

The Preparation and Characterization of Compounds of the Types PtEt₂diphos and PtEtClidiphos. Correlations of the ³¹P N.M.R. Spectral Parameters with Ring Size

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A series of compounds of the type PtEt₂diphos (diphos = 1,2-diphenylphosphinoethane, dppe; 1,3-diphenylphosphinopropane, dppp, and 1,4-diphenylphosphinobutane, dppb) has been prepared. Selective cleavage of one ethyl group by hydrogen chloride gives the chloroethyl derivative, PtEtClidiphos, in each case, although an attempt to prepare [PtCl(C₂H₄-dppp)]BF₄ by abstraction of hydride from PtEtCl-dppp using triphenylmethyl cation failed. Hydride abstraction occurs, but the ethylene is readily displaced by fluoroborate anion. Correlations of phosphorus chemical shifts and platinum-phosphorus coupling constants with ring size are noted for both series of compounds.

Introduction

There has been considerable interest in recent years in the use of platinum metal complexes of chelating diphosphines as homogeneous catalysts [1]. In many cases, however, the catalysts have been formed in solution and used *in situ*, with little being known of the nature of the species actually present in solution. As part of a study of model systems of such catalysts, we have investigated the chemical properties of a series of platinum(II) complexes of the types PtEtClidiphos and PtEt₂diphos containing the ligands 1,2-bisdiphenylphosphinoethane (dppe), 1,3-bisdiphenylphosphinopropane (dppp) and 1,4-bisdiphenylphosphinobutane (dppb). In addition, we have obtained ³¹P n.m.r. data for the complexes, noting correlations of chemical shifts and coupling constants with ring size and the nature of the ligands *trans* to the phosphorus atoms, and have attempted the formation of the cationic olefin complex, [PtCl(C₂H₄-dppp)]⁺BF₄⁻, via hydride abstraction from PtEtClidppp with trityl fluoroborate [2].

Experimental

Proton spectra were obtained on Varian T60 and on Bruker HX60 n.m.r. spectrometers. Phosphorus n.m.r. spectra were run on a Bruker HX60 spectro-

meter operating in the Fourier transform mode with broad-band proton decoupling. Infrared spectra were run on Nujol mulls or as KBr discs on a Perkin Elmer 180 spectrometer.

PtCl₂diphos

The compounds PtCl₂dppe, PtCl₂dppp and PtCl₂dppb were prepared by procedures similar to those of Watt and Cuddeback [3]. About 2 g of the ligand (48 mmol) in 40 ml ethanol were added to a stirred suspension of finely divided K₂PtCl₄ (2.0 g, 48 mmol) in 40 ml concentrated hydrochloric acid. The mixtures were refluxed with stirring for eight hours and cooled to give precipitates of the products in 80-90% yields. The dppb complex does not appear to have been previously prepared; its solubility in organic solvents is too low to recrystallize it or to obtain n.m.r. spectra.

The compounds *cis*-PtCl₂(PPh₃)₂ and *cis*-PtCl₂(PMePh₂)₂ were prepared by standard methods [4].

PtEt₂diphos, PtEt₂(PPh₃)₂, PtEt₂(PMePh₂)₂

Compounds of the type PtEt₂diphos were prepared by treating a suspension of 2.0 g PtCl₂diphos (~3 mmol) in 40 ml anhydrous ethyl ether with ~9 mmol of a standardized solution of ethyl lithium in petroleum ether (b.p. 30-60 °C) [5]. Reactions were stirred for one hour at 0 °C and one hour at room temperature, and then were treated with a few drops of methanol to destroy unreacted ethyl lithium. The solvent was removed *in vacuo*, the residue was extracted with methylene chloride and the products were precipitated by adding petroleum ether while the methylene chloride was boiled off. Yields were generally in the range 50-80%.

The compounds PtEt₂(PPh₃)₂ and PtEt₂(PMePh₂)₂ were prepared similarly; the former has been previously reported [6].

PtEtClidiphos

These compounds were prepared by treating solutions of about 0.5 g of the dichloro compounds in 15 ml methylene chloride at 0 °C with equivalent amounts of standardized solutions of HCl in ethyl ether, prepared by reacting acetyl chloride with

TABLE I. Melting Points and Analytical Data.

