Journal of Organometallic Chemistry, 397 (1990) 161–167
Elsevier Sequoia S.A., Lausanne
JOM 21100

Synthesis and structure of di-2-benzo[*b*]thienyl ditelluride

S. Kalyan Kumar, Harkesh B. Singh *
Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076 (India)

Kalyan Das and Umesh C. Sinha *
Department of Physics, Indian Institute of Technology, Powai, Bombay 400 076 (India)

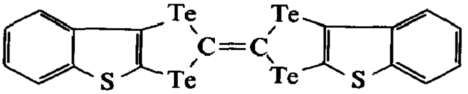
(Received April 19th, 1990)

Abstract

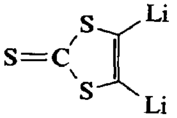
Attempted dilithiation of benzothiophene with lithium diisopropylamide (LDA) gave lithium benzothiophenetellurolate. Reaction of the tellurolate with 1,2-dibromoethane gave di-2-benzo[*b*]thienyl ditelluride, the crystal structure of which was determined by an X-ray diffraction study. The crystal consists of discrete molecules linked by weak intermolecular Te · · · Te and Te · · · S interactions, with no secondary intramolecular Te · · · S bonding.

Introduction

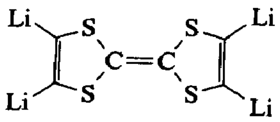
Substituted tetrathiafulvalenes (TTF) and their selenium and tellurium analogues, which incorporate several chalcogen atoms, have attracted much interest in the field of organic metals and superconductors [1]. The present study originated in an attempt to make benzothiophene-annulated tetratellurafulvalene (**1**) by the commonly used lithiation route [2].



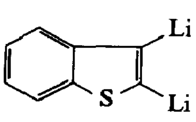
1



3



2



4

Prompted by the recent reports of proton/lithium exchange involving the vinylic protons of TTF (**2**) [3] and vinylene trithiocarbonate (**3**) [4] in the presence of strong

0022-328X/90/$03.50

base, and subsequent chalcogen insertion, we attempted the direct dilithiation of benzothiophene to give 2,3-ditellurated benzothiophene. In an attempt to generate the dilithio-derivative (4) by a "one pot" procedure we in fact obtained the ditelluride. The structure of the new compound was determined by an X-ray diffraction method.

Recent studies of the crystal structures of a variety of organotellurium derivatives by McWhinnie et al. [5–9] and others [10–12], have revealed the presence of intramolecular and intermolecular secondary bonds of various types and strengths. While examples of Te · · · N and Te · · · O secondary bonds are commonplace, there are only a few, recent, examples of intermolecular Te · · · S interactions [13,14]. It was of interest to look for possible Te · · · S contacts, and to see what effect these might have on the geometry of the molecule.

Experimental

Physical measurements

Elemental analyses for C and H were carried out with a Carlo Erba elemental analyzer model 1106. ^{1}H NMR spectra were recorded with Varian VXR 300 MHz instrument with TMS as internal standard. The mass spectrum was obtained at 70 eV. THe tellurium-containing mass peaks are given for ^{130}Te. The UV-Visible spectra in solution were recorded with a Shimadzu UV-260 spectrophotometer.

Synthesis

Synthesis of di-2-benzo[b]thienyl ditelluride. Lithium diisopropylamide was prepared by addition of 1.6 *M* n-butyllithium (11.3 ml, 19 mmol) to a cooled solution (−78 ° C) of diisopropylamine (1.72g, 17 mmol) in THF (35 ml). The mixture was stirred under argon at −78 ° C for 30 min, then benzothiophene (1.149 g, 8.56 mmol) in THF (10 ml) was added. The mixture was stirred at −78 ° C for 1 h, and to the yellow solution was added powdered tellurium (2.19g, 17.1 mmol). Stirring was continued at room temperature overnight, the resulting orange red solution was then treated with dibromoethane (1.61 g, 8.56 mmol) in THF (10 ml) at −78 ° C, the mixture stirred for 1 h at the same temperature and then for 8 h at room temperature, and finally added to water. Extraction with dichloromethane followed by drying ($CaCl_2$) and evaporation of the solvent gave a deep-orange solid. This was chromatographed on a silica gel column with a CH_2Cl_2/petroleum ether (1 : 5) mixture as eluent. The orange solid isolated was recrystallized twice from CH_2Cl_2 to give deep-red fine needles; yield: 2.61 g (58%), m.p. 189 ° C, MS, *m/e* (relative intensity) 526 (M^+ 1.3), 396(2), 266(100), 221(7), 133(28), 89(33), 63(7); ^{1}H NMR (DMSO-d_6) δ (ppm) 7.27–7.4 (several peaks, 4H), 7.76–8.00 (several peaks, 4H), 7.64 (S, 2H), Anal. Found: C, 36.18; H, 1.91. ($C_{16}H_{10}Te_2S_2$) calc.: C, 36.84; H, 1.91%. UV (λ_{max}) (CH_2Cl_2, nm): 356, 307, 267, 230.

