B_1]. Since ν(Pt–I) varied from 176 to 196 cm^{-1}, salts of the Magnus type can be excluded.

There is difference of opinion about the assignment of ν(Pt–N) in both cis and trans systems of the type PtL_2X_2. Allen and Theophanides[17] assigned ν(Pt–N) in *cis*- and *trans*-[$Pt(py)_2Cl_2$] to bands in the range 480–450 cm^{-1}. Deuteration studies however indicate[15] that these bands involve mainly ring deformational modes and it is assumed that ν(Pt–N) occurs at lower frequencies. Durig and coworkers[15] assigned ν(Pt–N) in the range 246–300 cm^{-1}, compared to the 260–300-cm^{-1} range of Clark and Williams;[18] in both cases L = py. In the present work, marginal assignments (cm^{-1}) for this mode can be made as follows: py, 291; 3-Me(py), 261; 5-Me(py), 256; 4-Et(py), 263 and 254; 3,5-Me_2py, 294 and 245. These are very weak bands in all cases and are not even observed for 4-Me(py) and 4-Et(py) unless concentrated mulls are employed. Hence we conclude that from both the present and earlier work, the assignment for ν(Pt–N) remains subject to question. This doubt is further accentuated by the fact that the trend in relative intensities within this series of complexes does not follow the order anticipated in relation to the nature and position of the substituents in the pyridine ring.

The first endotherm in the dta curves corresponds to the detachment of two ligands and this is confirmed by the weight losses computed from the corresponding tga curves. Only in the case of one ligand (4-Et(py)) was this endotherm resolved into a doublet, thus indicating that removal of the two ligands is a two-step process. The second endotherm corresponds to the loss of both ligand and iodine, but neither of these processes is complete over the temperature range encompassed by the second endotherms. Thereafter, both X-ray diffraction and infrared spectral data show that the decomposition product consists predominantly of elemental platinum together with some species containing Pt–I bonds and ligands. Minor but unexplainable endotherms in the dta curves and inflections in the tga curves are observed when conditions (heating rates, pressure, etc.) are changed; this suggests only that the final decomposition processes occur at different rates as the identity of the ligand is varied.

Finally, it should be noted that the heats of reaction reported above increase in the same order as the pK_b values of the pyridines; hence the effect of π-backbonding is small in comparison with that observed previously[19] for analogous complexes of cobalt(II).

Acknowledgments.—This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

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Protonation and Solvolytic Reactions of Some Low-Valent Platinum Complexes Containing Methoxydiphenylphosphine or *n*-Butoxydiphenylphosphine as Ligands

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The complexes Pt(*n*-BuOPPh$_2$)$_2$Cl$_2$, Pt(*n*-BuOPPh$_2$)$_4$, and Pt(MeOPPh$_2$)$_3$ have been isolated and the reaction between protonic acids and the zerovalent complexes has been found to give labile hydrides. The attempted preparation of Pt(MeOPPh$_2$)$_3$ in ethanol gave Pt(EtOPPh$_2$)$_3$, and the attempted preparation of complexes of P(OPh)$_3$ and P(O-*p*-tolyl)$_3$ by reaction with palladium salts in methanol gave solely Pd[P(OMe)$_3$]$_2$Cl$_2$. This latter compound is stable in ethanol in the absence of P(OPh)$_3$. The complex Pt(OPPh$_2$)$_2$(HOPPh$_2$)$_2$ has been synthesized and is considered to be a platinum(II)–diphenylphosphinato complex. The substitution products of this complex with P(OPh)$_3$ and P(O-*p*-tolyl)$_3$ have the stoichiometry Pt(OPPh$_2$)$_2$[HOP(OPh)$_2$]$_2$ and Pt(OPPh$_2$)$_2$[HOP(O-*p*-tolyl)$_2$]$_2$.

