# Reactions of Methylenecyclopropane with Some Hydridoplatinum(II) Complexes

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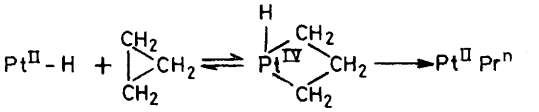
Methylenecyclopropane reacts with *trans*-[PtH($NO_3$)$L_2$] to give complexes with the (1—3-η-methylallyl)platinum cations [Pt($C_4H_7$)$L_2$]$^+$ (L = $PEt_3$, $PMe_2Ph$, or $PPh_3$). When L = $PEt_3$ or $PMe_2Ph$ the complexes contain the 1-methylallyl ligand only, but when L = $PPh_3$ the 2-methylallyl isomer is also formed. On the basis of deuterium-labelling studies, mechanisms for these reactions are proposed.

It is known that $Pt^{II}$ is able to insert into the C–C bond of cyclopropane derivatives to give platinacyclobutane derivatives.[1-3] From our interest in reactions of this kind, we have investigated reactions of some cyclopropyl derivatives with hydridoplatinum(II) complexes supposing that insertion reactions might occur by the general mechanism (1). With arylcyclopropanes and derivatives of cyclopropanecarboxylic acids these reactions did not occur readily, but methylenecyclopropane did react with hydridonitratoplatinum(II) complexes as described below, and in a preliminary communication.[4] Methylenecyclopropane has previously been shown to form stable olefin complexes with $Pt^0$,[5,6] and ring opening of methylenecyclopropane derivatives has been demonstrated with several transition-metal derivatives.[6-9] The mechanisms of such reactions have aroused much interest.

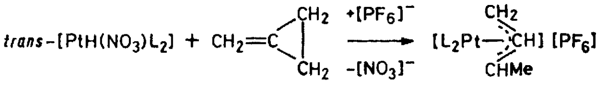


(1)

RESULTS AND DISCUSSION

Methylenecyclopropane did not react readily with complexes *trans*-[PtCl(H)$L_2$] (L = $PEt_3$, $PMe_2Ph$, or $PPh_3$) but reaction occurred at room temperature in each case with the corresponding nitrato-derivative *trans*-[PtH($NO_3$)$L_2$]. The greater reactivity of the nitrato-derivatives with alkenes is well established[10,11] and is ascribed to the ease of substitution of nitrate by the alkene to give an intermediate [PtH(alkene)$L_2$]$^+$. With methylenecyclopropane these intermediates could not be detected but the products were cationic 1—3-η-allylplatinum(II) complexes which were isolated as the hexafluorophosphate salts [equation (2)].

When L = $PEt_3$ or $PMe_2Ph$ the product was entirely the 1-methylallyl derivative as shown but, when L = $PPh_3$, a mixture of 1- and 2-methylallyl derivatives was formed in approximately equal amounts. The components were not separated but were readily identified



(2)

by the characteristic $^1H$ n.m.r. spectra (Table 1).[11-14] In each case the (1-methylallyl)platinum(II) complexes existed largely as the more stable *syn* isomer, although the *anti* isomer could also be detected in small amounts when L = $PEt_3$ or $PPh_3$.

The products arising from reaction of methylenecyclopropane with *trans*-[PtD($NO_3$)$L_2$] (L = $PEt_3$ or $PPh_3$) were investigated. When L = $PEt_3$ the product was shown to contain the (1—3-η-2-deuterio-1-methylallyl)platinum structure. The structure could not be determined unambiguously from the $^1H$ n.m.r. spectra since accidental overlap of peaks occurred, but investigation by $^{13}C$ n.m.r. spectroscopy was successful (Table 2). Assignments were made by comparison with $^{13}C$ n.m.r. spectra of other η$^3$-allyl derivatives.[15-18] It can be seen that the chief difference in the spectra of the ions [Pt($C_4H_7$)($PEt_3$)$_2$]$^+$ is in the intensity of the signal for $C^2$ (see Table 2 for nomenclature) which is much weaker in the deuterio-derivative. This is assigned as the carbon bound to deuterium and the lower intensity is due to loss of the Nuclear Overhauser Effect. The assignment is confirmed by the observation of further splitting of the $C^2$ signal in the deuterio-derivative due to the coupling $^1J$(DC). No lowering of intensity of the other signals was observed, suggesting that deuterium incorporation at the other carbon atoms of the allyl group was negligible.

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[1] F. J. McQuillin and K. G. Powell, *J.C.S. Dalton*, 1972, 2123.