synthesis of 2-methyltellurobenzo[b]thiophene [15]. To a solution of lithium 2-benzo[*b*]thiophene tellurolate (prepared as described above) in THF was added a solution of methyl iodide (2.43 g, 17.12 mmol). The mixture was stirred for 30 min at room temperature, and the usual work up gave a yellow semi-solid, which was recrystallised from hexane to give yellow crystals; yield: 2.1 g (88%); m.p. 39–40 ° C (lit. [15] 39 ° C) ^{1}H NMR (DMSO-d_6), δ (ppm) 2.25 (MeTe), 7.25–7.37 (multiplet, 2H), 7.64 (s, 1H), 7.76–7.98 (multiplet, 2H), UV (λ_{max}) (CH_2Cl_2, nm) 336, 293, 276.

X-Ray measurements

Reflection intensities were measured for a needle-like crystal, $0.2 \times 0.15 \times 0.34$ mm, using graphite monochromated Mo-K_α ($\lambda = 0.7107$ Å) radiation on an Enraf–Nonius CAD-4 diffractometer, operating in the ω–2θ scan mode. The cell parameters were determined from 25 reflections in the range $7 \leq \theta \leq 14°$. In total 3890 unique reflections were scanned in the range of $2 \leq \theta \leq 30°$. Two standard reflections [216 and 317] measured every minute showed no significant intensity variation. Lorentz and polarization corrections were applied. Direct methods located both of the Te atoms. Other non-H atoms were located from subsequent Fourier maps $|F_o|$s were corrected for absorption using a Fourier series to model the absorption surface based on the discrepancy between the $|F_o|$ and $|F_c|$ values [16,17]. The absorption coefficient for θ and μ; max. $A_{p,s} = 1.406969$, min. $A_{p,s} =$ 689217 and for θ: max. $A_\theta = 1.101846$, and min. $A_\theta = 0.906419$. All non-H atoms were refined with anisotropic thermal parameters. The H-atoms were fixed by geometry at C–H, 1.08 Å. In the final least-square refinements 181 parameters were refined using 2110 observed reflections with $|F_o| \geq 5.0\sigma\,|F_o|$, $R = 0.0945$.

MULTAN84 [18] and SHELX76 [19] were used respectively for the structure solution and refinements. The structure factors for the Te were taken from the *International tables for X-Ray Crystallography*, Vol. IV [20] and those for other atoms from SHELX76. The atomic coordinates, and the bond lengths and angles are listed in Tables 1 and 2 respectively. The general view of the molecule (Fig. 1) and the unit cell packing diagram (Fig. 2) were generated using PLUTO78 [21]. All the computations were carried out using CYBER-180/840.

Table 1

Atomic coordinates and equivalent temperature factors U_{eq} (Å$^2 \times 10^3$) for non-H atoms with e.s.d.'s in parentheses

