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Synthesis and characterization of $[C_5H_5Fe(CO)_2(ER_3)]BF_4$ complexes (E = N, P, As, Sb and Bi): crystal structure determination of $[C_5H_5Fe(CO)_2(Bi(C_6H_5)_3)]BF_4$ *

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Abstract

Group Vb donor ligands ER_3 (E = N, P, As, Sb and Bi; R = CH_3, C_2H_5, i-C_3H_7 and C_6H_5) react with $[C_5H_5Fe(CO)_2(THF)]BF_4$ under homogeneous or heterogeneous conditions to afford $[C_5H_5Fe(CO)_2(ER_3)BF_4$ complexes in good yields. Selected complexes of this type have also been obtained by oxidative cleavage of the Fe–Fe bond in $(Fe(C_5H_5)(CO)_2]_2$ with the ferricenium cation $[(C_5H_5)_2Fe]^+$ in the presence of ER_3. All the new complexes have been characterized by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy; The complex $[C_5H_5Fe(CO)_2(Bi(C_6H_5)_3)]BF_4$ has also been characterized by X-ray crystallography and shown to have a three-legged piano-stool geometry at the iron atom with a Fe–Bi distance of 2.570(1) Å. On the basis of NMR data, ligand substitution reactions, and comparison with results from the X-ray structures of related $E(C_6H_5)_3$ complexes (E = P, As and Sb) it is concluded that the Fe–E bond strength decreases in the order P > As > Sb > N > Bi, this is discussed.

Introduction

Donor ligands ER_3 with nitrogen or phosphorus as donor centers are two of the most common ligands used in inorganic [1] and organometallic systems [2]. Their higher analogues containing arsenic, antimony and bismuth donor centers have attracted much less interest; the numbers of known compounds containing these ligands generally decrease in the order As > Sb ≫ Bi [3,4]. During the last decade however, these ligands have attracted increasing interest due to a controversy about

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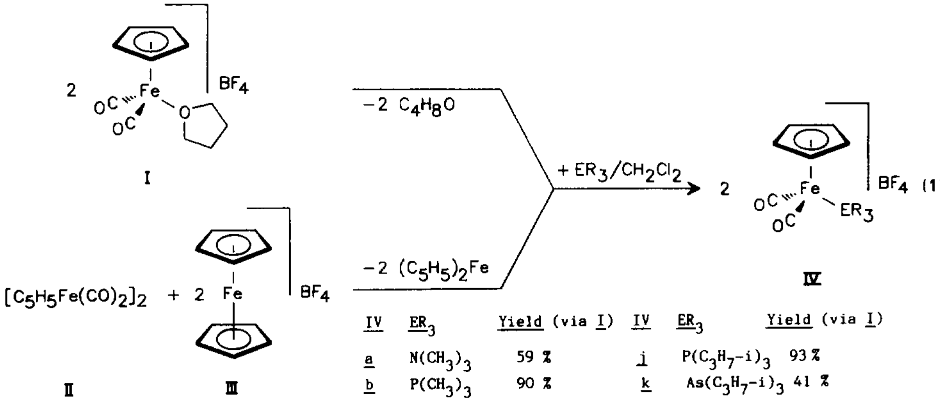
the relative σ and π contributions to the transition metal–ER_3 bond [5], but has been little of systematic investigation, especially in the case of bismuth donor ligands. Recent studies of the Fp^+ system ($Fp^+ = [C_5H_5Fe(CO)_2]^+$) attached to heavy Group VIb ligands $E'R_2$ indicates a strong increase in σ bond contribution in the order $E' = O \ll S < Se \ll Te$. This trend is nearly independent of the nature of R [6]. Investigations of the coordination behavior of selected Group Vb donor ligands ER_3 on the Fp^+ system have also been described [7].

We report here the crystal structure of $[Fp(Bi(C_6H_5)_3)]BF_4$, an important member of the $[Fp(E(C_6H_5)_3)]^+$ complex series [8], together with detailed spectroscopic data for Fp^+ complexes of Group Vb donor ligands. A preliminary communication has appeared [9].

Results and discussion

Complexes of the [Fp(L)]X type containing a wide variety of donor/acceptor ligands L have generally been obtained by replacement of labile coordinated ligands L′ such as THF [10]. This method is also applicable for Group Vb donor ligands ER_3, although the increasing reactivity of some of these ligands requires a change of the solvent used (see the Experimental section and Eq. 1). As alternative route to complexes IV involving the oxidative cleavage of the Fe–Fe bond in Fp_2 (II) by the ferricenium ion $[(C_5H_5)_2Fe]^+$ (III) in the presence of L can be used [11] (Eq. 1). Because of the increasing sensitivity and/or reactivity of uncoordinated ER_3 ligands [12], this latter method is only applicable for PR_3 and AsR_3 ligands. Under these conditions, $N(CH_3)_3$ affords paramagnetic and carbonyl-free coordination compounds of iron, while with $Sb(CH_3)_3$ only extensive decomposition is observed.



