in $[Cr(CO)_5(SnBu_2\{py\})]$ vs. $[Cr(CO)_5(Sn(CH\{SiMe_3\}_2)_2)]$ as a function of hybridization due to adduct formation. Structural distortion from octahedral toward idealized bicapped tetrahedron is attributed to a d^{10}-like configuration at iron. Hoffman, Howell, and Rossi have discussed[32] this distortion for $[Fe(CO)_4X_2]$ (X = halide) where X is strongly σ-electron donating.

Reduction by sodium amalgam of $[Fe(CO)_4(SnMe_2)]_2$ in various bases parallels closely reduction by hydride although the amalgam reduction route appears to be somewhat cleaner.

Acknowledgment. We wish to express our appreciation to the Robert A. Welch Foundation, the Research Corp., and the Dow Chemical Co. for support of our research. Thanks are also due to Professor Russell Geanangel at the University of Houston for measuring the ^{119m}Sn Mössbauer spectra and to Ms. Connie Merrill and Mr. Robert Saxton at Rice University for ^{57}Fe Mössbauer spectra. We would like to express our gratitude to Professor Lon J. Wilson (Rice) for use of his facilities and useful discussions. The authors thank Dr. Mark Andrews (Brookhaven Laboratories, Upton, NY) and Professor Richard Ernst (the University of Utah) for comments.

Registry No. $Na_2[Fe(CO)_4(SnMe_2)]$, 76705-09-4; $Na_2[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]$, 76705-10-7; $[Fe(CO)_4(SnMe_2)]_2$, 15418-00-5; $[Fe(CO)_4(Sn\text{-}n\text{-}Bu_2)]_2$, 15613-38-4; $Fe(CO)_4(SnMe_2\{THF\})$, 76705-11-8.

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[32] R. Hoffmann, J. M. Howell, and A. R. Rossi, *J. Am. Chem. Soc.*, **98**, 2484 (1976).

[33] P. G. Harrison and J. J. Zuckerman, *J. Am. Chem. Soc.*, **91**, 6885 (1969).

[34] P. G. Harrison and J. J. Zuckerman, *J. Am. Chem. Soc.*, **92**, 2577 (1970).

Contribution from Donnan Laboratories, Liverpool University, Liverpool L69 3BX, United Kingdom, and the Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

Preparation and Characterization of $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$: An A-Frame Methylplatinum Complex Cation

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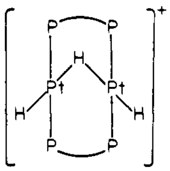
Received May 30, 1980

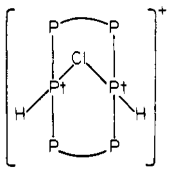
Reaction of $[PtCl_2(dppm)]$, dppm = bis(diphenylphosphino)methane, with methyllithium gives $[PtMe_2(dppm)]$, which, on reaction with HCl, gives $[PtClMe(dppm)]$ and the A-frame complex $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$, both of which have been isolated in pure form. The A-frame complex, previously thought to be a nonionic trimer, was characterized by comparison of its spectral properties (IR and ^1H and ^{31}P NMR) with those of the hexafluorophosphate salt $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ and by conductivity measurements. A third, probably dimeric, form of $[PtClMe(dppm)]$ has been isolated but not structurally characterized.

Introduction

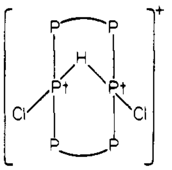
We recently synthesized[2] a series of hydridodiplatinum(II) complex ions, I–III, containing the ligand bis(diphenylphosphino)methane (dppm), and following this we have attempted the synthesis of analogous methyldiplatinum species $[Pt_2Me_nCl_{3-n}(\mu\text{-}dppm)_2]^+$ (n = 1–3). Accounts of the complex $[Pt_2Me_3(\mu\text{-}dppm)_2]^+$, analogous in molecular formula but not in structure with I, have recently been published,[3] and we now report on the complex ion $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$, analogous to II.



