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# Reaction of Lanthanides (La, Mischmetall) with $Cp_2ZrCl_2$ and Di- or Tetrahalogenoalkanes: New Formation and Studies of Five-Membered Zirconacycles

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Five-membered zirconacycles were generated in a new way, by simultaneously reducing $Cp_2ZrCl_2$ and di- or tetrahalogenoalkanes with La or mischmetall (an alloy of lanthanides) at room temperature. Zirconacyclopentane, formed by using 1,2-diiodoethane as an ethylene source, underwent ligand exchange with diphenylacetylene to afford the corresponding zirconacyclopentene and zirconacyclopentadiene complexes. Reaction monitoring with diphenylacetylene by GC-MS spectroscopy indicated that not only did the usual ligand exchange occur but also a direct homocoupling with a La-derived $Cp_2Zr$ equivalent could take place. Unsubstituted zirconacyclopentadiene, unavailable by classic methods, was formed by using tetrabromoethane as an acetylene source. It reacted with monosubstituted alkynes, in the absence of Cu or Ni additives, to afford monosubstituted benzene derivatives.

## Introduction

Numerous applications of zirconium in organic synthesis involve a furtive $Cp_2Zr(II)$ species, the so-called zirconocene.[1] Typically, zirconocene equivalents are generated by reducing $Cp_2ZrCl_2$ in the presence of stabilizing ligands.[2] Zirconocene chemistry has widely been developed since the introduction by E. Negishi in 1986 of a practical method for generating $Cp_2Zr$-butene, by treatment of $Cp_2ZrCl_2$with 2 equiv of *n*-BuLi at –78 °C and warming to room temperature.[3] In these conditions, transmetalation and a successive $\beta$-fragmentation occur.

We recently reported on an alternative, entirely room-temperature-based, protocol for the generation of an alkene-free zirconocene equivalent, by employing mischmetall (an alloy of Ce, La, Nd, and Pr) as reductant.[4] In addition to classic homodimerization of diphenylacetylene and enyne bicyclizations, reactions unprecedented with $Cp_2Zr$-butene have been carried out, involving coupling of terminal alkynes as well as intermolecular coupling of alkynes with imines. The real structure of the new zirconocene equivalent remains unknown at present.[5] Its chemical properties appear similar, but not identical, and seem complementary. Additional insight into the structure and chemistry of the lanthanide-originated $Cp_2Zr$ equivalent is necessary.

**Scheme 1. Reductive Generation of Ethylene and $Cp_2Zr$ Equivalent**

(a) $2\ Ln + 3\ ICH_2CH_2I \longrightarrow 2\ LnI_3 + 3\ H_2C{=}CH_2$

(b) $4\ Ln + 3\ Br_2CHCHBr_2 \longrightarrow 4\ LnBr_3 + 3\ HC{\equiv}CH$

(c) $3\ Cp_2ZrCl_2 + 2\ Ln \longrightarrow 3\ \text{"}Cp_2Zr\text{"} + 2\ LnCl_3$

In this paper we further focus on the reactivity pattern of $Cp_2Zr$ species, generated by reducing $Cp_2ZrCl_2$ with a pure lanthanide metal (La) or mischmetall. When reducing $Cp_2ZrCl_2$ and di- or tetrahalogenoalkanes with lanthanide metal, simultaneously in a one-reaction vessel, five-membered zirconacycles were formed and examined in comparison to those obtained in the classic way, by transmetalation, $\beta$-hydrogen fragmentation, and ligand substitution processes, according to Negishi−Takahashi protocols.[6]

## Results and Discussion

Several years ago, some of us reported on the preparation of lanthanide halogenides ($LnX_3$) by reacting a lanthanide metal (Ln = La, Nd, Pr, Sm, Gd and mischmetall) with halogenoalkanes.[7] In these dehalogenation reactions alkenes or alkynes are formed as depicted in Scheme 1, eq a and eq b.

