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Reactions of unstable compound $\{CpNiCH_3\}$ with acetylenes

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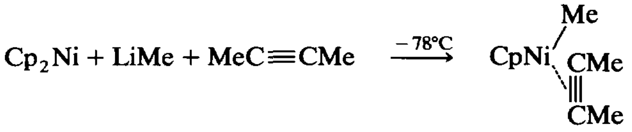
Abstract

The unstable compound $\{CpNiCH_3\}$ is formed in the reaction of nickelocene with methyllithium. This compound reacts with acetylenes to give thermolabile complexes of the type $CpNiMe(\eta^2\text{-}RC{\equiv}CR)$ **1** (R = Me, C_6H_5, $SiMe_3$). Complex **1** can react to give either: (i) the dinickel compound $(CpNi)_2(RC{\equiv}CR)$ **2**, or (ii) the labile compound $\{CpNi\text{–}(R)C{=}C(R)\text{–}CH_3\}$ **3**, which is formed by insertion of the alkyne. For R = Me, further complexation and insertion reactions followed by η-H elimination give the new stable η^3-allylNiCp compound **5**, the structure of which was determined by ^1H and ^{13}C NMR spectroscopy. When R = C_6H_5, η-H elimination is hindered for steric reasons and polymerization of diphenylacetylene occurs. For R = $SiMe_3$ steric hindrance makes coordination of the second $RC{\equiv}CR$ molecule to **3** impossible, preventing oligomerization of bis(trimethylsilyl)acetylene from occurring. γ-H elimination and further rearrangements of **3** give the η^3-allyl-nickel compound **6**. The mechanisms of reaction of $\{CpNiCH_3\}$ with acetylenes are discussed.

Introduction

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



$$Cp_2Ni + LiMe + MeC{\equiv}CMe \xrightarrow{-78^\circ C} CpNi(Me)(\eta^2\text{-}MeC{\equiv}CMe) \qquad (1)$$

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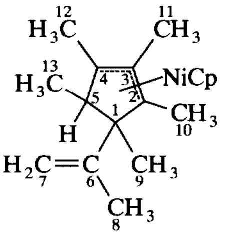
$$2\ \mathbf{1} \xrightarrow{>-30^\circ C} \underset{\mathbf{2}}{(CpNi)_2(MeC\equiv CMe)} + C_2H_6 + MeC\equiv CMe \qquad (2)$$

Tilney-Basset [2] synthesized complex **2** by reacting $Cp_2Ni(CO)_2$ with 2-butyne in a sealed tube in a CO atmosphere at 130°C. This method is inconvenient because toxic $Ni(CO)_4$ is used to synthesize the $Cp_2Ni(CO)_2$. The method we have developed is very simple. The reaction can be carried out over a very wide temperature range from -30°C to room temperature and the yield reaches 70%. This method can also be used to prepare dinickel compounds $(CpNi)_2(RC\equiv CR)$ **2** with other acetylenes ($R = C_6H_5$, $SiMe_3$).

Our previous studies showed that beside compounds **1** and **2**, other products are formed when Cp_2Ni reacts with MeLi in the presence of 2-butyne. The purpose of this work was to examine these other products formed in the above reaction and to explain why different products are formed by other acetylenes.

Results and discussion

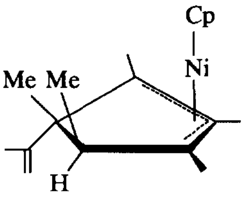
We have found that nickelocene reacts with methyllithium in the presence of 2-butyne to give complex **2** ($R = CH_3$) and a new compound **5**. Based on MS, ^1H NMR, ^{13}C NMR spectra and elemental analysis, we suggest that its structure is as follows:

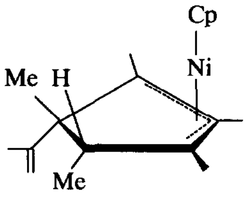


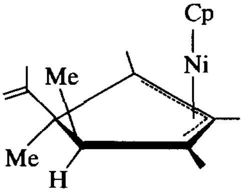
5

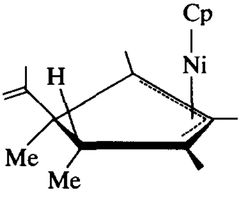
At room temperature compound **5** is a viscous, purple liquid, that is stable during high vacuum distillation at about 100°C. It oxidizes easily when exposed to air, but does not react with water or diluted hydrochloric acid.

