The First Low-Spin Nickel Complex with Two Coordinated Water Molecules, [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ − Synthesis and Structural Characterization

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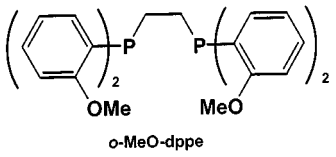
A series of nickel complexes of the didentate ligand 1,3-bis[di(*o*-methoxyphenyl)phosphanyl]propane (*o*-MeO-dppp) has been synthesized and characterized. The first low-spin nickel complex containing two coordinated water molecules, [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ (**1**), and compounds of the general formula [Ni(*o*-MeO-dppp)X_2] [X = Cl, Br, I, or trifluoroacetate (TFA)] are reported. Complex **1** has been characterized by X-ray crystallography. The nickel ion resides in a square-planar coordination environment with two phosphorus donors and two water molecules in a *cis* configuration (Ni–P distance 2.19 Å; Ni–O distance 1.97 Å). The structure of this complex and its behavior in solution are quite different from those of the complexes [Ni(*o*-MeO-dppp)X_2]. The halide complexes [Ni(*o*-MeO-dppp)Cl_2] (**2**) and [Ni(*o*-MeO-dppp)Br_2] (**3**) are seemingly mutually isostructural. In these complexes, the nickel ion also resides in a square-planar geometry, but with a significant tetrahedral distortion. The two different types of mono(*o*-MeO-dppp)nickel(II) complexes, i.e. [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ (**1**) and [Ni(*o*-MeO-dppp)X_2] [X = Cl (**2**), Br (**3**), I, or trifluoroacetate (TFA)] have been analyzed by electronic absorption and NMR spectroscopy. The differences in the crystal structures of **1** and **2** are helpful in rationalizing the fluxional behavior of these complexes, as has been studied by NMR spectroscopy.

Introduction

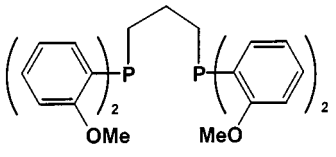
Recently, it was reported that selected diphosphanenickel(II) complexes are active catalysts in the homogeneous hydrogenation of 1-octene to *n*-octane.[1] In subsequent studies, it was observed that the catalytic hydrogenation activity of the nickel(II) catalyst incorporating the didentate phosphane ligand 1,3-bis[di(*o*-methoxyphenyl)-phosphanyl]propane (*o*-MeO-dppp) is much higher than that of a catalyst incorporating the ligand 1,2-bis[di-(*o*-methoxyphenyl)phosphanyl]ethane (*o*-MeO-dppe) (see Scheme 1).[2,3]

The presence of *ortho*-methoxy groups on the phenyl rings creates so-called hemi-labile ligands.[4] The enhanced enantioselectivities of hydrogenation catalysts bearing such methoxy groups have been attributed to possible metal−oxygen interactions.[5]

A systematic study was undertaken to investigate the nature of species in solution for both the *o*-MeO-dppe and *o*-MeO-dppp ligands, in order to obtain a better insight into the origin of the observed difference in catalytic activity. It appeared that the catalyst formed with the ligand *o*-MeO-dppe is involved in the auto-ionization equilibrium depicted in Scheme 2.[6]

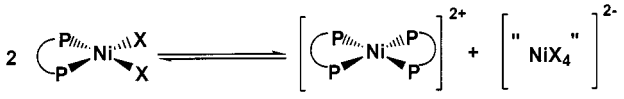


o-MeO-dppe



o-MeO-dppp

Scheme 1



Scheme 2

No bis(chelate) complexes of the unsubstituted ligand 1,3-bis(diphenylphosphanyl)propane (dppp) have hitherto been reported. The presence of the two bulky phenyl groups on each phosphorus atom in the C_3-bridged ligand presumably prevents the formation of the $[Ni(dppp)_2]^{2+}$ complex, which makes the possible auto-ionization reaction of *o*-MeO-dppp-containing nickel complexes doubtful. However, the formation of $[Ni(dppp)_2]^{n+}$ species in electrochemical experiments has been proposed.[7,8] In fact, bis(chelate) complexes have been observed with C_3-bridged ligands bearing smaller methyl groups on the phosphorus atoms[9] or with just one aryl group per phosphorus atom.[10] In the

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former case, the bite angle of the C_3-bridged ligand forces the nickel(II) center to adopt a tetrahedral geometry.

In this paper, the synthesis of nickel complexes with the propylene-bridged, sterically crowded ligand *o*-MeO-dppp is described, and the results of NMR investigations are reported.

Results and Discussion

Syntheses

The unique complex [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ (**1**) was obtained in analytically pure form from a mixture of nickel acetate, the ligand *o*-MeO-dppp, and ammonium hexafluorophosphate. This complex represents the first low-spin nickel complex with coordinating water molecules (see below). Complexes of the type [Ni(*o*-MeO-dppp)X_2] [X = Cl (**2**), Br (**3**), I, or trifluoroacetate (TFA)] were readily obtained by reaction of the ligand either with the corresponding nickel(II) salt (X = Cl or Br), or with nickel(II) acetate with subsequent addition of the appropriate acid (X = Cl, I, or TFA).

It would appear that in the case of *o*-MeO-dppp no bis(chelate) complex can be formed. In the presence of the weakly coordinating anion TFA, [Ni(*o*-MeO-dppp)$(TFA)_2$] was obtained, whereas from an aqueous reaction mixture complex **1** crystallized. Therefore, attempts were made to obtain a bis(*o*-MeO-dppp)nickel(II) complex from a dry, apolar solvent. Nickel(II) acetate was heated in vacuo to remove all water molecules and was subsequently mixed with *o*-MeO-dppp in dry dichloromethane. After four months, brick-red crystals had precipitated, which analyzed as [Ni(*o*-MeO-dppp)Cl_2]. The only possible source of the chloride anions in this compound was the chlorinated solvent. The formation of a nickel(II) dichloride species starting from a nickel(0) species in the presence of chloroform has been reported.[11] It appears that such reactions involve oxidative addition of chloroform to the nickel(0) center. It has also been found that in the Kharasch reaction[12] and in atom-transfer radical addition reactions (ATRA),[13] a nickel(II) chloride species can be formed by a radical pathway involving a nickel(III) species. In the present case, a radical pathway might be possible as the chloride compound is formed more rapidly in chloroform than it is in dichloromethane when starting from nickel(II) acetate and the ligand. No further attempts have been undertaken to elucidate the mechanism of the chloride abstraction.

