

breakdown to give smaller oligomer units. In fact, if water is added to an evaporated ethanol/water solution containing polymer crystals and mother liquor, the polymer crystals redissolve. Upon reevaporation, the first material to crystallize is the dimeric complex $\{[\text{Cu}(\text{bpm})(\text{H}_2\text{O})_2]_2(\text{bpm})\}(\text{ClO}_4)_4$ (3), as confirmed by X-ray crystallography.²⁵ As the mother liquor continues to evaporate, the dimeric crystals dissolve and polymer crystals reform. Presumably, this occurs because of the Cu:bpm ratio according to the following: (1) The first compound to form is the kinetically-favored, dimeric complex 3, with a Cu:bpm ratio of 2:3. (2) As this cation crystallizes (with ClO_4^-), the Cu:bpm ratio in solution increases, favoring the formation of larger oligomers. (3) As larger oligomers are formed, the thermodynamically-favored polymer (Cu:bpm ratio of 1:1) is formed by dissolution of the dimeric crystals to add to the chain length in solution. (4) Continued evaporation results in crystallization of the infinite-chain polymer complex.

Isolation of a single-crystal dimeric Cu(I) species, $\{[\text{Cu}(\text{bpm})]_2(\text{bpm})\}(\text{BPh}_4)_2$,²⁶ suggests that a mixed-valence system will be capable of forming ordered crystalline materials. Mixed-metal systems, such as Cu(II)/Fe(II), are also being investigated.

Acknowledgment. J.D.P. thanks the Office of Basic Energy Sciences, U.S. Department of Energy, for partial support of this work.

Supplementary Material Available: For 1 and 2, complete listings of atomic coordinates, distances and angles, anisotropic thermal parameters, and crystallographic data (10 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

(26) Morgan, L. W.; Pennington, W. T.; Petersen, J. D. Work in progress.

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Synthesis and Characterization of the New Mixed-Metal Cluster Complexes $[\text{Fe}_2\text{M}(\mu_3\text{-E})_2(\text{CO})_{10}]$ (M = W, E = Se, Te; M = Mo, E = S)

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Received August 15, 1991

Intense interest in transition-metal clusters continues because they represent possible conceptual bridges between homogeneous and heterogeneous catalysts and also because they represent synthetic challenges. A further challenge is represented by attempts to prepare mixed-metal clusters.

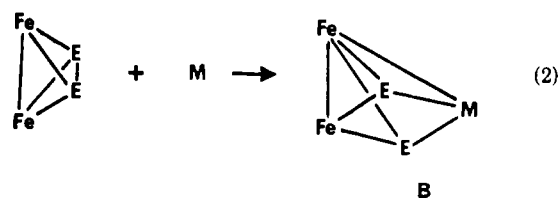
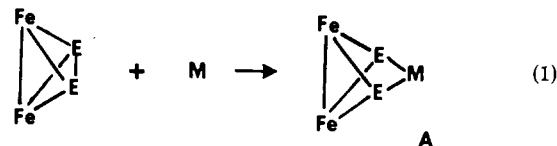
The oxidative addition of the E-E linkage of $(\mu\text{-E}_2)\text{Fe}_2(\text{CO})_6$ (E = S, Se, Te) to various low-valent, transition-metal species has yielded many mixed-metal complexes bridged by chalcogen atoms.¹ Seyferth and co-workers developed this method for the addition of various mononuclear species, such as Ni($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), Pd(PPh_3)₂, Pt(PPh_3)₂, CpCo, and Me₂Sn, across the S-S bond of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$.² Polynuclear metal carbonyl species, "Ru₃(CO)₁₁"³ and "Os₃(CO)₁₁"⁴ can also add across the Te-Te bond of $(\mu\text{-Te}_2)\text{Fe}_2(\text{CO})_6$. In general, the ag-

