# Some New Hydrido-complexes of Platinum(II) and their Reactions with Electrophiles

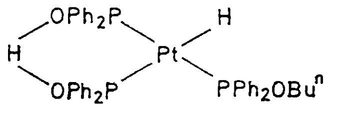
By **Pi-Chang Kong** and **D. Max Roundhill,*** Department of Chemistry, Washington State University, Pullman, Washington 99163, U.S.A.

The solvolysis of zerovalent platinum complexes of alkyl diphenylphosphinites in aqueous ethanol leads to the formation of hydridoplatinum(II) complexes. The compounds obtained from n-butyl diphenylphosphinite, isopropyl diphenylphosphinite, and methyl diphenylphosphinite have the respective stoicheiometries corresponding to $PtH(OPPh_2)(HOPPh_2)(Bu^nOPPh_2)$, $PtH(OPPh_2)(HOPPh_2)(Pr^iOPPh_2)$, and $PtH(OPPh_2)(HOPPh_2)_2$. $PtH(OPPh_2)(HOPPh_2)_2$ reacts with HCl to give $PtCl(OPPh_2)(HOPPh_2)_2$. $PtHCN(PPh_3)_2$ reacts with HBr, HCl, and $CF_3CO_2H$ to give $PtBrCN(PPh_3)_2$, $PtClCN(PPh_3)_2$, and $Pt(OCOCF_3)CN(PPh_3)_2$ respectively. The solvolysis of $Pd(Bu^nOPPh_2)_4$ in $Bu^nOPPh_2$, $N_2H_4$, and EtOH gives $Pd_2(OPPh_2)_4(HOPPh_2)_2$ which gives $Pd_2Cl_2(OPPh_2)_2(HOPPh_2)_2$ with HCl.

RECENTLY[1] we described the synthesis and chemistry of a number of alkyl diphenylphosphinite complexes of platinum. In that article we described the preparation of $Pt(Bu^nOPPh_2)_4$ and its solvolysis to $Pt(OPPh_2)_2(HOPPh_2)_2$. We also mentioned that another compound was formed in the solvolysis reaction which we considered to be a hydrido-complex of platinum. We now wish to present details of the synthesis and structure of this complex, as well as discussing some reactions of hydridoplatinum(II) complexes where the hydride ligand is opposite to a group having a high *trans* influence.

## RESULTS AND DISCUSSION

In the synthesis of $Pt(OPPh_2)_2(HOPPh_2)_2$ from $Pt(Bu^nOPPh_2)_4$ the conversion was achieved by allowing the reaction for the synthesis of $Pt(Bu^nOPPh_2)_4$ to continue for 4 days† rather than removing the product soon after its formation. When, however, the zerovalent platinum complex is isolated from the solution and stirred in a mixture containing a large proportion of water, the product is a hydridoplatinum(II) complex. The i.r. spectrum of this new compound shows a strong band for the Pt–H stretch at 2000 cm$^{-1}$. The intensity of this band is much greater than is usually found for hydridoplatinum(II) complexes, and it was because of this that we previously[1] suggested that the complex was a hydridocarbonyl. The stoicheiometry of this complex corresponds to the formula $PtH(OPPh_2)(HOPPh_2)(Bu^nOPPh_2)$, (I). The molecular weight data in $CHCl_3$ shows the complex to be monomeric. The complex gives a non-conducting solution in nitrobenzene. The extremely low frequency for ν(PtH) indicates that the hydrido-ligand is *trans* to diphenylphosphinato which has a very large *trans* influence.[2] An analogous complex (II) has been obtained from isopropyl diphenylphosphinite. In each case only two-thirds of the alkyl diphenylphosphinites incorporated into the complex are hydrolysed. The $^1H$ n.m.r. spectra of complexes (I) and (II) show the expected resonances for the phenyl, alkyl, and hydrido-hydrogens; the hydroxylic hydrogens are not observed as found in previous work.[1,3] The relative intensities of the alkyl : phenyl resonances confirms the presence of one alkyl group still present in the complex. This partial solvolysis appears unreasonable upon initial consideration, however Dixon has recently suggested that in



(I)

---

† We have since found that this reaction time can be shortened to 1 h by irradiating the reaction mixture with u.v. light.

[1] Pi-Chang Kong and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 749.

[2] J. Chatt and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 2745.

