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Functional Group Chemistry at the Zirconocene Backbone: Addition Reactions to Pendant Alkynyl Substituents

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The nickel-catalyzed cross-coupling of 2-bromoindene with propynyl- or (phenylethynyl)magnesium bromide gives the corresponding 2-alkynyl-substituted indenyl ligands. Subsequent deprotonation and transmetallation with the bis(tetrahydrofuran)zirconium tetrachloride adduct yields the corresponding bis(2-alkynylindenyl)dichloridozirconium complexes **4a** and **4b**, which cleanly add a $Co_2(CO)_6$ unit to their pairs of alkynyl substituents to give the dimetallic complexes **5a** and **5b**. Complex **5b** was characterized by an X-ray crystal structure analysis. Complex **4a** adds $HB(C_6F_5)_2$ to the alkynyl substituents to yield a mixture of α- and β-(borylalkenyl)metallocenes. Activation of these complexes with MAO gives active ethene polymerization catalysts, and the **4a**,**4b**,**6a**/MAO systems are also active in propene polymerization.

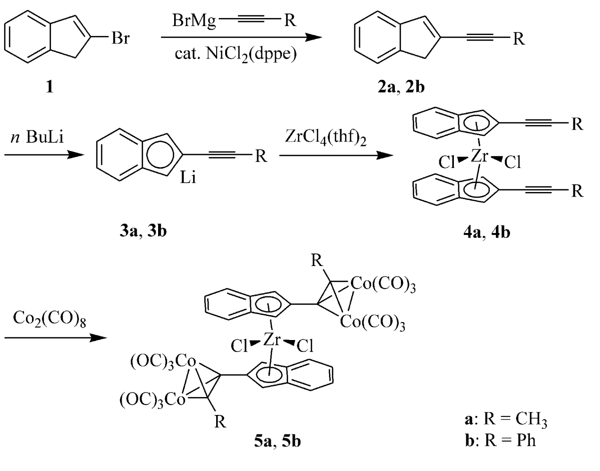
Introduction

Group 4 metallocenes that bear functional substituents at their cyclopentadienyl (Cp) or indenyl rings,[1] including amino acid, peptide- or carbohydrate-derived substituents,[2–4] have become of considerable interest lately, and such systems have contributed to the rapid growth of the emerging field of bio-organometallic chemistry.[5] The attachment of various types of alkenyl substituents has also been of considerable interest since this has allowed for the development of organic functional group chemistry at the framework of the pre-assembled bent metallocene systems. Prior to this development most Cp or indenyl substituents had been attached to the π-ligand framework early on at the ligand stage prior to the transmetallation step to the sensitive oxophilic early transition metal atom. An increasing number of examples are now known where pre-attached groups allow functional-group interconversions at the bent metallocene complex stage. This development includes addition reactions[6] but has also allowed a variety of important and useful carbon–carbon coupling reactions to be performed at the metallocene backbone such as the formation of novel *ansa*-metallocenes by intramolecular olefin metathesis (RCM),[7,8] photochemical [2+2] cycloaddition reactions,[9,10] and even by a variant of the Mannich reaction.[11] We have now extended this work to the chemistry of alkynyl-substituted zirconocenes and report here the synthesis and characterization of some key compounds and their typical reactions with a carbonylmetal $[Co_2(CO)_8]$ or a hydroboration reagent $[HB(C_6F_5)_2]$.

Results and Discussion

Synthesis and Characterization of the Bis(2-alkynylindenyl)zirconium Complexes

The alkynyl substituents used for this study were attached at the 2-positions of the indenyl ligands in the conventional way, namely at the organic ligand stage prior to the introduction of the group 4 transition metal atom, by coupling 2-bromoindene (**1**) with propynylmagnesium bromide in a reaction catalyzed by $[NiCl_2(dppe)]$. The cross-



Scheme 1.

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coupling reaction went smoothly, and product **2a** was isolated in 77% yield. The 2-phenylethynyl-substituted indenyl system **2b** was synthesized analogously (41% yield). Subsequent deprotonation was carried out by treatment with *n*-butyllithium to give **3a** or **3b**, respectively. Both these complexes were characterized spectroscopically. Typically, the alkynyl-substituted indenyllithium system **3a** exhibits a ^{1}H NMR singlet for the indenyl 1-H/3-H protons at δ = 6.45 ppm (2 H), an AA′BB′ pattern of signals (δ = 6.84 and 7.54 ppm) for the phenylene hydrogen atoms, and a sharp alkynyl CH_3 singlet at δ = 1.86 ppm. The alkynyl ^{13}C NMR resonances of **3a** appear at δ = 80.9 and 82.1 ppm, respectively.

Transmetallation of complexes **3a** and **3b** by treatment with $[ZrCl_4(thf)_2]$[12] cleanly gave the corresponding bis(2-alkynylindenyl)dichloridozirconium complexes **4a** (67% yield) and **4b**[13] (76% yield), respectively (see Scheme 1). Both these complexes were characterized by X-ray crystal structure analyses. Single crystals of complex **4a** (R = CH_3) were obtained from toluene (Figure 1). The X-ray crystal

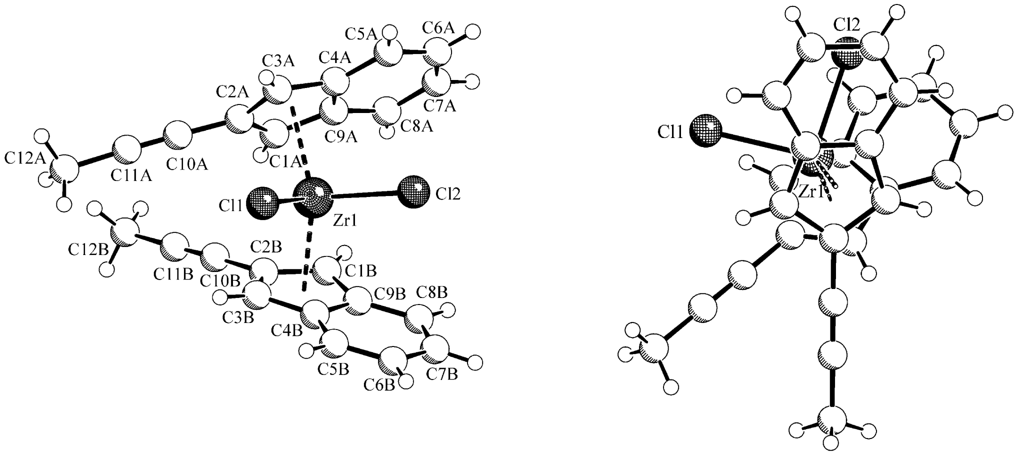


Figure 1. Two projections of the molecular structure of complex **4a** (R = CH_3) showing the typical bent metallocene conformation in the crystal. Selected bond lengths [Å] and angles [°]: Zr1–Cl1 2.442(1), Zr1–Cl2 2.405(1), Zr1–C1A 2.468(2), Zr1–C2A 2.485(2), Zr1–C3A 2.534(2), Zr1–C4A 2.639(2), Zr1–C9A 2.570(2), Zr1–C1B 2.510(2), Zr1–C2B 2.545(2), Zr1–C3B 2.523(2), Zr1–C4B 2.631(2), Zr1–C9B 2.588(2), C1A–C2A 1.420(3), C2A–C3A 1.420(2), C3A–C4A 1.420(2), C4A–C9A 1.439(2), C9A–C1A 1.426(2), C2A–C10A 1.430(2), C10A–C11A 1.188(3), C11A–C12A 1.466(3), C1B–C2B 1.411(3), C2B–C3B 1.432(2), C3B–C4B 1.428(2), C4B–C9B 1.424(3), C9B–C1B 1.434(3), C2B–C10B 1.440(2), C10B–C11B 1.185(2), C11B–C12B 1.469(3); Cl1–Zr–Cl2 95.45(2), C9A–C1A–C2A 108.2(2), C1A–C2A–C3A 108.2(2), C1A–C2A–C10A 126.0(2), C10A–C2A–C3A 125.7(2), C2A–C3A–C4A 108.2(2), C3A–C4A–C9A 107.8(2), C4A–C9A–C1A 107.4(2), C2A–C10A–C11A 178.6(2), C10A–C11A–C12A 178.6(2), C9B–C1B–C2B 107.5(2), C1B–C2B–C3B 108.8(2), C1B–C2B–C10B 125.1(2), C10B–C2B–C3B 126.0(2), C2B–C3B–C4B 107.0(2), C3B–C4B–C9B 108.1(2), C4B–C9B–C1B 108.0(2), C2B–C10B–C11B 177.7(2), C10B–C11B–C12B 178.2(2).

