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Reactions of nickelocene with diphenylmethyl- and triphenylmethyllithium

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Abstract

Reactions of nickelocene with diphenylmethyl- and triphenylmethyllithium have been studied. Several organonickel compounds were formed in these reactions. The products were separated by column chromatography and characterised by spectral methods. The presence of alkylated nickelocenes among products of both reactions has been confirmed. The crystal structures of two π-allyl cyclopentadienylnickel complexes have been determined by X-ray measurements. Bis(η^5-cyclopentadieny–η^3-cyclopentenylnickel) (**1**) crystallises in orthorhombic crystal system with eight molecules in a unit cell; space group *Pbca*, unit cell dimensions: $a = 10.134(3)$, $b = 11.801(3)$, $c = 26.753(7)$ Å. Compound **4** contains triphenylmethyl group η^3-bonded to NiCp unit. It crystallises in triclinic crystal system with four molecules in the unit cell; space group $P\bar{1}$; unit cell dimensions: $a = 9.8747(9)$, $b = 10.6331(10)$, $c = 19.569(2)$ Å and $\alpha = 93.793(8)$, $\beta = 102.000(8)$, $\gamma = 113.912(7)$°. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel; Clusters; π-Allyl complexes; Cyclopentadienyl; Crystal structure; Alkylation of nickelocene

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1. Introduction

We have previously found [1] that in the reaction of nickelocene with *tert*-butyllithium, processes of hydrogen elimination and of homolytic scission of Ni–C bonds proceed simultaneously. The free *t*-butyl radical $^{\bullet}C(CH_3)_3$, formed in the latter process, alkylates the cyclopentadienyl ring bonded to nickel.

The purpose of this work was to study reactions of nickelocene with diphenylmethyl- and triphenylmethyllithium. We wanted to find out whether the Ni–C bond in {CpNi–$CHPh_2$} and {CpNi–CPh_3} species, formed in the course of the reactions, underwent homolytic cleavage with the formation of free radicals $^{\bullet}CHPh_2$ and $^{\bullet}CPh_3$, respectively, and whether these radicals could alkylate cyclopentadienyl rings of nickelocene.

2. Results and discussion

The reactions of nickelocene with diphenylmethyl- and triphenylmethyllithium were carried out in THF at temperatures from −40°C to room temperature. The products were hydrolysed with deoxygenated water and separated by column chromatography on neutral alumina.

Several organonickel compounds are formed in the reaction of nickelocene with diphenylmethyllithium. The following compounds were isolated from the reaction mixture by column chromatography on neutral alumina: the previously described [2] π-allyl complex CpNi(η^3-C_5H_7) was identified on the basis of its ^1H-NMR and MS spectra; bis(cyclopentadienyl)(μ-cyclopentadiene)dinickel complex $(NiCp)_2(\mu\text{-}C_5H_6)$ of known structure [3,4], identified by spectral methods and a new, previously unknown π-allyl complex $(NiCp)_2(\eta^3\text{-}C_5H_6)_2$ (**1**). Complex **1** was eluted from chromatographic column (neutral alumina, eluent hexane) as the second, deep-red band. Its mass spectrum reveals the parent ion at *m*/*e* 378 (calculated for ^{58}Ni)

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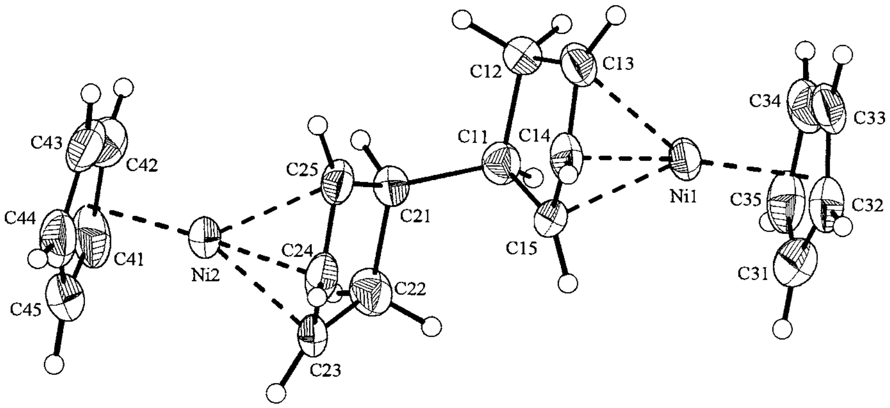


Fig. 1. ORTEP drawing of **1** with atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

of very low intensity with an isotopic pattern characteristic for two nickel atoms. The most intensive signal appears at *m*/*e* 189 and corresponds to the monomeric fragment $\{CpNi–\eta^3\text{-}C_5H_6\}^+$ of the dimeric π-allyl complex $(CpNi)_2(\eta^3\text{-}C_5H_6)_2$. The further fragments are characteristic also for other cyclopentadienyl nickel compounds and appear at *m*/*e* 123 $\{NiCp\}^+$ and 58 $\{^{58}Ni\}^+$.

