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Relativistically Parameterized Extended Hückel Calculations. 5. Charged Polyhedral Clusters of Germanium, Tin, Lead, and Bismuth Atoms

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Relativistically parameterized extended Hückel (REX) calculations are reported for the homonuclear clusters Ge_9^{4-}, Ge_9^{2-}, Sn_4^{2-}, Sn_5^{2-}, Sn_9^{4-}, Pb_5^{2-}, Pb_9^{4-}, and Bi_9^{5+}, the heteronuclear clusters $PbSn_4^{2-}$, $SnGe_8^{4-}$, $GeSn_8^{4-}$, $PbSn_8^{4-}$, and $TlSn_8^{5-}$, and the exopolyhedral cluster $CH_3Pb_9^{3-}$. The reported results include binding energies per atom, rearrangement energies, and charge distributions. Significant differences are found for the heavier element clusters between the results obtained by using the relativistic parameterization and those obtained by using the nonrelativistic parameterization. Relativistic effects appear to reduce the binding energy per atom in homonuclear clusters and to alter the charge distributions in the heteronuclear clusters AB_8^{q-}. The latter effects are discussed in terms of relativistic effects on the variation of atomic electronegativity with atomic charge.

I. Introduction

A particularly interesting series of inorganic compounds is those containing clusters of the group 3B, 4B, 5B, and 6B elements. X-ray crystal structure determinations have been reported for salts containing the polyatomic anions Sb_7^{3-},[1] Te_3^{2-},[2] Bi_4^{2-},[3] Sn_5^{2-} and Pb_5^{2-},[4] Sn_9^{4-},[5] Ge_9^{4-} and Ge_9^{2-},[6] As_{11}^{2-},[7] $Tl_2Te_2^{2-}$,[8] and Sn_4^{2-} and Ge_4^{2-}.[9] The salts typically contain Na^+ or K^+ complexed with the bicyclic 2,2,2-crypt ligand and are isolated from ethylenediamine solution. Some salts with related cationic clusters[10] are those containing Bi_5^{3+} and Bi_8^{2+},[11] Bi_9^{5+},[12] Se_4^{2+},[13] Se_8^{2+},[14] and Te_4^{2+}.[15,16] Some alloys whose structures have been interpreted in terms of clusters include NaPb (Pb_4^{4-}),[17] Na_3Hg_2 (Hg_4^{6-}),[18] KSn and β-NaSn (Sn_4^{4-}),[19,20] and Na_2Tl (Tl_4^{8-}).[21] Other alloy phases such as Na_9Sn_4,[22] $Na_{15}Sn_4$,[22] and Li_2Sn_5[23] do not readily admit of a cluster interpretation.

A particularly powerful technique for the identification of cluster species in solutions formed by extraction of Zintl phases with ethylenediamine (en) or ammonia is ^{119}Sn NMR.[24-26] Anionic clusters thus identified include $Sn_{9-x}Pb_x^{4-}$ (x = 0–9),[24] Sn_4^{2-},[25,26] $Sn_{9-x}Ge_x^{4-}$ (x = 0–9),[26] $TlSn_8^{5-}$,[26] and $SnTe_4^{4-}$.[26] A key observation is the fluxional nature of all of the above save $SnTe_4^{4-}$, resulting in a single ^{119}Sn chemical shift and a single $^{119}Sn-^{117}Sn$ nuclear spin coupling constant for a given cluster. By contrast the $SnTe_4^{4-}$ appears to be a "normal" tetrahedral species analogous to the SiO_4^{4-} orthosilicate ion.

We report here the results of a theoretical study of the structure and bonding of charged homonuclear clusters of Ge,

Table I. REX Parameters[a]

		$-\alpha_1$, eV		ζ_i	
element	orbital	rel	nonrel	rel	nonrel
Ge	4s	15.52	15.16	2.057	2.024
	$4p_{1/2}$	7.42	7.33	1.569	1.550
	$4p_{3/2}$	7.24		1.544	
Sn	5s	13.88	13.04	2.218	2.129
	$5p_{1/2}$	7.01	6.76	1.732	1.674
	$5p_{3/2}$	6.57		1.664	
Tl	6s	12.22	9.83	2.520	2.191
	$6p_{1/2}$	5.75	5.24	1.848	1.656
	$6p_{3/2}$	4.80		1.620	
Pb	6s	15.42	12.49	2.718	2.386
	$6p_{1/2}$	7.49	6.53	2.114	1.880
	$6p_{3/2}$	5.98		1.848	
Bi	6s	18.67	15.19	2.898	2.560
	$6p_{1/2}$	9.21	7.79	2.338	2.072
	$6p_{3/2}$	7.11		2.040	
C	2s	19.39	19.38	1.577	1.576
	$2p_{1/2}$	11.07	11.07	1.435	1.435
	$2p_{3/2}$	11.06		1.434	

[a] H(1s) parameters are $\alpha = -13.6$ eV and $\zeta = 1.0$.

Table II. Atomic Coordinates for C_{4v} A_9 Clusters

atom	x	y	z	atom	x	y	z
1	0	0	$-a$	6	0	c	d
2	b	b	0	7	$-c$	0	d
3	$-b$	b	0	8	0	$-c$	d
4	$-b$	$-b$	0	9	c	0	d
5	b	$-b$	0				

Table III. Coordinate Parameters for C_{4v} A_9 Clusters[a]

cluster	a, Å	b, Å	c, Å	d, Å
Ge_9^{4-} [b]	1.621	1.404	1.809	2.145
Sn_9^{4-} [c]	1.865	1.622	2.096	2.444
Pb_9^{4-}, Bi_9^{5+} [d]	1.977	1.718	2.221	2.590

[a] See Table II. [b] From ref 6. [c] From ref 5. [d] Sn_9^{4-} values scaled by 1.060.

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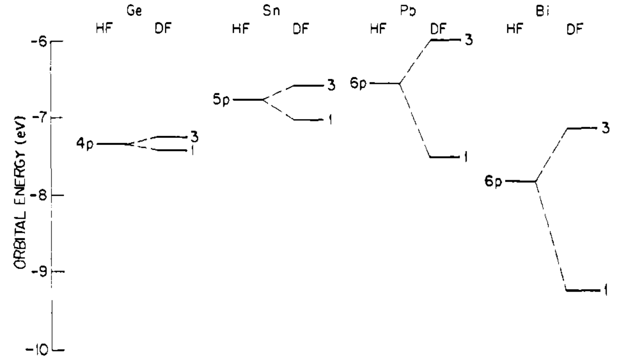

Figure 1. Nonrelativistic Hartree–Fock (HF) and relativistic Dirac–Fock (DF) orbital-energy parameters from ref 32 for the *n*p orbitals of Ge, Sn, Pb, and Bi. The labels 3 and 1 denote $j = {}^3/_2$ and ${}^1/_2$, respectively.

