1432 *Inorg. Chem.* **1989**, *28*, 1432-1434

Contribution from the Department of Chemistry,
Rice University, Houston, Texas 77251

Synthesis and Structure of $[PPN]_2[Tl_2Fe_6(CO)_{24}]$: Completion of a Series of Thallium–Iron Carbonyl Clusters

Juanita M. Cassidy and Kenton H. Whitmire*

Received August 8, 1988

The thallium–iron carbonyl $[Et_4N]_2[Tl_2Fe_4(CO)_{16}]$ is oxidized by $[Cu(MeCN)_4][BF_4]$ in MeOH to generate $[Et_4N]_2[Tl_2Fe_6(CO)_{24}]$. $[Et_4N]_2[Tl_2Fe_6(CO)_{24}]$ is also produced when HCl and CF_3SO_3H are used as oxidizing agents. Cation metathesis with [PPN]Cl occurs in MeOH in good yield. $[PPN]_2[Tl_2Fe_6(CO)_{24}]$ crystallizes in the monoclinic, centrosymmetric space group $P2_1/n$ with $a = 12.862$ (4) Å, $b = 21.256$ (4) Å, $c = 18.564$ (4) Å, $\beta = 108.06$ (2)°, $V = 4825$ (2) Å^3, $Z = 2$, and mol wt = 2493.25. Diffraction data were collected on a Rigaku AFC5S diffractometer using Mo Kα radiation. The structure refined to $R_F = 0.042$ and $R_{wF} = 0.049$ for 4660 reflections having $I > 3.00(\sigma(I))$. The structure of $[PPN]_2[Tl_2Fe_6(CO)_{24}]$ contains a Tl_2Fe_2 parallelogram with $d_{Tl-Fe} = 2.762$ (2) and 2.746 (2) Å. The two thalliums also bridge $Fe_2(CO)_6(\mu\text{-}CO)_2$ groups with $d_{Tl-Fe} = 2.746$ (2) and 2.765 (2) Å. The structure of $[PPN]_2[Tl_2Fe_6(CO)_{24}]$ completes a series of thallium–iron carbonyls, $[Et_4N]_4[Tl_4Fe_8(CO)_{30}]$ and $[Et_4N]_6[Tl_6Fe_{10}(CO)_{36}]$, previously reported.

Introduction

Main-group/transition-metal complexes have recently received a good deal of attention for their relationship to materials and solid-state chemistry.[1] Even so, structurally characterized transition-metal carbonyl compounds containing the main-group element thallium are limited.[2] Recently, we reported the X-ray structure analyses of the Tl–Fe carbonyls $[Et_4N]_2[Tl_2Fe_4(CO)_{16}]$ ($[Et_4N]_2$[I]), $[Et_4N]_4[Tl_4Fe_8(CO)_{30}]$ ($[Et_4N]_4$[II]), and $[Et_4N]_6[Tl_6Fe_{10}(CO)_{36}]$ ($[Et_4N]_6$[III]),[3] which are dimeric clusters formed through bonding of electron-rich iron carbonyls to electron-deficient thallium atoms. The structures show nonbonding Tl···Tl distances that range from 3.604 (3) to 3.859 (2) Å. No Tl–Fe carbonyl had been previously structurally characterized, and only one Tl–Fe compound had been reported—that of Hieber, formulated as $Tl_2Fe_3(CO)_{12}$[4] on the basis of elemental analysis. Herein we wish to present the Tl–Fe compound $[PPN]_2[Tl_2Fe_6(CO)_{24}]$ (PPN = bis(triphenylphosphine)nitrogen(1+)) ($[PPN]_2$[IV]) produced from the oxidation of $[Et_4N]_2$[I]. The structure of this cluster bears striking similarities to $[Et_4N]_4$[II] and $[Et_4N]_6$[III], and the cluster represents the missing member of this series of Tl–Fe carbonyls. The X-ray structure of $[PPN]_2$[IV] is discussed along with its structural comparisons to $[Et_4N]_4$[II] and $[Et_4N]_6$[III].

