www.elsevier.nl/locate/ica

Inorganica Chimica Acta 300–302 (2000) 200–205

Inorganica Chimica Acta

Synthesis and characterization of a series of novel nickel(II)/nickel(I) complexes. Crystal structures of [NiCl$_2$(dcpm)], [Ni(dcpm)$_2$](NO$_3$)$_2$·2EtOH, [Ni$_2$Cl$_2$(μ-dcpm)$_2$(μ-H)] and [Ni$_2$(μ-PCy$_2$)$_2$(PCy$_2$Me)$_2$]; dcpm = bis(dicyclohexylphosphino)methane

Charles E. Kriley [a,*], C. Joy Woolley [a], Matthew K. Krepps [a], Eric M. Popa [b], Phillip E. Fanwick [b], Ian P. Rothwell [c]

[a] *Department of Chemistry, 100 Campus Drive, Grove City College, Grove City, PA 16127, USA*
[b] *Department of Chemistry and Physics, Gyte Building, Purdue University Calumet, Hammond, IN 46323-2094, USA*
[c] *Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47907-1393, USA*

Received 27 August 1999; accepted 8 October 1999

Abstract

The complexes [(dcpm)NiCl$_2$] (**1**), [Ni$_2$Cl$_2$(μ-dcpm)$_2$(μ-H)] (**3**), [Ni$_2$(μ-PCy$_2$)$_2$(PCy$_2$Me)$_2$] (**4**) and [Ni(dcpm)$_2$](NO$_3$)$_2$·2EtOH (**2**), dcpm = bis(dicyclohexylphosphino)methane, have been prepared and characterized by ^{31}P, ^{1}H NMR (or EPR) as well as X-ray crystallography. The salt NiCl$_2$·6H$_2$O was found to react with dcpm to form the monomeric, four-coordinate, diamagnetic complex [(dcpm)NiCl$_2$] (**1**). Compound **1** was then reduced with ^{n}Bu$_3$SnH (or LiH with heating) in toluene at room temperature to form the air sensitive 'A-frame' complex [Ni$_2$Cl$_2$(μ-dcpm)$_2$(μ-H)] (**3**). The Ni–Ni bond distance for **3** was found to be 2.904(3) Å showing a lack of any Ni–Ni metal bonding. [Ni$_2$(μ-PCy$_2$)$_2$(PCy$_2$Me)$_2$] (**4**) was then formed by the reaction of **1** and excess LiH, heating to 90°C in an oil bath. [Ni$_2$Cl$_2$(μ-dcpm)$_2$(μ-H)] (**3**) was shown to be an intermediate in the synthesis of the bridging phosphido nickel complex. The Ni–Ni bond distance in **4** is 2.3910(8) Å corresponding to a single Ni–Ni metal bond. The reaction of Ni(NO$_3$)$_2$·6H$_2$O with dcpm in ethanol yields the square planar complex [Ni(dcpm)$_2$](NO$_3$)$_2$·2EtOH (**2**). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure complexes; Nickel complexes; Phosphine complexes; Dinuclear complexes

1. Introduction

Over the past 40 years a large number of four-coordinate nickel(II) phosphine complexes have been isolated and characterized [1]. It was initially thought that, due to steric strain, the bidentate phosphine dppm (bisdiphenylphosphinomethane) would only act as a monodentate ligand [2]. Since that time nickel(II) halides have been shown to react under controlled conditions with dppm to yield the monomeric, four-coordinate, low-spin chelated complexes [NiX$_2$(dppm)], where X is Cl, Br, or I [3]. Further reactivity of [NiX(L)$_2$] (L = monodentate phosphines) complexes was discovered by Schafer in 1979 when he synthesized the first nickel(I) bridged phophido complex [Ni$_2$(μ-SiMe$_3$)(PR$_3$)]$_2$ (R = n-C$_4$H$_9$, C$_2$H$_5$, and CH$_3$) from (R$_3$P)$_2$NiCl$_2$ and LiP(SiMe$_3$)$_2$ [4]. A crystal structure of [Ni$_2$(μ-t-Bu$_2$P)(PMe$_3$)]$_2$ was resolved by Atwood and co-workers in 1982 and until the present time has remained the only structurally characterized nickel complex of this type [5].

Reaction of Ni(COD)$_2$ (COD = cycloocta-1,5-diene) with dppm, and phenyl isocyanide dichloride (C$_6$H$_5$NCCl$_2$) or thionyl chloride (SOCl$_2$) has been shown to result in an 'A-frame' complex of the type [Ni$_2$Cl$_2$(μ-dppm)$_2$(μ-L)] [6]. Bimetallic nickel complexes

---

* Corresponding author. Fax: + 1-724-458 3855.

