Nickel Nitrosyl Complexes with Diphosphines. The Crystal and Molecular Structure of $[(dppe)(ON)Ni(\mu\text{-}dppe)Ni(NO)(dppe)][BF_4]_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$)†

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The preparation and characterization of several nitrosyl complexes of nickel with ditertiary phosphines (L–L) are reported. With the ligand $Ph_2PCH_2PPh_2$ (dppm) the mononuclear complex $[Ni(NO)(dppm)_2]BPh_4$ is obtained, in which one diphosphine acts as unidentate and one as a chelating ligand. With $R_2P(CH_2)_nPR_2$ (R = Ph or Me, n = 2 or 3) binuclear compounds $[Ni_2(NO)_2(L\text{–}L)_3]Y_2$ (Y = BF_4 or BPh_4) are formed, in which one diphosphine bridges two Ni(NO)(L–L) moieties. I.r., u.v.–visible, and ^{31}P n.m.r. data suggest a pseudo-tetrahedral co-ordination for the nickel atom with linear Ni–NO groups for both mono- and bi-nuclear species. Binuclear complexes containing phenyl-substituted diphosphines show an unusual low-temperature ^{31}P n.m.r. behaviour which is interpreted in terms of slow Ni–P bond rotation. A series of complexes $[Ni(NO)L(L\text{–}L)]Y$ [L = PHR_2, PR_3, or $P(OR)_3$; Y = BPh_4 or BF_4] has been prepared, and their low-temperature ^{31}P n.m.r. behaviour compared with that of the binuclear species. The structure of $[Ni_2(NO)_2(dppe)_3][BF_4]_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) has been determined by *X*-ray methods. Crystals are monoclinic, space group *C*2/*c* with $Z = 4$ in a unit cell of dimensions $a = 35.073(8)$, $b = 14.012(4)$, $c = 17.351(5)$ Å, and $\beta = 112.24(2)°$. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.0878$ for 2 029 observed reflections. In the cation one dppe ligand acts as a bridge between the two nickel atoms, while the other two chelate the two metals. One nitrogen atom from a terminal nitrosyl ligand completes the distorted tetrahedral co-ordination around each Ni atom. The Ni–N bond distance and the Ni–N–O bond angle are 1.67(2) Å and 168.2(14)°, respectively.

A large number of nickel nitrosyl complexes with phosphorus ligands have been reported, and the structures of several of these have also been determined by *X*-ray diffraction methods.[1] Although the $\{Ni(NO)\}^{10}$ complexes‡ can adopt two roughly equivalent geometries, *i.e.* pseudo-tetrahedral with a linear nitrosyl or square planar with strongly bent Ni–NO,[1a] to date all such complexes have been shown to possess a distorted tetrahedral co-ordination about the metal, with approximatively linear Ni–N–O groups.[2]

With unidentate phosphines and phosphites (L), complexes $[NiX(NO)L_2]$ (X = anionic ligand)[3–10] and $[Ni(NO)L_3]^+$ [11–14] have been isolated, while with tripod-like ligands (L′) the compounds $[Ni(NO)L']^+$ [L′ = $MeC(CH_2PEt_2)_3$ [15] or $N(CH_2CH_2PEt_2)_3$ [16]] are known. It should be noted that, in the case of $[Ni(NO)(PPh_3)_3]PF_6$, an equilibrium appears to take place in solution between tetrahedral and square-planar species, as indicated by low-temperature ^{31}P n.m.r. studies.[11] Four co-ordination is maintained also with bidentate ligands, which sometimes adopt unusual co-ordination modes. Thus $Ph_2PCH_2CH_2SEt$ forms a $[Ni(NO)(Ph_2PCH_2CH_2SEt)_2]^+$ species in which one of the ligand molecules is unidentate,[17] while two diphosphine bridges are present in the binuclear adduct $[(ON)(O_2N)Ni(\mu\text{-}dppe)_2Ni(NO_2)(NO)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[18] In solution, the latter is monomeric, $[Ni(NO_2)(NO)(dppe)]$, and probably adopts a distorted tetrahedral structure as in the related complexes $[NiCl(NO)(dppe)]$ [9] and $[Ni(NO)(PPh_3)(dppe)]^+$.[11] The chemistry of the dppe derivatives [18–20] has been the object of recent interest, in view of the application of the Ni–NO/Ni–NO_2 redox couple in oxygen-transfer reactions.[4,10,18–22]

The investigation outlined in this paper was prompted by our finding that dppe can also form a binuclear nickel nitrosyl complex $[(dppe)(ON)Ni(\mu\text{-}dppe)Ni(NO)(dppe)]^{2+}$. The ^{31}P n.m.r. spectra of this compound show a temperature-dependent behaviour, which is unexpected for the usual pseudo-tetrahedral $\{Ni(NO)\}^{10}$ derivatives. Since this suggests the possibility of a change in the stereochemistry around the metal atom, and maybe in the bonding mode of the NO group itself, it seemed interesting to investigate further the structure and stereochemistry of nickel nitrosyl complexes with diphosphines. Meek and co-workers[23] have previously reported an analogous study on the related $\{Rh(NO)\}^{10}$ derivatives with poly(phosphines).

We present here the results obtained with the diphosphines (L–L) $Ph_2P(CH_2)_nPPh_2$ [n = 1 (dppm), 2 (dppe) or 3 (dppp)], and $Me_2P(CH_2)_nPMe_2$ [n = 2 (dmpe) or 3 (dmpp)] in which both the σ-donor ability and the steric properties of the ligands are altered by changing the substituents at phosphorus as well as the length of the alkyl chain. Mono- and bi-nuclear complexes of the type $[Ni(NO)(L\text{–}L)_2]^+$ and $[Ni_2(NO)_2(L\text{–}L)_3]^{2+}$ have been prepared, in which the diphosphine can act as chelating, unidentate, or bridging between two Ni–NO moieties. Moreover, for comparative purposes, we have also synthesized

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† μ-1,2-Bis(diphenylphosphino)ethane-bis{[1,2-bis(diphenylphosphino)ethane]nitrosylnickel}bis(tetrafluoroborate).

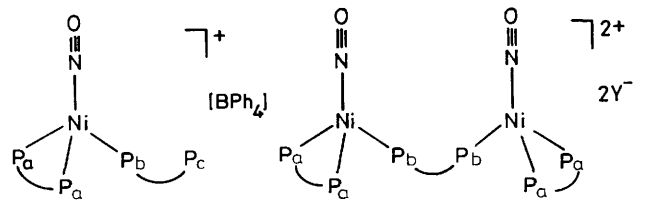
‡ In order to avoid ambiguities that can arise from the NO^+/NO^- formalism, Enemark and Feltham's notation $\{M(NO)\}^n$ is used, as described in ref. 1.

