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# Palladium-Catalyzed Cross-Coupling Reactions of Bromo-Substituted Group 4 Metallocenes

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*Summary: Pd-catalyzed Negishi reactions of Zr and Hf complexes bearing* $\eta^5$*-4-bromo-2-methylindenyl and* $\eta^5$*-2-bromoindenyl ligands with MeZnCl and various aryl- and heteroarylzinc reagents (RZnCl) give in high yields the respective complexes bearing* $\eta^5$*-4-R-2-methylindenyl and* $\eta^5$*-2-R-indenyl ligands, respectively.*

One of the most significant areas of growth in the last two decades has been the development of a new generation of olefin polymerization catalysts based on group 4 metallocenes.[1] These results form a solid basis for new advances in research and development of polymerization catalysts targeted mostly at *the design of new highly specific catalytic systems for the preparation of novel polyolefins* with a controlled set of properties, including morphology, uniform particle size distribution, and physicomechanical parameters. It is obvious that reasonable theoretical models for catalytic systems involving transition metals are too complex to allow computations at high levels of theory.[2] Therefore, for now and at least for the near future, there is no alternative to experimental screening of various catalysts, preferably using high-throughput approaches for both catalyst synthesis and testing. At present, new group 4 metallocene families are synthesized most often from the respective ligand families and simple metal derivatives, such as $MCl_n$ (or their complexes with donor ligands) and $M(NMe_2)_4$, where M = Ti, Zr, Hf, using transmetalation[1,3] and amine elimination reactions,[4] respectively. For chiral *ansa*-zirconocenes, transmetalation using the well-designed dichloride derivatives, such as substituted [biphenyl-2,2′-diylbis(oxy)]$ZrCl_2$[5] and particularly $[RN(CH_2)_3NR]ZrCl_2$,[6] is also widely used. These methodologies require preliminary ligand synthesis or modification of the ligand prior to metallocene preparation. Here, we demonstrate an alternative approach enabling synthesis of novel metallocenes starting from Br-substituted parent metallocene compounds. This synthetic method is based on the Pd-catalyzed Negishi cross-coupling reaction using group 4 metallocenes bearing Br-substituted ligands.[7] While similar modification of coordinated ligands in late-transition-metal complexes, particularly ferrocene derivatives, using catalytic cross-coupling reactions is well-known,[8] similar transformations of early-transition-metal complexes, which include highly polarized and reactive metal−ligand bonds,[9] have not previously been described.[10]

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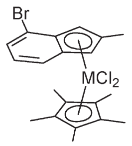
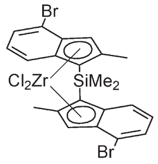
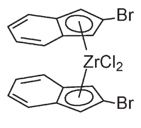
The three zirconocenes **1** and *rac*- and *meso*-**3** and the hafnium complex **2**, bearing the $\eta^5$-4-bromo-2-methylindenyl ligand, were selected for this study. Pd-catalyzed arylation of these metallocenes should result in new metal complexes having $\eta^5$-4-aryl-2-methylindenyl ligands. This ligand class is of particular importance, since $\eta^5$-4-aryl-2-methylindenyls are significant structural components of highly active commercial *ansa*-zirconocene polymerization catalysts that produce highly isotactic polypropylene (*i*PP).[1,12,13] One more complex selected for this study bears two $\eta^5$-2-bromoindenyl ligands. This zirconocene, **4**, can be used as a starting material in cross-coupling reactions to obtain the Waymouth-type complexes (2-arylindenyl)$_2$ZrCl$_2$, which are more recently believed to be multicentered catalysts that produce "elastomeric polypropylene" (*e*PP).[12,14]



**1** (M = Zr), **2** (Hf)



*rac*- & *meso*-**3**



**4**

Complexes **1** and **2** were obtained in 84 and 76% yields, respectively, via transmetalation between the lithium salt of 4-/7-bromo-2-methylindene and Cp*MCl$_3$ (M = Zr, Hf) in toluene. *rac*- and *meso*-**3** were synthesized from the Et$_3$Sn derivative of bis(4-bromo-2-methylindenyl)dimethylsilane and ZrCl$_4$ in toluene and then isolated in 21 and 29% yields, respectively. Finally, complex **4** was obtained in 77% yield from ZrCl$_4$ and 2 equiv of (2-bromoindenyl)lithium in CH$_2$Cl$_2$. Metallocenes **1**−**3** can be kept for a long time at room temperature, though complex **4** decomposes slowly under these conditions. Moreover, this compound was found to be extremely sensitive to moisture. Thus, complexes **1**−**4** represent two different types of the Br-substituted group 4 metallocenes bearing a halogen atom bonded to either (a) the Cp ring or (b) the benzene ring fused to the cyclopentadienyl fragment.

