

*N,N*-dibenzyl- $\alpha$ -fluoro- $\beta$ -alanine benzyl ester (**4**, Scheme I) in 90% yield.<sup>9</sup> The structure of **4** was established by <sup>1</sup>H and <sup>19</sup>F NMR, IR, and mass spectrometry. Hydrogenolysis of **4** over Pd/C 10% catalyst gave optically active  $\alpha$ -fluoro- $\beta$ -alanine, [ $\alpha$ ]<sub>D</sub> +29.1° (*c* 1.05, H<sub>2</sub>O).<sup>10</sup>

So that stereospecificity of the reaction could be examined, the diastereoisomeric threonine and allothreonine derivatives **2A** and **2B**, respectively, were subjected to the same reaction conditions (the products and yields are given in Table I). Inspection of the NMR spectra of the rearranged fluorinated products obtained indicated that only one diastereoisomer from each reaction (**5A** and **5B**) was formed. The stereochemical purity of the products was confirmed by GLC analysis of their *N*-trifluoroacetyl isopropyl ester derivatives. On the basis of the NMR data of **5A** and **5B** and particularly the chemical shifts of the  $\alpha$  hydrogen, we have assigned the threo configuration to the compound with the signal of higher field (**5A**) and the erythro configuration to the one of lower field (**5B**). In order to confirm this assignment, we subjected the monobenzyl derivative of **5A** to X-ray analysis. The crystal structure established the compound to have the threo configuration.<sup>11</sup>

The same reaction was also used with *threo*- and *erythro*-3-hydroxyleucine<sup>12</sup> derivatives (**3A** and **3B**, respectively) in order to produce the rearranged fluorinated products **6A** and **6B**, respectively. The stereochemical purity of the diastereoisomers **6A** and **6B** was shown by HPLC analysis (over silica SI 100, with CH<sub>2</sub>Cl<sub>2</sub>/hexane (2/3, v/v) as eluent). The assignment of the configuration was based on NMR data (similar to the previous case): **6A**, the threo configuration; **6B** the erythro configuration.

The stereospecificity of this reaction may be rationalized by the intermediacy of an aziridinium ion. The latter is probably formed by initial attack of DAST on the hydroxy group of the amino acid<sup>13</sup> and subsequent cyclization. Opening of the aziridinium ion by fluoride attack at the carbon atom  $\alpha$  to the carboxyl group yields the rearranged product.

Support for the suggested mechanism was obtained when fluorination of the *D*-isoserine<sup>14</sup> derivative **7** with DAST provided  $\alpha$ -fluoro- $\beta$ -alanine in identical yield and optical activity as obtained from *L*-serine, implying a common intermediate (**8**).

In addition, the isolation of both (2*R*,3*R*)-2-dibenzyl-amino)-3-fluorobutyric acid benzyl ester (26%) and  $\alpha$ -fluoro- $\beta$ -amino acid **5A** (60%) from fluorination of *N,N*-dibenzyl-*L*-threonine benzyl ester (**2A**) (see Table I) strongly suggests ring opening at either the  $\beta$  or the  $\alpha$  positions of the aziridinium intermediate.<sup>15</sup>

(8) W. J. Middleton and E. M. Bingham, *Org. Synth.*, **57**, 50 (1977).

(9) A solution of **1** (1.875 g, 5 mmol) in dry THF (10 mL) was added for 20 min to a stirred solution of DAST (0.72 mL, 5.5 mmol) in dry THF (10 mL) at room temperature. The reaction mixture was stirred for a further 30 min, and then ice was added to destroy the excess DAST. The mixture was diluted with EtOAc, washed with 5% NaHCO<sub>3</sub>, and concentrated in vacuo. Chromatography of the residue on silica gel (with 3.5% EtOAc in hexane as eluent) yielded 1.750 g of the rearranged fluorinated product **4**.

(10) The optical purity of **4** is under current investigation.

(11) The full X-ray structure has been established by Dr. F. Frolow and will be reported in a forthcoming publication.

(12) A. Shanzer, L. Somekh, and D. Butina, *J. Org. Chem.* **44**, 3967 (1979).

(13) W. J. Middleton, *J. Org. Chem.*, **40**, 574 (1975).

(14) Y. Shimohigashi, M. Waki, and N. Izumiya, *Bull. Chem. Soc. Jpn.*, **52**, 949 (1979).

