Inorganic Chemistry

Article

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Triple C−H Bond Activation of a Nickel-Bound Methyl Group: Synthesis and X-Ray Structure of a Carbide Cluster $(NiCp)_6(\mu_6\text{-}C)$

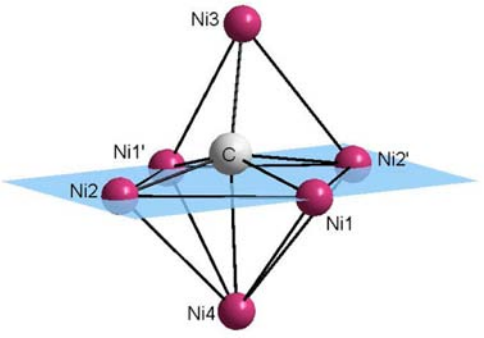
Włodzimierz Buchowicz,[†] Beata Herbaczyńska,[†] Lucjan B. Jerzykiewicz,[‡] Tadeusz Lis,[‡] Stanisław Pasynkiewicz,[†] and Antoni Pietrzykowski*,[†]

[†]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

[‡]Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-353 Wrocław, Poland

Supporting Information

ABSTRACT: A new hexanuclear cyclopentadienylnickel carbide cluster $(NiCp)_6(\mu_6\text{-}C)$ (**1**) was obtained through the thermolysis of the alkene complex $[NiCp(CH_3)(\eta^2\text{-}CH_2{=}CHC_4H_9)]$ (**4**). The X-ray molecular structure of **1** (monoclinic; $P2_1/c$; $Ni{-}C_{carbide}$ = 1.767(4)−2.109(4) Å) reveals a highly deformed octahedral arrangement of nickel atoms with two octahedron edges opened (Ni−Ni bonding distances = 2.410(1)−2.623(1) Å, Ni···Ni nonbonding distances = 3.107(2) and 3.108(2) Å). Cluster **1** is the first example of a homoleptic, cyclopentadienylnickel carbide cluster. Moreover, ^{13}C-labeling studies proved that the carbido ligand in cluster **1** originated from the Ni-bound methyl group. This transformation requires a triple C−H bond activation in the methyl group, which has not been observed so far for late transition metal compounds.



■ INTRODUCTION

Transition metal−carbide clusters are of great importance in contemporary organometallic chemistry and catalysis as they represent model compounds of intermediates adsorbed on metal surfaces.[1] Typical examples of metal−carbide clusters include early transition metal halide clusters[2] and late transition metal carbonyl clusters.[3] A few examples of terminal carbido ligands have also been reported.[4] The carbide carbon atom in clusters is most often derived from CO ligands,[3] small organic molecules (e.g., CCl_4),[2] or bridging CH_2 or CH groups via C−H bond activation.[5]

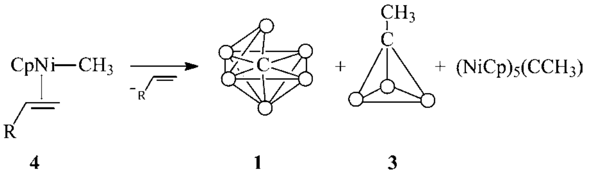
To the best of our knowledge, carbide clusters bearing cyclopentadienyl ligands are rare,[3j,k,5b] and only one example of a homoleptic, cyclopentadienyl carbide cluster, namely $[Rh_6Cp_6(\mu_6\text{-}C]^{2+}$, has been reported.[6] An unprecedented cyclopentadienylnickel carbide cluster $(NiCp)_6C$ (**1**) was described in addition to the other completely characterized products, i.e., $(NiCp)_3(\mu_3\text{-}CH)$ (**2**) and $(NiCp)_3(\mu_3\text{-}CCH_3)$ (**3**), in a preliminary communication on the thermolysis of the alkene complex $[NiCp(CH_3)(\eta^2\text{-}CH_2{=}CH(CH_2)_3CH_3)]$ (**4**).[7] This cluster was also observed in residues obtained from the reaction of nickelocene with methyllithium.[8] The formulation of **1** was derived from its mass spectra, and its structure has not been reported up to date.

In an effort to improve our knowledge on the formation and reactivity of cyclopentadienylnickel clusters, we have undertaken and report herein results of the complete structural analysis of this unique carbide cluster, **1**. Moreover, ^{13}C- and deuterium-labeling experiments allowed us also to explain the origin of the carbido and ethylidyne ligands in clusters **1** and **3**.

■ RESULTS AND DISCUSSION

Synthesis. The title cluster **1** was prepared by thermolysis of the alkene complex **4** under ambient conditions. The previously reported trinuclear ethylidyne cluster **3**[9−11] and a pentanuclear cluster tentatively formulated as $(NiCp)_5(CCH_3)$[7] were identified as the other major products of this reaction (Scheme 1).

