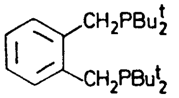
A *cis*-Dihydride of Platinum(II)

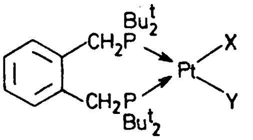
By Christopher J. Moulton and Bernard L. Shaw*
(*School of Chemistry, The University, Leeds* LS2 9JT)

Summary The first example of a *cis*-dihydride of platinum (II) is described.

Since the discovery of *trans*-[$PtHCl(PEt_3)_2$] many transition metal hydrides containing tertiary phosphines as stabilizing ligands have been prepared.[1] Monohydrides of the types [$PtHXL_2$] (X = anionic or radical ligand) of *trans*-configuration are particularly common whilst, in contrast, *cis*-monohydrides are rare: they can be prepared, however, by somewhat unusual methods such as the hydrogenolysis of a platinum–silicon bond[2] or by oxidative addition of a silicon hydride.[3] *trans*-Dihydrides of platinum(II), *trans*-[PtH_2L_2], are usually very unstable, *e.g.*, with L = PEt_3 or PPh_3, but it has been shown that with extremely bulky tertiary phosphines, *e.g.*, L = PBu^t_2Et or $P(cyclohexyl)_3$, stable, crystalline *trans*-dihydrides of this type can be prepared.[4] Hitherto, however, a *cis*-dihydride of platinum(II) has not been prepared. At first sight it would seem that very bulky tertiary phosphines could not be used to stabilize a *cis*-dihydride since phosphines with very large 'cone angles'[5] cannot normally be accommodated in mutually *cis*-positions. Moreover, we have found that a diphosphine such as $Bu^t_2P[CH_2]_3PBu^t_2$ prefers to bridge metal atoms rather than chelate.[6] It seemed possible, however, that the diphosphine $Bu^t_2PCH_2C_6H_4CH_2PBu^t_2$ (**1**)† which has very bulky end groups, might chelate since (i) the resultant seven-membered rings would allow the bulky PBu^t_2 end groups to be far apart, *i.e.*, the P–metal–P bond angle could be large and (ii) the stereochemistry and rigidity of the $CH_2C_6H_4CH_2$ framework would promote chelation and prevent bridging of two metal atoms. This proved to be the case for this diphosphine readily displaced t-butyl cyanide from *cis*-$[PtCl_2(Bu^tCN)_2]$ to give the chelate (**2**; X = Y = Cl). This dichloride was characterized by microanalytical and molecular weight data and by i.r. and n.m.r. spectroscopy. Moreover, it was reduced smoothly by sodium tetrahydroborate in ethanol to the *cis*-dihydride, $[PtH_2\{Bu^t_2PCH_2C_6H_4CH_2PBu^t_2\}]$ (**2**; X = Y = H), in virtually quantitative yield. This dihydride was characterized by microanalytical and molecular weight data and also by ^1H and ^{31}P n.m.r. (in $CDCl_3$) and i.r. spectroscopy. The ^1H n.m.r. pattern of the hydridic hydrogens is, as expected, second order, δ – 4·00 [$|^2J$(P–H, *trans*)$|$ 165, $|^2J$(P–H, *cis*)$|$ 22, and ^1J(Pt–H) 1008 Hz]. The t-butyl hydrogens give the expected doublet and methylene hydrogens a doublet with satellites due to ^{195}Pt coupling. The ^{31}P resonance is a singlet with satellites, δ (rel. to H_3PO_4) 46·37 p.p.m. [^1J(Pt–P) 2112 Hz], and ν(Pt–H) (Nujol mull) 2023s cm^{-1}: presumably the symmetrical and asymmetrical stretching frequencies occur at very nearly the same frequency. When treated with HCl in Et_2O the dihydride was converted into the mono-hydride $[PtHCl\{Bu^t_2PCH_2C_6H_4CH_2PBu^t_2\}]$ (**2**; X = H, Y = Cl). This monohydride had, as expected, a first order ^1H (hydride) n.m.r. pattern, δ – 7·69 [^2J(P–H, *cis*) 14, ^2J(P–H, *trans*) 190, and ^1J(Pt–H) 696 Hz], and rwo t-butyl doublets and two methylene doublets (with satellites). The ^{31}P n.m.r. spectrum showed signals at δ 24·59 [^1J(P–H) 2058 Hz (*trans*-H)] and 46·03 [^1J(P–H) 4199 (*trans*-Cl) and ^2J(P–P) 9·4 Hz] p.p.m. The i.r. spectrum showed absorptions at ν 2085s (Pt–H) and 282s (Pt–Cl) cm^{-1}. Even prolonged treatment with dry HCl in ether failed to convert this mono hydride into the dichloride (**2**; X = Y = Cl).



(1)



(2)

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† Made by treating *o*-$BrCH_2C_6H_4CH_2Br$ with $PHBu^t_2$ and subsequent treatment with a base.

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