Organometallics 1992, 11, 795–801

# A Novel Class of Nitrosyl A-Frames. Crystal and Molecular Structure of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BPh_4 \cdot CH_2Cl_2$

Francesco Neve* and Mauro Ghedini

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

Antonio Tiripicchio and Franco Ugozzoli

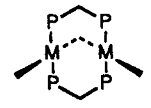
*Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy*

*Received August 8, 1991*

The reaction of $Pt_2Cl_2(\mu\text{-dppm})_2$ (dppm = bis(diphenylphosphino)methane) with an excess of $NO^+A^-$ in dichloromethane–methanol leads to the stable cationic species $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2]^+$, isolated as the $BF_4^-$ (**1a**) or $PF_6^-$ (**1b**) salt. The corresponding $BPh_4^-$ salt (**1c**) is obtained by treatment of **1a** with $NaBPh_4$. $Pt_2X_2(\mu\text{-dppm})_2$ species (X = Br, I) are also reactive toward $NO^+BF_4^-$, giving rise to the orange $[Pt_2Br_2(\mu\text{-NO})(\mu\text{-dppm})_2]BF_4$ (**2**) or the dark red $[Pt_2I_2(\mu\text{-NO})(\mu\text{-dppm})_2]BF_4$ (**3**). The reactivity of the platinum(I) precursors with the nitrosonium ion is compared with that of $Pd_2Cl_2(\mu\text{-dppm})_2$, which gives either a much less stable $\mu$-NO species or a non-nitrosyl Pd(II) complex. NMR characterization of complexes **1**–**3** at room temperature shows the presence in solution of nonfluxional, symmetrical A-frame structures. The crystal structure of the dichloromethane solvate $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2]BPh_4$ (**1c**) has been determined by X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 26.295$ (6) Å, $b = 16.338$ (4) Å, $c = 16.414$ (7) Å, $\beta = 106.99$ (2)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 4582 observed reflections to $R$ and $R_w$ values of 0.0501 and 0.0621, respectively. The cationic complex has an A-frame structure with terminal chloride and bridging dppm ligands and a bridgehead NO group, the nonbonding Pt–Pt separation being 3.246 (3) Å. The NO bridge is almost symmetric, with Pt(1)–N and Pt(2)–N bond distances of 1.947 (14) and 1.919 (16) Å and Pt(1)–N–O and Pt(2)–N–O angles of 120.4 (11) and 125.4 (12)°. This result contrasts with that previously found in the tetrafluoroborate salt of the same cation, but it is in agreement with theoretical studies predicting that the oscillation of the NO bridge from the symmetric to the asymmetric position requires a very low energy cost.

## Introduction

The small-bite bidentate ligand bis(diphenylphosphino)methane (dppm) is known to stabilize bimetallic systems[1,2] as well as mixed-metal clusters[3] when acting as a bridging group. Many binuclear species having a $M_2(\mu\text{-dppm})_2$ framework show the so-called "A-frame" structural arrangement (I).[4] In the idealized structure



I

each metal center has a square-planar geometry and a single atom (e.g. H, Cl, S, Se, O) or a small molecule (e.g. CO, $CS_2$, $SO_2$, SO, CNR, $N_2R^+$, $C_2R_2$) as the apex ligand.[5] Despite the large variety of bridgehead groups observed, a $\mu$-NO A-frame complex has not yet been reported. Unfavorable theoretical predictions, formulated by Hoffman and Hoffmann for an ideal nitrosyl model,[6] might have played a blocking role in pursuing such a species.

As part of our ongoing studies on the bimetallic activation of the NO ligand,[7] we are now able to report on the synthesis and characterization of stable platinum(II) $\mu$-NO A-frames. The complexes presented here are the result of a two-center oxidative addition of the nitrosonium ion ($NO^+$) to the binuclear species $Pt_2X_2(\mu\text{-dppm})_2$ (X = Cl, Br, I).[8,9] A preliminary account of this work has been previously reported.[10]

## Results and Discussion

Reaction of $Pt_2Cl_2(\mu\text{-dppm})_2$[11] with an excess of $NO^+A^-$ in dichloromethane–methanol at room temperature gave the new bimetallic complexes $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2]^+A^-$ (**1a**, A = $BF_4$; **1b**, A = $PF_6$) in good yield (eq 1). The reaction was accompanied by a color change from yellow to bright yellow-green.

---

[1] (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (b) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H.,; Ed.; Plenum: New York, 1983; p 167.

[2] Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

[3] (a) Braunstein, P.; de Meric de Bellefon, C.; Ries, M. *Organometallics* **1988**, *7*, 332. (b) Braunstein, P.; de Meric de Bellefon, C.; Ries, M.; Fischer, J.; Bouaoud, S.-E.; Grandjean, D. *Inorg. Chem.* **1988**, *27*, 1327 and references cited therein. (c) Bruno, G.; Lo Schiavo, S.; Rotondo, E.; Piraino, P.; Faraone, F. *Organometallics* **1987**, *6*, 2502. (d) Manojlovic-Muir, L.; Muir, K. W.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 2418.

[4] (a) Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726. (b) *J. Am. Chem. Soc.* **1977**, *99*, 6129.

[5] For recent examples of dppm A-frames, see: (a) Gong, J. K.; Fanwick, P. E.; Kubiak, C. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1190. (b) Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622. (c) Sharp, P. R.; Flynn, J. R. *Inorg. Chem.* **1987**, *26*, 3231.

[6] Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543.

[7] (a) Tiripicchio, A.; Tiripicchio Camellini, M.; Neve, F.; Ghedini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1651. (b) Neve, F.; Ghedini, M. *Inorg. Chim. Acta* **1990**, *175*, 111. (c) Ghedini, M.; Neve, F. *J. Chem. Soc., Dalton Trans.* **1984**, 1417. (d) Tiripicchio, A.; Manotti Lanfredi, A. M.; Ghedini, M.; Neve, F. *J. Chem. Soc., Chem. Commun.* **1983**, 97.

[8] Among the few examples of oxidative addition of $NO^+$ to dinuclear complexes reported, see: (a) Paul, P. P.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1990**, *112*, 2430. (b) Fjelsted, D. O. K.; Stobart, S. R.; Zavorotko, M. K. *J. Am. Chem. Soc.* **1985**, *107*, 8258. (c) Rabinowitz, H. N.; Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 1420.

[9] For an example of $NO^+$ reaction with a "$M_2(dppm)_2$" species which does not give rise to a bridging NO group, see: Ge, Y.-W.; Sharp, P. R. *Inorg. Chem.* **1991**, *30*, 1671.

[10] Ghedini, M.; Neve, F.; Mealli, C.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chim. Acta* **1990**, *178*, L5.

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

0276-7333/92/2311-0795$03.00/0

$$\mathrm{Pt_2Cl_2(\mu\text{-}dppm)_2} \xrightarrow{\mathrm{NO^+A^-}} \mathrm{[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]A} \quad (1)$$
$$\mathbf{1a},\ \mathrm{A = BF_4}$$
$$\mathbf{1b},\ \mathrm{A = PF_6}$$

The IR data ($\nu$(NO): **1a**, 1470 cm$^{-1}$; **1b**; 1468 cm$^{-1}$) are consistent with the presence of an NO ligand in the products. However, on the basis of these data alone, it cannot be said whether the coordination mode is bent terminal or bridging.

$[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BPh_4$ (**1c**) was obtained by metathetical exchange of $BF_4^-$ for $BPh_4^-$. It exhibits the same IR feature ($\nu$(NO) = 1476 cm$^{-1}$) observed for **1a** and **1b**.

