Heterobinuclear Nitrosyl Complexes. Part 2.[1] Crystal Structures of $[(Ph_3P)_2(NO)Ir(\mu\text{-dppn})(\mu\text{-Cl})PdCl][PF_6]_2$ and $[(Ph_3P)Cl_2Ir(\mu\text{-NO})(\mu\text{-dppn})PdCl]PF_6$ [dppn = 3,6-bis(2′-pyridyl)pyridazine] *

Antonio Tiripicchio and Marisa Tiripicchio Camellini
Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, I-43100 Parma, Italy
Francesco Neve and Mauro Ghedini
Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy

From the reactions of $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ or $[Ir(NO)(dppn)Cl(PPh_3)_2]PF_6$ with $[PdCl_2(NCPh)_2]$ the binuclear complexes $[(Ph_3P)_2(NO)Ir(\mu\text{-dppn})(\mu\text{-Cl})PdCl][PF_6]_2$ (**3**) and $[(Ph_3P)Cl_2Ir(\mu\text{-NO})(\mu\text{-dppn})PdCl]PF_6$ (**5**) respectively have been obtained. The structure of both these complexes have been determined by *X*-ray diffraction methods. Crystals of (**3**) are monoclinic, space group $P2_1/a$, with a = 22.365(9), b = 14.383(7), c = 18.525(7) Å, β = 115.17(2)°, and Z = 4. Crystals of (**5**) are monoclinic, space group Pn, with a = 15.754(7), b = 8.870(5), c = 14.453(7) Å, β = 111.42(2)°, and Z = 2. The structures have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.078 for 2 973 observed reflections for (**3**) and to R = 0.040 for 2 533 observed reflections for (**5**). In complex (**3**) a terminal bent NO group is bound to the Ir atom [Ir–N–O 123(3)°] with the dppn ligand and one Cl atom bridging the two metals [Ir ··· Pd separation 3.681(4) Å]. In (**5**) the dppn ligand and the nitrosyl group bridge the two metals, with Ir–N (nitrosyl) bond distances of 2.030(15) and 1.953(17) Å. The Ir ··· Pd separation is of 3.327(2) Å. According to these structural features the reaction scheme involving the heterobinuclear dppn nitrosyl complexes has been redesigned.

Homobinuclear transition-metal complexes containing bridging nitrogen monoxide are well known and many examples are reported in the literature.[2,3] In contrast, the synthesis of heteronuclear nitrosyl-bridged complexes represents a very recent development of the chemistry of NO. Thus up to now few members of this class of compounds have been described [1,4–7] and even less structurally characterized.[4–6]

A single-crystal *X*-ray analysis[4] has been carried on $[(Ph_3P)_2ClIr(\mu\text{-NO})(\mu\text{-dppn})CuCl][PF_6]_2$ (**4**) [dppn = 3,6-bis(2′-pyridyl)pyridazine], a complex in which the metals are held together by both the NO and the bis-chelating dppn ligand. In this compound the NO group is symmetrically bound to the metals.[4] A similar structural feature has been observed in $[(\eta\text{-}C_5H_5)Co(\mu\text{-NO})_2Mn(PMe_3)(\eta\text{-}C_5H_5)]$,[5] the only heterobinuclear species bridged only by NO groups. Finally, an asymmetrically bridging nitrosyl ligand has been found in the cluster $[N(PPh_3)_2][Fe_2W(\mu\text{-CO})(\mu\text{-NO})(\mu_3\text{-CR})(CO)_6(\eta\text{-}C_5H_5)]$, R = C_6H_4Me-4, with the NO group weakly bound to the iron atom of one Fe–W edge.[6]

In a previous paper[1] we described the syntheses of the heterobinuclear nitrosyl species $[IrPd(NO)(\mu\text{-dppn})Cl_2(PPh_3)_2][PF_6]_2$ and $[IrPd(NO)(\mu\text{-dppn})Cl_3(PPh_3)]PF_6$. On the basis of a spectroscopic characterization and by analogy with the similar IrCu compound (**4**), we suggested the presence of a bridging NO group in both those complexes. Now we report their *X*-ray analyses. These further investigations surprisingly show two different co-ordination modes, namely bent terminal in the complex cation of the 1:2 salt and bridging, as proposed, in that of the 1:1 salt. Therefore, according to these new findings, the reaction scheme for the heterobinuclear dppn nitrosyl complexes has been redesigned and discussed.

Results and Discussion

Crystal Structure of $[(Ph_3P)_2(NO)Ir(\mu\text{-dppn})(\mu\text{-Cl})PdCl][PF_6]_2$ (**3**).—The crystal structure of complex (**3**) consists of discrete heterobinuclear PdIr cations and of PF_6^- counter anions. A view of the cationic complex is shown in Figure 1 together with the atomic numbering scheme; relevant bond distances and angles are given in Table 1.

