ELSEVIER

Journal of Organometallic Chemistry 490 (1995) 189–195

Journal of Organometallic Chemistry

Reactions of nickelocene with methyl-, ethyl- and vinyl-lithium compounds. Hydrogen elimination and cyclopentadienyl ring hydrogenation

S. Pasynkiewicz *, W. Buchowicz, J. Popławska, A. Pietrzykowski, J. Zachara

Faculty of Chemistry, Warsaw Technical University, Koszykowa 75, 00-662 Warsaw, Poland

Received 3 August 1994

Abstract

It has been shown that bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel, $(NiCp)_2(\mu\text{-}C_5H_6)$, and ($\eta^5$-cyclopentadienyl)($\eta^3$-cyclopentenyl)nickel, $CpNi(\eta^3\text{-}C_5H_7)$, are formed in the reaction of nickelocene with methyl-lithium and with 1-phenyl-2-methylpropenyl-lithium. The compound $(NiCp)_2(\mu\text{-}C_5H_6)$ can be only formed as a result of the reduction of the cyclopentadienyl ring bonded to the nickel atom whereas the formation of $CpNi(\eta^3\text{-}C_5H_7)$ can be explained by the further hydrogenation of cyclopentadiene formed in the earlier reaction steps. $(NiCp)_2(\mu\text{-}C_5H_6)$ has been fully characterised spectrometrically and its X-ray structure determined. It crystallises in the orthorhombic system, space group *Pnma*, with four molecules per unit cell.

Keywords: Nickel; Lithium; Cyclopentadienyl; Nuclear magnetic resonance; X-ray diffraction; Crystal structure

1. Introduction

We have found previously that nickelocene reacts with methyl-lithium to form a (μ_3-ethylidyne)trinickel cluster [Eq. (1)] [1]:

$$LiCH_3 + NiCp_2 \xrightarrow[-LiCp;\ -CH_4]{0-20°C} (NiCp)_3(\mu_3\text{-}CCH_3) \qquad (1)$$

Clusters with more than three NiCp moieties are also formed in addition to the trinickel cluster. These multinuclear clusters will be the subject of further papers.

We have recently found that, in addition to the above clusters, the bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel complex $(NiCp)_2C_5H_6$ and a small amount of the π-allyl compound $CpNi(\eta^3\text{-}C_5H_7)$ are also formed in this reaction.

Bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel was first obtained by Fischer et al. in 0.5% yield (based on NiI_2) in the reaction of NiI_2 with NaCp in the presence of cyclopentadiene [2]. On the basis of ^1H NMR, IR and mass spectra, these authors have discussed possible structures for this compound. Pagueitte and Dahl studied the reactions of nickelocene with an equimolar amount of sodium naphtalenide in THF [3] and noted that $(NiCp)_2(\mu\text{-}C_5H_6)$ was formed besides other nickel complexes; however, no attempt was made to isolate this complex.

In this paper we report the formation of both the above complexes as a result of the reaction of nickelocene with methyl-lithium and 1-phenyl-2-methylpropenyl-lithium. Both complexes are formed as a result of cyclopentadienyl ring hydrogenation either by the agostic hydrogen from the methyl group bonded to nickel in the reaction of $NiCp_2$ with $LiCH_3$ or by the γ-H of the 1-phenyl-2-methylpropenyl group in the reaction of $NiCp_2$ with $LiC(C_6H_5)=C(CH_3)_2$.

2. Results

2.1. The $NiCp_2 + LiCH_3$ reaction

A mixture of nickel compounds is formed in the reaction of nickelocene with methyl-lithium. After hydrolysis and drying, this mixture was separated on a chromatographic column filled with neutral alumina employing 1:1 toluene/hexane as eluent. The first

---

* Corresponding author.

0022-328X/95/$09.50
SSDI 0022-328X(94)05166-6

pink band contained the π-allyl complex CpNi(η^3-C_5H_7), the second green band unreacted nickelocene while bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel, $(NiCp)_2(\mu\text{-}C_5H_6)$, was eluted as the third dark blue band.

After evaporating off the solvent, the first band was distilled under reduced pressure at 35–40°C when a few drops of a deep red liquid were obtained. This was identified as the π-allyl complex CpNi(η^3-C_5H_7) on the basis of its ^{1}H NMR spectrum [4].

When the solvents were partially evaporated from the third band, blue crystals were obtained. These were identified as the bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel complex $(NiCp)_2(\mu\text{-}C_5H_6)$ on the basis of their elemental analysis, ^{1}H, ^{13}C NMR and mass spectra.

The fourth brown band contained the tris(η^5-cyclopentadienyl)(μ_3-ethylidyne)trinickel cluster $(NiCp)_3C\text{-}CH_3$ as we have shown previously [1]. Further bands from the mixture contained clusters with more than three NiCp moieties.