Experimental Section

The title compound, $[PPN]_2$[IV], is moderately air sensitive, and all manipulations were performed on a Schlenk line using an oxygen-free nitrogen atmosphere, employing dried and distilled solvents. $[Et_4N]_2$[I],[3] $[Cu(MeCN)_4][BF_4]$,[5] and [PPN]Cl[6] were synthesized according to literature methods. The reagent $[Et_4N]$Br was used as received from the commercial source. Infrared spectra were recorded on a PE 1430 spectrophotometer. Analysis was performed by Desert Analytics Organic Microanalysis (Tucson, AZ).

Synthesis of $[Et_4N]_2[Tl_2Fe_6(CO)_{24}]$ Using $[Cu(MeCN)_4][BF_4]$. $[Et_4N]_2$[I] (1.765 g, 2.634 mmol) and $[Cu(MeCN)_4][BF_4]$ (0.846 g) were stirred for approximately 20 h in 100 mL of MeOH. The solution changed initially from brown-orange to brown and then finally to a greenish brown color with Cu^0 noticeable as a precipitate. The solution was filtered, leaving a brown to black solid plus the Cu^0 precipitate. The solid was dissolved in acetone, and the mixture was filtered and dried. More product was obtained from the MeOH filtrate upon concentration.

Table I. Crystallographic Data for $[PPN]_2[Tl_2Fe_6(CO)_{24}]$

chem formula	$Tl_2Fe_6C_{96}O_{24}N_2P_4H_{60}$	space group	$P2_1/n$ (No. 14)
cryst system	$a = 12.862$ (4) Å	λ	0.71069 Å
	$b = 21.256$ (4) Å	D_{calc}	1.72 g/cm^3
	$c = 18.564$ (4) Å	μ(Mo Kα)	43.72 cm^{-1}
	$\beta = 108.06$ (2)°	transmission coeff	0.8299–1.0000
	$V = 4825$ (3) Å^3		
Z	2	residuals: R; R_w	0.042; 0.049
temp	23 °C		
fw	2493.25		

IR (ν_{CO} in cm^{-1}, acetone): 2050 (w), 2027 (m), 2000 (vs), 1999 (vs, sh), 1978 (m, sh), 1966 (s), 1950 (m, sh), 1925 (m, sh), 1906 (s), 1789 (m). The compound is soluble in THF, acetone, and MeCN, slightly soluble in MeOH and CH_2Cl_2, and insoluble in diethyl ether, toluene, and hexane.

Synthesis of $[PPN]_2[Tl_2Fe_6(CO)_{24}]$. Excess [PPN]Cl was added to a MeOH solution of $[Et_4N]_2$[I] and $[Cu(MeCN)_4][BF_4]$, which had been prepared and allowed to stir for 20 h, as above. The solid was stirred for an additional 1 h, filtered out, and dissolved in CH_2Cl_2, and the solution was refiltered by using a fine frit. Diethyl ether was layered over the CH_2Cl_2 solution, a few volumes at a time, over a period of several hours, giving rise to large, black crystals. The crystals were washed with MeOH and dried. Yield: 1.05 g, 48% (based on iron). IR (ν_{CO} in cm^{-1}, CH_2Cl_2): 2050 (w), 2038 (s), 2000 (vs), 1961 (s), 1946 (s), 1936 (m, sh), 1906 (m), 1777 (m, br). IR (ν_{CO} in cm^{-1}, Nujol mull): 2030 (m), 2002 (s, sh), 1996 (s), 1967 (m, sh), 1959 (m), 1941 (m), 1926 (m), 1785 (m), 1764 (m). The compound is soluble in CH_2Cl_2, acetone, and THF, partially soluble in MeCN, very slightly soluble in MeOH, and insoluble in diethyl ether and hexane. Anal. Calcd: C, 46.25; H, 2.43; N, 1.12. Found: C, 46.22; H, 2.26; N, 1.17.

