

### Preliminary communication

## HYDRIDO(PHENYL)- AND HYDRIDO(METHYL)-PLATINUM(II) COMPLEXES VIA THERMALLY UNSTABLE METHOXO AND FORMATO COMPLEXES

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### Summary

Thermally stable hydrido(phenyl)- and hydrido(methyl)-platinum(II) complexes  $trans-[PtH(R)L_2]$  ( $R = Ph, L = PMe_3, PEt_3, PPh_3, P-i-Pr_3, P-t-BuMe_2, P-t-Bu_2Me$ ;  $R = Me, L = PPh_3, P-i-Pr_3$ ) are obtained in good yield by treatment of  $trans-[PtX(R)L_2]$  ( $X = Cl, OH, NHCOMe$ ) or  $trans-[PtR(MeOH)L_2]^+$  with methanolic sodium methoxide or sodium borohydride; thermally unstable *cis*-hydrido(methyls)  $PtH(Me)[Ph_2P(CH_2)_n PPh_2]$  ( $n = 2$  or  $3$ ) are formed by elimination of  $CO_2$  from the corresponding formates  $Pt(O_2CH)Me[Ph_2P(CH_2)_n PPh_2]$ .

Recently, a number of *trans*-hydrido-alkyls and -aryls of platinum(II) of general formula  $[PtH(R)L_2]$  have been prepared, e.g.  $L = PPh_3, R = CF_3$  [1],  $C(CN)_3$  [2],  $CH_2CN$  [3],  $CH_2CH_2CH_2CN$  [3];  $L = PCy_3^*$ ,  $R = C_6F_5, 1,3,5-C_6F_3H_2$  or  $1,3-C_6F_2H_3$  [4];  $L = PEt_3, R = C_6F_5$  [4], and it has been assumed that an electron-withdrawing substituent in the  $\sigma$ -alkyl or  $\sigma$ -aryl group is required for stability. The only reported exceptions in the nickel triad are  $trans-[NiH(R)L_2]$  ( $R = Me, Ph; L = PCy_3$ ) [5],  $trans-[PtH(R)(PEt_3)_2]$  ( $R = CH_2SiMe_3, Ph$ ) [6,7], which were not isolated in a pure state, and  $trans-[PtH(C_6H_9)(PPh_3)_2]$  ( $C_6H_9 = 1$ -cyclohexenyl) [8]. In the case of the nickel hydrides, ligand bulk may help to stabilize the complex.

We find that *trans*-hydrido(phenyl) complexes of platinum(II) can be isolated in >70% yield from: (1) reaction of hydroxo complexes  $trans-[Pt(OH)PhL_2]$  ( $L = PEt_3, PPh_3, P-t-Bu_2Me, P-t-BuMe_2$ ) [9,10] with methanol at 25–65°C; (2) reaction of cationic solvento species  $trans-[PtPh(MeOH)L_2]BF_4$  with methanolic sodium methoxide or sodium borohydride at –20 to +65°C; (3) reaction of chloro complexes  $trans-[PtClR(L)_2]$  with methanolic sodium

\*Cy = cyclohexyl

methoxide or sodium borohydride. Method (2) is suitable for the low-melting triethylphosphine complex ( $\nu(\text{PtH})$  1940  $\text{cm}^{-1}$  (liquid film)), which darkens above ca. 30°C but can be stored in benzene at room temperature for 24 h. This complex has recently been identified spectroscopically as a product of the reaction of  $[\text{Pt}_2\text{H}_2(\text{Ph})(\text{PEt}_3)_4]^+$  with chloride ion [7]. The complex *trans*- $[\text{PtH}(\text{Ph})(\text{PMe}_3)_2]$  is a colourless crystalline solid which is unstable in solution in benzene or dichloromethane at room temperature. The other members of the series are colourless, crystalline, air-stable complexes which can be recrystallized from dichloromethane/methanol. The similar hydrido-(methyl), *trans*- $[\text{PtH}(\text{Me})(\text{PPh}_3)_2]$ , is best made by treatment of the *N*-acetamido complex, *trans*- $[\text{Pt}(\text{NHCOMe})\text{Me}(\text{PPh}_3)_2]$  [8] with methanolic sodium methoxide, while *trans*- $[\text{PtH}(\text{Me})(\text{P-}i\text{-Pr}_3)_2]^*$  was prepared by reaction of *trans*- $[\text{Pt}(\text{OH})\text{Me}(\text{P-}i\text{-Pr}_3)_2]$  with methanol. Reaction of *trans*- $[\text{PtMe}(\text{MeOH})(\text{PPh}_3)_2]\text{BF}_4$  with sodium methoxide gives a mixture of the hydride and a methoxo-complex *trans*- $[\text{PtMe}(\text{OMe})(\text{PPh}_3)_2]$ , which undergoes  $\beta$ -elimination in refluxing methanol to give the impure hydride. Similar intermediate methoxo complexes are probably involved in the formation of the hydrido(phenyl) complexes\*\*.

