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# The preparation, reactivity, and crystal structure of a 1 : 1 adduct of dimethylzinc and ( – )-sparteine

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### Abstract

A 1 : 1 adduct of dimethylzinc and ( – )-sparteine has been prepared and characterized crystallographically; the complex is remarkably resistant to reaction with the atmosphere. The adduct is mononuclear with pseudo-tetrahedral coordination at the zinc atom. It reacts with benzoyl chloride to give acetophenone and with benzaldehyde to give (*R*)-1-phenylethanol with a 15% enantiomeric excess.

## 1. Introduction

There is considerable current interest in the use of alkylzinc reagents in two distinct areas of chemistry. Firstly, the reaction of dialkylzinc reagents with aldehydes can, in the presence of chiral ligands [1], occur with excellent stereoselectivity. However, such reactions have the disadvantage that simple dialkylzinc reagents are volatile pyrophoric liquids. Crystalline complexes containing one alkyl–zinc bond per zinc atom have been prepared using such ligands as exo-(*N*,*N*-dimethylamino)isoborneol [2] and tris-(3-tert-butylpyrazol-1-yl)borohydride [3]. However, there have been no previous reports of relatively air-stable complexes of simple dialkylzinc derivatives.

Secondly, adducts of dimethylzinc have found various applications in the development of organo-zinc reagents for use in the electronics industry. Adducts with simple ligands such as triethylamine and *N*,*N*,*N*′,*N*′-tetramethylethylene-diamine can be used as precursors and dopants in MOCVD [4,5]. Less volatile adducts, such as the compound formed with 4,4-bipyridyl, can be used for the purification of dimethylzinc for subsequent use in MOCVD. Our interest in developing the chemistry of dimethylzinc adducts led us to synthesize the complex formed by the naturally occurring tertiary amine ( – )-sparteine and dimethylzinc.

## 2. Experimental details

All experiments were carried out by use of standard Schlenk or glove box techniques. Metal alkyls were a gift from Epichem; all other chemicals were from B.D.H. Solvents were dried and degassed before use.

The $^{13}$C and $^{1}$H NMR spectra were recorded on a Bruker WP80 or AM250 pulsed Fourier transform NMR instruments and infrared spectra on a Mattson Polaris FT-IR spectrometer as Nujol mulls.

### 2.1. *Preparation of the 1 : 1 adduct 2 of dimethyl zinc and ( – )-sparteine*

The stoichiometric reaction, under nitrogen, of a frozen (liquid $N_2$) sample of dimethylzinc with a solution of ( – )-sparteine (**1**) in petroleum spirit results in the almost quantitative formation of a solid white adduct, **2**. The product was recrystallized twice from light petroleum (b.p. 60–80°C) to give white crystals (95%), m.p. 146°C.

### 2.2. *The reaction of 2 with benzoyl chloride*

A solution of **2** (0.41 g, 1.2 mmol) in THF (3 cm$^3$) was added to one of benzoyl chloride (0.116 cm$^3$, 1.0 mmol) in THF (4 cm$^3$). The mixture was stirred at 20°C

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for 18 h, then 2 M hydrochloric acid (20 cm$^3$) was added and the product extracted into $Et_2O$ (3 × 30 cm$^3$). The combined ethereal extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give an oil, which was dissolved in EtOH (4 cm$^3$). The solution was filtered, and the filtrate was added a solution of 2,4-dinitrophenylhydrazine in EtOH until the formation of the orange precipitate was complete. Acetophenone 2,4-dinitrophenylhydrazone (**3**) (124 mg, 41%) was filtered off; m.p. 248–249°C (lit. [12] 250°C).

### 2.3. The reaction of 2 with benzoyl chloride in the presence of $Pd(PPh_3)_4$

To a solution of benzoyl chloride (0.116 cm$^3$, 1.0 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in THF (3 cm$^3$) was added one of **2** (0.41 g, 1.2 mmol) in THF (8 cm$^3$). The orange mixture was refluxed for 3 h, then treated with 2,4-dinitrophenylhydrazone, as described above, to give **3** (195 mg, 65%); m.p. 246–248°C.

### 2.4. The reaction of 2 with benzaldehyde

A solution of **2** (1.37 g, 4.0 mmol) in THF (11 cm$^3$) was added to one of benzaldehyde (0.202 cm$^3$, 2 mmol) in THF (1 cm$^3$) The mixture was refluxed for 17 h then cooled and poured into 1 M aqueous citric acid (30 cm$^3$). The product was extracted into ether (3 × 30 cm$^3$) and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to give an oil. Flash chromatography on silica gel (40–60 $\mu$m), with the eluent progressively a changed from 1 : 1 dichloromethane/light petroleum (b.p. 40–60°C) to dichloromethane gave 1-phenylethanol (**4**) (0.095 g, 39%) as a colourless oil $[\alpha]_D^{20}$ +6.6° (*c* 4.3, MeOH), corresponding to a 15% excess of the (*R*)-enantiomer (lit. [13] $[\alpha]_D^{20}$ +45° (*c* 5, MeOH) for (*R*)-phenylethanol of > 98% e.e.); $\delta_H$ (80 MHz; $CDCl_3$) 1.50 (3H, d, $J = 6.5$ Hz, Me); 2.21 (1H, brs, OH); 4.88 (1H, q, $J = 6.5$ Hz, PhC*H*); 7.05–7.64 (5H, m, Ph).