IV	ER_3	Yield (via I)	IV	ER_3	Yield (via I)
a	$N(CH_3)_3$	59 %	j	$P(C_3H_7\text{-}i)_3$	93 %
b	$P(CH_3)_3$	90 %	k	$As(C_3H_7\text{-}i)_3$	41 %
c	$As(CH_3)_3$	73 %	l	$Sb(C_3H_7\text{-}i)_3$	32 %
d	$Sb(CH_3)_3$	79 %	m	$Bi(C_3H_7\text{-}i)_3$	25 %
e	$Bi(CH_3)_3$	42 %	n	$P(C_6H_5)_3$	98 %
f	$P(C_2H_5)_3$	91 %	o	$As(C_6H_5)_3$	85 %
g	$As(C_2H_5)_3$	55 %	p	$Sb(C_6H_5)_3$	89 %
h	$Sb(C_2H_5)_3$	40 %	q	$Bi(C_6H_5)_3$	51 %
i	$Bi(C_2H_5)_3$	see text			

Complexes IV were all isolated in medium to good yield as yellow to yellow-brown solids. After recrystallisation all the crystals are light yellow. Although all compounds except those containing bismuth ligands are air-stable, the solutions of IVa–m and IVq are somewhat sensitive. Increasing amounts of insoluble decomposition products were obtained upon changing the solvent from methylene chloride to the better donors acetone and acetonitrile, as previously observed for related $[Fp(X{=}ER_3)]^+$ compounds ($X = O$ to Te) [6c,6d]. All attempts to coordinate $Bi(C_2H_5)_3$ to give complex IVi were unsuccessful: Only insoluble carbonyl-free materials were obtained. It is not clear why this ligand, unlike other BiR_3 ligands, cannot be attached to the Fp^+ center.

Spectroscopic data for complexes IV are given in Table 1. On the basis of the results of Tolman [13] and Bartik [14] on $Ni(CO)_3(ER_3)$ complexes the $\nu(CO)$ IR frequencies have shown to correlate with donor/acceptor properties of the coordinated ligand. Within the limited resolution due to the polar nature of both solvent and complexes IV, no general trend can be detected in the $\nu(CO)$ frequencies. A much more generally applicable method for determination of donor/acceptor interactions between organometallic fragments and ligands L involves the ^{13}C CO NMR shifts, as extensively demonstrated for $M(CO)_n$ [15] ($M = Cr$, $n = 5$ or $M = Ni$, $n = 3$) and Fp^+ [16] fragments. Selected spectroscopic data for IV ($L = ER_3$, $R = CH_3$ and C_6H_5), along with those for related $Ni(CO)_3(ER_3)$ complexes for comparison, are given in Table 2. The data indicate the same overall trend, as shown, for example by the close resemblance between P and As in their complexes. Lack of comparable data for the coordination of BiR_3 ligands on the Ni^0 system prevents more detailed comparison.

In earlier investigations of other complexes containing Group Vb and VIb ligand coordinated to the Fp^+ fragment [6], the ^{13}C CO data for IVa–e ($L = E(CH_3)_3$) revealed the good donor properties of the coordinated $E(CH_3)_3$ groups. The observed high field shift for complexes with $P(CH_3)_3$ and $As(CH_3)_3$ may be accounted for in terms of additional backbonding. Larger variations in the ^{13}C CO data are observed for ER_3-containing complexes ($R = C_2H_5$ and i-C_3H_7), and are possibly due to steric effects. Upon changing R in $[Fp(ER_3)]BF_4$ from alkyl to aryl (complexes IVn–q, see Table 1 and 2) the donor properties of the coordinated $E(C_6H_5)_3$ ligands decrease on going from P to Bi as donor center. This may be the result of an increasing polarization of the E–C(phenyl) bond due to the decreasing electronegative of E. This effect can result in either a decreasing or an increasing Fe–E bond strength (the latter due to enhancement π-backbonding by the phenyl group).

