Some Cyclopropylplatinum Complexes

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The cyclopropylplatinum complex *cis*-$[Pt(\overline{CHCH_2CH_2})_2(PMe_2Ph)_2]$ has been prepared from *cis*-$[PtCl_2(PMe_2Ph)_2]$ and cyclopropyl-lithium. It reacts with methyl iodide to give $[Pt(\overline{CHCH_2CH_2})_2Me(I)(PMe_2Ph)_2]$, with allyl bromide or benzyl bromide to give $[PtBr_2(\overline{CHCH_2CH_2})_2(PMe_2Ph)_2]$, and with HCl to give *trans*-$[Pt(\overline{CHCH_2CH_2})Cl(PMe_2Ph)_2]$. The products of thermal decomposition of some of these complexes have been identified. The complex *trans*-$[Pt(\overline{CHCH_2CH_2})Cl(PMe_2Ph)_2]$ reacts with $Ag[NO_3]$ and $K[PF_6]$ to give the (1—3-η-allyl)platinum complex $[Pt(\eta\text{-}C_3H_5)(PMe_2Ph)_2][PF_6]$, and the corresponding 1-deuteriocyclopropylplatinum complex gives the (1—3-η-2-deuterioallyl)platinum complex.

CYCLOPROPYL derivatives of the transition elements have not been investigated extensively. The cyclopropyl-iron derivative $[Fe(C_3H_5)(\eta\text{-}C_5H_5)(CO)_2]$ has been shown to undergo reaction with electrophiles [1] such as sulphur dioxide and tetracyanoethylene to give expansion of the cyclopropyl ring, with $H[BF_4]$ to give the 1—2-η-propene complex $[Fe(\eta^2\text{-}CH_2{=}CHMe)(\eta\text{-}C_5H_5)(CO)_2][BF_4]$, and with a carbocation to remove H^- and give the allene complex ion $[Fe(\eta^2\text{-}CH_2{=}C{=}CH_2)(\eta\text{-}C_5H_5)(CO)_2]^+$. The cyclopropylnickel complex $[Ni(C_3H_5)(\eta\text{-}C_5H_5)(PPh_3)]$ also gives propene on treatment with acids.[2] Cyclopropyl-copper(I) complexes have been prepared in solution but not isolated,[3] and cyclopropylpalladium species have been suggested as short-lived reaction intermediates.[4] Thus the reaction of 1,2,3-triphenylcyclopropene with $[PdCl_2(NCPh)_2]$ is thought to involve a stereospecific σ-cyclopropyl- to 1—3-η-allyl-palladium rearrangement, as shown in equation (1).[4]

Following our general interest in oxidative-addition and reductive-elimination reaction of alkylplatinum complexes,[5] and in reactions of cyclopropane derivatives with platinum complexes,[6] we now report the synthesis and properties of some cyclopropyl-platinum(II) and -platinum(IV) complexes. A preliminary account of some of this work has been published.[7]

RESULTS AND DISCUSSION

The complex *cis*-di(cyclopropyl)bis(dimethylphenylphosphine)platinum(II) (1) was readily prepared by re-

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[1] W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **93**, 5299; A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *ibid.*, 1972, **94**, 4354; L. Cohen, W. P. Giering, D. Kenedy, C. V. Magatti, and A. Sanders, *J. Organometallic Chem.*, 1974, **65**, C57.

[2] J. M. Brown and K. Mertis, *J.C.S. Perkin II*, 1973, 1993.

[3] M. P. Periasamy and H. M. Walborsky, *J. Amer. Chem. Soc.*, 1975, **97**, 5930.

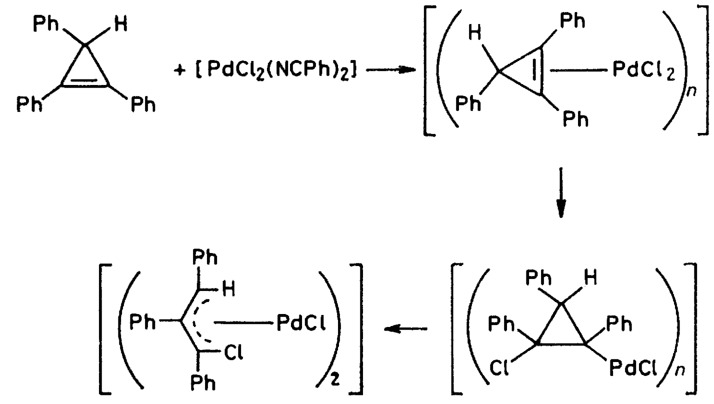
[4] P. Mushak and M. A. Battiste, *J. Organometallic Chem.*, 1969, **17**, P46; M. A. Battiste, L. E. Friedrich, and R. A. Fiato, *Tetrahedron Letters*, 1975, 45.