We reasoned that since both $Cp_2Zr$ equivalent (eq c) and unsaturated hydrocarbons (eqs a and b) can be generated by

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(1) For reviews, see: (a) *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, 2002. (b) Negishi, E. *Dalton Trans.* **2005**, 827. (c) New Aspects of Zirconium Containing Organic Compounds. In *Topics in Organometallic Chemistry*, Vol. 10; Marek, I., Ed.; Springer: Berlin, 2005. (d) Metallocenes in Regio- and Stereoselective Synthesis. In *Topics in Organometallic Chemistry*, Vol. 8; Takahashi, T., Ed.; Springer: Berlin, 2005. (e) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755.

(2) (a) Earlier experimental protocols employed Na or Mg as reductants, and typically alkynes or bipyridine as stabilizing ligands; see for example: Watt, G. W.; Drummond, F. O., Jr *J. Am. Chem. Soc.* **1970**, *92*, 826. (b) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1971**, *28*, 91. (c) Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65. (d) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193.

(3) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(4) Denhez, C.; Médégan, S.; Hélion, F.; Namy, J.-L.; Vasse, J.-L.; Szymoniak, *J. Org. Lett* **2006**, *8*, 2945.

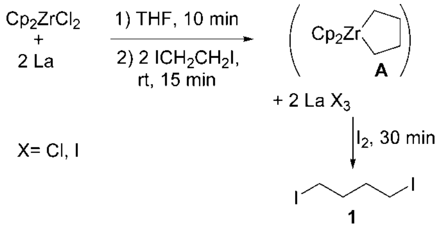
(5) One could speculate that oligomeric bimetallic species, which include zirconium and a chlorine-bridged lanthanide cooperating together, act in the reaction.

(6) (a) Negishi, E. In *Comprehensive Organic Synthesis*, Vol. 5; Paquette, L. A., Ed.; Pergamon: Oxford, 1991; p 1163. (b) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124.

(7) Lannou, M.-I.; Hélion, F.; Namy, J.-L. *Tetrahedron* **2003**, *59*, 10551.

10.1021/om701217e CCC: \$40.75

**Scheme 2. *In Situ* Formation of Zirconacyclopentane from $Cp_2ZrCl_2$, 1,2-Diiodoethane, and La**

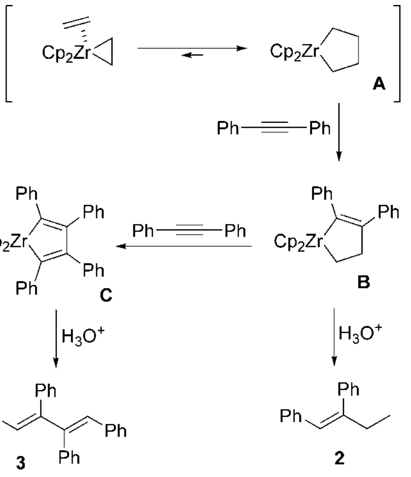


using lanthanide metal as reductant, the two reactions might be combined to produce alkene- or alkynezirconocenes. The feasibility of performing such transformations in a one-reaction vessel was then examined. In a preliminary experiment, a mixture of $Cp_2ZrCl_2$ (1 mmol) and the powdered La (2 mmol) was stirred at room temperature in 3 mL of THF until a deep red color appeared (typically after 10 min). A solution of 1,2-diiodoethane (2 mmol) in 2 mL of THF was then added. An exothermic process took place, and the reaction mixture turned bright green. After 15 min, iodine (2.5 mmol) was added and the reaction was next carried out at room temperature for an additional 0.5 h. Finally, hydrolytic workup, followed by extraction with ether and chromatography purification, afforded 1,4-diiodobutane (**1**) in 65% yield. This result indicated that *in situ* formed $Cp_2Zr$ equivalent and ethylene reacted together to form zirconacyclopentane (**A**), which further underwent iodination reaction to afford **1** (Scheme 2). A similar result was obtained by using mischmetall instead of La as reductant. Furthermore, the addition of 1-decene followed by iodination produced 1,4-diiodo-2-*n*-octylbutane in 70% yield.[8]

The dehalogenation of 1,2-diiodoethane by La to afford ethylene gas is known to be a very fast reaction.[9] However, a competing formation of **A** by the reaction of the $Cp_2Zr$ equivalent with 1,2-diiodoethane, possibly through a $\beta$-fragmentation from the intermediate $Cp_2IZrCH_2CH_2I$, cannot be ruled out. In fact, ethylene gas was demonstrated to form after a 10 min period, also when an equimolar amount of diiodoethane was added to "$Cp_2Zr$" (first generated from 1 equiv of $Cp_2ZrCl_2$ and 3/2 equiv of La). Further addition of $I_2$ to the reaction mixture gave **1**, albeit in low yield (15%).

