Stereoselectivity in the Complexing of Platinum(II) Chloride with Substituted Cyclopropanes

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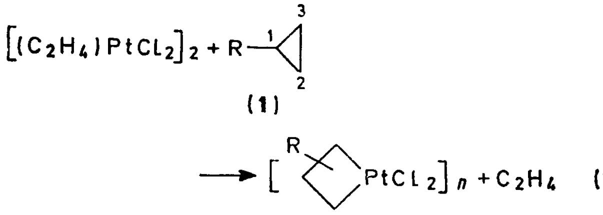
A series of mono-substituted cyclopropanes have been shown to displace ethylene from $[(C_2H_4)PtCl_2]_2$ with formation of substituted (propane-1,3-diyl)$PtCl_2$ derivatives, displacement being impeded or inhibited by electron withdrawing substituents. From the ^1H n.m.r. spectra of the bis-pyridine derivatives $(RC_3H_5)PtCl_2(py)_2$ it is shown that insertion occurs preferentially into the less substituted cyclopropane bond when R = n-C_6H_{13}, $PhCH_2$, *o*-$NO_2C_6H_4$, or Ph, but for R = *p*-MeC_6H_4 the principal product arises from insertion into the more substituted bond in the cyclopropane. *trans*-1,2-Diphenyl- and *trans*-1-methyl-2-n-butyl-cyclopropane undergo insertion of $PtCl_2$ into the less substituted cyclopropane bond, but *cis*-1-methyl-2-n-butylcyclopropane and bicyclo[4,1,0]heptane are preferentially isomerised to olefins. 1,2-Dicyclopropylethane yields a bis-$PtCl_2$ derivative.

TIPPER[1] showed that cyclopropane yields a dichloroplatinum derivative $(C_3H_6)PtCl_2$ which was subsequently[2] shown to arise as a result of insertion of a $PtCl_2$ residue into a carbon–carbon bond. This and the related reaction of cyclopropane with tetracarbonyldichlorodirhodium, reported by Wilkinson,[3] have become the precedents for a wide range of insertion and isomerisation reactions of strained cycloalkanes.[4]

The displacement reaction (1)



carried out using excess of a cyclopropane with dichloro(ethylene)platinum under refluxing ether has been shown[5] to be a convenient method of preparation of a range of substituted dichloro(propane-1,3-diyl)platinum derivatives. It was considered that the variation of reactivity of the cyclopropane (**1**) with the nature of the substituent group R, and the relative extent of ring fission along the 1,2- and 2,3-bonds would throw useful light on the nature of the insertion process.

The relative reactivity of monosubstituted cyclopropanes was compared by allowing equimolar amounts of different cyclopropanes to react competitively with dichloro(ethylene)platinum, and subsequent g.c. analysis of the unreacted material. This gave a reactivity sequence (**1**), R = n-C_6H_{13} > $PhCH_2$ > Ph > *o*-$NO_2C_6H_4$, and cyclopropanes (**1**), R = CN, $COCH_3$, or CO_2CH_3, failed to react. It was found that the excess of R-cyclopropane recovered from these experiments contained no products of isomerisation, and that the dichloro(propane-1,3-diyl)platinum derivatives (**2**) are decomposed by aqueous potassium cyanide to reform only the parent cyclopropane.

The reactivity sequence implies that the displacement reaction (1) depends on the electron donor capacity of the cyclopropane ring, and that the $PtCl_2$ residue acts as an electrophile. This conclusion is in agreement with the observed effect of electron withdrawing substituents on the rate of Ag^+-catalysed isomerisation of substituted cubanes,[6] and with current views[7] of the mechanism of Ag^+-induced rearrangement of bicyclo[1,1,0]butanes.

The structures of the dichloro(R-propane-1,3-diyl)platinum derivatives (**2**) were deduced[2] from the ^1H n.m.r. spectra of their bis-pyridine adducts (**3**).

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[1] G. F. H. Tipper, *J. Chem. Soc.*, 1955, 2045.

[2] D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, *J. Chem. Soc.*, **1961**, 738; N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Comm.*, 1966, 396; S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton, and N. F. Pilbrow, *J. Chem. Soc.* (*A*), 1969, 1227.

[3] D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 845.

[4] L. Cassar and J. Halpern, *Chem. Comm.*, 1970, 1082; L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515; P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, 1971, **93**, 1812; P. G. Gassman and F. J. Williams, *ibid.*, 1970. **92**, 7631.

[5] W. J. Irwin and F. J. McQuillin, *Tetrahedron Letters*, 1968, 1937; *cf.* D. B. Benson, *J. Organometallic Chem.*, 1970, **24**, 787.

[6] G. F. Koser, *Chem. Comm.*, 1971, 388; L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 6366.

[7] P. G. Gassman and T. G. Atkins, *J. Amer. Chem. Soc.*, 1971, **93**, 4597; M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masumune, *ibid.*, p. 4611.

Reaction with pyridine was carried out by stirring the chloro-polymer (**2**) in chloroform with a little pyridine for a few minutes and the solution was then filtered through a column of silica or alumina. It is unlikely that this mild treatment results in any rearrangement, and hence the structure of the trimethylene residue in (**3**) is taken to be representative of that in (**2**).

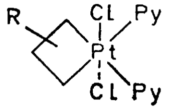
The bis-pyridine complexes, which may be purified by t.l.c. on silica gel in benzene, all exhibited a single ν(Pt–Cl) i.r. band (Table 1) consistent with trans-chloro-ligands as in (**3**).

