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Oxygen Atom Transfer Reactions. 3. The Crystal Structures of $Ni(NO_2)_2$dppe and $[Ni(ONO)(NO)dppe]_2$

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The crystal and molecular structures of $Ni(NO_2)_2$dppe·CH_2Cl_2 and $[Ni(ONO)(NO)dppe]_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) have been determined by X-ray crystallography. $Ni(NO_2)_2$dppe crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 11.880(6)$ Å, $b = 15.191(8)$ Å, $c = 17.162(6)$ Å and $\beta = 108.79(4)°$. The structure consists of discrete $Ni(NO_2)_2$dppe molecules well separated from solvent molecules. The square planar geometry about nickel is defined by the two phosphorus and two nitrogen atoms to which it is bonded. The P(1)–Ni–P(2) angle of the chelating dppe is 86.3(1)° and the N(1)–Ni–N(2) angle of the N-bonded nitro groups is 88.5(4)°. The nitro groups are approximately perpendicular to the square plane about nickel. Important interatomic distances are Ni–P(1) = 2.178(3) Å, Ni–P(2) = 2.182(4) Å, Ni–N(1) = 1.864(12) Å, and Ni–N(2) = 1.916(10) Å.

$[Ni(ONO)(NO)dppe]_2$ crystallizes in the monoclinic space group $P2_1/n$ with two molecules in a unit cell of dimensions $a = 15.528(11)$ Å, $b = 11.897(7)$ Å, $c = 15.023(13)$ Å, and $\beta = 110.71(5)°$. The structure consists of dimers bridged by two dppe ligands which form a ten-membered ring with the nickel atoms. The nickel atoms have distorted tetrahedral geometry with P(1)–Ni–P(2) = 112.4(1) and O(2)–Ni–N(1) = 140.0(4)°. The NO_2 group is bonded to nickel through one oxygen atom (Ni–O(N), 2.123(12) Å. The Ni–N–O angle of the nitrosyl group is 153.4(8)°. Important interatomic distances are Ni–P(1) = 2.271(4) Å, Ni–P(2) = 2.251(3) Å, and Ni–N(O) = 1.664(9) Å. While the crystal structure shows this complex to be a dimer in the solid state, molecular weight determinations indicate that it is monomeric in solution.

Introduction

The reaction of CO with square planar $Ni(NO_2)_2L_2$ complexes of tertiary phosphines has been shown to yield the corresponding nitro nitrosyl complexes according to reaction 1 [1, 2].

$$Ni(NO_2)_2L_2 + CO \rightarrow Ni(NO_2)(NO)L_2 + CO_2 \qquad (1)$$

Kinetic evidence indicates formation of a five coordinate carbonyl intermediate [3, 4], while ^{18}O labelling [2] of $Ni(NO_2)_2(PEt_3)_2$ demonstrates that the NO_2 ligand is the source of oxygen in the oxidation of CO to CO_2. An understanding of the mechanism of this reaction requires knowledge of the geometries of both reactant and product. Therefore, the present study was initiated to determine the molecular structure of $Ni(NO_2)_2$dppe (dppe = $Ph_2PCH_2CH_2PPh_2$), and the product from its reaction with CO, $Ni(NO_2)(NO)$dppe.

These complexes are of structural interest because of the constraints imposed on the coordination geometry of the nickel atom by the dppe ligand. Although the 89° bite angle of chelating dppe is compatible with the *cis* square planar geometry adopted by NiX_2dppe complexes, it is significantly smaller than the 113° commonly found for $NiNOXL_2$ and Ni(0) complexes of tertiary phosphines. The preparation of several related complexes including $Ni(CO)_2$dppe [5], $Ni(dppe)_2$ [6], and NiCl(NO)dppe [7] had been reported. Each was claimed to be tetrahedral and monomeric based on solution spectroscopy but no supporting crystallographic data was available for these complexes.

Additional interest in the structures of the title compounds arises from the structural versatility of the NO_2 ligand. This ligand most commonly functions as a unidentate nitro group although it can also act either as a monodentate or bidentate nitrito group. Complexes having monodentate nitro groups are quite common and are well documented crystallographically [8]. There is less direct evidence for the alternate coordination modes of NO_2 ligands. In addition, there are almost no crystallographic data on the complexes of unidentate nitrito groups although numerous complexes of this type have been claimed on the basis of spectroscopic data [8].

The crystal structures of $Ni(NO_2)_2$dppe and $Ni(NO_2)(NO)$dppe have been investigated in order to determine the coordination geometry about the nickel atom and to determine the bonding mode of the NO_2 ligands in these complexes.

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Experimental

All samples were manipulated under an atmosphere of dry nitrogen using standard Schlenk tube techniques. Solvents were reagent grade and purified by distillation under dry nitrogen immediately prior to use according to published procedures [9]. $Na^{15}NO_2$ (95% enriched) supplied by Prochem was used to prepare ^{15}N enriched samples. Solution molecular weights in 1,2-dichloroethane were determined by vapor pressure osmometry using a Hewlett Packard model 302B instrument calibrated with dppe in 1,2-dichloroethane.

Preparation of Complexes

$Ni(NO_2)_2$dppe was prepared by adding dppe (1.45 g, 3.64 mmol) to a solution of nickel nitrite [10] (0.686 g, 4.55 mmol) in 15 ml of warm methanol (50 °C). The light orange microcrystalline product was removed by filtration, washed with diethyl ether, and dried *in vacuo*.

IR: ν_{NO_2} = 1410, 1392, 1375; 1340, 1320, 1310; 819 cm^{-1}

$\nu_{^{15}NO_2}$ = 1380, 1365, 1350; 1315, 1297, 1288; 811 cm^{-1}

Anal. for $C_{26}H_{24}N_2O_4P_2Ni$: Calcd. (found): C% 56.9-(56.7); H% 4.4(4.2); N% 5.1(4.9); O% 11.7(11.4). Mol. Wt.: Calcd. (found) for $Ni(NO_2)_2$dppe: 548.65 (560 ± 20).

