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ELECTRON PRECISE VERSUS ELECTRON DEFICIENT BONDING IN $(Be_2C_2)_n$ RING SYSTEMS: CRYSTAL STRUCTURE OF $(Me_3N)(MeC{\equiv}C)Be(\mu\text{-}C{\equiv}CMe)_2Be(C{\equiv}CMe)(NMe_3)$

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Summary

The solid state structure of the 1/1 trimethylamine complex of dipropynylberyllium has been determined from X-ray data by direct methods. All non-hydrogen atoms were refined by least-squares methods with anisotropic temperature factors to an R value of 0.074 for the 1493 reflections classified as observed. The crystals of $[(MeC{\equiv}C)_2Be \cdot NMe_3]_2$ contain two independent centrosymmetric dimers in which the μ-alkynyl groups exhibit quite different types of interactions with the beryllium atoms. In one dimer the bridging alkynyl groups function as 1 electron donors leading to a predominantly electron-deficient Be_2C_2 ring system in which significant cross-ring metal–metal bonding is present, giving rise to a short Be...Be distance (2.319(6) Å). In the second dimer the ring is effectively electron-precise with the μ-alkynyl groups acting as $3e$ (σ,π) donors, with the associated Be...Be distance being considerably increased (2.549(6) Å).

Introduction

Organometallic compounds having electron-deficient bridged structures, such as those found for Group III elements are characterised by significant metal–metal interactions, the latter providing some stabilisation for associated species as compared to coordinatively unsaturated monomers. The carbon atom of μ-alkyl or μ-aryl groups are found to be approximately symmetrically placed between the two metal atoms (Type I), with the organic ligand thus functioning as a $1e$ donor. However,

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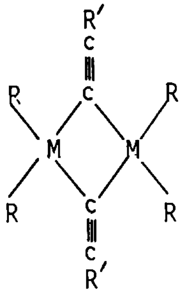
TABLE 1

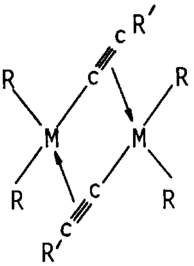
FRACTIONAL POSITIONAL PARAMETERS (Be, N and C$\times 10^5$; H$\times 10^3$) WITH e.s.d.'s IN PARENTHESES

Dimer **A**				Dimer **B**			
Atoms	*x*	*y*	*z*	Atoms	*x*	*y*	*z*
Be	56128(58)	47894(39)	−11183(62)	Be	−4321(61)	8448(38)	6500(64)
N	68839(32)	57565(22)	−14371(34)	N	−21253(32)	11310(22)	−4334(35)
C(1)	62202(37)	46416(25)	10011(40)	C(1)	8096(40)	6449(26)	−7728(45)
C(2)	70555(37)	44230(26)	20900(40)	C(2)	14505(44)	5488(28)	−19177(48)
C(3)	80174(44)	41488(31)	34524(46)	C(3)	21701(68)	4356(46)	−33826(68)
C(4)	54178(39)	36844(27)	−26549(43)	C(4)	1141(40)	16782(26)	25926(44)
C(5)	52915(43)	29434(28)	−37629(43)	C(5)	4388(42)	22128(26)	39721(44)
C(6)	51391(59)	20184(33)	−51481(53)	C(6)	8484(52)	28526(32)	56748(49)
C(7)	83715(46)	53993(36)	−13747(57)	C(7)	−27420(50)	3386(35)	−19789(51)
C(8)	64363(45)	59373(32)	−31206(48)	C(8)	−17635(50)	21185(32)	−8683(54)
C(9)	69882(50)	67325(31)	−2098(53)	C(9)	−32916(46)	12469(32)	5951(52)
H(1)	862	370	300	H(1)	180	80	−405
H(2)	870	478	414	H(2)	323	58	−325
H(3)	733	385	420	H(3)	240	−15	−350
H(4)	415	185	−575	H(4)	107	240	645
H(5)	560	220	−608	H(5)	0	313	600
H(6)	547	150	−466	H(6)	160	336	575
H(7)	865	527	−30	H(7)	−370	51	−252
H(8)	910	594	−150	H(8)	−201	22	−272
H(9)	829	478	−215	H(9)	−301	−33	−161
H(10)	722	638	−338	H(10)	−271	236	−145
H(11)	627	523	−399	H(11)	−135	266	8
H(12)	545	615	−323	H(12)	−93	201	−166
H(13)	772	722	−45	H(13)	−290	175	161
H(14)	738	663	89	H(14)	−414	154	16
H(15)	605	700	−31	H(15)	−364	54	88

