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Reactions of Platinum(II) Carboxylate Complexes with Tertiary Phosphines and Chlorinated Solvents

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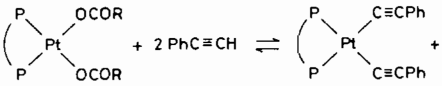
We have recently described the preparation of platinum(II) oxalate complexes containing bidentate ligands and their thermal reactions with phenylacetylene [1], and extension of this work to include malonate and benzoate complexes has shown that the equilibrium depicted in eqn. (1) is indeed a general



(1)

one. During the course of this work, we investigated the reactions of the platinum(II) carboxylates with tertiary phosphines, and the results of these studies are outlined below.

When a CH_2Cl_2 solution of $[Pt(OCOPh)_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) was treated with 1 mol equivalent of $PBu^n{}_3$, the $^{31}P\{^1H\}$ NMR spectrum showed the presence of two phosphorus-containing species, each of which gave rise to a first order spectrum typical of a platinum(II) complex containing three inequivalent phosphorus atoms [2]. On standing for six days, complete conversion to one of these took place. The final product was identified as $[PtCl(PBu^n{}_3)(dppe)]^+$, by comparison of its NMR parameters with those of an authentic sample prepared by reaction of $[PtCl_2(dppe)]$ with $PBu^n{}_3$ (Table I). When the reaction of $[Pt(OCOPh)_2(dppe)]$ with $PBu^n{}_3$ was performed in CH_3CN solution, only the first species was formed, and it was assigned the structure $[Pt(OCOPh)(PBu^n{}_3)(dppe)]^+PhCOO^-$. Removal of the solvent, followed by dissolution in CH_2Cl_2, resulted in quantitative conversion to $[PtCl(PBu^n{}_3)(dppe)]^+Cl^-$.

It seemed likely that the final product arose by displacement of Cl^- from the solvent by the carboxylate anion, and this was shown by the following experiments. When $[Pt(OCOPh)_2(dppe)]$ was treated with $PBu^n{}_3$ in benzyl chloride, $[PtCl(PBu^n{}_3)(dppe)]^+Cl^-$ was again produced. Passing the reaction mixture down a silica column allowed separation of benzyl benzoate, which was identified by thin layer chromatography and its ^1H NMR spectrum, by comparison with an authentic sample. Reaction of ammonium benzoate with $PhCH_2Cl$, in the presence of 18-crown-6, also produced benzyl benzoate. The mechanism in Scheme 1 is therefore proposed for the formation of $[PtCl(PBu^n{}_3)(dppe)]^+Cl^-$.

Treatment of CH_2Cl_2 solutions of [Pt(mal)(dppe)] (mal = malonate) with $PBu^n{}_3$, PEt_3 or $PMePh_2$ rapidly produced complexes of the type $[PtCl(PR_3)(dppe)]^+$. The $^{31}P\{^1H\}$ NMR parameters for the PEt_3 and $PMePh_2$ complexes are very similar to those

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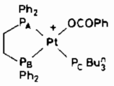
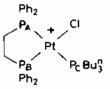
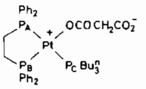
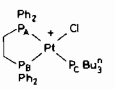
TABLE I. $^{31}P\{^1H\}$ NMR Data[a] for Complexes of the Type $[PtX(PBu^n{}_3)(P\ P)]^+$

Complex	Solvent	δP (ppm)[b]	^1J(Pt,P) (Hz)	^2J(P,P) (Hz)
	CH_3CN	P_A 52.3	2390	P_A, P_B not observed
		P_B 31.0	3475	P_A, P_C 356
		P_C 11.6	2435	P_B, P_C 18
	$CDCl_3$	P_A 53.2	2255	P_A, P_B 6
		P_B 42.8	3550	P_A, P_C 370
		P_C 8.3	2280	P_B, P_C 17
	$CDCl_3$[c]	P_A 50.6	2340	P_A, P_B 6
		P_B 30.5	3465	P_A, P_C 353
		P_C 12.8	2420	P_B, P_C 17
	$CDCl_3$	P_A −49.7	1865	P_A, P_B 66
		P_B −50.3	3040	P_A, P_C 408
		P_C 8.3	2310	P_B, P_C 20

[a] Spectra were measured at 20 °C on a JEOL FX-100 (40.2 MHz) or Varian XL-300 (121.4 MHz) NMR spectrometer. [b] Chemical shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding. [c] At −60 °C.

