K, indicative of weak antiferromagnetic coupling. A least-squares fit of the data for T = 4–300 K to the spin-only expression for two $S = {}^5/_2$ ions[12] yields best fit parameters g = 1.97 and J = −1.99 cm^{-1}. These values yield a mean discrepancy of 1.4% between observed and calculated χ values. The J value is very close to that previously reported for an O-bridged Mn(II) dimer with a Schiff base ligand.[15] The core of this latter dimer has a shorter Mn–Mn distance (3.300 vs 3.465 (2) Å) and corresponding smaller bridging Mn–O–Mn angles (101.2 (1) and 101.3 (1) vs 105.7 (2)°) than those we observe. Clearly, the small J values in these systems are not highly sensitive to variations in bridging geometry.

Only a few other structurally characterized examples of O-bridged Mn(II)–Mn(II) dimers exist. In the Schiff-base complex mentioned above, the bridging atoms are part of a larger chelating ligand. As in the present case, the Mn atoms are six-coordinate, but a number of the structure parameters differ significantly from those we observe.[15] A dinuclear O-bridged system in which the Mn(II) ions have a tetrahedral coordination geometry and are somewhat more strongly coupled (J = −5.0 cm^{-1}) than in the two six-coordinate dimers has recently been reported.[16] A bridging arrangement similar to that we observe is found in a polymeric Mn(II) complex derived from a substituted picolinic acid, but no magnetic data have been reported for this system.[17]

Acknowledgment. The X-ray diffractometer and the MicroVAX II computer were purchased with the assistance of NSF Grant CHE-85-14495. The SQUID magnetometer at the University of Southern California was also purchased with the aid of an NSF grant. We also thank Deborah Glover, an NSF-REU program participant, for experimental assistance.

Supplementary Material Available: Experimental details of the crystallographic study and listings of anisotropic temperature factors, hydrogen atomic positional parameters, bond distances, bond angles, and observed and calculated magnetic susceptibilities (9 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(15) Kessissoglou, D. P.; Butler, W. M.; Pecoraro, V. L. *Inorg. Chem.* **1987**, *26*, 495–503.

(16) Coucouvanis, D.; Greiwe, K.; Salifoglou, A.; Challen, P.; Simpoulos, A.; Kostikas, A. *Inorg. Chem.* **1988**, *27*, 593–594.

(17) Smith, G.; O'Reilly, E. J.; Kennard, C. H. L. *Aust. J. Chem.* **1981**, *34*, 891–896.

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"Electron-Deficient" Trigonal-Planar Tin- and Lead-Containing Iron Carbonyl Complexes: $[Et_4N]_2[E\{Fe(CO)_4\}_3]$ (E = Sn, Pb)

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Three-coordinate lead and tin complexes are rare. When the group IV atom is bonded to nonmetallic elements, pyramidal compounds are formed, among which are $[Li(THF)\{E(PBu^t{}_2)_3\}]$ (E = Sn, Pb; THF = tetrahydrofuran)[1] and $E[\eta^1\text{-}CH(PPh_2)_2][\eta^2\text{-}CH(PPh_2)_2]$ (E = Sn, Pb).[2] Planar arrays have been observed for $Ge(C_6H_2Me_3)_2({=}C\{C_6H_4\}_2)$[3] and metalated lead and tin atoms. Not long ago it was believed that the metalated species were only isolable as four-coordinate solvent-stabilized products,[4] but more recently several planar three-coordinate complexes have been structurally characterized, all showing evidence for a localized π-interaction between the group 14 element and a transition metal. Examples of this type of structure include $[(\mu_3\text{-}E)\{W(CO)_5\}_3]$ (E = Ge, Sn),[5] $[(\mu_3\text{-}E)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_3]$ (E = Ge,[6] Sn,[7] Pb[8]), $[R_2SnM(CO)_5]$ (R = C_5H_5, M = Cr, Mo, W; R = MeC_5H_5, M = Cr, W),[9] and $[(Me_3Si)_2CH]_2EM(CO)_5$ (E = Sn, M = Cr, Mo, W; E = Pb, M = Mo).[10] Lead also adopts a trigonal-planar coordination environment in the polymeric solid-state structure of Cp_2Pb.[11] We wish to report here the X-ray analyses of $[Et_4N]_2[E\{Fe(CO)_4\}_3]$ (E = Sn (**1**), Pb (**2**)), trigonal-planar main-group/transition-metal compounds.

