

# Synthesis, reactions and structure of bromo( $\eta^5$ -diphenylphosphinylcyclopentadienyl)nickel(II) dimer

Matthew S. Blais <sup>a</sup>, Robin D. Rogers <sup>b</sup>, Marvin D. Rausch <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA

<sup>b</sup> Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA

Received 28 May 1999; accepted 19 July 1999

Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday, and in recognition of his many outstanding contributions to organometallic chemistry.

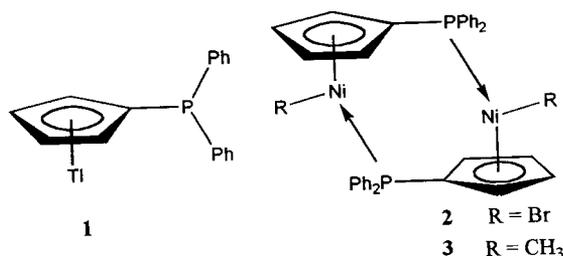
## Abstract

The reaction of diphenylphosphinylcyclopentadienylthallium (**1**) with  $\text{NiBr}_2 \cdot 2\text{DME}$  has produced  $\text{Ni}_2(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Br}_2$  (**2**) in quantitative yield. A reaction of **2** with methyl-lithium affords  $\text{Ni}_2(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CH}_3)_2$  (**3**) in high yield. Both **2** and **3** have been characterized by means of single crystal X-ray diffraction studies and shown to be homobimetallic, with cyclic dimeric structures. Each ligand bridges two metal centers via P coordination to one and  $\eta^5$ -coordination of the cyclopentadienyl moiety to a second  $\text{Ni}^{2+}$ . Each nickel atom is thus formally five-coordinate with average bonding parameters of Ni–Centroid (Cp), Ni–P, and Ni–X of 1.760(5), 2.154(5), Br: 2.301(8) Å (**2**) and 1.769(5), 2.113(5),  $\text{CH}_3$ : 1.944(1) Å (**3**). The P–Ni–X angles are compressed in **3** compared to **2** by an average of 4°. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Diphenylphosphinylcyclopentadienyl; Nickel; Homobimetallic; X-ray diffraction

## 1. Introduction

In 1983, we described a high yield synthesis of diphenylphosphinylcyclopentadienylthallium (**1**) and demonstrated the utility of this heterodifunctional reagent in the formation of a series of titanium-manganese heterobimetallic compounds [1]. In continuation of our studies on phosphinyl-substituted cyclopentadienyl derivatives of the transition metals, we report here on reactions of **1** leading to dimeric diphenylphosphinylcyclopentadienyl derivatives of a Group 10 metal, nickel.



## 2. Results and discussion

### 2.1. Synthetic studies

The serendipitous discovery of bromo( $\eta^5$ -diphenylphosphinylcyclopentadienyl)–nickel(II) dimer (**2**) resulted from an attempted synthesis of the corresponding disubstituted bis( $\eta^5$ -cyclopentadienyl)nickel compound,  $\text{Ni}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2$ . Several substituted nickelocenes have previously been prepared by reaction of two equivalents of a substituted cyclopentadienylthallium, -lithium or -sodium reagent with anhydrous nickel halides [2–5]. For this reason, it was anticipated that the reaction of two equivalents of **1** with  $\text{NiBr}_2 \cdot 2\text{DME}$  (DME = 1,2-dimethoxyethane) would yield  $\text{Ni}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2$ . On the other hand, there is a strong propensity to form monocyclopentadienylnickel compounds with a phosphine and a halide as the remaining ligands in the coordination sphere of nickel under a wide variety of reaction conditions [6–14].

