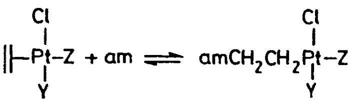
Platinum Complex containing a Four-membered Ring

By Ibrahim M. Al-Najjar and Michael Green*
(*Department of Chemistry, University of York, Heslington, York* YO1 5DD)
and S. John S. Kerrison and Peter J. Sadler*
(*Department of Chemistry, Birkbeck College, Malet Street, London* WC1E 7HX)

Summary ^1H, ^{13}C, and ^{195}Pt n.m.r. spectroscopy, together with ^{15}N-dimethylamine, have been used to elucidate the structure of a novel cyclic complex $[Me_2NCH_2CH_2Pt(Cl)PPh_3]$.

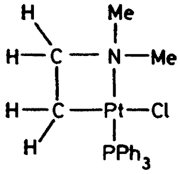
Olefins, activated by co-ordination to platinum, are frequently attacked nucleophilically by amines, with the result that a π-complex, (**1**), is transformed into a σ-bonded β-ammonioethanide compound, (**2**), see equation (1).[1–4]



(1)

(1) (2)

In this case, normally no further reaction occurs [apart from slow decomposition of (**1**) and (**2**)].[4] However, the following evidence leads us to believe that if am = Me_2NH, Y = PPh_3, and Z = Cl, a curious cyclization takes place leading to the formation of (**3**).



(3)

When (**1**, Y = PPh_3, Z = Cl) is dissolved in chloroform and stirred for 30 min with Me_2NH and the solvent removed *in vacuo*, white crystals, A, are formed. Washing of A with methanol and water, followed by drying *in vacuo* leads to B. The ^1H and ^{13}C n.m.r. spectra of A, B, and equimolar amounts of B and $Me_2NH_2{}^+Cl^-$ are identical. As A conducts in solution, it is formulated as $Me_2NCH_2CH_2PtCl(PPh_3)\cdot Me_2NH_2{}^+Cl^-$ and B, which is a non-conductor, will be shown to be (**3**). Microanalysis of B points to a 1:1:1 Pt:N:Cl stoicheiometry. Mass spectrometry gives no peaks greater than *ca.* m/e 564 (M^+), indicating only one platinum atom. The elucidation of the rest of the structure of B follows from its ^1H, ^{195}Pt, and ^{13}C n.m.r. spectra.

The Table summarizes the n.m.r. data for B. The following structural features emerge from the features indicated: (i) a σ CH_2–Pt bond: the values of $\delta(CH_2Pt)$ and of $J(^{195}Pt–^{13}C)$ in the ^{13}C n.m.r. spectrum;[5a] (ii) a fully σ-bonded NCH_2CH_2Pt unit: the 1:2:1 ^1H triplets, each with Pt satellites;[3,4] (iii) the absence of an NH proton on the Me_2NCH_2 group: $\delta(NCH_2)$ 4·25, *cf.* 4·35 for (**2**, am = py, Y = Me_2SO, *Z* = Cl)† and *ca.* 3·2 for (**2**, am = Z = many primary and secondary amines, Y = Cl);† (iv) Pt–P and Pt–N bonds: the sizes of the $^{195}Pt–^{31}P$ and $^{195}Pt–^{15}N$ couplings in the Pt n.m.r. spectrum, see (v) and (vi); (v) the *trans*-N–Pt–P arrangement as opposed to the geometry with *trans*-C–Pt–P and *trans*-Cl–Pt–N: compare $^1J(^{195}Pt–^{31}P)$ here of 4266 Hz with 3518 and 1719 Hz in *trans*-$[PtCl_2(NHMe_2)(PPh_3)]$[6] and *cis*-$[PtCl(CH_3)(PPh_3)_2]$[7] respectively, and also $^1J(^{195}Pt–^{15}N)$ here of 122 Hz with 171 and 312 Hz in *trans*-$[PtCl_2(^{15}NHMe_2)(PPh_3)]$[6] and *cis*-$[PtCl_2(NH_3)_2]$[8] respectively; (vi) the *cis*-C–Pt–P geometry: compare $^2J(^{13}C–Pt–^{31}P)$ here of 2·4 Hz with 9 and 104 Hz for the *cis*- and *trans*-coupling constants respectively in *cis*-$[Pt(CH_3)_2(PMe_2Ph)_2]$;[9] (vii) the proximity of the CH_3 protons to the Pt–P unit: Pt–H and P–H coupling in the ^1H n.m.r. spectrum; (viii) the closeness of the 2-C and Pt atoms in the NCH_2CH_2Pt ring: values of $^2J(^{13}C–C–Pt)$ are usually $<$ 100 Hz, not 145 Hz.[5b]

The absence of particularly close agreement between ^1J(Pt–P) and ^1J(Pt–N) in B and in the analogous compounds

---

† Run in $CDCl_3$ at *ca.* 30 °C.

