is a composite quantity of bonding and solvation effects where the negative contribution of Hg–Cl bond formation is more than compensated by the positive effects of Rh–Cl bond stretching and H_2O release. In addition, a "dilution of the 2+ charge" over the entire bridged complex would cause a reduction in electrostriction and consequently a small positive contribution to ΔS and ΔV.

The dissociation of the precursor complex, eq 2, exhibits a lower $\Delta H^{\ddagger}$ value than for the uncatalyzed reaction (cf. $\Delta H^{\ddagger} = 137 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -80 \pm 9$ J K^{-1} mol^{-1})[6] presumably due to a weakening of the Rh–Cl bond in the bridged species and also it shows a higher $\Delta S^{\ddagger}$ value because no new charge is created during the process. The large $\Delta H^{\ddagger}$ and a $\Delta S^{\ddagger}$ of almost 0 tend to favor a dissociative mechanism involving only Rh–Cl bond breaking. The positive $\Delta V^{\ddagger}$ value is also consistent with this mechanism, particularly as the corresponding values for the aquation of $RhCl_6^{3-}$ and $RhCl_5(OH_2)^{2-}$ are 21.5 ± 1.6 and 14.3 ± 0.5 cm^3 mol^{-1} (20 °C and $\mu = 4$ M).[8]

The $HgCl^+$ cation has catalytic activity almost identical with that of Hg^{2+} so that its increasing presence during the reaction should not affect the kinetics adversely. Indeed, the close similarity in activity helps to maintain pseudo-first-order conditions throughout the reaction even at the lowest Hg^{2+} concentrations. As may be expected, $HgCl_2$ exhibits only a slight catalytic effect with $k_{obsd} = 5 \times 10^{-5}$ s^{-1} at $[HgCl_2] = 5 \times 10^{-2}$ M at 28 °C.

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Registry No. *mer*-$RhCl_3(OH_2)_3$, 54630-78-3; Hg, 7439-97-6.

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B 1s Binding Energies in $MBPh_4$, Where M Is Na, K, Rb, Cs, and NH_4

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The purpose of this note is to describe the results of an X-ray photoelectron spectroscopy (XPS) study of the B 1s binding energy (BE) shifts in a series of tetraphenylborates, $MBPh_4$ where M is Na, K, Rb, Cs, and NH_4, which are isostructural.[1-5] It was anticipated that progressively increasing BE shifts would be observed on going from Na to Cs, as has been observed in similar studies.[6]

Samples of each compound were obtained as crystals, which were then ground to a fine powder and examined in a Vacuum Generators ESCA 3 photoelectron spectrometer. Several different support materials were tried (gold mesh, indium foil, silver paint, and adhesive tape), and each method gave essentially identical binding energies. Some sample discoloration after X-irradiation (300 W, 1 h) was noted for $NaBPh_4$ and NH_4BPh_4 and correlated with the appearance of a small shoulder on the high-BE side of the Na 1s, B 1s, and N 1s peaks. The samples were apparently stable to ultra-high vacuum in the absence of X-irradiation.

Table I. BE[a] Results and Selected Cation Properties[b] for $MBPh_4$

compd	B 1s, eV	C 1s, V	Δ, eV	cation ionic radius, Å	cation electronegativity
$NaBPh_4$	187.4	284.7	97.3	0.95	0.9
$KBPh_4$	186.7	283.0	96.5	1.33	0.8
$RbBPh_4$	186.5	283.2	96.5	1.48	0.8
$CsBPh_4$	189.6	285.5	96.5	1.69	0.7
NH_4BPh_4	187.9	284.4	95.9	1.43	

[a] Reproducibility for three determinations was ±0.15 eV.
[b] Obtained from "Handbook of Chemistry and Physics", 51st ed., Chemical Rubber Co., Cleveland, OH, 1970.

Average BE values for the C 1s and B 1s are given in Table I. The data were treated in terms of the relative shift of C 1s to B 1s, $\Delta = BE_{C\,1s} - BE_{B\,1s}$, which is independent of charging effects. Because the series of compounds $MBPh_4$ is isostructural, crystal field effects should be limited to those caused by the changing cation. The fairly large spacing between the B atom and the cations makes the choice of the boron atom as an internal reference a reasonable one. The size of the BPh_4 anion precludes large-scale model calculations on the $MBPh_4$ system, especially considering the rather narrow range of BE shifts observed. Thus an interpretation of trends in the data in terms of empirical parameters was considered.

