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SYNTHESIS OF SOME PLATINUM(II) DIPHOSPHINE COMPLEXES OF THE TYPE $[PtX_2(P\text{-}P)]$ ($X_2 = CO_3$; X = CH_3COO, CF_3COO, NCO)

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ABSTRACT

Treatment of aminobis(methylphosphine) complexes of platinum(II) with silver(I) salts in dichloromethane gives corresponding platinum(II) complexes of the type $[PtX_2(P\text{-}P)]$ where $X_2 = CO_3$; X= CH_3COO, CF_3COO, NCO; P-P = $(Cy_2PCH_2)_2NMe$, dcpam; $(Ph_2PCH_2)_2NMe$, dppam). The complexes have been characterised by using spectroscopic techniques such as ^{31}P-{^{1}H} and ^{1}H NMR, IR, and mass spectrometry.

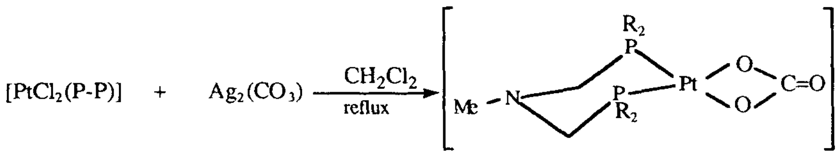
INTRODUCTION

The present work is part of a research program in the field of the synthesis of novel aminobis(methylphosphines) and platinum group metal complexes.[1,2] The phosphine platinum carbonate complexes are useful starting compounds for the synthesis of Pt(0) and Pt(II) complexes.[3] The carboxylate complexes of platinum(II) have been of interest and can be used to obtain zerovalent complexes.[4] The preparation of carbonate and acetate complexes would provide the opportunity to develop further the chemistry of these systems.

RESULTS AND DISCUSSION

In order to investigate the reactivity of dichloro derivatives of platinum(II) aminomethylphosphine complexes and also to obtain some zerovalent platinum complexes of aminomethylphosphines, the carbonate and acetate complexes **(2)**-**(6)** were prepared, Scheme 1. $[PtCl_2(dcpam)]$ **(1a)** and $[PtCl_2(dppam)]$[5] **(1b)** were refluxed with Ag_2CO_3 in dichloromethane. The insoluble silver salts were filtered off and diethyl ether was added to give pale yellow powdery samples of $[Pt(CO_3)(dcpam)]$ **(2)** and $[Pt(CO_3)(dppam)]$ **(3)**, respectively. Table I presents the $^{31}P-\{^1H\}$ NMR, IR and mass spectrometry data of the complexes **(2)**-**(6)**. The $^{31}P-\{^1H\}$ NMR spectra of these complexes showed more shielded signals with smaller one bond $^{195}Pt-^{31}P$ coupling constants, 3347 and 3355 Hz, as compared to the dichloride derivatives **(1a)** and **(1b)**, respectively. The reason for the small values of J(PPt) for the complexes **(2)** and **(3)** may be associated with the four-membered ring strain present in the carbonate complexes with a chelating phosphine, since the triphenylphosphine complex of $Pt(CO_3)$ exhibits a larger ^{195}Pt coupling to phosphorus, (J(PPt) = 3699 Hz) than its dichloride analogue (J(PPt) = 3577 Hz).[6] Table I also shows the coordination shifts of the complexes **(2)**-**(6)** along with the chemical shifts of the free ligands. The coordination shift values of the complexes (Δ), which can be defined by $\Delta = \delta(\text{complex}) - \delta(\text{free ligand})$, vary depending on the metal centres and the ligand itself. The values of Δ have been correlated for many metal phosphine complexes.[7-10] On comparison with the starting dichloride complexes, the ^1H NMR spectra of these complexes show no change in terms of phosphine protons. The ^1H NMR spectra data of complex **(5)** was, therefore, given as an example in the experimental section. These complexes were further characterised by

Scheme 1



P-P = dcpam , R = Cy; *(2)* ; dppam, R = Ph *(3)*

$$[\mathrm{PtCl_2(dcpam)}] \quad + \quad \mathrm{AgX} \quad \xrightarrow[\text{reflux}]{\mathrm{CH_2Cl_2}} \quad [\mathrm{PtX_2(dcpam)}]$$

$X = OCOCH_3$ *(4)*

$X = OCOCF_3$ *(5)*

X = NCO *(6)*

their IR and mass spectra. The IR spectra of the complexes (**2**)-(**5**) gave characteristic C=O bands in a range of 1659-1632 cm^{-1}, and (**6**) showed an N=C=O band[11] at 2228 cm^{-1}, Table I.

