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### Preliminary communication

## A NEW SYNTHESIS OF PLATINUM—CARBON BONDS

MAXWELL A. CAIRNS\*, KEITH R. DIXON\*\* and MARTIN A.R. SMITH\*\*\*

*Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 2Y2  
 (Canada)*

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### Summary

Syntheses of *cis*-[PtCl(CH<sub>2</sub>COCH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>], *cis*-[PtCl(CH<sub>2</sub>NO<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>], and *trans*-[Pt(C≡CPh)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] are described. The procedure involves reaction of *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] with Ag<sub>2</sub>O 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<sub>2</sub>, 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).



(diphos = 1,2-bis(diphenylphosphine)ethane, X = CH<sub>2</sub>COCH<sub>3</sub>, CH(COCH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>CN or CH<sub>2</sub>NO<sub>2</sub> [2])

Unfortunately, this procedure is severely restricted by the rarity of hydroxoplatinum complexes [4]. [Pt(OH)(CH<sub>3</sub>)(diphos)] [2] and *cis*-[Pt(OH)(C<sub>6</sub>F<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] [3] are almost the only well-characterised complexes with suitable,

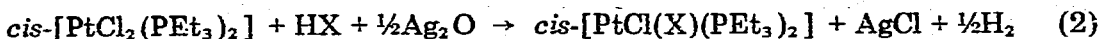
\*Present address: Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1W5.

\*\*Author to whom correspondence should be addressed.

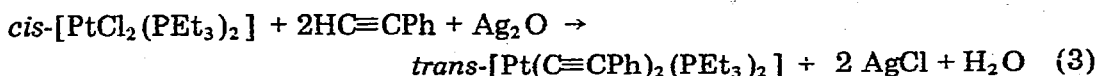
\*\*\*Present address: Bruker Limited, 5200 Dixie Road, Suite 116, Mississauga, Ontario, Canada, L4W 1E4.

terminal OH groups.

We now report that similar reactions may be achieved using platinum(II) chlorides with  $\text{Ag}_2\text{O}$  (prepared by addition of excess hydroxide to aqueous  $\text{AgNO}_3$ ) in the presence of an acidic C—H compound. The  $\text{Ag}_2\text{O}$  serves as a simple means of introducing a halide abstracting agent ( $\text{Ag}^+$ ) and a strong base ( $\text{O}^{2-}$ ) simultaneously. Thus reactions 2 and 3 proceed rapidly on stirring a small



(X =  $\text{CH}_2\text{COCH}_3$  or  $\text{CH}_2\text{NO}_2$ )



molar excess of  $\text{Ag}_2\text{O}$  with the platinum complex in acetone, nitromethane or  $\text{HC}\equiv\text{CPh}$ /benzene, respectively. Care is necessary to avoid absorption of  $\text{CO}_2$  by the  $\text{Ag}_2\text{O}$  since this results in production of  $[\text{Pt}(\text{CO}_3)(\text{PEt}_3)_2]$ . 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 micro-analyses and by the  $^1\text{H}$  and  $^{31}\text{P}$  NMR data collected in Table 1. The reactions

TABLE I

$^1\text{H}$  AND  $^{31}\text{P}$  NMR DATA<sup>a</sup>

Compound	$^1\text{H}$ for Pt—CH <sub>2</sub> group				$^{31}\text{P}$		
	$\delta$ (ppm)	$^2J(\text{Pt—H})$ (Hz)	$^3J(\text{P—H})$ ( <i>cis</i> ) (Hz)	$^3J(\text{P—H})$ ( <i>trans</i> ) (Hz)	$\delta$ (ppm)	$^1J(\text{Pt—P})$ (Hz)	$^2J(\text{Pt—P})$ (Hz)
<i>cis</i> -[PtCl(CH <sub>2</sub> COCH <sub>3</sub> )(PEt <sub>3</sub> ) <sub>2</sub> ]	-2.93	72	4.1	10.3	127.5 <sup>b</sup> 134.9 <sup>c</sup>	2004 <sup>b</sup> 3962 <sup>c</sup>	17
<i>cis</i> -[PtCl(CH <sub>2</sub> NO <sub>2</sub> )(PEt <sub>3</sub> ) <sub>2</sub> ]	-4.86	71	4.1	8.3	130.0 <sup>b</sup> 134.6 <sup>c</sup>	2098 <sup>b</sup> 3818 <sup>c</sup>	18
<i>trans</i> -[Pt(C≡CPh) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> ]					128.6	2370	

<sup>a</sup> Chemical shifts upfield (+) from  $\text{Si}(\text{CH}_3)_4$  or  $\text{P}(\text{OCH}_3)_3$ , external references. <sup>b</sup> *trans* to CH<sub>2</sub>. <sup>c</sup> *trans* to Cl.

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.

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