Scheme 1. The Synthesis of Cluster 1 from Complex 4 (R = *n*-C_4H_9, ○ = NiCp)



Structural Studies. Repeated crystallization from THF/hexane solutions afforded the paramagnetic cluster **1** as a gray powder in moderate yield.[12] Crystallization from THF/CH_2Cl_2 solution gave crystals of **1** suitable for X-ray studies. The structure was solved by direct methods and showed a distorted octahedron-like structure for the Ni atoms with the central C atom at the inversion center. The refinement with anisotropic temperature factors for all non-H atoms stopped with an *R* factor of ca. 10%. The molecule (Figure 1) showed elongated displacement ellipsoids for C1 and Ni3 atoms. Furthermore,

Received: April 24, 2012
Published: July 25, 2012

ACS Publications

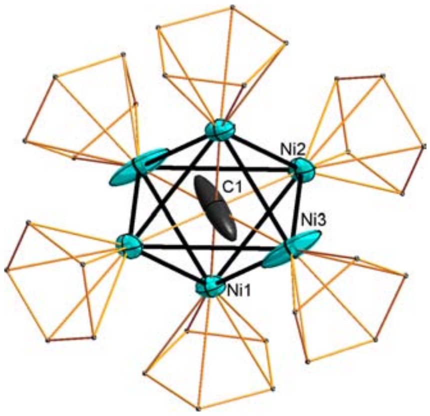


Figure 1. The ordered model of the cluster unit of the $(NiCp)_6(\mu_6\text{-}C)$ (**1**) molecule in the crystal **1**·$2CH_2Cl_2$, showing the elongated displacement ellipsoids of the Ni3 and C1 (when situated at the inversion center) atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity.

two relatively large peaks were observed on the difference-Fourier map near the Ni3 atom. In our opinion, the above factors indicate displacement of the C1 atom from the center of the inversion and distribution of the Ni3 atom between two positions. The cyclopentadienyl ring bonded to the Ni3 atom was also modeled in two positions. Further refinement gave a final *R* factor of 0.0497 and the cluster molecule shown in Figure 2. The asymmetric unit of **1**·$2CH_2Cl_2$ contains one-half of the cluster molecule and one slightly disordered CH_2Cl_2 molecule connected by weak C−H···Cl interactions (Figure S1, Supporting Information). The crystal data are collected in Table 1. Selected bond lengths and angles are listed in Table 2. The atom numbering scheme for **1** is shown in Figure 2.

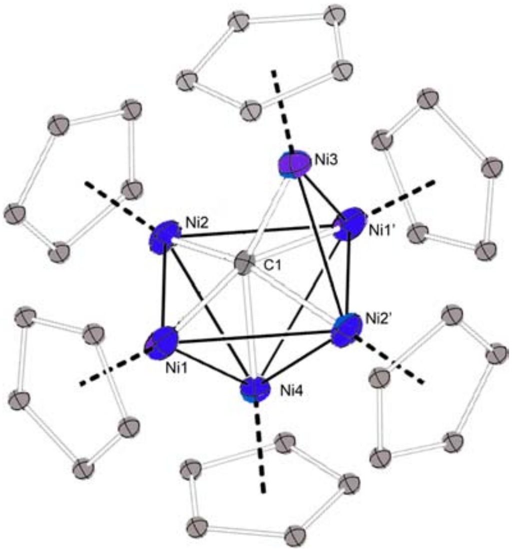


Figure 2. The structure of the final model of the $(NiCp)_6(\mu_6\text{-}C)$ (**1**) molecule showing the strongly deformed octahedron-like structure of Ni atoms around a central C atom, with atom labeling and 50% and 30% probability ellipsoids for Ni and C, respectively. H atoms are omitted for clarity.

The five Ni−C1 (carbide) distances are in the range of 1.767(4)−1.963(4) Å for Ni1, Ni1′, Ni2, Ni2′, and Ni3. These distances are shorter than in the other homoleptic nickel carbide clusters, that is, in $[Ni_8(CO)_{16}C]^{2-}$ (2.084(1) Å) and in $[Ni_9(CO)_{17}C]^{2-}$ (2.03(2), 2.15(2), and 2.81(3) Å).[3f] This is probably due to differences in the cluster sizes. The distance Ni4−C1 is significantly longer than the other five (2.109(4) Å), as the carbide atom is positioned out of the plane defined by Ni1, Ni1′, Ni2, and Ni2′ atoms by 0.389(1) Å toward Ni3 (Figure 3). Ten Ni−Ni distances are in the range of 2.410(1)−