X-ray Analysis of $[PPN]_2[Tl_2Fe_6(CO)_{24}]$. A crystal suitable for X-ray analysis was obtained from the synthesis above and was mounted on a glass fiber with epoxy cement. The crystal chosen was a black rectangular prism of dimensions 0.2 × 0.2 × 0.2 mm^3. Crystallographic data for $[PPN]_2[Tl_2Fe_6(CO)_{24}]$ are given in Table I. The programs used in solving the structure were part of the Molecular Structure Corp. data reduction and refinement programs (TEXSAN, version 2.0). Heavy atoms were located by using MITHRIL,[7] and all non-hydrogen atoms were determined and refined with cycles of least-squares difference maps until convergence was achieved. All atoms were refined anisotropically. The structural data were corrected for absorption (ψ scans) and decay. The possibility that the crystal structure of $[PPN]_2[Tl_2Fe_6(CO)_{24}]$ may include a mirror plane through the central Tl_2Fe_2 parallelogram is precluded by the orientation of the phenyl rings on the PPN cation; PPN$^+$ does not sit on a crystallographic site of symmetry. The generation of least-squares planes for the Tl_2Fe_2 ring and for the irons external to the ring resulted in a dihedral angle between these planes of 93.78°, significantly greater than the 90° that would be expected if a mirror plane were present in the anion.

An ORTEP diagram of the anion is shown in Figure 1. Atomic coordinates for $[PPN]_2$[IV] are shown in Table II, and selected bond dis-

---

(1) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. (b) Whitmire, K. H. *J. Coord. Chem.* **1988**, *17*, 95. (c) Hoffmann, R.; Wijeyesekera, S. D.; Sung, S.-S. *Pure Appl. Chem.* **1986**, *58*, 481.

(2) (a) $Tl[Co(CO)_4]$: Schussler, D. P.; Robinson, W. R.; Edgell, W. F. *Inorg. Chem.* **1974**, *13*, 153. (b) $Tl[CpMo(CO)_3]_3$: Rajaram, J.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 1313. (c) Reactivity studies of a number of simple thallium–metal carbonylates have been reported: Burlitch, J. M.; Theyson, T. W. *J. Chem. Soc., Dalton Trans.* **1974**, 828.

(3) Whitmire, K. H.; Cassidy, J. M.; Rheingold, A. L.; Ryan, R. R. *Inorg. Chem.* **1987**, *27*, 1347.

(4) Hieber, W.; Gruber, J.; Lux, F. *Z. Anorg. Allg. Chem.* **1959**, *300*, 275.

(5) Himmereich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488.

(6) Ruff, J. K.; Schlientz, W. D. *Inorg. Synth.* **1975**, *15*, 84.

(7) Gilmore, G. J. "MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data", University of Glasgow, Scotland, 1983.