Characterization of the Synthesized Complexes in the Solid Phase

The infrared spectra of all the synthesized nickel(II) complexes are very similar and also resemble that of the free ligand *o*-MeO-dppp. In the infrared spectrum of [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$, an additional band is observed at 1616 cm^{-1}, indicating that the complex contains coordinated water molecules. Diffuse reflectance absorption spectra of the halide compounds show only one strong band at around 20,000 cm^{-1}, as seen for the [Ni(dppp)X_2] complexes[14] (X = Cl, Br, or I), which can be ascribed to the $^1A_1 \rightarrow {}^1B_2$ transition for a square-planar geometry. This band shifts to higher energy in the order I (17,800 cm^{-1}) < Br (19,600 cm^{-1}) < Cl (20,600 cm^{-1}), consistent with the established spectrochemical series.[15] The positions of the strong absorption bands found for [Ni(*o*-MeO-dppp)$(TFA)_2$] and [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ at even higher energies (22,100 and 23,400 cm^{-1}, respectively) are also in accordance with the spectrochemical series.[15] The latter two complexes have also been assigned square-planar structures.

Crystal Structure of [Ni(o-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$ (1)

A molecular plot of the structure of the complex cation showing 50% probability ellipsoids is presented in Figure 1. Selected interatomic distances and angles are given in Table 1.

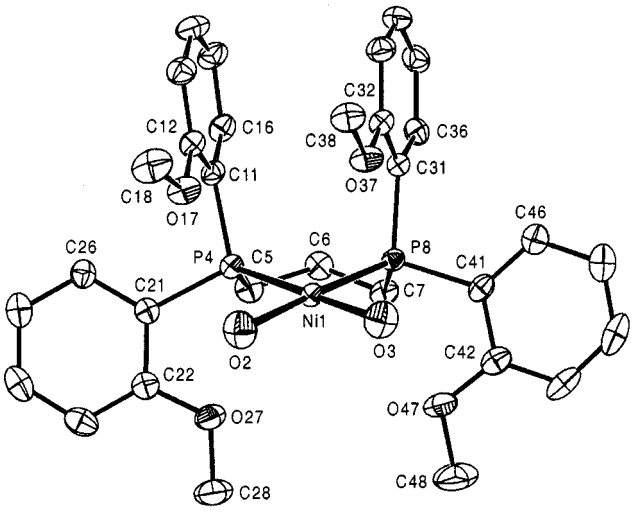


Figure 1. Displacement ellipsoid plot (50% probability) of the cationic unit in [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2 \cdot 0.6C_2H_5OH \cdot CHCl_3$ showing the atom-labeling scheme; hydrogen atoms are omitted for clarity

In complex **1**, the coordination geometry about the nickel(II) center is essentially square-planar with two phosphane donors and two water molecules in a *cis* configuration. The dihedral angle between the O−Ni−O and P−Ni−P planes does not deviate significantly from zero (2.06°). The water molecules are bound more tightly to the nickel center in a low-spin complex than in a high-spin complex, as indicated by the quite short Ni−O distances of 1.965(2) and 1.966(2) Å as compared to the Ni−O distance of 2.0418(8) Å in the octahedral complex [Ni$(H_2O)_6$](SiF_6).[16] The Ni−P distances are similar to that in the nickel(II) thiosalicylate complex [Ni(dppp)$(SC_6H_4CO_2)$] [2.1697(8) Å].[17] The bite angle of the bidentate phosphane ligand is 89.02(3)° in the present compound, similar to that of the unsubstituted analogue dppp in nickel complexes (87.3°).[18] The short Ni1···O37 distance [2.866(2) Å] indicates the presence of an electrostatic interaction between this

Table 1. Selected interatomic distances, angles, and torsion angles for [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$·0.6C_2H_5OH·$CHCl_3$ (**1**), [Ni(*o*-MeO-dppp)Cl_2] (**2**), and [Ni(*o*-MeO-dppp)Br_2] (**3**)

[a]	**1**		**2** (X = Cl)	**3** (X = Br)
Distances [Å]				
Ni1−O2	1.965(2)	Ni1−X1	2.2163(6)	2.3462(4)
Ni1−O3	1.966(2)			
Ni1−P4	2.1875(7)	Ni1−P4	2.1729(5)	2.1751(5)
Ni1−P8	2.1867(7)			
Ni1−O17	3.240(2)	Ni1−O17	3.3827(12)	3.4783(14)
Ni1−O27	3.230(2)			
Ni1−O37	2.866(2)			
Ni1−O47	3.385(2)			
		Ni1−H26	2.8711	2.8435
Angles [°]				
O2−Ni1−O3	85.87(10)	X1−Ni1−X1′	94.50(2)	92.85(2)
O2−Ni1−P4	92.31(8)	X1−Ni1−P4	88.55(2)	89.55(1)
O3−Ni1−P8	92.83(7)			
P4−Ni1−O3	177.80(8)	P4−Ni1−X1′	167.28(2)	166.59(1)
P8−Ni1−O2	177.92(8)			
P4−Ni1−P8	89.02(3)	P4−Ni1−P4′	91.17(2)	91.17(2)
Torsion Angles [°]				
Ni1−P4−C11−C12	−55.4(2)	Ni1−P4−C11−C12	61.50(16)	66.2(2)
Ni1−P8−C31−C32	31.3(2)			
Ni1−P4−C21−C22	−55.3(2)	Ni1−P4−C21−C22	−171.00(15)	−175.30(17)
Ni1−P8−C41−C42	61.0(2)			
P4−C5−C6−C7	55.9(3)	P4−C5−C6−C5′	−35.74(15)	−35.24(18)
C5−C6−C7−P8	−62.4(3)			

[a] Primed atoms at symmetry position: 1 − *x*, *y*, 1.5 − *z*.

ortho-methoxy group and the nickel(II) center. The two axial rings (rings 1 and 3) are stacked, as indicated by the small angle between the planes of these rings of 4.99(14)° and the short interplanar distance of 3.736 Å. The coordinated water molecules in **1** are involved in several hydrogen bonds. Based on the positions of the hydrogen atoms located from the difference Fourier map, these hydrogen bonds are all intermolecular, with the PF_6^- anion and the ethanol solvent as hydrogen-bond acceptors. There are additional short intramolecular O···O contacts (see Figure 2 and Table 2), for which, however, the X-ray experiment provides no evidence for hydrogen-bonding. It must be stated that all observed O···O and O···F distances are relatively long, except for O2···O17, thus an interaction of the coordinated water molecules with the *ortho*-methoxy groups of the ligand cannot be excluded.