(15) The formation of the  $\beta$ -fluoro product with retention of configuration implies neighboring group participation by the dibenzylamino group. DAST fluorination is known to otherwise proceed with inversion of configuration; see T. J. Tewson and M. J. Welch, *J. Org. Chem.*, **43**, 1090 (1978).

The formation of aziridinium ion intermediates in rearrangement reactions<sup>16</sup> and the participation of a carbonyl group in enhancing S<sub>N</sub>2 attack at the  $\alpha$ -carbon atom<sup>17</sup> are known. However, no case of opening of aziridinium ions at the carbon atom adjacent to the carbonyl group has, to our knowledge, been reported.

This method thus provides a useful route for the formation of  $\alpha$ -fluoro- $\beta$ -amino acids from  $\beta$ -hydroxy- $\alpha$ -amino acids in high stereospecificity and high yield. Further experiments are in progress to determine the detailed mechanism and stereochemical pathway of this rearrangement.

Registry No. **1**, 82770-40-9; **2a**, 82770-41-0; **2b**, 82770-42-1; **3a**, 82770-43-2; **3b**, 82770-44-3; **4**, 82770-45-4; **5a**, 82770-46-5; **5b**, 82770-47-6; **6a**, 82770-48-7; **6b**, 82770-49-8; **7**, 82770-50-1; DAST, 38078-09-0; (3*R*,3*R*)-2-(*N,N*-dibenzylamino)-3-fluorobutyric acid, 82770-51-2.

(16) D. R. Crist and N. J. Leonard, *Angew. Chem., Int. Ed. Engl.*, **8**, 962 (1969).

(17) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston: New York, 1959, p 284.

### Synthesis and Structure of Novel Mononuclear and Binuclear Zerovalent Platinum Complexes Involving Coordination by Tin Centers To Give Heteropolymetallic Arrays of Three or Five Atoms. A Unique Bridging Function for Bivalent Tin and a New Class of Platinum(0) Dimers

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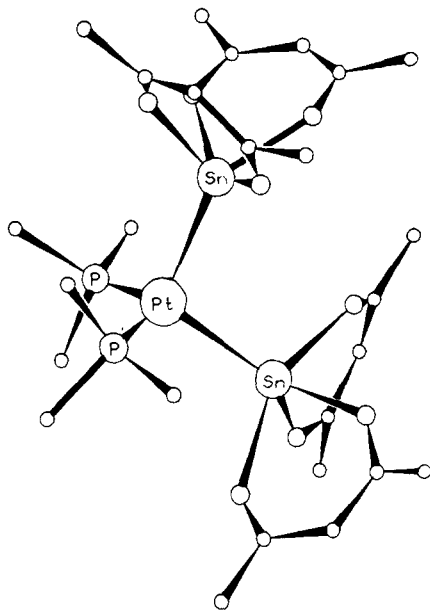
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Metal cluster chemistry is currently an extremely active area of research. This may be attributed<sup>1,2</sup> to (a) the importance of the contribution to bonding theory that has accrued through characterization of novel polyhedral geometries and (b) the potential significance in relation to catalytic applications of the incorporation into a single molecular framework of metal centers having different coordination properties. We describe representatives of two new types of heteropolymetallic species containing platinum and tin, which are related to one another by demonstrating tetrahedral coordination geometry characteristic of zerovalent platinum. Both also embody bivalent tin centers, in one structure as electron-pair donor sites in terminally bound ligating groups and in the other in a highly unusual bridging configuration, i.e., as a bridging stannylene.<sup>3</sup> So far as we are

(1) Ford, P. C.; Ungermann, C.; Laudis, V.; Moya, S. A.; Riuber, R. C.; Laine, R. H. *Adv. Chem. Ser.* **1979**, No. 173, 225. Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, **84**, 959. Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, **79**, 91.

(2) Stobart, S. R.; Dixon, K. R.; Eadie, D. T.; Atwood, J. L.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1980**, **19**, 931. Kraihanzel, C. S.; Sinn, E.; Gray, G. M. *J. Am. Chem. Soc.* **1981**, **103**, 960. Wrobleksi, D. A.; Rauchfuss, T. B. *Ibid.*, **1982**, **104**, 2314. Geoffroy, G. L.; Gladfelter, W. L. *Adv. Organomet. Chem.* **1980**, **18**, 207.