Table I. Crystal, Data Collection, and Refinement Parameters for **1** and **2**

empirical formula	$C_{28}H_{40}Fe_3O_{12}N_2Pb$ (**2**)	$C_{28}H_{40}Fe_3O_{12}N_2Sn$ (**1**)
fw	971.37	882.86
space group	$P2_1/c$ (No. 14)	
λ, Å	0.710 69	
temp, °C	23	
lattice params		
a, Å	10.959 (2)	10.910 (4)
b, Å	40.60 (1)	40.45 (1)
c, Å	17.455 (4)	17.461 (5)
β, deg	97.99 (2)	98.00 (2)
V, Å^3	7692 (4)	7630 (4)
Z	8	
D_{calc}, g·cm^{-3}	1.68	1.54
μ(Mo Kα), cm^{-1}	54.94	18.21
transmission coeff	0.4075–1.0000	0.7912–1.0000
residuals: R; R_w	0.065; 0.078	0.059; 0.071

Experimental Section

Compounds **1** and **2** were prepared simply by addition of $SnCl_2$ or $PbCl_2$ to $Fe(CO)_5$ dissolved in KOH/MeOH or from the reaction of $[Et_4N]_2[EFe_4(CO)_{16}]$ with CO as previously described.[12,13] Ir (ν_{CO} in cm^{-1}; CH_2Cl_2): **1**, 2021 w, 2002 w, 1977 s, 1904 s; **2**, 1973 s, 1895 s. The products are sparingly soluble in dichloromethane and methanol but insoluble in water, hexane, and diethyl ether.

X-ray Structural Analyses. X-ray-quality red, needlelike crystals of **1** (0.10 × 0.10 × 0.30 mm^3) were grown from a concentrated methanol solution, while black, needlelike crystals of **2** (0.50 × 0.20 × 0.20 mm^3) were obtained by cooling a concentrated methanol solution containing 2,2′-bipyridine and water. The data collection and refinement parameters for **1** and **2** are given in Table I. Reflections were collected for octants $+h,+k,\pm l$ for both **1** and **2**. For **1**, 10 500 reflections were measured, of which 9869 were independent and 4007 were observed ($I > 3.00\ (\sigma(I))$). For **2**, 10 741 reflections were measured, with 10 119 independent and 4343 observed reflections. Data were corrected for absorption and Lorentz/polarization effects. The analytical form of the scattering factors for the appropriate neutral atoms was corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[14] All programs employed were part of the Molecular Structure Corp. data reduction and refinement programs (TEXSAN, version 2.0). Heavy-atom positions were determined by the program Mithril[15] and subsequent

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(1) Arif, A. M.; Cowley, A. H.; Jones, R. A.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1446.

(2) Balch, A. L.; Oram, D. E. *Organometallics* **1986**, *5*, 2159.

(3) Lazraq, M.; Escudie, J.; Couret, C.; Satge, J.; Drager, M.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828.

(4) Brice, M. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 4529.

(5) Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O.; Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *282*, 331 and references cited therein.

(6) Gade, W.; Weiss, E. *J. Organomet. Chem.* **1981**, *213*, 451.

(7) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56.

(8) Kneuper, H.-J.; Herdtweck, E.; Herrmann, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 2508.

(9) Cornwell, A. B.; Harrison, P. G.; Richards, J. A. *J. Organomet. Chem.* **1976**, *108*, 47.

(10) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.

(11) Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* **1966**, *21*, 823.

(12) Whitmire, K. H.; Lagrone, C. B.; Churchill, M. R.; Fettinger, J. C.; Robinson, B. H. *Inorg. Chem.* **1987**, *26*, 3491.

(13) Esd's of average values are calculated with the scatter formula to give external estimates on the esd of an individual measurement: $\sigma = [\sum_{i=1}^{i=N}(d_i - d)^2/(N-1)]^{1/2}$.