Table I. Crystallographic Data for $\text{Fe}_2\text{WTe}_2(\text{CO})_{10}$

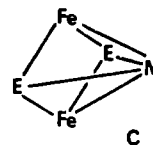
chem formula $\text{C}_{10}\text{Fe}_2\text{O}_{10}\text{Te}_2\text{W}$	fw 830.8
$a = 7.010$ (3) Å	space group $P\bar{1}$
$b = 9.591$ (2) Å	$T = 25$ °C
$c = 13.733$ (5) Å	$\lambda = 0.71073$ Å
$\alpha = 80.79$ (2)°	$\rho_{\text{calcd}} = 3.06$ g cm ⁻³
$\beta = 82.74$ (3)°	$\mu = 116.9$ cm ⁻¹
$\gamma = 84.73$ (3)°	$R(F)^a = 3.99\%$
$V = 901.7$ (6) Å ³	$R_w(F)^b = 4.39\%$
$Z = 2$	

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

glomeration of metal atoms frequently occurs in one of the two ways shown by eqs 1 and 2.



By the first route, a metal-containing group inserts into the E-E bond and no metal-metal bonds are formed. In the second route, insertion of a metal-containing group into the E-E bond is accompanied by the formation of an Fe-M bond to form a square-pyramidal $\text{Fe}_2\text{E}_2\text{M}$ core, in which the M atom occupies a basal site. Species such as B could be formed via A. For instance, $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{Fe}(\text{CO})_3\text{PPh}_3$ (structure A) readily undergoes decarbonylation to form $\text{Fe}_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-Te})_2$ (structure B).⁵ A third possibility (structure C) is the formation



of an Fe_2ME_2 square pyramid, in which M occupies the apex. Formation of C would involve insertion of M into the E-E bond, accompanied by cleavage of the Fe-Fe bond and formation of two Fe-M bonds. Examples of compounds with type C structures are far fewer than those exhibiting type A or B structures. In $(\text{C}_5\text{H}_4\text{COOMe})\text{CoFe}_2(\text{CO})_6(\mu_3\text{-S})_2$ ⁶ and $\text{Fe}_2\text{W}(\text{CO})_9(\text{PMe}_2\text{Ph})(\mu_3\text{-S})_2$,⁷ crystallographic analyses have revealed that the metal heteroatom occupies the apical site of a square pyramid. Rauchfuss has reported that $(\text{C}_5\text{H}_5)\text{RhFe}_2(\text{CO})_6(\mu_3\text{-Te})_2$ exists in two isomeric forms, one having a B-type structure and the other a C-type structure.^{1c}

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Fe}_2\text{WTe}_2(\text{CO})_{10}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
W	6058.7 (6)	2282.0 (4)	3364.1 (3)	37.8 (2)
Te(1)	4428.7 (9)	3857.8 (6)	1797.0 (5)	37.6 (2)
Te(2)	9156.1 (9)	2781.5 (6)	1963.5 (6)	41.7 (2)
Fe(1)	7180 (2)	5036 (1)	2311 (1)	38 (1)
Fe(2)	6469 (2)	1670 (1)	1346 (1)	41 (1)
O(1)	4509 (14)	7239 (10)	3088 (9)	83 (4)
O(2)	10292 (14)	5820 (12)	3305 (10)	89 (5)
O(3)	8090 (18)	6582 (11)	333 (7)	87 (4)
O(4)	7345 (18)	2811 (10)	-734 (8)	88 (5)
O(5)	8872 (16)	-1003 (9)	1386 (11)	97 (5)
O(6)	3044 (14)	264 (11)	1146 (11)	105 (6)
O(7)	2441 (16)	486 (11)	3790 (11)	103 (6)
O(8)	7814 (18)	-840 (10)	3861 (11)	100 (6)
O(9)	8805 (17)	2621 (14)	4975 (9)	99 (5)
O(10)	3347 (16)	4068 (13)	4799 (9)	94 (5)
C(1)	5500 (17)	6376 (11)	2790 (9)	49 (4)
C(2)	9091 (17)	5520 (12)	2900 (10)	56 (4)
C(3)	7788 (18)	6005 (11)	1121 (10)	54 (4)
C(4)	7019 (20)	2349 (12)	93 (10)	59 (5)
C(5)	7899 (19)	40 (11)	1406 (11)	60 (5)
C(6)	4353 (18)	803 (12)	1233 (11)	60 (5)
C(7)	3698 (19)	1143 (11)	3632 (12)	66 (5)
C(8)	7214 (20)	283 (13)	3682 (11)	64 (5)
C(9)	7855 (21)	2511 (15)	4408 (12)	71 (5)
C(10)	4283 (18)	3440 (14)	4275 (10)	61 (5)