(3) We take the term stannylene to refer to any subvalent tin compound, i.e., Sn(II) derivative, which is monomeric and molecular in character rather than polymeric or ionic in type. Connolly, J. W.; Hoff, C. *Adv. Organomet. Chem.* **1976**, **20**, 1. See also: Ewings, P. F. R.; Harrison, P. G.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1455. Stobart, S. R.; Churchill, M. R.; Hollander, F. J.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1979**, 911.

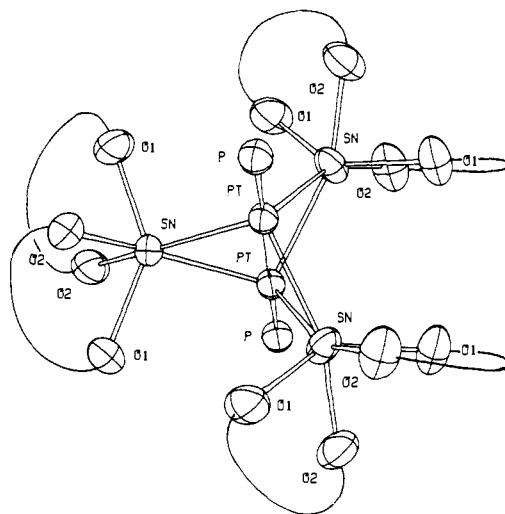


**Figure 1.** Molecular structure of complex 1. Phenyl rings have been omitted for clarity.

aware this second mode of coordination represents a unique situation.

On addition of a hexane solution<sup>4</sup> of  $\text{Sn}(\text{acac})_2$  to  $(\text{PPh}_3)_2\text{Pt}(\pi\text{-C}_2\text{H}_4)$  in benzene,<sup>5</sup> the reaction mixture instantly became yellow. Stirring (4 h) at ambient temperature followed by concentration and addition of hexane afforded pale orange crystals suitable for X-ray diffraction. Subsequently, an identical product (71%) was obtained through reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{Sn}(\text{acac})_2$  (2 equiv) in toluene solution and was formulated as  $(\text{PPh}_3)_2\text{Pt}[\text{Sn}(\text{acac})_2]_2$  (**1**, mp 183–185 °C dec) on the basis of microanalytical data.<sup>6</sup> The <sup>31</sup>P NMR spectrum<sup>7</sup> consisted of a singlet at 110.1 ppm flanked by satellite lines due to coupling with <sup>195</sup>Pt (<sup>1</sup>J = 5252 Hz) and <sup>117,119</sup>Sn (<sup>2</sup>J<sub>av</sub> = 445 Hz); the value of <sup>1</sup>J(Pt–P) confirms the characterization of compound **1** as a Pt(0) derivative, being in fact rather larger than those reported<sup>8</sup> for other zerovalent platinum complexes, including  $\text{Pt}(\text{PPh}_3)_n$  ( $n = 2\text{--}4$ ). The <sup>119</sup>Sn NMR spectrum comprised a triplet ( $\delta$  <sup>119</sup>Sn –601) with triplet sidebands [<sup>1</sup>J(<sup>119</sup>Sn–<sup>195</sup>Pt) = 12891 Hz] and further weak satellites attributable to <sup>117</sup>Sn–<sup>119</sup>Sn coupling (<sup>2</sup>J = 4517 Hz). These data establish that in solution two tin-containing ligands remain attached to Pt in **1** and imply bivalent<sup>9</sup> character for the tin nuclei. The <sup>195</sup>Pt NMR spectrum showed a triplet structure [with appropriate satellites arising from <sup>1</sup>J<sub>av</sub>(<sup>117,119</sup>Sn–<sup>195</sup>Pt)], proving that two phosphine ligands also coordinate the Pt center so that the complex is a four-coordinate species in solution.

