Amines were distilled from $CaH_2$. Alkynes were degassed, flushed with argon, and stored over molecular sieves (4 Å). All experiments were carried out under an argon atmosphere.

Catalysts **1** and **2** were synthesized according to a literature procedure.[14a,b] Imines **4b**–**h** and **5** were isolated after distillation of the crude hydroamination mixtures and were characterized by NMR spectroscopy, MS, IR spectroscopy, and elemental analyses. Identification of all other products was performed by comparison with authentic products. Compounds **4a** and **4i** were synthesized according to the procedures in references [16] and [9], respectively.

Example of a typical hydroamination experiment (**4b**, Table 2, entry 2): A solution of 1-octyne (3.2 mL, 2.4 g, 21.5 mmol) and *tert*-butylamine (3.5 mL, 2.4 g, 32.2 mmol) was treated with **1** (0.15 g, 0.43 mmol, 2 mol %) in toluene (6 mL). This mixture was heated to 85 °C and distilled under vacuum after 24 h. Product **4b** was obtained at 48–49 °C (0.1 mbar); yield: 2.9 g (75 %, >98 % (GC) anti-Markovnikov product); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 0.85$ (t, 3H, $CH_3$), 1.14 (s, 9H, C-$CH_3$), 1.21–1.34 (m, 8H, $CH_2$), 1.46 (m, 2H, $CH_2$), 2.20 (m, 2H, $CH_2$), 7.56 ppm (t, $^3J$ = 5.35 Hz, 1H, CH); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$ ($CH_3$), 22.6, 26.4, 29.1, 29.2 ($CH_2$), 29.6 (C-$CH_3$), 31.7, 36.4 ($CH_2$), 56.4 ($C_q$), 159.3 ppm (CH); IR (neat): $\tilde{\nu}_{C=N}$: 1671 cm$^{-1}$; MS (EI, 70 eV): $m/z = 184$ [$M^+$+1], 183 [$M^+$], 168 [$M^+ - CH_3$], 99 [$C_7H_{15}^+$], 84 [$C_4H_9NCH^+$], 57 [$C_4H_9^+$]; elemental analysis $C_{12}H_{25}N$ calcd (%) C 78.62, H 13.74, N 7.64; found C 78.19, H 13.99, N 7.42.

Received: December 21, 2001 [Z18425]


[1] Reviews: a) M. Nobis, B. Driessen-Hölscher, *Angew. Chem.* **2001**, *113*, 4105–4108; *Angew. Chem. Int. Ed.* **2001**, *40*, 3983–3986; b) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–703; c) J.-J. Brunet, D. Neibecker in *Catalytic Heterofunctionalization* (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, **2001**, pp. 91–141; d) T. E. Müller, M. Beller in *Transition Metals for Organic Synthesis*, *Vol. 2* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**, pp. 316–330; e) E. Haak, S. Doye, *Chem. Unserer Zeit* **1999**, *33*, 297–303; f) J. J. Brunet, D. Neibecker, F. Niedercorn, *J. Mol. Catal.* **1989**, *49*, 235–259; g) R. Taube in *Applied Homogeneous Catalysis with Organometallic Compounds*, *Vol. 1* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1996**, S. 507–520.

[2] a) J. Barluenga, F. Aznar, *Synthesis* **1975**, 704–705; b) J. Barluenga, F. Aznar, *Synthesis* **1977**, 195–196; c) J. Barluenga, F. Aznar, R. Liz, R. Rodes, *J. Chem. Soc. Perkin Trans. 1* **1980**, 2732–2737.

[3] D. Tzalis, C. Koradin, P. Knochel, *Tetrahedron Lett.* **1999**, *40*, 6193–6195.

[4] a) E. Haak, I. Bytschkov, S. Doye, *Angew. Chem.* **1999**, *111*, 3584–3586; *Angew. Chem. Int. Ed.* **1999**, *38*, 3389–3391; b) E. Haak, S. Doye, *Org. Lett.* **2000**, *2*, 1935–1937; c) I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2001**, 4411–4418; d) E. Haak, I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2002**, 457–463.

[5] a) A. M. Baranger, P. J. Walsh, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 2753–2763; b) P. J. Walsh, A. M. Baranger, R. G. Bergman, *J. Am. Chem. Soc.* **1992**, *114*, 1708–1719.

[6] Y. Li, T. J. Marks, *Organometallics* **1996**, *15*, 3770–3772.

