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Journal of Organometallic Chemistry 525 (1996) 287–289

Journal of Organometallic Chemistry

Preliminary communication

Hetero-*ansa*-metallocenes: I. Synthesis of the novel [1]-borylidene-bridged *ansa*-zirconocene dichloride

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Received 7 December 1995

Abstract

The first *ansa*-[1]-zirconocene dichloride with the boron bridge atom, $[(\mu\text{-PhB})(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ (5) is synthesised via subsequent transmetallation of $C_5H_4(SnMe_3)_2$ by $PhBCl_2$ and $ZrCl_4$. The unstable corresponding ligand — $PhB(C_5H_5)_2$ (1) — was synthesised and isolated in the form of pyridine (1 : 1) (2) and DABCO (2 : 1) (3) adducts.

Keywords: Zirconium; Boron; Bridging Ligand; Tin; *Ansa*-metallocene; Transmetallation

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Ansa-metallocenes with a one-membered bridge (i.e. with only one atom bonded to the two η^5-coordinated ligands) are extensively used for various olefin conversions and so have been intensively investigated in recent years [1]. The bridges were largely confined to a wide ranging carbon and silicon atoms, with other atoms present only in a few particular examples [2]. Syntheses by use of the 'ligand salt–metal complex' routes or 'metal amide–metal complex' are suitable in all cases. Cyclopentadienyl derivatives with two or more Alk_3Z-substituents (Z = Si, Ge, Sn) in the ring have long been known [3a], but they received only little attention as precursors of Group 4 metallocenes [3b–e], whereas the transmetallations of the mono-silylated and stannylated analogues have been much studied [3f–h].

We report below the first singly-bridged sandwich-type zirconium(IV) complex (5), having a boron atom in the one-membered bridge and opening the way to a novel class of *ansa*-metallocenes. At the same time we show that use of dimetallated Cp ligand allows the preparation of otherwise unattainable types of compound.

We first tried to synthesise the required ligand using Scheme 1.

The very unstable $PhBCp_2$ (1) reacts in solution with pyridine or DABCO forming (2) and (3) (1 : 1 and 2 : 1 adducts, respectively) in high yields [4,5]. An attempt to use (3) as a precursor of (1) failed indicating an impossibility to obtain anionic $[RBCp_2]^{2-}$ species and the unsuitability in this case of the commonly employed ligand salt–metal complex procedure.

It can be easily understood that the "metal amide–metal complex" route is also not suitable for these species too. Hence we decided to use the readily available bis-(trimethylstannyl) cyclopentadiene. All manipulations were carried out by use of Schlenk techniques. Pentane, heptane and toluene were freshly distilled from Na/K alloy prior to use.

When a solution of $C_5H_4(SnMe_3)_2$ (20 mmol) in toluene is treated with an equimolar amount (10 mmol) of $PhBCl_2$ at −60°C, one equivalent of Me_3SnCl is formed from each of the two different molecules of $C_5H_4(SnMe_3)_2$ to give the intermediate $PhB(C_5H_4SnMe_3)_2$ compound (4). See Scheme 2.

The latter is formed nearly quantitatively, as revealed by ^1H NMR spectroscopy. However, there is no need to isolate (4), because the subsequent addition of $ZrCl_4$ in situ gives the new complex (5) in 40% isolated yield after work up [6]. The light-yellow compound decomposes without melting when heated above 155°C. However, crystalline (5) is not very sensitive to moisture and

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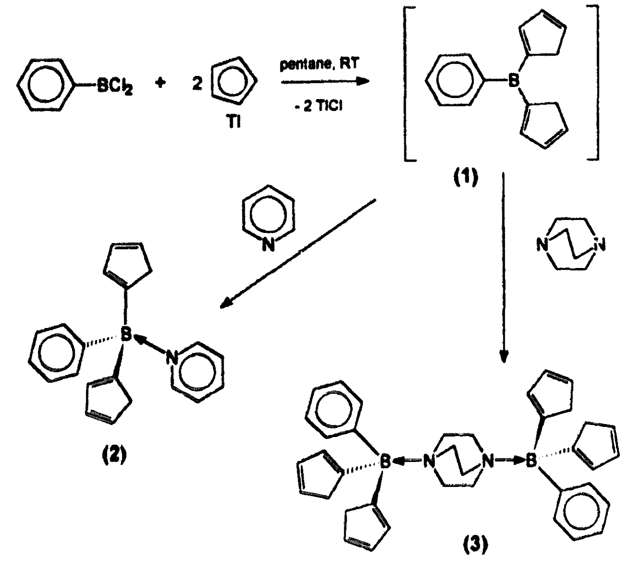
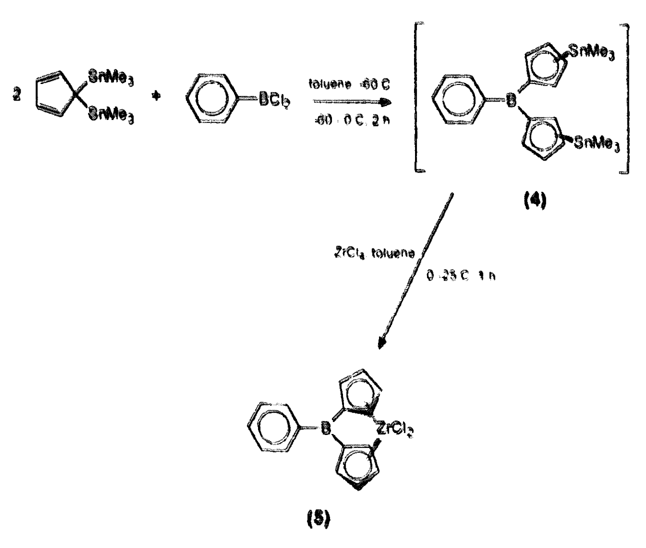
PII S0022-328X(96)06285-7



