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Reactions of the unstable compound $\{CpNiCH_3\}$ with 2-butyne. Formation of tetrameric complex $[CpNi–C(CH_3)=C(CH_3)_2]_4$

S. Pasynkiewicz, A. Pietrzykowski and M. Popławska

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

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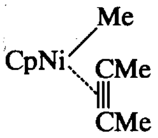
Abstract

One of the products of the reaction of $NiCp_2$ with $LiCH_3$ in the presence of 2-butyne, is the tetrameric complex $[CpNi–C(CH_3)=C(CH_3)_2]_4$ (**6**). The unstable monomer $\{CpNi–C(CH_3)=C(CH_3)_2\}$, which possesses a coordinatively unsaturated nickel atom, tetramerizes in such way that each nickel atom in the tetramer **6** forms a π-complex with the double bond of the next monomer molecule thus achieving a stable 18 electron configuration.

1. Introduction

We have previously shown that complex **1** is formed when nickelocene reacts with methyllithium in the presence of 2-butyne at −78°C (eqn. (1)) [1]. This complex decomposes above −30°C to form $(NiCp)_2(MeC{\equiv}CMe)$ (**2**) and ethane (eqn. (2)).

$$NiCp_2 + LiMe + MeC{\equiv}CMe \xrightarrow{-78°C} \qquad (1)$$



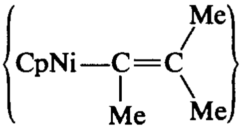
(**1**)

$$2\ \mathbf{1} \xrightarrow{>-30°C} (NiCp)_2(MeC{\equiv}CMe) + C_2H_6 + MeC{\equiv}CMe \qquad (2)$$

(**2**)

Besides the dinickel compound **2**, the labile compound $\{CpNi–(Me)C{=}C(Me)_2\}$ (**3**) is formed by the insertion of 2-butyne into the Ni–Me bond (eqn. (3)).

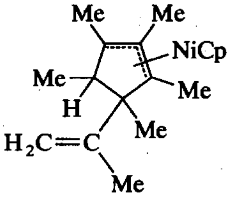
$$\mathbf{1} \longrightarrow \qquad (3)$$



(**3**)

In the presence of an excess of 2-butyne further complexation and insertion reactions followed by η-H elimination give the stable (η^3-allyl)NiCp compound **4** (eqn. (4)) [2].

$$\mathbf{3} \xrightarrow{2\,MeC{\equiv}CMe} \qquad (4)$$



(**4**)

Products **2** and **4** were isolated by column chromatography on neutral alumina using hexane as an eluent. The first (purple-red) fraction contained compound **4**, the second, unreacted nickelocene, and the third (green) fraction, compound **2**. A compound present in the last, dark brown fraction had not been characterized.

This work reports the isolation and characterization of the product additional to **2** and **4** that is formed in the reaction of nickelocene with methyllithium in the presence of 2-butyne.

2. Results

The new compound **6** that we have found to be formed in the reaction of nickelocene with methyllithium in the presence of an excess of 2-butyne was isolated chromatographically (neutral alumina, eluent hexane, last fraction) as a dark-brown solid. On the basis of its ^1H and ^{13}C NMR spectra we suggest that it is a tetramer $[CpNi–C(CH_3)=C(CH_3)_2]_4$. Its proposed structure is shown in Fig. 1. Each nickel atom of

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Correspondence to: Professor S. Pasynkiewicz.

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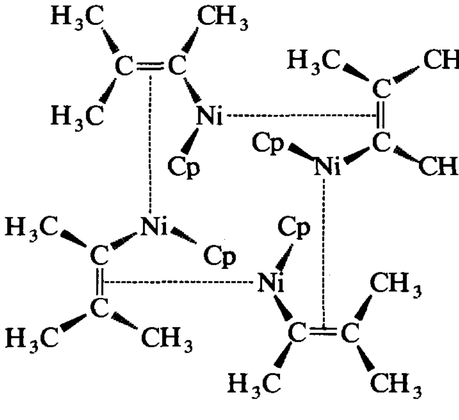


Fig. 1. Proposed structure of the tetramer **6**

tetramer **6** forms a π-complex with the double C=C bond of the next monomer molecule achieving a stable 18 electron configuration. Additionally, in contrast to a dimer or trimer, there are no internal strains in such a tetrameric form and each nickel atom is located perpendicular to a C=C bond.