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

[3] R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Organometallic Chem.*, in the press.

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

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

[6] M. Green and R. P. Hughes, *J.C.S. Chem. Comm.*, 1974, 686; M. Green, J. A. K. Howard, R. P. Hughes, S. C. Kellett, and P. Woodward, *J.C.S. Dalton*, 1975, 2007.

[7] R. Noyori, T. Ishigama, N. Hayashi, and H. Takaya, *J. Amer. Chem. Soc.*, 1973, **95**, 1674.

[8] P. Binger, *Angew. Chem. Internat. Edn.*, 1972, **11**, 309.

[9] R. Noyori and H. Takaya, *Chem. Comm.*, 1969, 525.

[10] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, 1970, 598.

[11] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1973, **12**, 357.

[12] J. Lewis, A. J. Deeming, and B. F. G. Johnson, *J.C.S. Dalton*, 1973, 1848.

[13] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1972, **11**, 1275.

[14] M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 1973, **12**, 991.

[15] B. E. Mann, R. Pietropaolo, and B. L. Shaw, *J.C.S. Dalton*, 1973, 2390.

[16] D. E. Axelson and C. E. Holloway, *J.C.S. Chem. Comm.*, 1973, 455.

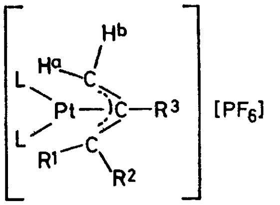
[17] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135.

[18] A. N. Nesmeyanov, E. I. Fedin, L. A. Fedorov, L. S. Isaeva, L. N. Lorens, and P. V. Petrovskii, *Doklady Akad. Nauk S.S.S.R.*, 1974, **216**, 816.

Our sample of *trans*-[PtD(NO$_3$)(PPh$_3$)$_2$] contained some 40% hydridoplatinum impurity but the $^1$H n.m.r. spectra of the products with methylenecyclopropane were sufficient to confirm the structures. Thus the signal due to the hydrogen atom R$^3$ (see Table 1) of the *syn*-1-methylallyl isomer was considerably weaker than for the unlabelled analogue indicating again the (2-deuterio-1-methylallyl)platinum structure. For the (2-methylallyl)platinum complex the methyl signal appears as a singlet and was somewhat weaker and broader (width at half-height 8 Hz) for the deuteriated complex than for the unlabelled species for which the width at half-height was 5 Hz. Thus, although the deuterium coupling was not fully resolved, the (2-deuteriomethylallyl)platinum structure is indicated.

TABLE 1

Hydrogen-1 n.m.r. spectra of the complexes in CDCl$_3$ solution

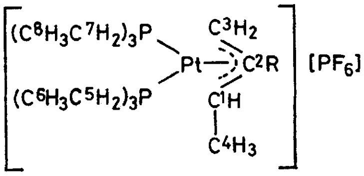


| L | R$^1$ | R$^2$ | R$^3$ | δ(H$^a$) | δ(H$^b$) | δ(R$^1$) | δ(R$^2$) | δ(R$^3$) |
|---|---|---|---|---|---|---|---|---|
| | | | | | | p.p.m. | | |
| PMe$_2$Ph [a] | H | H | H | 2.98 (dd) [b] | 4.32 (d) | | | 5.28 (m) |
| PMe$_2$Ph [c] | H | Me | H | 2.85 (dd) [d] | 4.0 | 4.0 | *e* | 4.99 |
| PPh$_3$ | H | Me | H | 2.92 (dd) [f] | 3.28 | 3.85 | 1.28 (dd) [g] | 5.29 (m) |
| PPh$_3$ | Me | H | H | 2.6 | *e* | 8.9 | 4.4 | 5.5 |
| PPh$_3$ | H | H | Me | 3.12 (d) [h] | 3.44 | | | 2.00 [i] |
| PEt$_3$ [j] | H | Me | H | 3.55 | 3.55 | 4.65 | *e* | 4.45 (m) |

[a] δ(MeP) 1.81 p.p.m. [d, *J*(PH) 9, *J*(PtH) 37 Hz]. [b] *J*(HH) 13, *J*(PH) 8 Hz. [c] δ(MeP) 1.90 [d, *J*(PH) 10, *J*(PtH) 40Hz] and 1.68 p.p.m. [d, *J*(PH) 10, *J*(PtH) 37 Hz]. [d] *J*(HH) 13, *J*(PH) 9 Hz. [e] Obscured. [f] *J*(HH) 12, *J*(PH) 7 Hz. [g] *J*(HH) 7, *J*(PH) 4 Hz. [h] *J*(PH) 9 Hz. [i] *J*(PtH) 62 Hz. [j] δ(CH$_2$P) 2.05 (m) and δ(C*H*$_3$CH$_2$) 1.08 (m) p.p.m.

