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Reactions of some Group 15 ligands with $[(\eta^5\text{-indenyl})\text{Fe}(\text{CO})_3]\text{BF}_4$

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Abstract

$[(\eta^5\text{-Indenyl})\text{Fe}(\text{CO})_3]\text{BF}_4$ (**I**) undergoes facile monocarbonyl substitution at room temperature in acetone by monophosphines, monophosphites and MPh_3 ($\text{M} = \text{As, Sb, Bi}$) ligands (**L**) to form $[(\eta^5\text{-Indenyl})\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$. Ditertiary phosphines, $\text{PPh}_2(\text{CH}_2)_n$ ($n = 1, 2, 4, 6, 8$) and both the arsines, $\text{AsPh}_2(\text{CH}_2)_2\text{AsPh}_2$ and $\text{AsMe}_2(\text{CH}_2)_5\text{AsMe}_2$ react similarly to form monosubstituted complexes *e.g.* $[(\eta^5\text{-Indenyl})\text{Fe}(\text{CO})_2(\eta^1\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)]\text{BF}_4$ and dimeric complexes, *e.g.* $\{[(\eta^5\text{-Indenyl})\text{Fe}(\text{CO})_2\text{-}\mu\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)]\text{BF}_4\}_2$. Prolonged refluxing of **I** with these ligands gives the chelates, *e.g.* $[(\eta^5\text{-Indenyl})\text{Fe}(\text{CO})(\eta^2\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)]\text{BF}_4$. The enhanced reactivity of the $[(\eta^5\text{-Indenyl})\text{Fe}(\text{CO})_3]^+$ cation over that of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ in solvents such as acetone may be attributed to the "indenyl" effect, *i.e.* ring slippage from η^5 to η^3 . However, no evidence was obtained for intermediates such as $[(\eta^3\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3(\text{acetone})]^+$, and so the effect must operate solely in the transition state of the reaction.

1. Introduction

In general, the cyclopentadienyl tricarbonyliron cation, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$, is relatively unreactive towards nucleophilic substitution by soft donors such as phosphines and phosphites. Carbonyl substitution often requires activation of a carbonyl group by oxidative decarbonylation using trimethylamine *N*-oxide (TMNO) or dimethylsulphoxide (DMSO) [1]. Alternatively, introduction of a labile ligand such as acetone or acetonitrile, by direct reaction of the iron dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ with acetone in the presence of Fe^{III} as oxidant to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}]^+$, provides a useful route to both phosphine and ditertiary phosphine substituted products *e.g.* $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$

$(\eta^1\text{-PPh}_2(\text{CH}_2)_2\text{PPh}_2)]^+$ [2]. Similarly, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})]^+$ has been used to prepare monosubstituted derivatives *e.g.* $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]^+$, disubstituted derivatives (chelates) *e.g.* $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]^+$ and metal-metal diphosphine-linked dimers *e.g.* $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\}^{2+}$ ($n = 2, 3$) [3]. In no case has direct ring attack by soft nucleophiles, such as phosphines been reported. However, with hard nucleophiles, *e.g.* hydride, both ring addition to form $[(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_3]$ and carbonyl substitution to form $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}]$ occur [4], preceded by initial attack at low temperatures at a carbonyl carbon atom with formation of the metal formyl intermediate $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CHO}]$ [5].

In contrast, relatively few studies have been reported on the analogous indenyl series where the possibility of the indenyl ring-forming ring-slipped (η^3)

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intermediates might be expected to lead to enhanced reactivity compared to that of the corresponding cyclopentadienyl species [6]. However, despite their observation that $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]^+$ undergoes monosubstitution fairly readily with various nucleophiles, Hammud and Moran [7] found the most versatile route to be that starting from the dimer in the presence of Fe^{III} , analogous to that used previously [2]. Interestingly, attack by a hard donor such as hydride has been shown by low-temperature ^1H NMR studies to involve an η^3 intermediate, $[(\eta^3\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3\text{H}]$ [8]. In this paper, we report the facile synthesis of a range of mono- and di-substituted derivatives and metal-metal diphosphine-linked dimers by direct reaction of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ with the ditertiary phosphines, $(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$ ($n = 1$, dppm, $n = 2$, dppe, $n = 4$, dppb, $n = 6$, dppe and $n = 8$, dppo) in acetone as solvent. The spectroscopic characterisation (IR, ^1H , ^{13}C and ^{31}P NMR) of these complexes is reported, together with the results of an X-ray structural determination of the chelate $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-Ph}_2\text{-PCH}_2\text{PPh}_2)]\text{BF}_4$.

2. Results and discussion

2.1. Monosubstituted complexes $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$

2.1.1. $L = \text{PR}_3$, $\text{P}(\text{OR})_3$ ($R = \text{alkyl, phenyl}$), MPh_3 ($M = \text{As, Sb, Bi}$)

Phosphines and phosphites generally react rapidly with I, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ in acetone as solvent, to give the monosubstituted products, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$. In dichloromethane the reaction is much slower, as noted previously for PPh_3 [3]. Thus neither $\text{P}(\text{OEt})_3$ nor $\text{P}(\text{OPh})_3$ reacts in CH_2Cl_2 even at higher temperatures, whereas they react rapidly in refluxing acetone. However, $\text{P}(\text{OMe})_3$ reacts rapidly at room temperature in both CH_2Cl_2 and acetone. No spectroscopic evidence was obtained for the intermediate $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{acetone})]\text{BF}_4$.

MPh_3 ($M = \text{As}$ and Sb) give monosubstituted $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{MPh}_3]\text{BF}_4$ in refluxing acetone, in contrast to BiPh_3 , which does not react with I even under vigorous conditions (e.g. prolonged refluxing or UV

