which via ring closure gives **16**.

Conclusions

We have shown here that considerable insight into the structures and dynamics of both 1:1 and 1:2 Pt(II)–L-methionine complexes in solution can be obtained via the use of high-field ^1H NMR spectroscopy, combined with ^{195}Pt and ^{15}N NMR spectroscopy, especially with the use of ^{15}N enrichment of L-MetH and polarization-transfer methods for observing ^{15}N resonances. The major thermodynamic products from reactions of 2 mol equiv of L-MetH with $[PtCl_4]^{2-}$ at pH* 7 are the three diastereomers of *cis*-[Pt(L-Met-*S*,*N*)$_2$] with only minor (10%) amounts of the analogous trans complexes. The cis complex undergoes reversible ring-opening at low pH to give four diastereomers of [Pt(L-MetH-*S*,*N*)(L-MetH$_2$-*S*)Cl]$^{2+}$.

The activation barriers for sulfur inversion are higher in the ring-closed compared to the ring-opened forms. We have shown for the 1:1 complex [Pt(L-MetH-*S*,*N*)Cl$_2$] that sulfur inversion in solution is accompanied by a change in the conformation of the six-membered chelate ring, whereas such a difference has not been observed in crystal structures of this and related complexes. Such conformational changes may be important for recognition processes involved in the transport and excretion of Pt(II)–methionine complexes.

Reactions of the anticancer drug cisplatin with the amino acid L-methionine are important because it has been suggested that certain products resulting from the reaction are nephrotoxic.[5] Renal ATPases appear to be more sensitive to inhibition by these products than by cisplatin alone.[38] A complex formulated as the trans isomer of [Pt(Met)$_2$] has been isolated from the urine of patients treated with the drug.[4] For reactions of $[PtCl_4]^{2-}$ with 2 mol equiv of L-MetH in aqueous solution near neutral pH the most stable form of the 1:2 complex is *cis*-[Pt(L-Met-*S*,*N*)$_2$], which exists as three diastereoisomers in equilibrium with minor amounts of the analogous diastereomers of the trans geometrical isomer. These same products, **6′A–C** and **7′A–C**, arise from similar reactions of cisplatin or *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with methionine. The use of combined ^1H, ^{15}N, and ^{195}Pt NMR spectroscopy on ^{15}N-enriched materials enabled a number of additional products to be identified, including monoammine complexes containing chelated or monodentate L-Met **12**, **13**, and **16**. Clearly each of these products may have significantly different biological activities and this may affect the interpretation of reported nephrotoxicity and anticancer data obtained from tests on reaction mixtures of cisplatin and methionine.[5] The products from these reactions now need to be separated and tested individually. The bischelated complexes **6′** and **7′** may be inactive and nontoxic; e.g., Melvik and Pettersen[39] found that the presence of excess methionine in culture media greatly reduced the toxicity of cisplatin toward cells. However, as we have shown, facile ring-opening reactions of the bischelated species can occur at low pH, and since some parts of biological cells (lysosomes) can be quite acidic, even bischelated species may become reactive.

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Supplementary Material Available: A figure showing ^{195}Pt NMR spectra at 297, 323, and 343 K of a 1:1 mixture of *cis*-$[PtCl_2(^{15}NH_3)_2]$ (110 mM) and [^{15}N]-L-MetH in 0.1 M deuteriated phosphate buffer, pH* 5.8 (1 page). Ordering information is given on any current masthead page.

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Oxidative Decarbonylation of Transition Metal Carbonyls by Arsenic Selenide Anions: Preparation and Structures of $[M(CO)_2(As_3Se_3)_2]^{2-}$ and $[M(AsSe_5)_2]^{2-}$ (M = Mo, W)

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The reactions of arsenic selenide anionic clusters with $M(CO)_6$ (M = Mo, W) were investigated and the products characterized by IR and ^{77}Se NMR spectroscopy and single-crystal X-ray diffraction of bis $(n\text{-}Bu)_4N^+$ salts in each case. The reaction of $As_4Se_6^{2-}$ with $M(CO)_6$ generates $[M(CO)_2(As_3Se_3)_2]^{2-}$ (I) in reasonable yield. Compound I contains two As_3Se_3 birdcage fragments bound to the metal center with the metal acting as a basal vertex, completing the birdcage structure of each fragment. The metal is also coordinated by two CO ligands, generating a bicapped trigonal prismatic ligand framework. The reaction of $As_2Se_6^{2-}$ with $M(CO)_6$ generates $[M(AsSe_5)_2]^{2-}$ (II). The metal center is in an irregular coordination environment with three terminal selenides from two $AsSe_5^{3-}$ ligands coordinated to the metal center. Molecule I can be converted to II by addition of red selenium. Reaction mechanisms for the formation of each product are proposed. Crystal data for $[(n\text{-}Bu)_4N]_2[[W(CO)_2(As_3Se_3)_2]$: space group $P\bar{1}$, $a = 11.575$ (3) Å, $b = 23.324$ (5) Å, $c = 30.663$ (6) Å, $\alpha = 95.63$ (2)°, $\beta = 100.01$ (2)°, $\gamma = 96.73$ (2)°, V = 8036 (3) Å^3, $Z = 6$, $R = 0.0753$. Crystal data for $[(n\text{-}Bu)_4N]_2[W(AsSe_5)_2]$: space group $C2/c$, $a = 18.240$ (6) Å, $b = 15.434$ (5) Å, $c = 18.003$ (5) Å, $\beta = 103.71$ (2), $V = 4923$ (2) Å^3, $Z = 4$, $R = 0.0716$.

Introduction

The coordination chemistry of transition metal sulfides is rich and varied,[1] and their importance in biological[2] and industrial catalytic processes[3] is a driving force for their continued study. Recent investigation of metal selenides and tellurides suggests that the heavier elements will lead to even more unusual chemistry.[4]

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The use of rings and cages containing group 15 elements further extends the structural possibilities by introducing one or more trivalent sites in the ligand framework.[5,6] We are currently expanding our explorations in this area to include complexes containing mixed groups 15/group 16 anions as ligands to metal centers.[7] It is known that nucleophilic tetrathio- and selenometalates react with binary group 15/group 16 clusters to generate several complexes whose unusual structural aspects can be attributed to the presence of one or more trivalent group 15 atoms.[6a,7]

$$MSe_4^{2-} + E_4Se_4 \rightarrow M_xSe_yE_z^{2-}$$

$$E = P, As$$

The novelty of these compounds has led us to investigate other potential routes to metal complexes containing mixed group 15/group 16 cage ligands.

