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Structure of Dichlorobis{bis(diphenylphosphino)methane}nickel(II)

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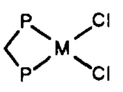
Nickel, palladium and platinum all form square planar complexes with $Ph_2PCH_2PPh_2$ (dppm) of stoichiometry $[MCl_2(dppm)]$, **1**, and $[M(dppm)_2]^{2+}$.[2-5] However, while the palladium and platinum complexes of formula $MCl_2(dppm)_2$ are formulated as ionic complexes with chelate dppm ligands $[M(dppm)_2]Cl_2$, **2**, the nickel complex has been formulated as the nonionic complex with monodentate dppm ligands *cis*-$[NiCl_2(dppm\text{-}P)_2]$, **3**.[6-8] The cationic $[Ni(dppm)_2]^{2+}$ and $[NiCl(dppm)_2]^+$, **4**, which is thought to have a square pyramidal stereochemistry at nickel, are only formed to a significant extent with noncoordinating anions such as perchlorate and tetraphenylborate.[5,9] Earlier, it had been thought that dppm would not chelate to nickel because of the ring strain in the resultant 4-membered ring.[6,7] The structures of complexes **1**–**4** were proposed on the basis of analytical data, magnetic properties, and IR and UV–visible spectroscopies.



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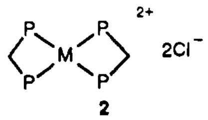

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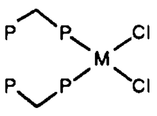

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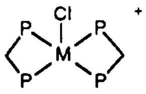

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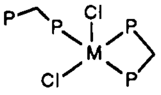

5

More recently, $[NiCl_2(dppm)_2]$ has been found very useful as a reagent for synthesis of homonuclear and heteronuclear dppm-bridged complexes containing nickel, as a catalyst precursor for the stereospecific cross-coupling of alkenyl halides and alkenyl Grignard reagents to give dienes or of alkyl halides with Grignard reagents in the presence of CO to give ketones, and also as a catalyst for the coupling of ethylene and butadiene to give 1,4,9-decatriene.[10-13]

While using $[NiCl_2(dppm)_2]$ as a precursor to dinickel complexes,[14] it was noted that recrystallization led to partial dissociation of dppm with formation of a mixture of large crystals of $[NiCl_2(dppm)]$, which are red-brown in color, and of $[NiCl_2(dppm)_2]$, which are black. Since both complexes had been formulated with square planar *cis*-$NiCl_2P_2$ chromophores, the great difference in appearance was surprising. The structure was therefore reinvestigated and found to be **5**, in which nickel has the unexpected coordination number of 5 and in which there are both monodentate and chelate dppm ligands. The earlier formulation as structure **3**,[6,7] which has not been questioned in later papers,[2c] is therefore incorrect.

Results

The diffuse reflectance spectrum of $[NiCl_2(dppm)]$ gave a single band at 19 800 cm^{-1} and that of $[NiCl_2(dppm)_2]$ gave two bands at 20 100 and 13 500 cm^{-1}. Clearly the extra ligand field band for $[NiCl_2(dppm)_2]$ at low energy (13 500 cm^{-1}) is responsible for its darker color in the solid state. Both $[NiCl_2(dppm)]$ and $[NiCl_2(dppm)_2]$ gave orange-red solutions in dichloromethane and the UV–visible spectra as $(1-2) \times 10^{-4}$ M solutions were essentially identical, both containing a ligand field band at 21 200 cm^{-1} ($\epsilon = 2.3 \times 10^3$ L mol^{-1} cm^{-1}), and two other bands at 29 600 cm^{-1} (shoulder) and 33 300 cm^{-1}. Addition of excess dppm to either solution caused a shift of the band to 21 100 cm^{-1}, but no new band appeared. This suggests that $[NiCl_2(dppm)_2]$ in dilute solution is essentially completely dissociated to $[NiCl_2(dppm)]$ and free dppm, and since there is no band at 13 500 cm^{-1}, the spectra clearly show that the solid-state structure of $[NiCl_2(dppm)_2]$ is not retained in dilute solution. The ^{31}P NMR spectrum of $[NiCl_2(dppm)]$ in CD_2Cl_2 solution at room temperature contained a broad singlet at $\delta = -51.0$ ppm (width at half-height 30 Hz) and at -90 °C this sharpened but the chemical shift was not significantly changed ($\delta = -50.4$ ppm, width at half-height 2 Hz). At room temperature $[NiCl_2(dppm)_2]$ failed to give a ^{31}P NMR resonance but, at -90 °C, a sharp singlet at -39.7 ppm was observed. When both $[NiCl_2(dppm)]$ and $[NiCl_2(dppm)_2]$ were present, two sharp resonances at -50.4 and -39.7 ppm were observed at -90 °C, thus showing that no exchange between the complexes was occurring at this temperature. The ^1H NMR spectrum of $[NiCl_2(dppm)]$ contained a broad resonance at $\delta = 3.62$ ppm due to the CH_2 protons of dppm at both room temperature and at -90 °C. The CH_2 protons of dppm in $[NiCl_2(dppm)_2]$ gave two broad resonances at $\delta = 4.20$ and 4.45 ppm, with partially resolved coupling, $J(HH) =$ ca. 15 Hz, at -90 °C but only an extremely broad peak at $\delta =$ ca. 4 ppm at room temperature. The phenyl ^1H resonances are also temperature dependent. At room temperature there are three resolved resonances at $\delta = 7.26$ (para) and 7.50 and 7.58 ppm (ortho and meta), but at -90 °C there are at least four resonances between 6.78 and 7.40 ppm. The average chemical shift changes from 7.5 ppm at room temperature to 7.2 ppm at -90 °C. These data were difficult to reconcile with the proposed structure **3**.