0020-1693/00/$ - see front matter
PII: S0020-1693(99)00460-0

of the general formula $[Ni_2X_2(\mu\text{-}PP)_2(\mu\text{-}L)]$ (X = halide, PP = diphosphine, and L = SO, C = CH_2, CNC_6H_5, small Lewis bases) can adopt three distinct conformations: 'mixed geometry', 'cradle' and 'A-frame'. Typically, 'A-frame' complexes contain square planar symmetry around the nickel metal center. Unlike palladium and platinum [7], only a small number 'A-frame' complexes of nickel have been structurally characterized [6].

Other factors that can be utilized in the study of nickel-phosphine chemistry are the use of poorly coordinating anions such as NO_3^-. The use of weakly coordinating anions has led to the synthesis of nickel(0) complexes containing two equivalents of a bidentate phosphine such as dppm [8]. The $[Ni(dppm)_2]$ complex has a tetrahedral coordination around Ni and is paramagnetic in nature.

Through the catalytic hydrogenation of aryl-phosphine ligands, gram quantities of various mono-, di-, and polydentate cyclohexyl phosphines have become available to study [9]. Many of these were previously either unavailable or difficult to chemically synthesize. The availability of these novel phosphines, in particular bis(dicyclohexylphosphino)methane (dcpm) [9] has provided the possibility of further development in the area of dinuclear transition metal phosphine chemistry.

We report here the preparation, characterization and reactivity of a series of nickel dcpm complexes.

2. Experimental

2.1. General procedures

NMR spectra were recorded by using a Varian Gemini 200 and 300 MHz spectrometer. EPR measurements were obtained on a Bruker ESP 300E system with an ER 4121 VT liquid-nitrogen variable-temperature controller. The operating microwave frequency was 9.45 GHz.

2.1.1. Preparation of complexes $[(dcpm)NiCl_2]$ (**1**)

To 50 ml of a methanol solution of $[NiCl_2]\cdot 6H_2O$ (0.28 g, 1.18 mmol) was added 50 ml of a toluene solution of dcpm (0.50 g, 1.22 mmol). An immediate color change from green to dark orange was observed upon the addition of the dcpm–toluene solution. The solution was then stirred for 12 h. Concentration of the resulting orange solution resulted in the formation of large orange blocks of pure product **1** in high yield (0.59 g, 94%). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.350 (s, 2H, CH_2), 1.0–2.6 (cyclohexyl). ^{31}P NMR ($CDCl_3$, 300 MHz): δ −32.469. *Anal.* Calc. for $NiC_{32}H_{54}Cl_2P_2$, $[(dcpm)NiCl_2]\cdot C_7H_8$: C, 60.98; H, 8.64; Cl, 11.25; P, 9.83. Found: C, 61.71; H, 9.44; Cl, 11.28; P, 10.65%.

2.1.2. $[Ni(dcpm)_2](NO_3)_2\cdot 2EtOH$ (**2**)

To 50 ml of a methanol solution of $[Ni(NO_3)_2]\cdot 6H_2O$ (0.506 g, 1.74 mmol) was added 50 ml of a toluene solution of dcpm (0.770 g, 1.88 mmol). An immediate color change from green to yellow was observed upon the addition of the dcpm–toluene solution. The solution was left to stir overnight under atmospheric pressure. A yellow solid was obtained upon stripping off the solvent. The yellow solid was then placed in a minimal amount of ethanol and refluxed until completely dissolved. Small crystals of $[Ni(dcpm)_2](NO_3)_2\cdot 2EtOH$ (**2**) were isolated after cooling the ethanol solution overnight in a freezer (1.63 g, 46.6%). No EPR signal was detected but the ^1H NMR was found to contain contact shifted peaks. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.1, 3.4, 8.6, and 9.1 (broad contact shifted peaks), 0.5–2.5 (cyclohexyl), 4.5 (broad, EtOH). ^{31}P NMR ($CDCl_3$, 300 MHz): δ −23.472.

2.1.3. $[Ni_2Cl_2(\mu\text{-}dcpm)_2(\mu\text{-}H)]$ (**3**)

To a 50 ml toluene solution of $[(dcpm)NiCl_2]$ (**1**) (0.20 g, 0.37 mmol) under nitrogen was added tributyltin hydride (0.44 g, 1.51 mmol). A green solution formed after stirring for approximately 12 h. Green colored crystals were obtained by stripping the solution to dryness and dissolving in a minimal amount of hexane and placing the resulting solution in the freezer overnight. It was also found that the desired product could be prepared by reacting **1** with an excess of LiH or NaH in toluene and heating the solution in an oil bath until the solution turned green in color (approximately 4 h). The complex was found to be EPR active showing a g value of 2.139 g at room temperature and $g_{\parallel} = 2.211$ g and $g_{\perp} = 2.071$ g at $T = 113$ K. Yield = 0.16 g (42%). *Anal.* Calc. for $Ni_2Cl_2P_4C_{50}H_{93}$: C, 59.67; H, 9.31; Cl, 7.05; P, 12.31. Found: C, 58.18; H, 9.60; Cl, 6.86; P, 10.74%.

