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Reactions of biscyclopentadienylnickel with lithium and magnesium aryls

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Abstract

The reaction of nickelocene with phenyllithium, *ortho*-, *meta*- and *para*-methylphenylmagnesium bromide, and 2-((dimethylamino)methyl)phenyllithium are studied. It was found that unstable compounds $\{CpNiC_6H_4R\}$ (R = H, *o*-, *m*-, *p*-CH_3) are formed in those reactions. For R = $CH_2N(CH_3)_2$, a stable compound, $CpNiC_6H_4CH_2N(CH_3)_2$, is formed due to intramolecular coordination. In other cases, mainly coupling reactions occur and biphenyl, bitolyl and higher coupling products are formed. Compound $\{CpNiC_6H_4R\}$ is also formed as a product of thermal decomposition of $Cp\{\eta^2\text{-}C_2H_4)NiC_6H_4R$. It reacts further to form the same products as above. The mechanism of the coupling reactions is proposed and discussed.

Introduction

Reactions of $NiCp_2$ with lithium alkyls: benzyl- [1], neopentyl- and trimethylsilylmethyl- [2] have been previously described. We have studied reactions of $NiCp_2$ with methyl-, ethyl- and n-propyllithium [3–5].

If unstable alkylcyclopentadienylnickel compounds formed in reaction 1 do not possess β-hydrogen atoms, then they undergo decomposition to form alkyl coupling products (eq. 2), trinickel clusters and corresponding alkanes (eq. 3)

$$NiCp_2 + RCH_2Li \rightarrow \{CpNiCH_2R\} + LiCp \qquad (1)$$

$$2\{CpNiCH_2R\} \rightarrow \frac{2}{n}(NiCp)_n + RCH_2\text{–}CH_2R \qquad (2)$$

$$3\{CpNiCH_2R\} \rightarrow (CpNi)_3CR + 2CH_3R \qquad (3)$$

$R = C_6H_5, CMe_3, SiMe_3$

For example, ethane, as a coupling product, and tris(η^5-cyclopentadienyl) (μ_3-alkylidyne)trinickel cluster, $(NiCp)_3C\text{–}CH_3$, are formed in the reaction of $NiCp_2$ with methyllithium [3].

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If a β-hydrogen atom is present in an alkyl group of alkyllithium compound, then alkene (eq. 4) and alkane (eq. 5) are formed in the reaction with $NiCp_2$.

$$\{CpNiCH_2CH_2R\} \rightarrow \{CpNiH\} + H_2C{=}CHR \qquad (4)$$

$$\{CpNiCH_2CH_2R\} + \{CpNiH\} \rightarrow \frac{2}{n}(NiCp)_n + CH_3{-}CH_2R \qquad (5)$$

The purpose of this work was to study the reactions of nickelocene with lithium and magnesium aryls. Aryl derivatives were chosen as they did not possess α-hydrogens and possessed non-typical β-hydrogen atoms.

Results

The reactions of nickelocene with phenyllithium, *ortho*-, *meta*- and *para*-methylphenylmagnesium bromide, and *ortho*-(dimethylaminomethyl)phenyllithium were studied (eq. 6).

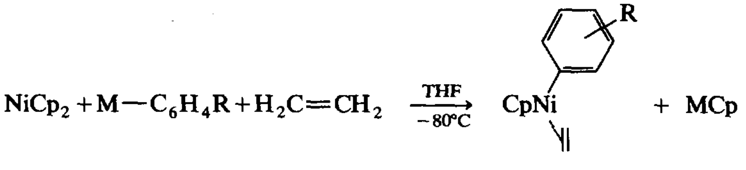
$$NiCp_2 + M{-}C_6H_4R \rightarrow \{CpNiC_6H_4R\} + MCp \qquad (6)$$

$R = H$, o-, m-, p-CH_3, o-$CH_2N(CH_3)_2$

$M = Li$, $MgBr$

The reactions were carried out at low temperature from −40°C to −20°C or at room temperature using THF, diethyl ether, hexane or their mixtures as solvents. Reaction products were then separated by chromatography on neutral alumina at room temperature or were hydrolyzed (alcoholyedyzed) prior to chromatographic separation.

