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# Nickel Mediated Coupling of Organic Ligands[*]

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Reactions of nickelocene, $NiCp_2$, with organolithium compounds RLi (R = $-C\equiv CPh$; $-CPh=CPh_2$; $-CPh_3$, $-CPh_2SiMe_3$), where R does not contain $\alpha$- and $\beta$-hydrogen atoms, have been studied. It was found that {CpNiR}, formed in the first step of the reaction, underwent coupling with the formation of $\{(NiCp)_2\}$ and R–R. As organolithium substrates are readily available, and yield of coupling products was high (from over 60% to ~ 90%), the studied reactions could be applied as synthetic methods for preparation of wide range of R–R type organic compounds. In order to improve yield of the products and to prevent very active $\{(NiCp)_2\}$ species from further reactions, $NiCp_2$ and LiR were reacted in the presence of $PhC\equiv CMe$, what led to the formation of only two products: $(NiCp)_2 \cdot PhC\equiv CMe$ complex and R–R. These products were easily separated by column chromatography on neutral alumina, leading to the isolation of R–R in high yield.

**Key words**: nickel, nickelocene, alkynes, coupling reactions

We have previously found that lithium and magnesium aryls react with nickelocene forming organic ligands coupling products [1]

$$MC_6H_4R + NiCp_2 \longrightarrow \{CpNiC_6H_4R\} + LiCp$$

where M = Li, MgX (1)

$$2\{CpNiC_6H_4R\} \xrightarrow{\text{coupling}} RC_6H_4\text{-}C_6H_4R + \{(NiCp)_2\}$$

The above reactions proceed at room temperature in high yield. Organolithium and -magnesium compounds are readily available. Therefore, one could expect that their reactions with nickelocene will find application in organic synthesis.

We have previously found that the unstable species $\{CpNiC_6H_4R\}$, formed in the reaction (1), gives not only coupling products but also reacts in other directions [2]. For R containing $\alpha$- or $\beta$-hydrogen atoms the main reaction pathway is hydrogen elimination [3]. If R contains $\alpha$-hydrogen, coupling reaction proceeds only in about 14% yield, and if R contains $\beta$-hydrogen it does not proceed at all [4]

$$2\{CpNiCH_2CH_3\} \longrightarrow H_2C{=}CH_2 + H_3C\text{-}CH_3 + \{(NiCp)_2\} \quad (2)$$

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[*] Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

Therefore, only reactions of nickelocene with organolithium or -magnesium compounds, where R does not contain $\alpha$- and $\beta$-hydrogen, seem to be promising for synthetic applications, and studies on these reactions were the purpose of this work.

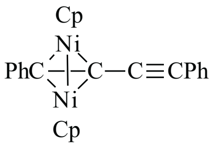
## RESULTS AND DISCUSSION

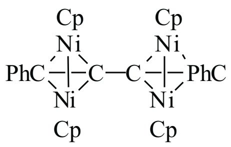
Reactions of nickelocene with RLi, where R = $-C\equiv CPh$; $-CPh{=}CPh_2$; $-CPh_3$, $-CPh_2SiMe_3$, have been studied. The reactions were carried out in THF at the temperature range from –60°C to room temperature.

***Reaction of nickelocene with lithium phenylacetylide.*** Lithium phenylacetylide reacted with equimolar amount of nickelocene already at –60°C. The reaction mixture was allowed to warm up to room temperature. It was then hydrolyzed with deoxygenated water, the organic layer was dried, concentrated to about 5 $cm^3$ and then separated by column chromatography on neutral alumina using hexane/toluene mixture as eluents. The reaction proceeded according to (3).

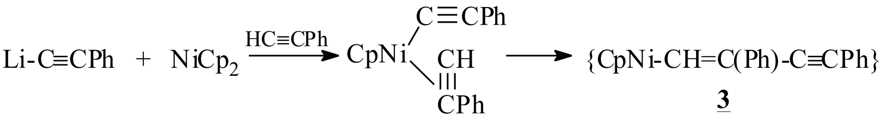
$$\begin{array}{l} Li\text{-}C\equiv CPh + NiCp_2 \longrightarrow \{CpNi\text{-}C\equiv CPh\} + LiCp \\ 2\{CpNi\text{-}C\equiv CPh \longrightarrow PhC\equiv C\text{-}C\equiv CPh + \{(NiCp)_2\} \end{array} \qquad (3)$$

1,4-Diphenylbutadiyne forms with $\{(NiCp)_2\}$ di-, **1**, and tetranickel, **2**, complexes.