The molecular structure<sup>10</sup> of complex **1** is shown in Figure 1. No closely related species exists in platinum group metal chemistry,



**Figure 2.** Molecular structure of complex 2. Carbon atoms have been omitted for clarity.

the zerovalent platinum center being stabilized by metal–metal interaction via electron donation from tin, which is itself subvalent in character. As such, the complex can be viewed as a highly reduced heteropolymetallic aggregate. It also joins a very limited range of compounds in which the geometry expected for four-coordinate  $\text{d}^{10}$  Pt(0) has been confirmed crystallographically,<sup>11–13</sup> with coordination by two  $\text{PPh}_3$  groups and two  $\text{Sn}(\text{acac})_2$  donors, as adduced from the NMR data, distributed around the central Pt atom in a distorted tetrahedral arrangement. The mean Pt–Sn distance is 2.558 (1) Å; the Pt–P bond length at 2.261 (4) Å is substantially shorter than those found in related four-coordinate complexes, being close to Pt–P in <sup>14,15</sup>  $\text{Pt}(\text{PPh}_3)_3$  or  $\text{Pt}(\text{P-}t\text{-Bu}_2\text{Ph})_2$ ; the P–Pt–P angle is wide (120.1°) despite the size of the tin-containing ligands.

Reaction of  $(\text{PPh}_3)_2\text{Pt}(\pi\text{-C}_2\text{H}_4)$  with  $\text{Sn}(\text{acac})_2$  (2 mol equiv) in refluxing toluene resulted in gradual deepening in color of the mixture; cooling after 6 h and concentration afforded a deep orange crystalline complex (**2**, 69%, decomposition point 92 °C). This compound was also isolated after refluxing compound **1** in toluene for 6 h. On the basis of <sup>31</sup>P, <sup>119</sup>Sn, and <sup>195</sup>Pt NMR spectroscopy the product was tentatively formulated as a binuclear platinum species possessing high molecular symmetry with coordination at Pt(0) by a single phosphine ligand and bridging Sn(II) units;<sup>16</sup> exact characterization of such a highly unusual arrangement was sought by using X-ray crystallography. The molecular structure<sup>17</sup> (organic fragments omitted for clarity), which is shown in Figure 2, consists of a trigonal bipyramid with the Pt atoms separated from one another by 2.593 (1) Å and with bond angles P–Pt–Sn = 118.9° and Sn–Pt–Sn = 98.6°. The two apical coordination positions at Pt are occupied by  $\text{PPh}_3$  molecules

(4) 2 mol equiv based on Pt; acacH = acetylacetonate.  $\text{Sn}(\text{acac})_2$  was synthesized as described elsewhere: Bos, K. D.; Budding, H. A.; Bulten, E. J.; Noltes, J. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 961.

(5)  $(\text{PPh}_3)_2\text{Pt}(\pi\text{-C}_2\text{H}_4)$  was prepared by using the published procedure: Blake, D. M.; Roundhill, D. M. *Inorg. Synth.* **1978**, *18*, 120.

(6) The <sup>1</sup>H NMR spectrum ( $\text{C}_6\text{H}_6$ ) contained signals at  $\tau$  3.2–3.8 (15, m), 5.76 (2, s) and 8.70 (12, s) attributable to  $\text{C}_6\text{H}_5$ , CH, and  $\text{CH}_3$  protons, respectively, and the IR spectrum (KBr pellet) showed bands near 1600  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{O})$  and at 1430, 1480  $\text{cm}^{-1}$ , characteristic of  $\text{PPh}_3$ .

(7) All NMR spectra were recorded by using a Bruker WM-250 spectrometer operating at 101.27, 93.28, and 53.27 MHz for <sup>31</sup>P, <sup>119</sup>Sn, and <sup>195</sup>Pt, respectively. Values for *J* are  $\pm 3$  Hz for <sup>31</sup>P and  $\pm 12$  Hz for the two metals. Chemical shifts are in ppm vs. external  $\text{P}(\text{OMe})_3$  (<sup>31</sup>P) and  $\text{SnMe}_4$  (<sup>119</sup>Sn).

(8) Pregosin, P. S.; Kunz, R. W. “<sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Phosphine Complexes”; Springer-Verlag: Berlin, 1979.

(9) For  $\text{Sn}(\text{acac})_2$  we observe  $\delta$  <sup>119</sup>Sn –702. See also: Kennedy, J. D.; McFarlane, W. *Rev. Silicon, Germanium, Tin Lead Compd* **1974**, *1*, 235. Smith, P. J.; Smith, L. *Inorg. Chim. Acta Rev.* **1973**, *7*, 11.

