

The activation of C–H bonds in terminal olefins by cyclopentadienylnickel species ¹

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Abstract

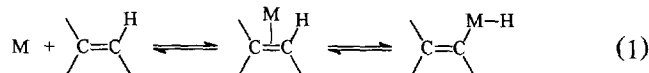
The alkylidynetrinickel clusters (NiCp)₃C(CH₂)₈CH₃ **1**, (NiCp)₃CCH₃ **2** and tetrakis(η⁵-cyclopentadienyl)dihydrotetranickel (NiCp)₄H₂ **3** were isolated from the reaction mixture of nickelocene with phenyllithium in the presence of 1-decene. (NiCp)₃C(CH₂)₄CH₃ and the clusters **2** and **3** were obtained in reaction with 1-hexene. In the presence of 2,4,4-trimethyl-1-pentene, cluster **3** was obtained as the main product of the reaction.

In the reaction with 1-decene, organic products (olefins, biphenyl, *o*-terphenyl, quaterphenyl) were identified by GC/MS analyses. The structure of **3** has been determined by X-ray diffraction and characterized by ¹H and ¹³C NMR, MS and IR. On the basis of organonickel and organic products formed, the mechanism of the sp²-hybridized C–H bond activation by cyclopentadienylnickel species has been discussed. © 1997 Elsevier Science S.A.

Keywords: C–H bond activation; Cyclopentadienylnickel clusters; Nickel

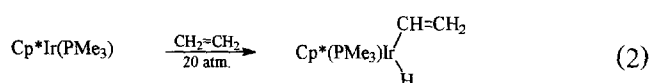
1. Introduction

Over the past few years, there has been much interest in the chemistry of coordinatively unsaturated transition metal complexes, particularly in the activation of alkyl C–H bonds by complexes of Ir, Rh, Re and W [1–4]. In the reactions of coordinatively unsaturated transition metals with alkenes and arenes, carbon–hydrogen bonds are more easily activated than sp³-hybridized C–H bonds in alkanes [5–7]. It has commonly been assumed that this is due at least partly to prior coordination of the metal to the π-electrons in the organic substrate followed by the oxidative addition step:

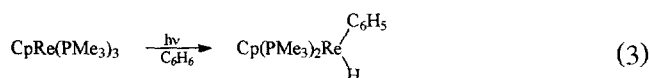


It was found that the insertion of the metal centre into the C–H bonds of alkenes occurred at temperatures

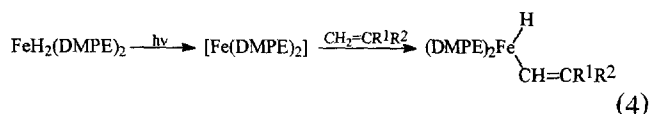
in the range 130–160 °C, leading to the formation of a stable vinyl hydride [8]:



The complex of rhenium reacts similarly with sp² C–H bonds [9] in alkenes or arenes:



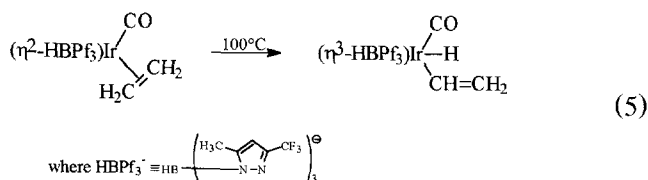
Irradiation of benzene or cyclopropane solutions of the above complex at 5–10 °C liberated trimethylphosphine and provided the products of C–H insertion. Similar results were obtained by Field and coworker [10] in the photochemically generated reaction of FeH₂(DMPE)₂ [DMPE = 1,2-bis-(dimethylphosphino)ethane] with olefins at low temperature:



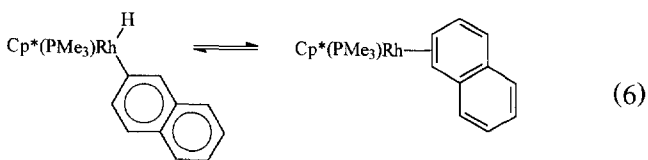
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¹ Dedicated to the memory of Professor Yuri Struchkov in recognition of his outstanding contributions to structural organometallic chemistry.

Bergman and coworkers [8,9] and Field and coworker [10] have found that the insertion of the metal centre into the sp^2 C–H bonds of alkenes or arenes occurs with concurrent, but not prior, formation of a π -complex. Graham and coworkers [11] showed that a hydridovinyliridium complex is more stable than its η^2 -ethylene isomer:



It was reasonable to assume that an η^2 -intermediate would be involved in the activation of olefinic C–H bonds by metal complexes. Jones and coworkers [12] proved the existence of an equilibrium between an η^2 -arene complex and its aryl hydride counterpart:



The above data show that the activation of sp^2 C–H bonds proceeds with coordinatively unsaturated transition metal complexes at elevated temperatures or upon irradiation.

Coordinatively and electronically unsaturated cyclopentadienylnickel complexes obtained by us in the reaction of nickelocene with phenyllithium appeared to be so reactive that they activated sp^2 C–H bonds in olefins at room temperature or even below. The hydridovinylnickel complex formed (in contrast to the hydridovinyl complexes of iridium, rhodium, rhenium) was unstable and reacted further to form trinickel clusters.

