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THE PREPARATION OF SOME BULKY DIHALO-, HALOHYDRIDO- AND DIHYDRO-PHOSPHINEPLATINUM(II) COMPOUNDS

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Summary

A series of dichloro-, hydridochloro- and dihydro-platinum(II) complexes have been prepared using bulky phosphine ligands, as $PtX_2(PR_3)_2$, $PtH(X)(PR_3)_2$ and $PtH_2(PR_3)_2$ (X = Cl, Br, I; R_3 = i-Pr_3, (cyclo-$C_6H_{11})_3$, (cyclo-$(C_6H_{11})_2$Ph). The dichloro compounds have been converted into the corresponding hydrido complexes with either hydrazine hydrate or sodium tetrahydroborate. In some cases, e.g. $PtH_2[P(cyclo\text{-}C_6H_{11})_3]_2$, variation had to be introduced owing to the limited reactivity of the dichloro compounds. The spectral properties (IR, NMR and mass spectra) of the various complexes are reported.

Introduction

While several monohydride derivatives of platinum(II) are known, e.g. PtCl(H)L_2 (where L = trialkylphosphine), the reported dihydride derivatives are relatively few in number, and generally less stable. The addition of hydrogen to Pt$(PEt_3)_3$ yields an unstable five coordinate species, $PtH_2(PEt_3)_3$, which dissociates to $PtH_2(PEt_3)_2$ above —30°C [1]. The reported preparation of several *trans*-PtH_2L_2 complexes by the addition of bulky phosphine ligands (L = Pcy_3, Pcy_2-i-Pr, Pcy_2Et, where cy = cyclohexyl) to an $Pt(acac)_2/AlR_3$ reaction mixture [2] has recently been disputed in a preliminary report of other such *trans*-$PtH_2(PR_3)_2$ complexes (R_3 = t-$BuMe_2$, t-$BuEt_2$, n-Bu_2-t-Bu, t-$Bu(CH_2Ph)_2$, t-Bu-n-Pr_2, t-Bu_2CH_2Ph, cy_3) prepared from either the corresponding chloro, $PtCl_2(PR_3)_2$ or hydridochloro, $PtCl(H)(PR_3)_2$, by treatment with $NaBH_4$ in ethanol [3]. Other reports have shown that bulky phosphines stabilise Pt—H bonds in PtH(X)(P-t-$BuPh_2)_2$ (X = Cl, Br, I) [4] and $PtCl(H)(Pcy_3)_2$, and that with other members of the Ni—Pd—Pt triad both hydride and tetrahydroborate groups may be stabilised as in MH(X)$(PR_3)_2$ (M = Ni, Pd; X = BH_4, Cl; R = cy, i-Pr) [5,6,7]. We have been studying bulky phosphineplatinum(II) compounds to determine whether the hydroborate

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derivatives may be similarly stabilised in this case, and to study further hydridoplatinum complexes.

Results and discussion

We have prepared a series of bulky phosphineplatinum (II) compounds, $PtX_2(PRR'_2)_2$, (where X = Cl, Br, I; R = R' = i-Pr, s-Bu, cy; R = Ph, R' = cy) as shown in Table 1. As expected, these all adopt a *trans* geometry in both the solid and solution states as shown by IR and NMR spectroscopy, and in one case by an X-ray analysis on $PtI_2[P(cy)_3]_2$ [8]. The compounds have also been identified by mass spectrometry. The preparative method consisted of adding the phosphine to an aqueous solution of potassium tetrachloroplatinate when the phosphine complex precipitated. The corresponding bromo and iodo compounds were obtained by adding the required alkali halide to the original reaction mixture. The chloro and bromo derivatives are very pale yellow crystalline solids, while the iodo analogues are yellow-orange. The melting points and analytical data are given in Table 1. The IR spectra of the compounds show the expected single Pt—halogen stretching mode near 340 cm^{-1} (chloro) and 250 cm^{-1} (bromo), but the absorption for the iodo compound was not detected since it occurred below 200 cm^{-1} (Table 1). The ^1H NMR spectra of the dicyclohexylphenyl- and tricyclohexyl-phosphine complexes showed broad complicated absorptions from the ligand protons. The compounds $PtX_2(P\text{-}i\text{-}Pr_3)_2$ and $PtCl_2(P\text{-}s\text{-}Bu_3)_2$ show simpler patterns; thus the former shows an approximately 1 : 3 : 3 : 1 quartet arising from the phenomenon of virtual coupling [9] with the latter showing broad singlets (three inequivalent hydrogen atoms) together with a triplet and a quartet respectively (Table 1, Fig. 1). In the mass spectra the molecular ions were observed for all the dichloro compounds, while for the compounds containing cyclohexyl and