**1**

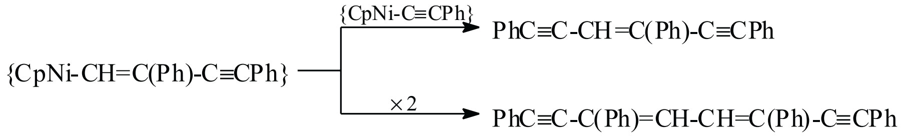

**2**

The yield of complexes **1** and **2** was 36% and 52% respectively. They were identified and characterized by means of spectroscopic methods ($^1H$ and $^{13}C$ NMR, EIMS). The molecular structure of analogous complexes of 1,4-di(trimethylsilyl)butadiyene with $\{(NiCp)_2\}$ have been determined by X-ray crystallography and published by us recently [5]. The complexes **1** and **2** can be decomposed by the reaction with gaseous hydrochloride to form 1,4-diphenylbutadiyne. The change of phenyl group of acetylene for other substituents will allow for synthesis of wide range of compounds with conjugated triple bonds system. If the reaction of nickelocene with lithium phenylacetylide was carried out in the presence of phenylacetylene, than besides the coupling reaction (3) also complexation followed by insertion of phenylacetylene into Ni–C bond occurred (4).



(4)

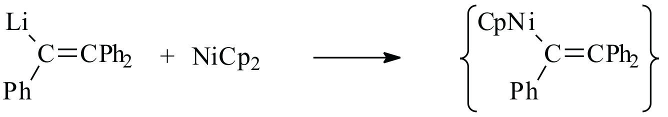
The unstable species **3** formed in the reaction (4) underwent coupling and cross-coupling reactions to form products with 6 and 8 carbon atoms and conjugated double and triple bonds system (5).



(5)

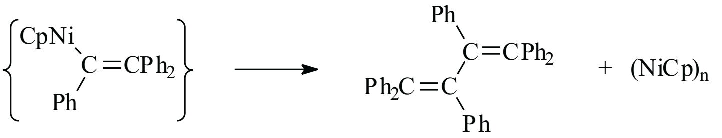
The products of the above reactions were identified by means of GC/MS.

***Reactions of triphenylvinyllithium with nickelocene***. Triphenylvinyllithium reacts with nickelocene forming unstable vinyl derivative of nickel (6).



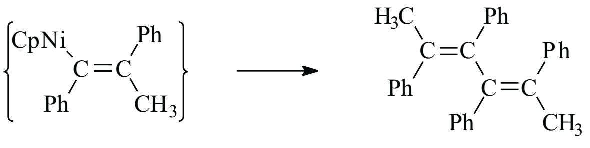
(6)

Due to the lack of $\alpha$- and $\beta$-hydrogen the unstable $\{CpNiC(Ph){=}CPh_2\}$ undergoes coupling to form hexaphenylbutadiene and cyclopentadienylnickel clusters (7).



(7)

The coupling is also the main course of the reaction if one phenyl group is replaced by methyl in *trans* position to the nickel atom (8). In contrary, if the methyl group is in *cis* position to the nickel atom then $\gamma$-H elimination is the dominant course of the reaction [6].

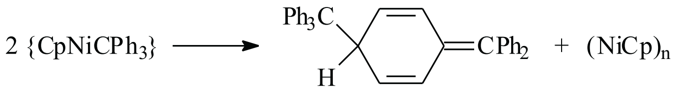


(8)

***Reaction of triphenylmethyllithium with nickelocene***. Triphenylmethyllithium reacts with nickelocene forming triphenylmethyl(cyclopentadienyl)nickel (9).

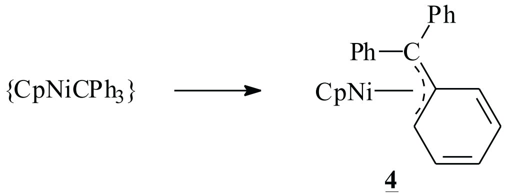
$$LiCPh_3 + NiCp_2 \longrightarrow \{CpNiCPh_3\} + LiCp \qquad (9)$$

One could expect that this species would readily undergo coupling due to the lack of $\alpha$- and $\beta$-hydrogen (10). It is known that hexaphenylethane exists as a dimer of triphenylmethyl radical and in equilibrium with the latter [7].