We have recently been utilizing the oxidative decarbonylation reaction as an entry to metal chalcogenides.[8] In this reaction, the coordination of an anionic polychalcogenide to a low-valent metal carbonyl center can result in electron transfer from the metal center to an element–element bond in the chain. This leads to oxidation of the metal center and shortening of the main group chain, often resulting in formation of unusual metal chalcogenide anions and clusters.[9]

$$W(CO)_6 + Se_4^{2-} \rightarrow WSe_4^{2-\,9a}$$

$$6W(CO)_6 + 2Te_4^{2-} \rightarrow [(W(CO)_3)_6(Te_2)_4]^{2-\,9c}$$

Reduction of mixed group 15/group 16 cages often results in formation of anionic clusters such as $As_2E_6^{2-}$[10,11] and $As_4E_6^{2-}$.[11,12] We were hopeful that coordination of these clusters to a low-valent metal center would result in oxidative rearrangement of the cages with resulting formation of unusual cluster complexes. This paper reports our initial results concerning the preparation of several unusual molybdenum and tungsten clusters obtained via oxidative decarbonylation of the parent carbonyls by anionic arsenic selenide cages.

Experimental Section

General Considerations. All arsenic selenide 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 purchased from Aldrich and were of the highest commercial grade. They were stored over activated sieves and bubbled with argon before use. All other reagents were purchased from Aldrich or Strem and used as received.

Carbon and hydrogen analyses were performed by Atlantic Microlabs, Atlanta, GA, and selenium and arsenic analyses were performed by Galbraith Labs, Knoxville, TN. Far-IR spectra were obtained on a Nicolet 20F far-IR instrument as Nujol mulls in sealed polyethylene bags. The ^{77}Se 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 arsenic selenide glass of formula "As_4Se_4" was obtained by a modification of the literature procedure[10] by melting equimolar amounts of the elemental powders in a sealed quartz tube at 600 °C for 18 h. K_2Se_3 was obtained by dissolving the elements in liquid ammonia at the correct ratio and stirring at −78 °C for 3 h.

Preparation of $[(C_4H_9)_4N]_2[W(CO)_2(As_3Se_3)_2]$ (Ia). In a typical reaction, 0.80 g (1.30 mmol) of As_4Se_4 and 0.06 g (2.61 mmol) of elemental sodium were combined in 10 mL of DMF and stirred for 4 h. The red solution was filtered onto 0.46 g (1.31 mmol) of $W(CO)_6$ and stirred at room temperature for 1 h. This solution was then heated to 100 °C under static vacuum for 8 h, after which 0.88 g (2.73 mmol) of $(n\text{-}Bu)_4NBr$ was added. The red solution was filtered and the DMF removed under vacuum. The tar was extracted with 10 mL of CH_2Cl_2 and the solution layered with 3 mL of diethyl ether. Storage at 4 °C overnight produced a white powder, which was removed by filtration. Addition of a fresh aliquot of ether and storage overnight at 4 °C produced red crystals in 30% yield. Anal. Calcd: C, 24.76; H, 4.37; As, 27.13; Se, 28.76. Found: C, 24.92; H, 4.35; As, 25.18; Se, 28.24. IR (cm^{-1}): 1989 (s), 1954 (m), 478 (m), 419 (m), 398 (m), 280 (m), 256 (s), 195 (s), 175 (s), 151 (s). ^{77}Se NMR ($\delta(Me_2Se)$ = 0 ppm) 322 (1 Se), 295 ppm (2 Se).

Preparation of $[(C_4H_9)_4N]_2[Mo(CO)_2(As_3Se_3)_2]$ (Ib). An arsenic selenide anion solution was prepared as described above and filtered onto 0.34 g of $Mo(CO)_6$ and stirred for 1 h at room temperature followed by heating to 100 °C under static vacuum, and stirring for 20 h. After workup as described above, red crystals were obtained in 20% yield. Anal. Calcd: C, 26.15; H, 4.62. Found: C, 26.99; H, 4.66. IR (cm^{-1}): 1990 (s), 1985 (m), 467 (m), 411 (m), 303 (m), 280 (m), 254 (s), 227 (m), 202 (s), 177 (s), 151 (s).

Preparation of $[(C_4H_9)_4N]_2[W(AsSe_5)_2]$ (IIa). Method A. An arsenic selenide solution was prepared as described above and added to 0.46 g (1.31 mmol) of $W(CO)_6$. After thermolysis as described above, the solution was cooled to room temperature, 0.40 g (5.06 mmol) of red selenium was added, and the solution was stirred at room temperature for 18 h. After addition of 0.88 g (2.73 mmol) of $(n\text{-}Bu)_4NBr$, the dark red solution was filtered and the DMF removed under vacuum. The red tar was extracted with 10 mL of CH_2Cl_2, filtered, and subjected to workup with diethyl ether as described above. Large dark red crystals could be isolated in 30% yield. Anal. Calcd: C, 23.88; H, 4.48; As, 9.33; Se, 49.13. Found: C, 24.60; H, 4.67; As, 9.25; Se, 49.78. IR (cm^{-1}): 259 (s), 227 (s), 214 (s). ^{77}Se NMR ($\delta(Me_2Se)$ = 0 ppm): 407 (2 Se), 562 (2 Se), 705 (2 Se), 831 (2 Se), 1070 ppm (2 Se).

Preparation of $[(C_4H_9)_4N]_2[W(AsSe_5)_2]$. Method B. A crystalline sample of $[(C_4H_9)_4N]_2[W(CO)_2(As_3Se_3)]$ was prepared as described above. A 0.40-g (0.24-mmol) sample of I was dissolved in 10 mL of DMF and 0.20 g (2.5 mmol) of red selenium added. The solution was stirred at room temperature for 12 h and filtered. The DMF was removed under vacuum and the red tar extracted with 10 mL of CH_2Cl_2. The solution was filtered and layered with 10 mL of diethyl ether and stored at 4 °C overnight. Filtration followed by addition of a fresh aliquot of ether produced the product (25% yield), which was identified by far-IR spectroscopy and a unit cell determination.

Preparation of $[(C_4H_9)_4N]_2[W(AsSe_5)_2]$. Method C. A Schlenk flask was charged with 0.30 g (0.487 mmol) of As_4Se_4 and 0.46 g (1.46 mmol) of K_2Se_3, and 10 mL of DMF was added. The solution was allowed to stir at room temperature for 4 h, filtered onto 0.34 g (0.96 mmol) of $W(CO)_6$, and stirred at room temperature for 1 h. The flask was then heated at 100 °C under static vacuum for 4 h and cooled to room temperature, and 0.91 g (2.82 mmol) of $(n\text{-}Bu)_4NBr$ was added. The solution was filtered and the DMF removed under vacuum. The tar was extracted with 10 mL of CH_2Cl_2, and the resultant solution was filtered and layered with 3 mL of diethyl ether. Storage overnight at 4 °C, filtration, and addition of a fresh aliquot of ether resulted in isolation of an orange crystalline product in 60% yield. The identity of the product was confirmed by far-IR spectroscopy and a unit cell determination.