[5] M. P. Brown, A. Hollings, K. J. Houston, R. J. Puddephatt, and M. Rashidi, *J.C.S. Dalton*, 1976, 786.

[6] R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J.C.S. Chem. Comm.*, 1976, 626.

[7] R. L. Phillips and R. J. Puddephatt, *J. Organometallic Chem.*, 1977, **136**, C52.

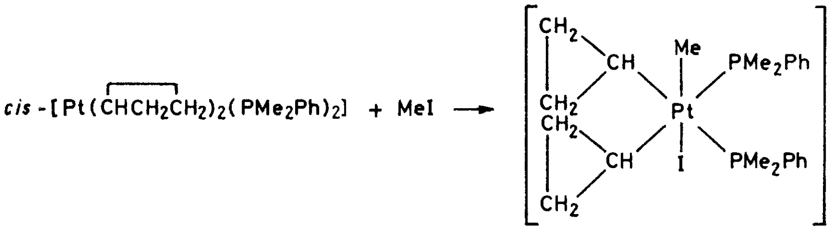
action (2). Reaction of complex (1) with hydrogen chloride then gave *trans*-$[\mathrm{Pt(\overline{CHCH_2CH_2})Cl(PMe_2Ph)_2}]$ (2). The stereochemistries of these σ-cyclopropylplatinum(II) complexes were readily determined from the ^1H n.m.r. spectra in the methylphosphorus region of the spectrum.[8] The cyclopropyl groups gave broad unresolved signals in the δ 0—1 p.p.m. region.



(1)

$$cis\text{-}[\mathrm{PtCl_2(PMe_2Ph)_2}] + 2\mathrm{Li(\overline{CHCH_2CH_2})} \longrightarrow \underset{(1)}{cis\text{-}[\mathrm{Pt(\overline{CHCH_2CH_2})_2(PMe_2Ph)_2}]} + 2\mathrm{LiCl} \quad (2)$$

Complex (1) underwent a simple oxidative-addition reaction with methyl iodide [equation (3)]. The methylplatinum resonance in the ^1H n.m.r. spectrum appeared as a triplet due to coupling with two equivalent ^{31}P atoms, and the coupling constant $^2J(PtH)$ 71 Hz is typical of a methylplatinum(IV) complex with the methyl group *trans* to iodide.[8] The methylphosphorus groups gave two doublets, indicating that the phosphine ligands are mutually *cis* and that there is no plane of symmetry containing the Pt–P bonds. Thus the stereochemistry (3), arising from the *trans* oxidative addition, is established.[8,9]

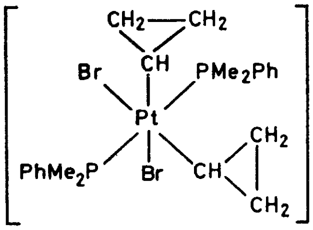


(3)

(3)

In contrast to this behaviour, reaction of (1) with allyl bromide or with benzyl bromide gave the complex $[\mathrm{PtBr_2(C_3H_5)_2(PMe_2Ph)_2}]$ of stereochemistry (4). The n.m.r. spectrum showed the presence of cyclopropyl groups and phosphine groups, but no allyl or benzyl signals were observed. The methylphosphorus resonance appeared as a triplet indicating that the phosphine ligands are mutually *trans* and this indicates the stereochemistry (4). The alternative structure with mutually *trans* cyclopropyl groups is considered unlikely since configurations with mutually *trans* alkyl groups are not favoured in platinum(IV) complexes.[8] It is interesting that both allyl bromide and benzyl bromide give oxidative-addition reactions with *cis*-$[\mathrm{PtMe_2(PMe_2Ph)_2}]$, but that *cis* rather than the more usual *trans* oxidative addition occurs.[10]

Thermal Stability of the Complexes.—The cyclopropylplatinum(IV) complexes have considerably higher thermal stability than similar ethylplatinum complexes. For example, the complex $[\mathrm{PtMeEt_2I(PMe_2Ph)_2}]$ decomposes rapidly at room temperature to give mostly ethane and ethylene by a mechanism involving initial β-elimination from an ethylplatinum group.[10] In contrast, (3) is stable in solution and the pure complex decomposes at the melting point of 142 °C to give methylcyclopropane and bicyclopropyl by intramolecular reductive elimination. Methylcyclopropane and bicyclopropyl were formed in the mol ratio 6 : 4, whereas, on the basis of statistical considerations only, the expected ratio would be 2 : 1. Thus it seems that cyclopropyl groups are