TABLE 1. Microanalyses and values of $\nu(\text{CO})$ for the complexes

Complexes	Anal. Found (calc.) (%) and IR		Spectra ($\nu(\text{CO}) \text{ cm}^{-1}$)
	C	H	
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$	41.83(42.01)	1.64(2.06)	2118 2069
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{PMe}_3)]\text{BF}_4 \cdot 1.5\text{H}_2\text{O}$	40.02(42.89)	4.11(4.60)	2046 2000
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{P n-Bu}_3)]\text{BF}_4 \cdot \text{H}_2\text{O}$	53.48(53.52)	6.60(5.92)	2043 1997
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me})]\text{BF}_4$	54.29(54.17)	3.89(4.14)	2048 2004
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{P}(\text{OMe})_3]\text{BF}_4$	38.14(38.40)	3.59(3.68)	2059 2016
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{P}(\text{OEt})_3]\text{BF}_4$	41.63(42.53)	5.03(4.59)	20.61 2018
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{P}(\text{OPh})_3]\text{BF}_4$		unsatisfactory	2068 2027
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{PPh}_3)]\text{BF}_4$	60.28(60.46)	3.87(3.85)	2050 2007
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{AsPh}_3)]\text{BF}_4$	56.09(56.17)	3.93(3.58)	2050 2007
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{SbPh}_3)]\text{BF}_4$	52.40(52.23)	3.33(3.33)	2045 2002
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppm})]\text{BF}_4 \cdot 1.5\text{H}_2\text{O}$	59.77(59.58)	4.03(4.27)	2047 2005
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$	62.21(62.70)	4.31(4.36)	1977
$\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-}(\text{dppm})\}\text{BF}_4\}_2$	54.52(54.80)	3.58(3.47)	2046 2003
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppm})]\text{BF}_4 \cdot \text{H}_2\text{O}$	61.26(60.85)	4.37(4.25)	2047 2005
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppe})]\text{BF}_4$	62.87(63.10)	4.63(4.56)	1976
$\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-}(\text{dppe})\}\text{BF}_4\}_2$	55.54(55.25)	3.75(3.63)	2046 2003
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppb})]\text{BF}_4$		unsatisfactory	2047 2005
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppb})]\text{BF}_4 \cdot 2\text{H}_2\text{O}$	60.77(61.24)	4.85(4.70)	1961
$\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-}(\text{dppb})\}\text{BF}_4\}_2$	56.41(57.05)	4.33(4.17)	2046 2003
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dpph})]\text{BF}_4 \cdot 4\text{H}_2\text{O}$	58.21(58.59)	4.53(4.65)	2047 2005
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dpph})]\text{BF}_4$	64.00(64.80)	5.81(5.30)	1955
$\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-}(\text{dpph})\}\text{BF}_4\}_2$	56.27(56.86)	4.32(4.20)	2046 2003
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppo})]\text{BF}_4 \cdot 1.5\text{H}_2\text{O}$	62.59(62.72)	5.93(5.23)	2047 2005
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppo})]\text{BF}_4 \cdot \text{H}_2\text{O}$	63.65(64.09)	5.68(5.47)	1954
$\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-}(\text{dppo})\}\text{BF}_4\}_2$	56.72(57.60)	4.37(4.46)	2046 2003
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dpae})]\text{BF}_4$	50.80(49.80)	3.42(3.59)	2047 2004
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dpae})]\text{BF}_4 \cdot \text{H}_2\text{O}$	54.95(54.72)	4.14(4.18)	1971
$\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-}(\text{dpae})\}\text{BF}_4\}_2$	51.75(51.75)	3.44(3.45)	2050 2009
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dmap})]\text{BF}_4$	40.95(40.32)	5.32(5.17)	1954

TABLE 2. ^1H and ^{13}C NMR spectral data

Complex	Chemical shift (ppm)	Assignment
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$	(202.71) (s, 3)	CO
	8.08–7.87 (dm, 4) (135.50–125.96)	A_2B_2 system = C(4,7-C5,6)
	6.68 (d, 2, $J = 2.75$ Hz) (78.22)	$(\text{CH})_{\text{C}} = (\text{C}2,3)$
	6.35 (t, 1, $J = 2.75$ Hz) (93.00)	$(\text{CH})_{\text{D}} = (\text{C}1)$
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{PPh}_3)]\text{BF}_4$	(106.87)	C8,9
	(210.00) (d, 2, $J = 24.7$ Hz)	CO
	7.78–7.31 (m, 19) (132.33–125.82)	A_2B_2 system + PPh_3
	6.10 (d, 2) (77.54)	$(\text{CH})_{\text{C}}$
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{P}(\text{OMe})_3)]\text{BF}_4$	5.55 (t, 1) (91.75)	$(\text{CH})_{\text{D}}$
	(104.59)	C8,9
	(207.36) (d, 2, $J = 38.57$ Hz)	CO
	7.74–7.54 (dm, 4) (132.33–125.10)	A_2B_2 system
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{P}(\text{OMe})_3)]\text{BF}_4$	5.94 (d, 2) (75.05)	$(\text{CH})_{\text{C}}$
	5.34 (t, 1) (91.75)	$(\text{CH})_{\text{D}}$
	(105.00)	C8,9
	3.87 (d, 9) (55.30)	CH_3
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{SbPh}_3)]\text{BF}_4$	(208.86) (s, 2)	CO
	7.58–7.73 (m, 19) (131.94–125.64)	A_2B_2 system + PPh_3
	6.38 (d, 2) (74.31)	$(\text{CH})_{\text{C}}$
	5.58 (t, 1) (88.94)	$(\text{CH})_{\text{D}}$
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppm})]\text{BF}_4$	(103.64)	C8,9
	(211.50) (d, 2)	CO
	7.75–7.25 (m, 24) (130.20–126.43)	A_2B_2 system + PPh_2
	5.85 (d, 2) (78.52)	$(\text{CH})_{\text{C}}$
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppm})]\text{BF}_4$	5.34 (t, 1) (95.43)	$(\text{CH})_{\text{D}}$
	(105.68)	C8,9
	3.72 (d, 2, $J = 11.73$ Hz) (29.79)	CH_2
	(212.33) (d, 2)	CO
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppe})]\text{BF}_4$	7.79–7.27 (m, 24) (131.40–126.77)	A_2B_2 system + PPh_2
	5.95 (d, 2) (78.38)	$(\text{CH})_{\text{C}}$
	5.52 (t, 1) (95.72)	$(\text{CH})_{\text{D}}$
	(106.16)	C8,9
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dpph})]\text{BF}_4$	3.83, 2.65 (m, 4) (29.33, 31.05)	CH_2
	(212.00) (d, 2)	CO
	7.83–7.33 (m, 24) (130.31–126.48)	A_2B_2 system + PPh_2
	5.99 (d, 2) (77.99)	$(\text{CH})_{\text{C}}$
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dpph})]\text{BF}_4$	5.52 (t, 1) (95.70)	$(\text{CH})_{\text{D}}$
	(105.74)	C8,9
	2.83, 2.10, 1.44 (m, 12) (24.84, 32.48)	CH_2
	(212.06) (d, 2)	CO
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppo})]\text{BF}_4$	7.98–7.48 (m, 24) (130.84–126.42)	A_2B_2 system + PPh_2
	6.15 (d, 2) (77.99)	$(\text{CH})_{\text{C}}$
	5.67 (t, 1) (95.52)	$(\text{CH})_{\text{D}}$
	(105.70)	C8,9
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$	2.95, 1.51, 1.43, 1.30 (m, 16) (24.78, 32.52)	CH_2
	(212.00) (d, 1)	CO
	7.75–7.25 (m, 24) (134.07–126.80)	A_2B_2 system + PPh_2
	5.91 (d, 2) (73.49)	$(\text{CH})_{\text{C}}$
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$	5.62 (t, 1) (89.81)	$(\text{CH})_{\text{D}}$
	(103.62)	C8,9
	5.16, 4.31 (dt, 2, $J = 10.73$ Hz) (44.71)	CH_2
	unresolved	CO
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppe})]\text{BF}_4$	7.63–6.97 (m, 24) (130.80–126.42)	A_2B_2 system + PPh_2
	5.32 (d, 2) (73.82)	$(\text{CH})_{\text{C}}$
	5.15 (t, 1) (92.22)	$(\text{CH})_{\text{D}}$
	(104.02)	C8,9
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dpac})]\text{BF}_4$	2.62 (bd, 4) (29.83)	CH_2
	(215.76) (s, 1)	CO
	132.54–127.39	A_2B_2 system + PPh_2
	70.99	$(\text{CH})_{\text{C}}$
$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dpac})]\text{BF}_4$	89.86	$(\text{CH})_{\text{D}}$
	101.60	C8,9
	28.22	CH_2