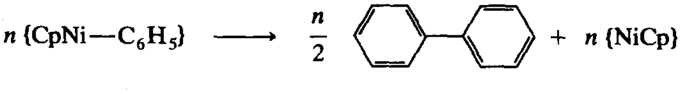
Cyclopentadienyl derivatives of lithium or magnesium formed in reaction 6 make isolation and identification of other products difficult. To avoid those difficulties we synthesized aryl(η^5-cyclopentadienyl)(η^2-ethene)nickel complexes (eq. 7). These complexes, stable below −20°C [6], were thermally decomposed by heating to room temperature, forming unstable $\{CpNiC_6H_4R\}$ without solid byproducts (eq. 8)



(7)

$$CpNi(\eta^2\text{-}H_2C{=}CH_2)C_6H_4R \xrightarrow[-80°C\text{ to room temperature}]{\Delta t} \{CpNi{-}C_6H_4R\} + H_2C{=}CH_2 \qquad (8)$$

$NiCp_2$ reacts with phenyllithium or phenylmagnesium bromide in THF within the temperature range −40°C to room temperature to give biphenyl as a main product and a mixture of cyclopentadienylnickel clusters $(NiCp)_n$ (eqs. 6, 9, 10)



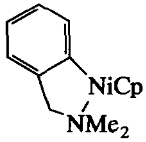
(9)

$$n\,\{NiCp\} \longrightarrow (NiCp)_6 + (NiCp)_4 + NiCp_2 + Ni \qquad (10)$$

An unstable product, {CpNi-C_6H_4R}, is formed in the reaction of $NiCp_2$ with *ortho-*, *meta-* and *para-*methylphenyllithium or magnesium bromide.

This product is identical to that formed during thermal decomposition of the corresponding ethylene complexes (eq. 8). The unstable compound, {CpNi–C_6H_4R}, reacts further to form bitolyl as a main product and a mixture of cyclopentadienylnickel compounds. The presence of a tri-nickel cluster (CpNi–$C_6H_4R)_3$ in the mixture was proved by means of ^1H and ^{13}C NMR and mass spectra.

If a dimethylaminomethyl group, Me_2NCH_2, is present in the ortho position as R in {CpNi–C_6H_4R}, then a stable 18-electron intramolecular coordination complex is formed.



This complex was isolated as brownish-green crystals (m.p. 95°C dec.) and fully characterized.

Discussion

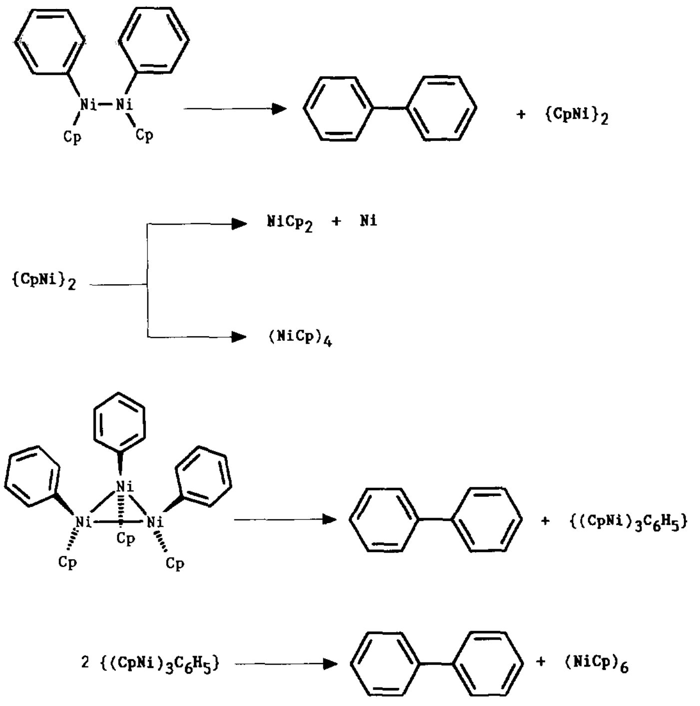
It was found previously [5] that in the reaction of $NiCp_2$ with alkyllithium or magnesium compounds, α-hydrogen elimination with the formation of a corresponding alkane R–CH_3 and tri-nickel cluster $(CpNi)_3C$–R, is the main reaction pathway, if a β-hydrogen atom is not present in an alkyl group (eq. 3). Coupling of the alkyl groups is another possible reaction pathway (eq. 2). The latter, however, seems to be a minor one as in the reaction of $NiCp_2$ with methyllithium, the molar ratio of methane (product of an α-hydrogen elimination reaction) to ethane (product of coupling of alkyl groups) is 7:1 [5].