To obtain aryl-/alkyl-substituted metallocenes from **1**−**4**, we have used Pd-catalyzed cross-coupling reactions with organozinc reagents (Negishi reaction). This reaction with aryl halides is known to proceed under mild conditions to give the desired cross-coupling products in high yields.[15] It should be noted that bromo-substituted zirconocenes and hafnocenes are very specific substrates for cross-coupling reactions, as they contain highly polarized and reactive metal−ligand (Cp′ and Cl) bonds.[9] Thus, the mildest conditions should be applied to exclude possible substitution of ligands in the coordination sphere of zirconium or hafnium, particularly a transfer of Br from ZnBrCl (formed from RZnCl during the catalytic reaction) to the transition metal, as well as the analogous transfer of the organic radical of the organozinc substrate resulting in undesirable aryl/alkyl zirconium/hafnium species. It should be noted that in comparison to the free Br-substituted ligand, the relatively high ionicity of Zr−-Cp′ and Hf−Cp′ bonds should increase the electron density on the Br-substituted metal-bound ligand, which in turn should reduce the reactivity of this substrate in the Negishi reaction, because oxidative addition of electron-rich aryl bromides to Pd$^0$ is slower.[15] This effect should be of particular importance for **4**, which has the Br substituent in the Cp fragment; hence, this substrate should be less reactive than **1**−**3**.

In the first series of experiments, we found that the palladium complex Pd(P$^t$Bu$_3$)$_2$[16] catalyzes cross-coupling reactions of metallocenes **1** and **2** with MeZnCl and various aryl- and heteroarylzinc reagents (Table 1). On the evidence of NMR spectroscopy, these reactions proceed even at room temperature to form the target zirconium and hafnium complexes involving 4-methyl-, 4-aryl-, and 4-heteroaryl-2-methylindenyl fragments in high or almost quantitative yield. No exchange of Cl ligands at Zr (or Hf) by Br was observed under the conditions studied. Though these reactions were performed on the 100−400 mg scale, in most cases, analytically pure products were isolated in good to high yield after treatment of the reaction mixtures by MeSiCl$_3$ (to remove an excess of organozinc reagent) and the following crystallization of the crude materials from common organic solvents (see the Supporting Information for experimental details). Treatment of the crude reaction mixtures by MeSiCl$_3$ was not applied during isolation of **25**−**28**, which have reactive functional groups. It should be noted that the synthesis of the zirconocenes bearing highly reactive cyano and carboxylic groups demonstrates a very important advantage of this chemistry, as the synthetic protocols for such promising metallocene targets have not been de-