TABLE 2 (continued)

Complex	Chemical shift (ppm)	Assignment
[(η^5 -C ₉ H ₇)Fe(CO)(η^2 -dmap)]BF ₄	unresolved	CO
	7.95–7.38 (m, 4)	A ₂ B ₂ system
	5.45 (d, 2) (<i>J</i> = 2.93 Hz)	(H) _C
	5.49 (t, 1) (<i>J</i> = 2.93 Hz)	(H) _D
	2.90, 2.12, 1.93 (bd, 10)	CH ₂
	1.43 (s, 12)	CH ₃
[(η^5 -C ₉ H ₇)Fe(CO) ₂] ₂ - μ -(dppm)][BF ₄] ₂	(211.44) (d, 4)	CO
	7.76–7.43 (m, 28) (130.48–126.53)	A ₂ B ₂ system + PPh ₂
	5.95 (d, 4) (78.56)	(CH) _C
	5.48 (t, 2) (96.00)	(CH) _D
	(105.61)	C8,9
	4.16 (t, 2, <i>J</i> = 7.51) (33.69)	CH ₂
[(η^5 -C ₉ H ₇)Fe(CO) ₂] ₂ - μ -(dpph)][BF ₄] ₂	(212.10) (d, 4, <i>J</i> = 23.10 Hz)	CO
	7.84–7.61 (m, 28) (130.48–126.52)	A ₂ B ₂ system + PPh ₂
	5.99 (d, 4) (78.03)	(CH) _C
	5.52 (t, 2) (95.72)	(CH) _D
	(105.74)	C8,9
	2.76, 1.45, 1.34 (m, 12) (24.86, 32.05, 32.50)	CH ₂
[(η^5 -C ₉ H ₇)Fe(CO) ₂] ₂ - μ -(dppo)][BF ₄] ₂	(211.10) (d, 4)	CO
	7.93–7.43 (m, 28) (130.48–126.50)	A ₂ B ₂ system + PPh ₂
	6.00 (d, 4) (78.07)	(CH) _C
	5.51 (t, 2) (95.60)	(CH) _D
	(105.74)	C8,9
	2.81, 1.35, 1.16 (m, 16) (24.86, 29.10, 32.16, 32.62)	CH ₂

The spectra were recorded in acetone-*d*₆ solution, TMS as internal standard. (m = multiplet, d = doublet, t = triplet, um = unresolved multiplet, bd = broad doublet).

radiation). However, the reaction of [(η^5 -C₉H₇)Fe(CO)₂Br] with BiPh₃ and AgBF₄ in CH₂Cl₂ at room temperature resulted in the appearance of new infrared peaks at 2068 cm⁻¹ and 2020 cm⁻¹, in place of those from I at 2118 cm⁻¹ and 2069 cm⁻¹, indicating formation of the monosubstituted derivative, but attempts to isolate this were unsuccessful.

2.1.2. *L* = ditertiary phosphines, Ph₂P(CH₂)_{*n*}PPh₂, (*n* = 1, (dppm); *n* = 2, (dppe); *n* = 4, (dppb); *n* = 6, (dpph) and *n* = 8, (dppo))

Complex I reacts with ditertiary phosphines in a 1 : 1 molar ratio in acetone at room temperature to give the

monosubstituted complexes, [(η^5 -C₉H₇)Fe(CO)₂(η^1 -dppa)]BF₄, where dppa denotes the general ditertiary phosphine ligand, diphenylphosphinoalkane. Analytical and spectroscopic data (IR; ¹H, ¹³C and ³¹P NMR) are given in Tables 1–3. Although the compounds show lower ν (CO) frequencies than the parent cation I, as expected when a CO group is replaced by a poorer π -acceptor ligand, there is no clear correlation between the decrease in ν (CO) and size of phosphine. Interestingly, there is very little variation in ν (CO) in the series [(η^5 -C₉H₇)Fe(CO)₂MPh₃][BF₄], M = P, As and Sb (Table 1), suggesting compensating electronic and steric effects in this series. It is also noteworthy

TABLE 3. ³¹P NMR data and coordination shifts

complex	δ (P _{FL})	δ (P _a)	δ (P _b)	δ (P _c)	Δ_{coord}	δ_{chel}	<i>J</i> (PP)
[(η^5 -C ₉ H ₇)Fe(CO) ₂ (η^1 -dppm)][BF ₄]	-23.60	-23.34	66.83	-	90.43	-	88.50
[(η^5 -C ₉ H ₇)Fe(CO) ₂ (η^1 -dppe)][BF ₄]	-12.50	-14.96	64.98	-	77.48	-	39.70
[(η^5 -C ₉ H ₇)Fe(CO)(η^2 -dppm)][BF ₄]	-23.60	-	-	26.93	-	-39.90	-
[(η^5 -C ₉ H ₇)Fe(CO)(η^2 -dppe)][BF ₄]	-12.50	-	-	93.68	-	28.70	-
[(η^5 -C ₉ H ₇)Fe(CO) ₂] ₂ - μ -(dppm)][BF ₄] ₂	-23.60	-	69.95	-	-	-	-
[(η^5 -C ₉ H ₇)Fe(CO) ₂] ₂ - μ -(dppe)][BF ₄] ₂	-12.50	-	61.89	-	-	-	-
[(η^5 -C ₉ H ₇)Fe(CO) ₂] ₂ - μ -(dppo)][BF ₄] ₂	-	-	61.94	-	-	-	-

(P_{FL}) = phosphorus atoms in the free ligand; (P_a) = uncoordinated phosphorus atoms; (P_b) = coordinated phosphorus atoms; (P_c) = chelated phosphorus atoms; $\Delta_{\text{coord}} = \delta$ (P_b) - δ (P_{FL}); $\Delta_{\text{chel}} = \delta$ (P_c) - δ (P_a), *J*(PP) = coupling (Hz) between the coordinated and uncoordinated phosphorus atoms. The spectra were recorded in acetone-*d*₆ solution, (85% H₃PO₄ as internal standard).

