Inorg. Chem. **1995,** *34,* 4385−4391

New Metal Carbonyl Complexes of Mixed Group 15/16 Anions: Structural Characterization of $[Fe(As_3Se_3)_2(CO)]^{2-}$, $[Mn(As_3Se_5)(CO)_3]^{2-}$, and $[Fe_2(AsTe_4)_2(CO)_4]^{2-}$

Thomas M. Martin, Paul T. Wood, George L. Schimek, William T. Pennington, and Joseph W. Kolis*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634

Received November 1, 1994[⊗]

The reactions of various mixed arsenic selenides and tellurides with metal carbonyls have been investigated. Several new clusters have been isolated and stucturally characterized. Iron carbonyl reacts with $As_4Se_6^{2-}$ to form $[Fe(As_3Se_3)_2(CO)]^{2-}$, which contains two $As_3Se_3^{2-}$ fragments attached to an Fe(CO) center. The compound is reminiscent of (and isoelectronic with) the previously reported $[M(As_3Se_3)_2(CO)_2]^{2-}$ (M = Mo, W). Crystallographic data: space group $P\bar{1}$, $a = 13.114(2)$ Å, $b = 19.250(2)$ Å, $c = 11.791(2)$ Å, $\alpha = 98.85(1)°$, $\beta = 108.81(1)°$, $\gamma = 88.86(1)°$, $V = 2782.7(7)$ Å^3, $Z = 2$, $R = 0.0721$, $R_w = 0.0931$. The same main group cage also reacts with $Mn_2(CO)_{10}$ to form $[Mn(As_3Se_5)(CO)_3]^{2-}$, which has a completely new topological framework. The structure is based on the As_4Se_4 type with one As vertex replaced by a $Mn(CO)_3$ fragment and the bound As containing a terminal As=Se bond. Crystallographic data: space group $P\bar{1}$, $a = 10.298(3)$ Å, $b = 11.649(3)$ Å, $c = 24.950(6)$ Å, $\alpha = 90.30(2)°$, $\beta = 94.32(2)°$, $\gamma = 106.35(2)°$, $V = 2863(1)$ Å^3, $Z = 2$, $R = 0.0464$, $R_w = 0.0539$. Iron carbonyl also reacts with $As_2Te_6^{2-}$ to form the first example of a transition metal arsenic telluride complex, $[Fe_2(AsTe_4)_2(CO)_4]^{2-}$. This dimer contains two $Fe(CO)_2$ fragments linked by two unusual $(Te_2)AsTe{-}Te$ ligands. Crystallographic data: space group $C2/c$, $a = 11.268(4)$ Å, $b = 21.228(9)$ Å, $c = 26.413(9)$ Å, $\beta = 100.32(3)°$, $V = 6216(4)$ Å^3, $Z = 4$, $R = 0.0646$, $R_w = 0.0613$. In addition to X-ray difffraction, these compounds were characterized by IR, far-IR, and ^{77}Se and ^{125}Te NMR. A more convenient preparation of the $As_2Te_6^{2-}$ salt is also reported.

Introduction

The coordination chemistry of metal sulfides has been investigated extensively,[1,2] due in part to their importance in industrial and biological processes.[3] While the corresponding selenium and tellurium systems have been less explored, recent work has shown some remarkable chemistry which is considerably different from that of the sulfides.[4] Workers in our laboratories have previously found that anionic polychalcogenides can coordinate to low-valent metal carbonyl centers, inducing electron transfer from the metal center to the chalcogen−chalcogen bonds in the chain.[5] This can lead to oxidation of the metal center, loss of some or all coordinated CO's, shortening of the polychalcogenide chain lengths, and formation of novel metal chalcogenide clusters.

However, since chalcogens tend to be divalent, their ability to form large, cage-type structures is somewhat limited, relative to atoms with greater connectivity, such as the group 15 elements. Incorporation of a trivalent pnictide into the chalcogen framework greatly increases the possibility of building topologically more complex clusters.[6] In a seminal paper by Rauchfuss and co-workers, it was shown that mixed 15/16 anionic cages could also be complexed to transition metal centers to form novel hybrid clusters.[7]

Recently, we extended this concept to the reactions of mixed group 15/16 anions with simple metal carbonyls. The simple mixed 15/16 anions such as $[As_2E_6]^{2-}$ (E = Se, Te)[8−10] and $[As_4Se_6]^{2-}$ [10,11] can easily be made by reduction of binary solids, while larger cages can be prepared as well.[12] The nature of the reducing agents can have a profound effect on the identity of the resultant cage anions, but in general, the synthetic procedures are straightforward and lead to convenient starting materials.[13] These mixed cage anions react with metal carbonyls similarly to the polychalcogenides, leading to the preparation of new hybrid clusters through an oxidative decarbonylation mechanism. Using this methodology, we have been able to prepare complexes such as $[M(As_3Se_3)_2(CO)_2]^{2-}$ (M = Mo, W)[14] and $[Fe_2(PSe_5)_2(CO)_4]^{2-}$.[15] This paper reports the extension of this chemistry to the synthesis and characterization of

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1995.

(1) (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 742. (b) Fenske, D.; Ohmer, J.; Hachgenie, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1277.

(2) (a) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987,** *31,* 89. (b) Coucouvanis, M.; Hydjikyriacou, A.; Draganjac, M.; Kanatzidis, M.; Heperuma, O. *Polyhedron* **1986,** *5,* 349. (c) Harmer, M. A.; Halbert, T. R.; Pan, W.-H.; Coyle, C. L.; Cohen, S. A.; Stiefel, E. I. *Polyhedron* **1986,** *5,* 314. (d) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 840.

(3) (a) Spiro, T. G., Ed. *Molybdenum Enzymes*; Wiley-Interscience: New York, 1985. (b) Coucouvanis, D. *Acc. Chem. Res.* **1991,** *24,* 1. (c) Holm, R. H. *Chem. Soc. Rev.* **1981,** *10,* 455. (d) Chianelli, R. R. *Cat. Rev.—Sci. Eng.* **1984,** *26,* 361. (e) Rakowski-Dubois, M. *Chem. Rev.* **1989,** *89,* 1.

(4) (a) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993,** *93,* 1037. (b) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990,** *100,* 223. (c) Kanatzidis, M. G.; Huang, S.-P. *Coord. Chem. Rev.* **1994,** *130,* 509. (d) Gysling, H. G. In *The Chemistry of Organic Selenium and Tellerium Compounds*; Patai, S., Rappaport, Z., Eds.; J. Wiley and Sons: New York, 1986; Vol. 1, p 679.

(5) Kolis, J. W. *Coord. Chem. Rev.* **1990,** *105,* 195 and references therein.

