Synthesis and *X*-Ray Crystal Structure of *ab*-Dimethyl-*df*-dinitro-*ce*-bis(triethylphosphine)platinum(IV)

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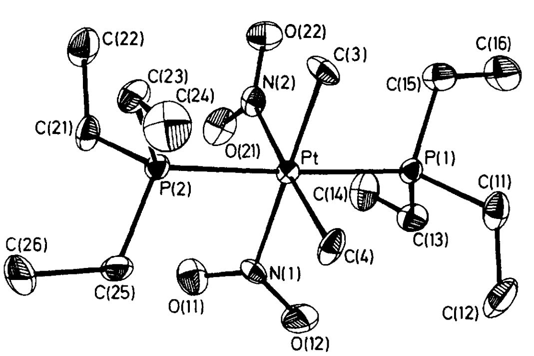
The interaction of nitric oxide with *cis*-$PtMe_2(PEt_3)_2$ gives a quantitative yield of $PtMe_2(NO_2)_2(PEt_3)_2$ whose structure has been determined by *X*-ray diffraction. The crystals of the complex are monoclinic, space group $P2_1$, with a = 7.278(1), b = 12.120(1), c = 11.867(1) Å, and β = 94.56(1)°. The structure was solved *via* the heavy-atom method and refined to an R value of 0.032 for 2 935 observed diffractometer data. The platinum(IV) atom has the expected octahedral geometry with *cis* methyls [Pt–C 2.077(9), 2.111(8) Å], *cis* nitro-groups [Pt–N 2.184(6), 2.198(8) Å], and *trans* phosphines [Pt–P 2.337(3), 2.430(3) Å].

TRANSITION and other metal alkyls and complex alkyls may react with nitric oxide [1,2] undergoing so-called insertion reactions in which alkyl groups are transferred from the metal to nitrogen; this transfer may be followed either by further reaction with NO to give *N*-nitroso-*N*-alkylhydroxylaminato-groups or by elimination of RN=NR from intermediates with η^2 or bridging RNO units and the concomitant formation of M=O bonds. However, the complex [3] *cis*-$PtMe_2(PEt_3)_2$ reacts smoothly with nitric oxide under oxygen-free conditions without transfer of methyl groups and instead the platinum(IV) nitro-complex, $PtMe_2(NO_2)_2(PEt_3)_2$, is formed quantitatively. Analytical and spectroscopic data (see Experimental section) are in accord with the structure determined by *X*-ray study.

RESULTS AND DISCUSSION

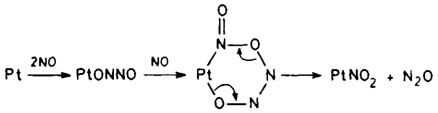
The complex (see Figure) has a *trans* P–Pt–P unit but the two methyl groups and the two NO_2 ligands are mutually *cis*. Such an arrangement of the NO_2 ligands would maximise the possibilities for d_π–N $p_\pi{}^*$ back donation, although only one of these ligands [containing N(2)] has the ideal orientation (*i.e.* coplanar with a metal co-ordination plane, *viz.* PtC_2N_2, dihedral angle = 8.6°). The second NO_2 plane lies almost halfway between the two most likely positions, with a dihedral angle (O_2N–PtC_2N_2) of 56.4°. In spite of this difference, the two Pt–N distances are essentially equal at 2.184(6) and 2.198(8) Å, and from this we deduce that the NO_2 groups are not demonstrating any significant π-acceptor strength. This situation may reflect the presence in the molecule of the two strong π-acceptor phosphine ligands. Confirmation of this general picture is obtained by comparing this structure with that of the complex $PtCl_2(NO_2)_2(en)$ (en = ethylenediamine) [4] in which the Pt–$N(NO_2)$ distances are slightly shorter at 2.00 and 2.14 Å.



Molecular structure of $PtMe_2(NO_2)_2(PEt_3)_2$

The two Pt–C distances in the complex are essentially equal, at 2.077(9) and 2.111(8) Å, but surprisingly the two Pt–P distances [2.337(3), 2.430(3) Å] differ significantly. We can only assume that the origin of this difference lies in intramolecular steric effects.

