Journal of Organometallic Chemistry, 347 (1988) 269–275
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Studies on binuclear complexes. Formation and molecular structure of $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$

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(Received June 8th, 1987; in revised from September 16th, 1987)

Abstract

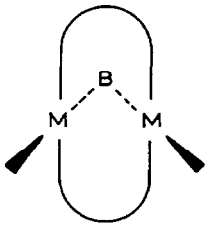
Under ambient conditions $(^1\eta\text{-dpm})_2NiCl_2$ was reduced by zinc powder in the presence of carbon monoxide to $(^1\eta\text{-dpm})_2Ni(CO)_2$ and $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$. The molecular structure of the latter complex was determined by X-ray crystallography. The complex crystallized in the monoclinic space group $C2/c$ with a 21.224(6), b 14.893(5), c 15.282(3) Å, β 100.43(2)°, $Z = 4$. The final values of $R = 0.075$ and $R_w = 0.081$ were obtained for 2082 independent reflections. The Ni–Ni distance is 2.694(1) Å. In this complex both nickel atoms have pseudotetrahedral configuration if the Ni–Ni bond is not taken into account. The molecular configuration is one of a W-frame with C_{2v} symmetry.

Introduction

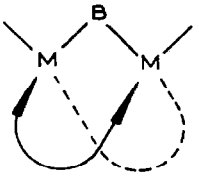
Binuclear complexes in which bis(diphenylphosphino)methane (dpm) holds two metal atoms have received considerable attention in recent years [1]. The A-frame structure containing dpm ligand forms readily in the presence of an apex ligand such as Cl, S, CO, PR_2 or others. Recently, Karsch pointed out [2] that the planar configuration of the metal atom in the A-frame changed to pseudotetrahedral when the oxidation number of the metal decreased and the complex then takes on a W-frame structure. By MO calculation the W-frame was shown to be a stable and

0022-328X/88/$03.50

quite a common structure although there are not very many examples as yet. Here we report the formation and the W-frame structure of $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$.



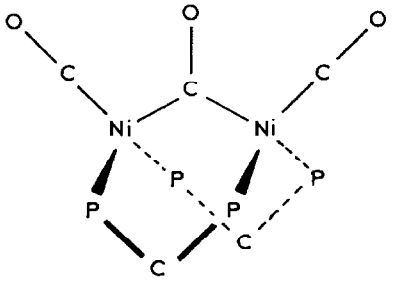
A-frame



W-frame

Results and discussion

Dpm is an $^1\eta$-coordinate ligand in $(dpm)_2NiCl_2$ [3]. Under ambient conditions $(dpm)_2NiCl_2$ was reduced by zinc powder in the presence of carbon monoxide. The major product $(^1\eta\text{-dpm})_2Ni(CO)_2$ was obtained along with a binuclear complex $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$ as a minor product. The binuclear complex is a stable yellow crystal under an inert atmosphere, but slowly turns dark in air. It is soluble in THF and CH_3OH. The possible pathway of formation of the binuclear complex



(I)

could even include the reduction-oxidative addition-reduction which we have described previously [4 *].

Description of molecular structure

The molecular structure of $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$(I) is shown in Fig. 1. Two nickel atoms and three carbonyls lie in one plane (Plane 1). Two nickel atoms with P(1), P(2) and P(1′), P(2′) lie in two other planes (Plane 2 and Plane 3, respectively). The dihedral angles are 105.6° between Plane 2 and 3 and 125.8° between Plane 1 and 2 (or 3). Plane 4 (P(1), C(100), P(2)) and Plane 5 (P(1), C(100), P(2)) are tilted towards each other and have a dihedral angles of 129.3° with Planes 2 and 3, respectively. The molecule possesses typical C_{2v} symmetry. The Ni–Ni distance is 2.694 Å. Both nickel atoms are of pseudotetrahedral configuration if the Ni–Ni bond is not taken into account. Bond angles of P(1)–Ni–C′, C′–Ni–C, C–Ni–P(1)

* Reference number with asterisk indicates a note in the list of references.