The changes in bond strength can be revealed by ligand substitution reactions [6a] as outlined in our preliminary communication [9] (see the Experimental section for a summary). Thus one equivalent of $P(CH_3)_3$ rapidly displaces all the other coordinated $E(CH_3)_3$ ligands in the related Fp^+ complexes, whereas under the same conditions $As(CH_3)_3$ and $Sb(CH_3)_3$ displace only $N(CH_3)_3$ and $Bi(CH_3)_3$. The $Sb(CH_3)_3$ complexes IVd on reaction with one equivalent $As(CH_3)_3$ in CD_2Cl_2 gives an equilibrium mixture of IVc and IVd, with substitution product IVc as the dominant species. The weak coordination of $Bi(CH_3)_3$ in complex IVe is also evident in the rapid decomposition of this complex in the presence of weak donor ligands such as acetone or acetonitrile. In the $E(C_6H_5)_3$ complex series IVn–q, one equivalent of $P(C_6H_5)_3$ in CD_2Cl_2 also displace all other coordinated ligands L

Table 1

^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and IR data for the complexes IV

Compound	^1H [a,b]	^{13}C [b,c]	^{31}P [b,d]	IR [d]
IVa	5.64 (s, 5 H, C_5H_5); 2.97 (s, 9 H, $N(CH_3)_3$)	211.69 (s, CO); 88.15 (s, C_5H_5): 62.03 ($N(CH_3)_3$)	–	2059s, 2011s
IVb	5.65 (d, 5 H, C_5H_5, $J(PH) = 1.7$); 1.89 (d, 9 H, $P(CH_3)_3$, $^2J(PH) = 11.7$)	210.21 (d, CO, $^2J(PC) = 26.3$): 88.21 s, C_5H_5): 19.77 (d, $P(CH_3)_3$, $^1J(PC) = 35.5$)	34.0	2054s, 2009s
IVc	5.62 (s, 5 H, C_5H_5); 1.83 (s, 9 H, $As(CH_3)_3$)	210.22 (s, CO): 87.20 (s, C_5H_5): 14.86 (s, $As(CH_3)_3$)	–	2051s, 2008s
IVd	5.60 (s, 5 H, C_5H_5): 1.64 (s, 9 H, $Sb(CH_3)_3$)	211.07 (s, CO): 86.67 (s, C_5H_5): 0.57 (s, $Sb(CH_3)_3$)	–	2046s, 2003s
IVe	5.64 (s, 9 H, C_5H_5); 2.33 (s, 9 H, $Bi(CH_3)_3$)	212.21 (s, CO): 86.07 (s, C_5H_5): −1.54 (s, $Bi(CH_3)_3$)	–	2053s, 2018s
IVf	5.69 (br s, 5 H, C_5H_5); 2.11 (m, 6 H, $P(C\mathit{H}_2CH_3)_3$); 1.21 (br t, 9 H, $P(CH_2C\mathit{H}_3)_3$, $J = 7.0$)	210.94 (d, CO, $^2J(PC) = 24$); 88.33 (s, C_5H_5); 21.54 (d, $P(\mathit{C}H_2CH_3)_3$; $^1J_{PC} = 30.9$), 8.06 (d, $P(CH_2\mathit{C}H_3)_3$; $^2J_{PC} = 3.4$)	59.0	2052s, 2007s
IVg	5.67 (s, 5 H, C_5H_5); 2.26 (q, 6 H, $As(C\mathit{H}_2CH_3)_3$, $^3J(HH) = 7.0$); 1.28 (t, 9 H, $As(CH_2C\mathit{H}_3)_3$, $^3J(HH) = 7.0$)	210.67 (s, CO); 86.90 (s, C_5H_5); 19.57 (s, $As(\mathit{C}H_2CH_3)_3$); 8.94 (s, $As(CH_2\mathit{C}H_3)_3$)	–	2050s, 2004s
IVh	5.74 (s, 5 H, C_5H_5); 2.36 (q, $Sb(C\mathit{H}_2CH_3)_3$, $^3J(HH) = 8.2$); 1.43 (t, 9 H, $Sb(CH_2C\mathit{H}_3)_3$, $^3J(HH) = 8.2$)	210.57 (s, CO); 85.99 (s, C_5H_5); 10.92 (s, $Sb(\mathit{C}H_2CH_3)_3$); 9.80 (s, $Sb(CH_2\mathit{C}H_3)_3$)	–	2046s, 2002s
IVj	5.46 (br s, 5 H, C_5H_5); 2.48 (m, 3 H, $P(C\mathit{H}(CH_3)_2)_3$); 1.33 (dd, 18 H, $P(CH(C\mathit{H}_3)_2)_3$, $^3J(HH) = 7.1$, $^3J(PH) = 15.5$)	211.37 (d, CO, $^2J(PC) = 22.4$); 87.05 (s, C_5H_5); 29.24 (d, $P(\mathit{C}H(CH_3)_2)_3$, $^1J(PC) = 23.2$); 20.08 (d, $P(CH(\mathit{C}H_3)_2)_3$, $^3J(PC) = 1.5$)	91.7	2052s, 2007s
IVk	5.76 (s, 5 H, C_5H_5); 2.85 (sep. $As(C\mathit{H}(CH_3)_2)_3$, $^3J(HH) = 7.2$); 1.41 (d, 18 H, $As(CH(C\mathit{H}_3)_2)_3$, $^3J(HH) = 7.2$)	212.40 (s, CO); 86.88 (s, C_5H_5); 30.71 (s, $As(\mathit{C}H(CH_3)_2)_3$); 20.45 (s, $As(CH(\mathit{C}H_3)_2)_3$)	–	2050s, 2006s
IVl	5.78 (s, 5 H, C_5H_5); 3.00 (sep, 3 H, $Sb(C\mathit{H}(CH_3)_2)_3$, $^3J(HH) = 7$); 1.52 (d, 18 H, $Sb(CH(\mathit{C}H_3)_2)_3$), $^3J(HH) = 7$)	211.23 (s, CO), 85.51 (s, C_5H_5); 23.73 (s, $Sb(\mathit{C}H(CH_3)_2)_3$), 21.63 (s, $Sb(CH(\mathit{C}H_3)_2)_3$)	–	2046s, 1999s
IVm	5.76 (s, 5 H, C_5H_5); 3.93 (sep, 3 H, $Bi(C\mathit{H}(CH_3)_2)_3$, $^3J(HH) = 7$); 1.91 (d, 18 H, $Bi(CH(C\mathit{H}_3)_2)_3$, $^3J(HH) = 7$)	210.47 9s, CO); 84.95 (s, C_5H_5); 26.08 (s, $Bi(\mathit{C}H(CH_3)_2)_3$); 24.53 (s, $Bi(CH(\mathit{C}H_3)_2)_3$)	–	2036s, 1994s
IVn	7.7–7.5 (m, 15 H, $P(C_6H_5)_3$); 5.65 (d, 5 H, C_5H_5, $^2J(PH) = 1.5$)	210.43 (d, CO, $^2J(PC) = 25.2$); 133.5 (d, *o*-C, $^2J_{PC} = 10.5$); 131.94 (d, C-1, $^2J(PC) = 52.2$), 132.81, (d, *p*-C, $^4J(PC) = 2.6$); 130.23 (d, *m*-C, $^3J(PC) = 11$); 89.73 (s, C_5H_5)	67.9	2059s, 2917s
IVo	7.68/7.48 (m/m, 9 H/6 H, $As(C_5H_5)_3$); 5.75 (s, 5 H, C_5H_5)	210.03 (s, CO); 132.85 (s, *o*-C); 132.39 (s, *p*-C); 130.65 (s, *m*-C); 130.20 (s, C-1); 88.36 (s, C_5H_5)	–	2057s, 2014s