that in the $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppa})]\text{BF}_4$ series, the $\nu(\text{CO})$ stretching frequencies are identical, and are not affected by the length of the hydrocarbon chain

separating the two phosphorus atoms. Indeed, even the two monosubstituted ditertiaryarsine complexes, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2)]\text{BF}_4$, and

TABLE 4. Bond distances (Å) and angles (deg) in $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$

<i>Bond distances</i>					
Fe ₁ -P ₁	2.204(2)	Fe ₁ -C ₉	2.177(8)	P ₂ -C ₂₃	1.817(7)
Fe ₁ -P ₂	2.207(2)	Fe ₁ -C ₃₅	2.741(8)	P ₂ -C ₂₉	1.805(7)
Fe ₁ -C ₁	2.087(8)	P ₁ -C ₁₀	1.825(7)	B ₁ -F ₁	1.343(11)
Fe ₁ -C ₂	2.071(8)	P ₁ -C ₁₁	1.820(7)	B ₁ -F ₂	1.359(11)
Fe ₁ -C ₃	2.077(8)	P ₁ -C ₁₇	1.821(7)	B ₁ -F ₃	1.347(12)
Fe ₁ -C ₈	2.173(7)	P ₂ -C ₁₀	1.844(7)	B ₁ -F ₄	1.358(11)
O ₁ -C ₃₅	1.146(7)	C ₁ -C ₂	1.404(10)	C ₁ -C ₈	1.421(10)
C ₂ -C ₃	1.362(10)	C ₃ -C ₉	1.424(10)	C ₄ -C ₅	1.367(11)
C ₄ -C ₉	1.412(10)	C ₅ -C ₆	1.382(11)	C ₆ -C ₇	1.312(11)
C ₇ -C ₈	1.450(10)	C ₈ -C ₉	1.444(10)	C ₁₁ -C ₁₂	1.390(10)
C ₁₁ -C ₁₆	1.384(10)	C ₁₂ -C ₁₃	1.406(11)	C ₁₃ -C ₁₄	1.388(11)
C ₁₄ -C ₁₅	1.320(10)	C ₁₅ -C ₁₆	1.390(10)	C ₁₇ -C ₁₈	1.367(9)
C ₁₇ -C ₂₂	1.382(9)	C ₁₈ -C ₁₉	1.376(10)	C ₁₉ -C ₂₀	1.365(11)
C ₂₀ -C ₂₁	1.363(11)	C ₂₁ -C ₂₂	1.407(10)	C ₂₃ -C ₂₄	1.389(10)
C ₂₃ -C ₂₈	1.394(9)	C ₂₄ -C ₂₅	1.413(11)	C ₂₅ -C ₂₆	1.362(11)
C ₂₆ -C ₂₇	1.389(11)	C ₂₇ -C ₂₈	1.386(10)	C ₂₉ -C ₃₀	1.392(9)
C ₂₉ -C ₃₄	1.378(10)	C ₃₀ -C ₃₁	1.398(10)	C ₃₁ -C ₃₂	1.355(11)
C ₃₂ -C ₃₃	1.349(11)	C ₃₃ -C ₃₄	1.405(10)		
<i>Bond angles</i>					
P ₂ -Fe ₁ -P ₁	74.7(1)	C ₃₅ -Fe ₁ -P ₁	90.9(2)	F ₃ -B ₁ -F ₂	109.6(9)
C ₁ -Fe ₁ -P ₁	108.2(2)	C ₃₅ -Fe ₁ -P ₂	94.9(2)	F ₄ -B ₁ -F ₁	108.9(9)
C ₂ -Fe ₁ -P ₁	92.2(2)	C ₃₅ -Fe ₁ -C ₁	156.9(2)	F ₄ -B ₁ -F ₂	107.0(9)
C ₁ -Fe ₁ -P ₂	102.4(2)	C ₃₅ -Fe ₁ -C ₂	126.5(3)	F ₄ -B ₁ -F ₃	112.4(9)
C ₂ -Fe ₁ -P ₂	138.5(2)	C ₃₅ -Fe ₁ -C ₃	92.9(3)	C ₂ -C ₁ -Fe ₁	69.7(5)
C ₂ -Fe ₁ -C ₁	39.5(3)	C ₃₅ -Fe ₁ -C ₈	124.6(6)	C ₈ -C ₁ -Fe ₁	73.8(5)
C ₃ -Fe ₁ -P ₁	122.2(2)	C ₃₅ -Fe ₁ -C ₉	91.9(3)	C ₈ -C ₁ -C ₂	106.5(7)
C ₃ -Fe ₁ -P ₂	161.2(2)	C ₁₀ -P ₁ -Fe ₁	95.6(2)	C ₁ -C ₂ -Fe ₁	70.9(5)
C ₃ -Fe ₁ -C ₁	66.2(3)	C ₁₁ -P ₁ -Fe ₁	128.8(2)	C ₃ -C ₂ -Fe ₁	71.0(5)
C ₃ -Fe ₁ -C ₂	38.3(3)	C ₁₁ -P ₁ -C ₁₀	109.8(3)	C ₂ -C ₃ -Fe ₁	70.6(5)
C ₈ -Fe ₁ -P ₁	144.3(2)	C ₁₇ -P ₁ -Fe ₁	118.3(2)	C ₃ -C ₂ -C ₁	110.5(8)
C ₈ -Fe ₁ -P ₂	96.5(2)	C ₁₇ -P ₁ -C ₁₀	107.2(3)	C ₉ -C ₃ -Fe ₁	74.3(5)
C ₈ -Fe ₁ -C ₁	38.9(3)	C ₁₇ -P ₁ -C ₁₁	103.0(3)	C ₉ -C ₃ -C ₂	108.9(8)
C ₈ -Fe ₁ -C ₂	64.4(3)	C ₁₀ -P ₂ -Fe ₁	95.0(2)	C ₉ -C ₄ -C ₅	117.0(8)
C ₈ -Fe ₁ -C ₃	65.1(3)	C ₂₃ -P ₂ -Fe ₁	119.9(2)	C ₆ -C ₅ -C ₄	122.9(9)
C ₉ -Fe ₁ -P ₁	161.1(2)	C ₂₃ -P ₂ -C ₁₀	107.5(3)	C ₇ -C ₆ -C ₅	122.9(9)
C ₈ -Fe ₁ -P ₂	123.5(2)	C ₂₉ -P ₂ -Fe ₁	120.1(2)	C ₈ -C ₇ -C ₆	118.5(8)
C ₉ -Fe ₁ -C ₁	65.8(3)	C ₂₉ -P ₂ -C ₁₀	107.0(3)	C ₁ -C ₈ -Fe ₁	67.3(4)
C ₉ -Fe ₁ -C ₂	64.4(3)	C ₂₉ -P ₂ -C ₂₃	105.5(3)	C ₇ -C ₈ -Fe ₁	127.3(5)
C ₉ -Fe ₁ -C ₃	39.0(3)	F ₂ -B ₁ -F ₁	108.6(9)	C ₉ -C ₈ -Fe ₁	70.7(4)
C ₉ -Fe ₁ -C ₈	38.8(3)	F ₃ -B ₁ -F ₁	110.3(8)	C ₇ -C ₈ -C ₁	134.0(7)
C ₉ -C ₈ -C ₁	107.9(7)	C ₂₈ -C ₂₇ -C ₂₆	118.4(9)	C ₂₇ -C ₂₆ -C ₂₅	121.5(9)
C ₉ -C ₈ -C ₇	118.1(7)	C ₃₀ -C ₂₉ -P ₂	119.6(6)	C ₂₇ -C ₂₈ -C ₂₃	121.2(8)
C ₄ -C ₉ -Fe ₁	127.0(6)	C ₃ -C ₉ -Fe ₁	66.7(4)	C ₃₄ -C ₂₉ -P ₂	120.6(5)
C ₈ -C ₉ -Fe ₁	70.5(4)	C ₄ -C ₉ -C ₃	133.6(8)	C ₃₄ -C ₂₉ -C ₃₀	119.7(7)
C ₈ -C ₉ -C ₄	120.5(7)	C ₈ -C ₉ -C ₃	105.9(8)	C ₃₂ -C ₃₁ -C ₃₀	119.2(8)
C ₁₂ -C ₁₁ -P ₁	122.4(6)	P ₂ -Fe ₁ -P ₁	93.7(3)	C ₃₄ -C ₃₃ -C ₃₂	120.6(9)
C ₁₆ -C ₁₁ -C ₁₂	119.3(7)	C ₁₆ -C ₁₁ -P ₁	118.3(6)	O ₁ -C ₃₅ -Fe ₁	177.9(6)
C ₁₄ -C ₁₃ -C ₁₂	118.9(9)	C ₁₃ -C ₁₂ -C ₁₁	119.5(8)	C ₃₁ -C ₃₀ -C ₂₉	120.1(7)
C ₁₆ -C ₁₅ -C ₁₄	121.0(9)	C ₁₅ -C ₁₄ -C ₁₃	121.4(9)	C ₃₃ -C ₃₂ -C ₃₁	121.6(9)
C ₁₈ -C ₁₇ -P ₁	119.3(5)	C ₁₅ -C ₁₆ -C ₁₁	119.9(8)	C ₃₃ -C ₃₄ -C ₂₉	118.8(7)
C ₂₂ -C ₁₇ -C ₁₈	119.9(7)	C ₂₂ -C ₁₇ -P ₁	120.8(5)	C ₂₈ -C ₂₃ -P ₂	119.8(6)
C ₂₀ -C ₁₉ -C ₁₈	119.6(9)	C ₁₉ -C ₁₈ -C ₁₇	120.7(8)	C ₂₅ -C ₂₄ -C ₂₃	118.6(8)
C ₂₂ -C ₂₁ -C ₂₀	119.2(8)	C ₂₁ -C ₂₀ -C ₁₉	121.2(9)	C ₂₈ -C ₂₃ -C ₂₄	119.9(7)
C ₂₄ -C ₂₃ -P ₂	120.0(6)	C ₂₁ -C ₂₂ -C ₁₇	119.3(7)	C ₂₆ -C ₂₅ -C ₂₄	120.4(9)