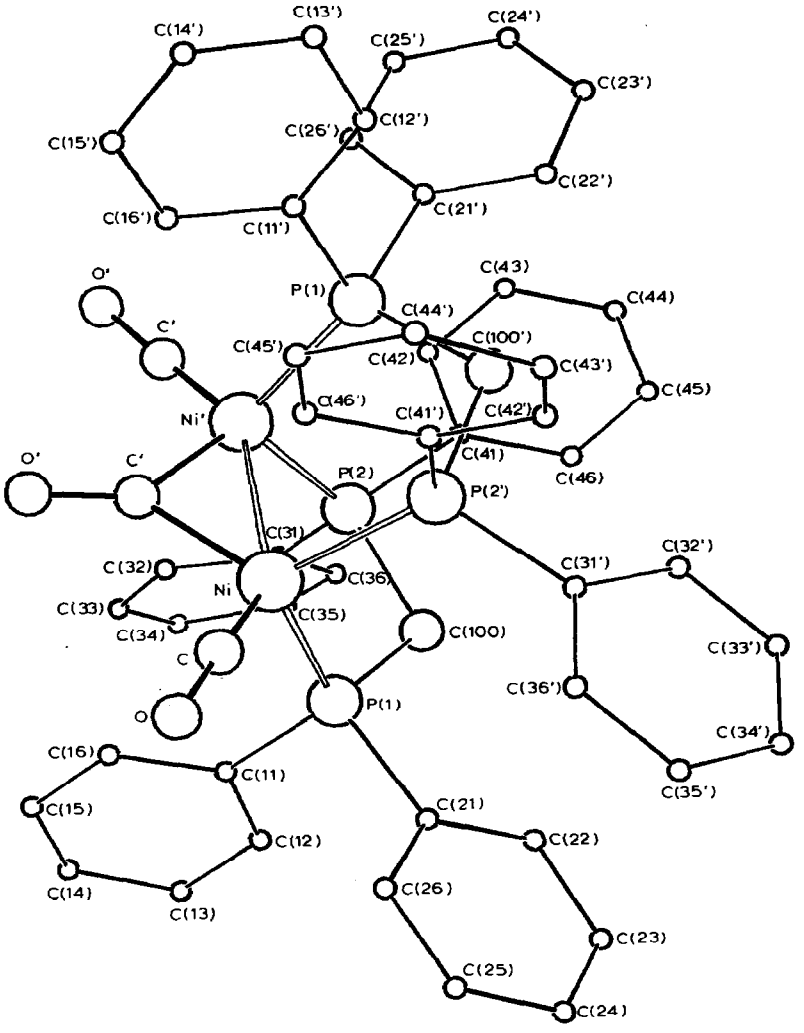


Fig. 1. The molecular structure of $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$.

and P(1)–Ni–P(2′) are 112.01°, 105.0°, 106.8° and 106.48°, respectively. In comparison with the known complex $Ni_2(\mu\text{-}(CF_3)_2PSP(CF_3)_2]_2(\mu\text{-CO})(CO)_2$ [5,6], the P–C–P angle (108.8°) of our complex is much larger than the P–S–P angle (95.7°). The same is true for the Ni–Ni distances (2.694 and 2.577 Å and the Ni–CO–Ni bond angles (89.8° and 81.0°). Also different are Ni–CO(terminal) distances (1.804 and 1.525 Å) and Ni–CO(bridging) distances (1.893 and 1.908 Å) and the vibration frequencies for carbonyls (1990, 1940, 1775 and 2088, 2075, 1994 cm^{-1}).

Experimental

Synthesis

The complex, $(dpm)_2NiCl_2$, was prepared by a published procedure [3]. Infrared spectra were recorded on a WFD-14 infrared spectrometer.

Table 1. X-ray diffraction data for $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$

Formula	$C_{53}H_{44}Ni_2O_3P_4$	d_{calcd} (g cm^{-3})	1.36
MW	969.4	Space group	Monoclinic; $C2/c$
a (Å)	21.224(6)	Scan mode	$\omega/2\theta$
b (Å)	14.843(5)	Radiation	Mo-K_α
c (Å)	15.282(3)	$2\theta_{max}$ (degree)	50
β (degree)	100.43(2)	No. of unique reflections	5046
V (Å^3)	4734.8	R	0.075
Z	4	R_w	0.081

An excess of zinc powder (2.0 g) was added to an absolute tetrahydrofuran (50 ml) solution of $(dpm)_2NiCl_2$ (2.5 g). Carbon monoxide was bubbled into the mixture for 6 h under ambient conditions with stirring. After filtration, the solvent was removed from the reaction mixture. Methanol was added and the extract was concentrated. Yellow crystals formed (0.2 g). M.p. 108 °C (dec.). Found: C, 65.54;

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms for $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$