Complexes **1a–c** are air-stable solids, which can be stored indefinitely. They are all soluble in chlorinated solvents such as dichloromethane and 1,1,2,2-tetrachloroethane, moderately soluble in acetone, and insoluble in common nonpolar solvents.

$Pt_2X_2(\mu\text{-}dppm)_2$ (X = Br, I) also reacted with $NO^+BF_4^-$ to give the orange $[Pt_2Br_2(\mu\text{-}dppm)_2]BF_4$ (**2**) and the dark red $[Pt_2I_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (**3**) in fairly good yields.

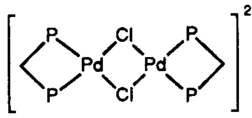
The synthesis of **3** is always accompanied by the formation of the dimeric $[Pt_2(\mu\text{-}I)_2(dppm)_2][BF_4]_2$ (**4**), which could be independently synthesized and structurally characterized.[12] A third unidentified product was occasionally observed in low percentage. Decreasing either the reaction temperature or the amount of $NO^+BF_4^-$ did not significantly improve the yield of the main product **3**.

The observed NO stretching frequencies are 1464 and 1455 cm$^{-1}$ for **2** and **3**, respectively. A regular trend (Cl > Br > I) for $\nu$(NO) can be therefore observed.

In order to test the expected different reactivity of $Pd_2Cl_2(\mu\text{-}dppm)_2$ vs that of the Pt homologue, the former was reacted with $NO^+BF_4^-$. Two different reaction products could be identified (eq 2).

$$\mathrm{Pd_2Cl_2(\mu\text{-}dppm)_2} \xrightarrow{\mathrm{NO^+BF_4^-}} \underset{\mathbf{5}}{\mathrm{[Pd_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4}} + \underset{\mathbf{6}}{\mathrm{[Pd_2(\mu\text{-}Cl)_2(dppm)_2][BF_4]_2}} \quad (2)$$

The orange-brown product **5**, formulated as $[Pd_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$, shows characteristic IR stretching frequencies at 1532 and 1046 cm$^{-1}$, which are assigned to $\nu$(NO) and $\nu$(BF), respectively. After being isolated, compound **5** decomposes in dichloromethane solution in a few hours. Its instability in solution prevented a complete characterization (see Experimental Section). Recrystallization attempts led to extensive decomposition. The elemental analysis of crude **5**, however, fits its formulation quite well. The second product, **6**, has been formulated as $[Pd_2(\mu\text{-}Cl)_2(dppm)_2][BF_4]_2$. On the basis of spectroscopic evidence (Experimental Section), and by analogy with **4**, compound **6** is assigned the chelated structure II.



II

Oxidation of $Pd_2Cl_2(\mu\text{-}dppm)_2$ is likely to generate **6**, for $NO^+$ is known to be a one-electron-oxidizing reagent.[13] No evidence has been found for the formation of monomeric species such as $Pd(dppm)Cl_2$.[14]

**Table I.** $^{31}P\{^1H\}$ **and** $^{195}Pt\{^1H\}$ **NMR Data**$^a$

| complex | $\delta(^{31}P)^b$ | $\delta(^{195}Pt)^c$ | $^1J$(PtP) | $^3J$(PtP) | $N^d$ |
|---|---|---|---|---|---|
| **1a** | −1.28 | −2141 | 3066 | +159 | 32 |
| **1b**$^e$ | −0.54$^f$ | | 3065 | +158 | 30 |
| **1c** | −0.45$^f$ | | 3068 | +159 | 32 |
| **2** | −1.93 | −2392 | 3022 | +155 | 31 |
| **3** | −3.48 | −2816 | 2983 | +152 | 29 |
| **5** | 5.96$^f$ | | | | |
| **6** | −50.43$^f$ | | | | |

$^a$ $\delta$ in ppm; $J$ in Hz. $^b$ In $CH_2Cl_2$ (80%)–acetone-$d_6$ (20%) at 32.44 MHz. $^c$ In $Cl_2CHCHCl_2$ (80%)–acetone-$d_6$ (20%) at 43.022 MHz. $^d$ $N = |^2J(P_AP_{A''}) + {}^4J(P_AP_{A'''})|$. $^e$ $\delta(PF_6^-) = -144.3$ ppm. $^f$ At 81.0 MHz.

**Table II.** $^1H$ **NMR Data**$^a$

| complex | $\delta(CH_a)$ | $\delta(CH_b)$ | $^2J(H_aH_b)$ | $^3J(PtH_a)$ | $J(PH_a)^b$ | $J(PH_b)^b$ |
|---|---|---|---|---|---|---|
| **1a** | 2.86 | 2.34 | 14.2 | 44 | 3.7 | 4.8 |
| **1b** | 2.86 | 2.39 | 14.2 | 44 | 3.7 | 4.8 |
| **1c** | 2.77 | 2.35 | 14.2 | 44 | 3.7 | 4.8 |
| **2** | 2.76 | 2.36 | 14.4 | 50 | 3.9 | 4.5 |
| **3** | 2.63 | 2.34 | 14.3 | 39 | 3.6 | 4.7 |

$^a$ In $CD_2Cl_2$ at 25 °C: $\delta$ in ppm; $J$ in Hz. $^b$ $J(PH) = |^2J(PH) + {}^4J(PH)|$.

The complexes **1–3** were all characterized by elemental analysis, conductivity measurements, and $^1H$, $^{31}P\{^1H\}$, and, in some cases, $^{195}Pt\{^1H\}$ NMR spectroscopy. The molecular structures of **1a**[10] and **1c** have been determined by X-ray crystallography. All of the spectroscopic and crystallographic evidence confirmed the formation of a novel class of nitrosyl A-frames.

**NMR Studies.** The NMR spectra of the complexes **1–3** are typical of symmetric A-frames of platinum.[11a] All data are collected in Tables I and II.

The $^{31}P\{^1H\}$ NMR spectra of **1a–c** showed the expected pattern for an AA′A″A‴ spin system with satellites due to coupling with $^{195}Pt$. The spectral parameters are given in Table I. Figure 1 shows the $^{31}P\{^1H\}$ NMR spectrum of **1a** in $CH_2Cl_2$ (80%)–acetone-$d_6$ (20%). The corresponding $^{195}Pt\{^1H\}$ NMR spectrum is shown in Figure 2. The triplet is due to coupling with adjacent $^{31}P$ atoms ($^1J$(PtP) = 3066 Hz). Long-range Pt–P coupling is responsible for additional splitting ($^3J$(PtP) = +159 Hz). The positive value found for $^3J$(PtP) (as obtained by analysis of the $^{31}P\{^1H\}$ spectrum) is indicative of a weak or absent metal–metal interaction.[11a,15] Negative $^3J$(PtP) coupling constants have indeed been observed for Pt A-frames containing a Pt–Pt bonding interaction.[3d,11b,16,17]

$^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of **2** and **3** display the same pattern seen for **1a**. The expected trend (Cl < Br < I) was observed for the upfield shift of both $^{31}P$ and $^{195}Pt$ resonances. The reverse order was found for $^1J$(PtP) (Table I).

Some decomposition of complexes **1–3** occurred in chlorinated solvent solutions after several hours. The decomposition was monitored by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy. New phosphorus signals due to decomposition products were found at −2.28, −2.87, and −7.23 ppm for dichloromethane solutions of **1a**, **2**, and **3**, respectively. The same species gave $^{195}Pt$ resonances as triplets at −3719 ($^1J$(PtP) = 2400 Hz), −4039 ($^1J$(PtP) = 2335 Hz), and −5076 ppm ($^1J$(PtP) = 2220 Hz), respectively. However, after several days the main signal in each spectrum was still that due to the A-frame species. It

---

[12] Neve, F.; Crispini, A.; Ghedini, M.; De Munno, G. *Inorg. Chim. Acta* **1990**, *176*, L23.

