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Transition metal complexes

VIII *. An unusual rearrangement of a butadienyl ligand via cyclometallation **

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Abstract

$Cp^*Ni(\eta^1,\eta^2\text{-}C_4HPh_4)$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) was prepared by reacting $Cp^*Ni(acac)$ with 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl and its structure determined by X-ray diffraction. Thermolysis of **1** in THF affords $Cp^*Ni(\eta^3$-1-benzyl-2,3-diphenylindenyl) (**2**) and $Cp^*Ni(\eta^3$-3-benzylyl-1,2-diphenylindene) (**3**). The structures of **2** and **3** were also determined by X-ray diffraction. A proposed mechanism of product formation is discussed.

Zusammenfassung

$Cp^*Ni(\eta^1,\eta^2\text{-}C_4HPh_4)$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) wurde aus $Cp^*Ni(acac)$ und 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl hergestellt und röntgenographisch charakterisiert. Die Thermolyse von **1** in THF lieferte $Cp^*Ni(\eta^3$-1-benzyl-2,3-diphenylindenyl) (**2**) und $Cp^*Ni(\eta^3$-3-benzylyl-1,2-diphenylinden) (**3**), deren Strukturen ebenfalls durch Einkristallstrukturanalysen bestimmt wurden. Für die Bildung von **2** wird ein Mechanismus vorgeschlagen.

1. Introduction

C–H bond activation by soluble metal complexes is well documented in the chemical literature, although even now the exact mechanisms involved are not well understood [2]. Cyclometallation represents a special case of C–H bond activation in which the activated C–H bond is attached to a ligand coordinated to the metal. Insertion of the metal into the C–H bond results in the formation of a metallacycle. Cyclometallations of aryl-containing ligands with N-, P-, As-, O-, or S-donating groups are well known and have been widely investigated [3]. In contrast, the cyclometallation of σ-C-bonded ligands is still relatively rare. We report here the rearrangement of a 1,2,3,4-tetraphenylbutadienyl ligand to an indenyl ligand via cyclometallation.

2. Results and discussion

The reactions described in this paper were discovered while attempting to prepare hydrocarbon-bridged transition metal complexes of the ferrol and fly-over type [4]. These complexes are thought to be intermediates in the cyclotri- and -tetramerization of alkynes [5]. We chose 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl as a suitable precursor for complexes of this type since Hoberg *et al.* [6] were able to obtain the bridging allyl complex shown in (1) from the reaction of nickel(II) bromide with 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl.

Thus $Cp^*Ni(acac)$ was reacted with 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl in ether at −40°C and allowed to warm up to room temperature (eqn. (2)). A brown compound **1** was isolated after chromatography. No dinuclear complex was obtained, and **1** was isolated in absence of moisture and by using superdry solvents. The analytical data suggested that **1** is a mononuclear complex in which one lithium atom is substituted by a

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* For Part VII, see ref. [1].

** Dedicated to Prof. Dr. h.c. mult. E.O. Fischer on the occasion of his 75th birthday.

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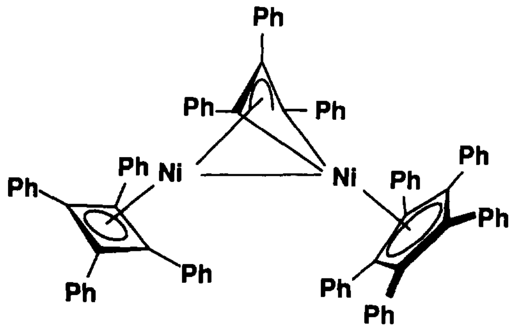


(1)

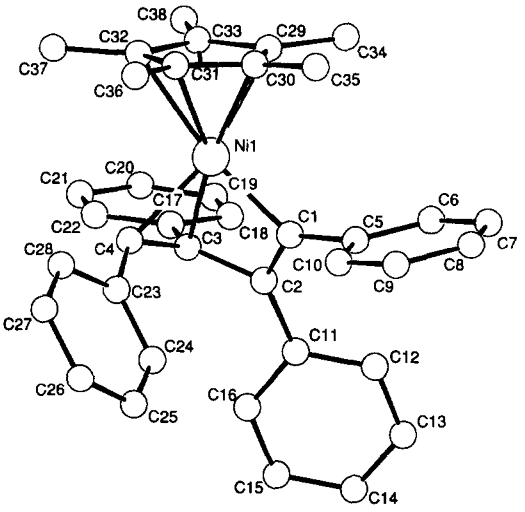
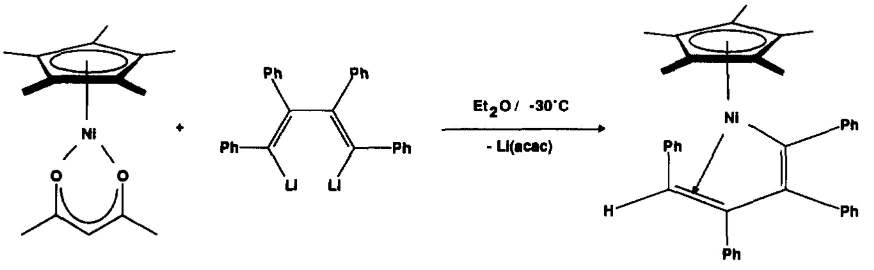


