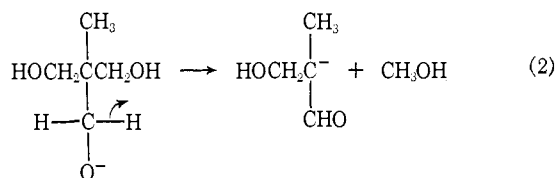
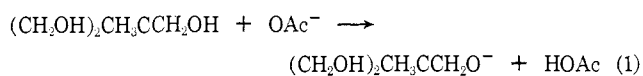


If the mechanism of the exchange were a simple proton transfer, the dianion  $[\text{CH}_2=\text{CO}_2^{2-} \leftrightarrow -\text{CH}_2-\text{COO}^-]$  would be an intermediate, but multicenter or intramolecular mechanisms are also possible.

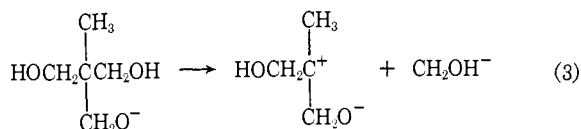
When dissolved in the ternary eutectic at 200°, trimethylolethane ( $\text{R} = \text{CH}_3$ ) and trimethylolpropane ( $\text{R} = \text{C}_2\text{H}_5$ ) decompose to the same products observed when the molten triols are heated at 240–260° with alumina:<sup>8</sup>  $\text{RC}(\text{CH}_2\text{OH})_3 \rightarrow \text{CH}_2=\text{CRCHO} + \text{CH}_3\text{OH} + \text{H}_2\text{O}$ .

The reaction was conducted in a vacuum system at 0.5 mm pressure, and the products were condensed in a cold trap. Trimethylolethane reacts quantitatively, with rate constant  $3.5 \times 10^{-5} \text{ sec}^{-1}$  after a 40-min induction period. The activation energy is low, roughly 7 kcal/mol, so that  $\Delta S^\ddagger$  is large and negative. The reaction is inhibited by acetic acid. The induction period is eliminated when sodium hydroxide, insoluble in the fused salt, is added.

These facts are consistent with a mechanism involving appreciable accumulation of the alkoxide ion (eq 1 and 2). The enolate ion loses hydroxyl ion to form  $\alpha$ -



methylacrolein. The internal displacement by hydride ion (eq 2) is formulated in preference to loss of formaldehyde from the original alkoxide ion. The formaldehyde would have to be quantitatively reduced to methanol before vaporizing from the hot solution into the vacuum; actually, formaldehyde was reduced neither by the fused acetate nor by ethanol or trimethylolethane in the melt. A dissociation to a tertiary carbonium ion and  $\text{CH}_2\text{OH}^-$  (not a known leaving group in ordinary solvents), as in eq 3, was proposed for the



alumina-catalyzed reaction. Assistance by the neighboring alkoxide would yield the epoxide. However, when the reaction was run with  $\text{CH}_3\text{C}(\text{CH}_2\text{OD})_3$ , no deuterium was found in the methyl group of the methanol (nor in the  $\alpha$ -methylacrolein) as would be expected if step 3 took place.

The usefulness of molten acetate eutectics as basic, nonvolatile solvents for high-temperature organic reactions is being investigated further.

**Acknowledgment.** We are very grateful for the support of the U. S. Army Research Office, Durham, N. C.

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Louis L. Burton, Thomas I. Crowell  
Department of Chemistry, University of Virginia  
Charlottesville, Virginia 22901

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## Metal Ion–Aromatic Complexes. VI. Benzene $\pi$ Complexes of Metals of the Third, Fourth, and Fifth Groups

Sir:

As part of a systematic study of metal ion–aromatic complexes, we have prepared and characterized a series of unusual complexes that are of import to the nature of the aromatic–metal bond.

