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Synthesis and Reactivity of Two *cis*-PtH_2(Diphosphine) Complexes (Diphosphine = 1,3-Bis(diphenylphosphino)propane and 1,4-Bis(diphenylphosphino)butane)

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Square planar Pt(II) complexes holding two hydride ligands in the *cis* position are quite rare. Since the first report [1] a few other examples have been found for Pt(II) species stabilized either by bulky chelating diphosphines [2, 3] or basic monophosphines [4, 5].

The interest in these complexes stems from facets ranging from catalysis [6] and mechanisms of fundamental organometallic reactions [7], to intermediates in the synthesis of Pt–Pt dimeric complexes [2]. More recently, Clark [8] suggested a *cis*-dihydride $\leftrightarrow \eta^2$-dihydrogen exchange to account for the dynamic behaviour of a series of *cis*-PtH_2(diphosphine) complexes. Besides the intrinsic interest, such a type of exchange could be of paramount importance for the understanding of H_2 activation on metallic catalysts. Moreover, the Horiuti–Polanyi hydrogenation mechanism [9], where H_2 activation is claimed to be rate determining, has been recently reconsidered in the light of experimental data, which suggest the facile reaction [10, 11]:

$$\text{Metal–}(H_2) + \text{unsaturated hydrocarbon} \longrightarrow \text{Metal (uns. hydroc.)} + H_2$$

This has a non-casual counterpart in the well-documented reaction [2–4, 8]:

$$cis\text{-}PtH_2(L_2) + \text{uns. hydroc.} \longrightarrow \text{Pt (uns. hydroc.)}(L_2) + H_2$$

Our interest in these topics [12, 13] spurred us to find new examples of *cis*-dihydride Pt(II) complexes and to study their reactivity and stability in the presence of H_2, ethylene and HCl.

Experimental

In the reactions oxygen was excluded by the standard techniques used for manipulation of air-sensitive compounds.

^1H and ^{31}P NMR spectra were recorded on a Varian FT 80A spectrometer operating at 79.542 and 32.203 MHz, respectively; IR spectra were registered on a Perkin-Elmer 983 spectrometer. Gas chromatographic/mass spectrometric analysis was carried out on a Finnigam-MAT 700 ion trap detector interfaced to a C. Erba Fractovap 4160 gas chromatograph.

Complexes $PtCl_2$(diphosphine) were prepared by reacting $PtCl_2$(COD) (COD = 1,5-cyclooctadiene) with the appropriate diphosphine ligand (Strem Chemicals).

Preparation of cis-$PtH_2(Ph_2P–(CH_2)_3–PPh_2)$ (2a)

2.00 g of $PtCl_2(Ph_2P–(CH_2)_3–PPh_2)$ are suspended in a 1:1 mixture of CH_2Cl_2/EtOH (10 ml) under H_2 atmosphere. The mixture is stirred at −10 °C for a few minutes, and solid $NaBH_4$ (0.5 g) is added in small amounts over 30 min. The resulting off-white suspension is left stirring for an additional 2 h. After this time a mixture of 5 ml MeOH and 20 ml EtOH is added and stirring is continued for 30 min. The suspension is quickly filtered in air and the white precipitate washed with H_2O, EtOH and n-hexane, and dried under vacuum. Yield 1.32 g (73%). *Anal.* Calc.: C, 53.2; H, 4.6. Found: C, 52.8; H, 4.7%.

The same procedure is used in the synthesis of complex **2b**.

Preparation of $Pt(C_2H_4)(Ph_2P–(CH_2)_3–PPh_2)$ (3a)

A 1:1 mixture of CH_2Cl_2/EtOH (5 ml) is saturated with ethylene at −78 °C. 0.5 g of complex **2a** are added to yield a white suspension. The mixture is allowed to reach room temperature under ethylene atmosphere and stirred for 1 h. The white suspension is filtered, washed with n-hexane and dried *in vacuo*. Yield 0.3 g (60%). *Anal.* Calc. C, 54.8; H, 4.7. Found: C, 54.5; H, 4.7%.