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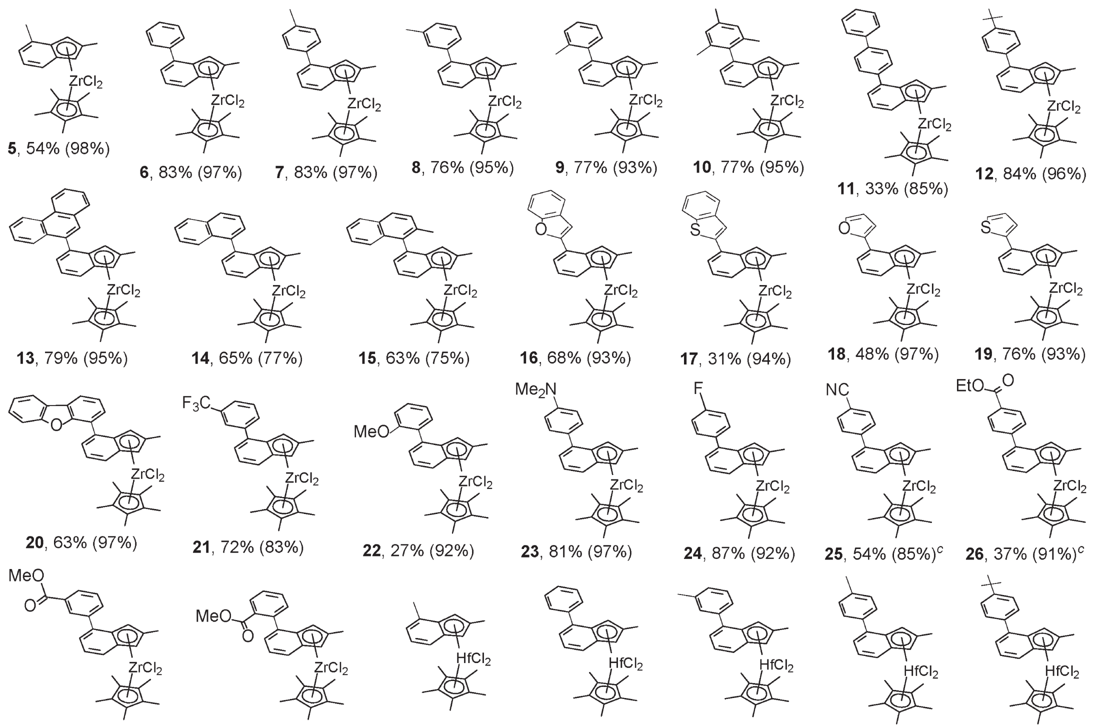
**Table 1. Products of the Pd-Catalyzed Cross-Coupling Reactions of 1 and 2 with RZnCl**[a,b]



**5**, 54% (98%)
**6**, 83% (97%)
**7**, 83% (97%)
**8**, 76% (95%)
**9**, 77% (93%)
**10**, 77% (95%)
**11**, 33% (85%)
**12**, 84% (96%)
**13**, 79% (95%)
**14**, 65% (77%)
**15**, 63% (75%)
**16**, 68% (93%)
**17**, 31% (94%)
**18**, 48% (97%)
**19**, 76% (93%)
**20**, 63% (97%)
**21**, 72% (83%)
**22**, 27% (92%)
**23**, 81% (97%)
**24**, 87% (92%)
**25**, 54% (85%)[c]
**26**, 37% (91%)[c]
**27**, 53% (86%)[c]
**28**, 75% (88%)[c]
**29**, 90% (99%)
**30**, 71% (95%)
**31**, 61% (97%)
**32**, 70% (97%)
**33**, 67% (98%)

[a] Reactions were carried out using 2 mol % of Pd(P$^t$Bu$_3$)$_2$ and a 1/1.50 ratio of **1** or **2** to organozinc reagent in THF at room temperature for 4 h, unless otherwise stated. The subsequent treatment of the reaction mixtures with MeSiCl$_3$ was used to decompose the excess organozinc reagent and isolate the product (except for compounds **26**–**28**). [b] The isolated yield of analytically pure metallocene is shown; the total yield (in parentheses) was determined by NMR spectroscopy. In all cases the studied conversion of **1** or **2** was >99%. [c] The reaction was carried out for 15 h.

scribed previously in the literature.[17] Their possible uses could range from supported catalysis to organic synthesis and material chemistry. Synthesis of **25**–**28** was achieved using the functionalized organozinc substrates obtained from the respective Grignard reagents recently developed by Knochel et al.[18] Alternatively, the functionalized organozinc compounds obtained via direct insertion of zinc into the aryl–halogen bond according to the Rieke protocol[19] or Knochel method[20] work as well. The isolated zirconocenes were unambiguously characterized by NMR spectroscopy, and additionally, **26**, bearing a 4-EtOC(O)C$_6$H$_4$ fragment, was studied by X-ray crystal structure analysis (Figure 1).