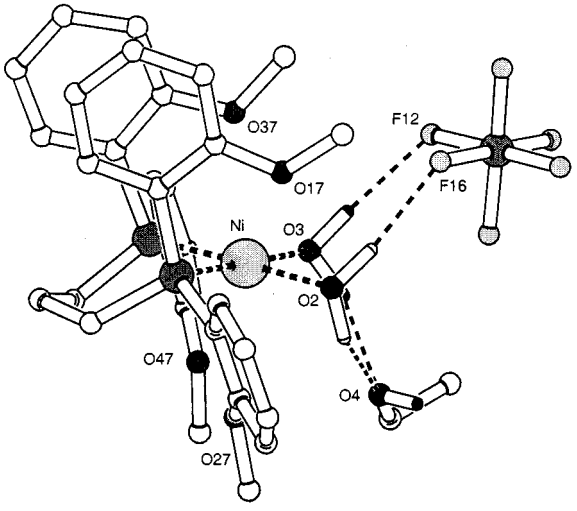


Figure 2. Crystal structure of **1** drawn such that all possible hydrogen-bond acceptors for the coordinated water molecules are visible

Table 2. Selected interatomic distances and angles concerning all possible hydrogen-bond acceptors in the crystal structure of [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$·0.6C_2H_5OH·$CHCl_3$ (**1**)

Distances [Å]		Angles [°]	
O2−O4	3.103(5)	Ni1−O2−O4	91.39
O2−F16	3.142(3)	Ni1−O2−F16	105.01
O2−O17[a]	2.873(3)	Ni1−O2−O17	81.77
O2−O27[a]	3.041(3)	Ni1−O2−O27	77.08
O3−O4	3.015(5)	Ni1−O3−O4	93.99
O3−F12	3.139(3)	Ni1−O3−F12	125.49
O3−O37[a]	3.121(3)	Ni1−O3−O37	63.94
O3−O47[a]	3.149(3)	Ni1−O3−O47	79.17

[a] Intramolecular contacts.

No crystal structure of a low-spin nickel complex with coordinated water molecules has hitherto been reported. However, the synthesis of the five-coordinate nickel(II) complex [Ni(dcpe)$(NO_3)_2(H_2O)$] has been reported by Connor and Riley.[19] It remains unclear as to whether this low-spin nickel complex really contains a coordinated water molecule, as this has not been proven unambiguously. The known structures of nickel complexes incorporating coordinated water molecules are all octahedral (high-spin) and do

not contain phosphane ligands.[20] The structures of nickel complexes incorporating phosphane ligands are predominantly square-planar (low-spin) or, due to steric constraints, are sometimes tetrahedral (high-spin). It seems that in complex **1** the electronic factors of the phosphorus atoms, which will favor a low-spin square-planar geometry, predominate over those of the water molecules, which would favor a high-spin octahedral geometry. It seems likely that the ligand *o*-MeO-dppp plays an important role in the formation of the low-spin nickel complex containing coordinated water molecules. The reaction of nickel(II) acetate with the unsubstituted ligand dppp in the presence of ammonium hexafluorophosphate results in a compound that can most probably be formulated as the dimeric hydroxo complex $[\{Ni(dppp)(\mu\text{-}OH)\}_2](PF_6)_2$.[21−23] Whereas the ligand *o*-MeO-dppp is able to stabilize the dicationic nickel atom through an interaction of one methoxy group with the metal center, in the case of dppp the complex is stabilized by the formation of two monocationic metal centers bridged by two hydroxy groups.

Crystal Structures of [Ni(o-MeO-dppp)Cl_2] (2) and [Ni(o-MeO-dppp)Br_2] (3)

A molecular plot of the structure of [Ni(*o*-MeO-dppp)Cl_2] (**2**) showing 50% probability ellipsoids is presented in Figure 3. Selected interatomic distances and angles are given in Table 1.

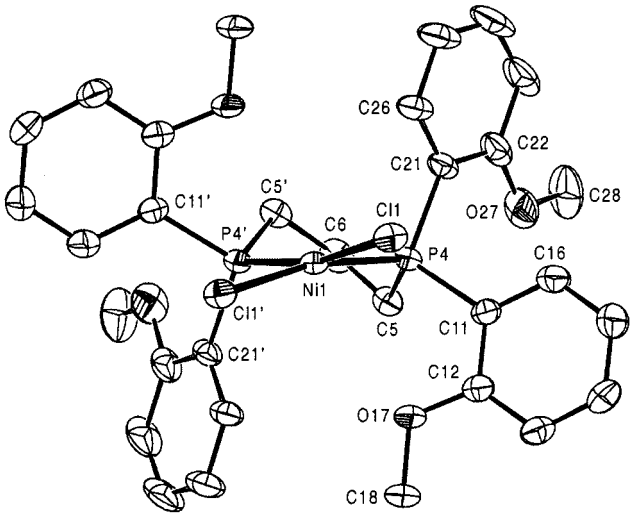


Figure 3. Displacement ellipsoid plot (50% probability) of [Ni(*o*-MeO-dppp)Cl_2] showing the atom-labeling scheme; hydrogen atoms are omitted for clarity; symmetry operation: $1 - x, y, 1.5 - z$

The complex [Ni(*o*-MeO-dppp)Br_2] is isostructural with [Ni(*o*-MeO-dppp)Cl_2], as can be seen from the crystallographic data in Table 3 and from the graphical representation in Figure 4a. Complexes **2** and **3** possess an exact, crystallographic twofold symmetry. In both complexes, the coordination geometry about the nickel(II) center is square-planar, with a significant tetrahedral distortion, as is evident from the dihedral angle between the X−Ni−X and P−Ni−P planes (16.65° for **2** and 19.45° for **3**). To date, no crystal structures of complexes of the parent ligand, [Ni(dppp)X_2] (X = Cl, Br, or I), have been reported. However, the structures of [Ni(*o*-MeO-dppp)X_2] [X = Cl (**2**) or Br (**3**)] resemble that of [Ni(*o*-MeO-dppe)I_2], which has been reported previously.[6] In Figure 4b, [Ni(*o*-MeO-dppe)I_2] and **2** are compared in a graphical representation. The Ni−P distances in **2** and **3** are similar to those in [Ni(*o*-MeO-dppe)I_2]. Due to the extra carbon atom in the bridge, the bite angles in **2** and **3** are larger than that in [Ni(*o*-MeO-dppe)I_2] [86.48(3)°]. The rather long Ni···O17 distances of 3.38 Å in **2** and 3.48 Å in **3** are indicative of an absence of any electrostatic interactions between the nickel ion and the *ortho*-methoxy groups. In Figure 3, it can be seen that the *ortho*-hydrogen atoms (H26, H26′) of the two axial aryl groups are directed towards the nickel atom. The Ni···H distances of 2.87 Å in **2** and 2.84 Å in **3** indicate the presence of either an agostic interaction or an Ni···H−C hydrogen bond, a phenomenon which has been observed previously.[6,24,25]