Suitable needle-shaped crystals for X-ray structure determination were grown by vapor diffusion over a period of four days using dichloromethane/diethyl ether. The complex crystallizes with one molecule of dichloromethane per molecule of nickel complex. To prevent evaporation of this solvent and consequent crystal decomposition, the crystal was coated with epoxy resin and mounted in a hollow glass capillary under a steam of nitrogen prior to data collection.

$Ni(NO_2)(NO)$dppe was prepared by the reaction of $Ni(NO_2)_2$dppe (0.219 g, 0.4 mmol) with CO in 5 ml of carefully degassed dichloromethane. Addition of 15 ml of hexane yielded blue-black microcrystals of product which were removed by filtration after 8 hours, washed with hexane, and dried *in vacuo*.

IR: ν_{NO} = 1750, $\nu_{^{15}NO}$ = 1715 cm^{-1}

Anal. for $C_{26}H_{24}N_2O_3P_2Ni$: Calcd. (found): C% 58.6-(58.3); H% 4.5(4.6); N% 5.3(5.1); O% 9.0(9.6). Mol. Wt.: Calcd. (found) for $Ni(NO_2)(NO)$dppe: 532.65 (535 ± 20).

Crystals of $[Ni(ONO)(NO)dppe]_2$ were obtained by generating a solution of $Ni(NO_2)(NO)$dppe in dichloromethane as described above. Vapor diffusion of diethyl ether into this solution over a period of two weeks yielded dark blue plate-shaped crystals suitable for data collection. Several crystals of appropriate size were coated with cyanoacrylate resin, mounted in hollow glass capillaries and sealed under nitrogen prior to data collection.

Collection and Reduction of X-ray Intensity Data

Each crystal was mounted on a Syntex $P2_1$ autodiffractometer controlled by a Nova 1200 computer. The longest dimension of each crystal was approximately parallel to the ϕ axis. Automatic centering, indexing and least-squares routines [11] provided the cell dimensions which are listed in Table I along with other important crystallographic data for each complex. Intensity data for the *hkl* octants were collected under the conditions listed in this table. The data were reduced to F_o^2 and $\sigma(F_o^2)$ by published procedures. Lorentz polarization factors were calculated on the assumption of 50% mosaicity and 50% perfection of the monochromator crystal. For $Ni(NO_2)_2$dppe, the intensities of the standard reflections exhibited an average decline of 12% during the first fifth of the data collection and a 3% decline thereafter. The average linear decomposition for the standards of $[Ni(ONO)(NO)dppe]_2$ was 10%.

Solution and Refinement of Structures

Neutral-atom scattering factors for the nonhydrogen atoms and corrections for the anomalous dispersion made for the nickel, phosphorus, and chlorine atoms were taken from the tables of Cromer and Waber [12]. Hydrogen atom scattering factors were taken from the calculations of Stewart, Davidson, and Simpson [13]. The structures were refined by full-matrix least-squares techniques minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = 4F_o/[\sigma^2(F_o^2) + (pF_o^2)]^2$. The factor to prevent overweighting of strong reflections, p, was set equal to 0.03. The discrepancy indices, R_1 and R_2, are defined in the usual manner.

$Ni(NO_2)_2dppe \cdot CH_2Cl_2$

The structure was solved by the heavy atom method in which the position of the nickel atom was readily determined from a three dimensional Patterson map. The remaining 37 nonhydrogen atoms were located by successive refinements and difference electron density maps. This structure was then refined to isotropic convergence. At this point, the unusually high temperature factor (β = 13.6 $Å^2$) of the dichloromethane carbon, C(3), suggested a possible disorder involving this atom. To investigate this possibility, the contribution of this carbon atom was removed from the calculated structure factors and five fourier planes were generated between the two chlorine atoms and perpendicular to the Cl(1)–Cl(2) vector. These planes were at the midpoint of the Cl(1)–Cl(2) vector

TABLE I. Crystallographic Data at 24 °C.[a]

molecular formula	$[Ni(NO)(ONO)dppe]_2$	$Ni(NO_2)_2dppe$
molecular weight	1065.3	548.65
crystal shape	plate	rectangular needle
crystal dimensions, mm	0.42 × 0.33 × 0.06	0.75 × 0.30 × 0.08
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
cell dimensions[b]		
a, A	15.528(10)	11.880(6)
b, A	11.897(7)	15.191(8)
c, A	15.023(13)	17.162(6)
deg	110.71(5)	108.79(4)
V, A^3	2596(3)	2932(2)
Z	2	4
d_{obs}[c], g cm^{-3}	1.37	1.46
d_{calc}, g cm^{-3}	1.36	1.44
radiation, A	(MoK_α) 0.71073	(MoK_α) 0.71073
monochromator	graphite crystal	graphite crystal
supplied power	50 kV, 30 mA	50 kV, 30 mA
data collection method	$\theta-2\theta$ scan	$\theta-2\theta$ scan
scan speed, deg min^{-1}	variable (3.0–29.3) determined as a function of peak intensity	variable (2.0–29.3) determined as a function of peak intensity
scan range (2θ), deg.	$MoK_{\alpha1}$ – 1.0 to $MoK_{\alpha2}$ + 1.0	$MoK_{\alpha1}$ – 1.0 to $MoK_{\alpha2}$ + 1.0
ratio of total background	0.5	0.5
time to peak scan time standard reflections	(052), (202), (–130) after every 97 readings	(006), (–504), (–322) after every 97 readings
decomposition of standards	10%	15%
2 limit, deg.	4.0–50.0	4.0–50.0
no. of unique data	5033	5612
no. of data used in the calculation	2249 $I > 3(I)$	2508, $I > 36(I)$
absorption coefficient (μ), cm^{-1}	9.64 (MoK_α)	10.03 (MoK_α)

