The molecular structure and numbering scheme for the title compound are shown in Figure 1. The molecular geometry involves two-coordinate[1,9] Cu atoms in discrete $CuBrP(mes)_3$ molecules. Complexes of the general formula $L_m(CuX)_n$ between tertiary phosphines (and arsines and other monodentate ligands) have been extensively studied and display a variety of stoichiometries and structures.[1,2,9] As mentioned, with the exception of dimeric $[CuClPCy_3]_2$,[5] the 1:1 complexes have tetrameric "cubane" or "chair" Cu_4X_4 cores. All monomeric species previously characterized by X-ray analyses involve three- and four-coordinated Cu(I) centers;[1,9] these include $CuCl(PPh_3)_3$, $CuCl(AsMe_2Ph)_2$, and several species not containing phosphine and arsine ligands.[10] The related compound $(Ph_3P)Cu(\eta^5\text{-}C_5H_5)$[11] is not strictly comparable as it does not contain a halide ion. Other species presented as monomeric, such as $CuX(SPPh_3)$,[12] are more likely ligand- or halide-bridged polymers.[1,9,10] There is evidence that various phosphine–copper(I) halide complexes dissociate in solution to products that include monomeric species, but no firm structural data are available.[13-15] The structure of $CuBrP(mes)_3$ is therefore noteworthy for several reasons: (i) it is the first[1,9] two-coordinate phosphine copper(I) halide complex: (ii) it confirms the expectation[1-3,5] that tetrameric M_4X_4 clusters will fragment into MX units if the associated ligand is sufficiently large; (iii) it demonstrates dramatically the steric effect for the largest known phosphine ligand, $P(mes)_3$.[7]

Each copper(I) atom is diagonally coordinated by a $P(mes)_3$ ligand (Cu–P = 2.193 (2) Å) and a terminal Br atom Cu–Br = 2.225 (1) Å). The Cu–P bond length is comparable to that reported in $[CuClPCy_3]_2$ (2.183 (2) Å)[5] and several 1:1 tetrameric complexes[16-18] while the Cu–Br bond distance appears to be very significantly shortened by comparison,[16-18] a result that is in keeping with the lower coordination number. The angles at the Cu and P atoms are Br–Cu–P = 173.7 (1)°, Cu–P–C(11) = 103.8 (2)°, Cu–P–C(21) = 108.0 (2)°, and Cu–P–C(31) = 111.7 (2)°. The Cu–P–C angles are markedly irregular as compared to M–P–C angles in other $P(mes)_3$ complexes,[7] indicative of steric interactions not observed in the earlier structures. We attribute the nonlinearity of the Br–Cu–P angle, and the irregularity of the Cu–P–C angles, to the repulsive interaction between mesityl rings of adjacent molecules. The benzene of solvation lies in a cavity between two almost parallel Cu–Br bonds related by a twofold axis with only van der Waals contacts between benzene carbons and Cu or Br (see the legend of Figure 1 for details).

Other bond distances in the $CuBrP(mes)_3$ molecule are in close agreement with those reported for other $P(mes)_3$ complexes[7] and in free $P(mes)_3$.[19] The P–C bond lengths are approximately equivalent, averaging 1.847 (6) Å. The C–C distances within the mesitylene rings average 1.395 (9) Å while the ring to methyl C–C distances are 1.512 (9) Å on average. The large C–P–C angles, averaging to 111.3 (3)°, reflect the much greater bulkiness of $P(mes)_3$ as compared to that of other phosphines (e.g. average C–P–C angles are 103° in PPh_3 complexes).[6] Detailed analyses of intramolecular and intermolecular interactions and calculation of θ and a "ligand profile"[4] of the $P(mes)_3$ ligand are under way.