2. Results and discussion

In a preliminary communication [13] we have found that nickelocene reacts with phenyllithium in the presence of 1-decene and 1-hexene to form tris(η^5 -cyclopentadienyl)(μ_3 -alkylidyne)trinickel clusters $(\text{NiCp})_3\text{CR}$ ($\text{R} = (\text{CH}_2)_8\text{CH}_3$ and $(\text{CH}_2)_4\text{CH}_3$ respectively). In this paper we present the results of isolation and characterization of all organonickel and organic products formed in these reactions. We have also studied the reaction of nickelocene with phenyllithium and a branched olefin (2,4,4-trimethyl-1-pentene) in order to find out whether the formation of the π -complex influenced the C–H bond activation.

The reaction of nickelocene with phenyllithium and

1-decene was carried out in THF at temperatures ranging from -60°C to room temperature. Products were separated by column chromatography on alumina using hexane/toluene mixture as eluents. The following products were isolated: two trinickel clusters $(\text{NiCp})_3\text{C}(\text{CH}_2)_7\text{CH}_3$ **1** and $(\text{NiCp})_3\text{CCH}_3$ **2** [14] and the hydridotetranickel cluster $(\text{NiCp})_4\text{H}_2$ **3**. The cluster **1** was identified by means of its ^1H and ^{13}C NMR and mass spectra. The ^1H NMR spectrum of **1** shows a singlet at 5.19 ppm characteristic of cyclopentadienyl-trinickel clusters, a triplet at 0.91 ppm of CH_3 protons and signals of all CH_2 protons at 1.34 to 3.74 ppm. A signal at 284.90 ppm in the ^{13}C NMR spectrum of **1** corresponds to methylidyne carbon and a signal at 87.90 ppm is characteristic of cyclopentadienyl carbons. The signals of the remaining nine carbon atoms of the alkyl group are observed from 14.30 to 57.90 ppm. A parent ion at m/e 508 (^{58}Ni calc.) was present in the mass spectrum of **1**. The signal had an isotopic pattern characteristic of three nickel atoms. The other fragments observed were at m/e 438 ($\text{M}-\text{C}_5\text{H}_{10}$) $^+$, 370 ($\text{M}-\text{C}_{10}\text{H}_{18}$) $^+$, 304 (Ni_3Cp_2) $^+$, 246 (NiCp_2) $^+$, 188 (NiCp_2) $^+$ and 123 (NiCp) $^+$. The last four fragments observed were typical of all alkylidynetrinickel clusters.

The cluster **2** was obtained in a small amount and was identified on the basis of its ^1H , ^{13}C NMR and mass spectra. The spectra of this cluster were identical with those of the previously described cluster $(\text{NiCp})_3\text{CCH}_3$ [14].

The cluster **3** $(\text{NiCp})_4\text{H}_2$ was isolated from the reaction mixture by column chromatography on alumina (eluent hexane/THF), repeated several times. It was recrystallized from hexane/THF solution to give black-brown crystals. The crystals did not melt up to 350°C .

The formation of tetranickelhydrido clusters of the general formula $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_x$ ($x = 1$ and 3) has been reported previously [15,16]. Tetrakis(η^5 -cyclopentadienyl)tetranickel trihydride $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_3$ was isolated from the reaction of $\text{CpNi}(\text{NO})$ with AlCl_3 and LiAlH_4 [15]. Dahl and coworker obtained the same compound by treatment of a THF solution of vacuum-sublimed nickelocene with an equimolar amount of sodium naphthalenide in THF [16]. They also reported the formation of $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}$ in this reaction, but the compounds $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_x$ ($x = 1$ and 3) were not isolated [16]. Schneider et al. [17] obtained an equimolar mixture of $\text{Ni}_4(\text{tBuCp})_4\text{H}_x$ ($x = 1$ and 3) by vaporising nickel atoms into a solution of *tert*-butyl substituted cyclopentadiene. All the tetranickelhydrido clusters mentioned above were paramagnetic, making NMR characterization impossible. $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_3$ has three additional electrons, which are all unpaired [15]. The structure of $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_3$ has been determined by X-ray diffraction [18]. The compound contains a pseudo-tetrahedral Ni_4 cluster; each nickel atom is co-

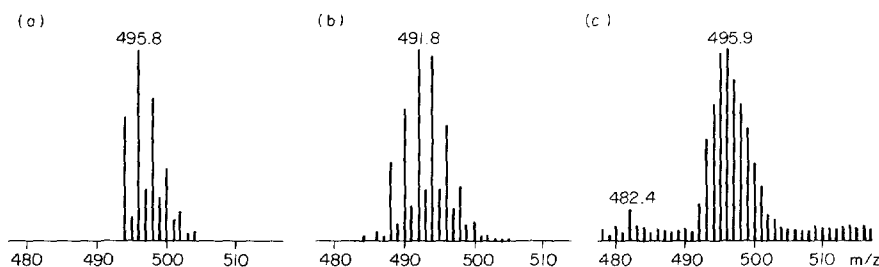


Fig. 1. Mass spectra of $(\text{NiCp})_4\text{H}_2$ at the m/e range 480–510: (a) calculated isotope pattern for $\text{C}_{20}\text{H}_{22}\text{Ni}_4$; (b) EIMS (70 eV); (c) LSIMS.

ordinated to a planar π -bonded cyclopentadienyl ring. Three of the four faces of the nickel tetrahedron are bridged by hydrogen atoms. The above structure has been confirmed by a single crystal neutron diffraction technique at low temperature [19]. The results obtained by both methods were in very good agreement with each other.