(14) *International Crystal Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

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Table II. Positional Parameters and *B*(eq) Values for $[\mathrm{Sn}\{\mathrm{Fe(CO)}_4\}_3]^{2-}$

atom	*x*	*y*	*z*	*B*(eq), Å^2
Sn1	0.7991 (1)	0.05551 (3)	0.23567 (7)	5.00 (7)
Fe1	0.7929 (3)	0.03897 (7)	0.0944 (1)	5.7 (2)
Fe2	0.8427 (3)	0.11530 (7)	0.2745 (2)	5.9 (2)
Fe3	0.7668 (3)	0.01106 (7)	0.3350 (1)	5.6 (1)
O11	0.783 (2)	0.0166 (4)	−0.065 (1)	12 (1)
O12	1.024 (2)	0.0074 (5)	0.161 (1)	14 (1)
O13	0.786 (2)	0.1077 (4)	0.0456 (8)	10 (1)
O14	0.562 (1)	0.0051 (4)	0.1086 (9)	9 (1)
O21	0.917 (2)	0.1816 (4)	0.320 (1)	16 (2)
O22	1.048 (1)	0.1073 (4)	0.1872 (9)	10 (1)
O23	0.610 (2)	0.1323 (5)	0.181 (1)	12 (1)
O24	0.813 (2)	0.0978 (4)	0.432 (1)	11 (1)
O31	0.709 (2)	−0.0370 (5)	0.445 (1)	14 (1)
O32	0.545 (2)	0.0498 (4)	0.349 (1)	12 (1)
O33	0.996 (2)	0.0322 (5)	0.425 (1)	11 (1)
O34	0.783 (2)	−0.0394 (4)	0.218 (1)	11 (1)
C11	0.790 (2)	0.0263 (5)	−0.001 (1)	8 (1)
C12	0.934 (2)	0.0196 (7)	0.134 (1)	10 (2)
C13	0.791 (2)	0.0809 (6)	0.070 (1)	7 (1)
C14	0.655 (2)	0.0186 (5)	0.103 (1)	6 (1)
C21	0.892 (2)	0.1548 (6)	0.300 (2)	10 (2)
C22	0.962 (2)	0.1097 (5)	0.220 (1)	6 (1)
C23	0.703 (2)	0.1253 (6)	0.217 (1)	8 (1)
C24	0.828 (2)	0.1047 (5)	0.368 (1)	7 (1)
C31	0.733 (2)	−0.0183 (6)	0.399 (1)	8 (1)
C32	0.635 (2)	0.0348 (5)	0.342 (1)	7 (1)
C33	0.909 (2)	0.0249 (6)	0.388 (1)	8 (1)
C34	0.776 (2)	−0.0186 (5)	0.263 (1)	8 (1)
Sn2	0.4139 (1)	0.29439 (3)	0.23172 (8)	5.43 (7)
Fe4	0.2567 (3)	0.33983 (7)	0.2430 (2)	5.9 (2)
Fe5	0.6428 (3)	0.30895 (8)	0.2385 (2)	6.6 (2)
Fe6	0.3395 (4)	0.23455 (7)	0.2175 (2)	7.8 (2)
O41	0.088 (2)	0.3907 (5)	0.273 (2)	17 (2)
O42	0.104 (2)	0.3123 (4)	0.112 (1)	10 (1)
O43	0.223 (2)	0.3055 (5)	0.382 (1)	13 (1)
O44	0.442 (1)	0.3894 (4)	0.222 (1)	10 (1)
O51	0.901 (2)	0.3246 (7)	0.254 (2)	18 (2)
O52	0.582 (2)	0.3465 (4)	0.098 (1)	11 (1)
O53	0.704 (2)	0.2395 (5)	0.232 (1)	13 (1)
O54	0.604 (2)	0.3445 (5)	0.377 (1)	10 (1)
O61	0.263 (2)	0.1665 (4)	0.191 (1)	15 (1)
O62	0.089 (2)	0.2537 (6)	0.243 (1)	12 (1)
O63	0.417 (3)	0.2407 (5)	0.066 (1)	16 (2)
O64	0.523 (2)	0.2217 (5)	0.351 (1)	14 (1)
C41	0.151 (2)	0.3704 (7)	0.256 (2)	13 (2)
C42	0.169 (2)	0.3232 (6)	0.164 (1)	8 (1)
C43	0.240 (2)	0.3196 (6)	0.324 (1)	8 (1)
C44	0.371 (2)	0.3687 (6)	0.233 (1)	7 (1)
C51	0.799 (3)	0.3179 (8)	0.249 (2)	11 (2)
C52	0.600 (2)	0.3300 (5)	0.155 (1)	7 (1)
C53	0.675 (2)	0.2683 (7)	0.234 (1)	9 (2)
C54	0.616 (2)	0.3302 (6)	0.320 (1)	7 (1)
C61	0.298 (3)	0.1936 (6)	0.203 (1)	10 (2)
C62	0.192 (3)	0.2477 (7)	0.238 (2)	9 (2)
C63	0.387 (3)	0.2385 (6)	0.129 (2)	12 (2)
C64	0.450 (3)	0.2279 (6)	0.298 (2)	10 (2)