Our preliminary attempts to characterize the title complex in solution have focused on NMR studies. The ^1H NMR spectrum shows the expected downfield shifts for methyl resonances and an increased $^4J(^{31}P-^1H)$ coupling constant (4 Hz) for the meta protons of the mesitylene rings. The main feature of the $^{13}C\{^1H\}$ NMR spectrum of $CuBrP(mes)_3$ is the lack of observable $^{31}P-^{13}C$ coupling and the 9 ppm downfield shift of the *ipso* carbon atoms (C(11), C(21), and C(31)) as compared to the position in free phosphine. The single resonance at −28.6 ppm (with respect to 85% H_3PO_4) in the $^{31}P\{^1H\}$ NMR spectrum of a $CDCl_3$ solution of $CuBrP(mes)_3$ at ambient temperature corresponds to a coordination chemical shift[20] of +7.2 ppm for $P(mes)_3$. In contrast, a coordination chemical shift of −15.9 ppm[21] was found for $P\text{-}t\text{-}Bu_3$ in the 1:1 $CuBrP\text{-}t\text{-}Bu_3$ complex (reported as dimeric in dichloroethane solution).[6] The $^{31}P\{^1H\}$ NMR spectrum of the green decomposition product obtained by exposure of $CuBrP(mes)_3$ to air for an extended period shows resonances due to uncomplexed $P(mes)_3$ and $OP(mes)_3$ only; an oxide cluster as proved[22] for the analogous PEt_3 tetramer is apparently not formed. Other NMR results and solution characterization measurements will be reported together with our continuing studies on analogous $CuXP(mes)_3$ complexes.

Acknowledgment. We thank NSERC of Canada for operating grants (to E.C.A. and G.F.) and Imperial Oil of Canada for a University Research Grant (to E.C.A. and J.M.).

Registry No. $[CuBrP(mes)_3]\cdot{}^1/_2C_6H_6$, 97920-99-5.

Supplementary Material Available: Listings of atom coordinates, temperature factors, bond distances and angles, and structure factors for the title compound (23 pages). Ordering information is given on any current masthead page.

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Received January 24, 1985

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(9) Examples of two-coordinate copper(I) are limited: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980; p 798. A recent report confirms two-coordination in $[(CuNEt_2)_4]$: Hope, H.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 936. Other examples are as follows. $[Cu(mes)_2]^-$: Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240. $[Cu(SC_{10}H_{13})_2]^-$: Koch, S. A.; Fikar, R.; Millar, M.; O'Sullivan, T. *Inorg. Chem.* **1984**, *23*, 122. $[Cu(C(SiMe_3)_3)_2]^-$: Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *264*, C23. $[Cu(2,6\text{-}Me_2C_6H_3O)_2]^-$: Fiaschi, P.; Floriani, C.; Pasquali, M.; Chiesi-Villa, A.; Grastini, C. *J. Chem. Soc., Chem. Commun.* **1984**, 888.

(10) Ellen, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.

(11) Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1970**, *92*, 2353.

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(13) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, 92, 4114.

(14) Lippard, S. J.; Mayerle, J. *Inorg. Chem.* **1972**, *11*, 753.

(15) Fife, D. J.; Moore, W. M.; Morse, K. W. *Inorg. Chem.* **1984**, *23*, 1684.

(16) Some comparative Cu–P and Cu–Br bond lengths are as follows: $[CuBrPEt_3]_4$, Cu–P = 2.1994 (22) Å, Cu–Br = 2.5436 (8) Å;[17] $[CuBrPPh_3]_4$, Cu–P = 2.201 (35) Å, Cu–Br = 2.495 (20) Å;[18] $[CuBrP(t\text{-}Bu)_3]_4$, Cu–P = 2.228 (4) Å, Cu–Br = 2.593 (2) Å.[6]

(17) Churchill, M. R.; DeBoer, B. G.; Mendak, D. J. *Inorg. Chem.* **1975**, *14*, 2041.

(18) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1427.

(19) Blount, J. F.; Maryanoff, C. A.; Mislow, K. *Tetrahedron Lett.* **1975**, *11*, 913.

(20) Coordination chemical shift is defined as δ(complex) − δ(free phosphine); negative values corresponding to upfield shifts are known for some Zn, Cd, and Cu complexes.[6]

(21) The chemical shift reported for free $P\text{-}t\text{-}Bu_3$ in ref 6 is corrected to +60.7 ppm, as reported in ref 1c.

(22) Churchill, M. R.; DeBoer, B. G.; Mendak, S. J. *Inorg. Chem.* **1975**, *14*, 2496.