Because our compound **3** was diamagnetic, we assumed that it possessed an even number of hydrido H atoms, i.e. 2 or 4.

Two signals were observed in the ^1H NMR spectrum of this compound: a singlet of C_5H_5 protons at 5.34 ppm and a singlet of hydride protons at -19.95 ppm. Establishing the stoichiometry from the relative integrals of the Cp and H signals was not a straightforward task; the large difference in chemical shifts of these two signals requires use of a wide spectral window that results in short acquisition times and a small number of measuring points per signal. Also, the differences in proton relaxation time lead to misleading integration values. Several carefully taken experiments using relaxation delays (8–60 s) between FID registration gave a Cp to H proton ratio 20.21 ± 0.2 (expected 20:2). Prolongation of the relaxation delays above 15 s did not change the integration values. A considerable broadening of the hydride proton signal (linewidth 5 Hz, while the linewidth of the Cp proton signal was 0.65 Hz) was observed. The cause of this phenomenon has not yet been clarified. Only one signal of the Cp carbon atoms at 82.60 ppm was observed in the ^{13}C NMR spectrum of **3**.

In EIMS (70 eV) at $150\text{--}170^\circ\text{C}$ a group of peaks at m/e 488–504 was present. These peaks were a result of overlapping of the parent ion at m/e 494 (^{58}Ni calc.) and of at least three other fragments at m/e 492 $(\text{NiCp})_4^+$, 490 $[(\text{NiCp})_4 - 2\text{H}]^+$ and 488 $[(\text{NiCp})_4 - 4\text{H}]^+$. Because the parent ion was of low intensity and the computer simulation did not give satisfactory results, a spectrum using the LSIMS(+) technique was recorded (*m*-nitrobenzyl alcohol was used as matrix). An intensive parent ion at m/e 495($\text{M} + \text{H}$) $^+$ and its fragments was observed (Fig. 1).

The IR spectrum of **3** (in polyethylene foil) showed the following absorption bands: 1260, 1000, 940, 805, 770 cm^{-1} . The lack of an absorption band of $\nu_{\text{Ni-H}}$ at

around 1100 cm^{-1} did not mean the absence of an Ni–H bond [17,20].

The crystal structure of **3** was determined by X-ray diffraction. The solving of the structure was based on the assumption that the molecule possessed two hydrogen atoms. The smaller volume of the unit cell ($3720.6(14)\text{ \AA}^3$) compared with the unit cell of $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_3$ [19] ($3832(6)\text{ \AA}^3$) gave additional evidence that the number of hydrogen atoms is 2. A very good agreement of the unit cell parameters of compound **3** with those of $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_3$ [19], and the same space group, led to the assumption that both compounds were isomorphic, and therefore solving the structure of **3**, the atomic coordinates were taken from Ref. [19]. Good refinement of structural parameters proved that it was a good model and led to the value $R_1 = 0.0409$. To determine which of the three hydrogen atoms, fixed initially in the molecule, was not present, the positional parameters and thermal factors of H(1), H(2) and H(3) atoms were unlocked. After several refinement cycles by means of full-matrix least-squares, it appeared that the positional parameters and thermal factors changed the most for the H(2) atom, which led to the conclusion that this atom should be removed from the molecule. The crystallographic basis for the hydride

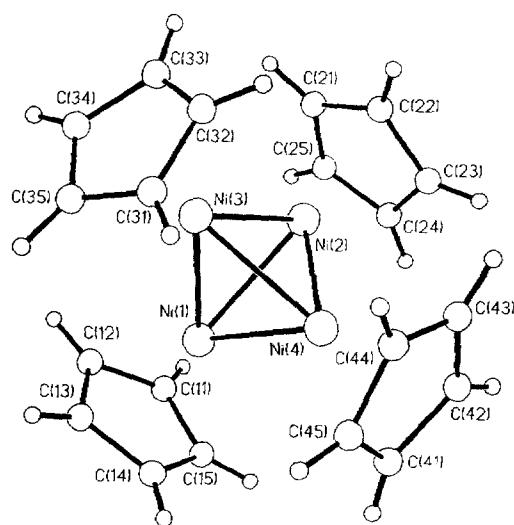


Fig. 2. A perspective view of an $(\text{NiCp})_4\text{H}_2$ molecule showing the atom numbering system.

H atom positions is very weak, and whilst consistent with the solution evidence it cannot be taken as corroborating it. Selected bond lengths and angles are listed in Tables 3 and 4 and are compared with those values for $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_3$ [19]. Fig. 2 shows a perspective view of the molecule, including the atom numbering system. Although the crystal structure of **3** is very similar to the structure of $\text{Ni}_4\text{Cp}_4\text{H}_3$ [19], there are considerable differences observed in bond lengths and angles (Tables 3 and 4), indicating that these are two different compounds.

The cluster **3** has been formed in several reactions of nickelocene with organolithium and magnesium compounds [21]. The hydrogen elimination from an organic ligand leads to the formation of unstable $\{\text{CpNiH}\}$ species. This species reacts further to form the cluster **3**.

