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# Reactions of nickelocene with phenyl- and methyllithium in the presence of bis(trimethylsilyl)acetylene

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Dedicated to Professor Pierre Braunstein in recognition of his outstanding contributions to organometallic chemistry

#### Abstract

Results of the reactions of nickelocene with phenyl- and methyllithium in the presence of bis(trimethylsilyl)acetylene have been reported. It was found that in the reaction of nickelocene with phenyllithium and bis(trimethylsilyl)acetylene three products were formed: di(cyclopentadienylnickel) complex with bis(trimethylsilyl)acetylene (NiCp)<sub>2</sub>( $\mu$ - $\eta^2$ - $\eta^2$ -Me<sub>3</sub>SiC=CSiMe<sub>3</sub>) (1); di(cyclopentadienylnickel) complex with phenyl(trimethylsilyl)acetylene (NiCp)<sub>2</sub>( $\mu$ - $\eta^2$ - $\eta^2$ -PhC=CSiMe<sub>3</sub>) (2) and tetra(cyclopentadienylnickel) complex with 1,4-bis(trimethylsilyl)-1,3-butadiyne (NiCp)<sub>4</sub>( $\mu$ , $\mu$ - $\eta^2$ - $\eta^2$ - $\eta^2$ - $\eta^2$ - $\eta^2$ - $\Omega^2$ -SiC=CSiMe<sub>3</sub>) (3). Phenyl(trimethylsilyl)-1,3-butadiyne were the products of coupling and cross-coupling of {CpNiPh} and {CpNiC=CSiMe<sub>3</sub>} formed as intermediate products of the reactions. All products were characterized by spectroscopic methods and crystal and molecular structures of compounds 1 and 3 were determined by single crystal X-ray measurements.

Keywords: Nickel; Nickelocene; Alkynes; Butadiynes; Crystal structures

### 1. Introduction

We have previously found that nickelocene reacts with methyllithium and diphenylacetylene forming many di-, tri- and tetranickel compounds [1-3]. The first step of the reaction of nickelocene with methyllithium is the formation of unstable 16-electron species {CpNiCH<sub>3</sub>} (Eq. (1)).

$$NiCp_2 + LiCH_3 \rightarrow \{CpNiCH_3\} + LiCp$$
(1)

Methyl(cyclopentadienyl)nickel reacts in many directions. In the presence in alkynes it forms stable di(cyclopentadienylnickel) complexes [4-12] or unstable nickelacyclopentadienyl ring (Eq. (2)).

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The species formed in the reaction (2) react further forming many isolated and fully characterized cyclopentadienylnickel compounds.

In this paper we present results of the reaction of nickelocene with phenyl- and methyllithium in the presence of di(trimethylsilyl)acetylene.

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### 2. Experimental

### 2.1. Reagents and general techniques

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Bis(trimethylsilyl)acetylene and lithium trimethylsilylacetylide (0.5 M solution in THF) were purchased from Aldrich. Methyl- and phenyllithium were prepared by conventional methods. Solvents were dried by conventional methods. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Varian Mercury 400 MHz instruments. Mass spectra were recorded on AMD-604 and AMD M-40 mass spectrometers.

### 2.2. Reactions of nickelocene with phenyllithium in the presence of bis(trimethylsilyl)acetylene

A solution of 0.92 g of NiCp<sub>2</sub> (4.8 mmol) and 1.1 cm<sup>3</sup> of bis(trimethylsilyl)acetylene (4.8 mmol) in 50 cm<sup>3</sup> THF was cooled to -55 °C. A solution of phenyllithium in THF (5.5  $\text{cm}^3$ , 5.3 mmol) was then added drop by drop within 1 h (temperature was maintained at -55--50 °C). The mixture was stirred at this temperature for the next hour and then it was allowed to warm up slowly to room temperature (r.t.). Stirring was continued overnight. The volatile substances were removed under reduced pressure, 10 cm<sup>3</sup> of THF and 40 cm<sup>3</sup> of C<sub>6</sub>H<sub>14</sub> were added and the products were hydrolyzed with 40  $\rm cm^3$  of the deoxygenated water. The organic layer was separated and dried, then solvents were evaporated, then residue was re-dissolved in toluene-C<sub>6</sub>H<sub>14</sub> mixture and chromatographed on Al<sub>2</sub>O<sub>3</sub> (deactivated with 5% of water) using  $C_6H_{14}$ -toluene mixture as eluent. Organic product, eluted with hexane before the first organometallic band, was identified as biphenyl by means of GC/MS analysis: *m/e* (relative intensity) 154  $(M^+, 100\%), 76 (13.8\%).$ 

