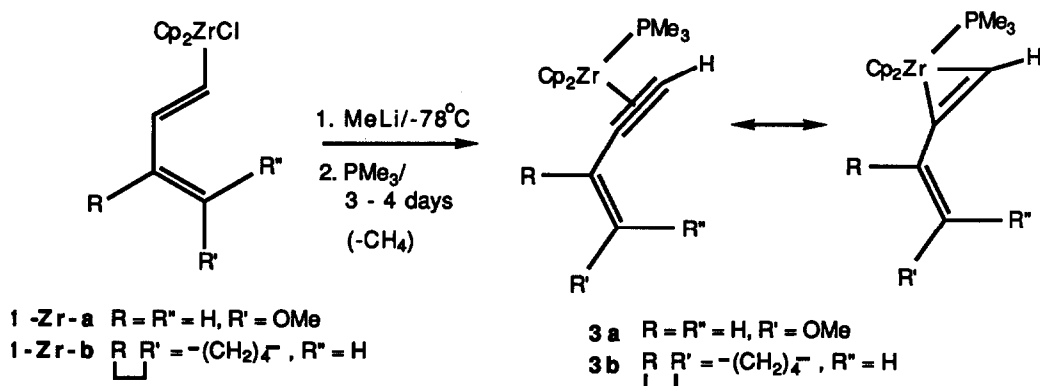


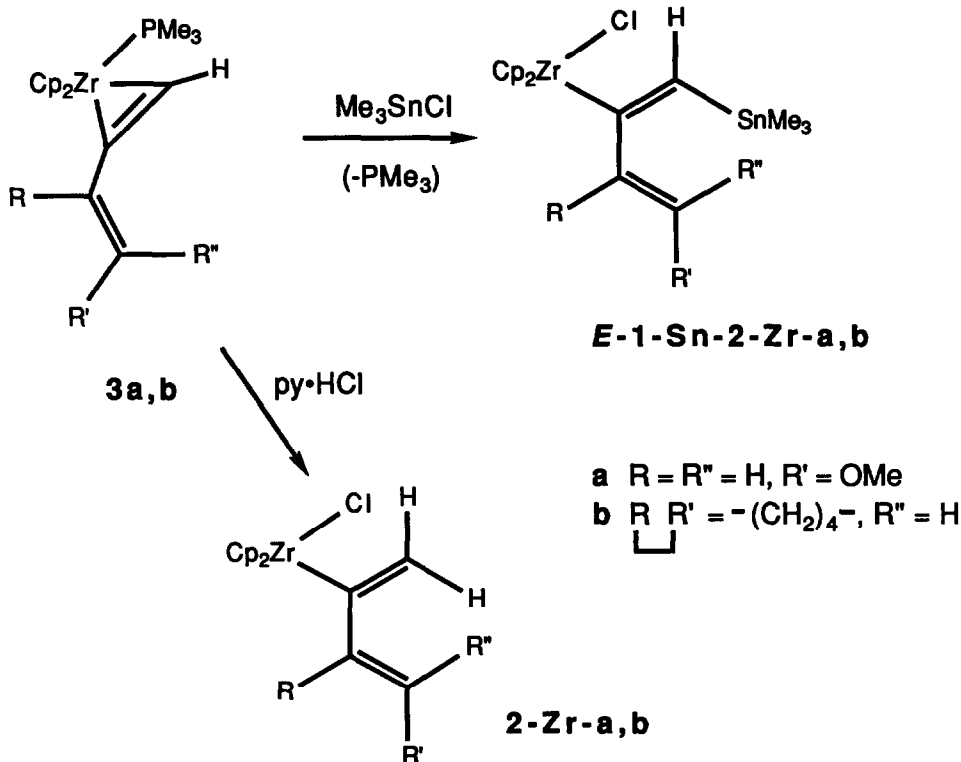
To effect the goal of converting the readily available enyne type starting materials to 2-substituted dienes, we developed an efficient strategy that utilizes the dienyl zirconium complexes **1-Zr** as the starting materials. Utilization of the Buchwald procedure⁷ followed by either "double transmetallation" or protonation, produces the 2-substituted dienes that we sought with additional flexibility to introduce functionality at the 1-position.

The dienyl zirconium reagents **1-Zr-a, b** react with MeLi at -78°C to generate⁷ the corresponding methyl-dienyl zirconocene derivatives ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(CH₃)CH=CH-CR=C(R')R'' **2a** and **2b**;⁸ as these materials are somewhat thermally labile, they were characterized in solution only and typically carried directly to the next step. Addition of PMe₃ (8 - 10 equiv) results in a slow elimination of methane and the formation of the zirconocene alkyne complexes⁹ **3a** and **3b** in good yields following the reported procedure.⁷

