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The first structurally characterized trinickel cluster with an open structure: Crystal and molecular structure of $\overline{\mathrm{CpNi}[\mu\text{-}\eta^4\text{-PhC=C(Ph)–C(Ph)=C}}\mathrm{Ph}]\mathrm{Ni}(\mu\text{-}\eta^2\eta^2\text{-PhC}\equiv\text{CPh})\mathrm{NiCp}$[1]

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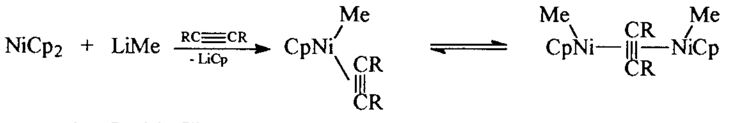
Abstract

Reaction of nickelocene with methyllithium in the presence of diphenylacetylene at the molar ratio of reactants 1:1:2 produces a trinickel cluster with an open structure. The cluster contains a bent arrangement of nickel atoms. Two of the alkyne units are linked via a carbon–carbon bond to produce a nickelacyclopentadienyl ring, while the third alkyne unit remains independently coordinated to the cluster via two π-bonds. Two Cp groups are bonded to two terminal nickel atoms. The cluster crystallizes from methylene chloride with solvent molecules in a monoclinic crystal system and $P2_1/n$ space group. Corresponding unit cell parameters were determined as: $a = 12.4385(13)$ Å; $b = 24.994(3)$ Å; $c = 13.9657(14)$ Å; $\beta = 91.457(8)°$; $V = 4340.4(8)$ Å^3; $Z = 4$.

Keywords: Nickel; Metal clusters; Nickelocene

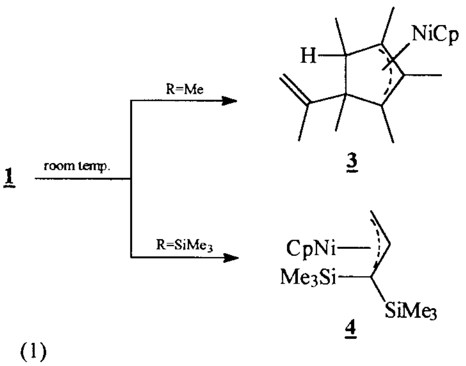
1. Introduction

We have previously found that nickelocene reacts with methyllithium in the presence of an excess of alkynes at − 78°C to form π-complexes **1** and **2** (Eq. 1) [1].



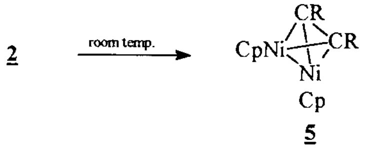
where R = Me; SiMe3 **1** **2** (1)

These complexes react further at room temperature. For R = CH_3 the complex **1** reacts to form π-allyl complexes **3** and for R = $Si(CH_3)_3$[bis(1,1-trimethylsilyl)-η^3allyl]cyclopentadienylnickel **4** was obtained (Eq. 2) [2]



(2)

The complex **2** warmed up to room temperature forms the dinickel compound **5** (Eq. 3).



(3)

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[1] Dedicated to the memory of Professor Mark E. Vol'pin.

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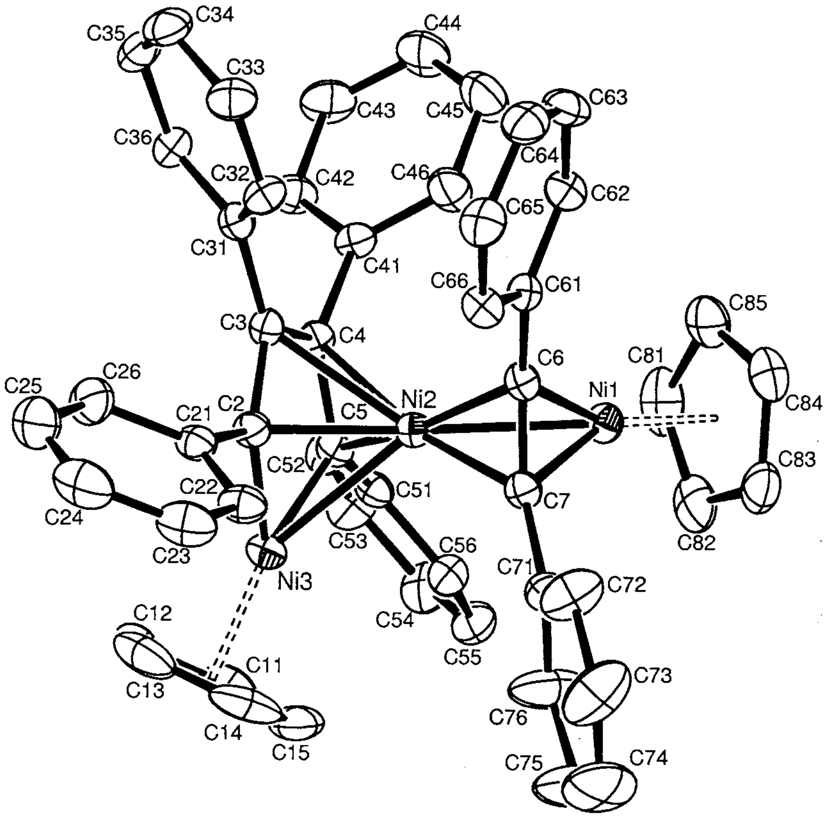


Fig. 1. The ORTEP-III drawing of **6** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms and the solvent of crystallization (CH_2Cl_2) have been omitted for clarity.