[13] Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317.

[14] Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267.

[15] Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J. *J. Organomet. Chem.* **1978**, *161*, C46.

[16] Sharp, P. R. *Inorg. Chem.* **1986**, *25*, 4185.

[17] Arsenault, G. J.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Treurnicht, I. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 86.

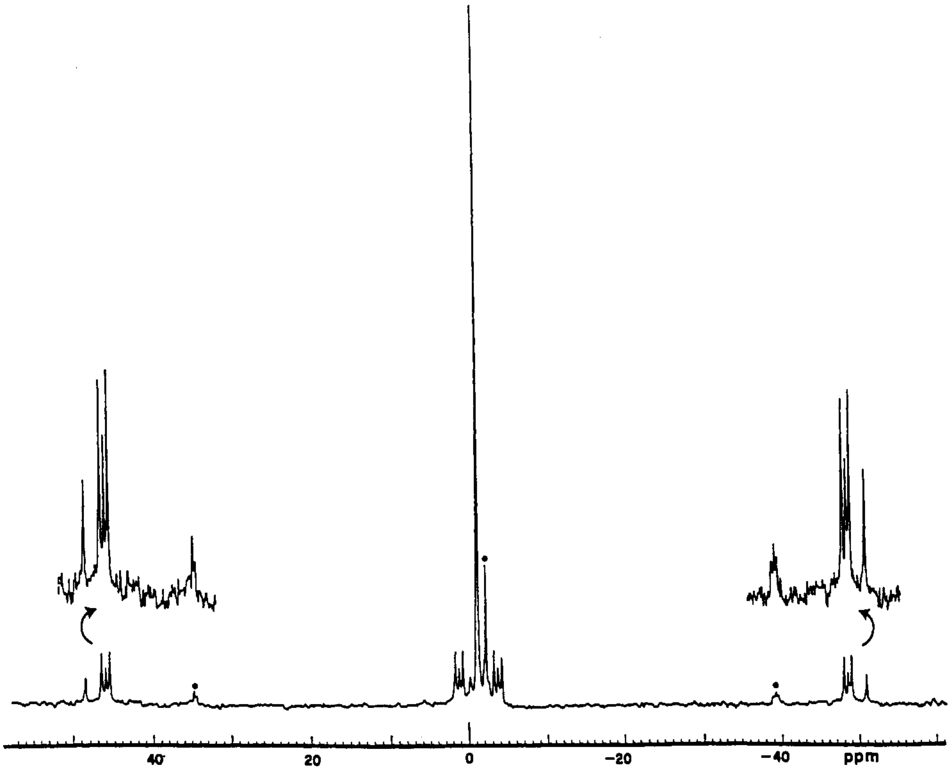


**Figure 1.** $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (**1a**). The peaks marked with an asterisk are due to an unidentified Pt species.

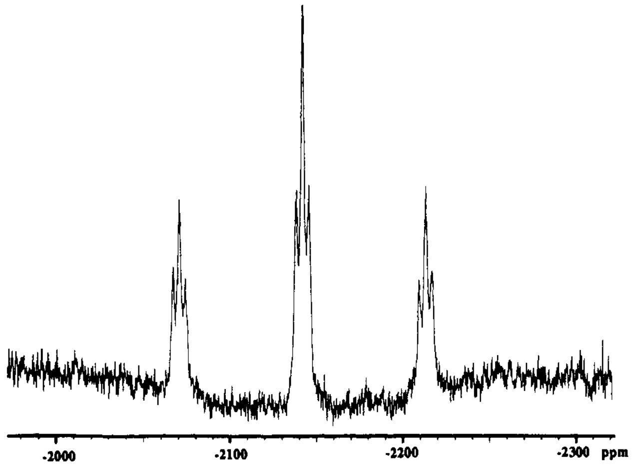


**Figure 2.** $^{195}Pt\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (**1a**).

should be noted that the partial decomposition is not a simple reductive elimination, as $[Pt_2X_2(\mu\text{-}dppm)_2]$ species were never detected.

$^1H$ NMR spectra are also indicative of A-frame structures with nonfluxional behavior (Table II). Since $CH_2$ protons of dppm are nonequivalent, an AB pattern is observed. Figure 3 shows the methylene region for **1c** at 200.133 MHz. Due to "virtual" coupling with four P nuclei, the high-field signal shows a quintet with AB coupling at 14.2 Hz. The low-field $CH_2$ resonance alone shows coupling to $^{195}Pt$ with $^3J(PtH)$ at ~40 Hz. A different magnitude of PtH coupling for nonequivalent methylene protons is a common feature of $^1H$ NMR spectra of dppm-bridged Pt dimers[18] or $Pt_2M$ clusters.[3d] Differences as large as 100 Hz have been reported.[17]

The broadening seen in $^{195}Pt$ satellites (Figure 3a) is possibly the result of a chemical shift anisotropy relaxation mechanism, as is often reported for platinum complexes.[19] In our case, both proton and phosphorus NMR spectra indeed have less resolved platinum satellites at higher magnetic field.

**Description of the Crystal Structure of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BPh_4\cdot CH_2Cl_2$ (1c).** Crystals of **1c** consist of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]^+$ cations, $BPh_4^-$ anions, and dichloromethane molecules of solvation, separated by normal contacts. A view of the cationic complex is shown in Figure 4 together with the atom-numbering scheme. Selected bond distances and angles are given in Table III. The structure of the complex is very close to a regular A-frame with terminal chloride and bridging dppm ligands and a bridgehead NO group. The nonbonding Pt···Pt separation, 3.246 (3) Å, determined by the oxidative insertion of $NO^+$ into the metal–metal bond of the percursor $[Pt_2Cl_2(\mu\text{-}dppm)_2]^{20}$ is longer than those found in $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2]$ (3.151 Å)[21] and $[Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-}dppm)_2]$ (3.094 Å).[22]

The slightly distorted square-planar coordination about each Pt atom is determined by two P atoms from two dppm ligands, by a Cl atom, and by the N atom of the bridging nitrosyl group. The Pt–P and Pt–Cl bond distances are practically equal to the two metals; the Pt–N distances are only slightly different (Pt(1)–N = 1.947 (14) Å and Pt(2)–N = 1.919 (16) Å). The displacements of the Pt(1), P(1), P(2), Cl(1), and N atoms from their mean

---

(18) (a) Hutton, A. T.; Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2121. (b) Puddephatt, R. J.; Thomson, M. A. *Inorg. Chem.* **1982**, *21*, 725.

(19) (a) Anklin, C. G.; Pregosin, P. S. *Magn. Reson. Chem.* **1985**, *23*, 67. (b) Lallemand, J.-Y.; Soulié, J.; Chottard, J.-C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.

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

(21) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1400.

(22) Cameron, T. S.; Gardner, P. A.; Grundy, K. R. *J. Organomet. Chem.* **1981**, *212*, C19.