A small amount of green NiCp<sub>2</sub> (eluent C<sub>6</sub>H<sub>14</sub>) was eluted. The next green band containing (NiCp)<sub>2</sub>(Me<sub>3</sub>SiC=CSiMe<sub>3</sub>) (1) was collected (yield 53%; eluent 10% toluene in C<sub>6</sub>H<sub>14</sub>). It was characterized by <sup>1</sup>H, <sup>13</sup>C NMR and EIMS. The results were in good agreement with those published in Refs. [11,13]. Green crystals, suitable for X-ray measurements, were obtained by re-crystallization from MeOH.

The third light-green band was eluted with 13% toluene in C<sub>6</sub>H<sub>14</sub> (yield 10%). It was identified as a dinickel compound (NiCp)<sub>2</sub>(Me<sub>3</sub>SiC=CPh) (**2**) based on its <sup>1</sup>H, <sup>13</sup>C NMR and mass spectra. <sup>1</sup>H NMR (acetone-d<sub>6</sub>),  $\delta$  (ppm): 7.25–7.58 (m, 5H, Ph), 5.25 (s, 10H, Cp), 0.33 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR (acetone-d<sub>6</sub>)  $\delta$  (ppm): 139.61–128.0 (Ph), 112.34 (C–Ph), 96.02 (C–Si), 87.79 (Cp), 1.15 (CH<sub>3</sub>); EIMS (EI, 70 eV) *m/e* calculated for <sup>58</sup>Ni (relative intensity, %): 420 (*M*<sup>+</sup>, 30%), 246 (100%), 188 (60%), 123 (25%).

The next brown–green band was eluted using 25% toluene in C<sub>6</sub>H<sub>14</sub>. The compound was identified as (NiCp)<sub>4</sub>(Me<sub>3</sub>SiC=C–C=CSiMe<sub>3</sub>) (3) (yield 5%). It was identified on the basis of its EIMS (70 eV) *m/e* calculated for <sup>58</sup>Ni (relative intensity, %): 686 ( $M^+$ , 60%), 498 (100%), 246 (30%), 188 (60%), 123 (20%), 73 (60%), 58 (40%); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$  (ppm): 5.07 (s, 20H, Cp), 0.45 (s, 18H, CH<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  (ppm): 101.57 (C–C), 96.92 (C–Si), 87.45 (Cp), 1.86 (CH<sub>3</sub>). Black crystals, suitable for X-ray analysis, were obtained from a mixture of C<sub>6</sub>H<sub>14</sub> with few drops of CH<sub>2</sub>Cl<sub>2</sub>.

## 2.3. Reaction of nickelocene with methyllithium in the presence of bis(trimethylsilyl)acetylene

A solution of methyllithium in  $Et_2O$  (4.6 cm<sup>3</sup>, 7.18 mmol) was added within 1 h at -55-65 °C to a solution of NiCp<sub>2</sub> 1.23 g (6.53 mmol) and bis(trimethylsilyl)acetylene 1.5 cm<sup>3</sup> (6.53 mmol) in 70 cm<sup>3</sup> of THF. The mixture was stirred at this temperature for the next hour, and then it was allowed to warm up slowly to r.t. The reaction mixture changed colour from green to brown-green. Stirring was continued overnight. The solution was concentrated, and then 10 cm<sup>3</sup> of THF and 50 cm<sup>3</sup> of  $C_6H_{14}$  were added, it was hydrolyzed with 60 cm<sup>3</sup> of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was re-dissolved in toluene-C<sub>6</sub>H<sub>14</sub> mixture and chromatographed on Al<sub>2</sub>O<sub>3</sub> (deactivated with 5% of water) using  $C_6H_{14}$  and  $C_6H_{14}$ -toluene as eluents. A small amount of green NiCp<sub>2</sub> (eluent  $C_6H_{14}$ ) was eluted. The next green band containing (NiCp)<sub>2</sub>(Me<sub>3</sub>SiC=  $CSiMe_3$  (1) (yield 25%) was collected (eluent 5% toluene in  $C_6H_{14}$ ). The third fraction was also collected ( $C_6H_{14}$ toluene 1:6), solvents were evaporated yielding a green solid identified as  $(NiCp)_2(Me_3SiC \equiv C - C \equiv CSiMe_3)$  (4) (yield 10%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>),  $\delta$  (ppm): 5.14 (s, 10H, Cp), 0.28–0.14 (s, 18H, CH<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ (ppm): 102.93 (Si-C-Ni), 102.74 (Ni-C-C), 99.21 (-C=C), 87.72 (Cp), 0.86 (C-Si); EIMS (EI, 70 eV) *m/e* calculated for <sup>58</sup>Ni (relative intensity, %): 440 ( $M^+$ , 100%), 246 (67%), 188 (13%), 123 (7%), 73 (10%), 58 The next brown-green band containing (2%).  $(NiCp)_4(Me_3SiC \equiv C - C \equiv CSiMe_3)$  (3) was collected (yield 8%; eluent 30% toluene in  $C_6H_{14}$ ).

