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REACTION OF ZIRCONOCENE DICHLORIDE WITH ALKYLLITHIUMS OR ALKYL GRIGNARD REAGENTS AS A CONVENIENT METHOD FOR GENERATING A "ZIRCONOCENE" EQUIVALANT AND ITS USE IN ZIRCONIUM-PROMOTED CYCLIZATION OF ALKENES, ALKYNES, DIENES, ENYNES, AND DIYNES[1]

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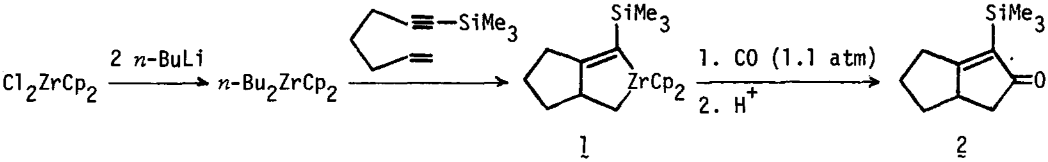
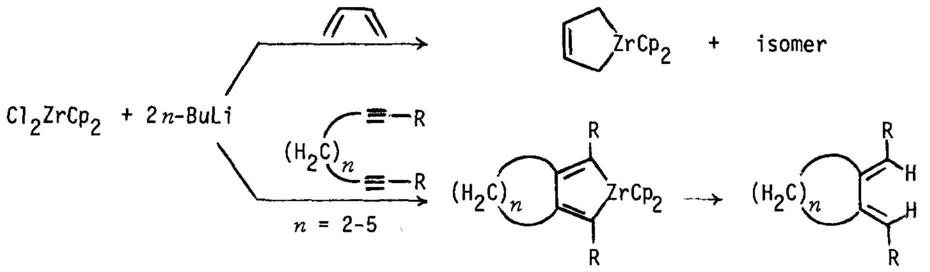
SUMMARY: Treatment of Cl_2ZrCp_2 with 2 equiv of alkylmetals (RM) containing Li or Mg, e.g., *n*-BuLi, in THF produces organozirconium species that act as sources of "$ZrCp_2$," the latter product being a convenient reagent for preparing zirconacycles.

We recently reported a bicyclization reaction of enynes[3] with a reagent generated by treating Cl_2ZrCp_2 with Mg (10 equiv) and $HgCl_2$ (1 equiv).[4] In view of the generally low chemoselectivity of Mg and the toxicity associated with $HgCl_2$, we sought an alternative procedure and have found that treatment of Cl_2ZrCp_2 with 2 equiv of *n*-BuLi in hexane for 1 h at -78°C in THF followed by addition of 7-trimethylsilyl-1-hepten-6-yne at -78°C and warming the mixture to room temperature produces the desired zirconabicyclic product 1 in essentially quantitative yield. As reported earlier,[3] 1 can be carbonylated to cleanly give 2-trimethylsilyl-3-oxobicyclo[3.3.0]oct-1-ene (2) in high yield (eq 1). Encouraged by these favorable results, we also tested EtMgBr (83%), *t*-BuLi (76%), and *t*-BuMgCl (trace) under essentially the same conditions and obtained 1 in the yields indicated in parentheses. Although the "$ZrCp_2$" equivalent has been generated by various methods including metal reduction of Cl_2ZrCp_2,[4] metal hydride reduction of $RZrCp_2Cl$[5] obtained by hydrozirconation of alkenes, and thermolysis or photolysis of Ph_2ZrCp_2,[6] the present method is more convenient than any previous method.



(1)

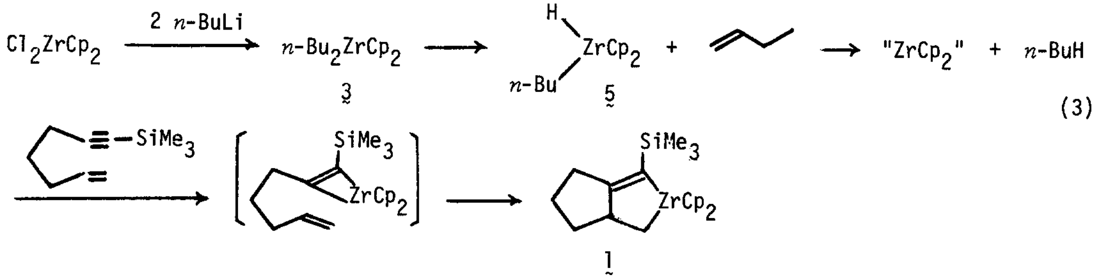
The *n*-BuLi-Cl_2ZrCp_2 reagent is also highly satisfactory for cyclizing dienes, such as butadiene,[6] and diynes (eq 2). The results of the diyne cyclization reaction are summarized in Table I. A similar diyne cyclization reaction with Cl_2TiCp_2 (1.28 equiv), 0.5% Na amalgam (3.36 equiv), and $PMePh_2$ (1.55 equiv) was recently reported.[7] However, the reaction of 1,5-diynes (*n* = 2) has not been reported, and silylated diynes reportedly give "severely diminished" yields of cyclization products.[7] We find that the reaction with the *n*-BuLi-Cl_2ZrCp_2 reagent proceeds smoothly to give satisfactory yields of the desired cyclic products (Table I). On the other hand, the corresponding *n*-BuLi-Cl_2TiCp_2 reagent generated analogously leads to very low yields of cyclization products along with byproducts that are not readily separable from the desired products.