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

Table 1. Analytical and conductivity data for the complexes

	Complex	Analysis (%)^a C	H	N	$\Lambda_M{}^b$/ Ω^{-1} cm^2 mol^{-1}
(**1**)	$[Ni(NO)(dppm)_2]BPh_4$	74.70(75.55)	5.45(5.50)	1.15(1.20)	52
(**2**)	$[Ni_2(NO)_2(dppe)_3][BF_4]_2$	60.35(60.60)	4.65(4.70)	1.75(1.80)	174
(**3**)	$[Ni_2(NO)_2(dmpe)_3][BF_4]_2$	27.10(27.00)	6.10(6.05)	3.40(3.50)	182
(**4**)	$[Ni_2(NO)_2(dppp)_3][BF_4]_2$	60.85(61.25)	4.90(4.95)	1.65(1.75)	173
(**5**)	$[Ni_2(NO)_2(dmpp)_3][BPh_4]_2$	62.95(63.35)	7.15(7.25)	2.10(2.15)	112
(**6a**)	$[Ni(NO)(PMePh_2)(dppe)]BPh_4$	75.00(75.15)	5.75(5.70)	1.45(1.40)	54
(**6b**)	$[Ni(NO)(PEtPh_2)(dppe)]BPh_4$	74.95(75.30)	5.75(5.85)	1.25(1.35)	48
(**6c**)	$[Ni(NO)\{P(C_6H_{11})Ph_2\}(dppe)]BPh_4$	75.85(76.00)	6.00(6.10)	1.25(1.30)	49
(**6d**)	$[Ni(NO)(PPh_3)(dppe)]BPh_4$	76.15(76.45)	5.60(5.55)	1.25(1.30)	51
(**6e**)	$[Ni(NO)(PMe_2Ph)(dppe)]BPh_4$	73.35(73.75)	5.80(5.85)	1.40(1.50)	56
(**6f**)	$[Ni(NO)(PMe_3)(dppe)]BPh_4$	72.40(72.15)	6.00(6.05)	1.55(1.60)	58
(**6g**)	$[Ni(NO)(PBu_3)(dppe)]BPh_4$	73.90(73.85)	7.05(7.10)	1.35(1.40)	52
(**6h**)	$[Ni(NO)(PHEt_2)(dppe)]BPh_4$	72.10(72.35)	6.20(6.20)	1.50(1.55)	54
(**6i**)	$[Ni(NO)\{PH(C_6H_{11})_2\}(dppe)]BPh_4$	73.45(74.10)	6.80(6.70)	1.30(1.40)	51
(**6j**)	$[Ni(NO)\{P(OMe)_3\}(dppe)]BPh_4$	69.05(68.40)	5.65(5.75)	1.40(1.50)	57
(**6k**)	$[Ni(NO)\{P(OEt)_3\}(dppe)]BPh_4$	69.80(69.15)	6.00(6.10)	1.35(1.45)	47
(**6l**)	$[Ni(NO)\{P(OBu)_3\}(dppe)]BPh_4$	70.25(70.45)	6.65(6.75)	1.25(1.30)	50
(**6m**)	$[Ni(NO)\{P(OPh)_3\}(dppe)]BPh_4$	72.80(73.15)	5.45(5.35)	1.30(1.25)	46
(**7a**)	$[Ni(NO)(PMePh_2)(dppp)]BPh_4$	74.90(75.30)	5.95(5.85)	1.30(1.35)	48
(**7b**)	$[Ni(NO)(PEtPh_2)(dppp)]BPh_4$	75.30(75.45)	5.90(5.95)	1.25(1.35)	56
(**7c**)	$[Ni(NO)\{P(C_6H_{11})Ph_2\}(dppp)]BPh_4$	75.50(76.10)	6.20(6.20)	1.20(1.30)	48
(**7d**)	$[Ni(NO)(PPh_3)(dppp)]BF_4$	63.35(63.55)	4.95(4.85)	1.60(1.65)	88
(**7e**)	$[Ni(NO)\{P(OMe)_3\}(dppp)]BPh_4$	68.65(68.65)	5.95(5.85)	1.40(1.50)	55

^{a} Required values are given in parentheses. ^{b} In nitromethane at 22 °C, for 10^{-3} mol dm^{-3} solutions.



	L-L	Y
(**1**)	dppm	
(**2**)	dppe	BF_4
(**3**)	dmpe	BF_4
(**4**)	dppp	BF_4
(**5**)	dmpp	BPh_4

a series of complexes of the type [Ni(NO)(L)(L–L)]Y (Y = non-co-ordinating anion). The dynamic behaviour of some of these compounds has been studied by ^{31}P n.m.r. spectroscopy, and the crystal structure of $[Ni_2(NO)_2(dppe)_3][BF_4]_2$ has been investigated in order to determine the co-ordination geometry around the metal atom.

Results and Discussion

All the new complexes were characterized by elemental analysis and conductivity (Table 1), i.r. and ^{31}P n.m.r. (Table 2), and u.v.–visible spectroscopy (Table 3).

The diphosphine derivatives of the $\{Ni(NO)\}^{10}$ group were prepared by the method of Booth and Chatt[3] by treating the appropriate nitrito-diphosphine complexes of nickel(II) with carbon monoxide. In the case of dppm, $[Ni(NO_2)(dppm)_2]BPh_4$ was used, while with dppe the starting material is a 1 : 1 mixture of $[Ni(dppe)_2][BF_4]_2$ and $NaNO_2$. With the ligands dppp and dmpp the nickel(II) complex was generated *in situ* from $NaNO_2$, $[Ni(H_2O)_6][BF_4]_2$, and the appropriate diphosphine in 1 : 1 : 2 molar ratio. Under the same experimental conditions dmpe forms a five-co-ordinate $[Ni(NO_2)(dmpe)_2]^+$ adduct, which does not react with carbon monoxide even at high pressures. Probably the strong co-ordinating ability of dmpe prevents the formation of the nitrocarbonyl intermediate, which is thought to be involved in the oxygen-transfer reaction leading to $\{Ni(NO)\}^{10}$ derivatives.[10,19,21] The nitrosyl-dmpe species was obtained instead by reacting $[NiCl(NO)(PPh_3)_2]$ and the diphosphine in alcohol in the presence of $NaBF_4$.

The complexes $[Ni(NO)(dppm)_2]BPh_4$ (**1**), $[Ni_2(NO)_2(dppe)_3][BF_4]_2$ (**2**), $[Ni_2(NO)_2(dmpe)_3][BF_4]_2$ (**3**), $[Ni_2(NO)_2(dppp)_3][BF_4]_2$ (**4**), and $[Ni_2(NO)_2(dmpp)_3][BPh_4]_2$ (**5**) are deep red or purple diamagnetic solids which possess a strong NO i.r. absorption in the 1 790—1 750 cm^{-1} region. All complexes have similar visible spectra both in the solid state and in dichloromethane solution, with two bands at 340—360 and 445—475 nm, and a shoulder on the lower-energy side at 510—545 nm. Infrared and electronic spectral data are strictly related to those reported for other pseudo-tetrahedral $[Ni(NO)L_3]^+$ complexes with linear Ni–NO groups.[11–16]