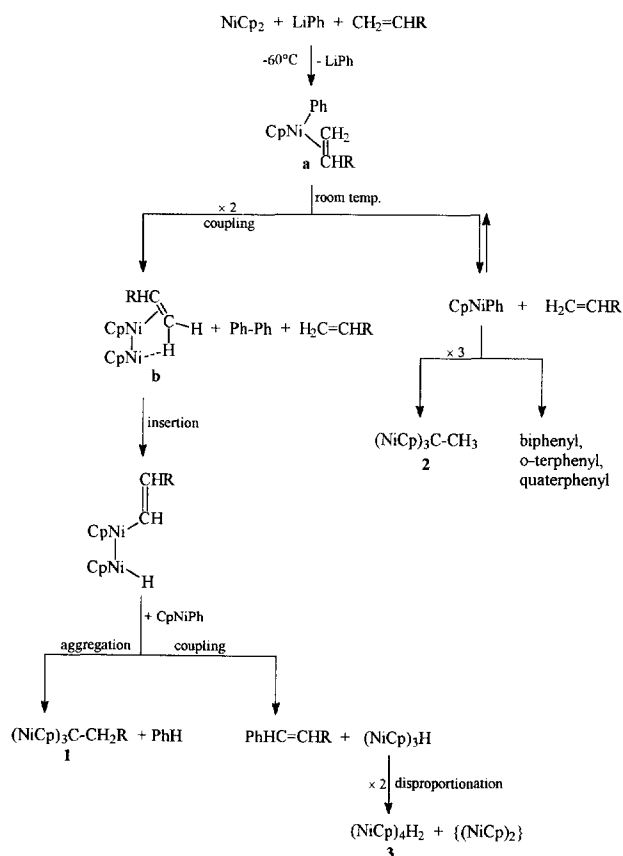
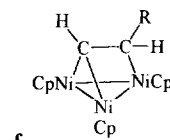
Besides the nickel clusters we have also identified biphenyl, *o*-terphenyl, 1,1':2',1'':2'',1''':2'''-quaterphenyl, 2-phenyldecane, 1-phenyl-1-decene (two isomers), 1,2-diphenyl-1-decene (two isomers), 1,1,2-triphenyl-1-decene and other not fully characterized olefins. These products were detected by means of GC/MS analyses.

It was also found that analogous products were formed in the reaction of nickelocene with phenyllithium in the presence of 1-hexene: $(\text{NiCp})_3\text{C}(\text{CH}_2)_4\text{CH}_3$ and the clusters **2** and **3**.

Keil and coworkers [22,23] have found that at low temperature (-60 to -80°C) nickelocene and phenyllithium in the presence of ethylene form a complex $\text{CpNiPh}(\eta^2\text{-CH}_2\text{CH}_2)$, which at elevated temperature (-10°C) undergoes an insertion reaction to form the unstable species $\{\text{CpNi-CH}_2\text{-CH}_2\text{-Ph}\}$. Therefore it can be assumed that in our studies of the reaction of nickelocene with phenyllithium in the presence of an excess of the liquid olefins (1-decene and 1-hexene) carried out at -60°C , a π -complex **a** stable under these conditions is formed (Scheme 1).

At room temperature the complex **a** can partially dissociate and exist in an equilibrium with $\{\text{CpNiPh}\}$ and the free olefin. We have previously shown that the unstable 16-electron species $\{\text{CpNiPh}\}$ undergoes a facile coupling reaction to form biphenyl and nickel clusters [24].

The complex **a** can also undergo coupling of phenyl groups before dissociation of the olefin to form the complex **b**. The activation of sp^2 C–H bonds in the coordinated olefin is caused by the presence of a coordinatively and electronically unsaturated dinickel centre. The insertion of the dinickel centre into the C–H bond of the olefin proceeds in the complex **b**. The unstable nickel hydride reacts with $\{\text{CpNiPh}\}$ to form a trinickel intermediate cluster **c** and benzene.

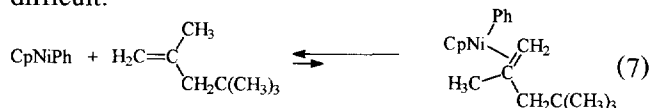


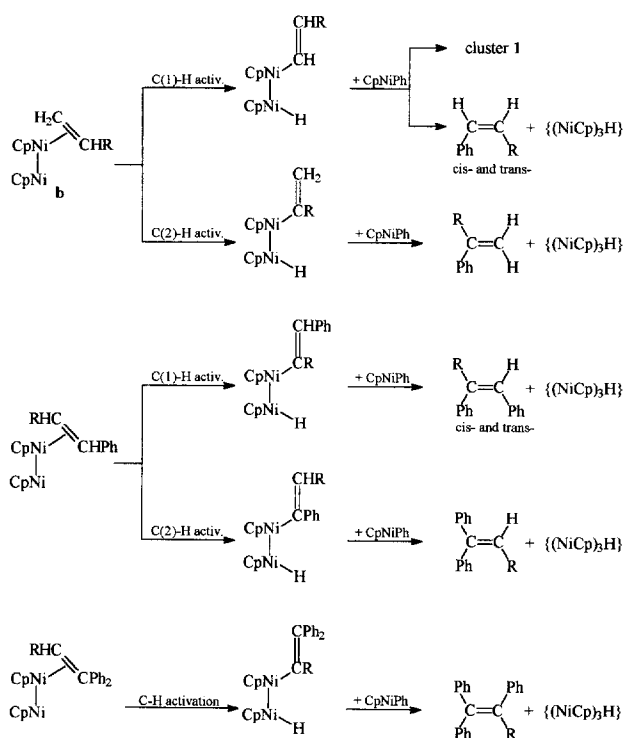
Scheme 1.