Table II. Positional Parameters and *B*(eq) for $[PPN]_2[Tl_2Fe_6(CO)_{24}]$

atom	*x*	*y*	*z*	*B*(eq), Å^2
Tl1	0.39385 (3)	0.05297 (2)	0.49607 (2)	3.47 (2)
Fe1	0.6133 (1)	0.05967 (7)	0.57769 (8)	4.14 (6)
Fe2	0.2264 (1)	0.09722 (8)	0.5446 (1)	4.43 (7)
Fe3	0.2747 (1)	0.15993 (7)	0.43842 (9)	4.21 (7)
O11	0.8491 (8)	0.0476 (5)	0.6538 (6)	8.7 (5)
O12	0.537 (1)	−0.0156 (5)	0.6832 (6)	8.7 (6)
O13	0.6175 (8)	0.1068 (5)	0.4306 (6)	7.6 (5)
O14	0.5738 (9)	0.1805 (5)	0.6390 (6)	9.6 (6)
O21	0.0665 (7)	0.0894 (4)	0.3911 (5)	5.8 (4)
O22	0.3898 (9)	0.0950 (5)	0.6964 (5)	8.4 (6)
O23	0.1513 (8)	−0.0338 (4)	0.5322 (6)	7.2 (5)
O24	0.043 (1)	0.1446 (5)	0.5902 (7)	9.6 (7)
O31	0.2934 (8)	0.2310 (4)	0.5788 (5)	7.5 (5)
O32	0.1251 (7)	0.2587 (5)	0.3635 (7)	9.6 (6)
O33	0.281 (1)	0.1058 (6)	0.2954 (5)	9.9 (7)
O34	0.4836 (7)	0.2270 (4)	0.4652 (6)	8.1 (5)
C11	0.757 (1)	0.0516 (6)	0.6238 (7)	5.9 (6)
C12	0.564 (1)	0.0123 (6)	0.6397 (7)	5.7 (6)
C13	0.614 (1)	0.0869 (6)	0.4870 (7)	5.2 (6)
C14	0.590 (1)	0.1326 (6)	0.6150 (8)	6.5 (7)
C21	0.146 (1)	0.1057 (5)	0.4362 (7)	4.4 (5)
C22	0.328 (1)	0.0941 (6)	0.6361 (8)	5.7 (6)
C23	0.186 (1)	0.0155 (6)	0.5366 (6)	4.6 (6)
C24	0.113 (1)	0.1274 (6)	0.5713 (8)	6.2 (7)
C31	0.275 (1)	0.1871 (6)	0.5398 (7)	5.5 (6)
C32	0.182 (1)	0.2204 (6)	0.3955 (8)	5.8 (6)
C33	0.280 (1)	0.1232 (7)	0.3520 (7)	5.6 (6)
C34	0.404 (1)	0.1999 (6)	0.4566 (8)	5.9 (6)
N1	0.2037 (8)	0.1220 (5)	0.9643 (5)	5.6 (5)
P1	0.1714 (2)	0.1339 (1)	0.8780 (1)	3.5 (1)
P2	0.2520 (2)	0.0893 (1)	1.0433 (2)	3.7 (1)
C1A1	0.1981 (9)	0.0681 (4)	0.8252 (6)	3.6 (5)
C1A2	0.121 (1)	0.0489 (5)	0.7568 (6)	4.6 (5)
C1A3	0.145 (1)	−0.0033 (6)	0.7184 (6)	5.0 (6)
C1A4	0.243 (1)	−0.0344 (6)	0.7469 (8)	6.2 (7)
C1A5	0.320 (1)	−0.0139 (6)	0.8141 (8)	6.5 (7)
C1A6	0.297 (1)	0.0355 (6)	0.8535 (7)	4.9 (6)
C1B1	0.0295 (9)	0.1533 (5)	0.8415 (6)	4.1 (5)
C1B2	−0.042 (1)	0.1315 (6)	0.8796 (7)	5.2 (6)
C1B3	−0.155 (1)	0.1448 (8)	0.848 (1)	7.1 (8)
C1B4	−0.192 (1)	0.1801 (8)	0.784 (1)	7.3 (8)
C1B5	−0.123 (1)	0.2029 (7)	0.7460 (9)	7.5 (8)
C1B6	−0.008 (1)	0.1883 (6)	0.7754 (8)	6.1 (7)
C1C1	0.2473 (8)	0.2001 (5)	0.8592 (6)	3.9 (4)
C1C2	0.2982 (9)	0.1970 (5)	0.8028 (6)	4.4 (5)
C1C3	0.359 (1)	0.2494 (7)	0.7915 (8)	6.1 (7)
C1C4	0.368 (1)	0.3012 (7)	0.834 (1)	6.5 (7)
C1C5	0.317 (1)	0.3051 (6)	0.8893 (9)	7.0 (7)
C1C6	0.252 (1)	0.2542 (6)	0.9024 (8)	5.9 (6)
C2A1	0.282 (1)	0.0067 (6)	1.0366 (7)	5.0 (6)
C2A2	0.200 (2)	−0.0302 (8)	0.9839 (8)	9 (1)
C2A3	0.226 (3)	−0.0931 (9)	0.977 (1)	13 (2)
C2A4	0.321 (3)	−0.120 (1)	1.022 (2)	14 (2)
C2A5	0.393 (2)	−0.085 (1)	1.074 (2)	14 (2)
C2A6	0.376 (1)	−0.0199 (7)	1.082 (1)	10 (1)
C2B1	0.3778 (9)	0.1280 (5)	1.0953 (6)	3.9 (5)
C2B2	0.415 (1)	0.1198 (6)	1.1751 (7)	5.5 (6)
C2B3	0.514 (1)	0.1481 (8)	1.2171 (8)	7.2 (8)
C2B4	0.574 (1)	0.1819 (7)	1.180 (1)	7.1 (8)
C2B5	0.537 (1)	0.1888 (6)	1.101 (1)	6.7 (8)
C2B6	0.438 (1)	0.1627 (6)	1.0590 (7)	5.5 (6)
C2C1	0.1586 (8)	0.0957 (5)	1.0974 (5)	3.7 (5)
C2C2	0.133 (1)	0.0449 (6)	1.1364 (7)	5.4 (6)
C2C3	0.063 (1)	0.0526 (8)	1.1804 (8)	7.0 (7)
C2C4	0.021 (1)	0.1119 (8)	1.1853 (9)	7.3 (8)
C2C5	0.044 (1)	0.1630 (7)	1.1450 (8)	7.1 (8)
C2C6	0.115 (1)	0.1552 (6)	1.1020 (7)	5.3 (6)