Comparison of the Structures of [Ni(o-MeO-dppp)-$(H_2O)_2$]$(PF_6)_2$ (1) and [Ni(o-MeO-dppp)X_2] (2 and 3)

In Figure 1 and Figure 3, it can be seen that the orientation of the diphosphane ligand in the two complexes is completely different. In **1**, the six-membered ring is in a chair conformation leading to two axial rings on one side of the coordination plane and two equatorial rings on the other. In **2** and **3**, two axial and two equatorial rings are again observed, but here the twist-boat conformation of the six-membered ring dictates alternating axial and equatorial positions of the aryl groups. The difference in conformation of the six-membered chelate ring in the two complexes may be related to the electrostatic interaction between the dicationic nickel center and the *ortho*-methoxy groups of the ligand. In **1**, all four *ortho*-methoxy groups lie in close proximity to the nickel(II) center, whereas in **2** and **3** only two *ortho*-methoxy groups point towards the nickel center (see torsion angles in Table 2). Complexes **2** and **3** are neutral, whereas **1** is a cationic complex, hence the nickel(II) center in **1** will have more electrophilic character than those in **2** and **3**. This provides a likely explanation for the presence of an electrostatic Ni···O interaction in **1**, while such an interaction is not significant in **2** and **3**. Moreover, the coordinated water molecules in **1** have the ability to form hydrogen bonds, resulting in an orientation of the ligand whereby possible hydrogen-bond acceptors lie in the proximity of these coordinated water molecules.

Characterization of the Synthesized Complexes in Solution

The essential preservation of the geometry seen in the solid-state upon dissolution is confirmed by a comparison of the electronic absorption spectra of **1** and **2** in CH_2Cl_2 solution with the diffuse reflectance electronic spectra of the solids. However, for the closely related nickel(II) species [Ni(dppp)X_2] (where X = Cl, Br, or I), both square-planar and tetrahedral species are observed in dichloromethane solution.[14] Apparently, the presence of the *ortho*-methoxy

Table 3. Crystal data and structure refinement details for [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$·0.6C_2H_5OH·$CHCl_3$ (**1**), [Ni(*o*-MeO-dppp)Cl_2] (**2**), and [Ni(*o*-MeO-dppp)Br_2] (**3**)

[a]	**1**	**2**	**3**
Empirical formula	$C_{31}H_{38}NiO_6P_2$·2PF_6 $CHCl_3$·0.6C_2H_6O	$C_{31}H_{34}Cl_2NiO_4P_2$ + solvent	$C_{31}H_{34}Br_2NiO_4P_2$ + solvent
Molecular mass	1064.21	662.13[a]	751.05[a]
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$ (No. 19)	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
Crystal size [mm]	0.56 × 0.38 × 0.25	0.30 × 0.12 × 0.06	0.39 × 0.11 × 0.06
Crystal color	red	red	red
a [Å]	12.6547(2)	19.3843(8)	19.8824(8)
b [Å]	16.8230(3)	12.6704(5)	12.2212(5)
c [Å]	21.0013(3)	16.4006(4)	16.7882(6)
β [°]	90	94.186(2)	97.312(2)
V [Å^3]	4470.97(12)	4017.4(2)	4046.1(3)
Z	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.581	1.095[a]	1.233[a]
μ [mm^{-1}]	0.85	0.72[a]	2.56[a]
refl. meas./unique	27890/10174	24644/4593	29261/4618
param./restraints	554/0	184/0	184/0
*R*1[b] (obs./all refl.)	0.0369/0.0408	0.0350/0.0465	0.0313/0.0356
*wR*2[c] (obs./all refl.)	0.0998/0.1025	0.0875/0.0905	0.0811/0.0827
GoF	1.043	1.058	1.078
Δρ (min./max.) [e Å^{-3}]	−0.37/0.71	−0.26/0.33	−0.87/0.71

[a] Derived values do not contain the contribution of the disordered solvent molecules. − [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$, $A = 0.0582$ (**1**), 0.0457 (**2**), 0.0387 (**3**), and $B = 2.2431$ (**1**), 1.2627 (**2**), 3.9813 (**3**).

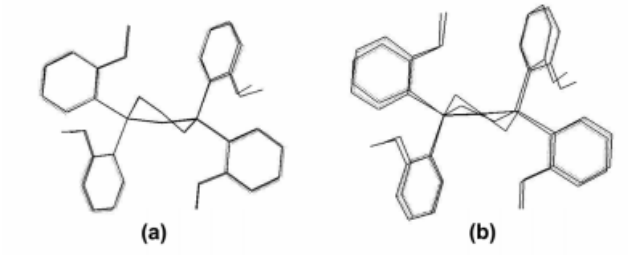


Figure 4. (a) Crystal structures of **2** and of **3** drawn such that the Ni and P atoms of the two structures are coincident; (b) crystal structures of **2** (wire) and of [Ni(*o*-MeO-dppe)I_2] drawn such that the Ni and P atoms of the two structures are coincident; in both representations, the perspective shown is that in which the depicted P atoms point away from the viewer, while the two other, not depicted coordinating atoms point towards the viewer

