Transition Metal–Carbon Bonds. Part 56.[1] Attack on Allene Complexes of Type *cis*-$[PtCl_2(PR_3)(C_3H_4)]$ by the Ambident Nucleophile, Acetoxime: Crystal Structure of $[PtCl(PMe_2Ph)\{ON(=CMe_2)CH=CMe\}]$ †

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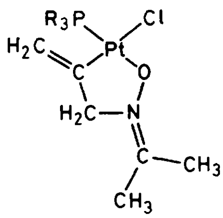
Treatment of *cis*-$[PtCl_2(PMe_2Ph)(C_3H_4)]$ with $Me_2C=NOH$ gives the title complex, the formation of which involves nucleophilic attack by nitrogen, a 1—3-hydrogen shift, and ring closure. Crystals are monoclinic, space group $P2_1/c$, with a = 10.208(3), b = 11.056(3), c = 15.305(2) Å, β = 102.49(2)°, and Z = 4; the final R factor was 0.025 for 3 171 independent F_o. A $^{31}P-\{^1H\}$ n.m.r. study of the conversion shows that some (unidentified) intermediates and minor products are formed.

We have shown that compounds of type *cis*-$[PtCl_2(PR_3)$(allene)] or *cis,cis*-$[Pt_2Cl_4(PR_3)_2$(buta-1,3-diene)] are attacked by amines to give ring compounds: four- or eight-membered with the allene complexes,[2] or two fused five-membered rings with the buta-1,3-diene complex.[3] In some cases zwitterionic intermediates were detected and/or isolated. In effect the diene–platinum complexes are extremely powerful alkylating agents, for example *cis,cis*-$[Pt_2Cl_4(PMe_2Ph)_2(\mu-C_4H_6)]$ alkylates dimethylamine rapidly even at −78 °C. These platinum–olefin complexes are probably more powerful alkylating agents than, for example, trifluoromethanesulphonates.

De Renzi *et al.*[4] have recently described the crystal structure of a complex of analogous type containing a four-membered ring, *viz.* $[PtCl(PPh_3)\{C(=CMe_2)CH_2NMe_2\}]$ formed by dimethylamine attack on a dimethylallene–platinum complex: this follows their extensive work in the area of amine attack on olefins co-ordinated to platinum. Green and co-workers[5] have also studied attack by amines on ethylene–platinum complexes of type $[PtCl_2(PR_3)(C_2H_4)]$ to give four-membered ring chelate compounds, and have recently extended their studies to platinum compounds containing substituted alkenes.[6]

We have now studied the alkylation of an oxime, acetoxime, by the allene complexes *cis*-$[PtCl_2(PR_3)(C_3H_4)]$ (PR_3 = PMe_2Ph or PEt_3). Oximes are ambidentate nucleophiles and their alkylation has been studied extensively.[7] Alkylation by alkyl halides or alkyl sulphates preferentially gives the *O*-alkyl ether, although *N*-alkylation to give a nitrone or *N*-oxide is a commonly occurring side reaction. By analogy with the work on attack by amines (see above) we expected that the oxime would first attack the terminal carbon atom of the co-ordinated allene with one nucleophilic centre (either N or O) but then the other nucleophilic centre (either O or N) would displace the labile chlorine in the *trans* position to the •• iary phosphine to give a five-membered ring chelate, either of type (1) or of type (2). We could not predict with any degree of certainty whether *N*-alkylation, giving (1), or *O*-alkylation, giving (2), would be preferred since several factors influence the position of attack on ambident nucleophiles, although the 'hardness' or 'softness' of the reaction centres appears to be a major factor.[8] The allene–platinum complex is probably a very soft, *i.e.* polarisable electrophile, and therefore one might expect *N*-alkylation to be preferred.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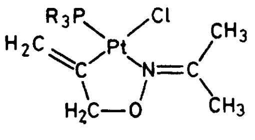
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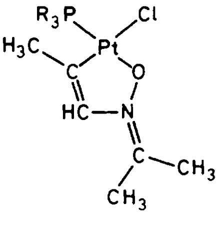
Results and Discussion