Zirconacyclopentanes are well-known intermediates, which are usually formed from dialkylzirconocenes through $\beta$-hydrogen fragmentation, leading to zirconacyclopropanes, and the cyclic carbozirconation ($\gamma$-ring expansion) sequence.[1,10] Both steps have been postulated to be concerted associative processes, and the reversible nature of the formation and interconversion of three- and five-membered zirconocenes has been mentioned.[11] The unusual way in which **A** was formed, and the particular chemical environment involved, encouraged us to further study the reaction medium. The *in situ* conversion of **A** (or zirconacyclopropane) into zirconacyclopentene **B** and zirconacyclopentadiene **C**, through the well-known ring expansion or/and ligand displacement,[1,12] would be especially considered (Scheme 3).

**Scheme 3. Generation of Zirconacyclopentene B and Zirconacyclopentadiene C**



To examine the formation of **B** and **C**, $Cp_2ZrCl_2$ was first reacted with La (2 equiv) and diiodoethane (2 equiv) as previously. After the bright green color appeared, diphenylacetylene (1 equiv) was added. The monitoring of the reaction by GC-MS was carried out by quenching aliquots with 1 M HCl regularly, within a 12 h period. These results are summarized in Figure 1.

During the first hour, diphenylacetylene was rapidly consumed, which was accompanied by a marked increase of the amount of (*Z*)-1,2-diphenylbutene (**2**) related to **B**.[13] After a 0.5 h period, 1,2,3,4-tetraphenylbutadiene (**3**) related to **C** started to form slowly, and simultaneously the formation of **2** slowed down. Finally, the amount of **2** remained constant after a 3 h period; nevertheless the amount of **3** continued to increase slowly and stabilized only after 4 h. These results suggested that at least two simultaneous reaction pathways could be responsible for the formation of **C**. The first would involve the ligand exchange sequence starting from **A**, as depicted in Scheme 3. The second would imply a hydrocarbon-free "lanthanide-derived" $Cp_2Zr$ equivalent.[4] The latter would still be (partially) active, toward the diphenylacetylene homodimerization, after a prolonged (3 h) reaction period. Anyway, a partial degradation of zirconocene took place in the reaction conditions.

In the next experiment, the hydrocarbon-free zirconocene equivalent was confirmed to couple diphenylacetylene, in a way competitive to that involving the ligand exchange from **A**, as depicted in Scheme 3. Thus, $Cp_2ZrCl_2$ was first reacted with La and diiodoethane. Differently from the experiment depicted in Figure 1 however, diphenylacetylene was added to the reaction mixture *only after a period of time* $T_1$ (Figure 2). The reactions were then carried out during 12 h. For $T_1 = 0$ (conditions very close to those previously employed, Figure 1), an important amount of **2** was obtained. The increase in $T_1$ up to 3 h resulted in a lower amount of **2** and a higher amount of **3**. If **C** had formed exclusively from **B** (and then from **A**), no variations in **C**/**B** (and consequently in **3**/**2**) ratio would have

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(8) Such alkene (or alkyne) intermolecular exchanges have been assumed to typically proceed through an initial cycloreversion leading to zirconacyclopropane (alkene-zirconocene), followed by a successive insertion reaction; see ref 1. An analogous "pair" selective reaction, using $Cp_2ZrCl_2$, 2 equiv of EtMgBr, and 1-decene, has been reported. Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266.

(9) The instantaneous formation of ethylene gas and a marked exothermic effect are observed; see also ref 7.

(10) (a) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (b) Negishi, E. *Chem. Scr.* **1989**, *29*, 457.