groups in the *o*-MeO-dppp ligand contributes to the stability of the square-planar geometry. It is difficult to ascertain whether this stabilization is due to the altered electronic or steric features of the diphosphane ligand resulting from the introduction of the *ortho*-methoxy groups. All the new nickel(II) complexes presented in this paper exhibit rather sharp ^{1}H NMR signals, which indicates that they are predominantly diamagnetic (low-spin) in solution. However, some paramagnetism is present, which is mainly manifested in the phosphorus NMR spectra. For [Ni(*o*-MeO-dppp)$(H_2O)_2$](PF_6) (**1**), one sharp resonance is observed in the $^{31}P\{^1H\}$ NMR spectrum at room temperature (δ = −9.8), whereas for [Ni(*o*-MeO-dppp)$(TFA)_2$], a rather broad signal is observed (δ = 4.7). For the complex [Ni(*o*-MeO-dppp)Cl_2] (**2**), a sharp ^{31}P NMR signal can only be observed at −60 °C (δ = 7.2). Apparently, at room temperature, the ^{31}P NMR signal for this complex is very broad, and is not discernible above the spectral noise. This broadening could perhaps be due to a geometric equilibrium (square-planar ⇄ tetrahedral), as at room temperature the ^{1}H NMR signals are also slightly broadened. These differences in line broadening for the various complexes can be related to their solid-state structures. The essentially square-planar geometry about the central nickel atom observed for **1** in the solid phase is retained in solution, whereas the tetrahedral distortion observed for **2** is reflected in the absence of a distinct resonance in the ^{31}P NMR spectrum at room temperature. The difference in the chemical shift (Δδ) of the phosphorus atom between the free and coordinated ligands in these complexes amounts to 30−40 ppm, which is comparable to that seen for other six-membered chelate systems.[26]

Fluxional Behavior of [Ni(*o*-MeO-dppp)Cl_2] and [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2$

The temperature-dependent ^{1}H NMR spectra of [Ni(*o*-MeO-dppp)Cl_2] (**2**) and [Ni(*o*-MeO-dppp)$(H_2O)_2$](PF_6) (**1**) in CD_2Cl_2 are shown in Figure 5 and Figure 6, respectively.

Both complexes exhibit fluxional behavior. At 25−35 °C, one set of aryl resonances and one methoxy resonance is observed for both complexes, indicating that the four functionalized aryl groups of the *o*-MeO-dppp ligand of both **1** and **2** are spectroscopically equivalent. On lowering the temperature, the ^{1}H NMR resonances of both complexes broaden and ultimately appear as double sets of resonances at −50 °C. The low-temperature spectrum of [Ni(*o*-MeO-dppp)Cl_2] (**2**) is in agreement with the crystal structure, in

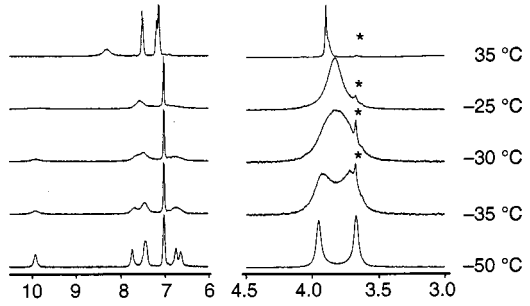


Figure 5. Two sections of the 400-MHz ^{1}H NMR spectra of [Ni(*o*-MeO-dppp)Cl$_2$] in CD_2Cl_2 as a function of temperature; section I: δ = 3−4.5, signals corresponding to the *ortho*-methoxy groups; section II: δ = 6−10.5, signals corresponding to the aryl groups; signals arising from the solvent or impurities are indicated with an asterisk

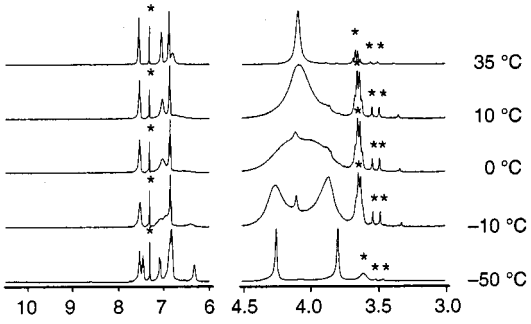


Figure 6. Two sections of the 400-MHz ^{1}H NMR spectra of [Ni(*o*-MeO-dppp)(H$_2$O)$_2$](PF$_6$)$_2$ in CD_2Cl_2 as a function of temperature; section I: δ = 3−4.5, signals corresponding to the *ortho*-methoxy groups; section II: δ = 6−10.5, signals corresponding to the aryl groups; signals arising from the solvent or impurities are indicated with an asterisk

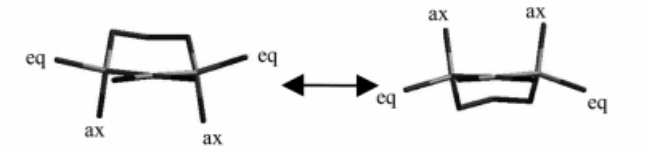
which pairs of the four aryl groups are equivalent: Two are oriented axially with respect to the six-membered chelate ring, while the other two are oriented equatorially. The observed fluxional behavior of **2** is best described as a rapid interchange of the equatorial and axial aryl groups (Scheme 3), which is a slow process on the NMR time scale at low temperature.

Scheme 3

In the low-temperature ^{1}H NMR spectrum of **2**, one of the *ortho*-aryl proton resonances is considerably shifted downfield and is found at δ = 9.9. This anomalous chemical shift can be attributed to the interaction of the two *ortho*-protons of the two spectroscopically identical axial aryl rings with the occupied d_{z^2} orbital of the nickel atom. The downfield shift of these protons in the ^{1}H NMR spectrum, together with the observed Ni···H interaction in the crystal structure of **2**, indicate that this interaction is better described as an Ni···H−C hydrogen bond rather than as an agostic interaction.[25] From the coalescence temperatures of the interconverting *ortho*-methoxy groups, and of two sets of the aryl protons, three estimates were obtained for the $\Delta G^{\ddagger}$ value[27] of the $(aryl)_{eq} \rightleftarrows (aryl)_{ax}$ exchange process: $\Delta G^{\ddagger}_{av}$ (**2**) = 47.6 kJ·mol^{-1}.

The low-temperature ^{1}H NMR spectrum of **1**, in which the fluxional behavior of the complex is in the slow exchange regime, is quite different from that of **2**. The resonances due to the aryl hydrogen atoms are all observed in the δ = 6−8 region, and none is observed further downfield like that seen for **2**, indicating that there is no Ni···H−C$_{aryl}$ interaction in **1**. This is in agreement with the crystal structure, which shows all four aryl rings to be oriented such that the *ortho*-methoxy groups are directed towards the nickel ion. Based on the crystal structure of **1**, four discrete sets of aryl resonances would be expected at low temperature; in fact, only two sets are observed. Apparently, a dynamic process is also operative at low temperatures.