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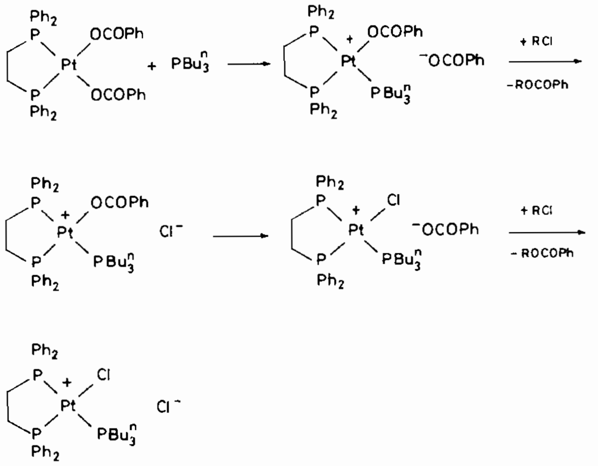

Scheme 1.

for $[PtCl(PBu^n_3)(dppe)]^+$ (Table I). When a $CDCl_3$ solution of [Pt(mal)(dppe)] was treated with PBu^n_3 at −60 °C, a complex of the form $[Pt(mal)(PBu^n_3)(dppe)]$ was produced (Table I). The carboxylate carbon resonance in the $^{13}C\{^1H\}$ NMR spectrum of [Pt(mal)(dppe)] (δC 173.8) was replaced by two resonances at δC 172.1 and 175.7, which suggests the presence of a monodentate malonate ligand. (A similar observation has been made for the $[Pt(C_2O_4)(PEt_3)_2]/PEt_3$ system [3]). On warming to ambient temperature, conversion to $[PtCl(PBu^n_3)(dppe)]^+$ occurred, and the $^{13}C\{^1H\}$ NMR spectrum exhibited a carbonyl resonance at δC 173.0, presumably due to $CH_2(COOCDCl_2)_2$. No reaction took place when [Pt(mal)(dppe)] was treated with PPh_3, $AsPh_3$ or $SbPh_3$, but in the presence of triethylamine the complex wass slowly converted to $[PtCl_2(dppe)]$. When PBu^n_3 was added to a $CDCl_3$ or CH_2Cl_2 solution of $[Pt(C_2O_4)(dppe)]$, the $[PtCl(PBu^n_3)(dppe)]^+$ cation was again produced, but significant amounts of $[Pt(C_2O_4)(PBu^n_3)_2]$ and other species were also present.

In none of the reactions of [Pt(mal)(dppe)] or $[Pt(C_2O_4)(dppe)]$ was a species of the type $[Pt(PR_3)_2(dppe)]^{2+}$ detected, even with excess tertiary phosphine. Indeed, treatment of $[PtCl_2(dppe)]$ with excess $PMePh_2$ does not yield $[Pt(PMePh_2)_2(dppe)]^{2+}$ unless $AgClO_4$ is added. This complex exhibits a second order $^{31}P\{^1H\}$ NMR spectrum, from which all the chemical shifts and coupling constants have been determined by analysis [4] and computer simulation of the spectrum (dppe: δP_A 48.8, $^1J(Pt, P_A)$ 2154 Hz; $PMePh_2$: δP_B −3.2, $^1J(Pt, P_B)$ 2376 Hz; $^2J(P_A, P_{A'})$ ±6.5 Hz, $^2J(P_A, P_B)$ 311.4 Hz, $^2J(P_A, P_{B'})$ −24.1 Hz, $^2J(P_A, P_{A'})$ ±25.5 Hz).

When $[Pt(C_2O_4)(dppm)]$ (dppm = bis(diphenylphosphino)methane) was treated with PBu^n_3 or PEt_3 in $CDCl_3$ solution, displacement of dppm occurred to yield $[Pt(C_2O_4)(PBu^n_3)_2]$ or $[Pt(C_2O_4)(PEt_3)_2]$. With [Pt(mal)(dppm)] the situation was more complicated, however. When a $CDCl_3$ solution of [Pt(mal)(dppm)] was treated with 1 mol equivalent of PBu^n_3 at −40 °C, the $^{31}P\{^1H\}$ NMR spectrum indicated that $[Pt(PBu^n_3)_2(dppm)]^{2+}$ was the only $PBu_3{}^n$-containing species present, but on warming to room temperature the resonances due to this complex disappeared, and $[Pt(mal)(PBu^n_3)_2]$ and $[PtCl(PBu^n_3)(dppm)]^+$ (Table I) were the major species present. (At low temperature the malonate dianion must react slowly with the solvent, since $[Pt(mal)(PBu^n_3)_2]$ is one of the final products.) With 2 mol equivalents of PBu^n_3 the platinum-containing products are $[Pt(PBu^n_3)_2(dppm)]^{2+}$ and $[Pt(mal)(PBu^n_3)_2]$. The reactions of [Pt(mal)(dppm)] with PEt_3 are similar, but with $PMePh_2$ the system is complicated further by the formation of the $[PtCl(PMePh_2)_3]^+$ cation. The complex $[PtCl(PMePh_2)(dppm)]^+$, obtained by treatment of $[PtCl_2(dppm)]$ with $PMePh_2$, undergoes fluxional behavior at room temperature, but the static $^{31}P\{^1H\}$ NMR spectrum was obtained at −40 °C. Addition of further $PMePh_2$ gave $[Pt(PMePh_2)_2(dppm)]^{2+}$, observable only at low temperature.

Since we have detected $[Pt(OCOPh)(PBu^n_3)(dppe)]^+$ in CH_2Cl_2 solution at ambient temperature, but could only prepare the analogous complex containing a monodentate malonate complex at −60 °C in $CDCl_3$, it appears that when one end of a dicarboxylate ligand is displaced, its reaction with a chlorinated solvent is particularly rapid.

Acknowledgements

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