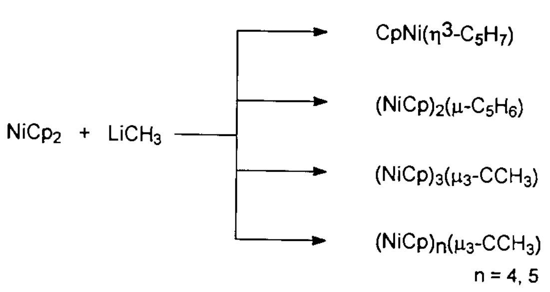
2.2. The $NiCp_2 + LiC(C_6H_5)=C(CH_3)_2$ reaction

Nickelocene reacts with 1-phenyl-2-methylpropenyllithium to form the unstable vinylnickel compound $\{CpNi-C(C_6H_5)=C(CH_3)_2\}$. As a result of further rearrangements the latter forms the π-allyl complex CpNi-[η^3-$CH_2C(CH_3)CH(C_6H_5)$], bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel $(NiCp)_2(\mu\text{-}C_5H_6)$ and higher nickel clusters. The mixture of products was separated chromatographically after hydrolysis (neutral alumina, eluent 1:1 toluene/hexane).

The first light green band was collected, the solvents evaporated and the residue distilled at 45–50°C under reduced pressure (10^{-3} Torr). A dark green oil (purple-red in the light of an electric bulb) was obtained. Two π-allyl isomers, *syn* and *anti* of (η^5-cyclopentadienyl)[η^3-1(phenyl)-2-(methyl)allyl]nickel were obtained and have been described [5].

Dark blue crystals precipitated on concentration of the second blue band. They were identified as bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel, $(CpNi)_2(\mu\text{-}C_5H_6)$, on the basis of their ^{1}H, ^{13}C NMR and mass spectra. The X-ray structure of this compound has also been determined.

3. Discussion



Scheme 1.

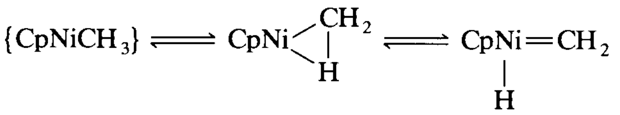
The reaction of nickelocene with methyl-lithium leads to the formation of a range of organonickel compounds (Scheme 1). We have previously described trinickel and higher clusters [1,6]. In this work we report the isolation and characterisation of two new compounds, $(NiCp)_2(\mu\text{-}C_5H_6)$ and CpNi(η^3-C_5H_7), formed in this reaction. The compound $(NiCp)_2(\mu\text{-}C_5H_6)$ has been obtained previously in the reaction of NiI_2 with NaC_5H_5 in the presence of 1,3-cyclopentadiene [Eq. (2)] [2]:

$$2NiI_2 + 4NaCp + C_5H_6 \longrightarrow (NiCp)_2C_5H_6 \quad (2)$$

Pagueitte and Dahl mentioned the possibility of the formation of $(NiCp)_2(\mu\text{-}C_5H_6)$ by the reduction of nickelocene with an equimolar amount of sodium naphtalenide in THF [3].

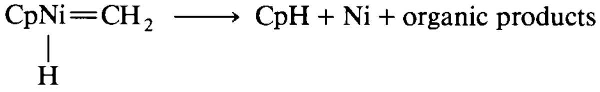
In our case this compound could be formed only as a result of the reduction of the cyclopentadienyl ring bonded to nickel. We have previously found that unstable $\{CpNiCH_3\}$ is formed in the reaction depicted in Eq. (3). This unstable compound undergoes α-H elimination to form nickel hydride [Eq. (4)]:

$$NiCp_2 + LiCH_3 \longrightarrow \{CpNiCH_3\} + LiCp \quad (3)$$



$$\{\mathrm{CpNiCH_3}\} \rightleftharpoons \mathrm{CpNi}\begin{smallmatrix}\mathrm{CH_2}\\ | \\ \mathrm{H}\end{smallmatrix} \rightleftharpoons \underset{\mathrm{H}}{\underset{|}{\mathrm{CpNi}}}=\mathrm{CH_2} \quad (4)$$

The latter hydride can react with $\{CpNiCH_3\}$ to evolve methane and form nickel clusters as a result of further reactions. It can also hydrogenate the cyclopentadienyl ring bonded to nickel to form cyclopentadiene [Eq. (5)]:



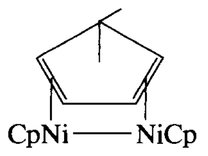
$$\underset{\mathrm{H}}{\underset{|}{\mathrm{CpNi}}}=\mathrm{CH_2} \longrightarrow \mathrm{CpH + Ni + organic\ products} \quad (5)$$

