Inorganica Chimica Acta
LETTER

$[Pt_2(\mu\text{-}NO)(\mu\text{-}dppm)_2Cl_2]BF_4$: the first A-frame complex with a nitrosyl bridgehead

Mauro Ghedini*, Francesco Neve
Dipartimento di Chimica, Università della Calabria,
I-87030 Arcavacata (CS) (Italy)

Carlo Mealli
Istituto per lo Studio della Stereochimica ed Energetica dei
Composti di Coordinazione, C.N.R., via J. Nardi 39,
I-50132 Florence (Italy)

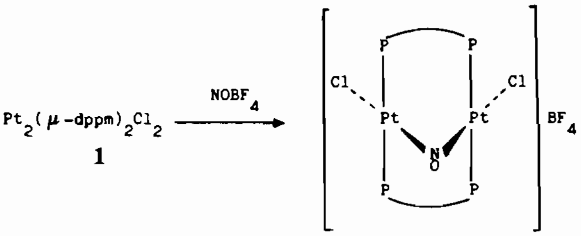
Antonio Tiripicchio and Franco Ugozzoli
Istituto di Chimica Generale ed Inorganica, Università di
Parma, Centro di Studio per la Strutturistica
Diffrattometrica del C.N.R., viale delle Scienze,
I-43100 Parma (Italy)

(Received September 4, 1990)

Typical A-frame complexes [1] are stabilized by the binucleating ligand bis(diphenylphosphino)-methane (dppm) [2] and by bridgehead atoms (e.g. H, Cl, S) or small molecules (e.g. CO, SO_2, CNR, C_2R_2). Among the latter, nitrosyl could also be a potential bridgehead occupant, although the corresponding A-frame derivative has not been reported as yet. As pointed out by Hoffman and Hoffmann [3], a small HOMO–LUMO gap, calculated for an ideal nitrosyl model, represents a source of thermodynamical instability and, in any event, geometrical distortions can be reasonably expected.

We are now able to present the synthesis and characterization of the first A-frame complex containing the NO group at the bridgehead position.

A yellow solution of the A-frame precursor $Pt_2(\mu\text{-}dppm)_2Cl_2$ (**1**) [4] in CH_2Cl_2 becomes yellow–green when an excess of $NOBF_4$ in methanol is added. Stirring (2 h), addition of diethyl ether and cooling (−20 °C) affords the precipitation of yellow–green, air stable crystals of the product **2** in 90% yield.



2

The analytically pure **2** exhibits ν(NO) at 1470 cm^{-1} (KBr). Its structure has been assigned on the basis of ^1H, $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR data. ^1H (200.133 MHz, CD_2Cl_2, 25 °C): $\delta(H_A)$ 2.34 (d q) $J(H_AH_B)$ 14.2, $^2J(PH_A)$ 4.8 Hz, $\delta(H_B)$ 2.86 ppm (m, doublet of quintets after ^{195}Pt decoupling), $J(H_AH_B)$ 14.2, $^2J(PH_B)$ 3.7, $^3J(PtH_B)$ 44 Hz. $^{31}P\{^1H\}$ (32.438 MHz, $C_2H_2Cl_4$–acetone-d_6 (20%), 25 °C, 85% H_3PO_4 as external standard): δ −1.28 ppm (s with complex ^{195}Pt satellites due to AA′A″A‴X and AA′A″A‴XX′ spin systems) $J(AX)$ 3066, $J(AX')$ +159, $J(AA'')$ 32, $J(AA''')$ 0 Hz. $^{195}Pt\{^1H\}$ (43.022 MHz, $C_2H_2Cl_4$–acetone-d_6 (20%), 25 °C, $Na_2[PtCl_6]$ in D_2O as standard): δ −2141 ppm (t t), $^1J(PtP)$ 3066, $^2J(PtP)$ +159 Hz. While the methylene protons of the ligand dppm have the AB pattern typical of A-frame structures, only one proton to ^{195}Pt coupling is observed in the ^1H NMR spectrum of **2**. The positive value of $^2J(PtP)$, +159 Hz, derived from both $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ spectra, excludes any major Pt–Pt bonding interaction [5]. The latter feature (Pt–Pt separation equal to 3.186(2) Å) has been confirmed by the X-ray analysis of the dichloromethane solvate of **2**.