(6) (a) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 1104. (b) Divaira, M.; Stoppioni, P.; Peruzzini, M. *Polyhedron* **1987,** *6,* 351. (c) Wood, P. T.; Woolins, J. D. *Transition Met. Chem.* **1986,** *11,* 358. (d) DiMaio, A. J.; Rheingold, A. L. *Chem. Rev.* **1990,** *90,* 169.

(7) Zank, G. A.; Rauchfuss, T. B.; Wilson, S. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984,** *106,* 7621.

(8) Belin, C. H. E.; *C. R. Acad. Sci. Paris, Ser. 2* **1984,** *298,* 691.

(9) Belin, C. H. E.; Charbonnel, M. M. *Inorg. Chem.* **1982,** *21,* 2504.

(10) Ansari, M.; Ibers, J. A.; O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Polyhedron* **1992,** *11,* 1877.

(11) Porter, E. J.; Sheldrick, G. M. *J. Chem. Soc. A* **1971,** 3130.

(12) Martin, T. M.; Wood, P. T.; Kolis, J. W. *Inorg. Chem.* **1994,** *33,* 1587.

(13) (a) Paul, P. P.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1993,** *115,* 3316. (b) Martin, T. M.; Schimek, G. L.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc., Dalton Trans.* **1995,** 501. (c) Martin, T. M.; Schimek, G. L.; Pennington, W. T.; Kolis, J. W. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1994,** *93−94,* 93.

0020-1669/95/1334-4385$09.00/0

two novel metal arsenic selenide anions, as well as the first metal arsenic telluride anionic cluster. In addition, a new synthetic route to $As_2Te_6^{2-}$ is reported, which is considerably more convenient than the one reported previously.[8]

Experimental Section

General Considerations. All group 15/16 anions are moderately air sensitive, and solutions were handled under purified argon using standard Schlenk techniques. Solids were handled in a Vacuum Atmospheres glovebox under argon. All solvents were distilled using standard drying techniques, stored over activated sieves, and degassed with argon before use. Reagents were purchased from Aldrich or Strem and used as received. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. IR spectra were taken on a Nicolet near-IR instrument as DMF solutions between CaF_2 plates, and far-IR spectra were obtained on a Nicolet 20F as Nujol mulls in sealed polyethylene bags. The ^{77}Se and ^{125}Te NMR spectra were obtained from samples dissolved in 2.5 mL of DMF, with 0.5 mL of CD_3CN added to obtain lock, and sealed in 10 mL tubes under vacuum. The SEM-EDAX data was obtained on a JEOL IC-848 scanning electron microscope. The compounds of nominal composition As_4Se_4, As_2Te_3, and Sb_2Se_3 were prepared by a modified literature procedure[11] whereby stoichiometric amounts of the elemental powders were melted in sealed quartz tubes at 650 °C for 10 h, while $[PPN][HFe(CO)_4]$ was prepared according to a standard literature procedure.[16]

Preparation of $[(C_6H_5)_4P]_2[Fe(As_3Se_3)_2(CO)]$ (I). Method A. In a typical reaction, 0.800 g (1.30 mmol) of As_4Se_4 and 0.102 g (2.60 mmol) of K were dissolved in 15 mL of dry DMF, and the mixture was stirred at ambient temperature for 12 h. The red-orange solution was filtered, and 0.085 mL (0.65 mmol) of $Fe(CO)_5$ was added. The resulting mixture was heated at 100 °C for 12 h. The brown solution was filtered onto 1.09 g (2.60 mmol) of Ph_4PBr, and the mixture was stirred for 1 h. This solution was filtered, and the filtrate was layered with 15 mL of freshly distilled diethyl ether. Storage of the reaction mixture at 4 °C overnight produced a white powder, which was removed by filtration. Addition of 10 mL of fresh ether and storage at 4 °C overnight produced brown rod-shaped crystals in 44% yield (based on Fe). Semiquantitative EDAX confirmed the presence of heavy elements in approximately correct ratios. Anal. Calcd for $C_{50.5}H_{43.5}N_{0.5}O_{1.5}P_2FeAs_6Se_6$: C, 35.21; H, 2.55. Found: C, 35.70; H, 2.64. IR (cm^{-1}): 1920(m), 525(s), 496(m), 341(w), 301(w), 269(w), 247(m), 223(m), 202(w). ^{77}Se NMR, ppm ($\delta_{^{77}Se}(Me_2Se) = 0$ ppm): 1590, 1559, 1327.

Method B. A combination of 0.300 g (0.487 mmol) of As_4Se_4 and 0.172 g (0.243 mmol) of $[PPN][Fe(CO)_4H]$ was dissolved in 15 mL of dry DMF, and the mixture was heated at 100 °C for 12 h. The resulting brown solution was filtered onto 0.410 g (0.974 mmol) of Ph_4PBr, and the mixture was stirred for 1 h. [Attempts to isolate the desired compound as its PPN^+ salt were unsuccessful.] The solution was filtered, and the filtrate was layered with 10 mL of diethyl ether. Storage of the solution at 4 °C overnight produced brown rod-shaped crystals in 38% yield (based on Fe). Analysis by ^{77}Se NMR and IR confirmed the identity of the anion in the title compound.

Preparation of $[(C_6H_5)_4P]_2[Mn(As_3Se_5)(CO)_3]$ (II). In a typical reaction, 0.800 g (1.30 mmol) of As_4Se_4 and 0.102 g (2.60 mmol) of K were dissolved in 15 mL of dry DMF and reacted at 25 °C for 12 h. The red-orange solution was filtered onto 0.500 g (1.30 mmol) of $Mn_2(CO)_{10}$, and the mixture was stirred at ambient temperature for 1 h. This solution was then heated at 100 °C for 12 h. After heating, 1.09 g (2.60 mmol) of Ph_4PBr was added. The red-orange solution was filtered, and the filtrate was layered with 10 mL of dry, freshly distilled diethyl ether. Storage of the reaction mixture at 4 °C overnight produced a white powder, which was removed by filtration. Addition of 10 mL of fresh ether and storage at 4 °C overnight produced red-orange cubic crystals in 38% yield (based on Mn). Semiquantitative EDAX confirmed the presence of heavy elements in approximately correct ratios. Anal. Calcd for $C_{54}H_{47}NO_4P_2MnAs_3Se_5$: C, 42.94; H, 3.14; N, 0.93. Found: C, 42.29; H, 3.15; N, 1.26. IR (cm^{-1}): 1979(s), 1890(s), 526(s), 452(w), 354(m), 321(m), 274(m), 235(m). ^{77}Se NMR, ppm ($\delta_{^{77}Se}(Me_2Se) = 0$ ppm): 1663, 1452, 1401.