Table III. Selected Bond Distances and Angles for $[\mathrm{Et_4N}]_2[\mathrm{Sn}\{\mathrm{Fe(CO)}_4\}_3]$

(a) Bond Distances (Å)			
Sn1–Fe1	2.548 (3)	Sn2–Fe4	2.541 (3)
Sn1–Fe2	2.539 (3)	Sn2–Fe5	2.552 (3)
Sn1–Fe3	2.556 (3)	Sn2–Fe6	2.554 (3)
(b) Bond Angles (deg)			
Fe1–Sn1–Fe2	119.2 (1)	Fe4–Sn2–Fe5	119.7 (1)
Fe1–Sn1–Fe3	119.0 (1)	Fe4–Sn2–Fe6	119.0 (1)
Fe2–Sn1–Fe3	121.8 (1)	Fe5–Sn2–Fe6	121.2 (1)

refinement. Difference maps were used to locate all non-hydrogen atoms. Since **1** and **2** are isomorphous, the atomic positions found for **2** were used as the starting point for the refinement of **1**. Atomic positional parameters for **1** are found in Table II, while some selected bond angles and distances are given in Table III. Corresponding parameters for **2** are given in Tables IV and V, respectively.

Table IV. Positional Parameters and *B*(eq) Values for $[\mathrm{Pb}\{\mathrm{Fe(CO)}_4\}_3]^{2-}$