(10)

But the yield of coupling product was low as $\{CpNiCPh_3\}$ was stabilized by the formation of $\pi$-allyl complex **4** (11).



**4**

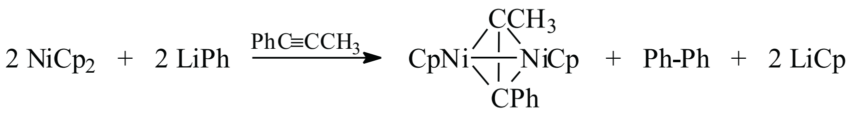
(11)

The complex **4** is stable and its structure was determined by spectral and crystallographic methods [8].

The coupling occurred also in the reaction of diphenyl(trimethylsilyl)methyllithiun with nickelocene (12)

$$LiC(SiMe_3)Ph_2 + NiCp_2 \longrightarrow \{CpNiC(SiMe_3)Ph_2\} \xrightarrow{x\ 2} [Ph_2(SiMe_3)Cl_2 \qquad (12)$$

In all the above reactions unstable $\{(NiCp)_2\}$ species were formed. These species were very active and led to the formation of wide range of organonickel and organic compounds. $\{(NiCp)_2\}$ could cleave tetrahydrofuran [9] and activate C–H bond in organic ligands [10]. The formation of many products in the reaction makes their separation difficult and decreases yields of isolated compounds. In order to avoid these difficulties we have carried out the reaction of nickelocene with phenyllithium in the presence of 1-phenylprop-1-yne. Only two products were formed besides cyclopentadienyllithium: di(cyclopentadienylnickel) complex with 1-phenylprop-1-yne (isolated in 73% yield) and biphenyl (isolated in 88% yield).



$$2\,NiCp_2 + 2\,LiPh \xrightarrow{PhC{\equiv}CCH_3} CpNi\overset{CCH_3}{\underset{CPh}{|}}NiCp + Ph\text{-}Ph + 2\,LiCp \qquad (13)$$

The role of 1-phenylprop-1-yne was to bind the formed $\{(NiCp)_2\}$ and to prevent it from further reactions. The yield of isolated products was therefore very high. This method can be applied in other reactions described above in order to increase the yield of coupling products.

## EXPERIMENTAL

All reactions were carried out under atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. Phenylacetylene and 1-phenyl-1-propyne were commercial products. Phenyl- and methyllithium solutions were prepared by standard procedures.

$^1$H and $^{13}$C spectra were measured on Varian Gemini–200 and Varian Mercury 400 MHz instruments. Mass spectra were recorded on AMD–604 and AMD M–40 mass spectrometers. GC/MS analyses were performed on a Hewlett Packard 5971 Series Mass Selective Detector with a HP 35 column (30 m×0.25 mm). The reported yields of crude products (*i.e.* after the first column chromatography) were based on the starting amount of nickelocene.

***Synthesis of lithium phenylacetylide.*** Lithium phenylacetylide was prepared by the method analogous to the literature one [11,12]. A solution of methyllithium (85 cm$^3$, 32.30 mmol) in $Et_2O$ was added within 4 h at –25°C to –20°C to a solution of phenylacetylene (3.22 cm$^3$, 29.37 mmol) in 20 cm$^3$ THF. The mixture was stirred at this temperature for the next hour, and then it was allowed to warm up slowly to room temperature. Stirred was continued overnight. The concentration of lithium phenylacetylide was 0.375 mol/dm$^3$. $^1$H NMR ($C_6D_6$): $\delta$ [ppm] 7.40÷6.94 (m, 5 H); $^{13}$C NMR ($C_6D_6$): $\delta$ [ppm] 131.59÷125 (Ph), 116.27 (PhC≡), 0.291 (≡CLi).