Its elemental analysis is entirely consistent with the proposed formula. The ^1H NMR spectrum (THF-d_8) provides little direct information on the structure of the complex because most of the protons are located in methyl groups on the periphery of the compound. However, the ^{13}C NMR spectrum is much more informative. Fourteen signals are identified, of which the one at 90.7 ppm is characteristic for the Cp group. Six methyl carbon signals are observed between 14.7 and 22.1 ppm, of which only the signal at 14.7 ppm shows the additional fine structure in the proton-coupled spectrum associated with a $CH_3(CH)$ group. The resonances at 111.7 (t) and 151.0 (s) ppm are typical for an isopropyliden unit, while the chemical shifts of the remaining signals are fully consistent with the proposed η^3-allyl structure. This structure and the ^{13}C signal assignments are also supported by the connectivities established in a 2D $^{13}C,^1H$ chemical shift correlated spectrum optimized for long range couplings ($^nJ(C,H)$) [3]; the ^1H assignments were also determined from this spectrum. In addition, the ^{13}C NMR spectrum shows that the major component of the sample (70%) is just one of the four possible diastereometric forms (the Ni-allyl unit is chiral and C_1 and C_5 are asymmetric):

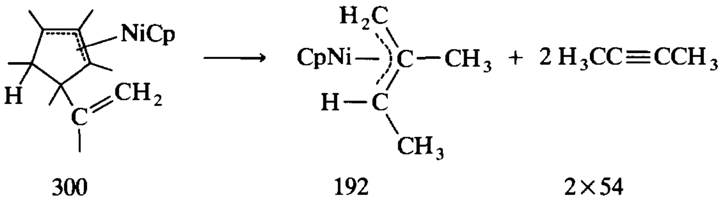




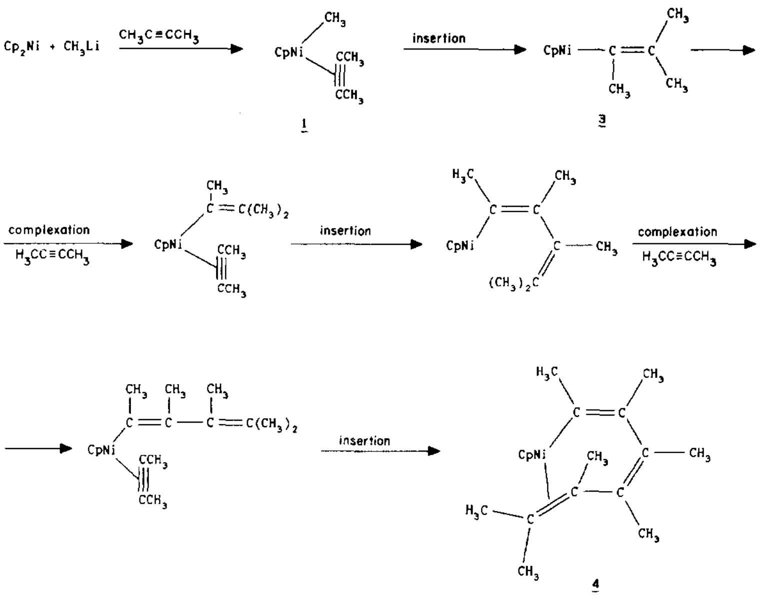




The mass spectrum shows a parent peak at *m/e* 300 (^{58}Ni) and the natural abundance of the ^{58}Ni and ^{60}Ni isotopes indicates the presence of one nickel atom in the molecule. Fragmentation of complex **5** also confirms the proposed structure. Although the molecular weights of the dinickel complex **2** and (η^3-allyl)NiCp **5** (Scheme 3) are both 300, their fragmentation in the mass spectra is different. Complex **2**, after 2-butyne abstraction, gives an ion $[(CpNi)_2]^+$ *m/e* 246 and further fragments $[Cp_2Ni]^+$ *m/e* 188, $[CpNi]^+$ *m/e* 123 and $[Ni]^+$ *m/e* 58. Complex **5** after CpH abstraction, gives an