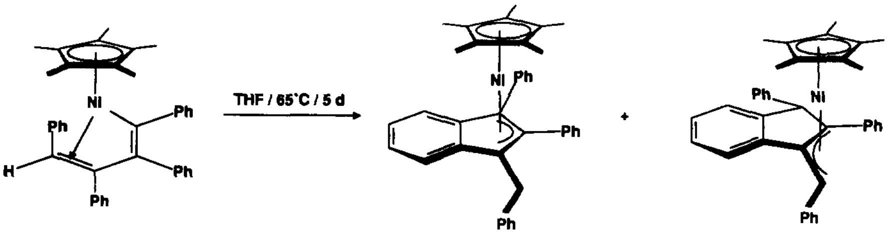
Fig. 1. Molecular structure of 1. Selected distances (Å) and angles (°) (average): Ni1–C1 1.923(9); Ni1 ··· C2 2.492(8); Ni1–C3 2.041(8); Ni1–C4 2.038(9); C1–C2 1.335(11); C2–C3 1.508(12); C3–C4 1.407(13); C1–C5 1.469(11); C2–C11 1.479(11); C3–C17 1.491(14); C4–C23 1.480(12); Ni1–C1–C2 98.2(6); C1–C2–C3 104.6(7); C2–C3–Ni1 87.9(5).

Cp*Ni-moiety and the other by a hydrogen atom, the source of which is not yet known. The results of the crystal structure analysis of 1 are summarized in Fig. 1 and reveal an η^1,η^2-C_4HPh_4 ligand bonded to one Cp*Ni-unit. There are two independent molecules in the asymmetric unit, but they differ only slightly in the conformation of the phenyl groups. 1 contains a coordinated (C3=C4) as well as an uncoordinated (C1=C2) olefinic C=C double bond. The uncoordinated double bond restrains the atoms Ni1, C1, C2, C3, C5 and C11 to coplanarity (RMS deviation = 0.06 Å) and as a result the phenyl group C11–C16 points away from the nickel atom. The coordinated double bond shows *trans* arrangement of the phenyl groups in contrast to 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl, where the phenyl groups are positioned in a *cis* configuration relative to the double bond. C4 carries an additional hydrogen atom and the C3–C4 bond has isomerized. *Cis / trans* isomerizations are well known [7] and it would appear that the *trans* isomer is thermodynami-



(2)

1



(3)

1 2 3

cally more favoured. The phenyl rings are twisted out of the planes of the butadiene double bonds and this can be attributed to steric causes. The steric shielding of the metal by the phenyl groups may also be the reason why no dinuclear complex was obtained in this reaction.

Complexes of the type CpNi(alkene)alkyl are known to undergo insertion of alkenes or alkynes into the Ni–C σ-bond [8] so similar reactions were attempted with **1**. Reaction of **1** with excess diphenylethyne or acetonitrile under vigorous conditions does, however, not result in insertion, but rather leads to a rearrangement of the butadienyl ligand and two products were isolated (eqn. (3)). Indeed, the same reaction occurs when **1** is refluxed in THF in the absence of any other reagent. **2**, a red solid, and **3**, a green solid were obtained according to ^{1}H-NMR in the ratio of 3:2 in quantitative yield. The crystal structures of **2** and **3** are shown in Figs. 2 and 3, respectively. **2** and **3** are isomers of **1**.

In **2** an indenyl moiety is coordinated to the nickel atom in an η^3-fashion. The Ni atom thus attains an 18e$^-$ configuration. The interatomic distances between Ni and C4 or C9 are, at 2.561(5) and 2.565(5) Å, much too large for direct Ni–C bonds. The C–C bond distances in the five-membered ring also rule out an η^5-coordination of the indenyl ligand to the metal and the C3–C4 and the C1–C9 distances are 0.4 Å longer than the C1–C2 and C2–C3 distances. The five-membered ring is not planar, but folded by 13° along the C1 ··· C3 axis. The projection of the metal atom onto the five-membered ring of the indenyl ligand deviates by 0.674 Å from the geometrical centre towards C2. This Δ-value [9] also supports the formulation of an η^3-coordination of the indenyl ligand. However, ^{1}H- and ^{13}C-NMR spectra show the presence of small amounts of a paramagnetic species, indicating some η^5-coordination in solution. This paramagnetic character results in line broadening of the nuclei in the vicinity of the spin carrying metal atom. It could be ruled out that the line broadening resulted from paramagnetic impurities since a mixture of **2** and **3** only shows broad lines for signals of **2**.