[a] The standard deviation of the least significant figure is given in parentheses in this and the following tables. [b] Cell dimensions were obtained from a least-squares refinement of setting angles of 15 reflections in the 2θ range 9 to 21 °C. [c] Density was determined by flotation using a solution of hexane and carbon tetrachloride.

and at intervals of 0.25 Å on either side of this point. Although there was considerable electron density in these planes, there was only one clearly defined peak. The position of highest electron density was therefore assigned as C(3). The carbon atoms of the phenyl rings were then treated as rigid groups (C–C = 1.383 Å, D_{6h} – 6/mmm symmetry) with individual isotropic thermal parameters. Refinement of the structure with an isotropic thermal parameter for C(3) and anisotropic thermal parameters for all remaining nonhydrogen, nongroup atoms converged with $R_1 = 0.083$ and $R_2 = 0.089$. The hydrogen atoms of the nickel complex were then placed at geometrically idealized positions (C–H = 1.08 Å), assigned an isotropic thermal parameter ($\beta = 5.0$ Å^2) and held fixed in subsequent refinements. Final refinements of this model [14] using 2406 independent reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ and $4.0° \leqslant 2\theta \leqslant 50.0°$ converged with $R_1 = 0.0795$ and $R_2 = 0.0820$. All parameter shifts during the final cycle of refinement were less than 0.08σ. The standard deviation of an observation of unit weight defined by $[\Sigma\omega(|F_o| - |F_c|)^2/(n - m)]^{1/2}$ was 2.37. The number of observations (n) was 2406 and the number of variables (m) was 170. The largest peak in the final electron density map was 0.994 e Å^{-3}. All of the prominent peaks on this map were closely associated with phenyl rings.

$[Ni(ONO)(NO)dppe]_2$

This structure was also solved by the heavy atom method in which Ni and P(1) were located from a three dimensional Patterson map. All remaining nonhydrogen atoms were located by successive refinements and difference electron density maps. This model was refined to convergence with isotropic phenyl carbon atoms and all other atoms anisotropic. Hydrogens were then assigned at geometrically idealized positions (C–H = 1.08 Å), assigned isotropic thermal parameters ($\beta = 5.0$ Å^2) and held fixed during subsequent refinements. After refining this model to convergence, the C–C distances for the phenyl carbons ranged from 1.300(14) to 1.443(14) Å. The phenyl rings were therefore treated as rigid groups (C–C = 1.383 Å, D_{6h} – 6/mm symmetry) with individual isotropic thermal parameters for each group

TABLE II. Final Parameters for the Non-hydrogen Atoms of $Ni(NO_2)_2((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)\cdot CH_2Cl_2$.[a]

Atom	x	y	z
Ni	0.23072(13)	0.19654(9)	0.16347(8)
Cl(1)	0.7606(6)	0.2434(5)	0.3653(4)
Cl(2)	0.8493(6)	0.3931(4)	0.3098(5)
P(1)	0.30314(26)	0.16883(18)	0.29472(16)
P(2)	0.06895(27)	0.23716(20)	0.18770(18)
O(1)	0.3491(12)	0.0721(7)	0.1140(7)
O(2)	0.4568(10)	0.1855(9)	0.1554(6)
O(3)	0.1096(9)	0.1983(7)	−0.0056(5)
O(4)	0.2106(8)	0.3146(6)	0.0427(5)
N(1)	0.3608(12)	0.1475(10)	0.1410(7)
N(2)	0.1755(9)	0.2400(7)	0.0528(6)
C(1)	0.0990(9)	0.2444(7)	0.3006(6)
C(2)	0.1764(9)	0.1651(7)	0.3355(6)
C(3)	0.8054(23)	0.3496(19)	0.3877(17)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	3.63(7)	3.08(6)	2.36(5)	0.43(7)	1.06(5)	0.14(6)
Cl(1)	16.3(5)	16.6(6)	17.3(6)	−3.7(4)	7.2(5)	0.7(4)
Cl(2)	17.7(6)	11.4(5)	20.2(6)	1.5(4)	6.1(5)	0.4(4)
P(1)	3.76(15)	3.02(15)	2.35(12)	−0.04(12)	0.89(11)	0.21(10)
P(2)	3.75(16)	4.22(17)	3.26(14)	0.80(13)	1.15(12)	0.25(12)
O(1)	16.3(11)	5.8(6)	8.8(7)	4.5(7)	6.2(7)	−0.7(5)
O(2)	6.4(6)	15.2(10)	6.7(6)	1.3(7)	3.0(5)	−0.9(7)
O(3)	11.5(7)	8.8(7)	3.0(4)	−3.1(6)	−0.1(4)	−1.0(5)
O(4)	9.0(6)	4.3(5)	5.8(5)	−0.8(5)	2.5(4)	1.8(4)
N(1)	6.0(7)	10.5(11)	3.5(6)	1.7(8)	1.7(6)	1.0(6)
N(2)	4.8(6)	5.3(6)	4.0(5)	1.0(5)	1.8(5)	−0.7(5)
C(1)	3.5(6)	4.9(6)	2.3(5)	1.2(5)	0.3(4)	−0.3(4)
C(2)	2.6(5)	5.2(7)	3.7(5)	−0.1(5)	1.0(4)	1.4(5)

Atom	B
C(3)	15.7(8)

[a] x, y, and z are in fractional monoclinic coordinates. Anisotropic thermal parameters are in the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. B is the isotropic thermal parameter in square angstroms of the given atom.

atom. Using this model final refinements based on the 2249 independent reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ and $4.0° \leqslant 2\theta \leqslant 50.0°$ converged with $R_1 = 0.0717$ and $R_2 = 0.0735$. All parameter shifts during the final cycle of refinement were less than 0.07σ. The standard deviation of an observation of unit weight, defined above was 2.18. The largest residual in the final difference electron density map was 1.037 e Å^{-3} located near ring P1R2.