The X-ray structure of **1** is shown in Fig. 1. It crystallises in an orthorhombic crystal system with eight molecules in a unit cell. The distances between nickel and carbon atoms engaged with π-allyl bonding system are 1.895 and 1.902 Å for middle carbon atoms (Ni(1)–C(14) and Ni(2)–C(24), respectively) and 1.999, 2.002, 2.008 and 2.003 Å for terminal carbon atoms (Ni(1)–C(13, 15) and Ni(2)–C(23, 25)). These values are almost identical with corresponding distances of known structures of other cyclopentadienylnickel compounds with π-allyl bonding system located in cyclopentenyl or cyclobutenyl rings [5–8].

Besides the above-described complexes, several other organonickel compounds were formed in this reaction. These compounds could not be separated by column chromatography. An analysis of a mass spectrum of its mixture indicates that they are mainly nickelocenes alkylated with the $^\bullet CHPh_2$ radical.

The reaction of nickelocene with triphenylmethyllithium led to the formation of several organonickel compounds. The main product was red–brown crystalline π-allyl compound (η^5-cyclopentadienyl)(7,7-diphenyl-1,2,7-η^3-benzyl)nickel (**4**). This compound has been obtained and spectrally characterised previously [9]. Compound **4** was isolated by column chromatography and crystallised from hexane. ^{1}H-NMR spectroscopy showed a singlet of cyclopentadienyl protons at $\delta = 4.95$ ppm and signals of aromatic and allylic protons in the 6.15–7.30 ppm region. ^{13}C-NMR spectroscopy revealed a signal due to cyclopentadienyl carbons at $\delta = 91.4$ ppm, a signal for benzyl carbon at 67.5 ppm, signals for phenyl carbons involved in π-allyl system at 97.8 and 103.4 ppm and signals for aromatic carbons in the 126.0–133.9 ppm region. In the mass spectrum the molecular ion appears at *m*/*e* 366 (calc. for ^{58}Ni) with isotropic pattern characteristic for one nickel atom. Its fragmentation was as follows: *m*/*e* (calc. for ^{58}Ni): 300 $(M-CpH)^+$; 243 $(CPh_3)^+$; 123 $(NiCp)^+$; 58 $(Ni)^+$. The last two fragments are characteristic of cyclopentadienyl nickel compounds. The crystal structure of compound **4** was determined by X-ray single crystal analysis and is shown in Fig. 2.

Compound **4** crystallises with two molecules in the asymmetric unit. Final geometry in the two independent molecules is essentially the same with disorder of cyclopentadienyl ring as the only differentiating factor. Compound **4** contains a benzyl ligand η^3-coordinated to a NiCp unit. The nickel atom is attached to the ligand at C(2), C(1) and C(7). C(1)–C(2) and C(1)–C(7) distances are typical for an allyl group η^3 bonded to a transition metal. The C(1)–C(7) bond is about 0.04 Å shorter than the corresponding C(7)–C(11) and C(7)–C(21) ones which confirms its engagement in π-al-

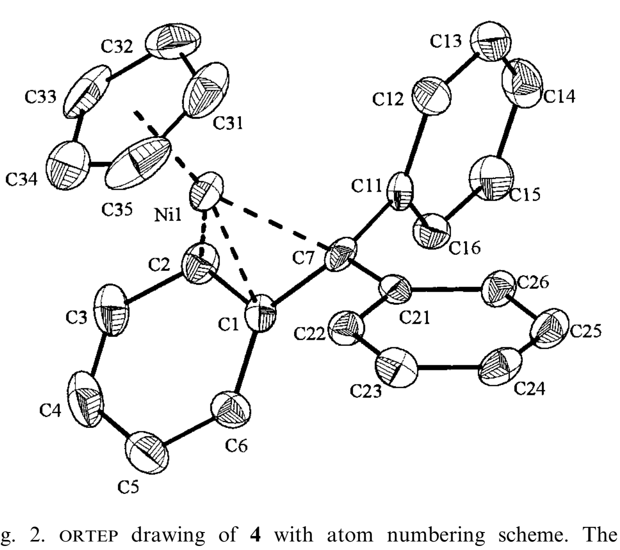
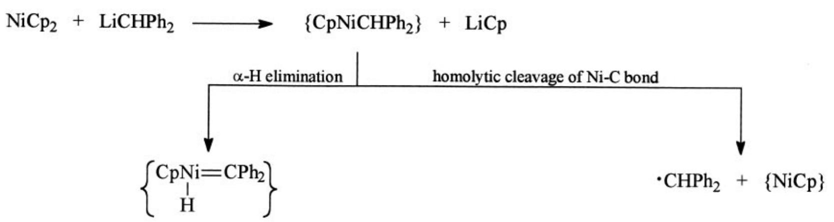


Fig. 2. ORTEP drawing of **4** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.



