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.

Acknowledgment. This research was supported by the National Science Foundation. T.B.R. is a fellow of the Camille and Henry Dreyfus and Alfred P. Sloan Foundations. L.E.B. is a UIF fellow. Mass spectra were obtained in the Mass Spectrometry Laboratory, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences (No. GM 27029). We thank Drs. Scott Wilson, Mark Draganjac, and Gregg Zank for help in solving the crystal structure of $CpMoFe(Te_2Br)(CO)_5$. We thank Johnson Matthey Inc. for loan of the iridium.

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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(5) (a) Dance, I. G.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1975**, 762. (b) Dance, I. G. *J. Am. Chem. Soc.* **1979**, *101*, 6264.

(6) Dance, I. G. *Inorg. Chem.* **1981**, *20*, 2155.

(7) Dance, I. G. *J. Am. Chem. Soc.* **1980**, *102*, 3445.

(8) Coucouvanis, D.; Kanatzidis, M.; Simhon, E.; Baenziger, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 1874.

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Table I. Cadmium-113 NMR Data for $[Cd_4(EPh)_6X_4]^{2+\,a}$

E	X	$\delta_{Cd}{}^{b}$	approx $\nu_{1/2}$, Hz
S	SPh	575^{c}	8^{c}
Se	SePh	$519^{d,e}$	$65^{d,e}$
S	Br	535	90
S	I	501	50
Se	Br	492	75
Se	I	441^{e}	85^{e}

[a] For acetone solutions at 295 ± 1 K; measured at 44.37 MHz. [b] Relative to external 0.1 M $Cd(ClO_4)_2(aq)$ at 295 ± 1 K. [c] Data from ref 11; $^2J(^{111}Cd\text{–}S\text{–}^{113}Cd) = 47$ Hz. [d] Data from ref 9. [e] In a ^{113}Cd-enriched sample.

$(EPh)_6Br_4]^{2-}$ (E = S or Se) can be obtained similarly by shaking an acetone solution of $(Me_4N)_2[Cd_4(EPh)_{10}]$ with a CCl_4 solution of Br_2 (eq 1b).[10] In all cases decolorization of the halogen is very rapid, the reaction being complete in less than 1 min under the conditions used. The new complexes are characterized by singlet ^{113}Cd NMR spectra; details of the spectra are given in Table I, which also includes data for $[Cd_4(EPh)_{10}]^{2-}$ for comparison.

The stepwise nature of the halogen oxidation was shown by a ^{113}Cd NMR study of $[Cd_4(SPh)_{10}]^{2-}$–I_2 mixtures. On addition of 2 molar equiv of I_2 to $[Cd_4(SPh)_{10}]^{2-}$ in acetone at 295 K, the spectrum of this species (Table I) is replaced by the singlet due to $[Cd_4(SPh)_6I_4]^{2-}$ (Table I). Solutions in which $0 < I_2/[Cd_4(SPh)_{10}]^{2-} < 2$ were studied by using ^{113}Cd enrichment; at ambient probe temperature the ^{113}Cd NMR spectra show signals in two regions, ca. 575 ppm and ca. 500 ppm,[12] with the intensity ratio I_{500}/I_{575} increasing with x. The lineshapes are non-Lorentzian, consistent with the existence of several unresolved overlapping lines, making it clear that the two regions of resonance are from equilibrium mixtures of $[^{113}Cd_4(SPh)_{10-x}I_x]^{2-}$ and not simply from mixtures of $[^{113}Cd_4(SPh)_{10}]^{2-}$ and $[^{113}Cd_4(SPh)_6I_4]^{2-}$ (**1***).[13] The two regions of resonance can be assigned to the component kernels, $^{113}CdS_4$ and $^{113}CdS_3I$, of the clusters $[^{113}Cd_4(SPh)_{10-x}I_x]^{2-}$, with $\delta_{Cd} \approx 575$ and ≈ 500, respectively. Evidently δ_{Cd} in these clusters is relatively insensitive to changes in substituent at a remote site.[14] Also, it is clear that exchange of ^{113}Cd between the two types of sites occurring in the clusters is slow on the ^{113}Cd NMR time scale.

When I_2 is added to $[^{113}Cd_4(SePh)_{10}]^{2-}$ in acetone, ^{113}Cd NMR spectroscopy at 295 K shows growth of a second region of resonance with $\delta_{Cd} \approx 440$ on the expected sequential replacement of SePh by I. At $I_2/[^{113}Cd_4(SePh)_{10}]^{2-} = 2$, the spectrum becomes the singlet of $[^{113}Cd_4(SePh)_6I_4]^{2-}$ (**2***) (Table I).

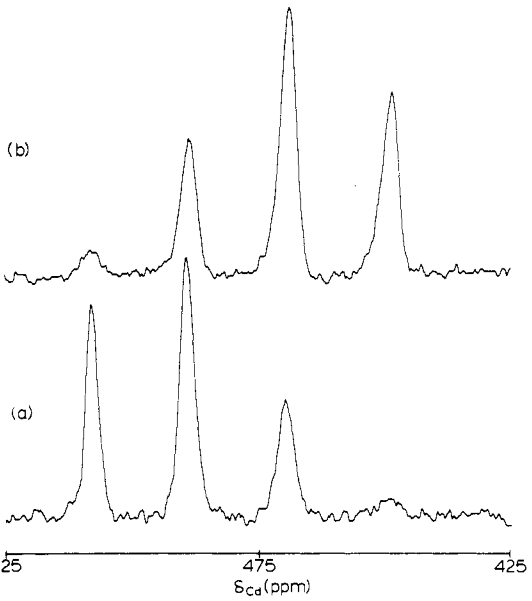
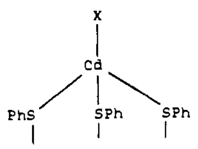
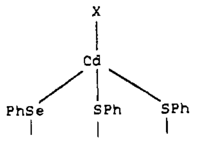