I



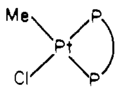
II



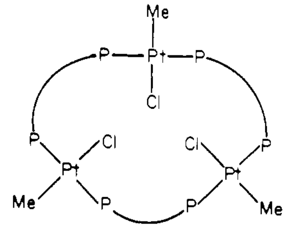
III

$\widehat{PP} = Ph_2PCH_2PPh_2$

Bennett and coworkers[4] have previously reported methylplatinum derivatives with dppm as ligand. They reported that $[PtClMe(cod)]$ (cod = 1,5-cyclooctadiene) reacted with dppm to give a monomeric form (IV) and an oligomeric form (V) of $[PtClMe(dppm)]$. The oligomeric form was tentatively identified as the trimer V by its molecular weight in chloroform, and this formulation was considered to be consistent with the ^1H and ^{31}P NMR spectra.

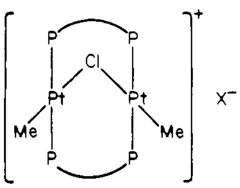


IV



V

We have developed routes to pure samples of both the monomeric and previously reported oligomeric forms of $[PtClMe(dppm)]$, and evidence is presented that the oligomeric form is actually an ionic A-frame dimer (VIa).



VIa, $X^- = Cl^-$
b, $X^- = PF_6^-$

Results and Discussion

We find that $[PtMe_2(dppm)]$ is a convenient starting material for the preparation of these chloromethyl complexes and is readily obtained by the action of methyllithium on $[PtCl_2(dppm)]$. It is worth noting that this reaction gives monomeric $[PtMe_2(dppm)]$, identical with the compound

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[1] (a) Liverpool University. (b) University of Western Ontario.

[2] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 516 (1978).

[3] M. P. Brown, S. J. Cooper, R. J. Puddephatt, M. A. Thomson, and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1117 (1979); A. A. Frew, L. Manojlovic-Muir, and K. W. Muir, *ibid.*, 624 (1980).

[4] T. G. Appleton, M. A. Bennett, and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 439 (1976).

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Table I. ^{1}H NMR Spectra of the Complexes in CD_2Cl_2 Solution

complex	δ(MePt)	^3J(PH), Hz	^2J(PtH), Hz	$\delta(CH_2P_2)$	^2J(PH), Hz	^3J(PtH), Hz
$[PtMe_2(dppm)]$	0.83	*a*	75	4.32	9	22.5^b
$[PtClMe(dppm)]$ (IV)	0.72	8.9	62	4.34	13.2	49
		3.0			8.5	
$[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ (VIa)	0.50	6.7	88	4.13^c		
	(0.51)^d	(6.5)^d	(88.0)^d	(4.13)^d		
$[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ (VIb)	0.51	6.6	88.2	4.09		

[a] $^3J(PH)_{cis} + {}^3J(PH)_{trans} = 0.6$ Hz; see Results and Discussion. [b] A value of 11.5 Hz was previously reported,[4] almost exactly half the true value. [c] Center of complex ill-resolved resonance. [d] Values reported by Bennett and co-workers[4] for the oligomeric form of [PtClMe(dppm)] (in $CDCl_3$) isolated by them.

reported previously[4] (see below). A dimeric form of $[PtMe_2(dppm)]$ also exists.[5]

Reactions between $[PtMe_2(dppm)]$ and hydrogen chloride (1:1 mole ratio) under various conditions are found to give good yields (60–80%) of chloromethyl complexes of empirical formula [PtClMe(dppm)]. Only insignificant amounts of $[PtCl_2(dppm)]$ are normally formed. The chloromethyl complexes isolated are the monomer *cis*-[PtClMe(dppm)] (IV), the ionic dimer $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]Cl$ (VIa), and an uncharacterized oligomeric form (VII) (probably also dimeric). The monomer (IV) has a ^{1}H NMR spectrum (Table I) in good agreement with that previously reported[4] and had ν(Pt–Cl) in the IR spectrum at 290 cm^{-1} (lit.[4] 292 cm^{-1}). It is further characterized by its ^{31}P spectrum (see below). In agreement with its formulation as a nonionic complex, the molar conductivity in nitromethane is negligible (Λ_M = 1.56 cm^2 Ω^{-1} mol^{-1}).

