reaction as well as with earlier pressure studies which were utilized to emphasize the mechanistic differences in competing concerted and nonconcerted processes.[11,14] The effect of pressure and viscosity on the *stereochemical* outcome of this reaction, which study is currently in progress, should provide even more clear-cut insights into these questions.

Acknowledgment. Support of this research in part by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are also indebted to Dr. Philip de Shong for his generosity in allowing us to use his high pressure apparatus at Penn State University.

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A New Type of Stable, Storable, and Selective Alkylating Reagent, R_4Pb

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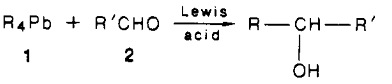
Needless to say, organomagnesium, organolithium, and organocopper derivatives are classical and widely used carbanionic alkylating reagents. Since the mid-1970s, a new current has appeared in this field. Several air-stable and storable reagents for the C–C bond formation of carbonyl compounds have been developed, which are normally used under nonbasic conditions.[1] Unfortunately, however, the transfer from the hitherto known reagents is limited to the particular functional groups such as allyl,[1b,c] alkynyl,[2] and enols.[1a] The transfer of alkyl groups is entirely unknown despite its potential synthetic importance.[3] We report for the first time a new method for the alkyl transfer via a stable and storable reagent, R_4Pb.

Tetraalkylleads[4] reacted quite smoothly with aldehydes in the presence of Lewis acids such as $TiCl_4$ and BF_3 (eq 1). The results are summarized in Table I. Titanium tetrachloride gave the best



$$\underset{\mathbf{1}}{R_4Pb} + \underset{\mathbf{2}}{R'CHO} \xrightarrow[\text{acid}]{\text{Lewis}} \underset{\mathbf{3}}{R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'} \qquad (1)$$

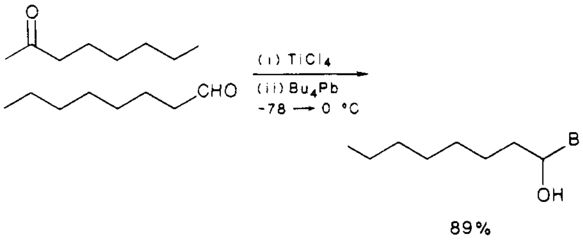
result among the Lewis acids examined. A possibility that $RTiL_n$ may be a real intermediate is eliminated by the following reasons. *n*-Alkyl groups and even a cyclohexyl group underwent the transfer reaction. It is well-known that *n*-alkyl and *sec*-alkyl titanium compounds of the type $Cl_3Ti–R$ (R = alkyl) easily undergo β-elimination reactions.[5] Further, formation of **3** by use of $BF_3{\cdot}OEt_2$ clearly indicates that transmetalation from R_4Pb to RBL_n does not take place under lower temperature, since RBL_n cannot alkylate aldehydes under the reaction conditions.

Table I. Alkyl Transfer from R_4Pb to Aldehydes[a]

entry	R_4Pb (**1**) R	R'CHO (**2**) R'	reaction condn temp (°C)	 **1** (equiv)	isolated yield of **3**, %
1	Et	C_6H_5	−78 → −30	1.8	96
2	Et	C_6H_{11}	−78 → −30	1.3	98
3	Et	$CH_3(CH_2)_6$	−78 → −30	1.3	94
4	Bu	C_6H_{11}	−78 → 0	1.3	84
5	Bu	C_6H_{11}	−78 → −30	1.3	70
6	Bu	$CH_3(CH_2)_6$	−78 → 0	1.3	88
7	Bu	$CH_3(CH_2)_6$	−78 → −30	1.3	73
8	C_6H_{11}	C_6H_{11}	−70 → 0	2.0	38
9	C_6H_{11}	C_6H_{11}	−70 → −30	1.3	32
10	C_6H_{11}	$CH_3(CH_2)_6$	−70 → 0	2.0	46
11	C_6H_{11}	$CH_3(CH_2)_6$	−70 → −30	1.3	41

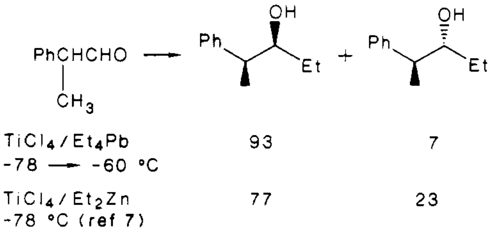
[a] The procedure of entry 1 is representative. To a solution of benzaldehyde (1 mmol) in CH_2Cl_2 (1 mL) was added at −78 °C a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 1.2 mmol), and then $Et_4Pb–CH_2Cl_2$ solution (1 M, 1.8 mmol) was added.[6] The reaction mixture was gradually warmed to −30 °C. Then, the reaction was quenched with aqueous $NaHCO_3$–MeOH. The product was isolated by column chromatography on silica gel (entries 1 ~ 3) or on alumina (entries 4 ~ 11), by using *n*-hexane–ether as an eluant. Excess Et_4Pb and Bu_4Pb were recovered and could be utilized repeatedly. When the reaction was incomplete (entries 4 ~ 11), the starting aldehyde was recovered.

As is apparent from Table I, transfer of an ethyl group occurs rapidly in essentially quantitative yields (entries 1–3). Transfer of a butyl group is relatively slow in comparison with ethyl transfer (entries 4–7), and cyclohexyl group can be transferred slowly at 0 °C (entries 9–11). Another important aspect of $R_4Pb/TiCl_4$ is its chemoselectivity. Only aldehydes underwent the alkylation in the presence of ketones (for example, eq 2). Cyclohexanone and related ketones did not react with Bu_4Pb at room temperature for a prolonged period of time.