(11) (a) Negishi, E.; Swanson, D. R.; Takahashi, T. *Chem. Commun.* **1990**, 1254. (b) Negishi, E.; Nguyen, T.; Maye, J. P.; Choueiry, D.; Suzuki, N.; Takahashi, T. *Chem. Lett.* **1992**, 2367. (c) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (d) Takahashi, T.; Fujimori, T.; Seki, T.; Saburi, M.; Uchida, Y.; Rousset, J.; Negishi, E. *Chem. Commun.* **1990**, 182.

(12) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444.

(13) The 1,4-dideuterated analogue was obtained after deuterolysis, thus demonstrating the formation of the zirconacycle intermediate.

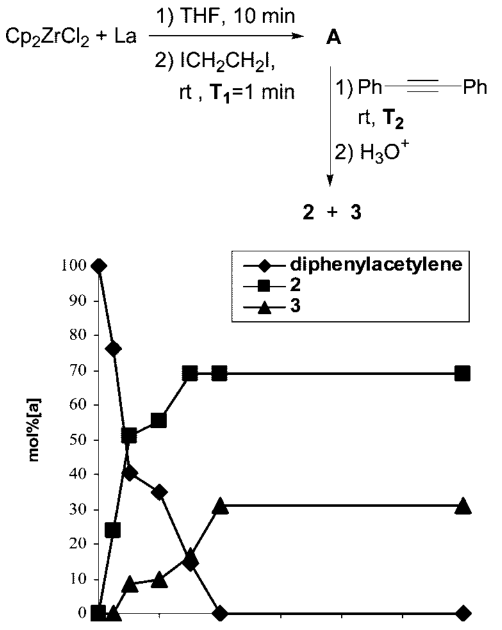


**Figure 1.** Reaction monitoring depending on the delay $T_2$ after the phenylacetylene addition. [a] = mol % of diphenylacetylene residual or included in compounds **2** and **3**.

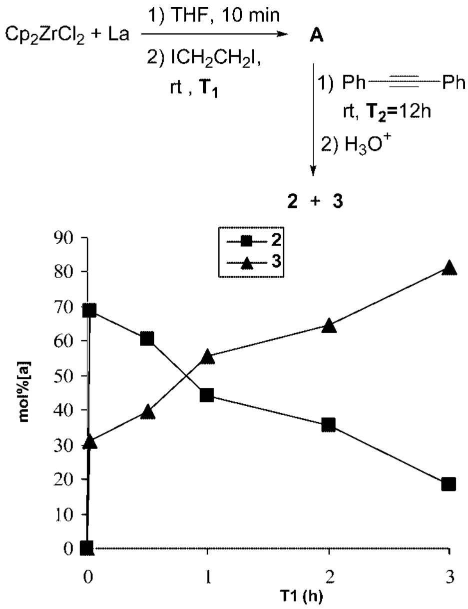
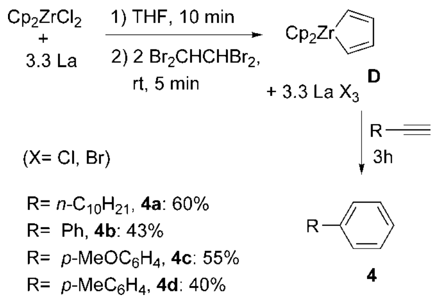


**Figure 2.** Reaction monitoring depending on the delay $T_1$ before the phenylacetylene addition. [a] = mol % of diphenylacetylene included in compounds **2** and **3**.

been observed with $T_1$. The results shown in Figure 2 suggest that during the period $T_1$ a progressive degradation (deactivation) of **A** took place, thus resulting in a lower amount of **2**. Simultaneously, a more stable hydrocarbon-free zirconocene equivalent would give the increased amount of **3**. Further studies are necessary to clarify the properties of the reacting species.