Preparation of $[(C_4H_9)_4N]_2[Mo(AsSe_5)_2]$ (IIb). Method A. A Schlenk flask was charged with 0.30 g (0.487 mmol) of As_4Se_4 and 0.46 g (1.46 mmol) of K_2Se_3 and 10 mL of DMF added. The solution was stirred for 4 h at room temperature and filtered onto 0.26 g (0.98 mmol) of $Mo(CO)_6$. The solution was heated to 100 °C for 2 h under static vacuum and allowed to cool to room temperature, and 0.91 g (2.82 mmol) of $(n\text{-}Bu)_4NBr$ was added with stirring. The solution was filtered and the DMF removed under vacuum. The purple black tar was extracted with 10 mL of CH_2Cl_2, filtered, and subjected to treatment with diethyl ether as described above. The product was isolated in 40% yield as large black crystals. IR (cm^{-1}): 266 (m), 246 (s), 226 (s), 204 (m), 158 (w). A unit

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Table I. Crystal Data

	Ia	IIa
formula	$C_{34}H_{72}N_2O_2As_6Se_6W$	$C_{32}H_{72}N_2As_2Se_{10}W$
fw	1648.09	1608.23
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	11.575 (3)	18.240 (6)
b, Å	23.324 (5)	15.434 (5)
c, Å	30.662 (6)	18.002 (5)
α, deg	95.63 (2)	
β, deg	100.01 (2)	103.71 (2)
γ, deg	96.73 (2)	
V, Å^3	8036 (3)	4923 (2)
Z	6	4
D_{calc}, g cm^{-3}	2.04	2.17
μ, cm^{-1}	95.7	104.1
transm coeff	0.52–1.00	0.46–1.00
no. of obsd data ($I > 3\sigma(I)$)	6799	2265
R^a	0.0753	0.0716
$R_w{}^b$	0.0775	0.0893

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)]^{1/2}$.

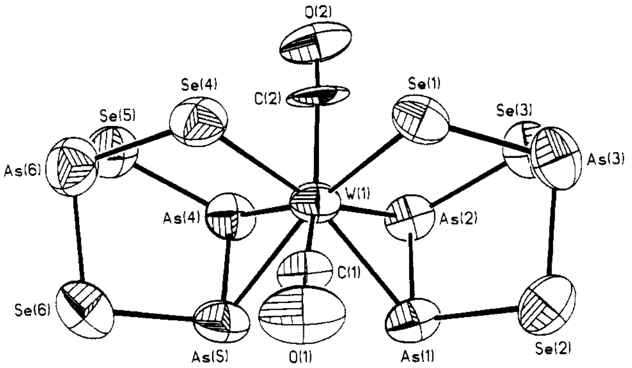

Figure 1. Thermal ellipsoid plot of the anion of Ia, $[W(CO)_2(As_3Se_3)_2]^{2-}$ (35% probability).

cell determination also showed it to be identical with the previously characterized species.[7b]

Preparation of $[(C_4H_9)_4N]_2[Mo(AsSe_5)_2]$. Method B. This conversion of $[(C_4H_9)_4N]_2[Mo(CO)_2(As_3Se_3)_2]$ to $[(C_4H_9)_4N]_2[Mo(AsSe_5)_2]$ was carried out exactly as described for method B for the corresponding tungsten compounds. The dark blue black crystalline product was characterized by far-IR spectroscopy and a unit cell determination.

X-ray Crystallography. Relevant crystallographic data for compounds Ia and IIa are given in Table I. All measurements were made at ambient temperature with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nicolet R3mV diffractometer. For Ia ω-scans were made at a fixed speed of 2.9°/min for 3.5° < 2Θ < 35° and 2°/min for 35° < 2Θ < 42°; for IIa $\omega/2\Theta$-scans were made at speeds ranging from 2 to 14.6°/min for 3.5 < 2Θ < 45°. Both structures were solved by direct methods and refined by full-matrix least-squares techniques using SHELXTL-PLUS and the standard Nicolet package of programs. Compound Ia crystallizes with three formula units per asymmetric unit; no symmetry relationship between formula units could be recognized. The anion of compound IIa possesses crystallographic 2-fold symmetry. Hydrogen atoms were not located for either compound. Due to computer constraints, the cations for each molecule of compound Ia were refined in blocks and were constrained as riding models with individual isotropic group thermal parameters in the final cycle. The parameters for the anions, which were refined anisotropically, did not vary significantly, regardless of the model used for the cations. All non-hydrogen atoms for IIa were refined anisotropically. Atomic coordinates and equivalent isotropic thermal parameters for the anions of compounds Ia and IIa are listed in Tables II and III, respectively. Selected distances and angles for the two compounds are given in Tables IV and V. Structure determination summaries and complete listings of coordinates, distances and angles, thermal parameters, and observed and calculated structure factors have been deposited as supplementary material.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (A^2 × 10^3) for Ia