Scheme 1.

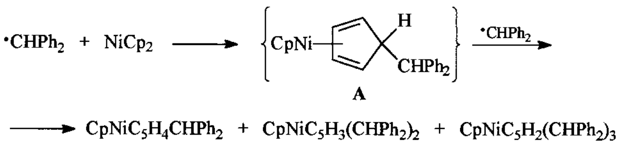
lyl bonding system. Another factor confirming the engagement of the C(1)–C(6) phenyl group in a π-allyl bonding system is a substantial differentiation of its C–C bond lengths (from 1.325 to 1.443 Å). Similar π-allyl systems were described for palladium, platinum [10] and rhenium [11] complexes.

Several other cyclopentadienylnickel compounds were formed in the above reaction. Chromatographic separation afforded monoalkylated nickelocene $CpNiC_5H_4CPh_3$ (**5**) together with the doubly alkylated nickelocene $CpNiC_5H_3(CPh_3)_2$. The presence of these nickelocenes was confirmed only by mass spectrometry. The molecular ion of **5** appeared at *m/e* 430, and the molecular ion of doubly alkylated nickelocene appeared at *m/e* 672.

Two other compounds were isolated and characterised from the reaction mixture. They were: ethylidyne-tri(cyclopentadienylnickel) cluster $(CpNi)_3CCH_3$ **6** and alkylidyne-tri(cyclopentadienylnickel) cluster $(NiCp)_3CCH_2CPh_3$ **7**. They were characterised by means of ^{1}H- and ^{13}C-NMR spectroscopy, and mass spectrometry. The crystal structure of **6** was published previously [12]. The clusters **6** and **7** were formed as a result of a cleavage of THF by cyclopentadienylnickel species as we described previously [13].

The course of the reaction of nickelocene with diphenylmethyllithium is presented in Scheme 1. Unstable 16-electron species $\{CpNiCHPh_2\}$ and LiCp are formed in the first step of this reaction. $\{CpNiCHPh_2\}$ reacts in two directions: α-hydrogen elimination and homolytic cleavage of the Ni–C bond with the formation of relatively stable radical $^{\bullet}CHPh_2$. Hydridocarbene $\{CpNi(H){=}CPh_2\}$, stabilised by two phenyl groups, is formed as a result of α-H elimination. This carbene acts as strong hydrogenating agent. It hydrogenates cyclopentadienyl ring of nickelocene to form unstable 19-electron species $\{CpNiC_5H_6\}$ (Scheme 2).

This species can stabilise by the formation of dimer **1** (in which both nickel atoms form π-allyl complexes), by the addition of {NiCp} species to form complex **2** or by further hydrogenation of a cyclopentadiene ring with the formation of the π-allyl complex **3**. In all these compound nickel achieves an 18-electron configuration. Compounds **2** and **3** were obtained previously and their structures were determined [2,4]. Compound **1** has not been previously described. The radical $^{\bullet}CHPh_2$ formed in the reaction of homolytic cleavage of the Ni–C bond alkylates the cyclopentadienyl ring of nickelocene to form unstable 19-electron species $\{CpNiC_5H_5CHPh_2\}$. Further reactions of this species with $^{\bullet}CHPh_2$ radicals lead to the formation of a mixture of alkylated nickelocenes (Eq. (1)).

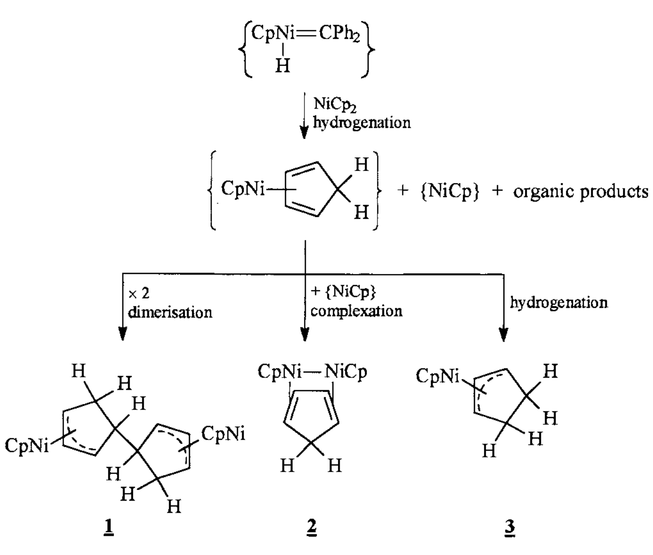


(1)