Table 1. Crystal Data and Structure Refinement Parameters for 1·$2CH_2Cl_2$

chemical formula	$C_{31}H_{30}Ni_6{\cdot}2CH_2Cl_2$
fw	924.66
λ (Å)	0.71073
T (K)	100(2)
cryst system	monoclinic
space group	$P2_1/c$
unit cell dimensions	
a (Å)	9.814(3)
b (Å)	9.298(3)
c (Å)	17.857(4)
β (deg)	98.50(3)
V (Å^3)	1611.6(8)
Z	2
D_c (Mg/m^3)	1.906
F(000)	936
habit	column
cryst size (mm)	0.3 × 0.2 × 0.2
μ (mm^{-1})	3.79
diffraction geometry	ω
Θ range (deg)	4.53−37.50
T_{min}, T_{max}	0.332, 0.552
number of reflns measured	40283
number of unique reflns	8462
$R_{(int)}$	0.0379
number of observed reflns	5596 [I > 2σ(I)]
refinement method	least-squares on F^2
number of params	246
final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0497, 0.1379
final R_1, wR_2 indices (all data)	0.0787, 0.1513
goodness-of-fit (S)	1.090
largest diff. peak and hole e Å^{-3}	1.71 and −1.21

Table 2. Selected Interatomic Distances [Å] and Angles [deg] in 1·$2CH_2Cl_2$

C1−Ni1	1.767(4)	Ni1−C1−Ni2	92.6(2)
C1−Ni1′[a]	1.963(4)	Ni1−C1−Ni3	120.8(2)
C1−Ni2	1.796(4)	Ni1−C1−Ni4	76.3(2)
C1−Ni2′[a]	1.936(4)	Ni1−C1−Ni1′[a]	155.9(2)
C1−Ni3	1.809(4)	Ni1−C1−Ni2′[a]	88.4(2)
C1−Ni4	2.109(4)	Ni2−C1−Ni3	119.1(2)
Ni1−Ni2	2.575(1)	Ni2−C1−Ni4	77.0(2)
Ni1−Ni2′[a]	2.584(1)	Ni2−C1−Ni1′[a]	86.7(2)
Ni1−Ni4	2.410(1)	Ni2−C1−Ni2′[a]	155.6(2)
Ni2−Ni4	2.444(1)	Ni3−C1−Ni4	153.3(2)
Ni3−Ni1′[a]	2.423(1)	Ni3−C1−Ni1′[a]	79.8(2)
Ni3−Ni2′[a]	2.423(1)	Ni3−C1−Ni2′[a]	80.6(2)
Ni4−Ni1′[a]	2.623(1)	Ni4−C1−Ni1′[a]	112.4(2)
Ni4−Ni2′[a]	2.590(1)	Ni4−C1−Ni2′[a]	108.6(2)
Ni2−Ni3	3.107(2)	Ni1′[a]−C1−Ni2′[a]	82.6(2)
Ni1−Ni3	3.108(2)		

[a] Symmetry transformations used to generate equivalent atoms: −*x* + 1, −*y* + 1, −*z* + 1.

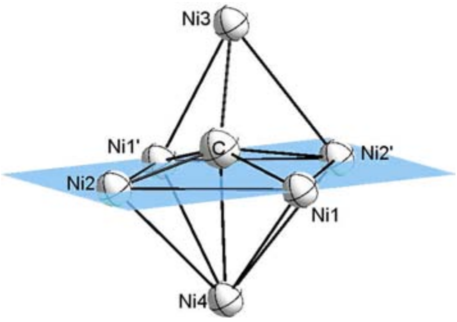


Figure 3. The Ni_6C core of the $(NiCp)_6(\mu_6\text{-}C)$ (**1**) molecule showing the position of the carbido ligand above the plane defined by Ni1, Ni1′, Ni2, and Ni2′ atoms.

2.623(1) Å, and on average (2.523 Å) are slightly longer than those observed in the octahedral clusters $(NiCp)_6$ (2.411(2)–2.438(2) Å) and $[(NiCp)_6]^+$ (2.419(2)–2.428(2) Å).[13] The other two Ni–Ni distances (Ni1–Ni3 = 3.108(2) Å and Ni2–Ni3 = 3.107(2) Å) are significantly longer than the others and indicate that the two edges of the Ni_6 octahedral core are open.