### 2.5. Crystallography

Data were recorded with a CAD4 diffractometer in the $\omega$–$2\theta$ scan mode; 1807 unique reflections were measured 1463 observed with $[F > 3\sigma F_o]$. The structure was solved by direct methods, as described previously [7,8], and refined with the inclusion of hydrogen atoms to $R = 0.0269$, $R_w = 0.0325$ for 309 parameters. Crystal data for $C_{17}H_{32}N_2Zn$, $M = 329.845$, $a = 12.582(2)$, $b = 11.248(2)$, $c = 12.099(2)$ Å, $V = 1712.28(0.5)$ Å$^3$, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.279$ g cm$^{-3}$, (Mo K$\alpha$) = 0.71069, $\mu = 12.738$ cm$^{-1}$. Atomic coordinates are shown in Table 1, a complete list of bond lengths and angles, and lists of thermal parameters, H atom coordinates, and anisotropic displacement factor coefficients have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

TABLE 1. Fractional atomic coordinates (× 10$^4$) for $C_{17}H_{32}N_2Zn$

| | *x* | *y* | *z* |
|---|---|---|---|
| Zn(1) | −1133(1) | −7929(1) | −7636(1) |
| N(1) | −2332(3) | −9332(3) | −7296(3) |
| N(2) | −2634(3) | −6859(3) | −7861(3) |
| C(1) | −312(5) | −7718(7) | −6218(5) |
| C(2) | −561(5) | −8143(9) | −9173(5) |
| C(3) | −1635(5) | −10352(5) | −7000(6) |
| C(4) | −2171(6) | −11560(5) | −6964(6) |
| C(5) | −2739(6) | −11804(5) | −8038(6) |
| C(6) | −3515(4) | −10807(5) | −8276(5) |
| C(7) | −2956(4) | −9597(5) | −8303(4) |
| C(8) | −3741(5) | −8580(5) | −8541(4) |
| C(9) | −4490(4) | −8416(5) | −7577(6) |
| C(10) | −3809(5) | −8002(5) | −6605(4) |
| C(11) | −3002(5) | −8977(5) | −6328(4) |
| C(12) | −3213(5) | −7397(5) | −8807(5) |
| C(13) | −3346(4) | −6771(4) | −6887(4) |
| C(14) | −2790(5) | −6172(6) | −5931(5) |
| C(15) | −2375(6) | −4938(6) | −6247(6) |
| C(16) | −1728(5) | −5008(5) | −7288(5) |
| C(17) | −2282(5) | −5651(5) | −8201(5) |

## 3. Results and discussion

The adduct was prepared in near quantitative yield from the reaction of **1** with dimethylzinc. Recrystallization from petroleum spirit gave single crystals suitable for an X-ray study. The structure of the adduct is shown in Fig. 1, and some of the more significant bond