$\{CpNiCH_3\}$ can also undergo a coupling reaction to form the fairly stable $(NiCp)_2$ [Eq. (6)]:

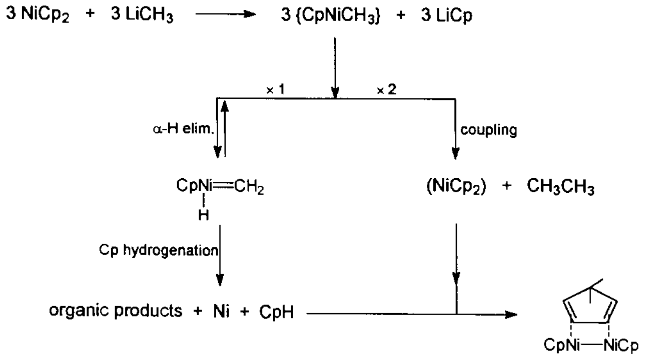
$$2\{CpNiCH_3\} \longrightarrow (NiCp)_2 + CH_3CH_3 \quad (6)$$

Complexation of $(NiCp)_2$ with cyclopentadiene forms the final product [Eq. (7)]:

$$(NiCp)_2 + C_5H_6 \longrightarrow$$



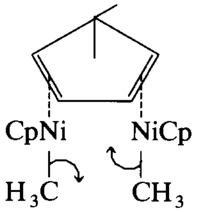
(7)



Scheme 2.

The course of above reactions is shown in Scheme 2. Stabilisation of $\{CpNiCH_3\}$ by complex formation with cyclopentadiene followed by ethane elimination also cannot be ruled out [Eq. (8)]:

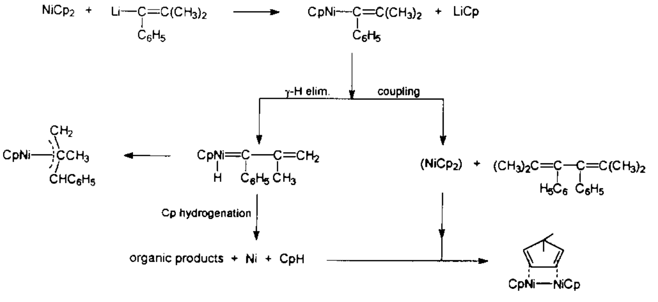
$2\{CpNiCH_3\} + C_5H_6 \longrightarrow$



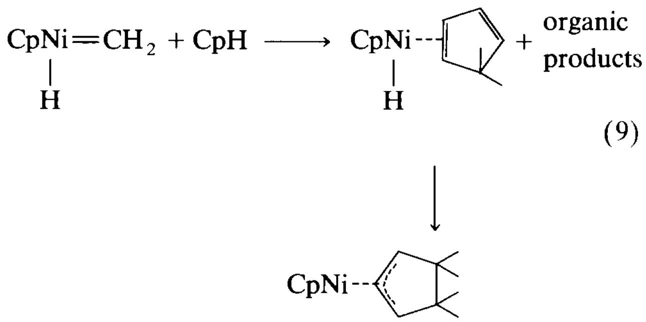
$$\xrightarrow[-C_2H_6]{} (NiCp)_2C_5H_6 \qquad (8)$$

The same compound, $(NiCp)_2(\mu\text{-}C_5H_6)$, is formed in the reaction of nickelocene with 1-phenyl-2-methylpropenyl-lithium, $[LiC(C_6H_5)=C(CH_3)_2]$, along with the π-allylnickel complex $CpNi[\eta^3\text{-}CH_2C(CH_3)CH\text{-}C_6H_5]$ described by us previously [5]. Because of the lack of α- and β-hydrogens in this reaction, γ-hydrogen elimination takes place (Scheme 3). The nickel hydride formed can hydrogenate the cyclopentadienyl ring bonded to the nickel atom or the π-allylnickel complex can be formed as a result of a hydrogen transfer to the α-carbon atom. The compound $(NiCp)_2$, generated in the coupling reaction, forms a complex with cyclopentadiene in later steps in the reaction.

A small amount of the π-allyl complex $CpNi(\eta^3\text{-}C_5H_7)$ is also formed in the reaction of nickelocene with methyl-lithium. This can be explained by the further hydrogenation of cyclopentadiene, formed in the earlier reaction steps [Eq. (5)], by the nickel hydride [Eq. (9)]:



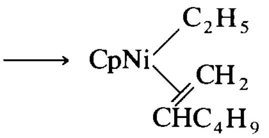
Scheme 3.