(10) Crystal data for **1**:  $\text{C}_{36}\text{H}_{38}\text{O}_8\text{P}_2\text{Sn}_2\text{Pt}$ ; mol wt 1353.4; orthorhombic; space group *Pca*2<sub>1</sub>;  $a = 19.327$  (5) Å,  $b = 12.811$  (2) Å,  $c = 21.978$  (2) Å;  $Z = 4$ ;  $\rho(\text{calcd}) = 1.649$   $\text{g cm}^{-3}$ ; Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å; Nonius CAD4 diffractometer;  $R = 0.033$  for 1967 observed reflections,  $I > \sigma(I)$ .

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(12) Albano, V. G.; Bellon, P. L.; Manassero, M. *Chem. Commun.* **1969**, 899.

(13) Eller, P. G.; Ryan, R. R.; Moody, D. C. *Inorg. Chem.* **1976**, *15*, 2442. Linsky, J. P.; Pierpont, C. G. *Ibid.* **1973**, *12*, 2959.

(14) Albano, V.; Bellon, P. L.; Scatturin, V. *Chem. Commun.* **1966**, 507.

(15) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

(16) Full analysis of the NMR data for compound **2** is obviously lengthy and will be described in detail elsewhere. In summary the <sup>195</sup>Pt spectrum shows coupling to only one <sup>31</sup>P nucleus with <sup>1</sup>J = 5545 Hz while the <sup>119</sup>Sn spectrum consists of triplets due to coupling to two equivalent <sup>31</sup>P nuclei (<sup>2</sup>J = 168 Hz); solution of the <sup>195</sup>Pt spectrum also establishes the existence of Pt–Pt coupling.

(17) Crystal data for **2**:  $\text{C}_{66}\text{H}_{72}\text{O}_{12}\text{P}_2\text{Pt}_2\text{Sn}_3$ ; mol wt 1865.5; trigonal; space group *R3c*(No. 167);  $a = 17.260$  (6) Å;  $\alpha = 60.56$  (2)°;  $V = 3682$  (3) Å<sup>3</sup>;  $Z = 2$ ;  $\rho(\text{calcd}) = 1.68$   $\text{g cm}^{-3}$ ; Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å; Picker diffractometer;  $R = 0.0399$  for 1150 observed reflections. An absorption correction was calculated by numerical integration. Data collection was to  $2\theta = 40^\circ$ , with 50-s step scans and equal time on background counting.

with Pt-P = 2.224 (4) Å while the three equatorially bridging ligands are symmetrically disposed with Pt-Sn = 2.680 (1) Å and Pt-Sn-Pt = 57.87 (3)°. This beautiful geometry represents the face-sharing of two distorted tetrahedral PPTSn<sub>3</sub> fragments, which constitute a series with the P<sub>2</sub>PtSn<sub>2</sub> configuration (1) and with the corresponding P<sub>3</sub>PtSn species (3), which we have also identified using NMR spectroscopy. The two Pt atoms are within bonding distance,<sup>18</sup> and the strong coupling between them [ $J(\text{Pt-Pt}) = 4663 \text{ Hz}$ ] is consistent with some degree of metal-metal bonding,<sup>19</sup> as is  ${}^2J(\text{P-Pt}) = 82$  and  ${}^3J(\text{P-P}) = 81 \text{ Hz}$ . As for complex 1, nonplanar coordination is characteristic of Pt(0) while the <sup>119</sup>Sn chemical shift (-563 ppm) is indicative of Sn(II). The narrow angle at the latter and the lengthening of Pt-Sn (0.12 Å) between compounds 1 and 2 incline us toward an interpretation based on delocalization of electron density between the five metal centers. Expressed in simple qualitative terms, this situation corresponds to interaction between three hybrid orbitals on each Pt with a single hybrid per Sn to give three bonding, three nonbonding, and three antibonding levels. The Pt(0) nuclei then retain "closed-shell" d<sup>10</sup> character while the Sn(II) atoms each contribute an electron pair to fill the three delocalized bonding orbitals. Superficially there is a resemblance between structure 2 and that of [Me<sub>2</sub>SnFe(CO)<sub>4</sub>]<sub>2</sub>, but the latter clearly incorporates quadrivalent tin and accordingly the angle at Sn is almost tetrahedral<sup>20</sup> with that at Fe quite narrow (77.4°). The electron count in another Sn(IV) derivative<sup>21</sup> [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>Sn<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub> is exact in terms of isolobal relationships<sup>22</sup> for a closo cluster, but delocalized metal-metal bonding tentatively proposed in a somewhat similar platinum-tin(IV) cluster<sup>23</sup> [(C<sub>8</sub>H<sub>12</sub>)<sub>3</sub>Pt<sub>3</sub>(SnCl<sub>3</sub>)<sub>2</sub>] does not appear to have been discussed further. A more realistic molecular orbital description of the intermetallic bonding in compound 2 will necessarily take account of interaction involving overlap of unfilled orbitals of comparable energy with the Pt filled-shell orbitals, similar to that put forward by Dedieu and Hoffmann<sup>24</sup> for unbridged Pt(0)-Pt(0) complexes of the type Pt<sub>2</sub>L<sub>4</sub>.

