Inorganica Chimica Acta, 44 (1980) L187–L188
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Multinuclear N.M.R. Studies on Cyclic Platinum Complexes

IBRAHIM M. AL-NAJJAR

Department of Chemistry, University of Gar Younis, El-Beida, Libya

MICHAEL GREEN, JAMIL K. K. SARHAN

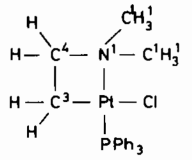
Department of Chemistry, University of York, Heslington, York YO1 5DD, U.K.

ISMAIL M. ISMAIL and PETER J. SADLER

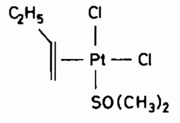
Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX, U.K.

Received November 13, 1979

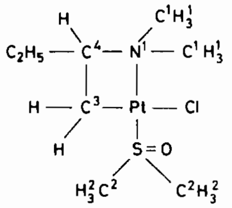
Recently we [1] reported the discovery of an unusual cyclic platinum complex (*1*). The complex was made from *cis*[$Me_2NHCH_2CH_2PtCl_2(PPh_3)$], ring closure involving the formation of a N–Pt bond *trans* to the triphenylphosphine ligand. We now show that cyclisation is not unique to phosphine complexes.



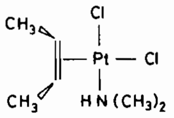
(1)



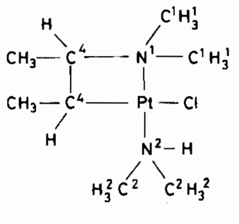
(2)



(3)



(4)



(5)

TABLE I. N.m.r. Parameters.[a]

δ/ppm		Description	J/Hz			
Complex (*3*)						
H^1	2.75	s, with sat	$^1J(Pt–H)$	46.5		
	2.65	s, with sat	$^1J(Pt–H)$	45.0		
C^1	49.6	d, with sat	$^2J(Pt–C)$	25.0	$^1J(C–N)$	5.6
	42.2	d, with sat	$^2J(Pt–C)$	26.4	$^1J(C–N)$	5.6
C^2	45.6	s, with sat	$^2J(Pt–C)$	72.0		
C^3	−14.7	s, with sat	$^1J(Pt–C)$	540.0		
C^4	82.2	s, with sat	$^2J(Pt–C)$	144.0	$^1J(C–N)$	4.3
Pt	−3602	d	$^1J(Pt–N)$	190		
Complex (*5*)						
H^1	2.72	s, with sat	$^3J(Pt–H)$	42.0		
H^2	2.66	s, with sat	$^3J(Pt–H)$	40.0		
C^1	47.4	s, with sat	$^2J(Pt–C)$	134.3	$^1J(C–N)$	<2
C^2	47.7	s, with sat	$^2J(Pt–C)$	130.6	$^1J(C–N)$	<2
C^3	−12.6	s, with sat	$^1J(Pt–C)$	682.4		
C^4	85.8	d, with sat	$^2J(Pt–C)$	172.0	$^1J(C–N)$	4.3
Pt	−2866	d of d	$^1J(Pt–N^1)$	239	$^1J(Pt–N^2)$	299

[a] Spectra run at *ca.* 27 °C; d = doublet, s = singlet, sat = Pt satellites; ^1H and ^{13}C δ-values relative to TMS, ^{195}Pt δ-values relative to external Na_2PtCl_6.

---

*Author to whom correspondence should be addressed.

Treatment of *cis*-[PtCl$_2$(η^2-1-butene)(SOMe$_2$)] (*2*) with an excess of Me$_2^{15}$NH in CDCl$_3$ containing a trace of sodium hydroxide yields a solution, the ^{1}H-, ^{13}C- and ^{195}Pt n.m.r. spectra of which indicate the formation of (*3*).

N.m.r. data are summarized in Table I, the following points being important in assigning formula (*3*). (i) The size of the ^{195}Pt–^{15}N coupling (190 Hz) indicates a one bond interaction (ii). In the N(CH$_3$)$_2$ group the two carbon atoms and the two sets of protons are non-equivalent, whereas they would be equivalent in an acyclic system. (iii) The N(CH$_3$)$_2$ proton and carbon resonances exhibit platinum coupling. (iv) The C^3 and C^4 resonances display coupling to nitrogen and to platinum indicating the proximity of both atoms. (v) ^{2}J(C^4–Pt) is rather large for a simple ^{2}J interaction [2]. (vi) The J(C–Pt) values of C^3 and C^4 are close to the corresponding parameters [1] in (*1*) which are 544 Hz and 145 Hz respectively.

