Structural and Spectroscopic Studies on Peroxymetallacyclic Complexes of Platinum †

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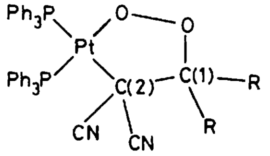
The ^{31}P and ^{13}C n.m.r. spectra of the adducts obtained from dioxobis(triphenylphosphine)platinum and tetracyanoethylene or 1,1-dicyano-2-methylpropene, $[\overline{Pt\{C(CN)_2CR_2OO}\}(PPh_3)_2]$ [R = CN (1a) and Me (1b)] respectively, have been examined. An *X*-ray structural study of the adduct (1b) shows a slightly distorted square-planar complex with the metallacyclic ring in a twist conformation.

Transient peroxymetallacyclic species have been considered as intermediates in rhodium-catalysed oxygenations of terminal olefins[1] where they might arise from reaction between the alkene and, for example, a peroxyrhodium species such as $RhCl(O_2)(PPh_3)_3$.[2] However, direct evidence for their involvement in these reactions is not available. In order to obtain more information about these little studied systems, we have examined the stable adducts (1a) and (1b) formed, respectively, from $[PtO_2(PPh_3)_2]$ and the electron-deficient alkenes tetracyanoethylene[3,4] and 1,1-dicyano-2-methylpropene.[4]



(1a); R = C≡N
(1b); R = Me

Table 1. Phosphorus-31 and ^{13}C n.m.r. data *

Signal	Compound (1a)	Compound (1b)
P_A	5.8, J(P–P) 21.5, $J(^{195}Pt–P)$ 2 990	7.6, J(P–P) 19.5, $J(^{195}Pt–P)$ 2 783
P_B	15.9, J(P–P) 21.5, $J(^{195}Pt–P)$ 3 392	18.0, J(P–P) 19.5, $J(^{195}Pt–P)$ 3 309
C_A	109.3, $J(^{195}PtCCC)$ 27.5	22.3, $J(^{195}PtCCC)$ 16.8
C_{B_1}	114.1 $J(^{195}PtCC)$ 62.8	119.1, $J(^{195}PtCC)$ 68.2
C_{B_2}	114.4, $J(^{195}PtCC)$ 47.1	119.4, $J(^{195}PtCC)$ 68.0

* Chemical shifts are in p.p.m. relative to H_3PO_4 for ^{31}P spectra and $SiMe_4$ for ^{13}C spectra; solvent in all cases is $CDCl_3$; J values are in Hz.