The reaction of NO co-ordinated to a metal in a complex with NO to give N_2O and NO_2, *i.e.* homogeneous disproportionation, is a well known reaction although the precise mechanisms involved are uncertain; [2] oxygen-transfer reactions between NO and other molecules such as CO are also known.[2,5] It seems reasonable to assume that we have a reaction of the type shown below where at some stage three NO molecules in some form must be bound simultaneously to the platinum atom.



The overall stoicheiometry of equation (1) has been

$$cis\text{-}PtMe_2(PEt_3)_2 + 6NO \longrightarrow PtMe_2(NO_2)_2(PEt_3)_2 + 2N_2O \quad (1)$$

confirmed by study in a closed system using very pure NO and analysing the gas after reaction by mass spectrometry, where N_2O but no NO_2 was detected.

That the rate of methyl transfer to co-ordinated NO is non-competitive with reactions leading to the nitro-complex is not surprising in view of the slowness of CO insertion into *cis*-$PtMe_2(PEt_3)_2$.[6]

It may be noted that the same nitro-compound is formed by interaction of *cis*-$PtMe_2(PEt_3)_2$ with NO_2–N_2O_4.

The oxidation of Pt^{II} to Pt^{IV} has been previously noted [7] in the interaction of NO with *cis*-$PtMe_2(PMe_2Ph)_2$. This was found to give *cis-cis-cis*-$PtMe_2(NO_2)_2(PMe_2Ph)_2$ which then isomerises to the more stable *cis-cis-trans* isomer and reacts further to give the products *trans*-$PtMe(NO_2)(PMe_2Ph)_2$ and *fac*-$PtMe_3(NO_2)(PMe_2Ph)_2$. By contrast to the present case, no N_2O was detected; also, NO_2 reacted to give a nitrato-complex. Oxidation of $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ by N_2O_4 does, however, lead to the iridium(III) dinitro-complex.[8]

EXPERIMENTAL

Microanalyses were by Imperial College Laboratory. Infrared spectra were recorded on a Perkin-Elmer 597, n.m.r. spectra on a Bruker WM-250 instrument.

Light petroleum had b.p. 30—40 °C. Nitric oxide (British Oxygen Co.) was purified by trap-to-trap distillation.

Dimethyldinitrobis(triethylphosphine)platinum(IV).—A thoroughly degassed (N_2) light petroleum (20 cm^3) solution of *cis*-$PtMe_2(PEt_3)_2$ (2 g) was treated with nitric oxide for *ca.* 10 min at room temperature. The pale yellow solution was concentrated to *ca.* 5 cm^3 and cooled to −30 °C to give pale yellow air-stable crystals which were washed with diethyl ether and dried. Yield 2.1 g, 93%; m.p. 110 °C [Found: C, 29.5; H, 6.8; N, 4.0; P, 9.2%; *M* (osmometric in CH_2Cl_2), 556. $C_{14}H_{36}N_2O_4P_2Pt$ requires C, 30.0; H, 7.0; N, 5.0; P, 11.0%; *M*, 553].

The compound is soluble in aromatic hydrocarbons, tetrahydrofuran, dichloromethane, and light petroleum, but sparingly soluble in diethyl ether.

The n.m.r. data (in C_6D_6 at *ca.* 20 °C, p.p.m.) were as follows: ^1H, δ 1.0 and 2.05 (multiplets for CH_3 and CH_2), 0.62 (partially obscured, Pt–CH_3); ^{31}P (referenced to external 85% H_3PO_4 at 101.27 MHz), δ 1.5 (t), J(P–Pt) = 1 959 Hz; ^{13}C (referenced to C_6D_6 at 62.9 MHz), δ −12.5 (main triplet), J(C–Pt) = 260.7 Hz with small additional splitting, J(C–P) = 4.5 Hz; ^{195}Pt (referenced to $PtCl_4^{2-}$ in D_2O at 53.65 MHz but converted into $PtCl_6^{2-}$ taking δ for $PtCl_4^{2-}$ at −1 614 p.p.m.[9]), linewidths *ca.* 1 000 Hz due to quadrupole broadening by ^{14}N, δ −3 520, J(Pt–P) = 2 062 Hz.