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

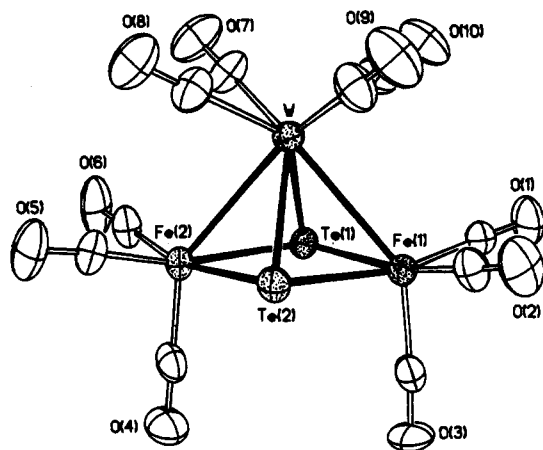
Table III. Bond Lengths (\AA)

W-Te(1)	2.736 (1)	W-Te(2)	2.736 (1)
W-Fe(1)	2.925 (1)	W-Fe(2)	2.898 (2)
W-C(7)	2.029 (13)	W-C(8)	2.015 (12)
W-C(9)	2.074 (17)	W-C(10)	2.036 (13)
Te(1)-Fe(1)	2.549 (2)	Te(1)-Fe(2)	2.545 (1)
Te(2)-Fe(1)	2.537 (1)	Te(2)-Fe(2)	2.543 (2)
Fe(1)-C(1)	1.807 (11)	Fe(1)-C(2)	1.781 (14)
Fe(1)-C(3)	1.768 (12)	Fe(2)-C(4)	1.747 (13)
Fe(2)-C(5)	1.773 (11)	Fe(2)-C(6)	1.800 (14)
O(1)-C(1)	1.126 (15)	O(2)-C(2)	1.147 (18)
O(3)-C(3)	1.138 (15)	O(4)-C(4)	1.154 (17)
O(5)-C(5)	1.160 (14)	O(6)-C(6)	1.122 (18)
O(7)-C(7)	1.109 (17)	O(8)-C(8)	1.120 (15)
O(9)-C(9)	1.109 (22)	O(10)-C(10)	1.122 (18)

Here, we report the synthesis and characterization of three new mixed-metal clusters of type C: $[\text{Fe}_2\text{W}(\mu_3\text{-Te})_2(\text{CO})_{10}]$, $[\text{Fe}_2\text{W}(\mu_3\text{-Se})_2(\text{CO})_{10}]$, and $[\text{Fe}_2\text{Mo}(\mu_3\text{-Se})_2(\text{CO})_{10}]$.

Room-temperature stirring of equimolar amounts of $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$ and $\text{W}(\text{CO})_5(\text{THF})$ in THF solvent afforded the new cluster $[\text{Fe}_2\text{W}(\mu_3\text{-Te})_2(\text{CO})_{10}]$ (**1**) in good yield. Similarly, the clusters $[\text{Fe}_2\text{W}(\mu_3\text{-Se})_2(\text{CO})_{10}]$ (**2**) (37% yield) and $[\text{Fe}_2\text{Mo}(\mu_3\text{-Se})_2(\text{CO})_{10}]$ (**3**) (31% yield) were obtained from the room-temperature reactions of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ with $\text{W}(\text{CO})_5(\text{THF})$ and $\text{Mo}(\text{CO})_5(\text{THF})$, respectively. All three compounds were characterized by infrared spectroscopy, mass spectrometry, and elemental analysis. Infrared spectra of **1-3** showed the presence of only terminally bonded carbonyl groups in identical patterns consisting of five bands. Mass spectra showed the molecular ion peaks for **1-3**, and elemental analysis confirmed their molecular formulas.