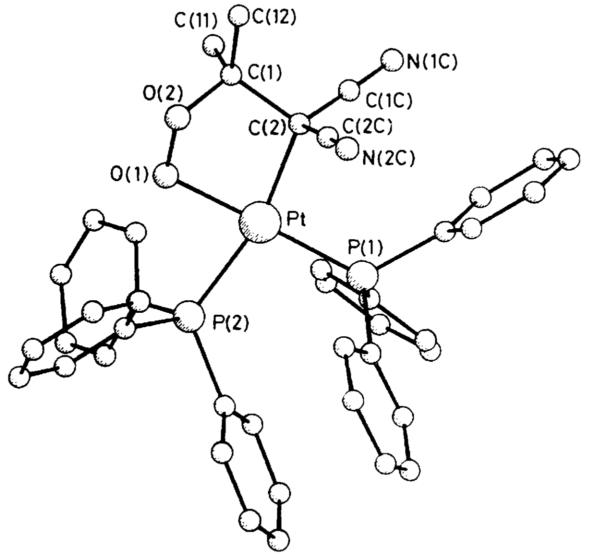


Figure 1. Molecular structure of $[\overline{Pt\{C(CN)_2C(Me)_2OO}\}(PPh_3)_2]$

Results and Discussion

Table 1 gives ^{31}P and ^{13}C n.m.r. spectral data for (1a) and (1b). Pidcock and co-workers[5] have shown that $^{195}Pt–P$ coupling decreases with increasing *trans* influence and Balimann and Pregosin[6] provide evidence for ^{31}P chemical shifts in phosphine complexes moving upfield with increasing *trans* influence; the P_A signals (Table 1) are therefore assigned to the phosphorus *trans* to C(2) in each case, as the cyano-substituted alkyl ligand is expected to have a greater *trans* influence than the peroxide ligand even though its σ-donor ability is likely to be less than that of a simple alkyl ligand. The *X*-ray crystallographic study of complex (1b) (see below) fully supports this conclusion. In the ^{13}C n.m.r. spectra, signals from the two quaternary carbon atoms in each complex could not be detected even when prolonged accumulation times were used. Presumably the relaxation times for these nucleii are very long. For complex (1b), the relative chemical shifts and the stronger $^{195}Pt–C$ coupling in the two signals labelled C_B in Table 1 clearly associate these with the cyano-carbons attached to C(2). Sheldon and Van Doorn,[4] in previously making this assignment, considered the two cyano-carbons to have the same chemical shift and to be split by $^{31}P–C$ coupling. However, there is no evidence for such coupling in the ^{31}P spectrum and it is reasonable to expect these carbons to have separate but similar chemical shifts. For complex (1a), heteronuclear coupling of *ca.* 50—70 Hz is only seen in the C_B signals which must, therefore, also originate from the two cyano-carbons nearest to the metal centre.

The structure of (1b) determined by *X*-ray structure analysis is shown in Figure 1. Selected bond lengths and angles are given in Table 2 and some least-squares planes in Table 3. The gross features of the structure are as expected, although there

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† *Supplementary data available* (No. SUP 23547, 38 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Selected bond lengths and angles for (1b) with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

O(1)–Pt	2.044(12)	C(2)–Pt	2.138(15)
P(1)–Pt	2.251(6)	P(2)–Pt	2.318(6)
O(2)–O(1)	1.462(15)	C(1)–O(2)	1.407(19)
C(2)–C(1)	1.608(22)	C(11)–C(1)	1.543(24)
C(12)–C(1)	1.551(22)	C(1C)–C(2)	1.376(22)
C(2C)–C(2)	1.447(23)	N(1C)–C(1C)	1.200(23)
N(2C)–C(2C)	1.148(22)	C(111)–P(1)	1.818(16)
C(121)–P(1)	1.819(17)	C(131)–P(1)	1.810(17)
C(211)–P(2)	1.849(17)	C(221)–P(2)	1.838(17)
C(231)–P(2)	1.839(19)		

(*b*) Bond angles (°)

C(2)–Pt–O(1)	82.4(6)	P(1)–Pt–O(1)	178.3(3)
P(1)–Pt–C(2)	99.1(5)	P(2)–Pt–O(1)	82.1(4)
P(2)–Pt–C(2)	164.2(4)	P(2)–Pt–P(1)	96.4(2)
O(2)–O(1)–Pt	107.5(8)	C(1)–O(2)–O(1)	107.9(11)
C(2)–C(1)–O(2)	105.3(12)	C(1)–C(2)–Pt	103.7(9)
C(111)–P(1)–Pt	119.9(5)	C(121)–P(1)–Pt	110.1(6)
C(121)–P(1)–C(111)	101.1(8)	C(131)–P(1)–Pt	110.8(6)
C(131)–P(1)–C(111)	103.1(8)	C(131)–P(1)–C(121)	111.3(8)
C(211)–P(2)–Pt	122.1(6)	C(221)–P(2)–Pt	111.9(6)
C(221)–P(2)–C(211)	103.3(8)	C(231)–P(2)–Pt	108.7(6)
C(231)–P(2)–C(211)	103.4(8)	C(231)–P(2)–C(221)	106.2(9)