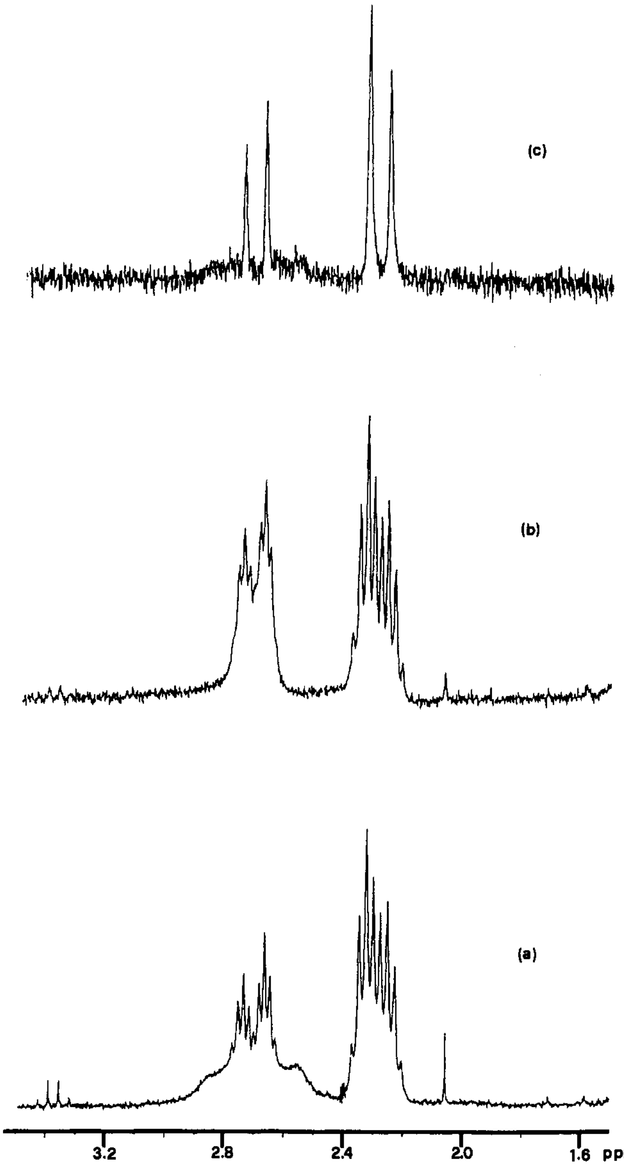
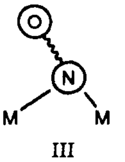


**Figure 3.** $^1H$ NMR spectra of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BPh_4$ (**1c**) in the methylene region: (a) fully coupled spectrum; (b) $^1H\{^{195}Pt\}$ spectrum; (c) $^1H\{^{31}P\}$ spectrum.

square plane are −0.038 (3), 0.077 (5), 0.078 (5), −0.002 (5), and −0.106 (16) Å, respectively; the analogous displacements for the atoms Pt(2), P(3), P(4), Cl(2), and N(1) are 0.008 (2), −0.032 (5), 0.006 (5), and 0.085 (15) Å. The dihedral angle between the coordination planes is 65.6 (2)°.

The NO bridge is almost symmetric, as shown by the Pt–N bond distances and by the Pt–N–Pt angles (Pt(1)–N–O = 120.4 (1)° and Pt(2)–N–O = 125.4 (12)°). Moreover, the two Pt···O distances are approximately equal (Pt(1)···O = 2.758 (13) Å and Pt(2)···O = 2.794 (13) Å).

It is now interesting to compare the structural features of **1c** with those already reported for the same cation in the tetrafluoroborate salt, $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (**1a**).[10] The only remarkable difference concerns the NO bridge, which in **1a** is significantly asymmetric. The NO can be seen as a pendulum (III), with the fulcrum at the oxygen atom (Pt–O = 2.74 (2) Å), frozen at ca. 7° of its oscillation toward Pt(2) (Pt(1)–N = 2.02 (2) Å and Pt(2)–N = 1.83 (2) Å). This asymmetry is not surprising, as extended Hückel molecular orbital calculations have shown that the oscillation of the NO pendulum up to ca. 8° from the symmetric position has an insignificant energy cost (Δ*E* < 0.06 eV).[10]



III

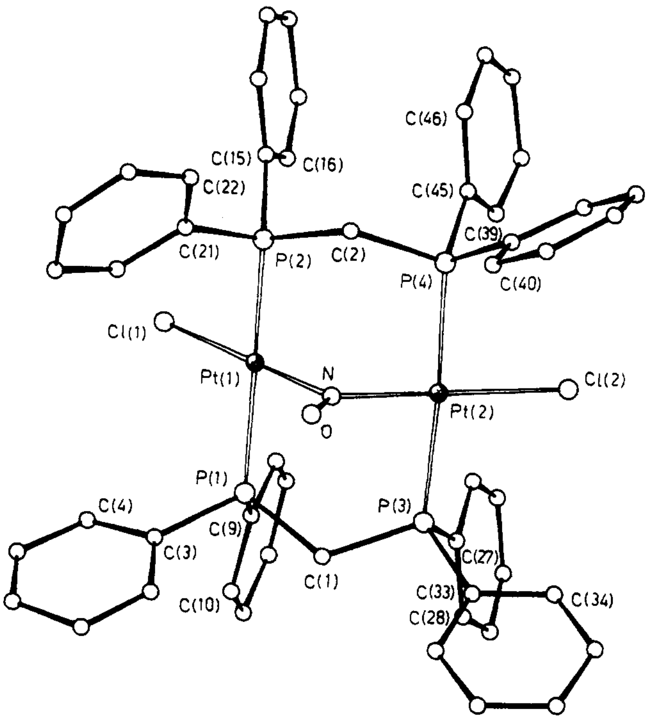


**Figure 4.** View of the cation of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2[BPh_4$ (**1c**) with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% level.