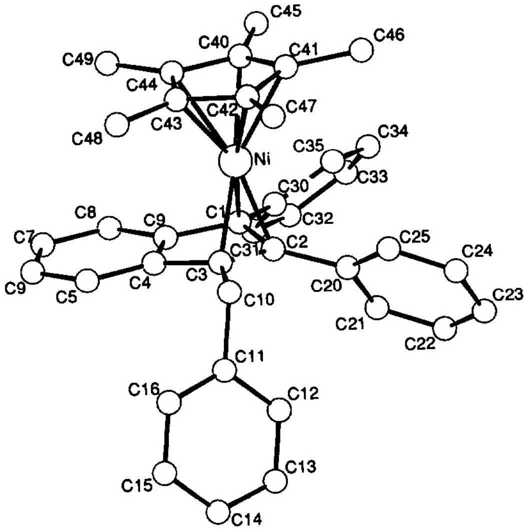


Fig. 2. Molecular structure of **2**. Selected distances (Å) and angles (°): Ni–C1 2.074(4); Ni–C2 1.942(4); Ni–C3 2.048(4); Ni ··· C4 2.561(5); Ni ··· C9 2.565(5); C1–C2 1.442(6); C2–C3 1.428(6); C3–C4 1.472(6); C4–C9 1.414(6); C1–C9 1.472(6); C1–C30 1.480(6); C2–C20 1.490(6); C3–C10 1.509(6); C10–C11 1.542(7); C1–C2–C3 106.4(4); C3–C10–C11 114.1(4).

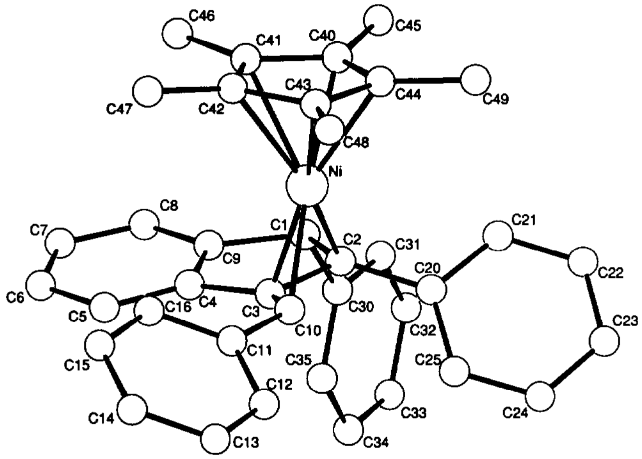


Fig. 3. Molecular structure of **3**. Selected distances (Å) and angles (°): Ni–C2 2.033(2); Ni–C3 1.935(2); Ni ··· C4 2.852(2); C1–C2 1.540(3); C2–C3 1.446(3); C3–C4 1.484(3); C4–C9 1.396(3); C1–C9 1.515(3); C1–C30 1.518(3); C2–C20 1.488(3); C3–C10 1.420(3); C10–C11 1.486(3); C1–C2–C3 108.6(2); C2–C3–C10 115.7(2); C3–C10–C11 128.6(2).

The structure of **3** is shown in Fig. 3. **3** contains a benzylylindene ligand η^3-coordinated to a Cp*Ni unit. C1 carries a hydrogen atom in a position endo to the metal atom. The nickel atom is attached to the ligand at C2, C3 and C10. The bond distances C2–C3 and C3–C10 are typical for an allyl group η^3-bonded to a transition metal and similar to the comparable C1–C2 and C2–C3 distances in **2**. C10 carries a *syn*-hydrogen atom. The phenyl ring attached to the side chain is situated in the thermodynamically favoured anti position of the allyl group. It appears that during the formation of **3** from **1** isomerization of the allyl group has occurred.

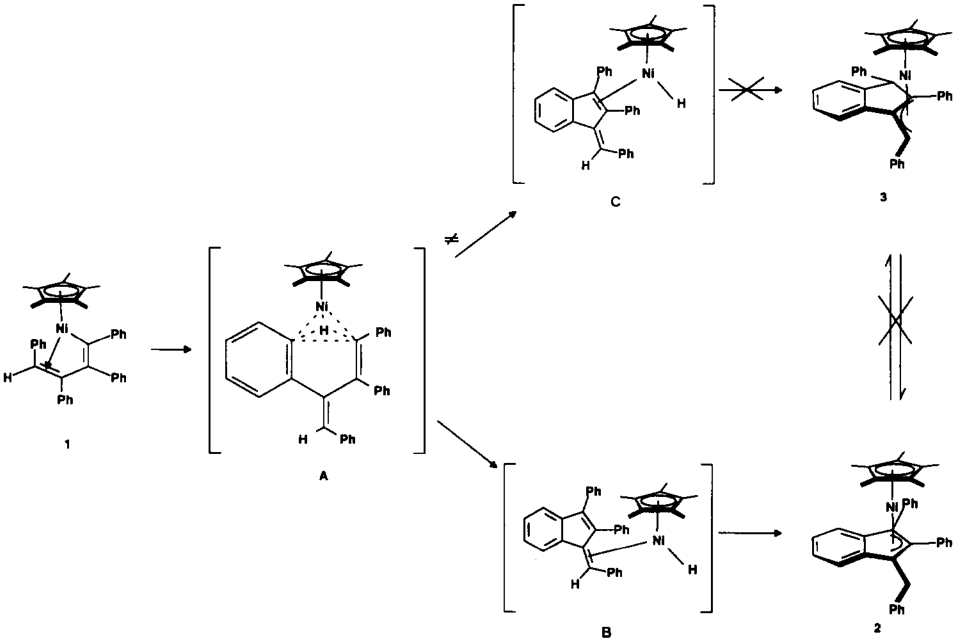
As both **2** and **3** contain asymmetric ligands, it is possible to gain some information about the mechanism of formation of **2** and **3** from **1** by inspection of the stereochemistry. C–H activation reactions are already known for the CpNi moiety, and bis(cyclopentadienyl)nickel is able to activate the C–H bonds of azobenzene to give the phenylazo nickel complex, cyclopentadienyl[2-(phenylazo)phenyl]nickel [10]. The first step in the thermolysis of **1** is therefore probably the loss of the C=C double bond (C3, C4) from the nickel atom, followed by rotation around the neighbouring C–C single bond of the butadienyl ligand. This allows the phenyl group to take up a position suitable for coordination of the metal atom to the C–H bond of the phenyl group [3,11]. Subsequent H-migration with simultanous formation of a new C–C bond could then lead to two products, depending on where the hydrogen is transferred to. Thus the reaction might take place via the transition state **A** (see Scheme 1).