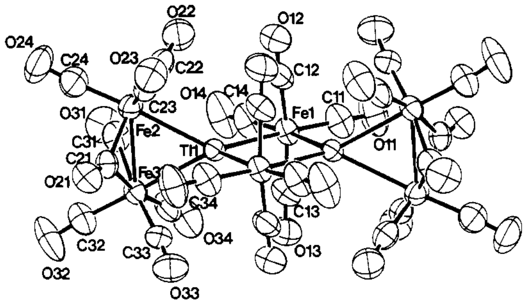


Figure 1. ORTEP diagram and atom-labeling scheme for the anion $[IV]^{2-}$, $[Tl_2Fe_6(CO)_{24}]^{2-}$.

Table III. Selected Distances and Angles for $[PPN]_2[IV]$

	(a) Bond Distances (Å)		
Tl1–Fe2	2.746 (2)	Fe2–Fe3	2.610 (2)
Tl1–Fe1*	2.746 (2)	Fe2–C21	1.97 (1)
Tl1–Fe1	2.762 (2)	Fe2–C31	2.02 (1)
Tl1–Fe3	2.765 (2)	Fe3–C21	2.01 (1)
Tl1···Tl*	3.507 (1)	Fe3–C31	1.97 (1)
	(b) Bond Angles (deg)		
Fe2–Tl1–Fe1	123.66 (5)	Fe1–Tl1–Tl1	50.24 (4)
Fe2–Tl1–Fe1	125.04 (5)	Fe3–Tl1–Tl1	151.03 (4)
Fe2–Tl1–Fe3	56.53 (5)	Tl1–Fe1–Tl1	79.11 (4)
Fe2–Tl1–Tl1	152.38 (4)	Fe3–Fe2–Tl1	62.11 (5)
Fe1–Tl1–Fe1	100.89 (4)	Fe2–Fe3–Tl1	61.36 (5)
Fe1–Tl1–Fe3	126.53 (5)	Fe2–C21–Fe3	82.0 (5)
Fe1–Tl1–Fe3	121.28 (5)	Fe3–C31–Fe2	81.7 (5)
Fe1–Tl1–Tl1	50.66 (4)		

Table IV. Comparison of Fe–Fe Distances

compd	d_{Fe-Fe}, Å	ref	compd	d_{Fe-Fe}, Å	ref
$Fe_2(CO)_9$	2.523 (1)	9	$[Et_4N]_4[II]$	2.788 (8)	3
$[PPN]_2[IV]$	2.610 (2)	*a*	$[Et_4N]_6[III]$	3.087 (5)	3

[a] This work.

tances and angles are given in Table III. Additional structural information is available (see supplementary material paragraph).