(9)

Since α-H and γ-H elimination reactions are much less facile than β-H elimination, we have carried out the reaction of nickelocene with ethyl-lithium in the presence of 1-hexene to obtain the complex $CpNi(C_2H_5)(\eta\text{-}C_6H_{11})$ [Eq. (10)]. Cyclopentadiene was then added to the reaction mixture.

$NiCp_2 + LiC_2H_5 + H_2C{=}CHC_4H_9$

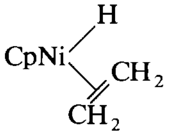


$$\longrightarrow CpNi(C_2H_5)(CH_2{=}CHC_4H_9) \qquad (10)$$

The $CpNi(C_2H_5)(\eta\text{-}C_6H_{11})$ formed readily eliminates the olefin to form the unstable compound $\{CpNiC_2H_5\}$ [Eq. (11)], which then undergoes β-H elimination to form the nickel hydride [Eq. (12)]:

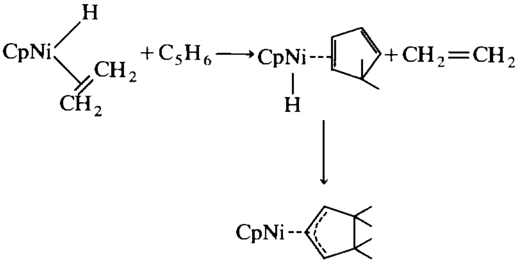
$$CpNi(C_2H_5)(\eta\text{-}C_6H_{11}) \longrightarrow \{CpNi-C_2H_5\} + H_2C{=}CHC_4H_9 \qquad (11)$$

$\{CpNi-C_2H_5\} \longrightarrow$



$$\{CpNi-C_2H_5\} \longrightarrow CpNi(H)(CH_2{=}CH_2) \qquad (12)$$

In the next step of the reaction, ethylene is replaced by cyclopentadiene and the latter is hydrogenated to form the π-allylnickel complex [Eq. (13)]:



(13)

If $NiCp_2$ is treated with ethyl-lithium in the presence of cyclopentadiene but in the absence of 1-hexene, the ethyl-lithium then reacts directly with cyclopentadiene leaving nickelocene unreacted. The reaction of nickelocene leading to the formation of the π-allyl complex $CpNi(\eta^3\text{-}C_5H_7)$ can be carried out in the presence of cyclopentadiene alone (without another

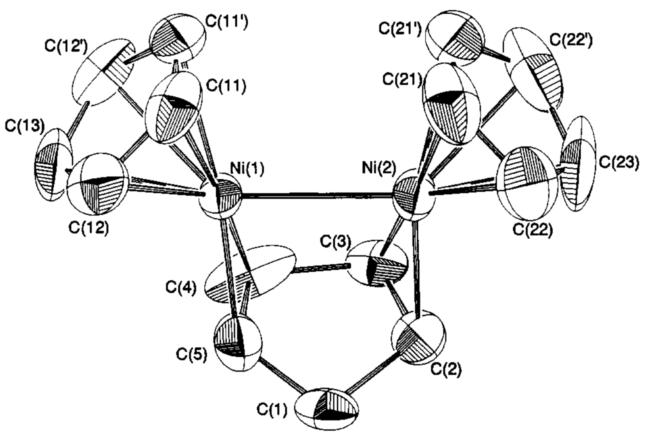


Fig. 1. ORTEP drawing of the $(NiCp)_2(\mu\text{-}C_5H_6)$ molecule showing the numbering system. Thermal ellipsoids are shown at the 50% probability level.

olefin) if instead of an alkyl-lithium an alkylmagnesium compound is used [4].

3.1. *Crystal structure*

Single crystal X-ray diffraction studies of $(NiCp)_2(\mu\text{-}C_5H_6)$ show that the compound crystallises in the orthorhombic system, space group *Pnma*, with four molecules per unit cell. Selected bond lengths and bond angles are listed in Tables 3 and 4 below. Fig. 1 shows a perspective view of the molecule including the atom numbering system. [2]

The nickel atoms lie on a crystallographic symmetry plane although the molecule does not itself possess such a plane (Fig. 1). All the atoms of the cyclopentadiene ring were refined with a site occupation factor equal 0.5. As a result the structure was refined as a superposition of two molecules leading to the crystallographic picture depicted in Fig. 2. This meant that the positional and thermal parameters of the cyclopentadiene ring carbon atoms had high esd values although the final *R* factor was low (2.81%). The structure depicted in Fig. 2 contains a mirror plane through Ni(1), Ni(2) and bisecting the two Cp rings. This may be due to statistical disorder in the crystal or to its racemic twinning. The two cyclopentadienyl rings are flat with the angle between the ring planes being 85.5(3)°. The two Ni–Cp(centroid) distances are 1.759(1) and 1.767(1) Å, while the 10 Ni–C(ring) distances average 2.12 Å. The Ni(1)–Ni(2) distance is 2.411(1) Å. These values are similar to ones reported previously [1].