In dichloromethane solution at room temperature the $[Ni(NO)(dppm)_2]^+$ cation is stereochemically non-rigid on the n.m.r. time-scale, its ^{31}P n.m.r. spectrum showing a single resonance at 8.5 p.p.m. When the temperature is lowered below −20 °C the singlet broadens, and at −70 °C the spectrum indicates the 'frozen' structure (**1**), in which one dppm ligand is unidentate with a dangling PPh_2 group. The spectrum, which is very nearly first order, shows three groups of signals (1 : 2 : 1 intensity ratio) centred at 33.5, 14.1, and −28.4 p.p.m. The high- and low-field doublets of triplets can be assigned to P_b and P_c, respectively, while the central doublet of doublets is due to P_a of chelating dppm. The chemical shift of the free end P_c is very close to that of free dppm. The $J(P_a–P_b)$ of 13.7 Hz is in accord with a pseudo-tetrahedral structure (**1**). Moreover, the observed variable-temperature n.m.r. behaviour suggests a rapid intramolecular exchange between bonded and free PPh_2 groups, which can occur either through a dissociative mechanism with opening of the chelate dppm ligands, or *via* an associative one, with formation of a five-co-ordinate inter-

Table 2. I.r. and ^{31}P n.m.r. data for the complexes

	I.r.[a]	^{31}P n.m.r.[b]				
Complex	ν(NO)/ cm^{-1}	$\delta(P_a)$/ p.p.m.	$\delta(P_{a'})$/ p.p.m.	$\delta(P_b)$/ p.p.m.	$J(P_a–P_b)$[c]/ Hz	T/K[d]
(1)	1 787	8.4[e]				
		14.1[f]		33.5	13.7	203
(2)	1 768	54.3		33.9		
		52.2	49.4	35.6		193
(3)	1 762	28.4		6.4		
(4)	1 769	20.0		29.9		
		21.7	19.5	33.2	*g*	153
(5)	1 752	−5.6		2.5	11.0	
(6a)	1 769	51.4		18.8		
		53.7		19.7		143
(6b)	1 774	50.4		33.5		
		53.1	48.1	35.0		143
(6c)	1 771	50.3		42.1		
		53.2	50.0	44.2	6.1	153
(6d)	1 781	49.5		38.3		
		50.3		39.8		143
(6e)	1 760	52.2		4.2		
(6f)	1 791	52.7		−6.8	3.4	
(6g)	1 785	52.1		18.2	2.2	
(6h)	1 772	53.4		−0.3	3.9	
(6i)	1 786	52.6		21.2		
(6j)	1 797	52.8		157.8	27.5	
(6k)	1 770	52.4		153.1	27.5	
(6l)	1 775	51.9		153.3	24.4	
(6m)	1 807	50.6		149.6	14.7	
(7a)	1 763	20.7		18.9		
		21.5		22.8		143
(7b)	1 777	20.2		32.7		
		22.1	20.0	36.0		143
(7c)	1 763	20.4		41.0		
		24.2	18.7	42.6	9.4[h]	173
(7d)	1 764	19.6		37.9		
		21.0		40.1		143
(7e)	1 774	22.9		157.5	25.9	

[a] In Nujol mull. [b] Lettering for P atoms as shown in diagrams for **(1)**—**(7e)**. Diphosphine P atoms labelled P_a and $P_{a'}$ when inequivalent. Solvents: CH_2Cl_2 (308—193 K), $CHF_2Cl–CD_2Cl_2$ (173—143 K). [c] Unless otherwise stated, $J(P_a–P_b)$ not observed or < 2 Hz. [d] Unless otherwise stated, T = 308 K. [e] Broad signal. [f] Other data are: $\delta(P_c) = -28.4$ p.p.m., $J(P_a–P_c) = 6.4$, $J(P_b–P_c) = 131.6$ Hz. [g] $J(P_a–P_{a'}) = 35.2$ Hz. [h] $J(P_a–P_{a'}) = 31.3$ Hz.

mediate, formally of nickel(II), involving bending of the NO group ($NO^+ \longrightarrow NO^-$).

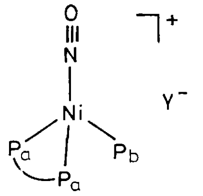
Complexes **(2)**—**(5)** behave as 1:2 electrolytes in nitromethane, and in this solvent a dimeric nature is suggested by conductivity measurements over a wide concentration range. The Onsager coefficients α, determined according to Onsager equation $\Lambda_0 = \Lambda_e + \alpha\sqrt{c_e}$ (Λ_0 and Λ_e = equivalent conductance at zero and c_e concentration, respectively), are in the range 3.5—4.2 ohm^{-1} $dm^{\frac{7}{2}}$ $mol^{-\frac{3}{2}}$, in good agreement with the values reported for 1:2 electrolytes.[24,25]

Evidence of a diphosphine-bridged structure for complexes **(2)**—**(5)** comes from the ^{31}P n.m.r. data (Table 2). In the case of **(2)** and **(3)** the room-temperature $^{31}P-\{^1H\}$ n.m.r. spectra exhibit two signals of 2:1 intensity ratio, with the more intense on the low-field side. On the basis of the co-ordination chemical shifts the lower-field signal can be assigned to the phosphorus atoms P_a of a chelating ligand, the high-field one to P_b of a molecule bridging two nickel atoms. In the case of **(4)** and **(5)** the room-temperature ^{31}P n.m.r. spectra show again two resonances (1:2 intensity ratio), but with the P_a signal upfield from P_b. This behaviour is in accord with the observation that for chelating diphosphines the co-ordination chemical shift depends on the chelate ring size, and is larger for five- than six-membered rings.[26] In this case, on going from complexes **(2)** and **(3)** to **(4)** and **(5)**, the signal of the chelating diphosphine shifts to higher field with respect to the bridging one. The structure of **(2)** has been confirmed by *X*-ray crystallography (see below). No fine structure is present in the ^{31}P n.m.r. spectra of **(2)**—**(4)**, while in the spectrum of dmpp analogue **(5)** the signals of chelate and bridging diphosphines appear as a doublet and a triplet, respectively, with $J(P–P) = 11.0$ Hz.