ion $[M - CpH]^+$ *m/e* 234 and also after five-membered ring cleavage and abstraction of two molecules of 2-butyne, gives an ion $[M - 2CH_3{\equiv}CCH_3]^+$ *m/e* 192 of 100% intensity, which suggests formation of the stable $[\eta^3\text{-allylNiCp}]^+$ ion. Further fragmentation of this ion gives $[CpNi]^+$ *m/e* 123 and $[Ni]^+$ *m/e* 58.



The formation of complex **5** can be explained by an insertion of complexed 2-butyne molecule into the Ni–CH_3 bond, vacation of a coordination position on the nickel atom, repeated formation of a complex with 2-butyne and further insertion (Scheme 1) until a six-membered ring is formed in **4**. The terminal double bond in complex **4** can form a π-complex with the nickel atom, blocking the free coordination position on the nickel atom and thus stopping 2-butyne oligomerization from taking place. Similar intramolecular coordination complexes have been described previously [4]. In complex **4** the hydrogen atom of the terminal methyl group lies close to the nickel atom. This makes η-H elimination and then formation of a five-membered ring possible, followed by migration of CpNi with formation of the η^3-allyl complex **5** (Scheme 2). Since the product is largely just one of the possible diastereoisomeric pairs of compounds, this reaction must proceed with a considerable degree of stereospecificity.



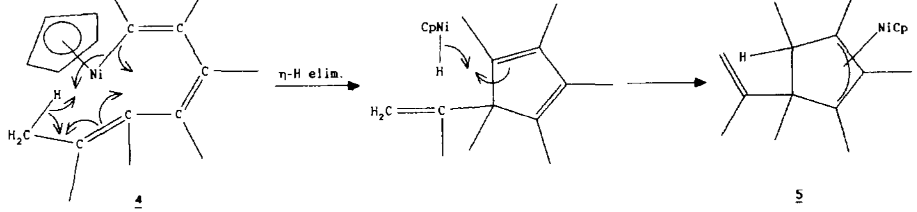
Scheme 1.

Maitlis *et al.* [5] have described a similar reaction of 2-butyne with $PdCl_2$ in the presence of triphenylphosphine. 5-Vinyl-1,2,3,4,5-pentamethylcyclopentadiene 25–65%, 5-(1-chlorovinyl)-1,2,3,4,5-pentamethylcyclopentadiene 10–65% and hexamethylbenzene 10–25% are formed in this reaction.

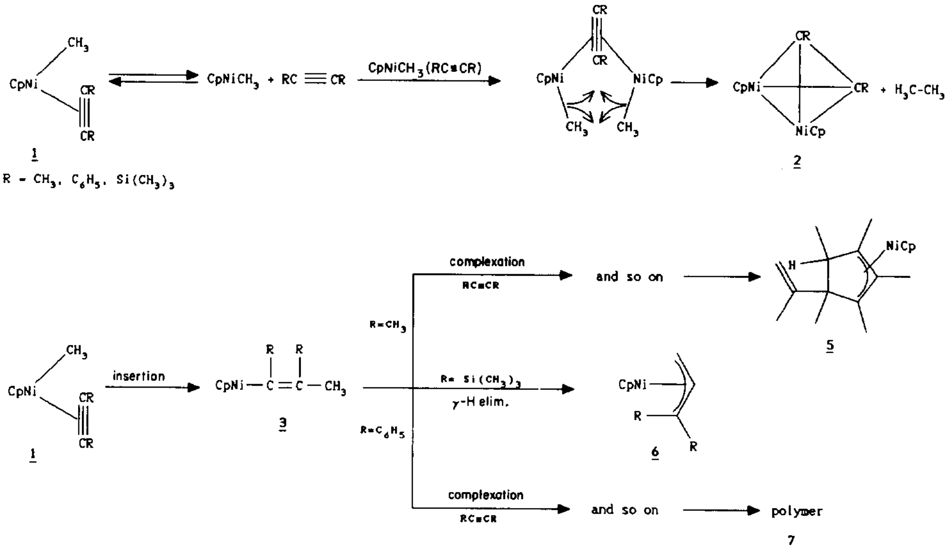
$$[Cl(Me_2C_2)_3PdCl]_2 + PPh_3 \longrightarrow C_5Me_5CH{=}CH_2 + C_5Me_5CCl{=}CH_2 + C_6Me_6$$

It can be assumed that the mechanism of the above reaction, similar to that of Cp_2Ni, consists of η-H elimination and further reactions of unstable palladium hydride.