[3] K. R. Dixon and A. D. Rattray, *Canad. J. Chem.*, 1971, **49**, 3996.

complexes containing both diphenylphosphinato- and diphenylphosphinous acid ligands co-ordinated to a metal atom, the two groups are held together as a symmetrical pair by strong hydrogen bonding.[3]

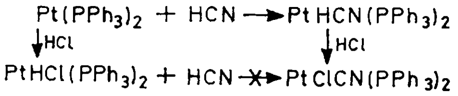
We have previously found that methyl diphenylphosphinite hydrolyses very rapidly, and in agreement with this we find that when the hydrido-complex is prepared with this ligand, complete hydrolysis occurs leading to the formation of complex (III), $PtH(OPPh_2)(HOPPh_2)_2$. This complex is insoluble in organic solvents. The compound dissolves in $H_2SO_4$ and the $^1H$ n.m.r. spectrum in this solvent confirms the absence of any methyl diphenylphosphinite as a ligand. The complex resembles (I) and (II) in showing a strong band for ν(PtH) at 1985 $cm^{-1}$.

Since the low value for ν(PtH) is due to the hydrogen being opposite a ligand of high *trans* influence, the hydrido-ligand should have 'hydridic' character. We have carried out a number of reactions with these hydridoplatinum(II) complexes and have found this to be a valid assumption. When compound (I) is stirred with $CCl_4$, $CHCl_3$ is formed. The hydrido-ligand in complex (I) is also lost with strong protonic acids such as HCl (with hydrogen evolution), and with electrophilic reagents such as MeI, $Ph_3CCl$, and $Ph_3CBr$. Complex (I) is unaffected by nucleophilic reagents such as ammonia, and by weak protonic acids such as nitromethane, pentane-2,4-dione, and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hfpd). These compounds have not previously been regarded as protonic acids to low-valent transition metal compounds, however, we have found that hfpd protonates $Pt(PPh_3)_4$ to form $[PtH(PPh_3)_3]CF_3COCHCOCF_3$. There has been no direct evidence for the protonation of $Pt(PPh_3)_4$ by either pentane-2,4-dione[4] or nitromethane, nevertheless we find that the addition of these compounds to $Pt(PMe_2Ph)_4$ forms[5] a hydrido-complex. These compounds are labile and the reaction occurs because of the higher basicity of $Pt(PMe_2Ph)_4$ as compared to $Pt(PPh_3)_4$. We have been unsuccessful in isolating the complexes of these anions with $[PtH(PMe_2Ph)_3]^+$, however, their formation is verified by the observation of singlets[1,6,7] in the $^1H$ n.m.r. spectrum at τ 19·8 for pentane-2,4-dione and at τ 20·6 for nitromethane. This observation of a hydridoplatinum complex formed by protonation with nitromethane is particularly interesting because of a recent paper proposing such an intermediate in the oxidative addition of nitromethane to $Pt(PPh_3)_2$ to give a difulminato-complex.[8]

The reaction of complexes (I) and (III) with HCl occurs with effervescence and the formation of $PtCl(OPPh_2)(HOPPh_2)_2$ as shown in equation (1). This

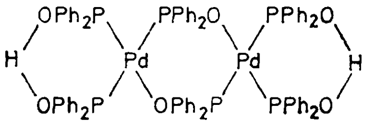
$$PtH(OPPh_2)(HOPPh_2)_2 + HCl \longrightarrow PtCl(OPPh_2)(HOPPh_2)_2 + H_2 \quad (1)$$

complex is also obtained from (I) and $Ph_3CCl$. This hydridic behaviour implies that other hydridoplatinum(II) complexes with the hydrogen opposite a ligand of high *trans* influence should be similar. We have verified this by reacting $PtHCN(PPh_3)_2$ with HCl, HBr, and $CF_3CO_2H$, when $H_2$ is liberated and $PtXCN(PPh_3)_2$ (X = Cl,[9,10] Br,[9,10] $OCOCF_3$) obtained. When HCN is passed through $PtHCl(PPh_3)_2$ under the same conditions no reaction occurs (Scheme).