The hydrogen transfer from α - to β -carbon atom with the mediated role of nickel atoms proceeds in this cluster, resulting in the formation of the stable alkylidyne-trinickel cluster **1**.

The mechanism of the formation of the cluster **2** is still not clear, and is under investigation.

The major product of the reaction of nickelocene with phenyllithium in the presence of 2,4,4-trimethyl-1-pentene was the cluster **3** $(\text{NiCp})_4\text{H}_2$. Traces of the trinickel clusters $(\text{NiCp})_3\text{CCH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$ and $(\text{NiCp})_3\text{CCH}_3$ were also detected. Another product was the dinickel complex $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$, described previously [25,26]. The different course of the reaction with 2,4,4-trimethyl-1-pentene (the branched olefin) than with the unbranched ones can be explained by steric hindrance, making the formation of the π -complex with nickel and therefore C–H activation in the olefin more difficult:

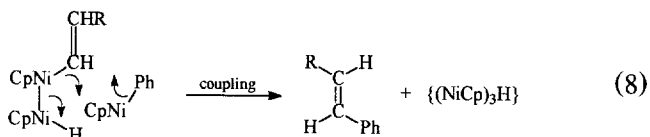




Scheme 2.

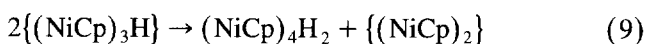
Further reactions of unstable $\{\text{CpNiPh}\}$ led to the formation of clusters **3** and coupling products. The phenyl ring coupling products, i.e. biphenyl, *o*-terphenyl, quaterphenyl and so on, have previously been described by us as β -H elimination products [24].

We have also found that olefins are formed in the reaction of nickelocene with phenyllithium in the presence of 1-decene, besides the nickel clusters, biphenyl and other phenyl ring coupling products. Five of these olefins were characterized by means of GC/MS analysis. Their formation can be explained by the possibility of the occurrence of the coupling reaction:



The olefin formed (1-phenyl-1-decene) can coordinate to $(\text{NiCp})_2$. This complex, after the transfer of a hydrogen atom, can react with $\{\text{CpNiPh}\}$ to form a new olefin (1,2-diphenyl-1-decene, two isomers). The reaction proceeds further with the formation of 1,1,2-triphenyl-1-decene (Scheme 2).

The unstable cluster $\{(\text{NiCp})_3\text{H}\}$ disproportionates to form the cluster **3** and $(\text{NiCp})_2$:



3. Conclusions

Electronically and coordinatively unsaturated nickel atoms in $\{(\text{NiCp})_2\}$ species formed in the reactions of nickelocene with phenyllithium in the presence of terminal olefins activate sp^2 C–H bonds of olefins at room temperature or lower. As a result of dinickel centre insertion into C–H bonds, the trinickel cluster $(\text{NiCp})_3\text{CCH}_2\text{R}$ and tetranickel cluster $(\text{NiCp})_4\text{H}_2$ are formed.

In contrast to the previously described paramagnetic tetranickelhydrido clusters possessing one and three hydride atoms in the molecule, the diamagnetic tetranickel cluster with two hydride atoms is easily formed in the reaction of nickelocene with organolithium or magnesium compounds.

4. Experimental details

All reactions were carried out under an atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. The olefins used were commercial products. Phenyllithium solutions were prepared from bromobenzene and lithium in THF by a standard procedure. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 and Varian Gemini instruments. Mass spectra were recorded on an AMD-604 mass spectrometer. GC/MS analyses were performed on a Hewlett Packard 5971 Series Mass Selective Detector with a HP 35 column (30 m $\times$ 0.25 mm). The reported yields of crude products (i.e. after the first column chromatography) were based on the starting amount of nickelocene.

4.1. Reaction of nickelocene with phenyllithium in the presence of 1-decene

A solution of NiCp_2 (0.65 g, 3.44 mmol) and 1-decene (1.3 cm³, 6.89 mmol) in 50 cm³ of THF was cooled to -60°C , then a solution of phenyllithium in THF (14 cm³, 3.50 mmol) was added during 1 h (The temperature was maintained from -60 to -50°C). The mixture was stirred at this temperature for the next hour, then allowed to warm slowly to room temperature (2 h). Stirring was continued overnight. The solution was concentrated to 10 cm³ (benzene was detected by GC in the distillate), then 40 cm³ of hexane was added; the products were hydrolysed with 40 cm³ of deoxygenated water. The organic layer was separated and dried, the solvents were evaporated, the residue was redissolved in toluene and chromatographed on Al_2O_3 (35 $\times$ 2 cm, deactivated with 5% water) using hexane and hexane/toluene mixtures as eluents. Organic products

eluted with hexane before the first organometallic band were collected and subjected to GC/MS analyses; the following compounds (selected) were identified: biphenyl, *o*-terphenyl, 1,1':2'',1''':2''',1''''-quaterphenyl, 2-phenyldecane (spectra in agreement with DATABASE \NBS75K.L), 1-phenyl-1-decene (two isomers). EIMS (70 eV) *m/e* (rel. int.) 216 (M^+ , 35%), 117 (64%), 104 (100%), 91 (47%); 216 (M^+ , 55%), 117 (100%), 104 (99%), 91 (35%); 1,2-diphenyl-1-decene (two isomers) 292 (M^+ , 13%), 193 (10%), 179 (100%), 165 (37%), 152 (9%); 292 (M^+ , 13%), 193 (8%), 179 (100%), 165 (22%), 152 (4%); 1,1,2-triphenyl-1-decene 368 (M^+ , 40%), 255 (100%), 241 (39%), 165 (11%); other isomers with molecular formula $C_{16}H_{24}$ and $C_{22}H_{28}$ were also detected but they cannot be identified unambiguously, only on the basis of mass spectra.