2.1.4. $[Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2]$ (**4**)

To 50 ml of a toluene solution of $[(dcpm)NiCl_2]$ (**1**) (0.20 g, 0.37 mmol) under nitrogen was added an excess amount of LiH (0.045g, 5.66 mmol). The solution was then heated in an oil bath at 90°C for 12 h, or until the solution turned dark red in color. The solution was then filtered and placed in the freezer. Red crystalline blocks of **4** formed overnight. Yield = 0.19 g (56%). ^1H NMR (C_6D_6, 300 MHz): δ 2.1 (s, 3H, CH_3), 0.8-2.8 (cyclohexyl). ^{31}P NMR (C_6D_6, 300 MHz): δ 23.569 (t, PCy_2, $J = 83.4$ Hz), 111.816 (t, PCy_2Me, $J = 83.4$ Hz).

2.2. X-ray crystallography

Preliminary examination and data collection were performed with Cu Kα (structure **3**) or Mo Kα (structures **1**, **2**, and **4**) radiation on an Enraf–Nonius CAD4 computer controlled kappa axis diffractometer equip-

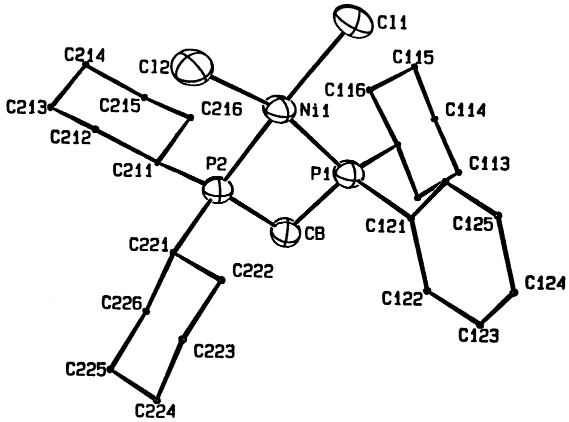


Fig. 1. Molecular structure of [(dcpm)$NiCl_2$] (**1**).

ped with a graphite crystal, incident beam monochromator. The crystallographic structure for [(dcpm)$NiCl_2$] (**1**) was solved using the Patterson–Heavy-atom method, which revealed the position of the Ni atom. The remaining atoms were located using DIRDIF [10] and succeeding difference Fourier synthesis. The crystallographic structure for [Ni(dcpm)$_2$](NO_3)$_2$·2EtOH (**2**) was solved using the structure solution program PATTY in DIRDIF92 [11]. The remaining atoms were located with succeeding difference Fourier synthesis. Hydrogen atoms were included in the refinement but were restrained to ride on the atom to which they were bonded. The crystallographic structures for [Ni_2Cl_2(μ-dcpm)$_2$(μ-H)] (**3**) and [Ni_2(μ-PCy_2)$_2$(PCy_2Me)$_2$] (**4**) were solved using the structure solution program SHELX-86 [12]. The remaining atoms were located in succeeding difference Fourier syntheses. Except as noted in the table of positional parameters, hydrogen atoms were located and added to the structure factor calculations but not refined.

Table 2
Selected bond distances (Å) and angles (°) for [$NiCl_2$(dcpm)] (**1**)

Ni(1)–Cl(1)	2.215(1)	Ni(1)–P(1)	2.152(1)
Ni(1)–Cl(2)	2.204(1)	Ni(1)–P(2)	2.142(1)
P(1)–C(B)	1.843(3)	P(2)–C(B)	1.838(4)
Cl(1)–Ni(1)–Cl(2)	97.60(4)	Ni(1)–P(1)–C(111)	123.2(1)
Cl(1)–Ni(1)–P(1)	95.93(4)	Ni(1)–P(1)–C(121)	111.6(2)
Cl(1)–Ni(1)–P(2)	167.50(5)	Ni(1)–P(1)–C(B)	95.9(1)
Cl(2)–Ni(1)–P(1)	163.34(4)	Ni(1)–P(2)–C(211)	114.7(1)
Cl(2)–Ni(1)–P(2)	92.20(4)	Ni(1)–P(2)–C(221)	120.5(1)
P(1)–Ni(1)–P(2)	75.89(4)	Ni(1)–P(2)–C(B)	96.4(1)
P(1)–C(B)–P(2)	91.7(2)		

All calculations were performed on a VAX computer. Refinement for structures **1**, **3**, **4** was carried out using MolEN [13], while refinement for structure **2** was performed on an AlphaServer 2100 using SHELX-93 [14]. Crystallographic drawings were carried out using the program ORTEP [15] and/or PLUTON [16]. Lorentz and polarization corrections were applied to the data.