The synthesis of **2** from **1** and  $\text{NiBr}_2 \cdot 2\text{DME}$  was performed under a variety of conditions, giving identical results. Variation of the solvent system or the ratio

\* Corresponding author.

of the reactants did not change the outcome. A large excess or a single equivalent of the thallium reagent **1** afforded the dimer **2** exclusively. Use of a single equivalent of **1** produced **2** in nearly quantitative yield. The  $^1\text{H-NMR}$  spectrum of **2** was consistent with the proposed structure. The product was readily crystallized from dichloromethane and hexane, and incorporated 1/2 mol of  $\text{CH}_2\text{Cl}_2$ , as shown by  $^1\text{H-NMR}$ , elemental analyses and by X-ray structural studies (vide infra). Dimer **2** was extremely air stable both as a solid and in solution.

A reaction of **2** with two equivalents of methyl-lithium caused a color change from purple to green. Purification of the reaction product by column chromatography and crystallization afforded methyl( $\eta^5$ -diphenylphosphinylcyclopentadienyl)nickel(II) dimer (**3**) in high yield. The  $^1\text{H-NMR}$  spectrum of **3** exhibited a doublet at  $\delta -0.94$  ppm, assignable to the methyl protons. The coupling constant,  $J_{\text{P-H}} = 5.88$  Hz, is consistent with phosphorus bonded to nickel in a dimeric structure.

Attempted synthesis of the dihydride analog of **3** from **2** and  $\text{NaH}$ ,  $\text{NaBH}_4$  or  $\text{LiAlH}_4$  were not successful, as were attempted polymerizations of ethylene, propylene or styrene using **3** and methylaluminumoxane (MAO).

## 2.2. Structural studies

Both **2** and **3** crystallize as discrete dimers with the diphenylphosphinylcyclopentadienyl ligands bridging two metal centers via P-donor coordination to one nickel position and  $\eta^5$  bonding of the cyclopentadienyl substituents to the second metal (Figs. 1 and 2). The two title compounds are very similar as is apparent by inspection of Figs. 1 and 2, however, despite the fact that both crystallize in the monoclinic space group  $P2_1/c$ , they are not isostructural. Compound **2** crystallizes as a hemi-methylene chloride solvate. (The presence of the disordered solvent does not appear to have any influence on the structure of the dimer.)

The coordination parameters of the formally 5-coordinate Ni(II) centers are summarized in Table 2. The two metals within a given compound show similar bonding patterns with a single exception. The P–Ni–Br angles in **2** differ by  $3.4^\circ$ , a difference of some  $85\sigma$ . There is also a small, but perhaps statistically significant variation in the Ni–P distances within each compound. The Ni–P distances differ by  $0.01\text{ \AA}$  in both **2** ( $8\sigma$ ) and **3** ( $15\sigma$ ).

When comparing bonding parameters between **2** and **3**, the differences expected by changing from  $\text{X} = \text{Br}$  to  $\text{CH}_3$  are manifest primarily in the Ni–P distances. The Ni–Br separations average  $2.301(8)\text{ \AA}$  in **2** versus the Ni– $\text{CH}_3$  bond distances of  $1.944(3)\text{ \AA}$ . Despite the closer approach of the methyl groups to Ni, the Ni–P

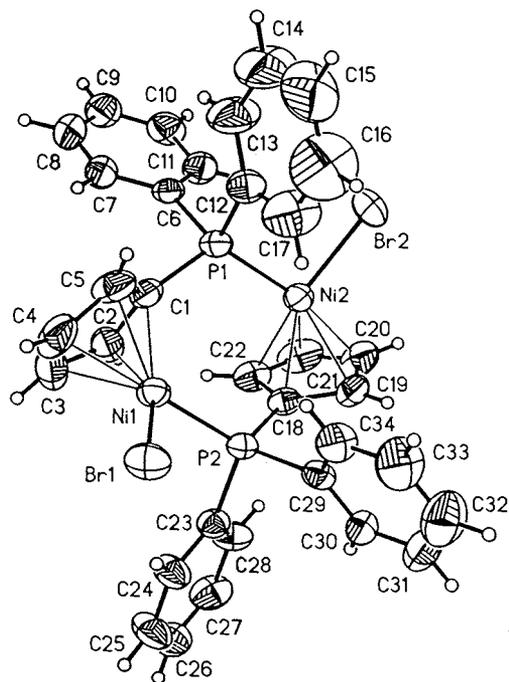


Fig. 1. ORTEP diagram (50% probability ellipsoids) and atom labeling scheme for **2**. The solvent molecule is omitted for clarity.