It is not obvious why the insertion of nickel into the C–H bond takes place selectively at the phenyl group attached to C3 of the butadienyl ligand. Certainly, the phenyl ring is able to rotate about the C–C single bond, and computer modelling shows that the *ortho* H atom on the phenyl group attached to C3 can approach the metal closely. The thermodynamically favoured five-membered transition complex involving the phenyl group attached to C2 [12] cannot be formed, because the phenyl group is held far from the reactive nickel centre by the sterically rigid double bond C1–C2. Insertion of the metal atom into the C–H bond of the phenyl group at C4 is possible but is less favoured on entropy grounds [13]. Hydrogen transfer to the metal results in a Cp*NiH moiety which can be coordinated to one of the two olefinic double bonds (Scheme 1, top and bottom). One would expect that coordination to the exocyclic double bond (**B**) should be thermodynamically favoured over the endocyclic one (**C**), which is more highly substituted. The subsequent insertion of the coordinated double bond into the Ni–H bond in **B** results in the observed complex **2**. How **3** may be formed is more difficult to ascertain since an isomerization of the allyl group [14] generated from **C** would result in the atom H1 in **3** being exo to the Ni atom and this is not observed. If the mechanism given in Scheme 1 is correct, isomerization must have occurred before formation of **A**. In any case, the different stability of the hydride intermediates correlates with the final product yields.

In conclusion, it is worth noting that the conversion of **2** to **3** and *vice versa* requires the same Ni mediated 1,4 hydrogen transfer that is probably necessary for the formation of **2** and **3** from **1**. Thermolysis of **2** or **3** does not, however, result in their interconversion, so the C–C bond formation appears to be the driving force in the thermolysis of **1**.

3. Experimental section

All reactions were carried out under argon and in oxygen- and moisture-free solvents. 1,4-Dilithium-1,2,3,4-tetraphenylbutadiendiyl [15] and Cp*Ni(acac) [16] were prepared by literature methods. ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker WM 400 FT, AC 200 or AM 200 instruments. The mass spectra



Scheme 1.

TABLE 1. Crystallographic and data collection parameters for **1–3**

	1	**2**	**3**
formula	$C_{38}H_{36}Ni$	$C_{38}H_{36}Ni$	$C_{38}H_{36}Ni$
mol wt	551.4	551.4	551.4
crystal size, mm	0.39 × 0.28 × 0.28	0.38 × 0.38 × 0.17	0.11 × 0.35 × 0.42
a, Å	24.812(2)	10.684(1)	9.153(1)
b, Å	24.812(2)	10.744(1)	10.735(3)
c, Å	24.812(2)	13.308(1)	15.417(4)
α, deg	113.69(1)	84.65(1)	77.15(3)
β, deg	113.69(1)	87.18(1)	79.89(2)
γ, deg	113.69(1)	73.45(1)	82.40(2)
V, Å^3	9490.9	1457.4	1447.1
D_{calcd}, g cm^{-3}	1.16	1.26	1.27
μ, cm^{-1}	10.10	6.91	6.96
$F(000)$, e	3504	584	584
Z	12	2	2
space group [no.]	$R\bar{3}$ [148]	$P\bar{1}$ [2]	$P\bar{1}$ [2]
diffractometer		Enraf-Nonius CAD4	
Kα X-radiation, λ, Å	0.71069	0.71069	0.71069
abs. correction	none	none	none
no. of measd reflcns	15332 [$\pm h$, $+k$, $+l$]	6951 [$\pm h$, $\pm k$, $+l$]	6834 [$\pm h$, $\pm k$, $+l$]
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.63	0.65	0.65
R_{av}	0.01	0.01	0.01
no. of indep reflcns	13015	6663	6587
no. of obsd reflcns ($I > 2\sigma(I)$)	8923	4965	5391
no. of refined params	704	352	352
R	0.068	0.061	0.069
R_w ($w = 1/\sigma^2(F_o)$)	0.087	0.077	0.050
Δ/σ	0.01	0.25	0.29
max. resid electron dens, e Å^{-3}	0.82	0.55	1.27

Structures were solved using heavy-atom methods, H-atom positions were calculated and kept fixed in the final refinement stages.

were obtained from a Finnigan MAT 311A/DF with an electron impact of 70 eV. The elemental analyses were determined by Mikroanalytisches Labor Dornis & Kolbe in Mülheim an der Ruhr, Germany.