The dppn molecule, acting as a quadridentate ligand, adopts a conformation suitable to chelate both Ir and Pd, on the same side, through one pyridyl and one pyridazinyl nitrogen atom. A chlorine atom, Cl(1), also bridges the two metals in a slightly asymmetric way [Ir–Cl(1) 2.395(11), Pd–Cl(1) 2.325(11) Å, Ir–Cl(1)–Pd 102.5(4)°]. The square-planar co-ordination of the Pd atom is completed by Cl(2); the octahedral co-ordination of the Ir atom involves also a nitrogen atom, N(3), from a terminal bent nitrosyl group, in the equatorial plane, and two phosphorus atoms from PPh_3 ligands, in the apical sites. The Ir ··· Pd separation is 3.681(4) Å. Each of the three rings of the dppn ligand is planar and the whole ligand is roughly planar, probably in order to allow the chelation of the two metals and the Cl bridge [dihedral angles between the central ring and the other two are 6.9(9) and 5.1(9)° respectively, the maximum deviation from the mean plane through the whole dppn being 0.15(3) Å]. Atoms Ir, Pd, Cl(1), Cl(2), and N(3) are almost coplanar with the dppn mean plane, the deviations from it being −0.054(2), 0.029(3), 0.02(1), 0.03(1), and −0.08(4) Å respectively, while the O atom is out of this plane by 0.45(4) Å.

It is noteworthy that the two bridges, the chlorine and the

---

* μ-[3,6-Bis(2′-pyridyl)pyridazine-$N'N''$:N^2N''']-μ-chloro-1-chloro-2-nitrosyl-2,2-bis(triphenylphosphine)-1-palladium-2-iridium bis(hexafluorophosphate) and μ-[3,6-bis(2′-pyridyl)pyridazine-$N'N''$:N^2N''']-1,2,2-trichloro-μ-(nitrosyl-*N*)-2-triphenylphosphine-1-palladium-2-iridium hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

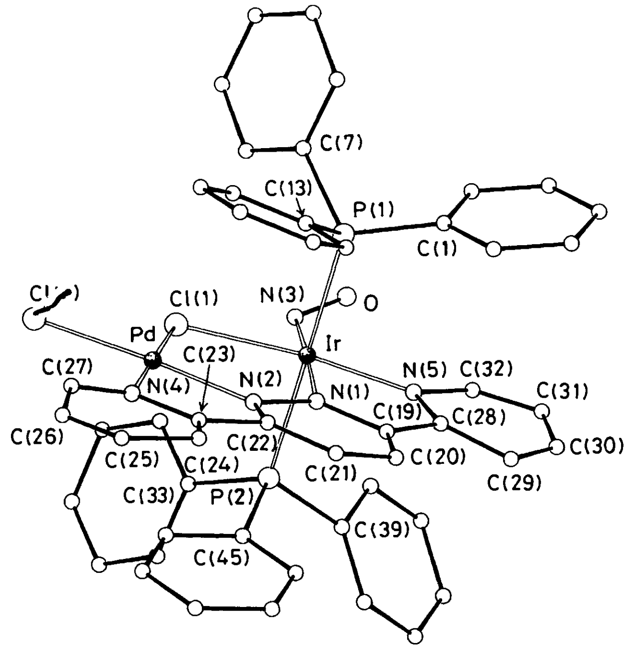


Figure 1. View of the cation $[(Ph_3P)_2(NO)Ir(\mu\text{-dppn})(\mu\text{-Cl})PdCl]^{2+}$ of compound (**3**) with the atomic numbering scheme

Table 1. Selected bond distances (Å) and angles (°) in complex (**3**)

Ir–P(1)	2.401(8)	Pd–N(4)	2.03(3)
Ir–P(2)	2.408(8)	N(3)–O	1.19(5)
Ir–Cl(1)	2.395(11)	N(4)–C(27)	1.38(5)
Ir–N(1)	2.12(3)	N(4)–C(23)	1.29(5)
Ir–N(3)	1.85(4)	N(1)–N(2)	1.40(5)
Ir–N(5)	1.98(3)	N(1)–C(19)	1.38(4)
Pd–Cl(1)	2.325(11)	N(2)–C(22)	1.45(5)
Pd–Cl(2)	2.246(13)	N(5)–C(28)	1.36(4)
Pd–N(2)	1.96(3)	N(5)–C(32)	1.38(5)
P(1)–Ir–P(2)	177.8(3)	P(2)–Ir–N(5)	88.9(9)
N(3)–Ir–Cl(1)	84.7(12)	P(2)–Ir–N(1)	89.0(9)
N(3)–Ir–N(5)	105.5(15)	P(2)–Ir–Cl(1)	88.3(3)
N(1)–Ir–N(5)	76.5(12)	Cl(1)–Pd–N(2)	96.1(9)
N(1)–Ir–Cl(1)	93.3(9)	Cl(1)–Pd–Cl(2)	88.5(4)
P(1)–Ir–N(3)	92.2(11)	Cl(2)–Pd–N(4)	94.7(9)
P(1)–Ir–N(5)	91.7(8)	N(2)–Pd–N(4)	80.8(12)
P(1)–Ir–N(1)	89.1(9)	Ir–Cl(1)–Pd	102.5(4)
P(1)–Ir–Cl(1)	90.8(4)	Ir–N(3)–O	123(3)
P(2)–Ir–N(3)	89.7(13)		

pyridazine, are almost coplanar, the dihedral angle between the PdCl(1)Ir and PdN(2)N(1)Ir planes being 3.5(8)°, so that the penta-atomic ring is nearly planar [torsion angles PdCl(1)IrN(1), Cl(1)IrN(1)N(2), IrN(1)N(2)Pd, N(1)N(2)PdCl(1), and N(2)PdCl(1)Ir are −2.4(9), 0.2(25), 3.2(38), −4.5(27), and 3.5(9)° respectively].