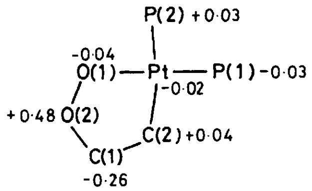

Figure 2. Distortion from square planarity (values in Å) of the co-ordination sphere

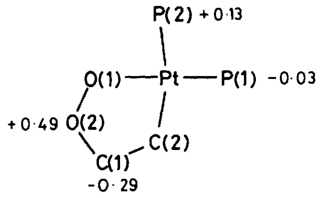

Figure 3. Conformation of the peroxymetallacyclic ring (values in Å)

are some points worthy of specific comment. The co-ordination sphere shows slight tetrahedral distortion with O(1), C(2), P(1), and P(2) lying out of the least-squares plane by ±0.03—0.04 Å, as shown in Figure 2. The metallacycle displays a *twist* conformation with O(2) and C(1) lying, respectively, 0.49 Å above and 0.29 Å below the Pt,O(1),C(2) plane (Figure 3). This conformation places the two methyl groups in pseudo-axial and pseudo-equatorial positions and leads to a contact distance of 3.56 Å between the carbon of the pseudo-axial methyl and the platinum atom. Thus there is little possibility for activation of a C–H bond at this methyl by the metal centre, as this bond will lie approximately perpendicular to the carbon–metal axis. This metallacyclic ring conformation also has a bearing on mechanistic considerations for the rhodium-catalysed oxygenations of 1-alkenes. If analogous

Table 3. Data for selected least-squares planes. Deviations from the planes (Å) are given in square brackets; atoms defining the plane are indicated (*); equations of planes refer to crystallographic axes

Plane 1 $8.971X + 22.042Y - 2.942Z = 3.267$

Pt* [0], O(1)* [0], C(2)* [0], O(2) [0.49], C(1) [−0.29], P(1) [−0.03], P(2) [0.13]

Plane 2 $9.197X + 21.450Y - 3.212Z = 3.225$

Pt [−0.02], O(1)* [−0.04], O(2) [0.40], C(1) [−0.26], C(2)* [0.04], P(1)* [−0.03], P(2)* [0.03]

Table 4. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Pt	1 578(1)	1 031	1 430(1)
O(1)	263(10)	1 407(3)	240(9)
O(2)	406(10)	1 420(3)	−894(9)
C(1)	425(13)	1 009(5)	−1 275(12)
C(2)	1 596(14)	803(4)	−217(12)
C(11)	−717(15)	763(6)	−1 485(15)
C(12)	572(16)	1 062(6)	−2 474(14)
C(1C)	1 534(17)	382(6)	−407(14)
N(1C)	1 472(19)	15(5)	−600(15)
C(2C)	2 696(15)	959(7)	−213(14)
N(2C)	3 552(15)	1 101(6)	−202(15)
P(1)	3 003(3)	619(1)	2 782(3)
C(111)	3 784(13)	248(4)	2 254(12)
C(112)	4 735(14)	375(6)	1 987(14)
C(113)	4 703(16)	5 081(8)	3 448(16)
C(114)	5 076(20)	4 669(8)	3 612(16)
C(115)	6 022(18)	4 529(6)	3 394(15)
C(116)	6 576(17)	4 832(5)	2 941(15)
C(121)	4 247(12)	931(5)	3 827(13)
C(122)	4 522(14)	1 276(6)	3 323(16)
C(123)	5 518(17)	1 519(6)	4 009(18)
C(124)	6 235(19)	3 561(8)	253(21)
C(125)	5 923(17)	3 899(8)	752(19)
C(126)	4 924(16)	4 161(6)	82(14)
C(131)	2 389(13)	298(5)	3 596(12)
C(132)	1 151(13)	282(4)	3 156(13)
C(133)	−603(17)	5 018(5)	1 281(17)
C(134)	−1 316(17)	227(6)	5 277(16)
C(135)	−2 547(19)	4 768(7)	−122(16)
C(136)	−3 123(16)	5 043(6)	402(15)
P(2)	1 235(4)	1 418(1)	2 859(3)
C(211)	2 239(14)	1 391(5)	4 510(13)
C(212)	3 122(14)	1 699(5)	5 018(14)
C(213)	3 886(17)	3 327(7)	1 276(17)
C(214)	3 777(19)	3 643(6)	2 000(16)
C(215)	2 905(17)	3 931(6)	1 475(15)
C(216)	2 098(16)	3 927(6)	210(14)
C(221)	−254(14)	1 316(5)	2 794(14)
C(222)	−1 069(15)	1 097(5)	1 773(16)
C(223)	−2 250(19)	1 026(8)	1 695(20)
C(224)	−2 517(19)	1 155(8)	2 626(23)
C(225)	−1 675(22)	1 354(7)	3 649(22)
C(226)	−549(15)	1 427(7)	3 730(17)
C(231)	1 252(15)	1 971(5)	2 498(15)
C(232)	1 831(17)	2 096(5)	1 812(15)
C(233)	1 892(22)	2 512(6)	1 569(20)
C(234)	1 408(26)	2 808(8)	2 003(23)
C(235)	822(26)	2 675(8)	2 716(27)
C(236)	723(20)	2 251(6)	2 967(19)
Cl(11)	7 151(11)	3 257(4)	3 636(11)
Cl(12)	8 201(15)	2 446(6)	4 236(16)
C(1S)	−1 708(38)	2 054(14)	−465(39)
Cl(21)	4 549(18)	2 160(6)	1 246(18)
Cl(22)	4 868(19)	2 366(7)	−726(19)
C(2S)	4 633(54)	2 027(20)	51(56)