When a mixture of *cis*[PtCl$_2$(η^2-*cis*-2-butene)(^{15}NHMe$_2$)] (*4*) and Me$_2^{15}$NH in CDCl$_3$ containing a trace of sodium hydroxide is allowed to stand for a few days, another cyclic complex is formed which we believe to be (*5*). Pertinent n.m.r. data are given in Table I. Important features in recognizing this cyclic compound are the occurrence of a ^{3}J(Pt–H^1) interaction as well as ^{3}J(Pt–H^2), the presence of ^{1}J(C^4–N^1) coupling and the large size of ^{2}J(Pt–C^4). The doublet of doublets with couplings of 239 and 299 Hz seen in the ^{195}Pt NMR spectra of (*5*) is consistent with the proposed structure. ^{1}J(^{195}Pt–^{15}N) values *trans* to aliphatic amines lie in the range 278–290 Hz [3] and, as in (*1*) and (*3*), cyclisation and deprotonation appear to decrease the coupling by *ca.* 50 Hz.

The ^{1}H and ^{13}C δ-values of H^1, C^1, C^3 and C^4 are close to those in (*3*) above, and also in (*1*). However there are contrasts between the three compounds in values of J(Pt–C). ^{2}J(Pt–C^1) rise sharply between (*1*), (*3*) and (*5*), *viz.* 11 Hz^1, *ca.* 26 Hz, *ca.* 134 Hz, while the corresponding ^{3}J(Pt–H^1) fall: 60 Hz^1, *ca.* 46 Hz, *ca.* 41 Hz, probably reflecting the difference in *trans* ligand. However while ^{1}J(Pt–C^3) are almost equal in (*3*) and (*1*), *viz.* 540 Hz and 544 Hz respectively, that in (*5*) of 682 Hz is much closer to the expected [2] value of *ca.* 650 Hz (Cl$^-$ being the *trans* ligand throughout). As *cis* effects in platinum compounds are usually small, this variation suggests that the larger *trans* influence of the π-bonding ligands PPh$_3$ and Me$_2$SO, compared with the amine, produces longer Pt–N^1 bonds, which, because of the ring structure, affect geometry in the Pt–C^1 region.

It is curious that the C^1 atoms are equivalent in (*5*) but not in (*3*). This implies that in this context the origin of non-equivalence is steric rather than electronic.

To conclude: the demonstration of the existence of these two cyclic complexes (and we have evidence for others such as the ^{15}N-piperidine analogue of (*3*)) suggests that the formation of this sort of compound may be general to platinum(II) chemistry and not limited just to phosphines. The fact that the amine system, as well as the SOMe$_2$ and PPh$_3$ complexes, can cyclize demonstrates that ring closure is not dependent on the presence of *trans*-labilizing or π-bonding ligands.

Turning to palladium systems, one can visualise this sort of ring complex as intermediates in the Wacker and Vinyl Acetate Processes, which in turn would imply an intramolecular mechanism [4].

Acknowledgments

We thank the SRC for support and a CASE award (to I.M.I.) with Johnson Matthey Ltd.

References

1 I. M. Al-Najjar, M. Green, S. J. S, Kerrison and P. J. Sadler, *J. Chem. Soc. Chem. Comm.*, 311 (1979).

2 B. E. Mann, *Adv. Organometal. Chem.*, *12*, 135 (1974).

3 P. S. Pregosin, H. Omura and L. M. Venanzi, *J. Am. Chem. Soc.*, *95*, 2047 (1973); S. J. S. Kerrison and P. J. Sadler, *J. Chem. Soc. Chem. Comm.*, 861 (1977).

4 T. Mejima and H. Kurosawa, *J. Chem. Soc. Chem. Comm.*, 610 (1977); J. E. Baechkrall, B. Aakermark and S. O. Ljunggren, *J. Chem. Soc. Chem. Comm.*, 264 (1977).