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Preparation of chelate bis(imine)nickel allyl systems by reaction of their corresponding butadiene complexes with electrophiles

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Abstract

The chelate 1,2-bis(imine)nickel(butadiene) complex **4a** (chelate ligand derived from condensation of biacetyl with 2,6-diisopropylaniline) adds the strong Lewis acid $B(C_6F_5)_3$ at the terminal carbon atom of the butadiene ligand to yield the dipolar substituted π-allyl-type betaine complex (lig)Ni[η^3-C_3H_4-$CH_2B(C_6F_5)_3$] (*Z*-**6a**). At 90 °C the kinetically formed product equilibrated with its *E*-**6a** isomer. Similarly, **4a** adds the boron Lewis acid (pyrrolyl)$B(C_6F_5)_2$ to yield the corresponding neutral dipolar π-allyl betaine complex *Z*-**7a**, that slowly equilibrated with *E*-**7a** over several hours at ambient temperature. Protonation of the butadiene ligand of complex **4a** was achieved by treatment with the neutral Brønsted acid (2H-pyrrol)$B(C_6F_5)_3$ to yield the [(lig)Ni(η^3-crotyl)$^+$][(pyrrolyl)$B(C_6F_5)_3^-$] salt **9a** (*Z*-/*E*-**9a** ratio = 90:10 upon preparation). At 298 K this salt rearranged to a 5:95 mixture of *Z*-**9a**/*E*-**9a** with a Gibbs activation energy of $\Delta G^{\ddagger}$ (298 K) = 22.3 ± 0.2 kcal mol^{-1}. Complex **4a** added [Ph_3C^+] to the butadiene ligand to yield the salt [(lig)Ni(η^3-C_3H_4-CH_2CPh_3)$^+$][$B(C_6F_5)_4^-$] (*Z*-**12a**), that proved isomerically stable under the applied reaction conditions. Similar reactions were carried out starting from the acenaphthylene 1,2-dione derived chelate bis(imine)Ni(butadiene) complex **4b**. The systems **6**, **7**, **9** and **12** were found to be active ethene polymerization catalysts in the presence of Al(*i*-Bu)$_3$.

Keywords: (Butadiene)nickel complexes; Boron Lewis acids; Metal boron betaines; (π-Allyl)nickel complexes; Ethene polymerization.

1. Introduction

(Allyl)nickel complexes have played an important role in the development of homogeneous catalysis using structurally well defined mono-nuclear transition metal complexes [1]. Most noteworthy in the early work is the chemistry of the neutral (allyl)Ni systems, which is of great importance, e.g. in the cyclooligomerization and cooligomerization of butadiene [2]. Chelate Schiff-base nickel cation complexes and related systems have been of interest in polymerization catalysis [3]. We had recently shown that strongly electrophilic neutral boranes, such as $B(C_6F_5)_3$ [4], can add to the butadiene ligands of a variety of metal complexes, especially of the early transition metals [5]. The borane addition occurs at a terminal CH_2 group of the butadiene ligand with formation of a substituted η^3-allyl moiety. The resulting complexes show a variety of features of typical (allyl)metal cation systems, only that the dipolar complexes **2** are overall neutral, because they have their counter anion covalently attached to the allyl ligand framework (see Scheme 1) [6,7].

In the case of the nickel systems, the addition of, e.g. $B(C_6F_5)_3$ to neutral L_nNi(butadiene) complexes of Ni(0) would then yield dipolar $L_nNi[C_4H_6{-}B(C_6F_5)_3]$ type complexes, featuring a local (allyl)Ni(II) type subgroup inside an overall neutral 'betaine' complex. We have prepared a few examples of such systems [8], that may chemically be placed at an intermediate position between the classical neutral (allyl)Ni complexes and the charged [(allyl)Ni$^+$] cations, by the addition of strongly electrophilic boranes to (butadiene)nickel complexes, and we have compared some of the chemical features of such dipolar systems with closely related (allyl)nickel cations that were made by H^+ or carbenium ion

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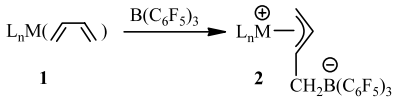


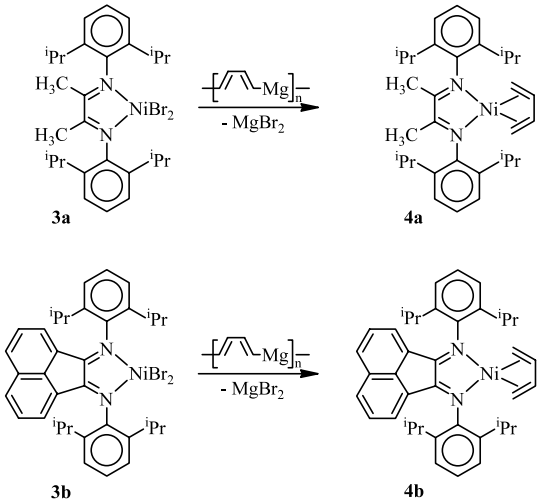
Scheme 1.

addition to the same (butadiene)nickel complex precursors.

2. Results and discussion

As the starting materials for our study we have employed the chelate bis(imine)nickel complex systems derived from **3a** and **3b**. The chelate ligands were synthesized by treatment of the corresponding 1,2-diketones with two molar equivalents of 2,6-diisopropylphenylamine under acidic conditions. Subsequent treatment with (dme)$NiBr_2$ gave the bis(imine)$NiBr_2$ complexes (**3a**, **3b**) that had previously been used extensively in homogeneous Ziegler–Natta catalysis [9,10]. The corresponding chelate bis(imine)Ni(butadiene) complexes (**4a**, **4b**) had been described by tom Dieck et al. [11]. They were prepared according to the literature procedure described by treatment of the complexes **3** with the 'butadiene–magnesium' reagent [12,13] (Scheme 2).

We then treated complex **4a** with $B(C_6F_5)_3$ (**5a**). One molar equivalent of the strong boron Lewis acid was rapidly added to give the product *Z*-**6a**, that was isolated in ca. 80% yield. We had characterized complex *Z*-**6a** by X-ray diffraction [8]. The X-ray crystal structure analysis had shown that the borane addition had taken place at the terminal $=CH_2$ group of the conjugated diene ligand. The NMR analysis of *Z*-**6a** showed the analogous structure to be present in solution. The C_4H_6-[B] ligand features four characteristical ^{13}C-NMR resonances at δ 54.3 (C1), δ 110.9 (C2), δ 100.7 (C3), and a broad C4 resonance at δ 26 (see Table 1). The ^{1}H-NMR spectrum of the C_3H_4-CH_2[B] section of *Z*-**6a** shows a six hydrogen pattern of signals that is typical for the presence of a *Z*-substituted η^3-allyl moiety [14]. It features the 1-H_{syn} and 1-H_{anti} signals at δ 2.48 and δ 2.57, respectively. Their mutual coupling (^2J) is so small that it was not resolved in this case. The 2-H (δ 4.88) shows a small *cis*-coupling constant with 1-H_{syn} [^3J(2-H,1-H_{syn}) = 7.2 Hz] and a large *trans*-coupling constant with 1-H_{anti} [^3J(2-H,1-H_{anti}) = 14.3 Hz]. Most significantly, the ^3J(2-H,3-H) coupling constant was found at 7.2 Hz, i.e. in the typical *cis*-range, which indicates the presence of the *Z*-**6a** isomer in solution under the applied conditions. The adjacent 4-H/H′ resonances occur at δ 2.00/1.03.



Scheme 2.

The attachment of the unsymmetrically substituted π-allyl moiety at the nickel center makes complex *Z*-**6a** chiral and the two halves of the substituted bis(imine) ligand have become different. Consequently, a pair of core methyl NMR resonances are observed (^{1}H: δ 1.16/1.15, ^{13}C: 19.5/18.4) and we have monitored a total of four isopropyl CH resonances (^{13}C: δ 30.6, 29.5, 29.1, 28.6) and eight isopropyl CH_3 signals (for details see Section 3) (Scheme 3).

Complex *Z*-**6a** rearranges at elevated temperature. During a period of 1 h at 90 °C (in toluene-d_8) it is equilibrated with its isomer *E*-**6a**. After 1 h a ca. 1:1 mixture of the two isomers was present in solution. From the mixture the typical NMR signals of the *E*-**6a** isomer were obtained. The ^{1}H-NMR spectrum features allyl resonances at δ 2.05, 1.39 (1-H_{syn}, 1-H_{anti}), δ 4.71 (2-H), and δ 4.00 (3-H) with coupling constants ^3J(2-H,1-H_{syn}) = 7.2 Hz, ^3J(2-H,1-H_{anti}) = 13.8 Hz, and ^3J(2-H,3-H) = 13.8 Hz. The latter clearly characterizes that the isomer *E*-**6a** had been formed subsequently upon thermolysis of *Z*-**6a**, which was formed under kinetic control. The acenaphthen-derived butadiene nickel complex **4b** was similarly converted to *Z*-**6b** (ca. 90% isolated, for details see Section 3).