Zirconacyclopentadienes, typically formed in the way shown in Scheme 3, were used in a number of synthetically useful transformations.[14] Nevertheless, this chemistry is mostly limited to the use of tetrasubstituted zirconacyclopentadienes, since only precursor disubstituted alkynes are compatible with the classical zirconocene formation conditions.[15] In contrast, terminal alkynes have recently been employed by using "lanthanide-derived" $Cp_2Zr$ equivalent to afford disubstituted zirconacyclopentadienes.[4] In the present work we studied the feasibility of preparing the unsubstituted analogue, i.e., zirconacyclopentadiene (**D**), which would formally derive from acetylene. In this reaction cheap and readily available 1,1,2,2-tetrabromoethane was used as acetylene precursor (Scheme 4).[16]

**Scheme 4. Insertion of Alkynes into Zirconacyclopentadiene (D)**



A mixture of $Cp_2ZrCl_2$ (1 mmol) and the powdered La (3.3 mmol) was stirred at room temperature until the deep red color appeared. A solution of 1,1,2,2-tetrabromoethane (2 mmol) in 1 mL of THF was then added. An exothermic process took place, and the reaction mixture turned green. At this stage, the reaction was quenched with $D_2O$, and (1*Z*,3*Z*)-1,4-dideuterobuta-1,3-diene was detected by $^1H$ NMR (benzene-$d_6$ was saturated with the collecting gas),[17] giving support to the *in situ* formation of **D**. Otherwise, addition of a monosubstituted alkyne (R = aryl or alkyl) and carrying out the reaction for an additional 3 h gave the monosubstituted benzene derivatives **4a**–**d**. Alkynes were entirely consumed, and small amounts of disubstituted dienes were also detected. A similar result was obtained by using mischmetall instead of La as reductant. Benzene derivatives are typically formed from zirconacyclopentadienes by using copper (CuCl) or nickel ($NiX_2(PPh_3)_2$) as additives.[14] To our knowledge, there is no report on the reactions of alkynes with zirconocenes to form benzene derivatives in Cu- or Ni-free conditions (without transmetalation).[18] The unprecedented formation of **4a**–**d** in the absence of the Ni or Cu salts might be due to a nonsubstitution pattern of the complex **D**. Additionally, it could involve a lanthanide halide-assisted reductive elimination process.

In summary, zirconacycle complexes have been generated in a new way from $Cp_2ZrCl_2$, lanthanide metals, and halogeno organic compounds. The reactions were monitored by GC-MS spectroscopy by quenching samples regularly. The initial step involves the *in situ* formation of both a hydrocarbon-free zirconocene equivalent and the alkene or alkyne component. The zirconocene and the unsaturated hydrocarbon thus formed reacted further to afford five-membered zirconacycles. When

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(14) Takahashi, T.; Li. Y. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.;Wiley-VCH: Weinheim, 2002; Chapter 2.

(15) (a) A few examples of Zr-mediated intramolecular coupling of terminal alkynes, involving an indirect generation of zirconocene-alkyne complexes from 2-bromoalkenes, have been reported. See: Barluenga, J.; Sanz, R.; Fananas, F. J. *Chem. Commun* **1995**, 1009. (b) Barluenga, J.; Sanz, R.; Fananas, F. J. *Chem.—Eur. J.* **1997**, *3*, 1324.

(16) Hélion, F.; Lannou, M.-I.; Namy, J.-L. *Tetrahedron Lett.* **2003**, *44*, 5507.

(17) Klärner, F-G.; Krawczyk, B.; Ruster, V.; Deiters, U. K. *J. Am. Chem. Soc.* **1994**, *116*, 7646.

(18) More recently, interesting oligomerization and cyclotrimerization reactions involving Zr/Cr system have been reported; see: Takahashi, T.; Liu, Y.; Iesato, A.; Chaki, S.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2005**, *127*, 11928.

using a dihalogenoalkane (diiodoethane) as an alkene source, the initial zirconacycloalkane intermediate underwent ring expansion and/or ligand displacement reactions with external alkynes to produce zirconacyclopentene and/or zirconacyclopentadiene complexes. When using tetrabromoethane as an alkyne (acetylene) source, the unsubstituted zirconacyclopentadiene, unavailable by classic methods, was obtained. It has been demonstrated to react with external alkynes, in the absence of Cu or Ni additives, leading to monosubstituted benzene derivatives. The presented reactions, carried out at room temperature, allow an alternative easy access to zirconacyclopentenes and zirconacyclopentadienes, which are useful synthetic intermediates. We are currently studying the use of these complexes associated with lanthanide salts as catalysts in some organic transformations.