TABLE 2

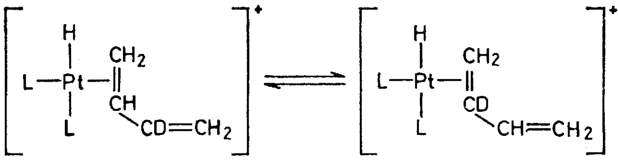
Carbon-13 n.m.r. spectra of the complexes



| | R = H | | R = D | |
|---|---|---|---|---|
| Atom | δ/p.p.m. | Intensity [a] | δ/p.p.m. | Intensity [a] |
| C$^1$ | 54.77 (d)<br>*J*(PC) 27.6 [b]<br>*J*(PtC) 86 | 0.12 | 54.6 (d)<br>*J*(PC) 28.0<br>*J*(PtC) 86 | 0.14 |
| C$^2$ | 111.49 (t) [c]<br>*J*(PC) 6 | 0.11 | 111.38 [c] | 0.04 |
| C$^3$ | 80.05 (d)<br>*J*(PC) 25.8<br>*J*(PtC) 74 | 0.16 | 79.80 (d)<br>*J*(PC) 26.0<br>*J*(PtC) 74 | 0.18 |
| C$^4$ | 14.88 | | 14.70 | |
| C$^5$,C$^7$ | 18.50 (d),<br>18.82 (d)<br>$^1$*J*(PC) 33.4<br>$^2$*J*(PtC) 69.5 | 1 | 18.36 (d),<br>18.68 (d)<br>$^1$*J*(PC) 33.3<br>$^2$*J*(PtC) 70.5 | 1 |
| C$^6$,C$^8$ | 8.28<br>*J*(PtC) 23.9 | 0.93 | 8.17<br>$^2$*J*(PtC) 25.0 | 0.99 |

[a] Total intensity with respect to the total intensity of peaks due to C$^5$ and C$^7$. [b] *J* values in Hz. [c] Low-intensity peak at δ 117.5 p.p.m. due to C$^2$ of *anti* isomer.

We interpret these results by the mechanism shown in the Scheme. The 1-methylallyl derivative is formed by addition of the Pt–H bond to the double bond of methylenecyclopropane to give a (cyclopropylmethyl)platinum(II) complex. Ring opening occurs next to give a but-3-enylplatinum(II) complex, which by β-elimination and reinsertion rearranges to the (1—3-η-1-methylallyl)platinum complex. There are good precedents for each of these steps but our attempts to prepare (cyclopropylmethyl)platinum complexes by alternative methods and so to demonstrate directly the sequence of reactions have been unsuccessful.[6,10-12,19,20] It should be noted that a co-ordinatively unsaturated platinum centre is required for all the steps, and that the proposed intermediate (4) must undergo insertion of the co-ordinated C=C bond into the Pt–H bond much faster than it undergoes the intramolecular isomerisation (3).[19]



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Interestingly, Attig[21] has recently reported the reaction (4), in which rearrangement of the but-3-enylplatinum derivative to the 1—3-η-allylplatinum isomer is presumably prevented by co-ordination of a carbonyl group, thus leaving no vacant co-ordination site on platinum.

When L = PPh$_3$ the reaction (see Scheme) to give the (2-methylallyl)platinum derivative is thought to proceed by insertion of the double bond into the Pt–H bond in the opposite sense to give a (1-methylcyclopropyl)platinum(II) species, which then undergoes direct ring opening to give the product. We have been able

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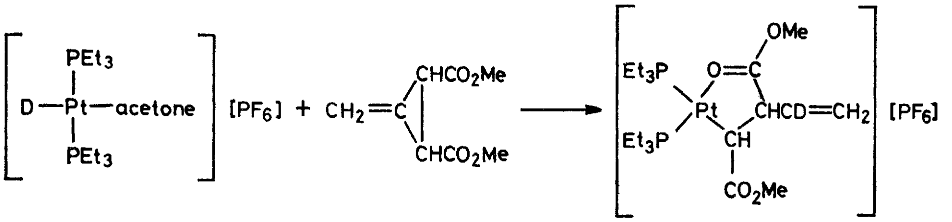
[19] J. M. Brown, J. A. Conneely, and K. Mertis, *J.C.S. Perkin II*, 1974, 905; J. M. Brown and K. Mertis, *ibid.*, 1973, 1993.