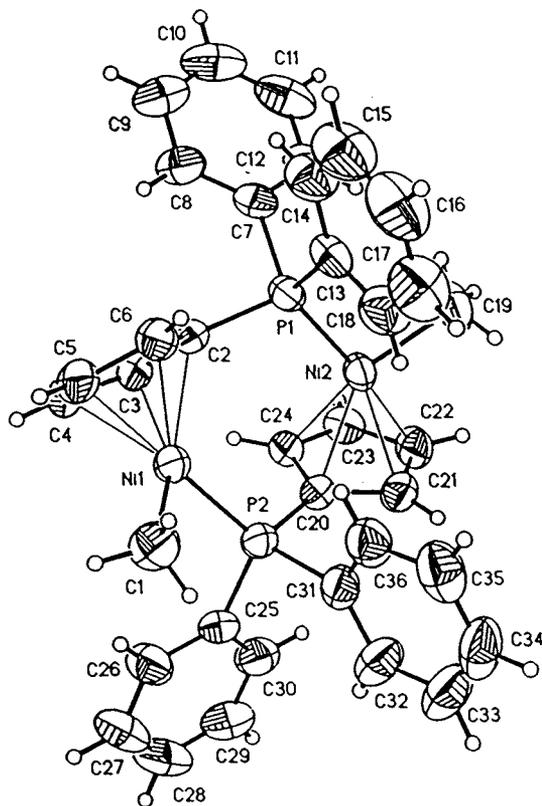


Fig. 2. ORTEP diagram (50% probability ellipsoids) and atom labeling scheme for **3**.

separations in **3** are shorter (2.113(5) Å average) than found for **2** (2.154(5) Å). As a result of these differences, the P–Ni–X angles are compressed in **3** compared to **2** by an average of 4°. (The average Ni–P separations in both **2** and **3** and the Ni–Br distance in **2** are shorter than corresponding distances found for 4-coordinate Ni(II) in Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>NiX<sub>2</sub> (X = Br [15], Cl [16]) and Yb(THF)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ni(CO)<sub>2</sub> [17] where the Ni–P distances range from 2.223 to 2.321 Å and the Ni–Br bond lengths are 2.351 and 2.344 Å.)

The Ni–C( $\eta^5$ ) interactions are almost identical in both compounds. All 20 Ni–C( $\eta^5$ ) distances have only a 0.1 Å range, and the individual Ni–C distances are essentially identical for all four unique Ni atoms. The four Ni–Centroid distances range from 1.755 to 1.774 Å, a difference of only 0.019 Å. The average Centroid–Ni–X angles are identical for both **2** and **3** (128°) and the 4° difference in Centroid–Ni–P angles may be the result of the longer Ni–P separations in **2**. There is also a 2° compression of the average Ni–P–Cp angle in **3** (115.8(1)° versus **2** (117.65(5)°).

### 3. Experimental

All operations were carried out under an argon atmosphere using Schlenk techniques unless otherwise noted. The argon was deoxygenated by BASF catalyst and dried with P<sub>2</sub>O<sub>5</sub> and molecular sieves. Reaction solvents were purified by distillation from sodium–potassium alloy under argon, except for dichloromethane which was distilled under argon from calcium hydride. Diphenylphosphinylcyclopentadienyl–thallium was prepared by a literature procedure [1]. All other reagents were obtained from Aldrich Chemical. Melting points are uncorrected and were determined under nitrogen in sealed capillary tubes. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. <sup>1</sup>H- and <sup>31</sup>P-NMR spectra were obtained on Bruker NR-80 or AC-200 spectrometers.