If the reactions of nickelocene with methyllithium were carried out in the presence of a large excess of diphenylacetylene the polydiphenylacetylene was formed with a very good yield (Eq. 4) [2].

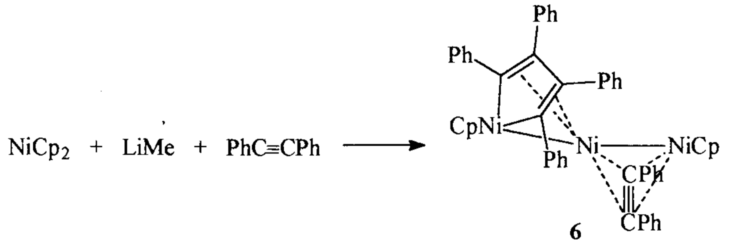
$$NiCp_2 + LiMe \xrightarrow[-\,LiCp]{PhC\equiv CPh} (PhC=CPh)_n \qquad (4)$$

The purpose of this work was to study the reactions of nickelocene with organolithium and -magnesium compounds and diphenylacetylene at the molar ratio of reactants 1:1:2, to isolate and characterize the products formed.

2. Results and discussion

We have found that 1 mol of nickelocene reacts with 1 mol of methyllithium in the presence of 2 mol of diphenylacetylene to form, unknown till now, a trinickel cluster with an open structure and that the reaction proceeded in a completely different way than if carried out with a large excess of diphenylacetylene (Eq. 5).

The molecular structure of **6** is shown in Fig. 1 and atomic coordinates, selected bond distances and angles are presented in Tables 2–4, respectively. The core of the compound forms a chain of three nickel atoms with Ni(1)–Ni(2) and Ni(2)–Ni(3) distances 2.3779(7) and 2.4404(7) Å, respectively, and Ni–Ni–Ni angle of 136.88(2)°. Ni(1) and Ni(2) atoms are at a typical single Ni–Ni bond distance. Two of the diphenylacetylene ligands have undergone carbon–carbon bond formation to produce an organic ligand containing four carbon atoms. This ligand forms two σ-bonds to Ni(3) forming a nickelacyclopentadienyl ring consisting of Ni(3), C(2), C(3), C(4) and C(5) atoms. The molecule can be treated as analogues one to the known complex (μ-diphenylacetylene)bis(η^5-cyclopentadienylnickel) $(NiCp)_2 \cdot (PhC{\equiv}CPh)$ **7** [3], where one Cp ring is replaced by a nickelacyclopentadienyl ring, that is schematically presented in Fig. 2. The ring is an envelope with Ni(3) deviated at 0.377(6) Å from the plane defined by C(2)–C(5) atoms. It can be treated as nearly planar



6

(5)

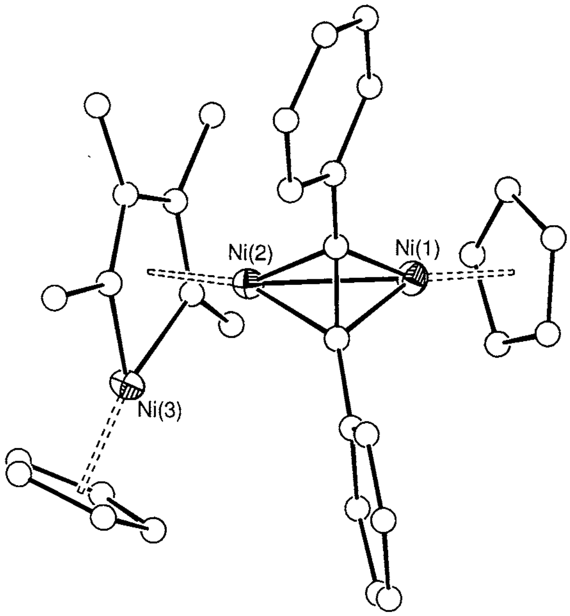


Fig. 2. A schematic presentation of the coordination modes of Ni atoms in **6**.

with maximum deviation from the mean plane defined by all five atoms of 0.1 13(2) Å for C(2). This ring can be considered as pseudoaromatic what appears in little differentiation of C–C distances and a substantial shortening of Ni(3)–C(2) (1.896(3) Å) and Ni(3)–C(5) (1.916(3) Å) from a typical $\mathrm{NiC_{alkyl}}$ single bond. We have estimated the lengths of a typical C–Ni bond as 1.944 Å (an average of 24 entries) and of typical C=Ni bond as 1.826 Å (from five entries) taking the data from Cambridge Crystallographic Database [4].