***Reaction of nickelocene with triphenylethylenelithium.*** Triphenylethylenelithium was prepared by the reaction of triphenylethylene chloride with lithium in THF according to the literature method [13]. A solution of triphenylethylenelithium in THF (28 mmol, 10 cm$^3$) was added within 1 h at –78°C to a solution of $NiCp_2$ (3.8 g, 20 mmol) in 100 cm$^3$ THF and kept at this temperature for 5 h. The reaction mixture was then allowed to warm up to room temperature and stirred for a further 12 h. The solvents were distilled off under reduced pressure and the residue was dissolved in 10 cm$^3$ THF and hydrolyzed by addition of 40 cm$^3$ 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 deactived with 5% water) using hexane/toluene as eluents. Organic products, eluted with hexane before the first organometallic band, were collected and subjected to GC/MS analyses. This band contained as 1,1,4,4,2,3-hexaphenylbutadien $(Ph)_2C{=}CPh{-}CPh{=}C(Ph)_2$ (yield 62%, eluent-hexane); EIMS (70 eV) m/e (rel. int.) 510 (M$^+$, 100%), 432 (54.2%), 344 (2.46%), 255 (2.18%), 155 (3.22%), 77 (13.2%). A small amount of $NiCp_2$ (eluent 10% toluene in hexane) was then eluted. The next brown band collected (eluent 50% toluene in hexane) contained unidentified organonickel compounds.

***Reaction of nickelocene with lithium phenylacetylide.*** A solution of $NiCp_2$ (1.27 g, 6.74 mmol) in 30 cm$^3$ THF was cooled to –40°C. A solution of lithium phenylacetylide in THF (19.7 cm$^3$, 7.41 mmol) was then added over 1 h (temperature was maintained at –40°C to –35°C). The mixture was stirred at this temperature for the next hour, and then it was allowed to warm up to room temperature. Stirring was continued overnight. The volatile substances were removed under reduced pressure, 10 cm$^3$ of THF and 50 cm$^3$ of toluene were added and the products were hydrolyzed with 50 cm$^3$ of the deoxygenated water. The organic layer was separated and dried, then solvents were evaporated, the residue was re-dissolved in a mixture hexane/toluene and chromatographed on $Al_2O_3$ (deactivated with 5% of water) using hexane/toluene mixture as an eluent. The first coloured band was identified as $NiCp_2$ (eluent hexane). The next dark green band containing $(CpNi)_2\cdot PhC{\equiv}C{-}C{\equiv}CPh$ was collected (yield 36%; eluent 30% toluene in hexane). The compound was characterized by $^1$H NMR ($C_6D_6$): $\delta$ [ppm] 7.68÷7.31 (m, 10 H, Ph), 5.36 (s, 10 H, Cp); $^{13}$C NMR ($C_6D_6$): $\delta$ [ppm] 138.80÷125.04, 99.75, 97.91, 88.77, 72.22, 69.11; EIMS (70 eV) m/e (calc. for $^{58}$Ni) 448 (M$^+$, 52%), 246 (100%), 188 (68%), 123 (26%), 58 (12%).

The next brown band was eluted with 50% toluene in hexane. It contained a compound identified as $(CpNi)_4\cdot PhC{\equiv}C{-}C{\equiv}CPh$ (yield 52%) by means of mass spectroscopy, $^1$H and $^{13}$C NMR. EIMS (70 eV) m/e (calc. for $^{58}$Ni) 696 (M$^+$, 70%), 508 (59%), 246 (20%), 188 (100%), 123 (67%), 58 (28%). $^1$H NMR ($C_6D_6$): $\delta$ [ppm] 7.22 ÷6.75 (m, 10 H, Ph), 5.16 (s, 20 H, Cp); $^{13}$C NMR ($C_6D_6$): $\delta$ [ppm] 138.16÷126.24, 94.75, 90.31, 86.27.