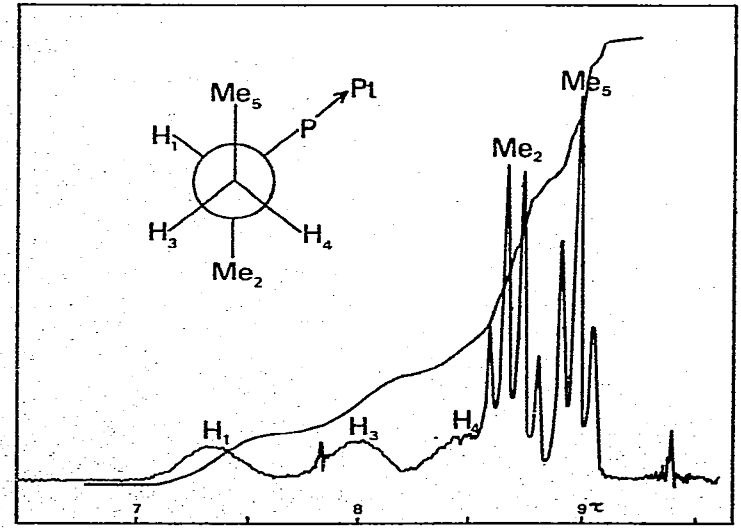

Fig. 1. The ^1H NMR spectrum of *trans*-$PtCl_2(P\text{-}s\text{-}Bu_3)_2$.

TABLE 1

ANALYTICAL, IR AND ^{1}H NMR DATA OF *trans*-PtX_2L_2 COMPOUNDS

X	L	M.p. (°C)	Analysis found (calcd.)(%)			Ir(cm^{-1})		^{1}H NMR^a		
			C	H	Halogen	ν(Pt—X)	ν(Pt—P)	$\tau(CH_3)^b$	τ(CH)	$^3J(CH_3—H)$
Cl	P-i-Pr_3	256	37.16 (36.86)	7.35 (7.17)	12.14 (12.12)	355	414	8.66	7.1	6.9
Br	P-i-Pr_3	263—265	31.73 (32.00)	6.08 (6.22)	23.99 (23.70)	249	418	8.63	7.1	6.6
I	P-i-Pr_3	202—205	28.36 (28.09)	5.33 (5.46)	33.02 (33.03)	—	—	8.62	6.6	6.6
Cl	P-s-Bu_3	152	42.86 (42.99)	8.13 (8.05)	10.40 (10.60)	333	—	8.71 (H(2)) 8.99 (H(5))	7.36 (H(1)) 8.02 (H(3)) 8.50 (H(4))	—
Cl	Pcy_2Ph	304—306	52.58 (53.07)	6.60 (6.34)	9.06 (8.72)	338	415	—	—	—
Br	Pcy_2Ph	309	47.71 (47.84)	5.83 (5.98)	17.95 (17.72)	244	419	—	—	—
I	Pcy_2Ph	302	43.23 (43.33)	5.99 (5.42)	24.65 (25.47)	—	—	—	—	—
Cl	Pcy_3	322—325	51.83 (52.29)	7.80 (7.99)	8.84 (8.59)	338	409	—	—	—
Br	Pcy_3	~310(dec.)	46.85 (47.21)	6.83 (7.21)	17.72 (17.49)	248	427	—	—	—
I	Pcy_3	289—291	43.12 (42.81)	6.92 (6.54)	25.68 (25.17)	—	—	—	—	—

^{a} J in Hz spectra of ligands containing cy group were unsatisfactory due to limited solubility, and complicated absorptions in the phenyl region. ^{b} In sec-butyl group, signals assigned according to $CH(1)(CH(2)_3)CH(3)H(4)(CH(5)_3)$; assignments for H(3) and H(4) may be reversed.

phenyl groups, fragmentation involved loss of these groups as integral mass units. The complexes containing the isopropyl group behaved similarly to the latter compounds but in addition the loss of 14 a.m.u. (CH_2) fragments was also observed. The iodo derivatives failed to show a molecular ion in some cases, and instead the highest mass ion was that which had lost one iodine atom (See Experimental).