The dimer (VIa) is characterized in solution by its ^{1}H and ^{31}P NMR spectra (see below) and by these spectra being identical with those of the cation in $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ (VIb). The latter is easily obtained from VIa by anion exchange using KPF_6. The formulation of VIa and VIb as 1:1 electrolytes is confirmed by their molar conductivities (at 10^{-3} M) in nitromethane (Λ_M = 67.4 and 76.2 cm^2 Ω^{-1} mol^{-1}, respectively), which fall within the range of 60–115 cm^2 Ω^{-1} mol^{-1} expected for salts of this type.[6,7] Further, the slopes B (117 and 147 cm$^{1/2}$ equiv$^{-1/2}$ Ω^{-1} for VIa and VIb, respectively) of the linear plots of ($\Lambda_0 - \Lambda_e$) vs. $C_e^{1/2}$, where Λ_e is the equivalent conductivity, Λ_0 is the equivalent conductivity at infinite dilution, and C_e is the equivalent concentration, are also characteristic of 1:1 electrolytes.[7,8] Crystalline VIa and VIb have similar IR spectra (Nujol mulls) except for the presence of PF_6^- absorptions in the spectrum of VIb. Since VIb may be expected to retain an ionic structure in the crystalline state, it appears likely that crystalline VIa is also ionic. Curiously both complexes lack absorptions in the 200–300-cm^{-1} region of the spectrum where ν(Pt–Cl) bands would be expected. The ^{1}H NMR spectrum observed by us for VIa is identical with that reported by Bennett and coworkers[4] for the oligomeric form of [PtClMe(dppm)] isolated by them, and the NMR data are compared in Tables I and II. We conclude, therefore, that we have isolated the same complex and that it was previously incorrectly characterized as the trimer V.

The other oligomeric form (VII) differs in its IR spectrum from VIa and shows a well-defined ν(Pt–Cl) band of medium intensity at 261 cm^{-1}. The relationship between VII and VIa is not clear since solutions in dichloromethane prepared from VII are identical (NMR) with those of VIa. Attempts to obtain its NMR spectrum in other solvents, e.g., C_6D_6, were unsuccessful due to lack of solubility. While it is possible that VII is merely a different crystalline modification of VIa, the differences in the ν(Pt–Cl) region of the spectrum suggest to us that the bonding between Cl and Pt is significantly different and that perhaps VII may be dimeric, but unlike VIa, nonionic.

Table II. $^{31}P\{^1H\}$ NMR Spectra of the Complexes[a]

	solvent	$\delta(^{31}P)$	^1J-(PtP), Hz	^2J-(PtP), Hz	J(PP), Hz
$[PtMe_2(dppm)]$	CH_2Cl_2	−36.7	1436		
$[PtClMe(dppm)]$ (IV)	CH_2Cl_2	−36.3^b	1248		42.5
		40.8^c	3876		42.5
$[PtClMe(dppm)]$ (IV)	$CHCl_3$	−34.8	1234		40
		−39.6	3891		40
$[Pt_2Me_2(\mu\text{-Cl})\text{-}(\mu\text{-dppm})_2]Cl$ (VIa)	CH_2Cl_2	10.2	3030^d	+30	33, 3^e
$[Pt_2Me_2(\mu\text{-Cl})\text{-}(\mu\text{-dppm})_2]Cl$ (VIa)	$CHCl_3$	10.6	3005	+34	31, 3^e
$[Pt_2Me_2(\mu\text{-Cl})\text{-}(\mu\text{-dppm})_2][PF_6]$ (VIb)	CH_2Cl_2	11.5	3030	+37	30, 4^e

[a] Reference $(MeO)_3PO$ in acetone. [b] P trans to methyl. [c] P trans to Cl. [d] Bennett and co-workers[4] quote a value of 3042 Hz. [e] $J_{AA''}$ and $J_{AA'''}$, respectively; see Results and Discussion.

In agreement with Bennett and co-workers we find that VIa is the most stable form in solution at room temperature. For example, samples of monomer IV or monomer IV/dimer VIa mixture when dissolved in dichloromethane change to pure dimer VIa over a period of 10–20 days. The change can be readily observed by NMR spectroscopy (^{1}H and ^{31}P). It is accelerated by addition of the more polar methanol (CD_3OD was used in the NMR studies) and is complete after only ~12 h in a 1:1 mixture of these solvents. The reverse change can be effected, but only partially, by treating the dimer with various solvents at elevated temperatures; e.g., refluxing with benzene produces ~30% monomer.