We initially studied the action of $Me_2C=NOH$ on *cis*-$[PtCl_2(PMe_2Ph)(C_3H_4)]$ in $CDCl_3$ by $^{31}P-\{^1H\}$ n.m.r. spectroscopy, with or without the presence of a base (sodium propan-2-oxide). At low temperatures, *e.g.* −60 to −20 °C, a mixture of phosphorus-containing species formed rapidly (see later), but at 20 °C a product characterised by δ(P) −14.5 p.p.m. and ^1J(Pt–P) 4 412 Hz predominated (up to *ca.* 80% of the total product). The yield of this product, as judged from the $^{31}P-\{^1H\}$ n.m.r. study, was virtually the same whether one or two moles of acetoxime per platinum were used, and addition of sodium propan-2-oxide made the yield worse. On a preparative scale we therefore treated a chloroform solution of the allene complex with acetoxime at *ca.* 20 °C. The species characterised by δ(P) −14.5 p.p.m. and ^1J(Pt–P) 4 412 Hz proved to be difficult to purify and was only isolated in *ca.* 20% yield (see Experimental section). Elemental analytical data (C, H, N, and Cl) were in good agreement with those expected for $C_{14}H_{21}ClNOPPt$ and the i.r. absorption spectrum (Nujol mull) showed a strong band at 296 cm^{-1}, assigned to ν(Pt–Cl). However, the ^1H and $^1H-\{^{31}P\}$ n.m.r. data showed the presence of a methyl and a methine group and that neither of the structures (1) or (2) is correct. The ^1H n.m.r. data were in agreement with either structure (3) or structure (4), *i.e.* a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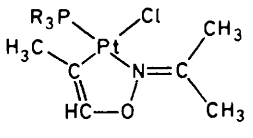
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† Chloro(1,4-dimethyl-3-oxo-3-azapenta-1,3-dien-1-yl-C^1O)-dimethylphenylphosphineplatinum.

Supplementary data available (No. SUP 23657, 23 pp.): structure factors, thermal parameters, H-atom co-ordinates, full bond length and angle data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

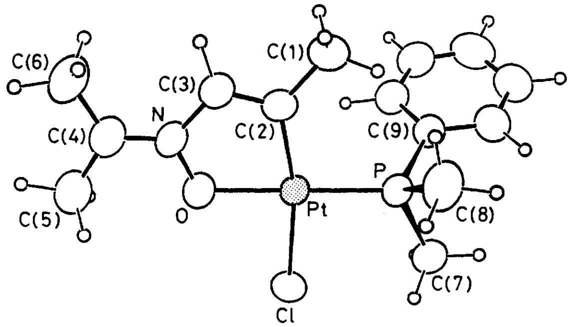

Figure. Molecular structure, showing the principal atomic numbering, of [PtCl(PMe$_2$Ph){ON(=CMe$_2$)CH=CMe}] (3)

1—3-hydrogen shift had occurred. The ^{1}H n.m.r. data (in CDCl$_3$) were as follows: δ 1.95 [^2J(PH) 11.0, ^3J(PtH) 40.4, PCH_3], 1.53 [J(PtH) 56, PtCCH$_3$], 6.73 [^3J(PtH) 61.5, PtC=CH], 2.41 and 2.27 p.p.m. [N=C(CH_3)$_2$]. The high value of ^1J(PtP), *viz.* 4 412 Hz, suggested that the phosphine was in the *trans* position to oxygen rather than nitrogen, *i.e.* structure (3) seemed more likely than (4). In order to establish this with certainty a crystal structure determination, by *X*-ray diffraction, was undertaken. This established that the structure was indeed (3; PR$_3$ = PMe$_2$Ph): the full structure is shown in the Figure, and Table 1 gives selected bond lengths and angles.

The co-ordination around Pt is, allowing for the effect of *C,O*-chelation, approximately square planar. The largest deviation from ideal geometry about Pt is the *trans* Cl–Pt–C(2) angle of 167.5(2)°, while the torsion angles * ω[P–Pt–C(2)–C(3)] and ω(Cl–Pt–O–N) are −177.3 and 173.1°, respectively. The absolute values of ω around the chelate ring are all <6.0°, and C(5)–C(4)–C(6) is coplanar (±1°) with C(3)–N–O. The C=N and C=C distances are normal and there are no remarkable bond lengths in the structure. It may be noted, however, that in the structure of the parent compound, *cis*-[PtCl$_2$(PMe$_2$Ph)(C$_3$H$_4$)],[9] the Cl *trans* to the η^2-allene is 2.316(3) Å from Pt; replacement of the η^2-C$_3$H$_4$ π interaction with Pt by a σ bond between C(2) and Pt consequent upon attack by the nucleophile leads to a lengthening of the Pt–Cl bond to 2.370(2) Å in (3). Similarly, the Pt–P bond in (3), where P is *trans* to O, is 0.050(5) Å shorter than that in the parent compound, where P is *trans* to Cl. The non-bonded intramolecular distances Pt···C(3) and Pt···N are 2.80 and 2.86 Å, respectively; there are no significant intermolecular contacts.