***Reaction of nickelocene with lithium phenylacetylide in the presence of phenylacetylene.*** A solution of lithium phenylacetylide in THF (8 cm$^3$, 6.72 mmol) was added within 1 h at –60 °C to –50°C to a solution of $NiCp_2$ (1.15 g , 6.11 mmol) with phenylacetylene (6.11 mmol, 0.67 cm$^3$) in 40 cm$^3$ THF and kept at this temperature for 1 h. The reaction mixture changed colour from green to red-brown. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The resulting brown solution was concentrated to 10 $\mathrm{cm^3}$, and then 50 $\mathrm{cm^3}$ toluene was added. The products were hydrolyzed with 40 $\mathrm{cm^3}$ of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was re-dissolved in toluene and separated by column chromatography on $\mathrm{Al_2O_3}$ (deactivated with 5% of water) using hexane/toluene mixtures as eluents. Organic products, eluted with hexane before the first organometallic band, were collected and subjected to GC/MS analysis. The following compounds (selected) were identified: 1,4-diphenylbutadiyne (PhC≡C–C≡CPh): m/e (rel. int.) 202 ($\mathrm{M^+}$, 100%), 150 (8.9%), 126 (3.8%), 101 (8.9%), 77 (1.96%); 1,4-diphenylbut-3-en-1-yn (PhC≡C–CH=CHPh): m/e (rel. int.) 204 ($\mathrm{M^+}$, 100%), 126 (8.52%), 101 (25.1%), 77 (6.63%); 1,4,6-triphenyl-hex-3-en-1,5-diyn (PhC≡C–CH=CPh–C≡CPh): m/e (rel. int.) 304 ($\mathrm{M^+}$, 11.9%), 228 (76.7%), 203 (27.1%), 102 (10.2%), 77 (20.4%); 1,4,6,8-tetraphenyl-octa-3,5-dien-1,7-diyn (PhC≡C–CH=CPh–CH=CPh–C≡CPh): m/e (rel. int.) 406 ($\mathrm{M^+}$, 63.7%), 329 (85.4%), 207 (12.7%), 102 (1.25%), 77 (18.0%). The first coloured band was identified as $\mathrm{NiCp_2}$ (eluent hexane), then a dark green band containing $(\mathrm{CpNi})_2$·PhC≡C–C≡CPh was eluted (yield 13%, eluent 22% toluene in hexane). The compound was characterized as in the reaction of nickelocene in the presence lithium phenylacetylide described above. The next green-brown band (eluent 35% toluene in hexane) consisted of a mixture of $(\mathrm{CpNi})_4$·PhC≡C–C≡CPh and $(\mathrm{CpNi})_2$·PhC≡C–CH=CPh–C≡CPh. It was evaporated to dryness, re-dissolved in hexane and purified by an additional column chromatography (eluent: 1% THF in hexane). The first compound isolated was identified as $(\mathrm{CpNi})_4$·PhC≡C–C≡CPh (yield 31%): EIMS (70 eV) m/e (calc. for $^{58}$Ni) 696 ($\mathrm{M^+}$, 100%), 508 (49%), 246 (22%), 188 (53%), 123 (25%), 58 (8%). $^1$H NMR($\mathrm{C_6D_6}$): $\delta$ [ppm] 7.22÷6.75 (m, 10 H, Ph), 5.16 (s, 20 H, Cp); $^{13}$C NMR ($\mathrm{C_6D_6}$): $\delta$ [ppm] 138.16÷126.24, 94.75, 90.31, 86.27. The next light-brown band was eluted with 5% THF in hexane. It was identified only by mass spectroscopy as $(\mathrm{CpNi})_2$·PhC≡C–CH=CPh–C≡CPh: EIMS (70 eV) m/e (calc. for $^{58}$Ni) 550 ($\mathrm{M^+}$, 30%), 362 (100%), 304 (82%), 246 (42%), 188 (45%), 123 (22%), 58 (16%).

The next brown fraction was also collected (toluene as eluent). It was identified as $(\mathrm{CpNi})_4$·PhC≡C–CH=CPh–C≡CPh (yield 2%). The compound was characterized only by mass spectroscopy: EIMS (70 eV) m/e (calc. for $^{58}$Ni) 798 ($\mathrm{M^+}$, 3%), 610 (12%), 246 (22%), 188 (53%), 123 (25%), 58 (8%).