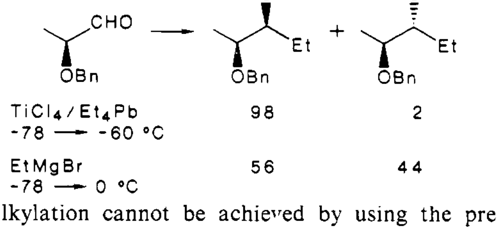


(2)

Very high 1,2- and 1,3-asymmetric induction was realized with this new reagent (eq 3–5). Especially noteworthy is the high asymmetric alkylation of eq 3 and 5. Such a high diastereoselective alkylation cannot be achieved by using the previous reagents. The ethylation of 2-phenylpropionaldehyde took place



(3)



(4)

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(1) (a) Silyl enol ethers: Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973**, 1011. (b) Allylsilanes: Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (c) Allyltins: Tagliavini, G.; Peruzzo, V.; Plazzogna, G.; Marton, D. *Inorg. Chim. Acta* **1977**, *24*, L24. Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919. (d) Allylboranes; allylaluminums, and related compounds react under nonbasic conditions, but they are air and moisture sensitive.

(2) (a) Stannylacetylenes: Yamamoto, Y.; Nishii, S.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, *102*. (b) Silylacetylenes: Kuwajima, I.; Nakamura, E.; Hashimoto, K. *Tetrahedron* **1983**, *39*, 975.

(3) Dialkylzinc compounds, which are moisture and air sensitive, transfer alkyl groups to aldehydes in the presence of $TiCl_4$ (ref 7).

(4) Et_4Pb and Bu_4Pb were prepared essentially according to the literature procedure: Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1950**, *72*, 1760. $(C_6H_{11})_4Pb$ was prepared as described in the literature: Gruttner, G. *Chem. Ber.* **1914**, *47*, 3257.

(5) *n*-Alkyl titanium compounds of the type $(i\text{-PrO})_3Ti–R$ do not undergo β-elimination reactions: (a) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: New York, 1985. (b) Seebach, D. *Mod. Synth. Methods* **1983**, *3*, 216.

(6) Clean reactions did not occur upon the reversed addition: (i) R_4Pb, (ii) $TiCl_4$, and then (iii) aldehydes. Apparently, the transmetalation took place first and $RTiL_n$ was involved as an intermediate in the reversed addition.

(7) Reetz, M. T.; Steinbach, R.; Wenderoth, B. *Synth. Commun.* **1981**, *11*, 261.

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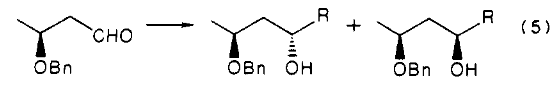

$TiCl_4/Et_4Pb$ −78 → −60 °C	78	22
$TiCl_4/Bu_4Pb$ −78 → −60 °C	91	9
BuMgBr −78 °C → room temperature	51	49

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.

(11) Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947; *Angew. Chem.* **1986**, *98*, 945.

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

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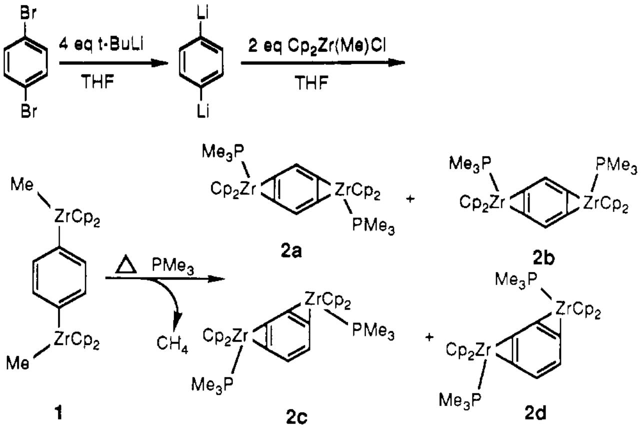
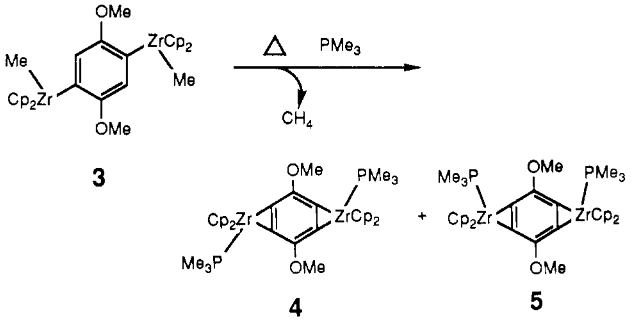
We recently reported the preparation and study of zirconocene complexes of benzyne,[1a] cyclohexyne,[1b] 1- and 3-hexyne,[1c] and thioaldehydes.[1d] In these cases the unstable organic fragment has previously been prepared in the free state, albeit with limited lifetimes. We became intrigued with the 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.

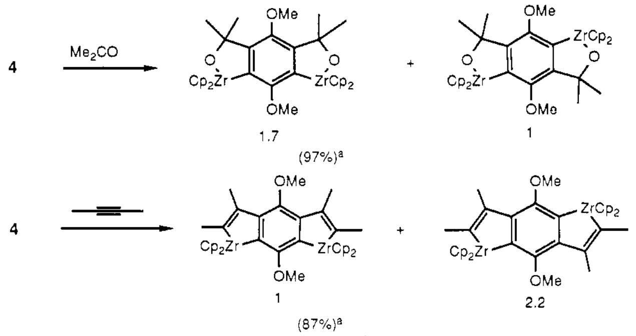
Scheme I



Scheme II



Scheme III



[a] Yield 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 ^{13}C NMR as a tool for its characterization.

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