Black, air-stable, rectangular parallelepiped-shaped crystals of **1** were grown by controlled evaporation of hexane solutions at room temperature, and an X-ray analysis was undertaken. An ORTEP diagram of the molecular structure of one molecule is shown in Figure 1. Tables I-IV give crystal data summary, fractional atomic coordinates, selected bond lengths, and bond angles for **1**, respectively. The metal core geometry can best be described as a Fe_2WTe_2 square pyramid in which the W atom is located at the apical site. There are four carbonyl groups associated with the W atom, while the two iron atoms have three carbonyl groups each. The equal W-Te(1) and W-Te(2) distances of 2.736 (1) \AA show that the W atom lies on the perpendicular bisector of the

**Figure 1.** ORTEP drawing of $\text{Fe}_2\text{W}(\mu_3\text{-Te})_2(\text{CO})_{10}$, illustrating the atom-numbering scheme.**Table IV.** Bond Angles (deg)

Te(1)-W-Te(2)	76.9 (1)	Te(1)-W-Fe(1)	53.4 (1)
Te(2)-W-Fe(1)	53.1 (1)	Te(1)-W-Fe(2)	53.6 (1)
Te(2)-W-Fe(2)	53.6 (1)	Fe(1)-W-Fe(2)	80.9 (1)
Te(1)-W-C(7)	88.0 (4)	Te(2)-W-C(7)	139.9 (5)
Fe(1)-W-C(7)	138.6 (4)	Fe(2)-W-C(7)	87.6 (5)
Te(1)-W-C(8)	136.0 (5)	Te(2)-W-C(8)	87.9 (4)
Fe(1)-W-C(8)	139.4 (4)	Fe(2)-W-C(8)	84.1 (5)
C(7)-W-C(8)	77.5 (5)	Te(1)-W-C(9)	139.6 (4)
Te(2)-W-C(9)	86.9 (4)	Fe(1)-W-C(9)	87.3 (4)
Fe(2)-W-C(9)	137.4 (4)	C(7)-W-C(9)	125.4 (6)
C(8)-W-C(9)	78.8 (6)	Te(1)-W-C(10)	88.0 (4)
Te(2)-W-C(10)	136.1 (4)	Fe(1)-W-C(10)	84.7 (4)
Fe(2)-W-C(10)	139.8 (4)	C(7)-W-C(10)	79.0 (5)
C(8)-W-C(10)	128.2 (6)	C(9)-W-C(10)	78.4 (6)
W-Te(1)-Fe(1)	67.1 (1)	W-Te(1)-Fe(2)	66.5 (1)
Fe(1)-Te(1)-Fe(2)	95.7 (1)	W-Te(2)-Fe(1)	67.3 (1)
W-Te(2)-Fe(2)	66.5 (1)	Fe(1)-Te(2)-Fe(2)	96.1 (1)
W-Fe(1)-Te(1)	59.5 (1)	W-Fe(1)-Te(2)	59.6 (1)
Te(1)-Fe(1)-Te(2)	84.0 (1)	W-Fe(1)-C(1)	107.5 (3)
Te(1)-Fe(1)-C(1)	90.9 (4)	Te(2)-Fe(1)-C(1)	166.9 (3)
W-Fe(1)-C(2)	107.2 (4)	Te(1)-Fe(1)-C(2)	166.6 (4)
Te(2)-Fe(1)-C(2)	89.9 (4)	C(1)-Fe(1)-C(2)	92.4 (6)
W-Fe(1)-C(3)	143.9 (4)	Te(1)-Fe(1)-C(3)	94.8 (5)
Te(2)-Fe(1)-C(3)	95.4 (4)	C(1)-Fe(1)-C(3)	97.1 (5)
C(2)-Fe(1)-C(3)	97.7 (6)	W-Fe(2)-Te(1)	59.9 (1)
W-Fe(2)-Te(2)	60.0 (1)	Te(1)-Fe(2)-Te(2)	84.0 (1)
W-Fe(2)-C(4)	145.4 (4)	Te(1)-Fe(2)-C(4)	95.6 (4)
Te(2)-Fe(2)-C(4)	96.0 (5)	W-Fe(2)-C(5)	103.7 (5)
Te(1)-Fe(2)-C(5)	163.5 (5)	Te(2)-Fe(2)-C(5)	89.4 (5)
C(4)-Fe(2)-C(5)	100.1 (6)	W-Fe(2)-C(6)	106.1 (5)
Te(1)-Fe(2)-C(6)	91.5 (4)	Te(2)-Fe(2)-C(6)	165.7 (5)
C(4)-Fe(2)-C(6)	97.9 (7)	C(5)-Fe(2)-C(6)	91.3 (6)
Fe(1)-C(1)-O(1)	177.5 (12)	Fe(1)-C(2)-O(2)	178.0 (12)
Fe(1)-C(3)-O(3)	175.4 (13)	Fe(2)-C(4)-O(4)	178.6 (11)
Fe(2)-C(5)-O(5)	175.9 (13)	Fe(2)-C(6)-O(6)	178.9 (14)
W-C(7)-O(7)	177.9 (12)	W-C(8)-O(8)	178.4 (14)
W-C(9)-O(9)	179.1 (10)	W-C(10)-O(10)	177.7 (13)

