

Isolation and Structural Characterization of *Geminal* Di(iodozincio)methane Complexes Stabilized with Nitrogen Ligands

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Supporting Information

ABSTRACT: Treatment of *gem*-di(iodozincio)methane with pyridine or diamine derivatives resulted in the isolation of a storable *gem*-di(iodozincio)methane species. Use of the sterically bulky bipyridine ligand gave a *gem*-di(iodozincio)methane complex, which allowed the first X-ray structural analysis of such species. This work represents a rare example of the isolation of an organometallic reactive species in Schlenk equilibrium and thus provides new insight into the design of efficient and storable organometallic reagents. The isolated *gem*-di(iodozincio)-methane complexes serve as effective methylene dianion synthons for olefination of carbonyl compounds.

Compounds with two metal atoms on the same carbon, categorized as *gem*-dimetalloalkanes ($R_2CM^1M^2$), constitute a classic and important class of organometallic reagents in organic synthesis.¹ Among them, *gem*-dimetallomethanes ($R = H$), such as Tebbe reagent ($Ti-CH_2-Al$), Nysted reagent ($Zn-CH_2-Zn$), and *gem*-dizincio-methanes ($Zn-CH_2-Zn$) are frequently employed in methylenation and related reactions.^{2–4}

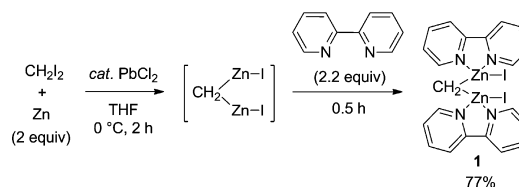
In contrast to the synthetic use, isolation and structural characterization of these reagents, apart from Tebbe reagent, are generally difficult due to their tendency to decompose via the Schlenk equilibrium, which results from their inherent instability. The structure of *gem*-di(iodozincio)methane ($CH_2(ZnI)_2$) was first proposed in the methylenation of a ketone and aldehydes by Fried and Miyano, in which they considered the reagent as a dianion derived from further reduction of Simmons–Smith reagents ($I-CH_2-ZnI$) with zinc.^{4a,b} Oshima, Takai, and Nozaki confirmed its structure indirectly by trapping with Me_3SnCl and demonstrated its wide synthetic utility.^{4c} Later, it was proved that these seminal outcomes were strongly dependent on the nature of the zinc used. After intensive studies, it was disclosed that the presence of trace amounts of lead was the key factor for the generation of *gem*-di(iodozincio)methane compounds.⁵ The reduction of a zinc carbenoid ($I-CHR-ZnI$) into *gem*-di(iodozincio)methanes ($RCH(ZnI)_2$) was dramatically accelerated by the use of a $PbCl_2$ catalyst, and a procedure for general preparation as a robust alkyldienation method for various carbonyl compounds was established. This alkyldienation reaction offers some advantages over typical olefination reaction such as the Wittig reaction,⁶ including expansion of the scope to easily enolizable or sterically hindered ketones,^{3,4c,h} high chemoselectivity,^{3,4i} and alkyldienation of ester carbonyl groups

with titanium salts.⁵ These features make them quite useful especially for the total synthesis of natural products.⁷ Recently, *gem*-di(iodozincio)methanes have been shown to be useful reagents for methylenation and ring-closing metathesis cascades of olefinic esters,⁸ 1,4-addition to enones, nickel-catalyzed carbocation of alkynes, and palladium-catalyzed sequential cross-coupling reactions.⁹

Despite numerous studies on their synthetic applications, crystallographic characterization of these useful reagents has remained elusive, presumably due to their tendency to decompose in solution via a Schlenk equilibrium and difficulties associated with producing single crystals.^{10,11} Matsubara et al. studied the structure of $CH_2(ZnI)_2$ species in THF using extended X-ray absorption fine structure, small angle neutron scattering, and anomalous X-ray scattering analysis.¹² We have long suspected that isolation and direct structural characterization would shed light on the exact nature of the reactive species, the origin of their unique selectivity, and their further synthetic application.¹³ Moreover, this study was expected to provide a new insight into the design of more efficient as well as storable *gem*-dimetallic reagents for olefination of carbonyl compounds. This report describes the synthesis and isolation of a series of storable *gem*-di(iodozincio)methane complexes and their first X-ray characterization. The performance of these complexes in the methylenation of several carbonyl compounds is also investigated.