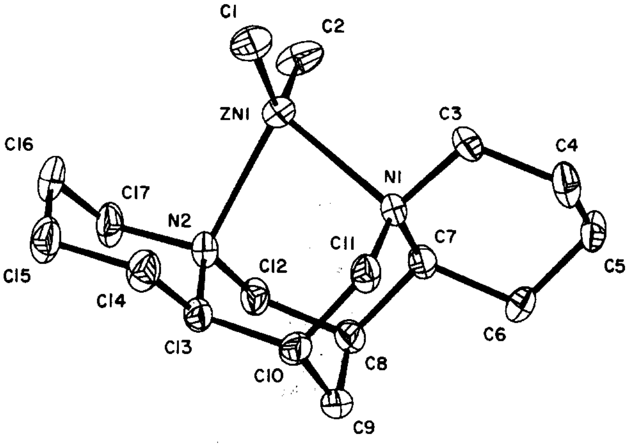


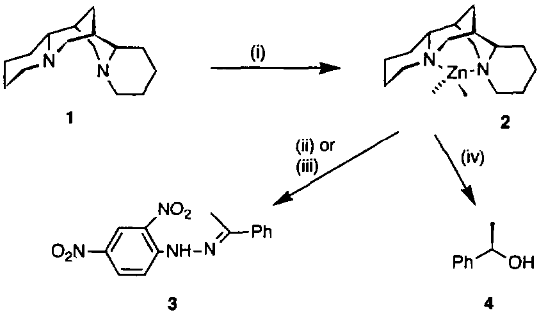
Fig. 1. Structure of the ( − )-sparteine adduct of dimethylzinc showing numbering scheme. Selected bond lengths (Å) and angles (°) for $C_{17}H_{32}N_2Zn$: N(1)–Zn(1) = 2.222(5), N(2)–Zn(1) = 2.256(6), C(1)–Zn(1) = 2.016(8), C(2)–Zn(1) = 2.008(8), N(2)–Zn(1)–N(1) = 80.4(2), C(1)–Zn(1)–N(1) = 105.9(3), C(1)–Zn(1)–N(2) = 118.0(3), C(2)–Zn(1)–N(1) = 109.2(4), C(2)–Zn(1)–N(2) = 104.6(4), C(2)–Zn(1)–C(1) = 128.2(4).

lengths and angles are shown in the legend. The compound is one of relatively few crystallographically characterized simple dialkyls of zinc. The others include (i) a rotaxane complex, $Et_2Zn(18\text{-crown-6})$ [8] (Zn–C = 1.957 Å and Zn–O = 2.867 Å), in which the alkyl is threaded through the macrocycle; (ii) the tetramethylethylenediamine adducts of methyl- or neopentyl-zinc [6] (Zn–C = 1.982 Å and Zn–N = 2.269 Å and Zn–C = 2.000 Å and Zn–N = 2.411 Å respectively), and (iii) the bis-1,3,5-trimethylhexahydro-1,3,5-triazine adduct of dimethylzinc [7] (Zn–C = 1.987 Å and Zn–N = 2.410 Å). These compounds are all monomeric, and contain 4-coordinate zinc atoms with pseudo-tetrahedral symmetry.

In **2**, a similar coordination environment is observed. The Zn–C bond length (av. 2.012(8) Å) is slightly longer than those in the other adducts reported to date [6–8]. This may be due to the much greater steric bulk of the (−)-sparteine ligand, which forces the two Zn–C bonds together; the C–Zn–C bond angle is the smallest (128.2(4)°) in any of these compounds. Another contributing factor may be the Lewis basicity of the sparteine since the Zn–N bonds are the shortest yet observed in such adducts (Zn–N(av.) = 2.239(6) Å). The constraints imposed on the adduct may also involve the very small N–Zn–N angle of (80.4(2)°), which is a direct result of the rigidity of the bidentate ligand.

The sparteine adduct has remarkable stability, with no apparent sign of decomposition after 3–4 days exposure to air, and is also involatile (m.p. 146°C). It is extremely difficult to remove dimethylzinc from the adduct, even under reduced pressure at elevated temperatures, and so the compound is unlikely to be of use in either the purification of dimethylzinc or growth of materials. However, it is possible that its resistance to atmospheric degradation could make it a potentially useful source of dimethylzinc for use in organic synthesis.

Traditionally the conversion of acyl chlorides into ketones is carried out by use of organocadmium reagents [9]. Less toxic reagents are of interest, *e.g.* manganese alkyl reagents have been considered [10]. Organozinc reagents are also known to effect this transformation, which can be facilitated by the use of low valent palladium species as catalysts [11], but the approach is not widely used, perhaps because of the difficulties of handling dialkylzinc reagents. Reaction of the complex **2** (1.2 mmol) with benzoyl chloride (1 mmol) in THF (20°C, 24 h) gave acetophenone, which was isolated as its 2,4-dinitrophenylhydrazone (**3**) (41% yield). When the reaction was performed under reflux (65°C, 3 h), in the presence of tetrakis(triphenylphosphine)palladium(0) (0.1 mmol), the yield of acetophenone 2,4-dinitrophenylhydrazone (**3**) increased to 65%.



Scheme 1. (i) $Me_2Zn$, light petroleum, 20°C, 95%; (ii) PhCOCl, THF, 20°C, 24 h, then 2,4-dinitrophenylhydrazine, 41%; (iii) PhCOCl, $(Ph_3P)_4Pd$, THF, 65°C, 3 h, then 2,4-dinitrophenylhydrazine, 65%; (iv) PhCHO, THF, 39% chemical yield, 15% e.e.

The reaction of **2** (Scheme 1) with benzaldehyde was also investigated. Benzaldehyde (2 mmol) was refluxed with **2** (4.0 mmol) in THF for 16 h, and aqueous work-up followed by flash chromatography gave (*R*)-phenylethanol (**4**) (39% yield) and 15% enantiomeric excess.

Thus complex **2** is a readily prepared, stable and conveniently handled derivative of dimethylzinc, which shows substantial reactivity towards electrophilic reagents and may have applications in organic synthesis.

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