Atom	x	y	z	U_{eq} [a]
Te(1)	0.9537(2)	0.2032(6)	0.1956(1)	52(3)
Te(1′)	0.8670(3)	0.9172(6)	0.1112(1)	54(3)
S(1)	0.7733(8)	1.0545(19)	0.2938(4)	49(8)
S(1′)	0.6863(9)	1.3274(22)	0.659(4)	56(8)
C(1)	0.8087(26)	1.2536(51)	0.2437(13)	37(12)
C(2)	0.7385(25)	1.4514(50)	0.2369(14)	35(12)
C(11)	0.6498(25)	1.4248(50)	0.2792(13)	34(12)
C(12)	0.5588(28)	1.5853(54)	0.2878(14)	42(12)
C(13)	0.4794(29)	1.5123(59)	0.3261(16)	58(12)
C(14)	0.4872(28)	1.3149(54)	0.3571(13)	44(12)
C(15)	0.5736(29)	1.1571(53)	0.3503(14)	45(12)
C(16)	0.6572(27)	1.2163(53)	0.3111(13)	40(12)
C(1′)	0.8138(27)	1.1940(51)	0.0556(14)	43(12)
C(2′)	0.8743(26)	1.2780(50)	0.0112(13)	37(12)
C(11′)	0.8115(30)	1.4739(54)	−0.0152(14)	48(12)
C(12′)	0.8389(34)	1.6156(61)	−0.0621(16)	66(12)
C(13′)	0.7700(41)	1.7862(64)	−0.0794(18)	85(13)
C(14′)	0.6674(42)	1.8294(57)	−0.0524(18)	84(12)
C(15′)	0.6375(37)	1.7092(57)	−0.0093(17)	66(12)
C(16′)	0.7109(32)	1.5160(57)	0.0109(15)	57(12)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star (\mathbf{a}_i \mathbf{a}_j)$.

Table 2

Bond distances (Å) and bond angles (°) (e.s.d's in parentheses)

Te(1′)–Te(1)	2.735(4)	C(14)–C(13)	1.328(46)
C(1)–Te(1)	2.109(30)	C(15)–C(14)	1.373(44)
C(1′)–Te(1′)	2.120(29)	C(16)–C(15)	1.415(44)
C(1)–S(1)	1.686(31)	C(2′)–C(1′)	1.366(43)
C(16)–S(1)	1.714(34)	C(11′)–C(2′)	1.462(43)
C(1′)–S(1′)	1.720(31)	C(12′)–C(11′)	1.404(47)
C(16′)–S(1′)	1.702(38)	C(16′)–C(11′)	1.383(50)
C(2)–C(1)	1.399(40)	C(13′)–C(12′)	1.321(52)
C(11)–C(2)	1.477(43)	C(14′)–C(13′)	1.414(65)
C(12)–C(11)	1.431(42)	C(15′)–C(14′)	1.275(57)
C(16)–C(11)	1.393(40)	C(16′)–C(15′)	1.467(49)
C(13)–C(12)	1.386(48)		
C(1)–Te(1)–Te(1′)	99.5(8)	C(15)–C(16)–S(1)	128.1(24)
C(1′)–Te(1′)–Te(1)	96.7(8)	C(15)–C(16)–C(11)	120.8(29)
C(16)–S(1)–C(1)	91.8(15)	S(1′)–C(1′)–Te(1′)	119.1(17)
C(16′)–S(1′)–C(1′)	89.7(17)	C(2′)–C(1′)–Te(1′)	124.6(20)
S(1)–C(1)–Te(1)	120.5(16)	C(2′)–C(1′)–S(1′)	116.3(22)
C(2)–C(1)–Te(1)	122.9(22)	C(11′)–C(2′)–C(1′)	108.0(27)
C(2)–C(1)–S(1)	116.6(22)	C(12′)–C(11′)–C(2′)	129.3(34)
C(11)–C(2)–C(1)	106.3(25)	C(16′)–C(11′)–C(2′)	112.5(30)
C(12)–C(11)–C(2)	126.2(27)	C(16′)–C(11′)–C(12′)	118.2(34)
C(16)–C(11)–C(2)	114.2(25)	C(13′)–C(12′)–C(11′)	119.9(40)
C(16)–C(11)–C(12)	119.6(30)	C(14′)–C(13′)–C(12′)	121.8(39)
C(13)–C(12)–C(11)	116.0(29)	C(15′)–C(14′)–C(13′)	121.8(37)
C(14)–C(13)–C(12)	124.3(32)	C(16′)–C(15′)–C(14′)	118.2(40)
C(15)–C(14)–C(13)	121.3(30)	C(11′)–C(16′)–S(1′)	113.4(27)
C(16)–C(15)–C(14)	117.9(27)	C(15′)–C(16′)–S(1′)	126.5(32)
C(11)–C(16)–S(1)	111.1(24)	C(15′)–C(16′)–C(11′)	120.1(35)

Crystal data. $C_{16}H_{10}S_2Te_2$; m.w. = 521.56, monoclinic, $P2_1/c$, $a = 11.939(3)$, $b = 5.624(3)$, $c = 23.475(5)$ Å, $\beta = 91.40(3)°$, $V = 1575.85$ Å^3, $Z = 4$, $D_{cal} = 2.29$ mg/mm^3, $T = 290$ K, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu = 3.67$ mm^{-1}, $F(000) = 968$.