[7] a) A. Haskel, T. Straub, M. S. Eisen, *Organometallics* **1996**, *15*, 3773–3775; b) M. S. Eisen, T. Straub, A. Haskel, *J. Alloys Compd.* **1998**, *271–273*, 116–122; c) T. Straub, A. Haskel, T. G. Neyroud, M. Kapon, M. Botoshansky, M. S. Eisen, *Organometallics* **2001**, *20*, 5017–5035.

[8] a) M. Tokunaga, M. Eckert, Y. Wakatsuki, *Angew. Chem.* **1999**, *111*, 3416–3419; *Angew. Chem. Int. Ed.* **1999**, *38*, 3222–3225; b) M. Tokunaga, Y. Wakatsuki, *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 587–596; c) M. Heider, J. Henkelmann, T. Ruehl, Eur. Pat. Appl. EP 646571, **1995** [*Chem. Abstr.* **1995**, *123*, 22925s]; d) Y. Uchimaru, *Chem. Commun.* **1999**, 1133–1134; e) I. Kadota, A. Shibuya, L. Mpaka Lutete, Y. Yamamoto, *J. Org. Chem.* **1999**, *64*, 4570–4571.

[9] C. G. Hartung, A. Tillack, H. Trauthwein, M. Beller, *J. Org. Chem.* **2001**, *66*, 6339–6343.

[10] J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 2923–2924.

[11] F. Pohlki, S. Doye, *Angew. Chem.* **2001**, *113*, 2361–2364; *Angew. Chem. Int. Ed.* **2001**, *40*, 2305–2308.

[12] a) Y. Shi, J. T. Ciszewski, A. L. Odom, *Organometallics* **2001**, *20*, 3967–3969; b) C. Cao, J. T. Ciszewski, A. L. Odom, *Organometallics* **2001**, *20*, 5011–5013.

[13] a) M. Beller, M. Eichberger, H. Trauthwein, *Angew. Chem.* **1997**, *109*, 2306–2308; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2225–2227; b) M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, T. E. Müller, A. Zapf, *J. Organomet. Chem.* **1998**, *566*, 277–285; c) M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, T. E. Müller, *Eur. J. Inorg. Chem.* **1999**, 1121–1132; d) M. Beller, O. R. Thiel, H. Trauthwein, C. G. Hartung, *Chem. Eur. J.* **2000**, *6*, 2513–2522; e) A. Tillack, H. Trauthwein, C. G. Hartung, M. Eichberger, S. Pitter, A. Jansen, M. Beller, *Monatsh. Chem.* **2000**, *131*, 1327–1334; f) M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, J. Herwig, T. E. Müller, O. R. Thiel, *Chem. Eur. J.* **1999**, *5*, 1306–1319; g) H. Trauthwein, A. Tillack, M. Beller, *Chem. Commun.* **1999**, 2029–2030.

[14] a) V. V. Burlakov, U. Rosenthal, P. V. Petrovskii, V. B. Shur, M. E. Vol'pin, *Organomet. Chem. USSR* **1988**, *1*, 526; b) V. V. Burlakov, U. Rosenthal, R. Beckhaus, A. V. Polyakov, Y. T. Struchkov, G. Oehme, V. B. Shur, M. E. Vol'pin, *Organomet. Chem. USSR* **1990**, *3*, 237–238; c) A. Tillack, C. Lefeber, N. Peulecke, D. Thomas, U. Rosenthal, *Tetrahedron Lett.* **1997**, *38*, 1533–1534; d) N. Peulecke, D. Thomas, W. Baumann, C. Fischer, U. Rosenthal, *Tetrahedron Lett.* **1997**, *38*, 6655–6656; e) N. Peulecke, A. Ohff, P. Kosse, A. Tillack, A. Spannenberg, R. Kempe, W. Baumann, V. V. Burlakov, U. Rosenthal, *Chem. Eur. J.* **1998**, *4*, 1852–1861; f) S. Pulst, F. G. Kirchbauer, B. Heller, W. Baumann, U. Rosenthal, *Angew. Chem.* **1998**, *110*, 2029–2031; *Angew. Chem. Int. Ed.* **1998**, *37*, 1915–1927; g) P. Arndt, A. Spannenberg, W. Baumann, S. Becke, U. Rosenthal, *Eur. J. Inorg. Chem.* **2001**, 2885–2890; Rosenthal's catalysts are now commercially available from Fluka.

[15] N. Peulecke, Ph.D. thesis, Rostock, **1997** describes an amination of trimethylsilylacetylene and phenylacetylene with aniline in the presence of **1** with a maximum yield of 50 %. However, other amines, such as *tert*-butylamine, do not react.

