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METAL COMPLEXES OF SUBSTITUTED PHOSPHINITES AND SECONDARY PHOSPHITES

D.M. ROUNDHILL *, R.P. SPERLINE and W.B. BEAULIEU

Department of Chemistry, Washington State University, Pullman, Washington 99164 (U.S.A.)

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CONTENTS

A. INTRODUCTION

Substituted phosphinous acids (R_2POH) and secondary phosphites (($(RO)_2POH$) are known for a wide variety of substituent groups R [1,2]. The compounds exist in two tautomeric forms, one of which is tricoordinate about phosphorus, and the other which is tetracoordinate about that atom. The position of this tautomeric equilibrium is dependent on the substituent R, but for simple aliphatic and aromatic substituents the equilibrium favors the tetracoordinate structure to the right (1).

$$\begin{aligned} &R_2POH \rightleftharpoons R_2PH(O) \\ &(RO)_2POH \rightleftharpoons (RO)_2PH(O) \end{aligned} \tag{1}$$

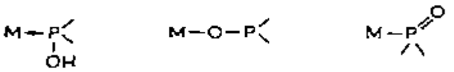
Nomenclature for disubstituted phosphinous acids and phosphites

R_2POH	Phosphinous acid	R_2PO^-	Phosphinito
$(RO)_2POH$	Phosphite	$(RO)_2PO^-$	Phosphito

These parent compounds are weak acids and treating them with strong base will yield the corresponding conjugate base (2). The focus of this review article is to compare and contrast the diverse coordination modes of these two compounds, and then to investigate the spectroscopy,

$$\begin{array}{ccc} R_2PH(O) & & R_2PO^- \\ & \xrightarrow{\text{Base}} & \\ (RO)_2PH(O) & & (RO)_2PO^- \end{array} \tag{2}$$

reactivity and structure of resulting complexes. The diversity of these compounds as ligands arises mainly from two factors. Firstly, the tricoordinate tautometic form of the acid structurally resembles a tertiary phosphine, and hence can coordinate to a metal ion in the well known manner of such ligands. Secondly deprotonation yields a uninegatively charged anion which resembles the ambidentate thiocyanate ion in being able to coordinate through two separate ends of the ligand (3). All the types of coordination are



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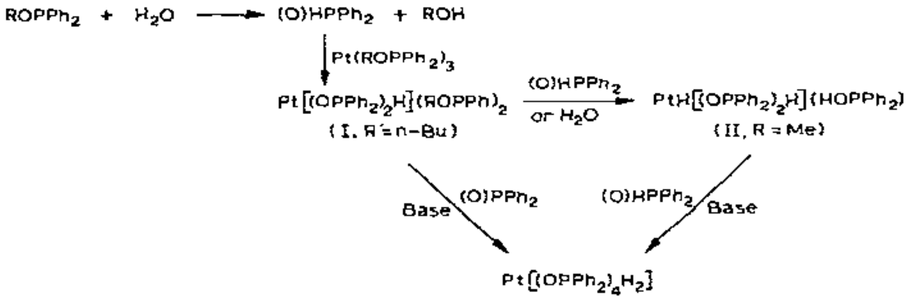
observed in metal complexes of substituted phosphinous acids and secondary phosphites, and discrimination between the various modes is an integral part of this chemistry.

B. ALKYL AND ARYL DERIVATIVES

Among the earliest characterized complexes of dialkyl phosphinites or phosphites are the dialkyl phosphito platinum(II) compounds. In 1944 Grinberg and Troitskaya [3] reported that treating K_2PtCl_4 with $P(OEt)_3$ in aqueous solution yields first $\{Pt[P(OEt)_3]_4\}PtCl_4$, then $Pt\{[OP(OEt)_2]_4H_2\}$ (4). This latter compound has both a tricoordinate diethyl phosphite and a diethyl phosphito conjugate base bonded to Pt(II) via the phosphorus atoms. The diethyl phosphite and phosphito ligands have been formed by hydrolysis of either coordinated or free triethyl phosphite. In a series of subsequent articles, Troitskaya et al. have used a similar procedure to prepare the methyl [4],

$$\begin{tikzcd} P(OEt)_3 \arrow[r, "K_2PtCl_4"] \arrow[d, "H_2O"', "-EtOH"] & \{Pt[P(OEt)_3]_4\}PtCl_4 \arrow[d, "H_2O"', "-EtOH"] \\ (EtO)_2PH(O) \arrow[r, "K_2PtCl_4"] & Pt\{[OP(OEt)_2]_4H_2\} \end{tikzcd} \qquad (4)$$

propyl [5—7] and butyl [5,8] derivatives. In parallel with their work on complexes of platinum(II), these workers have also prepared the palladium(II) derivatives with diethyl [9—14] and diisopropyl phosphite [13], in addition to the diisopropyl phosphito complex $Rh_3[OP(OPr)_2]_5[HOP(OPr)_2]Cl_4$ [15]. The method is also applicable to the preparation of the structurally analogous diphenyl phosphite [16] and diphenylphosphinite [17] complexes. The latter compound was obtained by a somewhat modified procedure since the Pt(O) compounds $Pt(ROPPh_2)_3$ (R = Me, n-Bu) were the precursors undergoing hydrolysis. This modification is probably unnecessary, however, if the desired product is $Pt[(OPPh_2)_4H_2]$ since it is likely that the conversion can be made directly from K_2PtCl_4. The reaction involving the zerovalent platinum complex is considered to involve the hydrolysis of the alkyl diphenylphosphinite to diphenylphosphinous acid, which subsequently undergoes oxidative additions to yield the intermediate platinum(II) hydride complex [18,19] (5). The intermediacy of the platinum hydrides is verified by the isolation of both



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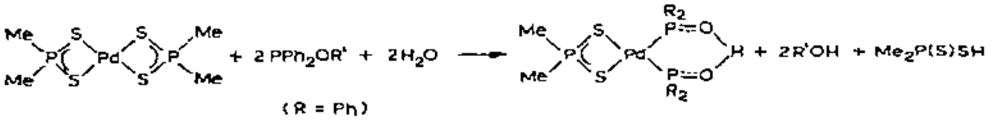
I and II, and by their subsequent conversion into the final product. With methyl diphenylphosphinite the only isolable hydride is complex II, which can also be formed by extensive hydrolysis of the complex I obtained from n-butyl diphenylphosphinite.