If a β-hydrogen atom is present in an alkyl group of lithium or magnesium compounds, then they react with $NiCp_2$ to form unstable {CpNiR} species. These species then undergo β-hydrogen elimination. If $R = C_2H_5$ or C_3H_7, then the product of decomposition of {CpNiR} species are an equimolar mixture of the corresponding alkane and alkene, $(CpNi)_n$ clusters [5] where $n = 6$ and 4, $NiCp_2$ and metallic nickel (eqs. 11, 10)

$$2\{CpNiC_2H_5\} \rightarrow C_2H_6 + C_2H_4 + 2\{NiCp\} \qquad (11)$$

The unstable compound {$CpNiC_6H_5$} (formed in the reaction of $NiCp_2$ with phenyllithium or phenylmagnesium bromide (eq. 6) or as a product of the thermal decomposition of phenyl(η^5-cyclopentadienyl) (η^2-ethene)nickel complex (eq. 8) does not possess an α-hydrogen atom and a β-hydrogen in the aromatic ring does not eliminate so easily like the β-hydrogen in an alkyl group. The lack of possibilities of α- and β-hydrogen elimination means that the main decomposition pathway of {$CpNiC_6H_5$} species is the coupling of phenyl groups to form biphenyl (eq. 9) and the formation of $(NiCp)_6$, $(NiCp)_4$ clusters, $NiCp_2$ and metallic nickel (eq. 10).

The unstable 16-electron compound, {$CpNiC_6H_5$}, probably forms di- or/and tri-nickel aggregates (Scheme 1) (the tri-nickel aggregate, where the nickel atom has 18 electrons, should be much more stable than the di-nickel one). Two or three



Scheme 1.

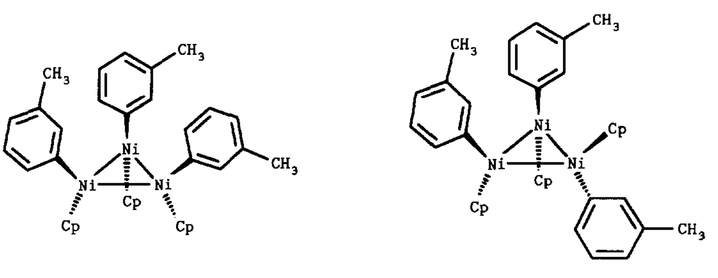
phenyl groups in aggregates could be positioned in unexpectedly close proximity to each other, resulting in interaction between the groups which would not take place if they were further apart. Coupling reactions can proceed via homolytic scission of the Ni–C bonds. It seems possible that homolytic cleavage generates short-lived radicals (to be distinguished from free radicals) which react with each other to form biphenyl.

The presence of tri-nickel aggregates $(CpNiC_6H_4CH_3)_3$ in the products of the reaction of $NiCp_2$ with *ortho*- and *para*-methylphenyllithium was proved by means of ^1H, ^{13}C NMR mass spectra. Those aggregates were not isolated in pure state because of their slow decomposition to bitolyl and $(CpNi)_n$ clusters. The tri-nickel cluster, $(CpNiC_6H_4CH_3)_3$, can exist in a form of two isomers **2c** and **2t** (Fig. 1). The ^1H NMR spectrum of this cluster shows the chemical shifts of aromatic protons at δ 7.35–7.00 ppm, C_5H_5 at 5.11 ppm and *m*-CH_3 at 2.33 and 2.25 ppm (integration ratio: found, 3.8 : 4.6 : 3.2; calc., 4 : 5 : 3).

The ^{13}C NMR spectrum shows two signals of C_5H_5 carbons at 88.56 and 88.38 ppm, two signals of CH_3 carbons at 21.78 and 21.73 ppm and six signals of aromatic carbons at 144.6, 138.4, 131.1, 127.2, 126.8, 124.4 ppm.

The presence of two signals of Cp carbon atoms in ^{13}C NMR, and two signals of the *m*-CH_3 group in ^1H NMR (integration ratio 2 : 1) and in ^{13}C NMR confirms the existence of the two isomers **2c** and **2t** (Fig. 1).