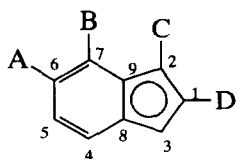


Fig. 1. Numbering of η^5 -indenyl system.

$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-Me}_2\text{As}(\text{CH}_2)_5\text{AsMe}_2)]\text{BF}_4$ show $\nu(\text{CO})$ values close to those for their phosphorus analogues.

The ^1H and ^{13}C NMR spectral data for the mono-substituted series are given in Table 2 (for numbering see Fig. 1) and, as expected, generally show similar patterns to those for I, except for additional splitting caused by ^{31}P coupling and additional ligand peaks. For example, the ^1H NMR spectrum of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppm})]\text{BF}_4$ consists of multiplets at 7.75–7.25 ppm assigned to the A₂ B₂ system and the phenyl protons, which are the most deshielded, a doublet at 5.85 ppm, assigned to the C protons, a triplet at 5.34 ppm assigned to the D proton, and finally a doublet at $\delta = 3.72$ ($J = 11.73$ Hz) assigned to the ligand CH₂ group. The ^1H NMR spectra of the other η^1 -dppa complexes are very similar except for the signals from ligand CH₂ protons.

The ^{13}C NMR spectra show the typical nine carbon pattern of the indenyl system, which is in agreement with previous reports [9]. The signals for the carbonyl carbons are split by the phosphorus atom in the phosphine and phosphite complexes, but not in the corresponding complexes with As and Sb ligands. For example, in the ^{13}C NMR spectrum of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppm})]\text{BF}_4$ the carbonyl carbons are the most deshielded, with a signal at 211.50 ppm, while the carbon atom in the CH₂ group (mixed with solvent peaks) is the most shielded carbon, appearing at 29.79 ppm. The C₂ carbon atom, which is equivalent to C₃, is less shielded than the methylene carbon and gives a signal at 78.52 ppm. The outer carbon C₁ gives a resonance at 95.43 ppm, the inner carbons C_{8,9} give a signal at 105.68 ppm, and the C_{4,7} and C_{5,6} carbons give signals at 126.43 ppm to 130.20 ppm respectively. These signals are overlapped by phenyl signals. The same pattern is observed for the complexes with longer methylene chains, such as dppe and dppo. The ^{31}P NMR spectra (Table 3) of the different $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppa})]\text{BF}_4$ complexes prove conclusively that the potentially bidentate phosphine ligands are coordinated in a monodentate mode to the metal atom because they contain two mutually coupled non-equivalent ^{31}P NMR resonance and a high-field signal with a chemical shift very similar to that for the free ligand [10,11]. The coordinated phosphorus atom shows

a downfield shift (*i.e.* the coordination shift) relative to that of the free ligand [3]. For example, the ^{31}P NMR spectrum of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppm})]\text{BF}_4$, shows two ^{31}P resonances, one at high-field -23.34 ppm assigned to the uncoordinated phosphorus atom, and one at low-field, 66.83 ppm, assigned to the coordinated phosphorus ($J(\text{PP}) = 88.50$ Hz). In $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dpp})]\text{BF}_4$ the phosphorus resonances are at -14.96 ppm and at 64.98 ppm, assigned to uncoordinated and coordinated phosphorus atoms, respectively ($J(\text{PP}) = 39.70$ Hz).

