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Preliminary communication

HYDROGENATION OF CATIONIC BIS(TERTIARY ALKYLPHOSPHINE)-RHODIUM(I) COMPLEXES. AN NMR STUDY

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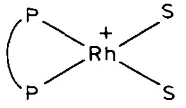
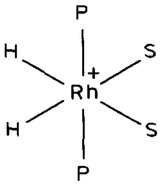
Summary

Rhodium hydrides have been observed in solution in the reaction of cationic rhodium(I) complexes of bis(tertiary phosphines) with hydrogen.

In the last few years considerable interest has been focused on the use of cationic phosphinerhodium(I) complexes ([L_2Rh(NBD)]ClO_4; L = tertiary phosphine, NBD = norbornadiene) as catalyst precursors for the hydrogenation of organic substrates [1]. A particular feature of the chemistry of these complexes is their behavior with hydrogen in the absence of substrate. When L_2 is a bidentate phosphine ligand, (P—P), such as dppe (1,2-bisdiphenylphosphinoethane), the catalyst precursor reacts with two moles of H_2 in methanol to give the rhodium(I) disolvate I as the only detectable species in solution [2]. However, when L is a monodentate tertiary phosphine the complex reacts with 3 moles of H_2 resulting in the rhodium(III) dihydride II [3]. Recently Brown and coworkers have demonstrated that I does in fact rapidly and reversibly add hydrogen, presumably to give a solvated cation such as III, but since III is not detectable, they conclude that the equilibrium constant for the reaction is very small [4].



(I)



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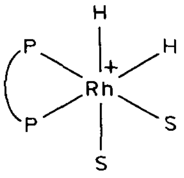

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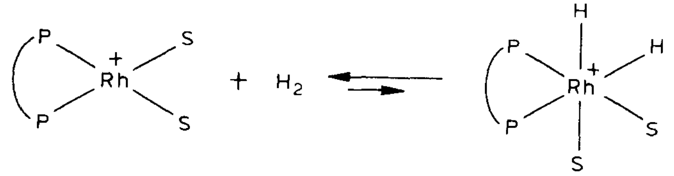
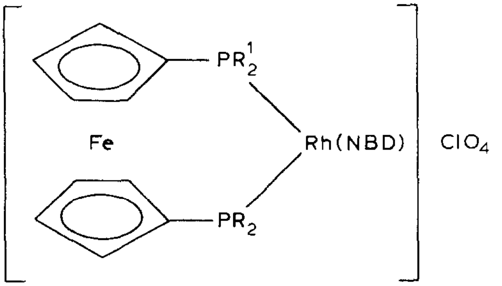
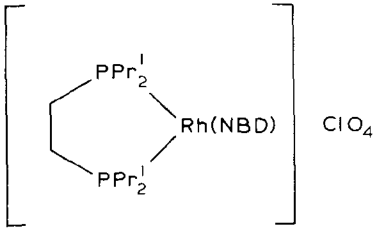


We have recently shown that when (P—P) is *rac*-$(PhBu^tPC_5H_4)_2Fe$ a bimetallic rhodium hydride species $[(P—P)HRh(H)_3RhH(P—P)]^+$ may be isolated from the reaction solution [5]. This is in contrast to the behavior of the dppe derived complexes described above [2]. However, there are two major differences between the two systems. Firstly, the ferrocene-based bis(tertiary phosphine) ligand is conventionally regarded as forming a 6-membered chelate ring (dppe forms a 5-membered ring) and secondly the ferrocenylphosphine contains alkyl groups and is thus more electron rich. We have therefore carried out an NMR study of the reaction of hydrogen with complexes IV and V [6] in order to determine some of the factors influencing hydride formation.



(IV)



(V)

(IVa: R = R^1 = Pr^i;
IVb: R = R^1 = Ph;
IVc: R = Ph, R^1 = Bu^t;
IVd: R = Ph, R^1 = Pr^i)

When a solution of IVa in $CDCl_3$ is treated with H_2 for 3—5 minutes, the color darkens considerably and the major species in the hydride region of the ^1H NMR spectrum exhibits two equal area multiplets indicated A in Fig. 1. The bridging hydride signal consists of a multiplet at δ —10.65 ppm from which a $^2J(PH)$ coupling of 75 Hz can be estimated. The broad quartet (J 20 Hz) at δ —20.30 ppm is in the terminal hydride region. The $^{31}P\{^1H\}$ NMR spectrum at this stage consists of only one signal (δ 65.66 (d) ppm, $J(RhP)$ 139 Hz) but the ferrocenyl ligand signals are doubled up indicating the molecule lacks a plane of symmetry through the chelate ring. These results are best explained in terms of the structure VI which may or may not contain weakly coordinated ClO_4 anions. It is quite reasonable to suppose that VI results from *cis*-dihydrogen addition to rhodium followed by rapid dimerisation.