Scheme 1.

can be easily handled. The one-pot synthesis is straightforward, preventing single-radical transfer reactions, which are so common for the precursor compounds such as bismetallated Cp. The ^{1}H NMR spectrum shows a Ph multiplet at 7.41–6.52 ppm and an AA′BB′ system of η^5-Cp signals at 6.28, 5.92 ppm. In the ^{13}C NMR spectrum there are signals from three types of Ph carbon atoms, at 137.44, 135.88 and 129.12 ppm, and from two types of η^5-Cp carbon atoms, at 125.96 and 115.76 ppm. Signals from carbon atoms linked with boron are not observed. The ^{11}B NMR spectrum consist of a broad singlet ($h_{1/2}$ = 4000 Hz) at 52.5 ppm. Therefore we conclude, that complex (5) is a [1]-borylidene bridged *ansa*-metallocene.

It is interesting to note that in diethyl ether (5) forms a yellow solution, whereas that in toluene, in which it is very soluble, is colorless. An attempt to dissolve (5) in DME gave a white insoluble solid.



Scheme 2.

We conclude that the use of bis-stannylated cyclopentadienes in *ansa*-metallocene chemistry allows easy access to novel [1]-boryliden-bridged *ansa*-zirconocenes. Studies of the properties of these species are in progress.

Acknowledgments

We thank ISF JAG-100, RFFI N 94-03-08418a and ISF a678-x (K.A.R.) grants for financial support.

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[4] Preparation of PhB$(C_5H_5)_2 \cdot C_5H_5N$, (2): to the stirred suspension of 8.62 g (32 mmol) CpTl in pentane (100 ml) at RT, $PhBCl_2$, 1.95 ml (2.38 g, 15 mmol) in heptane (100 ml) was slowly added. After 2 h the precipitate of TlCl was filtered off and C_5H_5N 1.6 ml (1.6 g, 20 mmol) in heptane was added. Light-yellow precipitate immediately formed. It was filtered off, washed with pentane and dried, yielding 3.48 g, 78% of (2). Decomp. 57°C. Anal. calcd for $C_{21}H_{20}BN$: C, 85.20; H, 6.78; N 4.71. Found C, 85.12; H, 6.85; N 4.68. ^{1}H NMR (Bruker WP-200SY, $CDCl_3$) d: 8.090, 7.421 (m, 5H, C*H*, Py-); 7.810, 7.283, 7.228 (m, 5H, C*H*, Ph-); 6.585, 6.506 (m, 6H, vin. C*H*, Cp); 2.992 (t, 4H, -CH_2-, Cp). ^{11}B NMR (Varian-VXR400, C_5D_5N) d: −4.5.

[5] Preparation of $[PhB(C_5H_5)_2]_2 \cdot C_6H_{12}N_2$, (3): to the stirred suspension of 14.54 g (54 mmol) CpTl in toluene (200 ml), $PhBCl_2$,

3.25 ml (3.97 g, 25 mmol) in pentane (50 ml) was slowly added. After 0.5 h the precipitate of TlCl was filtered off and 2.80 g of DABCO in hot toluene (100 ml) was added. A snow-white precipitate began, on cooling, to form. After 4 days at 0°C the product was filtered off, washed with pentane, and dried in vacuum. This procedure yields 5.55 g, 81% of (3) as a white microcrystalline solid. Decomp. 90°C Anal. calcd for $C_{38}H_{42}B_2N_2$: C, 83.23; H, 7.72; N 5.11. Found C, 83.01; H, 7.90; N 4.98. NMR (Varian-VXR400, $CDCl_3$) ^{1}H: d: 8.005, 7.840, 7.365 (m, 5H, C*H*, Ph-); 7.168, 6.80 (m, 6H, vin. C*H*, Cp); 2.868 (m, 4H, -CH_2-, Cp), 2.040 (m, 12H, -CH_2-, -DABCO-); ^{11}B: d: −4.3.

[6] Preparation of $[(\mu\text{-PhB})(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ (4): to the stirred solution of $C_5H_4(SnMe_3)_2$ 5.4 ml (7.83 g, 20 mmol) in toluene (30 ml) at −60°C, $PhBCl_2$, 1.30 ml (1.59 g, 10 mmol) was slowly added. The reaction mixture became yellow-orange. It was allowed to warm up to 0°C during 2 h, then $ZrCl_4$, 2.33 g (10 mmol) was added. The resulting orange solution was decanted from a white residue and reduced in volume. After 3 extractions of obtained oil with pentane, it became solid and turned yellow. The residue was washed with hot heptane five times and recrystallized from heptane/toluene, 5/1 mixture. The final yield of light-yellow microcrystalline powder of (5) was 40%. Anal. calcd for $C_{16}H_{13}ZrCl_2B$: C, 50.81; H, 3.46; Cl 18.75. Found C, 50.67; H, 3.62; Cl 18.31 NMR (Varian-VXR400, toluene-d^8) d: ^{1}H: 7.41 − 6.92 (m, 5H, Ph-), 6.28, 5.92 (t, q, 2H, 2H, AA′BB′, Cp-ring CH); ^{13}C: 137.44, 135.88, 129.12 (*C*H, Ph), 125.96, 115.76 (*C*H, C_5H_4); ^{11}B: 52.5.