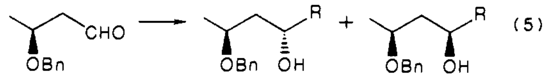

$TiCl_4/Et_4Pb$ -78 → -60 °C	78	22
$TiCl_4/Bu_4Pb$ -78 → -60 °C	91	9
BuMgBr -78 °C → room temperature	51	49

below -60 °C (eq 3), and the adduct was obtained in 64% yield in the ratio 93:7 (the aldehyde was recovered in 35% yield). Very high 1,2-asymmetric induction was observed in eq 4 (81% yield; 7% recovery of the aldehyde), but other reagents are also effective in asymmetric induction of this type of α-oxygen-substituted aldehydes.[8] The ethylation of the β-alkoxyaldehyde gave the adduct in 66% yield along with the recovered aldehyde (24%). Obviously, the present development provides a new stereo- and chemoselective alkylation procedure under non-carbanionic conditions.

It was rather curious that organolead compounds had been used only infrequently in organic synthesis, except $Pb(OAc)_4$, at the outset of our work.[9] The facile transfer from R_4Pb in comparison with R_4Sn is presumably due to the weak C-Pb bond.[10] The alkylation via R_4Pb clearly opens a door to the new area of organometallic-Lewis acid reagents,[11] and the full scope is now under active investigation.

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(8) For example: Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556.

(9) Lead-promoted allylation is reported: Tanaka, H.; Yamashita, S.; Hamatani, T.; Ikemoto, Y.; Torii, S. *Chem. Lett.* **1986**, 1611. See also: Tanaka, H.; Yamashita, S.; Katayama, Y.; Torii, S. *Ibid.* **1986**, 2043. For application of ((triphenylplumbyl)methyl)lithium and (bis(triphenylplumby)methyl)lithium in organic synthesis, see: Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410. Kauffmann, T.; Kriegesmann, R.; Rensing, A.; Konig, R.; Steinseifer, F. *Chem. Ber.* **1985**, *118*, 370. Kauffmann, T.; Rensing, A. *Ibid.* **1985**, *118*, 380. For α-alkynylation and α-arylation of ketones via organoleads, see: Moloney, M. G.; Pinkey, J. T.; Roche, E. G. *Tetrahedron Lett.* **1986**, *27*, 5025. Pinkey, J. T.; Rowe, B. A. *Aust. J. Chem.* **1983**, *36*, 789. Pinkey, J. T.; Kopinski, R. P. *Ibid.* **1983**, *36*, 311.

(10) The transfer from R_4Sn did not take place under the similar condition.

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Synthesis, Structure, and Reactions of a Zirconocene-Benzdiyne Complex

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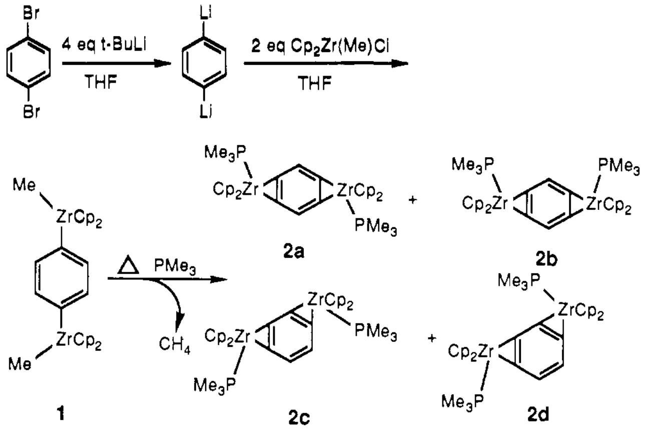
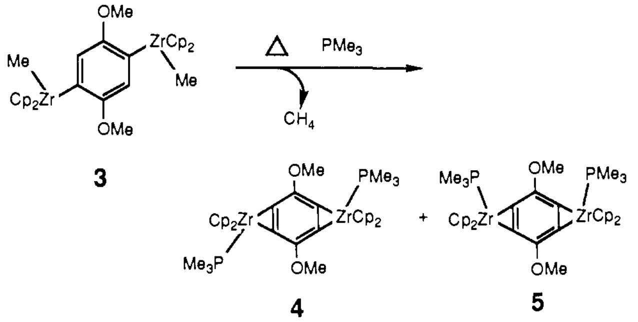
We recently reported the preparation and study of zirconocene complexes of benzyne,[1a] cyclohexyne,[1b] 1- and 3-hexyne,[1c] and thioaldehydes.[1d] In these cases the unstable organic fragment has previously been prepared in the free state, albeit with limited lifetimes. We became intrigued with the idea of preparing transition-metal complexes of organic molecules which are unlikely to be generated in their free state. To this end we have prepared the first example of a benzdiyne[2] species, in this case stabilized by two metal fragments.

