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Formation of an Azaplatinacyclobutane Compound from a Tertiary Amine by Elimination of an Alkene

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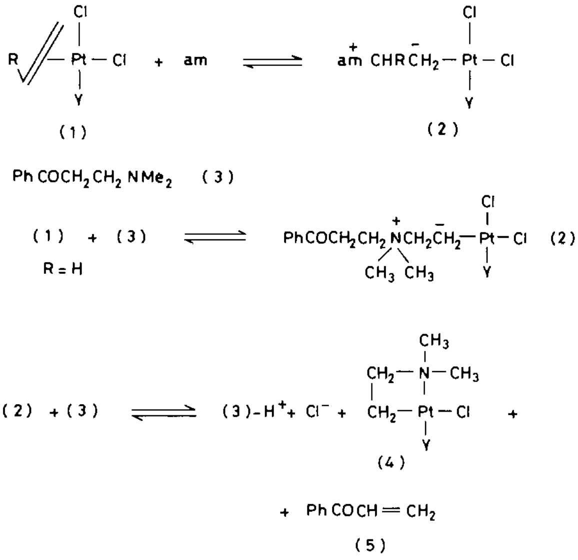

Amines (am) can attack (η-ethene)platinum(II) complexes (1; R = H) to form σ-2-ammonioethanide)-platinum(II) compounds [1–5]. In the present work, Mannich base (3), β-dimethylaminopropiophenone was used as amine. ^{195}Pt and ^{31}P n.m.r. were used for investigation of the reaction of Mannich base (3) with the olefin complexes (1) in which Y = PPh_3 and PBu_3^n at *ca.* 25 °C, and at *ca.* –40 °C. At low temperature, –40 °C, addition of excess of Mannich base (3) to (1) leads to the complete formation of the zwitterionic σ-compound (2).

This was characterized by ^{195}Pt and ^{31}P n.m.r. spectroscopy which gave respectively a doublet and triplet (1:4:1) with almost equal coupling constants of 4697 and 4684 Hz; this high value is typical of a Pt–P bond *trans* to Cl^-, enhanced by a *cis* alkyl group [6]. There is no further change at –40 °C either on standing or adding further base. However on warming the solution, for example to 25 °C, the cyclized compound (4) is produced in 100% yield. Its resonances are identical with ^{195}Pt, ^{13}C, ^{1}H and ^{31}P n.m.r. spectra obtained earlier from compound (4) formed by addition of $NHMe_2$ to the starting material (1) [7–9], identified in solution [9] and by elemental analysis [5]. Thus, Panunzi's [7] group has characterized by elemental analysis and osmometry. This suggests the elimination of phenylvinylketone (5), and the production of this compound was

TABLE I. ^{31}P N.m.r. and ^{195}Pt N.m.r., δ and J values in $CDCl_3$ at *ca.* 25 °C for R.T. and *ca.* –40 °C for L.T.

Compound	^{31}P N.m.r.^{a}				^{195}Pt N.m.r.^{b}			
	δ ppm		^1JPt–P, Hz		δ ppm		^1JPt–P, Hz	
	R.T.	L.T.	R.T.	L.T.	R.T.	L.T.	R.T.	L.T.
Cis-$PtCl_2(\eta\text{-}C_2H_4)PPh_3$ (1)	+12.6	+13.2	3262	3280	4038	–	3262	–
$PtCH_2CH_2NMe_2(Cl)PPh_3$ (4)	+10.0	+10.4	4272	–	3866	–	–	–
$Pt(C\bar{H}_2CH_2\overset{+}{N}(Me)_2CH_2CH_2COPh)(Cl)_2PPh_3$ (2)	–	+16.0	–	4684	–	4261	–	4697
$[PtCl_2(PPh_3)]_2$ (6)	+5.3	–	4100	–	3338	–	4106	–
Trans-$PtCl_2(N)(PPh_3)$ (7)	+4.8	–	3590	–	3652	–	3590	–
Cis-$PtCl_2(\eta\text{-}C_2H_4)P(Bu^n)_3$ (1′)	+5.0	+7.0	3040	3050	3998	4036	–	3057
$PtCH_2CH_2NMe_2(Cl)P(Bu^n)_3$ (4′)	–5.5	–	4047	–	3843	–	4038	–
$Pt(\bar{C}H_2CH_2\overset{+}{N}(Me)_2CH_2CH_2COPh)(Cl)_2P(Bu^n)_3$ (2″)		–1.6	–	4350	–	4206	–	4375
$[PtCl_2(PBu^n_3)]_2$ (6′)	+2.2	+3.4	3820	3742	3404	–	3801	–
Trans-$PtCl_2(N)P(Bu^n)_3$ (7′)	–5.5	–5.7	3344	–	3653	3667	3335	3291

For calibration of δ^{31}P n.m.r. for PPh_3 was –5.4 ppm, down field of 85% H_3PO_4 [11]. ^{a}δ-values relative to 85% H_3PO_4 for ^{31}P n.m.r. (+ upfield, – downfield) and ^{b}relative to Na_2PtCl_6 (all shifts are negative) for ^{195}Pt n.m.r. (using JEOL FX 100 MHz). ^{1}H and ^{13}C n.m.r. parameters of cyclic compound are similar to ref. [8]. ^{1}H n.m.r. of (5), consist of AMX systems for vinyl group, at δ 7.08, d–d, of 10.5 Hz; δ 6.41, d–d of 17.10 Hz and δ 5.93 Hz, d–d of 10.5 Hz; Ph complex at δ 7.3–8.

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verified from ^1H and ^{13}C spectra (the formation of free Cl^- was shown using silver nitrate).

Earlier work [4, 5] has hinted that ring formation of azaplatinacyclobutane complexes (4) is aided by bulky groups in am, in R and perhaps in Y. In the present work the tertiary amine, Mannich base, behaves like a bulky amine and yields of unstable σ-adducts (2) (only stable in solution at low temperature; when am is pyridine, the σ-product is found only at –40 °C [10]). By warming a solution of (2), cyclization takes place at room temperature and the more stable ring compound is formed (4).

Similar results are obtained when Y is PBu_3^n or $SOMe_2$, and for the analogous 1-butene and *cis*-2-butene complexes with Y = $SOMe_2$, and also for (1, Y = PPh_3) and α-(β-dimethylaminopropio)-naphthanone, Mannich base. These reactions provide the first examples of the formation of azaplatinacyclobutane ring from a tertiary amine by elimination of an alkene. However, quaternary ammonium salts decompose in basic media to give alkenes and tertiary amines.

The reaction is more complicated at 25 °C. Addition of one mol equivalent of the base (3) to (1, Y = PPh_3) in $CDCl_3$ at *ca.* 25 °C produces a ^{31}P n.m.r. spectrum corresponding to a mixture of four species (each of which has been characterized separately), namely, 10% of $[PtCl_2(PPh_3)]_2$ (6), $^1J(Pt-P)$ 4100 Hz; 10% of *trans*-$[PtCl_2(PPh_3)$(N-bonded base(3)$]$ (7), $^1J(Pt-P)$ 3590 Hz; 40% of the cyclized compound (4), $^1J(Pt-P)$ 4272, and the remaining 40% is the starting compound (1), see Table I. Addition of two equivalents of base (3) yields only two species (as shown by ^{31}P n.m.r. and ^{195}Pt n.m.r.); 70% of the cyclized compound (4) and 30% of the *trans* compound (7).

Similar results are obtained with (1, Y = PBu_3^n) at *ca.* 25 °C (each species has been characterized separately), see Table I.

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