TABLE 1

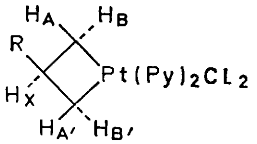
$(RC_3H_5)PtCl_2(py)_2$ complexes (**3**)

R	n-C_6H_{13}	$PhCH_2$	Ph	*o*-$NO_2C_6H_4$	*p*-MeC_6H
ν(PtCl), cm^{-1}	341	341	337	345	333
M.p.	125° (d)	114°	130°	220° (d)	105—107
R_F	0·7	0·5	0·5	0·55	

For (phenylpropane-1,3-diyl)bis(pyridine)dichloroplatinum the n.m.r. spectrum ($CDCl_3$) indicated structure (**4**, R = Ph), *viz.* H_x 5·9 (1H, m), no evident ^{195}Pt coupling, $H_{A,A',B,B'}$ τ 7·03 (4H, d, 9 Hz), satellites *J* ^{195}Pt–H 82 Hz, this signal becoming a singlet with the analogue (**4**, R = Ph, H_x = D), or on irradiation at τ 5·9. In C_6D_6 the spectra showed marked deshielding (Table 2), and improved resolution. At 220 MHz in C_6D_6 (**4**, R = Ph) showed a τ 6·6 signal as a pair of AB quartets, whence J_{AB} = 4·4 and J_{AX} = J_{BX} = 9 Hz, (**4**, R = Ph, H_x = D) giving the same J_{AB} value. The ^{195}Pt-satellites were not equally resolved, but at 220 MHz the higher field satellite showed six of the theoretical eight lines, whence $\nu_A - \nu_B$ = 5·5 and *J* ^{195}Pt–H_A and –H_B = 79 and 85 ± 2 Hz, these small differences leading to line coincidence in the lower field satellite, and indicating some ring bending.



(**3**)



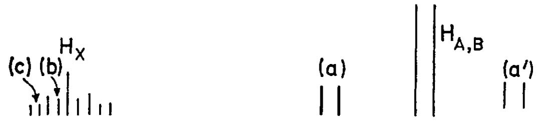
(**4**)

TABLE 2

Deshielding (Δ p.p.m.) for complexes (**3**) in C_6D_6 *vs.* $CDCl_3$ (90 MHz)

R	n-C_6H_{13}	$PhCH_2$	Ph	*p*-MeC_6H_4
$\Delta H_{A,B}$	0·54	0·3	0·39	0·30
ΔH_x	0·47	0·37	0·46	0·41

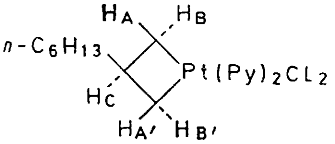
The *o*-nitrophenylcyclopropane derivative gave a similar spectrum (Table 3), and is therefore formulated as (**4**, R = *o*-$NO_2C_6H_4$). However, both complexes (**4**, R = Me and *o*-$NO_2C_6H_4$) showed the H_x proton as the expected quintet signal (at 220 MHz), but with minor signals (*cf.* Figure), and irradiation related lines (b) (c) with the (a) $H_{A,B}$ satellite for (**4**, R = Ph) and with the (a′) satellite for (**4**, R = *o*-$NO_2C_6H_4$). The minor signals may represent ^{195}Pt satellites; vicinal ^{195}Pt–H coupling is clearly observed in related acyclic analogues.[8,9]



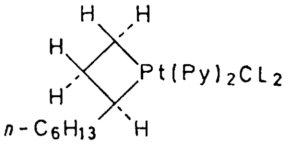
FIGURE

The benzylcyclopropane derivative is formulated as (**4**, R = $PhCH_2$), since H_x showed no apparent ^{195}Pt coupling; (**4**, R = $PhCD_2$) was also examined.

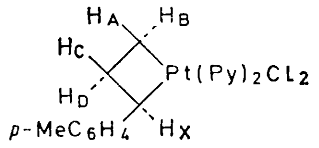
The $PtCl_2(py)_2$ derivative from n-hexylcyclopropane showed signals τ 7·25 and 7·57 (3 : 2), *cf.* the parent hydrocarbon: τ 9·6 and 10·0 (3 : 2), each with ^{195}Pt-satellites. The absence of satellites for the n-hexyl-α-CH_2 protons indicate structure (**5**) rather than (**6**), but this assignment is less definitive. However, taken together, the four cases (**4**, R = Ph, *o*-$NO_2C_6H_4$, $PhCH_2$, and n-C_6H_{13}) indicate a preference for insertion into the cyclopropane 2,3-bond. The possibility that this might derive from steric repulsion by the R-substituents was excluded by examination of the *p*-tolylcyclopropane derivative. This was characterised by a low field triplet, τ 5·07 (1H) with triplet satellites, *J* ^{195}Pt–H 102 Hz, and a 4H-signal τ 7·05 (t) with satellites, leading unambiguously to structure (**7**). However, a minor signal at τ 5·9, and a small τ 5·05 signal in the spectrum of (**4**, R = Ph) imply minor amounts of the alternative structure in each case, whilst (**4**, R = *o*-$NO_2C_6H_4$) appeared homogeneous. Thus 2,3- *vs.* 1,2-bond fission appears to fall: (**1**), R = *o*-$NO_2C_6H_4$ > Ph > *p*-MeC_6H_4. The n.m.r. data are collected in Tables 3 and 4.



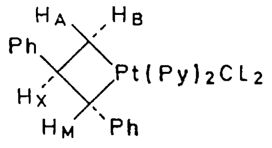
(**5**)



(**6**)



(**7**)



(**8**)

TABLE 3

N.m.r. data for complexes (**4**) and (**7**) in $CDCl_3$

	τ			$J_{H,H}$		J_{Pt-H}
(**4**)	A,A	B,B′	X *	A,B	AX,BX	A,B
R = H		7·34 †			7·5 †	84 †
n-C_6H_{13}		7·25, 7·58				
$PhCH_2$	7·3		6·79			81
Ph	7·03		5·9	4·4	9	79, 85
o-$NO_2C_6H_4$	7·02		5·44	4·4	9	80, 85
(**7**)	A,B,C,D		X		CX,DX	Pt–H_x
	7·05		5·07		9	102

* For (**4**, R = H) X = protons C,C′ on C_2. † Ref. 2 gives τ 7·5, 7·5 and 83 Hz respectively.