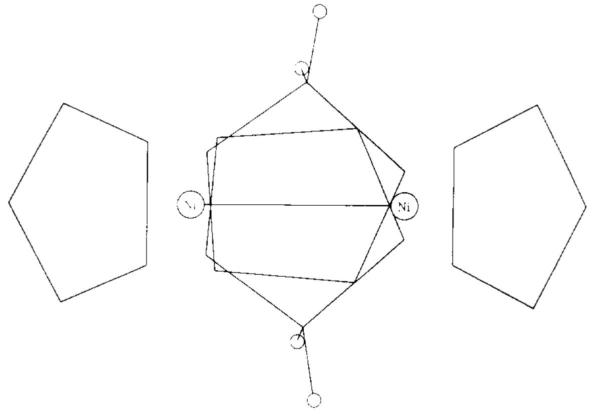


Fig. 2. Superposition of the cyclopentadiene ring in $(NiCp)_2(\mu\text{-}C_5H_6)$ showing the crystallographic picture of the molecule.

The cyclopentadiene ring is not flat. The C(1) atom is displaced from the plane passing through the C(2) ··· C(5) atoms in an opposite direction to that in which the nickel atoms are situated (Fig. 3). The ring is twisted in relation to the Ni–Ni axis (Fig. 2) resulting in differentiation of the Ni–C (double bond) distances from 2.02 Å to 1.92 Å. This is probably due to the fact that the Ni–Ni bond distance is significantly longer than the distance between the C=C bonds in the cyclopentadiene ring, leading to difficulty in the formation of a C=C π-bond to Ni and resulting in an unusually long C(3)–C(4) single bond (1.58 Å). All other bond parameters are unexceptional.

4. Experimental details

All reactions were carried out under an atmosphere of argon using Schlenk tube techniques. Solvents were

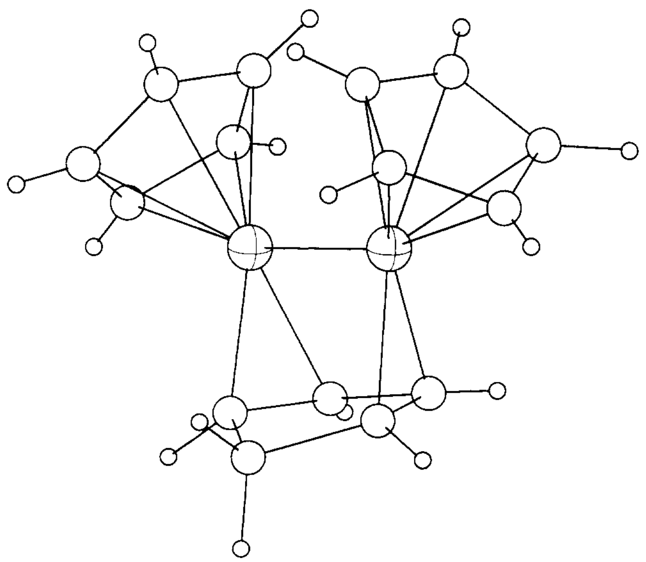


Fig. 3. A perspective view of $(NiCp)_2(\mu\text{-}C_5H_6)$ showing the bending in the cyclopentadiene ring.

---

[2] **Supplementary material available:** Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters; tables of calculated and observed structure factors have been deposited at the Cambridge Crystallographic Data Centre.

dried by conventional methods. ^1H and ^{13}C NMR spectra were measured on a Varian VXR-300 instrument. Mass spectra were recorded on an AMD-604 mass spectrometer.

4.1. Reaction of $NiCp_2$ with $LiCH_3$

A solution consisting of 18.4 mmol of $LiCH_3$ in 17 ml of Et_2O was slowly added to a solution of 13.6 mmol of $NiCp_2$ in 50 ml THF cooled to −70°C (1 h). The mixture was allowed to warm to ambient temperature (2 h) and was then stirred for a further 1 h. The reaction mixture was concentrated (solvents were distilled off under reduced pressure), 50 ml of pentane added and the mixture hydrolysed with deoxygenated water (100 ml). The separated organic layer was filtered through a G3 filter and dried using 4A molecular sieves. The solvents were distilled off under reduced pressure and the black solid remaining was dissolved in toluene (4 ml) and chromatographed on a column (60 cm × 3 cm, packed with neutral Al_2O_3 (II–III) in hexane) with 1 : 1 toluene/hexane as the eluent.