[16] N. Y. Grigor'eva, I. M. Avrutov, O. A. Pinsker, O. N. Yudina, A. I. Lutsenko, A. M. Moiseenkov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1985**, *8*, 1824–1835.


# Formation of a Butadienenickel-Based Zwitterionic Single-Component Catalyst for Ethylene Polymerization: An Alternative Activation Pathway for Homogeneous Ziegler–Natta Catalysts of Late Transition Metals**

Joachim W. Strauch, Gerhard Erker,* Gerald Kehr, and Roland Fröhlich

Homogeneous Ziegler–Natta catalysis has become very important in recent years.[1] In addition to the many reported catalysts based on metallocenes with metals from Group 4 and related systems, a variety of Ziegler–Natta systems of late

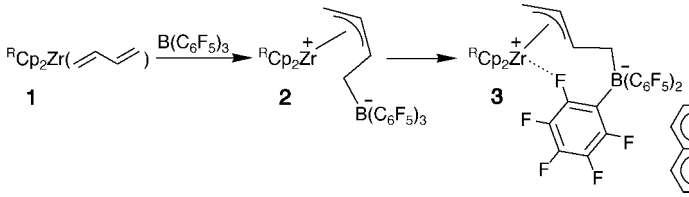
[*] Prof. Dr. G. Erker, Dipl.-Chem. J. W. Strauch, Dr. G. Kehr, Dr. R. Fröhlich[+]
Organisch-Chemisches Institut der Universität
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
Fax: (+49) 251-833-36503
E-mail: erker@uni-muenster.de

[+] X-ray crystal structure analysis.

[**] This work was supported by the Fonds der Chemischen Industrie (and the BMBF) and the Deutsche Forschungsgemeinschaft.

transition metal catalysts have significantly contributed to the expansion of this field, especially those derived from complexes with chelating imine ligands.[2] In all such systems, regardless of whether they are based on the early or late d-metal components, the catalytically active species is an alkylmetal complex cation $L_nMR^+$ (or its ion-pair equivalent[3]). In the case of the ubiquitous use of methylalumoxane (MAO) activation, this is usually generated in situ by alkylation of the corresponding metal dihalide derivative, followed by transfer of an alkyl anion equivalent. A variety of other activator components, for example $B(C_6F_5)_3$, $R_3C^+$, or $R_3NH^+$,[4] have also been used successfully for this purpose.

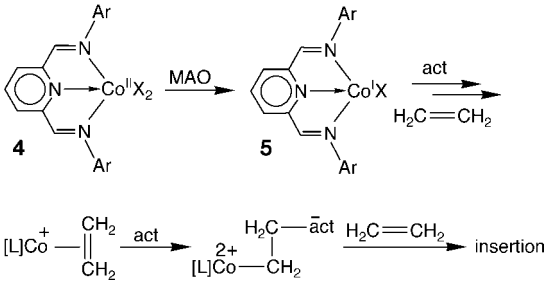
We have previously developed an alternative method of activation of homogeneous Ziegler–Natta catalysts containing metallocenes with transition metals from Group 4 and related systems: Treatment of the butadienezirconocene complexes **1** with $B(C_6F_5)_3$ results in the formation of the zwitterionic metallocene systems **3** (Scheme 1). These systems are active neutral single-component catalysts for olefin




Scheme 1. Formation of **3** by addition of $B(C_6F_5)_3$ to **1**.

polymerization that do not require the addition of further activating components.[5] The systems **3** have allowed some detailed mechanistic studies of the alkene C–C coupling steps taking place at such catalyst systems.[6] We report here, to our knowledge for the first time, the preparation of a related zwitterionic "butadiene-borate" Ziegler–Natta catalyst system of a late transition metal by addition of the electrophilic borane $B(C_6F_5)_3$ to a butadienenickel(0) complex.

