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Photoinduced alkyl group exchange of ethylzinc alkoxides: X-ray crystal structure of an iodomethylzinc methoxide†

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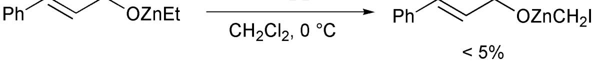
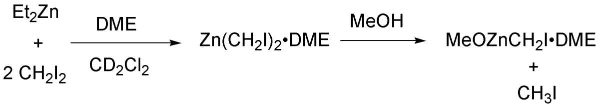
Irradiation of a solution of ethyl zinc alkoxides and CH_2I_2 leads to clean formation of iodomethylzinc alkoxides; these intermediates are important species generated in stereoselective cyclopropanation processes; no alkyl group exchange is observed in the absence of irradiation; the solid-state structure of $(MeO)_8Zn_7(CH_2I)_6$ is also reported.

The Simmons–Smith reaction has evolved over the years to become a general method to perform stereocontrolled cyclopropanation reactions.[1] The fact that a proximal basic group could direct the delivery of the methylene unit on prochiral alkenes was recognized early on and this was exploited on numerous occasions.[2] In particular, the cyclopropanation of prochiral allylic alcohols has been extensively studied and good to excellent diastereoselectivities can be obtained with cyclic and acyclic alkenes, regardless of the double bond geometry.[3] Surprisingly, while the nature of the species involved in these reactions has been highly debated, little has been unequivocally established. As a consequence, there is only scarce information on the intrinsic stereoselectivity of the various species involved in directed Simmons–Smith cyclopropanation reactions.[4] Among the possible intermediates, iodomethylzinc alkoxides are likely to be involved. These species are also invoked in the methods developed for the enantioselective cyclopropanation of allylic alcohols using chiral additives or catalysts.[5] Therefore, information on the solution and solid-state structure of iodomethylzinc alkoxides would be highly desirable. Herein, we report a new economical route toward these species along with the X-ray structure of iodomethylzinc methoxide.

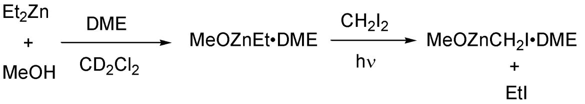
Heteroatom-substituted zinc carbenoids are typically prepared by the deprotonation of a substrate by the corresponding bis(halomethyl)zinc $[Zn(CH_2X)_2]$. One problem with this approach is the relative instability of these species. Indeed, they tend to decompose rapidly unless a complexing additive or low temperatures are used.[6] For that reason, we have been interested in developing an alternative approach to the preparation of heteroatom-substituted zinc carbenoids. A simple alternative would be to reverse the sequence of addition in order to perform the halogen–metal exchange between (heteroatom)ZnEt and the dihalomethane. However, this solution is not general since the rate of the halogen–metal exchange reaction depends on the nature of both species. For example, the rate of exchange of CH_2ICl is lower than CH_2I_2, often resulting in lower conversions. Also, while the exchange between Et_2Zn and CH_2I_2 is very rapid in various solvents,[7] the exchange between the ethylzinc alkoxide of cinnamyl alcohol and CH_2I_2 is extremely slow (eqn. (1)).[8] To circumvent this problem, we considered using the photoinduced zinc–iodide exchange reaction developed recently in our laboratories.[9] As a proof of concept, we synthesized $MeOZnCH_2I$ according to both methods.[10] The first approach involves deprotonation of MeOH with $Zn(CH_2I)_2{\cdot}DME$ (eqn. (2)).[11] In the second method, iodomethyl zinc methoxide is generated *via* deprotonation of MeOH with Et_2Zn, followed by photoinduced alkyl exchange involving CH_2I_2 (eqn. (3)).[12] The latter approach is advantageous, requiring only one equivalent of CH_2I_2.



(1)



$$\begin{matrix} Et_2Zn \\ + \\ 2\ CH_2I_2 \end{matrix} \xrightarrow[CD_2Cl_2]{DME} Zn(CH_2I)_2{\cdot}DME \xrightarrow{MeOH} \begin{matrix} MeOZnCH_2I{\cdot}DME \\ + \\ CH_3I \end{matrix} \quad (2)$$



$$\begin{matrix} Et_2Zn \\ + \\ MeOH \end{matrix} \xrightarrow[CD_2Cl_2]{DME} MeOZnEt{\cdot}DME \xrightarrow[h\nu]{CH_2I_2} \begin{matrix} MeOZnCH_2I{\cdot}DME \\ + \\ EtI \end{matrix} \quad (3)$$

In the photochemical approach, characteristic ^1H and ^{13}C NMR signals for the 'ZnCH$_2$I' species were observed both in the solution and solid states.[13] Upon standing at room temperature, colorless crystals suitable for X-ray analysis deposited in the NMR tube. The ORTEP is represented below (Fig. 1) with selected bond lengths and angles.