Because of the difficulty of structure determination in solution, the solid-state structure of $[NiCl_2(dppm)_2]$ was determined by an X-ray crystallographic study of its solvate **5**·C_6H_5Me and it led to formulation of the complex as $[NiCl_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$, **5**. In the crystal structure, molecules of the nickel complex are separated from those of the solvent molecules by normal van der Waals distances.

The molecular structure of **5** is shown in Figure 1 and is characterized by bond lengths and angles listed in Table I. The coordination geometry around the nickel atom is intermediate between trigonal bipyramidal [with P(2) and P(3) atoms at the axial sites] and square pyramidal [with a Cl(2) atom at the axial

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(1) (a) University of Glasgow. (b) University of Western Ontario.

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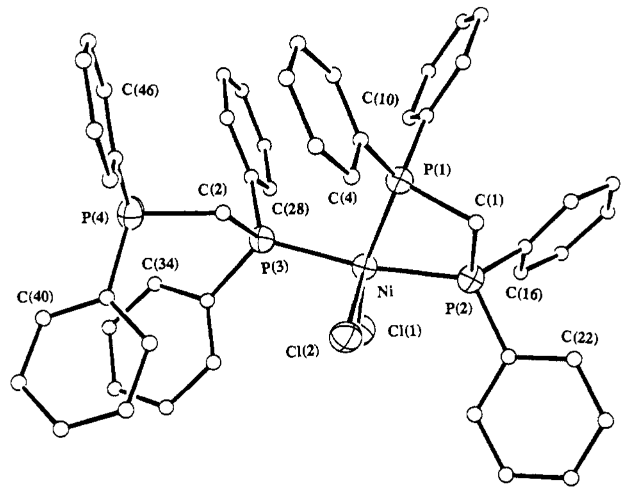

Figure 1. View of the molecular structure of [$NiCl_2(\eta^1$-dppm)(η^2-dppm)]. The carbon atoms are shown as spheres of arbitrary size, and the displacement ellipsoids for Ni, Cl and P atoms display 50% probability. In the phenyl rings, carbon atoms are numbered cyclically, C(*n*), C(*n* + 1), ..., C(*n* + 5), the C(*n*) atom being bound to phosphorus. In this drawing only the C(*n* + 1) atoms are labeled, for clarity.

Table I. Selected Interatomic Distances and Angles for [$NiCl_2$(dppm)$_2$]·C_6H_5Me