Since chlorophosphines are also hydrolytically unstable, a potential route to these dialkyl and diaryl phosphinito complexes is to treat the corresponding chlorophosphine complex with water. Such an approach has been used to prepare a wide range of diethyl and diphenylphosphinito complexes of platinum(II) [20]. These authors have prepared a wide range of monomeric and phosphinito bridged dimeric complexes with both the substituted phosphorus and arsenic analogs. The series of compounds has led the authors to propose that the order of bridging strength for a ligand between two platinum(II) centers follows the order: $Cl < Et_2PO < SEt < PPh_2$. Diphenylphosphinito complexes of both Ru(II) and Pd(II), the latter having also a coordinated dithiophosphate

$$cis\text{-}PtCl_2(PR_2Cl)(MR'_3)\left\{\begin{array}{l}\xrightarrow{OH^-} Pt_2(OH)_2(R_2PO)_2(MR'_3)_2 \xrightarrow{HCl} cis\text{-}PtCl_2(PR_2OH)\text{-}\\ \quad (MR'_3)\\ \xrightarrow{OR''^-} PtCl_2(R_2POR'')(MR'_3)\end{array}\right. \tag{6}$$

$(M = P, As;\ R = Ph, Et;\ R' = Me, Et;\ R'' = Me)$

ligand, have also been prepared by hydrolysis of the precursor methyl diphenylphosphinite complex [21,22] (6). Thus, prolonged exposure of the compound $Pd(S_2PMe_2)_2$ to a solution of excess methyl or ethyl diphenylphosphinite in dichloromethane or benzene led to the formation of the complex $Pd[(OPPh_3)_2H](S_2PMe_2)$ (7). This result further shows that adventitious traces of water in organic solvents can result in the formation of dialkyl or diaryl phosphinito and phosphito complexes from a tertiary phosphite ligand. This compound resembles other mixed ligand dialkyl phosphito complexes of Pd(II) and Pt(II) since Troitskaya et al. have prepared complexes containing a dimethyl phosphito ligand and a second coordinated group such as thiocya-



(7)

nate [11—13] or thiourea [23,24]. The ruthenium complex $(MeOPPh_2)_2(HOPPh_2)RuCl_3 \cdot Ru[(OPPh_2)_2H](HOPPh_2)$ prepared by these authors has been obtained under more vigorous conditions than those used for Pd(II) or Pt(II) complexes since the compound was formed after pyrolyzing the complex $[(MeOPPh_2)_3RuCl_3 \cdot Ru(MeOPPh_2)_3]Cl$ for 12 h at 120°C (8).

$$[(MeOPPh_2)_3RuCl_3 \cdot Ru(MeOPPh_2)_3]Cl \xrightarrow[12\,h]{120^\circ C} (MeOPPh_2)_2(HOPPh_2)RuCl_3 \cdot Ru[(OPPh_2)_2H] \qquad (8)$$

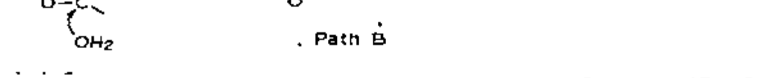
A further interesting example of the hydrolysis of a substituted phosphine leading to a complex of diphenylphosphinous acid is found with complexes of $Ph_2PC{\equiv}CCF_3$. Thus when the complex $PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ is allowed to stand for 5 h at room temperature in aqueous ethanol the complexes $\{PdCl[(OPPh_2)_2H]\}_2$ is formed [25]. It appears therefore that the alkynyl carbon bonded to phosphorus is susceptible to nucleophilic attack by water, resulting in the formation of diphenylphosphinous acid.

Although hydrolysis and alcoholysis of these dialkyl or diaryl phosphinite or phosphite ligands is a significant synthetic route to the desired product, the mechanistic details of the reaction remain relatively unknown and unexplored. Two types of reaction sequence are likely operable, although there is no verification yet that either pathway must be mutually exclusive for a particular reaction. The first pathway involves dissociation of the phosphite ester followed by hydrolysis or alcoholysis away from the metal center; and the second involves an activation of the alkyl group to nucleophilic attack by coordination of the phosphorus to an electron-poor metal center. The literature on the subject contains examples supportive of either pathway, but no attempt has been made to define boundary conditions on the metal center where one mechanism would be favored over the other one. The two pathways are shown diagrammatically in (9). Evidence in favor of the dissociative pathway with the phosphite being uncoordinated during hydrolysis (Path A) is to be found in comparative work on transesterification of tertiary phosphites coordinated to Fe(II) or Ru(II) as compared to those coordinated to Ni(0) [26]. For the complexes $MH_2[P(OR)_3]_4$ (M = Fe, Ru; R = Et, Ph), transesterification is too slow to be observed. For the kinetically labile complex $Ni[P(O\text{-}o\text{-tolyl})_3]_4$, however, transesterification does occur slowly. This

$$P(OR)_3 + H_2O \rightleftharpoons [HP(OR)_3]^+OH^- \rightleftharpoons HP(OR)_3OH \rightleftharpoons P(OR)_2OH + ROH$$

$$P(OR)_3 + R'OH \rightleftharpoons [HP(OR)_3]OR' \rightleftharpoons HP(OR)_3OR' \rightleftharpoons P(OR)_2OR' + ROH$$

Path A



(9)

observation is also supported by the result that attempted preparation of the complex $Pt(MeOPPh_2)_3$ in ethanol as solvent leads to the isolation of $Pt(EtOPPh_2)_3$ [17] (10). Such a pathway appears quite reasonable with a phosphite coordinated to a low-valent, kinetically labile metal ion.

$$2\,PtCl_4^{2-} + 6\,MeOPPh_2 + 6\,EtOH + N_2H_4 \rightarrow 2\,Pt(EtOPPh_2)_3 + 6\,MeOH + 4\,Cl^- + N_2 + 4\,HCl \qquad (10)$$