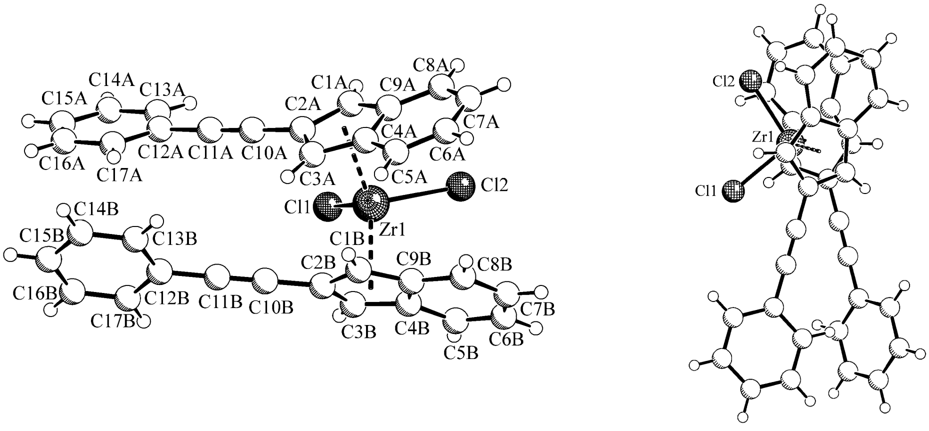


Figure 2. Two projections of the molecular structure of complex **4b**. Selected bond lengths [Å] and angles [°]: Zr1–Cl1 2.411(1), Zr1–Cl2 2.388(2), Zr1–C1A 2.525(2), Zr1–C2A 2.518(2), Zr1–C3A 2.465(2), Zr1–C4A 2.544(2), Zr1–C9A 2.595(3), Zr1–C1B 2.473(2), Zr1–C2B 2.485(2), Zr1–C3B 2.541(39, Zr1–C4B 2.632(2), Zr1–C9B 2.580(2), C1A–C2A 1.410(4), C2A–C3A 1.403(4), C3A–C4A 1.426(4), C4A–C9A 1.422(4), C9A–C1A 1.415(3), C2A–C10A 1.424(4), C10A–C11A 1.195(4), C11A–C12A 1.432(4), C1B–C2B 1.420(4), C2B–C3B 1.409(4), C3B–C4B 1.421(4), C4B–C9B 1.436(4), C9B–C1B 1.403(4), C2B–C10B 1.428(3), C10B–C11B 1.187(3), C11B–C12B 1.431(4); Cl1–Zr–Cl2 97.17(3), C9A–C1A–C2A 107.9(2), C1A–C2A–C3A 108.4(2), C1A–C2A–C10A 126.5(3), C10A–C2A–C3A 125.1(3), C2A–C3A–C4A 108.1(2), C3A–C4A–C9A 107.2(2), C4A–C9A–C1A 108.0(2), C2A–C10A–C11A 179.5(3), C10A–C11A–C12A 179.2(3), C9B–C1B–C2B 108.4(2), C1B–C2B–C3B 108.2(2), C1B–C2B–C10B 125.6(3), C10B–C2B–C3B 126.1(3), C2B–C3B–C4B 108.0(2), C3B–C4B–C9B 107.5(2), C4B–C9B–C1B 107.8(2), C2B–C10B–C11B 179.5(3), C10B–C11B–C12B 179.3(3).

structure analysis shows that linear propynyl substituents are attached at the C2 positions of each of the indenyl ligands [C2A–C10A 1.430(2), C10A–C11A 1.188(3), C11A–C12A 1.466(3) Å; C2A–C10A–C11A 178.6(2), C10A–C11A–C12A 178.6(2)°; C2B–C10B 1.440(2), C10B–C11B 1.185(2), C11B–C12B 1.469(3) Å; C2B–C10B–C11B 177.7(2), C10B–C11B–C12B 178.2(2)°]. The indenyl–C≡C–CH_3 units of complex **4a** are differentiated by an asymmetric metallocene conformational arrangement[14] where one of the propynyl groups at the bent metallocene wedge [Cl1–Zr–Cl2 95.45(2)°; Zr–Cl1 2.442(1), Zr–Cl2 2.405(1) Å] is oriented toward the lateral sector, whereas the other is found in the same sector but oriented markedly further toward the narrow bent metallocene back side. Both the indenyl rings are η^5-coordinated to the zirconium atom. The Zr–CH bond lengths lie in a narrow range [Zr–C1A 2.468(2), Zr–C2A 2.485(2), Zr–C3A 2.534(2) Å; Zr–C1B 2.510(2), Zr–C2B 2.545(2), Zr–C3B 2.523(2) Å], whereas the Zr–C indenyl bonds are slightly longer [Zr–C4A 2.639(2), Zr–C9A 2.570(2) Å; Zr–C4B 2.631(2), Zr–C9B 2.588(2) Å].

Single crystals of complex **4b** (R = Ph; Figure 2)[13] were obtained from dichloromethane/pentane (1:1) solution. The structure is similar to that of **4a**, except that the slightly more bulky phenylethynyl substituents are both oriented towards the same lateral sector of the bent metallocene wedge. The terminal phenyl substituents are oriented close to coplanar with their respective indenyl planes [deviations from coplanarity: 17.9° (A) and 15.4° (B)].

Complexation of the Alkynyl Substituents at the Bent Metallocene Stage

The zirconium complexes **4** were both treated with $[Co_2(CO)_8]$. As is often observed with purely organic acetylenes, the "organometallic" alkynyl systems **4a** and **4b** both react rapidly with the carbonylcobalt reagent to form the respective $[(alkyne)Co_2(CO)_6]$ complexes.[15–17] The products were isolated by crystallization from the toluene solution and obtained in 67% (**5a**) and 27% (**5b**) yield, respectively. Complex **5a** features a single ^{13}C NMR carbonyl resonance at δ = 199.9 ppm.[18] It shows three strong $\tilde{\nu}$(CO) IR bands at 2089, 2048, and 2019 cm^{-1} (plus one or two shoulders).[19] The ^{13}C NMR signals of the coordinated C≡C triple bond appear at δ = 83.7 and 95.4 ppm. Complex **5a** exhibits a single sharp ^1H NMR CH_3 signal at δ = 2.85 ppm (6 H) and a resonance for the indenyl 1-H/3-H protons at δ = 5.78 ppm (4 H).

Complex **5b** shows similar spectroscopic features [^1H NMR: δ = 5.93 (indenyl 1-H/3-H), 7.41/7.85 (indenyl 5/6-H/4/7-H) ppm; ^{13}C NMR: δ = 199.6 (CO), 83.1/92.8 (coordinated C≡C) ppm], and this complex was also characterized by X-ray diffraction. Single crystals were obtained by diffusion of pentane into a solution of **5b** in dichloromethane.

The crystal structure shows isolated molecules of the trinuclear metal complex **5b** (Figure 3) with each of the acetylene substituents coordinated to a $Co_2(CO)_6$ moiety. This results in a marked elongation of the C10–C11 bond in

