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TRANSITION METAL DIENYLS IN ORGANIC SYNTHESIS: A CONVENIENT PREPARATION OF σ-BONDED TIN AND ZIRCONIUM DIENYLS

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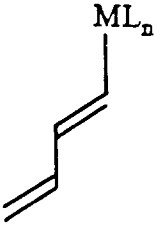
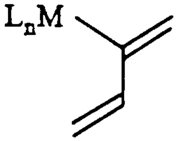
Abstract: Chemoselective hydrozirconation of 1-ene-3-yne molecules using $(\eta^5\text{-}C_5H_5)_2ZrHCl$, 1 represents the first general synthesis of zirconium dienyls, which, via transmetallation, can be stereoselectively transformed into synthetically useful tin dienyl derivatives.

The ability to utilise specifically functionalised 1,3-dienes in the Diels-Alder reaction is attractive, particularly if the functional groups can either activate the diene and/or are useful for subsequent elaboration. Typical modifications involve 1,3-dienes substituted with heteroatoms such as oxygen, sulfur or nitrogen-type donors.[2] In an effort to take advantage of this carbon-carbon bond forming reaction, we have extended the strategy to the synthesis and reactivity of 1,3-dienes which incorporate a transition metal moiety at either the 1- or the 2- position (A and B respectively).

A

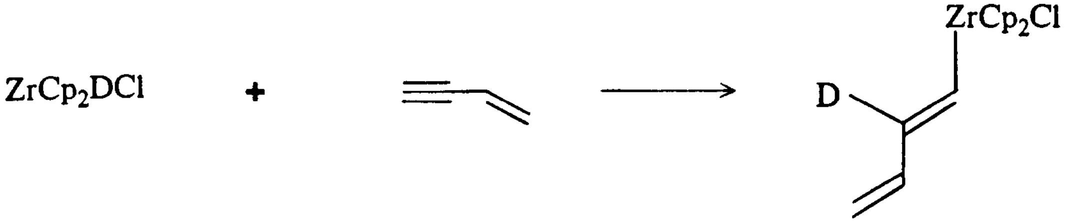




B

While transition metal complexes that contain 1,3-dienes bound in an η^4 fashion are commonplace[3], derivatives that have a transition metal σ-bonded to a diene are exceedingly rare[4,5]. Although the ability of metal-carbon σ-bonds to undergo further elaboration is well known[6], the influence of a transition metal unit on the reactivity of a diene, when the metal is σ-bonded to that diene, is virtually unknown[4]. We report here the synthesis of modified dienes of the type A where ML_n is $(\eta^5\text{-}C_5H_5)_2ZrCl$, and their transformation to organotin dienyl derivatives via a stereoselective transmetallation sequence[7]. One route to these types of molecules involves the hydrozirconation of 1-ene-3-yne molecules 2a - 2d,[8,9] as shown in Table 1.

These reactions proceed smoothly in a few hours at room temperature to generate the corresponding dienyl derivatives 3a - 3d in good yields (75-90%). A typical preparation for 3a - 3d involves portionwise addition of $(\eta^5\text{-}C_5H_5)_2ZrHCl$, 1, to a stirred solution of 2a - 2d in toluene. The completion of the reaction is indicated by formation of a homogeneous solution. The chemoselectivity of this reaction is quite remarkable; even though hydrozirconation of the alkene functionality is well established[10], we observe a complete preference for the alkyne over the alkene group, even for vinylacetylene **2a**[11]. To our knowledge, this is the first time that this type of chemoselectivity for metal-hydride addition has been observed[12]. The reaction of the deuterated analogue of **1**, $(\eta^5\text{-}C_5H_5)_2ZrDCl$, with these 1-ene-3-yne molecules is also revealing since the deuteron label is incorporated exclusively at the β-carbon, cis to the $(\eta^5\text{-}C_5H_5)_2ZrCl$ moiety.