Atom	x	y	z	B_{eq} (Å^2)
Ni	0.43953(7)	0.2044(1)	0.70405(9)	4.25(3)
P(1)	0.4015(1)	0.2745(2)	0.8105(2)	3.28(6)
P(2′)	0.4602(1)	0.3092(2)	0.6113(2)	3.35(6)
C(31)	0.4081(5)	0.4073(7)	0.5986(6)	3.2(2)
C(32)	0.4278(5)	0.4948(8)	0.6234(8)	4.5(3)
C(33)	0.03829(7)	0.5650(9)	0.6162(9)	6.2(4)
C(34)	0.3198(6)	0.5512(9)	0.5840(9)	5.9(9)
C(35)	0.2978(6)	0.4643(8)	0.5566(9)	6.1(3)
C(36)	0.3441(6)	0.393(1)	0.5637(9)	5.9(3)
C(21)	0.3835(5)	0.2067(8)	0.9042(7)	3.9(2)
C(22)	0.3922(6)	0.1131(8)	0.9022(8)	4.9(3)
C(23)	0.3782(6)	0.0619(8)	0.9729(8)	5.8(3)
C(24)	0.3571(6)	0.1013(9)	1.0434(8)	5.7(3)
C(25)	0.3442(7)	0.194(1)	1.0426(8)	6.7(3)
C(26)	0.3591(6)	0.2462(8)	0.9717(7)	5.3(3)
C(11)	0.3261(5)	0.3371(7)	0.7827(7)	4.0(2)
C(12)	0.2763(6)	0.292(1)	0.7380(9)	6.3(3)
C(13)	0.2171(6)	0.336(1)	0.714(1)	8.3(5)
C(14)	0.2084(6)	0.424(1)	0.737(1)	8.1(4)
C(15)	0.2590(6)	0.4702(9)	0.7845(9)	7.0(4)
C(16)	0.3210(6)	0.4287(8)	0.8095(8)	5.5(3)
C(41)	0.4552(5)	0.2753(8)	0.4953(7)	4.5(3)
C(42)	0.4450(7)	0.340(1)	0.4261(7)	6.6(4)
C(43)	0.4404(8)	0.314(1)	0.3393(9)	10.1(5)
C(44)	0.4481(6)	0.222(1)	0.3179(8)	9.9(5)
C(45)	0.4584(6)	0.159(1)	0.3855(9)	8.2(4)
C(46)	0.4592(5)	0.1835(9)	0.4757(7)	5.0(3)
C	0.3836(7)	0.154(1)	0.649(1)	9.9(5)
C	0.3352(5)	0.1128(8)	0.6011(9)	10.1(3)
C(100)	0.4591(5)	0.3601(7)	0.8647(8)	3.7(3)
C′	0.500	0.113(1)	0.750	5.9(5)
O′	0.500	0.0305(8)	0.750	8.6(4)

Table 3. Bond distances (Å) for $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$

Ni–Ni′	2.694(1)	C(22)–C(23)	1.396(6)
Ni–P(1)	2.204(1)	C(23)–C(24)	1.396(7)
Ni–P(2)	2.203(1)	C(24)–C(25)	1.404(7)
Ni–C	1.525(9)	C(25)–C(26)	1.413(6)
Ni–C′	1.908(6)	C(1)–C(12)	1.334(7)
P(1)–C(21)	1.847(4)	C(11)–C(16)	1.429(6)
P(1)–C(11)	1.833(4)	C(12)–C(13)	1.406(8)
P(1)–C(100)	1.851(4)	C(13)–C(14)	1.386(9)
P(2′)–C(31)	1.818(4)	C(14)–C(15)	1.441(7)
P(2′)–C(41)	1.827(5)	C(15)–C(16)	1.365(8)
P(2′)–C(100)	1.846(4)	C(41)–C(42)	1.414(7)
C(31)–C(32)	1.397(6)	C(41–C(46)	1.401(7)
C(31)–C(36)	1.382(6)	C(42)–C(43)	1.366(8)
C(32)–C(33)	1.403(7)	C(43)–C(44)	1.423(11)
C(33)–C(34)	1.356(7)	C(44)–C(45)	1.388(11)
C(34)–C(35)	1.410(8)	C(45)–C(46)	1.424(8)
C(35)–C(36)	1.433(7)	C–O	1.299(9)
C(21)–C(26)	1.367(6)	C′–O′	1.230(8)
C(21)–C(22)	1.403(6)		

Table 4. Bond angles (degree) for $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$