	x	y	z	U(eq)^a
W(1)	5371 (2)	7563 (1)	4017 (1)	84 (1)
Se(1)	3209 (4)	7211 (2)	4069 (1)	99 (2)
Se(2)	3810 (5)	5896 (2)	3468 (2)	124 (3)
Se(3)	4631 (5)	6088 (2)	4632 (2)	125 (3)
Se(4)	4701 (4)	8585 (2)	4035 (2)	110 (3)
Se(5)	7789 (5)	9034 (2)	4559 (2)	134 (3)
Se(6)	7046 (5)	8825 (3)	3390 (2)	137 (3)
As(1)	5659 (4)	6568 (2)	3608 (2)	105 (3)
As(2)	6212 (4)	6694 (2)	4388 (2)	100 (2)
As(3)	2998 (4)	6187 (2)	4089 (2)	117 (3)
As(4)	7593 (4)	7980 (2)	4370 (2)	109 (3)
As(5)	7087 (4)	7843 (2)	3583 (2)	110 (3)
As(6)	6350 (5)	9272 (2)	3990 (2)	130 (3)
O(1)	4044 (27)	7580 (14)	3018 (9)	143 (18)
O(2)	5453 (28)	7890 (15)	5049 (10)	141 (18)
C(1)	4548 (26)	7585 (15)	3374 (11)	67 (16)
C(2)	5385 (41)	7763 (21)	4683 (15)	136 (27)
W(2)	8601 (2)	7298 (1)	663 (1)	79 (1)
Se(7)	6427 (4)	6945 (2)	707 (2)	106 (3)
Se(8)	7157 (5)	5588 (2)	202 (2)	138 (3)
Se(9)	7833 (5)	5899 (2)	1361 (2)	129 (3)
Se(10)	7893 (4)	8301 (2)	598 (2)	116 (3)
Se(11)	10939 (5)	8801 (2)	1146 (2)	142 (3)
Se(12)	10282 (5)	8494 (3)	−20 (2)	149 (3)
As(7)	8990 (5)	6273 (2)	339 (2)	111 (3)
As(8)	9440 (4)	6490 (2)	1118 (2)	103 (2)
As(9)	6254 (4)	5936 (2)	783 (2)	130 (3)
As(10)	10807 (4)	7750 (2)	1011 (2)	103 (2)
As(11)	10333 (4)	7537 (2)	232 (2)	106 (3)
As(12)	9526 (5)	8978 (2)	547 (2)	141 (3)
O(3)	7376 (30)	7147 (17)	−342 (10)	156 (20)
O(4)	8609 (34)	7723 (19)	1685 (11)	158 (22)
C(3)	7667 (44)	7235 (22)	22 (15)	133 (27)
C(4)	8591 (59)	7655 (28)	1330 (16)	167 (34)
W(3)	7880 (2)	2288 (1)	2620 (1)	86 (1)
Se(13)	8506 (4)	1257 (2)	2602 (2)	111 (3)
Se(14)	6036 (5)	1003 (2)	3190 (2)	133 (3)
Se(15)	5470 (4)	833 (2)	2015 (2)	133 (3)
Se(16)	10078 (4)	2660 (2)	2633 (1)	100 (2)
Se(17)	9381 (5)	3951 (2)	3216 (2)	127 (3)
Se(18)	8727 (4)	3776 (2)	2041 (2)	122 (3)
As(13)	6056 (4)	1996 (2)	3000 (2)	108 (3)
As(14)	5699 (4)	1887 (2)	2213 (2)	109 (3)
As(15)	6823 (5)	572 (2)	2605 (2)	133 (3)
As(16)	7082 (4)	3173 (2)	2246 (1)	102 (2)
As(17)	7525 (4)	3273 (2)	3032 (2)	109 (3)
As(18)	10273 (4)	3679 (2)	2617 (2)	120 (3)
O(5)	8214 (33)	2035 (19)	1611 (12)	174 (22)
O(6)	9044 (26)	2193 (14)	3597 (9)	135 (17)
C(5)	8002 (49)	2107 (24)	1947 (18)	144 (33)
C(6)	8609 (5)	2264 (2)	3280 (2)	115 (26)

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

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for IIa

	x	y	z	U(eq)^a
W(1)	0	2367 (1)	2500	46 (1)
Se(1)	1666 (2)	1085 (2)	4062 (2)	79 (1)
Se(2)	403 (1)	1003 (1)	3236 (1)	63 (1)
Se(3)	1202 (2)	3253 (2)	4562 (1)	81 (1)
Se(4)	13 (1)	3265 (1)	3618 (1)	64 (1)
Se(5)	1347 (1)	2755 (1)	2620 (1)	59 (1)
As(1)	2008 (1)	2531 (2)	3936 (1)	73 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthagonalized U_{ij} tensor.

Results

Structure of $[(C_4H_9)_4N]_2[W(CO)_2(As_3Se_3)_2]$ (Ia). X-ray crystallographic results show two well-separated quaternary ammonium cations per cluster anion. There are three discrete, chemically similar $[W(CO)_2(As_3Se_3)_2]^{2-}$ clusters per asymmetric unit in the unit cell. Many fruitless attempts were made to locate a smaller or more symmetric unit cell. These included use of cell reduction programs such as TRACER, searching for relationships between coordinates of the heavy atoms, analysis of photographs, and examination of several different crystals. We see no obvious

Table IV. Selected Bond Distances and Angles for Ia

Distances (Å)			
W(1)–Se(1)	2.577 (5)	W(1)–Se(4)	2.591 (6)
W(1)–As(1)	2.615 (5)	W(1)–As(2)	2.624 (5)
W(1)–As(4)	2.640 (5)	W(1)–As(5)	2.632 (6)
W(1)–C(1)	2.043 (32)	W(1)–C(2)	2.046 (45)
Se(1)–As(3)	2.380 (7)	Se(2)–As(1)	2.445 (7)
Se(2)–As(3)	2.343 (8)	Se(3)–As(2)	2.446 (7)
Se(3)–As(3)	2.342 (7)	Se(4)–As(6)	2.376 (7)
Se(5)–As(4)	2.444 (7)	Se(5)–As(6)	2.350 (8)
Se(6)–As(5)	2.424 (8)	Se(6)–As(6)	2.334 (8)
As(1)–As(2)	2.348 (6)	As(4)–As(5)	2.364 (7)
O(1)–C(1)	1.142 (40)	O(2)–C(2)	1.120 (53)
Angles (deg)			
Se(1)–W(1)–Se(4)	84.6 (2)	Se(1)–W(1)–As(1)	93.4 (2)
Se(4)–W(1)–As(1)	153.0 (2)	Se(1)–W(1)–As(2)	94.2 (2)
Se(4)–W(1)–As(2)	153.7 (2)	As(1)–W(1)–As(2)	53.3 (1)
Se(1)–W(1)–As(4)	152.9 (2)	Se(4)–W(1)–As(4)	93.2 (2)
As(1)–W(1)–As(4)	100.3 (2)	As(2)–W(1)–As(4)	76.0 (2)
Se(1)–W(1)–As(5)	153.7 (2)	Se(4)–W(1)–As(5)	93.7 (2)
As(1)–W(1)–As(5)	76.4 (2)	As(2)–W(1)–As(5)	98.5 (2)
As(4)–W(1)–As(5)	53.3 (2)	Se(1)–W(1)–C(1)	79.4 (9)
Se(4)–W(1)–C(1)	76.6 (10)	As(1)–W(1)–C(1)	76.6 (10)
As(2)–W(1)–C(1)	129.1 (10)	As(4)–W(1)–C(1)	126.4 (9)
As(5)–W(1)–C(1)	74.7 (9)	Se(1)–W(1)–C(2)	78.1 (13)
Se(4)–W(1)–C(2)	78.6 (14)	As(1)–W(1)–C(2)	127.4 (14)
As(2)–W(1)–C(2)	75.5 (14)	As(4)–W(1)–C(2)	75.0 (13)
As(5)–W(1)–C(2)	127.3 (13)	C(1)–W(1)–C(2)	147.8 (17)
W(1)–Se(1)–As(3)	108.4 (2)	As(1)–Se(2)–As(3)	101.0 (2)
As(2)–Se(3)–As(3)	101.0 (3)	W(1)–Se(4)–As(6)	108.3 (2)
As(4)–Se(5)–As(6)	100.7 (2)	As(5)–Se(6)–As(6)	101.7 (3)
W(1)–As(1)–Se(2)	110.2 (2)	W(1)–As(1)–As(2)	63.6 (2)
Se(2)–As(1)–As(2)	103.5 (3)	W(1)–As(2)–Se(3)	110.1 (2)
W(1)–As(2)–As(1)	63.2 (2)	Se(3)–As(2)–As(1)	103.7 (2)
Se(1)–As(3)–Se(2)	100.1 (3)	Se(1)–As(3)–Se(3)	102.0 (2)
Se(2)–As(3)–Se(3)	96.7 (3)	W(1)–As(4)–Se(5)	110.1 (2)
W(1)–As(4)–As(5)	63.2 (2)	Se(5)–As(4)–As(5)	103.9 (3)
W(1)–As(5)–Se(6)	110.1 (3)	W(1)–As(5)–As(4)	63.5 (2)
Se(6)–As(5)–As(4)	103.3 (3)	Se(4)–As(6)–Se(5)	100.7 (3)
Se(4)–As(6)–Se(6)	101.5 (3)	Se(5)–As(6)–Se(6)	97.0 (3)
W(1)–C(1)–O(1)	176.8 (24)	W(1)–C(2)–O(2)	176.1 (45)