As regards the nitrosyl group, complex (**3**) can be considered to belong to the $\{MNO\}^8$ class, according to the Enemark and Feltham classification.[8] The N(3)–O distance, 1.19(5) Å, and the Ir–N(3)–O angle, 123(3)°, fall into the ranges reported for complexes with bent NO groups. The Ir–N(3) bond distance, 1.85(4) Å, is shorter than in the other six-co-ordinated iridium complex $[Ir(NCMe)_3(NO)(PPh_3)_2][PF_6]_2$ with a bent nitrosyl group, 1.965(20) Å.[9] The Ir–N(1) bond, 2.12(3) Å, much longer than the Ir–N(5) one, 1.98(3) Å, clearly shows the strong *trans*-bond effect of the bent nitrosyl groups.[10]

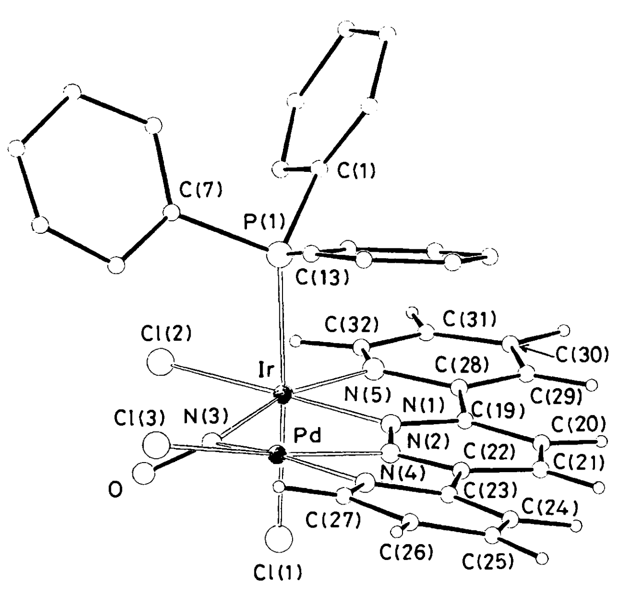


Figure 2. View of the cation $[(Ph_3P)Cl_2Ir(\mu\text{-NO})(\mu\text{-dppn})PdCl]^+$ of compound (**5**) with the atomic numbering scheme

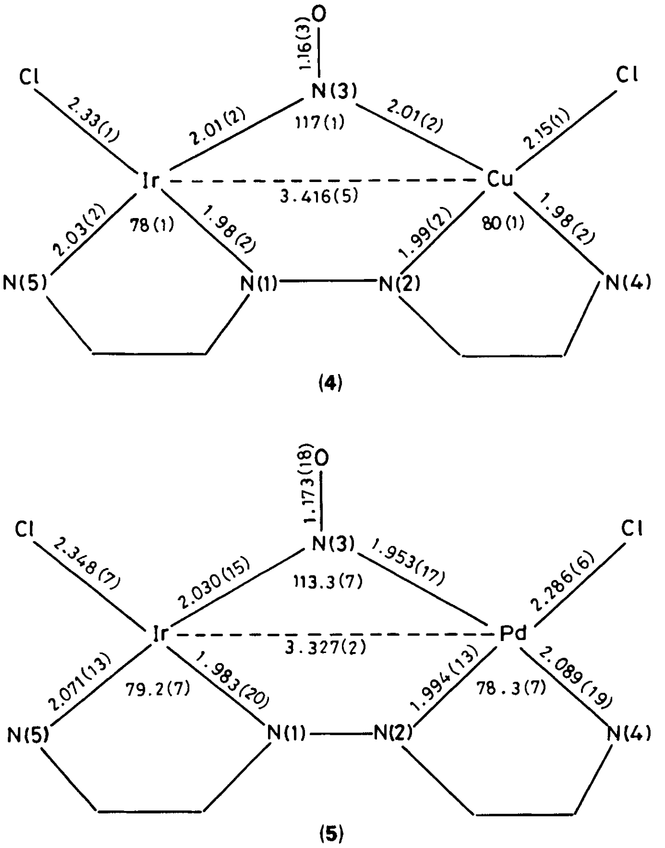
Table 2. Selected bond distances (Å) and angles (°) in complex (**5**)

Ir–P(1)	2.340(5)	Pd–N(4)	2.089(19)
Ir–Cl(1)	2.408(6)	N(3)–O	1.173(18)
Ir–Cl(2)	2.348(7)	N(4)–C(27)	1.38(3)
Ir–N(1)	1.983(20)	N(4)–C(23)	1.38(3)
Ir–N(3)	2.030(15)	N(1)–N(2)	1.31(3)
Ir–N(5)	2.071(13)	N(1)–C(19)	1.36(2)
Pd–Cl(3)	2.286(6)	N(2)–C(22)	1.36(3)
Pd–N(2)	1.994(13)	N(5)–C(28)	1.40(2)
Pd–N(3)	1.953(17)	N(5)–C(32)	1.34(3)
P(1)–Ir–Cl(1)	177.0(2)	Cl(1)–Ir–N(5)	87.2(4)
N(3)–Ir–Cl(2)	93.4(5)	Cl(1)–Ir–N(1)	88.5(6)
Cl(2)–Ir–N(5)	96.6(4)	Cl(1)–Ir–N(3)	84.0(5)
N(1)–Ir–N(5)	79.2(7)	N(3)–Pd–Cl(3)	93.6(5)
N(3)–Ir–N(1)	90.4(7)	N(3)–Pd–N(2)	91.1(6)
P(1)–Ir–N(3)	93.7(5)	N(2)–Pd–N(4)	78.3(7)
P(1)–Ir–Cl(2)	89.4(2)	Cl(3)–Pd–N(4)	97.6(5)
P(1)–Ir–N(5)	95.4(4)	Ir–N(3)–Pd	113.3(7)
P(1)–Ir–N(1)	93.4(6)	Ir–N(3)–O	121.7(13)
Cl(1)–Ir–Cl(2)	88.9(2)	Pd–N(3)–O	123.9(13)

Crystal Structure of $[(Ph_3P)Cl_2Ir(\mu\text{-NO})(\mu\text{-dppn})PdCl]PF_6$ (**5**).—In the crystals of complex (**5**) discrete heterobinuclear PdIr cations and PF_6^- anions are present. A view of the cation is shown in Figure 2 together with the atomic numbering scheme; relevant bond distances and angles are given in Table 2.