The most likely interpretation of the low-temperature spectrum of **1** is that the $(aryl)_{eq} \rightleftarrows (aryl)_{ax}$ exchange process (see Scheme 4) is slow on the NMR time scale, but that the two slightly differently oriented axial aryl groups observed in the crystal structure are still in rapid exchange by a windshield wiper type of motion, as a result of which each of the *ortho*-methoxy groups of the axial aryl rings points to the metal center for half of the time. One of the two *ortho*-methoxy resonances in the low-temperature spectrum of **1** is shifted considerably downfield (δ = 4.3) with respect to the other (δ = 3.8), as well as to those of the free ligand (δ = 3.64) and those of **2** (δ = 3.67 and 3.95). This downfield resonance is tentatively ascribed to the two rapidly interconverting (axial) *ortho*-methoxy groups interacting with the metal center. From the coalescence temperatures of the *ortho*-methoxy signals, and one of the aryl proton signals, two estimates were obtained for the $\Delta G^{\ddagger}$ value[27] of the $(aryl)_{eq} \rightleftarrows (aryl)_{ax}$ exchange process: $\Delta G^{\ddagger}_{av}$ (**1**) = 51.8 kJ·mol^{-1}.



Scheme 4

Auto-Ionization

As discussed above, a complex containing the [Ni(*o*-MeO-dppp)$_2$]$^{2+}$ moiety could not be obtained. However, it has been reported[6] that nickel(II) complexes containing the ligand *o*-MeO-dppe and weakly coordinating anions (such as TFA or OAc) are completely auto-ionized in polar solvents, as observed by ^{1}H NMR spectroscopy. Therefore, the complexes [Ni(*o*-MeO-dppp)(H$_2$O)$_2$](PF$_6$)$_2$ and [Ni(*o*-MeO-dppp)(TFA)$_2$] were dissolved in CD_3OD and ana-

lyzed by ^{1}H NMR. Neither complex is very soluble in methanol, and in the ^{1}H NMR spectra only the monochelate complexes are observed. It seems likely that the *o*-MeO-dppp ligand is too bulky to allow formation of a square-planar bis(chelate) complex. However, this is not solely an effect of the *ortho*-methoxy groups; no complexes containing the $[Ni(dppp)_2]^{2+}$ moiety have hitherto been reported, although the formation of such species in electrochemical experiments has been proposed.[7,8] The presence of the two aryl groups on each phosphorus atom in the C_3-bridged ligand clearly prevents the formation of a bis(chelate)Ni^{II} complex. In fact, bis(chelate) complexes are observed with C_3-bridged ligands bearing smaller methyl groups on the phosphorus atoms[9] or with just one aryl group per phosphorus atom.[10] However, in the former case, the chelate bite angle of the C_3-bridged ligand forces the nickel(II) center to adopt a tetrahedral geometry. Only one structure of a bis(chelate)nickel(II) complex containing C_3-bridged ligands with two aryl groups per phosphorus atom has been reported, namely that of $[Ni\{H_3CC(CH_2PPh_2)_2(CH_2OH)\}_2](BF_4)_2$.[28] In this structure, the nickel(II) center adopts a tetrahedral geometry and the chelate bite angle is somewhat reduced as a result of the substituents on the central carbon atom of the bridge, so that all eight aryl rings can be fitted in the rather limited space around the rather small nickel(II) ion. For the somewhat larger palladium(II) ion, a square-planar bis(*o*-MeO-dppp)palladium(II) complex is easily formed.[29] It seems that the combination of the large bite angle of *o*-MeO-dppp and the rather small nickel(II) ion prevents the formation of the $[Ni(o\text{-MeO-dppp})_2]^{2+}$ moiety. It is for this same reason that nickel(II) complexes containing the ligand *o*-MeO-dppp, unlike their *o*-MeO-dppe counterparts, are not involved in an auto-ionization equilibrium as depicted in Scheme 2.

Conclusion

The first low-spin, square-planar nickel(II) complex with two coordinated water molecules has been synthesized and the presence of the water molecules has been unambiguously proven. The ligand *o*-MeO-dppp appears to be able to stabilize the dicationic nickel atom through interactions of its methoxy groups with the metal center.

It appears that, in contrast to *o*-MeO-dppe-based complexes, nickel(II) complexes containing the ligand *o*-MeO-dppp are not involved in the auto-ionization equilibrium, $2\,[Ni(P{-}P)X_2] \rightleftarrows [Ni(P{-}P)_2]^{2+} + [\text{“}NiX_4\text{”}]^{2-}$. This is not solely an effect of the *ortho*-methoxy groups, as no complexes containing the $[Ni(dppp)_2]^{2+}$ moiety have hitherto been reported. The inability to form a bis(chelate) complex is most likely due to a combination of the large bite angle dictated by the C_3 bridge and the rather small nickel(II) ion. The absence of the bis(chelate) complex might be one of the reasons for the considerably better hydrogenation activity of catalysts based on this ligand, compared to those based on *o*-MeO-dppe. The lower sensitivity to variations in solvents and anions[3] of the catalysts containing *o*-MeO-dppp might also be related to the absence of the auto-ionization equilibrium.

Experimental Section

General Remarks: Elemental analyses were performed with a Perkin−Elmer 2400 Series II analyzer. − Infrared spectra were recorded with a Perkin−Elmer Paragon 1000 IR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000−300 cm^{-1}). − Solid-state electronic absorption spectra were obtained with a Perkin−Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. − Solution electronic absorption spectra were recorded from samples in 1-cm path length cells at ambient temperature, using the neat solvent as the reference. − ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Varian VXR-200 spectrometer at 200.06 MHz and 80.98 MHz, respectively, or with a Bruker WM-300 spectrometer at 300.13 MHz and 121.50 MHz, respectively. The variable-temperature ^{1}H NMR measurements were performed with a Varian INOVA-400 spectrometer equipped with a variable-temperature probe at 399.97 MHz. ^{31}P and ^{1}H chemical shifts are quoted in δ units relative to triphenylphosphane ($\delta_P = -6$) and residual protons in the deuterated solvent (CD_2Cl_2: $\delta_H = 5.24$), respectively.

Syntheses: All chemicals were either reagent grade and were used as received, or were synthesized as described below. Reactions were carried out under dry argon or dry nitrogen, unless stated otherwise, by using standard Schlenk techniques. Tris(*o*-methoxyphenyl)phosphane[30] and 1,3-bis[di(*o*-methoxyphenyl)phosphanyl]-propane (*o*-MeO-dppp)[31] were synthesized according to literature procedures. Generally, the complexes were obtained in yields of 40−80%; no attempts have been undertaken to optimize the yields.