Several anomalous features of the nitrito ligand remained: O(2)–N(2) = 1.097(14) Å while N(2)–O(3) = 1.192(13) Å. Thus the terminal oxygen, O(3), appears to have a shorter bond to N(2) than the oxygen (O(2)) bonded to both Ni and N(2). In addition, several angles about the nickel atom involving the nitrito group especially O(2)–Ni–N(1) (140.0(4)°), are severely distorted from tetrahedral. There is no evidence for steric crowding that would account for these distortions. Although these facts could be interpreted as resulting from the quality of the data set, they are also suggestive of disorder. Difference Fourier maps suggested the presence of another nitrito unit (occupancy approximately 20%) coplanar with and 180° from the established nitrito atom positions. The position of the metal-bonded oxygen was the same for each nitrito group. However, the low occupancy of the disordered nitrito atoms prevented their successful refinement.

Results

Description of Structures

Perspective views showing the numbering schemes of $Ni(NO_2)_2dppe\cdot CH_2Cl_2$ and $[Ni(ONO)(NO)dppe]_2$ are shown in Figs. 1 and 2 respectively. Selected

TABLE III. Final Group Parameters for $Ni(NO_2)_2((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)\cdot CH_2Cl_2$[a].

Group	x_c	y_c	z_c	ϕ	θ	ρ
P1R1	0.4665(5)	0.0000(4)	0.3623(3)	2.115(6)	−2.709(6)	−0.178(6)
P1R2	0.4537(4)	0.3352(3)	0.3847(3)	−2.990(12)	−1.987(5)	−0.889(11)
P2R1	−0.0278(6)	0.4224(4)	0.1083(4)	−1.062(7)	−2.708(6)	0.408(6)
P2R2	−0.1343(5)	0.0900(4)	0.1289(3)	−2.293(8)	2.432(5)	3.058(7)
Group	B_1	B_2	B_3	B_4	B_5	B_6
P1R1	3.96(24)	5.9(3)	6.6(3)	6.7(3)	9.4(5)	7.5(4)
P1R2	3.27(22)	4.23(25)	5.4(3)	5.22(28)	5.20(29)	4.82(28)
P2R1	4.49(26)	7.0(4)	8.6(4)	7.3(4)	8.3(4)	6.5(3)
P2R2	4.72(27)	6.7(4)	7.6(4)	8.1(4)	7.6(4)	5.8(3)

[a] x_c, y_c, and z_c are the fractional coordinates of the group origins. The angles ϕ, θ, and ρ (in radians) are the rotations necessary to bring about alignment (except for translation) of the group internal coordinate system with the fixed crystallographic coordinate system. B_i is the isotropic thermal parameter in square angstroms of the atom i in a given group. The rings are numbered so that atom C_1 is attached to P and atom C_4 is para to C_1. The standard deviations of the least significant digits are given in parentheses.

TABLE IV. Derived Parameters for the Group Atoms[a] for $Ni(NO_2)_2((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)\cdot CH_2Cl_2$.

Group	Atom	x	y	z
P1R1	C1	0.3960(7)	0.0731(5)	0.3336(5)
	C2	0.5140(8)	0.0736(5)	0.3371(5)
	C3	0.5845(6)	0.0005(7)	0.3658(5)
	C4	0.5371(9)	−0.0732(5)	0.3910(5)
	C5	0.4191(9)	−0.0737(5)	0.3875(6)
	C6	0.3486(6)	−0.0006(7)	0.3588(6)
P1R2	C1	0.3903(6)	0.2627(4)	0.3452(4)
	C2	0.4155(7)	0.3305(5)	0.2997(3)
	C3	0.4789(7)	0.4031(4)	0.3392(5)
	C4	0.5171(7)	0.4078(4)	0.4242(5)
	C5	0.4919(7)	0.3400(5)	0.4697(3)
	C6	0.4285(7)	0.2674(4)	0.4303(4)
P2R1	C1	0.0092(8)	0.3420(5)	0.1456(5)
	C2	−0.0937(8)	0.3473(6)	0.0788(6)
	C3	−0.1307(7)	0.4277(7)	0.0415(5)
	C4	−0.0648(10)	0.5028(5)	0.0710(6)
	C5	0.0381(9)	0.4974(5)	0.1378(6)
	C6	0.0752(7)	0.4170(7)	0.1751(5)
P2R2	C1	−0.0483(7)	0.1548(5)	0.1532(5)
	C2	−0.1519(9)	0.1619(5)	0.1730(5)
	C3	−0.2379(7)	0.0971(7)	0.1487(6)
	C4	−0.2203(8)	0.0252(6)	0.1046(6)
	C5	−0.1166(9)	0.0180(5)	0.0848(5)
	C6	−0.0306(7)	0.0829(6)	0.1092(5)

[a] x, y, and z are in fractional monoclinic coordinates. Estimated standard deviations (given in parentheses) are derived from those of the group parameters by NUCLS.

TABLE V. Parameters for the Fixed Hydrogen Atom Positions[a] for $Ni(NO_2)_2((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)\cdot CH_2Cl_2$.