Introduction

Protonation studies of substituted phosphine[1–6] and phosphite[7–11] complexes of nickel, palladium, and platinum have recently attracted attention from several groups of workers. The protonation of Pt(PPh$_3$)$_4$ has led to the formation of stable hydrides, although until recently[6] it has been considered that the addition of HX to Pd(PPh$_3$)$_4$ would lead to the formation of Pd(PPh$_3$)$_2$X$_2$ with the evolution of hydrogen. Studies at Du Pont[7–11] have considered the isolation and catalytic properties[12] of hydrides obtained by the protonation of phosphite complexes of Ni(0), where the products are considered to be pentacoordinate nickel(II) complexes. In addition to this work ^{1}H and ^{31}P nmr studies have been made on stereochemically nonrigid hydrides of Fe,[13] Ru,[14] and Os. In view of our interest

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in hydride complexes formed by protonation of $Pt(PPh_3)_4$ and recent work showing the differences between tertiary phosphine and phosphite complexes, we were interested in considering the effect of a mixed phosphine–phosphite ligand.

Experimental Section

Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. The platinum analysis was carried out by neutron activation analysis making use of the ^{199}Pt isotope ($t_{1/2}$ = 31 min with a γ emission of 542.7 keV). Irradiation was carried out for *ca.* 10 min and the samples were allowed to decay for 4 half-lives before counting the spectra. Molecular weight data were obtained by Galbraith Laboratories Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained on a Varian T 60 spectrometer as solutions in $CDCl_3$ using TMS as internal reference. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 700 spectrometer. Far-infrared spectra were obtained on either a Perkin-Elmer FIS 3 or a Beckman IR4 spectrometer as vaseline mulls. Melting points were obtained on a Fischer-Johns apparatus and are uncorrected. Mass spectra were obtained on a Varian M66 spectrometer. Methoxydiphenylphosphine and *n*-butoxydiphenylphosphine were gifts from Arapahoe Chemicals Inc., and platinum metals were obtained as chloro salts from Engelhard Industries Inc. Tri-*p*-tolyl phosphite (bp 175° (0.3 mm), $n^{24}D$ 1.5733) was prepared from the reaction between PCl_3 and *p*-cresol. Tetrakis(triphenyl phosphite)platinum(0) (mp 153°) was prepared from $Pt(PPh_3)_4$ and $P(OPh)_3$ in preference to the previously reported method.[15]

Dichlorobis(*n*-butoxydiphenylphosphine)platinum(II).—To a solution of Na_2PtCl_4 in acetone was added excess *n*-butoxydiphenylphosphine. The NaCl formed was filtered and the acetone solution was evaporated to dryness to give the *complex* which was washed with hexane and dried *in vacuo;* mp 175°. *Anal.* Calcd for $C_{32}H_{38}Cl_2O_2P_2Pt$: C, 49.1; H, 4.89; Cl, 9.06. Found: C, 48.9; H, 4.79; Cl, 9.48.

Tetrakis(*n*-butoxydiphenylphosphine)platinum(0).—To a hot (40–50°) ethanolic solution of *n*-butoxydiphenylphosphine (1.15 g) was added K_2PtCl_4 (0.4 g) in water (3 ml). The temperature of the stirred solution was raised to 60° until all the precipitate had dissolved and then the mixture was allowed to cool to 50°. An ethanolic solution of hydrazine (85%) was added dropwise to the stirred solution until a yellow precipitate of the *complex* was obtained which was filtered, washed with a small quantity of aqueous ethanol, and dried *in vacuo;* mp 85°. *Anal.* Calcd for $C_{64}H_{76}O_4P_4Pt$: C, 63.1; N, 6.21; P, 10.1. Found: C, 62.3; H, 6.14; P, 10.8. The complex is soluble in all common organic solvents including hexane.

Tris(methoxydiphenylphosphine)platinum(0).—To a hot methanolic solution of methoxydiphenylphosphine (1.08 g) was added dropwise a solution of K_2PtCl_4 (0.4 g) in water (4 ml). The mixture was stirred until all the solid had redissolved and 1 ml of a 50% solution of hydrazine (85%) in methanol was added dropwise. After stirring for 10 min the yellow *complex* which precipitated was filtered, washed well with aqueous methanol, and dried *in vacuo*. *Anal.* Calcd for $C_{39}H_{39}O_3P_3Pt$: C, 55.5; H, 4.66. Found: C, 55.4; H, 4.59.