The second pathway finds support in studies on the reactions of transition metal complexes of alkyl phosphinites or phosphites with nucleophiles. The alkyl diphenylphosphinites Ph_2POR (R = n-Bu, sec Bu, i-Pr) do not react with iodide ion in the absence of a transition metal ion, but in the presence of $FeCl_3$, $CoCl_2$ or $NiCl_2$, yields of up to 59% alkyl iodide are obtained after 1 h at ambient temperature [27]. The most definitive evidence comes from work on trialkyl phosphite cobalt dimethylglyoximate complexes [28]. These workers found that the dealkylation can be effected by halide or amine nucleophiles, and that the rate of formation of the dialkyl phosphite complex was significantly reduced in the presence of ligands which will substitute the coordinated phosphite (11). This mechanism is therefore well supported for a trialkyl phosphite coordinated to cobalt(III). It is to be anticipated, however,

$$CoCl(DH)_2[P(OMe)_3] + X^- \rightarrow CoCl(DH)_2[OP(OMe)_2] + MeX \qquad (11)$$

(DH is the monoanion of dimethylglyoxime)

that the reaction will be less favored for alkyl groups higher than methyl, not observed for R = aryl, and less favored for phosphites coordinated to metal centers having a greater electron density.

These results on cobalt(III) chemistry are in agreement with the ideas presented from earlier work on molybdenum(II) and iron(II) trialkyl phosphite complexes [29—31]. Complexes of type $\{\eta^5\text{-cpMo(CO)}_2[P(OR)_3]_2\}BPh_4$ under reflux conditions lose an alkyl group to give dialkyl phosphito complexes $\eta^5\text{-cpMo(CO)}_2[OP(OR)_2][P(OR)_3]_2$ (R = Me, Et, i-Pr, n-Bu). In this molybdenum case, coordination of the tertiary phosphite to a cationic metal center makes the alkyl group susceptible to nucleophilic attack, and here it appears that the nucleophile is the anion $\eta^5\text{-cpMo(CO)}_3^-$. This suggestion was made because the decomposition of a possible intermediate compound $\{\eta^5\text{-cpMo(CO)}_2[P(OMe)_3]_2\}\{\eta^5\text{-cpMo(CO)}_3\}$ gives a mixture of the compounds $\eta^5\text{-cpMo(CO)}_2[OP(OMe)_2][P(OMe)_3]_2$ and $\eta^5\text{-cpMo(CO)}_3Me$. Furthermore, even when the decomposition is carried out in the presence of excess trimethyl phosphite, the complex $\eta^5\text{-cpMo(CO)}_3Me$ is formed.

From these studies it does appear as if two competing routes are available for trialkyl phosphite hydrolysis in the presence of metal ions. Unfortunately though, despite considerable synthetic work on dialkyl phosphito complexes of platinum(II), no mechanistic information is available as to the pathway for their hydrolysis. Since there is evidence, however, that the first product from the reaction of trialkyl phosphites with tetrachloroplatinate(II) is the complex

$\{Pt[P(OR)_3]_4\}^{2+}PtCl_4^{2-}$, it appears likely that a nucleophilic displacement mechanism with Cl^-, OH^- or H_2O as nucleophile is operative on this cationic platinum(II) complex (12). The only argument against this suggestion is the observation that a similar method can be used to prepare the compound

$$PtCl_4^{2-} + P(OR)_3 \xrightarrow[-Cl^-]{} \{Pt[P(OR)_3]_4\}^{2+}PtCl_4^{2-} \xrightarrow[-Cl^-]{H_2O/OH^-} Pt\{[OP(OR)_2]_4H_2\} \qquad (12)$$

$Pt\{[OP(OPh)_2]_4H_2\}$, and nucleophilic attack at a phenyl carbon is an unlikely route. It is apparent that further kinetic, inhibition and labelling studies are necessary before these interesting questions can be adequately answered.

In addition to complexes of the diphenylphosphinito ligand, and complexes containing both a diphenylphosphinito and diphenylphosphinous acid group, a Mo(0) complex containing a coordinated diphenylphosphinous acid as the sole phosphorus ligand has been prepared. Thus the tricoordinate tautomer has been stabilized by coordination from treating the complex $Mo(CO)_5(PPh_2Cl)$ first with hydroxide, and then with acid [32a]. If, however, the hydrolysis of the parent compound is carried out in aqueous triethylamine, the anionic diphenylphosphinito pentacarbonyl molybdenum(0) complex is formed (13). In subsequent work the complex *cis*-$Mo(CO)_4(PPh_2Cl)_2$ has been found to react with aqueous triethylamine to give $[Et_3NH]\{Mo(CO)_4[(OPPh_2)_2H]\}$ [32b].

$$\begin{tikzcd}
Mo(CO)_5(PPh_2Cl) \arrow[r, "(i)\,OH^-", "(ii)\,H^+"'] \arrow[d, "H_2O + Et_3N"] & Mo(CO)_5(PPh_2OH) + Cl^- \\
Et_3NH[Mo(CO)_5OPPh_2] &
\end{tikzcd} \qquad (13)$$