The compounds (Table 1) are relatively inert towards displacement reactions, and we were unable to displace a halide ion with various neutral ligands (e.g. CO, PEt_3 and i-PrNC) to produce a cationic species as has been reported for the lower alkyl phosphine compounds [10]. A similar difficulty occurs on attempts to replace the chloride with other halide ions, and the preparative route mentioned above had to be used for the bromo and iodo compounds.

The ease of conversion of the dichloro derivative to the monohydride, $PtCl(H)(PR_3)_2$, varies with the phosphine used, and decreases in the order $P\text{-i-}Pr_3 > Pcy_2Ph > Pcy_3$, which correlates with the relative steric requirements of each ligand. Thus the complex $PtCl_2(P\text{-i-}Pr_3)_2$ may be converted to the monohydride by refluxing with hydrazine hydrate in 2-methoxymethanol for several hours, but with $PtCl_2(Pcy_2Ph)_2$ even longer reaction times are required, and only trace quantities are formed with $PtCl_2(Pcy_3)_2$. The addition of a small quantity of tri-*p*-tolylphosphine, or triphenylarsine, to the reaction mixture catalyses the formation of $PtCl(H)(Pcy_2Ph)_2$. We are unable to define the mechanism of this catalysis at present, but it would appear necessary for the added ligand [$(p\text{-}CH_3C_6H_4)_3P$ or $AsPh_3$] to enter the coordination sphere of the platinum to relieve the steric crowding which we assume otherwise inhibits the reaction. It is known, however, that when a bulky ligand is coordinated to the metal, a bimolecular type of substitution mechanism is no longer facile, and ligand exchange has been postulated to occur through an interchange dissocative process where the square-planar complex behaves as a pseudo-octahedral species and a molecule of solvent is involved in the rate-determining step [11]. We are investigating the mechanism further to determine whether the intermediate involves the loss of a halide ion or a phosphine ligand. At higher temperatures (>200°C) we have found that it is the latter group which is apparently eliminated in that when *trans*-PtI_2L_2 ($L = P\text{-i-}Pr_3$, Pcy_2Ph, Pcy_3) compounds are heated to their melting points (Table 1) a phosphine ligand is eliminated to produce the dimeric deep-red complex $Pt_2I_4L_2$. The corresponding chloro and bromo compounds do not behave in this way; no reaction occurred on heating and we were unable to isolate the dimeric species in these cases. Even in the iodo derivative the instability of the halogen bridge is demonstrated by reaction with carbon monoxide at ambient temperatures and pressure, with the reaction proceeding even more rapidly in refluxing chloroform solution:

$$Pt_2I_4(Pcy_3)_2 + 2CO \rightarrow 2\ cis\text{-}Pt(CO)I_2(Pcy_3)$$

The above modification for the hydride preparation was only partially successful for the preparation of $PtH_2(Pcy_3)_2$, and to improve the overall yield of this compound we devised a more circuitous route. When the arsine complex *cis*-$PtCl_2(AsPh_3)_2$ was treated with tricyclohexylphosphine and hydrazine hydrate in ethanol, the chlorohydrido compound *trans*-$PtCl(H)(Pcy_3)_2$ was formed as a pale yellow solid, in addition to some dichloride, *trans*-$PtCl_2(Pcy_3)_2$. Using this proce-