**Table III. Important Interatomic Distances (Å) and Angles (deg) for Complex 1c**

| | | | |
|---|---|---|---|
| Pt(1)–Cl(1) | 2.330 (5) | P(2)–C(15) | 1.790 (17) |
| Pt(1)–P(1) | 2.332 (5) | P(2)–C(21) | 1.779 (21) |
| Pt(1)–P(2) | 2.328 (5) | P(3)–C(1) | 1.823 (16) |
| Pt(1)–N | 1.947 (14) | P(3)–C(27) | 1.817 (19) |
| Pt(2)–Cl(2) | 2.322 (6) | P(3)–C(33) | 1.777 (16) |
| Pt(2)–P(3) | 2.335 (5) | P(4)–C(2) | 1.847 (17) |
| Pt(2)–P(4) | 2.329 (5) | P(4)–C(39) | 1.755 (15) |
| Pt(2)–N | 1.919 (16) | P(4)–C(45) | 1.803 (19) |
| N–O | 1.203 (23) | B–C(51) | 1.73 (3) |
| P(1)–C(1) | 1.873 (17) | B–C(57) | 1.68 (3) |
| P(1)–C(3) | 1.816 (17) | B–C(63) | 1.63 (3) |
| P(1)–C(9) | 1.793 (18) | B–C(69) | 1.66 (3) |
| P(2)–C(2) | 1.854 (14) | | |
| | | | |
| P(1)–Pt(1)–Cl(1) | 92.1 (2) | C(2)–P(2)–C(21) | 101.7 (8) |
| Cl(1)–Pt(1)–P(2) | 93.7 (2) | C(15)–P(2)–C(21) | 107.9 (8) |
| P(2)–Pt(1)–N | 86.2 (5) | Pt(2)–P(3)–C(1) | 112.8 (6) |
| N–Pt(1)–P(1) | 88.2 (4) | Pt(2)–P(3)–C(27) | 114.9 (6) |
| P(3)–Pt(2)–Cl(2) | 92.4 (2) | Pt(2)–P(3)–C(33) | 115.3 (6) |
| Cl(2)–Pt(2)–P(4) | 90.5 (2) | C(1)–P(3)–C(27) | 107.0 (8) |
| P(4)–Pt(2)–N | 88.9 (4) | C(1)–P(3)–C(33) | 101.0 (8) |
| N–Pt(2)–P(3) | 88.3 (5) | C(27)–P(3)–C(33) | 104.6 (7) |
| Pt(1)–N–Pt(2) | 114.2 (7) | Pt(2)–P(4)–C(2) | 110.4 (5) |
| Pt(1)–N–O | 120.4 (11) | Pt(2)–P(4)–C(39) | 116.1 (5) |
| Pt(2)–N–O | 125.4 (12) | Pt(2)–P(4)–C(45) | 116.9 (6) |
| Pt(1)–P(1)–C(1) | 112.4 (6) | C(2)–P(4)–C(39) | 102.9 (7) |
| Pt(1)–P(1)–C(3) | 111.2 (5) | C(2)–P(4)–C(45) | 105.2 (7) |
| Pt(1)–P(1)–C(9) | 118.9 (6) | C(39)–P(4)–C(45) | 103.8 (8) |
| C(1)–P(1)–C(3) | 102.7 (7) | C(51)–B–C(57) | 109.9 (14) |
| C(1)–P(1)–C(9) | 103.4 (8) | C(51)–B–C(63) | 103.4 (13) |
| C(3)–P(1)–C(9) | 106.7 (8) | C(51)–B–C(69) | 109.4 (15) |
| Pt(1)–P(2)–C(2) | 112.1 (5) | C(57)–B–C(63) | 114.3 (14) |
| Pt(1)–P(2)–C(15) | 119.1 (6) | C(57)–B–C(69) | 107.9 (15) |
| Pt(1)–P(2)–C(21) | 109.6 (6) | C(63)–B–C(69) | 111.8 (18) |
| C(2)–P(2)–C(15) | 105.1 (7) | | |

## Concluding Remarks

A small HOMO–LUMO gap in the MO diagram of a complex is a source of thermodynamical instability, unless geometrical distortions contribute to enhance the energy difference.

A theoretical analysis of the nitrosyl model $[Rh_2(\mu\text{-}NO)Cl_2(dpm')_2]^-$ (dpm' = $H_2PCH_2PH_2$), which is isoelectronic with $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]^+$, positioned the LUMO "only 0.75 eV above the $b_2$ HOMO".[6] This feature led the authors to conclude that a 34-electron species would have two electrons in the low-lying LUMO (of $b_1$ symmetry) and would therefore be stable. On the other hand, the 32-electron analogue was predicted to be unstable, and all distortions considered to relieve that small gap were destabilizing the model. However, the debridging of the NO ligand was disregarded, whereas as mentioned above, a low-degree of debridging (leading to an asymmetrically bound NO group) does not affect the stability of the model.

The present work clearly shows that the synthesis of μ-NO A-frames can be achieved and that the asymmetry of the bridgehead cannot be the stabilizing factor. Moreover, no further distortions from the ideal A-frame geometry can be observed.

In conclusion, μ-NO A-frames can be obtained and, at least in the platinum case, these are stable undistorted species. Finally, the otherwise possible asymmetry of the bridging NO ligand seems to be mainly associated with solid-state effects.

## Experimental Section

All reactions were performed under nitrogen in purified solvents. NMR spectra were recorded with Bruker AC 200 ($^1H$ and $^{195}Pt$) and Bruker NS 80 ($^{31}P$) spectrometers. Chemical shifts are quoted with respect to tetramethylsilane ($^1H$), 85% phosphoric acid ($^{31}P$), and $Na_2PtCl_6$ in $D_2O$ ($^{195}Pt$). Infrared spectra were recorded with a Perkin-Elmer 1330 spectrometer. Conductivity measurements were carried out using an LKB 5300 B Conductolyser conductivity bridge. The commercially available reagents dppm (bis(diphenylphosphino)methane; Aldrich), $NO^+BF_4^-$ (Aldrich), and $NO^+PF_6^-$ (Strem) were used as received. $Pt_2X_2(\mu\text{-}dppm)_2$ (X = Cl, Br, I)[11] and $Pd_2Cl_2(\mu\text{-}dppm)_2$[23] were synthesized by literature methods.

**$[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (1a).** A solution of $NO^+BF_4^-$ (0.077 g, 0.659 mmol) in dry methanol (3 mL) was added to a stirred suspension of $Pt_2Cl_2(\mu\text{-}dppm)_2$ (0.250 g, 0.203 mmol) in $CH_2Cl_2$ (15 mL). Within a few minutes the reaction mixture had become a yellow-green solution. After 2 h of stirring the solvent was removed under reduced pressure until formation of yellow-green crystals of **1a** was observed. The solid was filtered off, washed with diethyl ether, and dried in vacuo. The yellow-green filtrate was layered with diethyl ether and cooled to −20 °C. Overnight diffusion of the solvents gave a further crop of greenish yellow crystals of **1a**, total yield 0.244 g (89%). Anal. Calcd for $C_{50}H_{44}BCl_2F_4NOP_4Pt_2$: C, 44.59; H, 3.29; N, 1.04. Found: C, 44.43; H, 3.20; N, 0.98. IR (KBr, $cm^{-1}$): $\nu$(NO) 1470 (m). Conductivity ($CH_2Cl_2$ solution): $\Lambda_M$ = 48.4 $\Omega^{-1}$ $M^{-1}$ $cm^2$.

**$[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]PF_6$ (1b).** A solution of $NO^+PF_6^-$ (0.210 g, 1.2 mmol) in dry methanol (2 mL) was added to a stirred suspension of $Pt_2Cl_2(\mu\text{-}dppm)_2$ (0.230 g, 0.187 mmol) in $CH_2Cl_2$ (13 mL). A yellow-green microcrystalline solid precipitated from the resulting yellow solution within 1 h. Complete precipitation of **1b** was achieved by concentration of the reaction mixture. The solid (0.188 g, 71%) was removed by filtration, washed with methanol and diethyl ether, and dried in vacuo. Anal. Calcd for $C_{50}H_{44}Cl_2F_6NOP_5Pt_2$: C, 42.75; H, 3.16; N, 1.00. Found: C, 42.36; H, 3.07; N, 0.99. IR (KBr, $cm^{-1}$): $\nu$(NO) 1468 (m). Conductivity ($CH_2Cl_2$ solution): $\Lambda_M$ = 53.1 $\Omega^{-1}$ $M^{-1}$ $cm^2$.