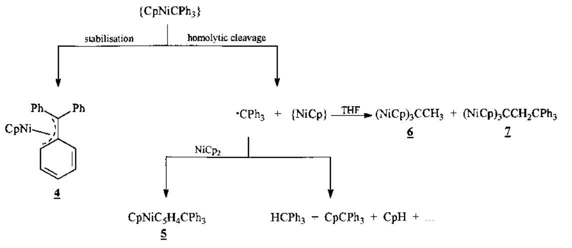
We were not able to separate this mixture by column chromatography. The compounds are paramagnetic and their presence was confirmed only by mass spectra of the mixture. The unstable species **A** does not dimerise as a similar species shown in Scheme 2, probably due to steric reasons.

The first step of the reaction of nickelocene with triphenylmethyllithium, leading to the formation of an unstable 16-electron cyclopentadienyl(triphenylmethyl)nickel $\{CpNiCPh_3\}$ (Eq. (2)), is analogous to the first step of the reaction of nickelocene with diphenylmethyllithium (Scheme 1).

$$NiCp_2 + LiCPh_3 \rightarrow \{CpNiCPh_3\} + LiCp \qquad (2)$$

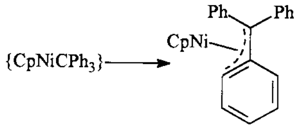


Scheme 2.



Scheme 3.

Further steps are rather different. The main reaction of $\{CpNiCHPh_2\}$ species is α-H elimination reaction (Scheme 1), while $\{CpNiCPh_3\}$ stabilises by the formation of a π-allyl complex (η^5-cyclopentadienyl)(7,7-diphenyl-1,2,7-η^3-benzyl)nickel (**4**), in which nickel achieves an 18-electron configuration (Eq. (3)).



4 (3)

In both reactions homolytic cleavage of the Ni–C bond, with the formation of free radicals $^{\bullet}CHPh_2$ and $^{\bullet}CPh_3$, respectively, takes place. $^{\bullet}CPh_3$, analogously to $^{\bullet}CHPh_2$, can substitute into the cyclopentadienyl ring of nickelocene to form $CpNiC_5H_4(CPh_3)$ identified by mass spectrometry in the second chromatographic band. The presence of $^{\bullet}CPh_3$ leads to the formation of several organic products such as $HCPh_3$, $C_5H_5(CPh_3)$, etc. Unstable, coordinately and electronically unsaturated {NiCp} species, formed by the decomposition of $\{CpNiCPh_3\}$, reacts with THF [13] to form two trinickel clusters $(NiCp)_3CCH_3$ and $(CpNi)_3CCH_2CPh_3$ (Scheme 3).

3. Experimental

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. Elemental analyses were performed on Perkin–Elmer 2400 analyser. ^{1}H- and ^{13}C-NMR spectra were measured on Varian Gemini-200, Varian VXR-300 and Varian-500 instruments. Mass spectra were recorded on AMD-604 and AMD M-40 mass spectrometers.

3.1. Reaction of nickelocene with diphenylmethyllithium

Diphenylmethyllithium was prepared by the reaction of diphenylmethyl chloride with lithium in THF [14].

A solution of diphenylmethyllithium in THF (9.1 mmol, 8 ml) was added within 1 h at −60 to −50°C to a solution of $NiCp_2$ (1.59 g, 8.4 mmol) in 95 ml THF and kept at this temperature for 1 h. The reaction mixture changed colour from green to red–brown on addition of diphenylmethyllithium. The reaction mixture was then allowed to warm up to r.t. and stirred overnight. The volatile substances were removed under reduced pressure; 5 ml of THF and 50 ml of hexane were added and the products were hydrolysed with 50 ml of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was redissolved in a 1:5 mixture of toluene and hexane and chromatographed on alumina (37 × 2 cm deactivated with 5% of water) using hexane–toluene mixtures as eluents. The following compounds were isolated and characterised.

$CpNi(\eta^3\text{-}C_5H_7)$ (**3**): A small amount of the first pink band eluted with 10% toluene in hexane. The compound has been characterised previously [2]. It was identified on the basis of its EIMS (70 eV) (molecular ion at $m/e = 190$ calc. for ^{58}Ni) and ^{1}H-NMR (C_6D_6) δ (ppm): 5.22 (s, 5H, Cp), 5.05 (s, 1H, CH), 3.90 (s, 2H, CH), 1.24 (d, 2H, $CH_{2\,egzo}$, $^3J = 13$ Hz), 0.77 (d, 2H, $CH_{2\,endo}$, $^3J = 13$ Hz).