2.2. Ditertiary phosphine bridged dimers $\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\mu\text{-}(\text{dppa})\}[\text{BF}_4]_2$

The complexes were prepared by refluxing the parent compound I with the appropriate ditertiary phosphine (dppa) in a 2:1 molar ratio in acetone for relatively short times (30 min to 1 h). Analytical and spectroscopic data are given in Tables 1–3; again the $\nu(\text{CO})$ stretching frequencies are virtually identical throughout the series and similar to those of the Cp series [12]. The ^1H and ^{13}C NMR spectra are very similar to those of the monosubstituted series and require no further comment.

The ^{31}P NMR spectra of $\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\mu\text{-}(\text{dppm})\}[\text{BF}_4]_2$ demonstrate conclusively that the ditertiary phosphine ligands are bridging ligands between two iron atoms, because there is only one ^{31}P NMR resonance in each complex shifted downfield relative to the free ligand. For example, for $\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\mu\text{-}(\text{dppm})\}[\text{BF}_4]_2$ the phosphorus signal is observed at 69.95 ppm.

2.3. Ditertiary phosphine chelates $\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\mu\text{-}(\eta^2\text{-dppa})\}[\text{BF}_4]$

The complexes in the chelate series may be prepared by prolonged refluxing of the parent compound I in an acetone solution and the appropriate ditertiary phosphine in 1:1 molar ratio. The reaction involves initial formation of the monosubstituted compound, *i.e.* $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppa})]\text{BF}_4$, as described above. Alternatively, the chelate may be produced by photolysis of the diphosphine-bridged metal dimer.

Analytical and spectroscopic data are given in Tables 1–3. In this series, and in contrast to the other series, *i.e.* the monosubstituted compounds and the metal–metal diphosphine-linked dimers, the carbonyl-stretching frequency is now influenced by the alkane chain length in the diphosphine, decreasing from 1977 cm^{-1} in the dppe chelate to 1954 cm^{-1} in the dppo chelate ($n = 1$ to $n = 8$), suggesting decreasing π -acceptor and/or increasing σ -donation by the diphosphine with increasing alkane chain length. Again the ^1H and ^{13}C NMR spectra require little comment, al-

though it should be noted that the ligand CH_2 protons are no longer equivalent and form an AB system; for example, in the case of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$, one proton appears at 5.16 ppm, as a sextet, and the other at 4.31 ppm, also as a sextet, each being split by the other ($J = 12.09$ Hz) and by the phosphorus atoms ($J = 10.44$ Hz).

The ^{31}P NMR spectra of the $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppa})]\text{BF}_4$ shows only a single resonance at low-field, as expected for the equivalently coordinated phosphorus atoms. For example, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$ shows a singlet at 26.93 ppm, whilst the dppe and dppo derivatives have signals at 93.68 ppm and 33.00 ppm respectively. The size of the chelate ring influences the ^{31}P chemical shifts as well as the carbonyl-stretching frequencies. The chelation shift is defined as the difference in ^{31}P chemical shift between the coordinated phosphorus atom of the monodentate complex, and the phosphorus atom of the corresponding chelated complex ($\delta_{\text{chelate}} - \delta_{\text{coord}}$) [3,10]. In $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$, (four-membered ring) the chelation shift is negative (-39.90 ppm), whereas $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppe})]\text{BF}_4$ (five-membered ring) shows a positive chelation shift (28.7 ppm). Similar chelation shifts have been observed for related complexes [3,13,14], where coordination shifts in all cases were positive, *i.e.* there was a shift to lower field on coordination.

2.4. Crystal structure of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$

The molecular structure of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$ as revealed by an X-ray diffraction study is shown in Fig. 2. The most important features of the structure are as follows: (a) the PFeP bite angle is 74.7° and the $\text{Fe} \cdots \text{C} \cdots \text{O}$ linkage is almost linear (177.9°); (b) the indenyl system (C_1 to C_9) is planar, with an average $\text{Fe} \cdots \text{C}$ (ring) bond distance of 2.117 \AA and an average FeP bond length of 2.206 \AA (Table 4), these values being similar to those reported for $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^2\text{-dppe})]\text{BF}_4$ [15,16].

2.5. Reactions of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ with ditertiary arsines

The ditertiary arsine ligands, $\text{Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2$ (dpae) and $\text{Me}_2\text{As}(\text{CH}_2)_5\text{AsMe}_2$ (dmap), react in the same way as the diphosphine ligands to form monosubstituted, dimeric, and chelate complexes (Tables 1 and 2). For example, dpae reacts with I in acetone at room temperature to give the monosubstituted complex $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dpae})]\text{BF}_4$, $\nu(\text{CO}) = 2047 \text{ cm}^{-1}$ and 2004 cm^{-1} , close to those of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{-AsPh}_3]\text{BF}_4$, $\nu(\text{CO}) = 2050 \text{ cm}^{-1}$ and 2007 cm^{-1} . $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dmap})]\text{BF}_4$, $\nu(\text{CO}) = 2051 \text{ cm}^{-1}$ and 2010 cm^{-1} , formed similarly. The dimeric complexes $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-(dpae)}][\text{BF}_4]_2$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-(dmap)}][\text{BF}_4]_2$, were prepared under very similar conditions to those employed for the corresponding diphosphine complexes. The chelates are only formed after prolonged refluxing in acetone. The arsine complexes, particularly the dinuclear ones, are less soluble than their diphosphine analogues.

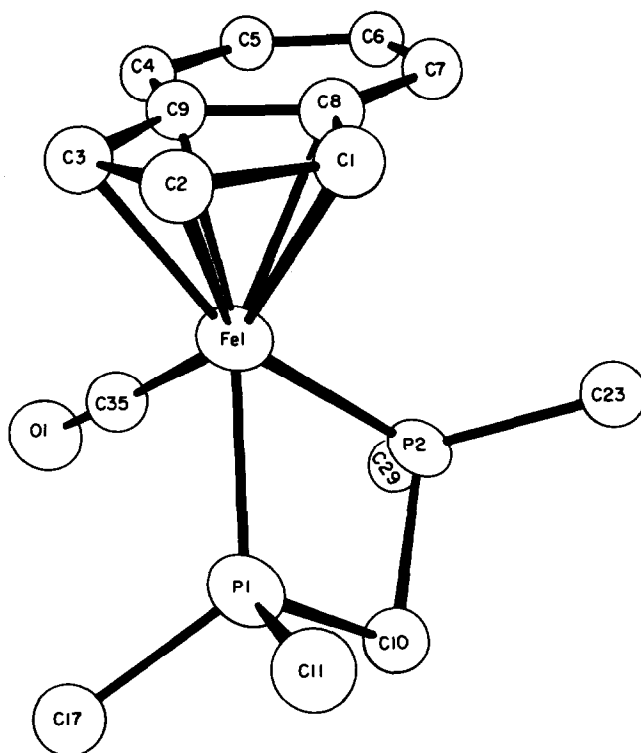


Fig. 2. X-Ray crystal structure of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$.