3.1. Synthesis of 1

A solution of 560 mg (1.91 mmol) Cp*Ni(acac) in ether was added to a suspension of 519 mg (1.00 mmol) 1,4-dilithium-1,2,3,4-tetraphenylbutadiendiyl in ether at −40°C. The mixture was allowed to warm to room temperature. During warming the colour of the solid changed to white. The solid was filtered off, a small amount of aluminium oxide was added to the solution and the solvent evaporated *in vacuo*. The residue was chromatographed on aluminium oxide using a solvent mixture of pentane/ether (1 : 1). The resulting brown solution was concentrated *in vacuo* and crystallized at 0°C. **1** was obtained in the form of large brown crystals. Yield: 310 mg (56%).

^{1}H-NMR (300 K, THF-d^8, 200.1 MHz): δ [ppm] = 6.83–7.89 (20H, m, phenyl-H), 4.71 (1H, s, C(4)-H), 1.18 (15H, s, C(6)-H); ^{13}C-NMR (300 K, THF-d^8, 50.3 MHz): δ [ppm] = 147.3 (s), 143.5 (s), 143.1 (s), 142.0 (s), 136.3 (s), 133.6 (s), 129.4 (d), 128.8 (d), 128.5 (d), 128.4 (d), 128.4 (d), 127.9 (d), 127.2 (d), 126.4 (d), 126.2 (d), 126.0 (d), 125.7 (d), 101.8 (s, C(5)), 79.7 (d, C(4)), 72.4 (s, C(3)), 8.8 (q, C(6))—numbering scheme shown below; MS (70 eV, 120°C): m/z 550 (M^+, 34%), 414 ($M^+ -$ Cp*H, 93%), 356 ($C_4Ph_4^+$; 15%); elemental analysis calculated for $C_{38}H_{36}Ni \times 0.5\ C_5H_{12}$ (587.44): C 82.80, H 7.21, Ni 9.99; found: C 82.87, H 7.12, Ni 9.94%.

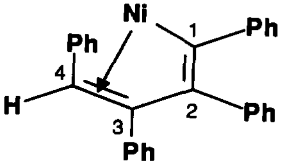


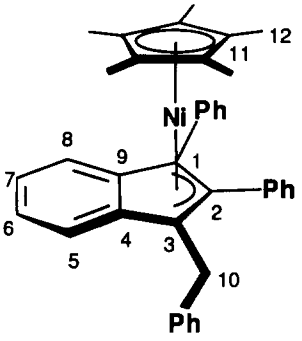
TABLE 2. Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) for **1**

Atom	x	y	z	U_{eq} [a]
Ni1	0.5411(1)	0.1761(1)	0.4165(1)	0.043(1)
Ni2	0.7429(1)	0.2115(1)	0.0585(1)	0.050(2)
C1	0.6537(3)	0.2629(3)	0.4920(3)	0.043(8)
C2	0.6562(3)	0.3209(3)	0.5315(3)	0.040(7)
C3	0.5725(3)	0.2789(3)	0.4973(3)	0.040(8)
C4	0.5370(3)	0.2216(3)	0.5017(3)	0.042(7)
C5	0.7152(3)	0.2607(3)	0.5027(3)	0.044(8)
C6	0.7531(4)	0.2816(4)	0.4767(4)	0.06(1)
C7	0.8066(4)	0.2729(4)	0.4847(4)	0.07(1)
C8	0.8235(4)	0.2435(5)	0.5185(4)	0.07(1)
C9	0.7867(4)	0.2220(4)	0.5446(4)	0.07(1)
C10	0.7327(4)	0.2301(4)	0.5365(4)	0.05(1)
C11	0.7226(3)	0.4075(3)	0.5974(3)	0.043(8)
C12	0.7901(3)	0.4488(4)	0.6090(4)	0.05(1)
C13	0.8520(4)	0.5300(4)	0.6718(4)	0.07(1)
C14	0.8480(4)	0.5716(4)	0.7242(4)	0.08(1)
C15	0.7817(5)	0.5326(4)	0.7131(4)	0.08(1)
C16	0.7195(4)	0.4511(4)	0.6507(4)	0.06(1)
C17	0.5294(3)	0.3004(3)	0.4640(3)	0.042(8)
C18	0.5570(3)	0.3445(3)	0.4453(3)	0.049(9)
C19	0.5182(4)	0.3662(4)	0.4162(4)	0.06(1)
C20	0.4518(5)	0.3443(5)	0.4041(5)	0.07(2)
C21	0.4236(4)	0.3012(5)	0.4228(5)	0.07(1)
C22	0.4626(4)	0.2803(4)	0.4533(4)	0.05(1)
C23	0.5747(3)	0.2173(3)	0.5617(3)	0.042(8)
C24	0.6523(3)	0.2776(4)	0.6334(3)	0.052(9)
C25	0.6815(4)	0.2705(4)	0.6882(4)	0.06(1)
C26	0.6342(4)	0.2021(4)	0.6716(4)	0.06(1)
C27	0.5576(4)	0.1418(4)	0.6012(4)	0.06(1)
C28	0.5274(3)	0.1493(4)	0.5471(3)	0.052(9)
C29	0.5054(4)	0.1209(4)	0.3027(3)	0.057(9)
C30	0.5216(4)	0.0836(4)	0.3314(3)	0.059(9)
C31	0.4665(4)	0.0492(3)	0.3376(3)	0.058(9)
C32	0.4185(4)	0.0677(3)	0.3172(3)	0.058(9)
C33	0.4411(4)	0.1089(4)	0.2928(3)	0.057(9)
C34	0.5470(5)	0.1600(5)	0.2833(4)	0.09(1)
C35	0.5793(5)	0.0732(4)	0.3404(4)	0.08(1)
C36	0.4592(5)	0.0004(4)	0.3606(4)	0.08(1)
C37	0.3497(4)	0.0405(4)	0.3128(4)	0.08(1)
C38	0.4013(5)	0.1342(4)	0.2609(4)	0.08(1)
C41	0.6885(3)	0.1859(3)	0.0941(3)	0.046(8)
C42	0.7289(3)	0.1737(3)	0.1344(3)	0.046(8)
C43	0.7874(4)	0.1864(4)	0.1237(3)	0.052(9)
C44	0.8489(4)	0.2617(4)	0.1572(3)	0.05(1)
C45	0.6229(3)	0.1807(3)	0.0812(3)	0.047(8)
C46	0.5444(4)	0.1079(4)	0.0228(4)	0.06(1)
C47	0.4840(4)	0.1049(5)	0.0123(5)	0.08(1)
C48	0.5006(5)	0.1730(6)	0.0598(5)	0.08(2)
C49	0.5764(5)	0.2446(5)	0.1162(5)	0.08(2)
C50	0.6375(4)	0.2490(4)	0.1271(4)	0.06(1)
C51	0.7267(4)	0.1546(3)	0.1833(3)	0.048(9)
C52	0.6611(4)	0.1203(4)	0.1760(4)	0.06(1)
C53	0.6627(5)	0.1064(4)	0.2249(5)	0.07(1)
C54	0.7299(6)	0.1272(4)	0.2827(5)	0.08(2)
C55	0.7945(5)	0.1594(4)	0.2899(4)	0.07(1)
C56	0.7934(4)	0.1733(4)	0.2404(4)	0.06(1)
C57	0.7770(5)	0.1156(5)	0.0788(4)	0.07(1)
C58	0.7030(5)	0.0395(5)	0.0202(5)	0.08(1)
C59	0.6920(7)	−0.0263(5)	−0.0225(6)	0.11(2)
C60	0.752(1)	−0.0193(9)	−0.009(1)	0.16(4)
C61	0.828(1)	0.055(1)	0.050(1)	0.16(4)

