DALTON
COMMUNICATION

Dimeric diphenylzinc adducts with cyclic thioethers

Ron S. Dickson,* Gary D. Fallon and Qian-Qian Zhang †

Department of Chemistry, Monash University, PO Box 23, Victoria 3800, Australia.
E-mail: ron.dickson@sci.monash.edu.au

Received 18th May 2000, Accepted 23rd May 2000
Published on the Web 31st May 2000

The 1 : 1 adducts formed between diphenylzinc and the cyclic thioethers $\mathrm{S(CH_2)}_n$ with $n = 3$ or 4 have dimeric structures with bridging phenyl groups.

Organo–zinc compounds that incorporate direct zinc–sulfur as well as zinc–carbon bonds are not common. In this communication, we report the first examples of complexes of the type $\mathrm{R_2ZnL}$ where L is a sulfur-donor ligand, and we describe the unexpected dimeric structure of these compounds which incorporate bridging phenyl groups.

The known organo–zinc–sulfur compounds include a few cyclic oligomers[1] and polymers[2] of the type $[\mathrm{RZn(SR')}]_n$. The pyridine adduct of one of these compounds, $[\mathrm{MeZn}\{\mathrm{S}(^t\mathrm{Bu})\}]$, has been isolated and characterised.[3] Several dithiocarbamate compounds of formula $[\mathrm{RZn(S_2CNEt_2)}]_2$ have also been characterised.[4,5] Interest in the latter was stimulated by problems encountered in the chemical vapour deposition of the important wide band gap semiconductor ZnS using conventional source compounds such as $\mathrm{R_2Zn}$ (R = Me, Et) and $\mathrm{H_2S}$.[6,7] The dithiocarbamate compounds can be used as single source precursors for the growth of ZnS.[4,5] Common structural features of the two classes of compounds described above are: (i) each zinc atom forms a single Zn–C bond; and (ii) in associated species, the bridging groups are bound through sulfur donor atoms. The unique features of the new compounds we have prepared are that they are adducts of $\mathrm{R_2Zn}$ compounds, and that the bridging groups in the dimeric stuctures have carbon rather than sulfur donor atoms.

Diphenylzinc was chosen for the initial study because it is expected to bind more strongly than would dialkylzinc compounds with Lewis bases. Under nitrogen, a solution of diphenylzinc in hexane was treated with one equivalent of trimethylene sulfide, and the reaction mixture was stirred at room temperature for several hours. A small amount of solid material was removed by filtration, and the filtrate was cooled to −78 °C. The white crystalline solid that deposited was isolated by filtration, washed with cold pentane, and dried in a nitrogen flow. The product was isolated in 55% yield based on the 1 : 1 adduct $[\mathrm{Ph_2Zn}\{\mathrm{S(CH_2)_3}\}]$.‡ The ^{1}H NMR spectrum confirmed the 1 : 1 ratio of $\mathrm{Ph_2Zn}$ to $\mathrm{S(CH_2)_3}$ in the product. The MS did not show a molecular ion, but peaks corresponding to the individual components $\mathrm{Ph_2Zn}$ and $\mathrm{S(CH_2)_3}$ were clearly present. The smell of the sulfur ligand was immediately evident if the compound was exposed to the atmosphere.

Repetition of the reaction with tetramethylene sulfide gave a similar result. Well formed crystals of $[\mathrm{Ph_2Zn}\{\mathrm{S(CH_2)_4}\}]$ were isolated after cooling the reaction solution.‡ An X-ray diffraction study revealed a dimeric structure with bridging phenyl groups (Fig. 1).§ Surprising aspects of the structure are its dimeric nature and the presence of bridging phenyl groups. In contrast to the dimeric or polymeric structures found for $\mathrm{R_2Be}$[8] and $\mathrm{R_2Mg}$[9] compounds, $\mathrm{R_2Zn}$ compounds are generally monomeric and the molecules are linear. Prior to this structure, alkynyl groups were the only organic groups able to form stable carbon-bridges between zinc atoms.[10] Adducts of $\mathrm{R_2Zn}$ compounds with O-donors such as dimethyl ether, 1,4-dioxane and 1,2-dimethoxyethane are also monomeric and contain 3-coordinate zinc.[11] A coordination of four is achieved in adducts such as $[\mathrm{R_2Zn(TMEN)}]$, but again the molecular structure is monomeric with a bidentate attachment of the N-donor ligand.[12] In the oligomeric and polymeric $[\mathrm{RZn(SR')}]_n$ compounds, it is the sulfur atoms that occupy the bridging positions.[1,2] The structure of $[\mathrm{Ph_2Zn}\{\mathrm{S(CH_2)_4}\}]$ does resemble that proposed for $[\mathrm{Et_2Mg(Et_2O)}]_2$ based on IR and Raman results.[13]

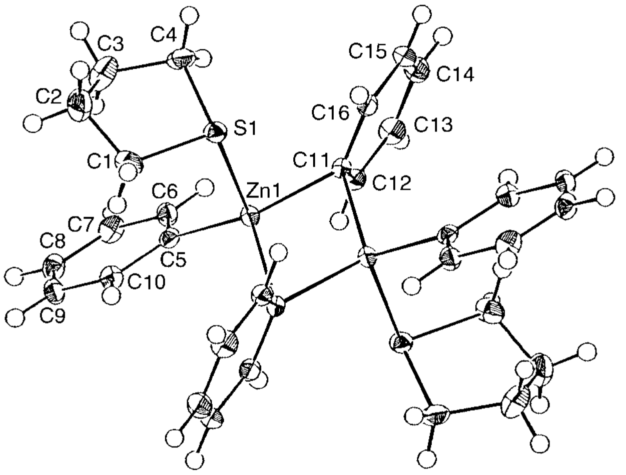

Fig. 1 Molecular structure and atom numbering scheme for $[\mathrm{Ph_2Zn}\{\mathrm{S(CH_2)_4}\}]_2$. Selected bond lengths (Å) and angles (°): Zn(1)–Zn(1) 2.4892(2), Zn(1)–S(1) 2.5025(5), Zn(1)–C(5) 1.983(2), Zn(1)–C(11) 2.114/2.261(2); Zn(1)–C(11)–Zn(1) 69.27(5), S(1)–Zn(1)–C(5) 111.59(5), S(1)–Zn(1)–C(11) 100.40(5), C(5)–Zn(1)–C(11) 121.98(7), C(11)–Zn(1)–C(11) 110.73(5).