For comparative purposes, we have also prepared a series of nitrosyl compounds of the type $[Ni(NO)L(L–L)]^+$ [L–L = dppe **(6a)**—**(6m)** or dppp **(7a)**—**(7e)**; L = PHR_2, PR_3, or $P(OR)_3$], which contain chelate rings of different size as well as unidentate phosphines and phosphites with different σ-donating ability and steric properties. The complexes were obtained either by treating carbon monoxide with a mixture of equimolar amounts of $[Ni(H_2O)_6][BF_4]_2$, $NaNO_2$, L–L, and L, or by treating the appropriate $[Ni(NO)L_3]^+$ with the diphosphine. The deep red to purple diamagnetic compounds are 1:1 electrolytes in nitromethane solution. Their i.r. spectra exhibit a strong NO stretching vibration in the 1 760—1 810 cm^{-1} region, which is typical for linear Ni–NO groups (Table 2). The u.v.–visible spectra closely resemble those of complexes **(1)**—**(5)**, and show a three-band system in the ranges 335—360, 435—475, and 505—540 nm (Table 3). In spite of the difference in the symmetry, these spectra are also similar to those of the $[Ni(NO)L_3]^+$ chromophore, which have been previously discussed in terms of configuration interaction.[1,12,16]

Table 3. U.v.-visible data for the complexes in CH_2Cl_2 solution

Complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1})		
(1)	340(1 840)(sh)	475 (760)	540 (640)(sh)
(2)	345(1 130)(sh)	470(1 210)	520(1 040)(sh)
(3)	360 (540)	445 (860)	510 (670)(sh)
(4)	360 (790)	470 (860)	545 (710)(sh)
(5)	355 (600)	445(1 180)	525 (820)(sh)
(6a)	345(1 060)	465(1 130)	520 (950)(sh)
(6b)	355 (880)	470(1 170)	530 (940)(sh)
(6c)	345(1 490)(sh)	470(1 170)	530 (950)(sh)
(6d)	360 (780)	475(1 080)	535 (880)(sh)
(6e)	355 (800)	455(1 100)	525 (790)(sh)
(6f)	340(1 650)(sh)	445(1 090)	525 (670)(sh)
(6g)	335(1 890)	465(1 150)	530 (880)(sh)
(6h)	350 (970)	450(1 160)	515 (900)(sh)
(6i)	355 (760)	465 (840)	530 (750)(sh)
(6j)	350 (910)	445(1 140)	505 (940)(sh)
(6k)	345 (990)	435(1 240)	505 (910)(sh)
(6l)	350 (940)	435(1 230)	505 (900)(sh)
(6m)	350 (940)	445(1 130)	510 (990)(sh)
(7a)	355 (780)	465 (990)	530 (790)(sh)
(7b)	355 (860)	465(1 030)	535 (810)(sh)
(7c)	355 (840)	470 (990)	540 (790)(sh)
(7d)	360 (860)	475(1 040)	540 (840)(sh)
(7e)	345 (890)	435(1 150)	505 (810)(sh)



L-L = dppe, Y = BPh_4

	L
(6a)	$PMePh_2$
(6b)	$PEtPh_2$
(6c)	$P(C_6H_{11})Ph_2$
(6d)	PPh_3
(6e)	PMe_2Ph
(6f)	PMe_3
(6g)	PBu_3
(6h)	$PHEt_2$
(6i)	$PH(C_6H_{11})_2$
(6j)	$P(OMe)_3$
(6k)	$P(OEt)_3$
(6l)	$P(OBu)_3$
(6m)	$P(OPh)_3$

L-L = dppp

	L	Y
(7a)	$PMePh_2$	BPh_4
(7b)	$PEtPh_2$	BPh_4
(7c)	$P(C_6H_{11})Ph_2$	BPh_4
(7d)	PPh_3	BF_4
(7e)	$P(OMe)_3$	BPh_4

As expected for a pseudo-tetrahedral structure, the ^{31}P n.m.r. spectra of complexes (**6a**)—(**6m**) and (**7a**)—(**7e**) consist of an AX_2 pattern. The *J*(P–P) values are near to 0 Hz for the derivatives with unidentate phosphines, and in the range 14—28 Hz when the unidentate ligand is a phosphite. Similar values have been found for the pseudo-tetrahedral nickel(0) complexes $[NiL_4]$ containing phosphines and phosphites.[27] As previously found in other series of phosphine[28] and phosphole[29] metal complexes, the co-ordination chemical shift of the ligand L in complexes (**6a**)—(**6m**), defined as $\Delta[\delta(^{31}P)] = \delta(^{31}P_{complex}) - \delta(^{31}P_{ligand})$, correlates linearly with the chemical shift of the free ligand. The correlation equation is $\Delta[\delta(^{31}P)] = -0.194\ \delta(^{31}P_{ligand}) + 43.5$ and the correlation coefficient, *R*, is 0.995. It should be noted that this equation can be used also for calculating the co-ordination chemical shift of the bridging diphosphine in complexes (**1**)—(**5**). If the experimental data for (**1**)—(**5**) are included, a correlation coefficient of 0.995 is obtained again, thus confirming that (**1**)—(**5**) and (**6a**)—(**6m**) possess the same overall geometry. Similarly, in the case of complexes (**7a**)—(**7e**), the equation is $\Delta[\delta(^{31}P)] = -0.184\ \delta(^{31}P_{ligand}) + 42.7$ ($R = 0.997$); when (**2**)—(**5**) are included, a slightly lower value of 0.992 is found for *R*.

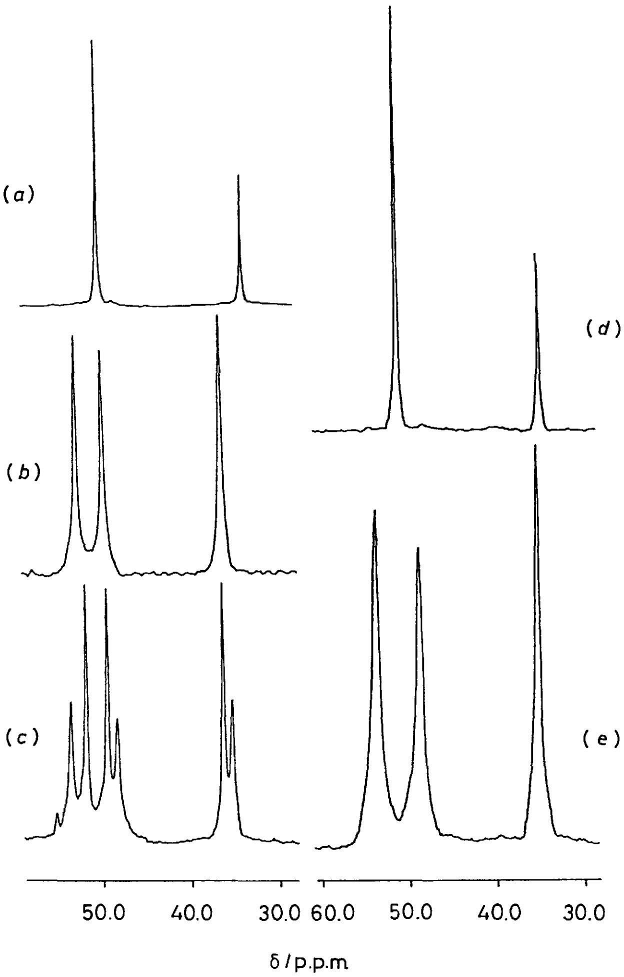


Figure 1. Variable-temperature ^{31}P n.m.r. spectra of complex (**2**) at (*a*) 308, (*b*) 203, (*c*) 143 K, and of (**6b**) at (*d*) 308 and (*e*) 143 K

The ^{31}P n.m.r. spectra of the binuclear complexes were also studied over a wide temperature range, in dichloromethane or CD_2Cl_2–CHF_2Cl solutions; some spectra of (**2**) and (**4**) at different temperatures are reported in Figure 1(*a*)—(*c*) and Figure 2(*a*), respectively. As the temperature of a solution of the dppp derivative (**4**) is lowered the ^{31}P resonance of the chelate diphosphine broadens and splits into a doublet. At −120 °C this signal is eventually resolved into four lines. At the same time, the ^{31}P signal of the bridging diphosphine remains sharp over the whole temperature range explored. Also in the case of (**2**), the singlet due to chelating dppe broadens as the temperature is lowered, and at −65 °C splits into a doublet. Below −100 °C this doublet slowly changes giving rise to a five-line system, while the resonance due to P_b begins to split into two signals [Figure 1(*c*)]. Apparently the limiting spectrum is not reached even at −130 °C, the lowest available temperature, and we were unable to reproduce the experimental spectrum by computer simulation. The spectral variations are entirely reversible with temperature. By contrast, the ^{31}P-{^1H} n.m.r.

