in benzene} resulted in further replacement of carbonyl groups and the formation of a new product characterised by means of elemental and mass spectral analysis as $[Fe_2(CO)_5(tedip)_2]$. The mass spectrum of this compound is typical of that of a metal carbonyl derivative revealing a molecular ion (*m/e* 768) and peaks corresponding to successive loss of carbonyl groups. The i.r. and ^1H n.m.r. spectral data for this species are summarised in Tables 2 and 3. The ^1H n.m.r. spectrum exhibits a single methylene multiplet and a single methyl triplet while the $^{31}P-\{^1H\}$ n.m.r. spectrum reveals a single resonance at +21.6 p.p.m. relative to $P(OMe)_3$. The solid-state i.r. spectrum contains four terminal and a single bridging carbonyl stretching band which is the number predicted for the structure of symmetry C_{2v} shown below (2) which has recently been established by *X*-ray crystallography.[13] The complex $[Fe_2(CO)_5\{F_2PN(Me)PF_2\}_2]$ has been shown to adopt a similar structure in the solid state.[8] The low-temperature (−158 °C) limiting $^{13}C-\{^1H\}$ n.m.r. spectrum of $[Fe_2(CO)_5(tedip)_2]$ * is consistent with the solid-state structure being retained in solution, the spectrum reveals a quintet at 280.0 p.p.m. [$^2J(P-C) = 18.9$ Hz] and two triplets at 221.3 [$^2J(P-C) = 14.8$ Hz] and 215.7 p.p.m. [$^2J(P-C) = 23.3$ Hz] (relative to $SiMe_4$).[13] The solution i.r. spectrum is very similar to the solid-state one apart from two shoulders on the bridging carbonyl peak. The presence of more than one bridging C–O stretching mode is attributed to the existence of a number of conformers in solution as described earlier for $[Fe_2(CO)_7(tedip)]$.



(2)

A second product was also isolated from this photochemical reaction but its formation was not reproducible while its yield was very much lower than that of $[Fe_2(CO)_5(tedip)_2]$. Characterisation of this compound was not achieved but its mass spectral data and elemental analysis (C and H only) were not inconsistent with it being $[Fe_2(CO)_6(tedip)_2]$. Its i.r. spectrum in the C–O stretching region was relatively simple [ν(C–O) at 2 022s, 1 985s, 1 952s, and 1 938s cm^{-1}, measured in cyclohexane] but its ^1H n.m.r. spectral data (two methyl triplets at τ 8.80 and 8.90) could not be reconciled in terms of a simple structure.

The reaction of $[Fe_3(CO)_{12}]$ with tedip in benzene under photochemical conditions was similar to the reaction involving $[Fe_2(CO)_9]$ in affording both $[Fe_2(CO)_7(tedip)]$ and $[Fe_2(CO)_5(tedip)_2]$. Although different products appeared to be formed in the reaction of these two compounds in cyclohexane under reflux, their isolation was not possible.

Irradiation of a solution of $[Mo(CO)_6]$ and tedip in benzene with u.v. light or refluxing of a solution of $[Mo(CO)_4(C_7H_8)]$ (C_7H_8 = bicyclo[2.2.1]heptadiene) and this ligand in the same solvent gave, as a major product, a compound whose i.r. spectrum indicated it to be of the type *cis*-$[M(CO)_4L_2]$ {ν(CO) at 2 039w, 1 949s, and 1 923vs cm^{-1}, measured in cyclohexane; *cf.* *cis*-$[Mo(CO)_4\{P(OMe)_3\}_2]$, ν(CO) at 2 037, 1 945, 1 926, and 1 921 cm^{-1}, measured in cyclohexane[16]}. Elemental analysis and a molecular-weight determination established the compound to be $[Mo(CO)_4(tedip)_2]$, in which the ligands are unidentate, and not $[Mo(CO)_4(tedip)]$ or $[\{Mo(CO)_4(tedip)\}_2]$. The presence of two methyl triplets in the ^1H n.m.r. spectrum of the compound is in agreement with this formulation.

