ELSEVIER

Journal of Organometallic Chemistry 488 (1995) 177–182

Journal of Organo metallic Chemistry

Oxidative η^2-iminoacyl formation by reaction of amidozirconocene complexes with tris(pentafluorophenyl)borane ☆

Bodo Temme, Gerhard Erker *

Organisch-Chemisches Institut der Universität Münster, Correnstraße 40, D-48149 Münster, Germany

Received 9 July 1994

Abstract

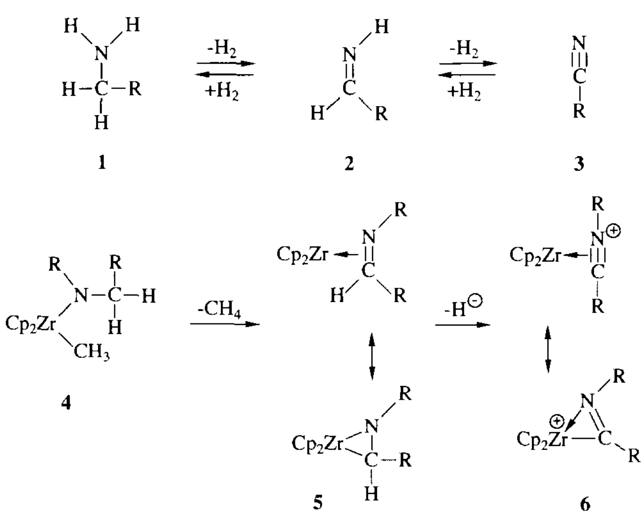
Methyl(*N*-pyrrolyl)zirconocene (**8a**) reacts with tris(pentafluorophenyl)borane selectively by transfer of the heterocyclic ligand to give the methylzirconocene cation, which is an active ethylene polymerization catalyst when generated in situ in toluene. In contrast, (diethylamido)methylzirconocene (**8b**) undergoes only transfer of the methyl group when treated with the $B(C_6F_5)_3$ Lewis acid, to give the (diethylamido)zirconocene cation (**10b**). The $[(Et_2N)ZrCp_2^+\ MeB(C_6F_5)_3^-]$ salt is not stable and rapidly reacts at room temperature with methane elimination and formation of a cationic (η^2-iminoacyl)metallocene system. The resulting $[Cp_2Zr(\eta^2\text{-}MeC{=}NEt)^+\ HB(C_6F_5)_3^-]$ species (**11b**) is isolated with an 84% yield. Methyl(*N*-piperidyl)zirconocene (**8c**) reacts similarly when treated with $B(C_6F_5)_3$ to give the (η^2-iminoacylium)zirconocene (**11c**) via the intermediate **10a**.

Keywords: Boron; Iminoacyl; Zirconocene

1. Introduction

Organic aldimines (**2**) can be reduced by the addition of dihydrogen to yield amines (**1**). They can also be oxidized and lose one equivalent of dihydrogen to give nitriles (**3**). In the coordination sphere of a Group 4 metallocene complex, formal equivalents of the **1**-to-**2** transformations are common; the thermally induced methane elimination from **4** to give **5** is a typical example [1] (Scheme 1). The (η^2-imine)zirconocene product (**5**) exhibits a pronounced σ-complex character and can probably be regarded as a metallacyclic three-membered ring system [2]. In a very formal sense the transformation of such an (η^2-aldimine)metallocene (**5**) to a cationic "(η^2-nitrilium)metal complex" (**6**) would correspond to the organic **2**-to-**3** oxidation on an organometallic level.

Of course, the resulting product **6** should really be termed a (η^2-iminoacyl)metallocene cation. A large number of (η^2-iminoacyl) Group 4 metal complexes are known [3], but only a very small number of (η^2-iminoacyl)metallocene cations (or structural equivalents thereof) have been described so far [4,5]. Such species are usually prepared by isonitrile insertion into neutral or cationic σ-hydrocarbyl metallocene complexes [3,6]. To our knowledge a cationic species of type **6** has never been prepared by a variant of the above-mentioned formal oxidation process starting from a dialkyl-



Scheme 1

☆ Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday.

* Corresponding author.

