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A Simple Preparative Route to the Complexes *trans*-[PtHCl(P(*p*-XC$_6$H$_4$)$_3$)$_2$] Involving Tin(II) Chloride and Hydrogen

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Platinum hydride complexes are recognized to be important intermediates in the homogeneously catalysed hydrogenation of unsaturated organic compounds by platinum salts [1]. Indeed, there is a substantial literature concerned with the mechanism of the insertion of olefins and acetylenes into the platinum–hydrogen bond [2]. For phosphine complexes the synthesis of complexes of the type *trans*-[PtHCl(PR$_3$)$_2$] can be accomplished in several ways: a) reaction of *cis*-[PtCl$_2$(PR$_3$)$_2$] with hydrazine hydrate or hydroxide in a refluxing alcohol [3]; b) addition of either strong [4] or weak [5] acids to an appropriate platinum(0) starting material [4, 5] or c) by reaction of a suitable substrate with the BH_4^- anion [6]. The first two methods require either relatively high temperatures or costly intermediates which must first be prepared.

It has been known for some time that tin(II) chloride combines with the complexes *cis*-[PtCl$_2$(PR$_3$)$_2$] to form an active hydrogenation catalyst [7, 8, 9]. Our own research concerned with the complexes [PtCl(SnCl$_3$)(PR$_3$)$_2$] [10, 11, 12] led us to consider the possibility that this tin–platinum catalyst might provide a convenient preparative route to these hydride complexes using only molecular hydrogen as reagent while working at room temperature. This hypothesis was bolstered by existing literature reporting the stability of hydridotrichlorostannate complexes of platinum(II) [13–15]. We report here a simple preparation of the complexes *trans*-[PtHCl(P(*p*-XC$_6$H$_4$)$_3$)$_2$] (X = OCH$_3$, CH$_3$, H, F, Cl, under very mild conditions, based on the *in situ* synthesis of active trichlorostannate complexes of platinum.

Results and Discussion

Synthesis

We find that good yields (70–95%) of the hydride complexes can be obtained when *cis*-[PtCl$_2$(P(*p*-XC$_6$H$_4$)$_3$)$_2$] complexes react with two equivalents of tin(II) chloride and hydrogen (see eqn. 1):

$$\begin{array}{l} \mathit{cis}\text{-}[\mathrm{PtCl_2P_2}] + 2\mathrm{SnCl_2} \xrightarrow[\text{RT}]{\mathrm{CHCl_3}} \mathit{trans}\text{-}[\mathrm{PtHClP_2}] \\ \text{1) } \mathrm{H_2} \qquad\qquad\qquad\qquad \mathrm{P} = \mathrm{P}(p\text{-}\mathrm{XC_6H_4})_3 \\ \text{2) } \mathrm{Me_4NCl} \end{array} \tag{1}$$

The yields were lower with tin/platinum ratios of one and three. The tetramethyl ammonium chloride serves to precipitate the sparingly soluble (Me$_4$N)-SnCl$_3$, thus freeing the platinum from coordination to tin. We have investigated the products of the reaction before addition of the ammonium salt, using ^{31}P NMR, and find a complicated mixture, some components of which are dynamic on the NMR time scale. After the precipitation, the reaction mixture contains *only product hydride and starting material*[*], suggesting that there are the equilibria shifted in favor of the *trans*-[PtHClP$_2$] complexes. The absence of by-products is especially advantageous since, after recrystallization, the contents of the filtrate can be recycled in another run, thus increasing the effective yield. Further, we find that starting from *trans*-[PtCl$_2$(P(*p*-CH$_3$C$_6$H$_4$)$_3$)$_2$] does not change yield. This is in contrast to the hydrazine hydrate method where only *cis*-starting materials can be used. The formation of a hydride ligand suggests that H$^+$ is set free and we confirm this in that a methoxide solution containing neutral red becomes acidic after contact with the exit gas.

We have successfully carried out the reaction beginning from *cis*-[PtCl$_2$(As(*p*-XC$_6$H$_4$)$_3$)$_2$], X = H, CH$_3$ and find ^{1}H NMR signals at −19.0 and −19.1 ppm respectively, which we assign to the hydride protons. Given the mild reaction conditions, this method offers an attractive alternative to classical platinum hydride syntheses for tertiary aryl phosphine and arsine complexes. We find that the yields are not as good for alkyl phosphine complexes and will combine these results together with the solvent dependence of the reaction in a more extensive report.

Experimental

All of the reactions were carried out in a Schlenk tube equipped with a gas-inlet adapter. A mixture of *cis*-[PtCl$_2$(P(*p*-CH$_3$C$_6$H$_4$)$_3$)$_2$] (880 mg, 1.0 mmol) and tin(II) chloride (380 mg, 2.0 mmol) was dissolved in 120 ml CHCl$_3$ and stirred, under nitrogen, for 0.5 h. During this period the solution became yellow in color. Hydrogen was then passed through

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[*] The starting material can appear as a mixture of *cis* and *trans* isomers.

TABLE I. Yields[a] and NMR Data for Hydride Complexes *trans*-$[PtHCl(E(p\text{-}XC_6H_4)_3)_2]$.

E	X	Yields (%)	δ $^{31}P^b$	$^1J(^{195}Pt, ^{31}P)$, Hz	δH^c	$^1J(^{195}Pt, H)$, Hz
P	Cl	>95%	26.9	3037	−16.2	1192
	F	80	26.0	3025	−16.2	1201
	H	70	28.4	3019	−16.2	1196
	CH_3	70	26.4	2996	−16.4	1212
	OCH_3	80	24.2	2965	−16.5	1230
As	H	50			−19.0	1044
	CH_3	60			−19.1	1057

[a] Based on the ^{31}P NMR spectra for phosphine complexes, or on the ^1H NMR Spectra with $PtHCl(PPh_3)_2$ as internal standard for arsine complexes. [b] Relative to external H_3PO_4. A positive value is to low field of the reference. [c] Relative to internal TMS.

the solution for 3 h with the exiting gas lead into a methanol solution of neutral red made basic with sodium methoxide. During this period the indicator solution turns from yellow to red due to the evolution of acid. The resulting yellow–orange reaction solution was then treated with an excess of tetramethylammonium chloride and stirred until the color disappeared. Filtration through celite was followed by destillation of the solvent to give product. The extent of the reaction was determined using $^{31}P\{^1H\}$ spectroscopy ($CH_2Cl_2/CDCl_3$). The NMR clearly shows that the product consists of some starting material and the desired hydride complex. The yields as determined by ^{31}P NMR are given in Table I. The pure hydride complex may be obtained after recrystallization from benzene/methanol (530 mg, 63% yield).

$^{31}P\{^1H\}$ spectra were measured as $CH_2Cl_2/CDCl_3$ solutions in 10 mm tubes using a Bruker HX-90 spectrometer operating in Fourier transform mode. Chemical shifts are relative to external H_3PO_4 and are accurate to ±0.1 ppm. Coupling constants are ±2 Hz. Typically 50° pulse angles and 0.7 sec acquisition times were employed.

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