Tris(ethoxydiphenylphosphine)platinum(0).—The preparation of this complex was carried out in a manner identical with that for the zerovalent $MeOPPh_2$ complex except that the solvent used was ethanol. The yellow *complex* which precipitated was again dried *in vacuo*. *Anal.* Calcd for $C_{42}H_{45}O_3P_3Pt$: C, 56.9; H, 5.12. Found: C, 55.8; H, 4.84.

Bis(diphenylphosphinato)bis(hydroxydiphenylphosphine)platinum(II).—This complex has been prepared using the four methods described.

(a) The reaction was carried out as for the preparation of $Pt(n\text{-}BuOPPh_2)_4$ except that instead of allowing the solution to cool to 50° the temperature is raised to 65° or above. The yellow precipitate redissolved and removal of the solvent gave a pale yellow oil. The addition of hexane and ethanol gave very pale yellow crystals which were recrystallized from $CHCl_3$ and an ethanol–hexane mixture to give the *complex;* mp 212°. *Anal.* Calcd for $C_{48}H_{42}O_4P_4Pt$: C, 57.5; H, 4.23; P, 12.4; Pt, 19.5; mol wt 1002. Found: C, 57.5, 57.6; H, 4.82, 4.10; P, 12.3, 12.7; Pt, 19.3; mol wt 790, 930. The complex is moderately soluble in $CHCl_3$.

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(b) A suspension of $Pt(n\text{-}BuOPPh_2)_4$ in ethanol was allowed to stand in air for 4 days in the presence of a small quantity of $n\text{-}BuOPPh_2$. The *complex* slowly formed as very pale yellow crystals in quantitative yield.

(c) A solution of $Pt(MeOPPh_2)_3$ in a 50:50 mixture of CH_2Cl_2 and hexane was allowed to stand at room temperature for 3 hr. The *complex* precipitated from solution in good yield.

(d) To a solution of K_2PtCl_4 (0.4 g) in water (5 ml) was added a solution of chlorodiphenylphosphine (2.0 g) in ethanol (10 ml). The solution was heated with stirring to 50° and hydrazine (2 ml of 85%) was slowly added. The solution changed color to deep yellow and then to pale yellow as the pale yellow complex precipitated; yield 0.78 g (82%).

Reaction with Triphenyl Phosphite.—To a pale yellow solution of bis(diphenylphosphinato)bis(hydroxydiphenylphosphine)platinum in $CHCl_3$ (15 ml) was added an excess of triphenyl phosphite, when the solution rapidly decolorized. The volume of the solution was reduced and hexane was added to give a white precipitate. Recrystallization from $CHCl_3$–hexane gave the phosphonato *complex* which was filtered, washed with hexane, and dried *in vacuo;* mp 153°. The yield was quantitative. *Anal.* Calcd for $C_{48}H_{42}O_8P_4Pt$: C, 54.1; H, 3.97; P, 11.6. Found: C, 53.3, 53.1; H, 3.83, 3.85; P, 11.7, 11.5.

Reaction with Tri-*p*-tolyl Phosphite.—Using a procedure similar to that used for triphenyl phosphite the *complex* with tri-*p*-tolyl phospite was obtained as colorless crystals, mp 180°. *Anal.* Calcd for $C_{52}H_{50}O_8P_4Pt$: C, 55.7; H, 4.49; P, 11.0. Found: C, 56.0; H, 4.82; P, 11.0.

Dichlorobis(trimethyl phosphite)palladium(II).—To a solution of Na_2PdCl_4 in methanol was added a slight excess of triphenyl phosphite or tri-*p*-tolyl phosphite and the solution was filtered to remove the NaCl formed. The solution was evaporated to a small volume and hexane was added to give the complex as white crystals, mp 135°. *Anal.* Calcd for $C_6H_{18}Cl_2O_6Pd$: C, 16.9; H, 4.26; P, 14.6. Found: C, 16.9; H, 4.01; P, 14.8.