We had recently described a heterocyclic variant of tris(pentafluorophenyl)borane (**5a**), namely *N*-pyrrolyl-bis(pentafluorophenyl)borane (**5b**) [15]. It is slightly less strongly electrophilic than the commonly used **5a**, but was shown to exhibit similar features as an activator component in homogeneous Ziegler–Natta catalysis [15] The Lewis acid **5b** adds cleanly to the butadiene ligands of either of the nickel complexes **4a** and **4b** to yield the dipolar (π-allyl)Ni[π-C_3H_4–CH_2–$B(C_6F_5)_2(NC_4H_4)$] 'betaine' complexes **7a** and **7b**. These complexes were isolated in > 70% yield in each case.

When the components **4a** and **5b** were mixed at −78 °C in toluene-d_8 and the solution was allowed to warm to room temperature a 90:10 mixture of the isomers *Z*-**7a** and *E*-**7a** was obtained. Again the *Z*-isomer proved to be the kinetically formed product. In the case of the **5b** addition product, the *Z*-**7a** ⇆ *E*-**7a**

Table 1
Selected ^{1}H- and ^{13}C-NMR chemical shifts of the *Z*- and *E*-allyl nickel products obtained from the addition of electrophiles to **4a** and **4b** [a]

Complex	$1H_{syn}$	$1H_{anti}$	2-H	3-H	4-H	4-H′	C1	C2	C3	C4
Z-**6a**	2.48	2.57	4.88	4.08	2.00	1.03	54.3	110.9	100.7	26 [d]
E-**6a** [c]	2.05	1.39	4.71	4.00	1.20	0.37	E	e	e	e
Z-**6b**	2.87	2.99	5.10	4.64	2.32	1.45	54.6	110.7	100.8	27 [d]
Z-**7a** [b]	2.52	2.08	5.00	4.12	1.36	1.15	53.8	110.8	97.5	25 [d]
E-**7a** [b]	2.24	1.73	4.57	3.68	0.87	0.10	e	114.4	99.0	e
Z-**9a**	2.86	2.53	5.56	3.62	0.60 [f]	–	58.3	115.5	79.2	14.9
E-**9a**	2.60	2.34	5.31	3.23	−0.03 [f]	–	59.7	119.4	80.1	15.0
E-**9b**	2.92	2.55	5.53	3.51	0.17 [f]	–	59.0	118.7	78.7	15.4
Z-**12a**	2.40	1.96	5.18	3.61	2.60	1.64	60.4	116.1	76.9	39.1
Z-**12b**	2.73	2.33	5.42	3.82	2.76	1.84	60.3	115.6	75.5	39.2

[a] In CD_2Cl_2 except **6a** and **6b** (toluene-d_8), 600 MHz (^{1}H), 150.8 MHz (^{13}C) at 298 K.
[b] At 268 K.
[c] At 358 K.
[d] Broad signal.
[e] Not determined.
[f] CH_3 group.

interconversion was, however, much faster then the *Z*-**6a** ⇆ *E*-**6a** conversion described above. In the case of the **7a** isomers it was sufficient to leave the system at room temperature for 6 h to achieve a 50% conversion to *E*-**7a**. Fig. 1 shows the TOCSY ^{1}H-NMR spectrum of the ca. 1:1 *Z*-/*E*-**7a** mixture featuring the well separated system of the six coupled proton resonances of the η^3-C_3H_4-CH_2-[B] subunit of the *E*-**7a** isomer (top) distinguished from the corresponding set of signals originating from the *Z*-**7a** isomer. A detailed analysis of the spectra showed again the typical small ^{3}J(2-H,3-H) = 8.0 Hz of *Z*-**7a**, whereas *E*-**7a** features a much larger value of ^{3}J(2-H,3-H) = 13.4 Hz (see also Table 1).

Complex *Z*-**7a** again features four diastereotopic isopropyl groups (^{1}H-NMR: δ 3.79, 3.15, 2.82, 2.56, each sept. 1 H, $CHMe_2$). Due to the chirality of the system, the methyl groups of each separate isopropyl group are diastereotopic, which gives rise to a set of each eight observed ^{1}H- and ^{13}C-NMR isopropyl-CH_3 resonances. The pyrrolyl ^{13}C-NMR resonances of *Z*-**7a** occur at δ 122.7 and δ 106.3. The corresponding signals of the isomer *E*-**7a** were observed at δ 123.0 and δ 106.0

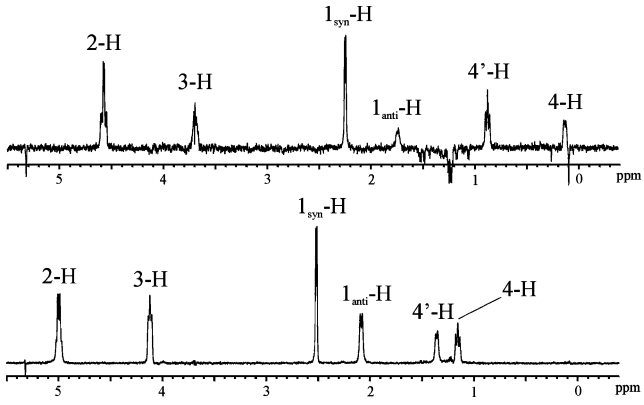
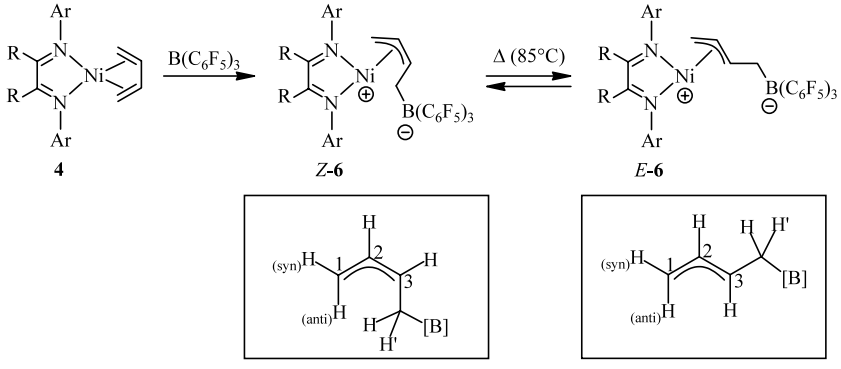


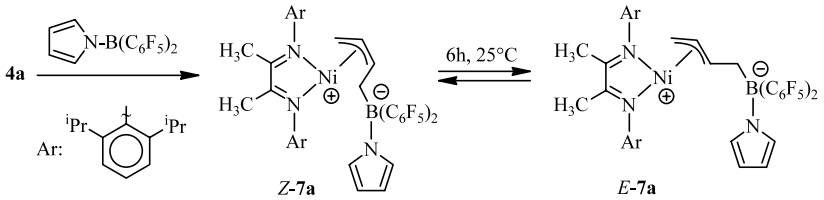
Fig. 1. TOCSY ^{1}H-NMR spectra of the (η^3-C_3H_4-CH_2-[B] subunit of *E*-**7a** (top) and *Z*-**7a** (bottom) (CD_2Cl_2, 600 MHz, 268 K).

(pyrrolyl[B] ^{13}C). The ^{11}B-NMR resonance of *Z*-**7a** is found at δ −6.9 (Scheme 4).

Protonation of the butadiene ligand in **4a** or **4b** should give rise to the formation of a cationic chelate [bis(imine)Ni(crotyl)$^{+}$] cation complex. As a suitable



Scheme 3.

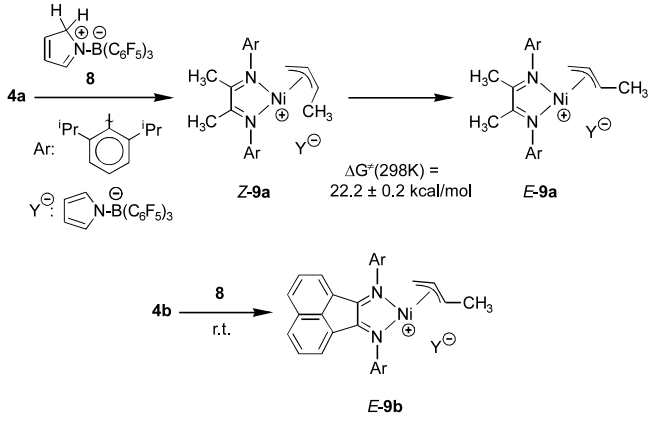


Scheme 4.