The cluster $(NiCp)_6(\mu_6\text{-}C)$ (**1**) bears 94 cluster valence electrons. That is four electrons more (delivered by the carbido ligand) than in the cluster $(NiCp)_6$, which adopts the octahedral skeletal *closo* structure.[13] This increase in the sum of valence electrons by four results in the cluster opening by breaking the two edges, which is in agreement with Wade's rules.[14] However, both clusters $(NiCp)_6$ and **1** bear two electron pairs too many for their structures, according to the conventional electron counting theories.[15] This phenomenon seems to be common for cyclopentadienylnickel clusters of a size higher than three nickel atoms. For example, cluster $(NiCp)_4$ would be a 60 VE system and should be stable with a tetrahedral structure. However, such a cluster has not been isolated so far. Additional electrons are necessary to stabilize its tetrahedral skeletal structure. These electrons can be delivered by hydrido[16] or by alkylidyne[17] ligands. Known tetrahedral Ni_4 clusters with other than cyclopentadienyl ligands, e.g., $Ni_4[CNC(CH_3)_3]_4[\mu_3(\eta^2)\text{-}C_6H_5C{\equiv}CC_6H_5]_3$,[18] $[Ni_4(CO)_4(\mu_3\text{-}CF_3C{\equiv}CCF_3)_3]$,[19] and $Ni_4(Cp^*Ga)_4(CO)_6$,[20] obey Wade–Mingos rules and possess 60 VE.

Reaction Pathways. To clarify the origin of the carbido and the carbyne ligands in clusters **1** and **3**, we have synthesized ^{13}C- and D-labeled complexes $[NiCp(^{13}CH_3)(\eta^2\text{-}CH_2{=}CH(CH_2)_3CH_3)]$ (**4-^{13}C**) and $[NiCp(CD_3)(\eta^2\text{-}CH_2{=}CH\text{-}(CH_2)_3CH_3)]$ (**4-d$_3$**). The thermal decomposition of **4-^{13}C** afforded $(NiCp)_6(\mu_6\text{-}^{13}C)$ (**1-^{13}C**), $(NiCp)_3(\mu_3\text{-}^{13}C^{13}CH_3)$ (**3-^{13}C$_2$**), and $(NiCp)_5(^{13}C^{13}CH_3)$ (Scheme 2). The presence of the ^{13}C atoms in all of these clusters was unambiguously deduced from the mass spectra (see Supporting Information).

Moreover, the thermal decomposition of **4-d$_3$** afforded $(NiCp)_6(\mu_6\text{-}C)$ (**1**), $(NiCp)_3(\mu_3\text{-}CCD_3)$ (**3-d$_3$**), and $(NiCp)_5(CCD_3)$ (Scheme 3). The presence of the CD_3 group in the isolated cluster **3-d$_3$** was unambiguously established from the MS and multinuclear NMR spectra.

The thermal decomposition of complexes $[NiCp(CH_3)(\eta^2\text{-}CH_2{=}CHR)]$ commences with the alkene dissociation (Scheme 4).[21] Thus, the highly unstable, 16 VE complex $\{NiCp(CH_3)\}$ readily undergoes α-H elimination. Three consecutive α-H eliminations and couplings with $\{NiCp(CH_3)\}$ molecules provide the intermediate tetranickel carbide cluster (Scheme 4, path a). Then, further aggregation of these reactive cyclopentadienylnickel species yields the cluster **1** (Scheme 4, path b).[22]

Accordingly, we conclude that the cluster **1** is formed from complex **4** as a result of a *triple C–H bond activation*.[23] There have been very few examples of activation of all three C–H bonds of a methyl group.[24] None of them involves a late transition metal-bound methyl group.

Taking into account our previous findings that solvents do not participate in the formation of **3**,[7] our results (Schemes 2 and 3) prove that the ethylidyne ligand in cluster **3** originates from *two* nickel-bonded methyl groups of complex **4**. The synthesis of **3** from complex **4** requires, in addition to *the triple C–H bond activation*, also a C–C bond formation. The exact course of the C–C bond forming reactions remains to be elucidated, but we wish to note that the partially exposed carbidic carbon atom in the intermediate cluster $\{(NiCp)_4C\}$ (Scheme 4) might be a suitable substrate for coupling reaction with nucleophilic $\{CpNiCH_3\}$, similarly as reported for cluster $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$ and CO.[25]

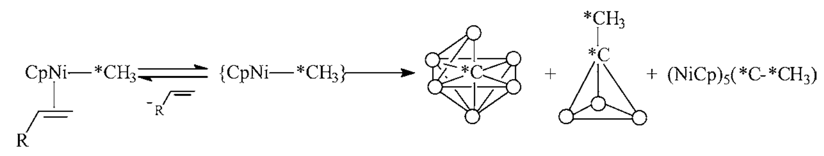
Stability on Alumina. The formation of the cluster **1** has been observed previously in few reports involving nickelocene chemistry.[7,8] However, as long as column chromatography on Al_2O_3 was routinely used to separate the reaction products, cluster **1** has not been isolated in a pure form. To check the stability of cluster **1** on Al_2O_3, we carried out a reaction of an isolated sample of **1** with neutral Al_2O_3 (deactivated with water). We observed that cluster **1** decomposed slowly upon interaction with the neutral Al_2O_3. The known cluster $(NiCp)_3(\mu_3\text{-}CH)$[7,11] (**2**) was detected by MS in the reaction mixture (Scheme 5). Moreover, two other clusters, preliminary formulated as $(NiCp)_3(CC_5H_5)$ and $(NiCp)_6C_2$, were also observed in the mass spectrum.