The carboxylate and isocyanate complexes (**4**), (**5**) and (**6**) were also synthesised by treating the dichloride derivatives of Pt(II) phosphine complexes with the relevant silver(I) salts. In their ^{31}P-{^{1}H} NMR spectra, the acetate complexes (**4**), (**5**) exhibited larger ^{195}Pt-^{31}P coupling constants than the starting dichloride compound due to the weaker *trans* influence of the oxygen atom, the J(PPt) values being consistent with phosphorus *trans* to oxygen.[12, 13] The relevant IR bands of the complex (**4**) and (**5**) are compared with that of silver(I) acetate $Ag(OOCCH_3)$ and triflouroacetate $Ag(OOCCF_3)$ as starting compounds of which the asymmetric C=O vibrations occur at 1574 and 1620 cm^{-1}, respectively, whereas the complexes (**4**) and (**5**) exhibit these bands at 1577 and 1637 cm^{-1}, respectively. The separation values of asym- sym bands ($\Delta\nu$) listed in Table I, are in agreement with the those reported in the literature.[14-17] The *cis* NCO coordinated complex (**6**) also gave a smaller ^{195}Pt coupling constant of J(PPt) 3345 Hz. which is in

TABLE I. ^{31}P-{^{1}H} NMR IR and Mass Spectra of Complexes (2)-(6)

^{31}P-{^{1}H} NMR				IR (cm^{-1})		Mass
Compound	δ^a	J(PPt)^a	Δ^a	C=O(sym,asym)	Δν	M$^+$
dcpam	-16.15					369
dppam	-27.53					
(2)	1.35	3347	17.5	1652, 1382	269	706
(3)	13.7	3355	13.8	1659, 1388	271	682
(4)	-0.47	3559	15.7	1577, 1364	213	705
(5)	1.72	3611	17.9	1637, 1400	271	759
(6)	0.82	3345	17.0	N=C=O, 2228		
Ag(OAC)				1574, 1338	236	
Ag(OACF$_3$)				1620, 1359	261	

^{a} ***Chemical shifts are in ppm, J values are in Hz.***

agreement with literature values.[11, 12] Although the difference between the coupling constant values of (5) and (6) was remarkable (270 Hz) the coordination shift values (Δ) were found very close.

EXPERIMENTAL

The melting points of the prepared complexes were recorded on a Gallenkamp melting point apparatus. The microanalytical data of some compounds were obtained on a Leco Corparation CHN-600 analyzer available in our department and some of them were carried out by Butterworth Labarotories Ltd. 54-56 Waldegrave Rd. Teddington, TW11, UK. The mass spectra of the compounds were obtained by using the FAB technique on a Kratos Concept Double Focusing Sector Mass Spectrometer. The ^{1}H NMR spectra were recorded at room temperature on a Bruker AM 300 spectrometer operating at 300.13 MHz with SiMe$_4$ (0.0 ppm) as internal reference, positive values being to high frequency (low field). The coupling constants J are in Hz. The ^{31}P NMR spectra were recorded in dichloromethane unless otherwise stated, either on a JEOL JMM-FX60 operating at 24.15 MHz or on a JEOL EM390 spectrometer operating at 36.24 MHz. with H$_3$PO$_4$ in D$_2$O as external reference.[17] The IR spectra were recorded on a Bio-Rad FTS 40 FTIR spectrophotometer. The solvents dichloromethane, diethyl ether and light petroleum ether were dried and distilled under nitrogen prior to use from the following drying agents: dichloromethane (calcium hydride); diethyl ether (sodium wire/benzophenone), light petroleum (40-60°C) (sodium).