Results

Synthesis of $[Et_4N]_2[IV]$/$[PPN]_2[IV]$. When $[Et_4N]_2[I]$ is stirred with $[Cu(MeCN)_4][BF_4]$ for approximately 20 h, $[Et_4N]_2[IV]$ results along with metallic copper. $Fe(CO)_5$ is also produced, as shown by the infrared spectrum of the filtrate. The product obtained as the $[Et_4N]^+$ salt, $[Et_4N]_2[IV]$, is soluble to a certain extent in most polar organic solvents but is insoluble in diethyl ether, toluene, and hexane. $[PPN]_2[IV]$ is produced in good yield directly from $[Et_4N]_2[IV]$ by cation metathesis. $[PPN]_2[IV]$ is soluble in CH_2Cl_2, acetone, THF, and MeCN and practically insoluble in MeOH. The infrared spectrum of $[PPN]_2[IV]$ is composed of several bands from 2050 to 1907 cm^{-1} along with a broad, weak bridging CO band at 1777 cm^{-1}. The Nujol mull infrared spectrum is similar and shows two bridging carbonyl bands at 1764 and 1785 cm^{-1}. $[PPN]_2[IV]$ can also be synthesized by using acids such as HCl and CF_3SO_3H as the oxidizing agents, although the yields obtained were much lower.

When a methanol solution of $[Et_4N]_2[I]$ is allowed to stand in the sunlight for extended lengths of time, or irradiated with ultraviolet light, $[Et_4N]_4[II]$ is produced along with smaller yields of $[Et_4N]_2[IV]$ and $[Et_4N]_6[III]$.

Structure of $[PPN]_2[IV]$. X-ray analysis shows that the asymmetric unit for $[PPN]_2[IV]$ consists of $[PPN]^+$ cations and $[Tl_2Fe_6(CO)_{24}]^{2-}$ anions in a 2:1 ratio. The anion is composed of a Tl_2Fe_2 planar parallelogram situated on a crystallographic inversion center, with the thalliums each bound to one additional $Fe_2(\mu\text{-}CO)_2(CO)_6$ group. The ring irons have a cis-pseudooctahedral geometry, with the carbonyls all bent in the direction of the ring. This distortion of octahedral geometry is especially apparent for the axial carbonyls (∠C12–Fe1–C13 = 154.0 (6)°). The thalliums are four-coordinate, severely distorted tetrahedra. All of the thallium–iron distances are similar.

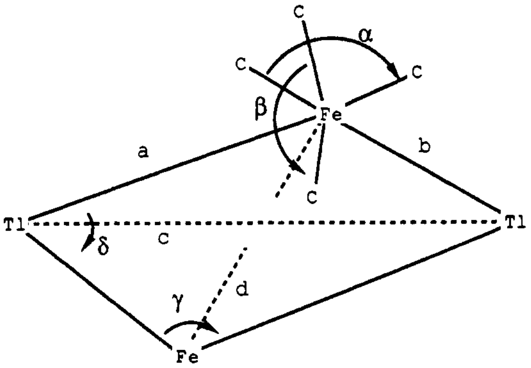
Discussion

$[PPN]_2[Tl_2Fe_6(CO)_{24}]$ is produced by treating $[Et_4N]_2[I]$ with $[Cu(MeCN)_4][BF_4]$ but can also be produced by using other oxidizing agents. In 1959, Hieber and co-workers reported a thallium–iron carbonyl compound synthesized by the addition of dilute HCl to a stirred solution of Tl_2CO_3 and $Fe(CO)_5$/KOH/MeOH. The formulation of this compound was deduced solely on the basis of elemental analysis to be $Tl_2Fe_3(CO)_{12}$.[4]

Table V. Comparison of Structural Parameters of the Tl_2Fe_2 Parallelograms of $[Et_4N]_2$[I], $[Et_4N]_4$[II], $[Et_4N]_6$[III], and $[PPN]_2$[IV][a]

compd	α, deg	β, deg	γ, deg	δ, deg	*a*, Å	*b*, Å	*c*, Å	*d*, Å
$[Et_4N]_2$[I]	97.1 (8)	144.4 (7)	80.0 (1)	100.0 (1)	2.632 (5)	3.038 (4)	3.658 (5)	4.352 (5)
$[Et_4N]_4$[II]	102.3 (17)	154.2 (18)	80.7 (1)	99.3 (1)	2.781 (5)	2.786 (6)	3.604 (3)	4.243 (8)
$[Et_4N]_6$[III]	103 (1)	151 (1)	82.8 (1)	97.1 (1)	2.790 (4)	2.815 (3)	3.706 (1)	4.205 (5)
$[PPN]_2$[IV]	99.9 (6)	154.0 (6)	79.11 (4)	100.89 (4)	2.746 (2)	2.762 (2)	3.507 (1)	4.247 (2)