TABLE 2 (*continued*)

Atom	x	y	z	U_{eq} [a]
C62	0.8410(6)	0.1235(6)	0.0945(6)	0.11(2)
C63	0.8894(3)	0.3426(4)	0.2255(3)	0.053(9)
C64	0.8733(4)	0.3609(4)	0.2745(4)	0.06(1)
C65	0.9144(4)	0.4382(4)	0.3362(4)	0.07(1)
C66	0.9735(4)	0.5002(4)	0.3519(4)	0.07(1)
C67	0.9909(4)	0.4832(4)	0.3049(4)	0.08(1)
C68	0.9498(4)	0.4057(4)	0.2434(4)	0.07(1)
C69	0.6527(4)	0.1452(4)	−0.0639(4)	0.08(1)
C70	0.6823(4)	0.2246(4)	−0.0151(4)	0.07(1)
C71	0.7623(4)	0.2785(4)	0.0235(3)	0.06(1)
C72	0.7842(4)	0.2339(4)	0.0026(4)	0.06(1)
C73	0.7148(5)	0.1512(4)	−0.0543(4)	0.07(1)
C74	0.5679(5)	0.0701(5)	−0.1197(4)	0.12(1)
C75	0.6315(5)	0.2424(6)	−0.0176(5)	0.09(2)
C76	0.8150(5)	0.3671(4)	0.0747(4)	0.08(1)
C77	0.8624(5)	0.2665(5)	0.0259(5)	0.08(1)
C78	0.7102(6)	0.0846(5)	−0.0965(5)	0.11(2)

[a] $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (\bar{\mathbf{a}}_i \cdot \bar{\mathbf{a}}_j)$.



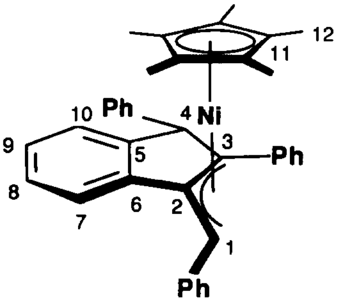
3.2. *Thermolysis of 1*

A solution of 414 mg (0.75 mmol) of **1** in THF was refluxed for five days during which the colour of the solution changed from brown to red-brown. Aluminium oxide was added to the solution and the solvent evaporated. The residue was chromatographed on aluminium oxide. A green phase was eluted with pentane/ether (10:1). The solution was evaporated to dryness and the residue recrystallized from pentane. **3** was obtained in the form of green needles. Yield: 110 mg (27%).

An orange red phase was eluted from the column with pentane/ether (1:1). The solution was concentrated *in vacuo* and crystallized at 0°C. The red crystals so obtained were recrystallized from ether. **2** occurs as red cubic crystals. Yield: 173 mg (42%).