Three signals of CH_3 groups at $\delta = 2.14$ ppm, 2.01 ppm and 1.43 ppm (integration ratio 1:1:1) are present in the ^{1}H NMR spectrum (C_6D_6) of complex **6** (Fig. 2). Signals at 2.14 ppm and 2.01 ppm correspond to protons of the geminal methyl groups $(CH_3)_2C=$ and a signal at 1.43 ppm corresponds to protons of the methyl group bonded to the same carbon atom to which the nickel atom is bonded. Protons of Cp groups appear as two singlets at 5.23 ppm and 5.22 ppm (difference of 1.36 Hz on 300 MHz spectrometer). The integration ratio of the above signals is 1:1 which indicates that in the tetramer **6**, the two cyclopentadienyl groups have a slightly different environment from that of the other two. The integration ratio of the signals of the Cp protons to the signals of the methyl protons is 5:9. The above data are fully consistent with the structure proposed for the tetramer (Fig. 1).

The ^{13}C NMR spectrum (Fig. 3) is also consistent with the proposed structure. Three signals of methyl carbon at $\delta = 13.71$ ppm, 17.02 ppm (signals of the geminal methyl carbons) and 31.12 ppm (signal of the methyl carbon bonded to the same carbon as the nickel atom) are present in the spectrum. Cyclopentadienyl carbon atoms give, like protons in ^{1}H NMR, two signals at $\delta = 87.91$ and 91.58 ppm. A signal at 169.18 ppm corresponds to the carbon atom bonded to one methyl group and to the nickel atom, and a signal at 102.99 ppm corresponds to the carbon atom bonded to two methyl groups.

Two possible conformers **6a** and **6b** of tetramer **6** are shown on Fig. 4. The drawings were made based on calculations of hypothetical coordinates of atoms using typical bond lengths and angles of nickel compounds [3–6].

Cyclopentadienyl groups in conformer **6b** are located alternately above and below the mean plane of the molecule. They have equivalent environments and only one signal of Cp protons in ^{1}H NMR and one signal of Cp carbons in ^{13}C NMR should be observable. If the conformer **6b** were present in the reaction products together with the conformer **6a** then three signals of Cp protons and Cp carbons should be observed. The presence of only two signals of equal