2.2.1. [(dcpm)$NiCl_2$] (1)

The molecule can be seen to adopt a distorted square planar geometry for the central $NiCl_2P_2$ core (Fig. 1). Crystal data and data collection parameters are given in Table 1. A listing of important bond distances and angles is found in Table 2. The Ni–P distances (average 2.147(5) Å) are typical for those found in related Ni–P complexes [17]. The P(1)–Ni(1)–P(2) bite angle is 75.89(4)°, typical for a square planar complex. The coordination around the phosphorus atoms is a distorted tetrahedral while all cyclohexyl groups are bonded in an equatorial manner to the phosphorus atoms.

Table 1
Crystal data and data collection parameters

	1	2	3	4
Formula	$NiCl_2P_2C_{25}H_{46}$	$Ni_2P_4O_8N_2C_{54}H_{104}$	$Ni_2Cl_2P_4C_{50}H_{93}$	$Ni_2P_4C_{50}H_{94}$
Formula weight	538.21	1150.76	1006.52	936.62
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$I4_1/a$ (no. 88)	$P2_1/n$ (no. 14)
Unit cell dimensions				
a (Å)	11.124(1)	10.493(3)	22.387(3)	10.662(2)
b (Å)	12.5206(8)	12.816(4)	22.387(3)	22.057(4)
c (Å)	19.783(2)	21.548(4)	20.742(3)	11.155(2)
α (°)	90	90	90	90
β (°)	97.224(9)	97.37(23)	90	96.39(1)
γ (°)	90	90	90	90
V (Å^3)	2733.5(8)	2873(2)	10395(4)	2607(1)
Z	4	2	8	2
D_{calc} (g cm^{-3})	1.308	1.330	1.286	1.193
Temperature (K)	293	296	293	293
Radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Cu Kα (1.54184 Å)	Mo Kα (0.71073 Å)
R	0.044	0.053	0.055	0.037
R_w	0.056	0.141	0.060	0.050

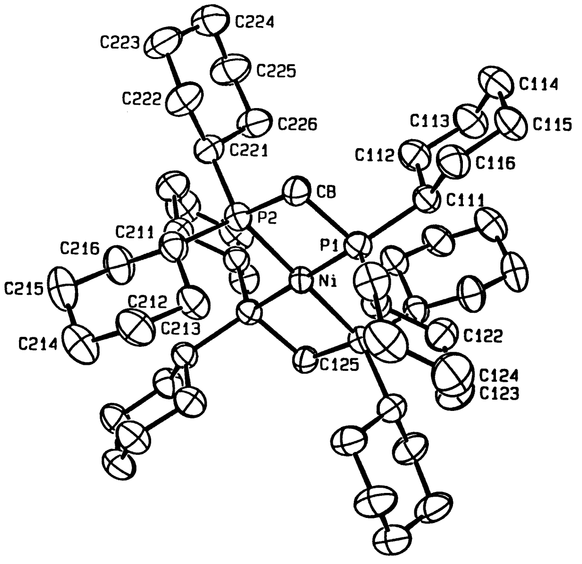


Fig. 2. Molecular structure of $[Ni(dcpm)_2](NO_3)_2 \cdot 2EtOH$ (**2**).

2.2.2. *$[Ni(dcpm)_2](NO_3)_2 \cdot 2EtOH$ (**2**)*

The coordination around the Ni atom can best be described as distorted square planar (Fig. 2). The P(1)–Ni–P(2) bite angle of 73.51(4)° is close to what is expected for a square planar, low spin, nickel d^8 complex. Crystal data and data collection parameters are given in Table 1. A listing of important bond distances and angles is found in Table 3. This is in contrast with the previously determined structure of $Ni(dcpm)_2$ [18], which was determined to have a distorted tetrahedral coordination around the nickel metal center. The coordination around the phosphorus atoms is again distorted tetrahedral while all cyclohexyl groups are bonded in an equatorial manner to the phosphorus atoms. The nitrate ion is extremely disordered, similar to the nitrate ion found in the square planar complex $[Ni(Ph_2CH_2CH_2PPh_2)_2](NO_3)_2$ [19]. In contrast to $[Ni(Ph_2CH_2CH_2PPh_2)_2](NO_3)_2$ our compound was found to crystallize with 2 equiv. of ethanol in the final structure.