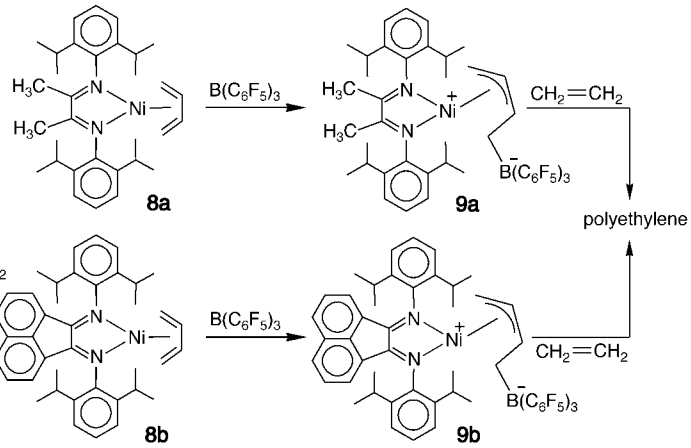
This development may be of specific importance in view of some recent observations made with late transition metal Ziegler–Natta catalysts. Treatment of bis(imine)halogenocobalt(II) chelate complexes **4** with MAO[7, 8] led to the reduction to the respective $Co^I$ complexes **5** rather than to alkylation (Scheme 2).[9, 10] Subsequent alkylation of **5** followed by methyl anion abstraction must then lead to a σ-alkyl ligand free cation which can be considered a direct precursor of the active catalyst species, although it lacks the essential metal–




Scheme 2. Reduction of **4** to give **5** and subsequent alkylation.

carbon σ bond.[11] One potential explanation for the observed catalytic olefin polymerization features of this system is based on the assumption that the activating Lewis acid might have been added to a cationic intermediate $[L]_nCo(ethylene)^+$ complex (see Scheme 2). Our new reaction, in which a bis(imine)nickel chelate complex participates, represents a vinylogous analogue of such an activation pathway in which a σ-alkyl group does not participate.

Treatment of [{biacetylbis(2,6-diisopropylphenylimine)}-$NiBr_2$] with the oligomeric "butadiene-magnesium" reagent[12] gave the known ($\eta^4$-butadiene)nickel complex (**8a**; Scheme 3).[13] The addition of $B(C_6F_5)_3$[14] to **8a** took place cleanly to yield the chelate complex **9a** (81% yield of isolated




Scheme 3. Formation of the catalysts **9a** and **9b** for the polymerization of ethylene.

product). Single crystals of **9a** for the X-ray structure analysis were obtained from benzene (Figure 1). The structure of **9a** shows the presence of the bis(imine) chelate ligand stabilizing the central Ni atom (Ni–N1 1.920(1), Ni–N2 1.951(1) Å). The C=N bonds in the five-membered metallacycle are short (C11–N1/C21–N2 1.289(2), C11–C21 1.493(2) Å). The planes of the bulky aryl groups are rotated considerably from the plane of the central metallacycle, but in different directions (dihedral angles C14-C13-N1-C11 −107.4(2), C24-C23-N2-C21 76.0(2)°), a structural feature that evidently occurs because of the unsymmetrical substitution pattern at the remaining ligand at the Ni center. The bulky $B(C_6F_5)_3$ reagent adds regioselectively at the terminal C4 carbon atom of the former butadiene ligand (C4–B 1.672(3) Å); the cisoid arrangement of the butadiene framework is preserved. Thus **9a** contains an *anti*-configurated monosubstituted $\eta^3$-allyl ligand (*Z*-configurated at the C2–C3 bond). The bulky borate group is rotated as much as possible away from the core of the nickel complex[15] (Ni-C3-C4-B 176.0(1)°, the Ni–C4 distance is 2.803(2) Å). The Ni–C1 (2.007(2) Å) and Ni–C3 bonds (2.048(2) Å) are slightly longer than the central Ni–C2 bond (1.968(2) Å) of the (π-allyl)nickel group. C1 and C3 of the π-allyl group lie almost in the bis(imine)nickel plane (N1-Ni-C3 169.1(1), N2-Ni-C1 172.4(1)°). The C1–C2 and C2–C3 bonds are equal in length (1.401(3) Å, C1-C2-C3 120.4(2)°), the C3–C4 bond as expected is longer (1.490(3) Å).

  1433-7851/02/4114-2544 $ 20.00+.50/0 *Angew. Chem. Int. Ed.* **2002**, *41*, No. 14