Selected bond distances and angles for $[\mathrm{Ph_2Zn}\{\mathrm{S(CH_2)_4}\}]_2$ are included in Fig. 1. As in the structures of $[\mathrm{Ph_3Al}]_2$[14] and $[(o\text{-Tol})_3\mathrm{Al}]_2$,[15] the bridge angles are acute (69.3°) and the bridging phenyl ring planes are perpendicular to the metal–metal axis. The Zn–C distances for terminal (1.983 Å) and bridging (2.114 Å) phenyl groups vary in the expected way. The Zn–S distances are 2.5025 Å; this is slightly longer than the sum of the covalent radii (2.35 Å) reflecting weak coordination of the ligand. There is a short Zn–Zn separation of 2.4892 Å which is within the sum of covalent radii for two zinc atoms. This close approach of the zinc atoms can be attributed to the need for good overlap between the Zn(sp^3) and C(sp^2) orbitals needed to generate the 3-centre, 2-electron bridge bonds.

Although these compounds are not sufficiently stable for CVD applications, they are inherently interesting because of their unique structure and as the first examples of diorgano-zinc–sulfur compounds.

Acknowledgements

We thank the China Scholarship Council for a scholarship (Q.-Q. Z.) and the Australian Research Council for financial support.

---

† Present address: Chemistry Department, Ocean University of Qingdao, Qingdao 266003, P. R. China.

DOI: 10.1039/b003985n

Notes and references

‡ The new compounds were characterised by recording their IR and NMR spectra. The compounds were unstable in air at ambient temperature and we were unable to obtain satisfactory microanalytical results for C,H and S. ^{1}H NMR data (C_6D_6, 298 K) for [$Ph_2Zn\{S(CH_2)_4\}$]: δ 7.66 (dd, 7.4 and 1.7 Hz, 4H, *o*-H of phenyl), 7.20–7.45 (m, 6H, *m*- and *p*-H of phenyl), 2.38–2.51 (m, 4H, SCH_2), 1.15–1.38 (m, 4H, CH_2).

§ Crystal data for $[Ph_2Zn\{S(CH_2)_4\}]_2$: $C_{32}H_{36}S_2Zn_2$, $M = 615.52$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.1004(2)$, $b = 17.0908$, $c = 11.0200(2)$ Å, $\beta = 108.825(1)°$, $V = 1441.67(5)$ Å^3, $T = -150$ °C, $Z = 2$, μ(Mo-Kα) = 18.28 cm^{-1}, $N = 23610$, N(unique) = 4212 ($R_{int} = 0.051$), $N_{obs} = 2821$ [$I > 2.50\sigma(I)$]. Data collected from a colorless tabular crystal (0.32 × 0.25 × 0.07 mm). All measurements made on a Nonius KappaCCD area detector. Hydrogen atoms were included but not refined. Final $R(F) = 0.035$, $R_w(F) = 0.039$. CCDC reference number 186/1996. See http://www.rsc.org/suppdata/dt/b0/b003985n/ for crystallographic files in .cif format.

1 G. W. Adamson, N. A. Bell and H. M. M. Shearer, *Acta Crystallogr., Sect. B*, 1982, **38**, 462.

2 G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1965, 1870.

3 M. A. Malik, M. Motevalli, J. R. Walsh, P. O'Brien and A. C. Jones, *J. Mater. Chem.*, 1995, **5**, 731.

4 M. A. Malik, M. Motevalli, J. R. Walsh and P. O'Brien, *Organometallics*, 1992, **11**, 3136.

5 P. O'Brien, J. R. Welsh, I. M. Watson. M. Motevalli and L. Henriksen, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2491.

6 P. J. Wright and B. Cockayne, *J. Crystal Growth*, 1982, **59**, 148.

7 H. M. Manasevit and W. I. Simpson, *J. Electrochem. Soc.*, 1971, **118**, 644.

8 A. I. Snow and R. E. Rundle, *Acta Crystallogr.*, 1951, **4**, 348; R. E. Rundle and A. I. Snow, *J. Chem. Phys.*, 1950, **18**, 1125.

9 E. Weiss, *J. Organomet. Chem.*, 1964, **2**, 314; E. Weiss, *J. Organomet. Chem.*, 1965, **4**, 101.

10 E. A. Jeffery, T. Mole and J. K. Saunders, *Aust. J. Chem.*, 1968, **21**, 137.

11 K. H. Thiele, *Z. Anorg. Allg. Chem.*, 1963, **322**, 71.

12 P. O'Brien, M. B. Hursthouse, M. Motevalli, J. R. Walsh and A. C. Jones, *J. Organomet. Chem.*, 1993, **461**, 5.

13 J. Kress and A. Novak, *Zh. Strukt. Khim.*, 1977, **18**, 852; J. Kress, *J. Organomet. Chem.*, 1976, **111**, 1.

14 J. F. Malone and W. S. McDonald, *Chem. Commun.*, 1967, 444.

15 M. Barber, D. Liptak and J. P. Oliver, *Organometallics*, 1982, **1**, 1307.