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pb1	0.7967 (1)	0.05603 (3)	0.23435 (6)	5.35 (6)
Fe1	0.7866 (4)	0.0383 (1)	0.0889 (2)	6.0 (2)
Fe2	0.8455 (4)	0.1174 (1)	0.2732 (3)	6.2 (2)
Fe3	0.7646 (4)	0.0108 (1)	0.3375 (2)	5.9 (2)
O11	0.771 (3)	0.0161 (7)	−0.068 (1)	13 (2)
O12	1.010 (3)	0.0036 (8)	0.147 (2)	16 (2)
O13	0.785 (2)	0.1064 (6)	0.043 (1)	10 (2)
O14	0.562 (2)	0.0040 (6)	0.107 (1)	9 (1)
O21	0.927 (3)	0.1832 (8)	0.316 (2)	18 (3)
O22	1.049 (2)	0.1080 (6)	0.182 (1)	9 (1)
O23	0.613 (2)	0.1362 (7)	0.180 (1)	12 (2)
O24	0.818 (2)	0.0995 (7)	0.433 (1)	11 (2)
O31	0.711 (3)	−0.0379 (7)	0.448 (2)	12 (2)
O32	0.543 (2)	0.0477 (6)	0.354 (2)	12 (2)
O33	0.993 (2)	0.0328 (7)	0.427 (2)	11 (2)
O34	0.776 (3)	−0.0397 (6)	0.218 (1)	11 (2)
C11	0.779 (3)	0.0280 (9)	−0.008 (2)	9 (2)
C12	0.923 (4)	0.019 (1)	0.126 (2)	13 (3)
C13	0.789 (3)	0.0791 (8)	0.067 (2)	7 (2)
C14	0.653 (3)	0.019 (1)	0.103 (2)	8 (2)
C21	0.894 (4)	0.1563 (8)	0.299 (3)	11 (3)
C22	0.968 (3)	0.1103 (7)	0.220 (2)	6 (2)
C23	0.711 (3)	0.1276 (9)	0.215 (2)	9 (2)
C24	0.834 (3)	0.106 (1)	0.368 (2)	8 (2)
C31	0.735 (4)	−0.019 (1)	0.400 (2)	9 (2)
C32	0.633 (3)	0.0351 (8)	0.344 (2)	7 (2)
C33	0.902 (3)	0.026 (1)	0.388 (2)	10 (2)
C34	0.769 (3)	−0.020 (1)	0.265 (2)	8 (2)
Pb2	0.4181 (1)	0.29440 (3)	0.22955 (7)	5.63 (6)
Fe4	0.2558 (3)	0.3411 (1)	0.2405 (3)	6.0 (2)
Fe5	0.6523 (4)	0.3094 (1)	0.2365 (3)	6.6 (2)
Fe6	0.3437 (5)	0.2331 (1)	0.2149 (3)	8.1 (3)
O41	0.087 (3)	0.3929 (7)	0.267 (3)	21 (3)
O42	0.106 (2)	0.3111 (6)	0.112 (1)	11 (2)
O43	0.217 (3)	0.3062 (7)	0.381 (1)	11 (2)
O44	0.445 (2)	0.3900 (5)	0.220 (2)	10 (2)
O51	0.909 (2)	0.3270 (8)	0.255 (2)	17 (3)
O52	0.594 (3)	0.3463 (8)	0.094 (1)	14 (2)
O53	0.707 (3)	0.2393 (6)	0.226 (2)	13 (2)
O54	0.615 (2)	0.3470 (6)	0.374 (1)	9 (1)
O61	0.261 (3)	0.1662 (7)	0.190 (2)	13 (2)
O62	0.088 (3)	0.254 (1)	0.241 (2)	14 (2)
O63	0.413 (4)	0.2386 (7)	0.062 (2)	17 (3)
O64	0.527 (3)	0.2187 (8)	0.345 (2)	15 (2)
C41	0.157 (3)	0.3738 (7)	0.255 (3)	10 (2)
C42	0.171 (3)	0.3248 (7)	0.163 (2)	7 (2)
C43	0.234 (3)	0.320 (1)	0.323 (2)	10 (3)
C44	0.377 (2)	0.3707 (7)	0.227 (2)	6 (2)
C51	0.807 (3)	0.3181 (8)	0.246 (2)	10 (2)
C52	0.607 (2)	0.3293 (6)	0.148 (2)	6 (2)
C53	0.690 (3)	0.268 (1)	0.235 (2)	9 (2)
C54	0.625 (3)	0.333 (1)	0.317 (2)	8 (2)
C61	0.296 (4)	0.194 (1)	0.200 (2)	12 (3)
C62	0.188 (5)	0.247 (1)	0.236 (3)	10 (3)
C63	0.392 (4)	0.237 (1)	0.125 (2)	10 (2)
C64	0.451 (4)	0.2260 (7)	0.295 (3)	10 (2)

Table V. Selected Bond Distances and Angles for $[\mathrm{Et_4N}]_2[\mathrm{Pb}\{\mathrm{Fe(CO)}_4\}_3]$

(a) Bond Distances (Å)			
Pb1–Fe1	2.627 (4)	Pb2–Fe4	2.624 (4)
Pb1–Fe2	2.619 (5)	Pb2–Fe5	2.624 (4)
Pb1–Fe3	2.629 (4)	Pb2–Fe6	2.622 (5)
(b) Bond Angles (deg)			
Fe1–Pb1–Fe2	119.4 (1)	Fe4–Pb2–Fe5	119.8 (1)
Fe1–Pb1–Fe3	118.6 (1)	Fe4–Pb2–Fe6	119.3 (2)
Fe2–Pb1–Fe3	122.0 (1)	Fe5–Pb2–Fe6	120.9 (2)

Results

Compounds **1** and **2** are formed upon treatment of a basic solution of $Fe(CO)_5$ with tin(II) chloride dihydrate and lead(II)