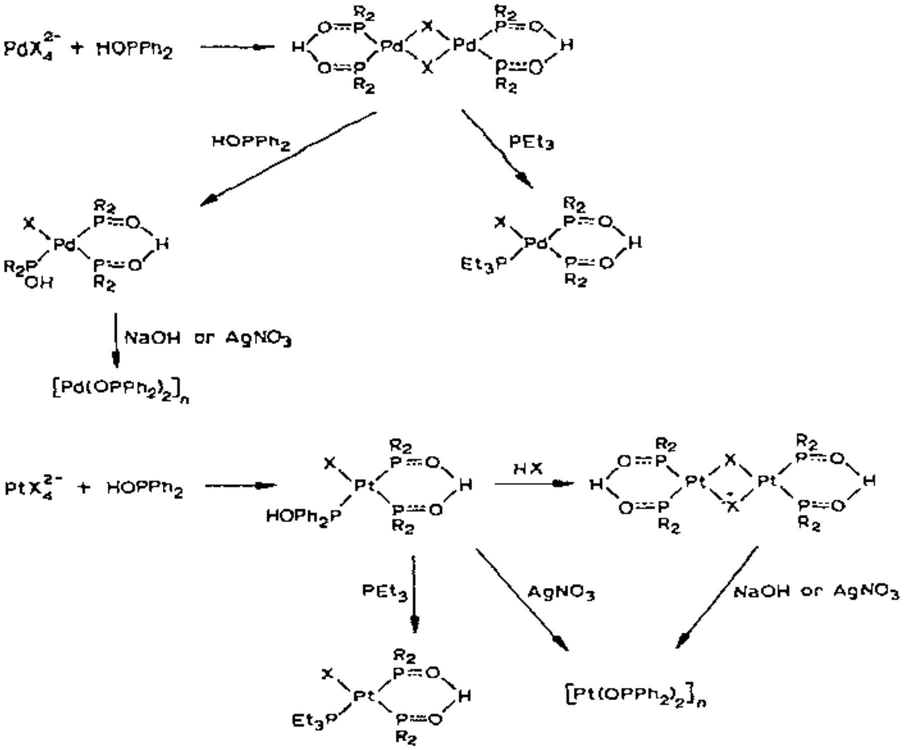
Diphenylphosphinito and dialkyl phosphito complexes have also been prepared using the isolated parent diphenylphosphinous acid and dialkyl phosphites as ligands. These acids are weak, but either before or after coordination of the phosphorus to the metal center, the proton can be transferred to a strong base to give a unidentate anionic ligand (14). It has been shown that addition of a strong base such as $LiNH_2$, NaH, LiPh or MeMgBr to the free

$$\begin{tikzcd}
 & M{-}PR_2(O) + X^- & \\
X{-}M \arrow[ur, "R_2PO^-"] \arrow[dr, "R_2POH"'] & & \\
 & X{-}M{-}PR_2OH \arrow[r, "Base"] & M{-}PR_2(O)
\end{tikzcd} \qquad (14)$$

dialkyl or diaryl phosphite leads to the formation of the O-bonded compound $MOP(OR)_2$ [33] (15). In a similar manner the silver diphenylphosphinite complex has been prepared from silver nitrate and the parent acid, although no

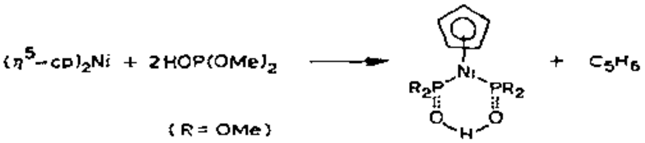
$$MY + HPO(OR)_2 \rightleftharpoons MOP(OR)_2 + HY \qquad (15)$$

serious attempt has been made to distinguish between an ionic structure $Ag^+OPPh_2^-$, and an O-bonded covalent one $AgOPPh_2$ [34]. This silver diphenylphosphinite compound has subsequently proven useful as a reagent in the preparation of a series of diphenylphosphinito platinum(II) and palladium(II) complexes. The silver compound was not isolated in this latter work, but a mixture of diphenylphosphinous acid and silver nitrate was used to prepare the complexes, some of which are shown in (16) [35].



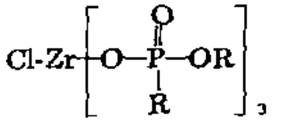
(16)

A nickel(II) complex with a coordinated dimethyl phosphito group has been prepared by treating nickelocene with dimethyl phosphite [36] (17). In



(17)

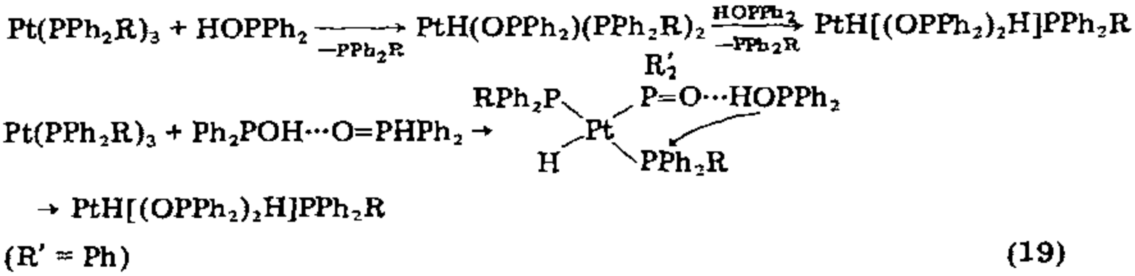
this case added base is not necessary since protonation of one ring yields cyclopentadiene. A series of dialkyl phosphito complexes of zirconium(IV) has been prepared by refluxing the appropriate dialkyl phosphite with zirconium tetrachloride in benzene as solvent. The resulting compounds Zr[OP(O)(OR)R]$_3$Cl and Zr[OP(O)(OR)R]$_2$Cl$_2$ (R = Et, n-Pr, n-Bu) are polymeric and the authors suggest structures of the type shown in (18) where the ligand is σ-bonded to the metal and one of the alkyl groups is bonded to phosphorus.



$$\mathrm{Cl\text{-}Zr}\left[\mathrm{O{-}\underset{R}{\underset{|}{\overset{O}{\overset{\|}{P}}}}{-}OR}\right]_3 \qquad (18)$$

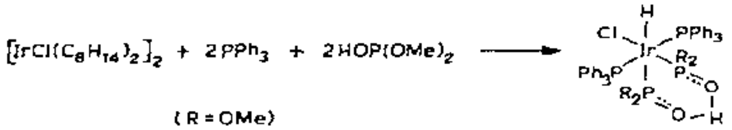
Such a product results from a Michaelis—Arbuzov rearrangement [37].

