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SYNTHESIS AND CHARACTERIZATION OF SOME *trans*-HYDRIDOMETHYLBIS(PHOSPHINE)-PLATINUM(II) AND -PALLADIUM(II) COMPLEXES

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Summary

Several *trans*-hydridomethylbis(phosphine)-platinum(II) and -palladium(II) complexes have been made by the reaction: *trans*-$M(H)Cl(PR_3)_2 + CH_3MgBr \rightarrow$ *trans*-$M(CH_3)(PR_3)_2 + MgClBr$ and their structures determined by ^1H NMR and IR spectroscopy. The complexes in which M = Pt and R = Cy (cyclohexyl) or i-Pr (isopropyl) are very stable in the solid state and in solution, while the compounds in which M = Pt, R = Et (ethyl) and M = Pd, R = i-Pr slowly decompose either in the solid state or in solution. The compound in which M = Pd and R = Cy was not isolated but was identified in solution.

Introduction

The importance of hydridoalkyl-transition metal complexes in catalytic and stoichiometric processes is widely recognized [1,2—4]. Several such complexes have been isolated at room temperature [5], and a few others have been identified in solution [1,3,6]. However, such complexes are still fairly rare.

We describe below what is to our knowledge one of the first successful syntheses of a series of hydridoalkyl complexes by a general method *.

Results and discussion

In earlier work [6] it was reported that the reaction between *trans*-$PtHCl(PPh_3)_2$ and CH_3MgBr quantitatively yields *cis*-$PtH(CH_3)(PPh_3)_2$ according to eq. 1.

$$trans\text{-}PtHCl(PPh_3)_2 + CH_3MgBr \rightarrow cis\text{-}PtH(CH_3)(PPh_3)_2 + MgClBr \qquad (1)$$

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* *Note added in proof.* Subsequent to the completion of these studies, a preliminary report appeared describing alternative approaches to the synthesis of these complexes [9].

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TABLE 1 [a]

^{1}H NMR AND INFRARED DATA

Compounds	δ M–*H* [c] (ppm)	δ M–C*H*$_3$ (ppm)	*J*(M, H) (Hz)	*J*(M, CH$_3$) (Hz)	*J*(H, CH$_3$) (Hz)	*J*(H, P$_1$P$_2$) [d] (Hz)	*J*(CH$_3$, P$_1$P$_2$) [d] (Hz)	M–H (cm^{-1}) [e]
I	–5.94	0.69	648.5	52.7	2.2	17.3	4.5	1925s
II [b]	–6.19	0.64	641.8	52.7	2.3	17.2	4.9	1925(br)
III	–4.92	0.59	676.5	52.3	2.3	19.2	5.6	1937(br)
IV	–6.73	0.13	—	—	2.8	11.1	4.5	1770(br)
V	–6.53	0.18	—	—	2.6	12.1	4.4	—

[a] NMR spectra determined in C_6D_6 at room temperature. [b] NMR spectra determined in $C_6D_5CD_3$. [c] M = Pd or Pt. [d] $P_1 = P_2$. [e] IR spectra determined in Nujol.

We have extended this approach to the synthesis of a variety of *trans*-hydridomethyl-platinum(II) and -palladium(II) complexes by the corresponding reactions of CH_3MgBr with *trans*-$PtHCl(PCy_3)_2$, *trans*-$PtHCl(P\text{-i-}Pr_3)_2$, *trans*-$PtHCl(PEt_3)_2$, *trans*-$PdHCl(P\text{-i-}Pr_3)_2$ and *trans*-$PdHCl(PCy_3)_2$ (Cy = cyclohexyl, Et = ethyl, i-Pr = isopropyl), according to eq. 2.

$$trans\text{-}MHCl(PR_3)_2 + CH_3MgBr \rightarrow trans\text{-}MH(CH_3)(PR_3)_2 + MgClBr \qquad (2)$$

In all cases the formation of the corresponding *trans*-hydridomethylbis(phosphine)-platinum(II) and -palladium(II) complexes was confirmed by ^1H NMR spectroscopy (see compounds I, II, III, IV, and V, Table 1). Their *trans*-configuration was unambigously assigned by ^1H NMR spectroscopy. In all cases, the signals due to the methyl and hydride protons were observed, as were the methyl—hydride, phosphorous—hydride and phosphorus—methyl couplings. In the case of platinum complexes the hydride—platinum and the methyl—platinum couplings were also observed. The IR spectra of the isolated compounds exhibited characteristic M—H stretching bands (see Table 1).

trans-$PtH(CH_3)(PCy_3)_2$ (I) and *trans*-$PtH(CH_3)(P\text{-i-}Pr_3)_2$ (II) were found to be very stable both in solution (benzene, toluene up to 100°C) and in the solid state (room temperature). *trans*-$PtH(CH_3)(PEt_3)_2$ (III) is stable in the solid state only at low temperatures (—30°C), and even then slowly changes colour from pale yellow to orange-red. In benzene solution at room temperature it decomposes slowly and turns black. The formation of methane as a decomposition product was confirmed by ^1H NMR spectroscopy and mass spectrometry. The higher stabilities of I and II compared to that of III may be due to inhibition by the bulky phosphine substituents of the *trans* → *cis* isomerisation and subsequent *cis*-reductive elimination.