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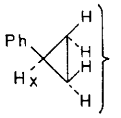
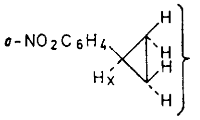
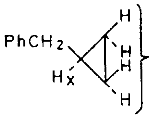
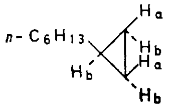
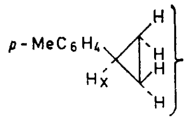
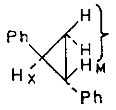
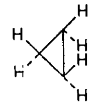
[8] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.

[9] S. F. A. Kettle, *J. Chem. Soc.*, 1965, 6664.

The pattern of reaction revealed by these examples of mono-substituted cyclopropanes was found to be repeated by two trans-1,2-disubstituted cyclopropanes, but not by examples of *cis*-1,2-disubstituted cyclopropanes which are discussed below.

TABLE 4

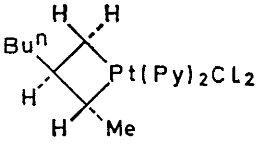
Downfield proton chemical shifts (Δ p.p.m. in $CDCl_3$ at 90 Hz) for $PtCl_2(py)_2$ trimethylene derivatives in comparison with the parent cyclopropanes

Cyclopropane	τ	Complex τ	Δ
 (a)	H_a 9·28 H_x 8·20	7·03 5·90	2·25 2·30
 (a)	H_a 9·14 H_x 7·64	7·02 5·44	2·1 2·2
 (a)	H_a 9·6 H_x 8·99	7·30 6·79	2·3 2·2
	H_a 10·0 H_b 9·6	7·58 7·25	2·42 2·35
 (a)	H_a 9·3 H_x 8·20	7·05 5·07	2·15 3·13
 (a)	H_a 8·65 $\left.\begin{matrix}H_m\\H_x\end{matrix}\right\}$ 7·90	6·80 4·88 5·25	1·85 3·02 2·65
	H 9·80	7·34	2·46

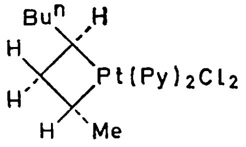
We examined *trans*-1,2-diphenyl- and *trans*-1-methyl-2-n-butyl-cyclopropane to investigate the influence of both aryl and alkyl substitution.

trans-1,2-Diphenylcyclopropane readily gave the $PtCl_2$ derivative in good yield with no concomitant isomerisation of residual cyclopropane. The bis-pyridine derivative [ν(Pt–Cl) 342 cm^{-1}] was characterised in the n.m.r. by a low field 1H signal as a doublet (*J* 10 Hz) at τ 4·88 with doublet ^{195}Pt-satellite (*J* ^{195}Pt–H 98 Hz) and a second 1H signal at τ 5·25 (m) showing no satellite signals. This leads unambiguously to a structure (**8**) and, in agreement, the A,B-protons appeared as a doublet (*J* 9 Hz) at τ 6·80 with ^{195}Pt satellites. Analysis of the A,B-proton signal was assisted by preparation of the dideuterium analogue (**8**, $H_M = H_x = D$) when H_A and H_B appeared as a single line (τ 6·8) with a low field Pt-satellite as a single peak, but with the higher field satellite as an AB-quartet. Thus, as for (**4**, R = Ph or o-$NO_2C_6H_4$) νH_A and νH_B and *J* ^{195}Pt–H_A and ^{195}Pt–H_B have slightly different values. In C_6D_6 solution the AB signal appeared as an AB-quartet (τ 6·5 at 90 MHz), and from this spectrum the following parameters could be derived: $J_{A,B}$ 4·4 Hz, ν_A τ 6·46 and ν_B 6·54, *J* ^{195}Pt–H_A and –H_B 77 and 84·5 ± 2 Hz. The values of these coupling constants agree closely with $J_{A,B}$ and *J* ^{195}Pt–H_A and –H_B derived from the complexes (**4**, R = Ph or o-$NO_2C_6H_4$), but *J* ^{195}Pt–H_M = 98 Hz is more in agreement with the corresponding value for H_x in (**7**) which also refers to a proton on an aryl substituted carbon atom.

trans-1-Methyl-2-n-butylcyclopropane gave a $PtCl_2$-$(py)_2$ derivative the n.m.r. spectrum of which showed a CH_3-signal as a doublet at τ 9·4 (*J* 7 Hz) together with doublet ^{195}Pt-satellites (*J* ^{195}Pt–H 24 Hz) attributable to vicinal ^{195}Pt–H coupling in a structure (**9**) or (**10**). The latter is contra-indicated by the absence of any apparent ^{195}Pt-satellite for the α-CH_2 protons of the n-butyl residue. The protons of the trimethylene group appeared as distinct 2H-signals at τ 7·07 and 7·6, *i.e.* reminiscent of the n-hexyl derivative (**4**, R = n-C_6H_{13}).

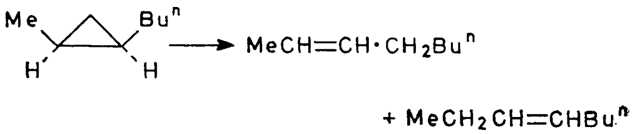


(**9**)

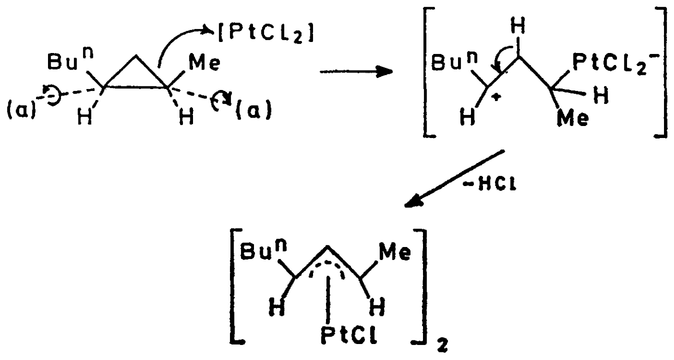


(**10**)