[20] S. Chemaly and J. M. Pratt, *J.C.S. Chem. Comm.*, 1976, 988.

[21] T. G. Attig, *J. Organometallic Chem.*, 1978, **145**, C13.

to demonstrate that cyclopropylplatinum to η-allylplatinum rearrangements occur readily when there is a vacant co-ordination site at platinum,[4] and further evidence for this mechanism is found in the work of Attig [equation (5)].[21] Again co-ordination of the carbonyl group to platinum presumably prevents the ring-opening reaction from occurring. It is interesting that Attig only found this mode of reaction for the triphenylphosphine complex, in the same way that we find formation of the (2-methylallyl)platinum complex only when L = $PPh_3$. There is no obvious explanation of this difference in the orientation of the initial addition of the Pt–H bond to the double bond of methylenecyclopropane species with L = $PPh_3$ and L = $PEt_3$ or $PMe_2Ph$.



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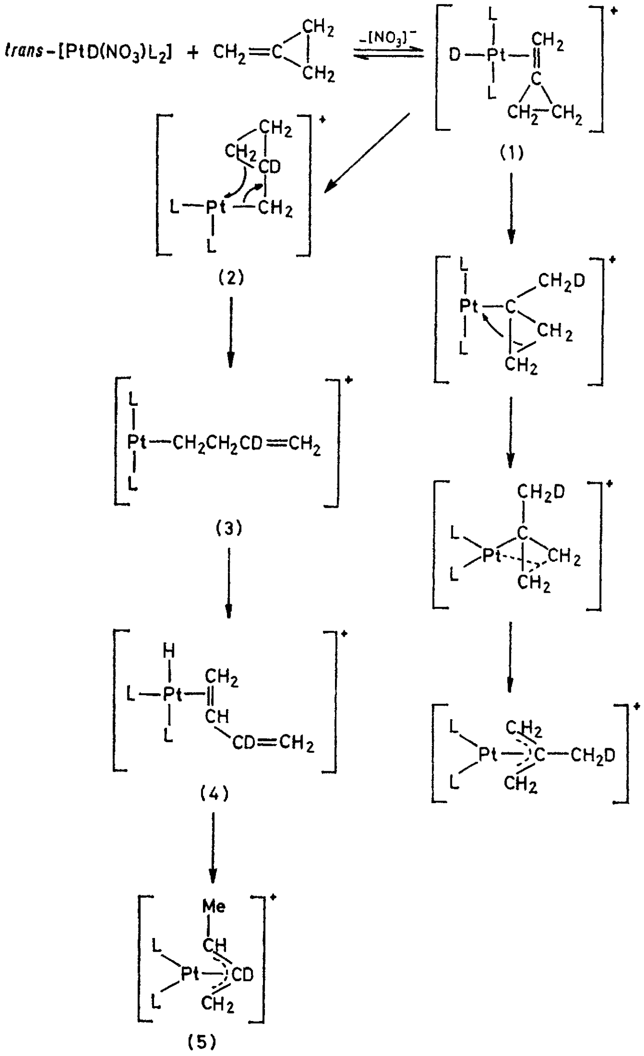

Scheme

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded using Perkin-Elmer R12b and Varian HA 100 spectrometers, $^{13}C$ n.m.r. spectra using a Varian XL 100 spectrometer.

Methylenecyclopropane was prepared using the literature method.[22] Impurities of methylcyclopropene were removed by stirring the impure gas over a 1% solution of potassium t-butoxide in dimethyl sulphoxide for 2—3 h.[23] The purity was determined by n.m.r. spectroscopy before use.[24] Hydridoplatinum(II) complexes were prepared by literature methods.[25,26]

*trans*-$[PtCl(D)(PEt_3)_2]$.—To a solution of *trans*-$[PtCl(H)(PEt_3)_2]$ (0.43 g) in tetrahydrofuran (thf) (5 $cm^3$) was added $D_2O$ (15 $cm^3$) and concentrated HCl (1 drop). The mixture was stirred at 70 °C for 1 h, then the organic solvent was evaporated *in vacuo* to leave a suspension of the *product* (80%), which was filtered off and dried *in vacuo*: ν(PtD) at 1 593 $cm^{-1}$, ν(PtH) absent.