In contrast to what was expected on the basis of steric effects, reactions 1 and 2 yield *cis*-$PtH(CH_3)(PPh_3)_2$, but *trans*-$PtH(CH_3)(PEt_3)_2$. The explanation for this difference could be similar to that invoked for PtL_2X_2 complexes [7], for which it was proposed that PPh_3, being more electronegative than PEt_3, favours the formation of the *cis*-isomer by increasing the strength of the Pt—P π-bond. The possibility of different mechanisms for reactions 1 and 2 cannot be excluded.

trans-$PdH(CH_3)(P\text{-i-}Pr_3)_2$ (IV) was found to be stable enough to be isolated as a solid, but was also characterized in solution, where it slowly decomposes to give methane. *trans*-$PdH(CH_3)(PCy_3)_2$ (V) is formed readily in benzene or toluene solution, where it is stable enough at room temperature to be characterized by ^1H NMR spectroscopy, but attempts to isolate it failed, notwithstanding the high stability of the corresponding complex I.

Further studies on the hydridoalkyl complexes are in progress.

Experimental

Proton NMR spectra were determined with a Bruker WH-90 spectrometer. IR spectra were determined with a Pye Unicam SP 1100 spectrophotometer.

trans-$PtHCl(PCy_3)_2$

1 g of *trans*-$PtHCl(PPh_3)_2$ was stirred at room temperature in a solution con-

taining 1 g of PCy_3 in 40 ml of ethanol. On boiling, the suspension dissolved to yield a clear solution, which was refluxed for 1 h. After cooling, the white precipitate of $PtHCl(PCy_3)_2$ was filtered off and washed with ether. Yield: approximately 50%. Further amounts were obtained by evaporating the filtrate, dissolving the residue in a minimum of toluene, adding ether, and cooling (total yield: 60—70%).

trans-$PtH(CH_3)(PCy_3)_2$ (I)

350 mg of *trans*-$PtHCl(PCy_3)_2$ were dissolved in 10 ml of toluene. 0.8 ml of 1.5 *M* CH_3MgBr was added and the solution was stirred for 0.5 h at room temperature. After cooling to —10° C, water was cautiously added. The mixture was filtered, the precipitate being washed carefully with toluene, and the filtrate was dried over Na_2SO_4. Evaporation to dryness gave a white precipitate which was crystallized at low temperature from toluene and methanol. Filtration gave 260 mg of *trans*-$PtH(CH_3)(PCy_3)_2$. (Yield approximately 75%). The compound was characterized by ^1H NMR and IR spectroscopy (see Table I). Elemental analysis Found: C, 57.14; H, 9.10; P, 7.88; ash, 25.90. $C_{37}H_{70}P_2Pt$ Calcd.: C, 57.56; H, 8.67; P, 8.03%.

trans-$PtH(CH_3)(P\text{-}i\text{-}Pr_3)_2$ (II)

This was made as described for I.

trans-$PtH(CH_3)(PEt_3)_2$ (III)

500 mg of $PtHCl(PEt_3)_2$ were dissolved in 10 ml of diethyl ether and 1.4 ml of 1.5 *M* CH_3MgBr were added. The mixture was kept for about 15 minutes at room temperature [8], then cooled in a bath at ca. —30° C, and water was cautiously added. Then solution was filtered by siphoning through a long steel needle containing a small wad of cotton, under N_2 pressure and at low temperature (ca. —30° C). The solution was then evaporated to dryness at —50° C and 10^{-3} mm Hg. After several hours a white compound separated and slowly turned yellow. (Yield: approximately 80%). The compound was fully characterized by ^1H NMR and IR spectroscopy (see Table 1). In benzene at room temperature, this compound decomposes slowly to give methane (NMR, mass spectrometry).

trans-$PdH(CH_3)(P\text{-}i\text{-}Pr_3)_2$ (IV)

To 0.7 g of $PdHCl(P\text{-}i\text{-}Pr_3)_2$ in 10 ml of diethyl ether, were added 1.8 ml of 1.25 *M* CH_3MgBr. The mixture was kept at room temperature for 20 minutes, then it was cooled to —30° C and 0.4 ml of degassed water was added slowly. The ethereal layer was separated at —30° C and evaporated to dryness at —20° C and 10^{-3} mm/Hg. The white solid obtained was identified by ^1H NMR and IR spectroscopy. (Yield: >90%).

trans-$PdH(CH_3)(PCy_3)_2$ (V)

To a solution of 0.118 g of $PdHCl(PCy_3)_2$ in 0.5 ml of toluene-d_8, were added 150 μl of 1.6 *M* CH_3MgBr. The *trans*-hydridomethyl compound was formed in quantitative yield and identified by ^1H NMR spectroscopy. It was not possible to isolate this compound as a solid.

References and notes

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