Frequently it is found that the complexes obtained using diphenylphosphinous acid or dialkyl phosphites as ligands have both a diphenylphosphinous acid and a diphenylphosphinito, or a dialkyl phosphite and a dialkyl phosphito, coordinated to the metal center. From a rather limited number of studies it does appear that after coordination of the phosphorus atoms to the metal, the acid proton is hydrogen bonded between the oxygens to give a pair of equivalent phosphorus atoms. This apparent stability of the ligating pair is an interesting detail, and it is possibly related to the additional bonding through this hydrogen bond. An interesting example of the formation of a phosphinito—phosphinous acid ligand pair comes from work on the oxidative addition of diphenylphosphinous acid to complexes $Pt(PPh_2R)_3$ (R = Me, Ph). The product is the platinum(II) hydride compound $PtH[(OPPh_2)_2H]PPh_2R$ [19] (19). Such a product is unusual since protonation of compounds PtL_3 commonly leads to the formation of an ionic complex $[PtHL_3]X$, or a covalent complex $PtHXL_2$, depending on the strength of the acid HX and the strength of the coordinate bond between platinum(II) and the conjugate base X^- [38]. The substitution of an additional coordinated PPh_2R group implies that further bonding is involved in the coordination of this PPh_2OH ligand, maybe through this hydrogen bonding. An alternative explanation is that diphenylphosphinous acid exists as a hydrogen bonded dimer in solvents of low dielectric constant, and that with the second phosphinous acid molecule already attached, the chelate effect ensures rapid substitution of the additional coordinated phosphine after the oxidative addition step has occurred. The concept that a chelating ligand would favor further phosphine substitution is justified by other work on the oxidative addition of the ligands $HSCH_2CH_2SMe$ and $HSCH_2CH_2SCH_2CH_2CH_2SMe$ to the compound $Pt(PPh_3)_3$, where again two phosphines are substituted in the formation of the hydride [39,40]. A similar result was also obtained with the oxidative addition of dimethyl phosphite to complexes of rhodium(I) and iridium(I) [41]. Thus when a solution containing $[IrCl(cyclooctene)_2]_2$ and two equivalents of triphenylphosphine is treated



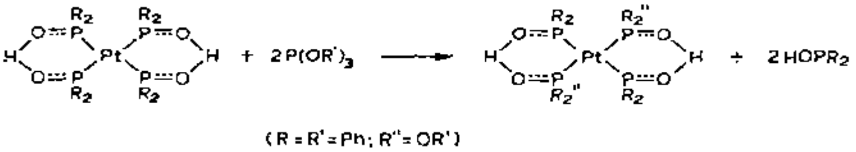
(19)

with dimethyl phosphite, the hydride $IrHCl\{[OP(OMe)_2]_2H\}(PPh_3)_2$ is formed (20).



(20)

An interesting type of reaction, but one which has received little attention, is the substitution between phosphinito and phosphito ligands coordinated to a metal center. One example is the reaction of the complex $Pt[(OPPh_2)_4H_2]$ with triphenylphosphite [17] (21). The product $Pt\{(OPPh_2)_2[OP(OPh)_2]_2H_2\}$ is obtained in good yield, but since in the hydrogen bonded structure it is not possible to distinguish between a coordinated diphenylphosphinous acid or diphenylphosphinito ligand, it is academic to try and identify which one is



(21)

substituted. It is surprising that two, and only two, phosphine ligands are substituted by phosphite, and this reaction deserves further investigation.

C. FLUORO DERIVATIVES

Although the compound $F_2HP(O)$ has been described by a number of workers [42—45], only recently has the compound been used as a ligand. Kruck et al. have prepared a number of metal complexes of the anion PF_2O^- by hydrolysis of the corresponding PF_3 complexes [46—49] (22). More recently difluorophosphinite complexes of palladium(II) and platinum(II) have been formed

$$2\,Ni(PF_3)_4 + Ba(OH)_2 \rightarrow Ba[Ni(OPF_2)(PF_3)_3]_2 + 2\,HF \qquad (22)$$

by treating the complexes MCl_2L_2 (L = py, PPh_3) with allyl difluorophosphinite [50—52] (23). The method has been expanded to use other alkyl difluorophosphinites, and both monomeric and chloro bridged complexes have been prepared.

$$PtCl_2(PEt_3)_2 + PF_2OR \rightarrow trans\text{-}PtCl(OPF_2)(PEt_3)_2 + RCl$$

(R = allyl or n-Bu)

$$PdCl_2(PEt_3)_2 + 2\,PF_2(OC_3H_5) \rightarrow [MCl(OPF_2)(PEt_3)]_2 + 2\,C_3H_5Cl \qquad (23)$$

If the complex *trans*-$PtCl(OPF_2)(PEt_3)_2$ is treated with allyl difluorophosphinite for an extended period of time in acetonitrile solvent at 80°C, the complex $Pt(OPF_2)_4^{2-}$ is formed (24). This method closely resembles the one first used to prepare the allylpyridinium salts of the palladium and platinum analogs of this ion [50]. Apparently the electron withdrawing fluorines on the phosphorus nuclei cause the protons on the oxygens to be strongly acidic and the complex is isolated as the deprotonated anion.

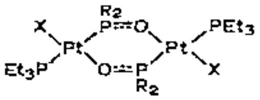
$$trans\text{-}PtCl(OPF_2)(PEt_3)_2 + 3\ C_3H_5OPF_2 \xrightarrow{80°C} [C_3H_5PEt_3]_2[Pt(OPF_2)_4] + C_3H_5Cl \qquad (24)$$

D. COMPLEXES OF PHOSPHOROUS ACID

Phosphorous acid is a dibasic acid having the structural formula $HP(O)(OH)_2$. It can therefore be regarded as the parent acid for dialkyl and diaryl phosphites, and should therefore have similar coordination chemistry to these esters. The anion should show similar ambidentate coordination behavior, and because of the large number of hydroxyl groups, the compounds should show good solubility in aqueous solution. The compounds which have been reported include $Pt\{[OP(OH)_2]_4H_2\}$ [53] and a series of multimetallic rhodium complexes [54—56]. The complexes can be prepared from complete hydrolysis of the trimethyl phosphite compound, or by treating salts of platinum(II) with phosphorous acid, either in solution or in the melt. The complex $Pt\{[OP(OH)_2]_4H_2\}$ is rather unstable, and decomposes to platinum metal in the presence of either acid or base. The complex has a strong absorption band at 368 nm and an emission band at 514 nm, and the excitation spectrum shows that the two are related [57]. Such an intense emission from an aqueous solution of a complex of platinum(II) is rather unusual, and further work needs to be done to identify the nature of the emission spectrum from this complex.