We have been unable to identify or isolate any of the intermediates in the conversion of *cis*-[PtCl$_2$(PMe$_2$Ph)(C$_3$H$_4$)] into (3) but report their ^{31}P-{^{1}H} n.m.r. parameters. The complex *cis*-[PtCl$_2$(PMe$_2$Ph)(C$_3$H$_4$)] in CDCl$_3$ at −60 °C shows δ(P) −9.2 p.p.m. and ^1J(PtP) 3 035 Hz. On adding one equivalent of acetoxime at −60 °C about half of this is converted into another species, δ(P) −20.3 p.p.m. and ^1J(PtP) 4 050 Hz, although minor species with δ(P) −11.1, −13.8, −20.0, and −24.3 p.p.m. are also produced. Little further change occurs in the temperature range −30 to −60 °C over a 1 h period although when the solution was warmed to 0 °C some of species (3) was produced. When stored at *ca.* −15 °C for 15 h species (3) was the major phosphorus-containing species and little further change occurred after a further period of 1 d at −15 °C. Minor species present in this solution showed δ(P) −17.8 p.p.m. and ^1J(PtP) 3 716 Hz, and δ(P) −24.1 and ^1J(PtP) 3 426 Hz (measured at −50 °C).

Table 1. Selected bond lengths (Å) and angles (°) for (3) with e.s.d.s in parentheses

Pt–Cl	2.370(2)	P–Pt–Cl	93.6(1)
Pt–P	2.200(2)	O–Pt–Cl	86.6(1)
Pt–O	2.059(4)	O–Pt–C(2)	81.0(2)
Pt–C(2)	1.991(6)	P–Pt–C(2)	98.8(2)
C(1)–C(2)	1.514(9)	P–Pt–O	179.7(1)
C(2)–C(3)	1.324(9)	Cl–Pt–C(2)	167.5(2)
C(3)–N	1.442(8)	C(1)–C(2)–C(3)	116.9(6)
N–O	1.350(6)	C(1)–C(2)–Pt	129.6(5)
N–C(4)	1.314(8)	Pt–C(2)–C(3)	113.4(5)
C(4)–C(5)	1.50(1)	C(2)–C(3)–N	118.6(6)
C(4)–C(6)	1.47(1)	C(3)–N–O	114.2(5)
P–C(7)	1.834(7)	N–O–Pt	112.4(3)
P–C(8)	1.837(6)	C(4)–N–C(3)	127.6(6)
P–C(9)	1.812(6)	C(4)–N–O	118.1(6)
C–C (phenyl)	1.36—1.42(1)	N–C(4)–C(5)	117.6(7)
	mean 1.39	N–C(4)–C(6)	122.2(7)
		C(5)–C(4)–C(6)	120.2(7)
		Pt–P–C(7)	115.2(2)
		Pt–P–C(8)	114.0(3)
		Pt–P–C(9)	116.2(2)

We have also shown that *cis*-[PtCl$_2$(PEt$_3$)(C$_3$H$_4$)] is attacked by acetoxime to give a product, almost certainly of type (3), characterised by its ^{31}P-{^{1}H} n.m.r. parameters: δ(P) 5.5 p.p.m. and ^1J(PtP) 4 255 Hz. It was not isolated in a pure state. In the conversion of complexes of type *cis*-[PtCl$_2$(PR$_3$)(C$_3$H$_4$)] to those of type (3) we suggest that nucleophilic attack by nitrogen on the co-ordinated allene is the first step, but do not know whether the 1–3-hydrogen shift occurs before, or after, cyclisation.

Experimental

The general techniques used were the same as in other recent papers from this laboratory.[2]

Action of Acetoxime on cis-[PtCl$_2$(PMe$_2$Ph)(C$_3$H$_4$)].—The oxime (24.7 mg) was added to a solution of the allene complex (150 mg) in a minimum amount of chloroform. The mixture was then filtered and evaporated under reduced pressure, after which light petroleum (b.p. 40—60 °C) was added and the mixture cooled to *ca.* −25 °C. This did not give crystals, so the mixture was evaporated to dryness and the residue dissolved in a minimum of acetone and n-hexane added. The solution was cooled to −25 °C and over several hours gradually gave the required compound (3; PR$_3$ = PMe$_2$Ph) (31.4 mg, 19%) as very pale brown prisms (Found: C, 35.05; H, 4.4; N, 2.85; Cl, 7.55. C$_{14}$H$_{21}$ClNOPPt requires C, 34.95; H, 4.4; N, 2.9; Cl, 7.55%).