The ready but slow conversion of IV to VIa and the more rapid conversion of VII permit pure VIa to be prepared from mixtures without difficulty. The oligomer VII is best prepared from the HCl/$[PtMe_2(dppm)]$ reaction when this is carried out in cold benzene. In our hands, this somewhat unpredictable reaction affords VII as the major product in about 50% of attempts when it then crystallizes directly from the reaction mixture in pure form. Preparation of pure monomer IV is fairly readily achieved from reactions carried out in a mixture of dichloromethane and methanol using the methanolysis of acetyl chloride as a convenient in situ route to the correct stoichiometric amount of hydrogen chloride.[6] Monomer IV appears to be the major product under these conditions and crystallizes more readily than the other products and thus may be separated in a pure form, although a mixture of IV and VIa is sometimes obtained. Pure or nearly pure monomer (NMR) may be readily recrystallized from dichloromethane/hexane. We have briefly examined the reaction between $[PtMe_2(dppm)]$ and $[PtCl_2(dppm)]$ as a

---

(5) The reaction between $[Pt_2Me_4(\mu\text{-SMe}_2)_2]$ and dppm affords the dimer $[Pt_2Me_4(\mu\text{-dppm})_2]$: R. J. Puddephatt and M. A. Thomson, to be submitted for publication.

(6) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

(7) J. R. Boehm, D. J. Doonan, and A. L. Balch, *J. Am. Chem. Soc.*, **98**, 4845 (1976).

(8) (a) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964); (b) A. L. Balch, *J. Am. Chem. Soc.*, **98**, 8049 (1976).

(9) H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, **59**, 411 (1973).

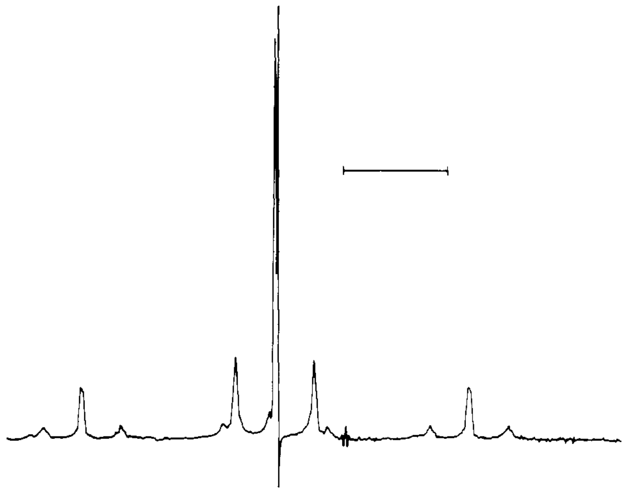

Figure 1. Gaussian-enhanced ^1H NMR spectrum (200 MHz) of $[PtMe_2(dppm)]$, showing only the methylplatinum resonance. The peak is centered at δ 0.83, and the bar represents 20 Hz.

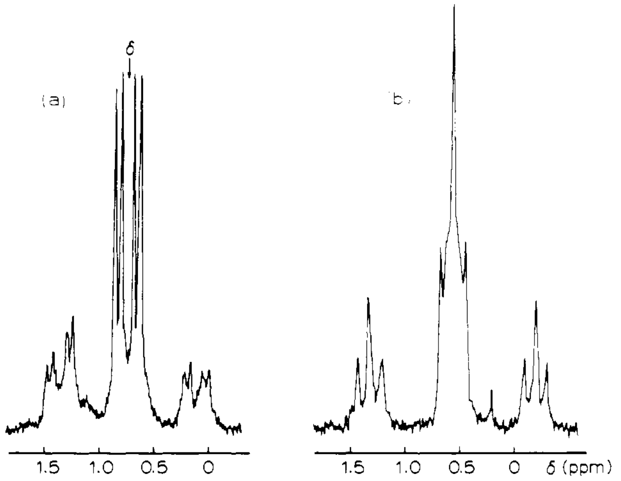

Figure 2. ^1H NMR spectra (60 MHz) of the methylplatinum groups of (a) $[PtClMe(dppm)]$ and (b) $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$.

possible means of preparing the chloromethyl complexes by an exchange process but without much success. However in boiling methanol this reaction produces the novel $[Pt_2Me_3(\mu\text{-}dppm)_2]^+$ cation, reported elsewhere.[3]