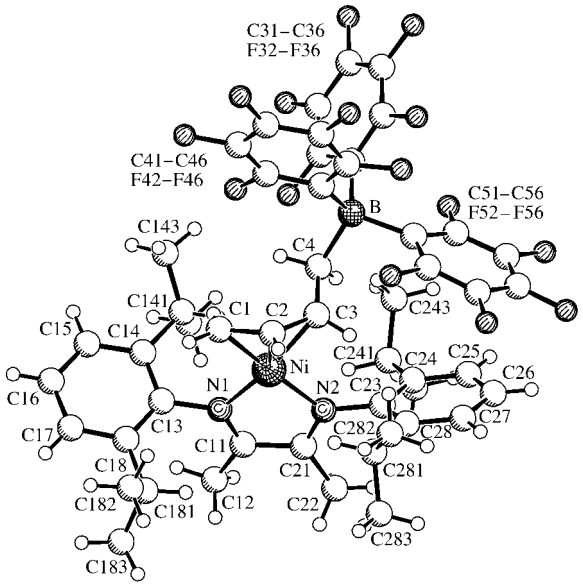



Figure 1. Stucture of complex **9a**. Selected bond lengths [Å] and angles [°]: Ni-C1 2.007(2), Ni-C2 1.968(2), Ni-C3 2.048(2), Ni-C4 2.803(2), Ni-N1 1.920(1), Ni-N2 1.951(1), C1-C2 1.401(3), C2-C3 1.401(3), C3-C4 1.490(3), C4-B 1.672(3), B-C31 1.659(3), B-C41 1.665(3), B-C51 1.653(3), N1-C13 1.448(2), N1-C11 1.289(2), C11-C21 1.493(2), C21-N2 1.289(2), N2-C23 1.449(2); C1-Ni-C2 41.3(1), C1-Ni-C3 73.7(1), C1-Ni-N1 103.5(1), C1-Ni-N2 172.4(1), C2-Ni-C3 40.8(1), C2-Ni-N1 141.2(1), C2-Ni-N2 131.4(1), C3-Ni-N1 169.1(1), C3-Ni-N2 101.1(1), N1-Ni-N2 82.7(1), Ni-C1-C2 67.9(1), Ni-C2-C1 70.9(1), Ni-C2-C3 72.7(1), Ni-C3-C2 66.5(1), Ni-C3-C4 103.7(1), C1-C2-C3 120.4(2), C2-C3-C4 127.2(2), C3-C4-B 114.4(1), C13-N1-Ni 124.7(1), C11-N1-Ni 114.5(1), C11-N1-C13 120.8(1), N1-C11-C21 114.5(2), C11-C21-N2 114.2(1), C23-N2-Ni 126.2(1), C21-N2-Ni 113.4(1), C21-N2-C23 120.2(1); for further values see text.

NMR spectra indicate an analogous structure of complex **9a** in solution. The signal patterns of the two bis(imine) ligands differ owing to the presence of the substituted $\eta^3$-allyl ligand ($^1$H and $^{13}$C NMR: signals of the methyl groups at $\delta =$ 1.16/1.15 and 19.5/18.4 ppm, respectively). The π-allyl group shows characteristic $^{13}$C NMR resonances at $\delta = 54.3$ (C1), 110.9 (C2), and 100.7 ppm (C3), and there is a broad signal ($\delta = 26$ ppm) corresponding to the C4 atom bound to the boron atom. The $^1$H NMR spectrum of **9a** shows the typical signals for π-allyl groups at $\delta = 2.57$ (1-H$_{syn}$), 2.69 (1-H$_{anti}$), and 4.88 (2-H$_{meso}$) with typical coupling constants of 7.2 Hz ($^3J$(H$_{syn}$,H$_{meso}$)) and 14.3 Hz ($^3J$(H$_{anti}$,H$_{meso}$)), and signals of the diastereotopic hydrogen atoms 4-H/4-H′ at $\delta = 2.00$ and 1.03 ppm. The acenaphthenequinonebis(imine)-derived complex **9b** was prepared analogously. It shows very similar spectroscopic features, and thus must be considered to have an analogous *anti*-configurated π-allyl unit.

Complexes **9a** and **9b** are active Ziegler–Natta single-component catalysts for ethylene polymerization, which do not require the presence of an additional activator component; however, some triisobutylaluminum was added as a "scrubbing agent" in the experiments on a preparative scale, as is usually done to prevent catalyst deactivation by hydrolysis pathways at the very low metal complex concentrations that were employed. At 25 °C and a monomer pressure of 2 bar, polyethylene(PE) was formed with the **9a** catalyst with an activity (*a*) of 159 kg(PE) mol(Ni)$^{-1}$ h$^{-1}$ bar(ethene)$^{-1}$. The catalyst **9b** is only slightly less active under the same conditions ($a = 106$). The resulting polyethylene has a branched structure, as typically formed with such homogeneous organometallic Ziegler–Natta nickel catalysts.[2, 16]

The catalysts **9a** and **9b** are the first examples of the successful application of the metal/butadiene/borane activation method to generate active homogeneous Ziegler–Natta catalyst systems based on typical late transition metal complexes. The isolated and structurally characterized complexes may be structurally and chemically related to the active intermediates in the recently disclosed "alkyl group free" Ziegler–Natta systems (Scheme 2).[7, 8] It appears that the addition of an activator component, such as B(C$_6$F$_5$)$_3$ or even potentially MAO, to a suitable metal alkene π complex might be a suitable general method for forming (or generating in situ) active homogeneous Ziegler–Natta-type catalysts for alkene polymerization.