Group	Atom	x	y	z
P1R1	H2	0.5514	0.1312	0.3186
	H3	0.6775	0.0011	0.3692
	H4	0.5934	−0.1308	0.4132
	H5	0.3832	−0.1325	0.4066
	H6	0.2571	−0.0023	0.3561
P1R2	H2	0.3860	0.3271	0.2336
	H3	0.4998	0.4561	0.3038
	H4	0.5676	0.4648	0.4551
	H5	0.5217	0.3445	0.5363
	H6	0.4079	0.2156	0.4661
P2R1	H2	−0.1447	0.2902	0.0539
	H3	−0.2094	0.4341	−0.0112
	H4	−0.0917	0.5671	0.0432
	H5	0.0907	0.5563	0.1628
	H6	0.1554	0.4123	0.2279
P2R2	H2	−0.1644	0.2181	0.2085
	H3	−0.3185	0.1033	0.1652
	H4	−0.2888	−0.0245	0.0857
	H5	−0.1051	−0.0375	0.0493
	H6	0.0489	0.0773	0.0926
C1	H1	0.0981	0.3043	0.3359
	H2	0.0155	0.2404	0.2508
C2	H1	0.1441	0.1068	0.3583
	H2	0.2725	0.1698	0.3675

[a] x, y, and z are in fractional monoclinic coordinates.

interatomic distances and angles for the nonhydrogen atoms of $Ni(NO_2)_2dppe\cdot CH_2Cl_2$ are given in Table VI. The corresponding data for $[Ni(ONO)(NO)dppe]_2$ are set out in Table XI.

$Ni(NO_2)_2dppe\cdot CH_2Cl_2$

The crystal structure consists of discrete molecules of the nickel complex well separated from dichloromethane molecules. The closest contact between

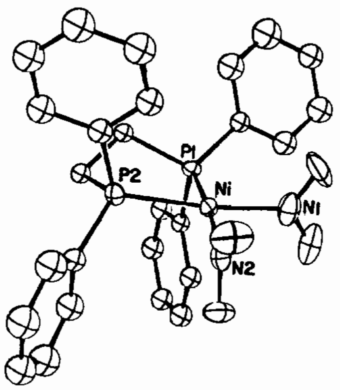

Fig. 1. ORTEP drawing of $Ni(NO_2)_2dppe$.

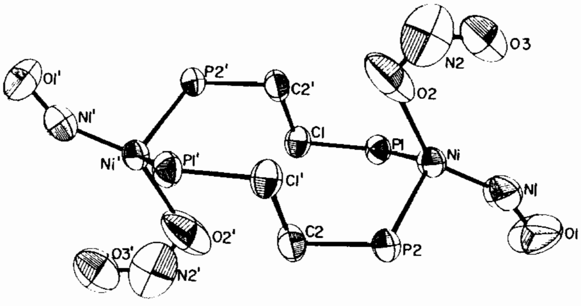

Fig. 2. ORTEP drawing of $[Ni(ONO)(NO)dppe]_2$ with phenyl rings eliminated for clarity.

the solvent molecule and the nickel complex is 2.905 Å found between Cl(1) and P1R1H2.

The coordination geometry about the nickel atom is essentially square planar with the central atom displaced only 0.17 Å from the plane defined by the phosphorus and nitrogen atoms to which it is bonded. The two N-bonded nitro groups are *cis* to each other in the square plane. The N(1)–Ni–P(1) and N(2)–Ni–P(2) angles are equivalent and are slightly larger than the N(1)–Ni–N(2) and P(1)–Ni–P(2) angles. This slight distortion from square planarity accommodates the restricted bite angle of dppe and minimizes crowding between the bulky phenyl rings of this ligand and the atoms of the nitro groups. The Ni–P bond lengths are equivalent and are typical of those reported for other Ni(II) phosphine complexes [15]. There is no evidence for disorder of the ethylene bridge which forms the backbone of the phosphine ligand. The average P–C(CH_2) distance

TABLE VI. Selected Interatomic Distances and Angles for $Ni(NO_2)_2((C_6H_5)_2(PCH_2CH_2P(C_6H_5)_2)\cdot CH_2Cl_2$ [a].

Distances			
Ni–N(1)	1.864(12)	P(1)–P1R1C1	1.817(8)
Ni–N(2)	1.916(10)	P(1)–P1R2C1	1.811(6)
Ni–P(1)	2.178(3)	P(2)–C(1)	1.857(10)
Ni–P(2)	2.182(4)	P(2)–P2R1C1	1.798(8)
N(1)–O(1)	1.227(14)	P(2)–P2R2C1	1.823(8)
N(1)–O(2)	1.229(14)	C(1)–C(2)	1.517(14)
N(2)–O(3)	1.229(11)	Cl(1)–C(3)	1.704(27)
N(2)–O(4)	1.240(11)	Cl(2)–C(3)	1.716(28)
P(1)–C(2)	1.854(10)	Cl(1)–Cl(2)	2.799(10)
Angles			
N(1)–Ni–N(2)	88.5(4)	C(2)–P(1)–Ni	107.3(3)
N(1)–Ni–P(1)	93.4(3)	C(2)–P(1)–P1R1C1	107.9(5)
N(1)–Ni–P(2)	172.8(5)	C(2)–P(1)–P1R2C1	104.6(5)
N(2)–Ni–P(1)	170.7(4)	P1R1C1–P(1)–P1R2C1	105.6(4)
N(2)–Ni–P(2)	92.9(3)	P1R1C1–P(1)–Ni	121.7(4)
P(1)–Ni–P(2)	86.3(1)	P1R2C1–P(1)–Ni	108.5(3)
O(1)–N(1)–O(2)	119.9(15)	C(1)–P(2)–Ni	109.3(4)
O(1)–N(1)–Ni	116.7(12)	C(1)–P(2)–P2R1C1	106.6(5)
O(2)–N(1)–Ni	123.3(13)	C(1)–P(2)–P2R2C1	104.4(5)
O(3)–N(2)–O(4)	120.7(10)	P2R1C1–P(2)–P2R2C1	108.4(5)
O(3)–N(2)–Ni	123.7(9)	P2R1C1–P(2)–Ni	115.6(4)
O(4)–N(2)–Ni	115.5(8)	P2R2C1–P(2)–Ni	111.8(4)
		Cl(1)–C(3)–Cl(2)	109.8(15)
P(2)–C(1)–C(2)	104.6(7)		
P(1)–C(2)–C(1)	106.9(7)		

[a] Distances in angstroms and angles in degrees. Standard deviations (given in parentheses) for the distances and angles involving the non-group atoms were calculated using a variance covariance matrix. Standard deviations for distances and angles involving the group atoms were calculated using only variances. The estimated variances for the carbon atoms of the rigid groups are those given in Table IV.