Previous studies have shown that the reaction of $[\{Fe(CO)_3(SR)\}_2]$ (R = Me or Et) with appropriate ditertiary phosphines (PX'P) in toluene or xylene under reflux gives $[\{Fe(CO)_2(SR)\}_2(PX'P)]$ in which the ligand bridges the two iron atoms (3).[17] The diphosphite tedip has now been found to also afford a bridged derivative, $[\{Fe(CO)_2(SMe)\}_2(tedip)]$, of structure analo-

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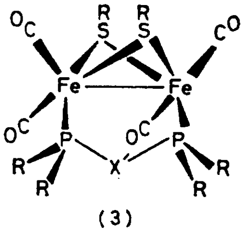
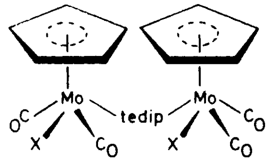
* Like $[Fe_2(CO)_7(tedip)]$, this compound is fluxional in solution.[13]

gous to that represented in (**3**), on reaction with $[\{Fe(CO)_3(SMe)\}_2]$ in refluxing xylene. The ^1H n.m.r. spectrum of this product contains two resonances corresponding to the SMe protons, both split into triplets as a result of coupling between the protons and the phosphorus nuclei, but significantly, with the coupling for the one being far greater than that for the other. It is assumed that the resonance with the larger coupling is associated with the methyl bonded to the sulphur positioned *trans* to the phosphorus ligand.



(3)

Treatment of $[Mo(cp)(CO)_3X]$ (X = Cl, Br, or I) with tedip in benzene at room temperature or under reflux afforded the bridged derivative $[\{Mo(cp)(CO)_2X\}_2(tedip)]$ as the major product. There was no evidence for the formation of chelated products in these reactions even when irradiated with u.v. light. The i.r. spectra of $[\{Mo(cp)(CO)_2X\}_2(tedip)]$ (X = Cl or Br) contain two terminal carbonyl stretching bands with the higher energy peak being more intense than the other. This is consistent with the compound occurring as the *cis,cis* isomer (4).[18,19] The *cis* isomers of type $[Mo(cp)(CO)_2(PR_3)X]$ do not reveal coupling between the phosphorus nuclei and the cyclopentadienyl protons [18] and thus the presence of two C_5H_5 resonances in the n.m.r. spectrum of $[\{Mo(cp)(CO)_2X\}_2(tedip)]$ (X = Cl or Br) is attributed to the two molybdenum atoms being in slightly different environments. In contrast to $[\{Mo(cp)(CO)_2X\}_2(tedip)]$ (X = Cl or Br), $[\{Mo(cp)(CO)_2I\}_2(tedip)]$ was obtained in three isomeric forms, three well separated bands were collected from the column employed to purify the product mixture from the reaction of $[Mo(cp)(CO)_3I]$ with tedip and each afforded a crystalline compound characterised as $[\{Mo(cp)(CO)_2I\}_2(tedip)]$. The relative intensities of the C–O stretching modes in the i.r. spectra of these isomers and their ^1H n.m.r. spectral data were consistent with their adopting *cis,cis* (4), *cis,trans* (5), and *trans,trans* (6) configurations respectively.[18,19]



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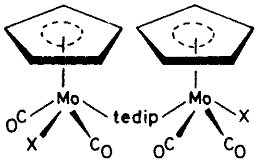

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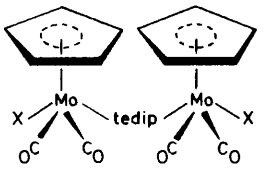

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Both the photochemical reaction of $[Mn(mcp)(CO)_3]$ (mcp = η-C_5H_4Me) with tedip and the thermal reaction of $[Fe(cp)(CO)_2(CH_3COCH_3)][SbF_6]$ with this ligand afforded oils with i.r. spectra (solution) containing at least two C–O stretching peaks, irrespective of the molar ratios employed $\{[Mn(mcp)(CO)_3]$ reaction: $\nu(CO)$ at 1 948(ip) (ip = inflection point), 1 938s, 1 888(ip), and 1 879s cm^{-1}, in cyclohexane; $[Fe(cp)(CO)_2(CH_3COCH_3)][SbF_6]$ reaction: $\nu(CO)$ at 2 073s and 2 023s cm^{-1}, in $CH_2Cl_2\}$. All attempts to separate the constituent components of these oils proved unsuccessful.