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

2496 *Inorg. Chem.* **1989**, *28*, 2496-2498

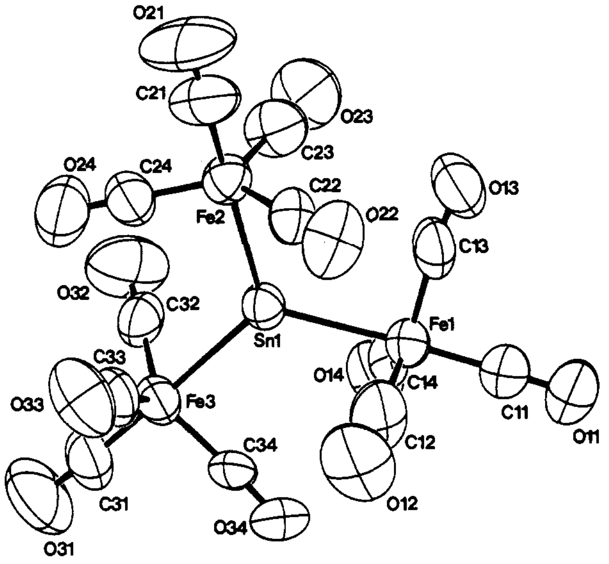

Figure 1. ORTEP diagram of one independent $[Sn\{Fe(CO)_4\}_3]^{2-}$ anion.

chloride or lead(II) acetate (eq 1; E = Sn, Pb), respectively, or upon exposure of $[Et_4N]_2[E\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ to pressures of CO gas (eq 2).[12,13]

$$2E^{2+} + 3[HFe(CO)_4]^- + 3OH^- \rightarrow E^0 + [E\{Fe(CO)_4\}_3]^{2-} + 3H_2O \tag{1}$$

$$[E\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]^{2-} + CO \rightarrow [E\{Fe(CO)_4\}_3]^{2-} + Fe(CO)_5 \tag{2}$$

X-ray analysis shows **1** and **2** to be isomorphous. The asymmetric unit consists of four disordered $[Et_4N]^+$ cations and two $[E\{Fe(CO)_4\}_3]^{2-}$ anions, with trigonal-planar main-group atoms coordinated to three essentially equivalent (noncrystallographically) trigonal-bipyramidal $[Fe(CO)_4]$ groups. The $[Sn\{Fe(CO)_4\}_3]^{2-}$ dianion is shown in Figure 1. The E atoms occupy axial positions on the metals. The mean deviation from planarity does not exceed 0.022 Å (Sn) or 0.020 Å (Pb) for either molecule in the asymmetric unit. The average E–Fe bond length, for both molecules in the asymmetric unit, is 2.548 (7) Å for Sn and 2.624 (4) Å for Pb. In comparison, the Pb–$Fe(CO)_4$ linkages in $[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ have an average Pb–Fe distance of 2.655 (6) Å.[13] The Fe–C distances for **1** and **2** range from 1.67 (3) to 1.78 (3) Å and from 1.66 (3) to 1.88 (5) Å, respectively. No iron–iron bonds are observed for **1** or **2**.