Preparations were carried out under a dry, oxygen free nitrogen atmosphere using standard Schlenk techniques. The silver(I) salts, Ag$_2$CO$_3$, Ag(OCOCH$_3$), Ag(OCOCF$_3$) and Ag(NCO) were, purchased from Aldrich Inc. and used without further purification. [PtCl$_2$(dcpam)] and [PtCl$_2$(dcpam)], were prepared by treating [PtCl$_2$(COD)] (COD = cyclooctadiene) with the novel phosphines (Cy$_2$PCH$_2$)$_2$NMe, dcpam; (Ph$_2$PCH$_2$)$_2$NMe, dppam, respectively, which were obtained by treating phosphonium salts of the type [R$_2$P(CH$_2$OH)$_2$]Cl (R = Cy, Ph) with methylamine in the presence of triethylamine as described in the literature.[5] The phosphonium salts were a gift of Dr. D. J. Law. Precious metal salts were obtained on loan from Johnson Matthey plc.

Synthesis of Carbonate Complexes

[Pt(CO$_3$)[(Cy$_2$PCH$_2$)$_2$NMe]] (2). Silver carbonate (0.66 g, 2.41 mmol) was added to a stirred solution of [PtCl$_2$(dcpam)] (**1a**) (0.30 g, 0.42 mmol) in dichloromethane (20 mL). The mixture was refluxed for 2 days. The solution was filtered through Celite. A pale yellow solid was obtained on addition of diethyl ether. Yield, 0.24 g (80.94 % based on Pt). M.p= 205 °C decomp. (Found: C, 47.42; H, 7.38; N, 1.82. C$_{28}$H$_{51}$NO$_3$P$_2$Pt requires: C, 47.58; H, 7.27; N, 1.98) ^{31}P-{^{1}H} δ= 1.35

ppm [J(PPt) 3347 Hz]. Mass spectrum: *m/z* 706; 706 (5.56 %)[M$^+$]. 646 (38.89 %) [Pt(dcpam)], 211 (7.41 %) [Cy_2PCH_2]. IR: ν(C-H aliph.) 2940, 2789; ν(C=O) 1652 (asym), 1382 (sym); ν(CH_2) 1446; ν(C-C) 1206; ν(C-O) 1095; ν(Cyclohexane) 1001, ν(N-CH_3) 847 cm^{-1}.

[Pt(CO_3){(Ph_2PCH_2)$_2$NMe}] (3). Silver carbonate (0.50 g, 1.80 mmol) was added to a stirred solution of [$PtCl_2${(Ph_2PCH_2)$_2$NMe}] (**1b**) (0.25 g, 0.36 mmol) in dichloromethane (20 mL). The mixture was refluxed for 24h and filtered through Celite. The product was precipitated with light petroleum. Yield 0.20 g (81.46 % based on Pt). M.p = 193 °C decomp. (Found: C, 49.35; H, 3.87; N, 1.98). $C_{28}H_{27}NO_3P_2Pt$ requires: C, 49.27; H, 3.99; N, 2.05 ^{31}P-{^1H}: δ= -13.7 ppm [J(PPt) 3355 Hz]. Mass spectrum: *m/z*:682, 682 (16.67%) [M$^+$]; 622 (51.85 %) [Pt(dppam)]; 199 (29.63%) [Ph_2PCH_2]. IR: ν(C-H arom.) 3052; ν(C-H aliph.) 2940, 2789; ν(arom.) 1627, 1577, 1481; ν(C=O) 1659 (asym), 1388 (sym); v(C-C) 1153; ν(C-O) 1102 cm^{-1}