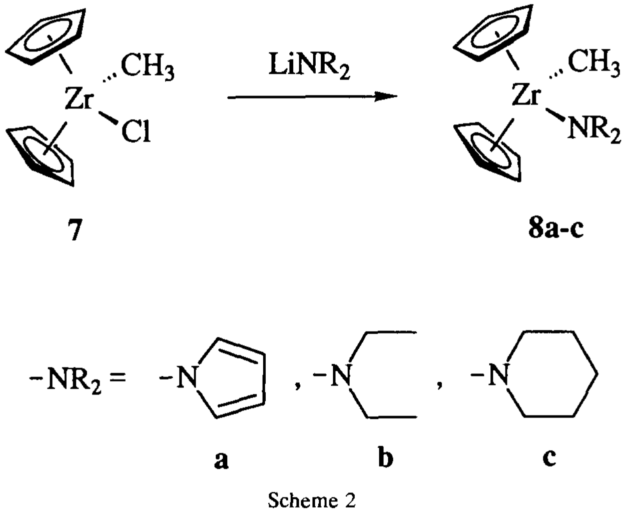
SSDI 0022-328X(94)00017-4

amidozirconocene system. We here report an example of such a transformation that we observed during an investigation of the reaction of alkyl(amido)zirconocene complexes with triarylborane Lewis acids.

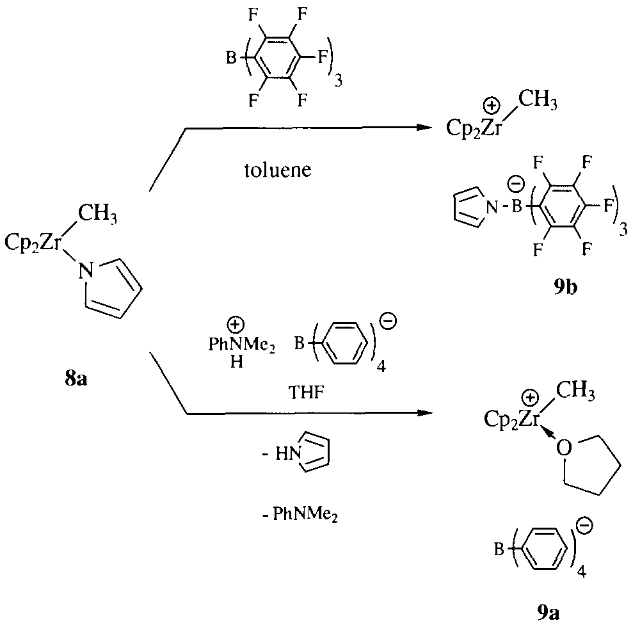
2. Results and discussion

Methylzirconocene chloride (7) was treated with *N*-pyrrolyllithium, lithium diethylamide or *N*-piperidyllithium respectively. In each case a clean halide substitution reaction was observed, and the corresponding amidobis(η-cyclopentadienyl)methylzirconium complexes (**8a**–**8c**) were isolated with good yields (about 80%) [7]. The (diethylamido)methylzirconocene complex **8b** exhibits an ^{1}H NMR Cp singlet at $\delta = 5.68$ ppm (10H) in benzene-d_6 solvent. The ^{1}H/^{13}C NMR resonance of the Zr–CH_3 appears at $\delta = 0.12/18.8$ ppm. The *N*-piperidylmetallocene complex **8c** shows very similar ^{1}H/^{13}C NMR chemical shifts for the corresponding resonances at $\delta = 5.67/109.4$ ppm (Cp) and 0.12/18.0 ppm (CH_3). The Cp resonance for the *N*-pyrrolylzirconocene complex **8a** is similar, at $\delta = 5.66/112.8$ ppm. However, we note that the Zr–CH_3 ^{1}H and ^{13}C NMR resonances are markedly shifted to higher δ values ($\delta = 0.41/30.2$ ppm) and so the carbanionic character of this σ-hydrocarbyl ligand must be less pronounced in the (*N*-pyrrolyl)zirconocene methyl complex **8a** than in its aliphatic amidozirconocene methyl complex counterparts **8b** and **8c**. Indeed, we have noticed quite substantial differences in chemical behaviour between complex **8a** and complexes **8b** and **8c** in their reactions with a strongly Lewis-acidic triarylborane (Scheme 2).

Complex **8a** was treated with one molar equivalent of the Bronsted-acid *N*,*N*-dimethylanilinium tetraphenylborate in tetrahydrofuran (THF) [8]. This leads selectively to the formation of free pyrrole and the salt **9a** of the THF adduct of the methylzirconocene cation [9]. Under these conditions the zirconium bound *N*-pyrrolyl ligand is more basic than the methyl ligand in the Zr–CH_3 bond. Complex **8a** exhibits similar behaviour when treated with the Lewis-acid tris(pentafluorophenyl)borane. Within the limits of detection, only transfer of the heterocyclic ligand system from zirconium to boron is observed, and we obtained the related salt of the methylzirconocene cation as its THF adduct (as in the salt **9a**) with an almost quantitative yield. Correspondingly, we generated $Cp_2ZrCH_3^+$ free of external stabilizing donor ligands in situ by treatment of **8a** with $B(C_6F_5)_3$ in toluene in the presence of ethylene. The obtained salt **9b** of the methylzirconocene cation is catalytically active under these conditions, as expected, and polymerizes ethylene with a moderate activity [$a \approx 600$ g polyethylene (g Zr)$^{-1}$ h^{-1}; mp (polyethylene) 124°C] [10] (Scheme 3).