Table V. Selected Bond Distances and Angles for IIa

Distances (Å)			
W(1)–Se(2)	2.503 (2)	W(1)–Se(4)	2.438 (2)
W(1)–Se(5)	2.489 (2)	Se(1)–Se(2)	2.432 (3)
Se(1)–As(1)	2.342 (4)	Se(2)–Se(2A)	2.708 (4)
Se(3)–Se(4)	2.418 (3)	Se(3)–As(1)	2.336 (4)
Se(5)–As(1)	2.415 (3)		
Angles (deg)			
Se(2)–W(1)–Se(4)	95.6 (1)	Se(2)–W(1)–Se(5)	89.8 (1)
Se(2)–W(1)–Se(2A)	65.5 (1)	Se(2)–W(1)–Se(4A)	149.2 (1)
Se(2)–W(1)–Se(5A)	114.1 (1)	Se(4)–W(1)–Se(5)	88.6 (1)
Se(4)–W(1)–Se(4A)	110.7 (1)	Se(4)–W(1)–Se(5A)	75.6 (1)
Se(5)–W(1)–Se(5A)	152.1 (1)	Se(2)–Se(1)–As(1)	103.1 (1)
W(1)–Se(2)–Se(1)	113.4 (1)	Se(4)–Se(3)–As(1)	103.1 (1)
W(1)–Se(4)–Se(3)	114.1 (1)	W(1)–Se(5)–As(1)	107.7 (1)
Se(1)–As(1)–Se(3)	101.3 (1)	Se(1)–As(1)–Se(5)	98.6 (1)
Se(3)–As(1)–Se(5)	100.4 (1)		

explanation for this unusual crystallographic behavior.

Cluster **Ia** contains a central tungsten atom which is coordinated by two arsenic and one selenium atom of two identical As_3Se_3 ligands (see Figure 1).[13] Each ligand cage combines with the metal to complete the formation of two corner-sharing birdcage P_4S_3 type structures[14] with the tungsten atoms in the base of each birdcage. In general, structures involving main group birdcages usually involve fragmentation of the cage[15] or oxidative addition of the metal center across a basal pnicogen–pnicogen bond.[6b,16] The geometry of a transition metal complex occupying the basal vertex of an E_3Q_3 cage (where E is a group 15 element and Q is a group 16 element) has been observed previously,[17] but two cages sharing one metal vertex is somewhat unusual.

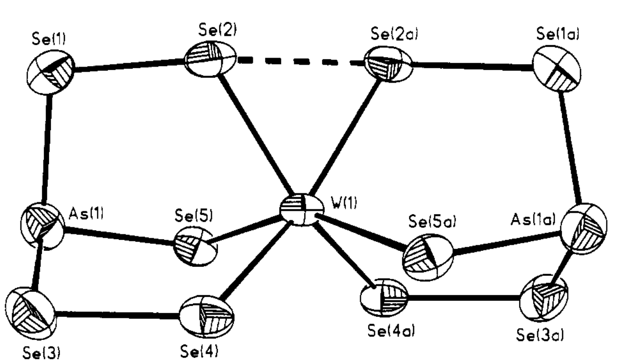

Figure 2. Thermal ellipsoid plot of the anion of IIa, $[W(AsSe_5)_2]^{2-}$ (35% probability).

The two cages are related by two noncrystallographic mirror planes passing through the center of the molecule. Thus the coordination geometry created by the cages is trigonal prismatic around the metal center. There are also two CO molecules coordinated to the metal, which pass through the two arsenic selenide square faces of the trigonal prism. These create an eight-coordinated metal center and complete the 18-electron count around the metal. The coordination geometry of eight coordinate molecular species is rarely bicapped trigonal prism;[18] however, this geometry is quite common in solid-state compounds.[19] The molybdenum analogue has a nearly identical unit cell and is assumed to be isostructural.[20]

The distances and angles of Ia (see Table IV) are commensurate with those observed with previously characterized metal arsenic selenide clusters.[7b] All three clusters per asymmetric unit have comparable distances and angles; W–Se distances average 2.584 (5) Å, and the W–As distances average 2.629 (9) Å, which are typical for these types of compounds. The basal arsenic atoms are clearly bonded to each other with an average As–As distance of 2.354 (8) Å. This distance is somewhat short for an As–As bond. For example the As–As bonds in As_4Se_4 are 2.567 (9) and 2.575 (10) Å.[21] The distance is not short enough to be a direct As═As double bond (ca. 2.224 Å)[22] but is similar to the distance of diarsines coordinated to transition metal centers (2.388 (7) Å).[23]

The angles of the coordinated arsenic atoms (As(1)–W(1)–As(5) = 76.4 (2) and As(2)–W(1)–As(4) = 76.0 (2)°) are somewhat more contracted than that of the coordinated selenides (Se(1)–W(1)–Se(4) = 84.6 (2)°). However all other distances and angles within the cages seem unremarkable. Also the coordinated CO molecules are nearly linear (W(1)–C(1)–O(1) = 176.8 (24)°) and the distances are normal.

Structure of $[(C_4H_9)_4N]_2[W(AsSe_5)_2]$ (IIa). The structure of IIa consists of two well-separated quaternary ammonium cations and a dianionic cluster. The molecule is isostructural with a

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(13) It is difficult to unambiguously assign the identity of arsenic and selenium atoms by crystallography alone. However, the elemental analysis indicates the presence of equal number of As and Se atoms and the ^{77}Se NMR spectrum displays a ratio of 2:1. These factors and the obvious presence of three divalent and three trivalent atoms in the cage all combine to lead to confidence in the assignment of atomic identity. The same logic can be applied to the assignation of atomic identities in II.

(14) Greenwood, N. N.; Earnshaw, A. *The Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1984; pp 581–586.

(15) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *Polyhedron* **1986**, *5*, 945.