TABLE VII. Final Parameters for the Non-hydrogen Atoms of $[\mathrm{Ni(ONO)(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)}]_2$.

Atom	x	y	z
Ni	0.46087(8)	0.05148(10)	0.18019(9)
P(1)	0.33312(16)	0.00555(21)	0.05428(18)
P(2)	0.58008(15)	−0.06392(21)	0.19517(16)
O(1)	0.4315(7)	−0.0341(8)	0.3368(7)
O(2)	0.5039(8)	0.1854(8)	0.1123(8)
O(3)	0.4567(7)	0.2793(8)	0.2002(7)
N(1)	0.4404(6)	0.0249(7)	0.2796(7)
N(2)	0.4879(8)	0.2656(13)	0.1389(9)
C(1)	0.6152(6)	−0.0888(8)	0.0919(6)
C(2)	0.6507(6)	0.0174(8)	0.0595(6)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	2.92(5)	3.31(6)	3.47(6)	0.24(5)	1.63(5)	0.00(6)
P(1)	2.92(11)	3.78(13)	3.46(12)	0.10(10)	1.78(10)	0.01(10)
P(2)	3.12(11)	3.24(12)	3.11(12)	0.26(10)	1.62(10)	−0.06(11)
O(1)	14.9(8)	9.1(7)	12.2(7)	4.6(6)	10.7(7)	5.9(6)
O(2)	9.3(6)	5.9(6)	8.7(7)	1.7(5)	1.1(5)	−3.6(5)
O(3)	11.2(7)	5.4(5)	9.0(7)	0.3(5)	4.4(6)	−1.9(5)
N(1)	5.4(5)	5.3(6)	6.4(5)	1.8(4)	3.5(4)	0.7(4)
N(2)	6.2(7)	12.2(12)	7.6(9)	−1.7(8)	1.8(6)	−0.1(8)
C(1)	4.0(5)	3.9(5)	3.4(5)	−0.1(4)	2.0(4)	−0.8(4)
C(2)	3.1(4)	4.1(5)	3.1(4)	−0.3(4)	1.4(4)	−0.2(4)

[a] x, y, and z are in fractional monoclinic coordinates. Anisotropic thermal parameters are in the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 3B_{23}klb^*c^*)]$.

TABLE VIII. Final Group Parameters for $[\mathrm{Ni(ONO)(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)}]_2$[a].

Group	x_c	y_c	z_c	ϕ	θ	ρ
P1R1	0.1688(3)	0.1831(4)	0.0148(3)	2.254(7)	2.204(4)	−2.910(7)
P1R2	0.2351(3)	−0.2180(4)	0.0916(3)	0.632(7)	−2.294(5)	−0.584(7)
P2R1	0.7670(3)	0.0106(4)	0.3596(3)	0.522(4)	−2.780(4)	−2.634(4)
P2R2	0.52961(28)	−0.3071(4)	0.2536(4)	−0.870(10)	−2.027(4)	−2.098(10)

Group	B_1	B_2	B_3	B_4	B_5	B_6
P1R1	3.28(19)	5.23(25)	7.1(3)	6.26(29)	5.11(25)	4.17(21)
P1R2	3.56(20)	5.48(26)	7.1(3)	6.9(3)	6.44(29)	5.64(26)
P2R1	3.13(19)	4.52(23)	5.90(26)	5.74(25)	5.39(26)	4.09(21)
P2R2	3.34(19)	5.44(26)	6.7(3)	6.00(28)	6.22(28)	5.26(25)

[a] x_c, y_c, and z_c are the fractional coordinates of the group origins. The angles ϕ, θ, and ρ (in radians) are the rotations necessary to bring about alignment (except for translation) of the group internal coordinate system with the fixed crystallographic coordinate system. B_i is the isotropic thermal parameter in square angstroms of the atom i in a given group. The rings are numbered so that atom C_1 is attached to P and C_4 is para to C_1. The standard deviations of the least significant digits are given in parentheses.

of 1.8654(10) Å is slightly longer than the P–C(C_6H_5) distance of 1.812(8) Å. All P–C distances are typical of those found in related transition metal phosphine complexes [16]. The geometry about each phosphorus atom is significantly distorted from tetrahedral. While the P1R1C1–P(1)–Ni angle of 108.5(3)° is equal within experimental error to that found in a regular tetrahedron, the P1R2C1–P(1)–Ni angle of 121.7(4)° is significantly larger. In the case of P(2), the corresponding angles are 115.6(4)° and 111.8(4)° respectively.

The N(1)–O(1)–O(2) and N(2)–O(3)–O(4) planes form dihedral angles of 96.5° and 86.4° respectively with the P(1)–P(2)–N(1)–N(2) plane. The Ni–N bond lengths of 1.846(10) and 1.916(19) Å differ by 5σ while the Ni–N–O angles span a range

TABLE IX. Derived Parameters for the Group Atoms[a] for $[Ni(ONO)(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)]_2$.

