9-Bromo-9-[(bromomagnesium)methylene]fluorene–Tetrahydrofuran (1/4) Structure of a MgBr/Br Carbenoid

Gernot Boche,* Klaus Harms, Michael Marsch and Achim Müller

Fachbereich Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

In the title compound the C–Br bond is 10 pm longer than in the corresponding vinyl bromide which, among others, is characteristic for the structure of a carbenoid.

The first X-ray crystal structure of a Li/Cl carbenoid[1] confirmed earlier suggestions from ^{13}C NMR investigations[2] and model calculations[3] of such species: as a main feature the C–Cl bond is remarkably longer (12 pm) than the same bond in the corresponding non-lithiated vinyl chloride. A similar situation is observed in Li/OR carbenoids (α-lithiated ethers).[4] On the other hand, in an (iodomethyl)zinc species of the type $(R_2O)_2Zn(CH_2I)_2$ 'the C–I bond lengths are normal for sp^3 carbon atoms'.[5] Here we report on the first X-ray crystal structure of a MgBr/Br carbenoid, namely that of 9-bromo-[9-[(bromomagnesium)methylene] fluorene–tetrahydrofuran (1/4) (**1**· 4 THF) (Fig. 1).‡

While in normal organomagnesium compounds the tetrahedral coordination is regarded to be typical,[6] the Mg atom in **1** is five-coordinate.[7] The C(1)–Mg bond length [219.0(10) pm] is longer than in other cases of C_{sp^2}–MgBr bonds (mean value of five aryl-MgBr bonds: 213.4 pm).[8] The Mg–Br(2) bond [251.7(3) pm] is somewhat shorter than the mean value of aryl Mg–Br bonds (255.1 pm).[8] The Mg–O bond lengths to the three Mg-bonded THF molecules are Mg–O(1) 204.5(7), Mg–O(2) 212.6(9) and Mg–O(3) 211.4(8) pm. The fourth THF molecule [O(4)–C(27)–C(28)–C(29)–C(30)] is not coordinated to the magnesium atom.

The C(1)–Br(1) bond length [200.6(10) pm] and the bond angles C(2)–C(1)–Br(1) [116.4(7)°] and C(2)–C(1)–Mg [147.3(8)°] are especially characteristic for the carbenoid nature of **1**. Thus, C(1)–Br(1) is 10 pm longer than the mean value of 63 C_{sp^2}–Br bonds (190.3 pm),[8] which corresponds to an elongation of 5.4%. (In the case of the vinylic Li/Cl carbenoid the C–Cl bond is 7.3% longer than in the corresponding vinyl chloride.[1]) The C(1)–Br(1) elongation concurs with the C(2)–C(1)–Br(1) bond angle being smaller (3.6°) and the C(2)–C(1)–Mg bond angle being much larger (27.3°) than the normal 120° angle at sp^2-hybridised carbon atoms. Thus, the α-elimination of $MgBr_2$ is indicated in the structure with the C(1)–Br(1) bond being transformed into the empty p orbital of the corresponding vinylidene. The greatly widened C(2)–C(1)–Mg bond angle [147.3(8)°] which leads to a shortening of the Mg–Br(1) distance to 312.9(3) pm (van der Waals contact of Mg and Br: 301 pm[8]) shows the approach of Mg to Br(1) which corresponds to a metal assisted ionization.[9] The elongation of the C(1)–Mg bond (see above) is in line with this notation. The raise in energy of the C(1)–Br(1) σ orbital in **1** compared to that in the non-metallated precursor, which goes along with a lowering of the C(1)–Br(1) σ* orbital, as found in model calculations of related compounds,[10] is in agreement with the facile α-elimination of $MgBr_2$ and the high electrophilicity of carbenoids such as **1**.

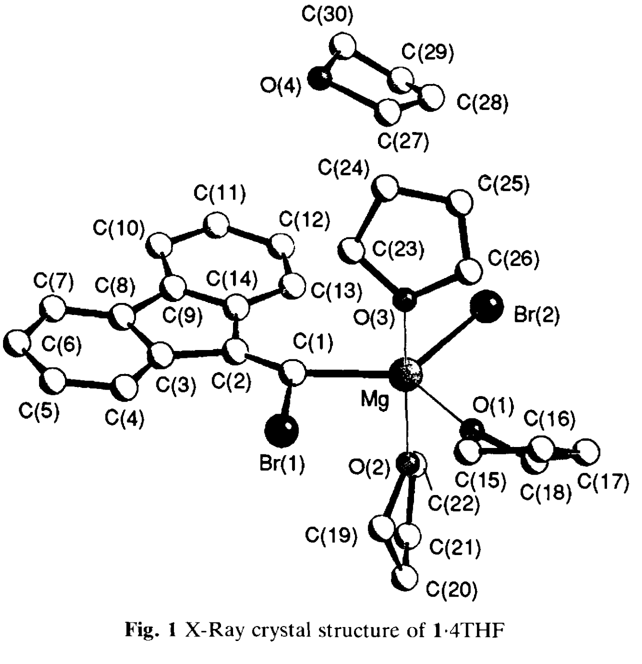

Fig. 1 X-Ray crystal structure of **1**·4THF

Financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (SFB 260) is gratefully acknowledged.