Crystallographic Studies.—Crystals suitable for *X*-ray work were obtained from toluene. Preliminary cell dimensions were obtained from photographs and refined using diffractometer setting angles. Intensity data were recorded on a CAD 4 diffractometer using monochromatised Mo-K_α radiation and an ω–2σ scan procedure,[10] and corrected for absorption empirically.[11] The structure was solved *via* the heavy-atom method and refined by full-matrix least squares. All atoms considered were assigned anisotropic thermal parameters. Hydrogen atoms were not included in the calculation of structure factors.

All computations were made using programs in the Enraf–Nonius SDP11/34 system.

Crystallographic data. $C_{14}H_{36}N_2O_4P_2Pt$, $M = 553.5$, Monoclinic, $a = 7.278(1)$, $b = 12.120(1)$, $c = 11.867(1)$ Å, $\beta = 94.56(1)°$, $U = 1\ 043.5$ Å^3, $D_m = 1.73$, $Z = 2$, $D_c = 1.76$ g cm^{-3}, $F(000) = 548$, space group $P2_1$, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 72.4 cm^{-1}. A total of 3 387 intensity data were measured, with 3 173 unique and 2 935 with $I > 1.5\sigma(I)$. Final R values were $R = 0.032$, $R' = [\Sigma(w\Delta)^2/\Delta wF_o^2]^{\frac{1}{2}} = 0.037$; the estimated standard deviation of an observation unit weight was 1.737.

TABLE 1

Atom fractional co-ordinates for $PtMe_2(NO_2)_2(PEt_3)_2$

Atom	x	y	z
Pt	0.234 16(3)	0.250 0(0)	0.244 43(2)
P(1)	0.352 7(3)	0.421 5(2)	0.172 8(2)
P(2)	0.122 5(3)	0.088 1(2)	0.321 2(2)
O(11)	−0.147(1)	0.214 2(7)	0.141 2(8)
O(12)	0.018(1)	0.281 6(8)	0.022 0(6)
O(21)	−0.082(1)	0.371 3(7)	0.342 4(7)
O(22)	0.163(1)	0.388 7(8)	0.447 8(6)
N(1)	−0.000 7(9)	0.246 8(11)	0.117 8(5)
N(2)	0.085 0(12)	0.352 9(6)	0.359 4(7)
C(11)	0.541(2)	0.406 7(9)	0.080 7(10)
C(12)	0.484(2)	0.371 6(13)	−0.038 1(10)
C(13)	0.188(2)	0.509 3(9)	0.090 3(9)
C(14)	0.029(2)	0.550 9(12)	0.151 4(13)
C(15)	0.453(2)	0.508 0(9)	0.288 8(10)
C(16)	0.505(2)	0.625 5(11)	0.255 7(14)
C(21)	−0.079(1)	0.111 2(10)	0.403 1(9)
C(22)	−0.035(2)	0.150 8(12)	0.524 1(10)
C(23)	0.283(2)	0.009 4(9)	0.417 6(8)
C(24)	0.434(2)	−0.052 6(11)	0.363 9(12)
C(25)	0.041(2)	−0.011 2(8)	0.213 5(8)
C(26)	−0.031(2)	−0.123 2(10)	0.256 1(12)
C(3)	0.469(1)	0.241 2(13)	0.360 8(8)
C(4)	0.384(1)	0.158 8(8)	0.135 0(8)

Final atomic fractional co-ordinates are given in Table 1, selected bond lengths and angles in Table 2; thermal parameters and lists of F_o/F_c have been deposited as Supplementary Publication No. SUP 23202 (14 pp.).*

TABLE 2

Selected bond lengths and angles for $PtMe_2(NO_2)_2(PEt_3)_2$

(*a*) Bond lengths (Å)

Pt–P(1)	2.430(3)	N(1)–O(11)	1.19(1)
Pt–P(2)	2.337(3)	N(1)–O(12)	1.23(1)
Pt–N(1)	2.184(6)		
Pt–N(2)	2.198(8)	N(2)–O(21)	1.24(1)
Pt–C(3)	2.111(8)	N(2)–O(22)	1.23(1)
Pt–C(4)	2.077(9)		

P–C(ethyl) 1.820(10)—1.845(10)

(*b*) Angles (°)

P(1)–Pt–P(2)	177.6(1)	O(11)–N(1)–O(12)	120(1)
N(1)–Pt–N(2)	92.2(3)	O(21)–N(2)–O(22)	117(1)
C(3)–Pt–C(4)	86.9(5)		

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