Complex **3b** is obtained in the same way.

Reaction of Complex 3a with HCl

0.32 g (0.5 mmol) of complex **3a** are dissolved in 10 ml of CH_2Cl_2 under ethylene at 0 °C, and treated with the stoichiometric amount of dry HCl in diethylether. Dilution of the resulting solution with diethylether affords complex **4a** as a white powder. Yield 0.25 g (75%).

The reaction of complex **3b** with HCl is carried out in the same way.

Results and Discussion

The dichloro complexes *cis*-$PtCl_2$(L–L) (**1a**: L–L = 1,3-bis(diphenylphosphino)propane = dppp;

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TABLE I. IR and NMR Data for Complexes *cis*-$PtH_2(L–L)$ and $Pt(C_2H_4)(L–L)$[a]

Complex	δH	$J(P–H)_{cis}$	$J(P–H)_{trans}$	J(Pt–H)	δP	J(Pt–P)	ν(Pt–H) (cm^{-1})
2a $PtH_2(dppp)$[b]	−2.21		152[c]	1080	8.6	1945	2014
2b $PtH_2(dppb)$[d]	−2.91	±19	±170	1076	22.7	2054	2006
3a $Pt(C_2H_4)(dppp)$	2.02[e]			61	13.6	2711	
3b $Pt(C_2H_4)(dppb)$	1.89[e]			62	25.3	2528	

[a] IR spectra are in CH_2Cl_2; NMR spectra are in CD_2Cl_2; chemical shifts are in ppm; coupling constants in Hz; ^{31}P shifts are quoted relative to 85% H_3PO_4. [b] At −70 °C. [c] $[J(P–H)_{cis} + J(P–H)_{trans}]$ (see text), J_{cis} and J_{trans} are opposite in sign. [d] At −80 °C. [e] Ethylene protons.

b: L–L = 1,4-bis(diphenylphosphino)butane = dppb) upon reaction with $NaBH_4$ under H_2 atmosphere afford the *cis*-dihydride complexes **2a** and **2b**, respectively:

$$\underset{\mathbf{1a,b}}{cis\text{-}PtCl_2(L–L)} \xrightarrow[NaBH_4,H_2]{CH_2Cl_2/EtOH} \underset{\mathbf{2a,b}}{cis\text{-}PtH_2(L–L)} \quad (1)$$

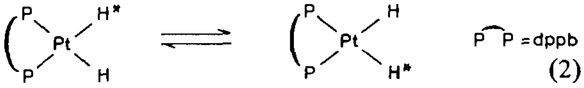
The preparative yields are generally good (>70%). Complexes **2a** and **2b** are recovered from the reaction mixture as white powders which can be safely handled in air for a short time; solutions of these species are air-sensitive but stable, when stored under H_2 atmosphere. The solutions are either colourless or pale-yellow, and turn dark-orange under vacuum or under the action of a nitrogen stream, which irreversibly leads to untractable products.

Complexes **2a** and **2b** have been characterized by analytical and spectroscopic data (IR, ^1H and ^{31}P NMR).

The infrared spectra, registered in CH_2Cl_2 solution, show a broad absorption at ~2010 cm^{-1} (see Table I) assigned to ν(Pt–H): this result agrees with the literature data which point out the difficulty in observing and assigning symmetrical and antisymmetrical Pt–H stretching vibrations in the case of *cis*-$PtH_2(L_2)$ species [1, 2].

The $^{31}P\{^1H\}$ NMR spectra of complexes **2a** and **2b** consist of a singlet flanked by ^{195}Pt satellites as expected from the magnetic equivalence of the two P atoms, under ^1H broad band decoupling conditions (the relevant data are reported in Table I); $^1J(Pt–P)$ values are in keeping with literature data.