The structure of this cation is comparable to that of (**3**) except for the replacement of the Cl bridge with a NO bridge and the co-ordination of two Cl atoms, one of them instead of a PPh_3 ligand, on the Ir atom. The Ir••• Pd separation, 3.327(2) Å, is shorter than in (**3**). Each of the three rings of the dppn ligand is planar; the central one is almost coplanar with the ring containing the atom N(5) [dihedral angle 1.9(6)°], while it is slightly bent with respect to the ring containing N(4) [dihedral angle 7.8(6)°]. The whole dppn ligand is roughly planar, the maximum deviation from the mean plane being 0.23(3) Å, with atoms Ir, Pd, Cl(2), and Cl(3) almost coplanar [deviating by 0.124(1), 0.114(2), 0.276(6), and −0.148(6) Å respectively] and with the nitrosyl group strongly out of plane [deviations of N(3) and O from the mean dppn plane are 0.55(2) and 1.20(2) Å].

The nitrosyl and pyridazine bridges are not coplanar



Scheme 1. Comparison of the most significant structural parameters (distances in Å, angles in °) in the cationic complexes $[(Ph_3P)Cl_2Ir(\mu\text{-}NO)(\mu\text{-}dppn)PdCl]^+$ (**5**) and $[(Ph_3P)_2ClIr(\mu\text{-}NO)(\mu\text{-}dppn)CuCl]^{2+}$ (**4**)

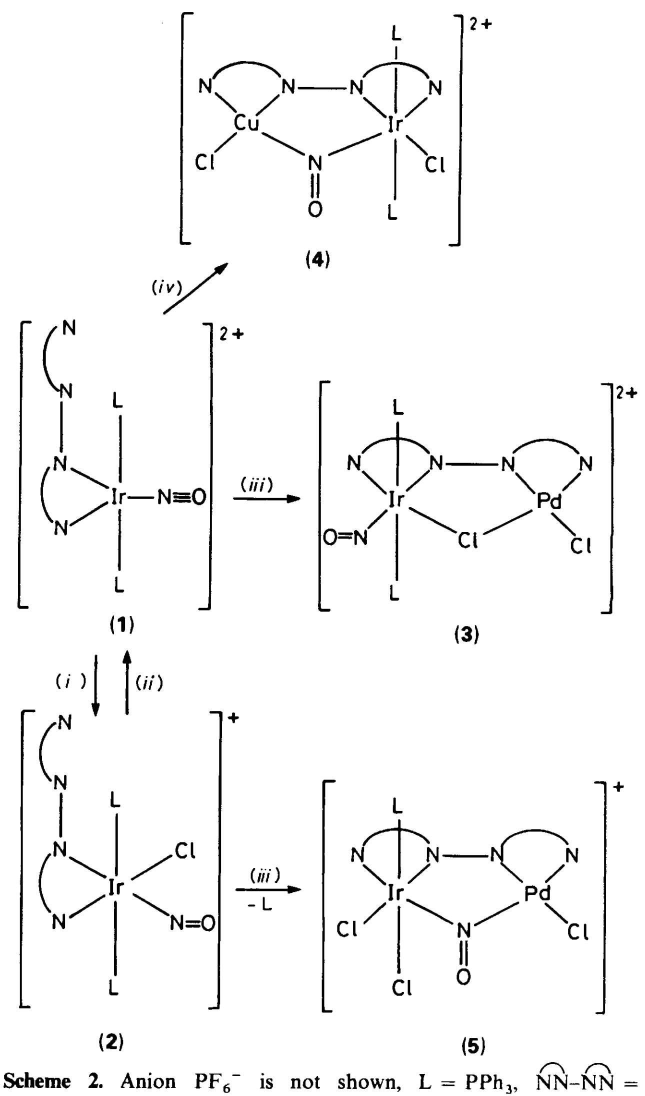
[dihedral angle between the PdN(3)Ir and PdN(2)N(1)Ir planes 23.4(8)°], in contrast to the chlorine and pyridazine bridges in (**3**). The nitrosyl group is bent away from the bulky PPh_3 ligand, whereas in (**3**) probably the bridging Cl atom is constrained to lie in the dppn plane in order to minimize the steric hindrance of the two PPh_3 ligands, above and below this plane. The bending of the NO group in (**5**) produces a remarkable distortion in the equatorial co-ordination of the Ir atom and especially in the square-planar co-ordination of the Pd atom, much greater than in (**3**). As a consequence the penta-atomic ring, formed by atoms Pd, N(3), Ir, N(1), and N(2), adopts a 'twist' conformation [torsion angles N(3)IrN(1)N(2), IrN(1)N(2)Pd, N(1)N(2)PdN(3), N(2)PdN(3)Ir, and PdN(3)-IrN(1) are −7.3(16), −6.9(20), 17.5(15), −20.8(8), and 18.5(9)° respectively].