TABLE. N.m.r. parameters of B.[a]†

δ/p.p.m.	Description	Assignment	J/Hz		
^{1}H n.m.r.					
0·65	(d of t, with sat.)[b]	$\mathrm{C}H_2\mathrm{Pt}$	^3J(H–H)8·1	^2J(Pt–H)88	^3J(P–H)2·5
2·7	(d, with sat.)[b]	$\mathrm{C}H_3\mathrm{N}$		^3J(Pt–H)35	^4J(P–H)3·4
4·25	(t, with sat.)[b]	$\mathrm{NC}H_2$	^3J(H–H)8·0	^3J(Pt–H)60	
7·4,7·7	(m)	$\mathrm{C_6}H_5$			
^{13}C n.m.r. (natural abundance)					
−20·37	(d, with sat.)	$C\mathrm{H_2Pt}$	^1J(Pt–C)543·8	^2J(P–C)2·4	
48·7	(d, with sat.)	$C\mathrm{H_3N}$	^2J(Pt–C)11·3	^3J(P–C)2·6	
71·55	(d, with sat.)	$\mathrm{N}C\mathrm{H_2}$	^2J(Pt–C)145·3	^3J(P–C)1·8	
127—133	(m)	$C_6\mathrm{H_5}$			
^{195}Pt n.m.r. (using ^{15}N)					
−3871[c]	(d of d)		^1J(Pt–P)4266	^1J(Pt–N)122	

[a] d = doublet, t = triplet, m = complex multiplet, sat. = Pt satellites. [b] Relative intensities, 1:3:1. [c] P.p.m. relative to external $\mathrm{Na_2PtCl_6}$.

in (v) may arise from unusual Pt–C and Pt–N bond lengths and/or the absence of strict tetragonal geometry at the platinum atom resulting from strain in the ring system.

^{1}H N.m.r. spectroscopy ($\mathrm{CDCl_3}$) of the products formed in solution by the reaction of (**1**,Y = $\mathrm{PPh_3}$, Z = Cl) with other amines shows $\delta(\mathrm{NC}H_2\mathrm{CH_2Pt})$ to lie in two ranges: (i) am = $\mathrm{MeNH_2}$, 2·4, $\mathrm{Pr^nNH_2}$, 2·3, $\mathrm{PhCH_2NH_2}$, 2·35, and $\mathrm{Pr^iNH_2}$, 2·4; (ii) am = $\mathrm{Bu^tNH_2}$, 4·35, $\mathrm{Et_2NH}$, 4·3, $\mathrm{PhCH_2(Me)NH}$, 4·4, and piperidine, 4·3. Since in B this δ value is 4·25 and in many examples of (**2**) it is 3·0 or less, it seems that the first group of amines form conventional adducts (**2**), but that the second give cyclic complexes analogous to (**3**). As the second group of amines is more bulky than the first, this interpretation indicates that the cyclization is brought about by steric factors.

The products formed by mixing the corresponding $\mathrm{Me_2SO}$ complex (**1**, Y = $\mathrm{Me_2SO}$, Z = Cl) and the aliphatic and alicyclic amines listed above, all, irrespective of size, give a $\mathrm{NC}H_2$ peak at δ 3·1—3·3 as expected for structure (**2**).† $\mathrm{Me_2SO}$ like $\mathrm{PPh_3}$, is *trans*-labilizing,[10] so that the formation of cyclic complexes is not prevented for kinetic reasons. However, extending the argument of steric factors, one can postulate that $\mathrm{Me_2SO}$ with its smaller size compared with $\mathrm{PPh_3}$ does not provide sufficient bulk to bring about cyclization, hence no compounds analogous to (**3**) are formed.

We thank the S.R.C. for grants and a studentship (to S.J.S.K.) and Johnson Matthey Ltd. for their support.

(*Received*, 17*th November* 1978; *Com.* 1239.)

[1] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, 1968, **90**, 4175.
[2] E. Benedetti, A. De Renzi, G. Paiaro, A. Panunzi, and C. Pedone, *Gazzetta*, 1972, **102**, 744.
[3] D. Hollings, M. Green, and D. V. Claridge, *J. Organometallic Chem.*, 1973, **54**, 399.
[4] I. M. Al-Najjar and M. Green, *J.C.S. Dalton*, 1979, in the press.
[5] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, (a) Tables I and XXIX; (b) Table XXXII.
[6] I. M. Al-Najjar, M. Green, S. J. S. Kerrison, and P. J. Sadler, *J. Chem. Research*, submitted for publication.
[7] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 368.
[8] S. J. S. Kerrison and P. J. Sadler, *J.C.S. Chem. Comm.*, 1977, 861.
[9] A. J. Cheney, B. E. Mann, and B. L. Shaw, *Chem. Comm.*, 1971, 431.
[10] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967.