Brønsted acid we have used the neutral 2H-pyrrol/$B(C_6F_5)_3$ adduct **8**. The reagent **8** is readily prepared by the addition of *N*-pyrrolyl lithium to $B(C_6F_5)_3$ followed by the reaction with hydrogen chloride in ether [16,17]. Compound **8** had successfully been applied previously as a suitable H^+ source for the protonolysis of sensitive early metal cation systems. The resulting [(pyrrolyl)$B(C_6F_5)_3^-$] anion shows a sufficiently low nucleophilicity [18] for the generation of such systems.

Proton transfer from **8** to **4a** took place readily. At low temperature, the *Z*-crotyl nickel cation complex *Z*-**9a** was rather selectively formed (*Z*-/*E*-**9a** = 90:10). During ca. 4 h at 298 K it rearranged to a 5:95 mixture of *Z*-**9a** and *E*-**9a**. The Gibbs activation energy of the thermally induced *Z*-**9a** to *E*-**9a** rearrangement was determined at $\Delta G^{\ddagger}$ (298 K) = 22.2 ± 0.2 kcal mol^{-1}. Again, the kinetically predominantly formed complex *Z*-**9a** is characterized by a coupling constant of ^3J(2-H,3-H) = 7.8 Hz, whereas the *E*-**9a** isomers features a much larger value of ^3J(2-H,3-H) = 13.4 Hz (for further details see Table 1 and Section 3) (Scheme 5).

The protonation of the acenaphthylene-derived Ni(butadiene) complex **4b** with **8** also proceeds cleanly. In this case only traces of the *Z*-**9b** isomer could be found. After work-up almost pure *E*-**9b** (^3J(2-H,3-H) = 13.3 Hz) was found (81% isolated).

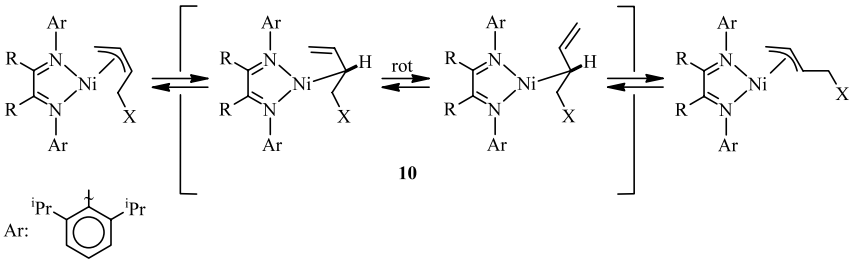


Scheme 5.

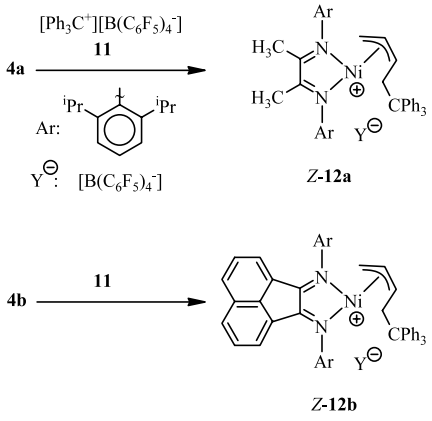
It is remarkable how different the rates of *Z*- to *E*-η^3-allyl isomerizations (qualitatively) are in the series of the complexes **6**, **7** and **9**. One obvious structural difference between these compounds lies in the steric bulk of the $-CH_2X$ group that is attached at the essential allyl sp^2 carbon atom C3, that needs to undergo an inplane inversion during the isomerization process. This is likely to occur through the corresponding σ-allyl intermediate (**10**) [19]. In **10** the nickel center together with its very bulky 2,6-diisopropylphenyl substituted chelate bis(imine) ligand will probably get closer to the allyl bound $-CH_2X$ substituent. Thus, the isomerization rate is likely to respond to the sterical features of the X-group that has become connected to the former butadiene C4 carbon center (see Scheme 6).

From this interpretation it is expected that the initially formed *Z*-isomer is ever more effectively protected from undergoing a subsequent thermally induced isomerization to the thermodynamically favored respective *E*-isomer if the substituent at C4 is increased in size. As an experimentally feasible extreme case we have, therefore, treated both the complexes **4a** and **4b** with trityl perfluorotetraphenylborate (**11**) [20]. In both cases the very bulky trityl cation electrophile added cleanly to the butadiene ligand to form the respective substituted chelate bis(imine) π-allyl nickel cation salts. In both cases only the *Z*-configurated products (*Z*-**12a**, *Z*-**12b**, see Scheme 7) were obtained. They were isolated in 76 and 89% yield, respectively. Both did not isomerize to their respective *E*-isomers. They proved to be stable with regard to isomerization under the applied conditions.

Both the betaine systems (**6**,**7**) and the substituted π-allyl nickel cation complexes (**9**) were low activity catalysts for ethene polymerization [10] in the presence of a ca. 50-fold excess of tri-isobutyl aluminum. It was checked in a NMR study, that the *Z*-**6a** system did not react itself even at 85 °C with a ca. twofold excess of Al(*i*-Bu)$_3$. So it remains to be resolved whether the added aluminum compound is actively involved in the polymerization process or if it merely acts as a moisture scavenger. In the latter case the systems **6** and **7** would serve as model catalyst systems for explaining possible olefin activation pathways at an increasingly observed homogeneous catalyst type that is derived from im-



Scheme 6.



Scheme 7.

Table 2
Ethene polymerization with the allyl nickel-type complexes [a]

Complex	μmol cat.	M_n [b] ($\times 10^3$)	D [b]	g PE [c]	Act [d]
6a	39	700	1.70	12.2	159
6b	33	130	1.98	15.3	231
7a	39	400	1.78	6.3	81
7b	33	140	1.94	5.0	76
9a	39	600	1.73	4.4	57
9b	33	220	1.82	4.5	68
12a	39	73	1.93	4.9	63
12b	33	[e]	[e]	5.5	78

[a] In 200 ml toluene at 25 °C, with 0.5 ml Al(*i*-Bu)$_3$ added, 2 bar ethene.
[b] M_n and polydispersity determined by GPC vs. polystyrene standard in THF at 35 °C.
[c] g Polyethylene obtained after 1 h reaction time.
[d] Catalyst activity in kg PE/mol cat × bar(ethene) × h.
[e] Insoluble polymer, M not determined.

mediate catalyst precursors that are lacking a necessary metal to carbon σ-bond [21–23]. The polyethylenes obtained at the **6**,**7**,**9**/Al(*i*-Bu)$_3$ catalyst (see Table 2) have a branched structure, as it is commonly observed at chelate bis(imine)Ni-derived catalyst systems [9,24]. The branching of the obtained polyethylenes was analyzed by ^{13}C-NMR spectroscopy [3b,25]. It was very similar for the samples listed in Table 2 which typically exhibited around 100 methyl branches per 1000 chain carbon atoms, half of which were randomly distributed and the remaining ones were 1,4-positioned to other CH_3 groups along the chain. In addition, the signals of very small amounts of longer branches (ethyl > propyl > butyl) could just be identified in the ^{13}C-NMR spectra of the polymer samples.

3. Experimental

General information: reactions with organometallic reagents were carried out under argon in Schlenk-type glassware or in a glove-box. Solvents were dried and distilled under argon prior to use. For additional general information, including a list of spectrometers and equipment used for physical characterization see Ref. [26]. NMR assignments were in most cases derived from a series of 2D-NMR experiments [27]. The boron reagents **5a** [4], **5b** [15] and **8** [16] were prepared as described in the literature. The (butadiene)nickel complexes **4a** and **4b** were synthesized according to literature procedures [11].

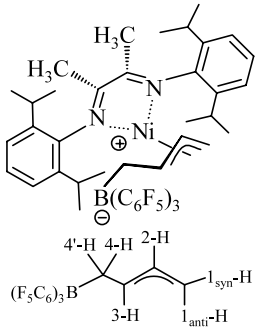
*3.1. Reaction of tris(pentafluorophenyl)borane (**5a**) with [biacetylbis(2,6-diisopropylphenylimin)](1,3-butadiene)nickel (**4a**), preparation of **6a***

3.1.1. NMR experiments

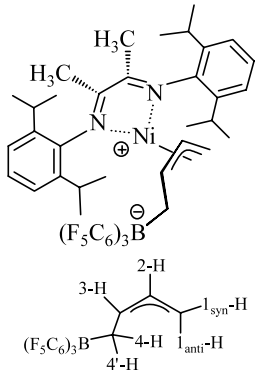
The betaine system **6a** was generated in situ by the slow addition of a solution of the (butadiene)nickel complex **4a** (20 mg, 38.6 μmol) in 0.5 ml of toluene-d_8 to a solution of 19.8 mg (39.6 μmol) of B(C$_6$F$_5$)$_3$ (**5a**) in 0.5 ml toluene-d_8 at ambient temperature. Initially, only the formation of ***Z*-6a** was observed. Warming to 90 °C resulted in the rearrangement to *E*-**6a**. After 1 h at 90 °C the NMR signals of a 1:1 mixture of *Z*-**6a** and *E*-**6a** were monitored. From the dark-purple colored solution the betaine precipitated as a dark colored solid during several days at room temperature (r.t.).

