

Hydrido(triphenylphosphine) and Hydrido(triphenylarsine) Complexes of Iridium(I)

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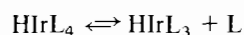
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In spite of the quite easy preparation of $\text{HRh}(\text{PPh}_3)_4$ ¹⁻⁴ and $\text{HRh}(\text{PPh}_3)(\text{AsPh}_3)_3$ ² the related iridium complexes, $\text{HIr}(\text{PPh}_3)_4$ (I) and $\text{HIr}(\text{AsPh}_3)_4$ (II), have not yet been prepared, even though there is no reason for this lack. During studies on the polarographic behaviour of rhodium(III) and iridium(III) hydrido complexes we have found that the electrochemical reduction proceeds *via* a two-electron uptake to yield the final metal(I) hydride.⁵ Thus our efforts have been focused on attempts to prepare by this procedure the new hydrido-complexes (I) and (II). On the other hand, the electrochemical reduction method has been confirmed as a simple and reliable procedure for the preparation of metal hydrides.⁶⁻⁸

Controlled potential electrolysis at about -2.2 V vs. SCE on the Hg electrode (at room temperature) of $\alpha\text{-HIrCl}_2\text{L}_3$ ($\text{L} = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}$) in acetonitrile/benzene (75/25 v/v) with tetraethylammonium perchlorate as supporting electrolyte and in the presence of a five-fold excess of the ligand produced the precipitation of a green-yellow crystalline solid. At the end of electrolysis the precipitate was separated, washed with acetonitrile and dried under vacuum. All the operations were performed under argon.

Both phosphine and arsine recovered compounds are air stable for several weeks in the solid phase but solutions decompose within minutes. Their infrared spectra (KBr disk) show a sharp peak at 2245 cm^{-1} (I) and 2220 cm^{-1} (II) assigned to the stretching mode $\nu(\text{Ir-H})$. The corresponding deuterido-complex obtained by the same procedure starting from

$\text{DlIrCl}_2(\text{PPh}_3)_3$ shows the Ir-D stretching shifted to 1610 cm^{-1} ($\nu_{\text{Ir-H}}/\nu_{\text{Ir-D}} \cong 1.4$). The elemental analyses fit very well with the formulas $\text{HIr}(\text{PPh}_3)_4$ and $\text{HIr}(\text{AsPh}_3)_4$. Calcd. for $\text{IrC}_{72}\text{H}_{61}\text{P}_4$: C, 69.61; H, 4.95; P, 9.97%. Found: C, 69.45; H, 4.91; P, 10.15%; mp $180 - 182^\circ\text{C}$ (decomp.). Calcd. for $\text{IrC}_{72}\text{H}_{61}\text{As}_4$: C, 69.98; H, 4.33; As, 21.13%. Found: C, 70.14; H, 4.29%; mp $220 - 225^\circ\text{C}$ (decomp.). These hydrides are moderately soluble in common organic solvents. Cryoscopic measurements suggest that they are dissociated in solution according to the equation



With this behaviour NMR measurements cannot give meaningful structural results. A similar phenomenon has been observed also for the complex $\text{HRh}(\text{PPh}_3)_4$.¹

The complexes react in benzene with the stoichiometric amount of HCl to give H_2IrClL_3 .

Further evidence supporting the correct formulation of the complexes as HIrL_4 can be derived by analogy with the electrochemical pattern of the related rhodium compound, $\text{HRhCl}_2(\text{PPh}_3)_3$. In this case the two-electron reduction product was identified as $\text{HRh}(\text{PPh}_3)_4$ by comparison with an authentic sample prepared according to Dewhirst *et al.*¹

Attempts to obtain crystals for X-ray investigations have failed.

References

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