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Novel Synthesis of Unbridged, Sterically Substituted Zirconocene Dichlorides from Fulvenes and Dialkylzirconium Dichlorides via Zirconium(IV) Hydride Transfer[1]

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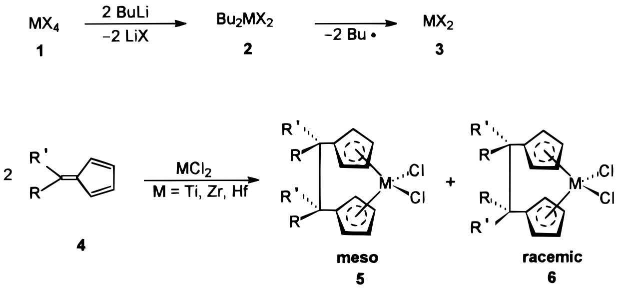
Summary: Unbridged, sterically substituted zirconocene dichlorides can be prepared in high yields by the interaction of a dialkylzirconium dichloride with 2 equiv of the appropriate fulvene in hydrocarbon medium with alkene displacement. The requisite dialkylzirconium dichloride can readily be produced by the alkylation of $ZrCl_4$ *in hydrocarbon media with 2 equiv of an alkyllithium reagent. Generating the* R_2ZrCl_2 *reagents in hydrocarbon media permits their use as hydrozirconating agents for a variety of polar unsaturated organic substrates.*

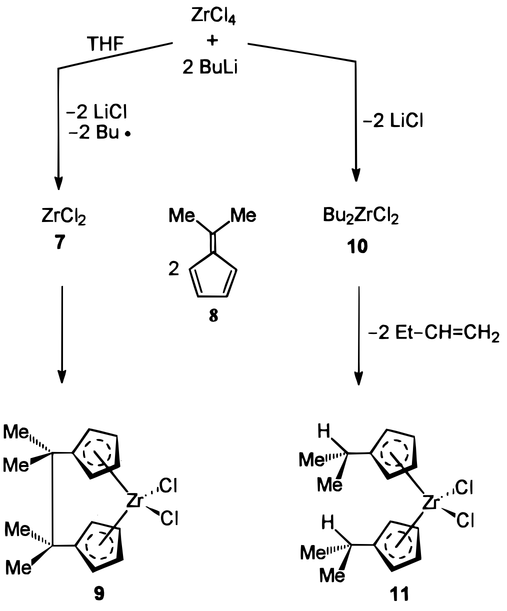
Recently, we reported the novel synthesis of *ansa*-metallocene dichlorides by the reductive dimerization of fulvenes with group 4 metal divalent chlorides.[2] The requisite metal dichlorides were found to be readily generated by the alkylative reduction of the specific metal tetrachloride with 2 equiv of an alkyllithium reagent at low to moderate temperatures in THF (Scheme 1). With unsymmetrically substituted fulvenes (**4**), varying ratios of *meso* and *racemic ansa*-metallocenes were produced (**5**:**6**) because of steric control of the manner of the *ansa* carbon−carbon bond formation.[3]

In the course of investigating the role of the medium on the generation of $ZrCl_2$ (**7**) from $ZrCl_4$ and 2 equiv of *n*-butyllithium (Scheme 2), we have observed a remarkable solvent effect: in THF the reaction, begun at −78 °C and completed at 25 °C, results in a black suspension of $ZrCl_2$ and LiCl, which reacts with 6,6-dimethylfulvene (**8**) to provide a high yield of *ansa*-zirconocene dichloride **9**, but in hexane or toluene the same interaction of $ZrCl_4$ and BuLi leads to a brown solution of di-*n*-butylzirconium dichloride[4] (**10**) with suspended LiCl that reacts with 6,6-dimethylfulvene to yield almost exclusively bis(isopropylcyclopentadienyl)zirconium dichloride (**11**) (Scheme 2).

Scheme 1



Scheme 2



This hydrozirconation of 6-substituted fulvenes by the di-*n*-butylzirconium dichloride generated in hexane or toluene from $ZrCl_4$ and BuLi has proved to be quite general (Scheme 3). The 6-phenyl-, 6-(1-naphthyl)-, and 6-(9-anthryl)fulvenes (**12a**−**c**) can individually be con-

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(1) Part 17 of the series Organic Chemistry of Subvalent Transition Metal Complexes. Part 16: Eisch, J. J.; Shi, X.; Owuor, F. A. *Organometallics* **1998**, *17*, 5219.

(2) Eisch, J. J.; Shi, X.; Owuor, F. A. *Organometallics* **1998**, *17*, 5219.