Scheme 2

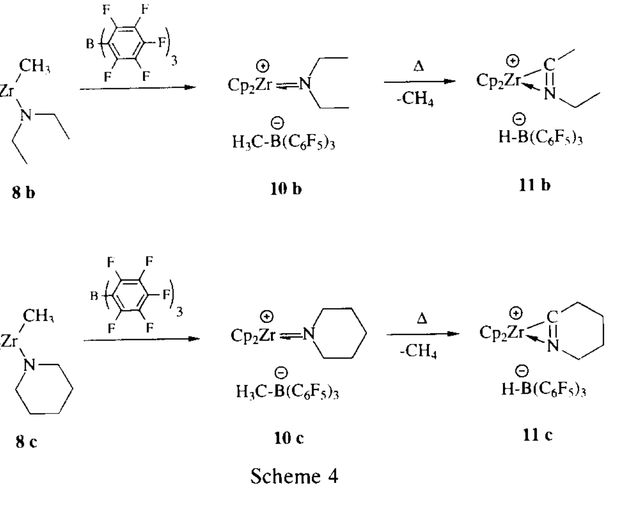


Scheme 3

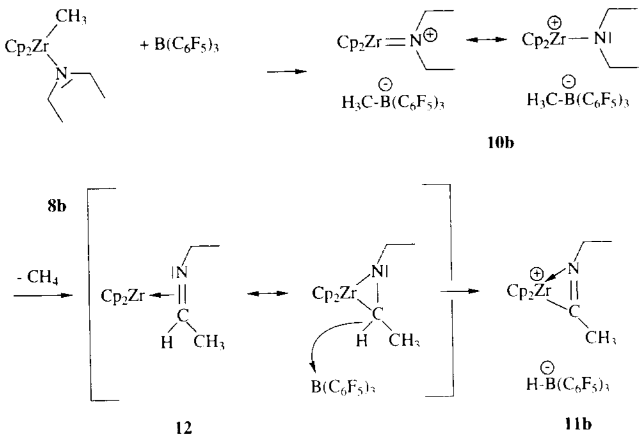
The reaction of (*N*-diethylamido)methylzirconocene (**8b**) with tris(pentafluorophenyl)borane takes a very different course. The reaction was carried out in a 1 : 1 molar ratio of the reagents and monitored directly by ^{1}H NMR spectroscopy in benzene-d_6. In a clean reaction a single new product is formed by means of methyl ligand transfer from zirconium to boron [11]. This product **10b** is characterized by ^{1}H NMR signals at $\delta = 5.51$ ppm (Cp) and $\delta = 3.02$ ppm (q) and 0.45 ppm (t, $^3J = 6.9$ Hz, ethyl); the methyl signal, at $\delta = 0.30$ ppm, is very broad. The presence of a tetracoordinated methyltriarylborate anion is confirmed by an ^{11}B NMR resonance at $\delta = -14.2$ ppm. These data indicate that the triarylborane Lewis acid has in this case abstracted the σ-methyl ligand from zirconium to give the salt **10b** of the cationic (diethylamido)zirconocene complex. We assume that this complex is formed as a tight ion pair with the weakly nucleophilic $MeB(C_6F_5)_3^-$ anion, as was observed for alkylzirconocene and hydridozirconocene cation complexes containing similar anionic components [12].