Table 3
Selected bond distances (Å) and angles (°) for $[Ni(C_{25}H_{46}P_2)_2](NO_3)_2 \cdot 2CH_3CH_2OH]$ (**2**)

Ni–P(2)	2.2836(11)	Ni–P(1)	2.3095(13)
Ni–P(2)	2.2836(11)	P(1)–C(B)	1.831(4)
Ni–P(1)	2.3095(13)	P(2)–C(B)	1.827(4)
P(2)–Ni–P(2)	179.9990(10)	C(B)–P(1)–Ni	93.80(14)
P(2)–Ni–P(1)	73.51(4)	C(111)–P(1)–Ni	121.14(14)
P(2)–Ni–P(1)	106.49(4)	C(121)–P(1)–Ni	116.22(14)
P(2)–Ni–P(1)	106.48(4)	C(B)–P(2)–C(221)	107.1(2)
P(2)–Ni–P(1)	73.51(4)	C(B)–P(2)–C(211)	104.1(2)
P(1)–Ni–P(1)	179.9980(10)	C(221)–P(2)–C(211)	106.1(2)
C(B)–P(1)–C(111)	106.3(2)	C(B)–P(2)–Ni	94.75(13)
C(B)–P(1)–C(121)	109.1(2)	C(221)–P(2)–Ni	121.20(14)
C(111)–P(1)–C(121)	108.3(2)	C(211)–P(2)–Ni	120.60(14)

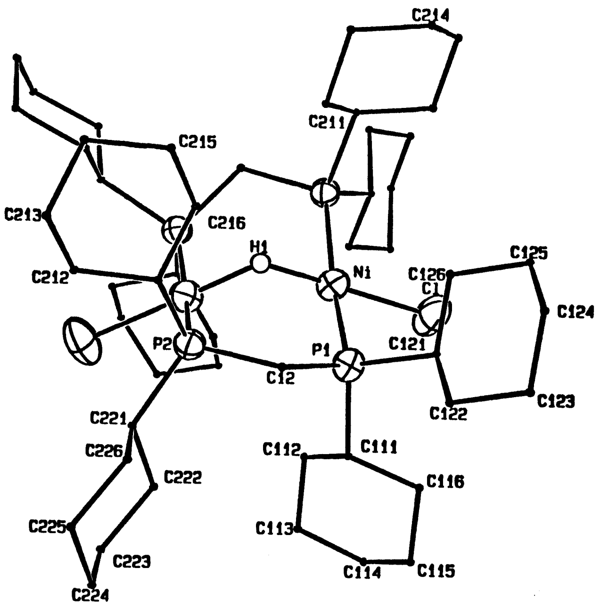


Fig. 3. Molecular structure of $[Ni_2Cl_2(\mu\text{-dcpm})_2(\mu\text{-H})]$ (**3**).

Table 4
Selected bond distances (Å) and angles (°) for $[Ni_2Cl_2(\mu\text{-dcpm})_2(\mu\text{-H})]$ (**3**)

Ni–Ni	2.904(3)	Ni–H(1)	1.61(5)
Ni–Cl	2.268(4)	P(1)–C(12)	1.84(1)
Ni–P(1)	2.212(3)	P(2)–C(12)	1.83(1)
Ni–P(2)	2.213(3)	Cl–Ni–P(2)	93.8(1)
Ni–Ni–Cl	154.6(1)	Cl–Ni–H(1)	179(1)
Ni–Ni–P(1)	87.7(1)	Ni–P(1)–C(12)	116.5(3)
Ni–Ni–P(2)	94.8(1)	Ni–P(2)–C(12)	114.5(3)
Ni–Ni–H(1)	26(4)	P(1)–C(12)–P(2)	115.3(5)
Cl–Ni–P(1)	89.7(1)	Ni–H(1)–Ni	128(8)
P(1)–Ni–P(2)	166.1(2)	P(2)–Ni–H(1)	87(1)
P(1)–Ni–H(1)	89.4(3)		

2.2.3. *$[Ni_2Cl_2(\mu\text{-dcpm})_2(\mu\text{-H})]$ (**3**)*

The structure of $[Ni_2Cl_2(\mu\text{-dcpm})_2(\mu\text{-H})]$ (**3**) can be seen in Fig. 3. Crystal data and data collection parameters are given in Table 1. A listing of important bond distances and angles is found in Table 4. Few examples of Ni 'A-frame' complexes have been structurally characterized. Currently only three such structures have been determined [6,21], this complex constituting the fourth example of this class and the only Ni hydride 'A-frame' complex known. The Ni–H bond distance was found to be 1.61(5) Å. The Ni–Ni distance of 2.904(3) Å shows the absence of any Ni–Ni bonding. The coordination around the phosphorus atoms is a distorted tetrahedral while all cyclohexyl groups are bonded in an equatorial manner to the phosphorus atoms.