E. REACTIONS

Much of the chemistry of these phosphinito and phosphito groups as ligands involves their coordination chemistry to platinum(II). It is not unexpected, therefore, that some effort has been devoted toward identifying their positions in the ground state *trans* influence, and the kinetic *trans* effect, series. From comparison of values for ν(Pt—Cl) in diphenylphosphinito complexes it is found that this ligand is high in the *trans* influence series [20]. This position has been confirmed by similar measurements of ν(Pt—H) in complexes $PtH[(OPPh_2)_2H](n\text{-}BuOPPh_2)$ [18], by the finding that the Hg—P bond distance in $Hg[OP(OEt)_2]_2$ is longer than in $HgCl[OP(OEt)_2]$, and by consideration of trends in the ^{31}P NMR spectra of similar Pt(II) complexes (section F). An interesting result has been discussed for diphenylphosphinito bridged complexes of Pt(II). The complex $[Pt_2X_2(OPPh_2)_2(PEt_3)_2]$ (X = Cl, Br) is tentatively assigned a structure with the bridging diphenylphosphinites and the halide in *trans* positions across the bridge (25). The halides are *trans* to the


(R = Ph; X = Cl, Br)

(25)

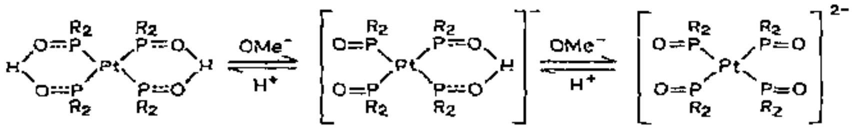
coordinated oxygen atoms of the diphenylphosphinito group, and interestingly they show low values for (Pt—X) indicative of a high *trans* influence for the oxygen end as well as that of the coordinated phosphorus end of the diphenylphosphinite ligand [20].

The kinetic *trans* effect for a P-bonded dialkyl phosphito ligand has been measured in a dimethylglyoximato cobalt(III) complex [59]. Trogler et al. studied the replacement of L by L′ in complexes $RR'P(O)Co(DH)_2L$ (L and L′ are phosphines, phosphites or heterocyclic N donors). The substituents used on the phosphinito or phosphito ligand are R=R′=OMe, Ph; R=OMe, R′=Ph. The kinetic *trans* effect order was found to be: $OPPh_2 \sim OPPh(OMe) > Me > OP(OMe)_2 \sim SO_3 \gg NO_2$, and the kinetics interpreted on a two-step sequence with $k_{obs} = k_1$ (26).

$$RR'(O)Co(DH)_2L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RR'P(O)Co(DH)_2 + L$$

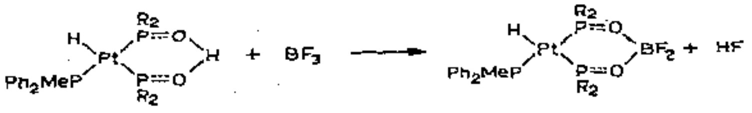
$$RR'(O)Co(DH)_2 + L' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RR'P(O)Co(DH)_2L' \qquad (26)$$

For P-bonded metal complexes of dialkyl or diaryl phosphinous acid or phosphites, the hydrogen bonded to the oxygen is acidic. This proton can be removed by titration with base, or substituted for by transition metal ions and by Lewis acids. For complexes such as $Pt\{[OP(OMe)_2]_4H_2\}$ the two acid proton can be sequentially removed by base, and two inflexions can be seen in a conductivity plot against added base (Fig. 1) [16,57] (27). This proton is observed as a broad line in the ^1H NMR spectrum, and resonates in the



(27)

region 10—15 ppm downfield of tetramethylsilane [19,60]. Treating complexes having both diphenylphosphinous acid and diphenylphosphinito, or dimethyl phosphite and dimethyl phosphito groups, with BF_3 [17,19,57,61, 62], $SiClMe_3$ [62] or transition metal acetylacetonates [57,60,63], leads to replacement of the acidic proton by BF_2, $SiMe_3$ or a transition metal ion. This method has been used to prepare complexes of the type shown in (28).


(R = Ph)