## 2.4. Reaction of nickelocene with lithium (trimethylsilyl)acetylide

A solution of 1.61 g of NiCp<sub>2</sub> (8.5 mmol) in 50 cm<sup>3</sup> THF was cooled to -55 °C. A solution of lithium (trimethylsilyl)acetylide (0.5 M inTHF; 16.5 cm<sup>3</sup>, 9.4 mmol) was then added within 1 h (temperature was maintained at -55--50 °C). The mixture was stirred at this temperature for the next hour, and then it was

allowed to warm up slowly to r.t. Stirring was continued overnight. The volatile substances were removed under reduced pressure, 30 cm<sup>3</sup> of toluene and 20 cm<sup>3</sup> of C<sub>6</sub>H<sub>14</sub> were added and the products were hydrolyzed with 50  $\text{cm}^3$  of the deoxygenated water. The organic layer was separated and dried, then solvents were evaporated, a residue was re-dissolved in toluene-C<sub>6</sub>H<sub>14</sub> mixture and chromatographed on Al<sub>2</sub>O<sub>3</sub> (deactivated with 5% of water) using  $C_6H_{14}$ -toluene mixture as eluent. The following compounds were isolated and characterized: NiCp<sub>2</sub>—a small amount in the first green band eluted with  $C_6H_{14}$ ;  $(NiCp)_2(Me_3SiC \equiv C - C \equiv$  $CSiMe_3$ ) (4)—the second green band eluted with 10% toluene in C<sub>6</sub>H<sub>14</sub> (yield 30%); (NiCp)<sub>4</sub>(Me<sub>3</sub>SiC=C-C=  $CSiMe_3$ ) (3)—the third band eluted as brown-green chromatographic band using 50% toluene in  $C_6H_{14}$ (yield 45%).

### 2.5. Crystal structure determination

Single crystals of **1** and **3** suitable for X-ray diffraction studies were placed in a thin-walled capillary (Lindemann glass) in a nitrogen atmosphere, plugged with grease and flame sealed.

All measurements of the crystal of 1 were performed on a Kuma KM4CCD  $\kappa$ -axis diffractometer with graphite-monochromated MoKa radiation. The crystal was positioned at 65 mm from the KM4CCD camera. 256 frames were measured at  $1.8^{\circ}$  intervals with a counting time of 15 s. The data were corrected for Lp. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw) programs. The structure was solved by direct methods using SHELXS-97 [14] and refined using SHELXL-97 [15]. The refinement was based on  $F^2$  for all reflections except those with very negative  $F^2$ . Weighted R factors wR and all goodness-of-fit S values are based on  $F^2$ . Conventional R factors are based on F with F set to zero for negative  $F^2$ . The  $F_o^2 > 2s(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on  $F^2$  are about twice as large as those based on F. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in Ref. [16]. The crystal structure of 1 is presented in Fig. 1. The crystal data, data collection and refinement parameters for the compound are given in Table 1. Selected bond lengths and bond angles are presented in Tables 2 and 3.