2.2.4. $[Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2]$ (4)

The structure of $[Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2]$ (**4**) can be seen in Fig. 4. Crystal data and data collection parameters are given in Table 1. A listing of important bond distances and angles is found in Table 5. The P(1)–Ni(1)–P(2) bond angle of 122.50° giving a trigonal planar coordination around nickel. A Ni–Ni bond distance of 2.3910(8) Å is indicative of a single Ni–Ni metal bond. The symmetry of the molecule is D_{2h} with coplanar Ni and P atoms and a linear arrangement of P(1)–Ni(1)–Ni(1)–P(1). The coordination around the phosphorus atoms is a distorted tetrahedral while all cyclohexyl groups are bonded in an equatorial manner to the phosphorus atoms.

3. Results and discussion

As has been previously shown with dppm, dcpm was found to react with $[NiCl_2]\cdot 6H_2O$ as well as $[Ni(NO_3)_2]\cdot 6H_2O$ to form the corresponding Ni(II) complexes (Figs. 1 and 2). In the case of $[NiCl_2]\cdot 6H_2O$ the expected complex, $[(dcpm)NiCl_2]$ (**1**), was formed in high yield, giving a diamagnetic, distorted square planar geometry around the NiP_2Cl_2 core (Scheme 1). The structure is indicative of a nickel d^8, $+2$ oxidation state with C_{2v} symmetry. All four of the complexes prepared in this study were found to contain phosphines resting in a tetrahedral environment, with the cyclohexanes being bound in an equatorial manner. The $[Ni(NO_3)_2]\cdot 6H_2O$ also reacts quantitatively with dcpm in ethanol forming $[Ni(dcpm)_2](NO_3)_2\cdot 2EtOH$ (Scheme 2). The NiP_4 core having a square planar geometry and a D_{4h} symmetry in the solid state. The ^1H NMR is characteristic of a paramagnetic, contact shifted NMR suggesting the possibility of a square planar/tetrahedral structure in solution. Again the nickel d^8 metal center has a $+2$ oxidation state.

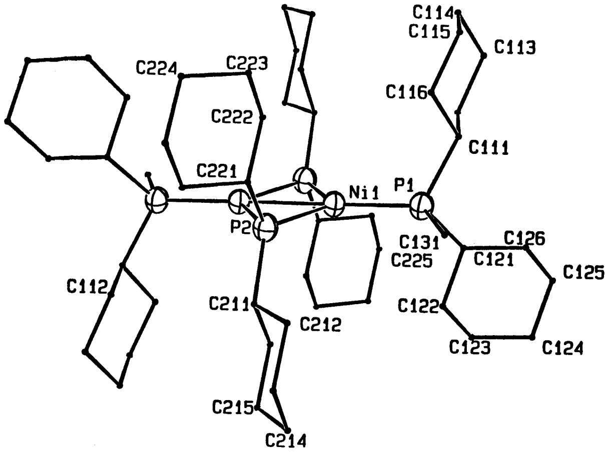
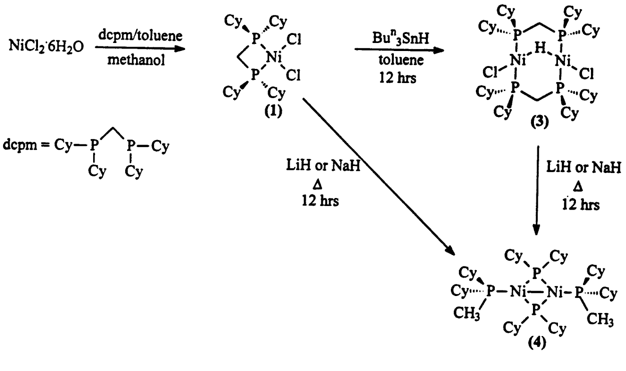


Fig. 4. Molecular structure of $[Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2]$ (**4**).

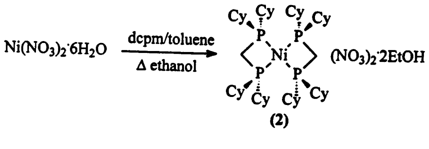
Table 5
Selected bond distances (Å) and angles (°) for $Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2$ (**4**)

