Nitrosyl Coupling in Transition Metal Complexes: the Molecular Structure of $[(Ph_3P)_2Pt(N_2O_2)]$

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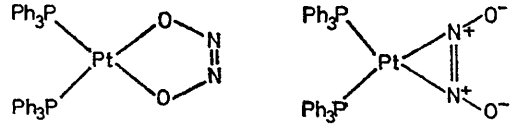
Summary A crystallographic study of $[(Ph_3P)_2Pt(N_2O_2)]$ shows that the two NO groups are coupled *via* the nitrogen atoms, forming a *cis*-hyponitrite ligand, which bonds to platinum through the oxygen atoms to give a PtONNO ring.

THE dinitrosyl complexes $[M(NO)_2(PPh_3)_2]^{n+}$ (M = Fe, Ru, or Os, $n = 0$; M = Co, Rh, or Ir, $n = 1$) react with CO to form N_2O and CO_2.[1] The unstable $[Pt(N_2O_2)(PPh_3)_2]$, which is obtained by the action of NO on $Pt(PPh_3)_3$ or $Pt(PPh_3)_4$,[2] undergoes a similar reaction with CO.[3] Spectroscopic evidence indicated a hyponitrite derivative of platinum (**1a**) or (**1b**), and the coupling of two NO ligands to produce an ONNO species may be an important reaction step with the former complexes. This is supported by the single crystal *X*-ray structure of $[Pt(N_2O_2)(PPh_3)_2]$ reported here which establishes structure (**1a**). The sample was prepared by the method of Ugo *et al.*;[2] the air-sensitive, yellow crystals were deposited as rectangular blocks from a benzene–dichloromethane mixture.



(1a) (1b)

Crystal data: $C_{36}H_{30}N_2O_2P_2Pt$, triclinic, $a = 12{\cdot}199(6)$, $b = 10{\cdot}747(6)$, $c = 15{\cdot}730(8)$ Å, $\alpha = 108{\cdot}75(4)$, $\beta = 95{\cdot}57(4)$, $\gamma = 69{\cdot}98(4)°$, $U = 1834.6$ Å^3, $Z = 2$, space group $P\bar{1}$; graphite-monochromated Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å,

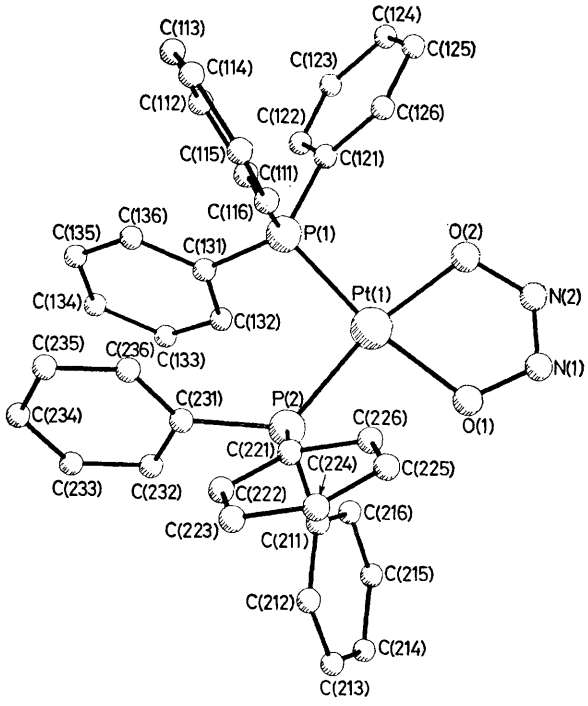


FIGURE. Molecular structure of $[(Ph_3P)_2Pt(N_2O_2)]$ (hydrogen atoms have been omitted for clarity). Bond lengths and bond angles are: Pt(1)–P(1), 2·22(1); Pt(1)–P(2), 2·27(1); Pt(1)–O(1), 2·00(2); Pt(1)–O(2), 2·03(3); O(1)–N(1), 1·39(5); O(2)–N(2), 1·32(3); and N(1)–N(2), 1·21(5) Å; ∠P(1)–Pt(1)–P(2), 99·8(4); ∠P(1)–Pt(1)–O(2), 89·4(8); ∠P(2)–Pt(1)–O(1), 92·8(7); and ∠O(1)–Pt(1)–O(2), 78·0(1·0)°.

$\mu = 37{\cdot}72$ cm^{-1}. Intensity data ($3{\cdot}0 \leqslant 2\theta \leqslant 50°$) were recorded on a Syntex $P2_1$ four-circle automatic diffractometer. The 1969 unique observed intensities [$I > 2{\cdot}5\,\sigma(I)$] were corrected for absorption, and the structure was solved by Patterson and Fourier methods. Least-squares refinement gives an R value of 0·108 (Pt and P atoms anisotropic; C, N, and O isotropic; and phenyl hydrogens, with a common fixed temperature factor, riding 1·08 Å away from the carbon positions). R can be further reduced by introducing a disordered benzene solvent molecule, but it is difficult to obtain chemically reasonable locations for the extra atoms.†

The Figure illustrates the molecular geometry and includes important bond lengths and angles. Although a (N,O) bridging *cis*-hyponitrite has been found[4] in $[(NH_3)_5Co{-}N_2O_2{-}Co(NH_3)_5]^{4+}$, there is apparently no previous crystallographic evidence for a bidentate hyponitrite ligand. The ON_2O group is planar, and makes a dihedral angle of 6·7° with the metal co-ordination plane.

The geometry of the remainder of the complex, and the molecular packing, are similar to that reported[5] in other $[(Ph_3P)_2PtL]$ complexes, where L is a bidentate ligand. In fact the compounds with L = CO_3, S_2CO, and N_2O_2 crystallise in $P\bar{1}$ space group with closely similar cell dimensions.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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