Crystal data for **3** were collected with subsequent  $\varphi$  and  $\omega$  scans on a Nonius KappaCCD diffractometer with graphite monochromated Mo K $\alpha$  radiation, using diffractometer control program 'Collect' [17]. Unit cell parameters and data reduction were processed with Denzo and Scalepak [18]. The structure was solved by



Fig. 1. The ORTEP drawing of 1 with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

direct methods using SHELXS-97 [14]. Full-matrix leastsquares refinement method against  $F^2$  values was carried out using the SHELXL-97 [15] program. All hydrogen atoms were placed in calculated positions and refined using a riding model. Crystallographic symmetry of 3 clearly indicates that the molecules are not related by symmetry; the unit cell being triclinic and containing twelve molecules of the complex. Search for higher symmetry failed at the early stage of structure solution and it became evident at the further stages that there are some significant differences in molecular conformation between some of the six molecules. Thermal disorder, illustrated by ORTEP plots, is different as well. And, although 'chemical' differences (in terms of bond lengths and angles) are very small and mostly insignificant in statistical terms, the six complex molecules are slightly different molecular species from the structural viewpoint. Atom numbering system has been kept the same in all six independent molecules, i.e., Ni1A-C1A distance corresponds, e.g., to Ni1D-C1D and Ni1G-C1G, etc.

The crystal structure of 3 is presented in Fig. 2.The crystal data, data collection and refinement parameters for the compound are given in Table 1. Tables 4 and 5 present the observed bond lengths and bond angles.

### 3. Results and discussion

Reactions of nickelocene with phenyl- or methyllithium and bis(trimethylsilyl)acetylene were carried out at molar ratios of reactants  $NiCp_2:LiR:Me_3SiC \equiv$  $CSiMe_3 = 1:1:1.1$  in THF. The reactants were mixed together at about -50 °C, and the reaction mixture was then allowed to warm up to room temperature and

Table 1 Crystal data and structure refinement for **1** and **3** 

	1	3
Empirical formula	C <sub>18</sub> H <sub>28</sub> Ni <sub>2</sub> Si <sub>2</sub>	C <sub>30</sub> H <sub>38</sub> Ni <sub>4</sub> Si <sub>2</sub>
Formula weight	418.00	689.62
Temperature (K)	293(2)	150(2)
Crystal system	monoclinic	triclinic
Space group, number	$P 2_1/n$	PĪ
a (Å)	9.264(2)	15.934(1)
b (Å)	15.862(3)	16.937(2)
c (Å)	14.863(3)	18.827(2)
α (°)	90	91.06(2)
β (°)	93.55(3)	90.58(2)
γ (°)	90	115.00(2)
V (Å <sup>3</sup> )	2179.9(8)	4603.2(6)
Ζ	4	6
$D_{\rm calc} ({\rm g}{\rm cm}^{-1})$	1.274	1.493
Absorption coeffi-	1.832	2.512
cient (mm <sup>-1</sup> )		
F(000)	880	2148
Crystal size (mm)	0.4  imes 0.3  imes 0.2	$0.25\times0.22\times0.14$
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å mator	), graphite monochro-
$\mu$ range (°)	3.60-21.00	2.16-19.78
Index ranges	$-9 \le h \le 4, -15 \le$	$0 \le h \le 15, -16 \le$
-	$k \le 15, -14 \le l \le 14$	$k \le 14, -17 \le l \le 17$
Reflections collected	7128	8006
Unique data	2321, $R_{\rm int} = 0.0996$	8006, $R_{\rm int} = 0.0000$
Refinement method	Full-matrix least-square	es on $F^2$
Data/restraints/para-	2321/0/227	8006/0/974
meters		
Final R indices $ I\rangle$		
$2\sigma(I)$ ]		
$R_1; wR_2$	0.0885; 0.1767	0.0482; 0.1287
<i>R</i> indices (all data)		
$R_1; wR_2$	0.1197; 0.1971	0.0627; 0.1353
Goodness-of-fit on	1.055	1.132
$F^{2 a}$	0 ( <b>***</b> ) 0 (***)	
Largest difference	0.657/-0.654	0.583/ -0.628
peak and hole ( $e A^{-3}$ )		
Weights $a, b$	0.0500; 21.1989	0.0694; 13.0071

<sup>a</sup> Goodness-of-fit =  $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ .

<sup>b</sup>  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|, \ wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}.$ 

<sup>c</sup>  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = [2F_o^2 + \max(F_o^2, 0)]/3$ .

stirred overnight. The mixture was hydrolyzed with deoxygenated water and the organic layer was separated by column chromatography on neutral alumina deactivated with 5% of water, using hexane-toluene mixture as an eluent.