Ni(1)–Ni(1)	2.3910(8)	Ni(1)–P(2)	2.1708(9)
Ni(1)–P(1)	2.1586(9)	Ni(1)–P(2)	2.1778(9)
Ni(1)–Ni(1)–P(1)	179.05(3)	C(111)–P(1)–C(121)	103.3(2)
Ni(1)–Ni(1)–P(2)	56.78(3)	C(111)–P(1)–C(131)	100.8(2)
Ni(1)–Ni(1)–P(2)	56.50(3)	C(121)–P(1)–C(131)	101.8(2)
P(1)–Ni(1)–P(2)	122.50(4)	Ni(1)–P(2)–Ni(1)	66.71(3)
P(1)–Ni(1)–P(2)	124.20(3)	Ni(1)–P(2)–C(221)	122.9(1)
P(2)–Ni(1)–P(2)	113.29(3)	Ni(1)–P(2)–C(211)	120.5(1)
Ni(1)–P(1)–C(111)	116.1(1)	Ni(1)–P(2)–C(211)	121.8(1)
Ni(1)–P(1)–C(121)	114.9(1)	Ni(1)–P(2)–C(221)	121.1(1)
Ni(1)–P(1)–C(131)	117.7(1)	C(211)–P(2)–C(221)	102.4(1)

A study of the reactivity of $[(dcpm)NiCl_2]$ (**1**) was then undertaken. It was found that by reacting **1** with $^nBu_3SnH$ (or LiH and heating for 4 h) in toluene a green, paramagnetic complex could be isolated, $[Ni_2Cl_2(\mu\text{-}dcpm)_2(\mu\text{-}H)]$ (**3**) (Scheme 1). The X-ray crystal structure of **3** shows that the dcpm ligand bonds in a bridging manner (Fig. 3) and that the coordination around each of the Ni metal centers (NiP_2HCl) is approximately square planar. The product is currently the only example of a nickel 'A-frame' complex with a bridging hydride in the apex position. The Ni–Ni bond distance of 2.904(3) Å shows the absence of any Ni–Ni bonding as can be seen in Table 6. The paramagnetic structure gives an EPR signal with a g value of 2.139 g at room temperature and $g_{\parallel} = 2.211$ g and $g_{\perp} = 2.071$ g at $T = 113$ K. Compound **3** has been found to react



Scheme 1.



Scheme 2.

Table 6
Ni–Ni bond lengths for selected nickel compounds [a]

Compound	d(Ni–Ni) (Å)	Reference
Ni–Ni metallic radii	2.492	
$[\mathrm{Ni_2(\mu dcpm)_2Cl_2(\mu H)}]$	2.904(3)	this work
$[\mathrm{Ni_2(\mu dppm)_2(NCS)_2(\mu C{=}CH_2)}]$	284.0(4)	[20]
$[\mathrm{Ni_2(\mu dcpm)_2Cl_2(\mu SO)}]$	3.308(1)	[6]
$[\mathrm{Ni_2(\mu dppm)_2Cl_2(\mu CNC_6H_5)}]$	2.917(4)	[6]
$[\mathrm{\{Ni(dippe)\}_2(\mu H)_2][BPh_4]}$	2.316(5) [b]	[21]
$[\mathrm{Ni_2(dcpp)_2(\mu H)_2}]$	2.441(1) [b]	[22]
$[\mathrm{Ni_2(dippp)_2(\mu H)_2}]$	2.438(1) [b]	[23]
$[\mathrm{Ni_2(\mu ^tBu_2P)(PMe_3)}]_2$	2.375(3) [b]	[5]
$[\mathrm{Ni(\mu(tBu)(H)P)(PMe_3)_2}]_2$	2.559(2) [b]	[24]
$[\mathrm{Ni_2(\mu Pcy_2)_2(Pcy_2Me)_2}]$	2.3910(8) [b]	this work

[a] dcpm = bis(dicyclohexylphosphino)methane; dppm = bis(diphenylphosphino)methane; dcpp = bis(dicyclohexylphosphino)propane; dippe = bis(diisopropylphosphino)ethane; dippp = bis(diisopropylphosphino)propane.

[b] Indicates actual Ni–Ni bonds.

with various organic molecules including alkynes and isocyanides. At this point no products have been isolated, but studies continue.

Heating $[\mathrm{Ni_2Cl_2(\mu\text{-}dcpm)_2(\mu\text{-}H)}]$ (**3**), for approximately 12 h, yields the red complex $[\mathrm{Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2}]$ (**4**) (Scheme 1). The desired complex can also be obtained from heating **1** with LiH in an oil bath for 12 h at approximately 90°C . A Ni–Ni bond distance of 2.3910(8) Å is indicative of a single Ni–Ni metal bond (Table 6). The linear P–Ni–Ni–P bonding gives a D_{2h} symmetry. Further reactivity of the complex has yet to be investigated.

4. Supplementary material

Crystal data and data collection parameters are contained in Table 1. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 133445 (**1**), 133446 (**2**), 133447 (**3**), and 133448 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ [fax +44-1223-336033] or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgements

We thank the Department of Energy, Grove City College and the Purdue Research Foundation for support of this research. Special thanks to Steve Boone, Central Missouri State University, for his technical advice.