On continued exposure to H_2 in the NMR tube a second species B in Fig. 1 develops at the expense of A. The ratio of the bridging (—13.52 ppm) to

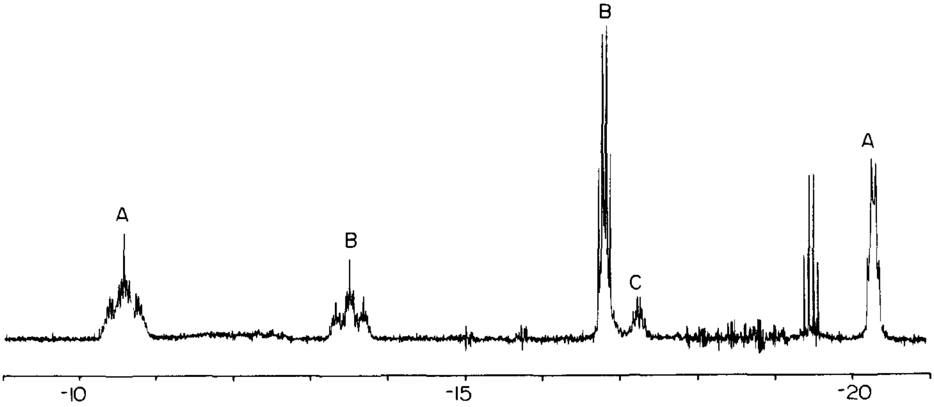
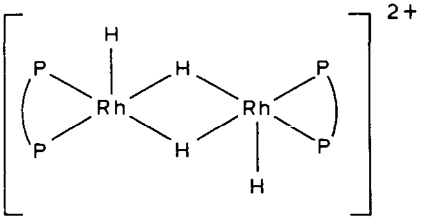
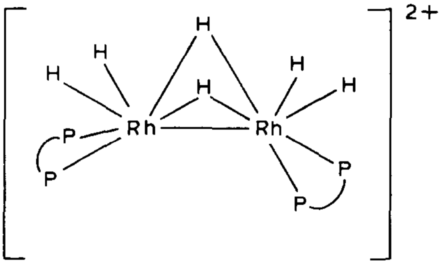


Fig. 1. The hydride region of the 400 MHz ^{1}H NMR spectrum of IVa on treatment with hydrogen ($CDCl_3$). The quartet at —19.5 ppm is due to an impurity.



(VI)

terminal (—16.82 ppm) multiplets in B is 1/2. There is one large ^2J(PH) coupling of 72 Hz(t) and one smaller one of 12 (t) or 20 Hz(t), the ambiguity arising because one of these values is the ^1J(RhH) coupling. The terminal region shows only a small ^2J(PH) coupling of 19 Hz(t) whilst the ^1J(RhH) coupling (22 Hz) has the appearance of a virtual triplet, presumably the result of ^1J(RhRh) coupling. The ligand resonances are again doubled so that a structure based on VI with two more terminal hydrogen atoms cannot be considered. Only an arrangement as in VII would account for the available data. A related structure is present in $[CpLRh(H)_3RhLCp]^+$ when L = PPr^i_3 [8]



(VII)

Species C at —17.30 (Fig. 1) seems to be the end product of hydrogenation. It contains only terminal hydrogen atoms ^2J(RhH) 22 Hz(d), ^2J(PH) 25 Hz(t). This could be ascribed to a fluxional species such as $[(P—P)RhH_4]^+$ (VIII).

Solution of V in CD_2Cl_2 lightens in color when treated with H_2. In the early stage a cation of structure VII predominates (—9.08(m), —18.63(m) ppm). Further reaction results in the disappearance of this species and the appearance of a new broad resonance at —18.30 ppm and a new bridged species (—8.25(m), —18.1(m) ppm) of unknown structure.

The three other rhodium complexes IVb, IVc, IVd when treated with H_2 in $CDCl_3$ react similarly. The main products appear to be bridged hydrides of structure VII; chemical shift data are as follows: IVb —11.4, —16.6; IVc —14.4, —15.4; IVd —12.1, —16.2 ppm.

Hydrides are also easily obtained from solutions of $[L_2Rh(NBD)]ClO_4$ in a variety of solvents when L_2 is a P—N bound ligand such as $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3(CHMeNMe_2)PPh_2\text{-}1,2)$ [9].

These results imply that a major factor influencing the reactivity of [bis(tertiary phosphine)]rhodium(I) complexes with molecular hydrogen is the nature of the phosphorus substituents. Chelate ring size should have little effect except when the ligand contains a long aliphatic chain as bridge e.g. $Ph_2P(CH_2)_5PPh_2$, when internal metallation to give hydrides is possible [2a,2c].

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6 Complexes IV and V were prepared by the procedure of Schrock and Osborn [3] from the appropriate ligands [7]. All complexes gave satisfactory analytical and spectral data. IVa: ^{31}P (δ 38.09 ppm w.r.t. 75% H_3PO_4, $J(RhP)$ 158.7 Hz), V: ^{31}P (δ 78.00 ppm w.r.t. 75% H_3PO_4, $J(RhP)$ 154 Hz).

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