We have previously reported the preparation and crystal structure of  $\text{Ag}(\text{I})$ ,<sup>1</sup>  $\text{Cu}(\text{I})$ ,<sup>2,3</sup> and  $\text{Hg}(\text{I})$ <sup>4</sup> benzene complexes. The first two are nonaxial complexes (*i.e.*, the metal ion does not lie in the sixfold symmetry axis of benzene) in agreement with theoretical predictions; however, the anion plays more than a passive role, as evidenced by the length of the M–Cl bonds. The third involves  $\text{Hg}_2^{2+}$  ions. Rundle and Corbett<sup>5</sup> reported the existence of a benzene complex of  $\text{Ga}(\text{I})$  which in the absence of analytical data was presumed to be the 1:1 complex,  $\text{C}_6\text{H}_6 \cdot \text{GaGaCl}_4$ ; further, they remarked that  $\text{GaAlCl}_4$  also complexes, but  $\text{TlAlCl}_4$  does not. By previously reported methods<sup>1–3</sup> we have prepared two benzene complexes of  $\text{Tl}(\text{I})$ :  $\text{C}_6\text{H}_6 \cdot 2\text{TlAlCl}_4$  and  $(\text{C}_6\text{H}_6)_2 \cdot \text{TlAlCl}_4$ . These are the only known organometallic complexes of  $\text{Tl}(\text{I})$  except for  $\text{TlC}_5\text{H}_5$ .<sup>6</sup> These have been characterized by, at least, duplicate chemical analysis of the inorganic components, and the benzene has been quantitatively determined by vpc after hydrolysis of the complex. *Anal.* Calcd for  $\text{C}_6\text{H}_6 \cdot 2\text{TlAlCl}_4$ : Tl, 49.58; Al, 6.55; Cl, 34.44;  $\text{C}_6\text{H}_6$ , 9.46. Found: Tl, 49.79; Al, 6.66; Cl, 34.48;  $\text{C}_6\text{H}_6$ , 8.31. Calcd for  $(\text{C}_6\text{H}_6)_2 \cdot \text{TlAlCl}_4$ : Tl, 38.62; Al, 5.10; Cl, 26.80;  $\text{C}_6\text{H}_6$ , 29.48. Found: Tl, 37.84; Al, 5.23; Cl, 25.95;  $\text{C}_6\text{H}_6$ , 28.53. Although these chemical analyses are not as accurate as we desire, we had sent samples to two commercial laboratories and they were notoriously poor, and we have performed these analyses ourselves by standard methods. Not only is care necessary to exclude oxygen and water vapor but the aromatic can be lost by prolonged exposure in a drybox. This is particularly true of  $(\text{C}_6\text{H}_6)_2 \cdot \text{TlAlCl}_4$ . These statements apply to the other analyses below. In general, these compounds are either insoluble in nonpolar solvents (except benzene) or the aromatic is stripped off so that further characterization in solution is not possible.  $(\text{C}_6\text{H}_6)_2 \cdot \text{TlAlCl}_4$  can be readily transformed into the more stable  $\text{C}_6\text{H}_6 \cdot 2(\text{TlAlCl}_4)$  under vacuum at ambient temperature. Infrared spectra of fluorocarbon mulls show no absorptions that would indicate a symmetry lower than  $\text{D}_{6h}$  for either of these complexes. This, nevertheless, is not definitive. Preliminary experiments indicate that  $\text{In}(\text{I})$  also forms benzene complexes. We have found no evidence for a 1:1  $\text{C}_6\text{H}_6 \cdot \text{Tl}(\text{I})$  complex.

It is interesting to note that the arguments of Rundle and Corbett based on the charge-transfer theory of Mulliken<sup>7</sup> can be used to predict a symmetric  $\text{C}_{6v}$  ferrocene sandwich-type structure for  $2\text{Bz} \cdot \text{Tl}(\text{I})$  since

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both the highest filled benzene orbitals and the lowest empty Tl(I) ( $p_x, p_y$ ) orbitals belong to the  $e_1$  irreducible representation of  $C_{6v}$  symmetry. These same arguments can be used to predict an inverted ferrocene structure of  $C_6H_6 \cdot 2Tl(I)$ , *i.e.*, metals on the sixfold axis on either side of the aromatic ring. However, these theoretical arguments assume a passive role for the  $AlCl_4^-$  entity, and we have shown that this is anything but the case for  $Ag(I)$ <sup>1</sup> and  $Cu(I)$ <sup>2,3</sup> as well as for the  $ClO_4^-$  ion in  $(C_6H_5C_6H_{11})_2 \cdot AgClO_4$ <sup>8</sup> and  $[m-(CH_3)_2-C_6H_4]_2AgClO_4$ <sup>9</sup>. This is particularly true for the  $(C_6H_6)_2 \cdot TlAlCl_4$  complex since benzene cannot be readily removed from this complex under vacuum at ambient temperature. The most likely structure for the  $C_6H_6 \cdot 2TlAlCl_4$  complex is one in which each Tl(I) coordinates to the aromatic ring as well as with, at least, one halogen of nearby  $AlCl_4^-$  groups.