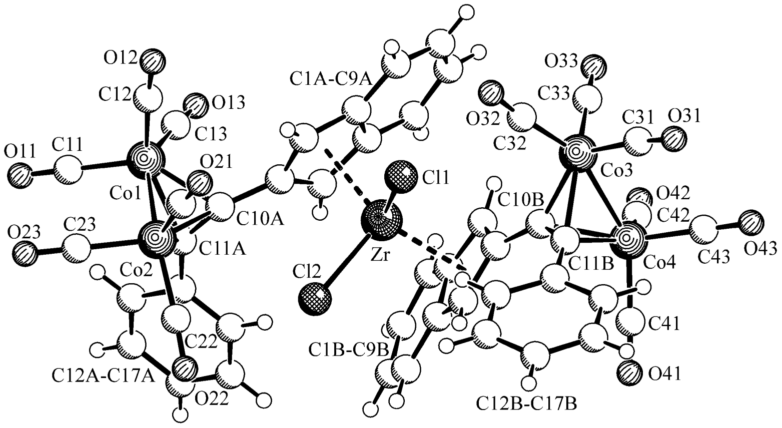


Figure 3. View of the molecular structure of complex **5b** (R = Ph). Selected bond lengths [Å] and angles [°]: Zr1–Cl1 2.422(1), Zr1–Cl2 2.415(1), Zr1–C1A 2.504(3), Zr1–C2A 2.588(3), Zr1–C3A 2.522(3), Zr1–C8A 2.553(3), Zr1–C9A 2.586(3), Zr1–C1B 2.561(3), Zr1–C2B 2.586(3), Zr1–C3B 2.463(3), Zr1–C8B 2.599(3), Zr1–C9B 2.531(3), C1A–C2A 1.410(4), C2A–C3A 1.428(4), C3A–C9A 1.432(4), C9A–C8A 1.434(4), C8A–C1A 1.435(4), C2A–C10A 1.453(4), C10A–C11A 1.342(4), C11A–C12A 1.472(4), C1B–C2B 1.414(4), C2B–C3B 1.421(4), C3B–C9B 1.441(4), C9B–C8B 1.430(4), C8B–C1B 1.426(4), C2B–C10B 1.462(4), C10B–C11B 1.346(4), C11B–C12B 1.465(4), Co1–Co2 2.461(1), Co1–C10A 2.004(3), Co1–C11A 1.950(3), Co2–C10A 1.955(3), Co2–C11A 1.980(3), Co3–Co4 2.462(1), Co3–C10B 1.962(3), Co3–C11B 1.964(3), Co4–C10B 1.996(3), Co4–C11B 1.979(3); Cl1–Zr–Cl2 95.69(3), C8A–C1A–C2A 108.4(3), C1A–C2A–C3A 107.9(3), C1A–C2A–C10A 126.9(3), C10A–C2A–C3A 124.8(3), C2A–C3A–C9A 108.0(3), C3A–C9A–C8A 107.4(3), C9A–C8A–C1A 107.5(3), C2A–C10A–C11A 142.6(3), C10A–C11A–C12A 141.6(3), C8B–C1B–C2B 108.0(3), C1B–C2B–C3B 108.5(3), C1B–C2B–C10B 123.5(3), C10B–C2B–C3B 127.5(3), C2B–C3B–C9B 107.3(3), C3B–C9B–C8B 107.6(3), C9B–C8B–C1B 107.8(3), C2B–C10B–C11B 139.2(3), C10B–C11B–C12B 142.5(3), Co1–C10A–Co2 76.8(1), Co1–C11A–Co2 77.5(1), Co3–C10B–Co4 76.9(1), C03–C11B–Co4 77.3(1).

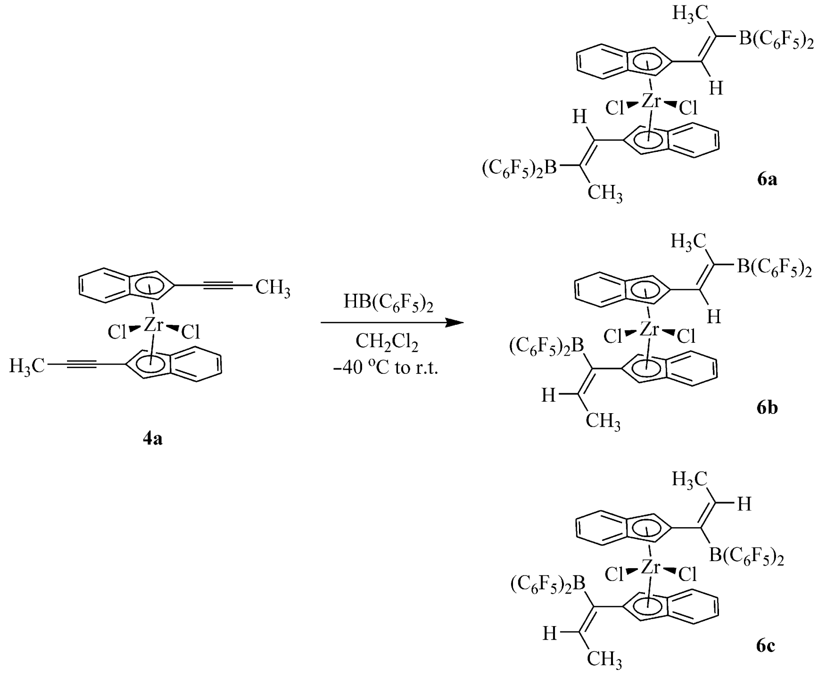
both these units [C10A–C11A 1.342(4), C10B–C11B 1.346(4) Å] with respect to the starting material **4b** (see above). The C10,C11,Co_2 unit forms a distorted tetrahedral substructure [unit B: Co3–Co4 2.462(1), C10B–Co3 1.962(3), C10B–Co4 1.996(3), C11B–Co3 1.964(3), C11B–Co4 1.979(3) Å]. Both ligands are again slightly different due to the specific conformational arrangement of the system, and both the very bulky $C_2(Ph)Co_2(CO)_6$ substituents are found oriented toward different lateral sectors of the bent metallocene wedge. The overall geometry deviates markedly from C_2 symmetry, with one of the substituents turned somewhat toward the front and the other toward the narrow metallocene backside. The indenyl ligands are quite uniformly η^5-coordinated to the zirconium atom [ring B: Zr–C3B 2.463(3), Zr–C2B 2.586(3), Zr–C1B 2.561(3), Zr–C8B 2.599(3), Zr–C9B 2.531(3) Å]. The coordinated acetylene groups in the pentanuclear complex are rotated only slightly out of the planes of their respective indenyl ligands [dihedral angles: C1A–C2A–C10A–C11A 170.6(4), C3B–C2B–C10B–C11B –171.5(4)°].

Hydroboration of the Alkynyl Substituents

Complex **4a** was employed as a substrate for a hydroboration reaction.[20] Thus, treatment of **4a** with the strongly electrophilic hydroboration reagent $HB(C_6F_5)_2$[21] in an approximate 1:2 molar ratio resulted in a clean addition to the C≡C triple bonds of both alkynyl substituents. The bis(hydroboration) product **6a** (see Scheme 2) was isolated in 27% yield from the reaction mixture. The characteristic NMR features of **6a** allowed us to assign its structure as that of the symmetrical regioselective β-borylalkenyl *cis* hydroboration product. It shows a slightly broadened ^1H NMR singlet for the alkenyl CH_3 (δ = 2.12 ppm) and =CH (δ = 7.02 ppm) groups (see Figure 4) and the alkenyl ^{13}C NMR resonances appear at δ = 146.8 (=C[B]) and 149.8 (=CH) ppm. Due to a rapid conformational equilibrium, the indenyl 1-H/3-H protons appear as a singlet at δ = 6.31 (4 H) ppm and the corresponding phenylene hydrogen atoms of the indenyl ligand core as an AA′BB′ pattern at δ = 7.65 and 7.30 (8 H) ppm.

However, hydroboration of **4a** with $HB(C_6F_5)_2$ (Piers' borane) turned out to be remarkably nonregioselective. This became evident when we treated a sample of **4a** with $[HB(C_6F_5)_2]$ in CD_2Cl_2 under slightly different experimental conditions and monitored the reaction directly by NMR spectroscopy without workup. This procedure revealed the formation of all three regioisomeric hydroboration products **6a**, **6b**, and **6c** in a 45:43:12 ratio. The symmetrical β,β-bis(hydroboration) product **6a**, which we had isolated earlier (see above), was one of the main products with the unsymmetrical α,β-bis(hydroboration) isomer **6b** being formed in almost equal amounts. This isomer was readily identified from the mixture by its typical ^1H NMR features. Thus, the signals for ligand I (α-B) occur at δ = 1.63 (d, ^3J = 7.2 Hz, 3 H), 5.71 (q, ^3J = 7.2 Hz, 1 H, =$CHCH_3$), 5.95 (s, 2 H, indenyl 1-H/3-H), and 7.39/7.82 (phenylene 4-H to 7-H) ppm, whereas the ^1H NMR resonances (β-B) of the "mixed" isomer (ligand II) appear at δ = 2.09 (s, 3 H), 6.01 (s, 2 H, indenyl 1-H/3-H), 7.01 (br. s, 1 H, CH=C[B]CH_3), and 7.26/7.59 (4-H to 7-H) ppm, as shown in Figure 4.

The third (and minor) isomer was assigned the structure of **6c**. This is the sterically most encumbered of the three products, which determines some of its properties. The symmetrical product **6c** was identified by observation of the typical NMR signals for ligand I [δ = 1.57 (d, ^3J = 7.2 Hz,



Scheme 2.