$(RC_5H_4)MoFe(Te_2X)(CO)_5$: Carbonyl Clusters Containing Hypervalent Main-Group Centers

Sir:

The associative binding of a Lewis base to a polynuclear metal carbonyl generally induces a change in the net metal–metal bond order of the cluster.[1] This pattern has been codified in various valence electron counting schemes.[2] In this report we describe

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(1) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. For recent examples see: Schneider, J.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1982**, *115*, 989. Bogan, L. E., Jr.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429. Adams, R. D.; Horvath, I. T.; Mathur, P. *J. Am. Chem. Soc.* **1984**, *106*, 6296.

(2) See: Mingos, D. M. P. *Inorg. Chem.* **1985**, *24*, 114. Teo, B.-K. *Inorg. Chem.* **1985**, *24*, 115 and references therein.

0020-1669/85/1324-3720$01.50/0

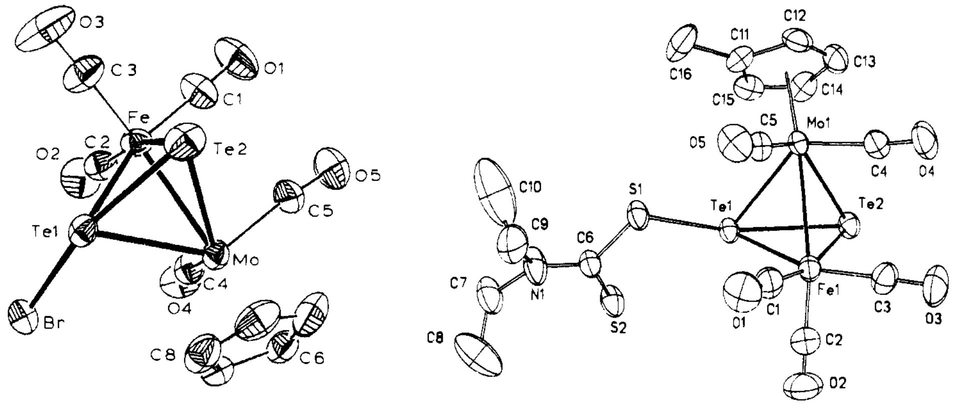


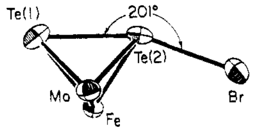
Figure 1. ORTEP drawing of the $(C_5H_5)MoFe(Te_2Br)(CO)_5$ and $(CH_3C_5H_4)MoFe(Te_2SC(S)NEt_2)(CO)_5$ molecules.

a violation of these rules in the form of a metal telluride cluster that binds simple Lewis bases at the main-group center. Structural studies on the adducts indicate hypervalent bonding involving a 4-coordinate, 10-electron Te center. An additional point of interest is our isolation of a stable complex of Te_2.

Bromination of the green $(RC_5H_4)_2Mo_2FeTe_2(CO)_7$[3] (R = H, Me, *i*-Pr) ($-78 \rightarrow +25$ °C, 3 h, CH_2Cl_2 solution, chromatographic workup) gives red $(RC_5H_4)Mo(CO)_3Br$ and a new compound of the formula $(RC_5H_4)MoFeTe_2Br(CO)_5$ (**1**·Br). The yields are optimal (75%)[4] when the reaction is conducted under an atmosphere of carbon monoxide (eq 1). The solid-state structure of

$$(RC_5H_4)_2Mo_2FeTe_2(CO)_7 + Br_2 + CO \rightarrow (RC_5H_4)MoFeTe_2Br(CO)_5 + (RC_5H_4)Mo(CO)_3Br \quad (1)$$

