

Preliminary communication

**STABILIZATION OF PLATINUM(II) HYDRIDES BY TRI-*t*-BUTYLARSINE;
 FACILE SYNTHESSES OF STABLE *trans*-PtH₂[As(*t*-Bu)₃]₂ AND
trans-PtHX[As(*t*-Bu)₃]₂ COMPLEXES**

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Summary

trans-PtH₂[As(*t*-Bu)₃]₂ was prepared in very good yield by a facile reaction of K₂PtCl₄ with As(*t*-Bu)₃ in alkaline ethanol. Treatment of *trans*-PtH₂[As(*t*-Bu)₃]₂ with CF₃CO₂H or HCl afforded *trans*-PtH(O₂CCF₃)[As(*t*-Bu)₃]₂ or *trans*-PtHCl[As(*t*-Bu)₃]₂, respectively, in almost quantitative yield.

Since the first report [1] of the preparation of stable dihydridoplatinum(II) complexes, *trans*-PtH₂L₂, where L is a bulky phosphine, there has been considerable interest in the preparation of stable hydrido complexes of platinum(II) and palladium(II). Although no stable dihydridopalladium(II) complex has yet been isolated, several synthetic routes have been reported [1—5] for the *trans*-PtH₂L₂ complexes. These include, (i) reactions of *cis*-PtCl₂L₂ or *trans*-PtHClL₂ complexes with either NaBH₄ or hydrazine hydrate, (ii) oxidative additions of molecular hydrogen or methanol to the platinum(0) complexes of bulky phosphines and (iii) reaction of Pt(CO)₄L₂ complexes with NaBH₄. We report here very convenient synthetic routes for the remarkably stable hydridoplatinum(II) complexes which are stabilized by tri-*t*-butylarsine ligands.

Reaction of commercially available K₂PtCl₄ with As(*t*-Bu)₃ in alkaline alcohol affords the new complex *trans*-PtH₂[As(*t*-Bu)₃]₂ (I) in about 80% yield. In a typical preparation, solid K₂PtCl₄ (1 mmol) was added to a solution of As(*t*-Bu)₃ (2.5 mmol) and KOH (3.5 mmol) in 25 ml ethanol and the mixture was stirred for 24 h at 30 to 40°C. A colourless solution was obtained by diluting the mixture with *n*-hexane and filtering off a grey residue. Concentration of the solution gave analytically pure *trans*-PtH₂[As(*t*-Bu)₃]₂ (other products were not looked for). Although the preparation of platinum(II) hydrides of the type *trans*-PtHCl(PR₃)₂ from the reduction of a Pt—Cl bond of the complexes *cis*-PtCl₂(PR₃)₂

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with alcoholic KOH has been known [6], the reaction reported here provides the first example of the preparation of a platinum(II) dihydride via reduction of both Pt—Cl bonds by ethanol.

The infrared spectrum of I shows a strong single band at 1775 cm^{-1} attributable to the Pt—H stretching frequency which compares well with the Pt—H stretching frequencies for the known *trans*-dihydridobis(tertiary phosphine)-platinum(II) complexes [1–6]. Its ^1H NMR spectrum, in deuterated benzene, consists of a single resonance in the *t*-butyl region (δ 1.54 ppm) and a characteristic triplet due to the hydrogens bonded to platinum (δ -3.78 ppm; $^1J(^{195}\text{Pt}-^1\text{H})$ 725 Hz).

Samples of I stored at room temperature for over three months were found to be unchanged as shown by analytical and spectroscopic data. In marked contrast with *trans*-PtH₂[P(*t*-Bu)₃]₂ [6] which rapidly undergoes intermolecular metalation in solution to give molecular hydrogen and the hydrido bridged dinuclear metalated complex, (PtH{P(*t*-Bu)₂PMe₂CH₂})₂ (I) was recovered almost unchanged after 24 h in benzene.

Treatment of I with CF₃CO₂H afforded *trans*-PtH(O₂CCF₃)[As(*t*-Bu)₃]₂ (II). *trans*-PtHCl[As(*t*-Bu)₃]₂ (III) was obtained by treating I with HCl. Like I, II and III are stable at room temperature in the solid state as well as in solution. The Pt—H stretching frequencies for II and III were observed at 2341 and 2348 cm^{-1} , respectively; the antisymmetric CO₂ stretching frequency for II was observed at ca. 1706 cm^{-1} . The ^1H NMR spectrum of II showed a singlet resonance due to *t*-butyl groups at 1.33 and a triplet due to the Pt—H hydrogen at -27.24 ppm ($^1J(^{195}\text{Pt}-^1\text{H})$ 1026 Hz). For III the *t*-butyl resonance was observed at 1.51 ppm and the triplet due to the hydrogen bonded to platinum was seen at -21.1 ppm ($^1J(^{195}\text{Pt}-^1\text{H})$ 970 Hz).

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