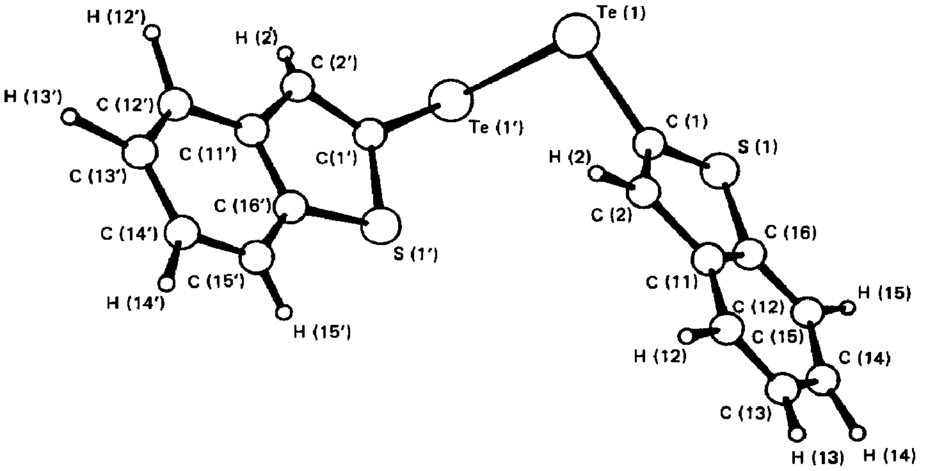


Fig. 1. Perspective view of one molecule of $C_{16}H_{10}S_2Te_2$.

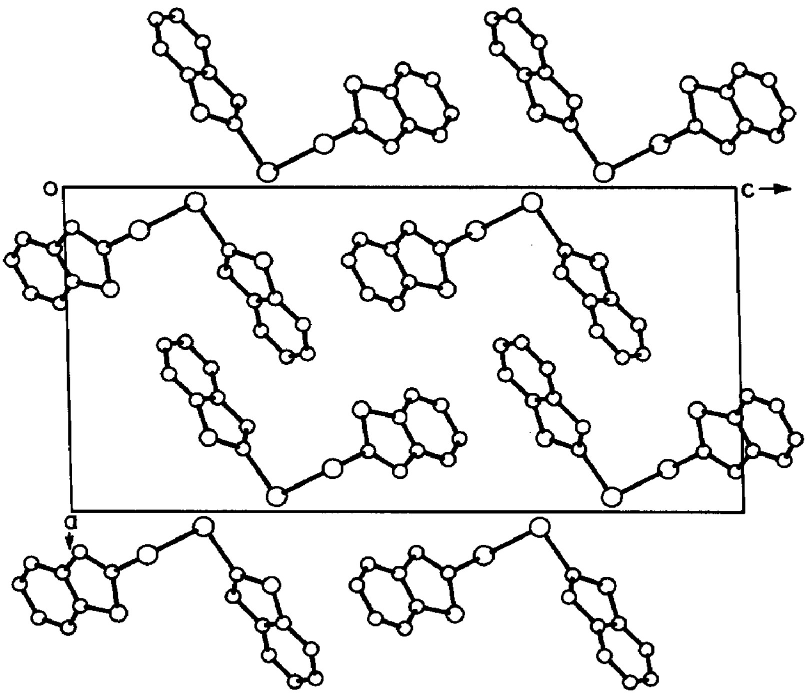
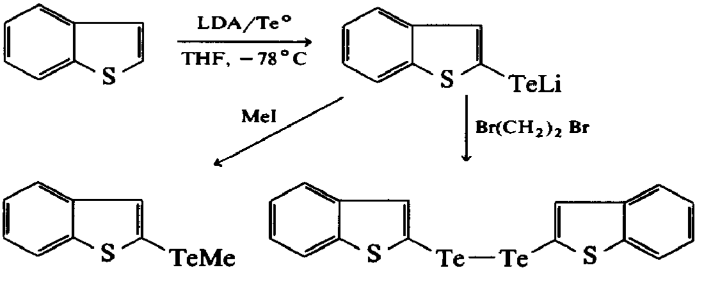


Fig. 2. Packing diagram.