Table 1 (continued)

Compound	^{1}H [a,b]	^{13}C [b,c]	^{31}P [b,d]	IR [d]
IVp	7.63 (s, 15 H, $Sb(C_6H_5)_3$); 5.84 (s, C_5H_5)	209.34 (s, CO); 135.52 (s, *o*-C); 132.34 (s, *p*-C); 130.86 (s, *m*-C); 128.67 (s, C-1); 87.00 (s, C_5H_5)	–	2052s, 2011s
IVq	7.71/7.58 (m/m, 6 H/9 H, $Bi(C_6H_5)_3$); 5.87 (s, C_5H_5)	208.95 (s, CO); 136.81 (s, *o*-C); 136.49 (br s, C-1); 131.89 (s, *m*-C); 131.50 (s, *p*-C); 86.68 (s, C_5H_5)	–	2055s, 2015s

[a] Chemical shifts (δ) in ppm, coupling constants in Hz; measurements at 297 ± 2 K. [b] Measured in dried and degassed acetone-*d*. [c] ^{1}H-Decoupled; chemical shifts are to high frequency of $Si(CH_3)_4$. [d] ^{1}H-Decoupled; chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [e] ν(CO) in cm^{-1}; measured in 1,2-$Cl_2C_2H_4$ solution; all values are ± 2 cm^{-1}.