This experiment clearly supports our previous suggestion that cluster **2** was actually formed during the chromatographic workup.[7] It also reasonably explains why cluster **1** was not isolated when column chromatography on alumina was applied to separate the reaction products.[11]

■ CONCLUSIONS

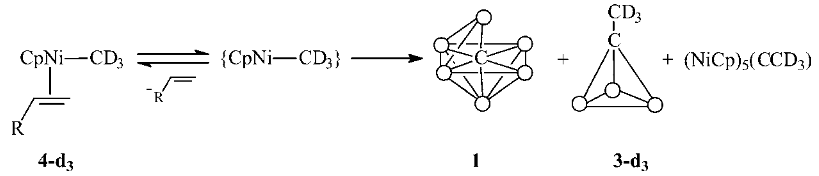
We have proved that the nickel-attached methyl group of complex **4** was transformed into the carbido and the carbyne ligands in clusters **1** and **3**, respectively. This process requires a *triple C–H bond activation* in the nickel bonded methyl group, which has not been observed so far for a late transition metal.

Scheme 2. Thermal Decomposition of Complex 4-^{13}C (R = n-C_4H_9, ○ = NiCp, *C = ^{13}C)

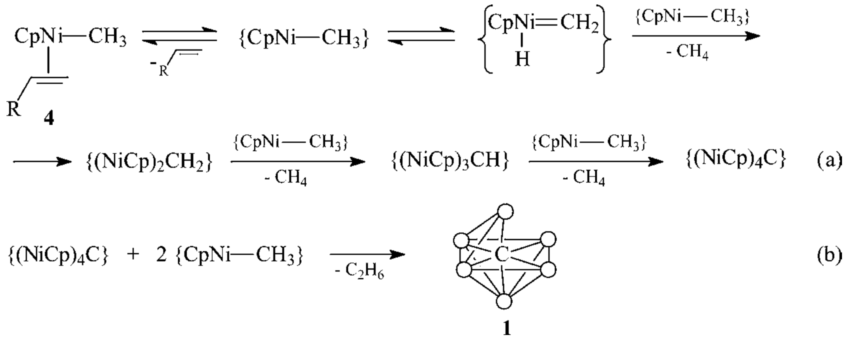


4-^{13}C **1-^{13}C** **3-^{13}C$_2$**

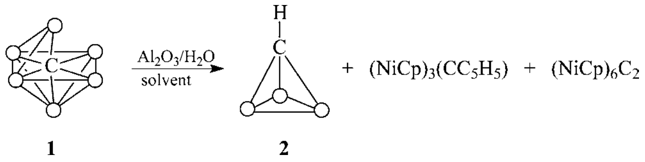
Scheme 3. Thermal Decomposition of the Deuterated Complex 4-d$_3$ (R = *n*-C_4H_9, ○ = NiCp)



Scheme 4. Plausible Pathways Leading to Cluster 1 (○ = NiCp)



Scheme 5. Decomposition of the Cluster 1 in the Presence of Alumina (○ = NiCp)



Moreover, the C−C bond was *selectively* formed from two carbon atoms that were originally bonded to the Ni atoms in the complex **4**, yielding the ethylidyne ligand of the cluster **3**.

The isolated and fully characterized cluster **1** represents the first example of a homoleptic, cyclopentadienylnickel carbide cluster. The X-ray structure of **1** reveals a partially exposed, carbidic carbon atom that could be considered as a model of surface intermediates in the Fischer−Tropsch C−C bond-forming chemistry.