*3.1.2. Preparation of **6a***

At −78 °C a precooled solution of $B(C_6F_5)_3$ (**5a**) (198 mg, 387 μmol) in 20 ml of toluene was added dropwise with stirring to a solution of 200 mg (387 μmol) of **4a** in 20 ml of toluene. The mixture was stirred for 30 min and then warmed to room temperature during 2 h. The dark-purple solution was stirred for 4 h at ambient temperature and then the solvent was removed in vacuo. The residue was suspended in pentane (30 ml). The resulting brown precipitate was washed with pentane (3 × 10 ml) and dried in vacuo to yield 321 mg (81%) of **6a**, m.p. 212 °C dec. Anal. Calc. for $C_{50}H_{46}BF_{15}N_2Ni$ (*M* 1029.4): C, 58.34; H, 4.50; N, 2.72. Found: C, 58.64; H, 4.81; N, 2.76%.



^{1}H-NMR (599.9 MHz, toluene-d_8, 358 K): $\delta = 7.03$ (t, 1H, $^3J_{HH} = 7.7$ Hz, *p*-Ph), 6.95 (d, 2H, $^3J_{HH} = 7.7$ Hz, *m*-Ph), 6.89 (t, 1H, $^3J_{HH} = 7.7$ Hz, *p*-Ph), 6.86 (d, 2H, $^3J_{HH} = 7.7$ Hz, *m*-Ph), 4.71 (d t, 1H, $^3J_{HH} = 13.8$ Hz, $^3J_{HH} = 7.2$ Hz, 2-H), 4.00 (ddd, 1H, $^3J_{HH} = 13.8$ Hz, $^3J_{HH} = 13.2$ Hz, $^3J_{HH} = 7.8$ Hz, 3-H), 2.95, 2.91, 2.62, 2.59 (each sept, each 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.05 (d, 1H, $^3J_{HH} = 7.2$ Hz, 1_{syn}-H), 1.39 (d, 1H, $^3J_{HH} = 13.8$ Hz, 1_{anti}-H), 1.27, 1.20 (each s, each 3H, NC–CH_3), 1.20 (br, 1H, 4′-H), 1.36, 1.31, 1.03, 0.99, 0.89, 0.87, 0.80, 0.72 (each d, each 3H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–CH_3), 0.37 (br, 1H, 4-H).



^{1}H-NMR (599.9 MHz, toluene-d_8, 298 K): $\delta = 7.26$ (t, 1H, $^3J_{HH} = 7.7$ Hz, *p*-Ph), 7.09 (d, 2H, $^3J_{HH} = 7.7$ Hz, *m*-Ph), 7.05 (t, 1H, $^3J_{HH} = 7.7$ Hz, *p*-Ph), 6.96 (d, 2H, $^3J_{HH} = 7.7$ Hz, *m*-Ph), 4.88 (dt, 1H, $^3J_{HH} = 14.3$ Hz, $^3J_{HH} = 7.2$ Hz, 2-H), 4.08 (br, 1H, 3-H), 3.73, 2.98, 2.64, 2.29 (each sept, each 1H, $^3J_{HH} = 7.2$ Hz, *i*-Pr–C*H*), 2.57 (d, 1H, $^3J_{HH} = 14.3$ Hz, 1_{anti}-H), 2.48 (d, 1H, $^3J_{HH} = 7.2$ Hz, 1_{syn}-H), 2.00 (br, 1H, 4′-H), 1.57, 1.49, 1.12, 1.01, 0.98, 0.97, 0.92, 0.77 (each d, each 3H, $^3J_{HH} = 7.2$ Hz, *i*-Pr–CH_3), 1.16, 1.15 (each s, each 3H, NC–CH_3), 1.03 (br, 1H, 4-H). ^{13}C{^{1}H}-NMR (150.8 MHz, benzene-d_6, 298 K): $\delta = 173.1$, 172.5 (each C=N), 148.1 (dm, $^1J_{CF} = 240$ Hz, *o*-B(C_6F_5)$_3$), 143.1, 141.1 (*ipso*-Ph), 138.4 (dm, $^1J_{CF} = 250$ Hz, *p*-B(C_6F_5)$_3$), 138.2, 137.6, 137.5, 136.0 (each quart. *C*-CH(CH$_3$)$_2$), 136.7 (dm, $^1J_{CF} = 250$ Hz, *m*-B(C_6F_5)$_3$), 128.0, 127.8, 124.2, 124.1, 123.8, 123.5 (each Ph), 110.9 (C2), 100.7 (C3), 54.3 (C1), 30.6, 29.5, 29.1, 28.6 (each *i*-Pr–*C*H), 26 (br, C4), 24.4, 24.2, 24.0, 23.9, 23.3, 22.7, 22.2, 22.1 (each *i*-Pr–*C*H$_3$), 19.5, 18.4 (each NC-*C*H$_3$). *ipso*-C of C_6F_5 not detected. ^{19}F-NMR (599.9 MHz, benzene-d_6, 298 K): $\delta = -166.5$ (m, 6F, *m*-B(C_6F_5)$_3$), -163.0 (t, $^3J_{FF} = 19$ Hz, 3F, *p*-B(C_6F_5)$_3$), −130.5 (m, 6F, *o*-B(C_6F_5)$_3$). ^{11}B{^{1}H}-NMR (64.2 MHz, benzene-d_6, 298 K): $\delta = -14.0$. IR (KBr): $\tilde{\nu} =$ 2971, 2932, 2874, 1643, 1517, 1459, 1388, 1283, 1223, 1085, 991, 898 cm^{-1}.

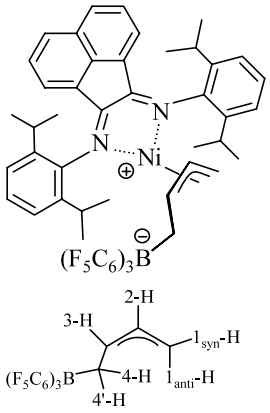
*3.2. Reaction of the (butadiene)Ni complex **4b** with $B(C_6F_5)_3$, formation of **6b***

3.2.1. NMR experiment

Complex **6b** was generated in situ by treatment of 30.0 mg (48.9 μmol) of **4b** in 0.5 ml toluene-d_8 with 25.0 mg (48.9 μmol) of $B(C_6F_5)_3$ (**5a**) in 0.5 ml of toluene-d_8 at ambient temperature. The NMR spectra of the product (see below) were obtained from this experiment.

*3.2.2. Preparation of Z-**6b***

The betaine **7** was prepared by treatment of $B(C_6F_5)_3$ (**5a**, 167 mg, 326 μmol) with **4b** (200 mg, 326 μmol) in a total volume of 40 ml of toluene analogously as described above to yield 334 mg (91%) of the dark violet product *Z*-**6b**, m.p. 182 °C (dec.). Anal. Calc. for $C_{58}H_{46}BF_{15}N_2Ni$ (*M* 1125.5): C, 61.90; H, 4.12; N, 2.49. Found: C, 62.09; H, 4.57; N, 2.40%.