Sn, Pb, and Bi atoms as well as a number of heteronuclear clusters. The study employs our relativistically parameterized extended Hückel method (REX),[27] which we have earlier applied to the study[28] of orbital energies for group 4 tetrahalides and tetramethyl compounds and to the description[29] of bonding in numerous compounds of uranium and other heavy elements. An extension of the REX method has been used in the calculation[30] of nuclear spin–spin coupling constants, while the REX program itself has been made publicly available.[31] Incorporating as it does not only spin–orbit splittings but also relativistic expansions and contractions of atomic orbitals, the REX method should provide a semiquantitative assessment of the importance of these effects in heavy-element clusters. Its dual relativistic and nonrelativistic parameterizations[27] are based on the atomic Dirac–Fock (DF) calculations of Desclaux.[32] An alternative theoretical tool for the investigation of these clusters is the effective potential method, which we have recently employed[33] in its nonrelativistic form in a study leading to predictions of a distorted tetrahedral equilibrium geometry and of fluxional behavior for Sn_4^{2-}. This latter study was motivated by the NMR investigations of Rudolph et al.[25,26] and paralleled the effective potential study of Te_4^{2+} by Rothman et al.[34] Both simple semiempirical,[11] SCF-MO-CNDO,[5,6] and INDO[35] calculations have been reported for a number of the cationic and ionic clusters.

II. A_9^q Clusters

The principal series of clusters that we have studied consists of Ge_9^{4-},Sn_9^{4-}, Pb_9^{4-}, and Bi_9^{5+}, their oxidation products A_9^{2-} and Bi_9^{7+}, and various substitutional derivatives. REX parameters for the elements Ge, Sn, Pb, and Bi are listed in Table I, with the important spin–orbit splittings of the *n*p atomic orbitals (AO's) being shown in Figure 1. Coordinates corresponding to a molecular symmetry of C_{4v} are given in Tables II and III and are based on idealizations of the observed Sn_9^{4-} and Ge_9^{4-} structures.[5,6] Coordinates for Pb_9^{4-} and Bi_9^{5+} were obtained by scaling the Sn_9^{4-} values by 1.060, the ratio of the average Bi–Bi distance[12c] (3.143 Å) in $Bi_9^{5+}(D_{3h})$ to the average Sn–Sn distance[5] (2.966 Å) in $Sn_9^{4-}(C_{4v})$. The use of the same extrapolated coordinates for $Pb_9^{4-}(C_{4v})$ and $Bi_9^{5+}(C_{4v})$ is based on the similarity of the average Pb–Pb distance[4] (3.08 Å) in Pb_5^{2-} to the Bi–Bi distance given above. Coordinates for the D_{3h} symmetry structure of these complexes are given in Tables IV and V and are based on idealizations of the observed Ge_9^{2-} and Bi_9^{5+} structures.[6,12c] Coordinates for $Sn_9^{4-}(D_{3h})$ were obtained by scaling the $Bi_9^{5+}(D_{3h})$ values by 0.944, the reciprocal of the scaling factor used previously. An alternate scaling based on the average Ge–Ge distance (2.598 Å) in $Ge_9^{2-}(D_{3h})$ leads to parameters for $Sn_9^{4-}(D_{3h})$ of a = 2.719 Å, b = 1.758 Å, and c = 1.682 Å; the resulting polyhedron has less height but a greater equatorial "bulge" than that described by the parameters in Table V. The polyhedra with D_{3h} and C_{4v} symmetries are shown in Figure 2.

Table IV. Atomic Coordinates for D_{3h} A_9 Clusters

atom	x	y	z
1	a	0	0
2	$-a/2$	$3^{1/2}a/2$	0
3	$-a/2$	$-3^{1/2}a/2$	0
4	$-b$	0	c
5	$b/2$	$3^{1/2}b/2$	c
6	$b/2$	$-3^{1/2}b/2$	c
7	$-b$	0	$-c$
8	$b/2$	$3^{1/2}b/2$	$-c$
9	$b/2$	$-3^{1/2}b/2$	$-c$

Table V. Coordinate Parameters for D_{3h} A_9 Clusters[a]

cluster	a, Å	b, Å	c, Å
Ge_9^{4-}, Ge_9^{2-} [b]	2.382	1.540	1.473
Sn_9^{4-} [c]	2.637	1.766	1.763
Pb_9^{4-}, Bi_9^{5+} [d]	2.794	1.871	1.868

[a] See Table IV. [b] Ge_9^{2-} coordinates from ref 6. [c] Bi_9^{5+} values scaled by 0.944. [d] From ref 12c for Bi_9^{5+}.

Table VI. Rearrangement Energies for A_9^q Clusters

cluster	ΔE-(REX)[a]	ΔE-(EHT)[a]	cluster	ΔE-(REX)[a]	ΔE-(EHT)[a]
Ge_9^{4-}	0.92	0.93	Ge_9^{2-}	−0.42	−0.55
Sn_9^{4-}	0.46	0.45	Sn_9^{2-} [b]	0.04	−0.21
Pb_9^{4-}	0.39	0.35	Pb_9^{2-} [b]	0.23	−0.27
Bi_9^{5+}	0.18	0.13	Bi_9^{7+} [b]	0.04	−0.44

[a] $\Delta E \equiv E(D_{3h}) - E(C_{4v})$, in eV. [b] Unknown species.

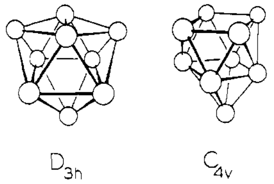

Figure 2. The nine-atom polyhedra with D_{3h} (left) and C_{4v} (right) symmetries.

