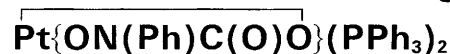


Insertion of Carbon Dioxide and of Unsaturated Carbon Compounds into the Platinum–Nitrogen Bond: the X-Ray Crystal Structure of



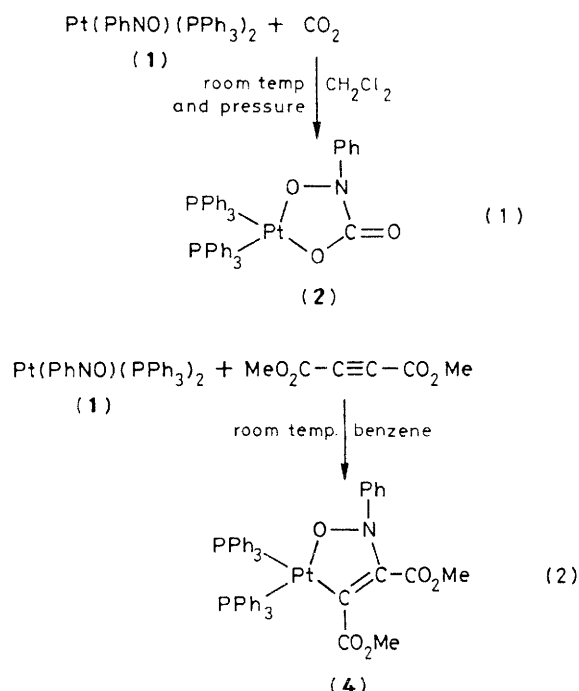
Pier Luigi Bellon, Sergio Cenini, Francesco Demartin, Maddalena Pizzotti, and Francesca Porta
Istituto di Chimica Generale and CNR Center, Via Venezian 21, 20133 Milano, Italy

$\text{Pt}(\text{PhNO})(\text{PPh}_3)_2$ reacts with unsaturated carbon compounds such as carbon dioxide, carbon disulphide, alkenes, and dimethyl acetylenedicarboxylate to give 1:1 adducts; X-ray studies on the adduct formed with carbon dioxide, $\text{Pt}\{\text{ON}(\text{Ph})\text{C}(\text{O})\text{O}\}(\text{PPh}_3)_2$, show that the entering molecule is inserted into the platinum–nitrogen bond of the η^2 -bonded nitroso ligand.

Much interest has recently been focused on the reactivity of unsaturated carbon compounds such as carbon dioxide and alkenes with complexes having a metal–nitrogen bond.^{1–3} The activation of carbon dioxide by transition metal complexes is of obvious interest in the search for alternative chemical feedstocks.⁴ In addition the metal-promoted C–N bond formation is a major achievement in the field of hydrocarbon functionalisation.⁵ In the reactions of molybdenum² and niobium³ aryl- and alkyl-nitroso derivatives with alkenes, the transfer of the RN residue of the η^2 -bonded nitroso ligand to the olefin was observed. Our interest in the reactivity and in the structural aspects of the metal–nitrogen bond^{6–8} has

led us to examine the reactions of the complex $\text{Pt}(\text{PhNO})(\text{PPh}_3)_2$ (1), having an η^2 -bonded arylnitroso ligand, with unsaturated carbon compounds. Compound (1), which can be obtained from $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ and nitrosobenzene,⁹ readily reacts with gaseous carbon dioxide, to give the one-to-one adduct (2)[†] [equation (1)]. Analogously, compound (1) reacts with carbon disulphide to give the corresponding one-to-one adduct, $\text{Pt}\{\text{ON}(\text{Ph})\text{C}(\text{S})\text{S}\}(\text{PPh}_3)_2$ (3); no reaction is

[†] Satisfactory elemental analyses have been obtained for all the compounds reported here.



observed with acetone. An unequivocal structural assignment was not possible for (2) from spectroscopic data, and so a single-crystal *X*-ray diffraction study was carried out.

Crystal data: $\text{C}_{43}\text{H}_{35}\text{NO}_3\text{P}_2\text{Pt} \cdot \text{CH}_2\text{Cl}_2$, $M = 955.73$; yellow monoclinic prisms; space group (from systematic absences) $P2_1/n$ (no. 14); $a = 13.416(2)$, $b = 13.900(3)$, $c = 21.573(3)$ Å, $\beta = 92.20(2)^\circ$, $U = 4020$ Å³, $Z = 4$, $D_c = 1.58$ g cm⁻³, $F(000) = 1896$ electrons; μ (Mo- K_α) = 39.26 cm⁻¹. Intensity data were collected on a Nonius CAD4 diffractometer with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å), in the 2θ range 6–50°. The structure, solved by conventional Patterson and Fourier methods using 2170 absorption-corrected reflections with $I \geq 3\sigma(I)$, has been refined by full-matrix least-squares down to $R = 0.10$. The refinement is not yet complete since both the solvent and the complex molecules appear to be heavily disordered; in the latter the disorder affects three phenyl rings of the phosphine ligands. The essential features of the metallo carbamate ring are however clearly seen at the present stage (see Figure 1).[‡]