To stabilize the generated *gem*-di(iodozincio)methane species, we first chose 2,2'-bipyridine as a ligand. The reaction of *gem*-di(iodozincio)methane, which can be easily prepared from zinc and diiodomethane using a catalytic amount of $PbCl_2$,⁵ with 2 equiv of 2,2'-bipyridine in THF at 25 °C for 30 min gave the bipy- $CH_2(ZnI)_2$ complex **1** as a pale yellow solid in 77% yield (Scheme 1). The formation of **1** was indirectly confirmed by NMR spectroscopy through the appearance of a new methylene

Scheme 1. Synthesis of bipy- $CH_2(ZnI)_2$ Complex **1**



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proton at -0.68 ppm in THF- d_8 . This singlet ($Zn-CH_2-Zn$) and a multiplet, which was assigned to $CH=N$, with an integration of 1:2, suggested the presence of two 2,2'-bipyridine ligands per a *gem*-di(iodozincio)methane unit. Elemental analysis also supported this proposed structural formula. Moreover, ESI-TOF-MS analysis clearly proved the presence of complex **1** even in the solution state (see Supporting Information). The corresponding *gem*-di(iodozincio)methane complex **2**, containing lutidine as a ligand, was synthesized in a similar manner in 76% yield. Complex **3** having a diamine ligand such as N,N,N',N' -tetramethylethylenediamine (TMEDA) was also prepared (Figure 1). The chemical shift of the active methylene

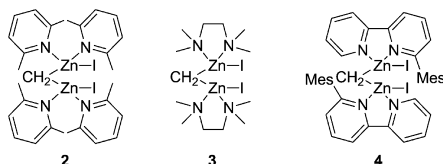
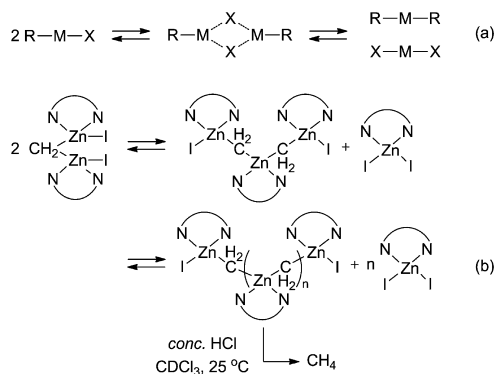


Figure 1. Structures of *gem*-di(iodozincio)methane complexes **2–4** with nitrogen ligands (Mes = 2,4,6-trimethylphenyl).

carbon in **3** was -0.76 ppm, compared with -0.55 ppm for that of **1** (both in $CDCl_3$), reflecting electron donation from the TMEDA ligand. Complexes **1–3** were soluble in dichloromethane and THF, but almost insoluble in hexane. Additionally, they were found to be stable in the solid state. No obvious decomposition was observed by NMR at 25 °C even after a year, when they were kept in the solid state under an argon atmosphere.

Unfortunately, all attempts to obtain suitable crystals for X-ray analysis by recrystallization led to the isolation of the diiodozinc complex **1'** (bipy- ZnI_2) with the corresponding nitrogen ligands (Figure S1 and Table S1).¹⁴ This can be understood by considering the change in chemical structure through a Schlenk equilibrium, which is often proposed for main-group metal-based organometallic reagents having metal–halogen bonds, such as Grignard and organozinc reagents (Scheme 2a).^{12c,15} The

