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# A Novel Method for the Synthesis of Platinum(II) Complexes of Ditertiary Arsines

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We report here a new method of preparation of platinum(II) complexes of ditertiary arsines starting from the solid potassium tetrachloroplatinate and the appropriate ligand in chloroform solution and subsequently, the exchange of chloride ion by the desired halogen or pseudohalogen, the latter being present as the insoluble sodium salt.

Previous methods of preparation of bidentate phosphino [1], arsino [2], stibino [3] and bismuthino [4] ligand complexes of nickel(II), palladium(II) and platinum(II) have involved either the addition of metal chloride in an alcohol to a solution of the appropriate ligand in chloroform or dichloromethane, or the addition of the ligand to a solution of the metal chloride in an alcohol followed by reflux. The resulting solutions were, in both cases, treated with an excess of the appropriate sodium halide or pseudohalide to yield the desired product. However, these methods may result in contamination of the product by unreacted metal chlorides that remain in solution as the chloro complexes and which may prove to be difficult to separate from the desired bromo, iodo or thiocyanato derivatives. The procedure outlined here eliminated the need for more than one solvent and, more importantly, ensures that there is no contamination from the chloro derivative, since the starting tetrachloroplatinate is insoluble in chloroform. We observe in our attempts to complex long-chain diarsines to $K_2PtCl_4$ that no reaction occurs until addition of the appropriate NaX (X = Br, I, SCN), even when the initial mixture is stirred for four days at room temperature or for eight hours under reflux. In contrast, when sodium halide or pseudohalide is added, immediate reaction occurs; the colourless solution of the ligand in chloroform takes on the colour characteristic of the desired complex and the tetrachloroplatinate passes smoothly into solution leaving behind the insoluble sodium chloride and excess sodium halide/pseudohalide. After filtration the complex in solution can be isolated simply by reduction in volume of the chloroform until precipitation occurs. By using an excess of the tetrachloroplatinate as compared with the ligand, no excess ligand is left in solution after exchange; hence the method provides a quick and clean route for the preparation of complexes from solution in an extremely pure form.

The method has wide applications for use in preparative coordination chemistry in situations where the solid metal chlorides do not react with ligands in solution above them and where the products of halogen exchange have to be obtained in an extremely pure form. The precise mechanism of complex formation under exchange conditions is not known but is currently under investigation.

## Experimental

1 mm of $K_2PtCl_4$ is placed in a clean dry 50 $cm^3$ round bottom flask and to this is added 1 mm of the appropriate ligand ($Ph_2As(CH_2)_xAsPh_2$, x = 10, 12) in 30 ml of chloroform. The mixture is stirred and a large excess of the appropriate sodium halide or pseudohalide NaX is added (X = Br, I, SNC). The mixture is stirred for 30 minutes, filtered and the resulting filtrate is reduced in volume to precipitate the desired complexes, $PtLX_2$.

## References

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