The Pauling's concept of the relation between the bond length $R(n)$ and the bond order n [5] (Eq. 6) was applied to calculate bond orders of Ni–C in **6**.

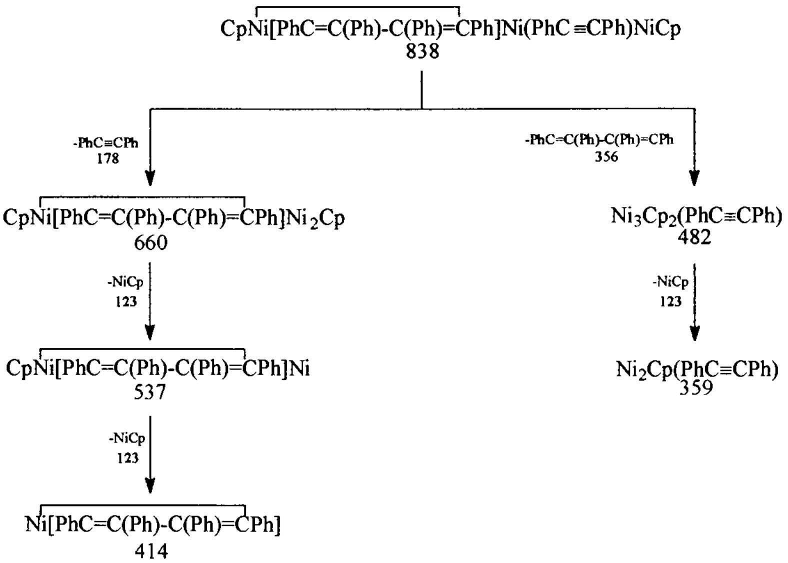
$$R(n) - R(1) = -c\ln(n) \qquad (6)$$

From that equation the value of constant c was estimated as 0.1702, taking bond lengths for the typical single, $R(1)$, and double, $R(2)$, Ni–C bonds. We have calculated bond orders of Ni–C in **6** to obtain values of 1.33 for Ni(3)–C(2) and 1.18 for Ni(3)–C(5) that confirms a contribution of nickel electrons to the nickelacyclopentadienyl ring π-bond system.

The nickelacyclopentadienyl ring acts as a five-electron donor, that causes all three nickel atoms associated with 18 electrons each. In terms of electron counting the complex **6** is a 50 electron cluster, consistent with the presence of two metal–metal bonds.

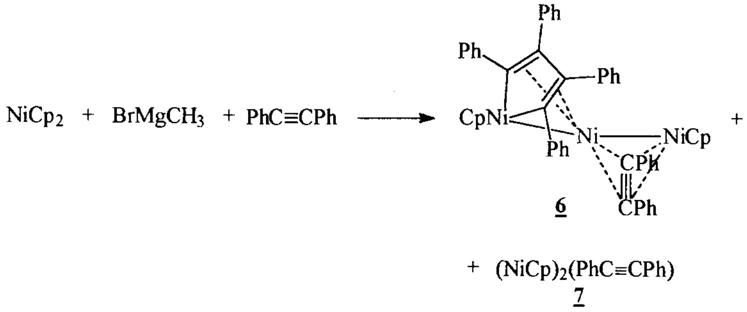
^{1}H-NMR spectrum reveals two different signals of Cp groups bonded to Ni(1) and Ni(3) at δ 5.14 and 4.56 ppm (integration ratio 1:1) and a complex system of overlapping aromatic proton signals at 6.75–7.22 ppm. ^{13}C-NMR shows two signals of cyclopentadienyl carbon atoms at δ 94.80 and 90.37 ppm, and two signals of nickelacyclopentadienyl ring carbon atoms (C(2; 5) at 176.85 ppm and C(3; 4) at 150.99 ppm). Carbon atoms of diphenylacetylene π-bonded to the Ni(1) and Ni(2) atoms appear at 102.12 ppm. Phenyl carbon atoms appear as several signals at 126.26. 138.17 ppm. The ^{1}H and ^{13}C-NMR spectra are consistent with the structure of **6** shown on Fig. 1. EIMS (70 eV) of **6** shows a parent ion at m/e 838 (^{58}Ni calc.). The signal has an isotopic pattern characteristic for three nickel atoms. The proposed fragmentation pattern is presented in Scheme 1.