Crystal data of **2**: $C_{50}H_{44}BCl_2F_4NOP_4Pt_2 \cdot 2CH_2Cl_2$, $M_r = 1516.55$, triclinic, $P\bar{1}$, $Z = 2$, $a = 12.344(6)$, $b = 16.742(4)$, $c = 14.355(7)$ Å, $\alpha = 73.82(3)$, $\beta = 83.87(3)$, $\gamma = 85.76(3)°$, $V = 2830(2)$ Å^3, $\rho_{calc} = 1.780$ g cm^{-3}, $F(000) = 1468$, $\mu(Mo\ K\alpha) = 54.4$ cm^{-1}. The intensities of 9515 independent reflections were collected on a Siemens AED diffractometer, $3 \leq \theta \leq 23°$, $\theta/2\theta$ scan technique and Nb-filtered Mo Kα radiation ($\lambda = 0.71073$ Å). The structure, solved by Patterson and Fourier methods, was refined by full matrix least-squares on the basis of 3436 observed reflections ($I \geq 3\sigma(I)$) to R and R_w values of 0.076 and 0.085, respectively. The SHELX system of computer programs was used [6]. Unfortunately, the quality of the crystalline sample is not the best, but it is worth mentioning that a second set of data, collected on another crystal from a different preparation, provided essentially the same results, including the structural feature of the asymmetric bridgehead. See also 'Supplementary material'.

The structure of the cation is depicted in Fig. 1 and is close to an A-frame with terminal chloride, bridging dppm ligands and a bridgehead NO group.

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

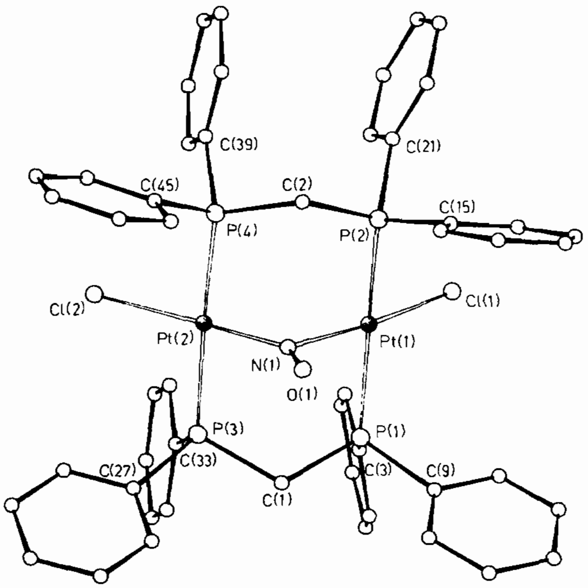


Fig. 1. View of the complex cation $[Pt_2(\mu\text{-}NO)(\mu\text{-}dppm)_2Cl_2]^+$ with the atomic numbering scheme. Selected interatomic distances (Å) and angles (°) are: Pt(1)...Pt(2) 3.186(2), N(1)–Pt(1) 2.02(2), N(1)–Pt(2) 1.83(2), N(1)–O(1) 1.17(3), Pt(1)–Cl(1) 2.317(8), Pt(1)–P(1) 2.346(11), Pt(1)–P(2) 2.342(11), Pt(2)–Cl(2) 2.317(10), Pt(2)–P(3) 2.315(11), Pt(2)–P(4) 2.345(11); P(1)–Pt(1)–P(2) 171.9(3), Cl(1)–Pt(1)–N(1) 173.8(8), P(3)–Pt(2)–P(4) 176.4(4), Cl(2)–Pt(2)–N(1) 178.1(8), Pt(1)–N(1)–Pt(2) 112(1), Pt(1)–N(1)–O(1) 117(2), Pt(2)–N(1)–O(1) 131(2).

The non-bonding Pt–Pt distance is probably associated with the oxidative insertion of the reacting NO^+ across the metal–metal bond of the precursor **1** (2.652(2) Å) [7].

Although the Pt–N–Pt angle of 112(1)° is close to that found in binuclear μ-NO complexes with no M–M bond [8], the asymmetry of the bridge in **2** is noteworthy. In fact, the Pt(1)–N and Pt(2)–N distances of 2.02(2) and 1.83(2) Å, respectively, are significantly different with a t value of 6.7 ($t = \Delta/\sqrt{(\sigma_1^2 + \sigma_2^2)}$). The asymmetry is also mirrored by the two Pt–N–O angles of 117(2) and 131(2)°, respectively. Since the two Pt–O distances are approximately equal (*c.* 2.77 Å), the NO group can be imagined as a pendulum with fulcrum at the oxygen atom and frozen at *c.* 7° of its oscillation toward Pt(2).

As it can be envisaged from Fig. 1, the square about the metal Pt(1) diverges from planarity slightly more than that about the metal Pt(2). Numerically, the feature is substantiated by larger displacements of the single ligand atoms from the mean coordination planes (the atoms Pt(1), P(1), P(2), Cl(1), N(1) have single displacements from their mean square plane of −0.015(3), 0.108(9), 0.106(9), −0.014(9) and −0.231(26) Å, respectively; the analogous displacements for the atoms Pt(2), P(3), P(4), Cl(2), N(1) are: 0.003(3), 0.007(10), 0.007(10), 0.007(10) and 0.050(25) Å, respectively) and by the angle P(1)–Pt(1)–P(2) somewhat smaller than P(3)–Pt(2)–P(4) (171.9(3) versus 176.4(4)°). Finally, to dismiss the possible argument that the NO asymmetry stems from poor crystallographic data, notice (Fig. 1) that the methylene groups of the two dppm ligands are symmetrically disposed, with an average P–C bond of 1.84(3) Å close to its ideal value.