A list of the calculated differences between the total orbital energies for the D_{3h} and C_{4v} forms of the none-atom clusters is given in Table VI. For the species with 40 valence electrons (including the *n*s electrons) the C_{4v} form is computed to be favored for all four elements. The REX and EHT (extended Hückel) parameterizations give essentially the same rearrangement energies for a given cluster. As in our earlier studies,[27-29] results labeled EHT refer to those obtained by using the REX formalism but with nonrelativistic parameters (Table I). The observed structures of Ge_9^{4-} and Sn_9^{4-} are essentially of C_{4v} symmetry, while that of Bi_9^{5+} is close to D_{3h} in $Bi(Bi_9)(HfCl_6)_3$[12c] but distorted somewhat toward C_{4v} in

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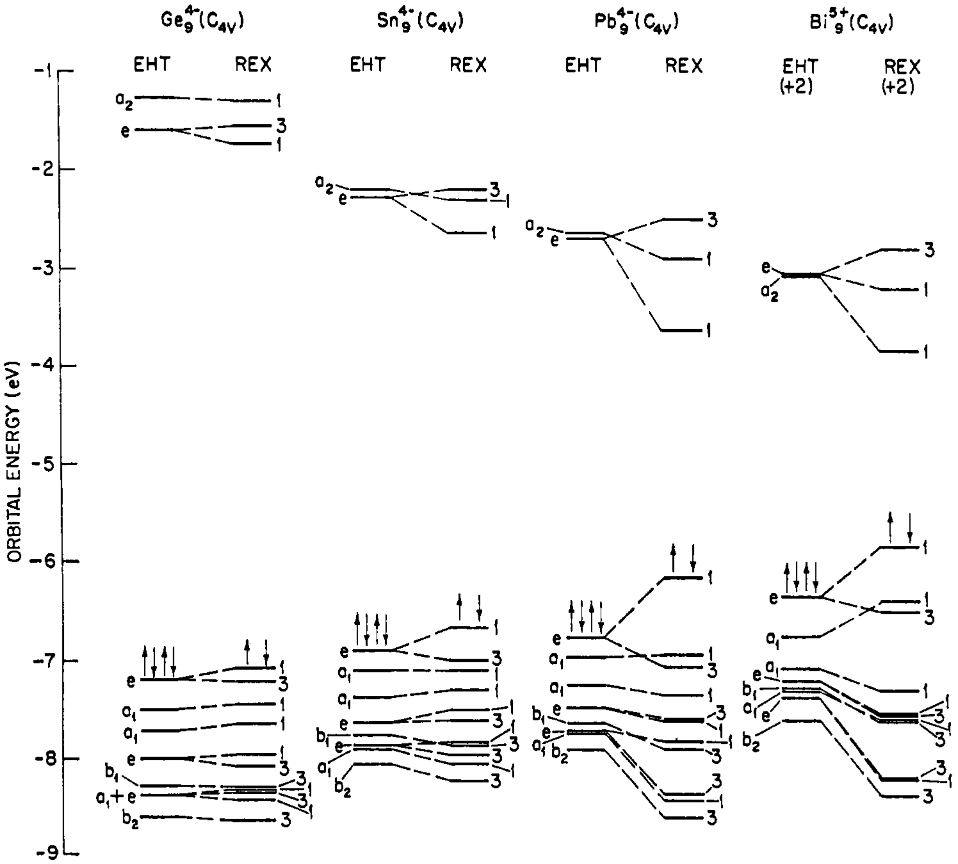

Figure 3. REX and EHT orbital energies for some homonuclear nine-atom clusters with C_{4v} symmetry. The relativistic orbital labels 1 and 3 denote the $e_{1/2}$ and $e_{3/2}$ irreducible representations of C_{4v}^{*}. Arrows denote the HOMO in each case. Values for Bi_9^{5+} have been shifted upward by 2 eV.

$Bi_{12}Cl_{14}$.[12] Although we are unable to account for the apparent stability of the D_{3h} form of Bi_9^{5+} relative to the C_{4v} form, we do note in Table VI a significant decrease in the rearrangement energy in going from Ge to Bi. The approximately 0.5 eV value for Sn_9^{4-} is certainly consistent with the fluxional behavior predicted for this complex by Corbett and Edwards[5] on the basis of SCF–MO–CNDO calculations and observed in solution NMR by Rudolph et al.[24] For the known oxidized cluster Ge_9^{2-} and the unknown oxidized clusters Sn_9^{2-}, Pb_9^{2-}, and Bi_9^{7+}, our findings (Table VI) are somewhat different. For Ge_9^{2-} both the REX and EHT parameterizations favor the D_{3h} structure, as observed,[6] but for the other clusters the stability of the D_{3h} form computed with the EHT parameterization is lost on going to the REX parameterization. Some further details of this effect are discussed in connection with the orbital energies. Our results are not dissimilar from the SCF–MO–CNDO results of Corbett and Edwards[5] for Sn_9^{4-} and of Belin, Corbett, and Cisar[6] for the two Ge_9^{q-} clusters. These authors were also unable to account satisfactorily for the structure of Bi_9^{5+}, although suggestions about packing forces were made. Barriers to the D_{3h}–C_{4v} interconversion in nine-atom clusters and in AB_9 complexes have also been computed[36] by using the points-on-a-sphere model. The results indicate a preference for D_{3h} symmetry for a variety of force-law exponents.

The computed Mulliken charges for the C_{4v} forms of Ge_9^{4-}, Sn_9^{4-}, and Pb_9^{4-} follow the same pattern, namely, that atoms on the open face (6–9 in Table II) are the most negative, followed by the apical atom (1), with the cn = 5 atom (2–5) (cn = coordination number) being the least negative. The REX values for these three positions in both Ge_9^{4-} and Sn_9^{4-} are 0.57–, 0.45–, and 0.32–, respectively, while for Pb_9^{4-} they are 0.54–, 0.38–, and 0.37–. In the last case the use of relativistic parameters tended to equalize the charges, as the corresponding EHT values are 0.57–, 0.46–, and 0.31–, respectively. The SCF–MO–CNDO values[5] for $Sn_9^{4-}(C_{4v})$ are somewhat different from our values, namely, 0.55–, 0.75–, and 0.25– for the three positions, the apical atom being the most negative and the overall distribution being more polarized than that which we find. However these results do agree with ours in having the cn = 5 site as the least negative.