Characterization of the Complexes by NMR Spectroscopy. The complex $[PtMe_2(dppm)]$ gives a singlet in the ^{31}P NMR spectrum (Table II) with satellites of one-fourth intensity, confirming that it is monomeric. In the ^1H NMR spectrum, the methylplatinum resonance normally appears as a triplet and could be taken to indicate a trans stereochemistry except that closer inspection reveals an unusual intensity distribution. However, with resolution enhancement, the central peak is resolved into a very closely spaced doublet $[^3J(PH)_{cis} + {}^3J(PH)_{trans} = 0.6$ Hz (Figure 1, Table I)] and confirms the expected cis stereochemistry, the *cis*-Me_2PtP_2 unit giving a second-order splitting pattern which has been discussed previously.[10]

The monomer *cis*-$[PtClMe(dppm)]$ (IV) gives an AB quartet in the ^{31}P NMR spectrum due to the nonequivalent ^{31}P atoms, and the satellites due to coupling with ^{195}Pt are of one-fourth intensity (Table II). The methylplatinum resonance appears as a doublet of doublets due to coupling with the nonequivalent ^{31}P atoms. This compound is thus positively characterized as IV.

The oligomer VIa is characterized as an ionic A-frame complex, by conversion to the hexafluorophosphate derivative VIb and by comparison of the spectral properties of these derivatives. The ^{31}P NMR spectra are particularly useful. Thus the isotopomer of VIb containing no ^{195}Pt atoms gives a singlet in the $^{31}P\{^1H\}$ NMR spectrum. That containing one ^{195}Pt atom gives rise to an [AA′A″A‴X] spin system, which can be analyzed to yield most of the coupling constants in the system. The spectrum is the same in general form as the $^{31}P\{^1H\}$ NMR spectrum of II, which has been discussed in detail previously,[2] and those of other complexes with the $Pt_2(\mu\text{-}dppm)_2$ skeleton and serves as strong evidence that this grouping is present. Bennett and co-workers were unable to observe the fine structure of the spectrum in their ^{31}P spectrum obtained by the INDOR technique and so were unable to deduce the true structure. However, their value of $^1J(PtP)$ for the oligomer of $[PtClMe(dppm)]$ is the same as for VIa and VIb within experimental error, and the ^1H NMR spectral parameters are also the same, so that there is no doubt that their oligomer is VIa. The arguments presented for structure V based on the ^1H NMR spectrum[4] are equally valid for structure VIa. Thus the methylplatinum resonance occurs as a distorted triplet due to coupling with ^{31}P as would be expected from the complex spin systems of both VIa and V, and arguments based on the magnitudes of PtH or PtP coupling constants will also fail to distinguish between structures VIa and V. In summary, the isolation of the ionic hexafluorophosphate derivative and its characterization as VIb by the ^{31}P NMR spectrum, together with the similarity of the infrared and NMR spectra of VIa and VIb, are sufficient proof of the structure proposed for VIa. This is also the structure expected by analogy with the hydride derivative II.

Experimental Section

The complex $[PtCl_2(dppm)]$ was prepared as previously described.[11] Microanalyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, Mülheim, West Germany. NMR spectra were recorded on a Varian XL-100 spectrometer, and the resolution-enhanced spectrum {of $[PtMe_2(dppm)]$} was recorded on a Bruker WH-200 spectrometer. Conductivity measurements were made in nitromethane at 25 °C over the concentration range of 5×10^{-3} to 10^{-4} M with use of a Phillips PR 9500 bridge, and the Λ_M values quoted are for 10^{-3} M solutions.

Preparation of $[PtMe_2(dppm)]$. A suspension of $[PtCl_2(dppm)]$ (3.22 g, 5.00 mmol) in diethyl ether (55 mL) was prepared in a flask (100 mL) under dry nitrogen, and methyllithium in ether (16 mL of 1.5 M solution, 24 mmol) was added dropwise at 0 °C with stirring. The contents of the flask slowly become orange-yellow, and stirring was continued for 2 h. The excess of methyllithium was hydrolyzed with saturated aqueous ammonium chloride (5 mL), more water added, and the ethereal layer separated. Slow addition of hexane gave $[PtMe_2(dppm)]$ (2.39 g, 79%) as off-white crystals. The product thus obtained appeared pure (IR, NMR), but when recrystallized from benzene and hexane (80% yield), it was pure white. Anal. Calcd for $[PtMe_2(dppm)]$: C, 53.2; H, 4.6; P, 10.2. Found: C, 53.1; H, 4.5; P, 9.8.