## Experimental Section

**Materials and Methods.** All reactions were performed under an atmosphere of argon using standard Schlenk techniques. Prior to use, tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Lanthanum and mischmetall ingots purchased from Aldrich and Fluka, respectively (minimum rare earth content is 99.0%), were powdered with a rasp under Ar. No steps to activate them were used. $^1H$ NMR spectra were recorded in $CDCl_3$ on a Brucker AC-360 MHz. $^{13}C$ NMR spectra were recorded in $CDCl_3$ on a Brucker AC-250 MHz. Chemical shifts are reported in delta ($\delta$) units, expressed in parts per million (ppm). High-resolution mass spectra (HRMS) were obtained with a MAT-95-S Finnigan. GC-MS were obtained with a DSQ-Thermo electron instrument. Infrared spectra were recorded on a Perkin-Elmer Spectrum One system. Spectral characteristics of all known compounds were in accordance with the literature data.[19–24]

**Preparation of 1,4-Diiodobutane (1).[19]** A mixture of $Cp_2ZrCl_2$ (292 mg, 1 mmol) and the powdered La (280 mg, 2 mmol) was stirred at room temperature in 3 mL of THF until the deep red color appeared (typically after 10 min). A solution of 1,2-diiodoethane (564 mg, 2 mmol) in 2 mL of THF was then added. An exothermic process took place, and the reaction mixture turned bright green. After 15 min, iodine (635 mg, 2.5 mmol) was added, and the reaction was next carried out at room temperature for an additional 0.5 h. Finally, hydrolytic workup, followed by extraction with ether and chromatography purification, afforded 1,4-diiodobutane (65% yield) as an orange oil. In an analogous experiment, when mischmetall (0.86 mmol) was used instead of La, **1** was obtained in 68% yield.

**Preparation of (*Z*)-1,2-Diphenylbutene (2)[20] and (*E*,*E*)-1,2,3,4-Tetraphenyl-1,3-butadiene (3).[21]** A mixture of $Cp_2ZrCl_2$ (292 mg, 1 mmol) and the powdered La (280 mg, 2 mmol) was stirred at room temperature in 3 mL of THF until the deep red color appeared (typically after 10 min). A solution of 1,2-diiodoethane (564 mg, 2 mmol) in 2 mL of THF was then added. An exothermic process took place, and the reaction mixture turned bright green. After the bright green color appeared, diphenylacetylene (178 mg, 1 mmol) was added. The reaction mixture was stirred for 12 h at room temperature and then quenched with HCl (1 N, 5 mL). The aqueous layer was extracted with $Et_2O$ (3 × 20 mL), and the organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel using a mixture of pentane/AcOEt as eluant. (*Z*)-1,2-Diphenylbutene: white solid, mp 170.8 °C. (*E*,*E*)-1,2,3,4-Tetraphenyl-1,3-butadiene: white solid, mp 182–184 °C.

**Preparation of Monosubstituted Benzene Derivatives 4.** A mixture of $Cp_2ZrCl_2$ (292 mg, 1 mmol) and the powered La (462 mg, 3.3 mmol) was stirred at room temperature until a deep red color appeared. A solution of 1,1,2,2-tetrabromoethane (691.28 mg, 2 mmol, 234 $\mu$L) in 1 mL of THF was then added. An exothermic process took place, and the reaction mixture turned green. After 5 min a monosubstituted alkyne was added (1 mmol). The reaction was next carried out at room temperature for an additional 3 h and then quenched with HCl (1 M, 5 mL). The aqueous layer was extracted with $Et_2O$ (3 × 20 mL), and the organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under vaccum. The residue was purified by column chromatography on silica gel using a mixture of pentane/AcOEt as eluant. All products in this study are known[22–24] and were identified by $^1H$ and $^{13}C$ NMR and GC-MS.

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**Supporting Information Available:** $^1H$ and $^{13}C$ NMR spectra for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Herve, A.; Rodriguez, A. L.; Fouquet, E. J. *Org. Chem.* **2005**, *70*, 1953.

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