References

[1] (a) H.H. Karsch, Chem. Ber. 116 (1983) 1643. (b) P. Hofmann, L.A. Perez-Moya, M.E. Krause, O. Kumberger and G. Muller, Z. Naturforsch, 45b (1990) 897.

[2] (a) J. Chatt, F.A. Hart, H.R. Watson, J. Chem. Soc. (1962) 2537. (b) G.R. Van Hecke, W. de Horrocks, Jr., Inorg. Chem. 5 (1966) 1968.

[3] C. Ercolani, J.V. Quagliano, L.M. Vallarino, Inorg. Chim. Acta 7 (1973) 413.

[4] C.F. Nobile, G. Vasapollo, P. Giannoccaro, A. Sacco, Inorg. Chim. Acta 48 (1981) 261.

[5] R.A. Jones, A.L. Stuart, J.L. Atwood, W.E. Hunter, R.D. Rogers, Organometallics 1 (1982) 1721.

[6] (a) J.K. Gong, P.E. Fanwick, C.P. Kubiak, J. Chem. Soc., Chem. Commun. 17 (1990) 1190. (b) S. Hinze, J.K. Gong, P.E. Fanwick, C.P. Kubiak, J. Organomet. Chem. C10 (1993) 458.

[7] (a) A.L. Balch, C.T. Hunt, C-L. Lee, M.M. Olmstead, J.P. Farr, J. Am. Chem. Soc. 103 (1981) 3764. (b) R.T. Puddephatt, Chem. Soc. Rev. 12 (1983) 99. (c) K.A. Azam, A.A. Frew, B.R. Lloyd, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, Organometallics 4 (1985) 1400. (d) P.G. Pringle, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1983) 889. (e) C.-L. Lee, B. Besenyei, B.R. James, D.A. Nelson, M.A. Lilga, J. Chem. Soc., Chem. Commun. (1985) 1175.

[8] K.K. Chow, C.A. McAuliffe, Inorg. Chim. Acta 10 (1974) 197.

[9] (a) J.S. Yu, I.P. Rothwell, J. Chem. Soc., Chem. Commun. (1992) 632. (b) C.A. Morgan, P.E. Fanwick, I.P. Rothwell, Inorg. Chim. Acta 224 (1994) 105. (c) I.P. Rothwell, Chem. Commun. (1997) 1331. (d) P.N. Riley, J.R. Clark, P.E. Fanwick, I.P. Rothwell, Inorg. Chim. Acta 288 (1999) 35.

[10] P.T. Beurskens, W.P. Bosman, H.M. Doesburg, R.O. Gould, Th. E.M. van den Hark, P.A.J. Prick, J.H. Noordik, G. Beurskens, V. Parthasarathi, H.J. Bruins Slot, R.C. Haltiwanger, M. Strumpel, J.M.M. Smits, Technical Report 1, Crystallography Laboratory Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1984.

[11] P.T. Beurskens, G. Admirall, G. Beurskens, W.P. Bosman S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF92 Program System, Technical Report, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

[12] G.M. Sheldrick, Institut fur Anorganische Chemie der Universitat Gottingen, Germany, 1986.

[13] C.K. Fair, MolEN Structure Determination System, Delft Instruments, The Netherlands, 1990.

[14] G.M. Sheldrick, SHELXS93. A Program for Crystal Structure Refinement, University of Gottingen, Germany, 1993.

[15] C.K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.

[16] A.L. Spek, PLUTON. Molecular Graphics Program, University of Ultrecht, The Netherlands, 1991.

[17] D.J. Brauer, C. Kruger, J. Organomet. Chem. 77 (1974) 423.

[18] C. Kruger, Y-H. Tsay, Acta Crystallogr., Sect. B 28 (1972) 1941.

[19] A.F. Williams, Acta Crystallogr., Sect. C 45 (1989) 1002.

[20] X.R. Fontaine, S.J. Higgins, B.L. Shaw, M. Thorton-Pett, W. Yichang, J. Chem. Soc., Dalton Trans. (1987) 1501.

[21] M.J. Tenorio, M.C. Puerta, P. Valerga, J. Chem. Soc., Dalton Trans. (1996) 1305

[22] B.L. Barnett, C. Kruger, Y.H. Tsay, Chem. Ber. 110 (1977) 3900.

[23] M.D. Fryzuk, G.K.B. Clentsmith, D.B. Leznoff, S.J. Rettig, S.J. Geib, Inorg. Chim. Acta 265 (1997) 169.

[24] R. Jones, N.C. Norman, M.H. Seeberger, J. Atwood, W.E. Hunter, Organometallics 2 (1983) 1629.