In the reaction of nickelocene with methyllithium and diphenylacetylene at the molar ratio of reactants 1:1:2, besides trinickel cluster **6**, the complex $(\mathrm{NiCp})_2(\mathrm{PhC{\equiv}CPh})$ **7** of known structure determined by Mills and Shaw [3], is formed with 50% yield. We have isolated it by column chromatography and identified by means of ^{1}H-NMR (singlet of cyclo-



Scheme 1.

pentadienyl protons at 5.33 ppm and multiplet of phenyl protons at 7.15 ppm), ^{13}C-NMR (cyclopentadienyl carbons at 87.76 ppm, alkyne carbons bonded to nickel at 138.45 ppm) and mass spectrometry [a parent ion at *m*/*e* 424 (^{58}Ni calc.; an isotopic pattern characteristic for two nickel atoms); 246 $(\mathrm{NiCp})_2^+$, 188$(\mathrm{NiCp_2})^+$ and 123 $(\mathrm{NiCp})^+$]. The other products formed in the above reaction were: small amount of diphenylacetylene polymer and a dinickel compound **8** of molecular weight 603 (determined from the mass spectrum), that corresponded to the formula $\mathrm{Ni_2Cp_2H(PhC{\equiv}CPh)_2}$. This compound has not been fully characterized yet. The products of the reaction of nickelocene with methylmagnesium bromide and diphenylacetylene at the molar ratio of reactants 1:1:2 were the compounds **6** and **7** (Eq. 7). The formation of compound **8** was not observed.

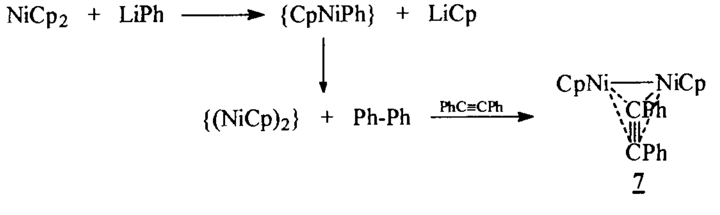


(7)

The main product of the reaction of nickelocene with phenyllithium and diphenylacetylene at the molar ratio of reactants 1:1:2 was the compound **7** (Eq. 8). The cluster **6** was not formed in this reaction.

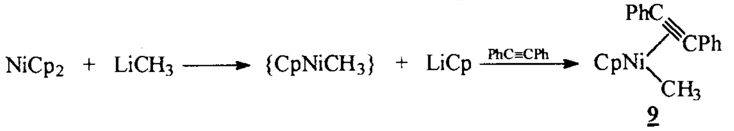
$$\mathrm{NiCp_2 + LiPh + PhC \equiv CPh \rightarrow (NiCp)_2\left(\underset{7}{Phc \equiv CPh}\right)} \tag{8}$$

Differences in the reaction course of methyl- and phenyllithium can be explained by differences of coupling reaction rates for the methyl and phenyl groups. We have previously shown that in the reaction of nickelocene with phenyllithium, diphenyl and the unstable active species $\{(\mathrm{NiCp})_2\}$ are formed with a high yield [6,7]. These species can easily form complexes with diphenylacetylene to produce compound **7** (Eq. 9).



(9)

Contrary to this, in the first step of the reaction of nickelocene with methyllithium in the presence of alkenes or alkynes, relatively stable complexes of the type **9** are formed (Eq. 10) [8]. These complexes react then further forming various products.



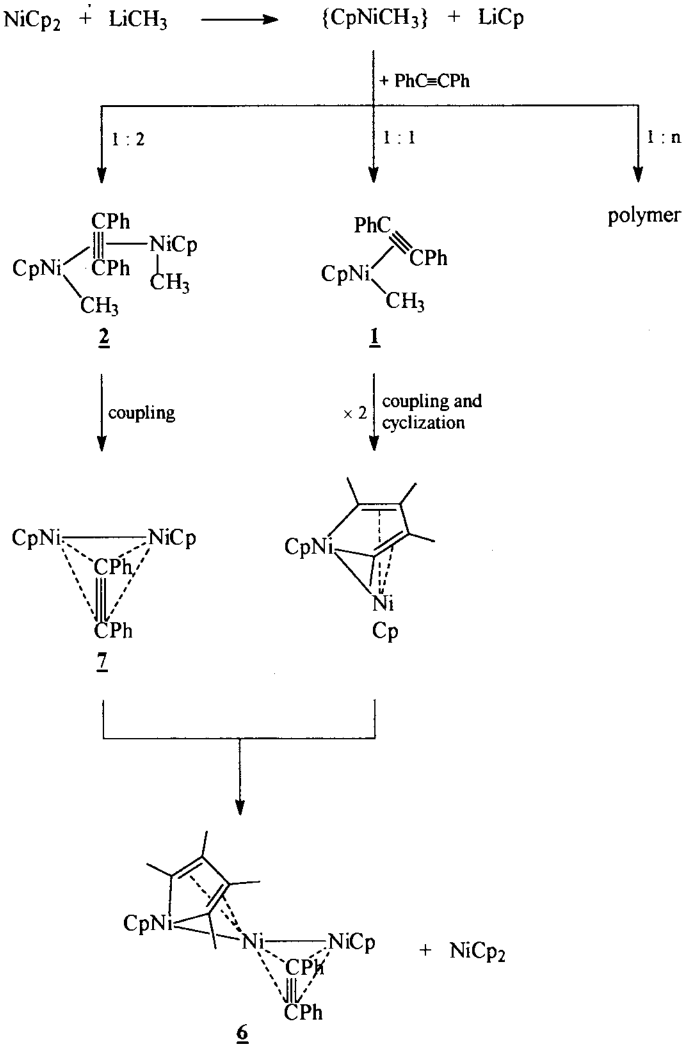
(10)

A proposition of the reaction course leading to the formation of the cluster **6** is presented on Scheme 2.