^{1}H-NMR (599.9 MHz, toluene-d_8, 298 K): $\delta = 7.40$ (t,

1H, $^3J_{HH} = 8.4$ Hz, *p*-Ph), 7.20 (d, 1H, $^3J_{HH} = 8.4$ Hz, *m*-Ph), 7.19-7.13 (m, 4H, *p*-, *m*-Ph), 7.13 (d, 1H, $^3J_{HH} =$ 7.8 Hz, napht.), 7.08 (d, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 6.62 (t, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 6.59 (d, 1H, $^3J_{HH} =$ 7.8 Hz, napht.), 6.54 (t, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 6.47 (d, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 5.10 (dt, 1H, $^3J_{HH} = 13.8$ Hz, $^3J_{HH} = 7.4$ Hz, 2-H), 4.64 (br, 1H, 3-H), 4.04, 3.41, 3.17, 2.84 (each sept, each 1H, $^3J_{HH} = 7.2$ Hz, *i*-Pr–C*H*), 2.99 (d, 1H, $^3J_{HH} = 13.8$ Hz, 1_{anti}-H), 2.87 (d, 1H, $^3J_{HH} = 7.4$ Hz, 1_{syn}-H), 2.32 (br, 1H, 4′-H), 1.57, 1.53, 1.20, 1.03, 0.96, 0.77, 0.74, 0.63 (each d, each 3H, $^3J_{HH} = 7.2$ Hz, *i*-Pr–CH_3), 1.45 (br, 1H, 4-H). $^{13}C\{^1H\}$-NMR (150.8 MHz, benzene-d_6, 298 K): $\delta = 170.4$, 170.2 (each *C*=N), 148.6 (dm, $^1J_{CF} = 240$ Hz, *o*-B(C_6F_5)$_3$), 145.3, 131.6, 131.3, 125.3 (each quart. napht.), 143.4, 141.9 (*ipso*-Ph), 137.2 (dm, $^1J_{CF} = 250$ Hz, *p*-B(C_6F_5)$_3$), 137.1, 139.3, 138.6 (each quart. *C*-CH(CH$_3$)$_2$), 138.4 (dm, $^1J_{CF} = 250$ Hz, *m*-B(C_6F_5)$_3$), 128.7, 128.6, 125.6, 125.1, 125.0, 124.8 (napht.), 128.0, 127.8, 124.2, 124.1, 123.8, 123.5 (Ph), 110.7 (C2), 100.8 (C3), 54.6 (C1), 30.8, 29.9, 29.5, 29.0 (each *i*-Pr–*C*H), 27 (br, C4), 25.2, 24.5, 24.1, 24.0, 23.4, 23.0, 22.4, 22.1 (each *i*-Pr–*C*H$_3$). ^{19}F-NMR (599.9 MHz, benzene-d_6, 298 K): $\delta = -166.2$ (m, 6F, *m*-B(C_6F_5)$_3$), −162.8 (t, $^3J_{FF} = 17$ Hz, 3F, *p*-B(C_6F_5)$_3$), −130.6 (m, 6F, *o*-B(C_6F_5)$_3$). $^{11}B\{^1H\}$-NMR (64.2 MHz, benzene-d_6, 298 K): $\delta = -14.0$. IR (KBr): $\tilde{\nu} = 2967$, 2932, 2874, 1644, 1516, 1458, 1389, 1276, 1084, 972, 799 cm^{-1}.

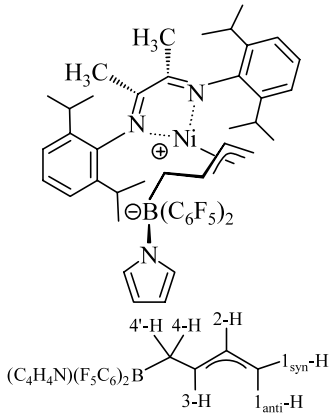
3.3. Addition of (*N*-pyrrolyl)B(C_6F_5)$_2$ (**5b**) to the (butadiene)nickel complex **4a**, formation of **7a**

3.3.1. NMR experiments

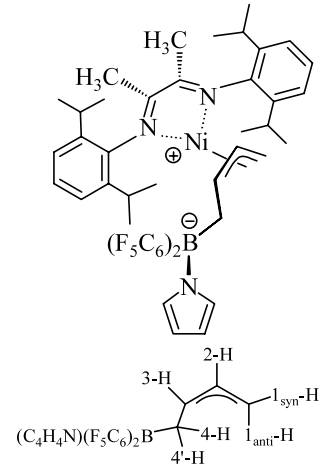
For the in situ generation of **7a** two separate solutions were prepared by dissolving **4a** (30.0 mg, 58.0 μmol) in 0.5 ml CD_2Cl_2 by **5b** (23.8 mg, 58.0 μmol) in 0.5 ml CD_2Cl_2. Then the borane solution was slowly added to the (butadiene)Ni solution by pipette. The resulting product solution was used to monitor the NMR spectra of **7a**.

3.3.2. Preparation of **7a**

At −78 °C a solution of 159 mg (386 μmol) of the boron reagent **5b** in 20 ml CH_2Cl_2 was added to a solution of **4a** (200 mg, 386 μmol) in 20 ml of dichloromethane. After 30 min the mixture was allowed to warm to r.t. and then stirred for 2 h. Solvent was removed in vacuo, the residue suspended in 50 ml of pentane and the solid collected by filtration. The product was washed with pentane (3 × 10 ml) and dried in vacuo to yield 292 mg (79%) of **7a**, m.p. 195 °C (dec.). Anal Calc. for $C_{48}H_{50}BF_{10}N_3Ni$ (*M* 928.4): C, 62.10; H, 5.43; N, 4.53. Found: C, 62.40; H, 5.86; N, 4.19%. A 90:10 mixture of *Z*-**7a** and *E*-**7a** was isolated. In solution a rearrangement was observed to yield a ca. 50:50 mixture of the isomers after 6 h at ambient temperature. Some NMR signals of the *E*-isomer were broad under the conditions of the NMR measurements.



^{1}H-NMR (599.9 MHz, CD_2Cl_2, 268 K): $\delta = 7.45$–7.26 (m, 6H, Ph), 6.39 (s, 2H, pyrrol), 5.85 (pt, 2H, pyrrol), 4.57 (d t, 1H, $^3J_{HH} = 13.4$ Hz, $^3J_{HH} = 8.0$ Hz, 2-H), 3.69 (br m, 1H, 3-H), 3.13, 3.05, 2.82, 2.71 (each sept, each 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.24 (d, 1H, $^3J_{HH} = 8.0$ Hz, 1_{syn}-H), 2.10-1.95 (br, 6H, NC-CH_3), 1.73 (m, 1H, 1_{anti}-H), 1.43, 1.32, 1.29, 1.28, 1.25, 1.22, 1.15, 1.08 (each d, each 3H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–CH_3), 0.87 (m, 1H, 4′-H), 0.10 (br, 1H, 4-H). $^{13}C\{^1H\}$-NMR (150.8 MHz, CD_2Cl_2, 268 K): $\delta = 147.5$ (dm, $^1J_{CF} = 230$ Hz, *o*-B(C_6F_5)$_3$), 138.1 (dm, $^1J_{CF} = 235$ Hz, *p*-B(C_6F_5)$_3$), 136.6 (d, $^1J_{CF} = 240$ Hz, *m*-B(C_6F_5)$_3$), 128.4, 128.2, 124.8 (br), 124.6 (br), 124.3 (br), 124.0 (each Ph), 123.0, 106.0 (pyrrol-*C*H), 114.4 (C2), 99.0 (C3), 29.6 (br), 29.5 (br), 29.1, 28.6 (each *i*-Pr–*C*H), 24.1, 23.6, 23.5, 23.3, 23.2, 23.1, 22.7, 22.6 (each *i*-Pr–*C*H$_3$).



^{1}H-NMR (599.9 MHz, CD_2Cl_2, 268 K): $\delta = 7.45$–7.26 (m, 6H, Ph), 6.20 (s, 2H, pyrrol), 5.80 (pt, 2H, pyrrol), 5.00 (dt, 1H, $^3J_{HH} = 15.0$ Hz, $^3J_{HH} = 8.0$ Hz, 2-H), 4.12 (br m, 1H, 3-H), 3.79, 3.15, 2.82, 2.56 (each sept, each 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.52 (dd, 1H, $^3J_{HH} = 8.0$ Hz, $^2J_{HH} = 1.8$ Hz, 1_{syn}-H), 2.10–1.95 (br,

6H, NC-CH_3), 2.08 (m, 1H, 1$_{anti}$-H), 1.51, 1.47 (each d, each 3H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–CH_3), 1.36 (br, 1H, 4′-H), 1.24-1.20 (m, 15H, *i*-Pr–CH_3), 1.15 (m, 1H, 4-H), 1.05 (d, 3H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–CH_3). ^{13}C{^{1}H}-NMR (150.8 MHz, CD_2Cl_2, 268 K): δ = 174.1 (br, *C*=N), 173.8 (*C*=N), 147.5 (dm, $^1J_{CF} = 230$ Hz, *o*-B(*C*$_6$F$_5$)$_3$), 143.8, 142.4 (*ipso*-Ph), 138.1 (dm, $^1J_{CF} = 235$ Hz, *p*-B(*C*$_6$F$_5$)$_3$), 138.8, 138.4, 138.3, 138.0 (each quart. *C*-CH(CH$_3$)$_2$), 136.6 (dm, $^1J_{CF} = 240$ Hz, *m*-B(*C*$_6$F$_5$)$_3$), 128.5, 128.4, 125.0, 124.5, 124.4, 124.3 (each Ph), 122.7, 106.3 (pyrrol), 110.8 (C2), 97.5 (C3), 53.8 (C1), 30.4 (br), 29.6 (br), 29.0, 28.6 (each *i*-Pr–*C*H), 25.0, 24.2, 24.1, 24.0, 23.7, 23.2, 22.4, 22.2 (each *i*-Pr–*C*H$_3$), 27, 20 (each br, NC-*C*H$_3$), 25 (br, C4). ^{19}F-NMR (599.9 MHz, benzene-d_6, 298 K): $\delta = -131.2$ (m, 6F, *o*-B(C$_6$*F*$_5$)$_3$), −158.4 (t, 3F, *p*-B(C$_6$F$_5$)$_3$), −162.6 (m, 6F, *m*-B(C$_6$*F*$_5$)$_3$). ^{11}B{^{1}H}-NMR (64.2 MHz, benzene-d_6, 298 K): $\delta = -6.9$. IR (KBr): $\tilde{\nu} = 2967$ (s), 2932 (w), 2731 (w), 1644 (m), 1458 (vs), 1385 (m), 1273 (w), 1215 (w), 1088 (s), 977 (s), 795 (m), 734 (m) cm^{-1}.