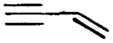
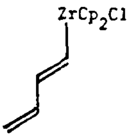
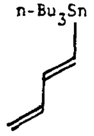
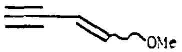
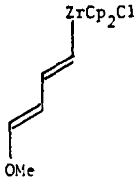
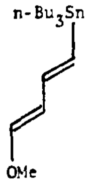
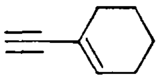
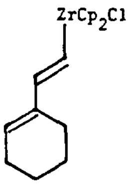
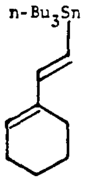
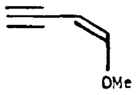
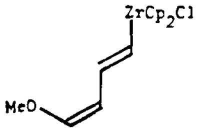
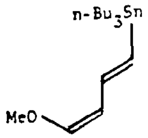


While the stereochemistry of the Zr-D addition to the alkyne functionality is not contentious[10], these reactions do suggest that the observed chemoselectivity is a kinetic preference for the alkyne versus the alkene rather than a thermodynamic preference.

Not only is the hydrozirconation procedure of 1-ene-3-yne molecules a general route to the required zirconium dienyl complexes, but these zirconium products are in turn useful reagents for the synthesis of a host of other metal or metalloid dienyl derivatives via transmetallation. Zirconium alkenyl derivatives transmetallate to a variety of Lewis acidic metal halides (i.e., $HgCl_2$, $AlCl_3$, $PdCl_2$, CuCl)[6b]. We have extended this reaction type to include organotin reagents[13]. For example, the reaction of the zirconium dienyl complexes **3a** and **3c** with $n\text{-}Bu_3SnCl$ in toluene at 100°C results in smooth formation of the corresponding tin dienyl complexes **4a** and **4c** in good yields, (75% and 90% respectively). The best yields for **4b** and **4d** (60% and 65% respectively) were obtained by reaction of **3b** and **3d** with $n\text{-}Bu_3SnCl$ in toluene at room temperature for 5-7 days. These complexes are readily separated from $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ by extraction with hexanes and filtration. We have confirmed that these reactions are stereoselective by ^1H NMR. In fact, the combination of the hydrozirconation of the 1-ene-3-yne molecules and the subsequent transmetallation to tin is an expedient synthesis of the organotin dienyl derivatives **4a** - **4d**. In comparison to the five step literature synthesis of **4a**[14], our procedure represents a significant and practical improvement.

Further work from our laboratory is focussing on the Diels-Alder reactions of these zirconium and tin dienyl reagents; in addition, we are expanding on the transmetallation theme.

Table 1. Synthesis of Organotin Dienyls via Hydrozirconation of 1-ene-3-ynes with $ZrCp_2HCl$ and subsequent transmetallation.[a]

ENTRY	1-ENE-3-YNES[b]	ZIRCONIUM DIENYLS	TIN DIENYLS
1	 2a	 3a	 4a
2	 2b	 3b	 4b
3	 2c	 3c	 4c
4	 2d	 3d	 4d

Satisfactory microanalysis, high resolution ^1H and ^{13}C NMR and IR spectra were obtained for all compounds synthesised

(a) Cp denotes η^5-C_5H_5

(b) 2a and 2d are commercially available from Pfaltz and Bauer and The Aldrich Chemical Co., respectively.

Acknowledgment

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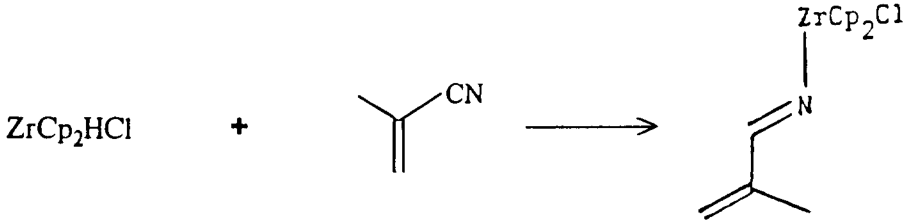
   (b) Carr, D.B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.
7. Carr, D.B.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 638.
8. For synthesis of **2b** and **2c** see: Brandsma, L. "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971.
9. Although **2b** was synthesised as a 4:1 E:Z mixture of geometric isomers, reaction of a 20% excess of **2b** with **1** resulted in clean formation of **3b**.
10. Labinger, J.A.; Schwartz, J. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 333 and refs. therein.
11. Similar selectivity was observed in reaction of **1** with α,β-unsaturated nitriles e.g., methacrylonitrile.



12. For an example of chemoselective hydroboration of **2c** see: Clark, G.M.; Polston, N.L.; Zweifel, G. *J. Am. Chem. Soc.* **1971**, *93*, 3395.
13. Reference 6(b) alludes to transmetallation reactions of zirconium alkenyl complexes with $SnCl_4$.
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