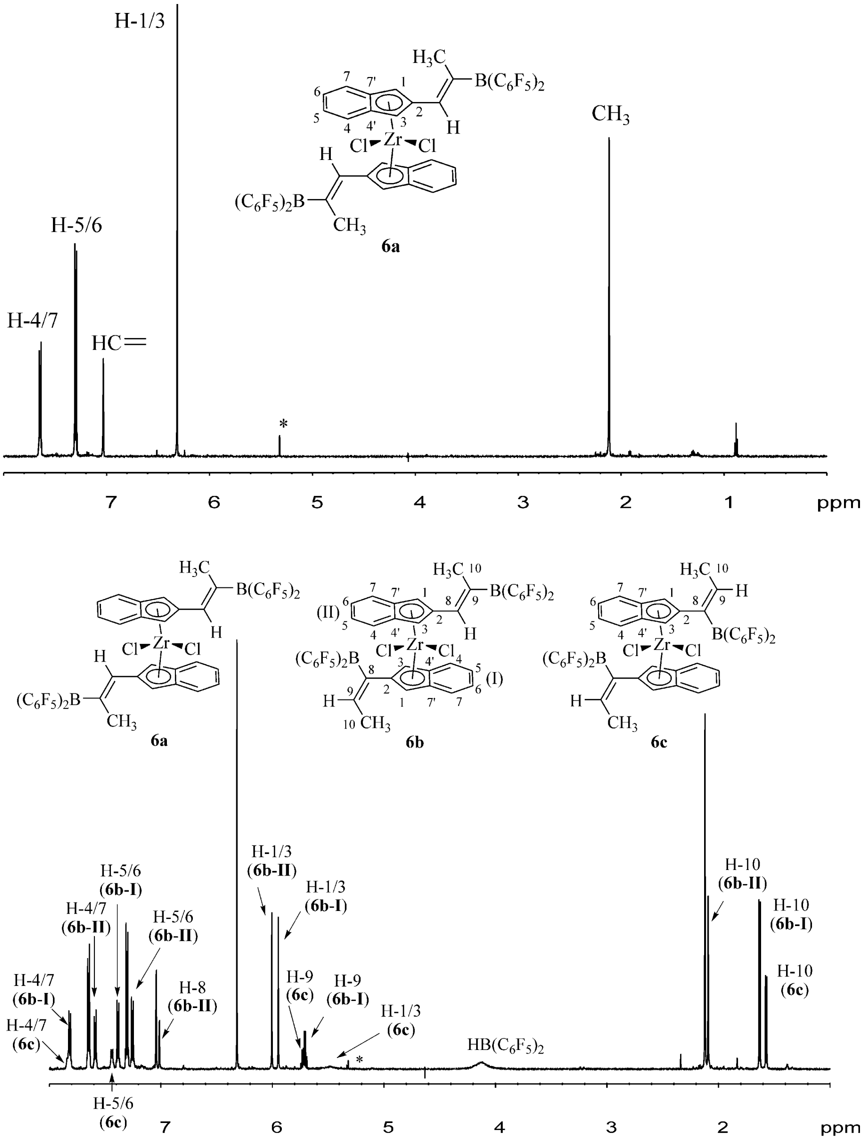


Figure 4. ^{1}H NMR spectra of **6a** (top) and the **6a/6b/6c** mixture (600 MHz, CD_2Cl_2, 298 K).

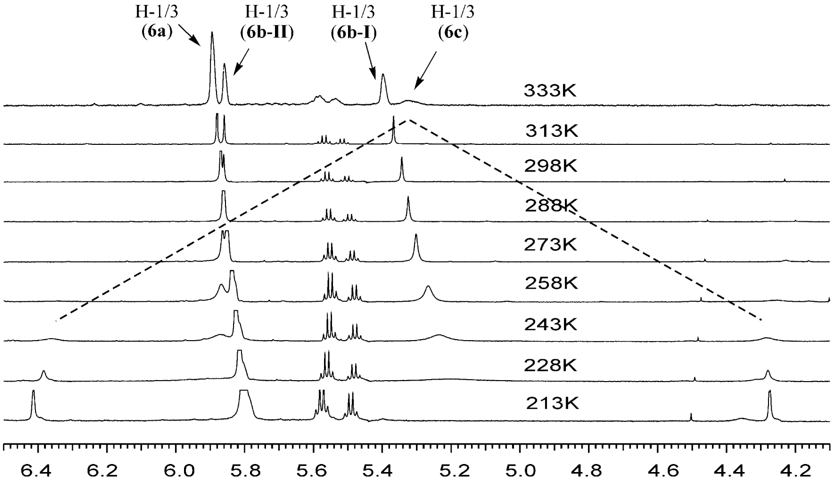


Figure 5. Temperature-dependent ^{1}H NMR spectra of the **6a/6b/6c** mixture of isomers ($C_6D_5CD_3$, 600 MHz).

6 H), 5.73 (q, ^3J = 7.2 Hz, 2 H, =CHCH$_3$), 7.44/7.82 (indenyl 4-H to 7-H) ppm]. The indenyl 1-H/3-H ^{1}H NMR resonance appears at δ = 5.49 ppm as a broad singlet at 298 K (600 MHz). However, hindered rotation around the indenyl C2 olefin C$_\alpha$ bond in this isomer (**6c**),[22] which is probably due to the increased steric bulk of the α-boryl-substituted alkenyl side-chain, means that decoalescence of the indenyl 1-H/3-H ^{1}H NMR resonance of complex **6c** is observed upon lowering the temperature (see Figure 5). This eventually leads to the observation of separate signals for the indenyl 1-H (δ = 4.27 ppm) and 3-H (δ = 6.41 ppm) protons (in C$_6$D$_5$CD$_3$, 600 MHz). A Gibbs activation energy barrier of $\Delta G^{\neq}$(293 K) = 12.5 ± 0.9 kcal mol^{-1} was determined for this rotational process at the coalescence temperature. A close inspection of the NMR spectra shown in Figure 5 also shows that the corresponding ligand I indenyl 1-H/3-H ^{1}H NMR resonance of the unsymmetrical isomer **6b** also broadens with decreasing temperature, although the limiting low-temperature NMR spectrum under static conditions could not be reached in this case.

Olefin Polymerization Reactions

Ethene polymerization reactions were carried out with the mononuclear zirconium complexes **4a** and **4b**, the dimetallic systems **5a** and **5b**, and the Zr/B system **6a**. In each case, the bent metallocene catalyst precursor was activated in toluene by treatment with a large excess (Al/Zr = 1280) of methylalumoxane (MAO).[23] As can be seen from Table 1, the metallocene catalysts derived from systems **4** are both very active, although the activity drops drastically upon going to the dimetallic systems **5**/MAO, which may be due to the enormous steric bulk of the alkynyl/Co$_2$(CO)$_6$ substituents. It is nevertheless remarkable that the presence of the highly functionalized carbonylmetal units does not interfere with olefin polymerization activity, except perhaps sterically. The system **6a**/MAO is again quite active in ethene polymerization, and it seems that here the attached CH=CMeB(C$_6$F$_5$)$_2$ groups primarily serve as inert substituents at the indenyl ligands.

Table 1. Ethene polymerization with the homogeneous **4a**, **4b**, **5a**, **5b**, and **6a**/MAO metallocene Ziegler–Natta catalyst systems.[a]

Polymer	Cat.	Zr cat. [mg]	Yield PE [g]	Activity[b]	M.p. [°C]
PE1	**4a**	11.7	30.7	1228	125
PE2	**4b**	14.8	38.2	1528	127
PE3	**5a**	26.0	2.95	118	124
PE4	**5a**	26.0	1.79	71	126
PE5	**5b**	29.1	0.47	19	126
PE6	**5b**	29.1	0.39	16	126
PE7	**6a**	29.0	14.2	568	124

[a] Reaction conditions: 200 mL of toluene, 20 mL of 1.6 M MAO solution in toluene, 2 bar of ethene, 30 min, 20 °C, 600 rpm of stirring, 2.5 × 10^{-5} mol of Zr catalyst (Al/Zr = 1280). [b] kg PE/[(mol Zr) h bar(ethene)].