Salt **10b** is thermally labile. Upon prolonged standing in benzene-d_6 solution it undergoes decomposition with methane formation to give a new cationic zirconium species that we have identified as the (η^2-iminoacyl)zirconocene cation; the counteranion is $HB(C_6F_5)_3^-$. The salt **11b** is thermally stable. We made it on a preparative scale by treatment of **8b** with $B(C_6F_5)_3$ followed by thermolysis and isolated it with a 84% yield. The (η^2-iminoacylium)zirconocene trisarylborohydride salt **11b** exhibits ^1H NMR signals at δ = 5.29 ppm (Cp), 2.89 and 0.61 ppm (^3J = 7.4 Hz, ethyl group) and 1.76 ppm (CH_3). The ^{13}C NMR resonance of the η^2-iminoacyl carbon atom is very characteristic at δ = 237.8 ppm. The corresponding iminoacyl ν(C=N) band appears in the IR spectrum at 1644 cm^{-1} (KBr). The presence of a borohydride is evident from the broad ν(B–H) band at 2369 cm^{-1}, very similar to that observed recently for the related $[(Cp_2ZrH)^+(HB(C_6F_5)_3)^-]$ salt at 2364 cm^{-1} [13]. The presence of the $[Ar_3B\text{–}H]^-$ anion is further supported by the ^{11}B NMR spectrum of the salt **11b** in THF-d_8; this shows a broad doublet at $\delta = -25.4$ ppm with $^1J_{BH}$ = 92 Hz. The overall composition of **11b** as $C_{32}H_{19}BNF_{15}Zr$ was confirmed by C, H, N elemental analysis. We thus conclude that the (diethylamido)methylzirconocene complex first loses a methyl group when treated with $B(C_6F_5)_3$ and then forms the (η^2-iminoacylium)zirconocene trisarylborohydride salt **11b** by extrusion of methane and hydride transfer (Scheme 4).

The methyl(*N*-piperidyl)zirconocene complex **8c** reacts analogously with $B(C_6F_5)_3$. By NMR monitoring we observed the rapid formation of **10c**, followed by methane elimination to give **11c**. The (η^2-iminoacylium)zirconocene triarylborohydride salt **11c** was not isolated but was identified by its very characteristic NMR resonances. It exhibits typical ^{13}C NMR resonances (in benzene-d_6) at δ = 235.7 ppm (iminoacyl-C), 109.7 ppm (Cp), 49.0 ppm ($N\text{–}CH_2$) and 34.9 ppm ($N{=}C\text{–}CH_2$).



Scheme 4



Scheme 5

The striking difference in the behavior of the amidozirconocene methyl complexes containing aromatic and aliphatic amido ligands toward the $B(C_6F_5)_3$ Lewis acid is probably due to a ground-state effect of the amidozirconocene moieties. The two series of compounds probably differ most in their ability to use the electron pair at nitrogen to compensate for the electron deficiency at the adjacent metal center [14]. In **8b** and **8c** the lone pair can be fully used and consequently the methyl group at zirconium is rather basic. In addition, the corresponding cation can also be substantially stabilized by electron donation from the adjacent nitrogen. In contrast, the nitrogen lone pair in the *N*-pyrrolyl metallocenes is involved in the heterocyclic aromatic 6π-electron system and cannot increase the electron density at the neutral or the cationic metal center, thus a different chemistry is observed than for the aliphatic amidozirconocene complexes.

Treatment of **8b** and **8c** with $B(C_6F_5)_3$ results in a remarkable sequence of formal ligand redox reactions that eventually lead to the (η^2-iminoacylium)zirconocene species (see above and Scheme 1). In a control experiment it was shown that the neutral starting material **8b** is stable up to about 150°C in respect of the thermally induced elimination of methane. We must therefore assume that the rapid CH_4 evolution from the $[(Cp_2Zr\text{-}NR_2)^+\ (CH_3BAr_3)^-]$ salt (or ion pair) does not proceed by way of the reverse reaction via **8b** but instead is a specific property of **10b** itself. Ion pair formation would undoubtedly assist the elimination of CH_4 from **10** to give the (η^2-ketimine)metallocene species **12** (Scheme 5). Under the reaction conditions this intermediate cannot be directly observed but is rapidly attacked by the strong Lewis acid $B(C_6F_5)_3$ and loses a hydride to give the salt of the stable (η^2-iminoacylium)$ZrCp_2$ cation, **11b**. This step in the overall amine to nitrilium ion redox reaction in the coordination sphere of the early transition metal center (see Scheme 1) is facilitated by the high hydride-abstracting ability of the very electron-deficient Lewis-acid triarylborane. In addition, we assume that it is further assisted, and the product further stabilized by tight ion pair formation by means of close fluoride–zirconium interaction, as was shown by X-ray diffraction to be present in related $[(Cp_2ZrR)^+RB(C_6F_5)_3^-)]$ species [12,13].

3. Experimental section

All reactions were performed in an inert atmosphere (argon) using Schlenk-type glassware or in a glove-box. Solvents were dried and distilled under argon prior to use. Methylzirconocene chloride (**7**) [15] and tris(pentafluorophenyl)borane [16] were prepared by published procedures. The amidolithium reagents were generated by treatment of the corresponding amines with *n*-butyllithium. For further general information, including details of spectrometers and equipment used for physical characterization, see [5].