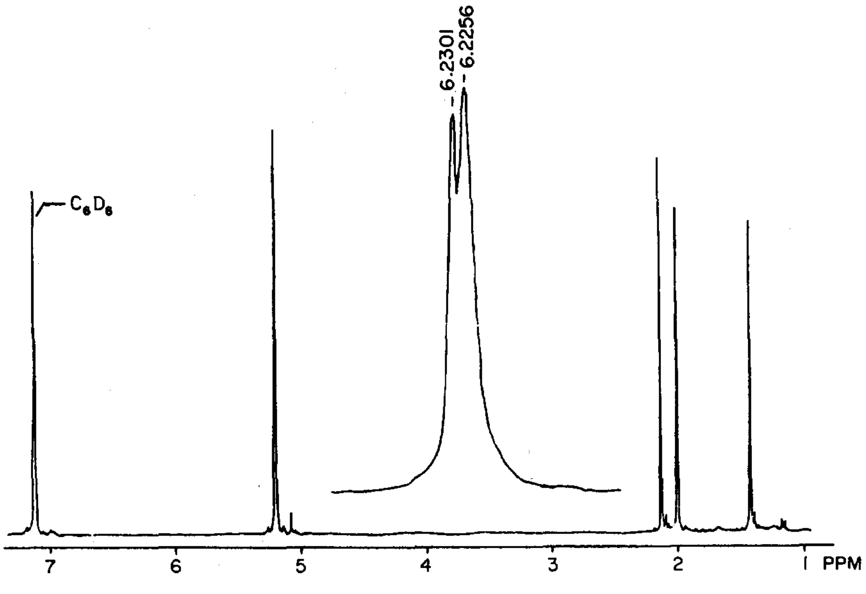


Fig. 2. ^{1}H NMR spectrum of **6** in C_6D_6

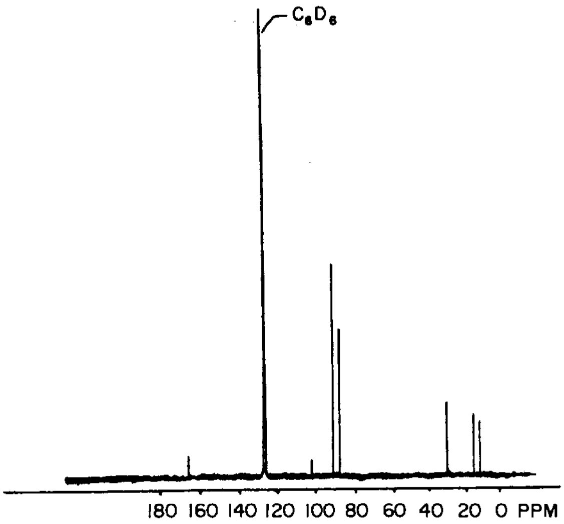


Fig. 3. ^{13}C NMR spectrum of **6** in C_6D_6

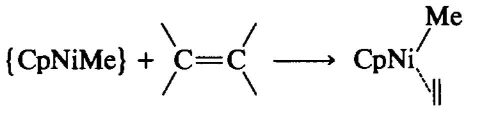
intensity indicates that tetramer **6** exists only in the form of the conformer **6a**.

There is no parent peak observed in the mass spectrum of the tetramer **6** (calc. 768 (^{58}Ni)) probably due to its stability being insufficient. The most intense signals in the mass spectrum appear at *m/e* 466 (100%) and *m/e* 410 (90%). The natural abundance of the ^{58}Ni and ^{60}Ni isotopes indicates the presence of three nickel atoms in the two fragments. It seems probable that the fragment of *m/e* 466 (^{58}Ni) consists of the trinickel core and the organic species C_7H_{13} $[(NiCp)_3C_7H_{13}]^+$. The fragment of *m/e* 410 is probably the parent ion of the already known trinickel cluster $[(NiCp)_3CCH_2CH_3]^+$ [3] formed in the chamber of the mass spectrometer. This suggestion was confirmed by the presence of the other fragments, typical for the fragmentation of this cluster *i.e.* $(Cp_2Ni_3CCHCH_3)^+$ *m/e* = 344 (^{58}Ni) and $(Cp_2Ni_3)^+$ *m/e* = 304 (^{58}Ni).

3. Discussion

Nickelocene reacts with methyllithium in THF to form the unstable compound {CpNiMe} (eqn. (5)). This compound associates and reacts further to form the tris (η^5-cyclopentadienyl) (μ_3-alkylidyne) trinickel cluster $(NiCp)_3CMe$ [3]. If the reaction of nickelocene with methyllithium is carried out in the presence of propene [7] or another olefin [8] then a complex CpNiMe(η^2-$H_2C{=}CHR$) is formed (eqn. (6)). In this reaction the unstable compound {CpNiMe} is stabilized by the formation of a π-complex with the olefin.

$$NiCp_2 + LiMe \longrightarrow \{CpNiMe\} + LiCp \qquad (5)$$



$$\{CpNiMe\} + {>}C{=}C{<} \longrightarrow CpNi\begin{smallmatrix}Me\\ \Vert\end{smallmatrix} \qquad (6)$$