(3) Preliminary single-crystal XRD data on the major stereoisomer (83%) of the *ansa*-zirconocene dichloride obtained by the reductive dimerization of 6-(1-naphthyl)fulvene with $ZrCl_2$ confirm that it is indeed the *racemic* isomer (personal communication from Professor A. L. Rheingold, University of Delaware).

(4) Attempts to generate $ZrCl_2$ in mixtures of THF and hydrocarbons and then to add the 6,6-dimethylfulvene led, to our surprise *and* dismay, to mixtures of tetramethylethylene(biscyclopentadienyl)zirconium dichloride and bis(isopropylcyclopentadienyl)zirconium dichloride! Our dismay became delight with the finding that in pure hydrocarbon medium (suspensions, rather than solutions) the hydrozirconation of fulvenes became the preponderant outcome. Since such hydrozirconating reagents range in appearance from brown to black, ongoing gasimetric studies of hydrolysis products are probing the question of the presence of both Bu_2ZrCl_2 and H_2ZrCl_2 in such reaction mixtures. For simplicity at this stage of our ongoing studies, we represent the hydride-transfer agent thought to be generated in such hydrocarbon solutions with the empirical formula Bu_2ZrCl_2 and thereby leave as open questions both the state of actual aggregation of such units and the possible role of *ate*-complexation of the LiCl.

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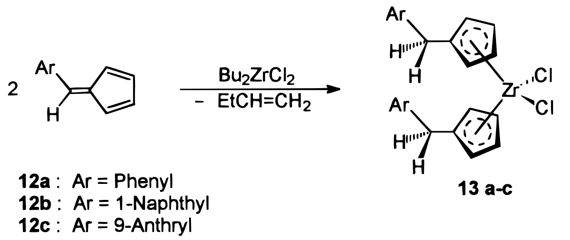
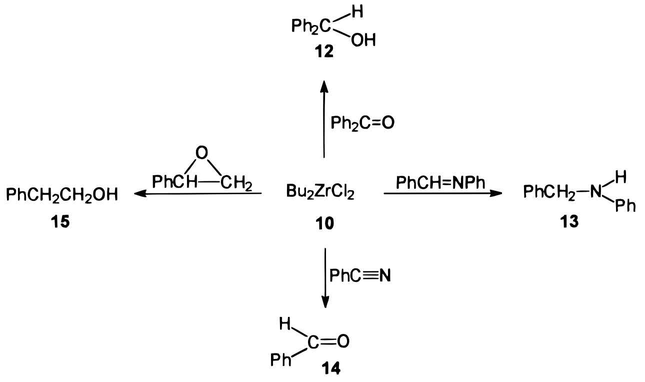
Scheme 3



Scheme 4

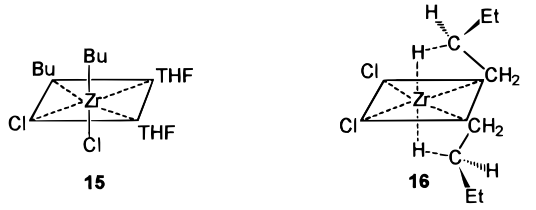


verted into their corresponding bis(benzylic cyclopentadienyl)zirconium dichlorides (**13a**−**c**) in a similar fashion (Scheme 3).

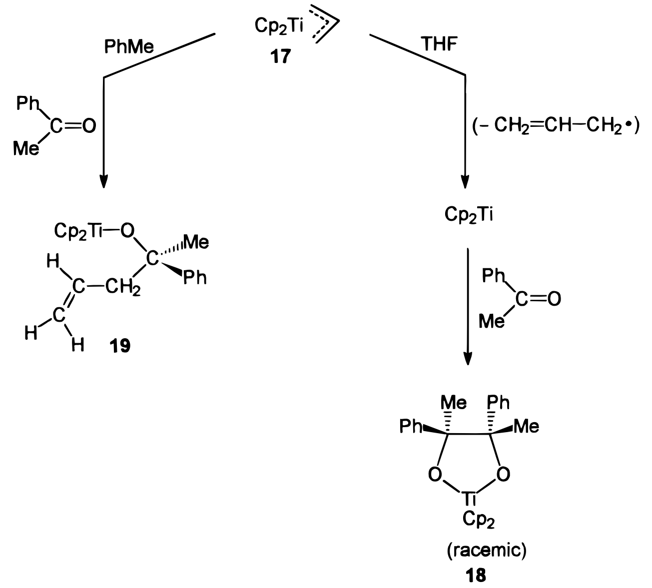
Because of such success, the capability of di-*n*-butylzirconium dichloride (**10**) of functioning as a hydrozirconating agent by zirconium(IV) hydride transfer was examined with other unsaturated organic compounds.[5] Addition of reagent **10** to the following organic substrates and subsequent hydrolysis effected monomolecular reduction in high yield: (1) benzophenone to benzhydrol (**11**); (2) benzalaniline to *N*-benzylaniline (**12**); (3) benzonitrile to benzaldehyde (**13**) (via the aldimine); and (4) styrene oxide to 2-phenylethanol (**14**) (Scheme 4). However, with ordinary alkenes and alkynes, such as 1-decene and 1-decyne, hydrozirconation by **10** is too slow to compete with the decomposition of **10** into **7**; as a consequence, 1-decyne is converted in the isomeric trimers normally produced with $ZrCl_2$.[6]

