Cl1	0.21192 (16)	0.25102 (16)	0.50436 (16)	5.21 (9)
Cl2	0.4529 (3)	0	0.31900 (19)	4.78 (15)
Cl3	0.9740 (3)	0	0.18939 (17)	5.18 (16)
O1	0.2603 (8)	0.3416 (5)	0.5096 (6)	9.9 (5)
O2	0.1057 (6)	0.2675 (7)	0.5069 (7)	10.7 (6)
O3	0.2267 (12)	0.1897 (8)	0.5469 (6)	13.4 (9)
O4	0.2295 (9)	0.2030 (8)	0.4532 (4)	10.5 (6)
O5	0.5489 (11)	0	0.3319 (4)	21.7 (27)
O6	0.3978 (10)	0	0.3672 (6)	8.4 (7)
O7	0.4229 (10)	0.0806 (7)	0.2866 (4)	11.3 (7)
O8	0.9492 (12)	0.0788 (7)	0.2232 (5)	12.1 (9)
O9	1.0755 (10)	0	0.1819 (11)	13.4 (14)
O10	0.9223 (16)	0	0.1429 (7)	17.4 (19)
N1	0.8616 (7)	0	0.3450 (5)	5.0 (6)
N2	1.0165 (5)	0.1576 (5)	0.3855 (4)	4.1 (3)
N3	1.0952 (7)	0	0.3286 (5)	4.3 (5)
N4	1.1158 (9)	0	0.4581 (5)	4.7 (5)
N5	0.9052 (9)	0	0.4690 (5)	5.0 (5)
N6	0.6091 (8)	0	0.1839 (5)	5.3 (6)
N7	0.4795 (6)	0.1572 (6)	0.1216 (5)	5.3 (4)
N8	0.3748 (7)	0	0.1645 (5)	3.7 (4)
N9	0.6258 (10)	0	0.0593 (5)	4.8 (5)
N10	0.4224 (9)	0	0.0394 (5)	4.4 (5)
C1	0.7999 (7)	0.0896 (8)	0.3531 (5)	5.5 (4)
C2	0.8533 (7)	0.1854 (8)	0.3435 (5)	5.7 (4)
C3	0.9272 (8)	0.2159 (7)	0.3856 (5)	6.0 (5)
C4	1.0830 (7)	0.1754 (7)	0.3374 (5)	5.3 (4)
C5	1.1541 (5)	0.0895 (6)	0.3314 (4)	4.8 (4)
C6	1.0664 (14)	0	0.5113 (7)	7.5 (10)
C7†	0.9695 (18)	0.0420 (14)	0.5130 (7)	4.9 (8)
C8	0.6753 (9)	0.0913 (13)	0.1876 (6)	9.1 (8)
C9	0.6163 (11)	0.1856 (11)	0.1907 (6)	8.3 (7)
C10	0.5663 (10)	0.2218 (8)	0.1383 (6)	7.9 (7)
C11	0.3924 (8)	0.1765 (6)	0.1575 (5)	5.7 (4)
C12	0.3183 (6)	0.0920 (8)	0.1534 (5)	5.6 (4)
C13	0.5865 (20)	0	0.0033 (10)	12.2 (17)
C14	0.4915 (14)	0	−0.0072 (9)	9.2 (16)