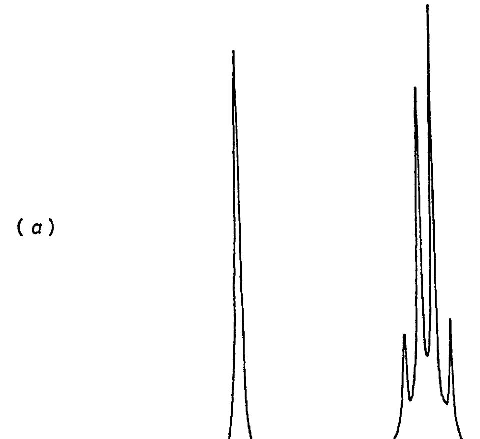


Figure 2. Low-temperature ^{31}P n.m.r. spectra of (*a*) complex (4) (153 K) and (*b*) complex (7c) (173 K)

spectra of both complexes (3) and (5), which contain the methyl-substituted diphosphines, do not show any significant changes between -130 and 35 °C.

The ^{31}P n.m.r. behaviour of complexes (2) and (4) suggests that the phosphorus atoms of the chelating diphosphine become inequivalent at low temperature. An attractive hypothesis is that the lowering of symmetry is the result of a change in the geometry of the complexes from pseudo-tetrahedral with a linear nitrosyl to square planar with a bent Ni–NO linkage. However, this appears unlikely at least in the case of complex (4), for which a limiting spectrum was obtained, since a *J*(P–P) value of only ±35 Hz is observed. It should be noted that the planar nickel(II) complexes $[NiX(L)(L\text{–}L)]^+$ (X = halide) exhibit *trans*- and *cis*-*J*(P–P) which are typically in the ranges 250—280 and -50 to -60 Hz, respectively.[30] Also a rapid equilibrium between two inequivalent planar structures, for which *J*(P–P) should be the average of *trans*- and *cis*-*J*(P–P), can be excluded on the same basis.

In this context, it seemed appropriate to study the low-temperature ^{31}P n.m.r. behaviour of $[Ni(NO)(PRPh_2)(dppe)]^+$ [R = Me (**6a**), Et (**6b**), C_6H_{11} (**6c**), or Ph (**6d**)] and $[Ni(NO)(PRPh_2)(dppp)]^+$ [R = Me (**7a**), Et (**7b**), C_6H_{11} (**7c**), or Ph (**7d**)]. In the case of the symmetric ligand PPh_3 the ^{31}P n.m.r. spectra of (**6d**) and (**7d**) are invariant down to -130 °C, the lowest available temperature. By contrast, with the asymmetric ligands $PRPh_2$ (R = Me, Et, or C_6H_{11}) the diphosphine signal broadens at temperature values which depend on the ring size of the diphosphine as well as on the bulkiness of group R. With dppe derivatives (**6a**)—(**6c**) the broadening appears at -100 ($PMePh_2$), -85 ($PEtPh_2$), and -60 °C [$P(C_6H_{11})Ph_2$]. For (**6b**) [Figure 1(*e*)] and (**6c**), the P_a resonance sharpens to two well separated signals of equal intensity at -120 and -100 °C, respectively; the limiting spectrum was not reached in the case of (**6a**).

The influence of steric effects is apparent also in the series (**7a**)—(**7c**). The spectra of complex (**7a**; L = $PMePh_2$) show sharp signals down to -130 °C, while in the case of (**7b**) and (**7c**) the ^{31}P resonances of the chelating diphosphine begin to broaden at -110 ($PEtPh_2$) and -40 °C [$P(C_6H_{11})Ph_2$]. Moreover, the limiting spectrum was obtained [Figure 2(*b*)] only in the case of the more hindered (**7c**). It is interesting that the related (**6g**), (**6j**), and (**7e**), containing symmetrical ligands such as PBu_3 and $P(OMe)_3$, or (**6h**) and (**6i**) with the less bulky $PHEt_2$ and $PH(C_6H_{11})_2$ ligands, exhibit ^{31}P n.m.r. spectra which are invariant over the temperature range +35 to -130 °C.

We conclude that all these $\{Ni(NO)\}^{10}$ derivatives possess a pseudo-tetrahedral structure also at low temperature. However, the rotation of the non-chelating, unsymmetrical phosphines around the Ni–P bond is slowed down at low temperature in the more crowded complexes, resulting in inequivalent phosphorus atoms in the Ni(NO)(L–L) fragment. The origin of the inequivalence of the diphosphine P_a atoms in the binuclear species (2) and (4) is probably the same, while the different behaviour of (3) and (5) may reflect the lower steric requirements of the Me_2P groups as compared to the Ph_2P. Thus, the low-temperature limiting spectra of complexes (2), (4), (**6a**)—(**6c**), and (**7a**)—(**7c**) can be interpreted as ABX patterns, in which the AB part is formed by the phosphorus atoms of the chelating diphosphine (P_a and $P_{a'}$) and X is P_b. In the case of dppp derivatives (4) and (**7c**) the $J(P_a\text{–}P_{a'})$ values are 35.2 and 31.3 Hz, respectively, while $J(P_a\text{–}P_b)$ and $J(P_{a'}\text{–}P_b)$ are small or negligible (Figure 2).

By contrast, in the dppe derivatives (2) and (**6a**)—(**6c**) there is no apparent coupling between the inequivalent phosphorus atoms of the diphosphine, which therefore give rise to two well separated signals (Figure 1). This is not surprising, since it is well known that the phosphorus atoms involved in five-membered chelate rings show *J*(P–P) values which are generally small or zero.[23,31] This is probably due to opposite signs of the 'through-the-metal' and 'through-the-chelate-ring' couplings.[32] In the case of the binuclear complex (2) the three-line resonance observed between -65 and -100 °C undergoes a further change below -100 °C [Figure 1(*b*) and (*c*)]. The splitting of the signals may indicate that the geometry of the complex is changing again, possibly from a tetrahedral to a square-planar structure with bending of the Ni–NO linkage. Unfortunately in the absence of the limiting spectrum it is not possible to evaluate the phosphorus–phosphorus coupling constants, which might be indicative of the geometry around the nickel atom.