Results and Discussion

The recent report of a platinum(II) hydride showing no detectable ^{31}P–H coupling[16] prompts us to present our results on the reactions of zerovalent platinum complexes with alkoxydiphenylphosphines as ligands, where we have observed a series of hydride complexes of platinum which show no coupling between ^{31}P and ^1H. The complex $Pt(n\text{-}BuOPPh_2)_4$ (τ_{OCH_2} 6.8 t, $\tau_{CH_2CH_2CH_3}$ 8.8 m) was readily obtained by the hydrazine reduction of *cis*-$Pt(n\text{-}BuOPPh_2)_2Cl_2$ (ν_{Pt-Cl} 316, 293 cm^{-1}) in the presence of excess $n\text{-}BuOPPh_2$. Using a similar procedure we have isolated the complex $Pt(MeOPPh_2)_3$[17] although for reasons we will discuss later we have not isolated the intermediate compound $Pt(MeOPPh_2)_2Cl_2$. Both these zerovalent complexes resemble $Pt(PPh_3)_4$ in being readily protonated to form a hydride. In the case of the triphenylphosphine system the platinum hydrides can usually be isolated, but with either $MeOPPh_2$ or $n\text{-}BuOPPh_2$ these complexes are extremely labile. When we attempted to isolate pure complexes we found that removal of the excess acid causes reversion to the yellow color of the zerovalent complex. If the solvent is removed while a slight excess of acid remains, we have been able to obtain the complexes as an impure colorless paste which shows a band in the ir spectrum in the 2000–2300-cm^{-1} region indicative of a platinum hydride. This dissociation of the hydride on attempted isolation is similar to that found with acetic acid and $Pt(PPh_3)_4$.[3] Although these complexes are labile, they will not

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(17) The difference in the coordination number for the zerovalent platinum complexes with $n\text{-}BuOPPh_2$ and $MeOPPh_2$ we consider to be of little consequence since there is undoubtedly an equilibrium of the type $PtL_4 \rightleftharpoons PtL_3 + L$ present, and if both complexes were separately required, we believe that by judicious manipulation of the concentration of the phosphine both the tris and tetrakis complexes could be isolated for each ligand.

undergo exchange with D_2 and do not react with butadiene as has been found for $Ni[P(O\text{-}p\text{-}tolyl)_3]_4H^+$.[10]

The characterization of the species in solution as a hydride has been confirmed by the presence of a high-field line in the ^1H nmr spectrum. With both $Pt(n\text{-}BuOPPh_2)_4$ and $Pt(MeOPPh_2)_3$ we found that even phenol will oxidatively add to form a hydride which is noteworthy since with $Pt(PPh_3)_4$ we have been unable to carry out this reaction under ambient conditions. This represents one of the few cases of the oxidative addition of phenol to form a hydride. In many cases, as can be seen in Tables I and II, the hydride resonance is a single sharp line which has a half-width of the order of 2 Hz which is much less than the 32 Hz which would be observed if the peak was an unresolved triplet of *trans*-$(ROPPh_2)_2Pt(H)X$.[2,5] Although the coupling between ^{31}P and ^1H is frequently absent, the coupling between the hydride and ^{195}Pt is readily observable. The values of J_{Pt-H} appear to be very similar to those obtained for stable triphenylphosphine hydride complexes of platinum(II) suggesting that it is phosphine exchange which is responsible for the disappearance of the P–H coupling in the spectrum. This explanation agrees with the results we have found for the tetrakis(triphenylphosphine)platinum(0)–trifluoroacetic acid system.[18] Tetrakis(triphenyl phosphite)platinum(0) is also readily protonated, and although the hydrides appear to be somewhat more stable than those obtained from the methoxydiphenylphosphine and *n*-butoxydiphenylphosphine complexes, the reductive elimination is still somewhat facile.