The mass spectrum of $(CpNiC_6H_4CH_3)_3$ shows a parent peak at *m/e* 642 (^{58}Ni) and the natural abundance of the ^{58}Ni and ^{60}Ni isotopes indicates the presence of three nickel atoms in the molecule. Fragmentation of this cluster gives



2c 2t

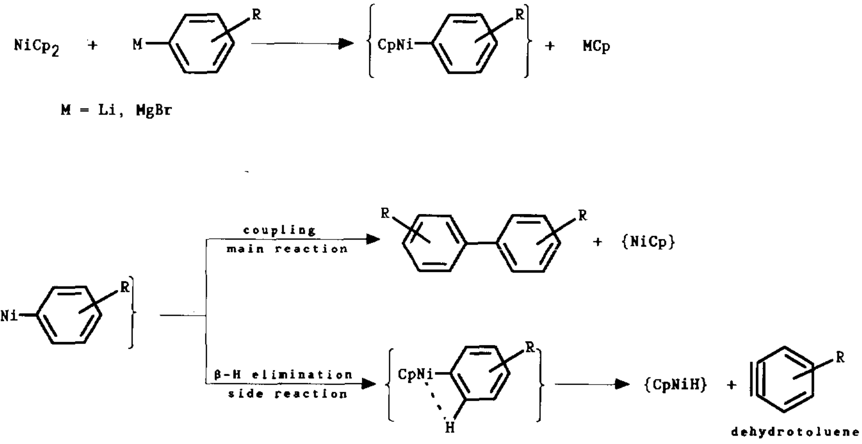
Fig. 1. Isomeric forms of the $(CpNiC_6H_4CH_3)_3$ cluster.

an ion $[(NiCp)_3(C_6H_4CH_3)_2]^+$ m/e 551. Other peaks present in the spectrum are bis(m-tolyl)$^+$ m/e 182 and fragments of $(NiCp)_n$ clusters: $[(NiCp)_6]^+$ m/e 738; $[Ni_5Cp_4]^+$ m/e 552; $[(NiCp)_4]^+$ m/e 494; $[Ni_4Cp_3]^+$ m/e 426; $[Ni_3Cp_2]^+$ m/e 306; $[(NiCp)_2]^+$ m/e 246; $[NiCp_2]^+$ m/e 188; $[NiCp]^+$ m/e 123; $[Ni]^+$ m/e 58.

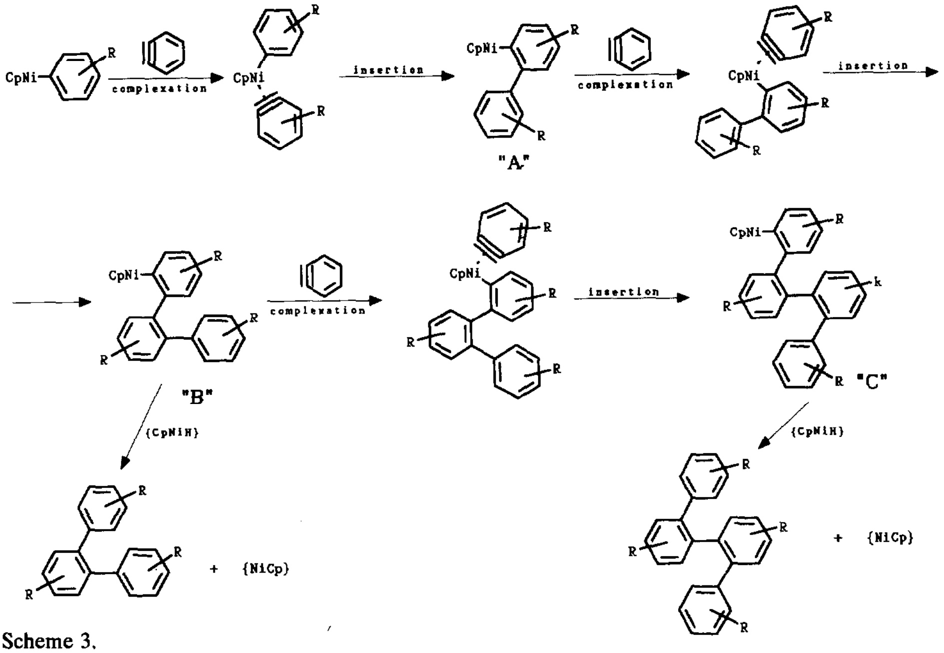
The above data are consistent with the proposition of the course of the coupling reaction shown in Scheme 1 and the formation of $(NiCp)_6$ and $(NiCp)_4$ clusters.