■ EXPERIMENTAL SECTION

General. All reactions and manipulations were carried out under an atmosphere of dry argon using Schlenk techniques. Solvents were distilled from potassium in the presence of benzophenone. Solutions of methyllithium were prepared from CH_3I and lithium in diethyl ether. Solutions of methyllithium-d$_3$ (from CD_3I, Armar, 99.5% D) and $^{13}CH_3Li$ (from $^{13}CH_3I$, Aldrich, 99% ^{13}C) were prepared in a similar way. Nickelocene was prepared according to the literature procedure.[26] Al_2O_3 (Sigma-Aldrich, neutral) was deactivated with 5% degassed water; 1-hexene (Sigma-Aldrich) was distilled under argon. ^1H NMR (400 MHz) and ^{13}C NMR spectra (101 MHz) were recorded on a Mercury-400BB spectrometer in benzene-d$_6$ at ambient temperature (unless otherwise noted). Mass spectra (EI, 70 eV) were measured on an AMD-604 mass spectrometer or Thermo-Finnigan TRACE DSQ GC/MS. Intensity data collection was carried out on a Kuma KM4 κ-axis diffractometer equipped with a CCD camera and an Oxford Cryosystem. All data were corrected for Lorentz, polarization, and absorption effects. Data reduction and analysis were carried out with the Kuma diffraction programs.[27] The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 data using the SHELXTL (version 6.1) program.[28] Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXTL default parameters.

Synthesis of [NiCp(CH$_3$)(η^2-CH$_2$=CH(CH$_2$)$_3$CH$_3$)] (4). A solution of nickelocene (1.445 g, 7.66 mmol) and 1-hexene (2.9 mL, 23.1 mmol) in THF (40 mL) and diethyl ether (60 mL) was cooled to −75 °C, and then a solution of methyllithium (7.70 mL, 9.19 mmol) in diethyl ether was added. The mixture was warmed slowly to −40 °C, stirred for 3 h, and then kept at −75 °C overnight. Water (40 mL) was added to the resulting red solution at −75 °C. The mixture was warmed to 5 °C, and the two layers were separated. Solvents from the organic layer were evaporated under reduced pressure at ca. −30 °C. The resulting oil was extracted with hexane (45 mL) at −75 °C. The solvent was evaporated under reduced pressure at ca. −30 °C. The resulting red oil was identified as [NiCp(CH$_3$)(η^2-CH$_2$=CH(CH$_2$)$_3$CH$_3$)].[11] ^1H NMR (400 MHz, benzene-d$_6$) δ ppm: 5.04 (s, Cp, 5H), 3.59 (b, =CH, 1H), 2.90 (b, =CH, 1H), 2.80 (b, =CH, 1H), 1.77 (b, CH$_2$, 2H), 1.36 (b, 2 × CH$_2$, 4H), 0.99 (b, CH$_3$, 3H), −0.62 (s, Ni-CH$_3$, 3H).

Thermal Decomposition of [NiCp(CH$_3$)(η^2-CH$_2$=CH(CH$_2$)$_3$CH$_3$)] (4). A solution of the freshly prepared [NiCp(CH$_3$)(η^2-CH$_2$=CH(CH$_2$)$_3$CH$_3$)] (**4**) in THF (100 mL) was stirred for seven days at room temperature, after which time the volatiles were evaporated under reduced pressure. EI-MS of the crude reaction mixture showed the presence of (NiCp)$_3$(μ_3-CCH$_3$) (**3**; M$^+$ at m/z = 396), (NiCp)$_5$(CCH$_3$) (M$^+$ at m/z = 642), and (NiCp)$_6$(μ_6-C) (**1**; M$^+$ at m/z = 750) (calcd. for ^{58}Ni). The residue was washed with hexane (5 × 30 mL), and the extracts were discarded. The remaining black solid was treated with THF (50 mL). The THF extract was filtered and reduced in volume to ca. 30 mL. Hexane (150 mL) was added, and the resulting solution was kept for two days at −75 °C. A gray precipitate settled down. The brown supernatant was discarded. The precipitate was dried under vacuum conditions and redissolved in THF (30 mL). Hexane (150 mL) was added, and the resulting suspension was kept overnight at −75 °C. This crystallization procedure was repeated five more times until the cluster (NiCp)$_6$(μ_6-C) (**1**) was obtained as a gray powder (0.063 g, 0.0835 mmol, 6.5% total yield, based on nickelocene in two step reaction). EI-MS m/z (calcd. for ^{58}Ni, rel. intensity): 750 (M$^+$, 8%), 627 ([M-NiCp]$^+$, 3%), 562 ([M-NiCp$_2$]$^+$, 31%), 496 ([M-NiCp$_2$-CpH]$^+$, 8%), 188 ([NiCp$_2$]$^+$, 100%), 123 ([NiCp]$^+$, 89%), 66 ([CpH]$^+$, 93%), 65 (Cp$^+$, 55%), 58 (Ni$^+$, 31%). HRMS calcd. for $C_{31}H_{30}Ni_6$: 749.84719. Found: 749.84499. Magnetic susceptibility measurements in a toluene solution using the Evans' method[29] are consistent with the presence of four unpaired electrons in the molecule (μ = 4.99 μ_B at 295 K). EPR measurements: repeatedly no signals were observed for the freshly prepared compound. ^1H NMR (400 MHz, benzene-d$_6$): no signals observed from −200 to +200 ppm at ambient temperature.