The **5**/MAO catalysts turned out to be inactive in propene polymerization under our applied reaction conditions. However, the **4a**,**4b**/MAO systems were quite active homogeneous metallocene Ziegler–Natta catalysts for propene polymerization. As can be seen from Table 2, both the mononuclear metallocene complexes **4a** and **4b** give very active propene polymerization catalysts when activated with MAO. A marked temperature dependence of the catalyst activity is observed in both cases, with a maximum at around 0 °C, which drops off upon either decreasing or increasing the reaction temperature. The molecular weight of the polypropylene formed with the **4a**/MAO catalyst system is high at –20 °C (M_w > 200000) but drops off rapidly to a mere 30000 at +40 °C. A similar trend is observed for the polypropylene obtained from the **4b**/MAO catalyst system, which starts at an even higher molecular weight at –20 °C (see Table 2). The boryl-functionalized **6a**/MAO catalyst is also active in propene polymerization, albeit slightly less than the former pair of metallocene catalyst systems.

The polypropylenes obtained are atactic, although in a certain temperature range (approx. 0 to +20 °C) a measurable positive deviation of the mmmm pentad content was noted. This is potentially due to some stereoblock polymer formation. Consequently, some of the polymer samples feature elastomeric properties, although of a clearly inferior quality to PP samples obtained from related 2-arylindene-

Table 2. Results of selected propene polymerization reactions employing **4/6a**/MAO catalyst systems.[a]

Polymer	Cat.	T [°C]	mmmm [%]	M_n[b]	M_w[b]	PDI	PP yield [g]	Activity[c]
PP1	**4a**	–20[d]	9.0	13.3	23.8	1.78	5.30	424
PP2	**4a**	–20[d],[e]	9.5	9.83	18.9	1.92	8.40	336
PP3	**4a**	0	12.6	5.79	13.7	2.37	41.4	1656
PP4	**4a**	+20	13.8	2.30	6.24	2.71	25.9	1036
PP5	**4a**	+40	11.8	0.92	2.98	3.26	10.9	436
PP6	**4b**	–20[d]	10.3	18.4	35.6	1.94	7.32	586
PP7	**4b**	0	16.0	6.83	19.8	2.90	41.3	1652
PP8	**4b**	+20	16.7	3.56	9.59	2.70	32.0	1280
PP9	**4b**	+40	13.4	1.17	3.67	3.14	18.4	736
PP10	**6a**	0	10.5	7.45	15.2	2.06	11.7	468
PP11	**6a**	+20	11.6	4.00	7.28	1.82	2.55	102

[a] Reaction conditions: 200 mL of toluene, 2.5 × 10^{-5} mol of Zr catalyst, 20 mL of 1.6 M MAO solution in toluene (Al/Zr = 1280), 2 bar of propene, 600 rpm of stirring, 30 min reaction time. [b] × 10^4 g mol^{-1}. [c] kg PP/[(mol Zr) h bar(propene)]. [d] 25 mL of liquid propene was used. [e] 60 min reaction time.

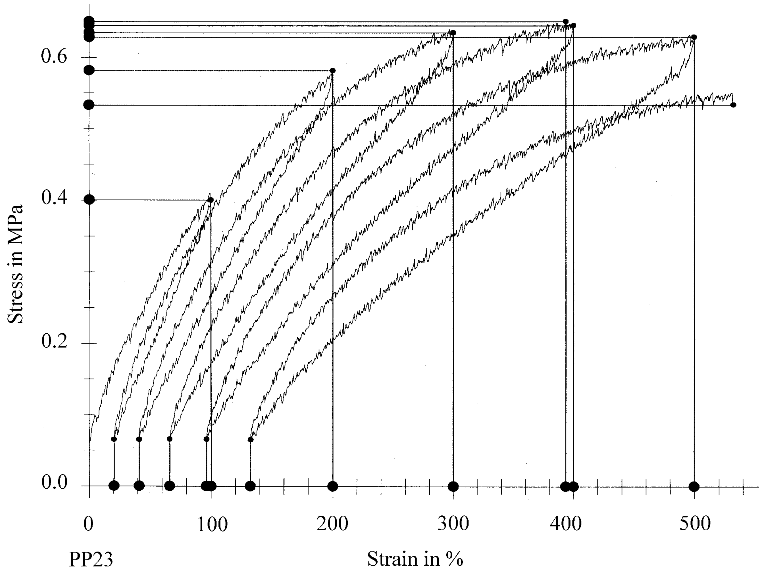


Figure 6. Stress vs. strain curve of an elastomeric polypropylene sample obtained at –20 °C with the **4b**/MAO catalyst system.

or -hetareneindene-derived catalyst systems.[22,24,25] A typical stress/strain behaviour of a polypropylene sample (PP23) obtained with the **4b**/MAO catalyst at –20 °C (60 min reaction time; see the Supporting Information for details) is shown in Figure 6.

Conclusions

This study has shown that alkynyl-substituted bent metallocenes can readily be synthesized by a route employing the respective preassembled ligand systems. The pendant alkynyl functionalities at the bent metallocene framework have been shown to cleanly undergo some typical reactions which are tolerated at the rather sensitive bent metallocene core. We have thus been able to add carbonylcobalt groups to the pair of substituted alkynyl groups to yield the heterodimetallic complexes **5** and have been able to utilize the alkynyl groups as building blocks in chemoselective (but not regioselective) hydroboration reactions. In all cases, the newly introduced functional groups tolerate the special conditions employed in the generation of active metallocene olefin polymerization catalysts. The results of our study add to the increasing evidence that a functional group chemistry can be developed at the bent metallocene stage if the specific features of the sensitive group 4 bent metallocene systems are adequately taken into account.

Experimental Section

General Considerations: All manipulations were carried out under argon using Schlenk-type glassware or in a glove box, unless otherwise noted. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use according to standard procedures. Melting points were determined with a TA Instruments DSC 2010. Mass spectra were recorded with a Finnigan MAT 8200 mass spectrometer. Elemental analyses were performed with a Foss-Heraeus CHN-O Rapid instrument. The IR spectra were recorded with a Varian 3100 Excalibur FT-IR spectrometer. NMR spectra were recorded with a Bruker AC200 P, a Varian 500 MHz INOVA or a Varian Unity Plus 600 NMR spectrometer. Most NMR assignments were based on a series of NOE, Tocsy, and 2D NMR experiments. Variable-temperature ^{1}H NMR experiments were conducted with a Varian Unity Plus 600 NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to solvent signals. Analysis of the elasticity of the polypropylenes was carried out with a Zwicki 1120 from Zwick company. 2-Bromoindene (**1**),[26] $[ZrCl_4(thf)_2]$[12], and $HB(C_6F_5)_2$[27] were prepared according to literature procedures. $[NiCl_2(dppe)]$, propynylmagnesium bromide thf solution (0.5 M), phenylacetylene, and $Co_2(CO)_8$ were commercially available.

Preparation of 2-(Prop-1-ynyl)indene (2a): thf (20 mL) was added to a mixture of 2-bromoindene (**1**; 3.90 g, 20 mmol) and $[NiCl_2(dppe)]$ (200 mg, 0.22 mmol, approx. 10 mol-%) in a Schlenk tube. The red suspension was stirred at 0 °C, and propynylmagnesium bromide (0.5 M solution in thf; 44 mL, 22 mmol) was added to the mixture dropwise. The mixture turned yellow. The water/ice bath was removed and the reaction mixture was refluxed for 3 h to afford a deep red mixture. Water (20 mL) was added to quench the reaction, and the product was extracted with diethyl ether (3 × 40 mL). The combined organic phases were washed successively with a saturated $NaHCO_3$ solution (2 × 30 mL) and brine (2 × 30 mL) and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuo, and the remaining yellow mixture was purified by column chromatography with pentane to give 2.38 g of colorless product (R_f = 0.14). Yield: 77%. M.p. 64 °C (DSC). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 2.07 (s, 3 H, CH_3), 3.48 (m, 2 H, 3-H), 6.95 (m, 1 H, 1-H), 7.20 [td, $J_{H,H}$ = 7.5, 1.2 Hz, 1 H, 5-H), 7.26 (tm, $J_{H,H}$ = 7.5 Hz, 1 H, 6-H), 7.34 (dm, $J_{H,H}$ = 7.5 Hz, 1 H, 7-H), 7.40 (dm, $J_{H,H}$ = 7.5 Hz, 1 H, 4-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): δ = 4.7 (CH_3), 43.2 (C-3), 77.0 (≡C–), 91.3 (≡C–Me), 121.3 (C-7), 123.8 (C-4), 125.7 (C-5), 126.9 (C-6), 128.8 (C-2), 135.9 (C-1), 143.0 (C-3a), 144.6 (C-7a) ppm. MS (EI): *m/z* (%) = 154.0 (100) [M^+]. IR (KBr): $\tilde{\nu}$ = 3067 (m), 2952 (w), 2895 (w), 2846 (w), 2760 (w), 2327 (w), 2219 (w), 1457 (s), 1386 (s), 1230 (m), 1201 (m), 847 (s), 744 (s), 714 (s), 599 (m) cm^{-1}. $C_{12}H_{10}$ (154.2): calcd. C 93.46, H 6.54; found C 93.07, H 6.46.