(2)

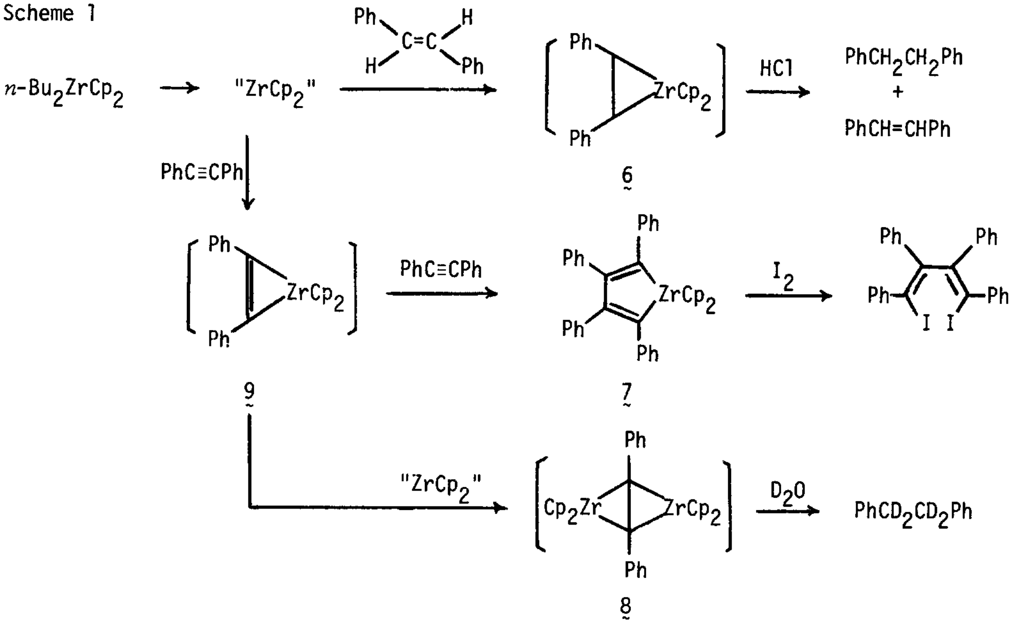
Examination of the *n*-BuLi-Cl_2ZrCp_2 reaction by ^1H NMR reveals the following mechanistic details. Upon addition of 2 equiv of *n*-BuLi to Cl_2ZrCp_2 placed in THF at -78°C cleanly shifts the Cp signal from 6.36(s) ppm for Cl_2ZrCp_2 to 5.93(s) ppm. Addition of 7-trimethylsilyl-1-hepten-6-yne to this mixture at -78°C does not cause any spectral change in the Cp region. At 20°C, however, a new singlet assignable to the Cp group of 1[3] at 5.96(br s) ppm emerges and grows at the expense of that at 5.93 ppm. This change obeys first order kinetics, $k_1 = (4.2\pm0.3)\times10^{-2}\ \text{min}^{-1}$ at 20°C. The initially formed product displaying the Cp signal at 5.93 ppm has been identified as *n*-Bu_2ZrCp_2 (3), since its treatment with 2 equiv of I_2 (-78°C to room temp) gives *n*-BuI (∿200%) and I_2ZrCp_2 (∿80%). Decomposition of 3 in the absence of the enyne is also a first-order process, the rate of which is essentially the same as the above cyclization, $k_1 = (4.6\pm0.4)\times10^{-2}\ \text{min}^{-1}$. When the above reaction is carried out in the presence of 2.2 equiv of $PMePh_2$, known $Cp_2Zr(PMePh_2)_2$ (4),[5] which shows a broad singlet at 4.98 ppm, is formed in 94% (by ^1H NMR). The first-order rate constant for this process is $(4.8\pm0.4)\times10^{-2}\ \text{min}^{-1}$ at 20°C. Furthermore, addition of 7-trimethyl-1-hepten-6-yne to 4 at 20°C provides within several minutes a 90% yield of 1. The results presented above clearly indicate that *n*-Bu_2ZrCp_2 (3) decomposes to give "$ZrCp_2$", which rapidly reacts with the enyne or $PMePh_2$ to provide 1 or 4, respectively, and that decomposition of 3 into "$ZrCp_2$" is the rate-determining step in the formation of 1. In the absence of any trapping agent, "$ZrCp_2$" decomposes rapidly to unidentified species.[8] Conversion of 3 into "$ZrCp_2$" does not involve reductive elimination of 3 to produce *n*-octane, since no *n*-octane is detected by GLC. On the other hand, 1-butene is formed in high yield (80-90%). The most likely course of the reaction is β elimination of 3 to produce *n*-Bu(H)$ZrCp_2$[9] (5) followed by its reductive elimination to give "$ZrCp_2$", which can then react with enynes, dienes and diynes via oxidative coupling and intramolecular carbometallation, as in eq 3.