The structure of complex (**5**) is comparable with that of (**4**), in which the Cu atom replaces the Pd and a PPh_3 ligand replaces the apical Cl. The most significant structural features of the two complexes are given in Scheme 1.

Complexes with nitrosyl groups bridging two metal centres not involved in a metal–metal bond are not very numerous. The most significant structural parameters in these complexes are reported for comparison in Table 3. It can be seen that these nitrosyl bridges are all symmetrical, independently of the nature of the metals and their co-ordination spheres.

Conclusion

The syntheses of the complexes (**3**) and (**5**) were achieved by reaction of equimolar amounts of $[PdCl_2(NCPh)_2]$ and $[Ir(NO)(dppn)(PPh_3)_2][PF_6]_2$ (**1**), or $[Ir(NO)(dppn)Cl(PPh_3)_2]PF_6$ (**2**), at room temperature, in dichloromethane or acetonitrile solution, respectively.[1]



Scheme 2. Anion PF_6^- is not shown, L = PPh_3, $\widehat{NN}\text{-}\widehat{NN}$ = dppn. (*i*) LiCl; (*ii*) $AgPF_6$; (*iii*) $[PdCl_2(NCPh)_2]$; (*iv*) $CuCl_2{\cdot}2H_2O$

Complex (**1**), with a linear Ir–NO linkage [ν(NO) 1 795 cm^{-1} (KBr)], easily reacts with $[PdCl_2(NCPh)_2]$ or $CuCl_2{\cdot}2H_2O$ giving rise to complexes (**3**) and (**4**) respectively. Both products have similar stoicheiometry but different NO structural features: bent terminal in (**3**) [ν(NO) 1 522 cm^{-1} (KBr)] and bridging in (**4**) [ν(NO) 1 525 cm^{-1} (KBr)].

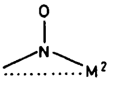
Alternatively, (**1**) reversibly adds a chloride ion affording the complex (**2**), whose Ir–NO moiety is bent [ν(NO) 1 502 cm^{-1} (KBr)]. The heterobinuclear (**5**) is then obtained by reaction of (**2**) with $[PdCl_2(NCPh)_2]$. Complex (**5**) is characterized by its Cl–Ir(μ-NO)Pd–Cl framework [ν(NO) 1 560 cm^{-1} (KBr)], formed by migration of a Cl atom from the Pd to the Ir. The latter metal, in turn, loses a PPh_3 ligand and is recovered as $[PdCl_2(PPh_3)_2]$.[1]

The reactivity summarized above merits the following remarks.

(*i*) A Cl–Ir(μ-NO)Pd–Cl framework is formed in complex (**5**). In order to explain this result it is useful to compare the reactions (**1**) ⟶ (**3**) and (**2**) ⟶ (**5**) (see Scheme 2).

The reaction (**1**) ⟶ (**3**) can be supposed to proceed through co-ordination of '$PdCl_2$' to the vacant dppn chelating site and the interaction of a Cl atom with the $\{IrNO\}^8$ fragment.[8] This

Table 3. The most significant structural parameters in complexes with nitrosyl bridging two metals not involved in a metal–metal bond (n.r. = not reported)



Complex	$M^1 \cdots M^2$ (Å)	M^1–N (Å)	M^2–N (Å)	N–O (Å)	M^1–N–M^2 (°)	Ref.
$[Pd_4(O_2CMe)_6(\mu\text{-}NO)_2]$		1.874	1.913	1.20	121.83	*a*
$[Pt_4(O_2CMe)_6(\mu\text{-}NO)_2]$	3.311(2)	1.912(15) (av.)	1.912(15) (av.)	1.22(3)	119.9(13)	*b*
$[NEt_4]_2[Pt_2(NO)(\mu\text{-}NO)Cl_6]$	3.287(3)	1.89(4)	1.93(3)	1.27(5)	119(2)	*c*
$[(Ph_3P)_2ClIr(\mu\text{-}NO)(\mu\text{-}dppn)CuCl][PF_6]_2$	3.416(5)	2.01(2)	2.01(2)	1.16(3)	117(1)	*d*
$[(Ph_3P)Cl_2Ir(\mu\text{-}NO)(\mu\text{-}dppn)PdCl]PF_6$	3.327(2)	2.030(15)	1.953(17)	1.173(18)	113.3(7)	*e*
$[Ir_2(\mu\text{-}pz)_2(\mu\text{-}NO)Cl_2(cod)_2]BF_4$	3.428(1)	2.096(9)	2.096(9)	n.r.	109.7(7)	*f*
$[Ru_4N(CO)_{12}(\mu\text{-}NO)]$	3.249(1)	2.025(6)	2.011(6)	1.227(7)	107.2(2)	*g*
$[Os_3(CO)_9(\mu\text{-}NO)_2\{P(OMe)_3\}]$	3.217(2)	2.072(14)	2.031(12)	1.227(18)	103.2(6)	*h*
		2.077(11)	2.050(13)	1.251(16)	102.4(5)	
$[Ru_3(CO)_{10}(\mu\text{-}NO)_2]$	3.150(1)	2.05(1)	1.99(1)	1.20(1)	102.5(4)	*i*
		2.03(1)	2.04(1)	1.24(1)	101.3(3)	
$[Os_3(CO)_9(NMe_3)(\mu\text{-}NO)_2]$	3.197(2)	2.05(1) (av.)	2.05(1) (av.)	n.r.	102.4(5)	*j*
$[Os_4H_3(CO)_{12}(\mu\text{-}NO)]$	n.r.	2.10(2)	2.10(2)	n.r.	n.r.	*k*
$[N(PPh_3)_2][Os_{10}C(CO)_{24}(\mu\text{-}NO)]$	n.r.	2.10(7)	2.10(7)	1.23(11)	n.r.	*l*
$[\{Co(meen)\}_2(\mu\text{-}NO)]BF_4$	2.770(2)	1.800(6)	1.817(6)	1.211(7)	99.9(3)	*m*