SCHEME

$Pt(PPh_3)_4$ reacts with HCl and HCN to form $PtHCl(PPh_3)_2$ and $PtHCN(PPh_3)_2$ respectively,[11] even in the presence of a large excess of acid. $PtCl_2(PPh_3)_2$ is not formed because the *trans* influence of the chloro-ligand is low and does not confer hydridic character to the hydrido-ligand, and $Pt(CN)_2(PPh_3)_2$ is not formed because HCN is too weak an acid to liberate hydrogen. When $PtHCN(PPh_3)_2$, however, is treated with HCl the hydridic hydrogen is liberated as $H_2$ in the strong acid medium giving $PtClCN(PPh_3)_2$. We believe that it is unnecessary to propose a dihydridoplatinum(IV) intermediate to explain these facts even though recently such complexes have been obtained.[12] In this respect it is pertinent that $PtHCl(PPh_3)_2$ does not react with HCN under ambient conditions even though the intermediate $PtH_2ClCN(PPh_3)_2$ would be a common one with the reaction of $PtHCN(PPh_3)_2$ with HCl, and the facile oxidative addition of HCN is well known.[13] Furthermore the oxidative addition–reductive elimination mechanism does not satisfactorily explain such reactions as that of $\{Rh[P(OMe)_3]_5\}BPh_4$[14] with an excess of HBr wherein the hydrido-complex initially formed is converted into $\{RhBr_2[P(OMe)_3]_4\}BPh_4$. Such a mechanism would require an eight-co-ordinate rhodium(V) intermediate.



(IV)

In an attempt to obtain the corresponding palladium complexes, $Pd(Bu^nOPPh_2)_4$ was allowed to solvolyse in

---

[4] I. R. Harvie and R. D. W. Kemmitt, *Chem. Comm.*, 1970, 198.

[5] H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707.

[6] R. Ugo, G. La Monica, S. Cenini, and F. Conti, *J. Chem. Soc.* (*A*), 1971, 522.

[7] K. Thomas, J. T. Dumler, B. W. Renoe, C. J. Nyman, and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 1795.

[8] W. Beck, K. Schorpp, and F. Kern, *Angew. Chem.*, 1971, **83**, 43.

[9] P. M. Treichel and R. W. Hess, *Chem. Comm.*, 1970, 1626.

[10] P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Amer. Chem. Soc.*, 1971, **93**, 5424.

[11] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 1966, **5**, 1128.

[12] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 854.

[13] H. Singer and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2516.

[14] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1693.

an inert atmosphere. The product is $Pd_2(OPPh_2)_4(HOPPh_2)_2$ (IV), which reacts with HCl to give $Pd_2Cl_2(OPPh_2)_2(HOPPh_2)_2$, a complex previously prepared by Dixon by an alternative route.[3]

## EXPERIMENTAL

Microanalyses were carried out by Chemalytics Inc., Tempe, Arizona, Galbraith Inc., Knoxville, Tennessee, or by using a Perkin-Elmer 240 elemental analyser. M.p.s were obtained on a Fischer–Johns apparatus and are uncorrected. Platinum metals were obtained from Engelhard Industries Inc. n-Butyl diphenylphosphinite, isopropyl diphenylphosphinite, and methyl diphenylphosphinite were obtained from Arapahoe Chemicals Inc. and used without prior purification. N.m.r. spectra were measured on a Varian T60 spectrometer. I.r. spectra were obtained as Nujol mulls on Perkin-Elmer 700 or 467 spectrometers.

*Hydridodiphenylphosphinato(diphenylphosphinous acid)(n-butyl diphenylphosphinite)platinum*(II), $PtH(OPPh_2)(HOPPh_2)(Bu^nOPPh_2)$.—Tetrakis(n-butyl diphenylphosphinite)platinum(0) was prepared as described previously [1] using $K_2PtCl_4$ (0·8 g). The zerovalent complex (1·0 g) was added to a solution containing ethanol (75%, 20 ml) along with the filtrate from the preparation of the zerovalent complex (6% of the total volume, 2 ml). The suspension was stirred for 3 days when the yellow colour slowly discharged. The colourless precipitate was filtered and recrystallised by adding ether to a saturated solution in $CH_2Cl_2$; yield 0·53 g (76%), m.p. 162° [Found: C, 56·2, 55·7; H, 4·6, 4·5; P, 10·9, 10·9%; *M* 830 ($CHCl_3$). $C_{40}H_{41}O_3P_3Pt$ requires C, 56·0; H, 4·8; P, 10·85%; *M*, 858].