Preparation of the Monomeric and Two Oligomeric Forms of $[PtCl(Me)(dppm)]$. Reactions between equimolar amounts of HCl and $[PtMe_2(dppm)]$ were carried out at 0 and 20 °C in dichloromethane, dichloromethane/methanol mixtures, and benzene while the experimental procedure and workup were varied slightly from experiment to experiment. Either standarized solutions of HCl in dichloromethane or benzene were used or weighed amounts of acetyl chloride were used to produce the stoichiometric amount of HCl by methanolysis.[9] Usually mixtures of the monomer IV and dimer VIa were obtained although in some experiments the oligomer VII was produced. The two procedures described below were found to be the most convenient routes to the pure complexes.

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(10) E. O. Greaves, R. Bruce, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 860 (1967); J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969); R. J. Goodfellow, M. J. Hardy, and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 2450 (1973).

(11) M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 951 (1977).

(a) Oligomer (VII) or Dimer $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (VIa). An aliquot of a standardized solution of hydrogen chloride in benzene (7.24 mL containing 1.64 mmol of HCl) was slowly added to $[PtMe_2(dppm)]$ (1.00 g, 1.64 mmol) in benzene (30 mL) kept at just above its freezing point. The solution was stirred during the addition (30 min) and then for a further 30 min. During this time an off-white solid formed in the yellow solution and was recovered by filtration to yield the oligomeric form VII of [PtCl(Me)(dppm)] (0.810 g, 78%) [ν(Pt–Cl) 261 cm^{-1}]. The ^{1}H NMR spectrum showed that it gave the cation $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ in dichloromethane-d_2 solution. A portion of VII (0.373 g) was recrystallized from dichloromethane/hexane to give the dimer $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (VIa) in 82% yield.

Six experiments similar to the above were carried out but VII was obtained as described from only three of these. The remainder gave instead fairly pure VIa (~70% yield) as the initial product. As a preparation if VII, the procedure is therefore somewhat unpredictable, but it is an excellent and reliable route to VIa since recrystallization of the initial product, irrespective of whether this is VII or VIa, affords pure VIa. Anal. Calcd for $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$: C, 49.6; H, 4.0; Cl, 5.6; P, 9.8. Found: C, 49.5; H, 4.1; Cl, 5.7; P, 9.9.

(b) The Monomer [PtCl(Me)(dppm)] (IV). A solution of acetyl chloride (0.119 g, 1.52 mmol) in dichloromethane (4.1 mL) was added over ~10 min at 20 °C with stirring to $[PtMe_2(dppm)]$ (0.927 g, 1.52 mmol) dissolved in dichloromethane (5 mL) and methanol (3.5 mL). The solution became somewhat deeper yellow and was then stirred for a further 15 min. The solvent was then mostly removed in a stream of nitrogen to produce a crop of white crystals in a small amount of yellow oily mother liquor. Benzene (~3 mL) was added to this mixture, diluting the mother liquor but not dissolving the crystals. These were recovered by filtration, washed with benzene, and dried, yielding [PtCl(Me)(dppm)] (0.614 g, 0.975 mmol, 64%). The ^{1}H NMR spectrum showed no trace of impurity. A portion of this product (0.14 g) was recrystallized from dichloromethane/hexane in 80% yield but the recrystallized material had an unchanged IR spectrum. A ν(Pt–Cl) band occurs at 290 cm^{-1} (lit.[4] 292 cm^{-1}). Anal. Calcd for [PtClMe(dppm)]: C, 49.6; H, 4.0; Cl, 5.6; P, 9.8. Found: C, 49.4; H, 3.9; Cl, 5.8; P, 9.9.

Preparation of $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ (VIb). A sample of potassium hexafluorophosphate (0.15 g, 0.81 mmol) was partially dissolved in methanol (5 mL) and the mixture added to the dimer $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (VIa) (0.200 g, 0.159 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for ~30 min at room temperature. Hexane was then added to precipitate the crude product together with the potassium salts. The latter were removed by washing the solid with water to leave $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ (0.194 g, 89%). Recrystallization from dichloromethane/hexane gave the pure product (0.145 g, 67% overall yield). Anal. Calcd for $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$: C, 45.6; H, 3.7; Cl, 2.6; F, 8.3; P, 11.3. Found: C, 45.5; H, 3.6; Cl, 2.8; F, 8.1; P, 11.3.