Table 2

Selected spectroscopic data for complexes IV and $Ni(CO)_3(L)$

L	$Fe(C_5H_5)(CO)_2(L)$ BF_4 (IV)			$Si(CO)_3(L)$		
	IR ν(CO) [a]	$\Delta\delta^{13}$C(CO) [b]	$\Delta\delta^{13}$C(α-C)(L) [c]	IR ν(CO) [a]	$\Delta\delta^{13}$C(CO) [b]	$\Delta\delta^{13}$C(αC)(L) [c]
$N(CH_3)_3$	2059	8.71	34.43	[d]	[d]	[d]
$P(CH_3)_3$	2054	7.23	3.30	2065	5.05	3.34
$As(CH_3)_3$	2051	7.24	4.30	[d]	4.46	3.12
$Sb(CH_3)_3$	2046	8.09	−2.69	[d]	4.99	1.37
$Bi(CH_3)_3$	2053	9.23	4.06	[d]	[d]	[d]
$P(C_6H_5)_3$	2059	7.45	−5.22	2070	4.30	−1.48
$As(C_6H_5)_3$	2057	7.05	−9.41	2073	4.16	−5.62
$Sb(C_6H_5)_3$	2052	6.36	−9.71	2074	4.86	−4.37
$Bi(C_6H_5)_3$	2055	5.97	−18.19	2072 [e]	[d]	[d]

[a] Data in cm^{-1} and measured in 1,2-$Cl_2C_2H_4$ for complexes IV [$(Fe(C_5H_5)(CO)_2(L)]$ BF_4; ± 2 cm^{-1}) or nonpolar solvents ($Ni(CO)_3(L)$; data from Ref. 28). [b] Data given as: δ^{13}C(CO)(complex) − δ^{13}C(CO)($[Fe(C_5H_5)(CO)_3]^+$ or $Ni(CO)_4$); δ^{13}C(CO)($[Fe(C_5H_5)(CO)_3]BF_4$) = 202.98 ppm acetone-d_6, ± 0.1 ppm [15]), δ^{13}C(CO)($Ni(CO)_4$) = 191.64 ppm (chloroform-*d*, ± 0.03 ppm [15]); data given in ppm. [c] Data given as: δ^{13}C(α-C)(complex) − δ^{13}C(αC)(uncoordinated ligand L); values are calculated using data from Refs. 9 and 28 and given in ppm. [d] To the best of our knowledge no data are available. [e] Data from Ref. 29.

from the complexes, but more slowly than $P(CH_3)_3$. Under the conditions used (CD_2Cl_2, room temperature, 12–24 h) no other $E(C_6H_5)_3$ ligand displaces a coordinated ligand L from $[Fp(E(C_6H_5)_3)]^+$ complexes. This indicates that either the bond strengths Fe–E(phenyl) are comparable, or, more probably, that is decreasing space for the substitution reaction around the metal center in these complexes. These ligand displacement reactions are consistent with a fall in the bond strength Fe–E in the order P > As > Sb > N > Bi.

Further evidence for these bonding trends should be provided by the results of X-ray structure determinations on $[Fp(E(C_6H_5)_3)]X$ complexes [8]. As an important member of this series, the X-ray structure of $[Fp(Bi(C_6H_5)_3)]BF_4$ (IVq) was determined (see Experimental section) [17*]. Atomic coordinates are given in Table 3 and selected bond distances and angles in Table 4. The structure of complex IVq is

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* Reference number with asterisk indicates a note in the list of references.

Table 3

Fractional atomic coordinates for $[Fe(C_5H_5)(CO)_2(Bi(C_6H_5)_3)]BF_4$ (IVq), with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*
Bi(1)	0.1745(1)	0.2269(1)	0.2657(1)
Fe(1)	0.2691(1)	0.1796(1)	0.4435(1)
C(1)	0.4508(11)	0.1321(9)	0.3840(7)
O(1)	0.5605(8)	0.0981(8)	0.3498(6)
C(2)	0.1997(9)	0.0264(9)	0.4706(6)
O(2)	0.1595(8)	−0.0706(6)	0.4986(5)
C(11)	0.0139(8)	0.3881(6)	0.2380(5)
C(12)	−0.1194(8)	0.3939(7)	0.3105(6)
C(13)	−0.2243(9)	0.4910(8)	0.2885(7)
C(14)	−0.1980(11)	0.5743(8)	0.1997(8)
C(15)	−0.0687(11)	0.5678(7)	0.1296(7)
C(16)	0.0397(8)	0.4737(7)	0.1516(5)
C(21)	−0.0839(8)	0.1247(7)	0.1684(5)
C(22)	−0.1584(9)	0.0384(8)	0.1296(6)
C(23)	−0.0989(10)	−0.0806(8)	0.1264(6)
C(24)	0.0332(10)	−0.1172(7)	0.1644(6)
C(25)	0.1070(8)	−0.0313(7)	0.2039(5)
C(26)	0.0509(8)	0.0890(7)	0.2062(5)
C(31)	0.3621(8)	0.2607(7)	0.1320(5)
C(32)	0.4702(10)	0.3441(8)	0.1370(6)
C(33)	0.5899(10)	0.3647(8)	0.0556(7)
C(34)	0.5995(8)	0.3031(8)	0.0290(7)
C(35)	0.4956	0.2200	−0.0346
C(36)	0.3740	0.1990	0.0478
C(41)	0.1962	0.1977	0.5993
C(42)	0.3414	0.2350	0.5731
C(43)	0.3497	0.3342	0.4922
C(44)	0.2020	0.3608	0.4730
C(45)	0.1114	0.2750	0.5395
B(1)	0.6732	0.3292	0.6585
F(1)	0.6173	0.2147	0.7028
F(2)	0.8021	0.3417	0.6950
F(3)	0.6990	0.3346	0.5539
F(4)	0.5688	0.4136	0.6863