Preparation of $[(C_4H_9)N]_2[Fe(AsTe_4)(CO)_2]_2$ (III). Method A. In a typical reaction, 0.600 g (1.13 mmol) of As_2Te_3 and 0.090 g (2.3 mmol) of K were dissolved in 15 mL of dry DMF, and the mixture was stirred at 25 °C for 12 h. To the resulting brown-purple solution was added 0.074 mL (0.56 mmol) of $Fe(CO)_5$, and the reaction mixture was allowed to proceed at ambient temperature for 4 h. The brown solution was filtered onto 0.726g (2.25 mmol) of $(n\text{-}Bu)_4NBr$, and the mixture was stirred for 1 h. The solution was filtered, and the filtrate was layered with 10 mL of dry, freshly distilled diethyl ether. Storage at 4 °C overnight produced a white powder, which was removed by filtration. Addition of 5 mL of fresh ether to the filtrate and storage at 4 °C overnight produced brown plates in 44% yield (based on Fe). Semiquantitative EDAX confirmed the presence of heavy elements in approximately correct ratios. Anal. Calcd for $C_{39}H_{79}N_3O_5Fe_2As_2Te_8$: C, 24.00; H, 4.09; N, 2.15. Found: C, 22.34; H, 3.82; N, 1.96. IR (cm^{-1}): 1960(s), 1916(s), 353(m), 213(m), 201(w), 181(m), 157(m). ^{125}Te NMR, ppm ($\delta_{^{125}Te}(Te(OH)_6) = 0$ ppm): 287, 234, −22.

Method B. In an alternative reaction, 0.208g (0.376 mmol) of $[PPN][Fe(CO)_4H]$ and 0.200 g (0.376 mmol) of As_2Te_3 were reacted in 15 mL of dry DMF at 100 °C for 12 h. At this point, 0.315 g (0.751 mmol) of Ph_4PBr [Attempts to isolate the desired compound as its PPN^+ salt were unsuccessful.] was added, and the reaction mixture was stirred for 1 h. The brown-red solution was filtered, and the filtrate was layered with 7 mL of diethyl ether. Storage at 4 °C overnight produced brown plates in 40% yield (based on Fe). Analysis by ^{125}Te NMR and IR confirmed the identity of the anion in the title compound.

Preparation of $[(C_6H_5)_4P]_2[As_2Te_6]$ (IV). In a typical reaction, 0.600 g (1.13 mmol) of As_2Te_3 and 0.090 g (2.3 mmol) of K were combined in 15 mL of dry DMF. The reaction mixture was stirred at 25 °C for 12 h. The resulting brown-purple solution was filtered onto 0.950 g (2.26 mmol) of Ph_4PBr, and the mixture was stirred for 1 h. The resultant mixture was filtered, and the filtrate was layered with 15 mL of dry, freshly distilled diethyl ether. Storage at 4 °C overnight produced large brown-purple cubes in 34% yield (based on As). Anal. Calcd: C, 36.18; H, 2.54. Found: C, 35.73; H, 2.56. The compound was structurally characterized by single-crystal X-ray diffraction: $P2_1/n$, $a = 10.81(3)$ Å, $b = 14.22(3)$ Å, $c = 16.94(3)$ Å, $\beta = 93.1(2)°$, $V = 2601(10)$ Å^3. The structure of the anion was not found to be significantly different from the one previously reported using a different counterion.[8] The full structure is presented in the supplementary material.

X-ray Structure Analysis. Intensity measurements were made at room temperature (22 °C) on either a Rigaku AFC7R diffractometer (I) or a Nicolet R3mV diffractometer (**II, III**) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Relevant crystallographic data are given in Table 1. Data were measured to $2\theta = 45°$ using an $\omega-2\theta$ (**I**) or ω (**II, III**) scan mode, at speeds of 32°/min (**I**) with up to three additional rescans of weak reflections to improve counting statistics, 2−14°/min (**II**) or 2°/min (**III**). Periodic measurement of three standard reflections indicated crystal and electronic stability (±2%) for all compounds. Lorentz and polarization corrections were applied to the data for each compound. A DIFABS[17] (0.80−1.42) absorption correction was applied to compound **I**, and a ψ-scan absorption correction was applied to **II** and **III**.

The structures were solved by direct methods and refined by full-matrix least-squares techniques using the SHELXTL-Plus package of programs, except for **I**, which was solved using the TEXSAN package. For **I**, carbon atoms were refined with isotropic thermal parameters and all other non-hydrogen atoms were refined anistropically. For **II**, the phenyl rings were treated as rigid groups with refined isotropic thermal parameters; all other non-hydrogen atoms were refined anisotropically. For **III**, the tellurium, arsenic, and iron atoms were refined anisotropically; all others were refined isotropically. Hydrogen atoms were included in the structure factor calculation for each compound at optimized positions ($d_{C-H} = 0.96$ Å) with a refined group thermal parameter (U_H: 0.09(1) Å^2 for **I**; 0.13(1) Å^2 for **II**; 0.24(5) Å^2 for **III**).

---

(14) O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992,** *31,* 888.

(15) Zhao, J.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* **1992**, 265.

(16) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978,** *17,* 297.

(17) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

Table 1. Crystallographic Data

	I	**II**	**III**
formula	$C_{50.5}H_{43.5}N_{0.5}O_{1.5}P_2FeAs_6Se_6$	$C_{54}H_{47}NO_4P_2MnAs_3Se_5$	$C_{39}H_{79}N_3O_5Fe_2As_2Te_8$
fw	1722.5	1510.37	1952.39
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	13.114(2)	10.298(3)	11.268(4)
b, Å	19.250(2)	11.649(3)	21.228(9)
c, Å	11.791(2)	24.950(6)	26.413(9)
α, deg	98.85(1)	90.30(2)	
β, deg	108.81(1)	94.32(2)	100.32(3)
γ, deg	88.86(1)	106.35(2)	
V, Å^3	2782.7(7)	2863(1)	6216(4)
Z	2	2	4
D_{calc}, g cm^{-3}	2.05	1.752	2.086
T, °C	22.0	22.0	22.0
λ, Å	0.7107	0.7107	0.7107
μ, mm^{-1}	7.83	5.23	5.24
transm coeff	0.428−1.000	0.67−1.00	0.90−1.00
no. of obsd data ($I > 3\sigma(I)$)	3814	1740	1064
no. of variables	358	275	158
$R(F_o)^a$	0.0721	0.0464	0.0646
$R_w(F_o)^b$	0.0931	0.0539	0.0613