TABLE 2

ANALYTICAL, IR AND ^2H NMR DATA OF *trans*-$PtH(X)L_2$ COMPOUNDS

X	L	M.p. (°C)	Analysis found (calcd.)(%)			IR(cm^{-1})^a ν(Pt—H)	^2H NMR^b			
			C	H	Halogen		τ(Pt—H)	τ(ligand)	^2J(P—H)	^1J(Pt—H)
Cl	P-i-Pr_3	129—131	39.24 (39.17)	7.37 (7.80)	6.32 (6.44)	2193	28.55	8.67(CH_3) 7.56(CH)	12.6	1285
Cl	Pcy_2Ph	196—198	55.39 (55.42)	6.99 (7.06)	4.36 (4.55)	2223	28.21	8.44(cy) 2.45(Ph)	12.5	1250
Cl	Pcy_3	235—237	54.49 (54.57)	8.22 (8.46)	5.06 (4.48)	2172	28.81	8.44(cy)	12.7	1282
I	Pcy_3	257—258	48.97 (48.92)	7.33 (7.59)	14.34 (14.38)	2158	23.9	—	11.1	—
H	P-i-Pr_3	53—55	42.25 (41.78)	7.97 (8.51)	—	1723	14.01	8.80(CH_3) 7.84(CH)	16.7	790
H	Pcy_2Ph	180—182	—	—	—	1765	13.18	8.52(cy) 2.48(Ph)	17.6	787
H	Pcy_3	—(dec.)	56.81 (57.10)	8.68 (8.98)	—	1720	13.06	8.39(cy)	18.8	790

[a] Recorded from KBr discs. [b] J in Hz, recorded from $CDCl_3$ solutions.

dure with the other phosphines, P-i-Pr_3 and Pcy_2Ph, yielded only the dichloride complexes, *trans*-$PtCl_2(PR_3)_2$ (R = cy_2Ph, i-Pr). It would appear therefore that in these latter two cases the rate of replacement of the arsine ligand is more rapid than the rate of formation of the hydride species, but with the bulky Pcy_3 ligand the two rates are comparable, and thus both the chlorohydrido and dichloride compounds are obtained. Unlike the dichloride, the chlorohydrido complex, *trans*-$PtClH(Pcy_3)_2$, does exchange chloride on treatment with lithium iodide in acetone to yield to corresponding *trans*-hydridoiodo complex.

The hydrides, *trans*-$PtCl(H)L_2$ (L = P-i-Pr_3, Pcy_2Ph, Pcy_3) and *trans*-PtH(I)-$(Pcy_3)_2$ are all air stable, colourless or pale yellow, crystalline compounds. The values of ν(Pt—H) for the hydrides are recorded in Table 2, and are discussed below with the spectra of the dihydride compounds. The mass spectra of these compounds show a low intensity molecular ion with the most intense peak arising from the loss of a halogen atom.

We have studied the reactions of the halohydrido compounds with the hydroborate ion to determine whether the corresponding hydridohydroborate species can be isolated. In every case when the two reactants are stirred together in acetonitrile solution in the absence of light, the sole product is the corresponding dihydride species, *trans*-PtH_2L_2, (L = P-i-Pr_3, Pcy_2Ph, Pcy_3). We have found no evidence for any hydroborate intermediate by interrupting the reaction at various stages, or by changing the solvent. The formulation of the dihydride is supported by elemental analysis, IR, NMR and (in part) mass spectrometric data. The compounds are stable when stored under nitrogen in the dark, but become discoloured on standing in the light for prolonged periods. The compound PtH_2-(P-i-$Pr_3)_2$ sublimes at 50°C/10^{-3} torr, and all three compounds slowly revert to the chlorohydrido compound on standing in chloroform solution. The IR spectra all show strong, single but fairly broad bands associated with ν(Pt—H) occurring at a much lower frequency (1710—1765 cm^{-1}) than the monohydride compounds (2158—2223 cm^{-1}) consistent with a *trans* geometry. The data are given in Table 2. The ^1H NMR spectra of the mono- and di-hydride compounds (Table 2) show considerable variations in the τ(Pt—H) and ^1J(Pt—H) values. Both sets of spectra show the expected 1 : 2 : 1 triplet at high-field from coupling of the hydride to the two equivalent ^{31}P nuclei, as well as the two satellites from the $^{195}Pt(I = \frac{1}{2})$ isotope, and are therefore consistent with a *trans* geometry. The data for the tricyclohexylphosphine derivative correspond well with the previously reported values when allowance is made for the different solvents used [4]. The τ(Pt—H) values correspond with the relative *trans* influence of the ligands in that the high-field shift is dependent upon, amongst other factors, the metal—hydrogen bond length with the shorter Pt—H bonds showing the higher field shift. Thus the increasing τ(Pt—H) values should be the reverse of the *trans* influence series, i.e. $Cl^- > I^- > H^-$, as is observed. Using the same arguments and, since the ^1J(Pt—H) values are dependent directly upon the proportion of *s*-character in the Pt—H bond, the value of ^1J(Pt—H) in the dihydride series should be less than in the monohydride series. Whilst this rationale allows an explanation of the experimental trends it gives no indication of the magnitude of such effects, and it may be that one or more of the other contributing factors do in fact predominate. The mass spectrum of $[PtH_2(i\text{-}Pr_3P)_2]$ showed only a weak molecular ion, and a fragmentation pattern which involved loss of the hydrogen atoms and isopropyl groups (see Experimental). Satisfactory spectra of the other two dihydrides could not be obtained due to decomposition, and only fragmentation patterns attributable to the ligands were obtained.