The complex formed (eqn. (6)) can be isolated in a pure state [7,8]. It is stable up to −20°C decomposing above this temperature to evolve the olefin molecule and forming the unstable compound {CpNiMe}. This decomposes further to form the same products as the compound formed in the reaction of nickelocene with methyllithium in the absence of olefin. Besides the decomposition of the complex CpNiMe(η^2-

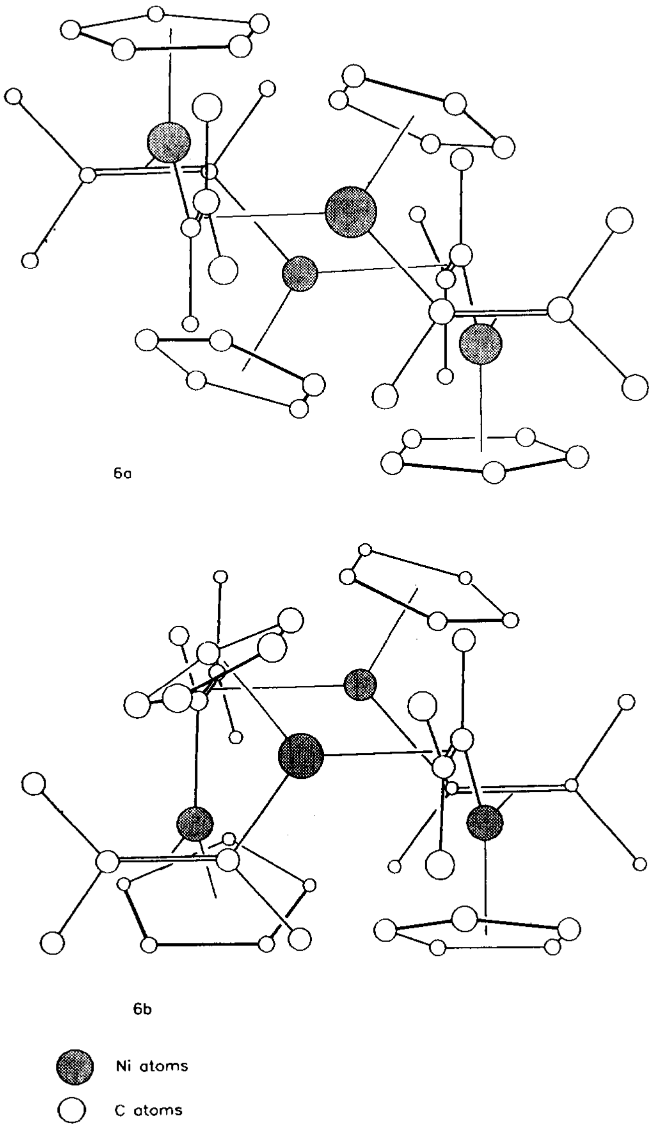
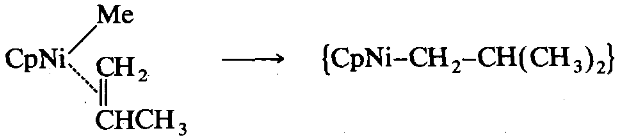


Fig. 4. Proposed structure of two conformers of a tetramer $[CpNi{-}C(CH_3){=}C(CH_3)_2]_4$