^1H, ^{13}C NMR and mass spectra show that besides $(CpNiC_6H_4CH_3)_3$, other tri-nickel clusters are also present in the products of the reaction of $NiCp_2$ with $M-C_6H_4CH_3$. Among them tris(η^5-cyclopentadienyl) (μ_3-metylidyne) tri-nickel cluster, $(CpNi)_3C-CH_3$, is formed in highest yield. It has not been isolated but its presence was proved by means of ^1H, ^{13}C NMR and mass spectra: ^1H NMR (toluene-d_8, 311 K): δ 5.19 (s, Cp, 15H); 3.67 (s, CH_3, 3H) ^{13}C NMR (THF-d_8, 311 K): δ 289.9 (s, μ_3C), 88.2 (d, Cp), 45.9 (q, CH_3). MS (70 eV, 100°C): M^+ m/e (^{58}Ni) 396. We cannot explain at present how the above cluster is formed.

In the reactions of $NiCp_2$ with o-, m- and p-methylphenyllithium, corresponding bitolyls were isolated and identified. MS (70 eV, 50–60°C): m/e 182 $[(CH_3C_6H_4)_2]^+$. The presence of coupling products of more than two tolyl groups was also detected in the reaction mixture by means of mass spectra: m/e 272 $[(CH_3C_6H_4)_2C_6H_3CH_3]^+$; m/e 362 $[(CH_3C_6H_3)_2(CH_3C_6H_4)_2]^+$.



Scheme 2.

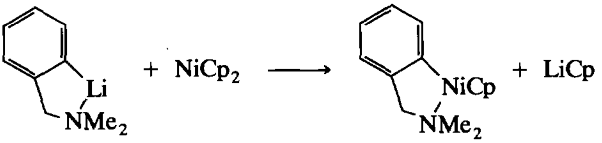


Scheme 3.

The coupling of aryl radicals is the main reaction pathway of the decomposition of $\{CpNiC_6H_4R\}$ (Scheme 2). To explain the formation of higher coupling products, we assumed that β-hydrogen elimination with the formation of dehydrotoluene could occur (Scheme 2).

A complex formation between dehydrotoluene and unstable $\{CpNiC_6H_4R\}$ species followed by an insertion reaction (Scheme 3) leads to the formation of a mixture of the higher coupling products. The same products can be formed in a cross-coupling reaction between A, B, C (Scheme 3) species and $\{CpNiC_6H_4R\}$ (Scheme 4). In all of the above cases, $(NiCp)_6$, $(NiCp)_4$ clusters, $NiCp_2$ and metallic nickel are formed in addition to organic products.

ortho-(Dimethylaminomethyl)phenyllithium reacts with $NiCp_2$ in a similar way as phenyl- and tolyllithium, but the possibility of an intramolecular complexation of nickel atom leads to the formation of a stable 18-electron cyclometallated compound (eq. 12)

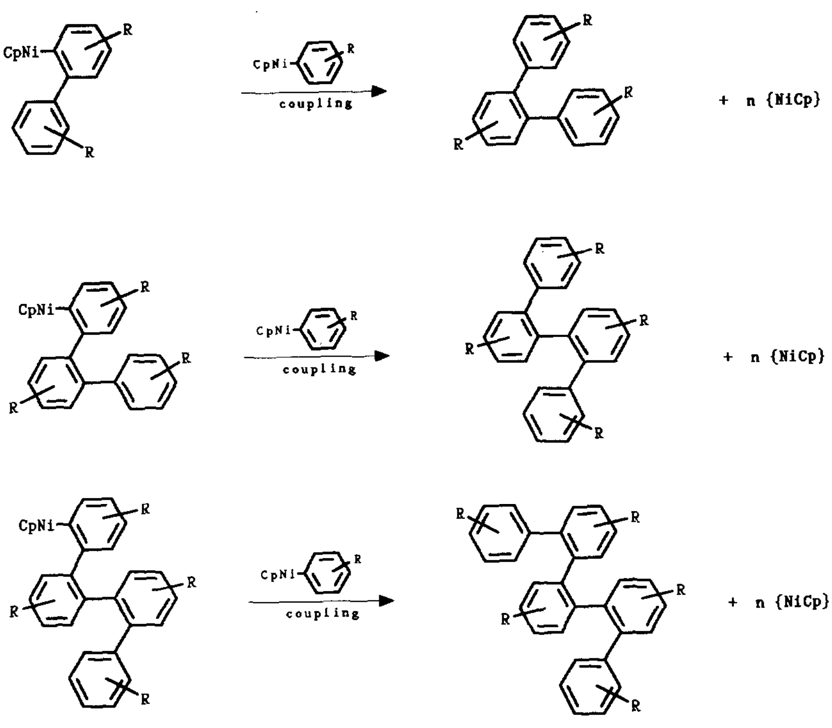


(12)

(2-((Dimethylamino)methyl)phenyl) (η^5-cyclopentadienyl)nickel does not undergo coupling or β-hydrogen elimination reactions up to 95°C.