Compound	M.P. (°C)	% Found		% Calc.	
		C	H	C	H
PtEt ₂ dppe	198–200 (decomp)	53.86	5.21	55.29	5.26
PtEt ₂ dppp	154–5	56.59	5.16	55.93	5.45
PtEt ₂ dppb	153–5	56.81	5.48	56.55	5.64
PtEt ₂ (PPh ₃) ₂	146	61.50	5.28	61.77	5.18
PtEt ₂ (PMePh ₂) ₂	94–95	54.94	5.29	55.13	5.55
PtEtCl ₂ dppe	190–200 (dec)	51.85	4.78	51.11	4.44
PtEtCl ₂ dppp	185–190 (dec)	50.89	4.47	51.83	4.65
PtEtCl ₂ dppb	180–200 (dec)	51.10	5.04	52.52	4.85
PtCl(BF ₄)dppp		44.44	3.59	42.90	3.89

methanol. Addition of acid was extended over 90 min in each case. The solutions were stirred a further 15 min and evaporated to dryness; the residues were then recrystallized from methylene chloride–petroleum ether to give the products in 70% yield.

Attempted Preparation of [PtCl(C₂H₄)dppp]BF₄

A solution of PtEtCl₂dppp in anhydrous tetrahydrofuran at 0 °C was treated under nitrogen with an equimolar amount of trityl fluoroborate for 30 min. The solvent was removed *in vacuo* and the residue was recrystallized from methylene chloride–petroleum ether to give PtCl(BF₄)dppp.

Melting points and analytical data are given in Table I, far infrared data in Table II.

TABLE II. Platinum–Chlorine Stretching Frequencies.

Compound	$\nu_{\text{PtCl}}(\text{cm}^{-1})^{\text{a}}$
PtCl ₂ dppe	292, 310
PtCl ₂ dppp	285, 309
PtCl ₂ dppb	288, 308
<i>cis</i> -PtCl ₂ (PPh ₃) ₂	292, 316
<i>cis</i> -PtCl ₂ (PMePh ₂) ₂	290, 314
PtEtCl ₂ dppe	283
PtEtCl ₂ dppp	289
PtEtCl ₂ dppb	282
PtCl(BF ₄)dppp	280

^aNujol mulls.

Discussion

¹H n.m.r. Spectra

Proton n.m.r. spectra were recorded for all diethyl derivatives. In all cases satisfactory integration of phenyl *versus* methyl/methylene regions was obtained, but the spectra were generally too complicated to interpret satisfactorily, particularly in view of complication by methylene protons in the chelating diphosphines. Phosphorus decoupling did not result

in significant spectral simplification, although sharpening of some peaks was observed.

³¹P n.m.r. Spectra

³¹P{¹H} spectra were obtained for all compounds except PtCl₂dppb, which is insoluble, and are listed in Table III. As expected, the ³¹P{¹H} spectra of the dichloro and diethyl compounds consist of 1:4:1 triplets, the satellites a result of coupling to ¹⁹⁵Pt. The spectra of the chloroethyl derivatives PtEtCl₂dppp and PtEtCl₂dppb exhibit central four-line AB quartets flanked by the weaker eight-line multiplets which are the AB portions of ABX spin systems (X = ¹⁹⁵Pt). In the case of PtEtCl₂dppe, J_{PP} was too small to resolve. The ³¹P chemical shifts of the diethyl and chloroethyl derivatives are very similar to those of the corresponding methyl compounds; data for the latter are also listed in Table III.

Listed in Table IV are the “coordination shifts”, Δ, of the dichloro and diethyl compounds, *i.e.* the difference in ³¹P chemical shift between the free and complexed phosphine [8], and the “ring contributions”, Δ_R, for the same compounds, *i.e.* the difference between the coordination shift of a *cis*-disubstituted phosphine complex and the coordination shift of a corresponding diphos complex [8].

As interesting feature of the ³¹P n.m.r. spectra is the extremely large downfield shift that occurs on coordination of dppe, a phenomenon which has been observed in a variety of compounds which contain phosphorus in a five member ring [7, 8]. It has been suggested that the observed shift is a consequence of a large “ring strain” introduced by the five-member chelate [9], an argument disputed by Grim [10], who maintained that if the “ring strain” was the cause of the anomalous chemical shift, large downfield coordination shifts should be observed for four-member dppm chelates, which is not generally the case. For a variety of transition metal complexes, it has been found that Δ_R for five-member rings is large and positive (a deshielding ring contribution), while four and six-member rings have negative (shielding)

TABLE III. ^{31}P NMR Data.