Synthesis of Acetate Derivatives of [PtX_2(dcpam)], X = $OCOCH_3$, $OCOCF_3$

[Pt($OCOCH_3$)$_2${(Cy_2PCH_2)$_2$NMe}].1/2 CH_2Cl_2 (4). Ag($OCOCH_3$) (0.19 g, 1.14 mmol) was added to a stirred solution of [$PtCl_2$(dcpam)] (0.20 g, 0.28 mmol) in dichloromethane (20 mL). The mixture was refluxed for 3h and filtered off through Celite. The pale yellow product was precipitated with light petroleum, filtered and dried. Yield: 0.14 g (66.38 % based on Pt). M.p = 215 °C decomp. (Found: C, 46.63; H, 7.35; N, 1.75. $C_{31}H_{57}NO_4P_2Pt$ requires: C, 46.86; H, 7.24; N, 1.1.74) NMR: ^1H δ= 1.20 - 1.85 [m, 40H CH_2 of Cy], 1.96 [s, 6H C-CH_3], 2.30 - 2.39 [m, 7H P-CH + N-CH_3], 2.55 [d, 4H PCH_2N J(HP) 2.74 Hz], 5.31 [s, CH_2Cl_2] ppm. ^{31}P-{^1H}: δ= -0.47 ppm [J(PPt) 3559 Hz]. Mass spectrum: *m/z*: 764; 764 (1.48 %) [M$^+$]; 705 (100 %) Pt($OCOCH_3$)(dcpam)]; 646 (4.13 %) [Pt(dcpa)]; 211 (1.85 %) [Cy_2PCH_2]. IR: ν(C-H aliph.) 2929, 2849, 2791; ν(C=O) 1577 (asym), 1364 (sym); ν(CH_2) 1445; ν(C-C) 1212; ν(C-O) 1097, ν(Cyclohexane) 1007, ν(N-CH_3) 852 cm^{-1}.

[Pt(OCOCF$_3$)$_2$[(Cy$_2$PCH$_2$)$_2$NMe]] (5). Ag(OCOCF$_3$) (0.25 g, 1.13 mmol) was added to a stirred solution of [PtCl$_2$(dcpam)] (0.20 g, 0.28 mmol) in dichloromethane (20 mL). The mixture was refluxed for 24 h and then filtered through Celite. The solvent volume was reduced and the product was then precipitated with light petroleum ether, filtered off and dried. Yield: 0.23 g (94.20 % based on Pt). M.p = 225 °C decomp. (Found: C, 45.27; H, 6.45; N, 1.78. $C_{31}H_{51}F_6NO_4P_2Pt$ requires: C, 45.64; H, 6.30; N, 1.72) ^{31}P-{^{1}H}nmr: δ = 1.72 ppm [J(PPt) 3611 Hz]. Mass spectrum: *m/z* 872; 872 (1.85 %) [M$^+$]; 759 (100 %) [Pt(dcpam)OCOCF]; 646 (9.26 %) [Pt(dcpam)]; 211 (2.78 %) [Cy$_2$PCH$_2$]. IR: ν(C-H aliph.) 2931, 2854, 2782; ν(C=O) 1637 (asym), 1400 (sym); ν(CH$_2$) 1446; ν(C-C) 1211, ν(C-F) 1174, ν(C-O) 1102; ν(Cyclohexane)1009; ν(N-CH$_3$) 854 cm^{-1}.

Synthesis of [Pt(NCO)$_2$(Cy$_2$PCH$_2$)$_2$NMe] *(6).* Ag(NCO) (0.16 g, 1.07 mmol) was added to a stirred solution of [PtCl$_2$(dcpa)] (0.10 g, 0.14 mmol) in dichloromethane (20 mL). The mixture was stirred for a further 24 h in the dark and filtered through Celite. The product was precipitated with diethyl ether to give a white solid. Yield: 0.09 g (88.06 %, based on Pt). M.p = 250 °C decomp. (Found: C, 47.63; H, 6.47; N, 5.50. $C_{29}H_{51}N_3O_2P_2Pt$ requires: C, 47.66; H, 7.04; N, 5.75) ^{31}P-{^{1}H}: δ= 0.81 ppm [J(PPt) 3345 Hz]. IR: ν(C-H aliph.) 2929, 2850, 2788; ν(NCO) 2228; ν(CH$_2$) 1445; ν(C-C) 1212; ν(C-O) 1094; ν(Cyclohexyl) 1005; ν(N-CH$_3$) 850 cm^{-1} .

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