Preparation and ^{31}P NMR Studies of Cationic Methyl Platinum(II) Complexes Containing Mixed Ligands

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The preparation of some new cationic methylplatinum(II) complexes containing mixed ligands of general formula, $[PtMe(\overset{\frown}{L\,L})(L')]^+PF_6^-$, 1 $[\overset{\frown}{L\,L} = Ph_2PC_2H_4PPh_2$ *and* $L' = Ph_2MeP$, Ph_3As *and* $(p\text{-}YC_6H_4)_3P$; $Y = F, H, CH_3, CH_3O, (CH_3)_2N]$ *and* $[PtMe(\overset{\frown}{L\,L'})(L'')]^+PF_6^-$, 2 $[\overset{\frown}{L\,L'} = Ph_2PC_2H_4AsPh_2$ *and* $L'' = (PhO)_3P$ *and* $(p\text{-}YC_6H_4)_3P$; $Y = F, CH_3, CH_3O]$ *has been described.*

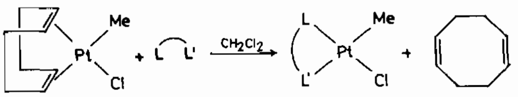
The ^{31}P *NMR spectra of complexes* 1 *and* 2 *consisting of 36 and 12 lines respectively are discussed. The* trans-*effect of the* para-*substituted phosphines has been related to their electronic parameters by measuring the platinum-phosphorous coupling constants (JPt–P) which follows the trend* $F < H < CH_3 < (CH_3)_2N$.

Introduction

We have been involved for some time in the synthesis and the spectroscopic studies of low symmetry complexes of platinum metals containing mixed ligands of variable electronic and steric parameters that can be useful in the studies like *trans*-effect of the ligands, and the asymmetric syntheses [1–4]. These complexes can also be useful catalysts since one or more weak donor ligands can be displaced readily by organic substrates [5]. There are, however, only a few reports of stable mixed ligands complexes of platinum available in literature [6–9]. In continuation of our investigations on the chemistry of mixed ligand complexes, here we describe the preparation and ^{31}P NMR studies of cationic methylplatinum complexes containing a chelating 'diphos' ($Ph_2PC_2H_4PPh_2$; dpe) or 'arphos' ($Ph_2PC_2H_4AsPh_2$; ape) ligand and a monodentate-tertiary phosphine ligand, R_3P.

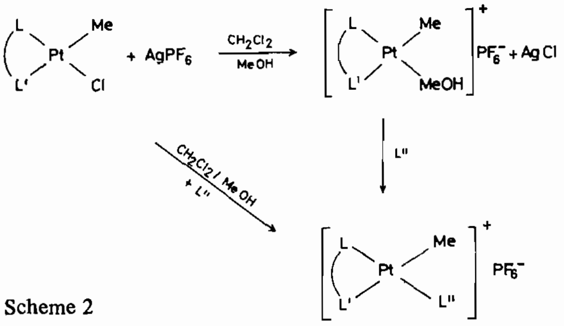
Results and Discussion

Reactions of chelating ligands such as 'diphos' ($Ph_2PC_2H_4PPh_2$) or 'arphos' ($Ph_2AsC_2H_4PPh_2$) with (COD)Pt(Me)Cl complex result in the displacement of cyclooctadienyl ligand and the complexes of the type *cis*-PtMe(Cl)($\overset{\frown}{L\,L'}$), 3 (where $\overset{\frown}{L\,L'}$ = diphos or arphos) can be isolated in almost quantitative yields (eqn. 1).



(1)

Treatment of complex 3 dessolved in CH_2Cl_2 with $AgPF_6$ in methanol gives the corresponding cationic methanol complex, *cis*-$[PtMe(MeOH)(\overset{\frown}{L\,L'})]^+$, 4. Although the complex 4 is stable in solution for several hours, generally, it is not isolated but used *in situ*. Reactions of complex 4 with ligands such as tertiary phosphines or arsines, afford the mixed ligand complexes of the type $[PtMe(\overset{\frown}{L\,L'})L'']^+$, (1 & 2) (Scheme 2).