with Group III compounds containing bridging ethynyl groups, there is clear structural evidence for the bridging ligand acting as a $3e$ donor so that it is strongly σ-bonded to one metal atom and weakly π-bonded to the other resulting in the bridging carbon atom being asymmetrically placed between the two metal atoms (Type II) [1]. Such an arrangement was first found in $(Ph_2AlC{\equiv}CPh)_2$ [2] and subsequently observed in $(Me_2AlC{\equiv}CMe)_2$ [3], $(Me_2InC{\equiv}CMe)_2$ [4] and $(Me_2GaC{\equiv}CPh)_2$ [5].



Type I



Type II

Evidence for similar type II π-interactions is less clear for Group II systems. In the complex $(MeBe(C{\equiv}CMe)NMe_3)_2$, although the bridging propynyl groups are tilted slightly towards one of the Be atoms, the structure is best considered as being essentially of type I with the propynyl group acting as a $1e$ donor [6]. Herein we report the structure of $[(MeC{\equiv}C)_2BeNMe_3]_2$, one of a limited number of structural studies of organoberyllium compounds containing $(Be_2C_2)_n$ ring systems. The crystal structure contains two independent molecules with structural parameters characteristic of type I and II, and thus this affords a unique opportunity for comparison of these two different types of bridging interactions.

Experimental

Crystals of $[(MeC{\equiv}C)_2BeNMe]_2$, recrystallised from benzene/hexane solution, were kindly supplied by Dr. B.R. Francis.

Crystal data

$C_{18}H_{30}Be_2N_2$, $M_r = 292.47$, triclinic, $P\bar{1}$, a 9.115(1), b 13.519(1), c 8.384(1) Å, α 102.8(1), β 99.0(1), γ 94.8(1)°, U 987.6 Å^3, $Z = 2$, D_c 0.89, D_m 0.90(1) gcm^{-3}, λ(Cu-K_α) 1.5418 Å, μ(Cu-K_α) 0.033 mm^{-1}, $F(000) = 320$.

Data collection and reduction

Intensity data were collected on a Hilger and Watts 4-circle diffractometer using Cu-K_α radiation and a θ–2θ scan. Two sets of equivalent reflections were recorded to the limit of $\theta = 20°$. The crystal used for data collection was a colourless plate of dimension 0.22 × 0.35 × 0.40 mm and was sealed inside a thin-walled capillary tube in an atmosphere of dry nitrogen. A total of 2576 independent reflections were measured of which 1493 had $I \geqslant 2\sigma(I)$ and were used for subsequent analysis. Corrections were made for Lorentz and polarisation effects but no corrections were applied for absorption. Unit cell dimensions were obtained by a least squares treatment of the positions of 12 high-order reflections.

Structure determination and refinement

Preliminary photographs showed the crystal to be triclinic and subsequent analysis confirmed the space group to be $P\bar{1}$. The structure was solved by direct methods and least squares refinement for Be, N and C with anisotropic temperature factors converged R to 0.074. The H atoms of the methyl groups attached to the alkynyl carbon atoms and those attached to the N atoms were given isotropic temperature factors (B) of 10.0 and 8.5 Å^2 respectively and were not refined. Atomic scattering factors were taken from International Tables [7]. Final positional parameters are given in Table 1; bond distances and angles are listed in Table 2. Lists of structure factors and thermal parameters are available on request from the authors (NAB).