The structural instability of Bu_2ZrCl_2 in THF and its relative stability in hydrocarbons at 25 °C likely has its origin in the coordination sphere existing about the Zr center: in THF **10** has presumably an octahedral coordination involving solvent ligands (**15**); and in hydrocarbons, without strong coordinating ligands, β-agostic C−H···Zr interactions may help stabilize Zr−C bonds to homolysis while also favoring heterolytic β-hydride elimination (**16**) (Scheme 5).[7]

Scheme 5



Scheme 6



That THF solvent can foster reductive elimination while a hydrocarbon solvent can stabilize a transition metal−carbon bond has already been observed in the interaction of η^3-allyltitanocene (**17**) with ketones: in THF **17** loses the allyl group, and the resulting titanocene causes the bimolecular reduction of the ketone (**18**): in toluene **17** simply adds its titanium−carbon bond to the ketone (**19**), like an ordinary alkylating agent[8] (Scheme 6).

The convenience and efficiency of synthesizing unbridged substituted zirconocene dichlorides from fulvenes and dialkylzirconocene dichlorides, as well as the smooth hydrozirconating action of this reagent on unsaturated substrates, are illustrated by the following experimental procedures:[9] To a white suspension of 1.24 g of $ZrCl_4$ (5.32 mmol) in 30 mL of anhydrous hexane, which had been cooled to −78 °C under an atmosphere of argon, was added slowly 6.65 mL of 1.6 M *n*-butyllithium (10.6 mmol). The suspension was then allowed to warm to 25 °C, where over 12 h it became dark brown.[10] Then 1.1 g of 6,6-dimethylfulvene in 30 mL of toluene was added and the resulting reaction mixture heated at reflux for 8 h. The cooled suspension was filtered, and the brown residue was washed with three 10 mL portions of $CHCl_3$. The combined filtrates were freed of solids in vacuo to yield essentially pure

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(5) The hydrozirconation of a wide variety of olefins and acetylenes by Schwartz's reagent, $(\eta^5\text{-}C_5H_5)_2ZrHCl$, had of course been established almost 25 years ago: Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115. Hart, D. W., Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.

(6) (a) Eisch, J. J.; Shi, X.; Alila, J. R.; Thiele, S. *Chem. Ber./Rec.* **1997**, *130*, 1175. (b) Shi, X. Doctoral Dissertation, State University of New York at Binghamton, May, 1996.

(7) Evidence of β-agostic C−H···Zr interactions is revealed in the single-crystal XRD data of a number of zirconocene derivatives, such as $Cp_2Zr(Cl)-CH_2-CH(AlEt_2)_2$, where via a Cl bridge between an Al center and Zr, the $Zr-C_1-C_2$ angle is drawn down to 75.4°. Although the putative agostic β-H is not observed directly, the angle contraction from 109° to 75° supports the operation of such an interaction: Kaminsky, W.; Kopf, Jürgen; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629.

(8) Eisch, J. J.; Boleslawski, M. P. *J. Organomet. Chem.* **1987**, *334*, C1.

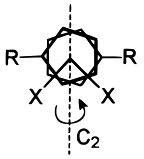
(9) All operations and reactions were carried out under an atmosphere of anhydrous, deoxygenated argon, and solvents and reaction vessels were likewise dried and deoxygenated before use. For relevant techniques: Eisch, J. J. *Organometallic Syntheses*; Academic Press: New York, 1981; Vol. 2, pp 3−62.

bis(isopropylcyclopentadienyl)zirconium dichloride (92%). Colorless samples of this derivative could be obtained either by flash column chromatography with a hexane−$CHCl_3$ gradient or by Soxhlet extraction of the crude reaction solids.[12a]

Alternatively, the di-*n*-butylzirconium dichloride can be generated completely in toluene, and after the room-temperature-stirring period, the 6-arylfulvenes **12a**−**c** can then be added and reaction at 65 °C commenced. Workup and isolation of the zirconocene dichlorides are carried out in the usual manner.[12b,13]