Experimental

All reactions were carried under argon by standard Schlenk technique. Solvents were dried and distilled under argon prior to use.



Scheme 4.

Reaction of $NiCp_2$ with MC_6H_5 (M = Li, MgBr)

A solution of $NiCp_2$ (1.41 g, 7.52 mmol) in THF was added dropwise to LiC_6H_5 (0.79 g, 9.4 mmol) placed in a Schlenk tube at −60°C. The colour of the reaction mixture changed from green to dark red. The mixture was stirred for 1 h and then warmed up to room temperature. The colour changed again to brown. The mixture was then filtered and the solvent was evaporated from the filtrate under reduced pressure. A black-grey greasy solid (1.03 g) was obtained. It was dissolved in a small amount of THF and chromatographed on neutral alumina using hexane as an eluent. No separation was observed. Part of the product was hydrolyzed with 20 cm^3 of water and the organic layer was separated. After evaporation of the solvent, the product was distilled at 90°C under vacuum with an oil pump. Biphenyl was identified as a product. ^1H NMR: δ 7.60 (m, *o*-H, 4H), 7.40 (m, *m*-H, 4H), 72.9 (m, *p*-H, 2H). MS: M^+ m/e 154. Similar results were obtained in the reaction of $NiCp_2$ with C_6H_5MgCl.

Synthesis of aryl(η^5-cyclopentadienyl)(η^2-ethene)nickel

A solution of 10–20 mmol of Cp_2Ni in 120 cm^3 of THF was saturated with ethylene at −78°C. A solution of aryllithium in diethyl ether (10% excess according to Cp_2Ni) was added dropwise to the above solution at −78°C. The reaction mixture was stirred at −50°C for 48 h. Solvents were distilled off at −78°C, 10^{-4} Torr. Diethyl ether (150 cm^3), cooled to −78°C, was added, the mixture was stirred at that temperature for a few hours. Insoluble LiCp was removed by filtration and the solvent was distilled off from the filtrate under reduced pressure. Pentane (200 cm^3) was added and the mixture was stirred for a further few hours. The remaining solid was again separated by filtration and the solvent was distilled off on a high vacuum line. Aryl (η^5-cyclopentadienyl) (η^2-ethene)nickel complexes were obtained by this method in 15–30% yield.

Synthesis of (η^5-cyclopentadienyl)(η^2-ethene)(3-methyl-phenyl)nickel

($3-CH_3C_6H_4$) ($\eta^2-H_2C{=}CH_2$)NiCp (0.6 g, 2.5 mmol, 18%) as a brownish-red solid was obtained by the method described above using 2.6 g (13.8 mmol) of $NiCp_2$ and 14 mmol of 3-methylphenyllithium. ^1H NMR (THF-d_8, 193 K): δ 5.38 (s, Cp, 15H), 3.88 (s, CH_2, 2H), 2.86 (s, CH_2, 2H), 6.6–7.0 (m, C_6H_4, 4H), 2.10 (s, *m*-CH_3, 3H).

Thermal decomposition of (η^5-cyclopentadienyl)(η^2-ethene)(3-methylphenyl)nickel

($3-CH_3C_6H_4$) ($\eta^2-H_2C{=}CH_2$)NiCp (1.2 g, 4.96 mmol) was placed in a Schlenk tube and slowly warmed up from −50°C to room temperature. The product of the thermal decomposition was a dark red solid which was dissolved in 5 cm^3 of hexane and chromatographed on neutral alumina (3×45 cm^2 column) using hexane as an eluent. Three fractions were collected.

Fraction I (light pink): A white, slightly pink coloured solid was obtained after evaporation of the solvent. It was sublimed at 150°C under reduced pressure giving 3,3′-dimethylbiphenyl as a white solid. ^1H NMR (THF-d_8, room temperature) δ 7.46–7.0 (H-aromatic); 2.33 (s, CH_3, 3H). MS: M^+ m/e 182 ($C_{14}H_{14}$), 272 ($C_{21}H_{20}$), 362 ($C_{28}H_{26}$).