Group	Atom	x	y	z
P1R1	C1	0.2409(4)	0.1089(5)	0.0287(5)
	C2	0.2427(4)	0.1836(6)	0.0998(4)
	C3	0.1706(5)	0.2578(6)	0.0860(5)
	C4	0.0966(4)	0.2573(6)	0.0009(6)
	C5	0.0948(4)	0.1826(6)	−0.0702(4)
	C6	0.1670(5)	0.1084(5)	−0.0564(4)
P1R2	C1	0.2759(4)	−0.1219(5)	0.0729(5)
	C2	0.2877(4)	−0.2238(6)	0.0343(4)
	C3	0.2469(5)	−0.3198(5)	0.0530(5)
	C4	0.1942(5)	−0.3141(5)	0.1103(6)
	C5	0.1824(5)	−0.2123(7)	0.1490(5)
	C6	0.2232(3)	−0.1162(5)	0.1303(5)
P2R1	C1	0.6867(3)	−0.0227(5)	0.2884(4)
	C2	0.7653(5)	−0.0877(4)	0.3099(5)
	C3	0.8456(4)	−0.0544(6)	0.3811(5)
	C4	0.8473(4)	0.0439(6)	0.4308(4)
	C5	0.7687(5)	0.1089(5)	0.4094(5)
	C6	0.6884(4)	0.0756(5)	0.3382(5)
P2R2	C1	0.5553(4)	−0.2043(5)	0.2279(5)
	C2	0.5147(5)	−0.2843(6)	0.1590(4)
	C3	0.4890(5)	−0.3871(6)	0.1847(5)
	C4	0.5040(5)	−0.4099(5)	0.2793(6)
	C5	0.5446(5)	−0.3299(7)	0.3482(4)
	C6	0.5702(4)	−0.2271(5)	0.3225(4)

[a] x, y, and z are infractional monoclinic coordinates. Estimated standard deviations (given in parentheses) are derived from those of the group parameters by NUCLS.

TABLE X. Parameters for the Fixed Hydrogen Atom Positions[a] for $[Ni(ONO)(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$.

Group	Atom	x	y	z
P1R1	H2	0.3021	0.1874	0.1667
	H3	0.1688	0.3170	0.1426
	H4	0.0404	0.3179	−0.0124
	H5	0.0350	0.1839	−0.1353
	H6	0.1639	0.0492	−0.1133
P1R2	H2	0.3302	−0.2265	−0.0094
	H3	0.2538	−0.4059	0.0231
	H4	0.1604	−0.3871	0.1274
	H5	0.1396	−0.2140	0.1922
	H6	0.2138	−0.0344	0.1619
P2R1	H2	0.7627	−0.1671	0.2707
	H3	0.9102	−0.1023	0.3988
	H4	0.9107	0.0724	0.4880
	H5	0.7691	0.1848	0.4523
	H6	0.6272	0.1284	0.3194
P2R2	H2	0.4986	−0.2652	0.0834
	H3	0.4586	−0.4547	0.1329
	H4	0.4848	−0.4898	0.3003
	H5	0.5531	−0.3499	0.4228
	H6	0.6046	−0.1641	0.3774
C1	H1	0.3306	0.1526	−0.1110
	H2	0.4431	0.1210	−0.0335
C2	H1	0.2835	−0.0424	−0.1138
	H2	0.3978	−0.0859	−0.0526

[a] x, y, and z are in fractional monoclinic coordinates.

of 7σ. There are no obvious sources for the disparity in Ni–N distances. This difference is likely an experimental artifact arising from the unsymmetric shape of the data crystal and the nonlinear decomposition of the crystal which occurred during data collection. The O–N–O angles are equivalent. The average Ni–N bond length of 1.890(11) Å is 0.107 Å shorter than that found in $Ni(NO_2)(NO)(PMe_3)_2$ [4]. The average Ni–P distance of 2.180(4) Å^2 is also shorter than that found in either $[Ni(ONO)(NO)dppe]_2$ or $Ni(NO_2)(NO)(PMe_3)_2$ [4]. Within experimental error, the remaining distances and angles do not differ significantly from those reported for related complexes.

[Ni(ONO)(NO)dppe]$_2$

This complex crystallizes in the monoclinic space group $P2_1/n$ with two discrete dimers per unit cell. The dimer spans two asymmetric units with each half related to the other by a crystallographic inversion center. Halves of the dimer are linked by two dppe ligands forming a ten membered ring including the two nickel atoms. The dppe bridges adopt a chair configuration with no evidence for disorder of the ethylene backbones of these ligands.

The bridging geometry of the dppe ligands allows each Ni atom to attain a distorted tetrahedral geometry. The dihedral angle of 90.4° between the P(1)–Ni–P(2) and O(2)–Ni–N(1) planes is similar to the idealized angle of 90° for a regular tetrahedron. While the P(1)–Ni–P(2) angle of 112.4(1)° is only slightly larger than that of a regular tetrahedron, the O(2)–Ni–N(1) angle of 140.0(4)° is considerably larger. Although the structure is distorted, the geometry at the nickel atoms is more closely related to tetrahedral than it is to square planar geometry.

The Ni–P(1) distance of 2.271(4) Å differs by 5–7σ from the Ni–P(2) distance of 2.251(3) Å. The Ni–N(01) bond length of 1.664(9) Å is typical of that found in other low symmetry $\{NiNO\}^{10}$ complexes and indicates considerable covalent bonding between the nickel and the nitrosyl ligand [4, 17]. The intermediate Ni–N(1)–O(1) angle of 153.4(8)° is similar to that found in closely related $\{NiNO\}^{10}$ complexes of other tertiary phosphines [17].

The nitrito group is bonded to nickel through oxygen as a unidentate ligand and adopts a *cis* configuration similar to that observed in $K_3Cu(NO_2)_5$ [18]. There is no bonding interaction between the

TABLE XI. Selected Interatomic Distances and Angles for $[Ni(ONO)(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)]_2$[a].