Nickelocene reacts with methyllithium in the presence of an excess of diphenylacetylene to form, as in the presence of 2-butyne and di(trimethylsilyl)acetylene [1], the previously described complex $(CpNi)_2(C_6H_5C{\equiv}CC_6H_5)$ **2** [2,6]. The yield of complex **2** ($R = C_6H_5$) is about 50% at room temperature in the presence of a fivefold excess of diphenylacetylene. Furthermore, a yellow solid polymer is



Scheme 2.



Scheme 3.

formed in the above reaction. This polymer does not dissolve in organic solvents, water or hydrochloric acid. It does not melt until 380°C and decomposes at 388°C.

It has been proved previously [1] that acetylenes form, with {$CpNiCH_3$}, thermolabile complexes of the type $CpNiMe(\eta^2\text{-}RC{\equiv}CR)$ **1** where $R = CH_3$, $Si(CH_3)_3$ (Scheme 3). These complexes react in two ways to give dinickel complexes **2** and the insertion reaction product **3**. This labile 16-electron complex **3** reacts further in the presence of excess of acetylenes (Scheme 3). The reaction path depends on the kind of R substituent in $RC{\equiv}CR$.

For $R = CH_3$, the following complexation and insertion reactions, and then η-H elimination, lead to the formation of the η^3-allyl complex **5**.

For $R = C_6H_5$, formation of the intramolecular π-complex **4** is impossible for steric reasons and the η-H elimination reaction does not occur. Therefore, the growing oligomer (complex catalysis) has a chain structure which allows further complexation and insertion reactions to occur, leading to the formation of the polymer **7** (Scheme 3).

When $R = SiMe_3$ the bulky substituents block a coordination position on the nickel atom in compound **3**. This prevents the formation of a complex with an additional molecule of $Me_3SiC{\equiv}CSiMe_3$. Therefore, neither the oligomerization reaction with the formation of this six-membered ring (as for 2-butyne) nor a linear polymerization reaction (as for diphenylacetylene) occurs. Instead, γ-H elimination takes place, followed by migration of the Me_3Si group from β-C to α-C to form the η^3-allyl complex **6** (Scheme 3).

Yields of products of the reaction of Cp_2Ni with CH_3Li in the presence of acetylenes depend on the reaction temperature and the molar ratio of the reactants $Cp_2Ni/RC{\equiv}CR$. Increasing the temperature favours the insertion reaction in complex **1** and therefore causes the yield of π-allyl complexes **5** and **6** or polymer **7** to increase (Scheme 3, Table 1). At low temperature, an acetylene

Table 1

Starting temperature (°C)	Yield of products (%)	
	5	**2**
−30	5	45
−20	10	38
+18	25	25

complexation reaction with two molecules of {CpNiCH$_3$} occurs more easily, leading to R–R elimination and the formation of the dinickel compound **2** (Scheme 3).

Experimental

All manipulations were carried out under dry argon by standard Schlenk tube techniques. Solvents were dried and deoxygenated prior to use by distillation over benzophenone radical anion. Chromatography was carried out on neutral alumina (Merck 90, activity I, 0.063–0.200 mm), deactivated with 3% of H_2O, with hexane as eluent. The ^{1}H NMR spectra were recorded on Bruker AM 200 and WH 400 NMR spectrometers and ^{13}C (75 MHz) and 2D ^{13}C,^{1}H chemical shift correlated spectrum ($\Delta_1 T = 0.05$ s for $^nJ(C,H) = 10$ Hz, $\Delta_2 T = 0.03$ s) on a Bruker WM 300 NMR spectrometer. The spectra were referenced indirectly to TMS via residual solvent signals. ^{1}H NMR (toluene-d_8, CHD$_2$): δ 2.03; (THF-d_8) δ 3.58. ^{13}C NMR (THF-d_8): δ 25.28.