***Reaction of nickelocene with triphenylmethyllithium***. Triphenylmethyllithium was prepared by the reaction of triphenylmethane with butyllithium. To a solution of triphenlymethyllithium in THF (12.6 mmol, 20 $\mathrm{cm^3}$), a solution of nickelocene (2.8 g, 10.5 mmol) in 30 $\mathrm{cm^3}$ THF was added within 1.5 h at –30 to –35°C and kept at this temperature for 3 h. The reaction mixture was then allowed to warm up slowly to room temperature and stirred overnight. Solvents were removed under reduced pressure and residue was dissolved in 10 $\mathrm{cm^3}$ of THF and 50 $\mathrm{cm^3}$ of hexane. The mixture was hydrolyzed with 50 $\mathrm{cm^3}$ of deoxygenated water. The organic layer was separated, dried and filtered through a bed of $\mathrm{Al_2O_3}$. After partial evaporation of the solvents, the mixture was chromatographed on neutral alumina (deactivated with 5% water). Organic compounds eluted before $\mathrm{NiCp_2}$ were collected. The dimer of triphenylmethyl radicals was identified by MS and $^1$H NMR. EIMS(70eV) m/e (rel. int.) 486 ($\mathrm{M^+}$, 14%), 243 (100%), 166 (26%); $^1$H NMR($\mathrm{C_6D_6}$): $\delta$ [ppm] 4.92 (s, 1H, aliphatic proton); 5.90÷6.45 (m, 4H, olefinic protons); 6.94–7.38 (m, 25H, aromatic protons). The separation and identification of other products were published previously [8].

***Reaction of nickelocene with diphenyl(trimethyl)silylmethyllithium***. Diphenyl(trimethyl)silylmethyllithium was prepared by the reaction of diphenyl(trimethyl)silylmethyl chloride with lithium. A solution of 18 $\mathrm{cm^3}$ (6.8 mmol) diphenyl(trimethyl)silylmethyllithium in THF was added to a solution of 1.17 g (6.2 mmol) $\mathrm{NiCp_2}$ in 30 $\mathrm{cm^3}$ of THF, drop by drop during 2 h at the temperature of –30°C to –35°C. Then the mixture was warmed up to room temperature and stirred overnight. The further procedure was analogical as in the previous reaction. The MS spectrum of the organic product does show the parent ion of bis[diphenyl(trimethyl)silylmethyl], but only fragments corresponding to $[\mathrm{Ph_2(SiMe_3)C}]^+$ (m/e 239); EIMS (70eV) m/e (rel. int.): 239 (100%), 165 (18%), 73 (92%).

***Reaction of nickelocene with phenyllithium in the presence of 1-phenyl-prop-1-yne***. A solution of $\mathrm{NiCp_2}$ (0.823 g, 4.37 mmol) with 1-phenyl-prop-1-yne (0.54 $\mathrm{cm^3}$, 4.37 mmol) in 45 $\mathrm{cm^3}$ THF was cooled to –78°C, then a solution of phenyllithium in THF (4.3 $\mathrm{cm^3}$, 4.81 mmol) was then added within 1 h (temperature was maintained at –78°C to –70°C). The reaction mixture changed colour from green to red-brown on addition of phenyllithium. The mixture was stirred at this temperature for the next hour, and then it was allowed to warm up slowly to room temperature. Stirring was continued overnight. The volatile substances were removed under reduced pressure, 10 $\mathrm{cm^3}$ of THF and 50 $\mathrm{cm^3}$ of toluene were added and the products were hydrolyzed with 50 cm$^3$ of the deoxygenated water. The organic layer was separated and dried, then solvents were evaporated, the residue was re-dissolved in a mixture hexane/toluene and chromatographed on $Al_2O_3$ (deactivated with 5% of water) using hexane/toluene mixture as an eluent. Organic products, eluted with hexane before the first organometallic band, were collected and identified as diphenyl (0.725 g, yield 88%; elem. anal. found: C, 92.9%; H, 6.4%; calc. for $C_{12}H_{10}$: C, 93.46%; H, 6.54%); EIMS m/e (rel. int.) 154 (M$^+$, 100%), 76 (13.8%). A small amount of green $NiCp_2$ (eluent: 3% toluene in hexane) was eluted. The next fraction was eluted with 40% toluene in hexane and identified as $(CpNi)_2 \cdot PhC{\equiv}CCH_3$ (yield 73%) by $^1$H and $^{13}$C NMR and mass spectroscopy. $^1$H NMR ($C_6D_6$): $\delta$ [ppm] 7.59 ÷ 7.109 (m, 5 H, Ph), 5.16 (s, 10 H, Cp), 2.46 (s, 3H, $CH_3$); $^{13}$C NMR ($C_6D_6$): $\delta$ [ppm] 139.00÷ 127.24, 100.68, 97.29, 87.75, 19.06; EIMS (70 eV) m/e (calc. for $^{58}$Ni) 362 (M$^+$, 60%), 246 (100 %), 188 (66%), 123 (15%), 58 (6%).

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