The point-charge approximation for XPS chemical shifts,[7] in terms of Δ defined above, may be written: $\delta\Delta = k\delta q + \delta V + \delta R$, where k is a constant, q is the charge on the host atom, V the external (crystal) potential energy, and R the relaxation energy, which may be considered as a sum of intra- and extraatomic terms. In general, δq and δV, where the change δ here is relative to $NaBPh_4$, have opposite sign for a given atom, but for the $MBPh_4$ series, δV should be dominated by changes in cation and be small compared to δq. The relaxation contribution, δR, should have the same sign as δq since it describes the adiabatic collapse of electronic charge toward the core hole following photoionization. Although this term cannot be evaluated directly, the relative contribution of δR to $\delta\Delta$ should approximate that of δq.

Overall, therefore, it is expected that Δ should decrease as cation size increases. Table I illustrates that this is, in general, the observed result. It had been expected that the relative shift for $RbBPh_4$ should lie between that of $KBPh_4$ and $CsBPh_4$. Cation size and empirical electronegativity values, listed in Table I, show a reasonable correlation with Δ, suggesting a decrease in anion–cation charge transfer as cation size is increased. This decrease implies a decrease in δq from Na to Cs and probably a decrease in δR, which should also be strongly influenced by the ability of the cation to neutralize a core hole, although this might be offset somewhat by the varying energy of the core hole on going from Na to Cs. Although these results are basically in agreement with what might be expected on the basis of simple parameters such as electronegativity and ionic size, the relatively small shifts observed preclude detailed examination at this stage. One further note is that the coincidence of Δ values for the Rb, NH_4, and K salts may be interpreted as indicating similar charge transfer in $MBPh_4$ from the anion to the cation for these cations. However, the lack of discrimination of XPS in this case may also mask changes in δR that effectively compensate for the anticipated trend in q on going from Na to K, Rb, Cs, and NH_4.

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Registry No. $NaBPh_4$, 143-66-8; $KBPh_4$, 3244-41-5; $RbBPh_4$, 5971-93-7; $CsBPh_4$, 3087-82-9; NH_4BPh_4, 14637-34-4.

Contribution from the Materials Science Center and the Department of Chemistry, Cornell University, Ithaca, New York 14853

Electrochemistry in Liquid Sulfur Dioxide. A New Synthesis of Hg_3AsF_6 and Hg_3SbF_6

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In a shared domain of chemistry and physics, low-dimensional synthetic metals such as TTF·TCNQ, Hg_3MF_6 (M = As, Sb), and $K_{1.75}Pt(CN)_4$ (KCP) have received considerable attention recently.[1-4] Redox-based synthetic procedures have generally been chemical in nature[5] although KCP has been prepared electrochemically;[6] an electrochemical preparation of a series of synthetic metals formed between an aromatic hydrocarbon (e.g., naphthalene, fluoroanthene, perylene) and a complex anion (MF_6; M = P, As, Sb, Bi) was recently reported,[7] and polyacetylene has been doped with AsF_6^- by an electrochemical method.[8] Although MF_6^- species are known for elements from many regions of the periodic chart,[9,10] further examples of mercury-chain compounds have not been forthcoming. With the goal of producing new mercury-chain compounds, we chose to employ the selectivity of electrochemical oxidation and hoped also to avoid the frequently intractable byproducts found in chemical preparations (e.g., SbF_3). We now report the synthesis of Hg_3AsF_6 and Hg_3SbF_6 at a mercury anode in liquid SO_2 solutions of the hexafluorometalates. Previous methods involve oxidation of Hg metal in liquid SO_2 by AsF_5 (or SbF_5) or $Hg_3(AsF_6)_2$ (or $Hg_3(Sb_2F_{11})_2$).[11,12] Another series of inorganic/organometallic mercury compounds, $Hg(M)_2$ (M = $Mn(CO)_5$, $Re(CO)_5$, $Fe(C_5H_5)(CO)_2$, or $Mo(C_5H_5)(CO)_3$) have also been prepared electrochemically.[13,14] The chemistry[15] and electrochemistry[16] of SO_2 solutions have been reviewed[17] and some recent voltammetric studies of $(CH_3)_4N^+$ [18] and $(C_6H_5)_3C^+$ [19] solutions indicate that trityl salts may have particular utility as electrolytes in SO_2.

