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A Simplified Synthesis of the hexamethylplatinate(IV) ion.

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Summary

Tetra-n-butylammonium hexachloroplatinate (IV) reacts with lithium methyl/lithium iodide in ether to give a solution containing lithium hexamethylplatinate (lV). With lithium methyl/lithium bromide in ether however, tetrabutylammonium hexamethylplatinate (IV) is precipitated together with lithium halides. Solid $[Bu_4N]_2[Pt(CH_3)_6]$ is stable under nitrogen at room temperature, but ether solutions of $[Pt(CH_3)_6]^{2-}$ decompose in a few minutes at room temperature in the absence of excess lithium methyl.

The hexamethylplatinate(IV) ion as a solution of its lithium salt in ether has recently been prepared by the reaction of halide-free lithium methyl with trimethylplatinum(IV) halides, $[Pt(CH_3)_3X]_4$ (X=Cl,I) [1,2]. Although the preparation of trimethylplatinum(IV) iodide has been greatly improved by the method of Baldwin and Kaska, [3], we now find that it is unnecessary to proceed to the hexamethylplatinate ion *via* isolation of this halo-methyl intermediate, or to use halide-free lithium methyl, and we here report a simplified route to the formation of the $[Pt(CH_3)_6]^{2-}$ anion directly from tetra-n-butylammonium hexachloroplatinate(IV).

Results and Discussion

Addition of an ether solution of lithium methyl/lithium iodide to a stirred slurry of tetrabutylammonium hexachloroplatinate(IV) in ether at

-78° gives a colourless solution of lithium hexamethylplatinate(IV), on warming to room temperature and filtering off precipitated lithium and tetrabutylammonium halides. The ^{1}H NMR and Raman spectra of this solution, which is stable at room temperature in the presence of excess lithium methyl, are in agreement with the spectra reported by Rice and Tobias [2], and the ^{195}Pt {^{1}H} spectrum shows a singlet due to $[Pt(CH_3)_6]^{2-}$ at δ = 358.3 p.p.m. (δ = 0 at 21.4 MHz when the ^{1}H resonance of $(CH_3)_4Si$ is at 100 MHz). A suspension of $K_2[PtCl_6]$ in ether reacts similarly with lithium methyl/lithium iodide solution, but starting with this salt the reaction requires stirring for 1-2 days at room temperature, and is accompanied by partial decomposition to platinum black.

The analogous reaction of $[Bu_4N]_2[PtCl_6]$ with lithium methyl/lithium bromide in contrast shows no sign of the ^{1}H resonance of the $[Pt(CH_3)_6]^{2-}$ ion in the resulting ether solutions. In this case the reaction proceeds to precipitate tetra-n-butylammonium hexamethylplatinate(IV), which is insoluble in ether, together with some lithium halide. This product is stable under nitrogen at room temperature and was characterized as substantially $[Bu_4N]_2[Pt(CH_3)_6]$ from its Raman spectrum [$\nu(Pt-CH_3)=509 cm^{-1}$] We were however unable to free this product completely of lithium halide by repeated washing with ether, and attempts to purify it by recrystallization at 0° from dichloromethane, nitromethane, acetonitrile or acetone also failed due to rapid decomposition in these solvents to platinum black.

The difference in the products of the reaction of $[Bu_4N]_2[PtCl_6]$ with lithium methyl/lithium iodide from those obtained with lithium methyl/lithium bromide appears to be due to the low solubility in ether of $[Bu_4N]I$, which precipitates from the reaction in the presence of iodide ions as the least soluble salt. This was confirmed by stirring the impure $[Bu_4N]_2[Pt(CH_3)_6]$, prepared by use of lithium methyl/lithium bromide, with a solution of anhydrous lithium iodide in ether at 0°, when solid $[Bu_4N]I$ was formed and $[Pt(CH_3)_6]^{2-}$ passed into solution. The resulting solution of $Li_2[Pt(CH_3)_6]$ could be stabilized by addition of lithium methyl, but in the absence of added CH_3Li it decomposed to platinum black in a few minutes at room temperature.

The reaction of lithium methyl with $K[AuCl_4]$ to give $Li[Au(CH_3)_4]$ has also been reported [4], but the reactions of lithium methyl with salts of the numerous other transition metal halogeno-anions have apparently been relatively little explored. Our observations relating to hexachloroplatinates, and preliminary observations on the reaction of lithium methyl with salts of the $[CuCl_4]^{2-}$ ion, suggest that this reaction is facilitated by use of tetraalkylammonium salts of the halogeno-anions rather than of alkali metal salts of these anions.

Experimental

All reactions were carried out under dry nitrogen or argon using Schlenk tube and syringe techniques. $[n\text{-}Bu_4N]_2[PtCl_6]$ was precipitated by addition of tetrabutylammonium chloride to an aqueous solution of potassium hexachloroplatinate(IV), and dried at 50° overnight. Anhydrous lithium iodide solution was prepared by reacting lithium metal with iodine in ether. Solutions of lithium methyl in ether were prepared from lithium metal and methyl bromide or iodide under argon, and were shown by analysis to contain approximately equimolar amounts of lithium methyl and lithium halide [5].

In a typical methylation of $[PtCl_6]^{2-}$, lithium methyl/lithium iodide solution (13 ml of 0.524 M solution in ether; 6.8 mmol.) was added dropwise to a slurry of tetra-n-butylammonium hexachloroplatinate(IV) (0.675g.; 0.76 mmol.) in 2 ml. ether at −78°. The mixture was allowed to warm to room temperature and the precipitated lithium and tetrabutylammonium halides were removed by filtration, to yield a colourless solution of $Li_2[Pt(CH_3)_6]$ containing excess lithium methyl.

References

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