(16) (a) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc. Dalton Trans.* **1985**, 291. (b) Ghilardi, C. A.; Midolini, S.; Orlandini, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 790.

(17) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* **1983**, 903.

(18) Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179.

(19) Hulliger, F. *Structural Chemistry of Layer-Type Phases*; D. Reidel: Dordrecht, The Netherlands, 1976.

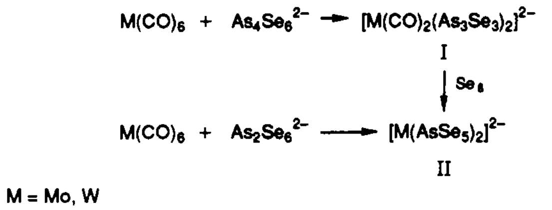
(20) Crystallographic data for the molybdenum analogue of Ia: $C_{34}H_{72}N_2O_2As_6MoSe_6$, fw = 1560.18, triclinic, $P\bar{1}$, a = 11.597 (6) Å, b = 23.315 (13) Å, b = 30.0663 (22) Å, α = 95.73 (5)°, β = 100.21 (5)°, γ = 96.07 (4)°, V = 8036 (9) Å^3, A = 6, D_{calc} = 1.934 g cm^{-3}.

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

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

(23) Elmes, P. S.; Leverett, P.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1971**, 747.

Scheme I



molybdenum analogue which has been previously prepared by a different method.[7b] The cluster has a tungsten center chelated by two $AsSe_5$ ligands (see Figure 2). Each ligand has three terminal selenide atoms bound to the metal center with an average W–Se distance of 2.48 (3) Å. All other distances and angles appear reasonable and are nearly identical with those of the previously reported molybdenum analogue.

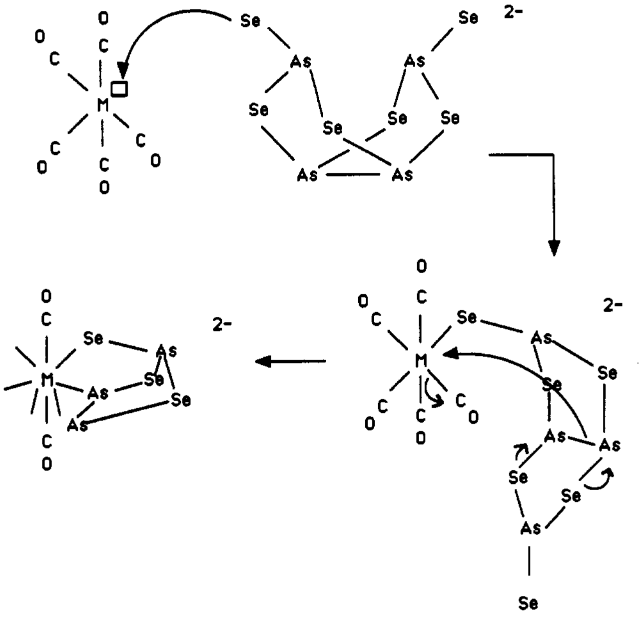
The two tridentate ligands are rotated relative to each other to a point between that expected for an octahedral and a trigonal prismatic coordination environment around the metal center. The result is a six-coordinate environment which is quite unsymmetrical. As in the previously reported molybdenum analogue,[7b] there is a close Se(2)···Se(2a) contact of 2.708 (4) Å between the two cages. There seems to be no electronic reason for any interaction, so it may be only due to the small size of the metal atom. The other selenium atoms have considerably longer nonbonded interactions (Se(4′)···Se(5) = 3.021 (4) Å).

Synthesis and Reactivity. Reaction of $M(CO)_6$ (M = Mo, W) with a solution containing a reduced arsenic selenide anion generates $[M(CO)_2(As_3Se_3)_2]^{2-}$ in reasonable yield. The arsenic selenide solution was prepared by reduction of As_4Se_4 glass with 2 equiv of sodium. The nature of this solution is not entirely understood. However it is known from previous work that reduction of As_4Se_4 with 2 equiv of elemental sodium followed by treatment with $(C_6H_5)_4PBr$ results in isolation of $As_4Se_6^{2-}$ in excellent yield.[11] Therefore, we assume that the predominant species in solution is $As_4Se_6^{2-}$. It cannot be the only compound because of mass balance. However, despite extensive investigation, this is the only species which could be characterized. We have obtained additional evidence that $As_4Se_6^{2-}$ is the active species in the cluster building reaction by isolating it as the $(C_6H_5)_4P^+$ salt and reacting it with $W(CO)_6$ to generate anion Ia. However, we have found that Ia is prepared most conveniently by performing the entire reaction in one pot with isolation of the product in reasonable yield by fractional crystallization.

In contrast, if the arsenic selenide solution is prepared by adding excess polyselenide in the form of K_2Se_3 to As_4Se_4, entirely different chemistry takes place. Any attempt to isolate a product from the arsenic selenide solution results in formation of $As_2Se_6^{2-}$ in good yield. Again, it is not known if other anionic clusters are present, but this is the only species which can be detected and characterized.[11] This reacts readily with $M(CO)_6$ to form $[M(AsSe_5)_2]^{2-}$. This is also an oxidative addition reaction with complete decarbonylation of the metal center (see Scheme I). Each terminal selenide on the ligand formally bears a negative charge so the whole ligand can be formally considered $AsSe_5^{3-}$. This imparts a tetravalent charge on the metal center. It is not known why I prefers to retain two carbonyl ligands, whereas II contains a very similar coordination and electronic environment but shows no apparent desire to retain carbonyl ligands.

We have also shown that I can be converted to II by the reaction of I with red selenium (Scheme I). This can be done using I which has been first isolated and characterized but is most conveniently carried out in one pot by reacting the dianion of I with red selenium in situ. The reaction is a formal displacement of the coordinated arsenic atoms of each cage with selenium atoms. Since there are no longer any As–As bonds, the $AsSe_5^{3-}$ ligands are isoelectronic with $As_3Se_3^{3-}$. However, since the conversion also takes place with loss of the CO ligands, the electron count around the metal center is lowered from 18 to 14. Also it can be noted that the arsenic atoms show no tendency to react with excess red selenium to generate $(Se{=}AsSe_5)^{3-}$ ligand cages. This is in keeping with the well-known reluctance of arsenic to assume a pentavalent state. It would appear that II is the most stable molecule in these systems as we have previously isolated and characterized IIb independently from the reaction of $MoSe_4^{2-}$ and As_4Se_4.[7b]

Scheme II



In general the reactions appear to proceed similarly for molybdenum and tungsten. However the tungsten compounds seem more stable and can be isolated easier and in generally higher yield than the corresponding molybdenum analogues.