Compound (2) represents the first genuine example of the insertion of carbon dioxide into a metal–nitrogen bond. It has in fact been recently recognized that what was previously thought to be a CO_2 insertion into the $\text{M}-\text{NR}_2$ bond is actually an amine-catalysed reaction which proceeds *via* the R_2NCO_2^- anion.¹⁰ This hypothesis was previously suggested by some of us for the reactions of the amido-complexes of rhenium(i) with carbon dioxide in the presence of secondary amines leading to the formation of carbamate derivatives.⁶ I.e., ¹H n.m.r., and ³¹P n.m.r. data for compound (2) are in agreement with its solid state structure. The organic ligand in (2) can be considered as a carbamic acid derivative. However, attempts to displace the oxygen atom bound to nitrogen by reaction of (2) with triphenylphosphine gave only $\text{Pt}(\text{PPh}_3)_2\text{CO}_3$.¹¹ Compound (1) also readily reacts with an alkyne-bearing electron-withdrawing substituent such as dimethyl acetylene

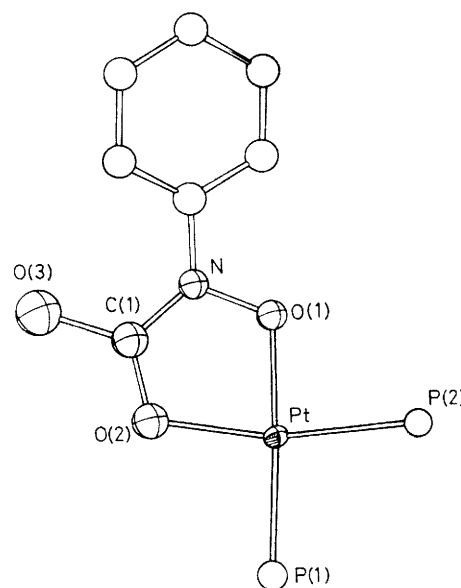


Figure 1. ORTEP view of the structure of $\text{Pt}\{\text{ON}(\text{Ph})\text{C}(\text{O})\text{O}\}(\text{PPh}_3)_2$ with the phenyl rings of the phosphine ligands omitted. Relevant bonding parameters are: Pt–P(1) 2.23(1), Pt–P(2) 2.22(1), Pt–O(1) 2.11(3), Pt–O(2) 2.05(3) Å. P(1)–Pt–P(2) 98.8(5), O(1)–Pt–O(2) 80.9(1.1)°.

dicarboxylate to give the one-to-one adduct (4) [equation (2)]. No reaction was observed between (1) and methylphenylacetylene. The need for a strongly electrophilic carbon atom in order that N–C bond formation should be promoted by (1) is confirmed by the fact that compound (1) does not react with an alkene such as β -cyano- β -phenylstyrene, but more activated alkenes such as tetracyanoethylene, β,β -dicyanostyrene, and fumaronitrile, are readily inserted to give the corresponding one-to-one adducts. These complexes are model compounds for intermediates which lead to aziridines and metal-oxo derivatives.³

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References

- M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, 1978, **17**, 3536, and references cited therein.
- L. S. Liebeskind, K. B. Sharpless, R. D. Wilson, and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 7061.
- A. R. Middleton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 1888.
- R. Eismberg and D. E. Hendriksen, *Adv. Catal.*, 1979, **28**, 79.
- 'Fundamental Research in Homogeneous Catalysis,' eds. M. Tsutsui and R. Ugo, Plenum Press, New York and London, 1977.
- G. La Monica, S. Cenini, F. Porta, and M. Pizzotti, *J. Chem. Soc., Dalton Trans.*, 1976, 1777.
- G. La Monica and S. Cenini, *J. Chem. Soc., Dalton Trans.*, 1980, 1145.
- P. L. Bellon, S. Cenini, F. Demartin, M. Manassero, M. Pizzotti, and F. Porta, *J. Chem. Soc., Dalton Trans.*, 1980, 2060.
- S. Otsuka, Y. Aotani, Y. Tatsuno, and T. Yoshida, *Inorg. Chem.*, 1976, **15**, 656.
- M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1977, **99**, 792.
- P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Am. Chem. Soc.*, 1970, **92**, 5873.

[‡] 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.

[§] Preliminary *X*-ray data have confirmed the structure of compound (4) suggested in equation (2).