Discussion

Formally, the main-group atom can be considered as a 4+ ion bonded to three two-electron-donor $Fe(CO)_4^{2-}$ groups, resulting in an E atom with six electrons, less than a filled octet. This electron deficiency might be removed through localized multiple bonding as in the group IV complexes $[(\mu_3\text{-}E)\{(\eta^5\text{-}C_5H_4R)Mn(CO)_2\}_3]$ (E = Ge,[6] Sn,[7] Pb;[8] R = H, CH_3), where one localized main-group/manganese double bond is observed. On the other hand, the extra electrons necessary to complete the octet around the main-group atom may be obtained from delocalized multiple bonds as in the transition-metal complexes $[NH_4]_4[Ir_3N(SO_4)_6(H_2O)_3]$,[16] $[(\mu_3\text{-}As)\{[Cr(CO)_5]_2[Mn(CO)_5]\}]$,[5] $[(\mu_3\text{-}As)\{[Cr_2(CO)_9][Mn(CO)_5]\}]$,[5] $[Na(THF)_2][Sb\{Cr(CO)_5\}_3]$,[5] and $Te\{MnCp(CO)_2\}_3$.[17] Several observations, however, suggest that **1** and **2** do not have multiple bonding. In both **1** and **2**, the E–Fe bond distances are equivalent and the angles around the central lead are nearly the same; thus, unquestionably no localized double bond is present. In **2**, the Pb–Fe bond lengths are shortened as compared to the Pb–$Fe(CO)_4$ distances in the electron-sufficient $[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$; however, this shortening is not as dramatic as that seen for some of the other main-group–transition-metal compounds where multiple bonding is invoked.[7] The longer Pb–$Fe_2(CO)_8$ linkages (2.832 (4) and 2.823 (4) Å) in $[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ are believed to result from the steric repulsions of the $Fe(CO)_4$ groups. This idea is supported by the shorter Pb–$Fe_2(CO)_8$ distances seen in $Pb[Fe_2(CO)_8]_2$ (2.606 (3) to 2.634 (5) Å). The Sn–Fe bond distances in **1** compare favorably with the average Sn–Fe single-bond distances in $Sn[Fe_2(CO)_8]_2$[18] (2.54 Å) and $Fe_3(CO)_9\{\mu_3\text{-}SnFe(CO)_2Cp\}_2$[19] (2.537 (4) Å). Since the symmetry of the $Fe(CO)_4$ group is C_{3v} with Sn(IV) or Pb(IV) occupying an axial site, the E atoms are not in the expected positions for maximizing multiple-bonding interactions. The equatorial positions on trigonal-bipyramidal $Fe(CO)_4$ would be preferred over the axial positions for the strongest π-interactions.[20] The E–Fe bond lengths in **1** and **2** may also be due to steric interactions of the $Fe(CO)_4$ groups; crowding is evident in molecular models of these compounds.

As with a number of other main-group/transition-metal carbonyl complexes, one notes that several of the Pb–Fe- and Sn–Fe-equatorial CO angles are slightly tilted toward the main-group atom (∠E–Fe–C(eq) range: **1**, 80.5 (8)–89.0 (7)°; **2**, 81 (1)–90 (1)°), so the electron deficiency at tin or lead may be lessened by donation from the π-clouds of the CO groups.

It is interesting to note that the anions adopt the planar geometries described and not equally probable pyramidal structures containing one Fe–Fe bond and a lone pair of electrons on the main-group element. Such forms may be interconverting in solution. Investigations into the reactivity of **1** and **2** are continuing.

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Supplementary Material Available: For **1** and **2**, crystallographic details, complete tables of crystal, data collection, and refinement parameters, bond distances and angles, positional parameters, and anisotropic thermal parameters, and ORTEP diagrams of both anions (35 pages); structure factor tables (57 pages). Ordering information is given on any current masthead page.

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(16) Ciechanowicz, M.; Griffith, W. P.; Pawson, D.; Skapski, A. C.; Cleare, M. J. *J. Chem. Soc., Chem. Commun.* **1971**, 876.

(17) Herberhold, M.; Reiner, D.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 59.

(18) Lindley, P. F.; Woodward, P. *J. Chem. Soc. A* **1967**, 382.

(19) McNeese, T. J.; Wreford, S. S.; Tipton, D. L.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1977**, 390.

(20) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

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Uranium Alkoxide Chemistry. 3. *tert*-Butyl Isocyanide Adducts of Tris(2,6-di-*tert*-butylphenoxy)uranium(III)[1]

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We recently reported the preparation and characterization of the first uranium(III) phenoxide complex, $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$ (**1**).[2] This uranium(III) compound is unusual because its coordination number is 3[3,4] and because the sterically demanding

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(1) Part 2: Burns, C. J.; Sattelberger, A. P. *Inorg. Chem.* **1988**, *27*, 3692.

(2) Van Der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 5924.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley & Sons: New York, 1988, Chapter 21.

(4) (a) The only other well-characterized UX_3 compounds, where X is a monodentate ligand, are $U[N(SiMe_3)_2]_3$[4b] and $U[CH(SiMe_3)_2]_3$.[4c] (b) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507. (c) Van Der Sluys, W. G.; Burns, C. J.; Sattelberger, A. P. *Organometallics* **1989**, *8*, 855.

0020-1669/89/1328-2496$01.50/0