$[Ni(o\text{-MeO-dppp})(H_2O)_2](PF_6)_2$ (1): A solution of $Ni(OAc)_2{\cdot}4H_2O$ (0.12 g, 0.5 mmol) in ethanol (15 mL) was mixed with a solution of *o*-MeO-dppp (0.28 g, 0.55 mmol) in chloroform (15 mL), to give a clear, dark-orange solution. A solution of NH_4PF_6 (0.16 g, 1 mmol) in ethanol (5 mL) was then added, which led to a slight lightening of the orange colour. After several days, orange crystals precipitated from the solution. These crystals proved to be suitable for X-ray diffraction analysis. − $C_{31}H_{38}F_{12}NiO_6P_4{\cdot}CHCl_3$ (1036.58): calcd. C 37.08, H 3.79; found C 37.08, H 3.72. − ^{1}H NMR (CD_2Cl_2, 35 °C): δ = 1.69 (m, 2 H, $CH_2CH_2CH_2$), 2.30 (s, H_2O), 2.51 (m, 4 H, $CH_2CH_2CH_2$), 4.09 (s, 12 H, OCH_3), 6.81 (m, 4 H), 6.91 (t, 4 H, arom. H), 7.05 (d, 4 H, arom. H), 7.55 (t, 4 H, arom. H). − ^{1}H NMR (CD_2Cl_2, −50 °C): δ = 1.67 (m, 2 H, $CH_2CH_2CH_2$), 2.58 (s, H_2O), 2.79 (m, 4 H, $CH_2CH_2CH_2$), 3.79 (s, 6 H, OCH_3), 4.25 (s, 6 H, OCH_3), 6.33 (m, 2 H, arom. H), 6.83 (m, 8 H, arom. H), 7.09 (m, 2 H, arom. H), 7.46 (t, 2 H, arom. H), 7.54 (t, 2 H, arom. H). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = −9.8 (s), 104.4 (septet, PF_6). − Diffuse reflectance electronic absorption of the solid: $\tilde{\nu}_{max}$ = 30,300 and 23,400 cm^{-1}. − Electronic absorption in CH_2Cl_2 [molar extinction coefficients (L mol^{-1} cm^{-1})]: $\tilde{\nu}_{max}$ = 30,900 (11,000) and 24,300 cm^{-1} (800).

$[Ni(o\text{-MeO-dppp})Cl_2]$ (2). − Method A: $Ni(OAc)_2{\cdot}4H_2O$ (50 mg, 0.2 mmol) was mixed with an equimolar amount of *o*-MeO-dppp (107 mg, 0.2 mmol) in ethanol (20 mL). The mixture was refluxed for 3.5 h and a clear orange solution was obtained. After the solution had cooled somewhat, HCl (1 M in Et_2O, 0.5 mL, 0.5 mmol) was added. The solution immediately turned red and after several

minutes a brick-red precipitate had formed. The solid was collected by filtration and dried in air. − **Method B:** $NiCl_2·6H_2O$ (0.35 g, 1.5 mmol) was dissolved in ethanol (10 mL) and then mixed with an equimolar amount of *o*-MeO-dppp (0.81 g, 1.5 mmol) dissolved in chloroform (10 mL). After a few seconds, a brick-red solid precipitated. The solid was collected by filtration and dried in air. Yield: 0.55 g (83%). − $C_{31}H_{34}Cl_2NiO_4P_2$ (662.15): calcd. C 56.23, H 5.18; found C 55.96, H 5.50. − ^{1}H NMR (CD_2Cl_2, 35 °C): δ = 1.67 (m, 2 H, $CH_2CH_2CH_2$), 3.07 (m, 4 H, $CH_2CH_2CH_2$), 3.90 (s, 12 H, OCH_3), 7.13 (m, 8 H, arom. H), 7.50 (t, 4 H, arom. H), 8.29 (m, 4 H, arom. H). − ^{1}H NMR (CD_2Cl_2, −50 °C): δ = 1.70 (m, 2 H, $CH_2CH_2CH_2$), 2.16 (m, 4 H, $CH_2CH_2CH_2$), 3.67 (s, 6 H, OCH_3), 3.95 (s, 6 H, OCH_3), 6.62 (m, 2 H, arom. H), 6.73 (m, 2 H, arom. H), 7.00 (m, 4 H, arom. H), 7.42 (m, 4 H, arom. H), 7.72 (m, 2 H, arom. H), 9.91 (m, 2 H, arom. H). − ^{31}P{^{1}H} NMR (H_3PO_4 external standard; $CDCl_3$): 25 °C: no peak; −60 °C: δ = 7.2 (s). − Diffuse reflectance electronic absorption of the solid: $\tilde{\nu}_{max}$ = 30,200 and 20,600 cm^{-1}. − Electronic absorption in CH_2Cl_2 [molar extinction coefficients (L mol^{-1} cm^{-1})]: $\tilde{\nu}_{max}$ = 31,300 (9,000) and 20,700 cm^{-1} (900).

[Ni(*o*-MeO-dppp)Br$_2$] (3): To a suspension of $NiBr_2$ (0.33 g, 1.5 mmol) in ethanol (10 mL) was added a solution of *o*-MeO-dppp (0.53 g, 1 mmol) in chloroform (10 mL) and the mixture immediately turned purple. After several minutes, a purple precipitate had formed. The solid was collected by filtration and dried in vacuo. Yield: 0.66 g (88%). Crystals of [Ni(*o*-MeO-dppp)Br_2] suitable for single-crystal X-ray diffraction analysis were obtained from an autoclave solution containing $NiBr_2$ (0.05 mmol) and *o*-MeO-dppp (0.055 mmol), in methanol (10 mL), dichloromethane (10 mL), toluene (4 mL), and 1-octene (15.6 mL). − $C_{31}H_{34}Br_2NiO_4P_2$ (751.05): calcd. C 49.58, H 4.56; found C 48.47, H 4.00. − Diffuse reflectance electronic absorption of the solid: $\tilde{\nu}_{max}$ = 29,600 and 19,600 cm^{-1}.