The red fraction was collected, the solvents distilled off and the residue distilled under reduced pressure (10^{-1} Torr) at 100°C. Several drops of a deep red, viscous liquid were obtained. $CpNi(\eta^3\text{-}C_5H_7)$: 1H NMR (THF-$d_8$) δ: 5.22 (t, 2-CH *meso*); 5.15 (s, H, in Cp); 4.03 (m, 1-CH *syn*, 3-CH *syn*); 1.31 (m, 4-CH, 5-CH *exo*); 0.89 (m, 4-CH, 5-CH *endo*) ppm. ^{13}C NMR (toluene-d_8) δ: 88.4 (d, C in Cp); 83.4 (d, C-2); 62.0 (d, C-1 and C-3); 31.2 (t, C-4 and C-5) ppm MS (70 eV) *m/e*: 190 (M^+).

The blue fraction was collected and on concentration of the solution blue crystals precipitated at low temperature. $(NiCp)_2(\mu\text{-}C_5H_6)$: ^1H NMR (THF-d_8) δ: 5.25 (s, –CH–); 5.08 (s, H in Cp); 2.89 (s, –CH–); 1.82 (s, –CH–) ppm. MS (70 eV) *m/e*: 123 (40%); 188 (100%); 246 (74%); 312 (M^+, 15%).

4.2. Reaction of $NiCp_2$ with 1-phenyl-2-methylpropenyllithium, $LiC(C_6H_5)=C(CH_3)_2$

An etheral solution of 1-phenyl-2-methylpropenyllithium (42 cm^3, 12.6 mmol) was added drop-by-drop to a solution of $NiCp_2$ (2.18 g, 11.5 mmol) in 120 cm^3 of Et_2O. The mixture was stirred at room temperature for 24 h, deoxygenated water (70 cm^3) added and the system stirred for a further 1 h. The mixture was filtered through a bed of alumina (2 cm high), the etheral layer separated and dried over molecular sieves. The solvent was evaporated under reduced pressure. The residue was dried under reduced pressure (10^{-1} Torr) at room temperature for 3–4 h. Sublimation of a small amount of $NiCp_2$ was observed leaving a viscous brown oil. Hexane (20 cm^3) was added, a black solid filtered off, the filtrate concentrated and chromatographed on alumina (deactivated with 2% water) using heptane as eluent.

The first, green fraction was identified as a mixture of (η^5-cyclopentadienyl)[η^3-1-*anti*-phenyl-2-methylallyl]nickel and (η^5-cyclopentadienyl)[η^3-1-*syn*-phenyl-2-methylallyl]nickel. The second, deep blue fraction was collected and concentrated under reduced pressure. The solution was placed in a freezer (−30°C) when small blue crystals were obtained after several days.

$(NiCp)_2(\mu\text{-}C_5H_6)$: ^1H NMR (C_6D_6) δ: 5.24 (s, –CH–); 5.08 (s, H in Cp); 2.88 (s, –CH–); 1.82 (s, –CH_2–) ppm. MS (70 eV) *m/e*: 123 (25%); 188 (100%); 246 (72%); 312 (M^+, 23%). ^{13}C NMR (C_6D_6) δ: 89.4 (Cp); 56.1 (–CH–); 54.3 (–CH–); 44.4 (–CH_2–) ppm.

4.3. Reaction of $NiCp_2$ with LiC_2H_5 in the presence of C_5H_6

To a solution consisting of 0.667 g of $NiCp_2$ (3.53 mmol) in 40 ml of Et_2O was added 1 ml (12.1 mmol) of C_5H_6. The solution was cooled to 3°C and then 17 ml (3.57 mmol) of an etheral solution of LiC_2H_5 was added drop by drop. Precipitation of a white solid was noted, the green colour of the solution remaining unchanged. The mixture was stirred at room temperature for 12 h, then filtered, the filtrate dried, the solvent distilled off under reduced pressure and the residue redissolved in hexane. The solution was chromatographed on Al_2O_3 (deactivated with 4% H_2O), using hexane as eluent. Only one fraction containing $NiCp_2$ was collected.

4.4. Reaction of $NiCp_2$ with LiC_2H_5 in the presence of 1-hexene and C_5H_6

To a solution consisting of 0.628 g of $NiCp_2$ (3.32 mmol) in 50 ml of THF was added 0.83 ml (6.64 mmol) of 1-hexene. The solution was cooled to −60°C and then 16 ml (3.36 mmol) of an etheral solution of LiC_2H_5 was added drop by drop, the temperature was maintained at −60°C to −50°C. A change of colour from green to brown was noted. After addition of LiC_2H_5 was complete, 1 ml (12.2 mmol) of C_5H_6 was added. The mixture was warmed slowly to room temperature and stirred for 12 h.