Preparation of 2-(Phenylethynyl)indene (2b): 2-Bromoindene (**1**; 3.90 g, 20 mmol) and [NiCl$_2$(dppe)] (200 mg, 0.22 mmol, 10 mol-%) were mixed, and thf (20 mL) was added. The red suspension **A** was stirred at 0 °C. Magnesium turnings (608 mg, 25 mmol) and thf (10 mL) were added to a three-necked, round-bottomed flask, and bromoethane (2.72 g, 25 mmol) in thf (20 mL) was added dropwise. The reaction was initiated by brief heating with a heat gun. The suspension was kept refluxing by the controlled addition of the C$_2$H$_5$Br solution. When the addition was finished, the mixture was stirred for another 1 h. The Grignard reagent solution was cooled to –78 °C, and phenylacetylene (2.55 g, 25 mmol) was added dropwise. The mixture was stirred at –78 °C for 1 h and then slowly warmed to room temperature. The resulting (phenylethynyl)magnesium bromide Grignard reagent **B** was added to suspension **A** at 0 °C. The mixture turned brown. The water/ice bath was then removed, and the reaction mixture refluxed for 3 h to give a brown mixture. Water (20 mL) was added to quench the reaction, and the product was extracted with Et$_2$O (3 × 40 mL). The combined organic phases were washed with a saturated NaHCO$_3$ solution (2 × 30 mL), then with brine (2 × 30 mL) and dried with anhydrous MgSO$_4$. The solvent was removed in vacuo, and the remaining yellow mixture was purified by column chromatography with pentane to give 1.79 g of the colorless product (R_f = 0.09). Yield: 41 %. M.p. 100 °C (DSC). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$, 298 K): δ = 3.64 (m, 2 H, 3-H), 7.17 (td, $J_{H,H}$ = 1.8, 0.8 Hz, 1 H, 1-H), 7.24 (td, $J_{H,H}$ = 7.4, 1.2 Hz, 1 H, 5-H), 7.30 (tdt, $J_{H,H}$ = 7.4, 1.2, 0.8 Hz, 1 H, 6-H), 7.36, 7.37 (m, 3 H, *p,m*-Ph), 7.41 (dm, $J_{H,H}$ = 7.4 Hz, 1 H, 7-H), 7.45 (dm, $J_{H,H}$ = 7.4 Hz, 1 H, 4-H), 7.52 (m, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD$_2$Cl$_2$, 298 K): δ = 43.1 (C-3), 86.9 (≡C–), 94.3 (≡C–Ph), 121.7 (C-7), 123.7 (*i*-Ph), 123.9 (C-4), 126.1 (C-5), 127.1 (C-6), 127.7 (C-2), 128.7 (*p*-Ph), 128.8 (*m*-Ph), 131.8 (*o*-Ph), 137.6 (C-1), 143.5 (C-3a), 144.5 (C-7a) ppm. MS (EI): *m/z* (%) = 216.1 (100) [M$^+$]. IR (KBr): ṽ = 3069 (w), 2959 (w), 2921 (w), 2351 (w), 2192 (w), 1597 (m), 1487 (m), 1458 (m), 1382 (m), 1207 (w), 862 (m), 755 (s), 714 (m), 687 (m) cm^{-1}. C$_{17}$H$_{12}$ (216.3): calcd. C 94.41, H 5.59; found C 94.33, H 5.37.

Preparation of 2-(Prop-1-ynyl)indenyllithium (3a): A solution of *n*BuLi in hexane (1.6 M; 12.7 mL, 20 mmol) was added dropwise to a solution of 2-(prop-1-ynyl)indene (**2a**; 3.13 g, 20 mmol) in diethyl ether (40 mL) at 0 °C, and the mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed in vacuo from the yellow suspension to give an orange solid, which was washed with pentane (60 mL). Filtration gave a yellow solid, which was dried in vacuo to yield 3.13 g of the product. Yield: 98 %. ^{1}H NMR (600 MHz, C$_6$D$_5$CD$_3$ with two drops of [D$_8$]THF, 298 K): δ = 1.86 (s, 3 H, CH$_3$), 6.45 (s, 2 H, 1-H, 3-H), 6.84 (m, 2 H, 5-H, 6-H), 7.54 (m, 2 H, 4-H, 7-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_5$CD$_3$ with two drops of [D$_8$]THF, 298 K): δ = 4.6 (CH$_3$), 80.9 (≡C–Me), 82.1 (≡C–), 96.7 (C-1, C-3), 110.4 (C-2), 116.6 (C-5, C-6), 120.2 (C-4, C-7), 128.0 (C-3a, C-7a) ppm.

Preparation of 2-(Phenylethynyl)indenyllithium (3b): A solution of *n*BuLi in hexane (1.6 M; 8.0 mL, 12.8 mmol) was added dropwise to a solution of 2-(phenylethynyl)indene (**2b**; 2.77 g, 12.8 mmol) in diethyl ether (40 mL) at 0 °C, and the mixture was kept at 0 °C for 2 h. The solvent was then removed in vacuo to give a sticky yellow solid, which was solidified by treatment with pentane (40 mL). Filtration gave a yellow solid, which was dried in vacuo to yield 2.52 g of the product. Yield: 88 %. ^{1}H NMR (600 MHz, C$_6$D$_5$CD$_3$ with two drops of [D$_8$]THF, 298 K): δ = 6.59 (s, 2 H, 1-H, 3-H), 6.86 (m, 2 H, 5-H, 6-H), 6.92 (m, 1 H, *p*-Ph), 7.02 (m, 2 H, *m*-Ph), 7.44 (m, 2 H, *o*-Ph), 7.57 (m, 2 H, 4-H, 7-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_5$CD$_3$ with two drops of [D$_8$]THF, 298 K): δ = 87.4 (≡C–Ph), 93.8 (≡C–), 97.5 (C-1, C-3), 108.7 (C-2), 117.0 (C-5, C-6), 120.4 (C-4, C-7), 126.4 (*p*-Ph), 126.8 (*i*-Ph), 128.5 (*m*-Ph), 128.7 (C-3a, C-7a), 131.1 (*o*-Ph) ppm.

Preparation of Bis[2-(prop-1-ynyl)indenyl]zirconium Dichloride (4a): 2-(Prop-1-ynyl)indenyllithium (**3a**; 0.96 g, 6.0 mmol) and ZrCl$_4$·2thf (1.13 g, 3.0 mmol) were added to a Schlenk tube, and the mixture was cooled to –78 °C. Cold toluene (30 mL, –78 °C) was added to the mixture, then the suspension was stirred at –78 °C for 2 h and slowly warmed to room temperature and stirred overnight. The resulting yellow suspension was filtered to give a yellow solution. CH$_2$Cl$_2$ (50 mL) was used to extract additional product from the remaining solid. The yellow solution was concentrated in vacuo. Crystallization at about –30 °C gave 0.95 g of the yellow product. Yield: 67 %. Crystals suitable for X-ray crystallography were obtained from toluene at about –30 °C. M.p. 223 °C (DSC). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$, 298 K): δ = 2.21 (s, 3 H, CH$_3$), 6.55 (s, 2 H, 1-H, 3-H), 7.20 (m, 2 H, 5-H, 6-H), 7.43 (m, 2 H, 4-H, 7-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD$_2$Cl$_2$, 298 K): δ = 4.8 (CH$_3$), 74.1 (≡C–), 93.4 (≡C–CH$_3$), 109.6 (C-1, C-3), 115.3 (C-2), 124.9 (C-4, C-7), 126.8 (C-3a, C-7a), 127.4 (C-5, C-6) ppm. IR (KBr): ṽ = 3110 (w), 2912 (w), 2843 (w), 2240 (m, C≡C), 1614 (w), 1436 (m), 1209 (m), 838 (s), 749 (s), 642 (m), 588 (w) cm^{-1}. C$_{24}$H$_{18}$Cl$_2$Zr (468.53): calcd. C 61.52, H 3.87; found C 61.42, H 3.63.