For the hydrozirconation of the polar, unsaturated organic substrates to yield reduced products **12**−**15**, the substrates are simply added to the preformed reagent **10** in toluene and allowed to react at reflux. Usual hydrolytic workup yields the reduced products **12**−**15** in 85−95% yields.[14]

In conclusion, it should be noted that zirconocenes **11** and **13a**−**c**, when combined with MAO, are all efficient polymerization catalysts for ethylene. Moreover, the unhydrolyzed hydrozirconation adducts, such as that obtained from benzophenone, $(Ph_2CHO)_2ZrCl_2$, are themselves suitable cocatalysts for ethylene polymerization as well. Finally, the unbridged, sterically substituted zirconocenes would appear to be especially promising candidates as isoselective catalysts for the polymerization of propylene, since they should tend to exist in a conformation having a C_2-symmetry axis (**20**).[15] Thus the hydrozirconations achievable with such dialkylzirconium dihalides make readily available broad classes of metallocene and nonmetallocene cocatalysts for olefin polymerization.



(20)

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(10) The individual treatment of $TiCl_4$ or $HfCl_4$, suspended in hexane or toluene at −78 °C, with 2 equiv of *n*-butyllithium and subsequent stirring at 25 °C, also led to hydrotitanating and hydrohafniating reagents, respectively, as evidenced by the reactions of such mixtures with benzophenone. With the titanium mixture, both tetraphenylethylene and benzhydrol were obtained in comparable amounts upon hydrolysis, evidence for the presence of both $TiCl_2$ (ref 11) and probably $BuTiCl_2$ or $HTiCl_2$. With the hafnium mixture, benzophenone was converted to benzhydrol in >90% yield (evidence for Bu_2HfCl_2 or H_2HfCl_2).

(11) Eisch, J. J.; Shi, X.; Lasota, J. *Z. Naturforsch.* **1995**, *50b*, 342.

(12) (a) Spectra of **11**: ^1H NMR ($CDCl_3$) δ 6.29 (t, 4H), 6.23 (t, 4H), 3.12 (septet, 2H), 1.21 (d, 12H); ^{13}C NMR δ 142.04, 114.63, 111.99, 28.74, 23.15. (b) Spectra of **12a**: ^1H NMR ($CDCl_3$) δ 7.3−7.5 (m, 10H), 6.25 (t, 4H), 6.05 (t, 4H), 4.07 (s, 4H); ^{13}C NMR δ 142.1, 129.8, 128.3, 127.9, 118.79, 113.59, 108.32.

(13) When the dialkylzirconium dichloride is thus generated in toluene or in THF and the solution suspension is heated at reflux in the absence of any fulvene or unsaturated organic substrate, a gas is evolved that is condensable at −90 °C (thus not H_2) but, when bubbled through a solution of Br_2 in CCl_4, does *not* discharge the color. Therefore, the evolved gas is principally butane, not butene. Furthermore, hydrolytic workup of the thermolyzed solution of Bu_2ZrCl_2 in toluene and ^1H NMR and GC analyses reveal that bibenzyl has been generated. Both observations, the formation of principally butane upon decomposition of Bu_2ZrCl_2 in THF or in toluene and the concomitant generation of bibenzyl in toluene, are consistent with the homolysis of the Ti−Bu bond being the chief pathway of the thermal decomposition of Bu_2ZrCl_2.

(14) The identity of the reduced products as benzhydrol (**12**), *N*-benzylaniline (**13**), benzaldehyde (**14**), and 2-phenylethanol was established by a detailed comparison of their spectral properties with those of authentic samples. Assurance that the acquired proton of these products stemmed from a transferred hydridic H of a Zr−H bond and was not introduced in the hydrolysis step was ascertained in the reaction of Bu_2ZrCl_2 with $Ph_2C{=}O$. Workup of this reaction mixture with D_2O resulted in the isolation of $Ph_2CH{-}OH(D)$, undeuterated on the benzylic carbon.

(15) (a) The test polymerizations of ethylene were carried out in the manner described in ref 2. (b) The steric bulk of such substituted zirconocenes should favor substituent projection from the nonplanar rings in a staggered manner, so as to give the structure a C_2-symmetry axis, as that possessed by bis(*tert*-butylcyclopentadienyl)zirconium dichloride and its many derivatives (cf. **20**): (Erker, G.; Muhlenberd, T.; Nolte, R.; Peterson, J. L.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1986**, *314*, C21. Krüger, C.; Nolte, M.; Erker, G.; Thiele, S. *Z. Naturforsch.* **1992**, *47b*, 995.