**Table IV. Summary of Crystallographic Data for Complex 1c**

| | |
|---|---|
| formula | $C_{74}H_{64}BCl_2NOP_4Pt_2\cdot CH_2Cl_2$ |
| mol wt | 1664.05 |
| cryst syst | monoclinic |
| space group | $P2_1/a$ |
| radiation (λ, Å) | graphite-monochromated Mo Kα (0.71073) |
| *a*, Å | 26.295 (6) |
| *b*, Å | 16.338 (4) |
| *c*, Å | 16.414 (7) |
| β, deg | 106.99 (2) |
| *V*, Å$^3$ | 6744 (4) |
| *Z* | 4 |
| $D_{calcd}$, g $cm^{-3}$ | 1.639 |
| *F*(000) | 3280 |
| cryst size, mm | 0.23 × 0.25 × 0.35 |
| μ(Mo Kα), $cm^{-1}$ | 44.85 |
| diffractometer | Philips PW 1100 |
| 2θ range, deg | 5–48 |
| rflns measd | ±*h*,*k*,*l* |
| no. of unique total data | 10378 |
| no. of unique obsd data [$I > 3\sigma(I)$] | 4582 |
| *R* | 0.0501 |
| $R_w$ | 0.0621 |

**$[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BPh_4\cdot CH_2Cl_2$ (1c).** $Pt_2Cl_2(\mu\text{-}dppm)_2$ (0.200 g, 0.163 mmol) was suspended in $CH_2Cl_2$ (12 mL) and $NO^+BF_4^-$ (0.062 g, 0.528 mmol) in dry methanol (2 mL) added with stirring. After 45 min the reaction mixture was reacted with $NaBPh_4$ (0.278 g, 0.812 mmol) in methanol (3 mL) for 4 h. Yellow needles of **1c** were obtained by evaporation of the solvents and crystallization from $CH_2Cl_2$–diethyl ether; yield 0.200 g (74%). Anal. Calcd for $C_{74}H_{64}BCl_2NOP_4Pt_2\cdot CH_2Cl_2$: C, 54.13; H, 4.00; N, 0.84. Found: C, 54.33; H, 4.05; N, 0.83. IR (KBr, $cm^{-1}$): $\nu$(NO) 1476 (m). Conductivity ($CH_2Cl_2$ solution): $\Lambda_M$ = 40.6 $\Omega^{-1}$ $M^{-1}$ $cm^2$. The presence of solvent was established by the crystallographic study. Its amount was also confirmed by $^1H$ NMR spectroscopy in acetone-$d_6$. The latter procedure was followed for all other compounds that crystallized with solvent molecules.

**Reaction of $Pt_2Br_2(\mu\text{-}dppm)_2$ with $NO^+BF_4^-$. $[Pt_2Br_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (2).** A solution of $NO^+BF_4^-$ (0.044 g, 5-fold excess) in dry methanol (1 mL) was added to a stirred suspension of $[Pt_2Br_2(\mu\text{-}dppm)_2]$ (0.100 g, 0.076 mmol) in $CH_2Cl_2$ (5 mL). The resulting yellow-orange solution was stirred for 1 h. Addition of diethyl ether (7 mL) gave, after cooling at −20 °C, an orange microcyrstalline solid, which was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.095 g (85% based on 0.5 $CH_2Cl_2$ of crystallization). Anal. Calcd for $C_{50}H_{44}BBr_2F_4NOP_4Pt_2\cdot 0.5$ $CH_2Cl_2$: C, 41.03; H, 3.07; N, 0.95. Found: C, 40.84; H, 3.11; N, 0.65. IR (KBr, $cm^{-1}$): $\nu$(NO) 1464 (m). Conductivity ($CH_2Cl_2$ solution): $\Lambda_M$ = 49.5 $\Omega^{-1}$ $M^{-1}$ $cm^2$.

**Reaction of $Pt_2I_2(\mu\text{-}dppm)_2$ with $NO^+BF_4^-$. $[Pt_2I_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (3).** $NO^+BF_4^-$ (0.020 g, 0.171 mmol) was added to an orange solution of $[Pt_2I_2(\mu\text{-}dppm)_2]$ (0.202 g, 0.146 mmol) in degassed $CH_2Cl_2$ (8 mL). After 5 min of stirring dry methanol (1 mL) was added. As the reaction progressed, the reaction mixture darkened in color. After 45 min addition of diethyl ether to the final dark red solution afforded dark red-black microcrystals of **3** and a yellow supernatant solution. The solid was filtered off, washed with methanol and diethyl ether, and dried in vacuo; yield 0.145 g (65%). Anal. Calcd for $C_{50}H_{44}BI_2F_4NOP_4Pt_2$:C, 39.26; H, 2.90; N, 0.92. Found: C, 39.50; H, 2.99; N, 0.87. IR (KBr, $cm^{-1}$): $\nu$(NO) 1455 (m). Conductivity ($CH_2Cl_2$ solution): $\Lambda_M$ = 56.2 $\Omega^{-1}$ $M^{-1}$ $cm^2$.

Slow evaporation of the solvents from the yellow mother liquor afforded a white precipitate. Recrystallization of this solid from acetone–diethyl ether afforded white-yellow prismatic crystals of $[Pt_2(\mu\text{-}I)_2(dppm)_2][BF_4]_2$, identified by comparison with a pure sample of the known compound.[12]

**Reaction of $Pd_2Cl_2(\mu\text{-}dppm)_2$ with $NO^+BF_4^-$.** An excess of $NO^+BF_4^-$ (0.835 mmol) in dry methanol (1 mL) was added to a red solution of $Pd_2Cl_2(\mu\text{-}dppm)_2$ (270 mg, 0.256 mmol) in $CH_2Cl_2$ (11 mL). The solution turned orange-brown within a few minutes. After 15 min of stirring, diethyl ether was added to the solution and the mixture cooled to −20 °C. Air-stable orange-brown

---

(23) (a) Balch, A. L.; Benner, L. S. *Inorg. Synth.* **1981**, *21*, 47. (b) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.

**Table V. Atomic Coordinates (×$10^4$) and Isotropic Thermal Parameters (Å$^2$ × $10^3$) with Esd's in Parentheses for the Non-Hydrogen Atoms of the Complex 1c**