$[CpNi(\eta^3\text{-}C_5H_6)]_2$ (**1**): The second orange–red band eluted with 10% toluene in hexane. It was recrystallised from hexane at about 0°C to afford red crystals (yield 10%). Anal. Calc. for $C_{20}H_{22}Ni_2$: C, 63.25; H, 5.84. Found: C, 63.70; H, 5.49%. EIMS (70 eV) m/e calc. for ^{58}Ni (relative intensity, %): 378 (1) [M^+]; 189 (100) [$(CpNiC_5H_6)^+$]; 123 (79) [$(NiCp)^+$]; 58 (24) [Ni^+]. The crystals were suitable for X-ray crystal structure measurements.

$(NiCp)_2(\mu\text{-}C_5H_6)$ (**2**): The third blue band eluted with 10% toluene in hexane (yield 10%). It was identified as a dinickel compound $(NiCp)_2(\mu\text{-}C_5H_6)$ [3,4] based on its ^{1}H-NMR and mass spectra: ^{1}H-NMR (C_6D_6) δ (ppm): 1.82 (s, 2H, CH_2), 2.87 (s, 2H, CH), 5.07 (s, 10H, C_5H_5), 5.24 (s, 2H, CH); EIMS (70 eV), m/e calculated for ^{58}Ni (relative intensity %): 312 [M^+] (36), 246 [$Ni_2Cp_2^+$] (100), 188 [$NiCp_2^+$] (69%), 123 [$NiCp^+$] (14), 58 [Ni^+] (3).

The remaining products were eluted as one brown chromatographic band using 50% toluene in hexane. It appeared to be a mixture of substituted nickelocenes: $CpNi(\eta^5\text{-}C_5H_4CHPh_2)$, $CpNi[\eta^5\text{-}C_5H_3(CHPh_2)_2]$, $CpNi[\eta^5\text{-}C_5H_2(CHPh_2)_3]$. Their presence in the mixture was confirmed by mass spectrometry. EIMS (70 eV) m/e (calculated for ^{58}Ni): $CpNi\text{–}\eta^5\text{-}C_5H_4(CHPh_2)$: 354 [$M^+$], 288 [$(M - C_5H_6)^+$]; $CpNi\text{–}\eta^5\text{-}C_5H_3(CHPh_2)_2$: 520 [$M^+$], 454 [$(M - C_5H_6)^+$]; $CpNi\text{–}\eta^5\text{-}C_5H_2(CHPh_2)_3$: 686 [$M^+$], 620 [$(M - C_5H_6)^+$].

*3.2. Crystal structure determination of **1***

A crystal of compound **1** was mounted on glass fibre and then flash-frozen to 100 K. Preliminary examination and intensities data collections were carried out on a KUMA KM-4 four-circle diffractometer [15] with an

Oxford Cryosystem–Cryostream in the ω–2θ mode using graphite-monochromated Mo–K_α radiation (0.71073 Å) up to $2\theta = 50°$. For collected intensities Lorentz polarisation and absorption corrections were applied. The structure was solved by direct method (SHELXS-97) [16] and refined on F^2 by a full-matrix least-squares program (SHELXL-97) [17]. The carbon bonded hydrogen atoms were included in the calculated positions and refined using a riding model. The crystal structure with the atom numbering system is presented in Fig. 1. Data collection and structure analysis parameters for **1** are given in Table 1, while selected bond lengths and angles are listed in Tables 2 and 3.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{20}H_{22}Ni_2$
Crystal size (mm)	$0.7 \times 0.3 \times 0.2$
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	10.134(3)
b (Å)	11.801(3)
c (Å)	26.753(7)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	3199.4(15)
Z	8
Formula weight	379.80
D_{calc} (g cm^{-3})	1.577
Temperature (K)	100(1)
Absorption coefficient (mm^{-1})	2.346
F(000)	1584
Radiation	Mo–K_α ($\lambda = 0.71073$ Å, graphite monochromator)
θ Range for data collection (°)	2.52–25.04
Scan type	ω–2θ
Index ranges	$0 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 31$
Reflections collected/unique	2347/2347 ($R_{Int} = 0.0000$)
Absorption correction	COSABS-99
Max. and min. transmission	1 and 0.743
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2347/0/221
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0302$ [a] wR_2 (refined) = 0.0874 [b]
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.0532P)^2 + 2.5130P$ [c]
R indices (all data)	$R_1 = 0.0631$; $wR_2 = 0.0967$
Largest difference peak and hole (e Å^{-3})	0.322 and −0.408

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Selected interatomic distances (Å) in **1** [a]