	Bond Lengths (Å)		
Ni–Cl(1)	2.228 (2)	Ni–Cl(2)	2.527 (2)
Ni–P(1)	2.192 (2)	Ni–P(2)	2.210 (2)
Ni–P(3)	2.218 (2)	P(1)–C(1)	1.834 (6)
P(1)–C(3)	1.803 (6)	P(1)–C(9)	1.813 (6)
P(2)–C(1)	1.834 (6)	P(2)–C(15)	1.820 (6)
P(2)–C(21)	1.818 (6)	P(3)–C(2)	1.824 (6)
P(3)–C(27)	1.815 (6)	P(3)–C(33)	1.821 (6)
P(4)–C(2)	1.854 (6)	P(4)–C(39)	1.843 (6)
P(4)–C(45)	1.831 (6)		
	Bond Angles (deg)		
Cl(1)–Ni–Cl(2)	107.2 (1)	Cl(1)–Ni–P(1)	156.1 (1)
Cl(1)–Ni–P(2)	94.8 (1)	Cl(1)–Ni–P(3)	92.9 (1)
Cl(2)–Ni–P(1)	93.5 (1)	Cl(2)–Ni–P(2)	88.9 (1)
Cl(2)–Ni–P(3)	93.2 (1)	P(1)–Ni–P(2)	73.3 (1)
P(1)–Ni–P(3)	97.9 (1)	P(2)–Ni–P(3)	171.1 (1)
Ni–P(1)–C(1)	93.1 (2)	Ni–P(1)–C(3)	127.0 (2)
Ni–P(1)–C(9)	114.2 (2)	C(1)–P(1)–C(3)	107.6 (3)
C(1)–P(1)–C(9)	106.3 (3)	C(3)–P(1)–C(9)	105.9 (3)
Ni–P(2)–C(1)	92.5 (2)	Ni–P(2)–C(15)	121.9 (2)
Ni–P(2)–C(21)	122.4 (2)	C(1)–P(2)–C(15)	106.3 (3)
C(1)–P(2)–C(21)	110.2 (3)	C(15)–P(2)–C(21)	101.9 (3)
Ni–P(3)–C(2)	112.9 (2)	Ni–P(3)–C(27)	113.1 (2)
Ni–P(3)–C(33)	117.2 (2)	C(2)–P(3)–C(27)	106.9 (3)
C(2)–P(3)–C(33)	102.2 (3)	C(27)–P(3)–C(33)	103.3 (3)
C(2)–P(4)–C(39)	104.4 (3)	C(2)–P(4)–C(45)	98.8 (3)
C(39)–P(4)–C(45)	102.4 (3)	P(1)–C(1)–P(2)	91.5 (3)
P(3)–C(2)–P(4)	117.1 (3)	P(1)–C(3)–C(4)	119.4 (4)
P(1)–C(3)–C(8)	122.2 (5)	P(1)–C(9)–C(10)	120.2 (4)
P(1)–C(9)–C(14)	120.3 (5)	P(2)–C(15)–C(16)	117.5 (5)
P(2)–C(15)–C(20)	122.3 (5)	P(2)–C(21)–C(22)	119.3 (5)
P(2)–C(21)–C(26)	121.0 (5)	P(3)–C(27)–C(28)	117.6 (5)
P(3)–C(27)–C(32)	123.9 (5)	P(3)–C(33)–C(34)	120.3 (4)
P(3)–C(33)–C(38)	119.9 (5)	P(4)–C(39)–C(40)	116.7 (5)
P(4)–C(39)–C(44)	125.2 (5)	P(4)–C(45)–C(46)	116.9 (5)
P(4)–C(45)–C(50)	125.7 (5)		

site]. The Ni–P and Ni–Cl(1) bond lengths are as expected; the Ni–P(2) and Ni–P(3) bonds are longer than Ni–P(1) due to the higher trans influence of the phosphine ligands compared to chloride. The Ni–Cl(2) bond [2.527 (2) Å] is ca. 0.30 Å longer than the Ni–Cl(1) bond. In the low-spin, square pyramidal nickel(II) complex [$NiCl(CH_2\{P(Ph)CH_2CH_2NH_2\}_2)]^+$ an even longer Ni–Cl bond [2.669 (7) Å] has been observed and its elongation has been ascribed to electronic effects.[15] A detailed inspection of the nonbonding intramolecular distances in **5**, however, suggests that steric effects may also be a factor in lengthening of the Ni–Cl(2) bond.

Table II. Crystallographic Data for [$NiCl_2(\eta^1$-dppm)(η^2-dppm)]·C_6H_5Me

formula	$C_{50}H_{44}Cl_2NiP_4 \cdot C_7H_8$	fw	990.53
a (Å)	10.851 (1)	space group	$P2_1/n$ (No. 14)
b (Å)	32.257 (3)	*T* (°C)	23
c (Å)	14.447 (1)	λ (Å)	0.71069
β (°)	96.248 (9)	ρ_{calc} (g cm^{-3})	1.309
V (Å^3)	5026.7 (8)	μ(Mo Kα) (cm^{-1})	6.55
Z	4	*R*	0.045
		R_w	0.058

^{a} $R = \sum||F_o| - |F_c||/|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$.