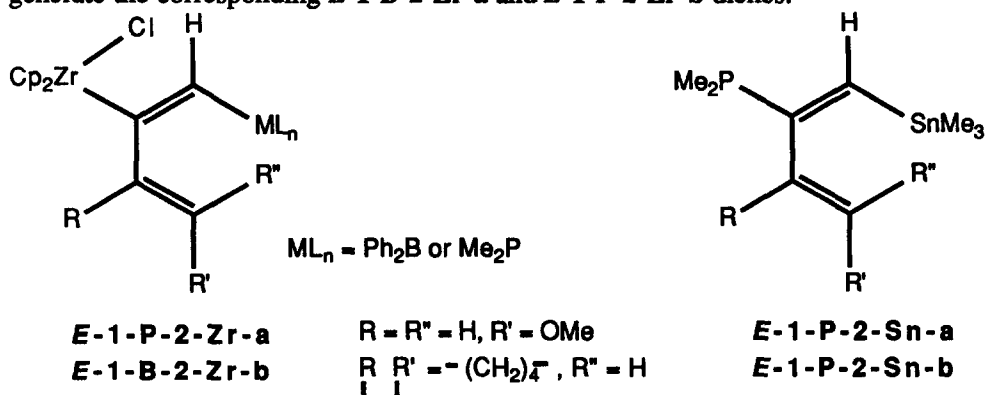


Since these formally Zr(II) alkyne derivatives can also be thought⁷ of as Zr(IV) metallocyclopropene complexes, there existed the possibility that transmetallation might be accessible. In fact, this has proven to be quite facile, but the stereochemistry of this "transmetallation" was completely unanticipated.

Addition of trimethylstannyl chloride to either **3a** or **3b** results in the formation of a single isomeric product¹⁰ having, in each case, the tin at the 1-position and the zirconium at the 2-position; the relative stereochemistry of the Sn and Zr moieties was ambiguous by NOE difference spectroscopy, but determined to be *trans* by a single-crystal X-ray structure (single-crystals of *E*-1-Sn-2-Zr-**b** were obtained from toluene/hexanes at -30°C). Thus the stereochemistry of this first "transmetallation" step proceeds with *inversion*. The parent 2-substituted zirconium dienyls can be accessed by reaction of **3a-b** with gaseous HCl (1 equiv) at -78°C , or more conveniently with pyridinium hydrochloride in toluene.



Preliminary findings hint at the potential of this strategy. With the zirconium in the two position, a subsequent "transmetalation" can be effected in analogy to previous studies.^{1,2,4,11} Addition of Me₂PCL to *E*-1-Sn-2-Zr-a,b cleanly produces the stannyl phosphines *E*-1-Sn-2-P-a,b. In addition, the first "transmetalation" also proceeds with Ph₂BBr or Me₂PCL to generate the corresponding *E*-1-B-2-Zr-a and *E*-1-P-2-Zr-b dienes.



These results collectively illustrate the flexibility of this "double transmetalation" procedure for the preparation of 1,2-dimetalated-1,3-dienes with a wide variety of substituents. The mechanism involved in the reaction of 3a-b with both HX and L_nMX systems, and the detailed reactivity of these new, highly functionalized dienes are currently under investigation.

Acknowledgment

Financial support was provided by NSERC of Canada in the form of an operating grant (M.D.F.) and a postdoctoral fellowship (R.F.A.). R. K. C. thanks Professor J. E. Drake for diffractometer time at the University of Windsor.