Distances			
Ni–O(2)	2.123(12)	P(1)–C(2)	1.842(9)
Ni–N(1)	1.664(9)	P(1)–P1R1C1	1.822(6)
Ni–P(1)	2.271(4)	P(1)–P1R2C1	1.828(7)
Ni–P(2)	2.251(3)	P(2)–C(1)	1.834(9)
N(1)–O(1)	1.155(9)	P(2)–P2R1C1	1.817(5)
O(2)–N(2)	1.097(14)	P(2)–P2R2C1	1.821(7)
N(2)–O(3)	1.92(13)	C(1)–C(2)	1.524(11)
Angles			
O(2)–Ni–N(1)	140.0(4)	C(2)–P(1)–P1R2C1	104.6(4)
O(2)–Ni–P(1)	96.4(3)	P1R1C1–P(1)–P1R2C2	101.8(3)
O(2)–Ni–P(2)	96.8(3)	P1R1C1–P(1)–Ni	113.8(3)
N(1)–Ni–P(1)	108.3(3)	P1R2C1–P(1)–Ni	113.6(3)
N(1)–Ni–P(2)	101.9(3)	C(1)–P(2)–Ni	119.4(3)
P(1)–Ni–P(2)	112.4(1)	C(1)–P(2)–P2R1C1	103.4(5)
O(1)–N(1)–Ni	153.4(8)	C(1)–P(2)–P2R2C1	103.5(5)
N(2)–O(2)–Ni	109.0(12)	P2R1C1–P(2)–P2R2C1	105.2(4)
O(2)–N(2)–O(3)	127.4(17)	P2R1C1–P(2)–Ni	113.9(4)
C(2)–P(1)–Ni	119.4(3)	P2R2C1–P(2)–Ni	110.0(4)
C(2)–P(1)–P1R1C1	105.1(4)		
C(2)–C(1)–P(2)	112.6(6)		
C(1)–C(2)–P(1)	111.0(6)		

[a] Distances in angstroms and angles in degrees. Standard deviations (given in parentheses) for the distances and angles involving the non-group atoms were calculated using a variance covariance matrix. Standard deviations for distances and angles involving the group atoms were calculated using only variances. The estimated variances for the carbon atoms of the rigid groups are those given in Table IV.

exo oxygen (O(3)) of the nitrito ligand and the nickel atom. The N(2)–O(3) distance of 1.192(13) Å is 0.095 Å longer than the N(2)–O(2) distance of 1.097 Å. This distortion probably arises from an unresolvable disorder involving this ligand. Despite this disorder, however, it is seen that the NO_2 ligand is coordinated to nickel as a unidentate nitrito group. Whithin experimental error, all of the C–P–C distances and angles differ insignificantly from those reported for related complexes [16].

Discussion

The results outlined above establish that $Ni(NO_2)_2dppe$ is square planar. Square planar geometry has been well documented crystallographically for many d^8 transition metal complexes [19]. The metrical details of $Ni(NO_2)_2dppe$ are consistent with the structures reported previously.

In the crystals selected for study, Ni(ONO)(NO)-dppe is dinuclear with the two nickel atoms bridged by two dppe ligands. Complexes bridged by two dppe ligands however are not common. To our knowledge, $[Ni(ONO)(NO)dppe]_2$ is the first example of a structurally characterized complex in which two bridging dppe ligands form a monocyclic system with two metal atoms [20]. The bridging by dppe ligands in the present complex permits the $\{NiNO\}^{10}$ group to adopt approximate tetrahedral geometry by relieving the steric constraint imposed by the 89° bite angle of dppe.

The distortion of the coordination sphere of the nickel atom from tetrahedral geometry has been observed for several monomeric $\{NiNO\}^{10}$ complexes with unidentate ligands. The bending of Ni–N–O linkage and apparently different Ni–P bond lengths in this complex have also been observed in a number of closely related $Ni(X)(NO)P_2$ complexes [17]. The low symmetry adopted by these complexes and the bending of the nitrosyl groups are in accord with the molecular orbital diagram for $\{NiNO\}^{10}$ complexes given in reference 21. A discussion of these structure-bonding relationships has also been presented in the preceding paper of this series [4].

Another interesting feature of these two structures is the linkage isomerism displayed by the NO_2 ligand. Each NO_2 group in $Ni(NO_2)_2dppe$ is bonded to the metal atom through the nitrogen atom. This mode of coordination has been well documented crystallographically and the metrical details of the present structure are consistent with these earlier reports [7]. In $[Ni(ONO)(NO)dppe]_2$, however, the NO_2 group is bonded to nickel as a unidentate nitrito ligand. Together with the structures reported for $Ni(Me_2NCH_2CH_2NH_2)_2(ONO)_2$ [22], $Cr(ONO)(NO)(C_5H_5N)_3 \cdot C_5H_5N$ [8] and $K_3Cu(NO_2)_5$ [18], this complex provides one of the few structurally characterized examples of unidentate nitrito coordination.

Infrared spectra of Ni(ONO)(NO)dppe taken immediately after preparation of the nitrosyl complex show predominantly N-bonded nitro groups. In addition, molecular weight determinations indicate that $\mathrm{Ni(NO_2)(NO)dppe}$ is monomeric in solution where it possibly adopts a distorted tetrahedral structure similar to that reported for bis(bis(dicyclohexylphosphino)methane)nickel [23]. Thus while the dppe bridged dimer with an O-bonded $\mathrm{NO_2}$ group is the crystallographic form of this complex, it is not the predominant form of this complex in solution. Investigations are in progress to determine how the constraints imposed by bidentate phosphine ligands affect the geometry of related Ni(0) complexes.

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Supplementary Material Available:

Group Parameters, derived parameters for the group atoms, parameters for the fixed hydrogen atom positions, and observed and calculated structure factors: Tables III, IV, V, and XII for $\mathrm{Ni(NO_2)_2 \cdot dppe \cdot CH_2Cl_2}$ and Tables VII, IX, X, and XIII for $\mathrm{[Ni(ONO)(NO)dppe]_2}$ (27 pages). Ordering information is given on any current masthead page.

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