3.1. Preparation of bis(η-cyclopentadienyl)methyl(N-pyrrolyl)zirconium (8a)

Methylzirconocene chloride (**7**) (1.0 g, 3.7 mmol) and *N*-pyrrolyllithium (0.30 g, 4.1 mmol) were mixed as solids; then THF (50 ml) was added and the mixture was stirred for 4 h at ambient temperature. The solvent was then removed in vacuo, and the residue taken up in 50 ml of toluene. The solution was filtered to remove lithium chloride and the solvent was removed in vacuo. The residual solid was washed with a small volume of pentane to give 0.88 g (79%) of **8a**, (melting point (m.p.), 89°C). ^1H NMR (benzene-d_6): δ 6.62, 6.57 (m, each 2H, pyrrol-H), 5.66 (s, 10H, Cp), 0.41 (s, 3H, CH_3). ^{13}C NMR (benzene-d_6): δ 112.8 (Cp), 110.3 and 109.4 (pyrrol-C), 30.2 (Zr-CH_3). IR (KBr): $\tilde{\nu}$ 3105, 3079, 2973, 2921, 2868, 1446, 1262, 1078, 1019, 808, 735, 644 cm^{-1}. Anal. Found: C, 58.25; H, 5.80; N, 4.82. $C_{15}H_{17}NZr$ (302.5) calc.: C, 59.55; H, 5.66; N, 4.63%.

3.2. Preparation of bis(η-cyclopentadienyl)(diethylamido)methylzirconium (8b)

Methylzirconocene chloride (**7**) (1.0 g, 3.7 mmol) was treated with 0.32 g (4.1 mmol) of lithium diethylamide in 50 ml of THF as described above, and work-up as before yielded 0.9 g (79%) of **8b** (m.p. 83°C). ^1H NMR (benzene-d_6): δ 5.68 (s, 10H, Cp), 3.02 (q, ^3J = 6.9 Hz, 4H, CH_2CH_3), 0.85 (t, ^3J = 6.9 Hz, 6H, CH_2CH_3), 0.12 (s, 3H, Zr–CH_3). ^{13}C NMR (benzene-d_6): δ 109.3 (Cp), 47.7 (N–CH_2–), 18.8 (Zr–CH_3), 15.5 (CH_2CH_3). IR (KBr): $\tilde{\nu}$ 3098, 2960, 2927, 2861, 2828, 2802, 1604, 1446, 1367, 1183, 1137, 1019, 992, 874, 801, 742, 571 cm^{-1}. Anal. Found: C, 57.88; H, 7.33; N, 4.35. $C_{15}H_{23}NZr$ (308.6) calc.: C, 58.39; H, 7.51; N, 4.54%.

3.3. Preparation of bis(η-cyclopentadienyl)methyl(N-piperidyl)zirconium (8c)

The above procedure was repeated starting from 1.0 g (3.7 mmol) of **7** and 0.37 g (4.1 mmol) of *N*-piperidyllithium in 50 ml of THF and gave 0.95 g (80%) of **8c** (m.p., 81°C). Complex **8c** was characterized only spectroscopically. ^1H NMR (benzene-d_6): δ 5.67 (s, 10H, Cp), 3.14 (m, 4H, CH_2), 1.38 (m, 6H, CH_2), 0.12 (s, 3H, Zr–CH_3). ^{13}C NMR (benzene-d_6): δ 109.4 (Cp), 57.9 (CH_2), 28.4 (CH_2), 25.9 (CH_2), 18.0 (Zr–CH_3). IR (KBr): $\tilde{\nu}$ 3104, 2967, 2927, 2868, 1446, 1361, 1269, 1098, 1019, 913, 801, 749 cm^{-1}.

3.4. Reaction of 8a with tris(pentafluorophenyl)borane, preparation of 9b

The zirconium complex **8a** (100 mg, 0.33 mmol) was mixed with 170 mg (0.33 mmol) of $B(C_6F_5)_3$, and 20 ml of toluene were added. The mixture was stirred for 30 min at room temperature, and the precipitated **9b** was filtered off, washed with 10 ml of pentane and dried in vacuo (yield, 250 mg (93%); m.p., 230°C (decomposition)). ^1H NMR (THF-d_8): δ 7.29 and 6.15 (m, each 2H, pyrrol-H), 6.91 (s, 10H, Cp), 0.52 (broad s, 3H, CH_3). ^{11}B NMR (THF-d_8): δ–14.9 (s). Anal. Found: C, 47.44; H, 2.26; N, 1.78. $C_{33}H_{17}BNF_{15}Zr$ (814.5) calc.: C, 48.66; H, 2.10; N, 1.72%.