[a] N. V. Podberezskaya, V. V. Bakakin, N. I. Kuznetsova, A. F. Danilyuk, and V. A. Likholobov, *Dokl. Akad. Nauk SSSR*, 1981, **256**, 870. [b] P. De Meester and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1973, 1194. [c] J. M. Epstein, H. White, S. B. Wild, and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1974, 436. [d] Ref. 4. [e] This work. [f] D. D. K. Fjeldsted, S. R. Stobart, and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1985, **107**, 8258; cod = cyclo-octa-1,5-diene, pz = pyrazolate. [g] J. P. Attard, B. F. G. Johnson, J. Lewis, J. M. Mace, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1985, 1526. [h] S. Bellard and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1980, **36**, 705. [i] J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 1972, **11**, 382. [j] B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *J. Chem. Soc., Chem. Commun.*, 1979, 916. [k] D. Braga, B. F. G. Johnson, J. Lewis, J. M. Mace, M. McPartlin, J. Puga, W. J. H. Nelson, P. R. Raithby, and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1982, 1081. [l] D. Braga, K. Henrick, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, and J. Puga, *J. Chem. Soc., Chem. Commun.*, 1982, 1083. [m] H. N. Rabinowitz, K. D. Karlin, and S. J. Lippard, *J. Am. Chem. Soc.*, 1977, **99**. 1420.

interaction induces the redox processes $Ir^I \longrightarrow Ir^{III}$ and $NO^+ \longrightarrow NO^-$ to form the (NO)–Ir(μ-Cl)Pd–Cl moiety. Since in the reaction (**2**) ⟶ (**5**) '$PdCl_2$' reacts with the co-ordinatively saturated complex (**2**) (formally containing an Ir^{III} and a NO^- group) the dissociation of a PPh_3 molecule is required. As a consequence the formation of the derivative $[PdCl_2(PPh_3)_2]$ is observed. So, in the first step '$PdCl_2$' should act as a PPh_3 scavenger leading to the formation of the intermediate '$[Ir(NO)(dppn)Cl(PPh_3)]^+$,' which can chelate more '$PdCl_2$.'

(*ii*) For the reported heterobinuclear nitrosyl complexes the NO stretching frequency is not diagnostic of its bonding mode. While complexes (**4**) and (**5**) showed ν(NO) values (1 525 and 1 560 cm^{-1}, respectively) normal for NO ligands bridging two metals, a lower value (1 522 cm^{-1}) was observed for complex (**3**) (*i.e.* the bent, terminal mode of nitrosyl co-ordination).

The reactivity displayed by (**1**) shows how the nitrosyl bonding mode can change step by step on going from a monometallic to a bimetallic species [*i.e.* linear (**1**) ⟶ bent (**2**) ⟶ bridging (**5**) or linear (**1**) ⟶ bent (**3**)]. Therefore, this chemistry may be a proper example of activation by polymetallic systems of the nitrogen monoxide involved in catalytic processes.

Experimental

The complexes $[(Ph_3P)_2(NO)Ir(\mu\text{-}dppn)(\mu\text{-}Cl)PdCl][PF_6]_2$ (**3**) and $[(Ph_3P)Cl_2Ir(\mu\text{-}NO)(\mu\text{-}dppn)PdCl]PF_6$ (**5**) were prepared as previously reported.[1]

Crystal Structure Determination of Complexes (**3**) *and* (**5**).—Crystals of both complexes were of very poor quality, enough to prevent very accurate structure determinations. Those selected for the data collections were of approximate dimensions 0.15 × 0.21 × 0.24 [(**3**)] and 0.25 × 0.28 × 0.34 mm [(**5**)]. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 carefully centred reflections (with θ in the range 10—15°).

Crystal data. (**3**), $C_{50}H_{40}Cl_2F_{12}IrN_5OP_4Pd$, M = 1 448.30, monoclinic, space group $P2_1/a$, a = 22.365(9), b = 14.383(7), c = 18.525(7) Å, β = 115.17(2)°, U = 5 393(4) Å^3, Z = 4, D_c = 1.784 g cm^{-3}, $F(000)$ = 2 832, $\mu(Mo\text{-}K_\alpha)$ = 30.84 cm^{-1}.

(**5**), $C_{32}H_{25}Cl_3F_6IrN_5OP_2Pd$, M = 1 076.50, monoclinic, space group Pn, a = 15.754(7), b = 8.870(5), c = 14.453(7) Å, β = 111.42(2)°, U = 1 880(2) Å^3, Z = 2, D_c = 1.902 g cm^{-3}, $F(000)$ = 1 036, $\mu(Mo\text{-}K_\alpha)$ = 43.56 cm^{-1}.