Fe(1)-Fe(2) segment. The average W-Fe distance (2.912 \AA) in **1** is longer than the average W-Fe distance (2.748 \AA) found in $\text{WFe}_2(\text{CO})_9(\text{PMe}_2\text{Ph})(\mu_3\text{-S})_2$, which has a metal-core geometry similar to that of **1**. The longer W-Fe bonds in compound **1** than in $\text{WFe}_2(\text{CO})_9(\text{PMe}_2\text{Ph})(\mu_3\text{-S})_2$ may be due to the larger size of the bridging tellurium ligands. Alternatively, the shorter average W-Fe bond distance in $\text{WFe}_2(\text{CO})_9(\text{PMe}_2\text{Ph})(\mu_3\text{-S})_2$ could be due to the presence of a phosphine group on the W atom. Substitution of phosphine ligands, which are not as effective as CO ligands in withdrawing electron density from metal atoms, should favor stronger metal-metal interaction.

Overall, **1** could be thought of formally as a metal-metal-exchange product of $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$, with one of the apical Fe(CO)₃ units being replaced by an isoelectronic W(CO)₄ fragment. However, we did not observe the formation of **1** when $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ and $\text{W}(\text{CO})_6$ solutions were photolyzed or thermolyzed. Both the tellurium ligands adopt the μ_3 bridging mode in **1** and

thereby function as four-electron donors to the cluster. In terms of electron-counting rules, **1** is a 50-electron cluster, and thus it adopts a nido-octahedral geometry, as predicted by the skeletal electron pair theory. To our knowledge, cluster **1** represents the first example of an iron-tungsten, mixed-metal cluster triply capped by two tellurium functionalities.

Although the mechanistic features have not been established, formation of **1-3** may occur by addition of $M(\text{CO})_5$ ($M = \text{Mo}, \text{W}$) across the E-E bond of $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ ($E = \text{Se}, \text{Te}$), followed by loss of one carbonyl group, cleavage of the Fe-Fe bond, and formation of two Fe-M bonds. Further studies are underway to explore the utility of **1-3** as synthons in mixed-metal cluster preparations.

Experimental Section

All reactions were performed under an atmosphere of pure argon by using standard Schlenk techniques. Solvents were purified, dried, and distilled under argon or nitrogen atmosphere prior to use. The compounds $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$ ⁸ and $M(\text{CO})_5(\text{THF})$ ⁹ ($M = \text{Mo}, \text{W}$) were prepared by established procedures. Since $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$ and $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ decompose in the solid state, freshly prepared solutions of these compounds were used. It is assumed that $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ ($E = \text{Te}, \text{Se}$) are formed in approximately 40% yield. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer as solutions in NaCl cells. Mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer at 70 eV for compounds **1** and **2** and 20 eV for compound **3**. Elemental analyses were performed on a Carlo-Erba automatic analyzer. Photochemical reactions were carried out in a water-cooled double-walled quartz vessel. A 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. was used.