$[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dmap})]\text{BF}_4$, $\nu(\text{CO}) = 2051 \text{ cm}^{-1}$ and 2010 cm^{-1} , formed similarly. The dimeric complexes $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-(dpae)}][\text{BF}_4]_2$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]_2\text{-}\mu\text{-(dmap)}][\text{BF}_4]_2$, were prepared under very similar conditions to those employed for the corresponding diphosphine complexes. The chelates are only formed after prolonged refluxing in acetone. The arsine complexes, particularly the dinuclear ones, are less soluble than their diphosphine analogues.

The ^1H NMR spectrum of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dmap})]\text{BF}_4$ shows a multiplet at 7.95–7.38 ppm assigned to the A_2B_2 protons, a triplet at 5.49 ppm ($J = 2.93$ Hz) assigned to the D proton, a doublet at 5.45 ppm ($J = 2.93$ Hz) assigned to the C protons, signals at 2.90, 2.12, and 1.93 ppm assigned to the $(\text{CH}_2)_5$ protons, and finally the singlet at 1.43 ppm assigned to the CH_3 protons. In the ^{13}C NMR spectrum of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dpae})]\text{BF}_4$, the most deshielded carbon is the carbonyl carbon at 215.76 ppm, with the $\text{C}_{5,6}$ and $\text{C}_{4,7}$ carbons and the phenyl carbons at 132.54–127.39 ppm respectively. The signal at 101.60 ppm is assigned to the $\text{C}_{8,9}$ carbons, that at 89.86 ppm to C_1 , that at 70.99 ppm to C_2 , C_3 , and that from the most shielded carbon, at 28.22 ppm, to the CH_2 groups of dpae.

The carbonyl ^{13}C NMR spectra of the above complexes show an interesting pattern. For example, in the

parent cation, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]^+$, the CO signal appears as a singlet at 202.71 ppm, while in $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{P}(\text{OMe})_3)]\text{BF}_4$ it is a doublet at 207.36 ppm ($J = 38.50$ Hz). In $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\text{PPh}_3)]\text{BF}_4$ it lies at 210.0 ppm ($J = 24.70$ Hz) and in $(\eta^5\text{-C}_9\text{H}_7)\text{-Fe}(\text{CO})_2\text{Br}$ as a singlet at 212.67 ppm. Thus the most shielded carbonyl carbon is present in $[(\eta^5\text{-C}_9\text{H}_7)\text{-Fe}(\text{CO})_3]\text{BF}_4$ and the most deshielded in $[(\eta^5\text{-C}_9\text{H}_7)\text{-Fe}(\text{CO})_2]\text{Br}$, which is the reverse of the order of the carbonyl-stretching frequencies of the complexes. Fenske and coworkers have reported studies [17–19], in which the carbonyl 5σ orbital, involved in dative bonding to the transition metal, was shown to have a negative overlap population, so that donation of electron density from this orbital strengthens the $\text{C}\cdots\text{O}$ σ bond. Secondly, as the extent of transition metal \rightarrow carbonyl π back-donation decreases, the electron density in the carbonyl π^* orbital also decreases, with concomitant increase in the $\text{C}\cdots\text{O}$ bond strength. Bodner and coworkers [20–22] noted a similar correlation between the carbonyl chemical shifts and the carbonyl-stretching frequencies of $\text{L}_n\text{Ni}(\text{CO})_{4-n}$ derivatives and the electron donor-acceptor abilities of the ligands. Thus the carbonyl chemical shifts in $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$ ($\text{L} = \text{CO}, \text{P}(\text{OMe})_3$ or PPh_3) and $(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{Br}$ are related to the electron donor-acceptor character of the ligand, where the carbonyl resonance is increasingly deshielded with increasing electron density at the transition metal; decreasing the metal positive charge tends to lower the carbonyl-stretching frequencies and raise the δ values for the carbonyl carbon atoms.

3. Conclusions

The above results clearly show an enhanced reactivity of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]^+$ over that of isoelectronic $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$ towards ligand substitution by ditertiary phosphines (L), providing a further example of the ‘indenylyl effect’. Although we were unable to obtain any evidence for a η^3 ring-slipped intermediate, the higher reactivity in acetone compared with that in dichloromethane as solvent suggests initial generation of $[(\eta^3\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3(\text{acetone})]^+$ as an intermediate followed by formation of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3\text{L}]^+$ and subsequent loss of CO.

No evidence was obtained for initial attack by diphosphines at a ring carbon atom to form either ring adducts or ring–ring diphosphine-linked dimers, in contrast to the behaviour of the related η^5 -cyclohexadienyl and η^5 -cycloheptadienyl tricarbonyliron cations which give stable ring adducts; e.g. $[(\eta^4\text{-C}_7\text{H}_5\text{-5-exo-dppm})\text{Fe}(\text{CO})_3]\text{BF}_4$ [23] and ring–ring linked dimers e.g. $[5,5'\text{-exo-PPh}_2(\text{CH}_2)_3\text{PPh}_2](\eta^4\text{-C}_6\text{H}_7)\text{-}$

$\text{Fe}(\text{CO})_3)_2]\text{BF}_4)_2$ [24]. Despite the higher reactivity of the indenyl-containing cation compared with the analogous cyclopentadienyl-containing cation, both species undergo only metal carbonyl substitution in their reactions with soft nucleophiles such as diphosphines. It appears that the indenyl effect, involving ring slippage from η^5 to η^3 of the five-membered ring, operates for soft nucleophiles only in the transition state. The loss of delocalization energy of the planar C_5 ring is too great for formation of a stable η^4 ring adduct as a final product, whereas in the related cation $[(\eta^5\text{-C}_7\text{H}_9)\text{Fe}(\text{CO})_3]^+$ ring puckering reduces the delocalization energy and so formation of ring adducts is energetically possible [25].

4. Experimental details

Solvents were freshly dried by standard methods. All reactions and work-up were carried out under high-purity nitrogen. Tertiary diphosphines (dppm, dppe, dppb, dppe and dppo) ($n = 1, 2, 4, 6$ and 8 , respectively) were obtained commercially, and used without further purification. Infrared spectra were recorded using a 0.1 mm CaF_2 cell on a Perkin Elmer 1720 FT spectrometer linked to a 3700 data station. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a JEOL GX 270 spectrometer. Analyses were performed by the Microanalytical Laboratory of the Chemical Services Unit of University College Dublin, and are given in Table 1 together with the infrared carbonyl-stretching frequencies of the new compounds. The starting complex $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ was prepared by the published method [7].

4.1. Preparation of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppa})]\text{BF}_4$

An equimolar amount of the ligand was added to a solution of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ (0.3 g, 0.878 mmol) in dry acetone (30 ml) at room temperature. The mixture was stirred under nitrogen and after 10 min the reaction was complete, as indicated by IR spectroscopy. The solvent was removed, and the residue recrystallised from dichloromethane–ether to give pure yellow products.