3.5. Reaction of 8b with tris(pentafluorophenyl)borane, generation of 10b

Bis(η-cyclopentadienyl)(diethylamido)methylzirconium (**8b**) (6 mg, 20 μmol) was treated with 10 mg (20 μmol) of $B(C_6F_5)_3$ in benzene-d_6 at ambient temperature. Spectroscopic monitoring revealed immediate formation of the salt **10b**. ^1H NMR (benzene-d_6): δ 5.51 (s, 10H, Cp), 3.02 (q, ^3J = 6.9 Hz, 4H, CH_2), 0.45 (t, ^3J = 6.9 Hz, 6H, CH_2CH_3), 0.30 (broad s, 3H, B–CH_3). ^{11}B NMR (benzene-d_6): δ – 14.2 (s). This initial product is not stable for long under the reaction conditions. After about 1 h it had almost completely disappeared to give **11b**. ^1H NMR (benzene-d_6): δ 5.29 (s, 10H, Cp), 2.89 (q, ^3J = 7.4 Hz, 2H, CH_2), 1.76 (s, 3H, N=C–CH_3), 0.61 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3): the ^1H resonance of the CH_4 co-product was observed at

$\delta = 0.15$ pm(s). ^{11}B NMR (benzene-d_6): δ −18.4 (broad s).

*3.6. Reaction of **8b** with tris(pentafluorophenyl)borane, preparation of **11b***

To a solution of **8b** (200 mg, 0.65 mmol) in 30 ml of toluene was added tris(pentafluorophenyl)borane (332 mg, 0.65 mmol). The mixture was stirred for 2 days at ambient temperature, the solvent was then removed in vacuo, and the residue was washed with 20 ml of pentane to leave 440 mg (84%) of **11b** (m.p., 56°C (decomposition)). ^{1}H NMR (see above). ^{13}C NMR (benzene-d_6): δ 237.8 (C=N), 148.7 (d, $^1J_{CF} = 238$ Hz), 139.8 (d, $^1J_{CF} = 247$ Hz), 137.7 (d, $^1J_{CF} = 248$ Hz), 121.4 (broad m, $B(C_6F_5)_3$), 109.7 (Cp), 43.6 (C=N–CH_2), 21.3 and 12.5 (CH_3). ^{11}B NMR (THF-d_8): δ −25.4 (d, $^1J_{BH} = 92$ Hz). Anal. Found: C, 47.46; H, 2.70; N, 1.79. $C_{32}H_{19}BNF_{15}Zr$ (804.5) calc.: C, 47.77; H, 2.38; N, 1.74%.

*3.7. Reaction of bis(η-cyclopentadienyl)methyl(N-piperidyl)zirconium (**8c**) with tris(pentafluorophenyl)borane, formation of **10c** and **11c***

The reaction was carried out only on an NMR scale. The products were not isolated. A mixture of **8c** (6 mg, 0.02 mmol) and $B(C_6F_5)_3$ (10 mg, 0.02 mmol) were dissolved in 0.5 ml of benzene-d_6. The mixture was transferred to an NMR tube that was sealed. Formation of **10c** was instantaneous. ^{1}H NMR (benzene-d_6): δ 5.48 (s, 10H, Cp), 3.04 (m, 4H, CH_2), 1.08 (m, 2H, CH_2), 0.91 (m, 4H, CH_2), 0.30 (broad s, 3H, B–CH_3). ^{11}B NMR (benzene-d_6): δ −14.1 (s). ^{13}C NMR (benzene-d_6): δ 148.6 (d, $^1J_{CF} = 238$ Hz), 139.2 (d, $^1J_{CF} = 247$ Hz), 137.6 (d, $^1J_{CF} = 248$ Hz), 125.0 (broad m, $B(C_6F_5)_3$), 113.3 (Cp), 62.8 (CH_2), 28.4 (CH_2), 24.4 (CH_2), −0.5 (broad m, B–CH_3). After 2 days at room temperature the primary product was almost completely converted to the final product **11c**. ^{1}H NMR (benzene-d_6): δ 5.31 (s, 10H, Cp), 2.81 (m, 2H, CH_2), 2.10 (m, 2H, CH_2), 1.00 (m, 4H, CH_2), *H*B resonance not observed. ^{11}B NMR (benzene-d_6): δ −17.0 (broad s). ^{13}C NMR (benzene-d_6): δ 235.7 (*C*=N), 148.8 (d, $^1J_{CF} = 239$ Hz), 139.8 (d, $^1J_{CF} = 249$ Hz), 137.6 (d, $^1J_{CF} = 249$ Hz), 122.0 (broad m, $B(C_6F_5)_3$), 109.7 (Cp), 49.0, 34.9, 22.7, 19.5 (CH_2).