Interaction of $(NiCp)_6(\mu_6\text{-}C)$ (1) with Alumina. $(NiCp)_6(\mu_6\text{-}C)$ (**1**; 0.026 g) was dissolved in toluene (10 mL). Al_2O_3 (6.0 g, deactivated with 5% of degassed water) was added, and the resulting slurry was stirred for eight days at room temperature. A red-brown solution was obtained which was decanted from the Al_2O_3. The remaining Al_2O_3 was subsequently washed with toluene (5 mL, then 4 × 2 mL) until the toluene washings were nearly colorless. Because the Al_2O_3 was yellow-brown and a black solid also remained, the Al_2O_3 was further washed with THF (5 mL, then 2 × 2 mL) until the extracts were nearly colorless (finally, the Al_2O_3 was light-yellow and small amounts of a black solid also remained). The combined toluene and THF washings were evaporated to dryness to leave 0.012 g of a dark solid. The EI-MS of this residue featured molecular peaks that were assigned to (calcd. for ^{58}Ni) $(NiCp)_3(\mu_3\text{-}CH)$ (**2**; m/z = 384), $(NiCp)_3(\mu_3\text{-}CC_5H_5)$ (m/z = 448), $(NiCp)_6(\mu_6\text{-}C)$ (**1** ; m/z = 750), $(NiCp)_6C_2$ (m/z = 762).

An analogous reaction performed in THF instead of toluene gave similar results albeit with apparently somewhat diminished yields of the soluble clusters.

Synthesis of $[NiCp(CD_3)(\eta^2\text{-}CH_2{=}CH(CH_2)_3CH_3)]$ (4-d_3). This complex was prepared similarly as described above for $[NiCp(CH_3)(\eta^2\text{-}CH_2{=}CH(CH_2)_3\ CH_3)]$ (**4**) from nickelocene (1.3733 g, 6.02 mmol), methyllithium-d_3 (11.0 mL, 6.65 mmol), and 1-hexene (2.50 mL, 20.3 mmol) in THF (60 mL) and Et_2O (60 mL). For **4-d_3**, ^{1}H NMR (400 MHz, benzene-d_6) δ: 5.04 (s, Cp, 5H), 3.54 (b, =CH, 1H), 2.93 (b, $=CH_2$, 1H), 2.75 (b, $=CH_2$, 1H), 1.30 (unresolved m, 3 × CH_2, 6H), 0.89 (b, CH_3, 3H). ^{13}C NMR (100 MHz, benzene-d_6) δ: 93.75 (s, Cp), 77.4 (b, =CH), 53.46 (s, $-CH_2-$), 38.3 (b, $=CH_2$), 34.63 (s, $-CH_2$), 22.65 (s, $-CH_2-$), 14.57 (s, CH_3), −20.9 (b, Ni-CD_3). EI-MS m/z (^{58}Ni, rel. intensity): 225 (M^+, 33%), 141 ($[CpNiCD_3]^+$, 43%), 123 ($[NiCp]^+$, 44%), 97 ($[NiC_3H_3]^+$, 9%), 84 ($[CH_2{=}CH(CH_2)_3CH_3]^+$, 51%), 69 ($[CH_2{=}CH(CH_2)_3]^+$, 43%), 66 ($[CpH]^+$, 19%), 65 ($Cp^+$, 16%), 58 ($Ni^+$, 9%), 56 ($[CH_2{=}CHCH_2CH_3]^+$, 100%).

Thermal Decomposition of $[NiCp(CD_3)(\eta^2\text{-}CH_2{=}CH(CH_2)_3CH_3)]$ (4-d_3). The sample of **4-d_3** prepared above was dissolved in cyclohexane and stirred at ambient temperature for seven days, after which time the volatiles were removed under reduced pressure. EI-MS of the crude reaction mixture showed the presence of $(NiCp)_3(\mu_3\text{-}CCD_3)$ (**3-d_3**; M^+ at m/z = 399), $(NiCp)_5(CCD_3)$ (M^+ at m/z = 645), $(NiCp)_6(\mu_6\text{-}C)$ (**1**; m/z = 750) (^{58}Ni). Column chromatography on Al_2O_3 of this residue (hexane/toluene 4:1) afforded cluster **3-d_3** (5.6% yield, two steps from nickelocene). ^{1}H NMR (400 MHz, benzene-d_6) δ: 5.15 (s, Cp). ^{2}H NMR (30.7 MHz, benzene) δ: 3.25 (s, $-CD_3$). ^{13}C NMR (125.8 MHz, benzene-d_6) δ: 289.3 (s, μ_3-C), 87.89 (s, Cp), 45.05 (septet, $-CD_3$, $^1J_{CD}$ = 19.4 Hz). EI-MS m/z (^{58}Ni, rel. intensity): 399 (M^+, 85%), 332 ([M-CpD]$^+$, 38%), 304 ($[Ni_3Cp_2]^+$, 49%), 246 ($[NiCp)_2]^+$, 15%), 188 ($[NiCp_2]^+$, 16%), 123 ($[NiCp]^+$, 13%). HRMS calcd. for $C_{17}H_{15}D_3Ni_3$: 398.96572. Found: 398.96689. The second fraction eluted with toluene consisted of a mixture of $(NiCp)_3(\mu_3\text{-}CCD_3)$ (**3-d_3**) and $(NiCp)_3(\mu_3\text{-}CH)$ (**2**).