4.2. Preparation of $\{[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2]\}_2\mu\text{-}(\text{dppa})\text{-}[\text{BF}_4]_2$

For the preparation of these complexes, a 2:1 ratio of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ to the free ligand was required. The reactants were mixed in dry acetone (30 ml) and the solution was refluxed for 30 min at room temperature until the $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ had disappeared as indicated by IR spectroscopy. The solution was concentrated to half its volume and addition of dry ether afforded dark yellow products.

TABLE 5. Crystal data for $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$

Crystal size (mm)	$0.25 \times 0.22 \times 0.35$
Formula	$\text{C}_{35}\text{H}_{29}\text{BF}_4\text{FeOP}_2$
M (a.m.u)	670.212
Triclinic space group	P1
<i>a</i> (Å)	10.538 (4)
<i>b</i> (Å)	11.415 (2)
<i>c</i> (Å)	15.027 (3)
α (°)	78.94(2)
β (°)	88.38 (2)
γ (°)	64.65(2)
<i>U</i> (Å ³)	1600.28
<i>Z</i>	2
<i>D_c</i> g cm ⁻³	1.39
μ cm ⁻¹	5.67
<i>F</i> (000)	688
Radiation Mo-K α	$\lambda = 0.7093 \text{ \AA}$
Graphite monochromator	
Diffractometer	Enraf-Nonius CAD4F
Orienting reflections range	25, $13 < 2\theta < 20^\circ$
Temperature (°C)	22
Scan method	$\omega/2\theta$
Data collection range	$2 < 2\theta < 48^\circ$
No. unique data	4874
Total $I > 3\sigma I$	2466
No. of parameters fitted	222
<i>R^a</i> , <i>R_w^b</i>	5.53%, 7.24%
Quality-of-fit indicator ^c	0.9
Largest shift/esd, final cycle	0.001
Largest positive peak (e Å ⁻³)	0.27
Largest negative peak (e Å ⁻³)	-0.13

^a $R = [\sum \|F_o\| - |F_c|] / \sum F_o$.

^b $R_w = \{[\sum w(|F_o - F_c|)^2] / [\sum w(|F_o|)^2]\}^{1/2}$; $w = 1/[(\sigma F_o)^2 + 0.00254 F_o^2]$.

^c Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$.

4.3. Preparation of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppa})]\text{BF}_4$

A solution of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ and an equimolar amount of the free ligands was refluxed in dry acetone under nitrogen. $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^1\text{-dppa})]\text{BF}_4$ was formed initially. After prolonged refluxing this intermediate disappeared, as indicated by IR spectroscopy. The solvent was removed *in vacuo*, and the oily products extracted with dichloromethane. Recrystallisation from hexane afforded orange and dark brown products.

The same procedure was used with the arsine ligands.

4.4. X-ray structure of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})(\eta^2\text{-dppm})]\text{BF}_4$

Crystal data and some experimental details are given in Table 5. The structure was solved by direct methods, SHELX86 [26], and refined by full-matrix least squares using SHELX76 [27]. Data were corrected for Lorentz and polarization effects but not for absorption. Hydro-

gen atoms were included in calculated positions with fixed thermal parameters. The iron, phosphorous, boron and fluorine atoms and the carbon monoxide group were refined anisotropically. The thermal parameters were terms U_{ij} of $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$.

The atomic scattering factors for non-hydrogen and hydrogen atoms, and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [28–30]. All calculations were performed

TABLE 6. Fractional atomic coordinates for $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^2\text{-dppm})]\text{BF}_4$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Fe ₁	0.10350(11)	0.50317(10)	0.23330(7)
P ₁	0.27060(2)	0.30730(2)	0.29320(1)
P ₂	0.29210(2)	0.53650(2)	0.24990(1)
O ₁	0.15570(6)	0.44940(5)	0.05240(4)
C ₁	-0.01740(8)	0.58300(8)	0.33770(5)
C ₂	-0.06100(9)	0.49530(8)	0.30900(6)
C ₃	-0.10550(8)	0.53690(8)	0.21940(5)
C ₄	-0.14190(9)	0.75130(8)	0.10290(6)
C ₅	-0.12570(9)	0.86510(9)	0.09740(6)
C ₆	-0.07640(9)	0.89520(9)	0.17010(6)
C ₇	-0.03470(9)	0.81380(8)	0.24980(6)
C ₈	-0.04810(8)	0.69050(7)	0.26300(5)
C ₉	-0.10350(8)	0.66180(7)	0.18730(5)
C ₁₀	0.41240(7)	0.35960(7)	0.28540(5)
C ₁₁	0.26800(7)	0.22490(7)	0.40910(4)
C ₁₂	0.36490(9)	0.20570(8)	0.47770(5)
C ₁₃	0.36050(10)	0.13650(9)	0.56490(6)
C ₁₄	0.26010(9)	0.08740(8)	0.58010(6)
C ₁₅	0.16830(9)	0.10600(8)	0.51480(5)
C ₁₆	0.17000(8)	0.17410(8)	0.42790(5)
C ₁₇	0.31890(7)	0.17490(6)	0.22970(4)
C ₁₈	0.21530(8)	0.15250(7)	0.19400(5)
C ₁₉	0.24850(9)	0.04960(8)	0.14920(5)
C ₂₀	0.38600(9)	-0.02870(9)	0.13810(6)
C ₂₁	0.49200(10)	-0.00930(8)	0.17300(5)
C ₂₂	0.45850(8)	0.09400(7)	0.22060(5)
C ₂₃	0.30440(7)	0.61960(7)	0.33890(5)
C ₂₄	0.30630(8)	0.74260(8)	0.31610(6)
C ₂₅	0.29940(9)	0.81160(10)	0.38620(6)
C ₂₆	0.29220(10)	0.75750(9)	0.47410(6)
C ₂₇	0.29150(9)	0.63410(8)	0.49780(6)
C ₂₈	0.29700(8)	0.56630(8)	0.42940(5)
C ₂₉	0.36270(7)	0.60150(6)	0.15200(4)
C ₃₀	0.27300(8)	0.68360(7)	0.07700(5)
C ₃₁	0.32740(9)	0.72950(8)	-0.00080(6)
C ₃₂	0.46790(9)	0.69210(8)	-0.00240(6)
C ₃₃	0.55680(10)	0.61090(8)	0.06910(6)
C ₃₄	0.50530(8)	0.56380(7)	0.14850(5)
C ₃₅	0.13750(7)	0.47020(7)	0.12440(5)
B ₁	0.17440(12)	0.79380(11)	0.73630(8)
F ₁	0.27340(5)	0.83120(5)	0.75550(4)
F ₂	0.12050(7)	0.76040(8)	0.81520(4)
F ₃	0.07080(7)	0.89330(6)	0.68020(5)
F ₄	0.23590(8)	0.68300(6)	0.70060(4)

on a VAX 8700 computer. The ORTEP program was used to obtain the drawings [31]. The atom coordinates are shown in Table 6. A table of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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