[Ni(*o*-MeO-dppp)I$_2$]: $Ni(OAc)_2·4H_2O$ (0.25 g, 1 mmol) was dissolved in ethanol (10 mL) and mixed with an equimolar amount of *o*-MeO-dppp (0.53 g, 1 mmol) in chloroform (10 mL). To the clear orange solution, HI (50% in water, 0.25 mL, 1.8 mmol) was added, and a purple solution was obtained. After several minutes, a dark-purple precipitate had formed. The solid was collected by filtration and dried in air. Yield: 0.61 g (72%). − $C_{31}H_{34}I_2NiO_4P_2·(CHCl_3)_{0.5}$ (904.74): calcd. C 41.82, H 3.84; found C 41.07, H 3.79. − Diffuse reflectance electronic absorption of the solid: $\tilde{\nu}_{max}$ = 24,300 and 17,800 cm^{-1}. − Electronic absorption in CH_2Cl_2 [molar extinction coefficients (L mol^{-1} cm^{-1})]: $\tilde{\nu}_{max}$ = 28,000 (10,000) and 17,800 cm^{-1} (1,600).

[Ni(*o*-MeO-dppp)(TFA)$_2$]: $Ni(OAc)_2·4H_2O$ (0.12 g, 0.5 mmol) was dissolved in methanol (1 mL) and a solution of *o*-MeO-dppp (0.27 g, 0.5 mmol) in dichloromethane (10 mL) was added. When a clear, dark-orange solution had been obtained, trifluoroacetic acid (0.1 mL, 1.3 mmol) was added. The reaction mixture was filtered and layered with diethyl ether, which resulted in the deposition of a dark-orange crystalline precipitate. Yield: 0.18 g (43%). − $C_{35}H_{34}NiF_6O_8P_2$ (817.27): calcd. C 51.44, H 4.19; found C 51.10, H 4.14. − ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 1.82 (m, 2 H, $CH_2CH_2CH_2$), 2.16 (m, 4 H, $CH_2CH_2CH_2$), 3.68 (d, 12 H, OCH_3), 6.95 (m, 8 H, arom. H), 7.49 (m, 4 H, arom. H), 8.36 (m, 2 H, arom. H). − ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 4.7 (br. s). − Diffuse reflectance electronic absorption of the solid: $\tilde{\nu}_{max}$ = 29,500 and 22,100 cm^{-1}.

Attempted Synthesis of [Ni(*o*-MeO-dppp)$_2$](TFA)$_2$: In an attempt to synthesize this compound, $Ni(OAc)_2·4H_2O$ (0.12 g, 0.5 mmol) was mixed with *o*-MeO-dppp (0.53 g, 1 mmol) in a mixture of dichloromethane (10 mL) and methanol (1 mL). When a clear, dark-orange solution had been obtained, trifluoroacetic acid (0.1 mL, 1.3 mmol) was added. The solvents were partially evaporated in vacuo and diethyl ether was added, which resulted in the deposition of an orange precipitate. The supernatant solution was decanted off and the solid residue was dried in air. − ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 4.8 (s), −37.2 (s). − When methanol was added to the compound, an orange solution was obtained and a white solid remained that analyzed as the free ligand. After filtration and evaporation of the solvent from the filtrate, an orange compound was obtained. This compound appeared to be the mono-chelate complex [Ni(*o*-MeO-dppp)$(TFA)_2$].

Attempted Synthesis of [Ni(*o*-MeO-dppp)$_2$](OAc)$_2$: In an attempt to synthesize a bis(*o*-MeO-dppp) complex, $Ni(OAc)_24H_2O$ (0.12 g, 0.5 mmol) was first dried in vacuo in order to remove all water molecules. It was then taken-up in dichloromethane to give a green solution. The ligand *o*-MeO-dppp (0.58 g, 1.1 mmol) was dissolved in dichloromethane (20 mL) to give a colorless solution. On mixing the two solutions, a green solution was initially obtained. However, after stirring overnight, a clear orange solution was obtained. After 4 months at 4 °C, brick-red crystals suitable for single-crystal X-ray diffraction analysis had formed. These crystals were characterized as [Ni(*o*-MeO-dppp)Cl_2].

X-ray Crystal Structure Determinations of [Ni(*o*-MeO-dppp)$(H_2O)_2$]$(PF_6)_2·(C_2H_5OH)_{0.6}·CHCl_3$ (1), [Ni(*o*-MeO-dppp)Cl_2] (2), and [Ni(*o*-MeO-dppp)Br_2] (3): Intensities were measured with a Nonius-Kappa CCD diffractometer with a rotating anode (Mo-K_α, λ = 0.71073 Å) at 150 K. The structure was solved by Patterson methods (DIRDIF-97[32]) and refined against F^2 of all reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 $Å^{-1}$ using the program SHELXL-97.[33] Non-hydrogen atoms were refined freely with anisotropic parameters; hydrogen atoms were refined as rigid groups. In the crystal structure of **1**, the hydrogen positions of the water and ethanol molecules were located from the difference Fourier map and were kept fixed during the refinement. The drawings were created and structure calculations and checks for higher symmetry were carried out using the program PLATON.[34] Further experimental details are given in Table 3. The crystal structures of **2** and **3** show large voids (1243 $Å^3$ for **2** and 1273 $Å^3$ for **3**), which are occupied by disordered solvent molecules (dichloromethane). Their contribution to the structure factors was assessed by back-Fourier transformation (program PLATON,[34] CALC SQUEEZE, 484 e^-/unit cell for **2**, 400 e^-/unit cell for **3**). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151615 (**1**), -151616 (**2**), and -151617 (**3**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[21] **[{Ni(dppp)(μ-OH)}$_2$](PF$_6$)$_2$4H$_2$O·0.3CHCl$_3$:** Following the same procedure as for the synthesis of [Ni(*o*-MeO-dppp)(H$_2$O)$_2$](PF$_6$)$_2$ but using dppp, an orange solid was obtained. − $C_{54}H_{54}F_{12}Ni_2O_2P_2$4H$_2$O·0.3CHCl$_3$ (1374.09): calcd. C 47.46, H 4.57; found C 47.51, H 4.63. − Electronic absorption in CH_2Cl_2 [molar extinction coefficients (L mol^{-1} cm^{-1})]: $\tilde{\nu}_{max}$ = 32,200 (15,000) and 22,500 cm^{-1} (1,300). − These data are indicative of a square-planar complex. The IR spectrum shows a sharp band at 3608 cm^{-1} attributable to an O−H stretching vibration. Elucidation of the crystal structure is in progress. Compare refs.[22,23]
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