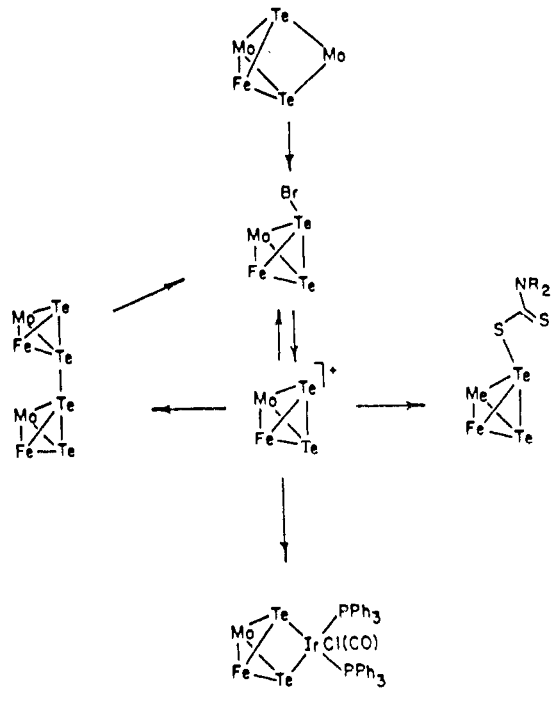
1·Br[5] consists of a tetrahedral $MoFeTe_2$ core with a bromine atom attached to one tellurium atom (Figure 1). The striking feature of this structure is the Te–Te–Br angle of 201°



which indicates the presence of a stereochemically active lone pair at the four-coordinate tellurium center. The coordination geometry of Te(1) closely resembles that found for telluranes (10-Te-4 species).[6] The Te···Te bond length of 2.807 (1) Å is very close to the 2.81 Å distance found in elemental tellurium.[7]

The ^1H NMR spectrum of **1**·Br (R = *i*-Pr) is temperature dependent: while the $i\text{-}PrC_5H_4$ ligand lies on a time-averaged symmetry plane at higher temperatures, the molecule is configurationally stable on the NMR timescale below -68 °C (toluene-d_8 solution, 200 MHz). A process that would explain this dynamic behavior involves bromide exchange via the intermediacy of $[(RC_5H_4)MoFe(Te_2)(CO)_5]^+$, $[\mathbf{1}]^+$. The latter can be prepared in near-quantitative yield from the reaction of **1**·Br and $AgSbF_6$.[8] Whereas solutions of **1**·Br are only feebly conducting, $[\mathbf{1}]SbF_6$ behaves as a 1:1 electrolyte in acetone solution. The spectroscopic properties of $[\mathbf{1}]SbF_6$ are slightly shifted from those of **1**·Br. The ^{125}Te NMR spectrum of the cation consists of a single resonance at 839 ppm upfield of neat Me_2Te, comparable to the resonance position for the unstable tetrahedrane $Fe_2(Te_2)(CO)_6$ (−733 ppm)[9] but quite different from that for $(MeC_5H_4)_2Mo_2FeTe_2(CO)_7$ (+1100 ppm).[3] $[\mathbf{1}]SbF_6$ can also be prepared in low yield by the treatment of solutions of $(C_5H_5)_2Mo_2FeTe_2(CO)_7$ with oxygen in the presence of $NaSbF_6$. Sodium borohydride reduction of $[\mathbf{1}]SbF_6$ gives a diamagnetic blue species analyzing as $[\mathbf{1}]_n$,[10] which

Scheme I



(Mo = $(RC_5H_4)Mo(CO)_2$, Fe = $Fe(CO)_3$)

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(3) Bogan, L. E., Jr.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 3843.

(4) For $(C_5H_5)MoFe(Te_2Br)(CO)_5$: Anal. Found: C, 17.57; H, 0.68; Br, 11.07; Te, 35.6; Fe, 9.30. Calcd: C, 17.36; H, 0.73; Br, 11.55; Te, 36.9; Fe, 8.07. Note that the mass spectrum of **1**·Br shows a strong peak corresponding to **1**·Br_2^+. FDMS: *m/e* 775 (M^+ + Br), 695 (M^+), 615 (M^+ − Br). IR (CH_2Cl_2): 2055 s, 2016 m, 2006 m, 1964 vw cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.41 s. Solution conductivity (acetone): $\Lambda = 2.75 \times 10^{-1}\ \Omega^{-1}$. For $(i\text{-}PrC_5H_4)MoFe(Te_2Br)(CO)_5$: IR ($CH_2Cl_2$): 2064 s, 2012 m, 2005 m, 1958 w cm^{-1}. ^1H NMR (toluene-d_8, −38 °C): δ 4.23 m (2 H), 4.07 m (2 H), 1.99 m (1 H), 0.65 d (6 H); −88 °C: δ 4.21 m (2 H), 3.88 m (1 H), 3.67 m (1 H), 1.75 m (1 H), 0.64 d (6 H).