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + gF_o^2]$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Fe(As_3Se_3)_2(CO)]^{2-}$

	x	y	z	$U_{eq}{}^a$
Se(1)	4451(2)	7319(2)	−817(3)	84(1)
Se(2)	4855(2)	7702(1)	2347(3)	78(1)
Se(3)	2652(2)	8476(1)	289(3)	65(1)
Se(4)	45(2)	6362(1)	−3016(2)	65(1)
Se(5)	−1295(2)	7153(2)	−1001(3)	74(1)
Se(6)	1088(2)	6198(1)	170(2)	56(1)
As(1)	3095(2)	6595(1)	−547(2)	61(1)
As(2)	3401(2)	6845(1)	1580(2)	57(1)
As(3)	4507(2)	8316(1)	678(3)	75(1)
As(4)	1153(2)	7402(1)	−1968(2)	61(1)
As(5)	194(2)	7943(1)	−678(2)	65(1)
As(6)	−528(2)	6069(1)	−1438(2)	66(1)
Fe(1)	1848(3)	7340(2)	204(3)	49(1)
P(1)	3428(4)	4640(3)	−3658(5)	43(2)
P(2)	1680(5)	10322(3)	−2456(5)	49(3)
O(1)	1397(16)	7854(10)	2411(17)	96(10)
C(1)	1669(16)	7679(10)	1535(19)	41(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Mn(As_3Se_5)(CO)_3]^{2-}$

	x	y	z	$U_{eq}{}^a$
Se(1)	−2543(3)	2193(2)	2178(1)	55(1)
Se(2)	−3927(3)	4407(3)	1737(1)	70(1)
Se(3)	−1667(3)	3588(3)	3482(1)	57(1)
Se(4)	−3087(4)	5836(3)	3047(1)	78(2)
Se(5)	−5204(3)	3420(3)	3881(1)	63(1)
As(1)	−3920(3)	3707(2)	3173(1)	48(1)
As(2)	−962(3)	3839(3)	2604(1)	58(1)
As(3)	−2025(3)	5532(3)	2275(1)	70(1)
Mn(1)	−4744(4)	2628(4)	2311(1)	50(2)
P(1)	1287(7)	8316(6)	4394(2)	47(3)
P(2)	280(7)	7664(6)	654(2)	48(3)
O(1)	−5949(28)	1244(22)	1312(8)	105(13)
O(2)	−7308(24)	3254(20)	2423(8)	81(11)
O(3)	−5636(24)	472(21)	2929(7)	85(11)
C(1)	−5446(36)	1825(31)	1689(10)	67(16)
C(2)	−6297(32)	3043(22)	2385(9)	47(12)
C(3)	−5241(35)	1318(33)	2691(12)	77(17)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients(Å^2 × 10^3) for $[Fe(AsTe_4)(CO)_2]_2{}^{2-}$

	x	y	z	$U_{eq}{}^a$
Te(1)	374(3)	−751(2)	5231(1)	55(1)
Te(2)	−1535(3)	−1607(2)	4990(2)	73(2)
Te(3)	−1637(3)	−380(2)	3857(1)	70(2)
Te(4)	−2823(3)	66(2)	5211(2)	69(2)
As(1)	−2962(5)	−781(3)	4496(2)	75(3)
Fe(1)	553(6)	−210(3)	4358(3)	59(3)
O(1)	1096(28)	589(15)	3572(13)	80(11)
O(2)	1040(28)	−1437(16)	3937(12)	86(12)
C(1)	811(49)	252(27)	3864(24)	103(22)
C(2)	859(44)	−925(26)	4094(20)	84(18)

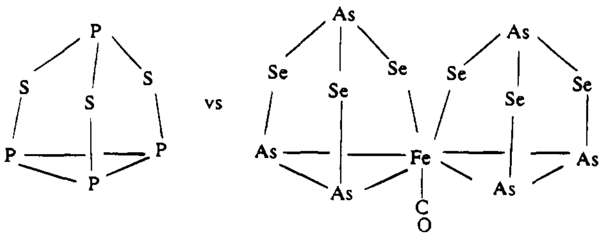
[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

All three compounds crystallize with molecules of DMF solvent included in the lattice. In all cases, these solvent molecules were poorly modeled with isotropic thermal parameters and hydrogen atoms were not included. In **I**, The DMF molecule is disordered about an inversion center ($^1/_2$, 0, $^1/_2$). In **II**, the DMF molecule occupies a general position but the carbonyl carbon is disordered (70/30) over two sites. In **III**, the DMF molecule is disordered over a 2-fold rotation axis ($^1/_2$, y, $^1/_4$).

Positional parameters of the anions are given in Tables 2−4 for compounds **I**−**III**, and selected distances and angles are listed in Tables 5−7 for the three compounds.

Results

Structure of $[(C_6H_5)_4P]_2[Fe(As_3Se_3)_2(CO)]$ (I). The dianion, $[Fe(As_3Se_3)_2(CO)]^{2-}$, contains two As_3Se_3 ligands, each coordinated to the central iron atom by two arsenic atoms and one selenium atom (see Figure 1). Each of the As_3Se_3 ligands chelates to the iron atom to form two corner-sharing birdcage fragments, each of which is isostructural with P_4S_3.[18]



The two rings are twisted and skewed, making for a very irregular coordination geometry around the metal center. There

Table 5. Selected Bond Distances and Angles for $[Fe(As_3Se_3)_2(CO)]^{2-}$

Distances (Å)			
Se(1)−As(1)	2.409(5)	Se(6)−As(6)	2.331(3)
Se(1)−As(3)	2.383(4)	Se(6)−Fe(1)	2.422(4)
Se(2)−As(2)	2.393(4)	As(1)−As(2)	2.381(4)
Se(2)−As(3)	2.365(5)	As(1)−Fe(1)	2.442(4)
Se(3)−As(3)	2.349(4)	As(2)−Fe(1)	2.440(4)
Se(3)−Fe(1)	2.421(4)	As(4)−As(5)	2.381(4)
Se(4)−As(4)	2.417(3)	As(4)−Fe(1)	2.446(4)
Se(4)−As(6)	2.364(4)	As(5)−Fe(1)	2.439(4)
Se(5)−As(5)	2.394(4)	Fe(1)−C(1)	1.691(23)
Se(5)−As(6)	2.357(4)	O(1)−C(1)	1.197(32)