The AA'XX' spin system of a *cis*-$PtH_2(L–L)$ species should give rise to a pattern of ten separate lines in the hydride region of the ^1H NMR spectrum (disregarding ^{195}Pt satellites). In this spectral region complex **2a** shows a deceptively simple AA'XX' pattern which consists of only six separate lines flanked by ^{195}Pt satellites. A six line pattern for a AA'XX' spin system should be obtained if either $J_{AA'}$ or $J_{XX'}$ are ~0 Hz; however in our case, computer simulation with these parameters leads to poor agreement between the intensity of the calculated lines and that of the observed ones (attempts to include possible couplings with the diphosphine protons were not made). It is likely that lower intensity lines are lost in the background and/or masked by some of the more intense ones. The spectral data obtained enable us to assign only $|J(P–H)_{cis} + J(P–H)_{trans}|$ and these results are reported in Table I. The ^1H NMR spectrum of complex **2a** is not affected by temperature, while that of complex **2b** shows a dynamic behaviour. The low temperature limiting spectrum is obtained at −80 °C and shows only four equal-intensity lines for the central part of the hydride region. This pattern is consistent with an AA'XX' spin system in which both $J_{AA'}$ and $J_{XX'}$ are ~0 Hz, and allows straightforward assignment of $J(P–H)_{cis}$ and $J(P–H)_{trans}$ (see Table I). Increasing the sample temperature to *ca.* 20 °C leads to the broadening of the external lines of the quartet, whereas the internal ones remain unchanged. In the meanwhile no variation is observed in the ^{31}P NMR spectrum, where the signals remain sharp and the coupling between ^{31}P and ^{195}Pt is retained. This overall behaviour is very similar to that observed by Clark [8] and is consistent with an intramolecular process [14] leading to mutual exchange of the two hydrido ligands:



(2)

By comparing our ^1H NMR data with those in the literature it may be concluded that a deceptively simple AA'XX' spin system is a commonly encountered feature for this type of complex which mostly shows only four lines in the hydrido region. Other common features are the following: the hydrides resonate at relatively low fields (they cover the range 0.65 to −4.00 ppm); $^2J(H–P)_{trans}$ are ~170 Hz, whereas $^2J(H–P)_{cis}$ are *ca.* one order of magnitude smaller; $^1J(H–Pt)$ are >1000 Hz significantly larger than those observed for platinum dihydrides having *trans* geometry.

Both complexes **2a** and **2b** react with ethylene according to reaction (3):

$$cis\text{-}PtH_2(L-L) + C_2H_4 \longrightarrow Pt(C_2H_4)(L-L) + H_2 \qquad (3)$$
$$\mathbf{2a,b} \qquad\qquad \mathbf{3a\ b}$$

This reaction does not lead to ethylene hydrogenation, as confirmed by GC-MS analysis. Complexes **3a** and **3b** are isolated as white powders, they are air-stable and the relevant spectroscopic data are reported in Table I.

Owing to our interest in the olefin hydroformylation with mono-hydrido Pt(II) species [15], we thought it interesting to study the reaction of complexes **2a** and **2b** with a stoichiometric amount of dry HCl, in order to obtain new *cis*-PtHCl(L–L) compounds [1]. However, all our attempts failed, since by reacting complexes **2a** and **2b** with a 1:1 stoichiometric amount of dry HCl we obtained a 50:50 mixture of the complexes **1a,b** and **2a,b**. The dichloro complexes **1a** and **1b** are the only products obtained by reacting complexes **2a** and **2b** with a two-fold stoichiometric amount of HCl.

Likewise, mono-hydrido-chloro complexes cannot be obtained by reacting complexes **3a** and **3b** with HCl: this reaction affords in good yield (>70%) the alkyl complexes *cis*-$PtCl(C_2H_5)(L-L)$ (**4a,b**) which have been identified by comparing their spectroscopic properties with those of authentic samples [16].

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