metallacycles are involved in these reactions, the position of the key migrating hydrogen would correspond to that of the pseudo-axial carbon in structure (1b). In such a case the prospect of metal C–H bond interaction appears to be remote, unless the ring system has considerable conformational flexibility.

Experimental

The peroxy complexes (1a), m.p. 178—182 °C (decomp.), and (1b), m.p. 180—184 °C (decomp.) were prepared by the method detailed in ref. 4 and the crystals used for *X*-ray work were obtained from methylene chloride–hexane solutions by slow concentration at 4 °C.

N.m.r. measurements were made using a JEOL PFT 100 n.m.r. spectrometer. Cell dimensions, crystal orientation and intensities were obtained using a CAD4 diffractometer with graphite-monochromated Mo-K_α radiation and previously described procedures.[7]

Crystal Data.—$C_{42}H_{36}N_2O_2P_2Pt\cdot CH_2Cl_2$, $M = 942.73$, Monoclinic, space group $P2_1/c$, $a = 12.361(2)$, $b = 32.244(3)$, $c = 12.314(4)$ Å, $\beta = 115.51(2)°$, $U = 4\,365(3)$ Å^3, $Z = 4$, $D_c = 1.431$ g cm^{-3}, $F(000) = 1\,704$, μ(Mo-K_α) = 33.5 cm^{-1}, λ(Mo-K_α) 0.710 69 Å.

7 849 Intensities were recorded, 7 639 of which were unique, 5 254 with $I > 3\sigma(I)$, $\omega/2\theta$ scan mode, $1.5 \leqslant \theta \leqslant 25°$. An empirical absorption correction was applied (max. : min. transmission ratio 1.00 : 0.59). The crystal decay during data collection was 20%, and a linear correction was applied.

The structure was solved by standard heavy-atom methods and refined by least squares. During the course of the refinement it became apparent that the structure also contained some methylene chloride of crystallisation, probably one molecule per host molecule, disordered over two sites. The final R value was 0.063. Unit weights were used since these gave acceptable agreement analyses. Final atomic co-ordinates are given in Table 4. Computers, programs, and scattering factors are as in ref. 7.

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