| | *x/a* | *y/b* | *z/c* | *U*$^a$ | | *x/a* | *y/b* | *z/c* | *U*$^a$ |
|---|---|---|---|---|---|---|---|---|---|
| Pt(1) | 1895 (1) | 2000 (1) | 3508 (1) | 538 (3) | C(34) | 917 (8) | −1707 (11) | 3010 (11) | 752 (55) |
| Pt(2) | 940 (1) | 710 (1) | 2713 (1) | 484 (3) | C(35) | 888 (9) | −2490 (12) | 2699 (12) | 854 (61) |
| P(1) | 2343 (2) | 978 (3) | 4434 (3) | 529 (17) | C(36) | 1331 (8) | −2875 (14) | 2631 (12) | 932 (65) |
| P(2) | 1492 (2) | 2928 (3) | 2438 (3) | 606 (18) | C(37) | 1798 (10) | −2473 (13) | 2831 (13) | 993 (69) |
| P(3) | 1412 (2) | −274 (3) | 3670 (3) | 496 (17) | C(38) | 1835 (8) | −1680 (12) | 3172 (12) | 806 (58) |
| P(4) | 509 (2) | 1748 (3) | 1797 (3) | 522 (18) | C(39) | 107 (6) | 1435 (9) | 792 (10) | 499 (42) |
| Cl(1) | 2222 (2) | 3019 (3) | 4519 (3) | 823 (21) | C(40) | 353 (7) | 1168 (9) | 194 (10) | 562 (45) |
| Cl(2) | 126 (2) | 157 (3) | 2711 (3) | 687 (20) | C(41) | 43 (8) | 880 (11) | −634 (13) | 781 (57) |
| N | 1608 (6) | 1150 (8) | 2668 (10) | 661 (78) | C(42) | −493 (7) | 884 (10) | −802 (13) | 744 (55) |
| O | 1838 (4) | 958 (7) | 2162 (8) | 719 (63) | C(43) | −751 (9) | 1124 (11) | −190 (12) | 825 (59) |
| C(1) | 2125 (6) | −74 (10) | 4026 (12) | 592 (72) | C(44) | −444 (7) | 1395 (10) | 596 (11) | 619 (49) |
| C(2) | 999 (6) | 2427 (9) | 1531 (9) | 466 (68) | C(45) | 84 (6) | 2419 (10) | 2178 (11) | 605 (48) |
| B | 3789 (7) | 7890 (16) | 1831 (12) | 787 (110) | C(46) | −137 (7) | 3107 (11) | 1700 (13) | 751 (55) |
| C(3) | 3047 (6) | 972 (9) | 4517 (10) | 546 (45) | C(47) | −492 (8) | 3619 (14) | 1957 (15) | 1058 (71) |
| C(4) | 3358 (7) | 1555 (12) | 5046 (12) | 789 (57) | C(48) | −642 (10) | 3439 (16) | 2689 (16) | 1164 (79) |
| C(5) | 3897 (8) | 1582 (12) | 5127 (12) | 849 (59) | C(49) | −442 (9) | 2702 (13) | 3137 (16) | 1106 (75) |
| C(6) | 4133 (8) | 1034 (11) | 4717 (12) | 826 (59) | C(50) | −73 (7) | 2229 (12) | 2920 (12) | 775 (58) |
| C(7) | 3838 (8) | 380 (13) | 4269 (13) | 954 (66) | C(51) | 4194 (7) | 8337 (11) | 1298 (11) | 691 (51) |
| C(8) | 3292 (8) | 384 (13) | 4163 (13) | 899 (63) | C(52) | 4087 (8) | 9114 (11) | 911 (12) | 801 (58) |
| C(9) | 2295 (6) | 958 (9) | 5501 (10) | 543 (44) | C(53) | 4410 (8) | 9390 (14) | 400 (13) | 937 (63) |
| C(10) | 2641 (7) | 432 (10) | 6084 (11) | 683 (52) | C(54) | 4806 (8) | 8968 (12) | 317 (13) | 860 (60) |
| C(11) | 2575 (8) | 351 (13) | 6908 (14) | 902 (64) | C(55) | 4929 (9) | 8212 (13) | 671 (13) | 942 (67) |
| C(12) | 2198 (7) | 839 (11) | 7119 (13) | 799 (57) | C(56) | 4615 (8) | 7905 (13) | 1151 (13) | 821 (62) |
| C(13) | 1875 (8) | 1357 (11) | 6545 (12) | 828 (60) | C(57) | 3240 (7) | 8464 (11) | 1712 (11) | 752 (55) |
| C(14) | 1930 (7) | 1419 (10) | 5734 (11) | 631 (50) | C(58) | 2740 (9) | 8074 (15) | 1417 (13) | 933 (68) |
| C(15) | 1153 (6) | 3796 (10) | 2696 (10) | 579 (46) | C(59) | 2276 (10) | 8515 (14) | 1320 (14) | 1052 (72) |
| C(16) | 978 (8) | 3816 (14) | 3409 (14) | 945 (66) | C(60) | 2305 (10) | 9326 (14) | 1510 (13) | 1071 (72) |
| C(17) | 672 (8) | 4412 (13) | 3622 (16) | 1054 (71) | C(61) | 2778 (8) | 9735 (15) | 1807 (13) | 979 (67) |
| C(18) | 501 (10) | 5095 (15) | 3024 (15) | 1117 (78) | C(62) | 3228 (10) | 9287 (13) | 1927 (13) | 1002 (69) |
| C(19) | 678 (8) | 5078 (13) | 2301 (14) | 896 (62) | C(63) | 3674 (7) | 6984 (10) | 1405 (11) | 616 (47) |
| C(20) | 973 (7) | 4448 (11) | 2125 (12) | 748 (55) | C(64) | 3810 (7) | 6223 (11) | 1825 (14) | 859 (61) |
| C(21) | 1968 (7) | 3293 (10) | 1946 (11) | 655 (50) | C(65) | 3689 (7) | 5531 (13) | 1386 (13) | 890 (64) |
| C(22) | 1827 (7) | 3578 (10) | 1115 (11) | 696 (52) | C(66) | 3441 (8) | 5514 (15) | 549 (15) | 1007 (72) |
| C(23) | 2221 (8) | 3827 (12) | 722 (15) | 957 (65) | C(67) | 3294 (8) | 6187 (12) | 128 (14) | 893 (62) |
| C(24) | 2735 (12) | 3802 (15) | 1167 (18) | 1284 (89) | C(68) | 3420 (7) | 6927 (11) | 572 (12) | 753 (54) |
| C(25) | 2915 (15) | 3488 (17) | 2031 (20) | 1662 (114) | C(69) | 4111 (8) | 7842 (12) | 2865 (13) | 894 (64) |
| C(26) | 2498 (9) | 3292 (13) | 2397 (17) | 1133 (78) | C(70) | 4588 (9) | 7379 (13) | 3181 (16) | 1089 (75) |
| C(27) | 1199 (6) | −403 (9) | 4620 (10) | 516 (42) | C(71) | 4822 (11) | 7216 (16) | 4089 (17) | 1238 (89) |
| C(28) | 1387 (7) | −1058 (11) | 5130 (11) | 694 (52) | C(72) | 4562 (11) | 7585 (15) | 4594 (21) | 1295 (92) |
| C(29) | 1214 (8) | −1173 (14) | 5852 (14) | 964 (68) | C(73) | 4109 (12) | 8038 (17) | 4377 (20) | 1413 (100) |
| C(30) | 907 (8) | −624 (13) | 6051 (15) | 941 (65) | C(74) | 3879 (9) | 8155 (12) | 3483 (14) | 961 (68) |
| C(31) | 716 (7) | 32 (11) | 5563 (12) | 771 (55) | Cl(3) | 1558 (5) | 6220 (8) | 645 (8) | 2683 (56) |
| C(32) | 867 (7) | 147 (11) | 4827 (11) | 680 (52) | Cl(4) | 3137 (5) | 1780 (9) | 677 (9) | 2988 (64) |
| C(33) | 1399 (6) | −1278 (9) | 3248 (10) | 551 (45) | C(75) | 1980 (15) | 5955 (22) | −24 (25) | 2109 (154) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

microcrystals of $[Pd_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (**5**) formed overnight. The solid was filtered and dried in vacuo; yield 217 mg (70% based on 0.5 $CH_2Cl_2$ of crystallization). Anal. Calcd for $C_{50}H_{44}BCl_2F_4NOP_4Pd_2 \cdot 0.5CH_2Cl_2$: C, 50.05; H, 3.74; N, 1.10. Found: C, 50.18; H, 3.67; N, 0.80. IR (KBr, cm$^{-1}$): $\nu$(NO) 1532 (m). $^1H$ NMR (200.133 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 2.87 (m, $J(H_aH_b)$ = 14.0, $J$(PH) ≈ 2.5 Hz, P–$CH_2$P), 1.81 (d qn, $J(H_aH_b)$ = 14.0, $J$(PH) = 4.5 Hz, P–$CH_2$–P). When the solution of **5** is allowed to stand in the NMR tube, the growth in the proton spectrum of new broad methylene resonances at 4.33 and 3.24 ppm was observed just minutes after the first run.

Further cooling of the yellow filtrate gave after a few days yellow microcrystals of $[Pd_2(\mu\text{-}Cl)_2(dppm)_2][BF_4]_2$ (**6**) in 22% yield. Anal. Calcd for $C_{50}H_{44}B_2Cl_2F_8P_4Pd_2$: C, 48.98; H, 3.62. Found: C, 49.39; H, 3.76. $^1H$ NMR (200.133 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 4.82 (t, $J$(PH) = 12.1 Hz, P–$CH_2$–P). Complex **6** decomposes in air as a solid after months.