The stereochemistry of the hydrides is established by the triplet hydride resonance with  $^{195}\text{Pt}$  satellites in their  $^1\text{H}$  NMR spectra, the chemical shifts and  $^1J(\text{PtH})$  values being as expected for H *trans* to a ligand of high *trans*-influence\*\*\*. In addition, the values of  $^1J(\text{PtP})$  obtained from  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra are typical of mutually *trans*-phosphine in planar platinum(II) complexes.

The magnitudes of  $^1J(\text{PtH})$  and  $\nu(\text{PtH})$  for *trans*- $\text{PtH}(\text{R})(\text{PPh}_3)_2$  (R = Me, Ph,  $\text{C}_6\text{H}_9$  or  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$ ) are similar, but they are smaller than the corresponding values for *trans*- $\text{PtH}(\text{CH}_2\text{CN})(\text{PPh}_3)_2$  (Table 1), consistent with a lower *trans*-influence for the cyanomethyl ligand [11]. The  $J(\text{PtH})$  data apparently indicate  $\text{CH}_3$  to be below  $\text{CF}_3$  in the NMR *trans*-influence series, whereas on the basis of  $^2J(\text{PtCH}_3)$ ,  $^2J(\text{PtCF}_3)$  and  $^1J(\text{PtP})$  data, it has been concluded [12] that the *trans*-influences of these two ligands are

TABLE 1

SELECTED IR AND  $^1\text{H}$  NMR SPECTRAL DATA FOR *trans*- $\text{PtH}(\text{R})(\text{PPh}_3)_2^a$ 

R	$\nu(\text{PtH})$	$\delta(\text{PtH})$	$^1J(\text{PtH})$	Ref.
Me	1936	-3.77	656	this work
Ph	1890 <sup>b</sup>	-5.71	600	this work
$\text{C}_6\text{H}_9$	1920 <sup>c</sup>	-4.64	608	[8]
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$	1950	-4.51	636	[3]
$\text{CH}_2\text{CN}$	2027	-7.32	746	[3]
$\text{CF}_3$	2073	-8.23	544	[1]

<sup>a</sup> IR data ( $\text{cm}^{-1}$ ) refer to Nujol mulls, except where indicated otherwise; NMR data refer to solutions in  $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ . <sup>b</sup> 1966  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ). <sup>c</sup> In  $\text{CH}_2\text{Cl}_2$ .

\*Satisfactory analytical data have been obtained for all new compounds reported here.

\*\**trans*- $[\text{Pt}(\text{OMe})\text{Ph}(\text{PEt}_3)_2]$  has been reported [14].

\*\*\**trans*- $[\text{PtH}(\text{Ph})(\text{PPh}_3)_2]$ :  $\delta(\text{CD}_2\text{Cl}_2, 32^\circ\text{C})$  5.71 ppm (t with  $^{195}\text{Pt}$  satellites, 1H, PtH,  $^2J(\text{PH})$  18.3 Hz,  $^1J(\text{PtP})$  600 Hz),  $\delta(\text{P})$  ( $\text{C}_6\text{H}_6, 30^\circ\text{C}$ ) 31.0 ppm ( $^1J(\text{PtP})$  3120 Hz). The data for the  $\text{PEt}_3$  complex agree with those given in ref. 7.

approximately equal. In the series *trans*-PtH(C<sub>6</sub>H<sub>4</sub>X)(PEt<sub>3</sub>)<sub>2</sub> (X = various substituents in *meta*- or *para*-positions) the magnitudes of  $\nu$ (PtH) and  $\delta$ (PtH) increase with the electron-withdrawing ability of X, but there are no consistent trends in  $^1J$ (PtH).