The solution was concentrated, 50 ml of hexane added and the system hydrolysed with 50 ml of deoxygenated water. The organic layer was separated, dried over molecular sieves and chromatographed on Al_2O_3 (4% H_2O) using hexane as eluent. The first red fraction was collected. The red solid obtained after evaporation of the solvent sublimed at 35–40°C under 10^{-1} Torr pressure. It was identified as $CpNi(\eta^3\text{-}C_5H_7)$ on the basis of its ^1H NMR spectrum. The second, green fraction was also collected and identified as $NiCp_2$.

4.5. X-ray structure determination

A deep red, well-shaped crystal of $(NiCp)_2(\mu\text{-}C_5H_6)$ was placed in a thin-walled capillary tube (Lindemann glass) in an inert atmosphere. The tube was plugged with grease, then flame-sealed and mounted on the goniometer head of a four-circle P3 (Siemens AG) diffractometer. The crystallographic data obtained, the parameters for data collection and the refinement procedure are presented in Table 1.

The crystal system, the orientation matrix and the unit cell parameters were obtained from the least-squares refinement of the angular positions measured for 25 reflections randomly found in the 2θ range between 5° and 22°. The intensities were collected up to $2\theta = 50°$ (max. $\sin\theta/\lambda = 0.60$) in the θ–2θ mode with the scan range 1.8° plus the $K\alpha_1 - K\alpha_2$ separation at various scan speeds between 3.7 and 29.3 deg. min^{-1}. Two check reflections (1 3 1) and (4 1 0), repeated every 70 reflections, showed a decay of 2.3%. The intensities were adjusted accordingly and corrected for the Lorentz polarisation effect. Since the absorption coefficient was comparatively high (μ = 3.04 cm^{-1}), an empirical correction based on collected azimuthal data (psi scan) was applied.

Table 1
Data collection and structure analysis parameters

Molecular formula	$C_{15}H_{16}Ni_2$
Crystal size (mm)	0.09×0.12×0.27
Crystal system	orthorhombic
Space group	P*nma*
Unit cell dimensions	
a	8.922(2) Å
b	10.386(2) Å
c	13.323(3) Å
Volume	1234.6(5) $Å^3$
Z	4
Formula weight	313.7
Density (calc.)	1.688 g cm^{-3}
Temperature (K)	293
Absorption coefficient	3.038 mm^{-1}
F(000)	648
Radiation	Mo Kα (λ = 0.71073 Å, graphite monochrom.)
2θ range	4.0–50.0°
Scan type	$2\theta-\theta$
Scan speed (variable)	3.66–29.30°(2θ) min^{-1}
Scan range (2θ)	1.80° plus Kα separation
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 12$, $-15 \le l \le 15$
Reflections collected	2538
Independent reflections	1165 (R_{int} = 1.79%)
Observed reflections	880 ($F > 3.0\sigma(F)$)
Min./max. transmission	0.8151/0.9653
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0005F^2$
No. of parameters refined	152
Final *R* indices (obs. data)	R = 2.81%, R_w = 2.75%
R index for all data	R = 4.46%
Goodness-of-fit	0.92
Largest and mean Δ/σ	0.005, 0.001
Data-to-parameter ratio	5.8
Residual extreme in final difference Fourier map	0.24/−0.39 e $Å^{-3}$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq} [a]	Site occup. factor
Ni(1)	523(1)	2500	−468(1)	35(1)	0.5
Ni(2)	2993(1)	2500	268(1)	42(1)	0.5
C(11)	−862(5)	1833(5)	692(3)	63(2)	1
C(12)	−1451(5)	1415(5)	−184(4)	66(2)	1
C(13)	−1814(7)	2500	−752(5)	72(3)	0.5
C(21)	2672(7)	1864(5)	1751(3)	76(2)	1
C(22)	4018(7)	1392(7)	1436(4)	90(3)	1
C(23)	4876(10)	2500	1216(7)	123(7)	0.5
C(1)	2873(12)	1165(11)	−1605(7)	49(3)	0.5
C(2)	3877(13)	2131(11)	−1041(9)	51(6)	0.5
C(3)	3232(14)	3340(12)	−1089(9)	45(4)	0.5
C(4)	1646(34)	3222(37)	−1609(21)	66(8)	0.5
C(5)	1544(27)	1942(37)	−1662(21)	58(11)	0.5

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Two space groups consistent with the reflection pattern were obtained. non-centrosymmetric $Pna2_1$ and centrosymmetric *Pnma*. The phase problem was solved in both space groups by direct methods using the SHELXS-86 program [7]. Since during further refinement in the $Pna2_1$ group severe correlation of most of the parameters occurred, the structure was refined as centrosymmetric. The observed $Pna2_1$ group correlation of the parameters could be due to statistical disorder in the crystal or to its racemic twinning (a parameter which multiplies the imaginary part of atomic scattering factors refined to zero).