The cluster **6** is the first structurally characterized trinickel cluster with a chain arrangement of nickel atoms. Based on spectroscopic evidences, a similar structure was proposed for $[\mathrm{Ni_3(C_5H_5)_2(CF_3C_2CF_3)_3}]$ obtained in the reaction of hexafluorobut-2-yne with $[\{\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{SCF_3})\}]$ [9]. A compound having the empirical formula $\mathrm{Ni_2Mo(CO)_2(PhC{\equiv}CH)_3CpCp^*}$ was obtained from the reaction of Cp*Ni(CO)I with $[\mathrm{CpMo(CO)_3}]^-$ and an excess of PhC≡CH [10]. Its molecular structure is similar to **6** and also reveals a chain arrangement of three metal atoms with molybdenum involved in metallacyclopentadiene ring. The other two structurally characterized examples of compounds with three-metal chains and metallacyclopentadiene rings are $\mathrm{(CO)_3Co\{\mu\text{-}\eta^4\text{-}C(Et){=}C(Et){-}C(Et){=}C(Et)\}W(CO)_2(\mu\text{-}\eta^2\eta^2\text{-}EtC{\equiv}CEt)Co(CO)_3}$ [11] and $\mathrm{(CO)_3Os\{\mu\text{-}\eta^4\text{-}C(Me){=}C(Me){-}C(Me){=}C(Me)\}Os(CO)_2(\mu\text{-}\eta^2\eta^2\text{-}MeC{\equiv}CMe)Os(CO)_3}$ [12].

3. Experimental details

All reactions were carried out under an atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. ^{1}H and ^{13}C-NMR spectra were measured on a Varian VXR-300 instru-



Scheme 2.

ment. Mass spectra were recorded on an AMD-604 mass spectrometer.

3.1. Reaction of nickelocene with methyllithium in the presence of diphenylacetylene

A solution of 2.27 g $NiCp_2$ (12.03 mmol) and 4.28 g of diphenylacetylene (24.06 mmol) in 100 cm^3 THF was cooled to $-55°C$, then a solution of methyllithium in Et_2O (27 cm^3, 13.23 mmol) was added over 1 h (temperature was maintained at -55 to $-50°C$). The mixture was stirred at this temperature for the next hour, then it was allowed to warm up slowly to room temperature. Stirring was continued overnight. The volatile substances were removed under reduced pressure, then 20 cm^3 of toluene and 60 cm^3 of hexane were added and the products were hydrolyzed with 60 cm^3 of the deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was re-dissolved in toluene/hexane mixture and chromatographed on Al_2O_3 (37 × 2 cm, deactivated with 5% of water) using hexane/toluene mixture as eluent.

A small amount of green $NiCp_2$ (eluent: 3% toluene in hexane) was eluted. The next green band containing $(NiCp)_2(PhC{\equiv}CPh)$ was collected (yield 53%; eluent 25% toluene in hexane). It was characterized by ^1H-NMR (C_6D_6) δ[ppm] 5 16 (s, 10H), 7.15 (m, 10H); ^{13}C-NMR (C_6D_6) δ[ppm] 139.22, 130.64–127.43, 87.76; EIMS (70 eV) m/e 424 (M^+, 60%), 246 (100%), 188 (60%), 123 (17%), 58 (5%).

The next brown band was eluted with 35% toluene in hexane. It was evaporated to dryness, re-dissolved in THF/hexane mixture and purified by additional column chromatography (eluent: 10% THF in hexane). The brown solid was obtained. It was identified as $(NiCp)_2(PhC{\equiv}CPh)_2H$ (yield 19.5%) by means of mass spectroscopy. EIMS (70 eV) m/e-603 (M^+, 70%), 537 (100%), 479 (50%), 424 (18%), 414 (65%), 359 (22%), 246 (27%), 188 (25%), 178 (30%), 123 (22%), 58 (8%).

The next brown-red fraction was also collected (eluent: 50% toluene in hexane). It was evaporated to dryness, re-dissolved in THF/hexane mixture and purified by additional column chromatography (eluent: 15% THF in hexane). The brown-red solid obtained was identified as $CpNi[\mu\text{-}\eta^4\text{-}PhC{=}C(Ph){-}C(Ph){=}CPh]Ni(\mu\text{-}\eta^2\eta^2\text{-}PhC{\equiv}CPh)NiCp$ (yield 15%), ^1H-NMR (C_6D_6) δ[ppm] 7.22–6.75 (m, 30H), 5.14 (s, 5H), 4.56 (s, 5H); ^{13}C-NMR (C_6D_6) δ[ppm] 176.85, 150.99, 138.16, 136.83, 131.36–126.26, 102.12, 94.80, 90.37; EIMS (70 eV) m/e 838 (M^+, 50%), 660 (90%), 602 (8%), 537 (27%), 484 (48%), 472 (20%), 414 (45%), 359 (33%), 246 (7%), 188 (7%), 178 (100%), 123 (37%), 58 (8%). The crystal structure was determined by X-ray analysis.