X-ray Crystal Structure Analysis of Complex 4a: Formula C$_{24}$H$_{18}$Cl$_2$Zr, *M* = 468.50, yellow crystal 0.30 × 0.20 × 0.15 mm, *a* = 27.904(1), *b* = 7.676(1), *c* = 19.846(1) Å, β = 109.61(1)°, *V* = 4004.3(6) Å^3, ρ = 1.554 g cm^{-3}, μ = 8.22 cm^{-1}, empirical absorption correction (0.791 ≤ *T* ≤ 0.887), *Z* = 8, monoclinic, space group *C*2/*c* (no. 15), λ = 0.71073 Å, *T* = 198(2) K, ω and ϕ scans, 13229 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] 0.67 Å^{-1}, 4881 independent (R_{int} = 0.041) and 4284 observed reflections [$I \geq 2\sigma(I)$], 246 refined parameters, *R* = 0.026, *wR*$_2$ = 0.064, max. residual electron density 0.28 (–0.75) e Å^{-3}.

Preparation of Bis[2-(phenylethynyl)indenyl]zirconium Dichloride (4b): 2-(Phenylethynyl)indenyllithium (**3b**; 1.33 g, 6.0 mmol) and ZrCl$_4$·2thf (1.13 g, 3.0 mmol) were mixed in a Schlenk tube and the mixture cooled to –78 °C. Cold toluene (40 mL, –78 °C) was added to the mixture, then the suspension was stirred at –78 °C for 2 h and then slowly warmed to room temperature and stirred overnight. The resulting yellow suspension was filtered to give a yellow solution. CH$_2$Cl$_2$ (50 mL) was used to extract additional product from the remaining solid. The yellow solution was concentrated in vacuo. Crystallization at about –30 °C gave 1.36 g of the yellow product. Yield: 76 %. Crystals suitable for X-ray crystallography were obtained from a mixture of dichloromethane and pentane at about +4 °C. M.p. 207 °C (DSC). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$, 298 K): δ = 6.75 (s, 2 H, 1-H, 3-H), 7.23 (m, 2 H, 5-H, 6-H), 7.39 (m, 2 H, *m*-Ph), 7.41 (m, 1 H, *p*-Ph), 7.49 (m, 2 H, 4-H, 7-H), 7.59 (m, 2 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (150.8 MHz, CD$_2$Cl$_2$, 298 K): δ = 83.8 (≡C–), 95.8 (≡C–Ph), 109.5 (C-1, C-3), 114.2 (C-2), 122.6 (*i*-Ph), 125.0 (C-4, C-7), 127.3 (C-3a, C-7a), 127.8 (C-5, C-6), 129.0 (*m*-Ph), 129.5 (*p*-Ph), 132.1 (*o*-Ph) ppm. IR (KBr): ṽ = 3107 (w), 3057 (w), 2216 (m, C≡C), 1635 (m, br.), 1535 (m), 1498 (m), 1440 (m), 1367 (w), 1205 (w), 834 (s), 758 (s), 692 (m), 644 (w), 530 (w) cm^{-1}. C$_{34}$H$_{22}$Cl$_2$Zr (592.67): calcd. C 68.90, H 3.74; found C 68.87, H 3.45.

X-ray Crystal Structure Analysis of Complex 4b: Formula C$_{34}$H$_{22}$Cl$_2$Zr, *M* = 592.64, yellow crystal 0.20 × 0.20 × 0.20 mm, *a* = 11.801(1), *b* = 13.040(1), *c* = 17.255(1) Å, *V* = 2655.3(3) Å^3, ρ = 1.428 g cm^{-3}, μ = 6.37 cm^{-1}, empirical absorption correction (0.883 ≤ *T* ≤ 0.883), *Z* = 4, orthorhombic, space group $P2_12_12_1$ (no. 19), λ = 0.71073 Å, *T* = 198(2) K, ω and ϕ scans, 20825 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] 0.67 Å^{-1}, 6439 independent (R_{int}

= 0.058) and 5423 observed reflections [$I \geq 2\sigma(I)$], 334 refined parameters, R = 0.038, wR_2 = 0.060, Flack parameter –0.05(3), max. residual electron density 0.58 (–0.50) e Å^{-3}.

Preparation of the Dimetallic Zr/Co Complex 5a: Complex **4a** (200 mg, 0.43 mmol) and $Co_2(CO)_8$ (301 mg, 0.88 mmol) were added to a Schlenk tube, which was cooled to –78 °C. Cold toluene (15 mL, –78 °C) was then added to the mixture, and the suspension was slowly warmed to room temperature with stirring. Filtration gave a brown solution from which the solvent was partly removed in vacuo. The concentrated solution was kept at about –30 °C for crystallization, and a brown solid was collected by filtration and dried in vacuo to yield 305 mg of the product. Yield: 67%. ^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 2.85 (s, 3 H, CH_3), 5.78 (s, 2 H, 1-H, 3-H), 7.39 (m, 2 H, 5-H, 6-H), 7.83 (m, 2 H, 4-H, 7-H) ppm. ^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2): δ = 22.6 (CH_3), 83.7, 95.4 (C≡C), 106.0 (C-1, C-3), 126.1 (C-5, C-6), 126.4 (C-3a, C-7a),126.6 (C-4, C-7), 142.3 (C-2), 199.9 (br., CO) ppm. M.p. 193 °C (DSC). IR (KBr): $\tilde{\nu}$ = 2964 (w), 2929 (w), 2904 (w), 2858 (w), 2089 (s), 2048 (s), 2019 (s), 1634 (m), 1427 (w), 1384 (w), 1258 (w), 1203 (w), 1146 (w), 1051 (m), 1011 (m), 820 (m), 750 (m), 637 (w), 516 (s), 469 (m), 415 (w) cm^{-1}. $C_{36}H_{18}Cl_2Co_4O_{12}Zr$ (1040.38): calcd. C 41.56, H 1.74; found C 41.55, H 1.60.

Preparation of the Dimetallic Zr/Co Complex 5b: Complex **4b** (302 mg, 0.51 mmol) and $Co_2(CO)_8$ (349 mg, 1.02 mmol) were added to a Schlenk tube, which was cooled to –78 °C. Cold toluene (15 mL, –78 °C) was then added to the mixture and the suspension was stirred and slowly warmed to room temperature. Filtration gave a brown solution from which the solvent was removed in vacuo. The brown residue was dissolved in a mixture of pentane (10 mL) and CH_2Cl_2 (5 mL). The solution was filtered and kept at about –30 °C for crystallization. The resultant brown solid was collected and dried in vacuo to yield 159 mg of the product. Yield: 27%. M.p. 209 °C (DSC). Crystals suitable for X-ray crystallography were obtained by diffusion of pentane into a CH_2Cl_2 solution of **5b** at room temperature. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 5.93 (br., 2 H, 1-H, 3-H), 7.37 (m, 1 H, *p*-Ph), 7.39 (m, 2 H, *m*-Ph), 7.41 (m, 2 H, 5-H, 6-H), 7.60 (m, 2 H, *o*-Ph), 7.85 (m, 2 H, 4-H, 7-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 83.1 (≡C–), 92.8 (≡C–Ph), 105.6 (br., C-1, C-3), 126.3 (C-5, C-6), 126.4 (C-3a, C-7a), 126.6 (C-4, C-7), 128.3 (*p*-Ph), 128.9 (*m*-Ph), 130.6 (*o*-Ph), 138.3 (*i*-Ph), 142.8 (C-2), 199.6 (br., CO) ppm. IR (KBr): $\tilde{\nu}$ = 3078 (w), 2087 (s), 2052 (s), 2021 (s), 1846 (m), 1635 (m), 824 (m), 750 (m), 693 (m), 648 (m), 508 (m), 512 (m), 459 (m) cm^{-1}. $C_{46}H_{22}Cl_2Co_4O_{12}Zr$ (1164.5): calcd. C 47.44, H 1.90; found C 47.34, H 1.81.