[a] Parameters are defined by the following:



Repeating his reaction resulted in a compound with an IR spectrum identical with that of $[Et_4N]_2$[IV]. Our results suggest that the Hieber compound was probably a dimer of the above formulation with two Tl^+ counterions: $Tl_2[Tl_2Fe_6(CO)_{24}]$. Also, from its solubility characteristics, Hieber's compound was most likely ionic, not neutral, as the original formulation might suggest. An attempt at protonating $[Et_4N]_2$[I] with CF_3SO_3H resulted in the formation of $[Et_4N]_2$[IV] along with $Fe(CO)_5$.

The anions $[IV]^{2-}$, $[II]^{4-}$, and $[III]^{6-}$ can be thought of as dimers of fragments derived from $Fe_2(CO)_6(\mu\text{-}CO)_3$ by successive replacement of the bridging carbonyls with isoelectronic $[\mu\text{-}TlFe(CO)_4]^-$ groups. Bridging carbonyls tend to shorten metal–metal-bond distances, while bulky main-group ligands have been shown to lengthen the bonds that they bridge.[8] Thus, we would expect that the Fe–Fe bond distances would increase in going from $Fe_2(CO)_9$ to $[Et_4N]_6$[III]. This is in fact the case, as shown in Table IV. As in $Fe_2(CO)_9$ (Fe–C(br) = 2.016 Å)[9] and $[Et_4N]_4$[II],[3] the bridging CO's are symmetrically placed for $[PPN]_2$[IV].

Similar to $[Et_4N]_4$[II] and $[Et_4N]_6$[III], $[PPN]_2$[IV] shows a central, planar Tl_2Fe_2 parallelogram containing an inversion center. The Tl$\cdots$Tl distances across the central parallelograms become progressively longer in going from $[PPN]_2$[IV] to $[Et_4N]_6$[III]. $[PPN]_2$[IV] shows the shortest Tl$\cdots$Tl distance of 3.507 (1) Å, while the Tl$\cdots$Tl distances in $[Et_4N]_4$[II] and $[Et_4N]_6$[III] are 3.604 (3) and 3.706 (1) Å, respectively. In comparison, the Tl$\cdots$Tl distances for thallium metal in the α form (room temperatures) are 3.4076 and 3.4566 Å. It is interesting to note that the difference between the Tl$\cdots$Tl distance in $[PPN]_2$[IV] and in the element is less than 0.1 Å. The Tl$\cdots$Tl distance in $[PPN]_2$[IV] is the shortest that we have encountered and may indicate some type of bonding interaction. The only isolated, but structurally uncharacterized, compound thought to contain a Tl–Tl bond is $K_2[Me_3TlTlMe_3]$, produced by reduction of trimethylthallium with potassium metal.[10] For comparison, long, but structurally significant, interactions between Se atoms in the organic superconducting materials $(TMTSF)_2X$ (TMTSF = tetramethyltetraselenafulvalene; X = $[PF_6]^-$, $[ClO_4]^-$, $[ReO_4]^-$) range from 3.873 to 4.138 Å.[11] The thallium atoms in $[PPN]_2$[IV] are formally in the +3 oxidation state, which makes them isoelectronic with closed-shell Au(I). Bonding interactions between Au(I) atoms in a number of dimeric and higher order cluster compounds have been observed,[12-20] and the nature of this interaction has been discussed.[21,22] A few metal carbonyl clusters with more than one gold atom also exhibit this phenomenon.[23,24]