Figure 3 displays some of the orbital energies for the A_9 clusters with assumed C_{4v} symmetry. Not shown are the energies of the nine MO's consisting primarily of the *n*s AO's. The spin–orbit splittings of the e HOMO's are 0.12, 0.32, 0.89, and 0.65 eV for the clusters of Ge, Sn, Pb, and Bi, respectively, while the splittings of the e LUMO's are 0.20, 0.43, 1.09, and 1.04 eV. By comparison, the atomic *n*p splitings (Table I and Figure 1) are 0.18, 0.44, 1.51, and 2.10 eV, respectively. The levels derived from the HOMO are ordered $e_{1/2}$ above $e_{3/2}$ (irreducible representations of C_{4v}^{*}, the "double-group" derived from the group C_{4v}), while those derived from the LUMO are ordered $e_{3/2}$ above $e_{1/2}$.

Figure 4 displays some of the orbital energies for the same A_9 clusters but with assumed D_{3h} symmetry. The EHT results for the D_{3h} clusters are principally characterized by the a_2'' HOMO lying above the degenerate e′ MO, while the EHT results for the C_{4v} clusters are characterized by the degenerate e HOMO lying above the a_1 MO. However, the REX level patterns are quite similar for the two symmetries of each cluster except Ge_9^{4-}, where for D_{3h} symmetry the $e_{5/2}$ (or a_2'') HOMO lies 0.99 eV above the next $e_{5/2}$ (or e′) MO. In short, large spin–orbit coupling reduces the structure dependence of the orbital energy pattern. For Ge_9^{4-}, with small spin–orbit coupling, the destabilization of the HOMO remains large for

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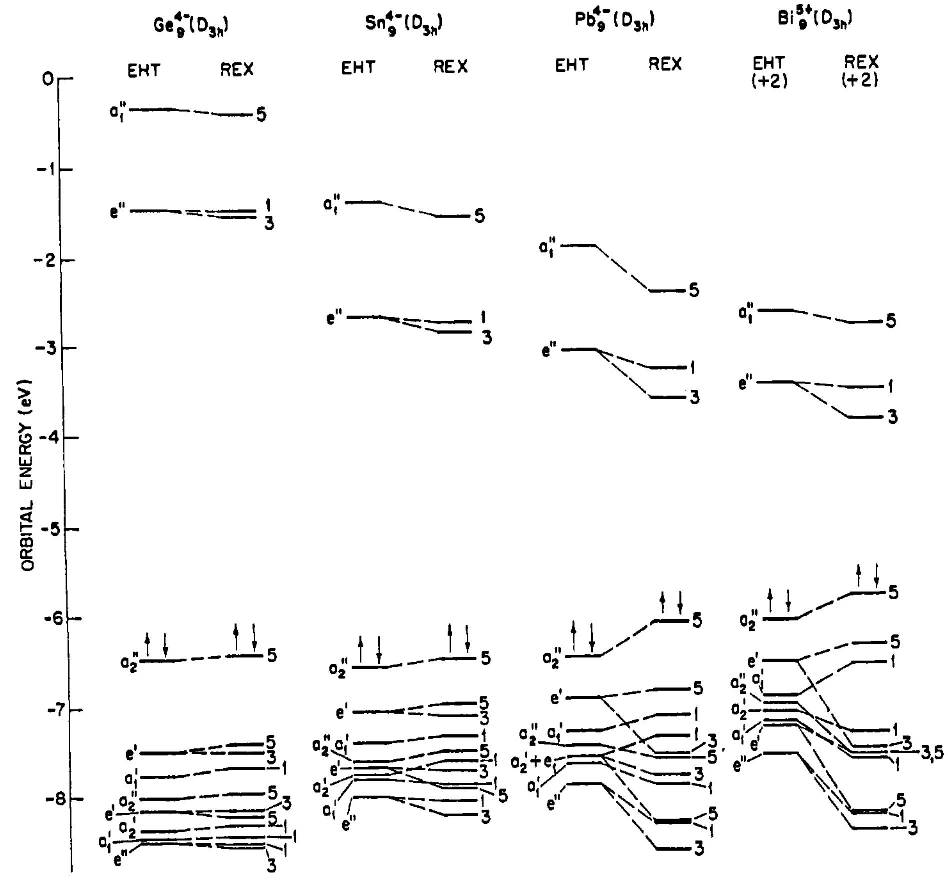

Figure 4. REX and EHT orbital energies for the D_{3h} symmetry form of the same nine-atom clusters shown in Figure 3. The labels 1, 3, and 5 denote the irreducible representations of $e_{1/2}$, $e_{3/2}$, and $e_{5/2}$ of D_{3h}^*. Values for Bi_9^{5+} have been shifted upward by 2 eV.

Table VII. HOMO–LUMO Separations for A_9 Clusters

cluster	symmetry	ΔE-(REX), eV	ΔE-(REX), eV
Ge_9^{4-}	C_{4v}	5.36	5.59
	D_{3h}	4.89	4.99
Sn_9^{4-}	C_{4v}	4.02	4.60
	D_{3h}	3.62	3.89
Pb_9^{4-}	C_{4v}	2.55	4.06
	D_{3h}	2.49	3.39
Bi_9^{5+}	C_{4v}	2.01	3.29
	D_{3h}	1.96	2.65

D_{3h} symmetry. Interestingly, the oxidized form Ge_9^{2-}, in which this orbital is vacant, displays the D_{3h} structure.[6] The spin–orbit splittings of the occupied e′ MO's just below the HOMO's of the D_{3h} forms are 0.08, 0.14, 0.70, and 1.16 eV for the clusters of Ge, Sn, Pb, and Bi, respectively, with $e_{5/2}$ above $e_{3/2}$ (irreducible representations of D_{3h}^*, the "double-group" derived from the group D_{3h}), while the splittings of the e″ LUMO's are 0.07, 0.11, 0.32, and 0.33 eV, with $e_{1/2}$ above $e_{3/2}$.

Another important feature of the orbital energies is the HOMO–LUMO separations given in Table VII. We note that the separations decrease in going from Ge_9^{4-} to Bi_9^{5+} and in going from the EHT to the REX parameterization, the latter effect undoubtedly attributable to the relativistic contraction of the $np_{1/2}$ AO's. Although the values are certainly sensitive to our bond distance assumptions, the trend toward lower energy electronic excitations in the heavier clusters appears to be significant. We also note that for the heavier clusters the separations are essentially the same for the C_{4v} and D_{3h} forms when the REX parameterization is employed. Thus the broadening of the absorption bands due to fluxional behavior is not predicted to be as great as it would be from the EHT results. We hope that absorption spectra of these clusters in solution will be obtained for comparison with these predictions.