*Complex* (II), *Hydridodiphenylphosphinato(diphenylphosphinous acid)(isopropyl diphenylphosphinite)platinum*(II), $PtH(OPPh_2)(HOPPh_2)(Pr^iOPPh_2)$.—M.p. 166° (Found: C, 55·4; H, 4·4; P, 11·0, 10·8. $C_{39}H_{39}O_3P_3Pt$ requires C, 55·5; H, 4·65; P, 11·0%).

*Hydridodiphenylphosphinatobis(diphenylphosphinous acid)platinum*(II), $PtH(OPPh_2)(HOPPh_2)_2$.—M.p. 220° (Found: C, 54·1, 54·0; H, 4·2, 3·9; P, 11·55, 11·05. $C_{36}H_{33}O_3P_3Pt$ requires C, 53·9; H, 4·15; P, 11·6%).

*Chlorodiphenylphosphinatobis(diphenylphosphinous acid)platinum*(II), $PtCl(OPPh_2)(HOPPh_2)_2$.—HCl Was passed through a stirred suspension of $PtH(OPPh_2)(HOPPh_2)_2$ in $CH_2Cl_2$. The colourless complex dissolved and the solution was allowed to stand for 1 h at room temperature. The volume of solvent was reduced to 1 ml and ether (20 ml) added to give the complex [4] as colourless crystals, m.p. 255° (Found: C, 50·6; H, 3·8; Cl, 5·25. $C_{36}H_{32}ClO_3P_3Pt$ requires C, 51·7; H, 3·85; Cl, 4·25%).

*Bromocyanobis(triphenylphosphine)platinum*(II).— HBr Was passed through a solution of $PtHCN(PPh_3)_2$ (225 mg) in benzene (20 ml). After 1 h the volume of solvent was reduced to 1 ml and ether added to give the complex as colourless crystals, yield 229 mg (92%), m.p. >300° (Found: C, 52·9; H, 3·7; N, 1·95. $C_{37}H_{30}BrNP_2Pt$ requires C, 53·8; H, 3·65; N, 1·7%).

*Chlorocyanobis(triphenylphosphine)platinum*(II).— M.p. >300° (Found: C, 56·5; H, 3·9; Cl, 4·85. $C_{37}H_{30}ClNP_2Pt$ requires C, 56·9; H, 3·85; Cl, 4·45%).

*Trifluoroacetatocyanobis(triphenylphosphine)platinum*(II).—M.p. 198° (Found: C, 54·7; H, 3·6; N, 1·6. $C_{39}H_{30}F_3NO_2P_2Pt$ requires C, 54·6; H, 3·5; N, 1·65%).

*Hydridotris(triphenylphosphine)platinum*(II) *1,1,1,5,5,5-Hexafluoropentane-2,4-dionate* $[PtH(PPh_3)_3]CF_3COCHCOCF_3$.—1,1,1,5,5,5-Hexafluoropentane-2,4-dione was added dropwise to $Pt(PPh_3)_4$ until the colour was discharged. Addition of ether gave the complex, m.p. 117° (Found: C, 60·0; H, 3·85. $C_{59}H_{47}F_6O_2P_3Pt$ requires C, 59·6; H, 4·0%).

*Tetrakis(diphenylphosphinato)bis(diphenylphosphinous acid)dipalladium*(II), $Pd_2(OPPh_2)_4(HOPh_2)_2$.—The brown precipitate obtained from $Na_2PdCl_4$, n-butyl diphenylphosphinite, and hydrazine was stirred for 24 h. Recrystallisation from methylene chloride and ether gave orange crystals, m.p. 177° (Found: C, 59·9; H, 4·5. $C_{72}H_{62}O_6Pd_2P_6$ requires C, 60·8; H, 4·4%).

*Dichlorobis(diphenylphosphinato)bis(diphenylphosphinous acid)dipalladium*(II), $Pd_2Cl_2(OPPh_2)_2(HOPPh_2)_2$.—Addition of HCl to the above compound gave the complex, m.p. 195° (Found: C, 52·7; H, 4·2. $C_{48}H_{42}Cl_2O_4Pd_2P_4$ requires C, 52·9; H, 3·9%).

This work was supported by the Graduate School Research Fund and by Cities Service Oil Company, Cranbury, New Jersey. We wish to thank Arapahoe Chemical Co., Boulder, Colorado, for gifts of methyl diphenylphosphinite and n-butyl diphenylphosphinite.

[3/919 *Received, 7th May,* 1973]