3.2. X-ray structure determination of **6**

A selected deep-violet crystal of **6**, crystallized from methylene chloride, was sealed inside a capillary (Lindemann glass) in an inert atmosphere and mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. Crystal data and details of data collection and refinement procedure are presented in Table 1. The orientation matrix was obtained from the least-squares refinement of the angular positions measured for 50 reflections randomly selected with $16.0° < 2\theta < 26.5°$. Two check reflections repeated every 70 reflections showed a decay of 4.6%. After correction for the Lorentz-polarization effect and crystal decomposition, the gaussian absorption correction was applied based on a well defined crystal shape. The phase problem was solved in the $P2_1/n$ space group by direct methods using the SHELXS program [13]. The structure was refined on F^2 by full-matrix least-squares method (SHELXL97 program [14]) with isotropic thermal parameters in the first step. After full convergence of the isotropic refinement, anisotropic thermal parameters were assigned for all non-H atoms. Although some of the H atoms could be found in subsequent difference Fourier maps, all were set riding in calculated positions with fixed isotropic thermal parameters $U_{iso} = 1.2U_{eq}(C)$. A single molecule of solvent, CH_2Cl_2, disordered over several orientations was located in the structure cavity. Four partially occupied molecules of CH_2Cl_2 were included in the refinement process giving no significant features in the final difference Fourier map. In the final stages of refinement the maximum shift/error ratios were less than 0.001. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Selected bond lengths and angles are presented in Tables 3 and 4. The same compound crystallizes also from hexane, without solvent molecules, in a triclinic crystal system and $P\bar{1}$ space group. Corresponding unit cell parameters were determined as: $a = 12.018(3)$ Å; $b = 13.287(3)$ Å; $c = 15.177(6)$ Å; $\alpha = 98.50(3)°$; $\beta = 106.25(3)°$; $\gamma =$

Table 1
Crystal data and structure refinement for 6

Empirical formula	$C_{52}H_{40}Ni_3 \cdot CH_2Cl_2$
Crystal size (mm)	$0.10 \times 0.17 \times 0.74$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions:	$a = 12.4385(13)$ Å $b = 24.994(3)$ Å $c = 13.9657(14)$ Å $\beta = 91.457(8)°$
Volume	4340.4(8) Å^3
Z	4
Formula weight	925.89
Density (calc.)	1.417 g cm^{-3}
Temperature (K)	293(2)
Absorption coefficient	1.447 mm^{-1}
$F(000)$	1912
Radiation	Mo–K$_\alpha$($\lambda = 0.71073$ Å, graphite monochromator)
θ range for data collection	2.17–25.06°
Scan type	$\omega - 2\theta$
Index ranges	$0 \le h \le 14$, $0 \le k \le 29$, $-16 \le l \le 16$
Reflections collected/unique	7939/7577 [$R_{int} = 0.0254$]
Absorption correction	Gaussian
Max. and min. transmission	0.8516 and 0.8007
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7577/103/587
Goodness-of-fit on F^2	0.969
Final R indices [$I > 2\sigma(I)$]	
$R_1 = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma(\lvert F_o\rvert)$	$R_1 = 0.0400$
$wR_2 = \{\Sigma[wF_o^2 - F_o^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$	$wR_2 = 0.0814$
Weighting scheme	$w^{-1} = [\sigma^2(F_o^2) + (0.0445P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
R indices (all data)	$R_1 = 0.0736$, $wR_2 = 0.0910$
Largest difference peak and hole	0.376 and -0.329 e Å^{-3}

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **6**[a]