Acknowledgments

Financial support from the Fonds der Chemischen Industrie, the Volkswagen-Stiftung, and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

References and notes

[1] S.L. Buchwald, M.W. Wannamaker and B.T. Watson, *J. Am. Chem. Soc., 111* (1989) 776; S.L. Buchwald, B.T. Watson, M.W. Wannamaker and J.C. Dewan, *J. Am. Chem. Soc., 111* (1989) 4486; R.B. Grossman, W.M. Davis and S.L. Buchwald, *J. Am. Chem. Soc., 113* (1991) 2321; N. Coles, R.J. Whitby and J. Blagg, Synlett., (1992) 143, and references cited therein.

[2] See for a comparison G. Erker, *Acc. Chem. Res., 17* (1984) 103; G. Erker, U. Hoffmann, R. Zwettler, P. Betz and C. Krüger, *Angew. Chem., 101* (1989) 644; *Angew. Chem. Int. Edn. Engl., 28* (1989) 630; M.J.S. Dewar and G.P. Ford, *J. Am. Chem. Soc., 101* (1979) 783; D. Cremer and E. Kraka, *J. Am. Chem. Soc., 107* (1985) 3800.

[3] See for a review L.D. Durfee and I.P. Rothwell, *Chem. Rev., 88* (1988) 1059; selected representative examples of other papers are R.D. Adams and D.F. Chodosh, *Inorg. Chem., 17* (1978) 41; F.H. Elsner and T.D. Tilley, *J. Organomet. Chem., 358* (1988) 169; G. Erker, R. Zwettler and C. Krüger, *Chem.* Cher. *122* (1989) 1377; S.M. Beshouri, D.E. Chebi, P.E. Fanwick, I.P. Rothwell and J.C. Huffman, *Organometallics, 9* (1990) 2375; F.R. Lemke, D.J. Szakla and R.M. Bullock, *Organometallics, 11* (1992) 876; and references cited in these papers.

[4] A.S. Guram and R.F. Jordan, *J. Org. Chem., 58* (1993) 5595; P.G. Cozzi, T. Carofiglio, C. Floriani, A. Chiesi-Villa, and C. Rizzoli, *Organometallics, 12* (1993) 2845; A.S. Guram, Z. Guo and R.F. Jordan, *J. Am. Chem. Soc., 115* (1993) 4902; R.F. Jordan and D.F. Taylor, *J. Am. Chem. Soc., 111* (1989) 778; R.F. Jordan, D.F. Taylor and N.C. Baenziger, *Organometallics, 9* (1990) 1546; A.S. Guram and R.F. Jordan, *Organometallics, 9* (1990) 2116, 2190; *Organometallics, 10* (1991) 3470; A.S. Guram, D.C. Swenson and R.F. Jordan, *J. Am. Chem. Soc., 114* (1992) 8991; Z. Guo, D.C. Swenson, A.S. Guram and R.F. Jordan, *Organometallics, 13* (1994) 766, and references cited therein.

[5] D. Röttger, G. Erker, M. Grehl and R. Fröhlich, *Organometallics, 13* (1994) in press.

[6] C. Valero, M. Grehl, D. Wingbermühle, L. Kloppenburg, D. Carpenetti, G. Erker and J.L. Petersen, *Organometallics, 13* (1994) 415.

[7] P.J. Walsh, F.J. Hollander and R.G. Bergman, *J. Am. Chem. Soc., 110* (1988) 8729; N. Coles, M.C.J. Harris, R.J. Whitby and J. Blagg, *Organometallics, 13* (1994) 190, and references cited therein.