The screening of phosphine ligands confirmed that Pd(P$^t$Bu$_3$)$_2$ and a mixture of Pd(dba)$_2$ with 2 equiv of P$^t$Bu$_3$ are the most active catalytic systems for the Negishi reaction of **1** with 2-*p*-tolylzinc chloride (Table 2). On the evidence of NMR spectroscopy, Pd(P$^t$Bu$_3$)$_2$ works effectively at 0.4 mol % concentration of Pd to give the respective coupling product in 73% yield (91% conversion of **1**) at room temperature for 2 h. On the other hand, the catalyst based on di-*tert*-butyl[2-(9-phenanthryl)phenyl]phosphine (entry 6) was found to possess moderate activity. Interestingly, other catalysts with bulky *o*-biphenylphosphine ligands or Xantphos were altogether less active in the coupling reaction studied. Surprisingly, whereas for Pd(P$^t$Bu$_3$)$_2$ we observed no exchange of the Cl ligand of Zr for Br, the catalysts based on Pd(dba)$_2$ gave mixtures of the respective zirconium dichloride and chloride–bromide complexes (in a ratio of 1 to 0.05–0.3 depending on the phosphine used).

These positive results laid a basis for the following study of more practical targets, i.e. *rac*-**3** and complex **4**, which, after being arylated, should form promising precatalysts for *i*PP and *e*PP synthesis, respectively. First, *rac*-**3** and 2.6 equiv of 2-*p*-tolylzinc chloride were shown to give the desired disubstituted cross-coupling product *rac*-**34** in almost quantitative yield in the presence of 2 mol % of Pd(P$^t$Bu$_3$)$_2$ in THF for 4 h at room temperature (Scheme 1). Similarly, *meso*-**3** gave pure *meso*-**30** under these conditions. Analytically pure *rac*- and *meso*-**34** were isolated in 85 and 79% yields after treatment of the reaction mixtures with MeSiCl$_3$. Therefore, *no epimerization of both starting ansa complexes and the respective chiral products was observed under the conditions employed.* It should be noted that possible epimerization of the racemic complexes in the presence of zinc salts[21] could be the only impediment to a high-yield synthesis of *rac*-**34** using the cross-coupling protocol.

The Negishi reaction of **4** bearing two $\eta^5$-2-bromoindenyl ligands was found to proceed more slowly than similar reactions of **1**–**3**. On the evidence of NMR spectroscopy, **4**

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(17) The only known approach to Zr complexes bearing a carboxylic group bonded to a $\eta^5$-Cp′ ligand via a $-CH_2CH{=}CH-$ or $-CH_2CH_2CH{=}CH-$ linker was found to be Ru-catalyzed metathesis of zirconocenes including vinyl functions.[11s,11t]

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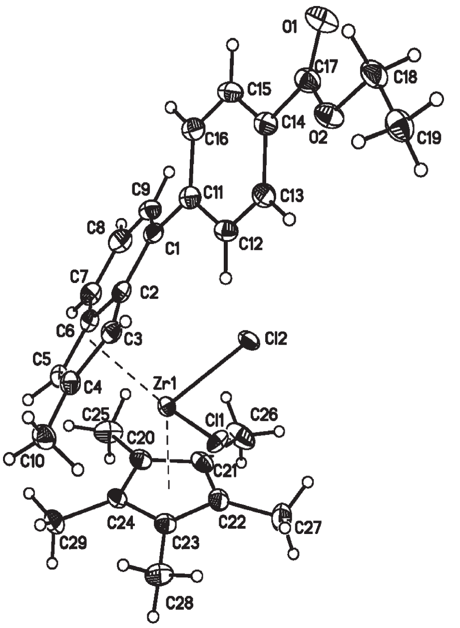
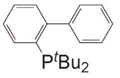
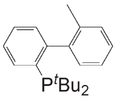
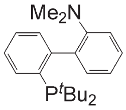
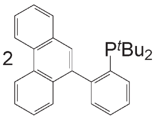


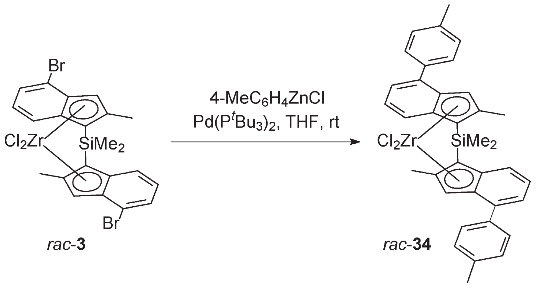
**Figure 1.** Molecular structure of **26**, including 50% thermal ellipsoids and the atom-labeling scheme.