Table 4

Selected bond distances (Å) and angles (°) for $[Fe(C_5H_5)(CO)_2(Bi(C_6H_5)_3)]BF_4$ (IVq)

Fe(1)–Bi(1)	2.570(1)	Fe(1)–C(1)	1.764(9)
Fe(1)–C(2)	1.788(9)	C(1)–O(1)	1.135(12)
C(2)–O(2)	1.129(11)	Bi(1)–C(11)	2.218(6)
Bi(1)–C(26)	2.218(8)	Bi(1)–C(31)	2.226(6)
Fe(1)–Bi(1)–C(11)	119.2(2)	Fe(1)–Bi(1)–C(26)	121.5(2)
Fe(1)–Bi(1)–C(31)	112.6(3)	Fe(1)–C(1)–O(1)	176.9(8)
Fe(1)–C(2)–O(2)	172.4(8)	Bi(1)–Fe(1)–C(1)	92.0(3)
Bi(1)–Fe(1)–C(2)	93.9(3)		

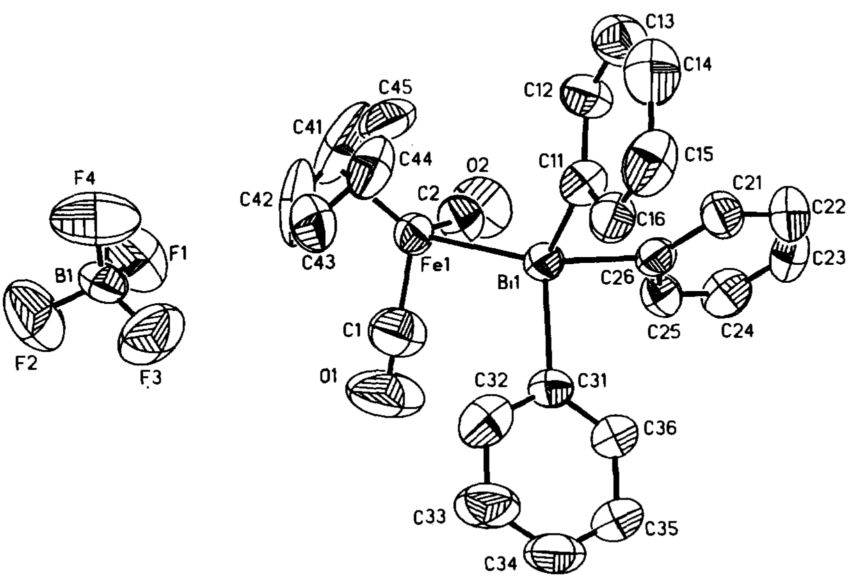

Fig. 1.

shown in Fig. 1, and is composed of discrete cations $[C_5H_5Fe(CO)_2(Bi(C_6H_5)_3)]^+$ and anions BF_4^- without any interactions between them. The coordination about the iron atom is pseudooctahedral ("three-legged piano-stool geometry") with the carbonyl (C(1) and C(2)) and triphenylbismuth ligands occupying three of the six positions and the cyclopentadienyl ring, acting in tridentate mode, occupying the remaining three positions. The observed Fe–Bi distance of 2.570(1) Å is slightly longer than the sum of the covalent radii (2.53 Å [18]), as expected for a bonding system which mainly involves sigma interactions, and also observed for the related $Cr(CO)_5$ complex [19]. Compared with corresponding distances in selected FeBi cluster compounds containing either Bi^{3-} or BiX^{2-} groups (X = halide or alkyl) (Fe–Bi 2.65 to 2.71 Å [20]), the cluster Fe–Bi bond is elongated by ca. 0.1 Å, and this can be attributed to the steric demands of the organometallic fragments, the multiple bridging nature of the Bi fragment, and in some cases oligomeric association in the solid state. The bond lengths and angles within the Fp^+ fragment are unexceptional when compared with those in related cationic (Fp(L)]X complexes [8,21]. Due to the limited quality of the X-ray structure determination of $Bi(C_6H_5)_3$ [22], the observed values for the Bi–C1 (phenyl) bond distances (2.218/2.226 Å) in IVq are in agreement with those in the uncoordinated ligand (2.21/2.25 Å).

