A Novel Catalytic Effect of Lead on the Reduction of a Zinc Carbeneoid with Zinc Metal Leading to a Geminal Dizinc Compound. Acceleration of the Wittig-Type Olefination with the RCHX₂-TiCl₄-Zn Systems by Addition of Lead

Kazuhiro Takai,*,† Tadahiro Kakuuchi, Yasutaka Kataoka, and Kiitiro Utimoto*
Division of Material Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan

Received March 14, 1994

Summary: A catalytic amount of lead promotes further reduction of zinc carbeneoid (ICH₂Zn) with zinc in THF to give a geminal dizinc compound (CH₂ZnZn), which is a key intermediate for the methylation of carbonyl compounds with a CH₂Zn, zinc, and TiCl₄ system.

Metals such as lithium, magnesium, and zinc are usually employed in organic synthesis without further purification. Thus, it is difficult to know the influence of trace impurities that are not eliminated completely by standard smelting methods.1,2 In 1978, we reported the methylation of aldehydes and ketones with a CH₂Br-TiCl₄-Zn system (eq 1).3 This reagent was modified for the alkylideneation of carbonyl groups of carboxylic acid derivatives (eq 2).4 Recently, we were informed that the reported yields could not be reproduced by following the protocol given for the latter reaction.5 Because all of the relevant organic and inorganic materials except zinc powder6 are purified as part of the procedure,7 we suspected the zinc powder of causing the difference.8

Analysis of fluorescent X-rays of both samples of zinc powder revealed that the effective lots of zinc contained 0.04-0.07 mol % of lead on the basis of zinc and that the less effective sample was free of lead.9 Addition of a catalytic amount (0.5 mol %) of lead powder (or PbCl₂10 to pure zinc powder showed the reproducible results originally reported.11 Moreover, addition of a catalytic amount of PbCl₂ revealed a remarkable acceleration of the methylation of carbonyl groups, especially in the case of a CH₂Cl₂-TiCl₄-Zn system (Figure 1).12 Treatment of 4-phenyl-2-butanone with a mixture of CH₂Cl₂, TiCl₄, and zinc in THF at 0 °C for 90 min produced the methylation product 2 in 5-8% yield. The reaction accelerated suddenly after the addition of PbCl₂ (1 mol % based on zinc) to the mixture, and the yield of 2 went up to 65%. When a catalytic amount of PbCl₂ was added to the zinc from the beginning, the methylation proceeded smoothly at 0 °C to give 2 in 81% yield within 30 min.

Treatment of dodecanal in the presence of Me₃SiCl with the filtrate derived from CH₂Cl₂, pure zinc powder, and a catalytic amount of PbCl₂ in THF furnished 1-tridecene in 72% yield,12 while the same reaction without PbCl₂ did not produce 1-tridecene at all (eq 3).13 This suggests that a catalytic amount of PbCl₂ (or lead), added to zinc, promotes further reduction of ICH₂Zn14-16 forming a methylene dianion equivalent, CH₂(ZnI)₂.17-20

---

1 Present address: Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushima, Okayama 700, Japan.


(5) The protocol was examined by Professors R. Yonogi and R. K. Boeckman, Jr., who check Organic Synthesis.

(6) Zinc dust (purity 98.87 wt % (>90 % on label), pyrometallurgy) was purchased from Wako Pure Chemical Industries Ltd., Japan.

(7) Zinc powder was simply washed several times with 5% hydrochloric acid in turn with water, methanol, and ether, and dried in vacuo according to the literature. Fieser, L. F.; Fieser, M. Organic Reactions: Wiley: New York, 1967; Vol. I. p 1276.

(8) We sent a sample of our zinc powder purchased from Wako to R. K. Boeckman, Jr. Reaction with zinc dust from Wako produced 1 in 85% yield, while that with zinc from Aldrich gave 1 in 39% yield. It was suggested that Wako zinc powder includes some unknown impurities which promote the reaction.

(9) The difference of the purity has proved to stem from the smelting method. Zinc powder (distilled zinc) derived by Pyrometallurgy contained 0.04-0.07 mol % of lead based on zinc. In contrast, zinc (electrolytic zinc) produced by hydrometallurgy was pure (>99.999%) and it did not contain lead.

(10) Lead powder (99.999% purity) and PbCl₂ (99.999% purity) were purchased from Rare Metallic Co., Japan.

(11) Yields and stereoselectivities of 1 with such potential catalysts (0.5 mol % of zinc) in THF at 25 °C for 4.5 h are as follows: FeCl₃, 14% (Z/E = 95/5); CoCl₂, 22% (96/4); NiCl₂, 0%; CuCl₂, 22% (95/5); AgCl, 28% (85/15); PtCl₂, 14% (92/8); AuCl₃, 26% (95/7); SnCl₃, 10% (96/4); BiCl₃, 13% (91/9); none, 10-15% (Z/E = 92-95/5).

(12) Geminal dimetallic compounds having weak nucleophilicity require Lewis acids such as Me₃Al, Me₃SiCl, Ti(O-i-Pr)₃ and BF₃-OEt₂ to promote methylation or alkylidenation. The Lewis acid-assisted reagents have different reactivity (e.g., aldehyde-selective methylation) from the present TiCl₄-containing reagent systems. The geminal methylation in the presence of PbCl₂ produced 1-tridecene in only 10% yield without Me₃SiCl.