Small amounts of $NiCp_2$ (hexane/toluene 9:1) were then eluted. A brown-red band was collected (hexane/toluene 1:1), evaporated to dryness, redissolved in hexane and purified by additional column chromatography (hexane/THF 95:5) to yield a brown-

Table 1

Data collection and structure analysis parameters

Empirical formula	$C_{20}H_{22}Ni_4$
Crystal size (mm ³)	$0.25 \times 0.30 \times 0.45$
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions:	$a = 28.005(6) \text{ \AA}$ $b = 9.151(2) \text{ \AA}$ $c = 14.901(3) \text{ \AA}$ $\beta = 103.02(3)^\circ$
Volume ($\text{\AA}^3$)	3720.6(14)
Z	8
Formula weight	497.22
Density (calc.) (g cm ⁻³)	1.775
Temperature (K)	293(2)
Absorption coefficient (cm ⁻¹)	39.80
$F(000)$	2032
Radiation	Mo K α ($\lambda = 0.71069 \text{ \AA}$, graphite monochromator)
2 θ Range for data collection	4.70 to 48.10°
Scan type	$\omega-2\theta$
Index ranges	$-0 \leq h \leq 31$, $-0 \leq k \leq 10$, $-16 \leq l \leq 16$
Reflections collected	3006
Independent reflections	2940 [$R_i = 0.0371$]
Observed reflections	1756 ($I > 3.5\sigma(I)$)
No. of parameters refined	218
Goodness-of-fit on F^2	1.060
Final R indices [$I > 3.5(I)$]	$R_1 = \sum(F_o - F_c)/\sum(F_o)$ $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$
Weighting scheme	$R_1 = 0.0409$ $wR_2 = 0.1017$ $w^{-1} = [\sigma^2(F_o^2) + (0.0886P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.00063(12)
Largest difference peak and hole (e $\text{\AA}^{-3}$)	0.615 and -0.631

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Ni(1)	0.13849(3)	0.47119(9)	0.03132(6)	0.0456(3)
Ni(2)	0.08114(3)	0.31066(10)	0.08156(6)	0.0518(3)
Ni(3)	0.11051(3)	0.25203(9)	-0.05226(6)	0.0458(3)
Ni(4)	0.16438(3)	0.23775(9)	0.09690(6)	0.0467(3)
C(11)	0.1295(3)	0.6935(9)	0.0577(8)	0.079(3)
C(12)	0.1259(4)	0.6746(9)	-0.0357(7)	0.080(3)
C(13)	0.1721(4)	0.6156(9)	-0.0440(7)	0.082(3)
C(14)	0.2013(3)	0.5995(10)	0.0420(8)	0.088(3)
C(15)	0.1755(4)	0.6475(10)	0.1053(7)	0.087(3)
C(21)	0.0066(5)	0.2815(39)	0.0621(16)	0.210(15)
C(22)	0.0306(8)	0.1616(21)	0.1056(19)	0.178(8)
C(23)	0.0584(5)	0.2093(18)	0.1892(10)	0.114(5)
C(24)	0.0519(6)	0.3521(17)	0.1971(9)	0.131(5)
C(25)	0.0195(7)	0.3921(23)	0.1204(15)	0.172(10)
C(31)	0.1376(7)	0.1092(25)	-0.1341(11)	0.157(8)
C(32)	0.0951(9)	0.0538(12)	-0.1156(9)	0.138(7)
C(33)	0.0583(5)	0.1368(15)	-0.1511(8)	0.110(4)
C(34)	0.0748(5)	0.2478(12)	-0.1942(6)	0.101(4)
C(35)	0.1240(6)	0.2312(18)	-0.1835(7)	0.112(5)
C(41)	0.2324(3)	0.2434(10)	0.1924(7)	0.090(3)
C(42)	0.1964(4)	0.1672(11)	0.2321(6)	0.081(3)
C(43)	0.1816(3)	0.0481(10)	0.1787(6)	0.077(2)
C(44)	0.2071(3)	0.0430(9)	0.1116(6)	0.075(2)
C(45)	0.2374(3)	0.1616(11)	0.1182(7)	0.074(2)

$$U_{eq}^* = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$$

red solid; $(NiCp)_3C(CH_2)_8CH_3$ (yield ca. 10%). 1H NMR (C_6D_6): δ [ppm] 5.19 (s, 15H, Cp), 3.74 (t, 2H, $J = 7.7$ Hz), 2.18 (m, 2H, $J = 7.5$ Hz), 1.70 (m, 2H, $J = 7.7$ Hz), 1.54–1.34 (unresolved multiplet, 10H), 0.91 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR (C_6D_6): δ [ppm] 284.90 (C methylidyne), 87.90 (Cp), 57.90, 36.05, 32.31, 30.47, 30.23, 30.21, 29.83, 23.08 (CH_2), 14.30 (CH_3). EIMS (70 eV) *m/e* (rel. int.) (^{58}Ni) 508 (M^+ , 74%), 438 (81%), 370 (76%), 304 (91%), 246 (50%), 188 (28%), 123 (10%). The cluster $(NiCp)_3CCH_3$ [14] was present in this sample in a small amount.