Angles (deg)			
As(1)−Se(1)−As(3)	100.3(2)	Se(3)−Fe(1)−Se(6)	178.3(2)
As(2)−Se(2)−As(3)	100.3(1)	Se(3)−Fe(1)−As(1)	98.7(2)
As(3)−Se(3)−Fe(1)	106.9(1)	Se(6)−Fe(1)−As(1)	80.8(1)
As(4)−Se(4)−As(6)	100.2(1)	Se(3)−Fe(1)−As(2)	98.3(1)
As(5)−Se(5)−As(6)	100.4(1)	Se(6)−Fe(1)−As(2)	80.0(1)
As(6)−Se(6)−Fe(1)	105.9(1)	As(1)−Fe(1)−As(2)	58.4(1)
Se(1)−As(1)−As(2)	103.0(1)	Se(3)−Fe(1)−As(4)	82.6(1)
Se(1)−As(1)−Fe(1)	109.7(1)	Se(6)−Fe(1)−As(4)	98.9(1)
As(2)−As(1)−Fe(1)	60.8(1)	As(1)−Fe(1)−As(4)	78.6(1)
Se(2)−As(2)−As(1)	105.2(2)	As(2)−Fe(1)−As(4)	136.8(2)
Se(2)−As(2)−Fe(1)	109.4(1)	Se(3)−Fe(1)−As(5)	81.9(1)
As(1)−As(2)−Fe(1)	60.9(1)	Se(6)−Fe(1)−As(5)	99.6(1)
Se(1)−As(3)-Se(2)	96.9(1)	As(1)−Fe(1)−As(5)	136.7(2)
Se(1)−As(3)-Se(3)	99.9(1)	As(2)−Fe(1)−As(5)	164.9(2)
Se(2)−As(3)-Se(3)	99.1(2)	As(4)−Fe(1)−As(5)	58.3(1)
Se(4)−As(4)−As(5)	102.4(1)	Se(3)−Fe(1)−C(1)	86.1(7)
Se(4)−As(4)−Fe(1)	109.3(1)	Se(6)−Fe(1)−C(1)	93.2(7)
As(5)−As(4)−Fe(1)	60.7(1)	As(1)−Fe(1)−C(1)	139.5(7)
Se(5)−As(5)−As(4)	105.3(1)	As(2)−Fe(1)−C(1)	81.1(7)
Se(5)−As(5)−Fe(1)	107.9(1)	As(4)−Fe(1)−C(1)	141.6(7)
As(4)−As(5)−Fe(1)	61.0(1)	As(5)−Fe(1)−C(1)	83.8(7)
Se(4)−As(6)−Se(5)	97.1(1)	Fe(1)−C(1)−O(1)	169.7(18)
Se(4)−As(6)−Se(6)	101.0(1)	Se(5)−As(6)−Se(6)	99.6(1)

Table 6. Selected Bond Distances and Angles for $[Mn(As_3Se_5)(CO)_3]^{2-}$

Distances (Å)			
Se(1)−As(2)	2.328(3)	As(1)−Mn(1)	2.454(4)
Se(1)−Mn(1)	2.503(6)	As(2)−As(3)	2.620(5)
Se(2)−As(3)	2.343(4)	Mn(1)−C(1)	1.801(27)
Se(2)−Mn(1)	2.508(5)	Mn(1)−C(2)	1.817(35)
Se(3)−As(1)	2.431(4)	Mn(1)−C(3)	1.770(35)
Se(3)−As(2)	2.354(3)	O(1)−C(1)	1.154(33)
Se(4)−As(1)	2.415(4)	O(2)−C(2)	1.146(44)
Se(4)−As(3)	2.358(5)	O(3)−C(3)	1.144(40)
Se(5)−As(1)	2.254(4)		

Angles (deg)			
As(2)−Se(1)−Mn(1)	102.3(2)	Se(2)−As(3)−As(2)	100.5(1)
As(3)−Se(2)−Mn(1)	100.9(1)	Se(4)−As(3)−As(2)	100.3(1)
As(1)−Se(3)−As(2)	91.3(1)	Se(1)−Mn(1)−Se(2)	86.4(2)
As(1)−Se(4)−As(3)	91.7(1)	Se(1)−Mn(1)−As(1)	94.2(2)
Se(3)−As(1)−Se(4)	91.8(1)	Se(1)−Mn(1)−C(1)	88.9(13)
Se(3)−As(1)−Se(5)	108.3(1)	Se(2)−Mn(1)−C(1)	85.5(10)
Se(4)−As(1)−Se(5)	108.1(2)	As(1)−Mn(1)−C(1)	176.7(12)
Se(3)−As(1)−Mn(1)	112.0(2)	Se(1)−Mn(1)−C(2)	175.9(8)
Se(4)−As(1)−Mn(1)	111.0(1)	Se(2)−Mn(1)−C(2)	89.6(8)
Se(5)−As(1)−Mn(1)	121.5(2)	As(1)−Mn(1)−C(2)	85.7(7)
Se(1)−As(2)−Se(3)	99.3(1)	C(1)−Mn(1)−C(2)	91.3(14)
Se(1)−As(2)−As(3)	99.4(1)	Se(1)−Mn(1)−C(3)	89.7(13)
Se(3)−As(2)−As(3)	100.8(2)	Se(2)−Mn(1)−C(3)	175.6(13)
Se(2)−As(3)−Se(4)	99.6(2)	As(1)−Mn(1)−C(3)	86.6(10)
Mn(1)−C(1)−O(1)	174.9(22)	C(1)−Mn(1)−C(3)	92.4(14)
Mn(1)−C(2)−O(2)	176.9(20)	C(2)−Mn(1)−C(3)	94.4(15)
Mn(1)−C(3)−O(3)	176.2(33)		

Table 7. Selected Bond Distances and Angles for $[Fe(AsTe_4)(CO)_2]_2^{2-}$

Distances (Å)			
Te(1)−Te(2)	2.800(5)	Fe(1)−C(1)	1.698(63)
Te(1)−Fe(1)	2.617(8)	Fe(1)−C(2)	1.730(56)
Te(1)−Fe(1A)	2.615(8)	Fe(1)−Te(4A)	2.626(8)
Te(2)−As(1)	2.570(7)	O(1)−C(1)	1.140(72)
Te(3)−As(1)	2.589(7)	O(2)−C(2)	1.194(65)
Te(3)−Fe(1)	2.607(8)	Te(1)−Te(1A)	3.464(4)
Te(4)−As(1)	2.592(7)	Fe(1)−Fe(1A)	3.921(8)
Te(4)−Fe(1A)	2.626(8)		

Angles (Deg)			
Te(2)−Te(1)−Fe(1)	105.1(2)	Te(1)−Fe(1)−C(2)	91.3(18)
Te(2)−Te(1)−Fe(1a)	104.7(2)	Te(3)−Fe(1)−C(2)	85.0(16)
Fe(1)−Te(1)−Fe(1a)	97.1(3)	C(1)−Fe(1)−C(2)	97.0(28)
Te(1)−Te(2)−As(1)	93.4(2)	Te(1)−Fe(1)−Te(1a)	82.9(3)
As(1)−Te(3)−Fe(1)	108.6(2)	Te(3)−Fe(1)−Te(1a)	84.6(2)
As(1)−Te(4)−Fe(1a)	108.9(2)	C(1)−Fe(1)−Te(1a)	90.3(21)
Te(2)−As(1)−Te(3)	100.0(2)	C(2)−Fe(1)−Te(1a)	167.1(18)
Te(2)−As(1)−Te(4)	98.8(2)	Te(1)−Fe(1)−Te(4a)	83.7(2)
Te(3)−As(1)−Te(4)	106.2(2)	Te(3)−Fe(1)−Te(4a)	175.1(4)
Te(1)−Fe(1)−Te(3)	99.8(3)	C(1)−Fe(1)−Te(4a)	88.8(18)
Te(1)−Fe(1)−C(1)	168.9(19)	C(2)−Fe(1)−Te(4a)	91.6(16)
Te(3)−Fe(1)−C(1)	88.1(18)	Te(1A)−Fe(1)−Te(4a)	99.2(3)
Fe(1)−C(1)−O(1)	172.0(53)	Fe(1)−C(2)−O(2)	175.7(46)

is also a single CO coordinated to the iron center, making it seven-coordinate. Transition metal complexes occupying the basal vertex of a Q_3E_3 cage (where Q is a group 15 element and E is a group 16 element) have been observed previously,[19] but complexes with two cages sharing a common metal vertex are rare. The overall structure is similar to the group 6 analogs $[M(As_3Se_3)_2(CO)_2]^{2-}$ (M = Mo, W).[14] However, the group 6 analogs contain two CO ligands and a much more regular bicapped trigonal prismatic coordination environment.