TABLE I

HIGH-FIELD NMR SPECTRA OF HYDRIDES FROM PROTONATION OF $Pt(n\text{-}BuOPPh_2)_4$

Acids	Solvent	τ_{Pt-H}	J_{Pt-H}	Multiplicity
Picric	CH_2Cl_2	15.0	...	s[a]
Phenol	CH_2Cl_2	15.8	808	s
H_2SO_4	CH_2Cl_2	14.8	...	t(2)[b]
CF_3COOH	CF_3COOH	15.0	836	t(2)
CF_3COOH[c]	$BuOPPh_2$	21.4	588	s
CH_3COOH	CH_3COOH (*A*)[d]	17.8	624	s
CH_3COOH	CH_3COOH (*A*/2)	17.1	760	s
CH_3COOH	CH_3COOH (*A*/4)	16.2	800	s
CH_3COOH	CH_3COOH (*A*/8)	15.7	820	s

[a] Singlet. [b] Pair of triplets. This pattern corresponds to the structure $[(n\text{-}BuOPPh_2)_3PtH]^+$. For the H_2SO_4 complex, J_{P-H}(trans) = 176 Hz and J_{P-H}(cis) = 16 Hz. For the CF_3COOH complex J_{P-H}(trans) = 173 Hz and J_{P-H}(cis) = 16 Hz. [c] Minimum quantity of acid to discharge the yellow color of the solution. [d] These ratios denote successive dilution of a solution of initial concentration *A* of the complex.

TABLE II

HIGH-FIELD NMR SPECTRA OF HYDRIDES FROM PROTONATION OF $Pt(MeOPPh_2)_3$

Acid	Solvent	Complex: acid ratio	τ_{Pt-H}	J_{Pt-H}	Multiplicity
Picric	$CDCl_3$		15.5	820	s
Phenol	$CDCl_3$	0.42	16.8	764	s
Phenol	$CDCl_3$	0.21	15.7	808	s
Phenol	$CDCl_3$	0.11	15.2	840	s
CF_3COOH	CF_3COOH		15.0	840	t(2)
CH_3COOH	CH_3COOH	0.62	18.2	708	s
CH_3COOH	CH_3COOH	0.50	17.6	724	s
HCOOH	HCOOH		14.6	840	t(2)
CH_3COSH	$CDCl_3$		19.2	950	s
C_6H_5COSH	$CDCl_3$		18.8	996	s

These results show that the nonobservance of P–H coupling in platinum hydrides is quite common in exchange systems and that slight changes in the phosphine ligand can have profound effects in the lability of the complexes obtained.

In the preparation of $Pt(MeOPPh_2)_3$ the use of an alcohol other than methanol leads to the substitution of the methoxy group. If the synthesis of $Pt(MeOPPh_2)_3$ is carried out in ethanol, the sole product is $Pt(EtOPPh_2)_3$. The product of the solvolysis reaction can readily be confirmed from the ^1H nmr of the complexes formed. The complex $Pt(MeOPPh_2)_3$ shows a resonance due to the methyl protons at τ 6.87 (CH_3OH, τ 6.63),[19] whereas in the complex $Pt(EtOPPh_2)_3$ the resonances due to the ethyl protons occur at τ 8.93 (CH_3) and τ 6.69 (CH_2) (C_2H_5OH, τ 8.83 and 6.41); in each case the relative areas of the phenyl and alkyl protons in the complex confirm the stoichiometry. The ligand n-$BuOPPh_2$ however appears to be much less readily solvolyzed by alcohols in these reactions since we have been able conveniently to prepare $Pt(n\text{-}BuOPPh_2)_4$ using ethanol as solvent without any evidence for the formation of the $EtOPPh_2$ complex.