The carbenoid $(MeO)_8Zn_7(CH_2I)_6$ has a centrosymmetric dicubane structure in which the central zinc atom is lying on the inversion center.[14] The Zn–C bond lengths of *ca.* 2.15 Å, the C–I bond and the Zn–C–I bond angles of *ca.* 111° are comparable

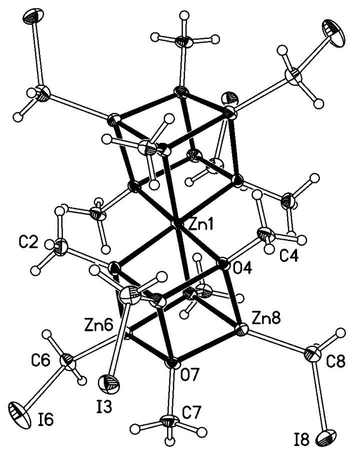


Fig. 1 ORTEP view of $(MeO)_8Zn_7(CH_2I)_6$. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles and torsion angles (°): I(3)–C(3) 2.152(6), I(6)–C(6) 2.152(6), I(8)–C(8) 2.145(6), Zn(1)–O(2) 2.094(3), Zn(1)–O(4) 2.107(3), Zn(3)–O(2) 2.063(3), Zn(3)–O(4) 2.035(3), Zn(3)–C(3) 1.968(6), Zn(8)–C(8) 1.964(6), O(2)–C(2) 1.436(6), O(5)–C(5) 1.434(6); Zn(3)–C(3)–I(3) 109.9(3), Zn(8)–C(8)–I(8) 112.3(3), O(2)i–Zn(1)–O(2) 180, O(2)i–Zn(1)–O(5) 98.32(13), O(2)–Zn(1)–O(5) 81.68(13), O(2)–Zn(1)–O(4) 81.65(13), O(2)–Zn(3)–O(4) 84.57(13), O(2)–Zn(3)–O(7) 83.68(14), Zn(1)–O(2)–Zn(6) 96.58(14); C(2)–O(2)–Zn(3)–C(3) −8.2(4), C(7)–O(7)–Zn(3)–C(3) −4.8(5), I(3)–Zn(3)–C(3)–O(7) −3.3(5), I(3)–Zn(3)–C(3)–O(2) 114.3(2).

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b110736d/

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to those reported for other zinc carbenoid complexes.[15] The cubes are distorted: all the Zn–O–Zn angles are greater than 90° (94–97°) and all the O–Zn–O angles are smaller than 90° (81–85°). The Zn–O skeleton structure can be compared to its methylated analogue, $Me_6Zn_7(OMe)_8$.[16] The latter is also distorted but in this case all the O–Zn–O angles are greater than 90° (93–98°) and all the Zn–O–Zn angles are smaller than 90° (81–86°).

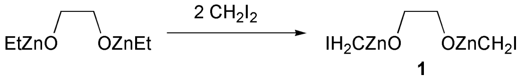
Interestingly, this system is preferred to the parent cubane compound, $(MeOZnCH_2I)_4$, and the X-ray crystal structure of its methylated cubane analogue $(MeOZnMe)_4$ has also been reported.[17] In fact, the equilibrium between both species has been proposed in studies on the methanolysis of dimethylzinc (eqn. (4)).[18] The parent equilibrium involving zinc carbenoids is

$$2(MeOZnMe)_4 \rightleftharpoons Me_2Zn + (MeO)_8Zn_7Me_6 \qquad (4)$$

also shown (eqn. (5)).

$$2(MeOZnCH_2I)_4 \rightleftharpoons Zn(CH_2I)_2 + (MeO)_8Zn_7(CH_2I)_6 \qquad (5)$$

The exchange reaction is also possible with the bis(ethylzinc alkoxide) derived from ethylene glycol (eqn. (6) and (7)). When 2 equivalents of CH_2I_2 were used (CD_2Cl_2, $h\nu$), both ethyl groups were exchanged to produce **1** in high yield (>95% by NMR). Quite interestingly, when only 1 equivalent of CH_2I_2 was used, 2 equivalents of ethyl iodide were generated (as determined by NMR) along with an insoluble white material which could be attributed to the oligomeric form of the *gem*-dizinc species **2**.



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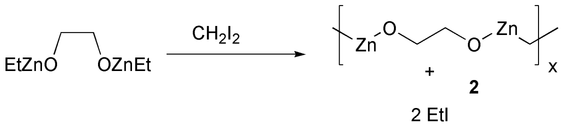

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10 The deprotonation approach can be monitored by following MeI [see ref. 5(*l*)] formation while the photoinduced approach involves monitoring EtI formation and CH_2I_2 consumption.

11 Dimethoxyethane (DME) is used as an additive to stabilize the zinc carbenoid. For precedence, see: A. B. Charette, S. Prescott and C. Brochu, *J. Org. Chem.*, 1995, **60**, 1081.

12 The reaction with CH_2I_2 barely proceeds (<10%) in the absence of irradiation or traces of oxygen.

13 Two signals were observed at *ca.* 1.5 ppm (^1H) and –32 ppm (^{13}C). This is probably due to different aggregates in solution; see: J. G. Noltes and J. Boersma, *J. Organomet. Chem.*, 1968, **12**, 425; the ^1H and ^{13}C NMR (solution) and ^{13}C CP-MAS NMR (solid-state) obtained are presented in the ESI†.

14 Intensity data were measured on a Brüker SMART CCD diffractometer using Mo-Kα radiation and the ω scan technique. Crystals of $C_{14}H_{36}I_6O_8Zn_7$ belong to the triclinic space group $P\bar{1}$ with a = 9.7182(6), b = 10.2310(5), c = 10.8825(5) Å, α = 66.8440(10), β = 68.2340(10), γ = 73.3540(10)°, V = 911.30(8) Å^3, Z = 1 and D_c = 2.8269 Mg m^{-3}. Data were collected at 173(2) K, and the structure was solved by direct methods and refined to R_f = 0.0430 and R_w = 0.1124 for 4288 reflections with $I = 2\sigma(I)$. CCDC reference number 161493. See http://www.rsc.org/suppdata/cc/b1/b110736d/ for crysallographic data in CIF or other electronic format.

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