Crystal Data.—C$_{14}$H$_{21}$ClNOPPt, M = 480.8, Monoclinic, space group $P2_1/c$, a = 10.208(3), b = 11.056(3), c = 15.305(2) Å, β = 102.49(2)°, U = 1 686.4(7) Å^3, Z = 4, D_c = 1.89 g cm^{-3}, $F(000)$ = 920, graphite-monochromated Mo-K_α radiation, λ = 0.710 69 Å, and μ(Mo-K_α) = 86.53 cm^{-1}.

Structure Determination.—Measurements were made on a crystal of dimensions 0.36 × 0.28 × 0.30 mm, using a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections having 35 < 2θ < 40°. Intensities of all independent reflections with 4 < 2θ < 45° were measured in the ω—2θ scan mode using scan speeds, according

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* The sign convention is that of W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

Table 2. Fractional co-ordinates (× 10^4) for non-hydrogen atoms of (3) with e.s.d.s in parentheses

Atom	x	y	z
Pt	2 789.7(2)	1 262.6(2)	2 261.8(1)
Cl	2 757(2)	638(2)	3 738(1)
P	3 927(2)	−334(2)	1 992(1)
O	1 734(4)	2 763(3)	2 513(2)
N	1 579(4)	3 585(4)	1 846(3)
C(1)	3 190(7)	1 760(6)	291(4)
C(2)	2 663(6)	2 125(6)	1 105(3)
C(3)	2 057(6)	3 188(6)	1 073(3)
C(4)	1 051(6)	4 638(6)	1 971(4)
C(5)	636(7)	4 841(6)	2 845(4)
C(6)	845(8)	5 592(6)	1 288(6)
C(7)	4 276(7)	−1 455(6)	2 895(4)
C(8)	5 600(6)	18(7)	1 799(4)
C(9)	3 150(6)	−1 247(6)	1 037(3)
C(10)	1 797(6)	−1 052(6)	595(4)
C(11)	1 219(7)	−1 789(6)	−101(4)
C(12)	1 924(9)	−2 684(7)	−394(4)
C(13)	3 253(8)	−2 928(7)	47(4)
C(14)	3 882(6)	−2 188(6)	752(4)

to a prescan intensity, between 2 and 29° min^{-1}, and with the scans running from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$. The 3 171 reflections with $I > 2\sigma(I)$ were used in the structure determination after correction for Lorentz, polarisation, and transmission factors ($A^* = 5.15$—12.13 for the full data set). Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms using the SHELX program system.[10] The H atoms, all of which were found in difference maps, were included in the calculation at idealised positions with C–H fixed at 1.08 Å. The refinement converged to $R = 0.025$ and $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.023$, employing the weighting scheme $w = 1/\sigma^2F_o$. A final difference map showed no significant residual electron density. Complex neutral-atom scattering factors were calculated from the analytical approximation and coefficients given in ref. 11. The final atomic co-ordinates and their standard deviations are given in Table 2.

Acknowledgements

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References

1 Part 55, A. R. H. Bottomley, C. Crocker, and B. L. Shaw, *J. Organomet. Chem.*, in the press.
2 J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 575.
3 J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1982, 457.
4 A. De Renzi, B. Di Blasio, G. Morelli, and A. Vitagliano, *Inorg. Chim. Acta*, 1982, **63**, 233 and refs. therein.
5 I. M. Al-Najjar, M. Green, S. J. S. Kerrison, and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1979, 311; I. M. Al-Najjar, M. Green, J. K. K. Sarhan, I. M. Ismail, and P. J. Sadler, *Inorg. Chim. Acta*, 1980, **44**, L187.
6 M. Green, J. K. K. Sarhan, and I. M. Al-Najjar, *J. Chem. Soc., Dalton Trans.*, 1981, 1565.
7 H. Metzger, in Houben-Weyl's 'Methoden der organischen Chemie,' Stickstoffverbindungen I, Teil 4, 4th edn., ed. E. Müller, Georg Thieme Verlag, Stuttgart, 1968, vol. 10/4, p. 217.
8 J. March, 'Advanced Organic Chemistry: Reactions, Mechanisms, and Structure,' 2nd edn., McGraw-Hill Kogakusha Ltd., Tokyo, 1977, p. 338.
9 J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 121.
10 G. M. Sheldrick, SHELX 76 Program System, University of Cambridge, 1976.
11 'International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

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