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8. **2a**: $^1\text{H NMR}$ (C_6D_6 , 400 MHz, $\text{C}_6\text{D}_5\text{H}$ at 7.15 ppm) δ 0.05 (s, 3H, CH_3), δ 3.17 (s, 3H, OCH_3), δ 5.46 (dd, $J_{\text{DC}} = 12$ Hz, $J_{\text{BC}} = 10$ Hz, 1H, H_C), δ 5.80 (s, 10H, Cp), δ 6.37 (dd, $J_{\text{AB}} = 19$ Hz, $J_{\text{BC}} = 10$ Hz, 1H, H_B), δ 6.58 (d, $J_{\text{CD}} = 12$ Hz, 1H, H_D), δ 6.98 (d, $J_{\text{AB}} = 19$ Hz, 1H, H_A).
- 2b**: $^1\text{H NMR}$ (C_6D_6 , 400 MHz, $\text{C}_6\text{D}_5\text{H}$ at 7.15 ppm) δ 0.08 (s, 3H, CH_3), δ 1.52 (m, 2H, $\text{H}_{\text{E}/\text{E}'}$), δ 1.60 (m, 2H, $\text{H}_{\text{E}'/\text{E}}$), δ 2.06 (m, 2H, $\text{H}_{\text{D}/\text{D}'}$), δ 2.14 (m, 2H, $\text{H}_{\text{D}'/\text{D}}$), δ 5.72 (bm, 1H, H_C), δ 5.80 (s, 10H, Cp), δ 6.47 (d, $J_{\text{BA}} = 19$ Hz, 1H, H_B), δ 6.95 (d, $J_{\text{AB}} = 19$ Hz, 1H, H_A).
- 3a**: $^1\text{H NMR}$ (C_6D_6 , 400 MHz, $\text{C}_6\text{D}_5\text{H}$ at 7.15 ppm) δ 0.98 (d, $J_{\text{PH}} = 5.9$ Hz, 9H, PCH_3), δ 3.47 (s, 3H, OCH_3), δ 5.32 (d, $J_{\text{PH}} = 1.6$ Hz, 10H, Cp), δ 7.01 (dd, $J_{\text{BC}} = 12$ Hz, $J_{\text{AB}} = 1.4$ Hz, 1H, H_B), δ 7.30 (d, $J_{\text{BC}} = 12.2$ Hz, 1H, H_C), δ 7.39 (dd, $J_{\text{PH}} = 4.1$ Hz, $J_{\text{AB}} = 1.4$ Hz, 1H, H_A). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.5 MHz) δ 0.8 (s). Anal. calc. for $\text{C}_{18}\text{H}_{25}\text{OPZr}$: C, 56.96; H, 6.64. Found: C, 57.15; H, 6.60. **3b**: $^1\text{H NMR}$ (C_6D_6 , 400 MHz, $\text{C}_6\text{D}_5\text{H}$ at 7.15 ppm) δ 0.98 (d, $J_{\text{PH}} = 5.8$ Hz, 9H, PCH_3), δ 1.75 (m, 2H, $\text{H}_{\text{D}/\text{D}'}$), δ 1.84 (m, 2H, $\text{H}_{\text{D}'/\text{D}}$), δ 2.47 (m, 2H, $\text{H}_{\text{C}/\text{C}'}$), δ 2.69 (m, 2H, $\text{H}_{\text{C}'/\text{C}}$), δ 5.34 (d, $J_{\text{PH}} = 1.7$ Hz, 10H, Cp), δ 6.27 (m, 1H, H_B), δ 7.53 (d, $J_{\text{PH}} = 4.1$ Hz, 1H, H_A). $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6 , 121.5 MHz, 85% H_3PO_4 at 0 ppm) δ 0.4 (s). Mass spectrum (EI, 70eV) calc. for $\text{C}_{21}\text{H}_{29}\text{PZr}$ (P^+), m/e 402. Found, m/e 326 (P-PMe_3) $^+$, m/e 220 (ZrCp_2) $^+$, and m/e 546 (very weak) ($\text{P-PMe}_3 + \text{ZrCp}_2$) $^+$. Anal. calc. for $\text{C}_{21}\text{H}_{29}\text{PZr}$: C, 62.49; H, 7.24. Found: C, 62.31; H, 7.38.
- 1-Sn-2-Zr-a**: $^1\text{H NMR}$ (C_6D_6 , 400 MHz, $\text{C}_6\text{D}_5\text{H}$ at 7.15 ppm) δ 0.27 (s with ^{117}Sn and ^{119}Sn satellites, $J(^{117}\text{Sn-H}) = 52$ Hz, $J(^{119}\text{Sn-H}) = 54.4$ Hz, 9H, SnMe_3), δ 3.33 (s, 3H, OCH_3), δ 5.76 (s, 10H, Cp), δ 6.38 (dd, $J_{\text{DC}} = 12.5$ Hz, $J_{\text{AC}} = 1.4$ Hz, 1H, H_C), δ 6.64 (d, $J_{\text{CD}} = 12.5$ Hz, 1H, H_D), δ 7.56 (d with single set of Sn satellites, $J_{\text{AB}} = 1.4$ Hz, $J_{\text{SnH}} = 24.5$ Hz, 1H, H_A). Anal. calc. for $\text{C}_{18}\text{H}_{25}\text{ClOSnZr}$: C, 43.00; H, 5.01. Found: C, 43.31; H, 5.07.
- 1-Sn-2-Zr-b**: $^1\text{H NMR}$ (C_6D_6 , 400 MHz, $\text{C}_6\text{D}_5\text{H}$ at 7.15 ppm) δ 0.23 (s with ^{117}Sn and ^{119}Sn satellites, $J(^{117}\text{Sn-H}) = 52$ Hz, $J(^{119}\text{Sn-H}) = 54.4$ Hz, 9H, SnMe_3), δ 1.55 (m, 2H, $\text{H}_{\text{E}/\text{E}'}$), δ 1.63 (m, 2H, $\text{H}_{\text{E}'/\text{E}}$), δ 1.98 (m, 2H, $\text{H}_{\text{D}/\text{D}'}$), δ 2.11 (m, 2H, $\text{H}_{\text{D}'/\text{D}}$), δ 5.28 (m, 1H, H_C), δ 5.78 (s, 10H, Cp), δ 7.22 (s with single set of Sn satellites, $J_{\text{SnH}} = 43$ Hz, 1H, H_A). Mass spectrum (EI, 70eV) calc. for $\text{C}_{21}\text{H}_{29}\text{ClSnZr}$ (P^+), m/e 526. Found, m/e 526 (weak), m/e 511 (P-PMe_3) $^+$, m/e 420 ($\text{P-C}_6\text{H}_{11}\text{Cl}$) $^+$. Anal. calc. for $\text{C}_{21}\text{H}_{29}\text{ClSnZr}$: C, 47.88; H, 5.55. Found: C, 48.20; H, 5.74.
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