The chlorohydrido compound $PtCl(H)(Pcy_2Ph)_2$ is converted to the dideuteride product $Pt^2H_2(Pcy_2Ph)_2$ on treatment with lithium deuteroborate, $LiBD_4$, as evidenced by the lack of any Pt—H absorption in the IR spectrum, and the appearance of a strong band at 1270 cm^{-1} [ν(Pt—H)/ν(Pt—^{2}H) 1.39]. We assume therefore the initial deuterohydrido product undergoes further exchange with the BD_4^- ion yielding the dideuteride product.

Experimental

All reactions were performed under a dry nitrogen atmosphere, the solvents were dried and distilled prior to use, and the uncorrected melting points were determined using a Gallenkamp MF-350 apparatus. Molecular weights were made with a Mechrolab 301A vapour pressure osmometer, and microanalyses were carried out by either the microanalytical laboratory at the University of Sheffield or by A. Bernhardt Laboratories, West Germany.

The IR spectra were obtained using Perkin—Elmer 457 and 180 spectrometers, or on a Research and Industrial Instruments Company F.S.-720 Fourier spectrometer (in the range 300—50 cm^{-1}). Routine proton NMR spectra were recorded using a Perkin—Elmer R12 (60 MHz) spectrometer, but the quoted values are from spectra obtained using either a Varian HA100 or Bruker WH90 spectrometers. The mass spectra were run using an AEI MS12 or V.G. Micromass 12 spectrometer. The phosphine ligands were prepared as described elsewhere [12, 13].

Preparations

Trans-Dichlorobis(triisopropylphosphine)platinum(II)

$P\text{-}i\text{-}Pr_3$ (1.95 g, 12.2 mmol) was added to K_2PtCl_4(2.5 g, 4.7 mmol) dissolved in 15 ml of water. After shaking for 3 h the complex was filtered off and recrystallised from chloroform/ethanol to yield yellow prisms. Yields averaged 60—65%. Mol. wt. ($CHCl_3$ solution), 581 (calcd. 586). The mass spectrum showed a molecular ion at *m/e* 590—584, and ions corresponding to the following fragments: $Pt(P\text{-}i\text{-}Pr_3)_2$, $PtP_2\text{-}i\text{-}Pr_5$, $PtP_2\text{-}i\text{-}Pr_4$, $PtP_2\text{-}i\text{-}Pr_3$, $PtP\text{-}i\text{-}Pr_2$ and PtP_2^+.

trans-$PtCl_2(Pcy_2Ph)_2$ and trans-$PtCl_2(Pcy_3)_2$

Two molar equivalents of the phosphine (usually about 2 g) was added to one of K_2PtCl_4 dissolved in a mixture of chloroform/water. The mixture was stirred vigorously and heated to reflux. After separation of the chloroform layer, when the colour of the starting material in the aqueous layer had been discharged and removal of the solvent achieved, the solids were obtained as yellow solids. They were recrystallized from dichloromethane/ethanol mixtures, and yields were 50—60%. For $PtCl_2(Pcy_2Ph)$ the mol. wt. ($CHCl_3$) was 842 (calcd. 814), but $PtCl_2(Pcy_3)$ was too insoluble for reliable measurements to be made. Both compounds show a molecular ion in their mass spectrum and also ions with *m/e* values corresponding to: $PtCl(Pcy_2Ph)_2$, $Pt(Pcy_2Ph)_2$, $PtClP_2cy_3Ph_2$, and $PtP_2cy_3Ph_2$, for $PtCl_2(Pcy_2Ph)_2$; and $Pt(Pcy_3)_2$, $PtClP_2cy_5$ and Pcy_3 for $PtCl_2(Pcy_3)_2$.