In contrast the reaction of $[Fe(cp)(CO)_2I]$ with tedip in benzene under reflux yielded a single neutral product. characterised as $[\{Fe(cp)(CO)I\}_2(tedip)]$. The dinuclear nature of this species was confirmed by a molecular-weight determination as well as from a comparison of the relative intensities of the cyclopentadienyl and ligand resonances in its ^1H n.m.r. spectrum.

Previous studies have revealed that reaction of the ditertiary phosphines $Ph_2PX'PPh_2$ (X' = CH_2, C_2H_2, C_2H_4, C_3H_6, or NEt) and the diphosphazane $(PhO)_2PN(Et)P(OPh)_2$ with $[\{Fe(cp)(CO)_2\}_2]$ produces $[\{Fe(cp)(CO)\}_2(Ph_2PX'PPh_2)]$ [4] or $[\{Fe(cp)(CO)\}_2\{(PhO)_2PN(Et)P(OPh)_2\}]$ [20] in which the ligand is bridged bidentate. Treatment of $[\{Fe(cp)(CO)_2\}_2]$ with tedip in cyclohexane under photochemical conditions or in benzene under reflux has now been found to lead to cleavage of the pyrophosphite and the formation of $[Fe(cp)(CO)_2\{P(O)(OEt)_2\}]$ previously isolated from the reaction of $[Fe(cp)(CO)_2Cl]$ with $P(OEt)_3$.[21] At least one other product was formed in this reaction but it could not be purified sufficiently for characterisation.

In all but one of the reactions discussed above from which crystalline derivatives were isolated, the tedip ligand afforded products in which it was either unidentate or bridged bidentate; there was no evidence of it functioning as a chelating agent. Similar behaviour was observed on reaction of this ligand with various platinum metal complexes.[22,23] These two sets of results are interpreted in terms of tedip being unable to function as a chelating ligand. By means of an electron diffraction study it was established that the P–O–P bond angle in F_2POPF_2 is 150°,[24] while the corresponding angle in $[Fe_2(CO)_5(tedip)_2]$ is *ca.* 120°.[13] A P–O–P bond angle of 120—150° for chelating tedip would give rise to an M–P–O bond angle considerably different to that required for a tetrahedrally disposed phosphorus atom. The inability of this ligand to adopt normal approximately tetrahedral M–P–O angles and at the same time to retain a large P–O–P angle would account for it not functioning as a chelating agent.

EXPERIMENTAL

The diphosphite $(EtO)_2POP(OEt)_2$ (tedip) and the various metal carbonyl and cyclopentadienyl metal carbonyl starting materials were either synthesised according to literature methods [25-29] or obtained commercially. All experiments were performed under dinitrogen. The photochemical reactions employed a Hanovia medium-pressure arc photochemical reactor. Chromatographic separations were carried out on an alumina column (50 × 1.5 cm; Merck acid washed alumina, activity III).

The i.r. spectra were recorded on Perkin-Elmer model 21 and 457 instruments. The ^{1}H n.m.r. spectra were obtained using Varian Associates HA100, A60A, and T-60 spectrometers. The ^{31}P-{^{1}H} n.m.r. spectra were measured on a JEOL PFT-100 Fourier-transform instrument. Mass spectra were recorded on an A.E.I. MS 9 spectrometer. The elemental analyses were obtained by the Microanalytical Laboratory, University of Sussex and the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany.

[{Fe(CO)$_4$}$_2$(tedip)].—A suspension of [Fe$_2$(CO)$_9$] (0.73 g, 2.0 mmol) and tedip (0.26 g, 1.0 mmol) in benzene (50 cm^3) was stirred at room temperature for 3 to 6 h. The solution was filtered and the solvent and [Fe(CO)$_5$] removed under reduced pressure to afford a red-brown oil. Attempts to purify this oil were unsuccessful with the product readily converting to [Fe$_2$(CO)$_7$(tedip)] on an alumina column. The compound was thus identified by spectroscopic means only.

[Fe$_2$(CO)$_7$(tedip)].—A suspension of [Fe$_2$(CO)$_9$] (1.09 g, 3.0 mmol) and tedip (0.39 g, 1.5 mmol) in benzene (50 cm^3) was stirred at room temperature for 6 h. The solution was filtered and the solvent removed under reduced pressure. The red-brown oil so obtained was dissolved in light petroleum and the solution irradiated with u.v. light for 8 h. The solution was concentrated and transferred to an alumina column. Elution with benzene–light petroleum (1 : 5) gave a red band which was collected. Removal of the solvent under reduced pressure afforded [Fe$_2$(CO)$_7$(tedip)] as a red crystalline solid which was recrystallised from light petroleum. Yield: 45%.