#### 3.1. Bromo( $\eta^5$ -diphenylphosphinylcyclopentadienyl)-nickel(II) dimer (**2**)

In a 250 ml Schlenk flask equipped with a pressure equalizing addition funnel and magnetic stirring bar were placed 1.09 g (0.0185 mol) of nickel powder and 50 ml of DME. Bromine (1.02 ml, 0.0195 mol) diluted in 50 ml of DME was added dropwise with vigorous stirring. The mixture was allowed to react for 2 h yielding an amber solution and a yellow precipitate. Into a separate 500 ml Schlenk flask were added 9.3 g (0.020 mol) of diphenylphosphinylcyclopentadienylthallium, 100 ml of DME and a magnetic stirring bar, and

the flask was sealed with a rubber septum. The addition funnel was removed from the first flask and replaced with a rubber septum. The nickel bromide solution and suspension were then transferred to the 500 ml flask via a 16 gauge cannula (50 ml of additional DME was injected into the 250 ml flask to rinse out any remaining nickel bromide into the reaction flask). During the addition, the contents of the flask changed from a colorless solution with a white suspension to a dark purple solution with a gray precipitate. The reaction mixture was stirred overnight and then filtered through a Schlenk frit containing a 2 cm pad of Celite. The solvent was removed under vacuum and the resulting solid (6.85 g, 95.5% yield) was dissolved in 100 ml of toluene, filtered, and concentrated to a volume of 50 ml. The flask was placed in a freezer at –20°C and the contents allowed to crystallize for 5 days. The crystals were collected (5.94 g, 82.2% yield) on a frit and thoroughly dried under vacuum (mp 318°C decomp.).

<sup>1</sup>H-NMR indicated the presence of toluene trapped in the crystals, therefore the product was recrystallized from dichloromethane. A subsequent <sup>1</sup>H-NMR spectrum indicated the presence of dichloromethane trapped in the crystals. Therefore a sample was ground to a fine powder, placed under high vacuum and heated to 50°C overnight. <sup>1</sup>H-NMR still indicated the presence of 1/2 mol of dichloromethane. X-ray quality crystals were grown by dissolving the purple crystals in dichloromethane, layering an equal volume of hexane on top, and allowing the solution to stand overnight. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  8.08–7.81 (m, 12 H, aromatic), 7.48 (m, 8 H, aromatic), 5.76 (br s, 4 H, C<sub>5</sub>H<sub>4</sub>), 5.25 (s, 1 H, CH<sub>2</sub>Cl<sub>2</sub>); 5.13 (br s, 4 H, C<sub>5</sub>H<sub>4</sub>). <sup>31</sup>P-NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $\delta$  25.10 (s). Anal. Found: C, 51.22; H, 3.51; Br, 19.3, Ni, 14.3%. C<sub>34.5</sub>H<sub>29</sub>Br<sub>2</sub>ClNi<sub>2</sub>P<sub>2</sub> Calc. 50.64; H, 3.37; Br, 19.53; Ni, 14.35%.

#### 3.2. Methyl( $\eta^5$ -diphenylphosphinylcyclopentadienyl)-nickel(II) dimer (**3**)

In a 500 ml Schlenk flask equipped with a magnetic stirring bar was added 200 ml of benzene and 3.85 (4.40 mmol) of bromo( $\eta^5$ -diphenylphosphinylcyclopentadienyl)-nickel(II) dimer. The solution was stirred until the solid completely dissolved and 6.00 ml of 1.4 M methyl-lithium (8.4 mmol) was slowly added by syringe. The reaction remained dark purple for several hours and then turned dark green with a white precipitate. Filtration of the solution and removal of the solvent under vacuum gave 4.26 g (96% yield) of an air-sensitive green solid. The crude product was chromatographed on alumina and eluted with hexane/benzene (1:1) to give a single green band. The solvent was removed and the resulting green solid was crystallized by dissolving it in a minimum of dichloromethane, layering hexane on the top, and allowing the solution to stand for 2 days.