[8] R.F. Jordan, R.E. La Pointe, P.K. Bradley and N.C. Baenziger, *Organometallics, 8* (1989) 2892; R. Taube and L. Krukowa, *J. Organomet. Chem., 347* (1988) C9; R.F. Jordan, P.K. Bradley, N.C. Baenziger and R.E. La Pointe, *J. Am. Chem. Soc., 112* (1990) 1289; D.M. Amorose, R.A. Lee and J.L. Petersen, *Organometallics, 10* (1991) 2191; J.J.W. Eshuis, Y.Y. Tan, A. Meetsma, J.H. Teuben, J. Renkema and G.G. Evens, *Organometallics, 11* (1992) 362; S. Collins and D.G. Ward, *J. Am. Chem. Soc., 114* (1992) 5460; H.D. Horton, *Organometallics, 11* (1992) 3271; M-H. Prosenc, C. Janiak and H.-H. Brintzinger, *Organometallics, 11* (1992) 4036; X. Yang, L. Lia and T.J. Marks, *J. Am. Chem. Soc., 115* (1993) 3392; M. Bochmann and S.J. Lancaster, *Organometallics, 12* (1993) 633; S.L. Borkowsky, N.C. Baenziger and R.F. Jordan, *Organometallics, 12* (1993) 486; Y.W. Alelyunas, N.C. Baenziger, P.K. Bradley and R.F. Jordan, *Organometallics, 13* (1994) 148; and references cited in these papers.

[9] R.F. Jordan, *Adv. Organomet. Chem., 32* (1991) 325.

[10] See for a review M. Bochmann, *Nachr. Chem. Tech. Lab., 43* (1993) 1220.

[11] See for a comparison G.G. Hlatky, H.W. Turner and R.R. Eckman, *J. Am. Chem. Soc., 111* (1989) 2728; M. Bochmann, G. Karger and A.J. Jaggar, *J. Chem. Soc., Chem. Commun.*, (1990) 1038; G. Erker, M. Albrecht, S. Werner and C. Krüger, *Z.*

Naturforsch., *45b* (1990) 1205; A.D. Horton and J.H.G. Frijns, *Angew. Chem.*, *103* (1991) 1181; *Angew. Chem., Int. Edn. Engl.*, *30* (1991) 1152; D.M. Amorose, R.A. Lee and J.L. Petersen, *Organometallics*, *10* (1991) 2191; G. Erker, M. Albrecht and C. Psiorz, *Z. Naturforsch.*, *46b* (1991) 1571; G.G. Hlatky, R.R. Eckman and H.W. Turner, *Organometallics*, *11* (1992) 1413; C.J. Schaverien, *Organometallics*, *11* (1992) 3476; C. Pellecchia, A. Grassi and A. Immirzi, *J. Am. Chem. Soc.*, *115* (1993) 1160; D.J. Gillis, M.-J. Tudoret and M.C. Baird, *J. Am. Chem. Soc.*, *115* (1993) 2543; C. Pellecchia, A. Immirzi, A. Grassi and A. Zambelli, *Organometallics*, *12* (1993) 4473; see also G. Erker, R. Noe, D. Wingbermühle and J.L. Petersen, *Angew. Chem.*, *105* (1993) 1216; *Angew. Chem., Int. Edn. Engl.*, *32* (1993) 1213; G. Erker, R. Noe and D. Wingbermühle, *Chem. Ber.*, *127* (1994) 805.

[12] X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc.*, *113* (1991) 3623; C. Sishta, R.M. Hathorn and T.J. Marks, *J. Am. Chem. Soc.*, *114* (1992) 1112.

[13] X. Yang, C.L. Stern and T.J. Marks, *Angew. Chem.*, *104* (1992) 1406; *Angew. Chem., Int. Edn. Engl.*, *31* (1992) 1375, and references cited therein.

[14] For examples exhibiting strong nitrogen lone-pair to zirconium back bonding see G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund and C. Krüger, *Organometallics*, *8* (1989) 911; M. Bochmann, L.M. Wilson, M.B. Hursthouse and M. Motevalli, *Organometallics*, *7* (1988) 1148; C.S. Christ, Jr., J.R. Eyler and D.E. Richardson, *J. Am. Chem. Soc.*, *122* (1990) 4778; A.S. Guram, R.F. Jordan and D.F. Taylor, *J. Am. Chem. Soc.*, *113* (1991) 1833; S.L. Borkowsky, N.C. Baenziger and R.F. Jordan, *Organometallics*, *12* (1993) 486; Y.W. Alelyunas, Z. Guo, R.E. La Pointe and R.F. Jordan, *Organometallics*, *12* (1993) 544.

[15] J.R. Surtrees, *J. Chem. Soc., Chem. Commun.*, (1965) 567.

[16] A.G. Massey and A.J. Park, *J. Organomet. Chem.*, *2* (1964) 245; J.L.W. Pohlmann and F.E. Brinckmann, *Z. Naturforsch.*, *20b* (1965) 5.