Scheme 2

This way, several complexes (1 & 2) with ligands of variable degree of electronic parameters have been prepared [*e.g. 1*: where $\overset{\frown}{L\,L'}$ = $Ph_2PC_2H_4PPh_2$ and L'' = Ph_3As, Ph_2MeP, $(p\text{-}YC_6H_4)_3P$; Y = F, H, CH_3, CH_3O, $(CH_3)_2N$; 2: where $\overset{\frown}{L\,L'}$ = $Ph_2PC_2H_4AsPh_2$ and L'' = $(PhO)_3P$, $(p\text{-}YC_6H_4)_3P$; Y = F, CH_3CH_3O], as air-stable crystalline white solids in high yields. These complexes can be recrystallized unchanged

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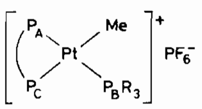
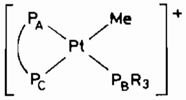
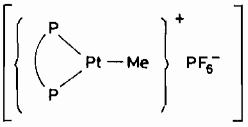
0020-1693/82/0000-0000/$02.75

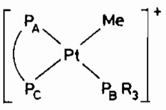
TABLE I. $^{31}P\{^{1}H\}$ NMR Spectral Data of  Complexes.[a]

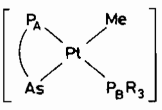
S No.	Complex	Chemical Shift (ppm)			$J^{31}P-^{31}P$ (Hz)			$J^{195}Pt-^{31}P$ (Hz)		
		$\delta(P_A)$	$\delta(P_B)$	$\delta(P_c)$	$J(P_AP_B)$	$J(P_AP_c)$	$J(P_BP_c)$	$J(PtP_A)$	$J(PtP_B)$	$J(PtP_c)$
1	$(p\text{-}FC_6H_4)_3P$	54.68 (dd)	26.16 (dd)	49.57 (dd)	386	7.4	18.5	2750	2780	1809
2	$(C_6H_5)_3P$	54.90 (dd)	23.61 (dd)	49.57 (dd)	381	7.4	18.5	2745	2776	1801
3	$(p\text{-}CH_3C_6H_4)_3P$	54.45 (dd)	21.93 (dd)	49.35 (dd)	381	7.4	18.5	2704	2786	1825
4	$(p\text{-}CH_3OC_6H_4)_3P$	53.76 (dd)	20.18 (dd)	49.42 (dd)	385	7.4	18.5	2671	2797	1805
5	$(p\text{-}Me_2NC_6H_4)_3P$	52.90 (dd)	17.97 (d)	49.57 (d)	385	7.4	18.5	2575	2804	1835
6	Ph_2MeP	53.91 (dd)	5.25 (d)	47.36 (d)	385	–	18.5	2682	2723	1772
7	$(C_6H_5)_3As$[b]	51.63 (s)	–	49.50 (s)				3303		1890

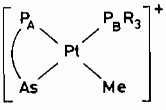
[a] Spectra were recorded in CH_2Cl_2/C_6D_6 at R. T. (dd) = double-doublet; (d) = doublet; (s) = singlet PF_6^- appeared as septet at δP – 144.69 ppm; JP–F 717 Hz. [b] Complex tended to disproportionate into  and Ph_3As and showed additional weak signals at δP = 14.47 ppm, JPtP = 1702 Hz.

from a mixture of solvents such as CH_2Cl_2/ether or CH_2Cl_2/hexane.