2: ^{1}H-NMR (300 K, THF-d^8, 400.1 MHz): δ [ppm] = 6.84–7.47 (15H, m, *H*-phenyl), 6.28 (1H, d ($J_{5/6}$ = 7.1 Hz), *H*-C(5)), 5.90 (1H, d ($J_{8/7}$ = 7.1 Hz), *H*-C(8)), 5.60 (1H, t ($J_{6/7}$ = 7.1 Hz), *H*-C(6)), 5.50 (1H, t, *H*-C(7)), 3.67 (1H, d ($J_{10/10a}$ = −15.1 Hz), *H*H$_a$C(10)), 3.44 (1H, d, H*H*$_a$ C(10)), 2.82 (15H, s, *H*-C(12)); ^{13}C-NMR (300 K, THF-d^8, 100.6 MHz): δ [ppm] = 151.1 (s), 147.6 (s), 144.4 (s), 137.8 (s), 133.2 (d), 132.7 (d), 131.5 (s), 129.5 (d), 128.7 (d), 127.7 (d), 127.6 (d), 127.5 (d), 127.5 (d), 126.6 (d), 125.4 (d), 124.6 (d), 123.1 (s), 109.6 (s, C(11)), 24.8 (t, C(10)), 4.9 (q, C(12))—numbering scheme shown below; elemental analysis calculated for $C_{38}H_{36}Ni$ (551.36): C 82.77, H 6.58, Ni 10.62; found: C 82.64, H 6.54, Ni 10.82%.

3: ^{1}H-NMR (300 K, THF-d^8, 400.1 MHz): δ [ppm] = 6.77–7.84 (15H, m, *H*-phenyl), 4.17 (1H, s, *H*-C(4)), 3.45 (1H, s, *H*-C(1)), 1.38 (15H, s, *H*-C(12)); ^{13}C-NMR (300 K, THF-d^8, 100.6 MHz): δ [ppm] = 143.4 (s, C(5)), 143.1 (s, C(6)), 149.9 (s), 141.0 (s), 140.8 (s), 130.7 (d), 129.8 (d), 128.5 (d), 128.4 (d), 128.2 (d), 128.0 (d), 127.2 (d), 126.6 (d), 126.4 (d), 126.3 (d), 126.2 (d), 124.7 (d), 122.5 (d), 100.7 (s, C(2)), 99.4 (s, C(11)), 80.8 (s, C(3)), 59.7 (d (J(CH) = 133 Hz), C(4)), 59.6 (d (J(CH) = 155 Hz), C(1)), 9.2 (q (J(CH) = 136 Hz), C(12))—numbering scheme shown below; elemental analysis calculated for $C_{38}H_{36}Ni$ (551.36): C 82.77, H 6.58, Ni 10.62; found: C 82.75, H 6.40, Ni 10.73%. The mass spectra of **2** and **3** were identical to that of **1**.



3.3. Crystal structure determinations

Atomic fractional coordinates for **1**, **2** and **3** are listed in Tables 2, 3 and 4, respectively, and crystal structure data are given in Table 4. Further details of crystal structure investigations (listings of structure factors, hydrogen atom positional parameters, anisotropic thermal parameters, distances and angles) may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-57313, the names of the authors and the journal citation.

TABLE 3. Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) for **2**

Atom	x	y	z	U_{eq} [a]
Ni	0.2041(1)	0.1854(1)	0.2600(1)	0.031(1)
C1	0.3247(4)	0.2820(4)	0.3164(3)	0.046(3)
C2	0.2472(4)	0.3491(4)	0.2317(3)	0.045(3)
C3	0.2946(4)	0.2739(4)	0.1477(3)	0.046(3)
C4	0.4235(4)	0.1843(4)	0.1731(3)	0.051(3)
C5	0.5178(5)	0.1007(5)	0.1160(4)	0.059(3)
C6	0.6286(5)	0.0202(5)	0.1632(4)	0.071(4)
C7	0.6451(5)	0.0196(6)	0.2655(4)	0.074(4)
C8	0.5522(5)	0.1048(5)	0.3235(4)	0.063(3)
C9	0.4414(4)	0.1880(4)	0.2772(3)	0.050(3)
C10	0.2469(5)	0.3045(4)	0.0409(3)	0.053(3)
C11	0.3198(5)	0.3864(4)	−0.0273(3)	0.052(3)
C12	0.2940(5)	0.5193(5)	−0.0150(4)	0.066(4)
C13	0.3584(6)	0.5938(5)	−0.0772(5)	0.074(4)
C14	0.4452(6)	0.5375(6)	−0.1522(4)	0.072(4)
C15	0.4694(5)	0.4072(6)	−0.1638(4)	0.071(4)
C16	0.4053(5)	0.3333(5)	−0.1014(4)	0.061(3)
C20	0.1502(4)	0.4800(4)	0.2313(3)	0.047(3)
C21	0.1856(5)	0.5821(4)	0.2678(4)	0.057(3)
C22	0.1000(6)	0.7067(5)	0.2645(4)	0.071(4)
C23	−0.0206(6)	0.7325(5)	0.2219(5)	0.076(4)
C24	−0.0571(5)	0.6321(6)	0.1868(4)	0.071(4)
C25	0.0266(4)	0.5064(5)	0.1905(3)	0.056(3)
C30	0.3120(4)	0.3291(4)	0.4185(3)	0.050(3)
C31	0.4195(5)	0.3437(5)	0.4659(4)	0.063(3)
C32	0.4039(6)	0.3932(6)	0.5602(4)	0.075(4)
C33	0.2827(6)	0.4275(6)	0.6083(4)	0.080(4)
C34	0.1752(5)	0.4162(6)	0.5603(4)	0.073(4)
C35	0.1886(5)	0.3665(5)	0.4669(3)	0.058(3)
C40	0.1269(6)	0.0779(5)	0.3726(4)	0.065(4)
C41	0.0207(5)	0.1448(5)	0.3087(4)	0.063(3)
C42	0.0587(5)	0.1093(5)	0.2107(4)	0.062(4)
C43	0.1829(5)	0.0110(5)	0.2140(4)	0.061(3)
C44	0.2227(5)	−0.0104(5)	0.3143(4)	0.064(4)
C45	0.1320(8)	0.0810(7)	0.4842(5)	0.101(6)
C46	−0.1055(7)	0.2375(6)	0.3402(6)	0.104(6)
C47	−0.0228(6)	0.1530(6)	0.1172(5)	0.091(5)
C48	0.2540(7)	−0.0586(6)	0.1265(5)	0.093(5)
C49	0.3447(7)	−0.1066(6)	0.3555(6)	0.095(5)