A comprehensive investigation of the properties of compounds typified by 1-3 is in progress, including development of related Ni and Pd chemistry. Since methanolic solutions containing chloroplatinic acid and stannous chloride provided the first effective catalyst for the reduction of ethylene under ambient conditions<sup>25</sup> and polynuclear Pt-Sn species have been implicated<sup>26</sup> in similar behavior, the possibility that the Pt(0)/Sn(II) systems will demonstrate parallel catalytic reactivity is being explored.

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**Registry No.** 1, 82918-18-1; 2, 82918-19-2; Sn(acac)<sub>2</sub>, 16009-86-2; (PPh<sub>3</sub>)<sub>2</sub>Pt(π-C<sub>2</sub>H<sub>4</sub>), 12120-15-9; Pt(PPh<sub>3</sub>)<sub>4</sub>, 14221-02-4; Pt, 7440-06-4; Sn, 7440-31-5.

**Supplementary Material Available:** Listings of crystallographic data for PtSn<sub>2</sub>(acac)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> and Pt<sub>2</sub>Sn<sub>3</sub>(acac)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub> (29 pages). Ordering information is given on any current masthead page.

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## Effectively Hypervalent First-Row Molecules. 1. Octet Rule Violations by OLi<sub>3</sub> and OLi<sub>4</sub>

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We have discovered computationally a large number of AX<sub>n</sub> molecules comprised of first-row elements whose unusual stoichiometries suggest violations of the octet rule.<sup>1</sup> The equilibrium geometries of these species involve polycoordinated central atoms, A, which therefore appear to have some hypervalent character. This communication deals with preliminary results on two such molecules, OLi<sub>3</sub> and OLi<sub>4</sub>. The former is known experimentally; gas-phase energies are available but not the geometry.<sup>2</sup>

The octet rule is very effective in predicting the optimum stoichiometry of AX<sub>n</sub> first-row molecules if X is hydrogen or an element (or group) toward the right of the periodic table. Thus, addition of a hydrogen atom to an oxygen atom to give the OH radical is exothermic by 101 kcal/mol; addition of a second hydrogen atom to give H<sub>2</sub>O is even better, releasing 118 kcal/mol.<sup>3</sup> However, the hypervalent species OH<sub>3</sub> and OH<sub>4</sub> appear to be only very weak van der Waals complexes between H<sub>2</sub>O and H or H<sub>2</sub>.<sup>4</sup>

If the bonded atom X is lithium rather than hydrogen, the situation is completely different. To illustrate this, we consider the compounds OLi<sub>n</sub> for n = 1-4. Table I gives calculated dissociation energies for OLi<sub>n</sub> → OLi<sub>n-1</sub> + Li. (These results were obtained by minimizing the Hartree-Fock/3-21G<sup>5</sup> energy to give the structure and then using the larger 6-31G\* basis<sup>6</sup> for MP2 correlated calculations<sup>7</sup> at these geometries. Zero-point corrections were made by using harmonic frequencies from the HF/3-21G surface<sup>8,9</sup> (see Table II). Clearly lithium does not respect the octet rule at all! The sequential addition of lithium atoms continues perfectly well after the second step and both OLi<sub>3</sub> and OLi<sub>4</sub> are indicated to be quite stable thermodynamically toward dissociation or loss of an electron. In further work to be described subsequently, OLi<sub>5</sub> and OLi<sub>6</sub> are also indicated to be stable molecules.

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