(5) For $(C_5H_5)MoFe(Te_2Br)(CO)_5$: triclinic, $P\bar{1}$; $a = 8.614$ (6), $b = 14.641$ (10), $c = 7.181$ (7) Å; $\alpha = 91.92$ (7), $\beta = 111.69$ (6), $\gamma = 99.34$ (6)°; $V = 826$ Å^3; $Z = 2$; D(calcd) = 2.782 g cm^{-3}; $\mu = 39.3$ cm^{-1} (Mo Kα). Of 4253 absorption-corrected reflections collected (Syntex P2$_1$ diffractometer, $3° < 2\theta < 55°$), 3216 ($F_o \geq 3\sigma(F_o)$) unique reflections were used in the solution and refinement of the structure. All non-hydrogen atoms were refined anisotropically. At convergence $R_F = 0.0576$ and $R_{wF} = 0.0598$. Selected distances (Å) and angles (deg): Te–Te, 2.807 (1); Mo–Te(1), 2.717 (1); Mo–Te(2), 2.776 (1); Fe–Te(1), 2.510 (1); Fe–Te(2), 2.573 (1); Mo–Fe, 2.876; Te–Te–Br, 158.9 (0); Te(2)–Te(1)–Mo, 60.3 (0); Te(2)–Te(1)–Fe, 57.6 (0).

(6) Cristofferson, G. D.; Sparks, R. A.; McCullough. *Acta Crystallogr.* **1958**, *11*, 782. Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(7) Donohue, J. "The Structures of the Elements"; Wiley: New York, 1974.

(8) For $[(MeC_5H_4)MoFeTe_2(CO)_5]SbF_6$: Anal. Found: C, 15.18; H, 0.78. Calcd C, 15.33; H, 0.82. FABMS: *m/e* 626 (M^+), 598, 570, 544, 520, 486. IR (CH_2Cl_2): 2079 s, 2031 m, 2022 m, 1981 vw cm^{-1}. ^1H NMR (acetone-d_6): δ 6.17 m (2 H), 6.05 m (2 H), 2.39 s (3 H). ^{125}Te NMR (vs. Me_2Te acetone/C_6D_6): 839 ppm (s) upfield. Solution conductivity (acetone): $\Lambda = 9.86 \times 10^{-2}\ \Omega^{-1}$.

(9) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1981**, *20*, 3583; **1983**, *22*, 1854.

undergoes mild bromination to give **1**·Br (Scheme I).

[**1**]SbF_6 is reactive toward electron-rich compounds via processes that appear to involve initial interaction of the substrate with the Te_2 center (Scheme I). With NaBr, **1**·Br is regenerated quantitatively. With NaS_2CNEt_2 (Na(dtc)), [**1**]SbF_6 reacts to give the corresponding neutral dithiocarbamate.[11] The structure of $(CH_3C_5H_4)_2MoFe(Te_2dtc)(CO)_5$ was shown crystallographically[12] to closely resemble that found for **1**·Br (Figure 1). The dithiocarbamate is monodentate; the Te(1)–S(1) distance is 2.562 (2) Å while the Te(1)–S(2) distance is 3.341 (2) Å. The only significant difference between the core structures of **1**·Br and **1**·dtc is the elongated Te···Te distance of 2.954 (1) Å in the latter, which may arise from the weak interaction of Te(1) with S(2).

[**1**]SbF_6 reacts smoothly with *trans*-$IrCl(CO)(PPh_3)_2$ to give $[(CH_3C_5H_4)MoFeIrTe_2(CO)_6(PPh_3)_2Cl]SbF_6$ via what appears to be an oxidative-addition process. ^1H and ^{31}P NMR spectroscopy show that the product exists as two isomers that differ in the relative orientation of the carbonyl and chloride ligands.[13]

To summarize, we have found that the coordination chemistry of these Te_2 complexes is localized at the main-group sites. It is striking that the binding of anions to the electron-precise cluster $[\mathbf{1}]^+$ involves expansion of the "octet" about tellurium and does not induce rupture of any bond within the cluster. These findings provide further incentives for the study of organo-transition-metal derivatives of the heavier main-group elements.[14] Finally, the present results indicate that the bonding in some cluster compounds that contain four-coordinate Te centers should be reevaluated in terms of a hypervalent bonding model.[15] Similar arguments may apply to some μ_4-S- and μ_4-PR-containing clusters.