We have also found that palladium complexes of phosphites undergo facile solvolytic exchange with an alcoholic solvent. The attempted preparation of $Pd[P(O\text{-}p\text{-}tolyl)_3]_2Cl_2$ from Na_2PdCl_4 and $P(O\text{-}p\text{-}tolyl)_3$ in methanol leads to the isolation of the methoxy complex $Pd[P(OMe)_3]_2Cl_2$ as the sole product. A synthesis for this trimethyl phosphite complex has recently been described in detail from $(PhCN)_2PdCl_2$.[20] however since the above replacement reaction occurs equally as well in good yield with triphenyl phosphite as with tri-*p*-tolyl phosphite, the preparation of $Pd[P(OMe)_3]_2Cl_2$ may usefully be carried out as a one-step synthesis from Na_2PdCl_4 and $P(OPh)_3$ in methanol. This trimethyl phosphite complex remains unchanged in ethanol at room temperature; however if a small quantity of triphenyl phosphite[21] is added to the solution, the ^1H nmr indicates that the exchange of the methyl groups for ethyl groups has occurred to the extent of about 25% in 3.5 hr.

We have attempted to prepare $Pd(n\text{-}BuOPPh_2)_4$, and although it is possible to obtain a yellow complex by the hydrazine reduction reaction, the product very rapidly decomposes in air and we have not been able to obtain microanalytical data.

In the preparation of $Pt(n\text{-}BuOPPh_2)_4$ we have found that if the temperature is allowed to rise above 65° the bright yellow precipitate redissolves giving a pale yellow compound which shows no resonance in the ^1H nmr spectrum due to the butoxy group. The same complex, the stoichiometry of which corresponds to $Pt(OPPh_2)_2(HOPPh_2)_2$, is formed by allowing the complex $Pt(MeOPPh_2)_3$ to stand for 3 hr or by the addition of hydrazine to a solution of K_2PtCl_4 and chlorodiphenylphosphine. The reactions and interconver-

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(19) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. 2, Pergamon Press, Elmsford, N. Y., 1966, pp 1115–1129.

(20) J. M. Jenkins and J. G. Verkade, *Inorg. Syn.*, **11**, 108 (1968).

(21) Triphenyl phosphite will slowly exchange with ethanol at room temperature and after 17 hr it appears that about 22% of the phenyl groups are converted into ethyl groups.

sions which have been carried out are shown in Figure 1. The complex is insoluble in common organic solvents except for $CHCl_3$ in which it is sparingly soluble. The microanalytical data for C, H, and P did not confirm whether it was the alkyl or the alkoxy group which had been lost because other formulas could be fitted to

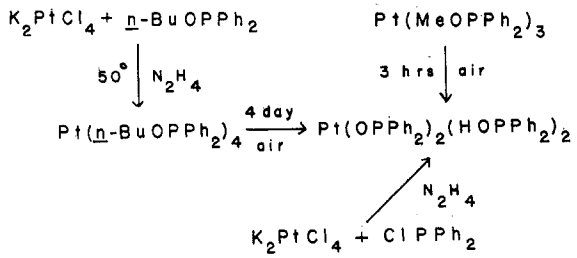

Figure 1.—Scheme of reactions.

the data, but the platinum analysis strongly suggested that the oxygen remains bonded to the phosphorus. The mass spectrum of the complex at 150° shows a highest peak at *m/e* 202 and other peaks at *m/e* 201, 125, and 124 from Ph_2POH^+, Ph_2PO^+, $PhPOH,^+$ and $PhPO^+$, respectively. This confirms that the oxygen has not been completely eliminated in the solvolysis reaction. The sample used for mass spectroscopy was prepared from $Pt(MeOPPh_2)_3$ but there is no significant peak at *m/e* 216 for the parent ligand, showing that the observed peaks are due to the complex and not to $MeOPPh_2$ present as an impurity. It appears possible that loss of the alkyl group may lead to dimerization and the formation of a chelating ligand; however the mass spectrum up to *m/e* 420 shows no evidence for such a species.