Preparation of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$. Solid $\text{Fe}_3(\text{CO})_9(\mu_3\text{-Se})_2$ (1.75 g, 3 mmol) was added to a solution of NaOMe (prepared by adding 0.63 g of Na, 11.6 mmol in 300 mL of MeOH), and the mixture was stirred for 12 h. The solution was diluted with hexane (200 mL) and water (200 mL) and acidified with 6 M HCl. After separation of the aqueous layer from the organic layer, the aqueous layer was further extracted with hexane (100 mL) and the combined organic extracts were washed with water (100 mL) and dried over anhydrous MgSO_4 . The organic solution was concentrated to 10 mL and chromatographed on a silica gel column, using hexane as eluant. A single purple band of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ was obtained. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2078 (s), 2038 (s), 2002 (m).

Preparation of $[\text{Fe}_2M(\mu_3\text{-E})_2(\text{CO})_{10}]$ ($M = \text{W}, E = \text{Se}, \text{Te}; M = \text{Mo}, E = \text{Se}$). In a typical experiment, $M(\text{CO})_5(\text{THF})$ ($M = \text{Mo}, \text{W}$) (0.1 mmol) in THF solvent (100 mL) was added to a THF solution containing $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ ($E = \text{Se}, \text{Te}$) (0.1 mmol), and the reaction mixture was allowed to stir at room temperature for 3 h. The solvent was removed in vacuo, and the residue was subjected to a chromatographic workup using a silica gel column. Elution with hexane afforded a violet band, identified as $\text{Fe}_2M(\text{CO})_{10}(\mu_3\text{-E})_2$ (**1**, $M = \text{W}, E = \text{Te}$; **2**, $M = \text{W}, E = \text{Se}$; **3**, $M = \text{Mo}, E = \text{Se}$).

1. Yield: 0.062 g, 75%. Mp: 156–158 °C dec. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2081 (w), 2044 (vs), 2034 (s), 2002 (s, br), 1964 (w). Mass: m/e 828 [M^+]. Anal. Calcd for $\text{C}_{10}\text{Fe}_2\text{O}_{10}\text{Te}_2\text{W}$: C, 14.45. Found: C, 14.52.

2. Yield: 0.027 g, 37%. Mp: 142–145 °C dec. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2087 (w), 2053 (vs), 2044 (vs), 2010 (s), 1969 (w). Mass: m/e 734 [M^+]. Anal. Calcd for $\text{C}_{10}\text{Fe}_2\text{O}_{10}\text{Se}_2\text{W}$: C, 16.35. Found: 15.91.

3. Yield: 0.020 g, 31%. Mp: 130 °C dec. IR (hexane; $\nu(\text{CO}), \text{cm}^{-1}$): 2090 (w), 2055 (vs), 2041 (vs), 2012 (s), 1972 (w). Mass: m/e 646 [M^+]. Anal. Calcd for $\text{C}_{10}\text{Fe}_2\text{MoO}_{10}\text{Se}_2$: C, 18.57. Found: 19.00.

X-ray Crystal Structure Determination of **1.** Crystal data are collected in Table I. The centrosymmetric triclinic space group was assigned from photographic evidence and was confirmed by the chemically rational results of refinement. ψ -scan data showed serious edge-effect aberrations for reflections with low glancing angles to the major face. Those making angles of $\leq 3^\circ$ were discarded; 242 data were eliminated. The remaining data were corrected for absorption using a laminar model, instead of the usual ellipsoidal form.

The structure was solved by direct methods. All atoms were anisotropically refined. All computations used SHELXTL (5.1) software (G. M. Sheldrick, Nicolet (Siemens), Madison, WI).

Acknowledgment. We are thankful to Dr. V. Manohar and Dr. K. Nagarajan, Searle Ltd., for providing us the mass spectral facility and to Dr. S. Bhaduri, Alchemie Research Centre, for

making available to us the elemental analyses. M.M.H. is grateful to the CSIR (New Delhi) for a research associateship, and R.S.R. thanks the Indo-Iraq Cultural Exchange Programme for the award of a research scholarship.