[a] $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (\bar{\mathbf{a}}_i \cdot \bar{\mathbf{a}}_j)$.

TABLE 4. Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) for **3**

Atom	x	y	z	U_{eq} [a]
Ni	0.2388(1)	0.3095(1)	0.3146(1)	0.030(1)
C1	0.4838(3)	0.0982(2)	0.2757(2)	0.034(1)
C2	0.3355(2)	0.1682(2)	0.2487(1)	0.030(1)
C3	0.3613(2)	0.2970(2)	0.2005(1)	0.030(1)
C4	0.5193(2)	0.3159(2)	0.1996(2)	0.034(1)
C5	0.6023(3)	0.4197(3)	0.1615(2)	0.049(2)
C6	0.7487(3)	0.4111(3)	0.1773(2)	0.058(2)
C7	0.8116(3)	0.3022(3)	0.2285(2)	0.058(2)
C8	0.7327(3)	0.1972(3)	0.2625(2)	0.047(2)
C9	0.5868(3)	0.2042(2)	0.2482(2)	0.035(1)
C10	0.2318(2)	0.3805(2)	0.1819(1)	0.031(1)
C11	0.2210(3)	0.5181(2)	0.1364(1)	0.033(1)
C12	0.1240(3)	0.5560(2)	0.0736(2)	0.046(2)
C13	0.1077(4)	0.6807(3)	0.0263(2)	0.057(2)
C14	0.1883(4)	0.7709(3)	0.0423(2)	0.059(2)
C15	0.2803(3)	0.7373(3)	0.1058(2)	0.057(2)
C16	0.2972(3)	0.6115(2)	0.1532(2)	0.045(2)
C20	0.2219(2)	0.0913(2)	0.2336(1)	0.032(1)
C21	0.1676(3)	−0.0082(2)	0.3016(2)	0.042(2)
C22	0.0623(3)	−0.0809(3)	0.2885(2)	0.052(2)
C23	0.0095(3)	−0.0576(3)	0.2081(2)	0.058(2)
C24	0.0650(3)	0.0374(3)	0.1395(2)	0.055(2)
C25	0.1712(3)	0.1100(2)	0.1519(2)	0.042(2)
C30	0.5436(2)	−0.0112(2)	0.2277(2)	0.037(1)
C31	0.5711(3)	−0.1351(3)	0.2742(2)	0.054(2)
C32	0.6319(4)	−0.2326(3)	0.2286(3)	0.072(3)
C33	0.6641(4)	−0.2073(3)	0.1369(3)	0.072(3)
C34	0.6344(4)	−0.0850(3)	0.0898(2)	0.065(2)
C35	0.5749(3)	0.0123(3)	0.1345(2)	0.052(2)
C40	0.2223(3)	0.2344(2)	0.4526(2)	0.040(1)
C41	0.3131(3)	0.3387(3)	0.4352(2)	0.045(2)
C42	0.2301(3)	0.4497(3)	0.3987(2)	0.046(2)
C43	0.0843(3)	0.4169(3)	0.3935(2)	0.044(2)
C44	0.0779(3)	0.2840(3)	0.4308(2)	0.040(1)
C45	0.2637(4)	0.1015(3)	0.5016(2)	0.057(2)
C46	0.4699(4)	0.3291(4)	0.4536(2)	0.070(2)
C47	0.2755(5)	0.5835(3)	0.3792(2)	0.076(3)
C48	−0.0420(4)	0.5122(3)	0.3638(2)	0.066(2)
C49	−0.0539(3)	0.2088(3)	0.4472(2)	0.058(2)

[a] $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (\bar{\mathbf{a}}_i \cdot \bar{\mathbf{a}}_j)$.

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