Thus *trans*-1,2-diphenylcyclopropane, certainly, and *trans*-1-methyl-2-n-butylcyclopropane, most probably, undergo fission along the less substituted edge of the cyclopropane ring. *cis*-1-Methyl-2-n-butylcyclopropane, however, was found to react quite differently. In refluxing ether with dichloro(ethylene)platinum the cyclopropane was consumed and replaced by two new products (65 : 35) recognised by g.l.c., and showing a broad n.m.r. signal at τ 4·9. The platinum complex formed in this reaction failed to yield a stable pyridine derivative, and when shaken in alcohol under hydrogen it was reduced to give a product which by t.l.c. analysis was found to contain two components, the main one (80%) being identified as n-octane. Thus *cis*-1-methyl-2-n-butylcyclopropane reacts by fission of the more substituted 1,2-bond to form a mixture of olefins:

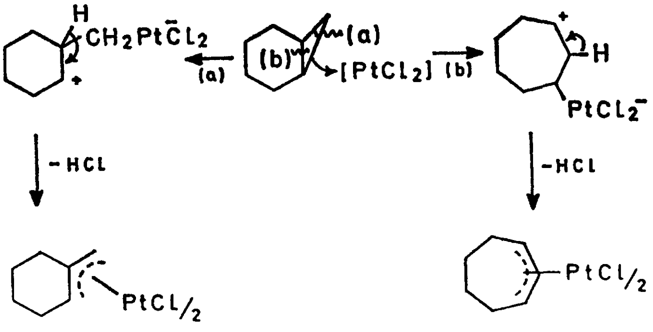


It is possible that an unstable (propane-1,3-diyl)$PtCl_2$ intermediate may intervene in this process, but coordination along the more substituted, 1,2-bond is not precedented among the examples described above, and in forming such a complex the compression between the *cis*-alkyl groups would be reduced by bond fission without carrying the reaction in the direction of the olefin. We are therefore led to consider an alternative, *e.g.*,

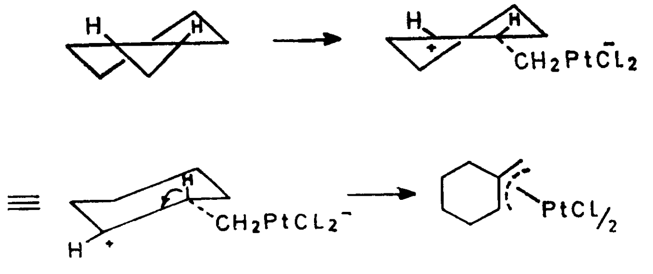


in which the electrophilic $PtCl_2$ residue reacts along a less substituted edge of the cyclopropane which is not, however, the bond broken. Some precedent is found[10] in the various reactions of cyclopropanes with electrophiles. If such a pathway is open, it is at first sight surprising that the behaviour of *cis*-1-methyl-2-n-butylcyclopropanes is exceptional. However, it is apparent that the transition to the olefinic or π-allylic derivative involves movement of the alkyl substituted centres as indicated by the arrows (a), and compression is already present in the ground state of the *cis*-disubstituted cyclopropane assisting movement in this sense, and is absent in the mono-substituted or *trans*-disubstituted analogues.

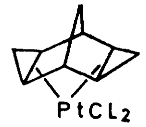
Bicyclo[4,1,0]heptane behaved similarly. With dichloro(ethylene)platinum in ether (1 h reflux) an orange complex was formed, and the residual solution, as well as the product from the orange complex decomposed by aqueous potassium cyanide solution, were shown by g.l.c. to yield methylenecyclohexane, 1-methylcyclohexene, and cycloheptene (*ca.* 2 : 2 : 1). Formation of these products may be rationalised



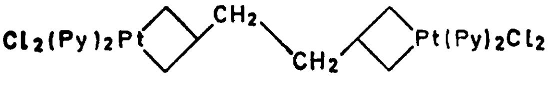
or, in more detail for route (a) which indicates the pathway for proton elimination.



One further variant was also examined, on analogy with the bidentate character of diolefins, and the known $PtCl_2$-derivative of *exo,exo*-tetracyclo[3,3,1,$0^{2,4}$,$0^{6,8}$]nonane[11] which is formulated as (**11**). However, 1,2-dicyclopropylethane gave a $PtCl_2$-complex, and a bis-pyridine derivative (m.p. 155° dec.) which analysed as $(py)_2PtCl_2\,C_3H_5CH_2CH_2C_3H_5PtCl_2(py)_2$ and showed n.m.r signals: τ 8·57 (4H), and 7·2—7·6 (10H) with ^{195}Pt-satellites, *J ca.* 80 Hz, consistent only with structure (**12**).



(**11**)



(**12**)

This range of examples serves to establish some generality for the reaction of cyclopropanes with $PtCl_2$. All the $PtCl_2$ trimethylene derivatives were found to reform only the parent cyclopropane by treatment with aqueous potassium cyanide. The reaction of dichloro-(2-phenylpropane-1,3-diyl)platinum with triphenylphosphine in chloroform similarly regenerated phenylcyclopropane with formation of *cis*-$(Ph_3P)_2PtCl_2$. The 2-phenylpropane-1,3-diyl complex in chloroform with carbon monoxide gave an unstable orange platinum carbonyl derivative (ν_{CO} 2120 cm^{-1}) and phenylcyclopropane. We have already described a similar displacement using propenylbenzene,[5] or by reduction.[12]

This chemical behaviour contrasts with that of alkylplatinum derivatives; $(Et_3P)_2Pt(Me)Cl$, $(PhMe_2P)_2Pt(Me)Cl_3$, and $(PhMe_2P)_2Pt(Me)_2Cl_2$ are stable,[13] yet we have been unable to obtain a phosphine analogue of the bis-pyridine dichloro(propane-1,3-diyl)platinum derivative. The difference presumably resides in the relatively great acceptor capacity of a Ph_3P ligand which would accentuate the marked electron transfer from the trimethylene residue apparent in the deshielding of the protons in the $PtCl_2(py)_2$ derivatives. In the stable phosphine platinum alkyls noted above[13] the CH_3-signal is found in the τ 9 region.