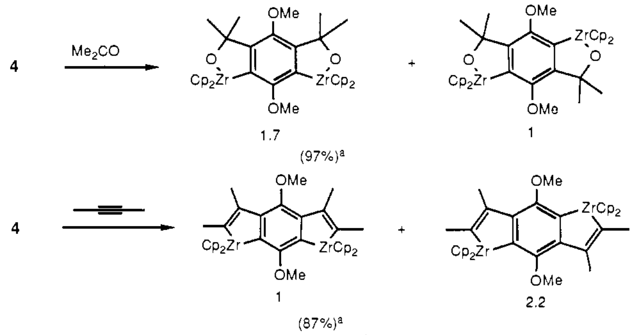
Scheme I



Scheme II



Scheme III



aYield determined by ¹H NMR.

Our initial attempts to synthesize a benzdiyne complex are shown in Scheme I. 1,4-Dilithiobenzene[3] was treated with 2 equiv. of zirconocene (methyl) chloride to give **1** in 90% yield.[4] Thermolysis of **1** at 70 °C in the presence of excess trimethylphosphine led to a mixture of the four possible isomers as evidenced by ¹H NMR. In order to prevent the formation of the regioisomeric products, we decided on the strategy shown in Scheme II. Compound **3** can be prepared as in the unsubstituted case in ca. 90% yield. Thermolysis of **3** over 48 h at 70 °C in benzene as before led to the deposition of **4** as beautiful plate-like crystals in 50% isolated yield. Its ¹H NMR spectrum shows only one methoxy signal. Examination of the remainder of the reaction mixture shows that both **4** and **5** are formed under these conditions but that **4** selectively crystallizes under the reaction conditions. Compound **4** has been characterized by ¹H NMR, elemental analysis, and X-ray crystallography.[5]

The X-ray crystal structure of **4**, shown in Figure 1, has several interesting features. First, the molecule possesses a center of symmetry with each $Cp_2Zr(PMe_3)$ unit displaced ca. 0.17 Å from

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(1) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (c) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (d) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590.

(2) Hart and co-workers have elegantly detailed the use of benzdiyne equivalents in organic synthesis: Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357. Hart, H.; Lai, C. Y.; Nwokogu, G.; Shamonilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6649.

(3) Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry 1*, Springer Verlag: Berlin, 1987; p 190.

(4) Except where noted, all yields refer to isolated yields.

(5) ¹H NMR (250 MHz, C_6D_6) δ 1.42 (d, J_P = 6 Hz, 18 H), 4.28 (s, 6 H), 5.41 (d, J_P = 3 Hz, 20 H). Anal. calcd. for $C_{34}H_{44}O_2P_2Zr_2$: 56.01, C; 6.08, H. Found: 55.97, C; 6.11, H. The extremely low solubility of **4** precluded the use of ¹³C NMR as a tool for its characterization.

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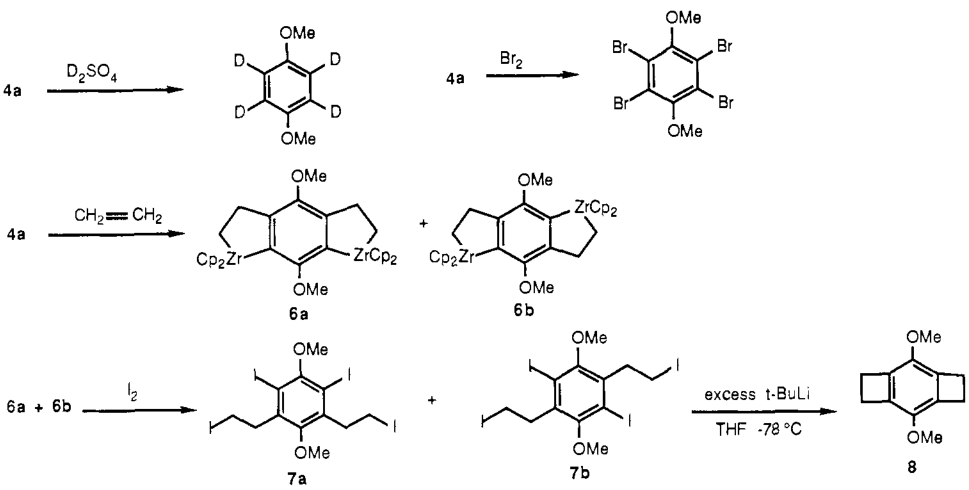
Scheme IV