(4)

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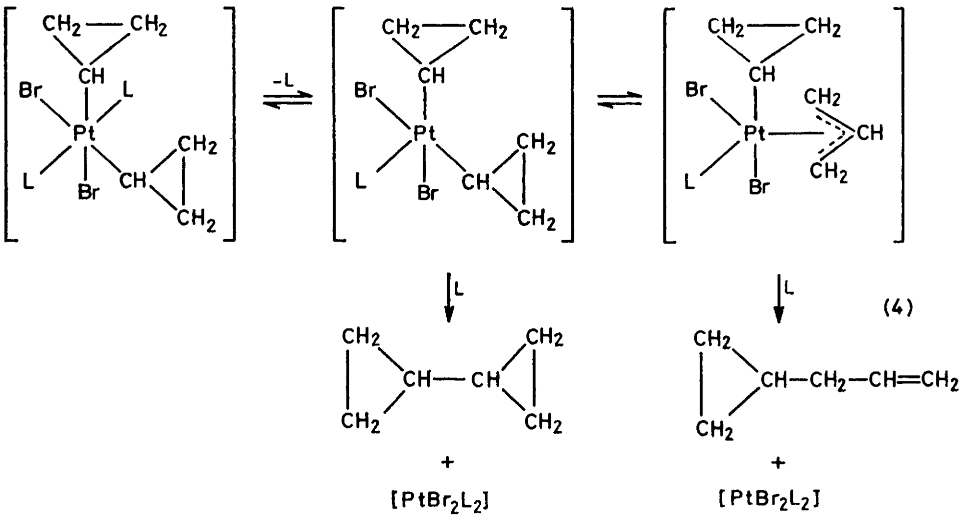
[8] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

[9] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1974, 2457.

[10] M. P. Brown, R. J. Puddephatt, C. E. E. Upton, and S. W. Lavington, *J.C.S. Dalton*, 1974, 1613.

eliminated slightly more readily than methyl groups on reductive elimination, and the order of ease of reductive elimination from $\mathrm{Pt^{IV}}$ can be obtained:[8-10] R = acetyl > allyl, ethyl > cyclopropyl > methyl > benzyl > phenyl > trifluoromethyl.

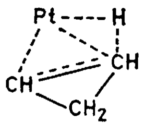
Some ring opening occurred on thermolysis of complex (4) to give a mixture of allylcyclopropane and bicyclopropyl in approximately equimolar proportions.



(4)

No biallyl was formed which is inconsistent with a mechanism involving cyclopropyl and allyl radicals and, from the known mechanisms of similar reductive eliminations and with the observation that σ-cyclopropyl to η-allyl rearrangements are possible,[7] we tentatively suggest mechanism (4) to account for the products. However it is not clear why allyl derivatives are not formed on decomposition of (3).

It is clear that cyclopropylplatinum complexes undergo β-elimination considerably less readily than do ethylplatinum complexes. This is probably due to the extra ring strain which would be introduced in the product, cyclopropene, of β-elimination from the cyclopropylplatinum group. However, although free cyclopropene is highly reactive, complexes of cyclopropene with $\mathrm{Pt^0}$ have high thermal stability[11] and it is clear that ring strain is relieved by complex formation. It is probable therefore that it is the transition state, in which the cyclopropene is partially formed but is only weakly coordinated, rather than the final product, which is particularly unstable, as illustrated below.

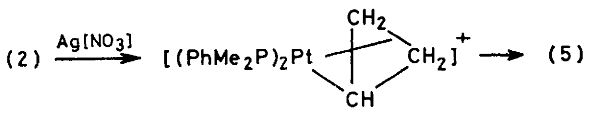


The β-elimination mechanism of decomposition probably occurs in the thermal decomposition of (1) which gives a mixture of cyclopropane and propene. A colourless platinum complex, which would be expected to be the cyclopropene complex $[\mathrm{Pt(C_3H_4)(PMe_2Ph)_2}]$, was formed also but we have been unable to purify and characterise it fully. This can be compared with the analogous decomposition of *cis*-$[\mathrm{PtEt_2(PMe_2Ph)_2}]$ when a mixture of ethene and ethane was evolved, and red polymeric products formed from the residual $[\mathrm{Pt(PMe_2Ph)_2}]$ were formed.[10]