The extent of the proton deshielding in complexes such as (**4**), (**5**), or (**8**) (*cf.* Table 3), and especially of the proton H_x (or H_c) is high relative to *e.g.* $[(C_2H_5)_3PtCl]_4$ which shows[9] signals for CH_2 at τ 7·7 and for CH_3 at 9·25. The deshielding in the (propane-1,3-diyl)$PtCl_2(py)_2$ series

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[10] S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 4013; J. R. Hendrickson and R. K. Boeckman, *ibid.*, 1971, **93**, 4491.

[11] H. C. Volgar, H. Hogeveen, and M. M. P. Gaasbeck, *J. Amer. Chem. Soc.*, 1964, **91**, 2137.

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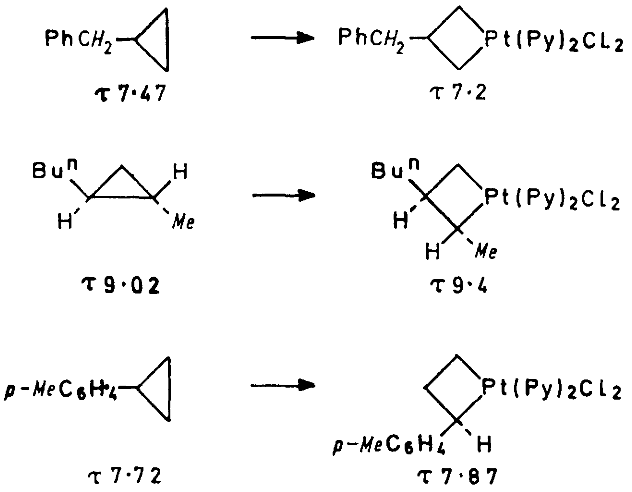
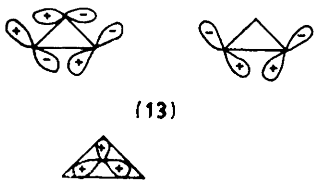
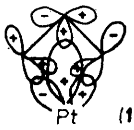
does not, however, extend to the protons of substituents, *viz*:



Thus the general proton deshielding of the trimethylene group appears to derive from these protons being very nearly equidistant from the PtCl$_2$(py)$_2$ residue, rather to an inductive process which should be transmitted.

In terms of the bent-bond model for cyclopropane, insertion of PtCl$_2$ may be rationalised as a process of rehybridisation as the electrons of the carbon–carbon bond overlap with a hybrid vacant orbital of the platinum. Using the Walsh[14,15] orbital picture, however, *cf.* (**13**) it is possible to represent the bonding as comprising a σ-donor component from the lowest cyclopropane orbital, together with a π-back donation into an antibonding level as in (**14**).


(**13**)



(**14**)

Such a picture could directly rationalise the general proton deshielding, and place the bonding of the trimethylene residue somewhere between a σ-alkyl- and a π-olefin-platinum derivative.

It may also be noted that the geminal proton–proton coupling $J_{\mathrm{HA,HB}} = 4{\cdot}4$ Hz found for (**4**, R = Ph] and (**8**) is small in comparison with values derived for methyl platinum and similar derivatives[16] (*ca.* 10 Hz), and for geminal coupling in cyclobutanes (10—17 Hz). The value of this coupling constant may be attributed to a specific electrophilic effect of the PtCl$_2$(py)$_2$ residue, but it is also consistent with a widened H$_A$–C–H$_B$ angle, and with the model (**14**) based on essentially sp^2-hybrid carbon units. This model also presents a dual pathway for vicinal ^{195}Pt–H coupling which may offer an alternative explanation to attributing the small value of this coupling constant to an angular relation approaching 90° between this proton and the molecular plane. J_{vic} ^{195}Pt–H is very small[2] in (C$_3$H$_6$)PtCl$_2$(py)$_2$, where there can be no deformation of the kind inferred in *e.g.* (**4**, R = Ph) which may be expected to reduce the Pt-vicinal-proton dihedral angle.

In the (propane-1,3-diyl)PtCl$_2$(py)$_2$ derivatives the n.m.r. data indicate that the trimethylene component is retained in the (90, 90)-geometry[15] and in this conformation cyclopropane represents an energy minimum[15] for a trimethylene residue. The reformation of the parent cyclopropane by a range of displacement reactions is therefore to be expected.

EXPERIMENTAL

Phenylcyclopropane[17] was obtained from 1-phenyl-1,3-dibromopropane using zinc–copper couple in dimethylformamide.

1-*Deuterio*-1-*phenylcyclopropane* was prepared by treatment of phenylcyclopropane (0·6 g) with sodium hydride (1·1 g) dissolved in [^{2}H$_6$]dimethyl sulphoxide (3 g) at 30—40° for 5 days. Dilution with D$_2$O and recovery gave a product (0·34 g), b.p. 175°, ν_{CD} 2240 cm^{-1}, showing [^{2}H$_0$] 31·6, [^{2}H$_1$] 68·1, and [^{2}H$_2$] 0·3% by mass spectral analysis. Of the n.m.r. signals for phenylcyclopropane, *i.e.* τ 2·88 (m, 5H), 8·18 (m, 1H), 9·15 (m, 2H) and 9·35 (m 2H) the τ 8·18 signal was very weak in the deuteriated product, and the τ 9·15 and 9·35 signals were essentially single lines.

o-*Nitrophenylcyclopropane*, b.p. 120°, 15 mmHg, prepared[18] using fuming nitric acid in acetic anhydride at −40°, showed i.r. bands at 750, 1610, 1525, 1508(sh), and 1350 cm^{-1}, and n.m.r. signals: τ 2—3 (m, 4H), 7·61 (m, 1H), 9·0 (m, 2H) and 9·3 (m, 2H).