Bromo and iodo derivatives of PtX_2L_2 (L = P-i-Pr_3, Pcy_2Ph and Pcy_3)

These were prepared essentially as reported for the chlorocomplexes except that the appropriate lithium halide was added in excess to the reaction mixture. Thus typically, the phosphine (2 g) and K_2PtCl_4 (0.5 mol equivalent with respect to the phosphine) were treated in the respective solvent in the presence of the lithium halide (10 mol equivalents with respect to platinum). All the compounds were recrystallised from chloroform/ethanol mixtures, and yields were similar to those of the chloro compounds. Molecular ions (M^+) were not observed in every compound; the major ions are outlined below:

$PtBr_2(P\text{-}i\text{-}Pr_3)_2$: M^+, $PtBr_2P_2\text{-}i\text{-}Pr_5$, $PtBr_2P_2\text{-}i\text{-}Pr_4$.

$PtI_2(P\text{-}i\text{-}Pr_3)_2$: M^+, $PtI(P\text{-}i\text{-}Pr_3)_2$, $PtP_2\text{-}i\text{-}Pr_5C_2H_5$, $PtI_2(P\text{-}i\text{-}Pr_3)$, $Pt(P\text{-}i\text{-}Pr_3)_2$.

$PtBr_2(Pcy_2Ph)_2$: Poorly resolved spectrum, weak M^+ ion observed.

$PtI_2(Pcy_2Ph)_2$: $PtIP_2cy_4Ph_2$, $PtP_2cy_4Ph_2$, Pcy_3H_2,Pcy_3H.

$PtI_2(Pcy_3)_2$: $PtI(Pcy_3)_2$, $Pt(Pcy_3)_2$, PtP_2cy_5, PtP_2cy_4, PtP_2cy_3, $PtIP_2cy_2$, $PtIP_2$, PtP_2cy.

trans-$PtCl_2$(P-s-Bu_3)$_2$

The solid complex $AgNO_3 \cdot P\text{-}s\text{-}Bu_3$ (3.78 g, 10 mmol) was added to a solution of K_2PtCl_4 (1 g, 2.5 mmol) in a 1 : 3 ethanol/water (30 ml) mixture. After shaking overnight the off-white solid was filtered off, dissolved in chloroform, and petroleum ether (60—80°) added. As the solvent slowly evaporated, yellow crystals of the product were deposited. (Yield 0.85 g, 53%). The mass spectrum showed a molecular ion at *m/e* 674—668.

Formation of bridged tetraiodide complexes, $Pt_2I_4L_2$

The respective diiodide complexes, PtI_2L_2 (L = P-i-Pr_3, Pcy_2Ph, Pcy_3), were heated to their melting points for about 0.5 h, after which time the orange colour of the solids had deepened to a dark red. Recrystallisation of the solids from CH_2Cl_2/EtOH mixtures afforded the pure $Pt_2I_4L_2$ compounds in near 80% yields.

$Pt_2I_4(P\text{-}i\text{-}Pr_3)_2$, m.p. 225—228°. Found: C, 17.92; H, 3.46; I, 41.50. $C_{18}H_{42}I_4P_2Pt_2$ calcd.: C, 17.73; H, 3.45; I, 41.7%.

$Pt_2I_4(Pcy_2Ph)_2$, m.p. 315° (dec.). Found: C, 29.02; H, 3.68. $C_{36}H_{54}I_4P_2Pt_2$ calcd.: C, 29.88; H, 3.74%.

$Pt_2I_4(Pcy_3)_2$, m.p. 335° (dec.). Found: C, 28.94; H, 4.42; I, 33.77. $C_{36}H_{66}I_4P_2Pt_2$ calcd.: C, 29.63; H, 4.53; I, 34.82%.