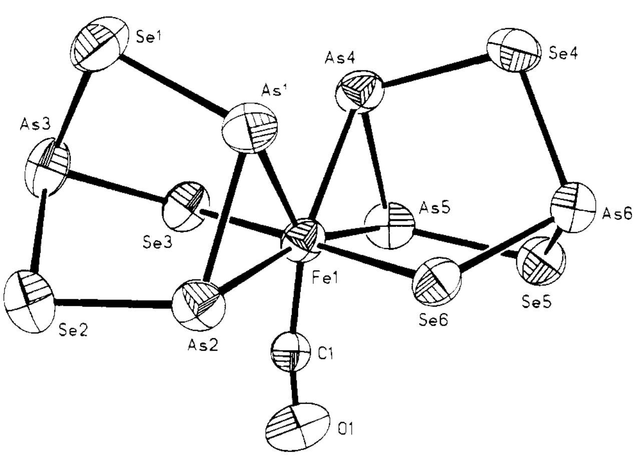


Figure 1. Thermal ellipsoid view of $[Fe(As_3Se_3)_2(CO)]^{2-}$ with thermal ellipsoids at 35%.

The bond distances and angles of $[Fe(As_3Se_3)_2(CO)]^{2-}$ (see Table 5) are in agreement with previously characterized metal arsenic selenide clusters with a few exceptions.[14,20] The average Fe−As bond distance is 2.436(7) Å and the average Fe−Se bond distance is 2.422(4) Å, which are normal for these types of compounds. The average As−As distance is 2.371(4) Å, indicating the arsenic atoms are bound to one another within each cage. This distance is short for an As−As single bond which typically falls between 2.56 and 2.58 Å in As_4Se_4.[21] While this distance is not short enough to be a direct As=As double

---

(18) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.

(19) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1983,** 903.

(20) (a) O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 710. (b) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *Polyhedron* **1986**, *5*, 945.

(21) Bastow, T. J.; Whitfield, H. J. *J. Chem. Soc., Dalton Trans.* **1973,** 1739.

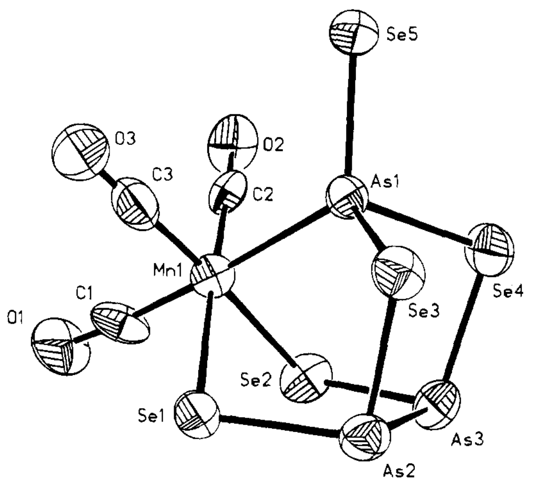


Figure 2. Thermal ellipsoid view of $[Mn(As_3Se_5)(CO)_3]^{2-}$ with thermal ellipsoids at 35%.

bond (2.224 Å),[22] it is similar to the As−As distance in $[M(As_3Se_3)_2(CO)_2]^{2-}$,[14] as well as the distance reported for a number of simple diarsines coordinated to transition metal centers (2.388(7) Å).[6d]

The bond angles of the coordinated arsenic atoms [As(2)−Fe(1)−As(3) = 58.5(1)° and As(4)−Fe(1)−As(5) = 58.2(1)°] are highly contracted compared to those of previously characterized complexes.[14] Furthermore, the average bond angles between the coordinated selenium atoms and the arsenic atoms in each cage are 99.8(7)°, which is somewhat larger than those angles in analogous structures (94.2(2)°).[14] All other angles within the cages are typical (see Table 5). Also, the coordinated CO molecule is nearly linear [Fe(1)−C(1)−O(1) = 171(2)°].

Another interesting aspect of dianion **I** is that the two As_3Se_3 cages are tilted slightly, pushing the arsenic atoms As(1) and As(4) toward one another. The distance between the arsenic atoms is 3.097(4) Å, which is too long for an As−As bond but is shorter than a van der Waals interaction (4.0 Å).[23] The tilting of the cages gives the central iron an unsymmetrical environment. Structures displaying a similar Se•••Se interaction have been reported previously,[20a] but there seems to be no obvious reason for this interaction in either case.

If each main group fragment is formally considered $[As_3Se_3]^{3-}$, then the oxidation state of the central iron atom is Fe^{4+}. Since each As_3Se_3 unit acts as a 6-electron donor, the presence of the single CO ligand along with the 4 metal electrons completes the 18-electron count around the iron. Alternatively, the short As−As distances suggest that the cage may contain some diarsine character with the diarsine donating 2 π-electrons.[20] This would make the charge of each cage formally −1, with the charge residing on the metal-bound selenium atom, and the central iron would be zerovalent. This description would also satisfy the 18-electron count around the metal. The IR stretching frequency associated with the CO ligand falls in an intermediate region, indicating some electron density build-up at the metal center (vide infra). However, the value is not at either extreme of the spectrum, suggesting that the electron density is partially delocalized throughout the cluster.

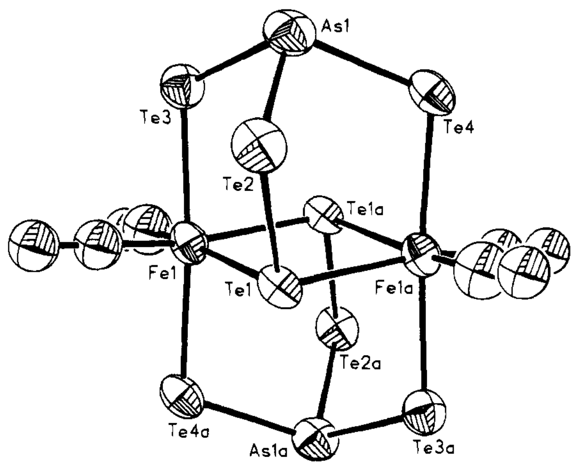
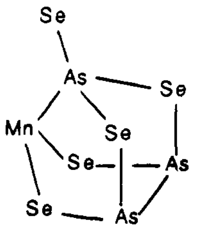
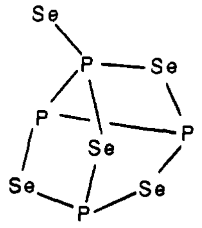


Figure 3. Thermal ellipsoid view of $[Fe_2(AsTe_4)_2(CO)_4]^{2-}$ with thermal ellipsoids at 35%.