## *Experimental Section*

**9a**: A solution of B(C$_6$F$_5$)$_3$ (198 mg, 387 μmol) in toluene (15 mL) was added dropwise with stirring to a solution of the butadienenickel complex **8a** (200 mg, 387 μmol) in toluene (15 mL) at −78 °C. The mixture was warmed to room temperature and then stirred for 2 h. The solvent was removed in vacuo and the residue suspended in pentane (20 mL). The product was collected by filtration, washed with pentane (2 × 20 mL), and dried in vacuo. Yield of **9a**: 321 mg (81 %), m.p. 212 °C (decomp); elemental analysis (%) calcd for C$_{50}$H$_{46}$BF$_{15}$N$_2$Ni (1029.4): C 58.34, H 4.50, N 2.72; found: C 58.64, H 4.81, N 2.76; $^1$H NMR ([D$_8$]toluene, 600 MHz, 298 K): $\delta = 7.26$ (t, 1H), 7.09 (d, 1H), 7.05 (m, 2H), 6.96 (2d, 2H; aryl), 4.88 (m, 1H; $^3J = 14.3$ Hz and 7.2 Hz, allyl 2-H), 4.21 (br., 1H; 3-H), 2.69 (d, 1H; 1-H$_{anti}$), 2.57 (d, 1H; 1-H$_{syn}$), 2.00, 1.03 (br. each 1H, 4-H/H′) 3.73, 2.98, 2.64, 2.29 (sept., each 1H; -C*H*Me$_2$), 1.57, 1.49, 1.12, 1.01, 0.98, 0.97, 0.92, 0.77 (d, each 3H; -CH(C*H*$_3$)$_2$), 1.16, 1.15 ppm (s, 3H each, N=C-CH$_3$); $^{13}$C NMR ([D$_6$]benzene, 150.8 MHz, 298 K): $\delta = 173.1$, 172.5 (-C=N-), 148.1 ($^1J_{C,F} =$ 240 Hz), 138.4 ($^1J_{C,F} = 250$ Hz), 136.7 ($^1J_{C,F} = 250$ Hz; *o*-, *p*-, *m*-B(C$_6$F$_5$)$_3$), 143.1, 141.1 (arom. C1), 138.2, 137.6, 137.5, 136.0 (arom. C2, C6), 128.0, 127.8, 124.2, 124.1, 123.8, 123.5 (arom. CH), 110.9 (allyl-C2), 100.7 (C3), 54.3 (C1), ∼26 (br., C4), 30.6, 29.5, 29.1, 28.6 (-*C*HMe$_2$), 24.4, 24.2, 24.0, 23.9, 23.3, 22.7, 22.2, 22.1 (-CH(*C*H$_3$)$_2$), 19.5, 18.4 ppm (-N=C-CH$_3$).

X-ray crystal structure analysis of **9a**: C$_{50}$H$_{46}$BF$_{15}$N$_2$Ni · 0.5 C$_6$H$_6$, $M_r =$ 1068.46, dark red crystal 0.50 × 0.40 × 0.30 mm, $a = 14.550(1)$, $b =$ 23.070(1), $c = 15.141(1)$ Å, $\beta = 99.91(1)°$, V = 5006.5(5) Å$^3$, $\rho_{calcd} =$ 1.418 g cm$^{-3}$, $\mu = 4.82$ cm$^{-1}$, empirical absorption correction via SORTAV ($0.795 < T < 0.869$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda =$ 0.71073 Å, T = 198 K, $\omega$ and $\varphi$ scans, 31004 reflections collected (± *h*, *k*, *l*), $((\sin\theta)/\lambda) = 0.65$ Å$^{-1}$, 11452 independent ($R_{int} = 0.035$) and 9345 observed reflections ($I > 2\sigma(I)$), 659 refined parameters, $R = 0.040$, w$R^2 =$ 0.93, max. residual electron density ±0.43 e A$^{-3}$, hydrogen atoms calculated and refined as riding atoms. Data set was collected with a Nonius Kappa CCD diffractometer, equipped with a rotating anode generator Nonius FR 591, for programs used see reference [17].