Compound	δ^a	$J_{\text{Pt-P}}$ (Hz)	J_{PP} (Hz)	Comments
PtCl ₂ dppe	41.1	3609		$\delta = 45.3, J = 3618$ [7] ^b
PtCl ₂ dppp	-5.6	3408		$\delta = -5.6, J = 3420$ [7] ^b
<i>cis</i> -PtCl ₂ (PPh ₃) ₂	14.2	3671		
<i>cis</i> -PtCl ₂ (PMePh ₂) ₂	-1.1	3620		$\delta = -1.2, J = 3616$ [7] ^b
PtEt ₂ dppe	45.1	1602		$\delta = 45.4, J = 1794$ for PtMe ₂ dppe [7] ^c
PtEt ₂ dppp	3.0	1592		$\delta = 3.2, J = 1790$ for PtMe ₂ dppp [7] ^b
PtEt ₂ dppb	18.5	1677		
<i>cis</i> -PtEt ₂ (PPh ₃) ₂	27.3	1709		
<i>cis</i> -PtEt ₂ (PMePh ₂) ₂	5.9	1667		$\delta = 6.4, J = 1851$ for <i>cis</i> -PtMe ₂ (PMePh ₂) ₂ [7] ^c
PtEtCl dppe	42.9 ^d , 42.0 ^e	4478 ^d , 1558 ^e	<2	$\delta = 42.0^d, 43.4^e, J = 4224^d, 1737^e$ for PtMeCl dppe ^b
PtEtCl dppp	6.8 ^d , 2.2 ^e	4418 ^d , 1483 ^e	20.6	$\delta = 5.1^d, 3.0^e, J = 4116^d, 1644^e$ for PtMeCl dppp ^b
PtEtCl dppb	18.3 ^d , 19.2 ^e	4574 ^d , 1577 ^e	13.2	
PtCl(BF ₄)dppp ^h	-7.7, -11.8	3144, 3556	27	

^appm from external H₃PO₄, positive shifts downfield. All spectra run in CDCl₃ unless otherwise noted. ^bIn CH₂Cl₂. ^cIn C₆H₆. ^d*trans* to Cl. ^eP *trans* to Et or Me. ^hIn CD₃CN.

TABLE IV. ^{31}P Coordination Shifts (Δ) and Ring Contributions (Δ_{R}).

Compound	Δ	Δ_{R}
PtCl ₂ dppe	53.4	42.2
PtCl ₂ dppp	11.4	-4.5
<i>cis</i> -PtCl ₂ (PMePh ₂) ₂	25.6	-
PtEt ₂ dppe	57.4	39.2
PtEt ₂ dppp	20.0	-2.9
PtEt ₂ dppb	34.0	12.6
<i>cis</i> -PtEt ₂ (PMePh ₂) ₂	32.6	-

contributions to chemical shift with Δ_{R} for the four-member systems being larger. These trends are reflected in this work in the dppe and dppp compounds listed in Table IV. We have also found that the seven-member ring structure in PtEt₂dppb results in a deshielding ring contribution which is about one third as large as that observed in dppe compound, which contains a five-member structure.

Palenik *et al.* [11] have recently published crystal data on a series of dichloropalladium complexes PdCl₂L (L = dpmm, dppe, dppp). The data indicate that the five-member ring dppe compound is less strained than either the four-member ring dpmm or six-member ring dppp compounds. Although no crystal structures have been done on the corresponding platinum compounds, it seems reasonable to expect this trend to be repeated. In qualitative terms it would thus appear that there is a correspondence

between ring strain and Δ_{R} – the more strained the system, the larger the shielding contribution of Δ_{R} to the observed chemical shift. If this is indeed correct, one would predict on the basis of the deshielding ring contribution to the observed chemical shift of PtEt₂dppb that an X-ray structure would show this compound to be less strained than the four or six-member ring analogs. There do not appear to be any crystal structures in the literature to either confirm or disprove this. The far infrared spectra (Table II) also appear to have little to say about the matter.