Benzylcyclopropane.—A commercial sample was used, i.r. bands: 700, 730, 1600 cm^{-1}, n.m.r. τ 2·8 (m, 5H), 7·47 (d, J 7 Hz, 2H), 9·0 (m, 1H), 9·25 (m, 2H), and 9·57 (m, 2H).

Dideuteriobenzylcyclopropane was obtained from benzylcyclopropane (0·8 g) with sodium hydride (0·25 g) in [^{2}H$_6$]dimethyl sulphoxide (2 ml) maintained at 30° for 7 days. The product (0·41 g) showed ν_{CD} 2340 cm^{-1}, and by mass spectral analysis: [^{2}H$_0$] 18·9, [^{2}H$_1$] 50·2, and [^{2}H$_2$] 30·9%.

p-*Tolylcyclopropane* was prepared from p-methylstyrene (19 g), methylene di-iodide (50 g) in ether (150 ml) with zinc–copper couple (15 g) and a reaction time of 4 days. The product (70%), b.p. 70°, 12 mmHg showed a strong i.r. band at 810 cm^{-1}, and n.m.r. signals: τ 3·05 (essentially a singlet, 4H), 7·72 (s, 3H), and 9·1—9·4 (m, 4H).

n-*Hexylcyclopropane*, prepared after Simmons[19] was purified by fractionation b.p. 148—150°, ν_{CH} 3050 cm^{-1}, n.m.r. signals: τ 9·1 (t, 3H), 8·7 (m, 10H), 9·6 (m, 3H), and 10·0 (m, 2H).

trans-1,2-*Diphenylcyclopropane* was obtained from the *cis–trans*-mixture prepared by the method of Beech *et al.*[20] by equilibration using sodio dimethyl sulphoxylate, *viz*: to a solution of sodium hydride (1 g) in dimethyl sulphoxide

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[19] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256.

[20] S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 1952, 4686.

(20 ml) under N_2, the *cis–trans*-mixture of 1,2-diphenylcyclopropane (7·3 g) was added and after 3·5 h the red solution was diluted with water. Recovery gave *trans*-1,2-diphenylcyclopropane (4·8 g), b.p. 159°, 12 mmHg, showing i.r. bands: 700, 740, 755, 780, and 1605 cm^{-1} for the aromatic protons, and n.m.r. signals: τ 2·9 (m, 10H), 7·9 (q, 2H), and 8·65 (q, 2H).

trans-1,2-*Deuterio*-1,2-*diphenylcyclopropane*. To a solution of sodium hydride (0·14 g) in [$^2H_6$]dimethyl sulphoxide (2 g) under nitrogen *trans*-1,2-diphenylcyclopropane (0·56 g) was added and the solution kept at 30—40° for 2 days. Dilution with D_2O (5 ml) and recovery then gave [$^2H_2$]diphenylcyclopropane, b.p. 115—120°, 0·5 mmHg homogeneous to g.l.c., showing by mass spectral analysis [$^2H_0$] 1·9, [$^2H_1$] 8·7, [$^2H_2$] 80·9, and [$^2H_3$] 8·5% and ν_{OD} 2250 cm^{-1}, n.m.r.: τ 2·9 (m, 10H), 8·67 (s, 2H), and no 7·9 signal.

cis- *and* trans-1-*butyl*-2-*methylcyclopropane*.—*cis*-Hept-2-ene (18 g) with methylene di-iodide (48 g) and zinc–copper couple (15 g) in ether (120 ml) for 2 days gave a product containing *cis*- (41%) and *trans*-1-n-butyl-2-methylcyclopropane (23%) (g.l.c. on Apiezon) which were separated by preparative g.l.c. (11 ft Apiezon at 100°), retention times: *cis*- 9 and *trans*- 8 min. cis-*Isomer*, ν_{CH} 3020 cm^{-1}, n.m.r.: $-(CH_2)_3-$ τ 8·67 (m, 6H), 1 $-CH_3-(CH_2)_3-$ and 2 $-CH_3$ 9·0 (m, 6H), cyclopropyl-H 9·39 (m, 3H) and 10·31 (m, 1H). trans-*Isomer*, ν_{CH} 3040 cm^{-1}, n.m.r.: $-(CH_2)_3-$ τ 8·7 (m, 6H), 1 $-CH_3-(CH_2)_3-$ and 2 $-CH_3$ 9·02 (triplet shape, 6H), cyclopropyl-H 9·80 (m, 4H).

Bicyclo[4,1,0]*heptane*, obtained, b.p. 115—117°, from cyclohexene showed ν_{CH} 3065 cm^{-1}, and n.m.r. signals: τ 8·3 (m, 4H), 8·8 (m, 4H), 9·25 (m, 3H) and 10·0 (m, 1H).

1,2-*Dicyclopropylethane* [19] was prepared from hexa-1,5-diene (25 g) with methylene di-iodide (75 g) in ether (150 ml) with zinc–copper couple (20 g) with a reaction time of 5 days. The crude product (dicyclopropylethane, 30%, 4-cyclopropylbut-1-ene, 35% and hexa-1,5-diene, 35% by g.l.c.) was fractionated to give 4-cyclopropylbut-1-ene, b.p. 97—98, and 1,2-dicyclopropylethane, b.p. 129°. The latter showed ν_{CH} 3085 cm^{-1}, and n.m.r. signals: τ 8·7 (m, 4H), 9·6 (m, 6H) and 10·0 (m, 4H).

Preparation of (*Propane*-1,3-*diyl*)$PtCl_2$ *Derivatives*. (i) Tetrachlorobis(ethylene)diplatinum [21] (0·1 g) and the appropriate cyclopropane (0·2 g) under dry ether was warmed to reflux for 1—3 h. The pale yellow to white insoluble product was filtered, washed with ether, and dried *in vacuo*. The ether solution was examined by g.l.c.