X-ray Crystal Structure Analysis of Complex 5b: Formula $C_{46}H_{22}Cl_2O_{12}Co_4Zr$, M = 1164.48, red crystal 0.40 × 0.10 × 0.02 mm, a = 8.364(1), b = 15.278(1), c = 18.277(1) Å, α = 95.95(1), β = 101.72(1), γ = 92.24(1)°, V = 2270.2(3) Å^3, ρ = 1.704 g cm^{-3}, μ = 18.32 cm^{-1}, empirical absorption correction (0.528 ≤ T ≤ 0.964), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 25819 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] 0.67 Å^{-1}, 10881 independent (R_{int} = 0.063) and 7915 observed reflections [$I \geq 2\sigma(I)$], 586 refined parameters, R = 0.047, wR_2 = 0.076, max. residual electron density 0.51 (–0.69) e Å^{-3}.

Preparation of Complex 6a: Complex **4a** (200 mg, 0.43 mmol) and $HB(C_6F_5)_2$ (295 mg, 0.85 mmol) were added to a Schlenk tube, which was cooled to –40 °C. Cold dichloromethane (10 mL, –78 °C) was then added to the mixture, and the suspension was stirred and warmed slowly to room temperature (approx. 40 min). Filtration gave a yellow solution from which the solvent was removed in vacuo to give an orange residue. Pentane (20 mL) was added to the mixture, and the suspension was stirred for about 30 min to give an orange precipitate. The orange solid was collected by filtration and dried in vacuo to afford 133 mg of the product. Yield: 27%. M.p. 151 °C (DSC). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 2.12 (d, $J_{\text{H,H}}$ = 1.3 Hz, 6 H, CH_3), 6.31 (s, 4 H, 1-H, 3-H), 7.02 (q, $J_{\text{H,H}}$ = 1.3 Hz, 2 H, =CH), 7.30 (m, 4 H, 5-H, 6-H), 7.65 (m, 4 H, 4-H, 7-H) ppm. ^{11}B NMR (64 MHz, CD_2Cl_2, 300 K): δ = 66 ($\nu_{1/2}$ = 3300 Hz) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 18.4 (CH_3), 108.4 (C-1, C-3), 114.4 (*i*-C_6F_5), 125.7 (C-4, C-7), 127.6 (C-5, C-6), 127.6 (C-3a, C-7a), 131.6 (C-2), 137.9 (dm, J = 252 Hz, C_6F_5), 143.3 (dm, J = 256 Hz, *p*-C_6F_5), 146.8 (=C–B), 146.9 (dm, J = 246 Hz, C_6F_5), 149.8 ($^1J_{\text{C,H}}$ = 159 Hz, =CH) ppm. ^{19}F NMR (546 MHz, CD_2Cl_2, 298 K): δ = –129.7 (2 F, *o*), –150.0 (1 F, *p*), –162.0 (2 F, *m*) ppm. IR (KBr): $\tilde{\nu}$ = 2964 (w), 2920 (w), 1647 (s), 1576 (m), 1519 (s), 1471 (s), 1389 (m), 1311 (m), 1287 (m), 1232 (m), 1100 (s), 974 (s), 902 (s), 837 (w), 805 (w), 747 (m), 688 (m), 634 (w), 578 (w) cm^{-1}. $C_{48}H_{20}B_2Cl_2F_{20}Zr$ (1160.4): calcd. C 49.68, H 1.74; found C 49.19, H 1.92.

Preparation of Complexes 6a, 6b, and 6c in CD_2Cl_2 in an NMR Tube: Complex **4a** (20 mg, 0.043 mmol) and $HB(C_6F_5)_2$ (59 mg, 0.17 mmol) were mixed, and CD_2Cl_2 (0.8 mL) was added at room temperature. The yellow solution was transferred to an NMR tube [a small amount of $HB(C_6F_5)_2$ remained undissolved], which was sealed for the NMR measurements. The resulting ratio of complexes **6a**/**6b**/**6c** was 45:43:12. **Complex 6a:** ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 2.12 (br. s, 6 H, CH_3), 6.31 (s, 4 H, 1-H, 3-H), 7.04 (br., 2 H, =CH), 7.30 (m, 4 H, 5-H, 6-H), 7.65 (m, 4 H, 4-H, 7-H) ppm. **Complex 6b:** ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 1.63 [d, ^3J = 7.2 Hz, 3 H, CH_3 (**6b-I**)], 2.09 [s, 3 H, CH_3 (**6b-II**)], 5.71 [q, ^3J = 7.2 Hz, 1 H, =CH (**6b-I**)], 5.95 [s, 2 H, 1-H, 3-H (**6b-I**)], 6.01 [s, 2 H, 1-H, 3-H (**6b-II**)], 7.01 [br, 1 H, =CH (**6b-II**)], 7.26 [m, 2 H, 5-H, 6-H (**6b-II**)], 7.39 [m, 2 H, 5-H, 6-H (**6b-I**)], 7.59 [m, 2 H, 4-H, 7-H (**6b-II**)], 7.82 [m, 2 H, 4-H, 7-H (**6b-I**)] ppm. **Complex 6c:** ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 1.57 (d, ^3J = 7.2 Hz, 6 H, CH_3), 5.49 (br, 4 H, 1-H, 3-H), 5.73 (q, ^3J = 7.2 Hz, 2 H, =CH), 7.44 (m, 4 H, 5-H, 6-H), 7.82 (m, 4 H, 4-H, 7-H) ppm. ^{11}B NMR (64 MHz, CD_2Cl_2, 300 K): δ = 62 ppm ($\nu_{1/2}$ = 2400 Hz). ^{19}F NMR (546 MHz, $C_6D_5CD_3$, 298 K): **6a**: δ = –129.8 (8 F, *o*), –148.70 (4 F, *p*), –161.1 (8 F, *m*) ppm; **6b**: δ = –129.8 (4 F, *o*), –148.1, (2 F, *p*), –160.9 (4 F, *m*), –127.8 (4 F, *o*), –152.7 (2 F, *p*), –163.4 (4 F, *m*) ppm; **6c**: δ = –127.9 (8 F, *o*), –151.7 (4 F, *p*), –162.9 (8 F, *m*) ppm.

X-ray Crystal-Structure Determination: Data sets were collected with a Nonius KappaCCD diffractometer equipped with a rotating anode generator. Programs used: data collection: COLLECT (Nonius B.V., **1998**); data reduction: Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326); absorption correction: SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33–37; R. H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421–426); structure solution: SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473); structure refinement: SHELXL-97 (G. M. Sheldrick, University of Göttingen, **1997**); graphics: SCHAKAL (E. Keller, University of Freiburg, **1997**). CCDC-650362 (**4a**), -650516 (**4b**) and -650363 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Polymerization Procedure (T > 0 °C): Polymerization reactions were performed in a thermostatted Büchi glass autoclave system. The autoclave was evacuated and filled with argon three times then charged with toluene (200 mL) and methylalumoxane (MAO)/

toluene solution (1.6 M, 14 mL). The catalyst-addition funnel was first dried with MAO/toluene solution (2 mL), and then 2.5×10^{-5} mol of Zr catalyst precursor in MAO/toluene solution (4 mL) was added to the funnel. The polymerization temperature was controlled by a cryostat. The autoclave was evacuated for a short time at the chosen temperature to remove most of the argon inside, and then it was charged with olefin monomer (2 bar of ethene or propene), the pressure of which was controlled with a bpc 1202 Büchi pressflow gas controller (with program "bls2"). The toluene solution in the autoclave was stirred at a speed of 600 rpm for 30 min to saturate it with monomer and then the catalyst was added rapidly into the autoclave to start the polymerization reaction. The polymerization was carried out for 30 min, and then the reaction was quenched by adding a mixture of methanol and a 2 N HCl aqueous solution (1:1, v:v; 20 mL). Excess monomer was vented, the toluene solution was poured into methanol (1 L), and the polymer precipitated at the bottom of methanol solution. It was stirred, filtered and washed with a suitable solvent and then collected and dried. Details of the low-temperature (–20 °C) propene polymerization are provided as Supporting Information.

Elastomer Analysis: Hysteresis curves for the elastomeric polymer were determined by first establishing a strain on the polymer sample of 0.5 N. The polymer was then stretched to twice its original length. Upon reaching the desired elongation, the polymer sample recovery was measured as the strain was released to 0.5 N. At this point, this process was continued for 200% elongation, 300% elongation, etc. until 10 iterations were completed or the polymer sample broke.

Supporting Information (see footnote on the first page of this article): Detailed NMR spectroscopic data of all compounds, determination of the rotation barrier of complex **6c** in solution, and detailed polymerization data.

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