Scheme 2. Schlenk Equilibrium for *gem*-Di(iodozincio)methanes



Schlenk equilibrium is known to proceed via self-transmetalation of *gem*-dizinciomethanes $R_2C(ZnX)_2$ to produce dimeric, trimeric, and oligomeric organozinc species (Scheme 2b). The methylene proton signal of the bipyridine complex **1** in CD_2Cl_2 disappeared gradually at room temperature, and the formation of an insoluble white solid was observed. The singlet 1H NMR resonances for other methylene protons were also found to be

absent after the complexes lutidine- $CH_2(ZnI)_2$ **2** and TMEDA- $CH_2(ZnI)_2$ **3** were kept in CD_2Cl_2 or $CDCl_3$ at 25 °C for 24 h.¹⁶ Diiodozinc complexes with the corresponding nitrogen ligands were isolated from the reaction mixture, and their presence confirmed by 1H and ^{13}C NMR spectroscopy as well as elemental analysis. These analytical data were consistent with the data obtained from an authentic sample prepared from the reaction of ZnI_2 with the corresponding nitrogen ligands (see Figure S3). Moreover, when the insoluble white solid was treated with conc. HCl in $CDCl_3$ at 25 °C, evolution of methane gas was observed by 1H NMR analysis (Figure S4). These observations demonstrate the decomposition of *gem*-di(iodozincio)methane complexes **1–3** by a Schlenk equilibrium in the solution state.

Since ligand exchange shown in Scheme 2b probably proceeds through a bimolecular associative process, we postulated that the bulky ligand 6-mesityl-2,2'-bipyridine (MesBipy) would prevent the Schlenk equilibrium and generate the more stable *gem*-di(iodozincio)methane species.¹⁵ When a mixture of *gem*-di(iodozincio)methane and 6-mesityl-2,2'-bipyridine (1:2 ratio) was stirred in THF at 25 °C, formation of a yellow precipitate was observed. Evaporation of the solvent followed by extraction with CH_2Cl_2 and cooling of the extract at -25 °C resulted in the formation of orange prisms. Note that the recrystallization should be done at a low temperature, as the Mesbipy- $CH_2(ZnI)_2$ complex **4** (Figure 1) was unstable in solution and decomposed to the corresponding diiodozinc complex **4'** after only 1 day at 25 °C. X-ray crystallographic analysis under a cold stream of nitrogen finally gave the molecular structure of *gem*-di(iodozincio)methane. Figure 2

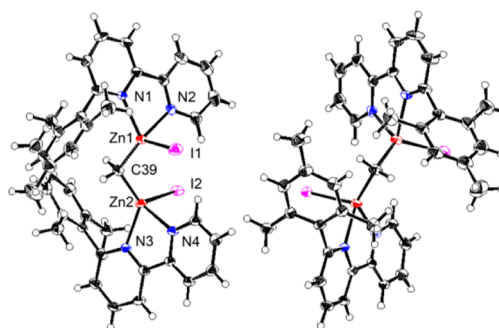


Figure 2. X-ray crystal structure of the *gem*-di(iodozincio)methane complex **4**. Left: side view; right: top view. Thermal ellipsoids are drawn at the 50% probability level. Co-crystallizing dichloromethane is omitted for clarity.

clearly shows the structure of **4**, which has two zinc centers bridged by a methylene ligand. Selected bond distances and angles are summarized in Table 1. The zinc center displays a distorted tetrahedral geometry. The $Zn-C-Zn$ bond angle

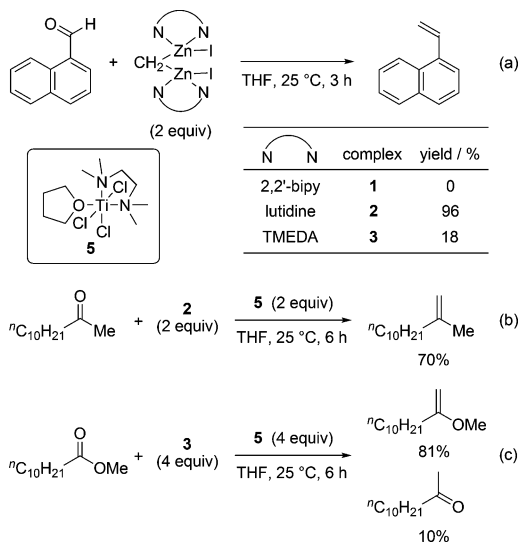
Table 1. Selected Bond Lengths (Å) and Angles (°) of **4**