In the four-membered $NiP_2C(1)$ chelate ring the methylene carbon atom is displaced from the NiP_2 plane by 0.672 (5) Å, to afford the C(1)· ·Ni separation of 2.934 (6) Å. All internal ring angles (Table I) are about 16° less than the ideal values for unconstrained P–Ni–P (90°), Ni–P–C, and P–C–P (ca. 109°) angles. Similar severe angular distortions have also been observed in other dppm chelates such as square planar [$PdCl_2$(dppm)],[2b] [$PtPh_2$(dppm)],[16] and [$Au(C_6F_5)_2$(dppm)]$^+$,[17] five-coordinate [$Fe(CO)_3$(dppm)],[18] and octahedral [$Mo(CO)_4$(dppm)][19] and [RhHCl(dppm)$_2$]$^+$ complexes.[20]

Discussion

The molecular structure of **5** reflects the stereochemical flexibility of the dppm ligands arising, in particular, from their ability to distort substantially the bond angles subtended at phosphorus and the methylene carbon atoms and to adopt different conformations about the P–CH_2 bonds. This flexibility, demonstrated in the present structure by the very different bond angles and conformations associated with the η^1- and η^2-dppm ligands, makes dppm a highly versatile ligand, capable of coordinating the metal atoms in η^1-terminal, η^2-chelate, and η^2-bridging modes and thus efficiently stabilizing mononuclear, binuclear, and cluster complexes.[21]

The NMR data for solutions of [$NiCl_2$(dppm)$_2$] are not consistent with a static structure **5**, as determined in the solid state. Thus, in **5** all phosphorus atoms are nonequivalent, but only one resonance, with a chemical shift consistent with chelating dppm, is observed in the ^{31}P NMR spectrum of [$NiCl_2$(dppm)$_2$] at –90 °C. It is, of course, possible that the molecule is fluxional even at –90 °C such that all phosphorus atoms become effectively equivalent, but we note that the ^1H NMR spectrum at –90 °C contains two resonances for the CH_2P_2 protons. Any form of fluxionality which leads to equivalence of all phosphorus atoms is expected to lead to equivalence of the CH_2P_2 protons also. Rapid reversible dissociation of dppm to give [$NiCl_2$(dppm)] at –90 °C is also shown not to occur, since separate resonances are observed when mixtures of the two complexes are present. Dissociation of dppm from [$NiCl_2$(dppm)$_2$] is negligible at low temperature at the concentrations used for NMR, since no signal due to [$NiCl_2$(dppm)] is observed in solutions of [$NiCl_2$(dppm)$_2$] under these conditions. The static structure **4** is consistent with the NMR data at –90 °C, since in this structure all ^{31}P atoms are equivalent but the CH_2P_2 protons are not. The cause of the loss of the ^{31}P signal in the ^{31}P NMR and the extreme broadening of the CH_2P_2 signal in the ^1H NMR at room temperature is not clear.

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Table III. Atomic Fractional Coordinates and Displacement Parameters (Å^2)