The reaction of nickelocene with phenyllithium and bis(trimethylsilyl) acetylene leads to the formation of three nickel complexes: di(cyclopentadienylnickel)complex with bis(trimethylsilyl)acetylene  $(NiCp)_2(\mu-\eta^2-\eta^2-Me_3SiC\equiv CSiMe_3)$  (1);  $(NiCp)_2(\mu-\eta^2-\eta^2-PhC\equiv CSiMe_3)$  (2) and tetra(cyclopentadienylnickel) complex with 1,4-bis(trimethylsilyl)-1,3-butadiyne  $(NiCp)_4(\mu,\mu-\eta^2-\eta^2-\eta^2-\eta^2-Me_3SiC\equiv C-C\equiv CSiMe_3)$  (3). Biphenyl was also formed as the result of coupling of two phenyl groups. All the above compounds were characterized by

Table 2 Selected bond lengths (Å) in 1 \*

Selected John lengths (11) III 1			
Ni(1)-C(1)	1.911(11)	Si(1)-C(1)	1.846(11)
Ni(1) - C(2)	1.988(12)	Si(2)-C(2)	1.715(13)
Ni(1)-C(10)	2.058(16)	Si(2)-C(7)	1.804(17)
Ni(1)-C(12)	2.046(18)	Si(2)-C(6)	1.820(15)
Ni(1)-C(9)	2.086(13)	Si(2)-C(8)	1.83(2)
Ni(1) - C(13)	2.101(16)	C(1) - C(2)	1.410(14)
Ni(1) - C(11)	2.163(17)	C(9) - C(10)	1.38(2)
Ni(1)-Ni(2)	2.341(2)	C(9)-C(13)	1.40(2)
Ni(2)-C(1)	1.912(10)	C(10) - C(11)	1.42(3)
Ni(2) - C(2)	2.005(11)	C(11) - C(12)	1.33(3)
Ni(2) - C(17)	2.04(2)	C(12) - C(13)	1.35(2)
Ni(2)-C(15)	2.062(19)	C(14) - C(15)	1.25(3)
Ni(2)-C(18)	2.078(19)	C(14) - C(18)	1.41(3)
Ni(2)-C(14)	2.076(16)	C(15)-C(16)	1.33(4)
Ni(2)-C(16)	2.09(2)	C(16) - C(17)	1.34(4)
Si(1)-C(3)	1.851(14)	C(17)-C(18)	1.30(4)
Si(1)-C(4)	1.831(15)	Ni(1)–Cp	1.736
Si(1) - C(5)	1.840(16)	Ni(2)-Cp	1.735

\* Estimated standard deviations in parentheses.

Table 3 Selected bond angles (°) in 1 \*

C(1)-Ni(1)-C(2)	42.3(4)	C(2)-C(1)-Ni(1)	71.7(6)
C(1) - Ni(1) - Ni(2)	52.3(3)	Si(1) - C(1) - Ni(1)	130.5(6)
C(2)-Ni(1)-Ni(2)	54.5(3)	C(2)-C(1)-Ni(2)	72.5(6)
C(1) - Ni(2) - C(2)	42.1(4)	Si(1) - C(1) - Ni(2)	132.0(6)
C(1) - Ni(2) - Ni(1)	52.2(3)	Ni(1)-C(1)-Ni(2)	75.5(4)
C(2) - Ni(2) - Ni(1)	53.8(3)	C(1)-C(2)-Si(2)	152.0(9)
C(4) - Si(1) - C(1)	108.4(7)	C(1)-C(2)-Ni(1)	65.9(6)
C(2)-Si(2)-C(7)	109.1(8)	Si(2) - C(2) - Ni(1)	132.1(6)
C(2)-Si(2)-C(6)	109.1(8)	C(1)-C(2)-Ni(2)	65.4(6)
C(7) - Si(2) - C(6)	109.2(12)	Si(2) - C(2) - Ni(2)	135.3(5)
C(2)-Si(2)-C(8)	109.4(9)	Ni(1)-C(2)-Ni(2)	71.8(4)
C(2)-C(1)-Si(1)	146.3(9)		

\* Estimated standard deviations in parentheses.

means of EI MS, <sup>1</sup>H and <sup>13</sup>C NMR. Crystal and molecular structure of compounds **1** and **3** were determined by single crystal X-ray analysis.