Data were collected at room temperature on a Siemens AED diffractometer using niobium-filtered Mo-K_α radiation (λ = 0.710 69 Å) and the θ—2θ scan technique, the individual profiles having been analysed according to Lehmann and Larsen.[11] All the reflections in the range 3—23 [(**3**)] and 3—24° [(**5**)] were measured. Of 8 115 and 3 274 independent reflections, 2 973 for (**3**) and 2 533 for (**5**), having $I > 2\sigma(I)$, were considered observed and used in the analyses. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collections. Corrections for absorption effects were applied[12] using the program ABSORB[13] [maximum and minimum values for the transmissions factors were 1.202 and 0.803 for (**3**) and 1.263 and 0.793 for (**5**)].

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all the non-carbon atoms and with the phenyl rings treated as rigid groups (C–C 1.395 Å) for complex (**3**) and with anisotropic thermal parameters for Ir, Pd, Cl, P, O, and N atoms for (**5**).[14] All the hydrogen atoms were placed at their geometrically calculated positions and introduced in the final structure-factor calculations. The weighting scheme used in the last cycles of

Table 4. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex (3)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ir	2 444(1)	1 265(1)	3 026(1)	C(13)	4 050(11)	620(19)	3 370(12)
Pd	2 951(1)	1 430(2)	1 383(2)	C(14)	4 319(11)	1 286(19)	3 045(12)
Cl(1)	2 748(5)	2 371(6)	2 275(5)	C(15)	4 644(11)	1 008(19)	2 584(12)
Cl(2)	3 229(6)	2 711(8)	903(7)	C(16)	4 700(11)	66(19)	2 447(12)
P(1)	3 582(4)	1 043(6)	3 929(5)	C(17)	4 431(11)	−600(19)	2 771(12)
P(2)	1 310(4)	1 464(6)	2 080(5)	C(18)	4 107(11)	−323(19)	3 233(12)
P(3)	3 033(7)	6 091(10)	3 543(11)	C(19)	2 347(14)	−738(21)	2 540(16)
P(4)	341(8)	7 330(10)	1 594(10)	C(20)	2 442(16)	−1 532(22)	2 130(19)
F(1)	2 507(15)	6 363(19)	2 733(19)	C(21)	2 673(14)	−1 414(23)	1 559(16)
F(2)	2 499(20)	6 408(20)	3 880(24)	C(22)	2 843(15)	−567(24)	1 373(18)
F(3)	3 261(13)	7 142(18)	3 575(17)	C(23)	3 025(17)	−315(26)	753(20)
F(4)	3 547(15)	5 967(21)	4 403(17)	C(24)	3 160(18)	−955(27)	352(21)
F(5)	3 605(17)	5 809(21)	3 334(20)	C(25)	3 332(25)	−647(37)	−353(28)
F(6)	2 817(14)	5 054(20)	3 509(20)	C(26)	3 381(22)	219(34)	−470(25)
F(7)	691(16)	6 829(26)	2 320(22)	C(27)	3 326(20)	840(30)	71(24)
F(8)	632(31)	6 931(53)	1 182(38)	C(28)	2 173(14)	−679(21)	3 203(16)
F(9)	−28(25)	7 693(32)	1 968(27)	C(29)	1 932(16)	−1 496(23)	3 410(19)
F(10)	39(18)	7 855(24)	827(23)	C(30)	1 803(19)	−1 378(30)	4 030(22)
F(11)	928(17)	7 956(25)	1 913(21)	C(31)	1 867(19)	−667(29)	4 387(21)
F(12)	−247(19)	6 698(20)	1 142(24)	C(32)	1 982(16)	116(24)	4 106(19)
O	2 379(15)	2 249(20)	4 226(21)	C(33)	1 012(11)	2 644(11)	1 729(13)
N(1)	2 516(13)	120(20)	2 345(20)	C(34)	1 353(11)	3 439(11)	2 122(13)
N(2)	2 698(13)	259(18)	1 717(16)	C(35)	1 083(11)	4 317(11)	1 859(13)
N(3)	2 370(20)	2 294(25)	3 583(20)	C(36)	472(11)	4 400(11)	1 203(13)
N(4)	3 148(14)	542(21)	661(15)	C(37)	130(11)	3 605(11)	811(13)
N(5)	2 167(13)	191(21)	3 485(16)	C(38)	400(11)	2 727(11)	1 074(13)
C(1)	3 638(11)	298(16)	4 724(12)	C(39)	722(11)	1 084(17)	2 451(14)
C(2)	3 649(11)	−669(16)	4 678(12)	C(40)	180(11)	510(17)	2 037(14)
C(3)	3 649(11)	−1 211(16)	5 302(12)	C(41)	−286(11)	352(17)	2 338(14)
C(4)	3 637(11)	−785(16)	5 973(12)	C(42)	−211(11)	767(17)	3 053(14)
C(5)	3 626(11)	182(16)	6 019(12)	C(43)	331(11)	1 341(17)	3 466(14)
C(6)	3 627(11)	724(16)	5 395(12)	C(44)	798(11)	1 499(17)	3 165(14)
C(7)	4 072(11)	2 091(13)	4 429(12)	C(45)	1 184(11)	790(16)	1 180(10)
C(8)	4 683(11)	1 931(13)	5 067(12)	C(46)	1 273(11)	1 274(16)	580(10)
C(9)	5 066(11)	2 678(13)	5 498(12)	C(47)	1 250(11)	802(16)	−88(10)
C(10)	4 839(11)	3 586(13)	5 291(12)	C(48)	1 138(11)	−155(16)	−157(10)
C(11)	4 227(11)	3 746(13)	4 652(12)	C(49)	1 049(11)	−640(16)	442(10)
C(12)	3 844(11)	2 999(13)	4 221(12)	C(50)	1 072(11)	−166(16)	1 111(10)