Table 1  
Summary of crystallographic data for **2** and **3**

	[Ni <sub>2</sub> (η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub> ]·0.5CH <sub>2</sub> Cl <sub>2</sub> ( <b>2</b> )	[Ni <sub>2</sub> (η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> ] ( <b>3</b> )
Color/shape	Black/parallelepiped	Black/parallelepiped
Empirical formula	C <sub>34.5</sub> H <sub>29</sub> Br <sub>2</sub> ClNi <sub>2</sub> P <sub>2</sub>	C <sub>36</sub> H <sub>34</sub> Ni <sub>2</sub> P <sub>2</sub>
Formula weight	818.21	645.99
Temperature (K)	294(2)	295(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	9.5697(1)	10.2364(2)
<i>b</i> (Å)	21.2031(4)	19.9515(4)
<i>c</i> (Å)	16.1565(3)	15.1014(2)
β (°)	100.9210(10)	99.235(1)
Volume (Å <sup>3</sup> )	3218.90(9)	3044.21(9)
<i>Z</i>	4	4
ρ <sub>calc</sub> (g cm <sup>-3</sup> )	1.688	1.409
μ (mm <sup>-1</sup> )	3.859	1.366
Radiation/λ (Å)	0.71073	0.71073
Measured/Independent/observed reflections	12748/4635 ( <i>R</i> <sub>int</sub> = 0.0638)/4067 ( <i>I</i> > 2σ( <i>I</i> ))	12007/4343 ( <i>R</i> <sub>int</sub> = 0.0477)/3937 ( <i>I</i> > 2σ( <i>I</i> ))
Relative transmission factors (%)	58.1/98.7	Not measured
Data/parameters	4623/377	4331/363
Goodness-of-fit	1.105	1.092
Weight parameters	0.0400, 5.7162	0.0345, 1.2595
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] data	<i>R</i> <sub>1</sub> = 0.0427, <i>wR</i> <sub>2</sub> = 0.1035	<i>R</i> <sub>1</sub> = 0.0289, <i>wR</i> <sub>2</sub> = 0.0757
<i>R</i> Indices (all data)	<i>R</i> <sub>1</sub> = 0.0501, <i>wR</i> <sub>2</sub> = 0.1097	<i>R</i> <sub>1</sub> = 0.0336, <i>wR</i> <sub>2</sub> = 0.0815

X-ray quality crystals were obtained, mp 195–196°C. A sample was powdered and placed under high vacuum overnight. Anal. Found: C, 66.33; H, 5.25%. C<sub>36</sub>H<sub>34</sub>Ni<sub>2</sub>P<sub>2</sub>. Calc.: C, 66.93; H, 5.31%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.87–7.36 (m, 20 H, aromatic), 5.36 (m, 8 H, C<sub>5</sub>H<sub>4</sub>), –0.94 (d, 6 H, *J*<sub>P–H</sub> = 5.88 Hz, CH<sub>3</sub>). <sup>31</sup>P-NMR (CH<sub>2</sub>Cl<sub>2</sub>) δ 34.89 (s).

### 3.3. X-ray data collection, structure determination and refinement for compounds **2** and **3**

Black single crystals of the title compounds were mounted on a fiber and transferred to the goniometer of a Siemens CCD area detector-equipped diffractometer (SMART). The space groups were determined to both be the centric *P*2<sub>1</sub>/*c* from the systematic absences,

although the two compounds are not isostructural. A summary of data collection parameters is given in Tables 1 and 2.

A methylene chloride molecule was found in difference Fourier maps of **2** disordered across a center of inversion. The disorder model chosen results in six different possible locations for the solvent molecule. The resolution required four atomic positions, two of which have partial occupancy by both Cl and C atoms. Position X(1) was refined with 1/3 occupancy Cl and 1/3 occupancy C, while position X(2) was 1/6 occupancy Cl and 1/6 occupancy C. The remaining two positions were refined as 1/3 (Cl(1A)) and 1/6 (Cl(1B)) occupancy Cl. The total occupancy corresponds to 1/2 molecule of methylene chloride in the asymmetric unit (per dimer of **2**).