The compound 1 crystallizes in monoclinic crystal system with four molecules in the unit cell. A comparison of crystallographic data of 1 with other structurally characterized complexes of acetylenes with di(cyclopentadienylnickel) [5-7,9,10] leads to the conclusion that bulky trimethylsilyl group have a substantial influence on distances and angles in the molecule. Although the Ni-Ni distance (2.341 Å) is almost identical as in the other complexes (2.33–2.34 Å), the Ni– $C_{ac}$  and  $C_{ac}$ – $C_{ac}$ are much longer in 1. Ni-Cac distances in 1 are not equal (1.911 and 1.988 Å for Ni(1) and 1.912 and 2.005 Å for Ni(2), respectively) what indicates that CpNi-NiCp moiety is located perpendicularly to  $C_{ac}-C_{ac}$ bond, but closer to one of the acetylenic carbon atoms. This was not observed for other reported complexes, where CpNi-NiCp moieties were symmetrically located



Fig. 2. The ORTEP drawing of **3** with atom numbering scheme (one of six molecules in the unit cell). The displacement ellipsoids are drawn at the 50% probability level.

Table 4						
Selected	bond	lengths	(Å)	in	3	*

Ni1E-C1E	1.902(19)	C1E-C1G	1.460(17)
Ni1E-C2E	1.930(16)	NilG-ClG	1.907(18)
Ni1E-C5E	2.100(16)	Ni1G-C2G	1.931(16)
Ni1E-C6E	2.108(18)	Ni1G-C4G	2.106(16)
Ni1E-C4E	2.104(12)	Ni1G-C3G	2.118(14)
Ni1E-C7E	2.103(22)	Ni1G-C6G	2.114(19)
Ni1E-C3E	2.132(19)	Ni1G-C5G	2.118(20)
Ni1E-Ni2E	2.359(5)	NilG-C7G	2.128(18)
Ni2E-C1E	1.898(19)	Ni1G-Ni2G	2.369(2)
Ni2E-C2E	1.934(15)	Ni2G-C1G	1.904(21)
Ni2E-C9E	2.072(15)	Ni2G-C2G	1.943(15)
Ni2E-C11E	2.092(16)	SilG-C2G	1.838(23)
Ni2E-C10E	2.109(22)	C1G-C2G	1.348(17)
Ni2E-C12E	2.118(23)	Ni1E-Cp	1.735
Ni2E-C8E	2.140(19)	Ni2E-Cp	1.752
Si1E-C2E	1.832(22)	Ni1G-Cp	1.737
C1E-C2E	1.346(17)	Ni1G-Cp	1.735

\* Estimated standard deviations in parentheses.

above  $C_{ac}-C_{ac}$  bond with equal Ni–C distances from 1.88 to 1.91 Å. This was not also observed for monodentate complex  $(Ph_3P)_2Ni(Me_3SiC=CSiMe_3)$ [19]. The  $C_{ac}-C_{ac}$  (1.410 Å) is longer than in other complexes (1.34–1.36 Å). The value 1.410 Å is in the range between double and single C–C bond. The longer C–C bond should cause a decreasing of the values of the Si– $C_{ac}-C_{ac}$  angles. Although the ethynyl ligand in **1** is as expected *cis*-bent, the Si– $C_{ac}-C_{ac}$  angles (146.3 and 152.0°) are larger than in other complexes (140–148°). This is probably due to a steric rather than electronic reason and caused by a repulsion of bulky trimethylsilyl