Atom	x	y	z	U_{eq}^{b}
Ni(1)	3643(1)	1677(1)	6624(1)	36(1)
Ni(2)	1978(1)	1346(1)	7176(1)	31(1)
Ni(3)	1210(1)	475(1)	7556(1)	37(1)
C(11)	1460(4)	−354(2)	7419(3)	58(1)
C(12)	454(4)	−265(2)	7777(4)	65(1)
C(13)	589(5)	−1(2)	8647(4)	82(2)
C(14)	1703(6)	63(2)	8827(3)	78(2)
C(15)	2226(4)	−163(2)	8061(4)	66(1)
C(2)	552(3)	1145(1)	7783(2)	36(1)
C(21)	126(3)	1262(1)	8748(2)	39(1)
C(22)	816(3)	1329(2)	9537(2)	47(1)
C(23)	415(4)	1393(2)	10453(3)	65(1)
C(24)	−669(5)	1385(2)	10580(3)	73(2)
C(25)	−1360(4)	1324(2)	9819(3)	71(1)
C(26)	−980(3)	1262(2)	8897(3)	58(1)
C(3)	229(3)	1427(1)	6947(2)	34(1)
C(31)	−499(3)	1897(1)	6936(2)	35(1)
C(32)	−353(3)	2315(2)	7569(3)	42(1)
C(33)	−1064(3)	2739(2)	7598(3)	52(1)
C(34)	−1962(3)	2744(2)	6983(3)	56(1)
C(35)	−2117(3)	2333(2)	6347(3)	50(1)
C(36)	−1404(3)	1909(2)	6322(3)	41(1)
C(4)	715(3)	1206(1)	6094(2)	33(1)
C(41)	617(3)	1493(1)	5146(2)	35(1)
C(42)	−139(3)	1340(2)	4449(2)	47(1)
C(43)	−252(4)	1622(2)	3606(3)	59(1)
C(44)	381(4)	2054(2)	3441(3)	71(1)
C(45)	1127(4)	2214(2)	4116(3)	80(2)
C(46)	1233(3)	1935(2)	4975(3)	55(1)
C(5)	1354(3)	752(1)	6286(2)	34(1)
C(51)	1866(3)	401(1)	5571(2)	35(1)
C(52)	1287(3)	204(2)	4775(3)	45(1)
C(53)	1717(3)	−188(2)	4203(3)	59(1)
C(54)	2732(4)	−380(2)	4385(3)	59(1)
C(55)	3333(3)	−179(2)	5145(3)	52(1)
C(56)	2902(3)	201(1)	5740(3)	42(1)
C(6)	2752(3)	1998(1)	7547(2)	33(1)
C(61)	2388(3)	2538(1)	7769(2)	32(1)
C(62)	2298(3)	2929(1)	7069(3)	41(1)
C(63)	1945(3)	3433(2)	7284(3)	51(1)
C(64)	1663(3)	3559(2)	8197(3)	55(1)
C(65)	1727(3)	3178(2)	8907(3)	52(1)
C(66)	2091(3)	2673(2)	8704(2)	43(1)
C(7)	3233(3)	1567(1)	7916(2)	35(1)
C(71)	3885(3)	1371(2)	8727(3)	45(1)
C(72)	4141(4)	1684(2)	9507(3)	69(1)
C(73)	4795(4)	1489(3)	10252(4)	97(2)
C(74)	5227(5)	992(3)	10199(4)	111(2)
C(75)	5023(6)	676(3)	9401(5)	138(3)
C(76)	4333(5)	865(2)	8688(4)	104(2)
C(81)	4046(4)	1459(2)	5222(3)	68(1)
C(82)	4790(4)	1233(2)	5872(4)	70(1)
C(83)	5312(3)	1647(2)	6359(3)	61(1)
C(84)	4887(3)	2130(2)	6009(3)	56(1)
C(85)	4109(4)	2011(2)	5301(3)	58(1)

[a] Positional and thermal parameters for disordered solvent molecule are included in supplementary materials.

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

Table 3
Selected inter-atomic distances (Å) in **6**[a]

Ni(1)–C(6)	1.899(3)	Ni(3)–C(5)	1.916(3)
Ni(1)–C(7)	1.907(3)	Ni(3)–C(13)	2.096(4)
Ni(1)–C(81)	2.106(4)	Ni(3)–C(12)	2.100(4)
Ni(1)–C(82)	2.107(4)	Ni(3)–C(11)	2.104(4)
Ni(1)–C(84)	2.116(4)	Ni(3)–C(14)	2.129(4)
Ni(1)–C(83)	2.119(4)	Ni(3)–C(15)	2.143(4)
Ni(1)–C(85)	2.122(4)	C(2)–C(3)	1.412(4)
Ni(1)–Ni(2)	2.3779(7)	C(2)–C(21)	1.489(4)
Ni(2)–C(7)	1.931(3)	C(3)–C(4)	1.459(4)
Ni(2)–C(6)	1.958(3)	C(3)–C(31)	1.482(5)
Ni(2)–C(2)	2.047(3)	C(4)–C(5)	1.408(5)
Ni(2)–C(5)	2.073(3)	C(4)–C(41)	1.508(4)
Ni(2)–C(4)	2.179(3)	C(5)–C(51)	1.485(4)
Ni(2)–C(3)	2.199(3)	C(6)–C(7)	1.330(5)
Ni(2)–Ni(3)	2.4404(7)	C(6)–C(61)	1.458(5)
Ni(3)–C(2)	1.896(3)	C(7)–C(71)	1.462(5)

[a] Estimated standard deviations in parentheses.

91.48(2)°; $V = 2295(1)$ Å^3, $Z = 2$. The quality of the crystal was insufficient for satisfactory structure refinement.

3.3. Reaction of nickelocene with phenyllithium in the presence of diphenylacetylene

A solution of phenyllithium in THF (8.5 cm^3, 7.7 mmol) was added to a solution of NiCp$_2$ (1.32 g, 7.0 mmol) and diphenylacetylene (2.5 g, 14.0 mmol) in 80 cm^3 THF. The reaction was carried out as described in Section 3.1. The following compounds were obtained: small amounts of unreacted NiCp$_2$, (CpNi)$_2$(PhC≡CPh) (yield 49.1%), (NiCp)$_2$(PhC≡CPh)$_2$H (yield 20.5%).