Treatment of *n*-Bu_2ZrCp_2 with 1 equiv of stilbene (-78°C to room temp) gives a zirconocene derivative tentatively identified as 6 in ca. 80% yield. The compound shows a singlet for the Cp group at 5.25 ppm. Interestingly, treatment of the reaction mixture with 3*N* HCl gives bibenzyl and stilbene in 79 and 7% yields, respectively. The reaction of *n*-Bu_2ZrCp_2 with 2 equiv of PhC≡CPh provides 7[11] in 94% yield, which exhibits a singlet for the Cp group at 6.22 ppm. Its iodinolysis gives (*Z*,*Z*)-1,4-diiodo-1,2,3,4-tetraphenyl-1,3-butadiene in 58% yield. On the other hand, the 1:1 reactant ratio leads to a different major product formed in 68% yield based on Zr (34% based on PhC≡CPh) and tentatively identified as a novel bicyclic compound 8 (^{1}H NMR singlet for the Cp group at 5.20 ppm) along with 7 (8%). Protonolysis of 8 with 3*N* HCl gives bibenzyl in 88%, while its deuterolysis with D_2O provides tetradeuteriobibenzyl with 92% deuterium incorporation. It is highly likely that 9 is a common intermediate for 7 and 8 and that the two reactions of 9 with PhC≡CPh on the one hand and with "$ZrCp_2$" on the other proceed at comparable rates (Scheme 1). The dual path nature of the reaction of "$ZrCp_2$" with alkynes should be an important factor in designing Zr-promoted cyclization of alkynes, enynes, and diynes.



(3)

Scheme 1



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(8) Decomposition of $Cp_2Zr(PMePh_2)_2$ has been investigated, and the product has been characterized [Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* 1981, *20*, 481].

(9) The intermediacy of 5 has been supported by preparing 5 by treatment of *n*-Bu(Cl)$ZrCp_2$ with LiAlH(OBu-*t*)$_3$ [Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* 1980, *100*, 3246] and observing the rate of its reaction with 7-trimethylsilyl-1-hepten-6-yne, which is essentially the same as that of decomposition of 3. Judging from the reported stability of monoorganohydridozirconocenes,[10] the presumed decomposition of 5 into "$ZrCp_2$" in the reaction must be promoted by the enyne, 1-butene, or THF. Monoorganohydridozirconocenes are also known to hydrozirconate alkenes and alkynes. Since there is no indication for hydrozirconation of the enyne with 5, it either does not compete with the bicyclization reaction or occurs competitively but is reversible.[10]

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Table I. Reaction of Diynes with "Zirconocene" Generated by Treatment of Zirconocene Dichloride with *n*-Butyllithium[a]

$R^1C{\equiv}C(CH_2)_nC{\equiv}CR^2$			Yield of bis(alkylidene)cycloalkane, %	
R^1	R^2	*n*	GLC	Isolated
Me	*n*-Bu	2	76	67
Et	Et	3	85	80
Me	Me	4	84	55
Me_3Si	Me_3Si	4	97	89
Me	Me	5	60	40

[a] Each reaction is carried out by treating Cl_2ZrCp_2 with 2 equiv of *n*-BuLi in hexane for 1 h at -78°C in THF followed by addition of a diyne at -78°C, warming the mixture to room temperature, and the standard workup with 3*N* HCl, $NaHCO_3$, and brine.

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