† Occupancy 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Ni1—N1	2.16 (1)	Ni2—N10	2.17 (1)
Ni1—N2	2.162 (7)	N1—C1	1.48 (1)
Ni1—N3	2.10 (1)	N2—C3	1.43 (1)
Ni1—N4	2.23 (1)	N2—C4	1.49 (1)
Ni1—N5	2.16 (1)	N3—C5	1.445 (9)
Ni2—N6	2.15 (1)	N6—C8	1.52 (2)
Ni2—N7	2.156 (7)	N7—C10	1.51 (1)
Ni2—N8	2.10 (1)	N7—C11	1.48 (1)
Ni2—N9	2.13 (1)	N8—C12	1.48 (1)
N1—Ni1—N2	92.9 (2)	N7—Ni2—N10	88.2 (3)
N1—Ni1—N3	95.7 (4)	N8—Ni2—N9	173.1 (4)
N1—Ni1—N4	170.9 (4)	N8—Ni2—N10	93.0 (4)
N1—Ni1—N5	90.4 (4)	N9—Ni2—N10	80.1 (5)
N2—Ni1—N2^{i}	160.2 (3)	Ni1—N1—C1	112.8 (6)
N2—Ni1—N3	80.3 (2)	C1—N1—C1^{i}	109.9 (8)
N2—Ni1—N4	88.6 (2)	Ni1—N2—C3	115.4 (6)
N2—Ni1—N5	99.4 (2)	Ni1—N2—C4	108.9 (6)
N3—Ni1—N4	93.5 (4)	C3—N2—C4	114.4 (8)
N3—Ni1—N5	173.9 (4)	Ni1—N3—C5	108.3 (6)
N4—Ni1—N5	80.4 (4)	C5—N3—C5^{i}	113.6 (8)
N6—Ni2—N7	93.3 (3)	Ni2—N6—C8^{i}	115.0 (7)
N6—Ni2—N8	96.7 (4)	C8—N6—C8^{i}	108 (1)
N6—Ni2—N9	90.2 (4)	Ni2—N7—C10	117.6 (7)
N6—Ni2—N10	170.3 (4)	Ni2—N7—C11	109.5 (6)
N7—Ni2—N7^{i}	160.5 (3)	C10—N7—C11	110.4 (9)
N7—Ni2—N8	80.5 (2)	Ni2—N8—C12	108.9 (6)
N7—Ni2—N9	99.1 (3)	C12—N8—C12^{i}	114.4 (8)
C1—N1—C1—C2	−178 (1)	C12—N8—C12—C11	−171 (1)
C4—N2—C3—C2	71.8 (8)	N1—C1—C2—C3	−72.4 (8)
C3—N2—C4—C5	−161 (1)	C1—C2—C3—N2	71.4 (9)
C5—N3—C5—C4	−171 (1)	N2—C4—C5—N3	54.2 (6)
C8—N6—C8—C9	−174 (1)	N6—C8—C9—C10	−74 (1)
C11—N7—C10—C9	76 (1)	C8—C9—C10—N7	70 (1)
C10—N7—C11—C12	−162 (1)	N7—C11—C12—N8	52.8 (7)

Symmetry code: (i) $x, -y, z$.

Data reduction, structure solution and structure refinement were carried out using *NRCVAX* (Gabe, Le Page, White & Lee, 1987). H atoms were located by theoretical calculation. H atoms attached to N5, C6 and C7 were not calculated. Atom C7 had a site occupation factor of 0.5.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans,trans-[$Ni_2(CN)_4(Me_2PCH_2PMe_2)_2$]

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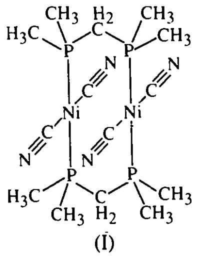
Abstract

The molecular structure of *trans,trans*-bis[μ-bis(dimethylphosphino)methane-*P*:*P*′]bis(dicyanonickel), [$Ni_2(CN)_4(C_5H_{14}P_2)_2$], is of the face-to-face type. It contains an eight-membered $Ni_2P_4C_2$ ring with an elongated chair conformation and a transannular Ni···Ni separation of 3.2085 (6) Å. The coordination geometry around the Ni atoms is square planar.

Comment

Binuclear transition metal complexes with bridging diphosphinomethane ligands, $R_2PCH_2PR_2$, interact with small molecules without fragmentation into mononuclear species and can provide models for the reactions which occur at the twofold sites on metal surfaces. Following our interest in the reactivity and structure of such complexes (Manojlović-Muir, 1988; Manojlović-Muir, Muir, Davis, Mirza & Puddephatt, 1992), we have determined the crystal structure of the nickel dimer *trans,trans*-$[Ni_2(CN)_4(dmpm)_2]$, (I), dmpm = $Me_2PCH_2PMe_2$.



(I)

The dimer comprises two *trans*-$Ni(CN)_2$ fragments bridged by two mutually *trans* dmpm ligands to form a face-to-face structure (Fig. 1). This type of molecular structure has been found in numerous binuclear complexes in which the bridging ligand is dppm, $Ph_2PCH_2PPh_2$ (Puddephatt, 1983; Chaudret, Delavaux & Poilblanc, 1988) and also in *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$ (Manojlović-Muir, Ling & Puddephatt, 1986).