Ring Opening of the Cyclopropyl Group.—The ability of $\mathrm{Pt^{II}}$ to insert into a carbon–carbon bond of cyclopropane is well known,[12,13] and a somewhat similar reaction might be expected to convert a σ-cyclopropylplatinum into 1—3-η-allylplatinum complex. This reaction was shown to occur on treating (2) with silver nitrate and then adding potassium hexafluorophosphate [equation (5)]. It seems that ionisation of the chloride

$$\mathit{trans}\text{-}[\mathrm{Pt}(\overline{\mathrm{CHCH_2CH_2}})\mathrm{Cl(PMe_2Ph)_2}] \xrightarrow[\mathrm{K[PF_6]}]{\mathrm{Ag[NO_3]}}$$
$$\underset{(5)}{[\mathrm{Pt}(\eta\text{-}\mathrm{C_3H_5})(\mathrm{PMe_2Ph})_2][\mathrm{PF_6}]} + \mathrm{AgCl} + \mathrm{K[NO_3]} \quad (5)$$

ligand is necessary for the reaction to occur, and an intermediate in which the far edge of the cyclopropyl group co-ordinates at the vacant site, and then undergoes ring opening, is suggested [equation (6)].



The prediction that no hydrogen migration occurs during the ring opening is found to be correct. Thus the complex *trans*-$[\mathrm{Pt}(\overline{\mathrm{CDCH_2CH_2}})\mathrm{Cl(PMe_2Ph)_2}]$ was prepared, and on treatment with $\mathrm{Ag[NO_3]}$ gave complex (6) as shown by the n.m.r. spectrum. Thus (5) gave $\delta(\mathrm{H_A})$ 2.93 [dd, $^3J(\mathrm{HH})$ 13, $^3J(\mathrm{PH})$ 8, $^2J(\mathrm{PtH})$ 42 Hz], $\delta(\mathrm{H_B})$ 4.30 [d, $J(\mathrm{HH})$ 7 Hz], and $\delta(\mathrm{H_C})$ 5.25 (m) p.p.m., while for (6) the signal due to $\mathrm{H_C}$ was

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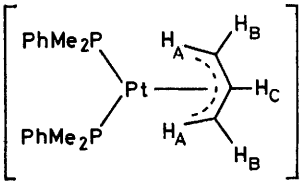
[11] J. P. Visser, A. J. Schipperijn, and J. Lukas, *J. Organometallic Chem.*, 1973, **47**, 433.

[12] D. B. Brown and V. A. Viens, *J. Organometallic Chem.*, 1977, **142**, 117.

[13] R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Organometallic Chem.*, 1978, **150**, 295.

absent and the H_A and H_B signals appeared as a doublet and singlet respectively with no HH coupling.



(5)

The observation that this cyclopropyl- to 1—3-η-allyl-platinum(II) transformation occurs readily lends support to the proposal of Battiste and his co-workers [4,14] that σ-cyclopropylmetal complexes may be intermediates in reactions where 1—3-η-allylmetal complexes are formed from cyclopropene or methylenecyclopropane derivatives.

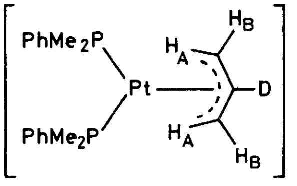
EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded using Perkin-Elmer R12b or Varian HA100 spectrometers. G.l.c.–mass spectrometry was carried out using a Pye series 104 gas chromatograph coupled with a Mikromass 601 mass spectrometer.

cis-*Di(cyclopropyl)bis(dimethylphenylphosphine)platinum*(II), (1).—Bromocyclopropane (3.62 g, 0.03 mol) in dry diethyl ether (50 cm^3) was added dropwise to a suspension of freshly prepared lithium shot (0.63 g, 0.09 mol) in diethyl ether (60 cm^3) cooled to 0 °C under an atmosphere of nitrogen. After stirring the mixture for 1 h, it was filtered under nitrogen to remove excess of lithium. The resulting solution of cyclopropyl-lithium was added dropwise to a suspension of *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (5.42 g, 0.01 mol) in diethyl ether (100 cm^3) at 0 °C under nitrogen. The mixture was allowed to warm to room temperature and stirred for 16 h, before hydrolysing with water. The ether layer was separated, dried, and then evaporated to give an oil. The oil was extracted with boiling light petroleum (b.p. 40—60 °C) and, on cooling the resulting solution to 0 °C, white crystals of *cis*-[Pt($\overline{\text{CHCH}_2\text{CH}_2}$)$_2$(PMe$_2$Ph)$_2$] were obtained, yield 1.46 g (26%), m.p. 104 °C; n.m.r. in C_6H_6, δ(MeP) 1.09 (d, $^2J + {}^4J$(PH) 7.5, ^3J(PtH) 19 Hz) and δ(C_3H_5) 0.75 p.p.m. (complex multiplet), integration PMe : C_3H_5 = 6 : 5 (Found: C, 47.7; H, 5.9. Calc. for $C_{22}H_{32}P_2Pt$: C, 47.7; H, 5.8%). The complex decomposed on heating to 120—130 °C.