The use of a stoichiometric amount of $NO^+BF_4^-$ lowered the yield of **5** to ~35%.

**X-ray Data Collection, Structure Determination, and Refinement for $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BPh_4 \cdot CH_2Cl_2$ (1c).** The crystallographic data are summarized in Table IV. Unit cell parameters were determined from the $\theta$ values of 30 carefully centered reflections, having 14.0 < $\theta$ < 16.8°. Data were collected at room temperature (22 °C) on a Philips PW 1100 diffractometer, using graphite-monochromated Mo K$\alpha$ radiation and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min$^{-1}$ and a scan width from $(\theta - 0.60)°$ to $(\theta + 0.60 + 0.346 \tan \theta)°$. A decay of about 15% of the initial intensity of a standard reflection, measured after 50 reflections, was observed during the data collection and corrected. The individual profiles have been analyzed by the method of Lehmann and Larsen.[24] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.367 and 0.802).[25] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms, except the carbon atoms of the phenyl rings and those of the dichloromethane molecule of solvation. All hydrogen atoms, except those of the solvent molecule, were placed at their geometrically calculated positions (C–H = 1.00 Å) and refining "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 482 variables; after the last cycles, no parameters shifted by more than 0.87 esd. The largest remaining peak (close to the Pt atom) in the final difference map was equivalent to about 0.87 e/Å$^3$. In the final cycles of refinement the weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the $K$ and $g$ values were 0.898 and 0.0017,

---

(24) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580.

(25) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158. Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109.

respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref. 26. All calculations were carried out on the Cray X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould Powernode 6040 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[27] The final atomic coordinates for the non-hydrogen atoms are given in Table V. The atomic coordinates of the hydrogen atoms are given in Table SI and thermal parameters in Tables SII and SIII (supplementary material).

**Acknowledgment.** We acknowledge financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and Johnson-Matthey Research Centre, Reading, England, for the generous loan of Pd and Pt salts. We also thank Dr. M. Grassi for the NMR experiments.

**Registry No.** **1a**, 133952-77-9; **1b**, 137966-74-6; **1c**, 137966-75-7; **1c**·$CH_2Cl_2$, 137966-76-8; **2**, 137966-78-0; **3**, 137966-80-4; **5**, 137966-82-6; **6**, 137966-84-8; $Pt_2Cl_2(\mu\text{-dppm})_2$, 61250-65-5; $Pt_2Br_2(\mu\text{-dppm})_2$, 61250-66-6; $Pt_2I_2(\mu\text{-dppm})_2$, 61289-07-4; $Pd_2Cl_2(\mu\text{-dppm})_2$, 64345-29-5; $[Pt_2(\mu\text{-I})_2(dppm)_2][BF_4]_2$, 132289-25-9; $^{195}Pt$, 14191-88-9.

**Supplementary Material Available:** Hydrogen atom coordinates (Table SI) and anisotropic and isotropic thermal parameters for the non-hydrogen atoms (Tables SII and SIII) (3 pages); observed and calculated structure factors from the final cycle of least-squares refinement (Table SIV) (27 pages). Ordering information is given on any current masthead page.

---

(26) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(27) Sheldrick, G. M. SHELX-76 program for crystal structure determination; University of Cambridge: Cambridge, England, 1976. SHELXS-86 program for the solution of crystal structures; University of Göttingen, Göttingen, Germany, 1986.

---

# Reactions of Unsaturated Dihydrido Carbonyl Complexes of Manganese(I) with Nitriles and Isonitriles. Preparation and Characterization of the First Binuclear $\mu,\eta^1,\eta^2$-NCR Derivatives

Francisco J. García Alonso, Manuel García Sanz, and Víctor Riera*

*Departamento de Química Organometálica, Universidad de Oviedo, E-33071 Oviedo, Spain*

Adela Anillo Abril, Antonio Tiripicchio,* and Franco Ugozzoli

*Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, Viale delle Scienze 78, I-43100 Parma, Italy*

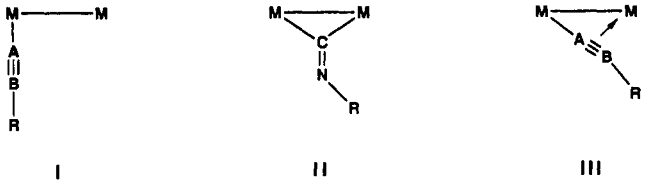
*Received May 17, 1991*

The unsaturated dihydrido binuclear carbonyl complexes $[Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-L-L})]$ (L-L = $Ph_2PCH_2PPh_2$, dppm (**1**), $(EtO)_2POP(OEt)_2$, tedip (**2**)) react under mild conditions with equimolecular amounts of nitriles NCR to give either $[Mn_2(\mu,\eta^1,\eta^2\text{-NCR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = Me (**3a**), Et (**3b**), Pr (**3c**), L-L = tedip, R = Me (**3d**), $^t$Bu (**3e**)) or $[Mn_2(\mu\text{-H})(\mu\text{-N=CHR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = Ph (**4a**), $CH_2Ph$ (**4b**), $CH{=}CH_2$ (**4c**), $CH_2CN$ (**4d**); L-L = tedip, R = Ph (**4e**), $CH{=}CH_2$ (**4f**)) depending on the nature of the nitrile substituent. The compounds **3** are the first binuclear complexes containing a bridging $\sigma,\pi$-nitrile. At room temperature isocyanides replace both hydrido ligands in **1** and **2** to give $[Mn_2(\mu,\eta^1,\eta^2\text{-CNR})(CO)_6(\mu\text{-L-L})]$ (L-L = dppm, R = $^t$Bu (**5a**); L-L = tedip, R = $^t$Bu (**5b**), 4-$MeC_6H_4$ (**5c**)) except in the case of *p*-tolyl isocyanide, which reacts with **1** to give $[Mn_2(\mu\text{-H})(\mu\text{-HC=N-4-MeC}_6H_4)(CO)_6(\mu\text{-dppm})]$ (**6**). The structures of **3a** and **4a** have been determined by X-ray diffraction methods. Crystals of **3a** are orthorhombic, space group $P2_12_12_1$ with $Z = 4$ in a unit cell of dimensions $a = 14.444$ (5), $b = 19.965$ (7), and $c = 11.207$ (5) Å. Crystals of **4a** are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 14.285$ (6), $b = 12.028$ (6), and $c = 10.902$ (6) Å and $\alpha = 86.74$ (3), $\beta = 105.32$ (2), and $\gamma = 97.59$ (2)°. Both structures have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1179 (**3a**) and 2118 (**4a**) observed reflections to $R$ and $R_w$ values of 0.0537 and 0.0693 (**3a**) and 0.0626 and 0.0738 (**4a**), respectively.

## Introduction

There is much current interest in the interactions between small unsaturated molecules and metal clusters. In fact, the presence of several metal atoms allows for a great diversity of ligand coordination modes and promotes a wide variety of useful substrate transformations, some of which are appropriate models for reactions catalyzed by transition-metal surfaces. In this sense, much work has been devoted to the reactivity of carbon monoxide and hydrocarbyl ligands with metal clusters, while nitriles, NCR, and isonitriles, CNR, which are among the most versatile groups both in organic and organometallic chemistry,[1,2] have received less attention.

**Chart I. Different Ways in Which Nitriles and Isonitriles Are Bonded to Two Metal Centers (ABR = CNR, NCR)**



0276-7333/92/2311-0801$03.00/0 © 1992 American Chemical Society