Received, 23rd March 1994; Com. 4/01748J

Footnotes

† Preparation of **1**·4 THF: 9-(dibromomethylene)fluorene (0.32 ml, 101 mg, 0.30 mmol) in THF (c = 0.94 mol dm^{-3}) was diluted with THF (3.5 ml), Et_2O (3.0 ml) and hexane (2.0 ml). The mixture was cooled to −30 °C and after dropwise addition of 0.13 ml (0.31 mmol) *n*-octylmagnesium bromide in Et_2O (c = 2.37 mol dm^{-3}) the solution was kept at −50 °C for 2 d. In order to obtain single crystals it was necessary to shake the flask after one day.

‡ *Crystal data for* **1**·4 THF: $C_{30}H_{40}Br_2MgO_4$; monoclinic, space group *Cc*, a = 929.0(2), b = 1936.8(4), c = 1715.9(3) pm, β = 99.63(2)°, Z = 4; data collection on a Siemens P4 diffractometer using Mo-Kα radiation, T = 223(5) K, ω scans. 5102 Reflections measured (θ_{max} = 25°), 4795 (R_{int} = 0.0449). Solution with direct methods with the Siemens SHELXTL PLUS (VMS)-package, full-matrix least-squares refinement on F^2 with all independent reflections with SHELXL-93, non hydrogen atoms anisotropic, hydrogen atoms with fixed isotropic thermal parameters on calculated positions, $wR2$ = 0.1730 (all unique data, calculated on F^2), goodness-of-fit (on F^2) = 0.956, conventional $R1$ [on F, for 2807 reflections with $I > 2\sigma(I)$] = 0.0636. Programs used: SHELXTL PLUS (VMS), Siemens Analytical XRAY Instruments, Inc., SHELXL-93, G. M. Sheldrick, Göttingen, 1993, and SCHAKAL 88B, E. Keller, Freiburg, 1988. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 G. Boche, M. Marsch, A. Müller and K. Harms, *Angew. Chem.*, 1993, **105**, 1081; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1032.

2 H. Siegel, K. Hiltbrunner and D. Seebach, *Angew. Chem.*, 1979, **91**, 845; *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 785; D. Seebach, H. Siegel, K. Müllen and K. Hiltbrunner, *Angew. Chem.*, 1979, **91**, 844; *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 784; D. Seebach, H. Siegel, J. Gabriel and R. Hässig, *Helv. Chim. Acta*, 1980, **63**, 2046; D. Seebach, R. Hässig and J. Gabriel, *Helv. Chim. Acta*, 1983, **66**, 308.

3 T. Clark and P. von R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1979, 883; *Tetrahedron Lett.*, 1979, 4963; *J. Am. Chem. Soc.*, 1979, **101**, 7747 and references cited therein; P. von R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk and N. G. Rondan, *J. Am. Chem. Soc.*, 1984, **106**, 6467, and references cited therein.

4 G. Boche, A. Opel, M. Marsch, K. Harms, F. Haller, J. C. W.

Lohrenz, C. Thümmler and W. Koch, *Chem. Ber.*, 1992, **125**, 2265; G. Boche, F. Bosold, J. C. W. Lohrenz, A. Opel and P. Zulauf, *Chem. Ber.*, 1993, **126**, 1873.

5 S. E. Denmark, J. P. Edwards and S. R. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 723.

6 Review: P. R. Markies, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets and A. L. Spek, *Adv. Organomet. Chem.*, 1991, **32**, 147.

7 Other cases with five-coordinated Mg: $MeMgBr\cdot 3THF$; M. Vallino, *J. Organomet., Chem.*, 1969, **20**, 1; P. R. Markies, G. Schat, S. Griffioen, A. Villena, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets and A. L. Spek, *Organometallics*, 1991, **10**, 1531. Higher coordination numbers are found in cases of intramolecular coordination and with polyethers.[6]

8 Cambridge Structural Database.

9 M. Duraisamy and H. M. Walborsky, *J. Am. Chem. Soc.*, 1984, **106**, 5035; G. Köbrich, *Angew. Chem.*, 1967, **79**, 15; *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 41.

10 G. Boche, F. Bosold and J. C. W. Lohrenz, *Angew. Chem.*, 1994, **106**, in the press; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, in the press.