Table 2  
Comparison of selected distances (Å) and angles (°)

Atoms	<b>2</b> Ni(1), P(2), Br(1), Cent1 <sup>a</sup>	<b>2</b> Ni(2), P(1), Br(2), Cent2 <sup>a</sup>	<b>3</b> Ni(1), P(2), C(1), Cent1 <sup>a</sup>	<b>3</b> Ni(2), P(1), C(19), Cent2 <sup>a</sup>
Ni–P	2.1593(13)	2.1489(13)	2.1081(7)	2.1186(7)
Ni–X	2.3019(8)	2.3002(9)	1.944(3)	1.944(3)
Ni–Cent <sup>a</sup>	1.755(2)	1.765(2)	1.764(1)	1.774(1)
Ni–C(Cp) range	2.090(5)–2.170(6)	2.073(5)–2.158(6)	2.079(3)–2.158(3)	2.086(2)–2.173(2)
Ni–C (Cp) avg	2.13(3)	2.12(3)	2.13(3)	2.14(3)
P–Ni–X	98.17(4)	94.77(4)	92.28(9)	92.34(9)
P–Ni–Cent	134.2	135.8	139.7	139.2
X–Ni–Cent	127.4	129.4	128.0	128.4

<sup>a</sup> Cent1 is the centroid of the five cyclopentadienyl ring carbon atoms bonded to Ni(1), Cent2 that for the cyclopentadienyl ring bonded to Ni(2).

Compound **3** was solved and refined without incident. The hydrogen atoms of both compounds (except those associated with the disordered solvent molecule in **2**) were placed in calculated positions and allowed to ride on the bonded atom with  $B = 1.2 \cdot U_{eqv}(C)$ . The methyl hydrogen atoms in **3** were included as a rigid group with rotational freedom at the bonded carbon atom ( $B = 1.2 \cdot U_{eqv}(C)$ ). Refinement of nonhydrogen atoms (except for the disordered solvent molecule in **2**) was carried out with anisotropic temperature factors.

## References

- [1] M.D. Rausch, B.H. Edwards, R.D. Rogers, J.L. Atwood, *J. Am. Chem. Soc.* 105 (1983) 3882.
- [2] E.O. Fischer, R. Jira, *Z. Naturforsch., Teil b* 8 (1953) 217.
- [3] H. Werner, T. Dernberger, *J. Organomet. Chem.* 198 (1980) 97.
- [4] W.P. Hart, D.W. Macomber, M.D. Rausch, *J. Am. Chem. Soc.* 102 (1980) 1196.
- [5] B.G. Conway, M.D. Rausch, *Organometallics* 4 (1985) 688.
- [6] G.E. Schroll, US Patent 3-054-815, *Chem. Abstr.* 58 (1963) (1962) 1494c.
- [7] W.K. Schropp, *J. Inorg. Nucl. Chem.* 24 (1962) 1690.
- [8] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, N. Hagi-hara, *J. Organomet. Chem.* 6 (1966) 86.
- [9] M. Van der Akker, F. Jellinek, *Rec. Trav. Chim. Pays-Bas* 86 (1967) 897.
- [10] Yu. A. Ustynyuk, T.I. Voevodskaya, N.A. Zharikova, N.A. Ustynyuk, *Dokl. Akad. Nauk SSSR*, 181 (1968) 372.
- [11] M.D. Rausch, Y.F. Chang, H.B. Gordon, *Inorg. Chem.* 8 (1969) 1355.
- [12] Ch. Moberg, M. Nilsson, *J. Organomet. Chem.*, 49 (1973) 243.
- [13] K.W. Barnett, *J. Chem. Educ.* 51 (1974) 422.
- [14] F. Mathey, *J. Organomet. Chem.* 87 (1975) 371.
- [15] I.R. Butler, W.R. Cullen, T.-J. Kim, S.J. Rettig, J. Trotter, *Organometallics* 4 (1985) 972.
- [16] U. Casellato, D. Ajo, G. Valle, B. Corain, B. Longato, R. Graziani, *J. Crystallogr. Spectrosc. Res.* 18 (1988) 583.
- [17] G.B. Deacon, C.M. Forsyth, W.C. Patalinghug, A.H. White, A. Dietrich, H. Schumann, *Aust. J. Chem.* 45 (1992) 567.