Ni′–Ni–P(1)	93.25(4)	C(31)–C(36)–C(35)	122.0(5)
Ni–Ni′–P(2)	93.06(4)	P(1)–C(21)–C(22)	118.5(3)
Ni′–Ni–C	149.5(3)	P(1)–C(21)–C(26)	120.7(4)
Ni′–Ni–C′	45.1(2)	C(22)–C(21)–C(26)	120.8(4)
P(1)–Ni–P(2′)	106.48(5)	C(21)–C(22)–C(23)	118.3(4)
P(1)–Ni–C	106.8(3)	C(22)–C(23)–C(24)	121.5(5)
P(1)–Ni–C′	112.01(7)	C(23)–C(24)–C(25)	120.2(5)
P(2′)–Ni–C	102.7(3)	C(24)–C(25)–C(26)	118.3(5)
P(2′)–Ni–C′	122.6(1)	C(21)–C(26)–C(25)	120.7(5)
C–Ni–C′	105.0(3)	P(1)–C(11)–C(12)	116.0(4)
Ni–P(1)–C(21)	118.0(2)	P(1)–C(11)–C(16)	121.6(4)
Ni–P(1)–C(11)	119.3(2)	C(12)–C(11)–C(16)	122.3(5)
Ni–P(1)–C(100)	110.7(2)	C(11)–C(12)–C(13)	119.2(6)
C(21)–P(1)–C(11)	99.3(2)	C(12)–C(13)–C(14)	121.9(6)
C(21)–P(1)–C(100)	103.9(2)	C(13)–C(14)–C(15)	118.8(6)
C(11)–P(1)–C(100)	103.5(2)	C(14)–C(15)–C(16)	121.4(6)
Ni–P(2′)–C(31)	116.5(1)	C(11)–C(16)–C(15)	116.4(5)
Ni–P(2′)–C(41)	116.5(2)	P(2′)–C(41)–C(42)	120.8(4)
Ni–P(2′)–C(100′)	116.5(2)	P(2′)–C(41)–C(46)	118.7(4)
C(31)–P(2′)–C(41)	100.9(2)	C(42)–C(41)–C(46)	120.4(5)
C(31)–P(2′)–C(00′)	102.6(2)	C(41)–C(42)–C(43)	120.9(7)
C(41)–P(2′)–C(100′)	101.3(2)	C(42)–C(43)–C(44)	119.8(8)
P(2′)–C(31)–C(32)	124.7(3)	C(43)–C(44)–C(45)	119.5(7)
P(2′)–C(31)–C(36)	117.2(4)	C(44)–C(45)–C(46)	121.1(7)
C(320–C(31)–C(36)	118.1(4)	C(41)–C(46)–C(45)	118.0(6)
C(31)–C(32)–C(33)	120.2(5)	Ni–C–O	178.3(7)
C(32)–C(33)–C(34)	121.9(6)	P(1)–C(100)–P(2)	108.8(2)
C(33)–C(34)–C(35)	119.9(5)	Ni–C′–Ni′	89.8(3)
C(34)–C(35)–C(36)	117.8(5)	Ni–C′–O′	135.1(2)

Table 5

The important least-squares planes and dihedral angles (degree) between the planes for $Ni_2(\mu\text{-dpm})_2(\mu\text{-CO})(CO)_2$

No. of Plane	Atom in the Plane					Dihedral Angle	2	3	4	5
1	Ni	Ni′	C′	C	C″	1	125.8	104.8	125.8	104.8
2	Ni	Ni′	P(2)	P(1)		2		129.3	105.6	26.5
3	P(2)	P(1)	C(100)			3			26.5	32.9
4	Ni	Ni′	P(1′)	P(2′)		4				129.3
5	P(1′)	P(2′)	C(100′)							

H, 4.57. $C_{53}H_{44}Ni_2O_3P_4$ calcd.: C, 65.61; H, 4.54%. IR (ν(CO), KBr disc): 1990, 1940 and 1775 cm^{-1}.

After the extraction the residue was dissolved in tetrahydrofuran, then methanol was added. White crystals formed (1.0 g). M.p. 128°C (Dec.). Found: C, 70.09; H, 5.50. $C_{52}H_{44}NiO_2P_4$ calcd.: C, 70.69; H, 4.98%. IR (μ(CO), KBr disc): 1991, 1926 cm^{-1}.

X-ray diffraction study

A crystal of approximate dimensions $0.2 \times 0.2 \times 0.3$ mm was mounted on a glass fiber. Data collection was performed on an Enraf–Nonius CAD-4 diffractometer with graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). A total of 5046 unique reflections was collected in the range of $2° < \theta < 25°$ using $\omega/2\theta$ scan mode, and 2082 reflections with $I > 3\sigma(I)$ were considered observed. LP and absorption corrections were applied to the data. The cell parameters and the conditions of data collection are listed in Table 1.

The structure was solved by direct method (MULTAN 82). The nickel atom in the asymmetric unit was found from an E-map. The coordinates of non-hydrogen atoms were obtained by several difference-Fourier synthesis. The equivalent isotropic thermal parameters and coordinates of non-hydrogen atoms were refined by full matrix least-squares method. The final R and R_w are 0.075 and 0.081, respectively. The maximum residual electron density peak on the final difference Fourier map is 0.72 e/Å^3.

All calculations were carried out by PDP 11/44 computer with the SDP-PLUS program system.

Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 2. The bond distances and bond angles are given in Table 3 and 4, respectively. The important least-squares planes and dihedral angles between the planes are given in Table 5.

Acknowledgement

The authors thank the National Foundation of Natural Sciences for financial support.

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