As expected, the *trans*-hydrido(alkyls) and -(aryls) are more stable towards reductive elimination of hydrocarbon RH than are the corresponding *cis*-complexes such as *cis*-PtH(R)(PPh<sub>3</sub>)<sub>2</sub> (R = Me, Ph) [13]. Thermal stability depends markedly on the bulk of the tertiary phosphine. Thus, PtH(Ph)-(P-*t*-Bu<sub>2</sub>Me)<sub>2</sub> is only 50% decomposed after 300 h at 160°C in *n*-decane, whereas PtH(Ph)(PEt<sub>3</sub>)<sub>2</sub> decomposes completely in less than 1 h at 65°C in the same solvent. In the latter case, the products are benzene, platinum metal, Pt(PEt<sub>3</sub>)<sub>3</sub> and another unidentified platinum-containing complex; decomposition is retarded in the presence of triethylphosphine (1 mol per mol of complex). Carbon monoxide causes rapid elimination of benzene from *trans*-PtH(Ph)(PEt<sub>3</sub>)<sub>2</sub> to give initially Pt(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>, which subsequently decomposes to give unidentified clusters. Dimethyl acetylenedicarboxylate readily inserts into the Pt—H bond of *trans*-PtH(Ph)(PEt<sub>3</sub>)<sub>2</sub> to give *trans*-PtPh{C(CO<sub>2</sub>Me)=CHCO<sub>2</sub>Me}(PEt<sub>3</sub>)<sub>2</sub>, but there is no reaction with acrylonitrile or ethylene.

Our preparative method can be extended to *cis*-hydrido(alkyls) of platinum(II) containing bidentate ligands such as Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (dppe) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (dppp). Treatment of the hydroxo(methyl) complexes Pt(OH)Me(dppe) [11] or Pt(OH)Me(dppp) [10] with formic acid, or of the cationic solvento species with sodium formate, gives initially the corresponding O-bonded formate complexes, characterized by IR and low temperature NMR spectra\*. These slowly lose CO<sub>2</sub>, both in solution at ca. -20°C and in the solid state at room temperature to form the hydrido(methyls), *cis*-PtH(Me)(dppe) and *cis*-PtH(Me)(dppp), which closely resemble *cis*-[PtH(ME)(PPh<sub>3</sub>)<sub>2</sub>] [13] in their spectroscopic properties\*\*. In contrast with the latter, thermal decomposition at room temperature does not give platinum metal, but rather an unidentified mixture of clusters presumably arising from the fragments [Pt(dppe)] or [Pt(dppp)].

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\*Pt(O<sub>2</sub>CH)Me(dppe):  $\delta$ (H) (CD<sub>2</sub>Cl<sub>2</sub>, -70°C) 0.24 ppm (dd with <sup>195</sup>Pt satellites, 3H, CH<sub>3</sub>, <sup>3</sup>J(PH) 2.5, 7.5 Hz, <sup>2</sup>J(PtH) 53.5 Hz), 8.44 ppm (d with <sup>195</sup>Pt satellites, 1H, O<sub>2</sub>CH, <sup>4</sup>J(PH) 13.4 Hz, <sup>3</sup>J(PtH) 70 Hz),  $\delta$ (P) (CH<sub>2</sub>Cl<sub>2</sub>, -74°C) 47.7 ppm (<sup>1</sup>J(PtP) 1841 Hz), 34.9 (<sup>1</sup>J(PtP) 4141 Hz); IR (Nujol) 2805w ( $\nu$ (CH)), 1630s ( $\nu$ (C=O)), 1300ms cm<sup>-1</sup> ( $\nu$ (C—O)).

\*\*PtH(Me)(dppe):  $\delta$ (H) (CD<sub>2</sub>Cl<sub>2</sub>, -70°C) -0.71 ppm (dd with <sup>195</sup>Pt satellites, 1H, PtH, <sup>2</sup>J(PH) 195, 15 Hz, <sup>1</sup>J(PtH) 1214 Hz), 0.81 ppm (dd with <sup>195</sup>Pt satellites, 3H, CH<sub>3</sub>, <sup>3</sup>J(PH) 7.1, 7.3 Hz, <sup>2</sup>J(PtH) 69 Hz),  $\delta$ (P) (CH<sub>2</sub>Cl<sub>2</sub>, -75°C) 48.9 (<sup>1</sup>J(PtP) 1792 Hz), 47.5 (<sup>1</sup>J(PtP) 1836 Hz); IR (Nujol) 1975 cm<sup>-1</sup> ( $\nu$ (PtH)).

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