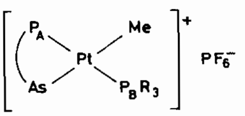
The ^{31}P NMR spectra of the complexes 1 ($\widehat{LL'}$ = $Ph_2PC_2H_4PCH_2$) and L″ = tertiary phosphine) consist of 36 lines with no loss of either phosphorus–phosphorus or platinum–phosphorus couplings, indicating that the integrity of the complexes were maintained in CH_2Cl_2/C_6D_6 solution. A 36-line spectrum is expected for the platinum complex (square planar geometry) with three magnetically non-equivalent phosphorus nuclei oriented in a manner as shown in structure 1. Although the chelating phosphine used in complex 1 is symmetrical and contains magnetically equivalent phosphorus nuclei (in the free phosphine), upon complexation with platinum to form complex 1, both phosphorus nuclei become magnetically non-equivalent due to the dissimilar groups at the respective *trans*-positions. Thus the phosphorus nuclei (represented by P_c in str. 1) *trans* to methyl group couples with both P_A and P_B in *cis* fashion [JP_cP_A = 7.4 Hz and JP_cP_B = 18.5 Hz) and appears as double-doublet associated with platinum satellites ($JPtP_c$ = 1772 to 1890 Hz). On the other hand, the phosphorus (P_A) of the chelating phosphine which is *trans* to the mono-dentate tertiary phosphine ligand (P_BR_3) displays a large *trans* coupling (with P_BR_3) ($JP_AP_B \approx 385$ Hz) and a smaller *cis* coupling (with P_c) (JP_AP_c = 7.4 Hz), thus appears as a double-doublet with platinum satellites ($JPtP_A \approx 2575$ to 2780 Hz). Similarly, the monodentate tertiary phosphine (P_BR_3) appears as double-doublet (*trans* $JP_BP_A \approx 385$ Hz and *cis* JP_BP_c = 18.5 Hz) associated with platinum satellites ($JPtP_B \approx 2723$ to 2804 Hz) (Table I).

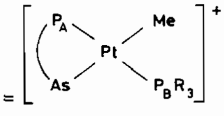

1


2A


2B

In all these complexes 1, since the chelating phosphine ($Ph_2PC_2H_4PPh_2$) is a constant component for one 'side' of each molecule, the values for $JPtP_A$ may well then reflect just the effect of the phosphine ligand of the *trans* position (*i.e.*, *trans*-influence of the phosphine ligand) [1, 2, 10, 11]. For aryl phosphine ligands, the dominant factor for *trans*-influence is electronic rather than steric as no appreciable steric bulkiness is changed by changing the substituents at the *para*- position [2, 12]. Upon examining the $JPtP_A$ values (Table I), it is observed that this value decreases as the electron donating tendency of the *para*-substituent on the phenyl

TABLE II. ^{31}P NMR Spectral Data of  Complexes.[a]

S No.	Complex P_BR_3 = 	Chemical Shift, + $\delta(P_A)$	δP (ppm) $\delta(P_B)$	$J^{31}P-^{31}P$ (Hz) $J(P_AP_B)$	$J^{195}Pt-^{31}P$ (Hz)	
					$J(Pt-P_A)$	$J(Pt-P_B)$
1	$(p\text{-}FC_6H_4)_3P$	57.19	21.70	388	2734	2845
2	$(p\text{-}CH_3C_6H_4)_3P$	56.81	17.32	385	2689	2841
3	$(p\text{-}CH_3OC_6H_4)_3P$	56.28	19.42	388	2649	2856
4	$(PhO)_3P$	53.08	110.27	588	2752	4853

[a] Spectra were recorded in CH_2Cl_2/C_6D_6 at room temperature. Signals due to PF_6^- appeared as septet at $\delta P \cong 177.70$ ppm with JP–F = 712 Hz. A 12 line spectrum is obtained for all the complexes.

phosphines increases, thus suggesting an increasing order of *trans*-effect. In other words, when electronic parameters (represented by ν cm^{-1}) [12] of the ligands $(p\text{-}YPh)_3P$ follow the order: Y = F > H > CH_3 > OCH_3 > $N(CH_3)_2$ then the *trans* effect follow the order: Y = $(CH_3)_2N$ > CH_3O > CH_3 > H > F. It is further observed that the $JPtP_B$ value in the substituted aryl phosphine ligands increases systematically (with an exception of Y = H) as the electron donating tendency of the *para*-substituent increases.