With the fourth group metals we have prepared  $(C_6H_6)_2Sn(AlCl_4)_2$  and  $(C_6H_6)_2Pb(AlCl_4)_2$  by the same methods. *Anal.* Calcd for  $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$ : Sn, 19.38; Al, 8.81; Cl, 46.32;  $C_6H_6$ , 25.48. Found: Sn, 18.85; Al, 9.19; Cl, 45.78;  $C_6H_6$ , 25.81. For this compound we have also been able to obtain single crystals for preliminary X-ray diffraction data and found the crystals to be monoclinic with  $a = 11.92 \text{ \AA}$ ,  $b = 17.46 \text{ \AA}$ ,  $c = 11.32 \text{ \AA}$ ,  $\beta \sim 90^\circ$ , and space group  $P2_1/n$ . With four  $(C_6H_6)_2Sn(AlCl_4)_2$  units per cell, the calculated density is  $1.73 \text{ g cm}^{-3}$  compared to the observed value of  $1.76 \text{ g cm}^{-3}$  found by flotation in a carbon tetrachloride–bromoform mixture. Hence, the molecular weight is that of  $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$  well within experimental error (1.7%). Mössbauer spectra<sup>10</sup> show a single line with an isomer shift of 1.6 mm/sec relative to  $Mg_2Sn$  as zero with no observable quadrupole splitting. The fluorocarbon mull infrared spectra give no indication of any symmetry less than  $D_{6h}$ . *Anal.* Calcd for dibenzene  $\cdot Pb(II)$  complex,  $(C_6H_6)_2Pb(AlCl_4)_2$ : Pb, 29.57; Al, 7.70; Cl, 40.47;  $C_6H_6$ , 22.27. Found: Pb, 28.81; Al, 7.60; Cl, 40.59;  $C_6H_6$ , 22.43. Preliminary X-ray single-crystal diffraction data show the crystals of this compound to be triclinic with  $a = 14.1 \text{ \AA}$ ,  $b = 8.76 \text{ \AA}$ ,  $c = 15.3 \text{ \AA}$ ,  $\alpha \sim \beta \sim \gamma \sim 90^\circ$ . With four  $(C_6H_6)_2 \cdot Pb(AlCl_4)_2$  entities per cell, the calculated density is  $1.96 \text{ g cm}^{-3}$  compared to the observed value of  $1.93 \text{ g cm}^{-3}$  measured by flotation in a carbon tetrachloride–bromoform mixture. The molecular weight is not as clear cut as in the case of  $(C_6H_6)_2 \cdot Sn(AlCl_4)_2$  because of the low crystal symmetry but is consistent with  $(C_6H_6)_2 \cdot Pb(AlCl_4)_2$ . As with the Tl(I) complexes no evidence is found in the infrared fluorocarbon mull spectra of an environment about the metal ion of symmetry lower than  $D_{6h}$ . Since these two compounds are isoelectronic in the valence shell with Tl(I), the same theoretical formalism is applicable and predicts a  $C_{6v}$  ferrocene sandwich-type structure. All the available evidence points to a symmetrical  $D_{6h}$  sandwich structure for  $(C_6H_6)_2M(AlCl_4)_2$  where M is Sn(II) and Pb(II). However, a quadrupole splitting should be observed in the Mössbauer spectra of  $(C_6H_6)_2Sn(AlCl_4)_2$  due to the fact that the sandwich structure has a point group symmetry lower than cubic. Nevertheless, there exist numerous examples where Sn does not show

a Mössbauer quadrupole splitting in low-symmetry environments if the atoms bonded directly to Sn have no unpaired electrons.<sup>11</sup> This is to our knowledge the first report of a  $\pi$  complex of Sn(II). In contrast, the structure of bis(cyclopentadienyl)tin(II) is generally accepted as that of a  $\sigma$ -bonded molecule.<sup>12</sup>

With the fifth-group metals we have prepared  $C_6H_6 \cdot BiCl_2AlCl_4$ . *Anal.* Calcd for  $C_6H_6 \cdot BiCl_2AlCl_4$ : Bi, 39.68; Al, 5.12; Cl, 40.39;  $C_6H_6$ , 14.81. Found: Bi, 38.92; Al, 4.96; Cl, 39.66;  $C_6H_6$ , 14.21. This formulation of a  $BiX_2^+$  ion is supported by the fact that the phase diagram of  $BiBr_3-AlBr_3$  shows the existence of a 1:1 compound.<sup>13</sup>

A reasonable view of the  $BiCl_2^+$  ion is that of an ion with an empty 6p orbital that can accept electrons from the  $e_1$  MO's of benzene. This would lead to the prediction that the Bi atom would be located above a carbon-carbon bond of the benzene ring with the empty orbital pointed toward the  $\pi$  orbitals of the ring. Again, the interaction of the anion may well change this over-simplified picture.

It would be expected that the infrared spectra of this compound would show significant lowering of the symmetry of the local environment of the benzene ring. No indications of lower symmetry have been found. However, infrared investigations of complexes that have been shown by X-ray crystallography to have lower symmetry about the aromatic ring have been equally uninformative, *e.g.*,  $C_6H_6 \cdot AgClO_4$ .<sup>14</sup>

Antimony and arsenic do not form similar complexes and the only benzene complexes we have been able to isolate up to this time are  $C_6H_6 \cdot 2SbCl_3$  and an analogous arsenic compound which were reported earlier by other workers.<sup>14</sup>

In general, the aromatic complexes of metal ions are less stable than the olefin complexes, and we predict that stable olefin complexes are possible for these ions. Experiments are under way in this direction.

We believe these are the first aromatic complexes reported of the above elements. The crystal structures of these compounds are under investigation in our laboratory at this time.

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Th. Auel, E. L. Amma

Department of Chemistry, University of South Carolina  
 Columbia, South Carolina 29208

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### The Oxidation of Platinum(II) Complexes by Hexachloroiridate(IV). Evidence for the Intermediate Formation of Platinum(III)

Sir:

The intermediate formation of platinum(III) in solution has been postulated in various reactions involving the platinum(II)–platinum(IV) redox couple, notably in certain photochemical and catalyzed substitution reactions of platinum(IV) complexes.<sup>1–3</sup> The

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