[Fe$_2$(CO)$_5$(tedip)$_2$].—A suspension of [Fe$_2$(CO)$_9$] (1.09 g, 3.0 mmol) and tedip (0.39 g, 1.5 mmol) in benzene (50 cm^3) was stirred at room temperature for 6 h. The solution was filtered and diluted with benzene to 150 cm^3. More tedip (0.52 g, 2.0 mmol) was added and the benzene solution irradiated with u.v. light for 15 h. The reaction mixture was filtered and the filtrate evaporated to dryness to afford a brown residue which was dissolved in a minimum of benzene–light petroleum and transferred to an alumina column. The latter was first eluted with light petroleum and benzene–light petroleum (1 : 5) to remove excess of ligand and [Fe$_2$(CO)$_7$(tedip)] and then with benzene–light petroleum (1 : 2) to give a red band which was collected. Removal of the solvent under reduced pressure and crystallization of the residue from light petroleum afforded [Fe$_2$(CO)$_5$(tedip)$_2$] as deep red crystals. Yield: 30%.

Elution of the column with benzene produced a yellow band which was collected. Removal of the solvent gave, in very low yield, a yellow crystalline solid which was not recrystallised. This species could not be characterised but is thought to be [Fe$_2$(CO)$_6$(tedip)$_2$] (see Results and Discussion).

[Mo(CO)$_4$(tedip)$_2$].—A solution of [Mo(CO)$_4$(C$_7$H$_8$)] (1.0 g, 3.3 mmol) and tedip (0.9 g, 3.5 mmol) in benzene (80 cm^3) was refluxed for 2 h. The solution was filtered and the solvent removed under reduced pressure to afford a colourless oil. This was dissolved in a minimum of light petroleum and transferred to an alumina column. Elution of the column with benzene–light petroleum (1 : 2) and subsequent removal of the solvent afforded [Mo(CO)$_4$(tedip)$_2$] as a colourless solid. Yield: 50% based on tedip.

[{Fe(CO)$_2$(SMe)}$_2$(tedip)].—A solution of [{Fe(CO)$_3$(SMe)}$_2$] (1.6 g, 4.3 mmol) and tedip (1.3 g, 5.0 mmol) in xylene (80 cm^3) was refluxed for 1 h. The solvent was removed under reduced pressure to afford a red oil which was dissolved in a minimum of benzene–light petroleum and the solution transferred to an alumina column. Elution of the column with benzene–light petroleum afforded a red band which was collected. Removal of the solvent under reduced pressure and crystallisation of the residue from light petroleum gave [{Fe(CO)$_2$(SMe)}$_2$(tedip)] as red crystals. Yield: 30%.

[{Mo(cp)(CO)$_2$Cl}$_2$(tedip)].—A solution of [Mo(cp)(CO)$_3$Cl] (0.6 g, 2.1 mmol) and tedip (0.6 g, 2.3 mmol) in benzene (50 cm^3) was stirred at room temperature for 2 days. The solution was filtered, concentrated to a small volume, and light petroleum added. Orange crystals of [{Mo(cp)(CO)$_2$Cl}$_2$(tedip)] which separated were recrystallised from benzene–light petroleum. Yield: 30%.

[{Mo(cp)(CO)$_2$Br}$_2$(tedip)].—A solution of [Mo(cp)(CO)$_3$Br] (1.0 g, 3.1 mmol) and tedip (0.8 g, 3.1 mmol) in benzene (70 cm^3) was refluxed for 2 h. Isolation and purification of [{Mo(cp)(CO)$_2$Br}$_2$(tedip)] was effected as for the chloro-derivative. Yield: 30%.