Structure of $[(C_6H_5)_4P]_2[Mn(As_3Se_5)(CO)_3]$ (II). The manganese arsenic selenide cluster, $[Mn(As_3Se_5)(CO)_3]^{2-}$, has been characterized as its $[PPh_4]^+$ salt (see Figure 2) and has a unique cluster framework. At first glance, it appears similar to the cage-type structure P_4Se_5,[18] with one pnictide vertex replaced by a $Mn(CO)_3$ fragment. However, the two species are not isostructural in that the connectivity within each cage is different.





Rather the cluster can be viewed as being derived from As_4Se_4, with one arsenic vertex replaced by an $Mn(CO)_3$ fragment and another arsenic vertex containing a terminal selenide linkage.

To our knowledge, this is the first manganese arsenic selenide cage reported, but the bond distances in $[Mn(As_3Se_5)(CO)]^{2-}$ (see Table 6) are in reasonable agreement with other known metal arsenic selenides.[14,20a] The Mn−As distance is 2.454(4) Å and the Mn−Se distances average 2.506(6) Å, which are normal for these cage-type compounds. The As−Se distances within the cage average 2.37(4) Å, which is typical for As−Se single bonds. However, the terminal Se(5)−As(1) bond is somewhat shorter [2.254(4) Å], suggesting the presence of an arsenic selenium double bond. Finally, the As−As bond distance of 2.620(5) Å is similar to the As−As bond distances in As_4Se_4 [2.567(9) and 2.575(10) Å],[21] indicating the presence of an As−As single bond.

The cluster contains a manganese carbonyl fragment which is coordinated by two selenium atoms and one arsenic atom as well as three carbonyl ligands in a pseudooctahedral environment. The angles between adjacent atoms coordinated to the manganese center range between 86(1) and 94(1)°, and those atoms trans to one another average 176(1)°. Also, the coordinated CO molecules are nearly linear [average 176(2)°], and the carbon−oxygen bond distances are normal for carbonyl ligands bound to metal centers (average C−O = 1.15(4) Å). If the arsenic selenide framework is viewed as a trianion donating six electrons to the metal center, then the charge on the manganese atom is formally 1+, with an 18-electron count. As with **I**, the IR stretching frequencies of the CO ligands of **II** fall in the region indicative of intermediate negative charge build-up at the metal center, suggesting delocalization of the negative charge throughout the cluster.

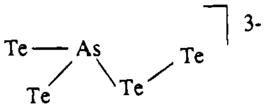
Structure of $[(n\text{-}C_4H_9)_4N]_2[Fe(AsTe_4)(CO)_2]_2$ (III). The anionic cluster **III** contains two iron dicarbonyl fragments

---

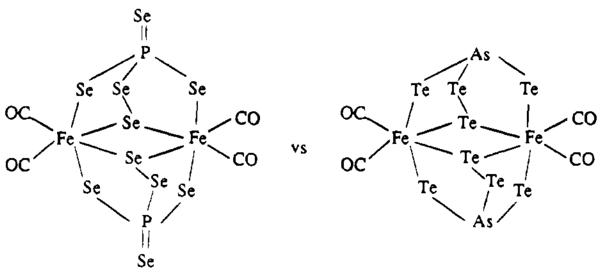
(22) Cowley, A. H. *Polyhedron* **1984,** *3,* 389.

(23) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

bridged by a tellurium atom from each of two unusual $AsTe_4$ groups (see Figure 3). Rather than the expected tetrahedral geometry, the $AsTe_4{}^{3-}$ group contains a trivalent arsenic bound to a ditelluride.



This unusual atomic arrangement is in keeping with the reluctance of arsenic to assume the pentavalent state. Although $[Fe(AsTe_4)(CO)_2]_2{}^{2-}$ is the first metal arsenic telluride reported, the overall geometry of the cluster is related to $[Fe(PSe_5)(CO)_2]_2{}^{2-}$, which was prepared earlier in this laboratory.[15]



If the terminal selenium atoms bound to the capping phosphorus atoms are disregarded, the conformations of the two cores are nearly identical. The cluster $[Fe(AsTe_4)(CO)_2]_2{}^{2-}$ has an inversion center at the center of the four-membered ring formed by Fe(1), Fe(1a), Te(1), and Te(1a).

The bond distances in $[Fe(AsTe_4)(CO)_2]_2{}^{2-}$ (see Table 7) are in agreement with previously characterized compounds.[8] The average As−Te distance of 2.58(1) Å is consistent with the As−Te distances of 2.603 and 2.571 Å reported for $[As_2Te_6]^{2-}$ and $[As_{10}Te_3]^{2-}$, respectively.[8,24] Furthermore, a typical Te−Te distance of 2.800(5) Å is observed between Te(1) and Te(2). Also, the Fe−Te distances of *ca.* 2.62 Å are commensurate with other Fe−Te bond distances described previously.[25] The intramolecular Fe(1)−Fe(1a) and Te(1)−Te(1a) distances of 3.921 and 3.464 Å, respectively, indicate no transannular Fe−Fe or Te−Te interaction.

Each iron is in a distorted octahedral environment. Adjacent atoms coordinated to the metal center are nearly orthogonal (82.9(3)−99.8(3) Å). However, the atoms trans to one another have angles which deviate significantly from ideal (169(2)−176(5)°). The coordinated CO ligands are slightly bent from the expected linear arrangement [Fe(1)−C(1)−O(1) = 172(5)°; Fe(1)−C(2)−O(2) = 176(5)°], but the Fe−C distances fall within the normal range for such M−CO coordination (Fe(1)−C(1) = 1.70(6) Å; Fe(1)−C(2) = 1.73(6) Å).

Each $AsTe_4$ unit is a trianion resulting in a formal oxidation state for the iron atoms of 2+. The $AsTe_4$ ligands act as 4-electron donors to each iron atom and the CO ligands donate two electrons each, thus completing the 18-electron count at each iron.