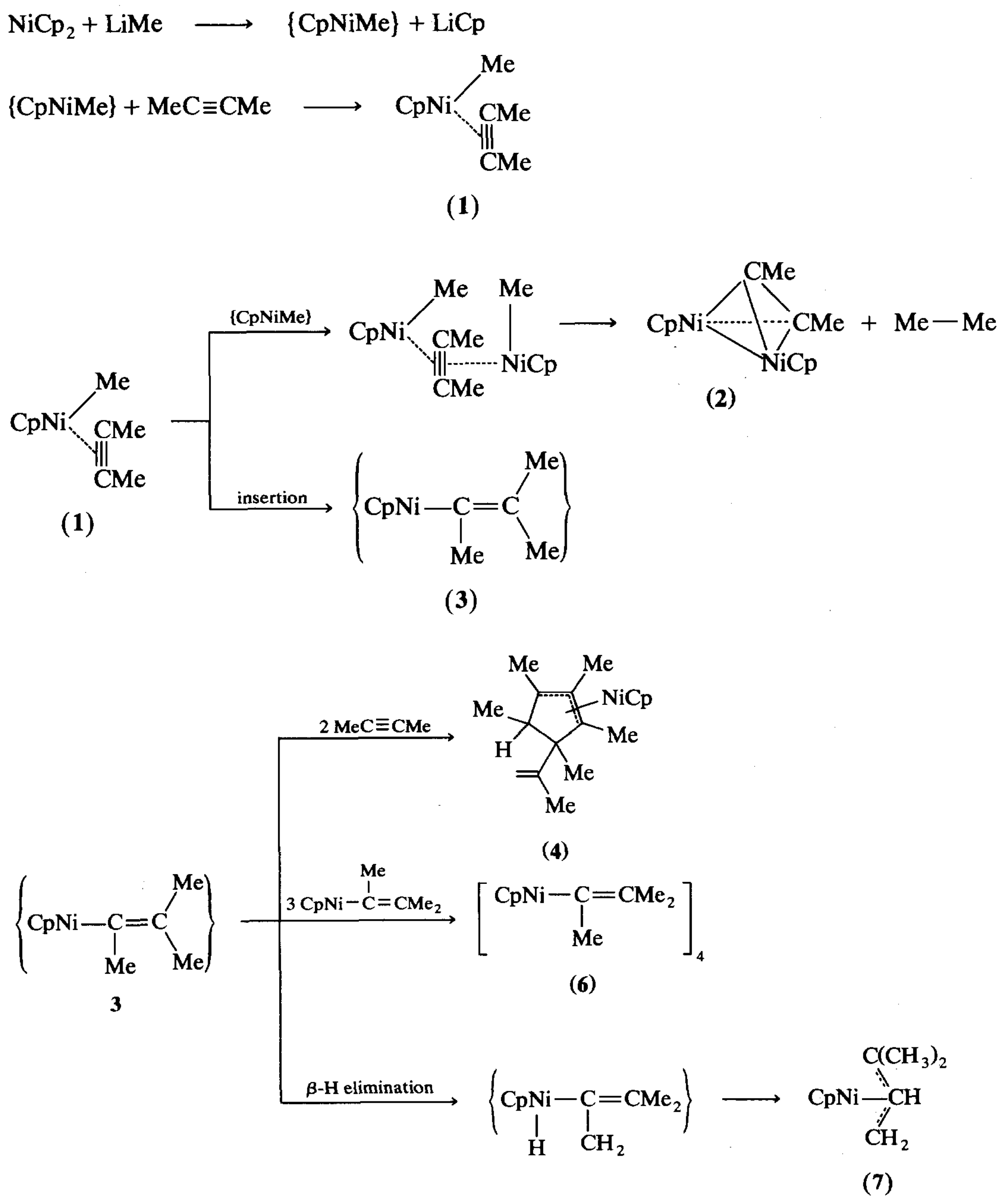
$H_2C{=}CHCH_3$), the olefin insertion reaction occurs (eqn. (7)).



$$CpNi(Me)(\eta^2\text{-}CH_2{=}CHCH_3) \longrightarrow \{CpNi\text{-}CH_2\text{-}CH(CH_3)_2\} \qquad (7)$$

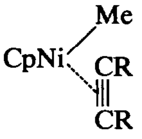
Because a β-hydrogen atom is present in the insertion product, the β-H elimination reaction occurs easily [9]. Neither excess of the olefin nor increase of its pressure lead to polymerization of the olefin. This is probably because β-H elimination occurs much quicker than complexation followed by insertion reactions.