Table 5. Fractional atomic co-ordinates (× 10^4) with (e.s.d.s) in parentheses for the non-hydrogen atoms of complex (5)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ir	5 000	2 195(1)	5 000	C(8)	5 787(15)	−2 033(26)	3 451(17)
Pd	4 841(1)	17(2)	6 804(1)	C(9)	6 526(18)	−3 044(30)	3 614(21)
Cl(1)	5 366(3)	4 428(6)	6 017(4)	C(10)	7 124(16)	−3 325(27)	4 640(19)
Cl(2)	6 338(4)	2 554(6)	4 668(5)	C(11)	6 972(20)	−2 669(30)	5 348(22)
Cl(3)	5 938(4)	−1 665(6)	7 684(4)	C(12)	6 296(14)	−1 609(26)	5 270(17)
P(1)	4 720(3)	−25(5)	4 062(4)	C(13)	3 857(11)	−1 105(19)	4 312(13)
P(2)	5 312(6)	5 324(10)	586(7)	C(14)	2 960(12)	−661(22)	3 957(14)
O	6 431(9)	1 344(19)	6 773(10)	C(15)	2 298(14)	−1 383(24)	4 226(16)
N(1)	3 838(11)	2 064(20)	5 234(15)	C(16)	2 557(15)	−2 573(23)	4 912(17)
N(2)	3 788(9)	1 279(16)	5 982(10)	C(17)	3 461(15)	−3 093(24)	5 300(17)
N(3)	5 660(9)	1 112(20)	5 303(11)	C(18)	4 111(12)	−2 335(20)	4 999(13)
N(4)	3 821(11)	−689(21)	7 309(11)	C(19)	3 133(13)	2 916(23)	4 642(15)
N(5)	4 167(9)	3 543(16)	3 860(11)	C(20)	2 312(13)	2 895(22)	4 800(15)
F(1)	6 431(14)	5 197(22)	990(15)	C(21)	2 228(13)	1 975(22)	5 567(15)
F(2)	5 304(13)	3 762(26)	101(18)	C(22)	2 988(12)	1 138(22)	6 127(14)
F(3)	5 322(13)	4 532(23)	1 565(15)	C(23)	3 020(15)	131(23)	6 927(17)
F(4)	4 275(17)	5 427(30)	248(19)	C(24)	2 327(18)	−149(32)	7 250(20)
F(5)	5 478(15)	6 914(25)	1 078(17)	C(25)	2 415(23)	−1 156(43)	7 954(27)
F(6)	5 366(15)	6 205(28)	−375(18)	C(26)	3 201(22)	−2 041(36)	8 347(24)
C(1)	4 288(11)	217(19)	2 692(13)	C(27)	3 931(16)	−1 782(27)	8 021(19)
C(2)	4 810(13)	1 206(23)	2 342(16)	C(28)	3 278(11)	3 743(19)	3 842(13)
C(3)	4 632(18)	1 277(31)	1 339(20)	C(29)	2 636(12)	4 566(21)	3 138(14)
C(4)	3 939(18)	273(30)	671(20)	C(30)	2 885(14)	5 347(24)	2 422(16)
C(5)	3 394(17)	−648(31)	1 065(20)	C(31)	3 778(14)	5 284(24)	2 474(16)
C(6)	3 614(13)	−682(23)	2 108(15)	C(32)	4 390(13)	4 392(24)	3 216(17)
C(7)	5 714(11)	−1 286(20)	4 277(13)				

refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.6326$ and 0.5988 and $g = 0.005$ for (**3**) and 0.002 for (**5**). The final atomic co-ordinates for the non-hydrogen atoms are given in Tables 4 [(**3**)] and 5 [(**5**)]. Final R and $R' = 0.078$ and 0.094 for (**3**) and 0.040 and 0.050 for (**5**). Atomic scattering factors, corrected for the anomalous dispersion of Ir, Pd, Cl, and P, were taken from ref. 15. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna, and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Acknowledgements

We thank the Italian Ministero della Pubblica Istruzione and Consiglio Nazionale delle Ricerche (C.N.R.) for financial support and Johnson Matthey Ltd. for the generous loan of iridium and palladium salts.

References

1 M. Ghedini and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1984, 1417.
2 R. D. Feltham and J. H. Enemark, *Top. Inorg. Stereochem.*, 1981, **12**, 155.
3 B. F. G. Johnson, B. L. Haymore, and J. R. Dilworth, 'Comprehensive Co-ordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 99.
4 A. Tiripicchio, A. M. Manotti Lanfredi, M. Ghedini, and F. Neve, *J. Chem. Soc., Chem. Commun.*, 1983, 97.
5 W. P. Weiner, F. J. Hollander, and R. G. Bergman, *J. Am. Chem. Soc.*, 1984, **106**, 7462.
6 E. Delgado, J. C. Jeffery, M. D. Simmons, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 869.
7 S. W. Carr and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1986, 1815.
8 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.
9 M. Lanfranchi, A. Tiripicchio, G. Dolcetti, and M. Ghedini, *Transition Met. Chem. (Weinheim, Ger.)*, 1980, **5**, 21.
10 D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2760.
11 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
13 F. Ugozzoli, *Comput. Chem.*, 1987, **11**, 109.
14 G. M. Sheldrick, SHELX76, Program for crystal structure determination, University of Cambridge, 1976.
15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 14*th September* 1989; *Paper* 9/05098A