Fraction II (green): Green crystals of $NiCp_2$ were obtained as a result of the sublimation of the green solid left after evaporation of the solvent. MS: M^+ m/e 188 (^{58}Ni).

The third fraction was eluted with hexane/THF (4 : 1). A brown solid obtained after evaporation of the solvents was identified as [CpNi(*m*-$CH_3C_6H_4$)]$_3$. ^1H NMR (THF-d_4, room temperature) δ 5.11 (s, Cp, 5H); 2.33 (d, CH_3, 3H); 2.25 (d, CH_3, 3H), 7.35–7.0 (m, H-aromatic, 4H). ^{13}C NMR (THF-d_4, 311 K): δ 144.6, 138.4, 131.1, 126.8, 124.4, 115.8 (C-aromatic); 88.6 (d, JC,H = 174 Hz, C_5H_5); 88.4 (d, JC,H = 174 Hz, C_5H_5); 21.8 (q, JC,H = 126 Hz, CH_3); 21.7 (q, JC,H = 126 Hz, CH_3).

Reaction of $NiCp_2$ with 4-methylphenylmagnesium bromide

A solution of *p*-$CH_3C_6H_4MgBr$ (7 mmol) in diethyl ether was added dropwise to a solution of 1.16 g $NiCp_2$ (6.2 mmol) cooled to 0°C in 50 cm^3 of THF. The colour of the reaction mixture changed from green to black-brown immediately. After stirring at 0°C for 2 h, the mixture was warmed up to room temperature, then cooled down again to 0°C and 10 cm^3 of C_2H_5OH was added. Hexane (50 cm^3) was added to separate the layers. The black-red upper layer was separated and solvents were distilled off under reduced pressure. A red-grey solid (0.48 g) was obtained. The product was chromatographed on neutral alumina (3×40 cm^2 column) using hexane/C_2H_5OH (9 : 1) as eluent. The first fraction contained mainly *p*-bitolyl. ^1H NMR (THF-d_8, room temperature): δ 7.46 (d, *ortho*-H aromatic, 4H); 7.18 (d, *meta*-H aromatic, 4H); 2.33 (s, *p*-CH_3, 6H). MS: M^+ m/e

182. Higher coupling products were also present in this fraction. MS: M^+ m/e 272 ($C_{21}H_{20}$); M^+ m/e 362 ($C_{28}H_{27}$).

The second fraction contained $NiCp_2$. MS: m^+ m/e 188. The third red-black fraction contained mainly $[CpNi(p\text{-}CH_3C_6H_4)]_3$. ^1H NMR (THF-d_8, room temperature) δ 7.0–7.46 (m, H-aromatic); 5.11 (s, C_5H_5); 2.25 (s, p-CH_3), 2.33 (s, p-CH_3). MS (70 eV, 180°C): M^+ m/e 642 (^{58}Ni).

Reaction of $NiCp_2$ with 2-((dimethylamino)methyl)phenyllithium

$2\text{-}(CH_3)_2NCH_2C_6H_4Li$ (0.85 g, 6 mmol) was added to a solution of 1.03 g (5.48 mmol) of $NiCp_2$ in 20 cm^3 of THF. The reaction mixture was stirred at room temperature for 2 h, then reduced in volume to about 5 cm^3 and chromatographed on neutral alumina (4 × 15 cm^2 column) using hexane as eluent. The first green fraction contained $NiCp_2$. MS: M^+ m/e 188 (^{58}Ni).

A brown-green solid was obtained after evaporation of the solvent from the second fraction, and was recrystallized from hexane. Brown-green crystals of $2\text{-}(CH_3)_2NCH_2C_6H_4NiCp$ (0.75 g, 2.9 mmol, 53% yield) were obtained; m.p. 92°C (dec.).

Anal. Found: C, 64.72; N, 5.36; H, 6.70. $C_{14}H_{18}NNi$ calc.: C, 65.17; N, 5.42; H, 6.64%. ^1H NMR ($CDCl_3$, room temperature): δ 6.86 (m, H-aromatic, 4H); 5.20 (s, C_5H_5, 5H); 3.61 (s, CH_2, 2H); 2.50 (s, CH_3, 6H).

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