Table VIII. REX Results for AB_8^{q-} Clusters with C_{4v} Frameworks

cluster	substn site[a]	relative energy, eV	$q(A)$[b]	$q(B_{av})$[c]
$SnGe_8^{4-}$	ap	0	0.07–	0.50–
	eq	0.23	0.13+	0.52–
	ba	0.31	0.14–	0.48–
$GeSn_8^{4-}$	ap	0.24	0.86–	0.39–
	eq	0.03	0.80–	0.40–
	ba	0	1.01–	0.37–
$PbSn_8^{4-}$	ap	0.10	0.39–	0.45–
	eq	0	0.25–	0.47–
	ba	0.10	0.50–	0.44–
$TlSn_8^{5-}$	ap	0.10	0.58–	0.55–
	eq	0	0.28–	0.59–
	ba	0.50	0.61–	0.55–
$TlSn_8^{3-}$	ap	0.47	0.21+	0.40–
	eq	0	0.49+	0.44–
	ba	0.30	0.26+	0.41–

[a] ap ≡ apical (cn = 4), eq ≡ equatorial (cn = 5), ba ≡ basal (cn = 4). [b] Mulliken charge for heteroatom A. [c] Averaged Mulliken charge for atoms B.

III. AB_8^{q-} and RA_9^{q-} Clusters

Since some of the most interesting experimental results on nine-atom clusters have come from the solution NMR studies of the systems $Sn_{9-x}Pb_x^{4-}$ (x = 0–9),[24] $Sn_{9-x}Ge_x^{4-}$ (x = 0–9),[26] and $TlSn_8^{5-}$,[26] we have performed REX calculations on the monosubstituted heteronuclear species $SnGe_8^{4-}$, $GeSn_8^{4-}$, $PbSn_8^{4-}$, and $TlSn_8^{5-}$. In Table VIII we show the relative total orbital energies for the three different substitution sites possible for each cluster with a C_{4v} framework. Undistorted Ge_9^{4-} coordinates (Tables II and III) were used for $SnGe_8^{4-}$, while undistorted Sn_9^{4-} coordinates were used for the ASn_8^{4-} (A = Ge, Pb, Tl^-) clusters. This assumption is somewhat drastic but is hoped not to lead to erroneous trends. The substitution sites labeled ap, eq, and ba refer to the apical (cn = 4), equatorial (cn = 5), and basal (cn = 4) positions, or atom sets 1, 2–5, and 6–9, respectively, as given in Table II. From Table VIII we see that whereas the eq site is preferred for Pb and Tl^- substitution in Sn_9^{4-}, the lower coordination ba site is preferred for Ge in Sn_9^{4-}. The tabulated Mulliken charges show that Pb or Tl^- substitution is accompanied by electron transfer to the remaining Sn atoms, while Ge substitution is accompanied by electron withdrawal. Substitution of Sn in Ge_9^{4-} is also accompanied by electron transfer from Sn to the remaining framework atoms and shows a preference for the ap site. The charge shifts accompanying Ge substitution are excessive, but there is a consistency between the charge shifts for the series $GeSn_8^{4-}$, Sn_9^{4-}, and $PbSn_8^{4-}$ and the corresponding ^{119}Sn NMR chemical shifts.[26] Specifically the shifts for Na_4GeSn_8 and Na_4PbSn_8 in en are +7.05 and −42.07 ppm relative to Na_4Sn_9 in en, with a positive sign denoting a shift to lower field (higher frequency). Table VIII includes entries for both $TlSn_8^{5-}$ and $TlSn_8^{3-}$. Experimental evidence[26] for the former in solution appears convincing; the high Tl character of its HOMO (38.5%) would lead to rather disparate charges between Tl and Sn for the unreported oxidized form.

Another key feature of an AB_8^{q-} cluster is the shift of the HOMO–LUMO separation relative to that of B_9^{q-}. For $GeSn_8^{4-}$, $PbSn_8^{4-}$, and $TlSn_8^{5-}$, the separations are 3.81, 3.86, and 3.49 eV, respectively, as compared to 4.02 eV for Sn_9^{4-}, while that for $SnGe_8^{4-}$ is 5.70 eV as compared to 5.36 eV for Ge_9^{4-}. The AB_8^{q-} values are all for the respectively preferred substitution sites. The large separation for $SnGe_8^{4-}$ as compared to that for Sn_9^{4-} should lead to a comparatively small paramagnetic contribution to the ^{119}Sn chemical shift for the former cluster. The observed[26] value of −6.56 ppm (upfield) for Na_4SnGe_8 relative to that for Na_4Sn_9, both in en, may reflect such a reduction in the paramagnetic contribution.

There is evidence[37] that a cluster such as Pb_9^{4-} reacts in solution with ethyl halides to form Et_4Pb. The reaction resembles the commercial synthesis of the latter from Na–Pb alloys and EtBr. We carried out a REX calculation on the model system $CH_3Pb_9^{3-}$, in which a CH_3^+ was attached to a cn = 4 site of Pb_9^{4-}. The Pb–C distance was taken as 2.303 Å, the value found[38] by electron diffraction for $(CH_3)_4Pb$. A C–H distance of 1.09 Å and ideal tetrahedral bond angles for the CH_3 group were assumed. As expected, there is a withdrawal of electron density from the framework; computed charges are as follows: H, 0.07+; C, 0.71−; the unique Pb, 0.55+; and the average of the remaining Pb's, 0.33−. The Pb–C bond order is a substantial 0.285. Although exaggerated by the noniterative nature of our MO method, these results do suggest a weakening of framework bonding by alkylation, which, if continued, would lead to a fragmentation of the cluster.