Figure 1. Cadmium-113 NMR spectra, measured at 260 K and 44.37 MHz, of mixtures of $[^{113}Cd_4(SPh)_6I_4]^{2-}$ (**1***) and $[^{113}Cd_4(SePh)_6I_4]^{2-}$ (**2***) in acetone. (a) **1***/**2*** ≈ 2; the spectrum results from 2008 50° (11 μs) pulses at 3-s intervals with proton decoupling during the 0.5-s acquisition time. In the recording, the digital resolution is 2.4 Hz/point, and a 20-Hz line broadening has been applied. (b) **1***/**2*** ≈ 0.5; the spectrum results from 2027 transients obtained and processed as in part a.

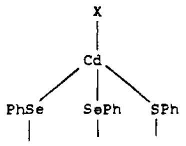
In the ^{113}Cd NMR spectra of mixtures of **1*** and **2*** in acetone at 295 K, a total of four broad resonances are found with chemical shifts ~500, ~480, ~462, and ~440 ppm, approximately equally spaced, and bounded approximately by the chemical shifts of **1*** and **2***. These spectra are better resolved at reduced temperature as shown in Figure 1.[16] The spectra are readily interpreted in terms of the occurrence among members of the series $[(\mu\text{-}SPh)_x(\mu\text{-}SePh)_{6-x}(CdI)_4]^{2-}$ of four different first coordination spheres I–IV (X = I) with δ_{Cd} in the sequence 500–440 (at 295 K), respectively, relatively insensitive to changes beyond the first coordination sphere as noted above for $[Cd(EPh)_{10-x}I_x]^{2-}$ also.[14] Thus the predominance of terminal iodine substitution in $[Cd_4(SPh)_x(SePh)_{6-x}I_4]^{2-}$ is clearly evident. Similarly, in their reduced-temperature ^{113}Cd NMR spectra, mixtures of $[^{113}Cd_4(SPh)_6Br_4]^{2-}$ and $[^{113}Cd_4(SePh)_6Br_4]^{2-}$ show resonances in four regions, attributable to I–IV (X = Br), indicating that bromine substitution also occurs mainly terminally.



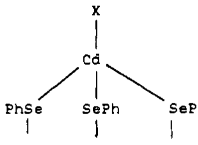
I



II



III



IV

The straightforward synthesis described here seems to be a viable general route to a wider range of halogen- and pseudohalogen-substituted metal chalcogenate clusters, and we are currently exploring this possibility.

Acknowledgment. This work was funded by an Operating Grant from the Natural Sciences and Engineering Research Council of Canada to P.A.W.D.

Registry No. $(Me_4N)_2[Cd_4(SPh)_6I_4]$, 98541-24-3; $(Me_4N)_2[Cd_4(SePh)_6I_4]$, 98576-61-5; $(Me_4N)_2[Cd_4(SPh)_6Br_4]$, 98541-26-5; $(Me_4N)_2[Cd_4(SePh)_6Br_4]$, 98541-28-7; $(Me_4N)_2[Cd_4(SPh)_{10}]$, 84493-87-8; $(Me_4N)_2[Cd_4(SePh)_{10}]$, 98541-30-1; I_2, 7553-56-2; Br_2, 7726-95-6.

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[10] Colorless crystals of $(Me_4N)_2[Cd_4(EPh)_6X_4]$ (E = S or Se; X = Br or I), were obtained in more than 85% yield by recrystallization from C_6H_{12}/Me_2CO after removal of Ph_2E_2 by extraction with Et_2O. The presence of Ph_2E_2 in the extract was confirmed by ^{13}C NMR. Anal. Calcd for $C_{44}H_{54}Cd_4I_4N_2S_6$: C, 30.02; H, 3.09; N, 1.59. Found: C, 30.06; H, 3.14; N, 1.53. Anal. Calcd for $C_{44}H_{54}Cd_4I_4N_2Se_6$: C, 25.88; H, 2.66; N, 1.37. Found: C, 26.13; H, 2.82; N, 1.40. Anal. Calcd for $C_{44}H_{54}Br_4Cd_4N_2S_6$: C, 33.61; H, 3.46; N, 1.78. Found: C, 33.36; H, 3.48; N, 1.77. Anal. Calcd for $C_{44}H_{54}Br_4Cd_4N_2Se_6$: C, 28.51; H, 2.94; N, 1.51. Found: C, 28.36; H, 2.66; N, 1.82. Cadmium-113 NMR data characterizing the new compounds are given in Table I.

[11] Dean, P. A. W.; Vittal, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 6436.

[12] All ^{113}Cd NMR chemical shifts are given relative to external 0.1 M $Cd(ClO_4)_2(aq)$ at 295 ± 1 K.

[13] In nonlabile $[Cd_4(SPh)_{10-x}I_x]^{2-}$ ($x = 1$–3), ^{113}Cd–^{113}Cd nuclear spin–spin coupling should occur, but this was not observed and because of signal overlap we were unable to extract the ^{113}Cd NMR spectra of the individual components of the equilibrium mixture.

[14] An analogous "local environment" effect has been observed earlier[15] in the ^{7}Li NMR spectra of tetrameric $Li_4R_{4-n}X_n$; we thank a reviewer for drawing our attention to this similarity.

[15] Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 2174.

[16] δ_{Cd} has a large temperature dependence (see also ref 11).