**Table 2. Influence of the Catalyst Structure on the Cross-Coupling Reaction of 1 with *p*-Tolylzinc Chloride**[a]

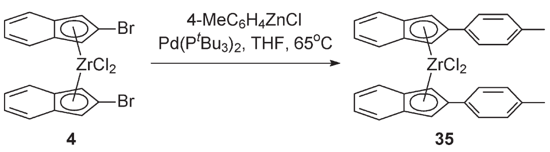
| Entry | Catalyst | Yield, %[b] | Conv., %[c] |
|---|---|---|---|
| 1 | Pd(P$^t$Bu$_3$)$_2$ | 90 | 93 |
| 2 | Pd(dba)$_2$ / 2 P $^t$Bu$_3$ | 91 | 93 |
| 3 | Pd(dba)$_2$ / 2  | 20 | 33 |
| 4 | Pd(dba)$_2$ / 2  | 33 | 54 |
| 5 | Pd(dba)$_2$ / 2  | 16 | 38 |
| 6 | Pd(dba)$_2$ / 2  | 82 | 87 |
| 7 | Pd(dba)$_2$ / Xantphos[d] | 21 | 25 |

[a] Reactions were carried out using 1 mol % of Pd catalyst and a 1/1.50 ratio of **1** to *p*-tolylzinc chloride in THF at room temperature for 1 h. The subsequent treatment with MeSiCl$_3$ was applied to decompose the excess organozinc reagent. [b] Yield of (4-*p*-tolyl-2-methylindenyl)Cp*ZrCl$_2$ on the evidence of NMR spectroscopy. [c] Conversion of **1** on the evidence of NMR spectroscopy. [d] Xantphos = 9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene.

**Scheme 1. Negishi Reaction of *rac*-3 with *p*-Tolylzinc Chloride**



**Scheme 2. Negishi Reaction of 4 with *p*-Tolylzinc Chloride**



and 2.6 equiv of *p*-tolylzinc chloride gave the desired Waymouth-type complex **35** in 67% yield (with almost quantitative conversion of **4**) in the presence of 4 mol % of Pd(P$^t$Bu$_3$)$_2$ after 3 h at 65 °C (Scheme 2). The loss of product is likely due to the instability of **4** in solution. For instance, this complex has a ca. 15 h half-life in C$_6$D$_6$ solution at 20 °C, and our attempts to carry out the synthesis of **35** at this temperature failed, since **4** decomposed more quickly than it reacted to form the target aryl-substituted product. It should be noted that no formation of the unsymmetrical complex (2-bromoindenyl)(2-*p*-tolylindenyl)ZrCl$_2$ was detected by NMR spectroscopy in all cases studied. Also, we did not observe a transfer of the *p*-tolyl or Br fragment to the Zr atom. Finally, the analytically pure **35** was isolated in 40% yield after treatment of the reaction mixture with MeSiCl$_3$ and the following crystallization of the product from toluene−hexanes.

In conclusion, we have demonstrated a new methodology for the synthesis of aryl-/alkyl-substituted group 4 metallocenes, which are known to be components of promising olefin polymerization catalysts. Whereas usually the desired metallocenes are synthesized by starting from well-designed cyclopentadienyl-type ligands and group 4 metal precursors, the above-described cross-coupling approach is more practical and enables easy access to a large library of precatalysts from a single bromo-substituted parent metallocene. This useful technique can be applied both for the synthesis of target complexes including metallocenes bearing highly reactive functionalities, such as cyano and carboxylic groups, and for high-throughput development of new promising olefin polymerization catalysts. The study of other halo-substituted group 4 metal complexes, their cross-coupling chemistry, and, particularly, the respective functionalized derivatives is underway.

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**Supporting Information Available:** Text, tables, figures, and CIF files giving synthetic procedures, characterization data for new compounds, and details of the X-ray crystal structure determinations of **2** and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.