Spectroscopy. All compounds have been characterized by IR, far-IR, NMR, and SEM-EDAX, as well as elemental analyses. Infrared spectroscopy of $[Fe(As_3Se_3)_2(CO)]^{2-}$ revealed the presence of one C−O stretch at 1920 cm^{-1}, in agreement with the solid state structure. The manganese complex has a spectrum with two peaks at 1979 and 1890 cm^{-1}, whereas $[Fe(AsTe_4)(CO)_2]_2{}^{2-}$ contains two C−O stretches at 1960 and 1916 cm^{-1}. Far-IR spectroscopy is also useful for identification of these complexes. The IR stretches below 400 cm^{-1} are associated with the bonds between the heavy elements, but specific assignments of the stretches is rather difficult. However, the heavy elements in each complex give distinctive bands which are unique for each of the compounds and each spectrum is a "fingerprint" for a specific complex.

The ^{77}Se NMR of the dianion $[Fe(As_3Se_3)(CO)]^{2-}$ has three distinct resonances at 1590, 1559, and 1327 ppm, in a ratio of 1:1:1, which are in agreement with its solid state structure. The resonances at 1590 and 1559 ppm are characteristic of selenium atoms within a cage or ring.[24] The single resonance at 1327 ppm can be assigned to the metal-bound selenium atom within the ring. For $[Mn(As_3Se_5)(CO)_3]^{2-}$, the ^{77}Se NMR also shows three resonances [1663, 1452, 1401 ppm] characteristic for metal cage compounds, in a ratio of 2:2:1. The downfield resonance at 1663 ppm is typical of a selenium within a main group ring, whereas the resonance at 1452 ppm is in the region of a metal-bound Se. This leaves the resonance of intensity 1 at 1401 ppm to be assigned to the terminal selenide. The ^{125}Te NMR of $[Fe(AsTe_4)(CO)_2]_2{}^{2-}$ has three resonances at chemical shifts of 287, 234, and −22 ppm. The resonances are in a ratio of 1:1:2 with the peak of intensity 2 assigned to the metal-bound tellurium atoms and the lower field resonances at 287 and 234 ppm assigned to the arsenic-bound and metal-bound ditelluride units, respectively.

Synthesis and Reactivity. Reduction of the As_4Se_4 glass with 2 equiv of potassium produces a solution containing soluble anionic arsenic selenides. Although the nature of this solution is not completely understood, it has been shown that addition of Ph_4PBr produces $[As_4Se_6]^{2-}$ in good yield.[10] Reaction of $Fe(CO)_5$ with this solution produces $[Fe(As_3Se_3)_2(CO)]^{2-}$ in reasonable yield. Despite the obvious observation that the dianion is not the only species in solution, it is assumed that it is the anion which reacts with the metal carbonyls to form the observed products. This is supported by the observation that reaction of premade $[Ph_4P]_2[As_4Se_6]$ with $Fe(CO)_5$ in DMF also leads to $[Fe(As_3Se_3)_2(CO)]^{2-}$ in reasonable yield. Furthermore, if As_4Se_4 glass is reacted with $[HFe(CO)_4]^-$ in DMF at 100 °C, the same cluster complex is obtained. The yields in both methods were approximately equivalent. It has also been found that $[Fe(As_3Se_3)_2(CO)]^{2-}$ can be prepared most convienently by performing the entire reaction in one vessel with isolation of the product by fractional crystallization.

The $[Mn(As_3Se_5)(CO)_3]^{2-}$ cluster can be prepared by reduction of As_4Se_4 glass with 2 equiv of an alkali metal, followed by heating in the presence of $Mn_2(CO)_{10}$. Addition of the appropriate cation leads to formation of **II** in good yield.

The reduction of a glass of nominal composition As_2Te_3 with 2 equiv of potassium generates a solution containing several arsenic telluride anions. All the species have not yet been identified, but addition of Ph_4PBr to the solution produces $[Ph_4P]_2[As_2Te_6]$ in good yield. However, it is not clear if it is the predominant product in solution, or is in equilibrium with other compounds. Addition of $Fe(CO)_5$ to the original arsenic telluride solution leads to formation of $[Fe_2(AsTe_4)_2(CO)_4]^{2-}$ in good yield. As with $[Fe(As_3Se_3)_2(CO)]^{2-}$, the anion of **III** could be formed by reaction of the previously isolated $[As_2Te_6]^{2-}$ with $Fe(CO)_5$.

An alternative route to the formation of $[Fe(AsTe_4)(CO)_2]_2{}^{2-}$ has also been found. Instead of reacting the previously reduced 15/16 anions with $Fe(CO)_5$, $[HFe(CO)_4]^-$ is reacted with the arsenic telluride glass. The reaction proceeds cleanly at elevated temperatures and yields from each method are comparable.

---

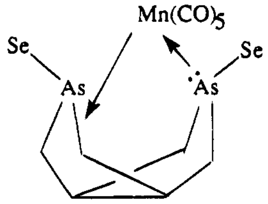
(24) Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* **1987,** 196.

(25) Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 913.

Discussion

We have shown previously that anions formed by reduction of group 15/16 neutral compounds will induce oxidation of a low-valent metal center with loss of some or all coordinated carbonyl ligands.[14,15] A mechanism for these reactions has been proposed, which involves nucleophilic attack at a vacant metal coordination site by a formally anionic terminal selenide from $[As_4Se_6]^{2-}$.[14] Inversion of the main group ring brings the desired atoms near the metal center. Oxidative addition with breakage of As−Se bonds generates the stable five-membered rings (M−Se−As−Se−As). Although the proposed mechanism can be invoked for the formation of $[Fe(As_3Se_3)_2(CO)]^{2-}$, the route to the formation of $[Mn(As_3Se_5)(CO)_3]^{2-}$ and $[Fe(AsTe_4)(CO)_2]_2^{2-}$ is not obvious.

The formation of $[Mn(As_3Se_5)(CO)_3]^{2-}$ can be accounted for by the attack of an arsenic atom upon a vacant metal coordination site followed by oxidative additon across two As−Se bonds. However, the driving force for such a reaction is not readily apparent.



This paper reports our continued extension of the oxidative decarbonylation reaction to mixed group 15/16 cages. We have shown that new hybrid metal carbonyl main group cage complexes can be synthesized. The path to the formation of these complexes can be accomplished by two procedures: (1) formation of the anionic main group complex with subsequent reaction with the metal carbonyl or (2) reaction of the neutral main group complex with the anionic iron carbonyl monohydride. The novel shapes and connectivity of these clusters indicate that the limit of topological design has not been reached. Investigations are continuing with the focus on the reactivity of the metal main group anions, as well as the further synthesis of new and larger cages containing heavier main group elements.

Acknowledgment. We are indebted to the National Science Foundation for support of this work (Grant CHE-9102548) and for funding for the diffractometer (Grant CHE-9207230).

Supplementary Material Available: Tables giving complete crystallographic experimental details, distances and angles, positional parameters for all atoms, anisotropic thermal parameters, and optimized hydrogen atom coordinates of molecules **I**−**IV** and a thermal ellipsoid plot of **IV**, along with text giving structure determination details and crystal data for **IV** (18 pages). Ordering information is given on any current masthead page.

IC941253U