Zr1-C1	2.194(8)	Å	C1-Zr1-C2	35.2(2)	°
Zr1-C2	2.253(7)		C1-C2-Zr1	74.8(5)	
C1-C2	1.345(11)		C2-C1-Zr1	70.0(4)	
C2-C3	1.398(11)		C1-C2-C3	121.1(6)	
C3-C4	1.401(10)		C2-C3-C4	118.8(7)	
C3-O1	1.412(9)		C6-C1-C2	120.1(6)	
Zr1-P1	2.667(2)				
Zr1-Zr2	6.640				

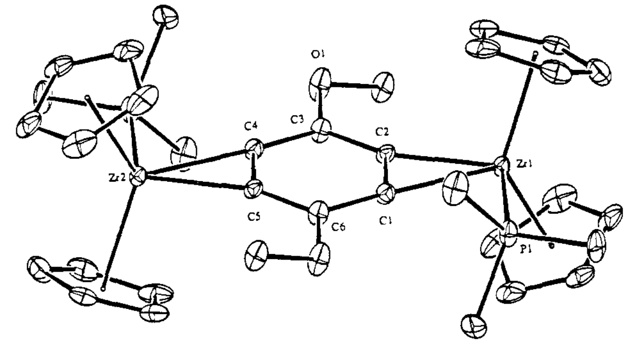


Figure 1.

the plane of the aromatic ring. Although not significantly to within 3σ, the two carbon-carbon "triple" bonds appear shorter than the other carbon-carbon bonds in the aromatic ring. This indicates that there is a great deal of π-back-bonding occurring to reduce the enormous strain which would exist in the free benzdiyne species.

Compound **4** undergoes bis-coupling reactions with unsaturated organic species to form the novel bis-metallacycles, as shown in Scheme III, which were not isolated but were characterized by ^1H NMR.

That **4** is in some ways equivalent to an aromatic tetraanion is indicated by its reactions as shown in Scheme IV. Treatment of **4** with excess D_2O/D_2SO_4 in THF provides a 93% yield of 2,3,4,5-tetradeuterio-1,4-dimethoxybenzene. In a similar fashion, **4** yields the known 2,3,4,5-tetrabromo-1,4-dimethoxybenzene[6] in 92% yield upon treatment with bromine. Heating **4** in benzene under 1 atm. of ethylene provides a 5:1 ratio of the bis-metallacycles **6a** and **6b** in quantitative yield. These isomers were not separated and were characterized by ^1H and ^{13}C NMR of the mixture. They can be converted to a mixture of regioisomeric tetraiodides **7a** and **7b** in 96% yield upon exposure to excess iodine.[8] Treatment of **7** (as the mixture of regioisomers) with excess *tert*-butyllithium in THF at −78 °C provided a 81% yield of the benzbicyclobutane[9] after flash chromatography.

In short, we have prepared, characterized, and undertaken an initial study of the reactions of the first transition-metal complex of a benzdiyne. We are continuing work in this area to increase regiochemical control of the coupling reactions of these diynes. In addition we have begun work on the synthesis of the 1,3-benzdiyne isomer as well as of the triyne species.

Acknowledgment. We would like to thank the National Institutes of Health (GM-34917), the Camille and Henry Dreyfus Foundation (for a Distinguished New Faculty in Chemistry Grant), and Dr. Alfred Bader and Firmenich SA for their generous financial support of this work. In addition, E.A.L. thanks the National Science Foundation for a graduate fellowship, and we thank the Biomedical Research Support-Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase X-ray diffraction equipment (NIH Grant S10 RR02243).

Supplementary Material Available: Preparation and spectroscopic characterization of compounds, crystallographic data and procedures, ORTEP diagram of **4**, bond distances and angles, and a table of final positional and thermal parameters (6 pages); table of observed and calculated structure factors for **4** (12 pages). Ordering information is given on any current masthead page.

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Metal Carbonyl Promoted Rearrangement of Cyclopropenes to Naphthols

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The carbene-alkyne cycloaddition with CO incorporation using carbenechromium complexes produces phenol derivatives.[3] Common examples involve arylcarbene ligands (as in **1**, Scheme I) and produce naphthohydroquinones as illustrated with the formation of **2** in Scheme I, path a. The process has been developed as a methodology and applied in specific syntheses.[4-7] There are several general limitations: (a) the starting arylcarbene complexes are available only by reaction of an aryllithium reagent with $Cr(CO)_6$;[8,9] (b) general success has been obtained only with alkoxy-substituted carbene ligands, leading specifically to naphthohydroquinones; and (c) the process is stoichiometric in chromium. Mechanisms have been proposed, involving initial

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(1) NIH Postdoctoral Fellowship holder.

(2) Undergraduate research student; results are taken in part from the Senior Thesis of M. C. Lee.

(3) For a recent review and leading reference, see: Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

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