IV. Variation of Electronegativity with Charge

The substitution trends noted in section III resemble those discussed by Rudolph[39] and by Williams[40] for site preferences in boranes and carboranes in that relatively electropositive substituents show a preference for high-cn sites, while relatively electronegative substituents show a preference for low-cn sites. The trends can be related to the effective atomic electronegativities implied by our choices of REX orbital energy parameters. A characteristic of noniterative semiempirical methods such as EHT is the implication of atomic electronegativities that are erroneously independent of the degree of occupancy of orbitals such as the np AO's. By contrast, the relativistic subshell structure associated with the use of different orbital energies for $np_{1/2}$ and $np_{3/2}$ AO's implies an electronegativity with a limited charge dependence even within the restrictions of a noniterative MO scheme. To illustrate this dependence, we first review the generalization of the Mulliken electronegativity scale. It should be noted, however, that this dependence is limited and by no means fully compensates for the shortcomings of a noniterative method.

The electronegativity χ of a chemical species, atomic or molecular, has been defined[41] as the negative of its electronic chemical potential μ, the latter being the derivative of the energy E with respect to the number of electrons N, so that

$$\chi(N) = -\mu(N) = -(\partial E/\partial N)_v \qquad (1)$$

where the subscript v indicates the constancy of the potential. The energy may be taken to a good approximation[42,43] as a quadratic function of N

$$E(N) = a_1N + a_2N^2 \qquad (2)$$

where both E and N are taken to be zero for a neutral species, so that N represents the electron *excess* (positive for an anion, negative for a cation). Calibrating eq 2 by setting $E(-1) = -a_1 + a_2 = \text{IE}$ (ionization energy) and $E(+1) = a_1 + a_2 = -\text{EA}$ (negative of electron affinity) and using ordinary rather than partial derivative notation, we have[41]

$$\chi(N) = -\mathrm{d}E/\mathrm{d}N = (\text{IE} + \text{EA})/2 - (\text{IE} - \text{EA})N \qquad (3)$$

a linear function of N reducing to the familiar Mulliken expression (IE + EA)/2 for a neutral species ($N = 0$). The Mulliken expression may thus be viewed[41] as a finite difference approximation to the derivative $-\mathrm{d}E/\mathrm{d}N$ evaluated at the point $N = 0$, with this approximation being exact, given the quadratic form of eq 2. It should be emphasized that N for an isolated species is a discrete rather than a continuous variable, although in applications to atoms or fragments which are a part of an extended system (molecule) it is taken to be continuous.

Changing the variable to the charge q, which varies as $-N$, we have for the finite difference approximation to the derivative $\mathrm{d}E/\mathrm{d}q$

$$\chi(q) = [E(\mathrm{A}^{q+1}) - E(\mathrm{A}^{q-1})]/2 \qquad (4)$$

where $E(\mathrm{A}^{q+1})$ and $E(\mathrm{A}^{q-1})$ denote energies for the species A with charges $q + 1$ and $q - 1$, respectively. With independent particle models, such as REX or EHT, for which E is a sum of orbital energies, eq 4 reduces to

$$\chi(q) = -(\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2 \qquad (5)$$

where ϵ_{HOMO} and ϵ_{LUMO} are orbital energies for the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular (or atomic) orbitals of the species with charge q. For the group 4B atoms, eq 5 reduces to eq 6, where p* and p denote

$$\chi(q \geq 1+) = -\epsilon_{\mathrm{p}*} \qquad (6\mathrm{a})$$

$$\chi(q = 0) = -(\epsilon_{\mathrm{p}*} + \epsilon_{\mathrm{p}})/2 \qquad (6\mathrm{b})$$

$$\chi(q \leq 1-) = -\epsilon_{\mathrm{p}} \qquad (6\mathrm{c})$$

$p_{1/2}$ and $p_{3/2}$, respectively. For group 3B, relationships 6a–6c hold for $q \geq 0$, $q = 1-$, and $q \leq 2-$, respectively, while for group 5B they hold for $q \geq 2+$, $q = 1+$, and $q \leq 0$, respectively. Values of χ in units of electronvolts are given in Table

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Table IX. Effective Atomic Electronegativities from REX Parameters

element	charge	χ(REX)[a]	χ(EHT)[a]
Ge	$^1/_2-$	7.24	7.34
	0	7.40	
	$^1/_2+$	7.43	
Sn	$^1/_2-$	6.55	6.77
	0	6.80	
	$^1/_2+$	6.99	
Pb	$^1/_2-$	5.98	6.52
	0	6.74	
	$^1/_2+$	7.50	
Tl	$^3/_2-$	4.79	5.23
	1−	5.26	
	$^1/_2-$	5.73	
Bi	$^1/_2+$	7.12	7.78
	1+	8.16	
	$^3/_2+$	9.20	

[a] See eq 1-3; units of χ are eV.

IX; the EHT values also given in Table IX are independent of q but do reflect the order $\chi(\mathrm{Ge}) > \chi(\mathrm{Sn}) > \chi(\mathrm{Pb})$. A division of all χ values by 3.15 would place them on a more customary scale. As mentioned earlier, the slight degree of charge dependence for χ as given by eq 6 is far from adequate; instead of the step change due to the spin–orbit splitting, there should be a greater and continuous variation in $\chi(q)$ due to electrostatics.

As the average atomic charges of $^4/_9-$ and $^5/_9+$ for clusters $A_9{}^{4-}$ and $A_9{}^{5+}$ are approximately $^1/_2-$ and $^1/_2+$, respectively, it is useful to apply the Mulliken definition to fractionally charged atomic species, yielding the general relationship

$$\chi(q) = E(\mathrm{A}^{q+1/2}) - E(\mathrm{A}^{q-1/2}) \qquad (7)$$

holding for half-odd-integral q. There is no division by 2 since the energy difference is that between species differing by only one electron. For $q = {}^1/_2-$, eq 7 reduces to χ = EA. Values of EA as obtained[44] from photodetachment thresholds for gaseous Ge and Sn atoms are 1.2 ± 0.1 and 1.25 ± 0.10 eV, respectively, while the value as obtained[45] from photoelectron spectroscopy for the gaseous Pb atom is 0.365 ± 0.008 eV. These values indicate the ordering $\chi(\mathrm{Ge}) \approx \chi(\mathrm{Sn}) > \chi(\mathrm{Pb})$ for this fractional negative charge, reflecting the large relativistic destabilization of $6p_{3/2}$ (occupied in Pb^-) as compared to that of $5p_{3/2}$ (occupied in Sn^-). Thus relativity reverses for neutral or slightly negative q inequalities such as $\chi(\mathrm{Pb}) > \chi(\mathrm{Sn})$, which obtain for sufficiently positive q. The REX values for $q = {}^1/_2-$ given in Table IX also satisfy $\chi(\mathrm{Sn}) > \chi(\mathrm{Pb})$ but do not have χ(Ge) as close to χ(Sn) as indicated by the empirical EA values or as suggested[26] by the small variations in ^{119}Sn chemical shifts for the series $\mathrm{Sn}_{9-x}\mathrm{Ge}_x{}^{4-}$ as compared to the larger variations for the series $\mathrm{Sn}_{9-x}\mathrm{Pb}_x{}^{4-}$. The large electronegativity difference between negatively charged Sn and Ge implied by our REX parameters is the cause of the exaggerated charge shifts for Sn–Ge clusters (Table VIII). The results for Sn–Pb and Sn–Tl clusters are expected to be more meaningful as the key feature that our REX parameters do reflect in a limited way is the greater rate of change of electronegativity with respect to charge for Tl, Pb, or Bi as compared to In, Sn, or Sb.