Ni(1)–C(13)	1.999(4)	C(12)–C(13)	1.511(6)
Ni(1)–C(14)	1.895(4)	C(13)–C(14)	1.389(6)
Ni(1)–C(15)	2.002(4)	C(14)–C(15)	1.410(6)
Ni(1)–C(35)	2.078(5)	C(21)–C(25)	1.527(6)
Ni(1)–C(34)	2.082(5)	C(21)–C(22)	1.549(6)
Ni(1)–C(31)	2.087(5)	C(22)–C(23)	1.506(6)
Ni(1)–C(33)	2.104(4)	C(23)–C(24)	1.399(6)
Ni(1)–C(32)	2.165(4)	C(24)–C(25)	1.404(6)
Ni(2)–C(23)	2.008(4)	C(31)–C(32)	1.399(7)
Ni(2)–C(24)	1.902(4)	C(31)–C(35)	1.411(7)
Ni(2)–C(25)	2.003(4)	C(32)–C(33)	1.386(7)
Ni(2)–C(41)	2.086(5)	C(33)–C(34)	1.409(7)
Ni(2)–C(42)	2.089(4)	C(34)–C(35)	1.403(7)
Ni(2)–C(45)	2.091(5)	C(41)–C(42)	1.401(7)
Ni(2)–C(43)	2.109(5)	C(41)–C(45)	1.409(7)
Ni(2)–C(44)	2.159(4)	C(42)–C(43)	1.410(7)
C(11)–C(15)	1.508(6)	C(43)–C(44)	1.372(7)
C(11)–C(21)	1.541(5)	C(44)–C(45)	1.395(7)
C(11)–C(12)	1.547(6)		

[a] Estimated S.D. values in parentheses.

Table 3
Selected bond angles (°) in **1** [a]

C(14)–Ni(1)–C(13)	41.67(17)	C(14)–C(15)–C(11)	110.0(3)
C(14)–Ni(1)–C(15)	42.30(16)	C(14)–C(15)–Ni(1)	64.8(2)
C(13)–Ni(1)–C(15)	67.39(17)	C(11)–C(15)–Ni(1)	104.2(3)
C(24)–Ni(2)–C(25)	42.05(18)	C(25)–C(21)–C(11)	113.0(3)
C(24)–Ni(2)–C(23)	41.81(18)	C(25)–C(21)–C(22)	102.1(3)
C(25)–Ni(2)–C(23)	67.67(18)	C(11)–C(21)–C(22)	113.1(3)
C(15)–C(11)–C(21)	112.9(3)	C(23)–C(22)–C(21)	103.9(4)
C(15)–C(11)–C(12)	102.7(3)	C(24)–C(23)–C(22)	110.0(4)
C(21)–C(11)–C(12)	113.6(3)	C(24)–C(23)–Ni(2)	65.1(2)
C(13)–C(12)–C(11)	103.1(3)	C(22)–C(23)–Ni(2)	102.3(3)
C(14)–C(13)–C(12)	110.5(4)	C(23)–C(24)–C(25)	105.6(4)
C(14)–C(13)–Ni(1)	65.2(2)	C(23)–C(24)–Ni(2)	73.1(2)
C(12)–C(13)–Ni(1)	103.0(3)	C(25)–C(24)–Ni(2)	72.8(2)
C(13)–C(14)–C(15)	105.0(4)	C(24)–C(25)–C(21)	109.6(4)
C(13)–C(14)–Ni(1)	73.2(2)	C(24)–C(25)–Ni(2)	65.1(2)
C(15)–C(14)–Ni(1)	72.9(2)	C(21)–C(25)–Ni(2)	103.6(3)

[a] Estimated S.D. values in parentheses.

3.3. Reaction of nickelocene with triphenylmethyllithium

A solution of triphenylmethyllithium in THF (28 mmol, 10 ml) was added within 1 h at −78°C to a solution of $NiCp_2$ (3.8 g, 20 mmol) in 100 ml THF and kept at this temperature for 5 h. The reaction mixture was then allowed to warm up to r.t. and stirred for a further 12 h. The solvents were distilled off under reduced pressure and the residue was dissolved in 10 ml THF and followed by addition of 40 ml of deoxygenated water. The organic layer was separated, dried and filtered through a bed of Al_2O_3. After partial evaporation of the solvent the mixture was chromatographed on alumina (37 × 2 cm deactivated with 5% water) using hexane–toluene mixtures as eluents. Four bands were separated:

The first band was concentrated and left for crystallisation at 3°C to give red–brown crystals of CpNi(η^3-$C_6H_5CPh_2$) (**4**) (yield 36%). The crystals were suitable for X-ray crystal structure measurements (see Section 3.4). The compound was also characterised by ^{1}H- and ^{13}C-NMR spectroscopy, and mass spectrometry. ^{1}H-NMR (THF-d_8) (atom numbering is shown at the scheme below) δ ppm: 7.30–7.15 (m, 13H, H aromatic), 6.15 (m, 2H, H-2, 2′ and H-6), 4.93 (s, 5H, Cp); ^{13}C-NMR δ ppm: 146.7 (C-6), 133.9 (C-3, 3′), 131.6 (C-7), 128.3 (C-8), 126.2 (C-9), 126.0 (C-4), 103.4 (C-1), 97.8 (C-2, 2′), 91.4 (Cp), 67.5 (C-5); EIMS (70 eV) *m*/*e* calculated for ^{58}Ni (relative intensity, %): 366 [M^+] (35), 300 [$(M-C_5H_6)^+$] (38), 243 [CPh_3^+] (34), 165 [$PhCC_6H_4^+$] (100).