The next brown fraction was also collected (hexane/toluene 1:1) and evaporated to dryness to yield a black solid; small crystals were obtained from hexane/THF solution; $(NiCp)_4H_2$ (yield ca. 10%). No melting observed up to $350^\circ C$. 1H NMR (C_6D_6): δ [ppm] 5.34 (s, Cp), -19.95 (s, H). ^{13}C NMR (C_6D_6): δ [ppm] 82.60 (d, $^1J_{C-H} = 174$ Hz, Cp). IR (neat, polyethylene foil) ν [cm^{-1}]: 1260, 1000, 940, 805, 770, 670. EIMS (70 eV) *m/e* (rel. int.) M^+ overlapped with fragments appearing at 488–504 where 494 (99%), 492 (100%) and 490 (70%); 428 (42%) and 426 (61%) overlapped with 424 (52%); 374 (16%), 306 (18%), 246 (15%), 188 (39%), 123 (24%). LSIMS(+) (*m*-nitrobenzyl alcohol) *m/e* ($M + H$) $^+$ (^{58}Ni) 495 overlapped with M^+ , ($M - H$) $^+$, ($M - 2H$) $^+$.

4.2. Reaction of nickelocene with phenyllithium in the presence of 1-hexene

The reaction was carried out as the previous one, using a solution of NiCp_2 (1.37 g, 7.25 mmol) and 1-hexene (2.0 cm^3 , 16 mmol) in 100 cm^3 of THF and a solution of phenyllithium in THF (33 cm^3 , 7.26 mmol). A brown-red fraction consisting of two clusters (ca. 4:1) was collected; $(\text{NiCp})_3\text{C}(\text{CH}_2)_4\text{CH}_3$ (main product): ^1H NMR (C_6D_6): δ [ppm] 5.17 (s, 15H, Cp), 3.69 (t, 2H, $J = 8.3 \text{ Hz}$), 2.13 (m, 2H, $J = 8.78 \text{ Hz}$), 1.63 (m, 2H, $J = 7.5 \text{ Hz}$), 1.48 (m, 2H, $J = 7.4 \text{ Hz}$), 1.02 (t, 3H, $J = 7.2 \text{ Hz}$); ^{13}C NMR (C_6D_6): δ [ppm] 295.57 (C methylidyne), 87.88 (Cp), 57.79, 35.64, 32.55, 23.13 (CH_2), 14.41 (CH_3). $(\text{NiCp})_3\text{CCH}_3$ (side product): ^1H NMR (C_6D_6): δ [ppm] 5.15 (s, 15H, Cp), 3.71 (s, 3H, CH_3). ^{13}C NMR (C_6D_6): δ [ppm] C methylidyne not observed, 88.01 (Cp), 46.01 (CH_3) [14]. EIMS (70 eV) mixture, m/e (rel. int.) (^{58}Ni) 452 (M^+ , 3%), 396 (M^+ , 65%), 330 (76%), 304 (95%), 246 (32%), 188 (26%), 123 (14%). The cluster $(\text{NiCp})_4\text{H}_2$ was also formed in this reaction. The organic products were not identified.

Table 3
Selected interatomic distances (Å) in $(\text{NiCp})_4\text{H}_2$ (this work) and $(\text{NiCp})_4\text{H}_3$ determined by X-ray [18] and neutron [19] diffractions *

	Compound		
	$(\text{NiCp})_4\text{H}_2$ 3	$(\text{NiCp})_4\text{H}_3$ [18]	$(\text{NiCp})_4\text{H}_3$ [19]
Ni(1)–Ni(2)	2.417(1)	2.459(3)	2.490(3)
Ni(1)–Ni(3)	2.397(1)	2.469(3)	2.464(3)
Ni(1)–Ni(4)	2.393(1)	2.484(3)	2.478(3)
Ni(2)–Ni(3)	2.383(1)	2.469(3)	2.458(3)
Ni(2)–Ni(4)	2.386(1)	2.451(3)	2.454(3)
Ni(3)–Ni(4)	2.392(1)	2.454(3)	2.471(3)
Ni(1)–C(11)	2.098(8)	2.17(2)	2.145(5)
Ni(1)–C(12)	2.105(8)	2.14(2)	2.134(5)
Ni(1)–C(13)	2.091(8)	2.13(2)	2.125(5)
Ni(1)–C(14)	2.090(8)	2.15(2)	2.134(5)
Ni(1)–C(15)	2.092(8)	2.14(2)	2.140(5)
Ni(2)–C(21)	2.059(12)	2.12(2)	2.112(6)
Ni(2)–C(22)	2.054(12)	2.15(2)	2.098(6)
Ni(2)–C(23)	2.073(10)	2.16(2)	2.139(4)
Ni(2)–C(24)	2.102(11)	2.11(2)	2.155(5)
Ni(2)–C(25)	2.078(12)	2.14(2)	2.147(5)
Ni(3)–C(31)	2.047(11)	2.08(2)	2.080(5)
Ni(3)–C(32)	2.045(10)	2.07(2)	2.083(6)
Ni(3)–C(33)	2.110(9)	2.17(2)	2.138(5)
Ni(3)–C(34)	2.126(9)	2.18(2)	2.156(4)
Ni(3)–C(35)	2.081(9)	2.13(2)	2.123(4)
Ni(4)–C(41)	2.105(8)	2.05(2)	2.139(5)
Ni(4)–C(42)	2.113(8)	2.12(2)	2.136(4)
Ni(4)–C(43)	2.113(8)	2.07(2)	2.148(5)
Ni(4)–C(44)	2.131(8)	2.16(2)	2.160(5)
Ni(4)–C(45)	2.115(7)	2.12(2)	2.145(6)

* Estimated standard deviations in parentheses.