The $^1$H NMR spectrum of the supernatant solution of CH$_2$I$_2$ and zinc (3 equiv) in THF-$d_8$ showed a characteristic singlet at 1.40 ppm that was assigned to ICH$_2$ZnI (or Zn-(CH$_2$I)$_2$), according to Denmark's results. Several small peaks corresponding to CH$_2$I, CH$_3$I, and THF were also observed. When a catalytic amount of lead and 2 equiv of zinc were added to the solution of ICH$_2$I$_2$ with (5 mol % based on zinc) in THF-$d_8$ at 25 °C for 1 h. The peak at -0.78 ppm disappeared upon addition of a drop of water to the NMR tube. Upon treatment of a filtered solution derived from CH$_2$I$_2$ and zinc in THF with Me$_3$SnCl at 40 °C for 20 h, ICH$_2$SnMe$_3$ was produced in 50% yield along with CH$_2$(SnMe$_3$)$_2$ in 2% yield. Meanwhile, trapping of the active species in the filtered solution of the lead-containing system with Me$_3$SnCl and LiI at 40 °C for 20 h furnished CH$_2$(SnMe$_3$)$_2$ in 26% yield; ICH$_2$SnMe$_3$ was not obtained. The yield of CH$_2$(SnMe$_3$)$_2$ was increased to 42% by addition of CuC$_2$2LiCl at -60 °C, before trapping with Me$_3$SnCl at -60 to 25 °C, over a period of 5 h.22

The accelerating effect of lead on the reduction of a zinc-carbenoid to a geminal dizinc compound might be explained as shown in Scheme 1. Transmetalation from the zinc-carbenoid 3 with lead(II)23 produces lead-carbenoid 4,21 which is readily reduced by zinc to give geminal lead zinc compound 5.24 Transmetalation from lead to zinc with zinc(II) affords geminal dizinc compound.

![Figure 1. Yields of 2 by means of the CH$_2$X$_2$-TiCl$_4$-Zn systems.](image-url)

**Scheme 1**

1. CH$_2$I$_2$ THF, 25 °C, 0.5 h
2. Me$_3$SiCl (1.0)
3. Zn slow
4. fast
5. fast
6. slow

(X = I or Cl)
6. Reduction of the lead-carbenoid 4 with zinc could proceed faster than that of the zinc-carbenoid 3, since the lead-carbon bond is more covalent than the zinc-carbon bond.25

The Wittig-type olefination of carbonyl compounds can be accomplished with geminal dimetallic compounds (LnM2CHR2MLn2)12,13 or the Schrock-type metal-alkylidene complexes (LnM=CHR).26 The present reagent derived from RCHX2, TiCl4, zinc, and a catalytic amount of PbCl2 has the following features, which are typical for titanium-based reactive species:27,28 (i) the methylenation reagent is effective for highly enolizable ketones30 and (ii) olefination of carboxylic acid derivatives proceeds under mild conditions.4 We are tempted to assume that the key intermediate of the methylenation is the Tebbe-type complex (9 or 10)29,31 or a titanium-containing geminal dimetallic compound (7 or 8),31 which is produced by transmetalation from the geminal dizinc compound 6 (Scheme 2).

Effects of a catalytic amount of lead on other zinc-mediated reactions are under investigation.

Acknowledgment. The authors thank Prof. Ryoji Noyori, Dr. Hsiao Yi, Prof. Robert K. Boeckman, Jr., Dr. Alan T. Johnson, and Prof. Jeremiah P. Freeman, who kindly informed us of the results of their attempts to reproduce the alkylidenation and thus initiated these studies in a fruitful manner. We also thank Prof. Hiroshi Takataki and Mr. Yoshihiji Honda of Environment Reservation Center of Kyoto University for the analysis of fluorescent X-ray. Financial supports from the Ministry of Education, Science, and Culture of Japan and Asahi Glass Foundation for Sciences are gratefully acknowledged.

Supplementary Material Available: Typical procedure for methylenation of 4-decanone (eq 1) and pentylenation of ethyl benzoate (eq 2) and 1H NMR spectra of ICH2ZnI and CHZ(ZnI) in THF-de (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(29) (a) In 1983, J. J. Eisch reported the Tebbe-type reagent, CplTI-(CH2)2-ZnX2, prepared by treatment of CplTICl2 with CH2(ZnI) in THF. See also: Bruin, J. W.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. Tetrahedron Lett. 1983, 24, 3935-3938.
(30) Reported stereoselectivities of carboxylic acid derivatives with Schrock-type metal-alkylidene complexes are moderate. In contrast, alkylidenation of carbonyl compounds with geminal dimetallic compounds proceeds under high stereocontrol. Because the alkylidenation of ester carboxylic acid groups with the RCHBr-TiCl5-Zn-TMEDA system produces Z-isomers of alkenyl ethers stereoselectively, the possibility of geminal dimetallic compounds 7 and 8 could not be neglected.