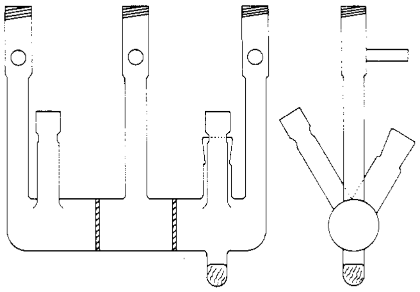

Figure 1. Front and end views of the electrochemical cell.

Experimental Section

Materials. SO_2 (Matheson) was drawn from the cylinder as a liquid and distilled from P_2O_5 under argon. Triple-distilled mercury (Merck) was used as received. $(CH_3)_4NAsF_6$ was prepared from $(CH_3)_4NOH$ (Aldrich) and $HAsF_6·6H_2O$ (Ozark-Mahoning) in methanol and purified by a literature method.[20] $(C_6H_5)_3CSbF_6·BF_3$ was prepared in situ from SbF_5 (Alfa) and $(C_6H_5)_3CBF_4$ (Alfa). $(CH_3)_4NPF_6$ was prepared by a method analogous to that for $(CH_3)_4NAsF_6$. $(CH_3)_4NMoF_6$ was prepared from $(CH_3)_4NI$ (Eastman) and MoF_6 (Pfaltz & Bauer) in SO_2 after the method of Hargreaves and Peacock;[21] the white solid was dissolved in SO_2 to afford a clear colorless solution which, upon saturation with BF_3, turned yellow. Except for the preparation and purification of $(CH_3)_4NAsF_6$ and $(CH_3)_4NPF_6$ (which are not hydrolyzed), all manipulations were performed in flame-dried glassware under purified argon atmospheres.[22] A PAR Model 173 potentiostat supplied the constant potential. Current was monitored with a Hewlett-Packard Model 7128A strip chart recorder.

The Cell (Figure 1). The electrolysis cell employed in these reactions consisted of a horizontal 140-mm (25-mm o.d.) Pyrex tube divided into three chambers (50, 40, and 50 mm) by two 20-mm sintered glass frits (M porosity). Three 75-mm stems (10-mm o.d.) emerged vertically from the top (one from each end, one from the center) and were capped by Rotaflo TF2/18 (0–8 mm) Teflon stopcocks, from which parallel 20-mm stems (7-mm o.d.) extended to the rear. The anode chamber had a 12-mm i.d. × 20-mm deep well and also two 10-mm o.d. necks 50 mm long tilting 30° from vertical (one forward, one back) which terminated with O-ring adapters. The cathode chamber had one similar tube tilting forward. The three 7-mm stems were connected by short pieces of butyl tubing to a yoke possessing a male 10/30 ₮ joint. Its mate had a glass-to-metal seal which was connected by Swagelock fitting to $^1/_4$-in. copper tubing leading to a T-bore stopcock atop a 90-cm capillary tube Hg bubble/manometer. The third stopcock arm was connected via butyl tubing to the argon/vacuum manifold.[22]

The working electrode consisted of 20 g of Hg in the well into which was immersed a glass-sealed platinum-wire electrode. The Ag/AgCl reference electrode was a coiled 0.020-in. Ag wire shielded in a 7-mm glass tube plugged with glass wool and possessing a small vent 2 cm from the end. The wire was oxidized by a $1^1/_2$ V dry cell in 1 M HCl for 1 min. The wire was sealed at the external end in a 5–10 mm thick epoxy plug (Torr-seal). The counterelectrode was a 5 mm × 20 mm × 0.025 mm Pt foil welded to a glass sealed 0.030-in. Pt wire. All three electrodes were sealed with Viton O-rings.

Electrochemical Syntheses. The electrolysis cell was set up as described above and carefully vacuum tested (<0.003 T) and then flamed dry. The stopcocks were replaced by septa under argon flush,

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