Table 4

Selected bond angles ($^\circ$) in $(\text{NiCp})_4\text{H}_2$ (this work) and $(\text{NiCp})_4\text{H}_3$ determined by X-ray [18] and neutron [19] diffraction *

	Compound		
	$(\text{NiCp})_4\text{H}_2$ 3	$(\text{NiCp})_4\text{H}_3$ [18]	$(\text{NiCp})_4\text{H}_3$ [19]
Ni(4)–Ni(1)–Ni(3)	59.9(1)	59.4(1)	60.0(1)
Ni(4)–Ni(1)–Ni(2)	59.5(1)	59.5(1)	59.2(1)
Ni(3)–Ni(1)–Ni(2)	59.4(1)	60.1(1)	59.5(1)
Ni(3)–Ni(2)–Ni(4)	60.2(1)	59.8(1)	60.4(1)
Ni(3)–Ni(2)–Ni(1)	59.9(1)	60.2(1)	59.7(1)
Ni(4)–Ni(2)–Ni(1)	59.8(1)	60.8(1)	60.2(1)
Ni(2)–Ni(3)–Ni(4)	60.0(1)	59.7(1)	59.7(1)
Ni(2)–Ni(3)–Ni(1)	60.7(1)	59.7(1)	60.8(1)
Ni(4)–Ni(3)–Ni(1)	59.9(1)	60.6(1)	60.3(1)
Ni(2)–Ni(4)–Ni(3)	59.8(1)	60.5(1)	59.9(1)
Ni(2)–Ni(4)–Ni(1)	60.8(1)	59.8(1)	60.7(1)
Ni(3)–Ni(4)–Ni(1)	60.1(1)	60.0(1)	59.7(1)

4.3. Reaction of nickelocene with phenyllithium in the presence of 2,4,4-trimethyl-1-pentene

The reaction was carried out similarly, from a solution of NiCp_2 (0.85 g, 4.50 mmol) and 2,4,4-trimethyl-1-pentene (1.65 cm^3 , 10.4 mmol) in 65 cm^3 of THF and a solution of phenyllithium in THF (10.5 cm^3 , 4.93 mmol). The following compounds were obtained.

– Organic products: biphenyl, *o*-terphenyl, 1,1':2',1'':2'',1''':quaterphenyl (spectra in agreement with DATABASE \ NBS75K.L), 1-phenyl-2,4,4-trimethyl-1-pentene (two isomers). EIMS (70 eV) m/e (rel. int.) 188 (M^+ , 47%), 131 (54%), 117 (56%), 97 (70%), 91 (50%), 57 (100%), major isomer presumably *trans* 188 (M^+ , 7%), 131 (100%), 117 (10%), 91 (18%), 57 (21%), minor isomer presumably *cis*.

– $(\text{NiCp})_2(\mu\text{-C}_5\text{H}_6)$ (trace). EIMS (70 eV) m/e (rel. int.) 312 (M^+ , 14%), 246 (61%), 188 (100%), 123 (32%), 58 (9%) [25,26].

– $(\text{NiCp})_3\text{CCH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$ (trace). EIMS (70 eV) m/e (rel. int.) (^{58}Ni) 480 (M^+ , 55%), 414 (37%), 356 (34%), 330 (43%), 304 (96%), 246 (52%), 188 (39%), 123 (21%), 71 (35%), 57 (54%). ^1H NMR (C_6D_6): δ [ppm] (partial spectrum) 5.17 (s, 15H, Cp), 1.06 (s, 9H, $\text{C}(\text{CH}_3)_3$).

– $(\text{NiCp})_4\text{H}_2$ (yield 20%).

When this reaction was repeated using 5:1 molar excess of the olefin, similar results were obtained (i.e. only traces of the trinickel cluster were formed).

4.4. Crystal structure determination of $(\text{NiCp})_4\text{H}_2$

The measurements were carried out at room temperature with the crystal placed in a glass capillary. Preliminary Weissenberg photography showed the crystal system and approximate unit cell dimensions. All measure-

ments were carried out on a Kuma KM-4 computer-controlled κ -axis diffractometer with graphite monochromated Mo K α radiation. The intensity stability was monitored by measurement of three standards every 100 reflections. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data collection and structure analysis parameters are given in Table 1, fractional atomic coordinates in Table 2. Selected bond lengths and angles are listed in Tables 3 and 4. The structure was refined by full-matrix least-squares method using SHELXL-93 [27] with anisotropic thermal parameters for non-H atoms. The hydrogen atoms were put in calculated positions and introduced as fixed contributors in the final stage of refinement. Scattering factors were those incorporated in SHELXL-93. Hydrogen atom coordinates, anisotropic displacement parameters, and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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