

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 R₄Pb 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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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 benzdiyne² species, in this case stabilized by two metal fragments.



Our initial attempts to synthesize a benzdiyne complex are shown in Scheme I. 1,4-Dilithiobenzene³ 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 Cp₂Zr(PMe₃) unit displaced ca. 0.17 Å from

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

^{(5) &}lt;sup>1</sup>H NMR (250 MHz, C₆D₆) 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 C₃₄H₄₄O₂P₂Zr₂: 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.



C

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-dimethoxybenzene⁶ 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 ¹³C 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% vield of the benzbicyclobutane9 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 1,3benzdiyne isomer as well as of the triyne species.

excess t-BuLi THE -78 °C

 OM_{c}

OMe

8

OMe

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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.

Metal Carbonyl Promoted Rearrangement of **Cvclopropenes 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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