Complexes $[PtMe(PR_3)(\widehat{LL'})]^+$ (2) containing the chelating 'arphos' ($\widehat{LL'}$ = $Ph_2AsC_2H_4PPh_2$) ligand are capable of forming both the *trans* (str. **2A**) or *cis* (str. **2B**) isomers. However, in the present studies only the *trans*-isomers have been obtained. The *trans* configuration has been ascertained on the basis of their ^{31}P NMR spectra which show a 12-line spectrum with a large phosphorus–phosphorus coupling ($JP_AP_B \approx 385$ Hz) in all the cases (Table II). Again, in these cases, the *trans*-effect of the *para*-substitutes phenyl phosphine is reflected by the value of platinum–phosphorus ($JPtP_A$) and the same trend is observed here as found in the case of complexes **1**.

Experimental

Diethyl ether was dried over $LiAlH_4$. Methanol was dried and distilled over magnesium metal. Dichloromethane was dried over anhydrous $CaSO_4$. Other solvents used were of spectroanalyzed grade and used without further purification. All the phosphine ligands were commercial samples used without further purification. $CODPtMe_2$ was prepared from the reaction of methyl lithium with $CODPtCl_2$ in diethyl ether. CODPt(Me)Cl was prepared from the reaction of $CODPtMe_2$ with equimolar amount of HCl. ^{1}H NMR spectra were obtained in CH_2Cl_2 solution with TMS as internal standard, on a Varian A-60 or T-60 spectrometer. ^{31}P NMR spectra were obtained in CH_2Cl_2/C_6D_6 solution on a Brucker-60 F.T. instrument and H_3PO_4 was used as an external standard. Microanalyses were performed by M.H.W. Microanalytical Lab., Phoenix, Arizona.

Preparation of [Pt($\widehat{LL'}$)(Me)Cl] (3) [$\widehat{LL'}$ = $Ph_2PC_2H_4PPh_2$ or $Ph_2PC_2H_4AsPh_2$]

Complex **3** was prepared from the reaction of 'diphos' or 'arphos' with CODPt(Me)Cl complex in CH_2Cl_2. Typically, when $Ph_2AsC_2H_4PPh_2$ (1.10 g; 2.5 mmol) was added to a solution of CODPt(Me)Cl (0.88 g, 2.50 mmol) in CH_2Cl_2 stirred magnetically at room temperature, a white insoluble solid appeared immediately. The reaction mixture was further stirred for ≈1 h and was concentrated. The insoluble solid was filtered, washed with hexane and ether and dried under reduced pressure. Yield (≈86%). *Anal.* Found: C, 47.4; H, 4.02; Cl, 5.10. Calcd. for $[PtMe(Cl)(Ph_2AsC_2H_4PPh_2)]$: C, 47.2; H, 3.96; Cl, 5.16%.

Preparation of $[PtMe(CH_3OH)(\widehat{LL'})]^+PF_6^-$ (4) [($\widehat{LL'}$) = ($Ph_2PC_2H_4PPh_2$) or ($Ph_2AsCgH_4PPh_2$)]

The methanol cation, **4**, was prepared under anaerobic conditions by the slow addition of a methanolic solution of an equimolar amount of $AgPF_6$ to a rapidly stirred CH_2Cl_2 solution of complex **3**. The white precipitate of AgCl formed during the reaction time (1 h) was centrifuged and filtered. The filtrate was reduced to small volume *in vacuo*. Careful addition of hexane or diethyl ether provided the crystalline solid of **4**, which was filtered, recrystallized from CH_2Cl_2/ether/hexane and dried *in vacuo*. Generally **4** was not isolated, but was used *in situ* for further reactions as described below.

TABLE III. Analytical Data of $[\mathrm{PtMe}(\widehat{L\,L'})L'']^+PF_6^-$ Complexes.