Crystal Structure of $[Ni_2(NO)_2(dppe)_3][BF_4]_2$ (2).—The unit cell of (2) contains four dimeric cationic complexes, with each half related to the other by a crystallographic inversion centre, and $[BF_4]^-$ anions, distributed partially on two-fold axes and partially on general positions (these latter also disordered and distributed in two positions of equal occupancy factors). A perspective view of the cationic complex together with the atomic numbering scheme is given in Figure 3, selected bond distances and angles in Table 4.

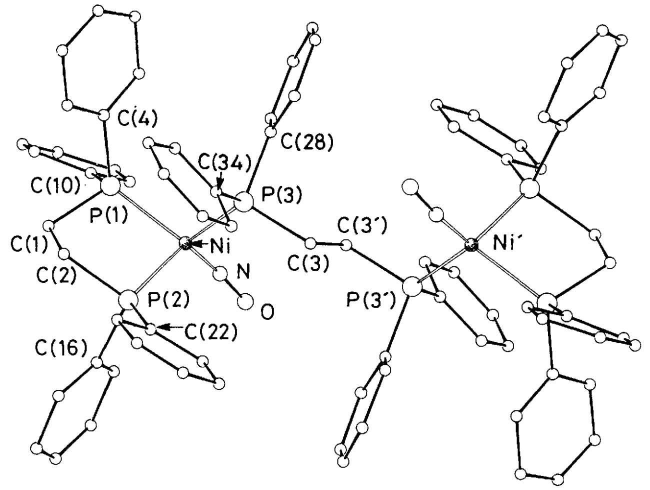


Figure 3. View of the cationic complex [(dppe)(ON)Ni(μ-dppe)Ni(NO)(dppe)]$^{2+}$ with the atomic numbering scheme

Table 4. Selected bond distances (Å) and angles (°) for complex (**2**)*

Ni–P(1)	2.274(5)	C(1)–C(2)	1.57(2)
Ni–P(2)	2.243(5)	P(2)–C(2)	1.83(2)
Ni–P(3)	2.261(4)	P(2)–C(16)	1.84(1)
Ni–N	1.67(2)	P(2)–C(22)	1.80(2)
N–O	1.13(2)	P(3)–C(3)	1.87(2)
P(1)–C(1)	1.81(1)	P(3)–C(28)	1.81(1)
P(1)–C(4)	1.82(2)	P(3)–C(34)	1.83(2)
P(1)–C(10)	1.78(2)	C(3)–C(3′)	1.51(2)
N–Ni–P(1)	120.2(5)	P(1)–C(1)–C(2)	109.0(11)
N–Ni–P(2)	117.0(5)	C(1)–C(2)–P(2)	107.3(11)
N–Ni–P(3)	113.5(5)	Ni–P(2)–C(2)	104.5(5)
P(1)–Ni–P(2)	88.4(2)	Ni–P(2)–C(16)	117.3(5)
P(1)–Ni–P(3)	109.5(2)	Ni–P(2)–C(22)	121.3(5)
P(2)–Ni–P(3)	105.1(2)	Ni–P(3)–C(3)	113.0(5)
Ni–N–O	168.2(14)	Ni–P(3)–C(28)	115.4(5)
Ni–P(1)–C(1)	105.1(6)	Ni–P(3)–C(34)	117.2(5)
Ni–P(1)–C(4)	121.9(6)	P(3)–C(3)–C(3′)	109.7(9)
Ni–P(1)–C(10)	117.0(6)		

* The primed atoms are related to the unprimed ones by the transformation $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

In the cation one dppe ligand acts as a bridge between the two nickel atoms, while the other two dppe ligands chelate the two metals. The distorted tetrahedral co-ordination around each Ni atom is completed by an N atom from a terminal nitrosyl. In spite of the severely distorted tetrahedral bond angles, the dihedral angle between the P(1)–Ni–P(2) and N–Ni–P(3) planes is 91.3(2)°, only a little larger than the theoretical value of 90° for a regular tetrahedron. An inspection of the bond angles in the co-ordination sphere of the Ni atom reveals that all the N–Ni–P angles [range 113.5(5)—120.2(5)°] are larger than the P–Ni–P ones [range 88.4(2)—109.5(2)°], probably due to a repulsive effect of the nitrosyl ligand towards the bulky PPh$_2$ groups. The bond distance of the nickel atom with the nitrogen of the nitrosyl ligand [1.67(2) Å] is comparable with those found in neutral nickel complexes such as [Ni(N$_3$)NO)(PPh$_3$)$_2$], [Ni(NCS)(NO)(PPh$_3$)$_2$], [Ni(NO$_2$)(NO)(PMe$_3$)$_2$],[7,8,10] and [{Ni(ONO)(NO)(dppe)}$_2$][18] [1.686(7), 1.648(5), 1.652(7), and 1.664(9) Å, respectively], but is significantly longer than those found in other cationic nickel complexes [1.581(12), 1.58(1), and 1.59(2) Å].[13,15,16]

The five-membered chelate ring adopts a 'twist' conformation with the C(1) and C(2) atoms deviating by −0.283(16) and 0.511(16) Å from the mean plane, and the Ni, P(1), and P(2) atoms almost in this plane [deviations 0.004(2), −0.002(4), and −0.024(4) Å, respectively].

The value of 168.2(14)° for the Ni–N–O angle is in the range reported for related {Ni(NO)}^{10} complexes, and closer to those found in cationic[14–16] than in neutral complexes.[7,8,10,18] The N–O bond distance of 1.13(2) Å is typical of low-symmetry {Ni(NO)}^{10} complexes.

The Ni–P bond distances involving the chelating dppe ligand are 2.243(5) and 2.274(5) Å, while the Ni–P distance involving the bridging dppe is 2.261(4) Å. The slight asymmetry of the Ni–P distances for the chelating dppe ligand could be attributed to the steric hindrance of the bulky PPh$_2$ groups rather than to electronic effects. Each P atom of the chelating dppe shows one axial and one equatorial Ph group (with respect to the mean chelation plane), and those disposed towards the PPh$_2$ group of the bridging dppe ligand have Ni–P–C angles which are larger by *ca.* 4° than those disposed towards the nitrosyl group.

Experimental

Organic solvents were reagent grade, purified by standard methods, and distilled just before use. The nickel salts, NaBF$_4$, NaBPh$_4$, and NaNO$_2$ were reagent grade, and were used without further purification. The diphosphines dppm, dppe, and dppp were purchased from Strem Chemicals and used as received; dmpp was prepared according to the reported method.[33] The ligands P(OMe)$_3$, P(OEt)$_3$, and P(OBu)$_3$ were obtained from EGA Chemie, and were purified by distillation under nitrogen. The unidentate phosphines were either commercially available (Fluka and Strem Chemicals) or synthesized by literature methods. Complexes [NiCl(NO)(PPh$_3$)$_2$],[11] [Ni(L-L)$_2$][BF$_4$]$_2$,[34] and [Ni(NO$_2$)(dppm)$_2$]BPh$_4$[35] were synthesized according to literature methods.