Spectroscopy. These compounds have been characterized by several spectroscopic methods. Infrared spectroscopy of I confirms the existence of the two coordinated carbonyl ligands with two peaks in the expected C–O stretching region. We have also found that far-IR spectroscopy is an extremely useful tool for identification of these cluster species. The heavy elements display very distinctive bands in this region, which are presumably due primarily to heavy element stretches (Figure 3). While it is difficult to assign specific bands to particular modes, the well-resolved bands lead to definitive fingerprint patterns.

We have also obtained ^{77}Se NMR spectra of the tungsten species Ia and IIa (see Figure 4). These are in agreement with the structures observed in the solid state. The ^{77}Se NMR spectrum of Ia contains two resonances in a 2:1 ratio as expected. This is consistent with the idealized C_{2v} symmetry of the molecule, which would render Se(2), Se(3), Se(5), and Se(6) equivalent. The chemical shifts are at somewhat higher fields than commonly observed for binary tungsten selenides.[24] However the selenide coordinated to the metal center is downfield relative to the cage selenide, which is consistent with results for binary metal selenides.

The ^{77}Se NMR spectrum of IIa is also consistent with the observed solid-state structure in that five resonances of equal intensity are observed. This would be expected if both cages are equivalent, but all selenium atoms in each cage are unique. Again the shifts are somewhat more downfield than in typical binary tungsten selenides. We have been unable to get clean, reasonable spectra for the molybdenum compounds despite several attempts. They do not appear to be visibly decomposing in solution, and we do not have an obvious explanation for our inability to obtain satisfactory spectra for the molybdenum compounds.

Discussion

This paper reports our first examples of the successful extension of the oxidative decarbonylation reaction to polynuclear main group anions containing group 15 anions. Previously we have

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[24] Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747.

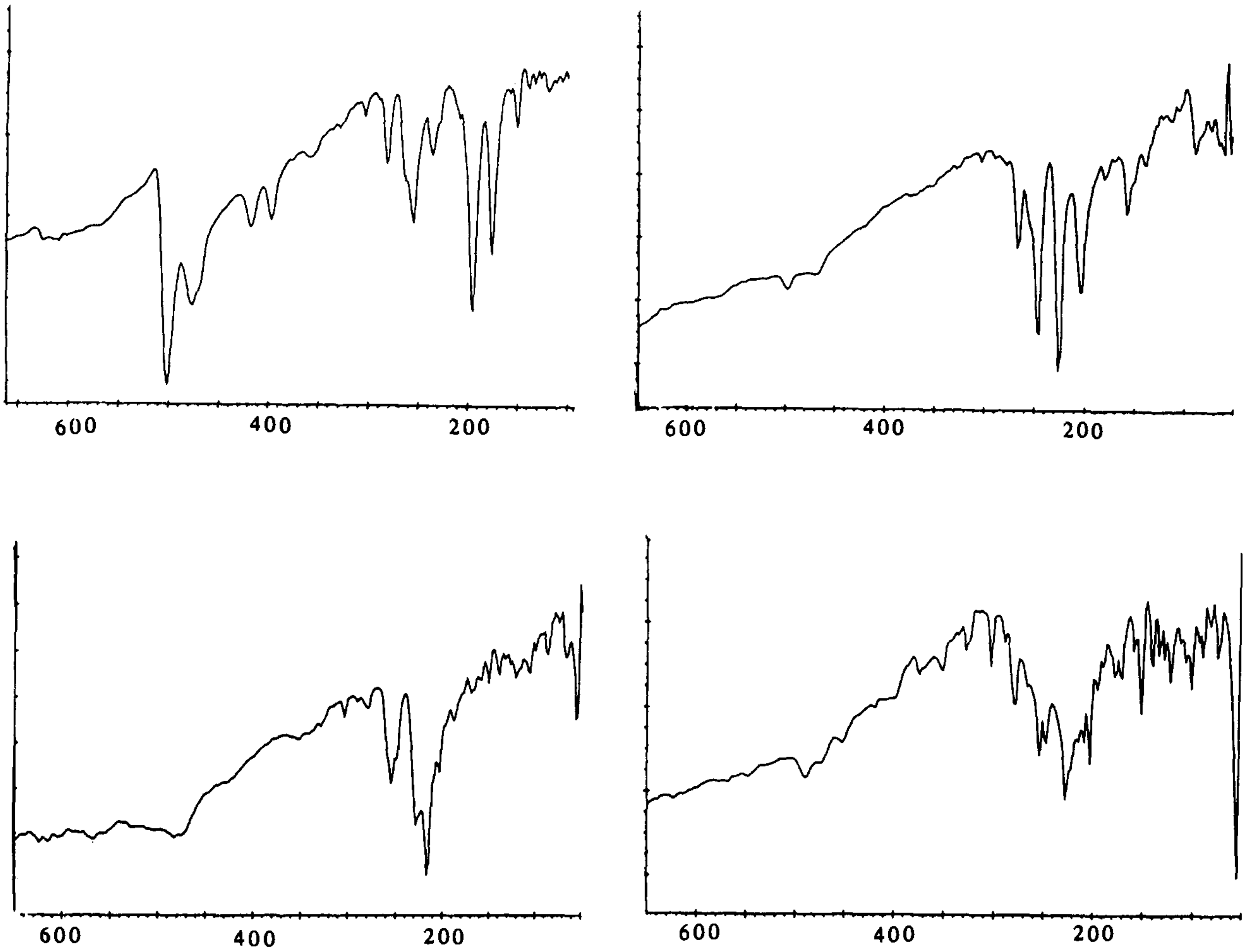
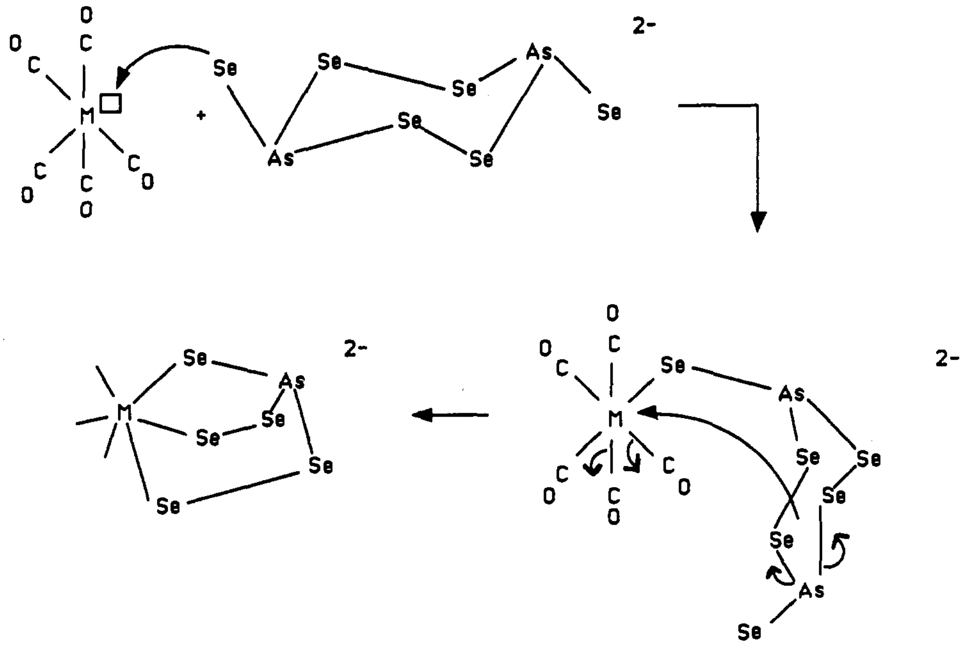