For comparison, selected data from the X-ray structure determinations of $[Fp(E(C_6H_5)_3)]X$ (E = P, As, Sb and Bi, cations IVn,o,p,q) and related complexes are given in Table 5. Adopting the method of Lappert et al. [19], subtraction of the tetrahedral covalent radii for P (1.10), Sb (1.36) and Bi (1.46 Å) from the Fe–E distance yields differences for the Fe radius of 1.140 (E = P), 1.117 (Sb) and 1.110 Å (Bi; lit. value for Fe: 1.07 Å [18]), following the trend observed for the $Cr(CO)_5(E(C_6H_5)_3)$ complexes [19,23] (Cr: 1.322 (C = P), 1.317 (As), 1.257 (Sb) and 1.245 Å (Bi; lit value for Cr: 1.15 Å [18])) and $Fe(CO)_4(E(C_6H_5)_3)$ complexes [24] (Fe: 1.144 (E = P) and 1.112 (Sb)). These observations are not in accord with trends

Table 5

Comparison of X-ray structure determinations on organometallic complexes containing group Vb donor ligands $E(C_6H_5)_3$

	$Fe(C_5H_5)(CO)_2(E(C_6H_5)_3)^+$ [8]				$Cr(CO)_5(E(C_6H_5)_3)$ [19,23]				$Fe(CO)_4(E(C_6H_5)_3)$ [24]	
	E = P	As	Sb	Bi [a]	P	As	Sb	Bi	P	Sb
Bond lengths (Å)										
M–E	2.240(1)	2.336(1)	2.477(1)	2.570(1)	2.422(1)	2.4972(5)	2.6170(3)	2.705(1)	2.244(1)	2.472(1)
M–E (calc.)	(2.17)	(2.28)	(2.43)	(2.53)	(2.354)	(2.494)	(2.609)	(2.709)	(2.17)	(2.43)
M–C_5H_5 (av.)	2.094	2.070	2.095	2.077	–	–	–	–	–	–
M–C(O) (av.)	1.776	1.779	1.784	1.772	1.845 [b]	1.859 [b]	1.865 [b]	1.86 [b]	1.795 [b]	1.765 [b]
C–O (av.)	1.134	1.137	1.136	1.132	1.154 [b]	1.147 [b]	1.13 [b]	1.14 [b]	1.139 [b]	1.138 [b]
E–C (av.)	1.817	1.930	2.109	2.220	1.828	1.947	2.133	2.216	1.831	2.125
E–C (calc.)	(1.83)	(1.94)	(2.09)	(2.19)	(1.83)	(2.017)	(2.09)	(2.19)	(1.83)	(2.09)
Bond angles (°)										
C–M–C [c]	96.4	96.0	92.9	94.8	–	–	–	–	–	–
C–M–E (av.)	91.3	91.5	94.2	93.0	174.3 [b]	174.7 [b]	175.0 [b]	175.7 [b]	178.3 [b]	178.1 [b]
M–C–O (av.)	178.2	178.6	178.5	174.7	–	–	–	–	178.9 [b]	179 [b]
C–E–C (av.)	104.8	104.5	101.5	101.1	102.6	101.4	99.2	98.7	103.9	101.8
R	0.059	0.039	0.035	0.0239	0.043	0.030	0.025	0.042	0.061	0.024

[a] This work. [b] *trans* CO. [c] Carbon atoms of the carbonyl groups.

expected for systems with π bonding, where the transition metal–E bond length should be fall as a result of additional back-bonding [19].

In agreement with our interpretation of σ interactions as the main bonding force for coordination of heavy Group Vb ligands ER_3 to the Fp^+ fragment, earlier investigations of the formation of adducts of ER_3 ligands with inorganic and organic compounds also indicated only weak acceptor properties for the heavy Group Vb ligands ER_3 [25].

Experimental

Materials. $[C_5H_5Fe(CO)_2]_2$ (Strem), $E(C_6H_5)_3$ ($E = P$, As, Sb; Aldrich and $E = Bi$; Alfa), ER_3 ($E = N$, $R = CH_3$; Aldrich, $E = P$, $R = CH_3$, C_2H_5 and i-C_3H_7; Strem), ECl_3 ($E = P$-Bi; Aldrich), $(C_5H_5)_2Fe$ and $HBF_4 \cdot (C_2H_5)_2O$ (both Aldrich) were obtained from commercial sources and used without further purification. All reactions were conducted in oven-dried Schlenk tubes and dried solvents, degassed under nitrogen, were used.