Infrared and u.v.–visible spectra were recorded on DS 702 G and Uvidec 505 Jasco spectrophotometers, respectively. ^{31}P-{^{1}H} N.m.r. spectra were recorded on a Bruker WP 80 SY spectrometer. Spectra at temperatures lower than 183 K were run in CD$_2$Cl$_2$–CHF$_2$Cl solutions. Positive ^{31}P chemical shifts are downfield from 85% H$_3$PO$_4$ as external standard. Conductance data were measured on a Metrohm E 518 conductivity bridge. Microanalyses were performed by the Microanalytical Laboratory of the Istituto di Chimica, Università di Udine. Analytical and physical data for the complexes are given in Table 1.

Preparations.—[Ni(NO)(dppm)$_2$]BPh$_4$ (**1**). The complex [Ni(NO$_2$)(dppm)$_2$]BPh$_4$ (2.39 g, 2.0 mmol) was dissolved in dichloromethane (20 cm^3) and stirred under a carbon monoxide atmosphere for 1 h. After addition of propan-2-ol (30 cm^3), dichloromethane was pumped off until a purple solid separated. Yield: 2.02 g (86%).

[Ni$_2$(NO)$_2$(dppe)$_3$][BF$_4$]$_2$ (**2**). A slurry of NaNO$_2$ (0.28 g, 4.0 mmol) and [Ni(dppe)$_2$][BF$_4$]$_2$ (4.12 g, 4.0 mmol) in acetone–methanol (100 cm^3, 1:1) was stirred in a carbon monoxide atmosphere until a purple solution formed (*ca.* 48 h). The solution was filtered and its volume reduced to *ca.* 50 cm^3. The resulting purple microcrystals were collected, washed with propan-2-ol, and recrystallized from dichloromethane–propan-2-ol. Yield 2.26 g (73%).

[Ni$_2$(NO)$_2$(dmpe)$_3$][BF$_4$]$_2$ (**3**). The complex [NiCl(NO)(PPh$_3$)$_2$] (1.28 g, 2.0 mmol) and dmpe (0.50 cm^3, 3.0 mmol) were stirred in methanol (20 cm^3) for *ca.* 16 h. A methanol solution (30 cm^3) of NaBF$_4$ (0.33 g, 3.0 mmol) was then added slowly. Upon elimination of dichloromethane *in vacuo*, a purple solid formed, which was filtered off, washed with ethanol, and recrystallized from dichloromethane–propan-2-ol. Yield 0.36 g (45%).

Table 5. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for the non-hydrogen atoms of complex (**2**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ni	3 575(1)	2 922(2)	983(1)	C(24)	3 635(6)	−1 122(15)	1 537(12)
P(1)	4 152(1)	3 239(3)	728(2)	C(25)	3 281(7)	−1 163(16)	1 668(12)
P(2)	3 912(1)	1 699(3)	1 786(2)	C(26)	3 090(6)	−350(15)	1 810(12)
P(3)	3 097(1)	2 238(3)	−153(2)	C(27)	3 304(5)	534(13)	1 872(10)
O	3 235(4)	4 175(11)	1 792(9)	C(28)	2 950(4)	2 930(11)	−1 101(8)
N	3 381(4)	3 748(10)	1 426(9)	C(29)	2 739(5)	2 482(13)	−1 865(11)
C(1)	4 546(4)	2 466(12)	1 428(9)	C(30)	2 622(5)	3 084(15)	−2 586(12)
C(2)	4 349(4)	1 474(12)	1 474(10)	C(31)	2 728(6)	4 013(14)	−2 498(13)
C(3)	2 595(4)	2 027(9)	−39(9)	C(32)	2 901(6)	4 435(16)	−1 789(13)
C(4)	4 176(5)	3 032(12)	−286(9)	C(33)	3 015(5)	3 885(12)	−1 039(10)
C(5)	4 382(5)	2 286(13)	−413(11)	C(34)	3 217(4)	1 059(10)	−451(8)
C(6)	4 382(6)	2 119(15)	−1 236(13)	C(35)	3 048(4)	252(11)	−320(9)
C(7)	4 180(6)	2 721(14)	−1 786(12)	C(36)	3 164(5)	−680(14)	−523(10)
C(8)	3 990(6)	3 444(15)	−1 713(13)	C(37)	3 454(5)	−666(13)	−869(11)
C(9)	3 983(5)	3 659(13)	−882(11)	C(38)	3 633(6)	163(14)	−991(11)
C(10)	4 376(5)	4 393(12)	1 012(9)	C(39)	3 513(5)	1 054(13)	−823(10)
C(11)	4 787(7)	4 536(17)	1 066(13)	F(1)	5 331(4)	−1 577(10)	2 905(9)
C(12)	4 951(8)	5 501(19)	1 310(14)	F(2)	4 909(5)	−431(12)	2 991(11)
C(13)	4 746(7)	6 130(15)	1 421(12)	F(3)	3 266(7)	3 360(16)	4 565(13)
C(14)	4 335(7)	6 102(16)	1 301(13)	F(4)	3 238(8)	3 518(21)	5 942(14)
C(15)	4 162(6)	5 131(14)	1 108(11)	F(5)	2 859(10)	4 414(20)	5 033(23)
C(16)	4 156(4)	1 915(11)	2 913(9)	F(6)	2 717(13)	2 909(34)	4 791(33)
C(17)	4 103(5)	2 791(14)	3 207(12)	F(3A)	3 008(8)	4 237(17)	5 614(17)
C(18)	4 287(6)	2 930(15)	4 100(13)	F(4A)	2 865(14)	3 428(33)	4 361(19)
C(19)	4 493(6)	2 210(14)	4 593(12)	F(5A)	2 728(13)	2 963(29)	5 445(29)
C(20)	4 548(5)	1 319(13)	4 289(12)	F(6A)	3 372(12)	3 021(37)	5 502(36)
C(21)	4 378(5)	1 159(12)	3 410(10)	B(1)	5 000	−1 026(33)	2 500
C(22)	3 671(4)	556(11)	1 726(8)	B(2)	3 019(9)	3 479(21)	5 131(18)
C(23)	3 833(5)	−270(12)	1 556(10)				

$[Ni_2(NO)_2(dppp)_3][BF_4]_2$ (**4**). The ligand dppp (1.65 g, 4.0 mmol) was added to a methanol solution (30 cm^3) containing $NaNO_2$ (0.14 g, 2.0 mmol) and $[Ni(H_2O)_6][BF_4]_2$ (0.68 g, 2.0 mmol). After filling the reaction vessel with carbon monoxide, the reaction mixture was stirred for 48 h, during which purple crystals formed, which were filtered off, washed with ethanol, and recrystallized from dichloromethane–ethanol. Yield 1.29 g (81%).

$[Ni_2(NO)_2(dmpp)_3][BPh_4]_2$ (**5**). The ligand dmpp (0.66 cm^3, 4.0 mmol) was added *via* a syringe to a deoxygenated methanol solution (20 cm^3) containing $[Ni(H_2O)_6][BF_4]_2$ (0.68 g, 2.0 mmol) and $NaNO_2$ (0.14 g, 4.0 mmol). After filling the reaction vessel with carbon monoxide, the slurry was refluxed for 2.5 h to give a purple solution. Addition of $NaBPh_4$ (1.37 g, 4.0 mmol) induced the precipitation of purple crystals which were recrystallized twice from dichloromethane–methanol. Yield 0.81 g (62%).