trans-*Chloro(cyclopropyl)bis(dimethylphenylphosphine)-platinum*(II), (2).—A solution of HCl (0.14 mmol) in diethyl ether was added to a solution of (1) (0.08 g, 0.14 mmol) in diethyl ether (5 cm^3). The white precipitate which formed was recrystallised from benzene–light petroleum, to give *trans*-[Pt($\overline{\text{CHCH}_2\text{CH}_2}$)Cl(PMe$_2$Ph)$_2$], 0.03 g (38%), m.p. 156 °C; n.m.r. in C_6H_6, δ(MeP) 1.68 [t, $^2J + {}^4J$(PH) 6.6, ^3J(PtH) 30 Hz] and δ(C_3H_5) 0.35 p.p.m. (complex multiplet) (Found: C, 42.2; H, 5.1; Cl, 6.5. Calc. for $C_{19}H_{27}ClP_2Pt$: C, 41.6; H, 5.0; Cl, 6.5%).

(1—3-η-*Allyl)bis(dimethylphenylphosphine)platinum*(II) *Hexafluorophosphate*, (3).—A solution of Ag[NO$_3$] (0.453 mmol) in methanol was added to (2) (0.25 g, 0.453 mmol) in methanol (15 cm^3). After 10 min the solution was filtered to remove AgCl, and excess of K[PF$_6$] in water (2 cm^3) was added. The precipitate of [Pt(η-C_3H_5)(PMe$_2$Ph)$_2$][PF$_6$] was filtered off and recrystallised from methanol, yield 0.18 g (60%), m.p. 166 °C. It was identical (m.p. and n.m.r. spectrum) with an authentic sample.[15]



(6)

Di(cyclopropyl)bis(dimethylphenylphosphine)iodo(methyl)-platinum(IV), (3).—Methyl iodide (0.5 cm^3) was added to a solution of (1) (0.20 g) in benzene (0.5 cm^3). After 24 h at room temperature, the colourless crystals which formed were filtered off and recrystallised from dichloromethane–methanol, yield 0.21 g (83%), m.p. 142—144 °C (decomp.); n.m.r. in $CDCl_3$, δ(PMe) 1.95 [d, $^2J + {}^4J$(PH) 8, ^3J(PtH) 11 Hz] and 1.80 [d, $^2J + {}^4J$(PH) 8, ^3J(PtH) 11 Hz], δ(PtMe) 0.35 [t, ^3J(PH) 7.5, ^2J(PtH) 71 Hz], and δ(C_3H_5) 0.50 p.p.m. (complex multiplet) (Found: C, 40.2; H, 5.3; I, 17.8. Calc. for $C_{23}H_{35}IP_2Pt$: C, 39.7; H, 5.1; I, 18.2%).

Dibromodi(cyclopropyl)bis(dimethylphenylphosphine)-platinum(IV), (4).—Allyl bromide (0.5 cm^3) in diethyl ether (0.5 cm^3) was added to a solution of (1) (0.2 g) in benzene (0.5 cm^3). After 48 h at room temperature the colourless crystals which formed were filtered off and recrystallised from dichloromethane–methanol, yield 0.10 g (39%), m.p. 190—191 °C (decomp.); n.m.r. in $CDCl_3$, δ(PMe) 2.20 [t, $^2J + {}^4J$(PH) 7.2, ^3J(PtH) 16 Hz] and δ(C_3H_5) 0—1 p.p.m. (complex) (Found: C, 37.3; H, 4.5; Br, 22.9. Calc. for $C_{22}H_{32}Br_2P_2Pt$: C, 37.0; H, 4.5; Br, 22.4%). The same product was formed in a similar reaction using benzyl bromide instead of allyl bromide.

Thermal-decomposition Studies.—The complex (*ca.* 0.01 g) was heated slowly to the melting point, at which decomposition with effervescence occurred. The volatile products were collected on the vacuum line in a trap cooled in liquid nitrogen, and were then analysed by g.l.c.–mass spectrometry. Satisfactory agreement between the g.l.c. retention time and the mass spectrum of the component of the product mixture with those for an authentic sample was obtained in each case.

The involatile product of decomposition of (4) was identified as *cis*-[PtBr$_2$(PMe$_2$Ph)$_2$] by the n.m.r. spectrum, but in other cases the platinum-containing products could not be identified.

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[14] R. Noyori and H. Takaya, *Chem. Comm.*, 1969, 525.
[15] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1972, **11**, 1275.