Table 5 Selected bond angles (°) in **3** \*

C1E-Ni1E-C2E	41.1(4)	C1G-Ni1G-Ni2G	51.5(3)
C1E-Ni1E-Ni2E	51.6(3)	C2G-Ni1G-Ni2G	52.5(3)
C2E-Ni1E-Ni2E	52.5(4)	C1G-Ni2G-C2G	41.0(4)
C1E-Ni2E-C2E	41.1(4)	C1G-Ni2G-Ni1G	51.6(4)
C1E-Ni2E-Ni1E	51.7(3)	C2G-Ni2G-Ni1G	52.1(3)
C2E-Ni2E-Ni1E	52.3(3)	C2G-C1G-C1E	144.9(9)
C2E-C1E-C1G	143.5(9)	C2G-C1G-Ni2G	71.1(6)
C2E-C1E-Ni1E	70.6(6)	C1E-C1G-Ni2G	132.0(7)
ClG-ClE-NilE	130.2(7)	C2G-C1G-Ni1G	70.4(6)
C2E-C1E-Ni2E	70.9(6)	C1E-C1G-Ni1G	133.5(7)
Ni1E-C1E-Ni2E	76.8(4)	Ni2G-C1G-Ni1G	76.9(4)
C1E-C2E-Si1E	145.1(7)	C1G-C2G-Si1G	147.0(8)
C1E-C2E-Ni2E	68.0(1)	C1G-C2G-NilG	68.5(5)
Si1E-C2E-Ni2E	133.7(5)	SilG-C2G-NilG	135.3(5)
C1E-C2E-Ni1E	68.3(6)	C1G-C2G-Ni2G	67.9(6)
Si1E-C2E-Ni1E	135.9(5)	Si1G-C2G-Ni2G	132.2(5)
Ni2E-C2E-Ni1E	75.3(4)	Ni1G-C2G-Ni2G	75.4(4)

\* Estimated standard deviations in parentheses.

groups. Although the crystal structure is of poor quality  $(R_1 = 0.0885)$  and the bond lengths and angles cannot be discussed in details, the general trends are as expected.

The compound **3** is the example of tetranuclear nickel diyne complex in which every two nickel atoms are bridged by C=C bond in  $\eta^2$ , $\eta^2$ -bridging mode. This is a rare example of structurally characterized of this type nickel complexes. The only other one was reported in Ref. [20]. Four carbon atoms of the diyne are almost coplanar (torsion angle C-C-C-C is 178.8°). The Ni-Ni distances (2.359 and 2.369 Å) are close to those reported for the dinickel-alkyne complexes in the bridging mode [5-7,9,10], but much shorter than in

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bridging divne complexes (2.655 and 2.687 Å) [20,21]. The average Ni-C distance of 1.919 Å is very close to those reported for 1,4-bis(trimethylsilyl)-1,3-butadiyne complexes with Ni(0) in the  $\eta^2$ ,  $\eta^2$ -bridging mode [21] and is slightly longer than those (1.901 [21] and 1.909 Å [22]) in the monodentate mode. In contrary the average Ni–C distance in the  $\eta^2$ ,  $\eta^2$ -bridging mode is shorter than that of complexes of other diynes (from 1.947 to 1.988 Å) [20,23,24]. The Ni-C distances between the nickel atom and the inside carbon atoms of the diyne are shorter than those between the nickel atom and the outside carbon atoms (Ni-Cac: 1.902, 1.930, 1.907, 1.931, 1.898, 1.934, 1.904, 1.943 Å; see the Table 4 to check which Ni-C distance correspond to which Ni-C bond). This phenomenon was observed also for other nickel complexes with trimethylsilyl derivatives of diyne [21,22] and nonsymmetrically substituted alkynes [25] in both: bridging and monodentate modes, and was probably due to steric reasons. The influence of the Me<sub>3</sub>Si group on the complexation of alkynes was described and discussed due to steric as well as electronic reasons [8,25,26].

The reaction of nickelocene with methyllithium and bis(trimethylsilyl)acetylene gave some different products. Compounds **1** and **3** were formed as in the reaction with phenyllithium, but there was no analogous compound to **2**, e.g.  $(NiCp)_2(\mu-\eta^2-\eta^2-CH_3C\equiv CSiMe_3)$ . The new product isolated form this reaction was di(cyclopentadienylnickel)complex with bis(trimethylsilyl)butadiyne  $(NiCp)_2(\mu-\eta^2-\eta^2-Me_3SiC\equiv C-C\equiv CSiMe_3)$  (**4**).

We have previously shown that nickelocene reacts with phenyl- or methyllithium in the presence of diphenylacetylene or 2-butyne forming unstable nickelacyclopentadienyl species, which reacts further forming a variety of organonickel compounds [1-3] (Eq. (3)).