Results and discussion

Treatment of benzothiophene with two equivalent of LDA followed by addition of elemental tellurium under the conditions employed in the preparation of **2** and **3** yielded only a monotellurated derivative. The resulting tellurolate anion when quenched with iodomethane gave a known telluride [15]. Interestingly, quenching with 1,2-dibromoethane yielded a novel ditelluride (**6**) (Scheme 1). Our failure to obtain an ethane-bridged telluroether is due the great ease of elimination from this dibromide [22]. The ditelluride could have potential as an agent in organic synthesis [23].



5

6

Scheme 1

The crystal structure of **6** consists of $C_{16}H_{10}S_2Te_2$ molecules linked by intermolecular Te $\cdots$ Te and Te $\cdots$ S contacts. The torsion angle, C(1)–Te(1)–Te(1′)–C(1′), is 88.5 (9) [24]. The Te–Te bond distance (2.735(4) Å) is slightly longer than is usual in ditellurides (2.697–2.715 Å) [25–29], but is in good agreement with twice the Pauling single bond covalent radii of Te (1.37 Å) and close to that in the recently reported bis[2-(hydroxyimino methyl)phenyl] ditelluride (2.746 Å) [5].

The average Te–C distance (2.11(1) Å) is in good agreement with the sum of the Pauling single bond covalent radii of Te (1.37 Å) and sp^2 hybridized C (0.74 Å), and with the values in the crystals of analogous compounds. The average C–S distance is 2.705(33) Å and the C–S–C angle is 90.7(17)°, which are comparable with the values in other benzothiophene derivatives. The geometry of the organic residue is unexceptional. The benzothienyl ring systems are planar, but they are inclined to one another at an angle of 11.0(3)°.

Examination of the intermolecular distances shows that the shortest distance between the Te atoms Te(1) $\cdots$ Te(1)$^{(i)}$ $[(i) \rightarrow 2-x,\ -\frac{1}{2}+y,\ \frac{1}{2}+z]$, is 3.939(5) Å. This distance is less than the van der Waals distance of 4.12 [30] or 4.40 Å [31], and could be considered as indicating a very weak interaction between the molecules. Another significant intermolecular interaction is between Te(1) and S(1)$^{(i)}$, 3.81(2) Å. Although this is less than the sum of the van der Waals radii (4.05 Å) or (3.86 Å), it appears to indicate only a very weak secondary interaction between these atoms. The bond angle at Te(1′), C(1)–Te(1′)–Te(1), 99.5(8)°, is larger than that at Te(1′), Te(1)–Te(1′)–C(1′), 96.7(8)°.

The large R value of 0.094 requires some comment. In the final refinements, high peaks within 1.20 Å of the Te atoms with large maxima, 2.06 e/Å^3, and minima, -1.88 e/Å^3 were observed in the difference Fourier map, indicating thermal motion of the tellurium atoms. Similar maxima and minima on the Fourier map were observed by Zingaro et al. in the case of bis(N,N-dimethylaminoformyl)ditelluride [29]. No change in the intensities of the check reflections was observed, suggesting that there was no decomposition during collection of the X-ray data. This was further confirmed by exposing a filter paper impregnated with the solution of the compound to ultraviolet radiation and finding that no decomposition occurred. Thus anisotropic motion of the tellurium atoms is responsible for the large R value.

Acknowledgements

HBS and SKK thank Board of Research in Nuclear Sciences, Department of Atomic Energy, Government of India for the financial support. Authors are grateful to Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, (Madras) for extending the instrumental facilities.

References

1 (a) T. Suzuki, H. Yamochi, S. Srdanov, K. Hinkelmann and F. Wudl, J. Am. Chem. Soc., 111 (1989) 3101; (b) H. Urayama, H. Yamochi, G. Saito, K. Narawa, T. Sugano, M. Kinoshita and J. Tanaka, Chem. Lett., (1988) 55.