V. $A_4{}^{2-}$ and $A_5{}^{2-}$ Clusters

As a final section we present some REX results for smaller clusters of Sn and Pb. The $\mathrm{Sn}_4{}^{2-}$ cluster, characterized by X-ray crystallography[9] and solution NMR,[25,26] was the subject of our recent nonrelativistic effective potential investigation,[33] which led to a prediction of a compressed tetrahedral equilibrium geometry with D_{2d} symmetry characterized by a polar angle of 67° and a Sn–Sn edge length of 3.11 Å. Also predicted was a low-energy barrier (40 kJ mol^{-1}) to pseudorotation through an elongated tetrahedral structure. The observed structure[9] is a distorted tetrahedron characterized by an average Sn–Sn distance of 2.96 Å and by large thermal ellipsoids. As we are unable to optimize bond lengths meaningfully in the REX or EHT procedures, we carried out REX calculations for a series of compressed tetrahedral structures assuming a fixed Sn–Sn distance of 3.0 Å, close to the observed value. We located a minimum-energy structure with a polar angle of 72°, corresponding to a somewhat more flattened tetrahedron than that found by the effective potential method. This minimum was found to be stable with respect to further distortion leading to a C_{2v} symmetry structure.

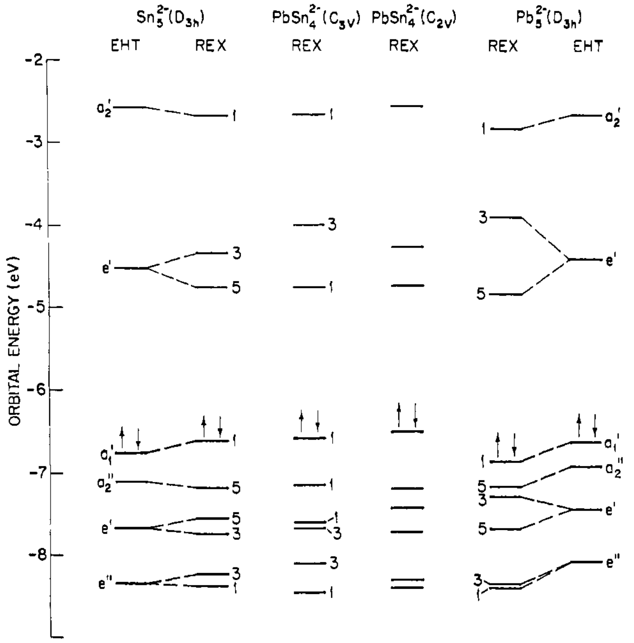

Figure 5. REX and EHT orbital energies for some five-atom clusters. The C_{3v} and C_{2v} forms of $\mathrm{PbSn}_5{}^{2-}$ are apically and equatorially substituted, respectively. The relativistic orbital labels 1, 3, and 5 denote the irreducible representations $e_{1/2}$, $e_{3/2}$, and $e_{5/2}$ of D_{3h}^{*} or $e_{1/2}$ and $e_{3/2}$ of C_{3v}^{*}.

The next clusters considered were the trigonal bipyramidal (D_{3h}) $\mathrm{Sn}_5{}^{2-}$ and $\mathrm{Pb}_5{}^{2-}$ clusters. Using the observed[4] bond lengths of $R_{\mathrm{ap,eq}}$ = 2.89 and $R_{\mathrm{eq,eq}}$ = 3.10 Å for $\mathrm{Sn}_5{}^{2-}$, with corresponding values of 3.00 and 3.24 Å for $\mathrm{Pb}_5{}^{2-}$, we obtained the orbital energies shown in Figure 5, together with REX values for $\mathrm{PbSn}_4{}^{2-}$ with the Pb atom in the ap (C_{3v}) and in the eq (C_{2v}) substitution sites. While the a_1' HOMO of $\mathrm{Sn}_5{}^{2-}$ is slightly raised in going to the REX parameterization, that for $\mathrm{Pb}_5{}^{2-}$ is slightly lowered, reflecting the relativistic stabilizations of both 6s and $6p_{1/2}$ AO's. The spin–orbit splittings of the e'(occupied) and e'(LUMO) levels are 0.15 and 0.42 eV for $\mathrm{Sn}_5{}^{2-}$ and, correspondingly, 0.40 and 0.92 eV for $\mathrm{Pb}_5{}^{2-}$. The equatorial atoms are found to be the more negative, with calculated charges being 0.32− (ap) and 0.45− (eq) for $\mathrm{Sn}_5{}^{2-}$ and 0.27− (ap) and 0.48− (eq) for $\mathrm{Pb}_5{}^{2-}$. A slight (0.07 eV) preference is computed for the C_{3v} or ap substituted form of $\mathrm{PbSn}_4{}^{2-}$ relative to the C_{2v} or eq form. Also negligible is the computed difference (0.05 eV) between the energy of the D_{3h} form of $\mathrm{Sn}_5{}^{2-}$ and the slightly higher value for a C_{4v} form with both $R_{\mathrm{ap,eq}}$ and $R_{\mathrm{eq,eq}}$ taken as 3.0 Å.