The molecular structure of the nickel dimer, characterized by the atomic parameters listed in Table 1, is exactly centrosymmetric. It contains an eight-membered dimetallacycle, $Ni_2P_4C_2$, which adopts an elongated chair conformation with the CH_2 groups displaced in opposite directions from the Ni_2P_4 plane. The NiP_2C_2 units eclipse each other, as is evident from the torsion angles C(2)—Ni—Ni′—C(1′) and P(1)—Ni—Ni′—P(2′) of −1.1 (2) and 0.9 (1)°, respectively. They are tilted with respect to the Ni_2P_4 plane [torsion angle C(1)—Ni—P(1)···P(2′) = 125.3 (1)°] to afford short intramolecular C(2)···Ni′ and C(2′)···Ni distances [2.901 (2) Å], which may indicate the presence of very weak Ni—CN semi-bridging interactions. The coordination geometry around each Ni atom is square planar. The intramolecular Ni···Ni separation [3.2085 (6) Å] is much longer than those [2.439 (1)–2.694 (1) Å] considered indicative of Ni—Ni σ-bonding (Manojlović-Muir, Muir, Davis, Mirza & Puddephatt, 1992).

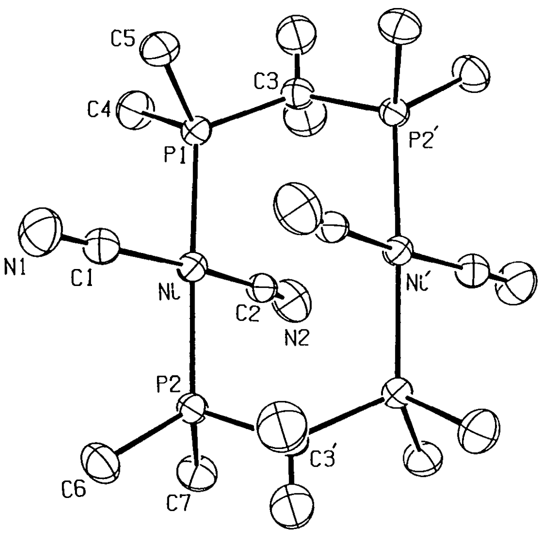


Fig. 1. The molecular structure of (I). All H atoms, except those attached to C(3) and C(3′), have been omitted for clarity. The midpoint of the Ni→Ni′ vector coincides with a crystallographic centre of symmetry. Atoms with primed labels are related to those in Table 1 by the symmetry operation −*x*, −*y*, −*z*. Displacement ellipsoids are shown at the 50% probability level.

The bite of the dmpm ligands, *i.e.* the intraligand P···P distance and the P—CH_2—P angle [3.142 (1) Å, 118.6 (2)°] are practically the same as those [3.140 (3) Å, 116.8 (6)°] in *trans,trans*-$[Pt_2I_2Me_2(\mu\text{-dmpm})_2]$. The metal–ligand bond lengths (Table 2) are in agreement with those previously observed in d^8-nickel complexes (Hope, Olmstead, Power & Viggiano, 1984; Bianchini, Masi, Meli & Sabat, 1986).

Experimental

The compound was prepared by reaction of $NiCl_2.6H_2O$ with dmpm and $NaBH_3CN$ in ethanolic solution; it was recrystallized from a CH_2Cl_2/acetone mixture (Mirza & Puddephatt, 1989).

Crystal data

$[Ni_2(CN)_4(C_5H_{14}P_2)_2]$
$M_r = 493.68$
Monoclinic
$P2_1/n$
$a = 9.148$ (2) Å
$b = 11.461$ (2) Å
$c = 10.220$ (2) Å
$\beta = 90.271$ (15)°
$V = 1071.5$ (4) Å^3
$Z = 2$
$D_x = 1.530$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 23 reflections
$\theta = 12$–17°
$\mu = 2.066$ mm^{-1}
$T = 296$ K
Prism
0.80 × 0.48 × 0.48 mm
Orange–red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.24$, $T_{max} = 0.35$
6433 measured reflections
3124 independent reflections

2166 observed reflections [$I \geq 3\sigma(I)$]
$R_{int} = 0.048$
$\theta_{max} = 30°$
$h = 0 \rightarrow 12$
$k = -16 \rightarrow 16$
$l = -14 \rightarrow 14$
2 standard reflections
frequency: 120 min
intensity decay: 2.9%