bond lengths (Å)		bond angles (°)	
Zn1–N1	2.091(4)	Zn1–C39–Zn2	117.0(2)
Zn1–N2	2.146(4)	N1–Zn1–N2	77.56(14)
Zn1–C39	1.944(5)	C39–Zn1–I1	118.21(13)
Zn1–I1	2.7013(9)	N2–Zn1–I1	94.04(12)
Zn2–N3	2.163(5)	N3–Zn2–N4	76.96(16)
Zn2–N4	2.127(4)	C39–Zn2–I2	125.23(14)
Zn2–C39	1.961(4)	N4–Zn2–I2	98.57(10)
Zn2–I2	2.6533(8)		

117.0° was larger than the previously reported Mg–C–Mg bond angle (112.2°) for $(\text{Me}_3\text{Si})_2\text{C}(\text{MgBr})_2$.^{14a} Two mesityl rings point in the same direction, located as if to “protect” the active methylene carbon from a Schlenk equilibrium. The two Zn–C bond distances, 1.944(5) and 1.961(4) Å, are much shorter than that reported for the *gem*-dizinciomethanes (CR_2Zn_2) (longer than 2.024 Å).¹⁰ Note that these previously reported *gem*-dizinciomethanes do not have halide atoms attached to the zinc atom and are more stable due to the absence of a tendency to decompose via the Schlenk equilibrium. The presence of substituents on the methylene carbon atoms to further stabilize these complexes might also be a reason for the longer Zn–C bond. The current Zn–C bond distances are even shorter than those of the iodomethylzinc carbenoid species $[\text{Zn}(\text{CH}_2\text{I})_2]$ (typically longer than 1.995 Å)¹¹ but are comparable to the typical Zn–C bond length (1.9–2.1 Å).

While the *gem*-di(iodozincio)methane complexes under discussion are stable in the solid state, some of them can be utilized as methylenation reagent for the carbonyl compounds. For example, 1-ethynylphthalene was obtained in 82% yield when 2 equiv of the lutidine- $\text{CH}_2(\text{ZnI})_2$ complex **2** was employed as a methylenation reagent (Scheme 3a). In sharp

Scheme 3. Methylenation of Aldehydes, Ketones, and Esters with *gem*-Di(iodozincio)methane Complexes

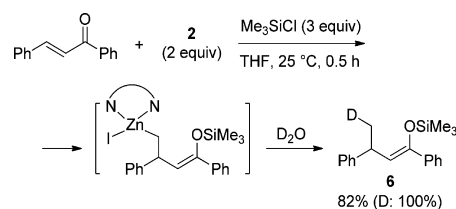


contrast, the bipy- $\text{CH}_2(\text{ZnI})_2$ complex **1** did not show any activity for this transformation. Although the TMEDA- $\text{CH}_2(\text{ZnI})_2$ complex **3** afforded the expected olefin, the yield was quite low. The same lutidine- $\text{CH}_2(\text{ZnI})_2$ complex **2** promoted the methylenation of ketones such as 2-dodecanone, furnishing 2-methyl-1-dodecene in 70% yield when the TMEDA-titanium complex **5**¹⁷ was used as an additive (Scheme 3b).¹⁸ Other additives, including $\text{BF}_3 \cdot \text{OEt}_2$, TiCl_4 , $\beta\text{-TiCl}_3$, MnCl_2 , Me_3SiOTf , AlCl_3 , and ZnI_2 , were totally ineffective, and the expected 2-methyl-1-dodecene was not obtained in any of these reactions. While the role of the titanium additive is unclear at the moment, the formation of a titanium methylidene species and activation of the ketone as a Lewis acid are considered the most likely modes of action.^{5,19} The use of a combination of TMEDA- $\text{CH}_2(\text{ZnI})_2$ complex **3** and TMEDA-titanium complex **5** promoted methylenation of esters, affording a mixture of 2-methoxy-1-decene and 2-dodecanone in 81% and 10% yields, respectively (Scheme 3c).²⁰ These results are comparable to