(ii) The dichloro(propane-1,3-diyl)platinum derivatives formed in (i) (0·1 g) in chloroform (1 ml) and pyridine (0·1 g) was stirred for a few minutes. The derived bis(pyridine) complex was chromatographed on silica gel or alumina usually with chloroform as solvent, and the recovered material recrystallised either from ethanol, or from a benzene–hexane mixture.

Dichloro(2-*phenylpropane*-1,3-*diyl*)*platinum*, yield 90%, dec. 135° (Found: C, 28·2; H, 2·7; Cl, 18·3; Pt, 51·1. $C_9H_{19}Cl_2Pt$ requires: C, 28·1; H, 2·6; Cl, 18·5; Pt, 50·8%). I.r.: 1605m, 1495m, 1420w, 1385w, 1355w, 1310w, 1295w, 1260m, 1205w, 1125m, 1079m, 1070m, 1035s, 1005w, 905w, 805w, 770m, 695s cm^{-1}.

trans-*Dichlorobis*(*pyridine*)(2-*phenylpropane*-1,3-*diyl*)-*platinum* (**4**, R = Ph).—Yield 65%, m.p. 130° (from ethanol). (Found: C, 41·7; H, 3·7; N, 5·2; Cl, 13·2; Pt, 36·6. $C_{19}H_{20}Cl_2N_2Pt$ requires: C, 42·1; H, 3·7; N, 5·2; Cl, 13·0; Pt, 36·0%). I.r.: 3080m, 3000m, 2940m, 1603s, 1493m, 1487m, 1450s, 1358w, 1260w, 1240m, 1219s, 1155m, 1072s, 1044s, 1015s, 908w, 757s, 697s, and 337 cm^{-1}.

Dichloro[2(o-*nitrophenyl*)*propane*-1,3-*diyl*]*platinum*.—Yield 80%, dec. 148° (Found: C, 25·3; H, 2·0; N, 3·4. $C_9H_9Cl_2NO_2Pt$ requires: C, 25·2; H, 2·1; N, 3·3%). I.r.: 1608m, 1575w, 1520s, 1508sh, 1415w, 1350s, 1138m, 1100m, 1027m, 856m, 787m, 745m cm^{-1}.

trans-*Dichlorobis*(*pyridine*)[2(o-*nitrophenyl*)*propane*-1,3-*diyl*]*platinum*, (**4**, R = *o*-$NO_2C_6H_4$).—Yield 89%, from ethanol, dec. 220°) Found: C, 38·8; H, 3·4; N, 7·3. $C_{19}H_{19}Cl_2N_3O_2Pt$ requires: C, 38·9; H, 3·2; N, 7·2%). I.r.: 1605s, 1575w, 1520s, 1508m, 1487w, 1452s, 1365m, 1250w, 1223w, 1217m, 1074s, 1046m, 1018m, 846m, 787m, 761s, 740m, 695s, and 345 cm^{-1}.

Dichloro(2-*benzylpropane*-1,3-*diyl*)*platinum*.—Yield 90%, dec, 123° (Found: C, 30·0; H, 2·9; Cl, 17·6. $C_{10}H_{12}Cl_2Pt$ requires: C, 30·2; H, 3·0; Cl, 17·8%). I.r.: 1609m, 1496s, 1455m, 1410w, 1148m, 1115w, 1096s, 1070w, 1033m, 745m, 700s cm^{-1}.

trans-*Dichlorobis*(*pyridine*)(2-*benzylpropane*-1,3-*diyl*)*platinum* (**4**, R = $PhCH_2$).—Yield 55%, m.p. 114° (from benzene–hexane) (Found: C, 43·2; H, 4·0; N, 5·2. $C_{20}H_{22}Cl_2N_2Pt$ requires: C, 43·2; H, 4·0; N, 5·0%). I.r.: 1605s, 1495m, 1485m, 1450s, 1360w, 1245w, 1220m, 1155w, 1100w, 1075s, 1045m, 1015m, 760s, 700s, and 341 cm^{-1}.

Dichloro(1-p-*tolylpropane*-1,3-*diyl*)*platinum*.—Yield 85%, dec. 125° (Found: C, 28·1; H, 3·0; Cl, 18·6. $C_{10}H_{12}Cl_2Pt$ requires: C, 30·2; H, 3·0; Cl, 17·8%). I.r.: 1605m, 1510m, 1445m, 1420m, 1380w, 1350w, 1310w, 1260w, 1210w, 1185m, 1120m, 1100w, 1035m, 1020m, 905w, 820s, 720w cm^{-1}.

trans-*Dichlorobis*(*pyridine*)(1-p-*tolylpropane*-1,3-*diyl*)*platinum* (**7**).—Yield 85%, from benzene–hexane, dec. 105—107° (Found: C, 43·1; H, 4·1; N, 4·9. $C_{20}H_{22}Cl_2N_2Pt$ requires: C, 43·2; H, 4·0; N, 5·0%). I.r.: 2980w, 2920m, 2900m, 1600s, 1505m, 1485m, 1445s, 1350w, 1260w, 1220m,sh, 1215m, 1185w, 1150w, 1035w, 1105w, 1075m,sh, 1070s, 1040s, 1015s, 900w, 880w, 840w, 825m, 765m,sh, 760m, 720w, 700s, and 333 cm^{-1}.

Dichloro(2-n-*hexylpropane*-1,3-*diyl*)*platinum*.—Yield 80%, dec. 120° (Found: C, 27·5; H, 4·6; Cl, 17·9. $C_9H_{18}Cl_2Pt$ requires: C, 27·5; H, 4·6; Cl, 18·1%). I.r.: 2860s, 1450s, 1400m, 1370m, 1135m, 1085s, and 715 cm^{-1}.

trans-*Dichlorobis*(*pyridine*)(2-n-*hexylpropane*-1,3-*diyl*)-*platinum* (**5**).—Yield 80% from benzene-hexane, darkened 125°, dec. 220° (Found: C, 41·1; H, 5·3; N, 5·4. $C_{19}H_{28}N_2PtCl_2$ requires: C, 41·4; H, 5·1; N, 5·1%). I.r.: 2900s, 1595s, 1480m, 1460w, 1440s, 1370w, 1350w, 1230m, 1210s, 1150m, 1130w, 1090w, 1065m, 1010m, 750s, 690s, and 340 cm^{-1}.