CCDC-180390 contains the supplementary crystallographic data for this paper. These data can be can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

**9b**: Treatment of **8b** (200 mg, 326 μmol) with B(C$_6$F$_5$)$_3$ (16.7 mg, 326 μmol) was carried out analogously to that for **9a**. Yield **9b**: 334 mg (91 %), m.p. 182 °C (decomp); elemental analysis (%) calcd for C$_{58}$H$_{46}$BF$_{15}$N$_2$Ni (1125.5): C 61.90, H 4.12, N 2.49; found: C 62.09, H 4.57, N 2.40; $^1$H NMR ([D$_6$]benzene, 600 MHz, 298 K): $\delta = 7.40$ (t, 1H), 7.20 (d, 1H), 7.19–7.13 (m, 4H; Ph), 7.13, 7.08, 6.62, 6.59, 6.54, 6.47 (acenapht. H), 5.10 (1H; allyl 2-H), 4.64 (1H; 3-H), 2.99 (1H; 1-H$_{anti}$), 2.87 (1H; 1-H$_{syn}$), 2.32, 1.45 (br., each 1H; 4-H/H′), 4.04, 3.41, 3.17, 2.84 (sept., each 1H; -C*H*Me$_2$), 1.57, 1.53, 1.45, 1.20, 1.03, 0.96, 0.77, 0.74 ppm (d, each 3H; -CH(C*H*$_3$)$_3$).

  1433-7851/02/4114-2545 $ 20.00+.50/0 

Polymerization reactions: A 1-L glass autoclave was charged with toluene (200 mL) and triisobutylaluminum (0.5 mL). The mixture was stirred (700 rpm), thermostated at 25 °C, and saturated with ethylene (2 bar). The polymerization reaction was started by the injection of a solution of the respective zwitterionic complex in toluene, generated in situ by treatment of **8a** or **8b** (ca. 35 μmol) with an equimolar amount of $B(C_6F_5)_3$ in toluene (8 mL). After 1 h the reaction was quenched by adding aqueous HCl in methanol (15 mL). The polymer was precipitated with additional methanol (100 mL), collected by filtration, washed with 6 N aqueous HCl (100 mL), water (200 mL), acetone (50 mL), and then dried in vacuo.

Received: March 20, 2002 [Z18937]


[1] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255 – 1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143 – 1170.

[2] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448 – 468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428 – 447; S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169 – 1203.

[3] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015 – 10031.

[4] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99 – 149; X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623 – 3625; J. C. W. Chien, W.-M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.* **1991**, *113*, 8570 – 8571; M. Bochmann, A. J. Jaggar, J. C. Nicholls, *Angew. Chem.* **1990**, *102*, 830 – 832; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 780 – 782; review: E. Y.-X. Chen, T. J. Marks, *Chem.Rev.* **2000**, *100*, 1391 – 1434.

[5] B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem.* **1995**, *107*, 1867 – 1869; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1755 – 1757; review: G. Erker, *Acc. Chem. Res.* **2001**, *34*, 309 – 317.

[6] M. Dahlmann, G. Erker, M. Nissinen, R. Fröhlich, *J. Am. Chem. Soc.* **1999**, *121*, 2820 – 2828; M. Dahlmann, G. Erker, K. Bergander, *J. Am. Chem. Soc.* **2000**, *122*, 7986 – 7998.

[7] T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2001**, *113*, 4855 – 4858; *Angew. Chem. Int. Ed.* **2001**, *40*, 4719 – 4722.

[8] V. C. Gibson, M. J. Humphries, K. P. Tellmann, D. F. Wass, A. J. P. White, D. J. Williams, *Chem. Commun.* **2001**, 2252 – 2253.

[9] Electron transfer had previously been observed or used in activation processes of metallocene Ziegler – Natta catalysts: R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325 – 387.

[10] For recent evidence of electron-transfer processes occurring in $B(C_6F_5)_3$ activation chemistry see, for example: C. J. Harlan, T. Hascall, E. Fujita, J. R. Norton, *J. Am. Chem. Soc.* **1999**, *121*, 7274 – 7275; C. J. Beddows, A. D. Burrows, N. G. Connelly, M. Green, J. M. Lynam, T. J. Paget, *Organometallics* **2001**, *20*, 231 – 233; R. J. Kwaan, C. J. Harlan, J. R. Norton, *Organometallics* **2001**, *20*, 3818 – 3820.