$[Ni(NO)L(dppe)]BPh_4$ [L = $PMePh_2$ (**6a**), $PEtPh_2$ (**6b**), $P(C_6H_{11})Ph_2$ (**6c**), PPh_3 (**6d**), PMe_2Ph (**6e**), PMe_3 (**6f**), PBu_3 (**6g**), $PHEt_2$ (**6h**), $PH(C_6H_{11})_2$ (**6i**), $P(OMe)_3$ (**6j**), $P(OEt)_3$ (**6k**), $P(OBu)_3$ (**6l**), *or* $P(OPh)_3$ (**6m**)]. Nitrogen-saturated dichloromethane solutions (15 cm^3) containing dppe (0.80 g, 2.0 mmol) and the appropriate ligand L (2.0 mmol) were added to a stirred methanol solution (30 cm^3) of $[Ni(H_2O)_6][BF_4]_2$ (0.68 g, 2.0 mmol) and $NaNO_2$ (0.14 g, 2.0 mmol) under a carbon monoxide atmosphere. Purple or deep red solutions were formed (1—6 h), where from red or purple crystals separated upon addition of $NaBPh_4$ (1.37 g, 4.0 mmol). The products were filtered off, washed with diethyl ether, and recrystallized from dichloromethane–ethanol. Yields 47—82%.

$[Ni(NO)L(dppp)]BPh_4$ [L = $PMePh_2$ (**7a**), $PEtPh_2$ (**7b**), *or* $P(C_6H_{11})Ph_2$ (**7c**)]. A dichloromethane solution (20 cm^3) containing dppp (0.41 g, 1.0 mmol) and the ligand L (1.0 mmol) was added to a methanol solution (30 cm^3) of $[Ni(H_2O)_6][BF_4]_2$ (0.34 g, 1.0 mmol) and $NaNO_2$ (0.069 g, 1.0 mmol) under a carbon monoxide atmosphere. After shaking for 6 h, a solution of $NaBPh_4$ (0.68 g, 2.0 mmol) in propan-2-ol (30 cm^3) was added, and the solution was concentrated until purple crystals separated, which were filtered off, washed with ethanol, and recrystallized from dichloromethane–propan-2-ol. Yields: (**7a**), 61; (**7b**), 74; (**7c**), 57%.

$[Ni(NO)(PPh_3)(dppp)]BF_4$ (**7d**). A dichloromethane solution (20 cm^3) containing dppp (0.41 g, 1.0 mmol) and PPh_3 (0.26 g, 1.0 mmol) was added to $[Ni(H_2O)_6][BF_4]_2$ (0.34 g, 1.0 mmol) and $NaNO_2$ (0.069 g, 1.0 mmol) dissolved in methanol (30 cm^3) under a carbon monoxide atmosphere. After shaking for 6 h, propan-2-ol (20 cm^3) was added; the dichloromethane was pumped off until purple crystals separated, which were recrystallized from dichloromethane–propan-2-ol. Yield 0.55 g (65%).

$[Ni(NO)\{P(OMe)_3\}_3]BPh_4$. The ligand $P(OMe)_3$ (0.71 cm^3, 6.0 mmol) was added *via* a syringe to a methanol solution (20 cm^3) of $[Ni(H_2O)_6][BF_4]_2$ (0.68 g, 2.0 mmol) and $NaNO_2$ (0.14 g, 2.0 mmol) under a carbon monoxide atmosphere. After stirring for 12 h, $NaBPh_4$ (1.37 g, 4.0 mmol) was added. The deep red crystals which precipitated thereupon were filtered off, washed with ethanol, and recrystallized from dichloromethane–ethanol. Yield 1.15 g (74%).

$[Ni(NO)\{P(OMe)_3\}(dppp)]BPh_4$ (**7e**). The ligand dppp (0.82 g, 2.0 mmol) and $[Ni(NO)\{P(OMe)_3\}_3]BPh_4$ (1.56 g, 2.0 mmol) were suspended in methanol (30 cm^3). Upon dropwise addition of dichloromethane a clear solution formed, which was stirred for 2 h. Evaporation of the dichloromethane *in vacuo* afforded red crystals which were filtered off, washed with ether, and recrystallized from dichloromethane–ethanol. Yield 1.44 g (76%).

Crystal Structure Determination of $[Ni_2(NO)_2(dppe)_3][BF_4]_2$ (**2**).—Purple-red crystals of complex (**2**) were grown by slow diffusion of ethanol into a dichloromethane solution of the complex. A crystal of approximate dimensions 0.20 × 0.32 × 0.35 mm was used for *X*-ray data collection. Unit-cell parameters were obtained by least-squares refinement of the θ values of 21 carefully centred reflections (θ 14—27°).

Crystal data. $C_{78}H_{72}B_2F_8N_2Ni_2O_2P_6$, $M = 1\,546.31$, monoclinic, space group $C2/c$, $a = 35.073(8)$, $b = 14.012(4)$, $c = 17.351(5)$ Å, $\beta = 112.24(2)°$, $Z = 4$, $D_c = 1.301$ g cm^{-3}, $F(000) = 3\,192$, $\mu(\text{Cu-}K_\alpha) = 22.81$ cm^{-1}.

Data were collected at room temperature on a Siemens AED diffractometer using nickel-filtered Cu-K_α radiation ($\lambda = 1.541\,78$ Å) and the θ—2θ scan technique, the individual profiles having been analysed according to Lehmann and Larsen.[36] All reflections with θ in the range 3—65° were measured. Of 6 299 independent reflections, 2 029 having $I > 2\sigma(I)$ were considered observed and were used in the analysis. The intensity of one standard reflection was measured after each 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A correction for the absorption effects was applied,[37] using the program ABSORB[38] (maximum and minimum transmission factors 1.223 and 0.818, respectively).

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic and then with anisotropic thermal parameters for Ni, P, O, N, C(1), C(2), and C(3) atoms only, because of the limited number of observed reflections.[39] The $[BF_4]^-$ anion was found distributed partially on a special position (two-fold axis, occupancy factor 0.3750 for the B atom and 0.7500 for the F atoms), and partially on a general position, with the F atoms disordered and distributed in two positions of equal occupancy factors (0.6250 for B and 0.3125 for F for each of the two images). The hydrogen atoms were placed at their geometrically calculated positions (C–H 1.0 Å), and introduced in the final structure-factor calculation. The weighting scheme used in the last refinement cycles was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 1.2074$ and $g = 0.0044$. The final atomic co-ordinates for the non-hydrogen atoms are given in Table 5. Final R and R' values were 0.0878 and 0.0961, respectively. Atomic scattering factors corrected for anomalous dispersion were taken from ref. 40. All calculations were performed on the GOULD POWERNODE 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del Consiglio Nazionale delle Ricerche, Parma.

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

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