Two Ni atoms and some of carbon atoms were found on the most appropriate E-map. The equivalent

Table 3
Bond lengths (Å) between non-hydrogen atoms in $(NiCp)_2(\mu\text{-}C_5H_6)$ [a]

Ni(1)–Ni(2)	2.411(1)	Ni(1)–C(4)	1.970(30)
		Ni(1)–C(5)	1.922(28)
Ni(1)–C(11)	2.096(5)		
Ni(1)–C(12)	2.125(5)	C(11)–C(12)	1.352(7)
Ni(1)–C(13)	2.119(6)	C(12)–C(13)	1.396(7)
Ni(1)–C(11′)	2.096(5)	C(11)–C(11′)	1.385(9)
Ni(1)–C(12′)	2.125(5)		
		C(21)–C(22)	1.364(9)
Ni(2)–C(21)	2.102(4)	C(22)–C(23)	1.413(9)
Ni(2)–C(22)	2.140(6)	C(21)–C(21′)	1.321(11)
Ni(2)–C(23)	2.101(9)		
Ni(2)–C(21′)	2.102(4)	C(1)–C(2)	1.541(15)
Ni(2)–C(22′)	2.140(6)	C(2)–C(3)	1.383(17)
		C(3)–C(4)	1.580(33)
Ni(2)–C(2)	1.952(11)	C(4)–C(5)	1.334(54)
Ni(2)–C(3)	2.019(12)	C(1)–C(5)	1.437(31)

[a] Estimated standard deviations in parentheses.

Table 4
Selected bond angles (°) in $(NiCp)_2(\mu\text{-}C_5H_6)$ [a]

C(2)–C(1)–C(5)	98.0(15)	Ni(2)–Ni(1)–C(5)	84.5(7)
C(1)–C(2)–C(3)	109.1(10)	Ni(2)–Ni(1)–C(4)	81.3(9)
C(2)–C(3)–C(4)	108.8(17)	Ni(1)–Ni(2)–C(2)	90.3(3)
C(3)–C(4)–C(5)	99.3(24)	Ni(1)–Ni(2)–C(3)	74.5(4)
C(1)–C(5)–C(4)	120.0(24)		

[a] Estimated standard deviations in parentheses.

reflections were averaged. The resulting 1165 unique reflections had the internal consistency index $R_{\text{int}} = 1.79\%$. The structure was refined using the full-matrix least-squares technique (SHELX-76 program [8]) with isotropic thermal parameters on the first step, thus resulting in an R value equal to 0.098. The positions of the remaining carbon and cyclopentadiene hydrogen atoms were determined on the differential Fourier map. After refinement with anisotropic thermal parameters, geometrical construction was used to place the hydrogen atoms of the cyclopentadienyl rings. The weighting scheme with $w(F)^{-1} = \sigma^2(F) + 0.0005F^2$ gave a satisfactory variance analysis. This resulted in a final value of the R factor of 2.81% after full convergence of the refinement.

The final atomic coordinates and equivalent temperature factors with their esd's for non-hydrogen atoms are listed in Table 2. A perspective view of the molecule (ORTEP [9]) with the atom numbering system is shown in Fig. 1. Selected bond lengths and bond angles are given in Tables 3 and 4.

Acknowledgements

The authors thank the State Committee for Scientific Research for financial support of this work (Grant No. 2 0638 91 01).

References

[1] H. Lehmkuhl, C. Krüger, S. Pasynkiewicz and J. Popławska, *Organometallics*, 7 (1988) 2038.
[2] E.O. Fischer, P. Mayer, C.G. Kreiter and J. Müller, *Chem. Ber.*, *105* (1972) 3014.
[3] M.S. Paquette and L.F. Dahl, *J. Am. Chem. Soc.*, *102* (1980) 6623.
[4] H. Lehmkuhl, A. Rufińska, R. Benn, G. Schroth and R. Mynott, *Liebigs Ann. Chem.*, (1981) 317.
[5] S. Pasynkiewicz, A. Pietrzykowski, W. Buchowicz and M. Popławska, *J. Organomet. Chem.*, *463* (1993) 235.
[6] S. Pasynkiewicz, *J. Organomet. Chem.*, *387* (1990) 1.
[7] G.M. Sheldrick, *SHELXS-86 Program for Crystal Structure Determination*, University of Göttingen, Germany, 1986.
[8] G.M. Sheldrick, *SHELX-76 Program for Crystal Structure Determination*, University of Cambridge, Cambridge, UK, 1976.
[9] C.K. Johnson, *ORTEP*, *Report ORNL-5138*, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.