Dichloro(trans-1,2-*diphenylpropane*-1,3-*diyl*)*platinum*.—Yield 80%, dec. 163° (Found: C, 39·3; H, 3·4, Cl, 15·3. $C_{15}H_{14}Cl_2Pt$ requires: C, 39·2; H, 3·0; Cl, 15·4%). I.r.: 1602m, 1494m, 1450m, 1417w, 1295w, 1230w, 1185w, 1160w, 1125m, 1078w, 1051m, 1034m, 1004m, 914w, 865w, 835w, 758s, 702s, 692s cm^{-1}.

trans-*Dichlorobis*(*pyridine*)(trans-1,2-*diphenylpropane*-1,3-*diyl*)*platinum* (**8**).—Yield 65%, (from ethanol) m.p. 116° (Found: N, 4·6. $C_{25}H_{24}Cl_2N_2Pt$ requires: N, 4·5%). I.r.: 1602m, 1490m, 1448s, 1217m, 1154w, 1070m, 1043m, 1014m, 786w, 755s, 696s and 342 cm^{-1}.

Dichloro(trans-2-*n-butyl*-1-*methylpropane*-1,3-*diyl*)*platinum*.—Yield 60%, m.p. (dec.) 119° (Found: C, 25·1; H, 4·2. $C_8H_{16}Cl_2Pt$ requires C, 25·4; H, 4·2%). I.r.:

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[21] J. Chatt and M. L. Searle, *Inorg. Synth.*, 1957, **5**, 210.

2900s, 1445m, 1420m, 1360m, 1140m, 1095m, 1070m, 1020m, 975w, and 725w cm^{-1}.

Dichlorobis(pyridine)(trans-2-*n-butyl*-1-*methylpropane*-1,3-*diyl)platinum*, (**9**).—Prepared and purified by t.l.c. R_f 0·7 in $CHCl_3$ on silica gel proved rather unstable in solution. By working rapidly the n.m.r. spectrum could be recorded, but the substance was not analysed.

Tetrachloro-μ-(2,2′-*ethylenedipropene*-1,3-*diyl*)-*diplatinum*.—Yield 95%, dec. 115° (Found: C, 16·9; H, 2·6; Cl, 20·3. $C_8H_{14}Cl_4Pt_2$ requires, 15·0; H, 2·2; Cl, 22·1%). I.r.: 2920m, 1615m, 1500w, 1450m, 1440m, 1420m, 1410m, 1095m, 1015m, 1825w, and 760 m cm^{-1}.

Tetrachlorotetra(pyridine)-μ-(2,2′-*ethylenedipropane*-1,3-*diyl*)-*diplatinum*, (**12**).—Yield 65% from benzene–hexane, dec. 155° (Found: C, 34·9; H, 3·4; N, 5·7%. $C_{28}H_{34}Cl_4N_4Pt_2$ requires: C, 35·1; H, 3·6; N, 5·9). I.r.: 2930m, 1615m, 1605m, 1490m, 1455s, 1405w, 1360w, 1250w, 1220m, 1155w, 1075m, 1045w, 950w, 875w, 775s, 765m and 695s cm^{-1}.

Reactions of (*Propane*-1,3-*diyl*)$PtCl_2$ *Complexes*.—(i) The complex (0·05 g) with potassium cyanide (0·2 g) in water (0·5 ml) slowly dissolved. The organic moiety extracted into ether (0·25 ml), analysed by g.l.c. contained in each case only the parent cyclopropane.

(ii) Dichloro(2-phenylpropane-1,3-diyl)platinum (0·07 g) with triphenylphosphine (0·1 g) in chloroform (5 ml) heated under reflux for 0·5 h gave after evaporation a white solid which was washed with hexane. The hexane extract contained only phenylcyclopropane by g.l.c. analysis. The solid, recrystallised from chloroform was identified as *cis*-dichlorobis(triphenylphosphine)platinum by comparison with an authentic sample.

(iii) Dichloro(2-phenylpropane-1,3-diyl)platinum (0·1 g) in chloroform (3 ml) at 0° was treated with carbon monoxide for 15 min and the solvent removed *in vacuo*. The remaining orange complex washed with hexane gave an extract containing only phenylcyclopropane (g.l.c.) but the residual solid, ν_{CO} 2120 cm^{-1}, decomposed in solution or in air to give a black residue.

Reaction of cis-1-*n-Butyl*-2-*methylcyclopropane with Zeise's Dimer*.—Tetrachlorobis(ethylene)diplatinum (0·31 g) and *cis*-1-n-butyl-2-methylcyclopropane (0·28 g) in ether (2 ml) was warmed to reflux during 3 h. The filtered complex, decomposed with aqueous potassium cyanide gave a product which by g.l.c. analysis contained none of the parent cyclopropane but two new products. Hydrogenation of the complex by shaking in ethanol under hydrogen gave a product containing two components the major (80%) having the same g.l.c. retention as n-octane by direct comparison. The ether reaction medium by g.l.c. analysis showed none of the original cyclopropane but the same two products as from KCN-decomposition of the complex and in the n.m.r. a broad proton signal at τ 4·9.

Reaction of Bicyclo[4.1.0]*heptane with Zeise's Dimer*.—Tetrachlorobis(ethylene)diplatinum (0·1 g) with bicyclo-[4,1,0]heptane (0·15 g) in ether (2 ml) warmed for 1 h gave an orange coloured complex, which when decomposed with aqueous KCN was shown to contain methylenecyclohexane, 1-methylcyclohexene, and cycloheptene as discussed above. The ethereal reaction solution contained these three olefins together with bicyclo[4.1.0]heptane. The olefins were synthesised for comparison.

We are grateful to British Petroleum for award of a studentship to K. G. P.

[2/075 *Received*, 13*th January*, 1972]