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Supplementary Material Available: Tables of atomic coordinates and temperature factors, bond lengths and angles, anisotropic thermal parameters, hydrogen coordinates and temperature factors, and structure factors for $(CH_3C_5H_4)_5MoFe(Te_2S_2CNEt_2)(CO)_5$ and $(C_5H_5)MoFe(Te_2Br)(CO)_5$ (40 pages). Ordering information is given on any current masthead page.

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(10) For $[(i\text{-}PrC_5H_4)MoFeTe_2(CO)_5]_n$: Anal. Found: C, 23.81; H, 1.66; Fe, 8.97; Te, 38.6. Calcd: C, 23.83; H, 1.69; Fe, 8.52; Te, 38.95. FABMS: *m/e* 727, 700, 657 (M^+), 627, 599, 575, 547, 516. IR (CH_2Cl_2): 2361 m, 2340 m, 2064 m, 2047 m, 2000 s,br cm^{-1}. ^1H NMR (CD_2Cl_2, −35 °C): δ 5.44 m (2 H), 5.36 m (2 H), 2.59 m (1 H), 1.20 d (6 H). [**1**] has the same valence electron count as $[Fe_2S_2(CO)_6]^-$, which exists as a dimer; see: Bose, K. S.; Sinn, E.; Averill, B. A. *Organometallics* **1984**, *3*, 1126.

(11) For $(MeC_5H_4)MoFe(Te_2SC(S)NEt_2)(CO)_5$: Anal. Found: C, 24.81; H, 2.20; N, 1.77. Calcd: C, 24.82; H, 2.21; N, 1.81. FABMS: *m/e* 780 (M^+), 721, 698, 667, 653, 628. IR (c-C_6H_{12}): 2052 s, 2002 m, 1989 m, 1944 w cm^{-1}. For $(i\text{-}PrC_5H_4)MoFe(Te_2SC(S)NEt_2)(CO)_5$: Anal. Found: C, 28.71; H, 2.59; N, 1.68. Calcd: C, 28.96; H, 2.84; N, 1.88. ^1H NMR (toluene-d_8, 22 °C): δ 4.83 m (2 H), 4.70 m (2 H), 3.57 q (4 H), 2.35 m (1 H), 0.96 t (6 H), 0.79 d (6 H). At −88 °C the two low-field signals of the 22 °C NMR spectrum are split into three broadened singlets: δ 4.80 m (1 H); 4.58 m (1 H), 4.12 m (2 H), 3.29 b (4 H), 1.85 m (1 H), 0.83 b (6 H), 0.66 d (6 H).

(12) For $(MeC_5H_4)MoFeTe(TeS_2CNEt_2)(CO)_5$: monoclinic, $P2_1/c$; a = 10.885 (2), b = 21.216 (4), c = 10.156 (3) Å; β = 100.79 (2)°; V = 2304.0 $Å^3$; Z = 4; D(calcd) = 1.96 g cm^{-3}; μ = 39.3 cm^{-1} (Mo Kα). Of 4390 absorption-corrected reflections collected (Nicolet R3 diffractometer, $4° \leq 2\theta \leq 50°$), 3654 ($F_o \geq 3\sigma(F_o)$) unique reflections were used in the solution (automated Patterson) and refinement (blocked cascade) of the structure. All non-hydrogen atoms were refined anisotropically, with all hydrogen atoms in idealized locations. At convergence R_F = 0.0343, R_{wF} = 0.0343, GOF = 1.22, and the highest peak (final difference map) was 0.56 e $Å^{-3}$ (associated with thermally active Et groups). Selected distances (Å) and angles (deg): Te–Te, 2.954 (1); Mo–Te(1), 2.740 (1); Mo–Te(2), 2.792 (1); Fe–Te(1), 2.517 (1); Fe–Te(2), 2.575 (1); Mo–Fe, 2.894 (1); Te(1)–S(1), 2.562 (2); Te–Te–S, 153.9 (0); Te(2)–Te(1)–Mo, 58.6; Te(2)–Te(1)–Fe, 55.5 (0).