3.4. Reaction of (*N*-pyrrolyl)B(C$_6$F$_5$)$_2$ (**5b**) with **4b**, formation of **7b**

A solution of **5b** (134 mg, 326 μmol) in 20 ml of dichloromethane was added dropwise at −78 °C to a solution of **4b** (200 mg, 326 μmol) in 20 ml of dichloromethane. Work-up analogously as described above yielded 242 mg, (72%) of complex **7b**, m.p. 201 °C (dec.). Anal. Calc. for $C_{56}H_{50}BF_{10}N_3Ni$ (*M* 1024.5): C, 65.65; H, 4.92; N, 4.10. Found: C, 65.65; H, 4.36; N, 3.85%. IR (KBr): $\tilde{\nu} = 2963$ (s), 2932 (w), 2870 (w), 1644 (m), 1601 (w), 1501 (vs), 1458 (vs), 1385 (w), 1262 (m), 1088 (vs), 986 (m), 957 (s), 779 (s), 756 (m) cm^{-1}. The NMR spectra of the product **7b** were very broad, even when generated in situ, so that a characterization by NMR could not be achieved.

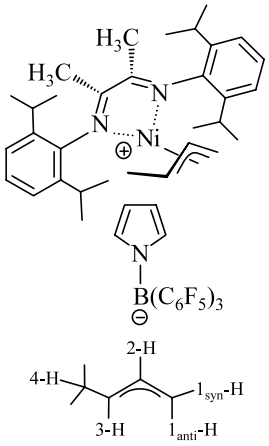
3.5. Reaction of **4a** with the 2H-pyrrol/B(C$_6$F$_5$)$_3$ adduct **8**, formation of **9a**

3.5.1. NMR experiments

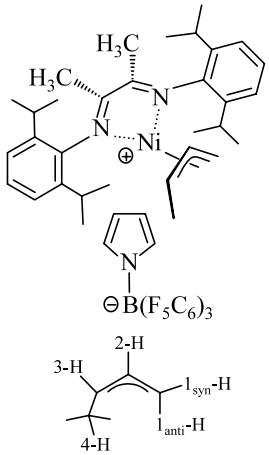
Complex **9a** was generated in situ by combining solutions of **4a** (20.0 mg, 38.7 μmol) in 0.5 ml CD_2Cl_2 and of **8** (22.4 mg, 38.7 μmol) in 0.5 ml of CD_2Cl_2. The NMR spectroscopic characterization of the products was carried out using the resulting product solution.

3.5.2. Preparation of **9a**

A solution of **8** (168 mg, 290 μmol) in 20 ml of dichloromethane was cooled to 0 °C. To this a solution of 150 mg (290 μmol) of **4a** in 20 ml of CH_2Cl_2 was added. The mixture was stirred for 6 h and worked up analogously as described above to yield 274 mg (86%) of **9a**, m.p. 204 °C. Anal. Calc. for $C_{54}H_{51}BF_{15}N_3Ni$ (*M* 1096.5): C, 59.15; H, 4.69; N, 3.83. Found: C, 58.90; H, 5.09; N, 3.39%. Initially a 90:10 ratio of *Z*-**9a** and *E*-**9a** was found that changed during 10 h at ambient temperature in solution to *Z*-**9a**:*E*-**9a** = 5:95.



^{1}H-NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 7.42-7.33 (m, 6H, Ph), 6.56 (s, 2H, pyrrol), 5.84 (s, 2H, pyrrol), 5.31 (ddd, 1H, $^3J_{HH} = 13.4$ Hz, $^3J_{HH} = 13.2$ Hz, $^3J_{HH} = 7.2$ Hz, 2-H), 3.30 (sept, 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 3.23 (dq, 1H, $^3J_{HH} = 13.4$ Hz, $^3J_{HH} = 6.3$ Hz, 3-H), 3.10, 2.81, 2.60 (each sept, each 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.60 (dd, 1H, $^3J_{HH} = 7.2$ Hz, $^2J_{HH} = 2.1$ Hz, 1$_{syn}$-H), 2.34 (dd, 1H, $^3J_{HH} = 13.2$ Hz, $^2J_{HH} = 2.1$ Hz, 1$_{anti}$-H), 2.16, 2.13 (each s, 3H, NC–CH_3), 1.41, 1.40, 1.35, 1.34, 1.28, 1.27, 1.21, 1.19 (each d, each 3H, $^3J_{HH} = \sim 6.8$ Hz, *i*-Pr–CH_3), −0.03 (d, 3H, $^3J_{HH} = 6.3$ Hz, 4-H). ^{13}C{^{1}H}-NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 176.8, 176.7 (each *C*=N), 148.4 (dm, $^1J_{CF} = 240$ Hz, *o*-B(*C*$_6$F$_5$)$_3$), 143.9, 141.7 (*ipso*-Ph), 137.7 (dm, $^1J_{CF} = 235$ Hz, *p*-B(*C*$_6$F$_5$)$_3$), 138.5, 138.0, 137.8, 137.5 (each quart. *C*–CH(CH$_3$)$_2$), 137.0 (dm, $^1J_{CF} = 240$ Hz, *m*-B(*C*$_6$F$_5$)$_3$), 129.4, 129.3, 125.5, 125.4, 125.2, 125.1 (Ph), 125.0, 105.9 (pyrrol), 119.4 (C2), 80.1 (C3), 59.7 (C1), 30.2, 29.8, 29.7, 29.5 (each *i*-Pr–*C*H), 24.5, 24.2, 23.8, 23.6, 23.3, 23.2, 23.1, 22.9 (each *i*-Pr–*C*H$_3$), 20.4, 20.1 (each NC-*C*H$_3$), 15.0 (C4).



^{1}H-NMR (599.9 MHz, CD_2Cl_2, 298 K): $\delta = 7.43$-7.40 (m, 6H, Ph), 6.56 (s, 2H, pyrrol), 5.84 (s, 2H, pyrrol), 5.56 (ddd, 1H, $^3J_{HH} = 14.5$ Hz, $^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 7.8$ Hz, 2-H), 3.62 (dq, 1H, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 6.3$ Hz, 3-H), 3.38 (sept, 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 3.09, 2.90 (each sept, each 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.86 (dd, 1H, $^3J_{HH} = 8.5$ Hz, $^2J_{HH} = 2.7$ Hz, 1_{syn}-H), 2.65 (sept, 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.53 (dd, 1H, $^3J_{HH} = 14.5$ Hz, $^2J_{HH} = 2.7$ Hz, 1_{anti}-H), 2.14, 2.12 (each s, 3H, NC–CH_3), 1.48, 1.46, 1.38, 1.34, 1.27, 1.25, 1.22, 1.14 (each d, each 3H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–CH_3), 0.60 (d, 3H, $^3J_{HH} = 6.3$ Hz, 4-H). ^{13}C{^{1}H}-NMR (150.8 MHz, CH_2Cl_2, 298 K): δ = 177.0, 176.8 (each *C*=N), 148.4 (dm, $^1J_{CF} = 240$ Hz, *o*-B(C_6F_5)$_3$), 143.5, 142.7 (*ipso*-Ph), 137.7 (dm, $^1J_{CF} = 235$ Hz, *p*-B(C_6F_5)$_3$), 138.6, 138.3, 138.0, 137.5 (each quart. *C*-CH(CH_3)$_2$), 137.0 (dm, $^1J_{CF} = 240$ Hz, *m*-B(C_6F_5)$_3$), 129.2, 129.1, 125.3, 125.2, 125.0, 124.9 (Ph), 125.0, 105.9 (pyrrol), 115.5 (C2), 79.2 (C3), 58.3 (C1), 30.4, 30.1, 29.4 (2x) (each *i*-Pr–*C*H), 24.6, 24.5, 24.3, 24.1, 23.5, 23.4, 23.2, 23.0 (each *i*-Pr–*C*H_3), 20.9, 20.0 (each NC–*C*H_3), 14.9 (C4). ^{19}F-NMR (599.9 MHz, benzene-d_6, 298 K): δ = −130.3 (m, 6F, *o*-B(C_6F_5)$_3$), −157.2 (t, 3F, *p*-B(C_6F_5)$_3$), −162.6 (m, 6F, *m*-B(C_6F_5)$_3$). ^{11}B{^{1}H}-NMR (64.2 MHz, benzene-d_6, 298 K): $\delta = -8.5$. IR (KBr): $\tilde{\nu} = 2971$ (m), 2874 (w), 1644 (m), 1516 (s), 1462 (vs), 1385 (m), 1277 (w), 1215 (s), 1088 (s), 980 (s), 795 (w) cm^{-1}.