Acknowledgment. We thank the SRC for a research studentship (to S.J.C.), the NSERC (Canada) for financial support (to R.J.P.), NATO for a travel grant (to M.P.B. and R.J.P.), Johnson-Matthey Ltd. for the generous loan of platinum, and Bruker Ltd. for the resolution-enhanced 200-MHz NMR spectrum.

Registry No. IV, 76584-41-3; V, 59335-15-8; VIa, 76648-80-1; VIb, 75862-29-2; VII, 76648-81-2; $PtMe_2(dppm)$, 52595-90-1; $PtCl_2(dppm)$, 52595-94-5; methyllithium, 917-54-4; HCl, 7647-01-0.

Contribution from the Department of Chemistry,
University of Malaya, Kuala Lumpur, Malaysia

Mixed-Ligand Complexes of Palladium. 5. Diaqua(ethylenediamine)palladium(II) Complexes of Ethanolamine, L-Serine, L-Threonine, L-Homoserine, and L-Hydroxyproline

MENG-CHAY LIM

Received April 3, 1980

The reactions of $[Pd(en)(OH_2)_2]^{2+}$ (en = ethylenediamine) with ethanolamine, L-serine, L-threonine, L-homoserine, and L-hydroxyproline in 0.1 M KNO_3 at 25 °C have been studied by potentiometric titrations. The results obtained can be explained by equilibria i and ii, where L = neutral ethanolamine or the anionic form of the amino acids; charges have been

$$[Pd(en)(OH_2)_2] + L \overset{K_1}{\rightleftharpoons} [Pd(en)L] + 2H_2O \tag{i}$$

$$[Pd(en)L] \overset{K_1'}{\rightleftharpoons} [Pd(en)(LH_{-1})] + H^+ \tag{ii}$$

left out for simplification. The values of log K_1 and pK_1' of these complexes suggest that, for ethanolamine, the neutral alcohol group coordinates to palladium, for L-serine, L-threonine, and L-homoserine, the neutral alcohol groups do not coordinate to the metal center, but coordinations occur upon deprotonations of the alcohol groups, and, for L-hydroxyproline, both the neutral alcohol group and the deprotonated alkoxyl group derived therefrom do not coordinate to the metal center.

The β-alcohol group in the side chain of the amino acid serine has been found to play an essential role in the functioning of a number of proteolytic enzymes, e.g., chymotrypsin and subtilisin.[1] It is of interest to investigate the coordinating ability of such alcohol groups to metal ions. As pointed out recently, there appears to be no general agreement regarding the participation of the β-alcohol groups in chelate formation in the metal complexes of serine and threonine.[2] While basicity-adjusted binding strength indicates weak chelation of the groups to hexacoordinate metal ions such as Co^{2+}, Ni^{2+}, and Zn^{2+}, X-ray structural studies in the solid state do not support this conclusion.[2-6] On the other hand it has been reported that in basic solutions Cu^{2+} promotes the ionization of the alcohol hydrogens from its bis complex with threonine with pK's of 10.3 and 11.3.[7]

No stability constants of palladium complexes of serine or threonine have been reported. In connection with our study of the mixed-ligand complexes of palladium with asparagine and glutamine, we have shown that owing to the very high

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(1) S. A. Bernhard, "The Structure and Function of Enzymes", W. A. Benjamin, New York, 1968 Chapter 8.

(2) R. Bruce Martin, *Met. Ions Biol. Syst.*, **9**, Chapter 1 (1979).

(3) D. Van der Helm and M. B. Hossain, *Acta Crystallogr., Sect. B*, **B25**, 457 (1969).

(4) D. Van der Helm and W. A. Franks, *Acta Crystallogr., Sect. B*, **B25**, 451 (1969).

(5) D. Van der Helm, A. F. Nicholas, and C. G. Fisher, *Acta Crystallogr., Sect. B*, **B26**, 1172 (1970).

(6) H. C. Freeman, J. M. Guss, M. J. Healy, R.-P. Martin, C. E. Nockolds, and B. Sarkar, *J. Chem. Soc. D*, 225 (1969).

(7) P. Grenouillet, R.-P. Martin, A. Rossi, and M. Ptak, *Biochim. Biophys. Acta*, **322**, 185 (1973).

0020-1669/81/1320-1377$01.25/0