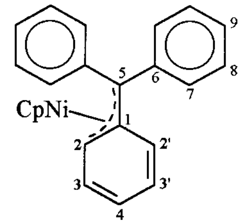


Table 4
Crystal data and structure refinement for **4**

Empirical formula	$C_{24}H_{20}Ni$
Crystal size (mm)	0.42 × 0.21 × 0.052
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.8747(9)
b (Å)	10.6331(10)
c (Å)	19.569(2)
α (°)	93.793(8)
β (°)	102.000(8)
γ (°)	113.912(7)
Volume (Å^3)	1811.2(3)
Z	4
Formula weight	367.11
D_{calc} (g cm^{-3})	1.346
Temperature (K)	293(2)
Absorption coefficient (mm^{-1})	1.531
F(000)	768
Radiation	Cu–K$_\alpha$ (λ = 1.54184 Å, graphite monochromator)
θ Range for data collection (°)	4.61–72.92
Scan type	ω–2θ
Index ranges	$-11 \le h \le 12$, $-13 \le k \le 13$, $-24 \le l \le 0$
Reflections collected/unique	7650/3691 (R_{int} = 0.0353)
Completeness to 2θ = 72.92° (%)	51.0
Absorption correction	ψ-scan
Max. and min. transmission	99.89 and 87.41
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3691/15/469
Goodness-of-fit on F^2	1.061
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0652 [a] wR_2 (refined) = 0.1317 [b]
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.0657P)^2 + 0.0000P$ [c]
R indices (all data)	R_1 = 0.0829; wR_2 = 0.1413
Extinction coefficient	0.0036(3)
Largest difference peak and hole (e Å^{-3})	0.507 and −0.343

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] $P = (F_o^2 + 2F_c^2)/3$.

The second deep-red band afforded after recrystallisation from hexane dark crystals of $(NiCp)_3CCH_3$ (yield 10%). The structure of this cluster has been determined previously [12]; therefore, it has been identified by means of ^{1}H- and ^{13}C-NMR spectroscopy, and mass spectrometry. ^{1}H-NMR (C_6D_6) δ ppm: 5.15 (s, 15H, Cp), 3.71 (s, 3H, CH_3); ^{13}C-NMR δ ppm: 289.2 (C-methylidyne), 88.0 (Cp), 46.0 (CH_3); EIMS (70 eV) *m*/*e* calculated for ^{58}Ni (relative intensity, %): 396 [M^+] (50), 330 [$(M-C_5H_6)^+$] (50), 246 [$Ni_2Cp_2^+$] (42), 188 [$NiCp_2^+$] (95), 123 [$NiCp^+$] (100).

The third dark red band contained a small amount of CpNi(η^5-$C_5H_4CPh_3$) (**5**) together with doubly alkylated CpNi(η^5-$C_5H_3(CPh_3)_2$). The compounds were characterised by EIMS (70 eV) of their mixture. Molecular ions appeared at *m*/*e* (calculated for ^{58}Ni) 430 for CpNi($C_5H_4CPh_3$) and at 672 for $CpNiC_5H_3(CPh_3)_2$.

The solvents from the fourth brown band were evaporated and the residue was recrystallised from a 6:1 hexane–toluene mixture giving dark brown crystals of a new alkylidynetri(cyclopentadienylnickel) cluster $(NiCp)_3CCH_2CPh_3$ (yield 8%). The cluster was characterised by ^{1}H- and ^{13}C-NMR spectroscopy, and mass spectrometry. ^{1}H-NMR (C_6D_6) δ ppm: 7.64–7.06 (m, 15H, C_6H_5), 5.44 (s, 2H, CH_2), 4.95 (s, 15H, C_5H_5); ^{13}C-NMR δ ppm: 285.1 (C-alkylidyne), 148.1 (C-1 phenyl), 131.3 (C-3,5 phenyl), 128.3 (C-2,6 phenyl), 126.3 (C-4 phenyl), 88.0 (Cp), 69.7 (CH_2), 61.7 (*C*Ph_3); EIMS (70 eV) *m*/*e* calculated for ^{58}Ni (relative intensity, %): 638 [M^+] (18), 572 [$(M-C_5H_6)^+$] (20), 395 [$M-CPh_3^+$] (100), 123 [$NiCp^+$] (6).