We conclude this section with a presentation in Table X of the binding energies (BE) per atom (energies of atomization per atom) for these and the other homonuclear clusters considered in our study. Also included are our values[27] for

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Table X. Binding Energies for Clusters[a]

cluster	symmetry	BE/atom	
		REX	EHT
Ge_9^{4-}	C_{4v}	1.81	2.08
Ge_9^{2-}	D_{3h}	1.88	2.17
Sn_4^{2-}	D_{2d}	2.28	2.90
Sn_5^{2-}	D_{3h}	2.02	2.70
Sn_9^{4-}	C_{4v}	2.02	2.65
Sn_9^{2-} [b]	C_{4v}	2.00	2.62
Pb_5^{2-}	D_{3h}	1.14	2.77
Pb_9^{4-}	C_{4v}	1.25	2.85
Pb_9^{2-} [b]	C_{4v}	1.20	2.80
Bi_4^{0} [c]	T_d	1.48	3.13
Bi_4^{2-} [c]	D_{4h}	1.40	2.85
Bi_9^{5+}	D_{3h}	1.49	3.45
Bi_9^{7+} [b]	D_{3h}	1.33	3.39

[a] BE/atom for $A_n^{q-} \equiv (1/n)[qE(A^-) + (n-q)E(A^0) - E(A_n^{q-})]$, in eV; BE/atom for A_n^{q+} given similarly, with $E(A^+)$ replacing $E(A^-)$. [b] Unknown species. [c] Reference 27.

$Bi_4^0(T_d)$ and $Bi_4^{2-}(D_{4h})$. We note a nearly constant value for all clusters of a given element, although Sn_4^{2-} is especially stable, while Bi_4^{2-} with its slightly antibonding excess electrons is comparatively less stable. Oxidized clusters such as the unknown Pb_9^{2-} and Bi_9^{7+} are also comparatively less stable. Of particular note is the fact that the use of the relativistic parameterization decreases the BE/atom for a given cluster; the percentage decreases from the larger EHT values are approximately 13%, 24%, 56%, and 57% for clusters of Ge, Sn, Pb, and Bi, respectively. This relativistic weakening of homopolar bonds, which we have previously noted,[27] reflects a tendency toward inertness for groups 4B and 5B with increasing atomic number. Similar effects for other groups have been discussed in recent reviews[46,47] and in effective potential studies[48] of Tl_2. By contrast, Hartree-Fock-Slater studies[49] of Au_2 and Hg_2^{2+} as compared to those of Ag_2 and Cd_2^{2+} indicate a relativistic strengthening of bonds for these *ns* and *ns*^{2} elements.

VI. Summary

In this present installment of our series of investigations of the effects of relativity on chemical bonding and structure, we have applied the REX method to the study of a number of charged clusters of Ge, Sn, Pb, and Bi atoms. Particular emphasis has been placed on the properties of both homonuclear and heteronuclear nine-atom clusters. These properties include structural rearrangement energies, charge distributions, and binding energies. The example of substitutional site preferences for heteroatoms is used to introduce a more general discussion of the role of relativity in modifying the variation of atomic electronegativities with atomic charge. Some predictions are made concerning the expected electronic absorption spectra of many of the complexes.

Acknowledgment. We wish to thank Professor R. W. Rudolph (deceased) for many valuable discussions about these heavy-element clusters and for permission to quote some results of his ^{119}Sn NMR investigations prior to publication. We also wish to thank the University of Michigan Computing Center for the use of its facilities.

Registry No. Ge_9^{4-}, 59457-98-6; Ge_9^{2-}, 64826-71-7; Sn_4^{2-}, 78413-16-8; Sn_5^{2-}, 61583-40-2; Sn_9^{4-}, 12597-40-9; Pb_5^{2-}, 58798-64-4; Pb_9^{4-}, 67417-86-1; Bi_9^{5+}, 39448-36-7; $SnGe_8^{4-}$, 76845-90-4; $GeSn_8^{4-}$, 76845-83-5; $PbSn_8^{4-}$, 67660-32-6; $TlSn_8^{5-}$, 76845-91-5; $PbSn_4^{2-}$, 78987-31-2; Sn_9^{2-}, 79068-86-3; Pb_9^{2-}, 79068-85-2; Bi_9^{7+}, 79068-84-1; $TlSn_8^{3-}$, 78987-32-3.

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Molecular Systematics in Metal Tetrathiolenes. A Novel 2-, 4-, 6-, 8-, and 12-Electron-Donating Ligand System upon Coordination to One, Two, Two, Three, and Four Metals, Respectively

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New synthetic and structural evidence has led to a unified pattern of the versatile coordination chemistry of the tetrathiolene ligands: tetrathionaphthalene (TTN, $C_{10}H_4S_4$), tetrachlorotetrathionaphthalene (TCTTN, $C_{10}Cl_4S_4$), and tetrathiotetracene (TTT, $C_{18}H_8S_4$). These ligands can act as, formally, 2-, 4-, 6-, 8-, and 12-electron (*n*e) donors (assumed to be neutral) when coordinated to one, two, two, three, and four metals, respectively. Molecular designs via electronic, steric, and reactivity controls give rise to an unusual array of novel metal tetrathiolene complexes or clusters. This paper reports the preparations, characterization, and chemical and physical properties of the following novel systems: (a) 2e systems, $(Ph_3P)_2(CO)XIr(TCTTN)$ where X = Cl, H; (b) 4e systems, $(Ph_3P)_4Pt_2(TTN)$ (reported elsewhere); (c) 6e systems, $(Ph_3P)_2(CO)_2I_2Ir_2(TCTTN)$; (d) 8e systems, $(Ph_3P)_2Pt(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$; (e) 12e systems, $(Ph_3P)_2(CO)_2H_2Ir_2(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$. Single-crystal X-ray structural determinations revealed that the 2e systems $(Ph_3P)_2(CO)XIr(TCTTN)$ have an octahedrally coordinated iridium with two triphenylphosphines in a trans configuration and an equatorial plane containing two sulfur atoms from TCTTN, the carbonyl group, and the X atom; the molecule as a whole, however, deviates significantly from planarity. High-pressure liquid chromatography using gel permeation was used to help separate and identify the products.

Recently we reported the preparations and structures of two distinctly different bimetallic complexes $(Ph_3P)_4Pt_2(TTN)$[1] and $(Ph_3P)_2(CO)_2Br_2Ir_2(TTN)$[2] based on the tetrathiolene (TTL) ligands:[1-6] tetrathionaphthalene (TTN, $C_{10}H_4S_4$),[7] tetrachlorotetrathionaphthalene (TCTTN, $C_{10}Cl_4S_4$),[8] and

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