	x	y	z	U
Ni	0.11239 (6)	0.14650 (2)	0.15547 (5)	0.031
Cl(1)	0.02768 (13)	0.19809 (5)	0.22921 (11)	0.049
Cl(2)	−0.06329 (11)	0.10524 (4)	0.07115 (10)	0.041
P(1)	0.25377 (12)	0.11597 (4)	0.08203 (10)	0.033
P(2)	0.12539 (12)	0.18213 (5)	0.02626 (10)	0.036
P(3)	0.12554 (12)	0.10562 (5)	0.27961 (10)	0.033
P(4)	0.08366 (13)	0.01383 (5)	0.34075 (10)	0.039
C(1)	0.1938 (5)	0.1383 (2)	−0.0308 (4)	0.038
C(2)	0.1223 (5)	0.0507 (2)	0.2497 (4)	0.038
C(3)	0.2728 (5)	0.0610 (2)	0.0654 (4)	0.035
C(4)	0.1767 (5)	0.0384 (2)	0.0165 (4)	0.047
C(5)	0.1863 (6)	−0.0038 (2)	0.0079 (5)	0.059
C(6)	0.2890 (6)	−0.0252 (2)	0.0491 (5)	0.067
C(7)	0.3844 (6)	−0.0030 (2)	0.0967 (5)	0.067
C(8)	0.3756 (5)	0.0395 (2)	0.1064 (4)	0.052
C(9)	0.4088 (4)	0.1367 (2)	0.1095 (4)	0.040
C(10)	0.4357 (5)	0.1611 (2)	0.1856 (4)	0.049
C(11)	0.5551 (6)	0.1765 (2)	0.2075 (5)	0.066
C(12)	0.6461 (5)	0.1668 (2)	0.1525 (6)	0.073
C(13)	0.6213 (5)	0.1415 (2)	0.0770 (6)	0.077
C(14)	0.5028 (5)	0.1264 (2)	0.0544 (5)	0.057
C(15)	0.2328 (5)	0.2253 (2)	0.0217 (4)	0.046
C(16)	0.2132 (6)	0.2595 (2)	0.0734 (5)	0.069
C(17)	0.2881 (8)	0.2947 (2)	0.0671 (6)	0.094
C(18)	0.3778 (7)	0.2947 (2)	0.0064 (7)	0.102
C(19)	0.3995 (7)	0.2600 (3)	−0.0420 (8)	0.112
C(20)	0.3265 (6)	0.2250 (2)	−0.0356 (6)	0.085
C(21)	−0.0108 (5)	0.2010 (2)	−0.0458 (4)	0.039
C(22)	−0.0005 (6)	0.2125 (2)	−0.1374 (5)	0.067
C(23)	−0.1020 (6)	0.2279 (2)	−0.1918 (5)	0.074
C(24)	−0.2120 (6)	0.2320 (2)	−0.1571 (5)	0.077
C(25)	−0.2241 (6)	0.2203 (3)	−0.0675 (5)	0.077
C(26)	−0.1227 (5)	0.2045 (2)	−0.0110 (4)	0.057
C(27)	0.2651 (4)	0.1142 (2)	0.3584 (4)	0.040
C(28)	0.2828 (5)	0.1532 (2)	0.3971 (4)	0.056
C(29)	0.3880 (6)	0.1624 (2)	0.4571 (5)	0.075
C(30)	0.4771 (6)	0.1332 (3)	0.4760 (5)	0.083
C(31)	0.4622 (5)	0.0947 (2)	0.4369 (6)	0.078
C(32)	0.3563 (5)	0.0849 (2)	0.3783 (5)	0.059
C(33)	0.0023 (4)	0.1095 (2)	0.3552 (4)	0.035
C(34)	0.0262 (5)	0.1004 (2)	0.4501 (4)	0.041
C(35)	−0.0715 (5)	0.0964 (2)	0.5044 (4)	0.049
C(36)	−0.1912 (5)	0.1017 (2)	0.4643 (4)	0.053
C(37)	−0.2143 (5)	0.1116 (2)	0.3720 (5)	0.064
C(38)	−0.1172 (5)	0.1155 (2)	0.3175 (4)	0.049
C(39)	−0.0862 (5)	0.0083 (2)	0.3205 (4)	0.043
C(40)	−0.1436 (5)	−0.0074 (2)	0.3917 (4)	0.055
C(41)	−0.2712 (6)	−0.0123 (3)	0.3844 (5)	0.076
C(42)	−0.3424 (6)	0.0001 (3)	0.3049 (5)	0.088
C(43)	−0.2882 (6)	0.0163 (3)	0.2335 (5)	0.083
C(44)	−0.1595 (5)	0.0204 (2)	0.2400 (5)	0.067
C(45)	0.1377 (5)	−0.0341 (2)	0.2905 (4)	0.041
C(46)	0.2554 (6)	−0.0474 (2)	0.3228 (4)	0.058
C(47)	0.3031 (6)	−0.0838 (2)	0.2919 (5)	0.078
C(48)	0.2335 (7)	−0.1080 (2)	0.2263 (5)	0.084
C(49)	0.1189 (7)	−0.0946 (3)	0.1947 (6)	0.092
C(50)	0.0701 (6)	−0.0585 (2)	0.2264 (5)	0.067
CS(1)	0.2953 (11)	0.1929 (4)	0.6977 (9)	0.176 (5)
CS(2)	0.4020 (10)	0.1858 (4)	0.7374 (9)	0.161 (5)
CS(3)	0.4522 (13)	0.1528 (5)	0.7820 (10)	0.196 (6)
CS(4)	0.3731 (11)	0.1132 (4)	0.7716 (9)	0.173 (5)
CS(5)	0.2503 (11)	0.1202 (4)	0.7187 (9)	0.172 (5)
CS(6)	0.1964 (12)	0.1534 (5)	0.6860 (10)	0.182 (5)
CS(7)	0.1956 (13)	0.2111 (5)	0.6542 (11)	0.210 (6)

[a] For the solvent atoms, C(S1) to C(S7), U is the isotropic displacement parameter and for other atoms, $U = 1/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*(\vec{a}_i\cdot\vec{a}_j)$.