The reaction of phenyllithium with nickelocene and bis(trimethylsilyl)acetylene differs from the reaction with diphenylacetylene or 2-butyne. Bulky  $Si(CH_3)_3$  substituents prevent acetylene units from a coupling and the formation of nickelacyclopentadienyl ring. On the other hand a similarity of trimethylsilyl group to acidic hydrogen in acetylene [27] facilitates the reaction of phenyllithium with bis(trimethylsilyl)acetylene and the formation of lithiumacetylide (Eq. (4)).

$$LiPh + Me_{3}Si-C=C-SiMe_{3}$$
  

$$\rightarrow Li-C=C-SiMe_{3} + PhSiMe_{3}$$
(4)

Therefore, nickelocene can simultaneously react with phenyllithium and lithium acetylide forming unstable species {CpNiPh} and {CpNiC=CSiMe<sub>3</sub>} (Eq. (5)).

NiCp<sub>2</sub> 
$$\xrightarrow{\text{LiPh}}$$
 {CpNiPh} + LiCp  
 $\xrightarrow{\text{Li-C=C-SiMe_3}}$  {CpNi-C=C-SiMe<sub>3</sub>} + LiCp (5)

These species readily undergo coupling reactions due to the lack of easily accessible  $\alpha$ - and  $\beta$ -hydrogen atoms [28] (Eqs. (6) and (7)).

$$\{CpNiPh\} \rightarrow \{CpNi-NiCp\} + Ph-Ph$$
 (6)

$$\{CpNi-C=C-SiMe_3\} \\ \rightarrow \{CpNi-NiCp\} + Me_3Si-C=C-C=C-SiMe_3$$
(7)

The formation of  $Me_3SiC \equiv C - C \equiv CSiMe_3$  by coupling by the two alkynyls at Ni was described in Ref. [29].

Cross coupling reaction also may occur resulting with the formation of phenyl(trimethylsilyl)acetylene (Eq. (8))

$$\{CpNiPh\} + \{CpNi-C=C-SiMe_3\}$$
  

$$\rightarrow \{CpNi-NiCp\} + Ph-C=C-SiMe_3$$
(8)

Reactions of bis(trimethylsilyl)acetylene and the products of reaction (7) and (8) with  $\{(NiCp)_2\}$  species lead to the formation of final products (Eq. (9)).



The reaction of methyllithium with nickelocene and bis(trimethylsilyl)acetylene proceeds differently that in case of phenyllithium.  $\{(NiCp)_2 \cdot (CH_3C \equiv$ the  $CSi(CH_3)_3$ , a compound analogues to 2, has not been formed in this reaction. In contrary to {CpNiPh}, {CpNiCH<sub>3</sub>} does not undergoes coupling and crosscoupling reactions but forms complex with  $Me_3SiC=$ CSiMe<sub>3</sub> [13], what decreases its reactivity and may lead to the formation of  $\{CpNi-C=CSiMe_3\}$  and SiMe<sub>4</sub>. {CpNi-C=CSiMe<sub>3</sub>} reacts further according to the Eq. (7). {NiCp}<sub>2</sub>, formed in this reaction, reacts with bis(trimethylsilyl)acetylene and bis(trimethylsilyl)butadivne present in the reaction mixture forming final products 1, 3 and 4 (Eqs. (10) and (11)).



{CpNi-NiCp} + Me<sub>3</sub>Si-C=C-C=C-SiMe<sub>3</sub> ----



To confirm the course of reactions leading to the formation of bis(trimethylsilyl)butadiyne (Eqs. (4), (5) and (7)), we have prepared lithium(trimethylsilyl)acetylide and reacted it with nickelocene. Compounds 3 and 4 were formed in this reaction.

Lithium(trimethylsilyl)acetylide was prepared in the reaction of methyllithium with bis(trimethylsilyl)acetylene (Eq. (12)).

$$LiMe + Me_3Si - C \equiv C - SiMe_3 \rightarrow Li - C \equiv C - SiMe_3$$
 (12)

Lithium(trimethylsilyl)acetylide reacts with nickelocene according to the reaction (5) forming unstable cyclopentadienylnickel(trimethylsilyl)acetylide. The latter undergoes coupling with the formation of bis(trimethylsilyl)butadiyne and bis(cyclopentadienylnickel) species according to the Eq. (7). These intermediate products form final complexes **3** and **4** (Eq. (11)).

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 198415 and 198416 for compounds **1** and **3**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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