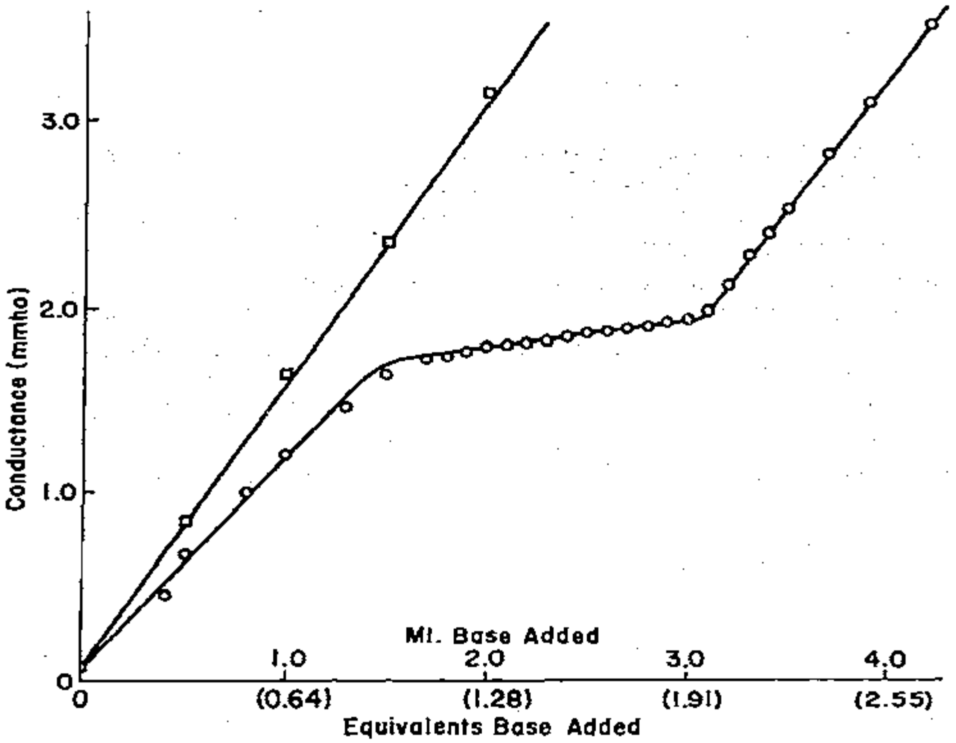
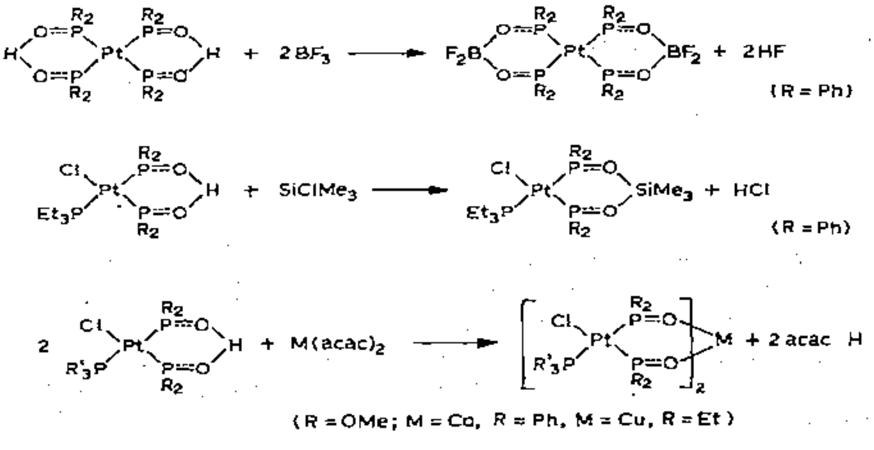
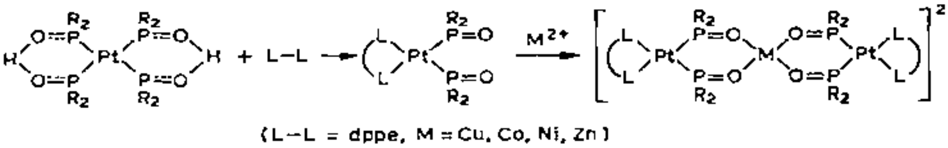


Fig. 1. Conductivity titration for the addition of a standard solution of sodium methoxide to Pt{[OP(OMe)$_2$]$_4$H$_2$} in methanol solvent.



(28)

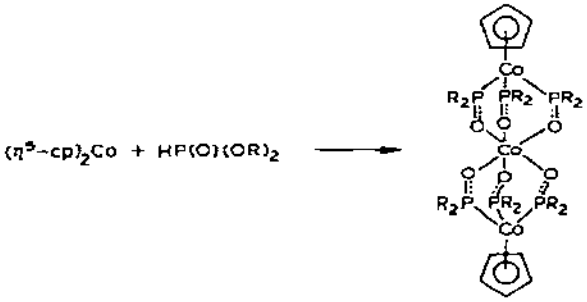
Similar mixed metal complexes can be prepared from Pt[OP(OMe)$_2$]$_2$L-L: (L-L) = 1,2-bis(diphenylphosphino)ethane (dppe), *o*-phenylenebis(dimethylarsine) (diars). These complexes can be prepared by treating Pt[OP(OMe)$_2$]$_4$H$_2$ with the appropriate chelate [17,60,63]. Since the dimethyl phosphito ligand is deprotonated in the uncharged complex, the compounds can be used to prepare cationic mixed metal oligomers (29). From work on the pseudotetrahedral cobalt(II) complexes the dimethyl phosphito ligand has a ligand field



(29)

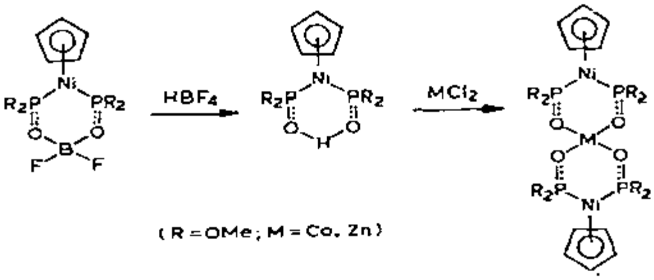
strength and nephelauxetic parameter B comparable to that of SCN^- [60].

These complexes are similar to the "triple sandwich" complexes prepared from $(\eta^5\text{-cp})_2Co$ or $(\eta^5\text{-cp})_2Ni$ and $HP(O)(OR)_2$ (R = Me, Et, Ph). In the case of cobalt the complex $(\eta^5\text{-cp})_2Co_3[OP(OR)_2]_6$ is isolated directly from the reaction [64—66] (30) but for the case of nickelocene the monomeric complex is obtained without subsequent complexation, and the second metal or



(30)

BF_2 can be subsequently substituted [36], (31). Treating the compound $(\eta^5\text{-cp})_2Co_3[OP(OR)_2]_6$ with HBF_4 gives a cationic complex $\{\eta^5\text{-cp}\ Co[OP(OR)_2]_3BF\}BF_4$. A single crystal structure for the complex with R=Et shows the tris(diethylphosphito) fluoroborate anion coordinated to the metal as a tridentate cage-forming chelate ligand [66b].



(31)

F. SPECTROSCOPY

The major portion of the spectroscopic work carried out with these complexes involves NMR studies.