The infrared spectrum of the complex shows bands at 1103 and 1100 cm^{-1} rather than a sharp band in this region diagnostic of a coordinated tertiary phosphine. This spectrum resembles those obtained with diphenylphosphinato complexes,[22] although it is difficult to assign the band at 985 cm^{-1} since the molecular weight data show the complex to be monomeric.[23] The proposed structure for the complex $Pt(OPPh_2)_2(HOPPh_2)_2$, as shown in Figure 2, represents a platinum(II) com-

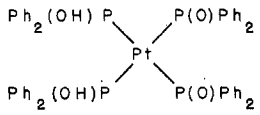

Figure 2.—Suggested structure of bis(diphenylphosphinato)-bis(hydroxydiphenylphosphine)platinum(II). The stereochemistry of the complex has not been deduced.

plex formed by hydrolysis of the alkoxydiphenylphosphine. The infrared spectrum shows a broad and rather imprecise band in the hydroxyl region at 3500 cm^{-1} but the resonance cannot be found in the ^1H nmr spectrum because of the strong hydrogen bonding.[22] The divalent oxidation state is suggested by the good stability of the complex to air; we have been able to recover it unchanged after bubbling a mixture of O_2 and CO_2 through a solution in $CHCl_3$. This reaction usually leads to carbonate formation in Pt(0) complexes of triphenylphosphine,[24] and we have found the carbonate ($\nu_{C=O}$ 1680 cm^{-1}) is also obtained with $Pt(BuOPPh_2)_4$.

The ligand appears to be displaced with both bis(diphenylphosphino)ethane and KCN but in neither case have we been able to obtain it in a pure state.[25] The diphenylphosphinatoplatinum compound reacts with triphenyl phosphite and tri-*p*-tolyl phosphite giving air-stable colorless crystalline complexes. The microanalytical data can only be interpreted if a phenyl (or *p*-tolyl) group has been lost from the triaryl phosphite and this was confirmed by integration of the phenyl against the methyl protons in the tri-*p*-tolyl phosphite complex. The stoichiometries of the complexes correspond to the formulas $Pt(OPPh_2)_2[HOP(OPh)_2]_2$ and $Pt(OPPh_2)_2[HOP(O\text{-}p\text{-}tolyl)_2]_2$ and show a strong band in the infrared spectrum at 1590 cm^{-1} characteristic of phenyl phosphite complexes in addition to the bands found in the spectrum of $Pt(OPPh_2)_2(HOPPh_2)$. The analytical and nmr data however do not confirm whether the $OPPh_2$ or the $HOPPh_2$ group has been lost, and an alternative structure would be $Pt[OP(OPh)_2]_2(HOPPh_2)_2$. It appears more likely however that solvolysis would occur by hydrogen exchange than by phenyl exchange, and the suggested formulation is further enforced by the mass spectrum of the complex from triphenyl phosphite which shows a strong peak at *m/e* 234 for the $HOP(OPh)_2$ group but no observable peak at *m/e* 202 for $HOPPh_2$.

In addition to the above complexes we have obtained from the reaction of *n*-$BuOPPh_2$ with platinum salts a further product which appears to be a carbonyl hydride. Structural details will be published at a later date along with further chemistry of these hydrolysis products.

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

(23) This band at 985 cm^{-1} implies bridging diphenylphosphinato ligands, and it is possible that the molecular weight data are misleading since it has of necessity been obtained only in $CHCl_3$. However in order to maintain the stoichiometry it would be necessary to postulate either pentacoordinate Pt(II) or four diphenylphosphinato bridges between the platinum atoms, neither of which appears probable at present although such dimeric structures cannot be completely eliminated.

(24) (a) C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Commun.*, 407 (1967); (b) P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5873 (1970).

(25) The oily products from either reaction have identical infrared spectra, strong bands being obtained which are assignable to OH, PH, and P=O groups. This spectrum is not unexpected since the displaced hydroxydiphenylphosphine would be in equilibrium with the phosphine oxide as shown by the equation[22] $Ph_2POH \rightleftharpoons Ph_2P(H)O$.