(13) For $[(MeC_5H_4)MoFeTe_2IrCl(PPh_3)_2(CO)_6]SbF_6$: Anal. Found: C, 35.07; H, 2.34; P, 3.79; Fe, 3.57. Calcd: C, 34.38; H, 2.27; P, 3.77; Fe, 3.40. IR (CH_2Cl_2): 2060 s, 2035 m, 1998 m cm^{-1}. ^1H NMR (acetone-d_6): δ 7.57 m (30 H), 6.41 m and 6.08 m (2.5 H), 6.23 m and 5.96 m (1.48 H), 2.97 s (3 H). ^{31}P NMR (acetone): δ −11.9 s, −12.6 s.

(14) Lewis-acidic main-group ligands are known for arsenic (Sigwarth, B.; Zsolnai, L.; Scheidsteger, O.; Huttner, G. *J. Organomet. Chem.* **1982**, *235*, 43), antimony (Kaul, H.-A.; Greissinger, D.; Malisch, W.; Klein, H.-P.; Thewalt, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 60), and phosphorus (Gross, E.; Jörg, K.; Fiederling, K.; Göttlein, A.; Malisch, W.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 738).

(15) See: Kiang, T.; Zare, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 4024. Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

Simple Synthesis and ^{113}Cd NMR Spectroscopic Characterization of the Fully Terminally Substituted Clusters $[(\mu\text{-}EPh)_6(CdX)_4]^{2-}$ (E = S or Se; X = Br or I)

Sir:

The tetranuclear anions $[\mu\text{-}SPh)_6(MSPh)_4]^{2-}$, having an adamantane-like cage structure, are known for a variety of divalent metal ions, including Zn,[1] Cd,[2] Mn,[3] Fe,[4] and Co,[5] but the substitution chemistry of these clusters as such has not been studied in detail. Analogous heteroligated clusters $[(\mu\text{-}SPh)_6(MSPh)_x(MX)_{4-x}]^{2-}$ and related species have normally been synthesized from mixtures of M^{2+}, SPh^-, and X^-, $[M(SPh)_4]^{2-}$ and MX_2, or basic salts of M(II), PhSH, and X^-, in an appropriate ratio.[5b,6-8] Only for Fe(II) have fully terminally substituted anions, $[(\mu\text{-}SPh)_6(FeX)_4]$ (X = Cl or Br), been prepared in this way.[8] For the Zn(II)[6] and Co(II)[5b] clusters, double terminal substitution by halogens has so far proved to be the limit via this route.

Recently we demonstrated[9] by use of ^{113}Cd NMR that the PhE^- ligands of $[Cd_4(EPh)_{10}]^{2-}$ (E = S or Se) can be replaced by RE'^- by redox reaction with organic dichalcogenides, $R_2E'_2$. The success of this study with pseudohalogen-like $R_2E'_2$ led us to investigate reaction of $[Cd_4(EPh)_{10}]^{2-}$ with the halogens themselves. Reported here are stepwise oxidative substitution reactions of $[Cd_4(EPh)_{10}]^{2-}$ (X = S or Se) with I_2 and Br_2, which lead to $[Cd_4(EPh)_6X_4]^{2-}$ (E = S or Se; X = Br or I) in high yield, and the characterization of the series $[(\mu\text{-}SPh)_x(\mu\text{-}SePh)_{6-x}(CdX)_4]^{2-}$ (X = Br or I) by ^{113}Cd NMR.

The anions $[Cd_4(EPh)_6I_4]^{2-}$ (E = S or Se) are obtained by the direct quantitative reaction of I_2 with $(Me_4N)_2[Cd_4(EPh)_{10}]$ in acetone, according to eq 1a.[10] The corresponding [Cd$_4$-

$$[Cd_4(EPh)_{10}]^{2-} + 2X_2 \xrightarrow[\text{room temp}]{\text{acetone}} [Cd_4(EPh)_6X_4]^{2-} + 2Ph_2E_2 \tag{1}$$

(a) X = I (in acetone) (b) X = Br (in CCl_4)

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