Refinement

Refinement on F
$R = 0.029$

$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

$wR = 0.033$
$S = 1.79$
2166 reflections
165 parameters
$w = 1/\sigma^2(|F_o|)$
$(\Delta/\sigma)_{\max} = 0.095$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni	0.16989 (3)	0.00730 (2)	0.03877 (3)	0.0234 (1)
P(1)	0.09649 (7)	0.08798 (5)	0.22127 (6)	0.0243 (2)
P(2)	0.23627 (7)	−0.07689 (5)	−0.14487 (6)	0.0232 (2)
N(1)	0.3709 (3)	0.2106 (2)	−0.0081 (3)	0.0468 (8)
N(2)	0.0258 (3)	−0.2143 (2)	0.1149 (3)	0.0497 (9)
C(1)	0.2938 (3)	0.1338 (2)	0.0077 (2)	0.0318 (8)
C(2)	0.0698 (3)	−0.1313 (2)	0.0854 (2)	0.0286 (7)
C(3)	−0.0926 (3)	0.0564 (2)	0.2671 (2)	0.0275 (7)
C(4)	0.1952 (4)	0.0359 (3)	0.3640 (3)	0.0430 (10)
C(5)	0.1115 (4)	0.2448 (2)	0.2310 (3)	0.0382 (9)
C(6)	0.3955 (3)	−0.0233 (3)	−0.2304 (3)	0.0371 (9)
C(7)	0.2725 (3)	−0.2321 (2)	−0.1398 (3)	0.0351 (9)

Table 2. *Selected geometric parameters* (Å, °)

Ni—P(1)	2.190 (1)	Ni—P(2)	2.198 (1)
Ni—C(1)	1.869 (3)	Ni—C(2)	1.896 (3)
P(1)—C(3)	1.830 (3)	P(1)—C(4)	1.813 (4)
P(1)—C(5)	1.806 (3)	P(2)—C(3′)	1.824 (3)
P(2)—C(6)	1.810 (3)	P(2)—C(7)	1.810 (3)
N(1)—C(1)	1.140 (4)	N(2)—C(2)	1.076 (4)
P(1)—Ni—P(2)	178.0 (1)	P(1)—Ni—C(1)	90.3 (1)
P(1)—Ni—C(2)	89.4 (1)	P(2)—Ni—C(1)	91.4 (1)
P(2)—Ni—C(2)	89.0 (1)	C(1)—Ni—C(2)	170.8 (2)
Ni—P(1)—C(3)	115.4 (1)	Ni—P(1)—C(4)	113.1 (2)
Ni—P(1)—C(5)	116.3 (2)	C(3)—P(1)—C(4)	101.4 (2)
C(3)—P(1)—C(5)	104.7 (2)	C(4)—P(1)—C(5)	104.2 (2)
Ni—P(2)—C(3′)	109.1 (1)	Ni—P(2)—C(6)	119.3 (2)
Ni—P(2)—C(7)	117.3 (1)	C(3′)—P(2)—C(6)	101.8 (2)
C(3′)—P(2)—C(7)	106.1 (2)	C(6)—P(2)—C(7)	101.5 (2)
Ni—C(1)—N(1)	178.2 (3)	Ni—C(2)—N(2)	173.1 (3)
P(1)—C(3)—P(2′)	118.6 (2)		

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. The non-H atoms were assigned anisotropic displacement parameters. H atoms were located in a low-angle $\Delta\rho$ map and their coordinates and isotropic displacement parameters were refined. All calculations were performed using the *GX* program package (Mallinson & Muir, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2-Acetylbicyclo[2.2.1]heptyl-C^3,O)(2,2′-bipyridyl)palladium(II) Trifluoromethanesulfonate 0.5-Diethyl Ether Solvate

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Abstract

The norbornyl moiety in the title compound, $[Pd(C_9H_{13}O)(C_{10}H_8N_2)]CF_3SO_3.0.5C_4H_{10}O$, is selectively *cis*, *exo* substituted on the 2 and 3 positions with the acetyl substituent bonded intramolecularly *via* its O atom to the palladium(II) centre.

Comment

The title compound (I) was prepared *via* norbornene insertion into the Pd—C(acetyl) bond. In most cases, such alkene-insertion products are unstable and readily undergo β-hydrogen elimination (Dekker, Elsevier, Vrieze, van Leeuwen & Roobeek, 1992). The structure determination was undertaken to establish the bonding of the 3-acetyl-2-norbornyl group and the stereochemistry of the insertion reaction.

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