In summary, this work has given a definitive solution to the structure of [$NiCl_2$(dppm)$_2$] in the solid state, but the structure in solution is still to be settled. In the concentrated solutions required for NMR, the structure is clearly not either **3** or **5**, but is perhaps **4**$^+$Cl$^-$. In dilute solution, as required for studies of the UV–visible spectra, it is likely that dissociation of dppm to give [$NiCl_2$(dppm)] occurs to a major extent. The chemistry is much more complex than was previously thought.

Experimental Section

The complex [$NiCl_2$(dppm)$_2$] was prepared by the literature method,[6] by mixing solutions of $NiCl_2\cdot 6H_2O$ in ethanol with dppm in toluene. The volume of solvent was reduced, CH_2Cl_2 was added to redissolve some precipitate, and the mixture was layered with pentane. A mixture of red-brown crystals of [$NiCl_2$(dppm)] (Anal. Calcd for $C_{25}H_{22}Cl_2NiP_2$: C, 59.4; H, 4.0. Found: C, 58.35; H, 4.3) and black crystals of $NiCl_2$(dppm)$_2$·toluene (Anal. Calcd for $C_{50}H_{44}Cl_2NiP_4$·toluene: C, 69.05; H, 5.25. Found: C, 68.1; H, 5.25) was obtained. These were separated by hand picking large crystals, and the pure compounds were used for characterization purposes. Both complexes were diamagnetic in the solid state (Gouy method) at room temperature.

X-ray Structure Analysis of [$NiCl_2(\eta^1$-dppm)(η^2-dppm)]·C_6H_5Me, 5·C_6H_5Me. The diffraction measurements were made on black crystals of **5**·C_6H_5Me by using graphite monochromated radiation and an Enraf-Nonius CAD4 diffractometer.

The unit cell dimensions (Table II) were determined by a least squares treatment of the setting angles for 23 reflections with $12 \le \Theta \le 17°$. An investigation of the diffraction pattern revealed a primitive crystal lattice and the $2/m$ Laue symmetry. Systematic absences of reflections established the $P2_1/n$ (No. 14) space group symmetry.

Intensities of reflections were measured by continuous $\Theta/2\Theta$ scans of $(0.80 + 0.35 \tan\Theta)°$ in Θ. The scan speeds were adjusted to give $\sigma(I)/I \le 0.03$, subject to a time limit of 90 s. Two strong reflections were measured every 2 h, but their intensities showed only random fluctuations not exceeding 3.5% of the mean values. The integrated intensities (q = 0.03)[22] of 9192 reflections measured were corrected for Lorentz, polarization, and absorption effects. The last correction was made by the empirical method of Walker and Stuart.[23] The intensities of 726 symmetry-related reflections were averaged to give 363 independent ones and R(internal) of 0.037. Of 8829 unique reflections measured, only 4648, which had $I \ge 3\sigma(I)$, were used in the structure analysis.

The crystal structure was solved by the heavy atom method. The position of the Ni atom was obtained from a Patterson function, and those of the remaining non-hydrogen atoms were obtained from the appropriate difference electron density maps. The hydrogen atoms, except those in the solvent molecule, were included in the structural model in calculated positions (C–H = 1.0 Å) and allowed to ride on the carbon atoms to which they are bonded; only their individual isotropic displacement parameters were refined. All non-hydrogen atoms of the nickel complex were assigned anisotropic displacement parameters, and the carbon atoms of the solvent molecule, isotropic displacement parameters. The structure was refined by block-diagonal least-squares techniques. The final atomic coordinates and displacement parameters are shown in Table III.

All calculations were carried out by using the GX program package.[24] Neutral atom scattering factors were taken from ref 25.

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Supplementary Material Available: Tables giving atomic coordinates and isotropic displacement parameters, including hydrogen atom locations, anisotropic displacement parameters, bond lengths, and bond angles (8 pages). Ordering information is given on any current masthead page.

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