[11] For a formally related homogeneous alkyl-free Group 4 metal Ziegler – Natta catalyst see: J. Cano, P. Royo, M. Lanfranchi, M. A. Pellinghelli, A. Tiripicchio, *Angew. Chem.* **2001**, *113*, 2563 – 2565; *Angew. Chem. Int. Ed.* **2001**, *40*, 2495 – 2497, J. Jin, D. R. Wilson, E. Y.-x. Chen, *Chem. Commun.* **2002**, 708 – 709, and references therein.

[12] H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, K. Lee, A. Nakamura, *Organometallics*, **1982**, *1*, 388 – 396, and references therein.

[13] J. C. M. Sinnema, G. H. B. Fendesak, H. tom Dieck, *J. Organomet. Chem.* **1990**, *390*, 237 – 250.

[14] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245 – 250; A. G. Massey, A. J. Park in *Organometallic Synthesis*, *Vol. 3,* (Eds.: R. B. King, J. J. Eisch), Elsevier, New York, **1986**, p. 461.

[15] For structurally related metallocene complexes with metals of Group 4 see: J. Karl, G. Erker, R. Fröhlich, *J. Organomet. Chem.* **1997**, *535*, 59 – 62; M. Dahlmann, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **2000**, *19*, 2956 – 2967.

[16] The resulting polyethylene contains mostly methyl branches, as expected: L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414 – 6415; C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 11664 – 11665; C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics* **1997**, *16*, 2005 – 2007; B. L. Small, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 7143 – 7144; S. A. Svejda, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **1999**, *121*, 10634 – 10635; NMR characterization: G. B. Galland, R. F. de Souza, R. S. Mauler, F. F. Nunes, *Macromolecules* **1999**, *32*, 1620 – 1625.

[17] Programs used: data collection COLLECT (B. V. Nonius, **1998**), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymol.* **1997**, *276*, 307 – 326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33 – 37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421 – 426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467 – 473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**).


## Photoactivatable Synthetic Ras Proteins: "Baits" for the Identification of Plasma-Membrane-Bound Binding Partners of Ras**

Jürgen Kuhlmann,* Andreas Tebbe, Martin Völkert, Melanie Wagner, Koji Uwai, and Herbert Waldmann*

The regulation of cell growth and differentiation by proteins of the Ras superfamily[1] requires the correct subcellular distribution of the small GTP-binding proteins (GTP = guanosine triphosphate).[2] The biological function of Ras is strictly dependent on its correct translocation to the plasma membrane, and this localization is directly linked to posttranslational S-farnesylation and S-palmitoylation of Ras.[3]

The real mechanism of translocation is still the subject of debate. On the one hand for K-Ras$^B$, which embodies a polycationic hexalysine stretch and a farnesyl thioether at the C terminus, a model was proposed in which unspecific but highly anionic "sites" (formed at least in part by the lipid bilayer) at the plasma membrane instead of a classical specific proteinaceous receptor are responsible for association of this Ras isoform with the plasma membrane.[4] On the other hand for H- and N-Ras, which have S-farnesyl and S-palmitoyl substituents at the C terminus, a membrane-trapping model[5] was postulated in which a prenyl protein specific palmitoyl-

[*] Dr. J. Kuhlmann, Dipl.-Biochem. A. Tebbe,
Dipl.-Biochem. M. Wagner
Max-Planck-Institut für molekulare Physiologie
Abteilung Strukturelle Biologie
Otto-Hahn-Strasse 11, 44227 Dortmund (Germany)
Fax: (+49) 231-133-1435
E-mail: juergen.kuhlmann@mpi-dortmund.mpg.de
Prof. Dr. H. Waldmann, Dipl.-Chem. M. Völkert, Dr. K. Uwai
Max-Planck-Institut für molekulare Physiologie
Abteilung Chemische Biologie
Otto-Hahn-Strasse 11, 44227 Dortmund (Germany)
and
Fb. 3, Organische Chemie, Universität Dortmund
Otto-Hahn-Strasse 6, 44227 Dortmund (Germany)
Fax: (+49) 231-133-2499
E-mail: herbert.waldmann@mpi-dortmund.mpg.de

[**] We thank Christine Nowak for excellent technical assistance, Lilianna Wielitzek for help with the UV exposure system, and Fred Wittinghofer for continuous encouragement. The work was supported by the Fonds der Chemischen Industrie and the Alexander von Humboldt Foundation.

  1433-7851/02/4114-2546 $ 20.00+.50/0 