Instrumentation. NMR spectra were recorded on Varian XL-300 spectrometers as ca. 5% solutions in dried and degassed acetone-d_6 with internal TMS (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P) as reference. All measurements were performed in 5 mm NMR tubes at 293 ± 2 K. IR spectra ($\nu(CO)$) were recorded with $1,2\text{-}Cl_2C_2H_4$ solutions in 0.1 mm CaF_2 cells on a Perkin Elmer 298 IR spectrometer, and were calibrated against a polystyrene standard.

The FAB(+)-MS spectrum of complex IVe were measured on a VG micromas 7070 double focusing high resolution mass spectrometer equipped with a VG data system 2000 with solutions in 3-nitrobenzyl alcohol/methylene chloride mixtures at room temperature.

Synthesis. $[Fp(L)]BF_4$ complexes IV were obtained as previously described: $L = E(CH_3)_3$ [9] (except for $E = Bi$, see below) and $L = E(C_6H_5)_3$ [9] (except for $E = Bi$, all complexes were obtained by oxidative cleavage of the Fe–Fe bond in Fp_2 by $[(C_5H_5)_2Fe]BF_4$ [26]; yields are < 90%). For all other complexes ($R = C_2H_5$ and i-C_3H_7, BiR_3) the following method was used: To an ethereal solution of 15 mmol of ER_3 ($E = As$, Sb, $R = C_2H_5$, i-C_3H_7; $E = Bi$, $R = CH_3$, i-C_3H_7 and C_6H_5; prepared from RMgX and ECl_3, ratio 3.2 : 1 in ether [12], with the excess of RMgX destroyed with degassed acetone) was added 2.0 g (6.0 mmol) of $[Fp(THF)]BF_4$ [8], and the resulting suspension stirred for 12 to 16 h at room temperature. After evaporation of the solvent, the products were extracted with methylene chloride, precipitated with ether, and recrystallized from methylene chloride/ether (1 : 1 to 1 : 4).

Since the new complexes all belong to the same series, their purities were confirmed only by spectroscopic methods. The sensitivity of complexes IVe and IVl prevented elementary analysis, but for complex IVe, low resolution FAB(+) data were obtained (amu): 481 (23%, $[M + BF_2]^+$), 431 (100%, $[M]^+$), 375 (12%, $[M - 2CO]^+$), 209 (8%, $[Bi]^+$), 186 (16%, $[Fe(C_5H_5)_2]^+$) and 177 (14%, $[Fp]^+$).

Ligand substitution reactions. A solution of a weighed amount of IVa–e ($R = CH_3$) or IVn–q ($R = C_6H_5$) in purified and degassed CD_2Cl_2 was transferred under nitrogen into an 5 mm NMR tube. Prior to addition of about 1.2 eq. ER_3 from a syringe, the purity of the starting material was checked by ^1H ($R = CH_3$) or ^{13}C NMR ($R = C_6H_5$) spectroscopy. After the solutions had been thoroughly mixed, they were stored in the dark at room temperature and the spectra checked after 12 and 24 h.

Crystallography. Crystal data for IVe: $C_{25}H_{20}BBiF_4FeO_2$, $M = 703.6$, crystals obtained as orange plates by slow diffusion of ether into a dilute methylene chloride/acetone solution were triclinic, space group $P\bar{1}$—C^1_i (No. 2), $a = 8.975(3)$, $b = 10.873(3)$, $c = 13.040(4)$ Å, $\alpha = 81.99(2)$, $\beta = 80.59(3)$, $\gamma = 86.05(3)°$, $V = 1241.59$ Å^3, $Z = 2$, $D_c = 1.883$ g cm^{-3}, $F(000) = 672$, Mo-K_α radiation, and $\mu = 76.88$ cm^{-1}.

Intensity data were collected from a crystal of dimensions 0.19 × 0.228 × 0.532 mm on an AED II diffractometer (θ–2θ mode; $7.89 < 2\theta < 37.12°$) equipped with an ECLIPSE computer using the SHELXTL [27] program system. The merging R index was 0.0239 for 3475 unique data ($I > 2.5\sigma(I)$) after empirical absorption correction (7 reflexes) using transmission factors between 0.69 and 1.00. The structure was solved by Patterson-Fourier synthesis followed by blocked-matrix least square refinement (all nonhydrogen atoms anisotropic, hydrogen atoms at calculated positions). Refinement converged at $R = 0.035$ and $R_w = 0.0291$ for 307 parameters. A complete table of bond lengths and angles, a table of thermal parameters, and a list of observed and calculated structures are available from H.S.

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