3.4. Crystal structure determination of **4**

An X-ray diffraction experiment was performed on a Nonius BV MACH3 diffractometer using a crystal sealed in a quartz capillary tube. Crystal stability was monitored every 100 reflections and it showed a 16% loss of intensity. The unit cell parameters were obtained by the least-squares fit of the setting angles for 25 reflections. These, along with selected details of data collection, structure solution and refinement procedures, are shown in Table 4. The intensities were corrected for Lorentz, polarisation and ψ-scan based absorption factors using the MOLEN system [18]. Due to

Table 5
Selected interatomic distances (Å) in **4** [a]

Ni(1)–C(1)	1.978(6)	C(15)–C(16)	1.377(9)
Ni(1)–C(2)	2.055(6)	C(21)–C(26)	1.391(8)
Ni(1)–C(7)	2.013(6)	C(21)–C(22)	1.392(8)
C(1)–C(7)	1.458(8)	C(22)–C(23)	1.380(8)
C(11)–C(7)	1.495(8)	C(23)–C(24)	1.389(9)
C(21)–C(7)	1.503(8)	C(24)–C(25)	1.344(9)
C(1)–C(2)	1.443(8)	C(25)–C(26)	1.399(9)
C(1)–C(6)	1.416(9)	C(31)–C(35)	1.374(11)
C(2)–C(3)	1.415(9)	C(31)–C(32)	1.402(11)
C(3)–C(4)	1.325(10)	C(32)–C(33)	1.397(10)
C(4)–C(5)	1.420(11)	C(33)–C(34)	1.386(11)
C(5)–C(6)	1.355(9)	C(34)–C(35)	1.347(11)
C(11)–C(16)	1.386(8)	Ni(1)–C(31)	2.074(8)
C(11)–C(12)	1.389(8)	Ni(1)–C(33	2.092(7)
C(12)–C(13)	1.381(9)	Ni(1)–C(32)	2.112(8)
C(13)–C(14)	1.382(10)	Ni(1)–C(34)	2.130(8)
C(14)–C(15)	1.381(10)	Ni(1)–C(35)	2.150(9)

[a] Estimated S.D. values in parentheses.

Table 6
Selected bond angles (°) in **4** [a]

C(1)–Ni(1)–C(7)	42.9(2)	C(1)–C(7)–C(11)	118.0(5)
C(1)–Ni(1)–C(2)	41.9(2)	C(1)–C(7)–C(21)	119.5(6)
C(7)–Ni(1)–C(2)	73.8(2)	C(11)–C(7)–C(21)	114.9(5)
C(6)–C(1)–C(2)	117.9(6)	C(1)–C(7)–Ni(1)	67.3(3)
C(6)–C(1)–C(7)	127.0(6)	C(11)–C(7)–Ni(1)	110.3(4)
C(2)–C(1)–C(7)	114.6(6)	C(21)–C(7)–Ni(1)	117.8(4)
C(3)–C(2)–C(1)	118.3(7)	C(2)–C(1)–Ni(1)	71.9(4)
C(4)–C(3)–C(2)	121.6(8)	C(1)–C(2)–Ni(1)	66.2(3)
C(3)–C(4)–C(5)	121.0(8)	C(7)–C(1)–Ni(1)	69.8(3)
C(6)–C(5)–C(4)	119.8(8)	C(6)–C(1)–Ni(1)	121.3(4)
C(5)–C(6)–C(1)	121.3(7)	C(3)–C(2)–Ni(1)	120.5(5)

[a] Estimated S.D. values in parentheses.

the 2D crystal, only 51.1% of the collected data were considered as observed and an NZ test showed non-centrosymmetric distribution of *E* values. Therefore, the structure was solved in the non-centrosymmetric $P1$ space group. Direct methods performed with the use of SHELXS-97 [16] program yielded four molecules gathered in two clusters. The space group was then changed to $P\bar{1}$ and the origin of the coordinate system was moved using a 0.666, 1.1463, − 1.858 translation vector. The structure was refined by the full-matrix least-squares method using the SHELXL-97 program [17]. A model with a 0.8:0.2 occupancy ratio and restricted C–C distances was introduced for the cyclopentadienyl ring in one of the two asymmetric molecules. All H atoms were fixed in geometrically calculated positions and were assigned isotropic displacement parameters with values equal to $1.2U_{eq}$ of the parent atom. Correction for secondary extinction was introduced in the final refinement.

The crystal structure with the atom numbering system is presented in Fig. 2, and selected bond lengths and bond angles for **4** are listed in Tables 5 and 6.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-139775 and -139776 for compounds **1** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; http: http://www.ccdc.cam.ac.uk).

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