those reported by one of the present authors previously, using freshly prepared *gem*-di(iodozincio)methane $\text{CH}_2(\text{ZnI})_2$.^{4c,h,5b} Note that one significant drawback of the previously employed *gem*-di(iodozincio)methanes was their instability; the reagents needed to be prepared beforehand and titrated in order to determine the factor. In contrast, the *gem*-di(iodozincio)-methane complexes with nitrogen ligands prepared in this work were quite stable.²¹ In the current study, 8 month-old powders of **2** and **3** were found to remain effective reagents for methylenation, as shown in Scheme 3.

Further utility was demonstrated by the stereoselective 1,4-addition reaction of *gem*-di(iodozincio)methane to enones.^{9g} In the presence of chlorotrimethylsilane, an addition reaction of the lutidine- $\text{CH}_2(\text{ZnI})_2$ complex **2** with chalcone proceeded efficiently via the formation of a silyl enol ether of β -zinciomethyl ketone followed by deuteration to furnish the deuterated (*Z*)-silyl enol ether **6** in 82% yield (Scheme 4).

Scheme 4. Stereoselective 1,4-Addition Reaction of a *gem*-Di(iodozincio)methane Complex to Chalcone



In conclusion, this study shows that the sterically crowded bipyridine ligand provides a unique environment for isolation of the first example of structurally characterized *gem*-di(iodozincio)methane species. The resulting complexes serve as sources of storable methylenation reagents for carbonyl compounds, including aldehydes, ketones, and esters. This result also revealed changes in reactivity of the *gem*-di(iodozincio)-methane species depending on the ligands used. As zinc atoms can easily be replaced with other transition metals by transmetalation, this study will open up new perspectives on the design and development of synthetically useful *gem*-dimetallomethane species that are difficult to access by conventional protocols.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (18) Complexes **1** and **3** (2 equiv each) with TMEDA-titanium complex **5** afforded 2-methyl-1-dodecene in 50% and 4% yields, respectively, under the reaction conditions shown in Scheme 3b.
- (19) For the review of methylenation by titanium reagents, see: (a) Hartley, R. C.; McKiernan, G. J. *Tetrahedron* **2007**, *63*, 4825. Other possibilities for the role of additives, such as releasing a free *gem*-di(iodozincio)methane species from its precursor **3** by removal of the TMEDA ligand or activation of halomethylzinc species by coordination, cannot be ruled out completely. For a related work, see: (b) Nakamura, E.; Hirai, A.; Nakamura, M. *J. Am. Chem. Soc.* **1998**, *120*, 5844. For the DFT study on the methylenation mechanism using free *gem*-di(iodozincio)methane species, see: (c) Sada, M.; Komagawa, S.; Uchiyama, M.; Kobata, M.; Mizuno, T.; Utimoto, K.; Oshima, K.; Matsubara, S. *J. Am. Chem. Soc.* **2010**, *132*, 17452. See also (d) Yoshino, H.; Kobata, M.; Yamamoto, Y.; Oshima, K.; Matsubara, S. *Chem. Lett.* **2004**, *33*, 1224.
- (20) NMR analysis clarified that 2-dodecanone was formed *in situ* before the aqueous workup by keto–enol tautomerization of 2-methoxy-1-decene under the current reaction conditions.
- (21) Lutidine- $\text{CH}_2(\text{ZnI})_2$ complex **2** was relatively stable against air and heat ($\sim 50^\circ\text{C}$) but unstable against water. See Scheme S1 for the detail.