3.6. Protonation of **4b** with the (2H-pyrrol)/B(C_6F_5)$_3$ adduct **8**, formation of *E*-**9b**

3.6.1. NMR experiments

Complex *E*-**9b** was in situ generated by the slow dropwise addition of a solution of 18.9 (32.6 μmol) of **8** in 0.4 ml of CD_2Cl_2 to a solution of 20.0 mg (32.6 μmol) of complex **4b** in 0.4 ml of CD_2Cl_2. Only the isomer *E*-**9a** was detected by NMR spectroscopy.

3.6.2. Preparation of *E*-**9b**

The reaction of **8** (189 mg, 326 μmol) with **4b** (200 mg, 326 μmol) was carried out at 0 °C in 40 ml CH_2Cl_2 analogously as described above. After stirring for 4 h at ambient temperature and the usual work-up 316 mg (81%) of the product *E*-**9b** was obtained, m.p. 212 °C (dec.). Anal. Calc. for $C_{62}H_{51}BF_{15}N_3Ni$ (M 1192.6): C, 62.44; H, 4.31; N, 3.52. Found: C, 62.25; H, 4.51; N, 3.26%.

^{1}H-NMR (599.9 MHz, CD_2Cl_2, 298 K): $\delta = 8.19$ (d, 2H, $^3J_{HH} = 8.0$ Hz, napht.), 7.57 (t, 2H, $^3J_{HH} = 8.0$ Hz, napht.), 7.54 (m, 2H, Ph), 7.48-7.44 (m, 4H, Ph), 6.80, 6.78 (each d, each 1H, $^3J_{HH} = 8.0$ Hz, napht.), 6.57, 5.88 (each s, each 2H, pyrrol), 5.53 (d t, 1H, $^3J_{HH} = 13.3$ Hz, $^3J_{HH} = 7.1$ Hz, 2-H), 3.66 (sept, 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 3.51 (dq, 1H, $^3J_{HH} = 13.3$ Hz, $^3J_{HH} = 6.4$ Hz, 3-H), 3.51, 3.14 (each sept, each 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.92 (dd, 1H, $^3J_{HH} = 7.1$ Hz, $^2J_{HH} = 2.1$ Hz, 1_{syn}-H), 2.90 (sept, 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.55 (dd, 1H, $^3J_{HH} = 13.3$ Hz, $^2J_{HH} = 2.1$ Hz, 1_{anti}-H), 1.48 (2 ×), 1.43, 1.42, 1.13, 1.11, 1.01, 0.98 (each d, each 3H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–CH_3), 0.17 (d, 3H, $^3J_{HH} = 6.4$ Hz, 4-H). ^{13}C{^{1}H}-NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 173.2, 173.1 (each *C*=N), 148.4 (dm, $^1J_{CF} = 240$ Hz, *o*-B(C_6F_5)$_3$), 147.8, 132.0 (napht.), 143.4, 141.3 (*ipso*-Ph), 138.8 (dm, $^1J_{CF} = 235$ Hz, *p*-B(C_6F_5)$_3$), 139.6, 139.4, 138.5, 138.4 (each quart. *C*–CH(CH_3)$_2$), 136.7 (dm, $^1J_{CF} = 240$ Hz, *m*-B(C_6F_5)$_3$), 129.6, 129.5, 126.5, 126.2, 125.2 (2 ×) (each Ph), 125.4, 105.8 (pyrrol), 118.7 (C2), 78.7 (C3), 59.0 (C1), 30.4, 30.1, 29.9, 29.6 (each *i*-Pr–*C*H), 24.9, 24.4, 23.8, 23.6, 23.3, 23.2, 23.0, 22.7 (each *i*-Pr–CH_3), 15.4 (C4). ^{19}F-NMR (599.9 MHz, benzene-d_6, 298 K): δ = −130.7 (m, 6F, *o*-B(C_6F_5)$_3$), −157.2 (t, 3F, *p*-B(C_6F_5)$_3$), -163.1 (m, 6F, *m*-B(C_6F_5)$_3$). ^{11}B{^{1}H}-NMR (64.2 MHz, benzene-d_6, 298 K): δ = −8.2. IR (KBr): $\tilde{\nu} = 2968$ (m), 2870 (w), 1644 (m), 1516 (s), 1462 (vs), 1277 (w), 1088 (m), 980 (m), 760 (w) cm^{-1}.

3.7. Reaction of **4a** with [Ph_3C^+][B(C_6F_5)$_4^-$] (**11**), formation of *Z*-**12a**

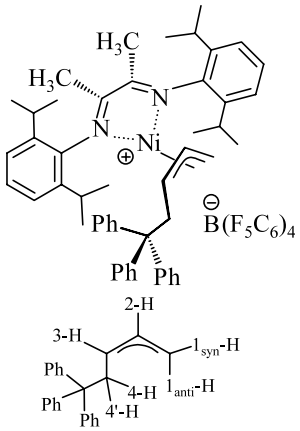
3.7.1. NMR experiments

Complex *Z*-**12a** was in situ generated by adding a solution of **4a** (53.5 mg, 58.0 μmol) in 0.5 ml CD_2Cl_2 to a solution of 30.0 mg (58 μmol) of **11** in CD_2Cl_2 at ambient temperature. The brown–violet solution was used to characterize the product by NMR spectroscopy; only the signals of *Z*-**12a** were observed.

3.7.2. Prepraration of *Z*-**12a**

A mixture of the reagents **11** (535 mg, 580 μmol) and **4a** (300 mg, 580 μmol) were placed in a Schlenk flask. Pre-cooled (−78 °C) dichloromethane (40 ml) was added. The mixture was stirred for 30 min at −78 °C, then allowed to warm to r.t. and stirred for further 4 h. Solvent was removed in vacuo and the residue sus-

pended in pentane (30 ml). The resulting solid was collected by filtration, washed with pentane (3 × 10 ml) and dried in vacuo to yield 634 mg (76%) of *Z*-**12a**, m.p. 243 °C. Anal. Calc. for $C_{75}H_{61}BF_{20}N_2Ni$ (*M* 1439.8): C, 62.57; H, 4.27; N, 1.95. Found: C, 63.07; H, 4.65; N, 1.85%.



^{1}H-NMR (599.9 MHz, CD_2Cl_2, 298 K): $\delta = 7.65$ (t, 1H, $^3J_{HH} = 7.8$ Hz, *p*-Ph), 7.56 (d, 1H, $^3J_{HH} = 7.8$ Hz, *m*-Ph), 7.50 (d, 1H, $^3J_{HH} = 7.8$ Hz, *m*-Ph), 7.36 (t, 1H, $^3J_{HH} = 7.8$ Hz, *p*-Ph), 7.32 (d, 1H, $^3J_{HH} = 7.8$ Hz, *m*-Ph), 7.28 (d, 1H, $^3J_{HH} = 7.8$ Hz, *m*-Ph), 7.16–7.12 (m, 9H, *o*- and *p*-CPh_3), 6.83–6.81 (m, 6H, *m*-CPh_3), 5.18 (dt, 1H, $^3J_{HH} = 15.0$ Hz, $^3J_{HH} = 8.2$ Hz, 2-H), 3.61 (ddd, 1H, $^3J_{HH} = 12.7$ Hz, $^3J_{HH} = 8.2$ Hz, $^2J_{HH} = 3.5$ Hz, 1H, 3-H), 3.38, 3.03, 3.02, 2.56 (each sept, each 1H, $^3J_{HH} =$ 6.8 Hz, *i*-Pr–C*H*), 2.60 (dd, 1H, $^2J_{HH} = 12.7$ Hz, $^2J_{HH} = 3.5$ Hz, 4′-H), 2.40 (dd, 1H, $^3J_{HH} = 8.2$ Hz, $^2J_{HH} = 1.6$ Hz, 1_{syn}-H), 2.18, 2.11 (each s, each 3H, NC-CH_3), 1.96 (dd, 1H, $^3J_{HH} = 15.0$ Hz, $^2J_{HH} = 1.6$ Hz, 1_{anti}-H), 1.64 (t, 1H, $J_{HH} = 12.9$ Hz, 4-H), 1.67, 1.44, 1.34, 1.26, 1.22, 1.20, 1.17, 1.12 (each d, each 3H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–CH_3). ^{13}C{^{1}H}-NMR (150.8 MHz, CD_2Cl_2, 298 K): $\delta = 177.2$, 176.7 (each *C*=N), 148.5 (dm, $^1J_{CF} = 250$ Hz, *o*-B(C_6F_5)$_4$), 145.5 (*ipso*-CPh_3), 143.2, 143.0 (*ipso*-Ph), 138.6 (dm, $^1J_{CF} = 250$ Hz, *p*-B(C_6F_5)$_4$), 139.0, 138.1, 137.9, 137.3 (each quart. *C*–$CH(CH_3)_2$), 136.7 (dm, $^1J_{CF} = 250$ Hz, *m*-B(C_6F_5)$_4$), 129.1, 128.4, 126.7 (*o*-, *m*- and *p*-Ph-CPh_3), 129.7, 129.3, 125.8, 125.6, 125.1, 124.9 (each Ph), 116.1 (C2), 76.9 (C3), 60.4 (C1), 58.1 (*C*Ph_3), 39.1 (C4), 30.6, 30.2, 29.7, 29.2 (each *i*-Pr–*C*H), 24.9, 24.8, 24.0, 23.9, 23.7, 23.5, 23.2, 22.8 (each *i*-Pr–*C*H_3), 20.8, 20.0 (each NC–*C*H_3). ^{19}F-NMR (599.9 MHz, benzene-d_6, 298 K): $\delta = -133.6$ (m, 6F, *o*-B(C_6F_5)$_3$), −164.3 (t, 3F, *p*-B(C_6F_5)$_3$), −168.1 (m, 6F, *m*-B(C_6F_5)$_3$). ^{11}B{^{1}H}-NMR (64.2 MHz, benzene-d_6, 298 K): $\delta = -14.9$. IR (KBr): $\tilde{\nu} =$ 3063 (w), 2971 (s), 2932 (m), 2874 (w), 1644 (s), 1515 (vs), 1466 (vs), 1381 (s), 1277 (m), 1088 (vs), 980 (vs), 722 (s) cm^{-1}.