Reaction of nickelocene with 2-butyne in the presence of methyllithium

Nickelocene (2.5 g, 13.24 mmol) was dissolved in 100 ml of THF, followed by 2-butyne (14.3 g, 20.7 ml, 265 mmol). The mixture was maintained at the temperature given in Table 1 and methyllithium (14.56 mmol) in 29.2 ml of diethyl ether was added dropwise. The mixture was allowed to warm to ambient temperature and stirred overnight. The solvents were then evacuated under reduced pressure, at room temperature. The residue was extracted with hexane (3 × 70 ml) and the combined extracts were concentrated to 6 ml. The resulting mixture of products was chromatographed. The first fraction afforded compound **5** as a purple oil. The second fraction gave a small amount of unreacted nickelocene and the third gave green crystals of compound **2** (R = CH$_3$). The yields are given in Table 1.

Compound 5. Elemental analysis: Found C, 71.83; H, 8.75. $C_{18}H_{26}Ni$ calc. (MW 301.10): C, 71.80; H, 8.70%. ^{1}H NMR (toluene-d_8) δ 0.62 (3H, H_{13}); 0.68 (3H, H_9); 1.12 (3H, H_{10} or H_{12}); 1.22 (3H, H_{12} or H_{10}); 1.76 (3H, H_8); 1.91 (3H, H_{11}); 4.89 [1H, H_7(E)]; 5.02 (5H, Cp); 5.10 [1H, H_7(Z)]. H_5 signal observed. ^{13}C NMR (THF-d_8): δ 14.7 (q, C_{13}); 14.9 (q, C_{11}); 16.9 (q, C_{10}); 17.6 (q, C_{12}); 21.6 (q, C_9); 22.1 (q, C_8); 52.8 (d, C_5); 56.8 (s, C_1); 79.0 (s, C_4); 80.8 (s, C_2); 90.7 (d, Cp); 99.6 (s, C_3); 111.7 (t, C_7); 151.0 (s, C_6). Mass spectrum (EI): $[M]^+$ m/e 300 (78%), $[M-CpH]^+$ m/e 234 (75%), $[M-2CH_3C{\equiv}CCH_3]^+$ m/e 192 (100%), $[CpNi]^+$ m/e 123 (22%), $[Ni]^+$ m/e 58 (12%).

Compound 2. (R = CH$_3$) m.p. 54–55°C (lit. m.p. 55°C [2]). ^{1}H NMR (THF-d_8): δ 2.13 (CH$_3$); 5.04 (Cp). ^{13}C NMR (THF-d_8): δ 100.5 (s), 87.6 (d), 17.9 (q).

Reaction of nickelocene with diphenylacetylene in the presence of methyllithium

Nickelocene (1 g, 5.3 mmol) and diphenylacetylene (14.15 g, 79.5 mmol) were dissolved in 75 ml of THF. Methyllithium (5.83 mmol) in 6.2 ml of diethyl ether was added during 5 min at room temperature. The colour of the reaction mixture changed from dark green to brown. After 30 min, a precipitate was formed. The reaction mixture was allowed to stand at room temperature for 15 h, and the yellow precipitate was filtered off and washed with THF three times. The filtrate was evaporated and dissolved in hexane to give a dark solution and another portion of yellow solid. The combined solids (11.7 g) were washed with hexane, water and diluted hydrochloric acid. This yellow product is insoluble in all common organic solvents, water and mineral acids, and decomposes at 388°C without melting. Hexane was evaporated from the solution and a residue chromatographed, to give 541 mg (yield 48%) of compound **2** ($R = C_6H_5$) $(CpNi)_2(C_6H_5C{\equiv}CC_6H_5)$ as black crystals. m.p. 148–150°C (lit. m.p. 149–150°C [2]). ^{1}H NMR (THF-d_8) 7.04–7.18 (m, 10H, C_6H_5), 5.16 (s, 10H, 2Cp).

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