2 F. Wudl and E. Aharon-Shalom, J. Am. Chem. Soc., 104 (1982) 1154.

3 (a) E. Aharon-Shalom, J.Y. Becker, J. Bernstein, S. Bittner, and S. Shaik, Tetrahedron Lett., 26 (1985) 2783; (b) N. Iwasawa, G. Saito, K. Imaeda, T. Mori, and H. Inokuchi, Chem. Lett., (1987) 2399, and references therein; (c) A.M. Kini, B.D. Gates, M.A. Beno, and J.M. Williams, J. Chem. Soc., Chem. Commun., (1989) 169.

4 P.J. Nigrey, J. Org. Chem., 53 (1988) 201.

5 K.Y. Abid, N. Al-Salim, M. Greaves, A.A. West and W.R. McWhinnie and T.A. Hamor, J. Chem. Soc., Dalton Trans., (1989) 2263.

6 N. Al-Salim, W.R. McWhinnie and T.A. Hamor, J. Chem. Soc., Dalton Trans., (1988) 2263.

7 N. Al-Salim, W.R. McWhinnie and T.A. Hamor, J. Chem. Soc., Chem. Commun., (1986) 453.

8 M.A.K. Ahmed, A.E. McCarthy, W.R. McWhinnie and F.J. Berry, J. Chem. Soc., Dalton Trans., (1986) 771.

9 R.E. Cobbledick, F.W.B. Einstein, W.R. McWhinnie and F.H. Musa, J. Chem. Res. (M)., (1979) 1901.

10 N.W. Alcock, Adv. Inorg. Chem. Radiochem., 15 (1972) 1.

11 N.W. Alcock, W.D. Harrison and C. Hoves, J. Chem. Soc., Dalton Trans., (1982) 251.

12 J. Lamotte, H. Campsteyn, L. Dupont and M. Vermeire, Cryst. Struct. Commun., 6 (1977) 749.

13 S. Huseby, F.J. Berry and W.R. McWhinnie (Eds.), in Proceedings of the Fourth International Conference on the Organic Chemistry of Se and Te, University of Aston, Birmingham, 1983, p. 298.

14 S. Huseby, K. Maartmann-Moc and Q. Mikalson, Acta. Chem. Scand., 43 (1989) 615.

15 L. Engman and M.P. Cava, Organometallics, 1 (1982) 470.

16 F. Ugozzoli, Comput. Chem., 11 (1987) 109.

17 N. Walker and D. Stuart, Acta Cryt., A39 (1983) 158.

18 P. Main, G. German and N.M. Woolfson, MULTAN84, A computer program for the automatic solution of crystal structures from X-ray diffraction data, University of York, England, 1989.

19 G.M. Sheldrick, SHELX76, Program for crystal structure determination and refinement, University of Cambridge, England, 1976.

20 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974.

21 W.D.S. Motherwell and W. Clegg, PLUTO78, Program for drawing crystal and molecular structure, University of Cambridge, England, 1978.

22 (a) H.M.K.K. Pathirana and W.R. McWhinnie, J. Chem. Soc., Dalton Trans., (1986) 2003; (b) E.G. Hope, T. Kemmitt, and W. Levason, Organometallics, 7 (1988) 78.

23 L. Engman and M.P. Cava, J. Org. Chem., 47 (1982) 3946.

24 W. du Mont, L. Lange, H.H. Karsch, K. Peters, E.M. Peters and H.G. von Schnering, Chem. Ber., 121 (1988) 11.

25 S. Ludlow and A.E. McCarthy, J. Organomet. Chem., 219 (1981) 169.

26 M.R. Spirlet, G. Van der Bossche, O. Dideberg and L. Dupont, Acta Crystallogr., B35 (1979) 1727.

27 G. Llabres, O. Dideberg and L. Dupont, Acta Crystallogr., B28 (1972) 2438.

28 H. Kruse, R.E. Marshe and J.D. McCullough, Acta. Cryst., 10 (1957) 201.

29 R.A. Zingaro, C. Herrera and E.A. Meyers, J. Organomet. Chem., 306 (1986) C36.

30 A. Bondi, J. Phys. Chem., 68 (1964) 441.

31 L. Pauling, The Nature of the Chemical Bond, 3rd Ed., Cornell University Press, Ithaca, New York, 1960.