Of the three thallium–iron compounds, $[PPN]_2$[IV] exhibits the shortest Tl_2Fe_2 ring Tl–Fe bond distances as well as the largest and smallest Fe–Tl–Fe and Tl–Fe–Tl ring angles, respectively (see Table V). The thallium atoms of the parallelograms exhibit a distorted tetrahedral geometry, while the ring irons are arranged as cis pseudooctahedra with the CO's, especially the axial CO's, tilted toward the Tl_2Fe_2 parallelogram. In $[Et_4N]_2$[I], $[Et_4N]_4$[II], and $[Et_4N]_6$[III], the equatorial carbonyls on the terminal $Fe(CO)_4$ groups are also bent toward the thallium atom.

The Tl–Fe bonds in $[PPN]_2$[IV] are essentially equivalent, ranging from 2.746 (2) to 2.765 (2) Å, and can best be described as "covalent" bonds with the thalliums and irons each sharing bonding electrons. In this manner each of the thallium atoms acquires a filled octet of electrons. The Tl–Fe bonds in $[PPN]_2$[IV] compare favorably with the central Tl–Fe bonds in $[Et_4N]_4$[II] and $[Et_4N]_6$[III], which range from 2.706 (6) to 2.786 (6) Å and 2.713 (3) to 2.815 (3) Å, respectively.

Acknowledgment. The Robert A. Welch Foundation and the National Science Foundation (Grant CHE-8421217) are gratefully acknowledged for support of this research.

Registry No. $[Et_4N]_2$[I], 113218-98-7; $[PPN]_2$[IV], 119656-33-6; $[Et_4N]_2$[IV], 119656-34-7; $[Cu(MeCN)_4][BF_4]$, 15418-29-8; HCl, 7647-01-0; CF_3SO_3H, 1493-13-6; Fe, 7439-89-6; Tl, 7440-28-0.

Supplementary Material Available: Listings of complete crystallographic data, anisotropic thermal parameters, and complete bond distances and angles for $[PPN]_2$[IV] (9 pages); a table of calculated and observed structure factors for $[PPN]_2$[IV] (32 pages). Ordering information is given on any current masthead page.

---

(8) Whitmire, K. H.; Lagrone, C. B.; Churchill, M. R.; Fettinger, J. C.; Biondi, L. V. *Inorg. Chem.* **1984**, *23*, 4227.

(9) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.

(10) Wilkie, C. A.; Oliver, J. P. In *Organometallic Compounds*; Coates, G., Wade, K., Eds.; Methuen: London, 1967; Vol. 1, p 372.

(11) Thorup, N.; Rindorf, G.; Soling, H. *Phys. Scr.* **1982**, *25*, 868.

(12) Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85.

(13) Fackler, J. P., Jr.; Basil, J. D. *Organometallics* **1982**, *1*, 871.

(14) Weinstock, J.; Sutton, B. M.; Kuo, G. Y.; Walz, D. T.; DiMartino, M. J. *J. Med. Chem.* **1974**, *17*, 139.

(15) Crane, W. S.; Beall, H. *Inorg. Chim. Acta* **1978**, *31*, L469.

(16) Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801.

(17) Calabro, D. C.; Harrison, B. A.; Palmer, G. T.; Moguel, M. K.; Rebbert, R. L.; Burmeister, J. L. *Inorg. Chem.* **1981**, *20*, 4311.

(18) Hesse, R. In *Advances in the Chemistry of the Coordination Compounds*; Kirschner, S., Eds.; Macmillan: New York, 1961; pp 314–320.

(19) For similar Cu(I) and Ag(I) compounds, see: Schmidbaur, H.; Jurgen, A.; Buchner, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 415.

(20) Briant, C. E.; Gilmour, D. I.; Mingos, D. M. P. *J. Organomet. Chem.* **1984**, *267*, C52.

(21) Mingos, D. M. P. *Phil. Trans. R. Soc. London, A* **1982**, *308*, 75.

(22) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171.

(23) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Organomet. Chem.* **1982**, *231*, C59.

(24) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Raithby, P. R.; Taylor, M. J. *Polyhedron* **1982**, *1*, 105.