As already recalled, a distortion of some sort was predicted for **2** prior to its synthesis, but not defined in nature [3]. On the basis of the experimental evidence for the incipient NO debridging, we now calculate, at the extended Hückel level [9], that the oscillation of the NO pendulum up to ≅8° from the equilibrium position (symmetric bridge) has an insignificant energy cost ($\Delta E < 0.06$ eV). Also, no cause, determinant for debridging, can be found from either the analysis of the frontier orbitals nor from a significant variation of the HOMO–LUMO gap.

Importantly, the flat energy surface implies that the possibility of observing an asymmetric NO bridgehead is not unrealistic, this being mainly associated with solid state effects. Recall in fact that the NMR spectra contain no trace of two asymmetric metal environments in solution.

Finally, we have found that by substituting CO for NO in our model, the same computational trend persists with only a slightly larger destabilization for the CO oscillation ($\Delta E < 0.15$ eV). Accordingly, it cannot be excluded that A-frames with asymmetric CO (or another π-acceptor) as a bridgehead may be observed in some cases. Unfortunately, the existing experimental data are not statistically significant. Thus, in spite of the large standard deviation ($Pt\text{–}C_{bridge} = 1.97(9)$ Å), the symmetry of the bridge is crystallographically imposed by a C_2 axis in the A-frame $Pt_2(\mu\text{-}CO)(\mu\text{-}dam)_2Cl_2$ [10]. Conversely, the different Pd–C distances of 1.84(5) and 1.95(6) Å in $Pd_2(\mu\text{-}CO)(\mu\text{-}dam)_2Cl_2$, dam = bis(diphenylarsino)methane [11], and of 1.98(3) and 2.04(3) Å in $Pd_2(\mu\text{-}CNCH_3)(\mu\text{-}dppm)_2(CNCH_3)_2$ [12] have a t value as low as 1.4 in both cases.

In conclusion, the asymmetry of the bridgehead does not seem to have a primary importance in stabilizing this first example of a nitrosyl A-frame, rather it provides an indication of the low energetics associated with the bridge-bonding network in this type of compound.

Supplementary material

Atomic coordinates are available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge

CB2 1EW, U.K., on quoting the names of the authors and the journal citation. Thermal parameters and a list of observed and calculated structure factors are available from the authors on request.

Acknowledgements

Ministero dell'Università e della Ricerca Scientifica e Tecnologica and Consiglio Nazionale delle Ricerche (C.N.R.) are gratefully acknowledged for financial support. We also thank Johnson Matthey Research Centre, U.K., for the loan of platinum salt, and Dr M. Grassi for obtaining the NMR spectra.

References

1 C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc., 99* (1977) 6129; *Inorg. Chem., 19* (1980) 2726.

2 (a) R. J. Puddephatt, *Chem. Soc. Rev., 12* (1983) 99; (b) A. L. Balch, in L. H. Pignolet (ed.), *Homogeneous Catalysis with Metal Phosphine Complexes*, Plenum, New York, 1983, p. 167; (c) B. Chaudret, B. Delavaux and R. Poilblanc, *Coord. Chem. Rev., 86* (1988) 191.

3 D. M. Hoffman and R. Hoffmann, *Inorg. Chem., 20* (1981) 3543.

4 (a) M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *J. Chem. Soc., Dalton Trans.,* (1977) 951; (b) M. C. Grossel, J. R. Batson, R. P. Moulding and K. R. Seddon, *J. Organomet. Chem., 304* (1986) 391.

5 M. P. Brown, J. R. Fischer, S. J. Franlin, R. J. Puddephatt and K. R. Seddon, *J. Organomet. Chem., 161* (1978) C46.

6 G. M. Sheldrick, *SHELX*, program for crystal structure determination, University of Cambridge, U.K., 1976.

7 M. P. Brown, R. J. Puddephatt, M. Rashidi, Lj. Manojlovic-Muir, K. W. Muir, T. Solomun and K. R. Seddon, *Inorg. Chim. Acta, 23* (1977) L33.

8 (a) A. Tiripicchio, A. M. Manotti-Lanfredi, M. Ghedini and F. Neve, *J. Chem. Soc., Chem. Commun.,* (1983) 97; (b) D. O. K. Fjeldsted, S. R. Stobart and M. J. Zawarotko, *J. Am. Chem. Soc., 107* (1985) 8258.

9 R. Hoffmann, *J. Chem. Phys., 39* (1963) 1397; R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys., 36* (1982) 2179, 2872.

10 M. P. Brown, A. N. Keith, Lj. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *Inorg. Chim. Acta, 34* (1979) L223.

11 R. Colton, M. J. McCormick and C. D. Pannan, *J. Chem. Soc., Chem. Commun.,* (1977) 823.

12 M. M. Olmstead, H. Hope, L. S. Benner and A. L. Balch, *J. Am. Chem. Soc., 99* (1977) 5502.