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Preliminary communication

A NEW SYNTHESIS OF PLATINUM—CARBON BONDS

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Summary

Syntheses of *cis*-$[PtCl(CH_2COCH_3)(PEt_3)_2]$, *cis*-$[PtCl(CH_2NO_2)(PEt_3)_2]$, and *trans*-$[Pt(C{\equiv}CPh)_2(PEt_3)_2]$ are described. The procedure involves reaction of *cis*-$[PtCl_2(PEt_3)_2]$ with Ag_2O and acidic C—H bonds to precipitate AgCl and generate a Pt—C bond. The method may represent a new general route to platinum—carbon bonds.

The traditional synthetic methods for platinum—carbon bond formation involve either Grignard or organolithium reagents with platinum(II) halides or oxidative addition reactions to platinum(0) tertiary phosphine complexes. The Grignard and organolithium routes are not generally applicable to organo substituents containing active functional groups (eg. X = CO, NO_2, CN, etc.) and the specialised nature of the oxidative addition reaction also places limitations on the types of complex which are accessible [1]. More recently, two groups of workers [2,3] have reported synthesis of organoplatinum complexes containing functional groups by reactions of hydroxoplatinum complexes with acidic C—H compounds (e.g. eq. 1).

$$Pt(OH)(CH_3)(diphos) + HX \rightarrow Pt(X)(CH_3)(diphos) + H_2O \qquad (1)$$

(diphos = 1,2-bis(diphenylphosphine)ethane, X = CH_2COCH_3, $CH(COCH_3)_2$, CH_2CN or CH_2NO_2 [2])

Unfortunately, this procedure is severely restricted by the rarity of hydroxoplatinum complexes [4]. $[Pt(OH)(CH_3)(diphos)]$ [2] and *cis*-$[Pt(OH)(C_6F_5)(PPh_3)_2]$ [3] are almost the only well-characterised complexes with suitable,

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terminal OH groups.

We now report that similar reactions may be achieved using platinum(II) chlorides with Ag_2O (prepared by addition of excess hydroxide to aqueous $AgNO_3$) in the presence of an acidic C—H compound. The Ag_2O serves as a simple means of introducing a halide abstracting agent (Ag^+) and a strong base (O^{2-}) simultaneously. Thus reactions 2 and 3 proceed rapidly on stirring a small

$$cis\text{-}[PtCl_2(PEt_3)_2] + HX + \tfrac{1}{2}Ag_2O \rightarrow cis\text{-}[PtCl(X)(PEt_3)_2] + AgCl + \tfrac{1}{2}H_2 \qquad (2)$$

$(X = CH_2COCH_3 \text{ or } CH_2NO_2)$

$$cis\text{-}[PtCl_2(PEt_3)_2] + 2HC{\equiv}CPh + Ag_2O \rightarrow$$
$$trans\text{-}[Pt(C{\equiv}CPh)_2(PEt_3)_2] + 2\,AgCl + H_2O \qquad (3)$$

molar excess of Ag_2O with the platinum complex in acetone, nitromethane or $HC{\equiv}CPh$/benzene, respectively. Care is necessary to avoid absorption of CO_2 by the Ag_2O since this results in production of $[Pt(CO_3)(PEt_3)_2]$. Presumably reactions 2 and 3 involve simultaneous generation of an active platinum cation by halide abstraction and a carbanion by proton abstraction.

The acetylide was characterised by comparison of spectroscopic data with those obtained for an authentic sample prepared by the literature method [5]. The other complexes were characterised by satisfactory C, H and N microanalyses and by the ^1H and ^{31}P NMR data collected in Table 1. The reactions described may be the basis of a new route to platinum—carbon compounds containing functional groups and further work is in progress to establish their generality.

TABLE I

^1H AND ^{31}P NMR DATA[a]

Compound	^1H for Pt—CH_2 group				^{31}P		
	δ (ppm)	^2J(Pt—H) (Hz)	^3J(P—H) (*cis*) (Hz)	^3J(P—H) (*trans*) (Hz)	δ (ppm)	^1J(Pt—P) (Hz)	^2J(P (Hz)
cis-$[PtCl(CH_2COCH_3)(PEt_3)_2]$	−2.93	72	4.1	10.3	127.5^b 134.9^c	2004^b 3962^c	17
cis-$[PtCl(CH_2NO_2)(PEt_3)_2]$	−4.86	71	4.1	8.3	130.0^b 134.6^c	2098^b 3818^c	18
trans-$[Pt(C{\equiv}CPh)_2(PEt_3)_2]$					128.6	2370	

[a] Chemical shifts upfield (+) from $Si(CH_3)_4$ or $P(OCH_3)_3$, external references. [b] *trans* to CH_2. [c] *trans* to Cl.

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