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

C(6)–Ni(1)–C(7)	40.90(14)	C(5)–Ni(2)–Ni(3)	49.43(9)
C(6)–Ni(1)–Ni(2)	53.07(10)	C(4)–Ni(2)–Ni(3)	74.28(9)
C(7)–Ni(1)–Ni(2)	52.18(10)	C(3)–Ni(2)–Ni(3)	73.96(9)
C(7)–Ni(2)–C(6)	39.97(14)	Ni(1)–Ni(2)–Ni(3)	136.88(2)
C(7)–Ni(2)–C(2)	123.07(13)	C(2)–Ni(3)–C(5)	83.45(14)
C(6)–Ni(2)–C(2)	121.32(13)	C(2)–N’(3)–Ni(2)	54.61(10)
C(7)–Ni(2)–C(5)	144.19(14)	C(5)–Ni(3)–Ni(2)	55.26(10)
C(6)–Ni(2)–C(5)	158.30(13)	C(3)–C(2)–C(21)	123.4(3)
C(2)–Ni(2)–C(5)	76.02 ∼ 13)	C(3)–C(2)–Ni(3)	114.7(2)
C(7)–Ni(2)–C(4)	167.23(13)	C(3)–C(2)–Ni(2)	76.5(2)
C(6)–Ni(2)–C(4)	131.14(13)	Ni(3)–C(2)–Ni(2)	76.37(12)
C(2)–Ni(2)–C(4)	68.36(12)	C(2)–C(3)–C(4)	111.8(3)
C(5)–Ni(2)–C(4)	38.56(12)	C(2)–C(3)–Ni(2)	64.84(19)
C(7)–Ni(2)–C(3)	146.49(13)	C(4)–C(3)–Ni(2)	69.80(18)
C(6)–Ni(2)–C(3)	116.04(13)	C(5)–C(4)–C(3)	113.2(3)
C(2)–Ni(2)–C(3)	38.64(12)	C(5)–C(4)–Ni(2)	66.64(18)
C(5)–Ni(2)–C(3)	68.05(13)	C(3)–C(4)–Ni(2)	71.29(18)
C(4)–Ni(2)–C(3)	38.92(12)	C(4)–C(5)–Ni(3)	113.7(2)
C(7)–Ni(2)–Ni(1)	51.25(10)	C(4)–C(5)–Ni(2)	74.8(2)
C(6)–Ni(2)–Ni(1)	50.83(10)	Ni(3)–C(5)–Ni(2)	75.31(11)
C(2)–Ni(2)–Ni(1)	172.11(10)	C(7)–C(6)–Ni(1)	69.9(2)
C(5)–Ni(2)–Ni(1)	111.78(9)	C(7)–C(6)–Ni(2)	68.9(2)
C(4)–Ni(2)–Ni(1)	116.73(9)	Ni(1)–C(6)–Ni(2)	76.10(12)
C(3)–Ni(2)–Ni(1)	141.93(9)	C(6)–C(7)–Ni(1)	69.2(2)
C(7)–Ni(2)–Ni(3)	117.05(10)	C(6)–C(7)–Ni(2)	71.1(2)
C(6)–Ni(2)–Ni(3)	151.42(10)	Ni(1)–C(7)–Ni(2)	76.57(12)
C(2)–Ni(2)–Ni(3)	49.02(10)		

[a] Estimated standard deviations in parentheses.

3.4. Reaction of nickelocene with methylmagnesium bromide in the presence of diphenylacetylene

To a solution of NiCp$_2$ (1.43 g, 7.6 mmol) and diphenylacetylene (2.71 g, 15.2 mmol) in 90 cm^3 THF, a solution of methylmagnesium bromide in Et$_2$O (6.2 cm^3, 8.36 mmol) was added within 1 h at 55–65°C. The mixture was stirred at this temperature for the next hour. It was allowed to cool down slowly to room temperature. Stirring was continued overnight. The solution was concentrated, then 10 cm^3 of toluene and 60 cm^3 of hexane were added, it was hydrolyzed with 60 cm^3 of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was re-dissolved in hexane and chromatographed on Al$_2$O$_3$ (37 × 2 cm, deactivated with 5% of water) using hexane and hexane/toluene as eluents.

A small amount of green NiCp$_2$ was eluted with hexane. The next green band containing (CpNi)$_2$(PhC≡CPh) was collected (eluent: 12% toluene in hexane). The next brown-red band was eluted with 50% toluene in hexane. It was evaporated to dryness, re-dissolved in hexane and purified by additional column chromatography (eluent: 5% THF in hexane). The brown-red solid was obtained. It was identified as CpNi[μ-η^4-PhC=C(Ph)–C(Ph)=CPh]Ni(μ-$\eta^2\eta^2$-PhC≡CPh)NiCp.

4. Supplementary materials

Tables of anisotropic thermal parameters, hydrogen atom coordinates and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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