Registry No. **1**, 138606-17-4; **2**, 138606-18-5; **3**, 138606-19-6; $\text{Fe}_2(\text{CO})_6(\mu\text{-Te}_2)$, 76185-27-8; $\text{W}(\text{CO})_5(\text{THF})$, 36477-75-5; $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$, 76185-26-7; $\text{Mo}(\text{CO})_5(\text{THF})$, 53248-43-4; Fe, 7439-89-6; W, 7440-33-7; Mo, 7439-98-7.

Supplementary Material Available: Tables of crystallographic data (Table S1) and anisotropic displacement parameters (Table S2) (2 pages); a listing of structure factor amplitudes (Table S3) (8 pages). Ordering information is given on any current masthead page.

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A High-Yield One-Step Synthesis of *trans*-[Cr([14]aneN₄)Cl₂]Cl and Its Conversion to *trans*-[Cr([14]aneN₄)(H₂O)₂](CF₃SO₃)₃

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Received August 9, 1991

Introduction

Acid-stable macrocyclic complexes of chromium(II) are rare.^{1,2} The *trans*-Cr([14]aneN₄)(H₂O)₂²⁺ complex ([14]aneN₄ = 1,4,8,11-tetraazacyclotetradecane, hereafter L) is exceptional in this respect.¹ However, the synthetic routes to its immediate precursor, *trans*-CrL(H₂O)₂³⁺, that were available until now are laborious,³⁻⁵ and the isolation of the solid perchlorate salt is outright dangerous.

Here we report a simple, one-step synthesis of *trans*-[CrLCl₂]Cl and its safe and easy conversion to *trans*-[CrL(H₂O)₂](CF₃SO₃)₃.

Experimental Section

[14]aneN₄ (Lancaster), CrCl₃·6H₂O (Baker), dmf (Fisher), and 2,2-dimethoxypropane (Aldrich) were used without purification.

Preparation of *trans*-[CrLCl₂]Cl. A hot (nearly boiling) solution of 2.5 g (12.5 mmol) of L in dmf was added to a solution of 3 g (11.3 mmol) of CrCl₃·6H₂O in 50 mL of dmf and 10 mL of CHC(OCH₃)₂CH₃ at 100 °C. The mixture was stirred and boiled for 30 min, during which time the bluish-gray solid precipitated. After the mixture was cooled to room temperature, the product was filtered out, washed with acetone, and air-dried. Yield: 3.6 g (90%). Cr analysis: 14.3% (calcd 14.5%).

cis-[CrLCl₂]Cl was prepared in the same way, except that CrCl₃·6H₂O (3 g, 11.3 mmol) was used in excess over L (2 g, 10 mmol). Yield: 3.2 g (90%).

Preparation of *trans*-CrL(H₂O)₂³⁺. A deaerated suspension of 1 g of *trans*-[CrLCl₂]Cl in 50 mL of 0.15 M CF₃SO₃H was placed on Zn/Hg under argon. Within several seconds, the gray suspension turned into a dark-pink solution of *trans*-CrL(H₂O)₂³⁺. In another 5–10 min, the color changed to a cherry red (*trans*-CrL(H₂O)₂²⁺). The solution was transferred into a beaker and bubbled with a stream of O₂ for a few minutes. This was followed by ion exchange on SP-Sephadex C-25. The small amounts of dichloro and monochloro complexes were eluted with 0.1 and 0.2 M CF₃SO₃H, respectively, and the major peachy-orange band of *trans*-CrL(H₂O)₂³⁺ was eluted with 1 M CF₃SO₃H. Slow evaporation in a hood over several days yielded large red crystals of *trans*-[CrL(H₂O)₂](CF₃SO₃)₃. After filtration and recrystallization from H₂O/CF₃SO₃H, the solid was dried under vacuum. Yield: 0.70 g (34%). Cr analysis: 7.07% (calcd 7.07%).

The monochloro and dichloro complexes that had been eluted first were combined and used as a starting material in subsequent preparations.

Preparation of *trans*-[CrLCl₂]Cl from *cis*-[CrLCl₂]Cl. To a suspension of 1 g of *cis*-[CrLCl₂]Cl in boiling dmf were added 5 mL of CH₃(OC-

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