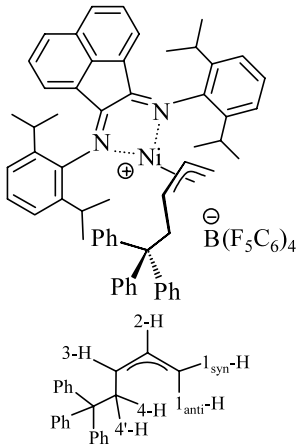
3.8. Reaction of $[Ph_3C^+][B(C_6F_5)_4^-]$ (**11**) with **4b**, formation of *Z*-**12b**

3.8.1. NMR experiments

For the NMR spectroscopic characterization *Z*-**12b** was generated in situ by slowly adding a solution of **11** (45.1 mg, 48.9 μmol) in 0.5 ml CD_2Cl_2 to a solution of **4b** (30.0 mg, 48.9 μmol) in 0.5 ml CD_2Cl_2. Only the formation *Z*-**12b** isomer was observed.

3.8.2. Preparation of *Z*-**12b**

Analogously as described above **11** (150 mg, 245 μmol) and **4b** (226 mg, 245 μmol) were reacted at −78 °C in dichloromethane (30 ml). The mixture was warmed to room temperature during 2 h and then stirred for 6 h. Work-up as described above yielded 300 mg (80%) of *Z*-**12b**, m.p. 245 °C. Anal. Calc. for $C_{83}H_{61}BF_{20}N_2Ni$ (*M* 1535.9): C, 64.91; H, 4.00; N, 1.82. Found: C, 64.58; H, 4.12; N, 1.99%.



^{1}H-NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 8.20 (d, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 8.19 (d, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 7.77 (t, 1H, $^3J_{HH} = 7.8$ Hz, *p*-Ph), 7.65 (dd, 2H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.2$ Hz, *m*-Ph), 7.59 (t, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 7.56 (t, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 7.48 (t, 1H, $^3J_{HH} = 7.8$ Hz, *p*-Ph), 7.44 (dd, 2H, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz, *m*-Ph), 7.39 (dd, 1H, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz, *m*-Ph), 7.18–7.14 (m, 9H, *o*- und *p*-CPh_3), 6.83–6.81 (m, 6H, *m*-CPh_3), 6.77 (d, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 6.74 (d, 1H, $^3J_{HH} = 7.8$ Hz, napht.), 5.42 (dt, 1H, $^3J_{HH} = 15.6$ Hz, $^3J_{HH} = 8.1$ Hz, 2-H), 3.82 (ddd, 1H, $^3J_{HH} = 12.8$ Hz, $^3J_{HH} = 8.1$ Hz, $^3J_{HH} = 3.3$ Hz, 1H, 3-H), 3.58, 3.43, 3.34, 3.01 (each sept, each 1H, $^3J_{HH} = 6.8$ Hz, *i*-Pr–C*H*), 2.76 (dd, 1H, $^2J_{HH} = 12.8$ Hz, $^3J_{HH} = 3.3$ Hz, 4′-H), 2.73 (dd, 1H, $^3J_{HH} = 8.1$ Hz, $^2J_{HH} = 1.6$ Hz, 1_{syn}-H), 2.33 (dd, 1H, $^3J_{HH} = 15.6$ Hz, $^2J_{HH} = 1.6$ Hz, 1_{anti}-H), 1.84 (t, 1H, $J_{HH} = 12.8$ Hz, 4-H), 1.69, 1.54, 1.30, 1.28, 1.14, 1.02, 1.00, 0.96 (each d, each 3H, $^3J_{HH} = \sim 6.8$ Hz, *i*-Pr–

CH_3). $^{13}C\{^1H\}$-NMR (150.8 MHz, CD_2Cl_2, 298 K): $\delta = 173.7$, 172.8 (each *C*=N), 148.5 (dm, $^1J_{CF} = 240$ Hz, *o*-B(C_6F_5)$_4$), 145.6 (*ipso*-CPh_3), 143.0, 142.9 (*ipso*-Ph), 138.6 (dm, $^1J_{CF} = 240$ Hz, *p*-B(C_6F_5)$_4$), 139.6, 138.7, 138.0, 137.6 (each quart. *C*–$CH(CH_3)_2$), 136.6 (dm, $^1J_{CF} = 240$ Hz, *m*-B(C_6F_5)$_4$), 133.8, 133.6, 130.0, 129.9, 126.1, 126.0 (napht.), 129.8, 129.5, 129.4, 126.3, 125.3 (each Ph), 129.1, 128.4, 126.8 (*o*-, *m*- und *p*-CPh_3), 115.6 (C2), 75.5 (C3), 60.3 (C1), 57.9 (CPh_3), 39.2 (C4), 30.5 (2x), 30.0, 29.6 (each *i*-Pr–*C*H), 25.4, 24.7, 24.1, 23.9, 23.9, 23.6, 23.4, 22.8 (each *i*-Pr–CH_3). ^{19}F-NMR (599.9 MHz, benzene-d_6, 298 K): $\delta = -133.1$ (m, 6F, *o*-B(C_6F_5)$_3$), −163.9 (t, 3F, *p*-B(C_6F_5)$_3$), −168.0 (m, 6F, *m*-B(C_6F_5)$_3$). $^{11}B\{^1H\}$-NMR (64.2 MHz, benzene-d_6, 298 K): $\delta = -14.5$. IR (KBr): $\tilde{\nu} = 3067$ (w), 2967 (vs), 2932 (m), 2874 (m), 1644 (s), 1612 (s), 1512 (vs), 1462 (vs), 1273 (s), 1088 (vs), 996 (vs), 776 (s) cm^{-1}.

3.9. Ethene polymerization

A 1-l thermostated glass autoclave (Büchi) was charged with 200 ml of dry toluene under argon. Triisobutylaluminum (0.5 ml) was added. The solution was then saturated with ethene at 2 bar with rapid stirring (700 U min^{-1}) at 25 °C. After 45 min the polymerization reaction was started by injection of a solution of ca. 35 μmol of the nickel catalyst in 10 ml toluene. After a reaction time of 1 h the mixture was quenched by adding 10 ml of a 1:1 mixture of methanol and 2 N aqueous HCl. After 20 min stirring and evaporation of excess ethene the formed polyethylene product was precipitated by adding 100 ml of methanol. The polymer was collected by filtration, washed with 2 N aqueous HCl, water and acetone (each 3 × 50 ml) and then dried over night at 50 °C in vacuo. For the characterization by ^{13}C-NMR spectroscopy (90.6 MHz) the respective polymer samples (ca. 60 mg) were dissolved in toluene-d_8 with heating, and the ^{13}C-NMR spectra recorded at 353 K. The typical NMR spectra of branched polyethylene were obtained [8,25]. The molecular weights and polydispersities of the polyethylene samples were obtained by GPC using an Agilent Series 1100 refractive index detector. The gel permeation chromatography was carried out in THF at 35 °C using two columns (100.000 and 1.000 Å). The M_n values listed in Table 2 are relative to a polystyrene standard.

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