The cluster $(NiCp)_3(\mu_3\text{-}CCD_3)$ (**3-d_3**) was also obtained from a reaction of nickelocene with methyllithium-d_3 in THF, as analogously described for methyllithium.[9]

Synthesis and Thermal Decomposition of $[NiCp(^{13}CH_3)(\eta^2\text{-}CH_2{=}CH(CH_2)_3CH_3)]$ (4-^{13}C). This complex was prepared as described above for **4** using a solution of $^{13}CH_3Li$ (obtained from 1.0 g of $^{13}CH_3I$ (7.0 mmol), 0.11 g of Li (15.7 mmol) in 7.0 mL of Et_2O), nickelocene (0.70 g, 3.70 mmol), and 1-hexene (1.50 mL, 12 mmol) in THF (20 mL) and Et_2O (20 mL). **4-^{13}C** was dissolved in THF (30 mL) and decomposed at room temperature for seven days. MS of the crude reaction mixture showed the presence of $(NiCp)_3(\mu_3\text{-}^{13}C^{13}CH_3)$ (**3-$^{13}C_2$**; M^+ at m/z = 398; calcd. for $(^{58}NiC_5H_5)_3{}^{13}C_2H_3)$, $(NiCp)_5(^{13}C^{13}CH_3)$ (M^+ at m/z = 644; calcd. for $(^{58}NiC_5H_5)_5{}^{13}C_2H_3)$, and $(NiCp)_6(\mu_6\text{-}^{13}C)$ (**1-^{13}C**; M^+ at m/z = 751; calcd. for $(^{58}NiC_5H_5)_6{}^{13}C)$.

X-Ray Crystal Structure Determination of $(NiCp)_6(\mu_6\text{-}C)$ (1). Several attempts were made to obtain crystals of X-ray quality. The first procedure was as follows: The crude solid of **1** (ca. 0.05 g) was dissolved in THF (5 mL). The solution was filtered to remove some insolubilities, and aliquots of the filtrate were placed in 5 mm NMR tubes. CH_2Cl_2 was carefully layered over the solutions (CH_2Cl_2/THF = 2:1), and the tubes were kept at −75 °C for seven days. The dark-red monoclinic crystals ($\mathbf{1}\cdot 2CH_2Cl_2$) suitable for X-ray measurements were formed at the bottom of the tubes as almost hexagonal columns. A single crystal was selected at approximately 0 °C and immediately placed on the diffractometer at −173 °C.

The second form of crystals suitable for X-ray measurements was obtained by crystallization from THF/hexanes at room temperature and the third one from THF/*n*-heptane at −75 °C. The second form (**1**) crystallizes as tetragonal needles and the third one ($\mathbf{1}\cdot 3C_4H_8O$) as long needles in a hexagonal crystal system. Discussion on the interatomic distances and angles was not possible due to a disorder in the crystals. Crystallization procedures, crystal data, and structure refinement parameters for these two forms are given in the Supporting Information. Crystallographic data for the structures reported in this paper have been deposited as supplementary publication nos. CCDC 867930, 867931, and 867932. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The crystal structure of $\mathbf{1}\cdot 2CH_2Cl_2$ (Figure S1); crystallization procedures, crystal data, and structure refinement parameters of the polymorphs **1** and $\mathbf{1}\cdot 3C_4H_8O$. CIF files of all polymorphs; EI MS spectra of the crude reaction mixture of decomposition of $[NiCp(^{13}CH_3)(\eta^2\text{-}CH_2{=}CH(CH_2)_3CH_3)]$ (**4-^{13}C**). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: anpietr@ch.pw.edu.pl.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Faculty of Chemistry of the Warsaw University of Technology for a financial support of this work.

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