[{Mo(cp)(CO)$_2$I}$_2$(tedip)].—A solution of [Mo(cp)(CO)$_3$I] (1.8 g, 4.8 mmol) and tedip (1.2 g, 4.8 mmol) in benzene (80 cm^3) was refluxed for 3 h. The solvent was removed under reduced pressure to afford a red oil which was dissolved in a minimum of benzene–light petroleum and transferred to an alumina column. Elution with benzene–light petroleum (1 : 1) afforded two distinct orange bands which were collected. In both cases the solvent was removed under reduced pressure and the orange crystalline residue recrystallised from benzene–light petroleum. The product eluted first was proposed to be *cis,cis*-[{Mo(cp)(CO)$_2$I}$_2$(tedip)] while that eluted second was proposed to be *cis,-trans*-[{Mo(cp)(CO)$_2$I}$_2$(tedip)] (see Results and Discussion). Yields: 10% of each.

Elution of the column with benzene–light petroleum (2 : 1) afforded a third orange band which was collected. The complex *trans,trans*-[{Mo(cp)(CO)$_2$I}$_2$(tedip)] was isolated in crystalline form from this solution as above. Yield: 5%.

Reaction of [Mn(mcp)(CO)$_3$] *with* tedip.—A solution of [Mn(mcp)(CO)$_3$] (1.75 g, 8.0 mmol) and tedip (1.04 g, 4.0 mmol) in tetrahydrofuran (150 cm^3) was irradiated with u.v. light for 12 h. The solvent was removed under reduced pressure and the residue dissolved in a minimum of light petroleum and transferred to an alumina column (activity 1). The column was eluted with light petroleum to remove [Mn(mcp)(CO)$_3$] followed by benzene–light petroleum (1 : 1) which produced a yellow band which was collected. Removal of the solvent under reduced pressure afforded an orange oil with elemental analyses (C and H) intermediate between those required for [Mn(mcp)(CO)$_2$(tedip)] {or [Mn(mcp)(CO)(tedip)]} and [{Mn(mcp)(CO)$_2$}$_2$(tedip)]. Attempts to isolate a crystalline product or products from this oil were unsuccessful.

Reaction of [Fe(cp)(CO)$_2$(CH$_3$COCH$_3$)][SbF$_6$] *with* tedip.—A solution of tedip (0.5 g, 2.0 mmol) in acetone (50 cm^3) was added dropwise to a stirred solution of [Fe(cp)(CO)$_2$(CH$_3$COCH$_3$)][SbF$_6$] {prepared *in situ* from [Fe(cp)(CO)$_2$I] (1.21 g, 4.0 mmol) and Ag[SbF$_6$] (1.38 g, 4.0 mmol)} in acetone (75 cm^3) and the solution stirred for another 30 min. The solvent was removed under reduced pressure to afford a red-orange oil which on attempted crystallisation produced an oil again irrespective of the choice of solvent. The elemental analyses (C and H) for this oil were intermediate between those required for $[Fe(cp)(CO)_2(tedip)][SbF_6]$ {or $[Fe(cp)(CO)(tedip)][SbF_6]$} and $[\{Fe(cp)(CO)_2\}_2(tedip)][SbF_6]_2$.

$[\{Fe(cp)(CO)I\}_2(tedip)]$.—A solution of $[Fe(cp)(CO)_2I]$ (2.0 g, 6.6 mmol) and tedip (1.2 g, 4.7 mmol) in benzene (100 cm^3) was refluxed for 2 days. The solvent was removed under reduced pressure to afford a green oil which was dissolved in a minimum of benzene–light petroleum and transferred to an alumina column. Elution of the column with benzene produced a green band which was collected. Removal of the solvent gave $[\{Fe(cp)(CO)I\}_2(tedip)]$ as a green oil which solidified on standing. Yield: 45%.

Reaction of $[\{Fe(cp)(CO)_2\}_2]$ *with* tedip.—A solution of $[\{Fe(cp)(CO)_2\}_2]$ (1.06 g, 3 mmol) and tedip (0.84 g, 3.2 mmol) in cyclohexane (150 cm^3) was irradiated with u.v. light for 15 min. The solvent was removed under reduced pressure and the residue dissolved in a minimum of light petroleum and transferred to an alumina column. The column was eluted first with light petroleum and benzene and then with chloroform to produce a long yellow band. This was collected in two fractions but both contained at least two compounds. The chloroform was removed under reduced pressure and both residues dissolved in a minimum of light petroleum. Storage at 0 °C for 12 h led to the separation in both cases of yellow crystals of $[Fe(cp)(CO)_2\{P(O)(OEt)_2\}]$. Yield: 30%.

Attempts to isolate a product or products from the mother-liquors proved unsuccessful.

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