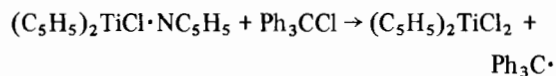
In the series of diethyl compounds, the platinum–phosphorus coupling constant increases in the order dppp(1592) < dppe(1602) < PMePh₂(1667) < dppb(1677) < PPh₃(1709). This order of increasing $J_{\text{Pt-P}}$ is the same in the series of analogous dichloro compounds, *i.e.* dppp(3408) < dppe(3609) < PMePh₂(3620) < PPh₃(3671). In the series of ethyl–chloro derivatives, this order holds for both phosphorus *trans* to chloride and phosphorus *trans* to ethyl, *i.e.* for $J_{\text{Pt-P}}$ (*trans* to ethyl), dppp(1483) < dppe(1558) < dppb(1577), for $J_{\text{Pt-P}}$ (*trans* to chloride), dppp(4418) < dppe(4478) < dppb(4574). The larger *trans* effect of ethyl relative to chloride is reflected in smaller $J_{\text{Pt-P}}$ observed in the diethyl compounds than in the dichloro derivatives [12]. Data on the corresponding dimethyl compounds [7] further indicate that ethyl exerts a larger *trans* influence than methyl. There is no apparent parallel between increasing coupling constant and chemical shift or Δ_{R} in this series of compounds.

Reaction of Trityl Cation and (PtC₂H₅Cl)dppp)

Reaction of PtEtCl₂dppp with trityl tetrafluoroborate led to the isolation of a white solid. Treatment of an acetonitrile solution of the product with excess cyanide ion in a sealed tube followed by mass spectral examination of the gas above the solution indicated that no ethylene was present. When the reaction of PtEtCl₂dppp with Ph₃CBF₄ in a sealed tube was carried out, however, the mass spectrum indicated the evolution of ethylene, as well as of ethane. The ³¹P-{¹H} spectrum of the product in acetonitrile consists of a twelve line AB + ABX pattern whose chemical shifts and coupling constants are given in Table III. The spectrum is similar to, although not the same as, the ³¹P-{¹H} spectrum of PtCl(NO₃)dppp in acetonitrile, prepared by treating PtCl₂dppp with one equivalent of silver nitrate. The infrared spectrum confirms the presence of tetrafluoroborate in the compound, while the far infrared spectrum shows a peak assignable to νPt-Cl at 280 cm⁻¹. All analytical and spectroscopic evidence indicates that the product is PtClBF₄dppp.

An interesting feature of the ³¹P-{¹H} spectrum of this compound is the marked broadening of the upfield half of the central four line pattern, which does not occur in the spectrum of PtClNO₃dppp. Conductivity studies suggest that these compounds are extensively dissociated in acetonitrile solution [13], and the line-broadening in the case of PtClBF₄dppp may be either a result of coupling to fluorine, or of an exchange process of the anion with a coordination site on the metal ion.

The mechanism of formation of PtCl(BF₄)dppp is not certain. The ethylene evolved is doubtless the result of decomposition of the desired product, [PtCl(C₂H₄)(dppp)]⁺BF₄⁻. The formation of ethane is more difficult to explain. One possible mechanism involves a one electron oxidation of PtEtCl₂dppp to a platinum(III) species, which might then undergo homolytic platinum-carbon bond cleavage to yield ethyl radical. Interaction of this radical with solvent would produce ethane. There is precedent for this type of one electron oxidation by trityl cation in the work of Matkovski *et al.* [14] with titanium(III), *i.e.*



We have been unable, however, to detect the stable trityl radical that should be generated by this path-

way, either in the UV-visible or ESR spectrum. The product Ph₃CH, however, which would be produced either by the hydride abstraction or ultimately by the radical reaction, has been isolated from the reaction.

The results indicate that the desired cation, [PtCl(C₂H₄)(dppp)]⁺, is formed but is unstable. In light of the stability of cations of the type *trans*-[Pt(NH₃)₂(C₂H₄)(Cl)]⁺ [15], it might reasonably be expected that the instability is due to the high *trans* effect of the phosphorus *trans* to ethylene. We note that the ligands bromide and iodide, which also have high *trans* effects, appear to destabilize ethylene complexes of platinum [16].

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