For several series of diphenyl phosphito and dialkyl phosphito complexes of palladium(II) and platinum(II) the ^{1}H and ^{31}P NMR spectra have been reported and discussed. The ^{31}P NMR spectra of complexes Pt{[OP-(OR)$_2$]$_4$H$_2$} (R = Me, Et, Ph) show a single resonance for the magnetically equivalent phosphorus nuclei indicative of a symmetrically bonded proton between the oxygens [60,67]. It is probable, however, that the proton rapidly exchanges between the oxygen atoms in a manner resembling that of acetylacetone [68,69], but there is no reported attempt to verify this at present. In the ^{31}P NMR spectral region the diphenyl phosphito group resonates at high fields when *trans* to chloride, and at lower fields when *trans* to phosphorus [67]. These chemical shift differences can be in the range of 20—40 ppm. Interpretation of the values obtained for the coupling constants suggests that they are a measure of the *s*-component of the Pt—P bonds, and that the origin of these large differences in coupling constants is likely differences in covalency. Since high *s*-character leads to a stronger bond, the coupling constants can be used to measure the strength of Pt—P bonds and determine the *trans* influence of ligands.

A complete analysis of the ^{31}P NMR spectrum of the complex [{Pt[OP-(OMe)$_2$]$_2$dppe}$_2$Zn](ClO$_4$)$_2$ has been made. The spectrum is complex since it is an AA′BB′ pattern superimposed on an AA′BB′X (X = ^{195}Pt, $I = 1/2$, 33% abundance) one [70]. Interestingly the ^{195}Pt satellite portion of the spectrum is not symmetrically flanked about the center portion of the spectrum (Fig. 2), but it has been found by calculation that this feature can be fit by iterative assignments assuming the above symmetries. It is apparent therefore that the unsymmetrical ^{195}Pt satellite portion of the spectrum is a consequence of second-order effects in the coupling of ^{31}P with ^{195}Pt.

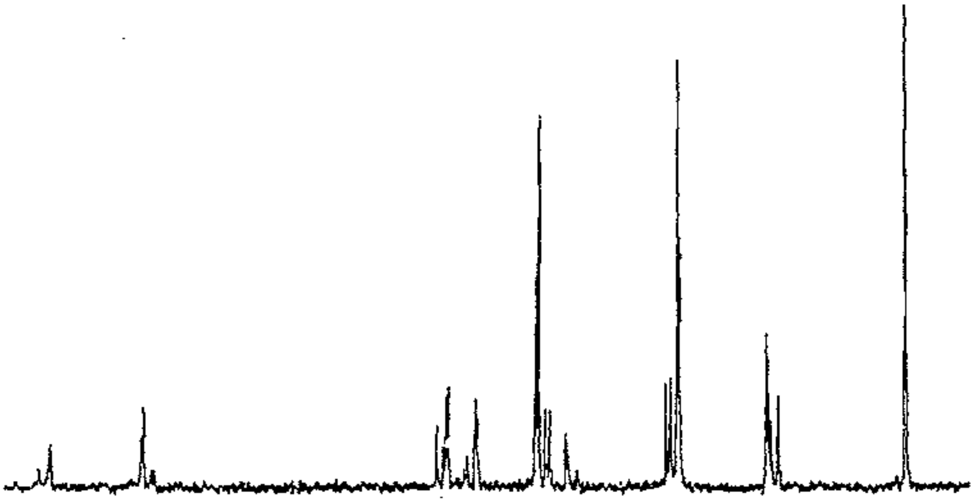
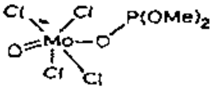


Fig. 2. ^{31}P NMR spectrum of the complex [{Pt[OP(OMe)$_2$]$_2$dppe}$_2$Zn](ClO$_4$)$_2$.

The infrared spectra of diphenylphosphinite complexes show bands mainly due to ν(P—O). These bands are observed in the 850—1150 cm^{-1} region and have been assigned as ν(P—OH)(terminal) ca. 880, ν(P—O)(bridge) ca. 1010, and ν(P—O)(terminal) ca. 1100 cm^{-1} [20]. The bands are frequently broad and may be obscured by other intense bands.

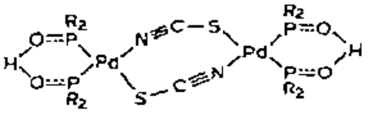
G. STRUCTURES

Single crystal x-ray structures have been solved for the compounds $HgCl[OP(OEt)_2]$ [71] and $Hg[OP(OEt)_2]_2$ [58]. The angles Cl—Hg—P and P—Hg—P are 173.3° and 165.9° respectively, and the corresponding Hg—P distances are 2.40 Å and 2.41 Å. The two respective values of the P=O distance are 1.44 Å and 1.46 Å. The structure of the complex $PtCl(OPF_2)(PEt_2Ph)_2$ shows a P-bonded difluorophosphinito ligand with a Pt—P distance of 2.199 to the PF_2O ligand [72]. The P—O bond distance of 1.471(17) is slightly longer than the value of 1.436(2) Å observed in POF_3. For the complex $\{MoOCl_4[OP(OMe)_2]\}^{n-}$ the dimethyl phosphito ligand is O-bonded to molybdenum with an Mo—O distance of 2.18(2) Å [73] (32).



(32)

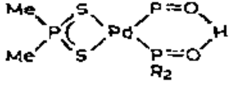
Two structures have been solved which show the symmetrical arrangement of phosphorus ligands in palladium complexes having both a coordinated diphenylphosphinous acid and diphenylphosphinito ligand. In the complex $\{Pd(SCN)[(OPPh_2)_2H]\}$ the non-bridging phosphine ligands are symmetrically hydrogen bonded with a short O—O distance of 2.421(7) Å and equal P—O distances of 1.549(6) and 1.536(6) Å [25]. A similar short O—O separation of 2.414(20) Å is found in the compound $Pd[(OPPh_2)_2H](S_2PMe_2)$ [21] (33).



(R = Ph)

(33)

The P—O distances are again short, 1.545(14) Å. The structure of the compound $(MeOPPh_2)_2(HOPPh_2)RuCl_3Ru[(OPPh_2)_2H](HOPPh_2)$ has also been solved, and the data further verify the basic ideas about these hydrogen bonded phosphinito ligands [22] (34).



(R = Ph)

(34)

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