S No.	Complex: $[\mathrm{PtMe}(\widehat{L\,L'})L'']^+PF_6^-$ $(\widehat{L\,L'})$ = $Ph_2PC_2H_4PPh_2$ L'' =	Solvent of Crystallization	M.P. (°C)	Analysis (%) Found (calcd.)	
				C	H
1	$(p\text{-}FC_6H_4)_3P$	CH_2Cl_2	260 (d)	50.9	3.72
				(50.5)	(3.65)
2	$(C_6H_5)_3P$	CH_2Cl_2/hexane	185	52.0	4.10
				(52.3)	(4.07)
3	$(p\text{-}CH_3C_6H_4)_3P$	CH_2Cl_2/hexane	155	54.8	4.59
				(54.5)	(4.54)
4	$(p\text{-}CH_3OC_6H_4)_3P$	CH_2Cl_2/hexane/ether	148	52.6	4.52
				(52.1)	(4.34)
5	$(p\text{-}(CH_3)_2NC_6H_4)_3P$	CH_2Cl_2/ether	–	53.1	4.96
				(53.5)	(4.98)
6	Ph_2MeP	CH_2Cl_2/hexane	175	51.0	4.25
				(50.4)	(4.20)
7	$(C_6H_5)_3As$ $(\widehat{L\,L'})=Ph_2PC_2H_4AsPh_2$	CH_2Cl_2/hexane	180	51.2	3.96
				(51.0)	(3.97)
8	(*p*-FC6H4)3P	CH_2Cl_2/hexane	–	48.8	3.72
				(48.5)	(3.50)
9	$(p\text{-}FC_6H_4)_3P$	CH_2Cl_2/ether	142	52.4	4.51
				(52.3)	(4.36)
10	$(p\text{-}CH_3OC_6H_4)_3P$	CH_2Cl_2/hexane	130	50.6	4.34
				(50.1)	(4.18)
11	$(Ph_3O)_3P$	CH_2Cl_2/ether	171	49.2	3.84
				(48.8)	(3.79)

Preparation of $[\mathrm{PtMe}(PR_3)(\widehat{L\,L'})]^+PF_6^-$ *(1 & 2)* $[(\widehat{L\,L'}) = Ph_2PC_2H_4PPh_2)$ *or* $(Ph_2AsC_2H_4PPh_2)]$

A solution of complex **4** (0.5 mmol) was prepared in CH_2Cl_2/CH_3OH by the above described procedure and PR_3 (0.5 mmol) was introduced with stirring. After being stirred for ≈2 h, the solution was reduced to small volume *in vacuo* and the dropwise addition of diethyl ether or hexane resulted in the formation of white crystalline solid. The solid was isolated, recrystallized from CH_2Cl_2/ether/hexane, washed with diethyl ether and dried *in vacuo* (Yield: 70–85%). Analytical data are given in Table III and ^{31}P NMR spectra in Tables I and II.

References

1 H. C. Clark, A. B. Goel, R. G. Goel and S. Goel, *Inorg. Chem., 19,* 3220 (1980).

2 A. B. Goel, S. Goel and H. C. Clark, *Syn. React. Inorg. Met. Org. Chem., 11,* 289 (1981).

3 H. C. Clark, A. B. Goel and C. S. Wong, *J. Organometal. Chem., 190,* C101 (1980).

4 H. C. Clark, A. B. Goel and S. Goel, *Inorg. Chem., 18,* 2803 (1979).

5 H. C. Clark, C. Billard and C. S. Wong, *J. Organometal. Chem., 190,* C105 (1980).

6 J. Chatt and L. M. Venanzi, *J. Chem. Soc,.,* 3858 (1955); 2445 (1957).

7 F. H. Allen and S. N. Sze, *J. Chem. Soc., A,* 2054 (1971).

8 C. Eaborn, K. J. Odell and A. Pidcock, *J. Chem. Soc., Dalton Trans.,* 1288 (1978).

9 J. A. Davies, F. R. Hartley and S. G. Murray, *Inorg. Chem., 19,* 2299 (1980).

10 A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc., A,* 1707 (1966).

11 F. H. Allen, A. Pidcock and C. R. Waterhouse, *J. Chem. Soc., A,* 2807 (1970).

12 C. A. Tolman, *Chem. Rev., 77,* 313 (1977).