Figure 3. Far-IR spectra of metal arsenic selenide clusters (bands near 500 cm^{-1} are due to counterion): (a) $[W(CO)_2(As_3Se_3)_2]^{2-}$ in Ia (top left); (b) $[Mo(CO)_2(As_3Se_3)_2]^{2-}$ in Ib (top right); (c) $[W(AsSe_5)_2]^{2-}$ in IIa (bottom left); (d) $[Mo(AsSe_5)_2]^{2-}$ in IIb (bottom right).

Scheme III



shown that anionic polychalcogenide chains react with low-valent metal carbonyls. They readily form metal chalcogenide complexes by coordination of the chain to the metal center followed by electron transfer from the metal center to the main group chain.[8,9] This results in oxidation of the metal center, with loss of some or all of the carbonyl ligands, and cleavage of the polychalcogenide chain. It was felt that if this reaction could be generalized to include other main group anionic clusters, it could provide a convenient entry to new transition metal–main group clusters.

Originally it was thought that a chalcogen–chalcogen linkage was necessary to induce oxidative decarbonylation. However the reaction of molybdenum and tungsten carbonyl with $As_4Se_6^{2-}$, which contains no direct Se–Se bonds, proceeds readily to generate $[M(CO)_2(As_3Se_3)_2]^{2-}$. We propose a tentative mechanism as

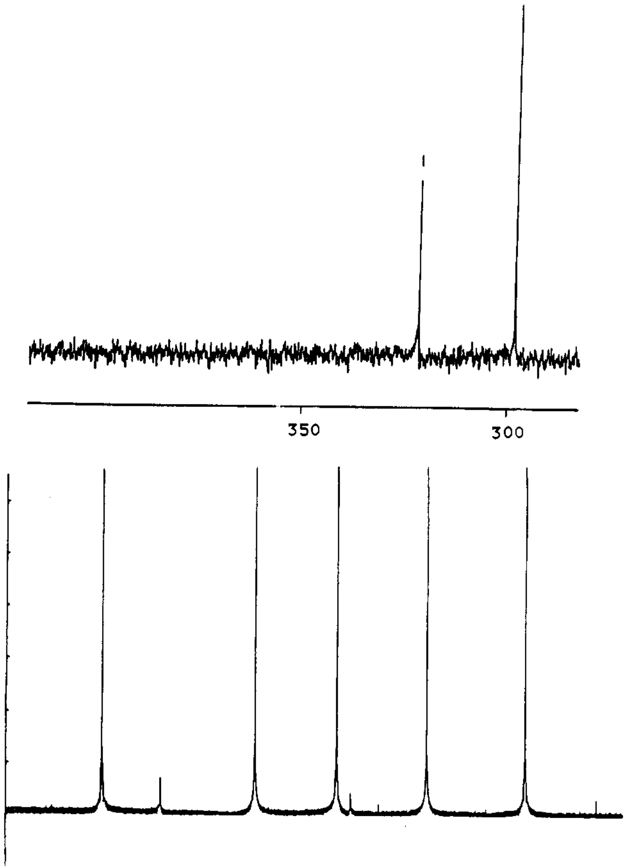


Figure 4. ^{77}Se NMR spectra of $[W(CO)_2(As_3Se_3)_2]^{2-}$ in Ia (top) and $[W(AsSe_5)_2]^{2-}$ in IIa (bottom).

shown in Scheme II. It is postulated to involve nucleophilic attack at a vacant metal coordination site by a formally anionic terminal selenide. Inversion of bridging selenium atoms move the arsenic atoms near the metal center, and oxidative addition with breakage of As–Se bonds generates the cage ligand, which contains stable five-membered (M–Se–As–Se–As) rings. We acknowledge that this mechanism is highly speculative, but it does have the advantage of retaining the correct atomic connectivity.

If each cage fragment in I is formally considered as $As_3Se_3^{3-}$, then the oxidation of the metal center is M^{4+}. Since each cage functions as a six-electron donor, the presence of the two CO ligands completes the 18-electron count around the metal. Alternatively each cage can be assigned a −1 charge locallized on the terminal selenide, in which case the metal center is formally zerovalent. In this case each cage contains a diarsine which acts as a two-electron π-donor to the metal center.[22] This would also complete the 18-electron count around the metal and is in line with the observed bond distances (vide supra). The IR stretching frequencies of the coordinated CO ligands fall in a region indicating some negative charge buildup at the metal center. However, they are between the values expected for the two extreme cases, indicating some delocalization throughout the cluster.

A particularly simple and elegant approach to understanding structure on these types of molecules is the use of topological charge stabilization. This theory states that the most electronegative elements will migrate to the vertex with the highest negative charge density as determined by simple extended Huckel calculations.[25] In the case of the birdcage structure, the least electronegative element should appear in the base of the birdcage.[25b] Thus it is not surprising for an electron rich transition metal to occupy this vertex.

A reaction mechanism similar to that invoked for I can be used to account for the formation of II (see Scheme III). Nucleophilic attack by a terminal selenide of $As_2Se_6^{2-}$ followed by ring inversion causes the selenide atoms to migrate near the metal center. Then oxidative addition to the metal center leads to formation of the observed product which again contains two five-membered rings.

Thus we have shown that several anionic main group cages and rings can undergo rearrangement when coordinated to low-valent metal centers forming unusual cage complexes. Although the development of main group cage chemistry is not as extensive as might be expected, there is sufficient evidence to indicate that the mixed main group cages could lead to an enormous variety of new transition metal–main group clusters.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE-8802217) for support of this work. J.W.K. also acknowledges support in the form of an Alfred P. Sloan Foundation Fellowship.

Supplementary Material Available: Listings of crystallographic details, atomic coordinates, complete bond distances and angles, and anisotropic thermal parameters for Ia and IIa and thermal ellipsoid plots of the other two anionic clusters in the asymmetric unit of Ia (16 pages); listings of observed and calculated structure factors for each structure (73 pages). Ordering information is given on any current masthead page.

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(25) (a) Gimarc, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 1979. (b) Gimarc, B. M.; Joseph, P. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 506.