(1—3-η-1-*Methylallyl*)*bis*(*triethylphosphine*)*platinum*(II) *Hexafluorophosphate*.—Methylenecyclopropane (36 $cm^3$) was condensed into a Carius tube containing a solution of *trans*-$[PtH(NO_3)(PEt_3)]$ (0.195 g) in benzene (3 $cm^3$). The tube was sealed. After 48 h at 25 °C the tube was opened and the yellow oil which had formed was dissolved in water and added to excess of aqueous $K[PF_6]$. The white precipitate of the *product* was recrystallised from ethanol, yield 0.10 g, m.p. 233 °C (decomp.) (lit.,[12] 219—222 °C) (Found: C, 30.4; H, 6.1; F, 18.0; Pt, 31.7. Calc. for $C_{16}H_{37}F_6P_3Pt$: C, 30.4; H, 5.9; F, 18.05; Pt, 30.9%).

(1—3-η-2-*Deuterio*-1-*methylallyl*)*bis*(*triethylphosphine*)-*platinum*(II) *Hexafluorophosphate*.—To a solution of *trans*-$[PtCl(D)(PEt_3)_2]$ (0.495 g) in dry thf (3 $cm^3$) was added a solution of $Ag[NO_3]$ (0.165 g) in $D_2O$ (0.5 $cm^3$) and thf (2 $cm^3$). The mixture was filtered to remove AgCl, and the filtrate was transferred to a Carius tube. Methylenecyclopropane (25 $cm^3$) was condensed into the tube and the tube sealed and left to stand at 25 °C for 48 h. The solution was evaporated and the residue was dissolved in ethanol and then treated with excess of aqueous $K[PF_6]$. The precipitate of the *product* was recrystallised from methanol, yield 0.35 g.

(1—3-η-*Methylallyl*)*bis*(*triphenylphosphine*)*platinum*(II) *Hexafluorophosphate*.—This was prepared in a similar way from *trans*-$[PtCl(H)(PPh_3)_2]$ (0.364 g), $Ag[NO_3]$ (0.081 g),

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[22] R. Koster, S. Arora, and P. Binger, *Angew. Chem. Internat. Edn.*, 1969, **8**, 205.

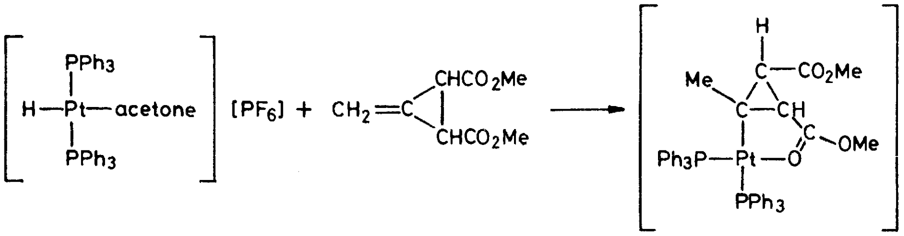
[23] I. S. Krull and D. R. Arnold, *Org. Prep. Procedures*, 1969, **1**, 283.

[24] B. C. Anderson, *J. Org. Chem.*, 1962, **27**, 2720.

[25] H. C. Clark and H. Kurosawa, *J. Organometallic Chem.*, 1972, **36**, 399.

[26] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

and methylenecyclopropane (20 cm$^3$), followed by excess of K[PF$_6$], yield 0.284 g (Found: C, 52.0; H, 4.3. Calc. for $C_{40}H_{37}F_6P_3Pt$: C, 52.2; H, 4.1%).



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*Bis(dimethylphenylphosphine)*(1—3-η-1-*methylallyl*)-*platinum*(II) *Hexafluorophosphate*.—Methylenecyclopropane (36 cm$^3$) was condensed into a Carius tube containing a solution of *trans*-[PtCl(H)(PMe$_2$Ph)$_2$] (0.46 g) in acetone (9 cm$^3$). Silver nitrate (0.146 g) dissolved in the minimum volume of water was added to the frozen (−196 °C) reaction mixture. The tube was then sealed *in vacuo* and set aside at 25 °C for 48 h. The solution was filtered to remove AgCl and the solvent was evaporated from the filtrate. The residue was dissolved in hot ethanol (5 cm$^3$) and added to excess of K[PF$_6$] in water. The white precipitate of the *product* was recrystallised from ethanol, yield 0.22 g, m.p. 135—136 °C (decomp.) (lit.,[13] 135—137 °C) (Found: C, 35.8; H, 4.2. Calc. for $C_{20}H_{29}F_6P_3Pt$: C, 35.8; H, 4.35%).

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