The bridge cleavage of $Pt_2I_4(Pcy_3)_2$ with carbon monoxide was achieved by passing the gas through a refluxing chloroform solution (50 ml), containing 0.2 g of the tetraiodide complex, for about 0.5 h. The resulting yellow solution was evaporated to dryness and the product identified as $Pt(CO)I_2(Pcy_3)$. Found: C, 22.34; H, 3.10. $C_{19}H_{33}I_2OPPt$ calcd.: C, 22.56; H, 3.27%. The mass spectrum showed ions at *m/e* values from M, PtI_2Pcy_3, $PtI_2(CO)Pcy_3$, $PtI_2(CO)P$, $PtI(CO)P$ and Pcy_3. Attempted recrystallisation of the product from CH_2Cl_2/EtOH led to evolution of carbon monoxide and the reformation of the tetraiodide complex.

Formation of trans-$PtCl(H)L_2$ (L = P-i-Pr_3, Pcy_2Ph)

Hydrazine hydrate (1 ml) was added to a suspension of *trans*-$PtCl_2(P\text{-}i\text{-}Pr_3)_2$

(1.0 g) in 2-methoxymethanol (20 ml) and the mixture refluxed for 3 h. The solid slowly dissolved to give a yellow solution, and after removal of the solvent, washing with water, and recrystallisation from $CH_2Cl_2/MeOH$ by slow evaporation, the hydride $PtCl(H)(P\text{-i-}Pr_3)_2$ was obtained as a pale yellow solid. Yield 0.57 g, 60%. The hydride, $PtCl(H)(Pcy_2Ph)_2$ was prepared in similar yields except several mg. of tri-*p*-tolylphosphine or $AsPh_3$ were added. The mass spectrum showed peaks at *m/e* masses corresponding to *M*, $PtH(Pcy_2Ph)_2$, PtP_2cyPh_2.

Formation of trans-PtCl(H)(Pcy₃)₂

Hydrazine hydrate (1 ml) and excess tricyclohexylphosphine (1 g) were added to a stirred suspension of $PtCl_2(AsPh_3)_2$ (1.0 g) in ethanol (40 ml), and the mixture refluxed for 0.5 h. The yellow solid deposited was filtered from the hot solution, and after recrystallisation from $CH_2Cl_2/EtOH$ by slow evaporation, the hydride was obtained as fine colurless needles. The mass spectrum showed *m/e* masses from *M*, $PtCl(Pcy_3)_2$, $Pt(Pcy_3)_2$. The iodide, $PtH(I)(Pcy_3)_2$ was prepared from $PtCl(H)(Pcy_3)_2$ by the action of sodium iodide in acetone solution over a period of 24 h. The mass spectrum showed *m/e* masses from *M*, $PtI(Pcy_3)_2$, $PtH(Pcy_3)_2$, $Pt(Pcy_3)_2$.

Formation of dihydride complexes trans-PtH₂L₂ (L = P-i-Pr₃, Pcy₂, PhPcy₃)

All the dihydrides were prepared by the same method. Thus a five molar excess of lithium tetrahydroborate was added to the corresponding hydridochloro compound (~0.5 g) in acetonitrile, and after stirring for 24 h the solvent was removed in vacuo. The hydride $PtH_2(P\text{-i-}Pr_3)_2$ was sublimed from the residue at $50°C/10^{-3}$ torr, and the other two hydrides were extracted rapidly with CH_2Cl_2, and precipitated by adding methanol. The solids were dried in vacuo after filtration. The yields and mass spectrum $[PtH_2(P\text{-i-}Pr_3)_2]$ for the hydrides were as follows: $PtH_2(P\text{-i-}Pr_3)_2$, (65%), *m/e* from *M*, $Pt(P\text{-i-}Pr_3)_2$, $PtHP_2\text{-i-}Pr_5$, $PtH_2P_2\text{-i-}Pr_4$, $PtH_3P_2\text{-i-}Pr_3$, $PtP_2\text{-i-}Pr_2$, PtP_2. $PtH_2(Pcy_2Ph)_2$ (35%), $PtH_2(Pcy_3)_2$ (45%).

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