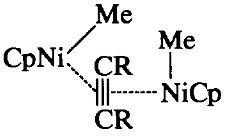
If the reaction of nickelocene with methyllithium is carried out in the presence of acetylenes then unstable



Scheme 1.

{CpNiMe} forms two complexes **1** and **5** at the molar ratios of components 1:1 and 1:2. These complexes are probably kinetically unstable.

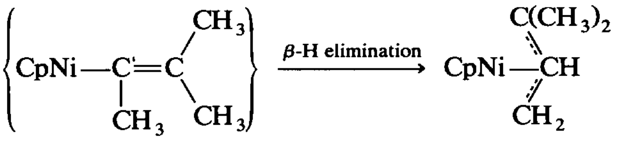

(1)


(5)

Complex **5** decomposes above −30°C to evolve ethane and forming the dinickel compound $(NiCp)_2(RC{\equiv}CR)$. Complex **1** undergoes insertion reaction forming the labile compound **3** {$CpNi{-}C(CH_3){=}C(CH_3)_2$}. In the presence of an excess of 2-butyne this compound undergoes consecutive complexation and insertion reactions to form the stable cyclic π-allylnickel complex **4** [2].

At the same time a stabilization of complex **3** occurs by its association to form the tetramer **6**. Each nickel atom of **6** forms a π complex with the C=C double bond of the next molecule of {$CpNi{-}C(CH_3){=}C(CH_3)_2$} achieving the 18 electron configuration (Fig. 1).

Besides compounds **2**, **4** and **6**, a small quantity of the π-allyl complex η^3-C_5H_9NiCp, **7**, is present in the products of the reaction of nickelocene with methyllithium in the presence of 2-butyne. **7** is formed as a result of the β-H elimination reaction occurring in compound **3** (eqn. (8)).



(3) (7)

(8)

Complex **7** is formed in low yield due to the stabilization of compound **3** by formation of a complex with 2-butyne [2] or by its association to the tetramer **6**. All the pathways of the reaction of nickelocene with methyllithium in the presence of 2-butyne are shown in Scheme 1.

4. Experimental details

All manipulations were carried out under dry argon. Solvents were dried and distilled over the benzophenone radical anion and deoxygenated prior to use. Chromatography was carried out on neutral alumina (Merck 90, 0.063–0.200 mm, deactivated with 2% of water). The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer. The spectra were referenced indirectly to TMS *via* residual solvent signals; ^1H NMR: C_6D_6, $\delta = 7.15$; ^{13}C NMR: C_6D_6, $\delta = 128.00$.

Nickelocene (2.5 g, 13.2 mmol) and 2-butyne (3.57 g, 66.2 mmol) were dissolved in 60 ml of THF. The mixture was kept at −30°C and 11.5 ml of methyllithium in diethyl ether (14.5 mmol) was added at this temperature. After two hours the reaction mixture was allowed to warm to room temperature and the stirring was continued for a further 15 h. The solvents were then evacuated under reduced pressure and deoxygenated water and hexane were added to the resulting mixture. The organic layer was separated, dried with molecular sieves and concentrated. The residue was chromatographed with hexane as eluent.

The first fraction gave 199 mg (5%) of the purple-red π-allyl complex **4**. The second light-green fraction afforded 154 mg of unreacted nickelocene. The next gave 1.8 g (45%) of dinickel complex **2**. The fourth fraction gave 0.5 g of complex **6** as a dark-brown solid.

^1H NMR (C_6D_6): δ (ppm) 1.43 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 5.23 (split into two signals at δ 5.2256 and 5.2301 ppm, a difference of 1.36 Hz, 5H, Cp).

^{13}C NMR (C_6D_6): δ (ppm) 13.71 (q), 17.02 (q), 31.12 (q), 87.90 (d), 91.59 (d), 102.99 (s), 169.18 (s).

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