Description and discussion of the structure

The structure is found to contain two independent centrosymmetric dimers (**A**, **B**) in which the Be_2C_2 rings are crystallographically constrained to be planar (Fig. 1, 2). The planarity of the four-membered ring system leads to a highly distorted tetra-

TABLE 2

BOND DISTANCES (Å) WITH e.s.d.'s IN PARENTHESES AND BOND ANGLES (°) e.s.d's ≈ 0.3° (Symmetry Code none x, y, z; (′) $-x, -y, -z$, Dimer **B**, $1.0-x, 1.0-y, -z$, Dimer **A**)

	Dimer **A**	Dimer **B**		Dimer **A**	Dimer **B**
Be–C(1)	1.836(6)	1.763(7)	C(1)–Be–C(1′)	103.4	96.2
Be–C(1′)	1.904(6)	2.042(6)	C(1)–Be–C(4)	115.0	121.1
Be–N	1.766(6)	1.782(6)	C(1)–Be–N	107.2	107.0
Be–C(4)	1.719(6)	1.735(6)	C(1′)–Be–N	105.8	106.4
N–C(7)	1.474(5)	1.483(5)	C(4)–Be–N	112.0	111.5
N–C(8)	1.486(5)	1.484(5)	C(4)–Be–C(1′)	112.6	112.9
N–C(9)	1.469(5)	1.467(5)	Be–C(1)–Be′	76.6	83.8
C(1)–C(2)	1.200(5)	1.188(5)	C(2)–C(1)–Be	154.9	168.6
C(2)–C(3)	1.463(5)	1.466(7)	C(2)–C(1)–Be′	128.5	100.2
C(4)–C(5)	1.190(5)	1.198(5)	C(1)–C(2)–C(3)	177.5	177.1
C(5)–C(6)	1.487(6)	1.469(5)	C(1)–C(2)–Be′	32.0	52.4
C(3)–H(1)	0.913	0.872	C(5)–C(4)–Be	177.3	175.9
C(3)–H(2)	1.014	0.953	C(4)–C(5)–C(6)	179.8	178.9
C(3)–H(3)	1.068	0.825	C(7)–N–C(8)	107.0	109.1
C(6)–H(4)	0.944	0.997	C(7)–N–C(9)	109.6	107.8
C(6)–H(5)	1.009	0.939	C(7)–N–Be	108.5	112.5
C(6)–H(6)	0.935	0.912	C(8)–N–C(9)	108.2	108.4
C(7)–H(7)	0.955	0.989	C(8)–N–Be	110.2	106.7
C(7)–H(8)	0.980	0.980	C(9)–N–Be	113.1	112.2
C(7)–H(9)	0.929	1.040			
C(8)–H(10)	0.975	1.037			
C(8)–H(11)	1.050	0.955			
C(8)–H(12)	0.964	1.083			
C(9)–H(13)	0.973	0.960			
C(9)–H(14)	0.979	0.957			
C(9)–H(15)	0.955	1.070			

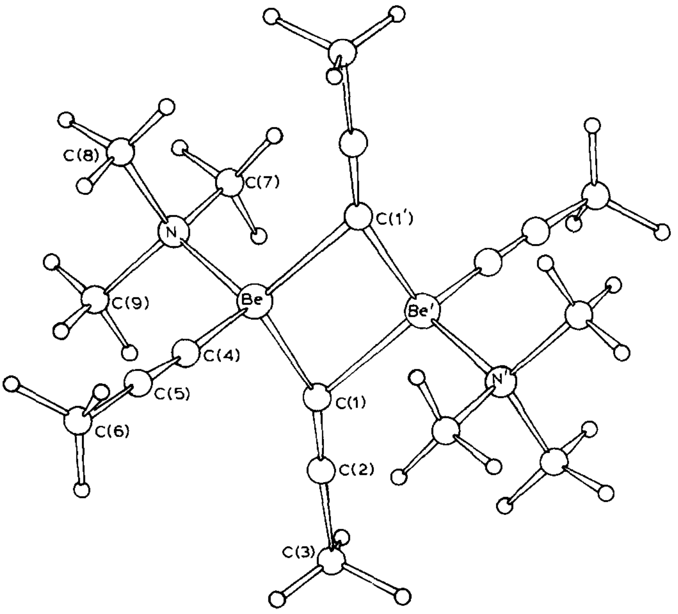


Fig. 1. Structure of $[(MeC{\equiv}C)_2BeNMe_3]_2$, Dimer **A** (Type I).

hedral coordination about beryllium, with bond angles ranging from 103.4 to 115.0° (dimer **A**), and from 96.2 to 121.1° (dimer **B**). Within these two dimers, the μ-alkynyl groups are found to adopt quite different orientations with respect to the

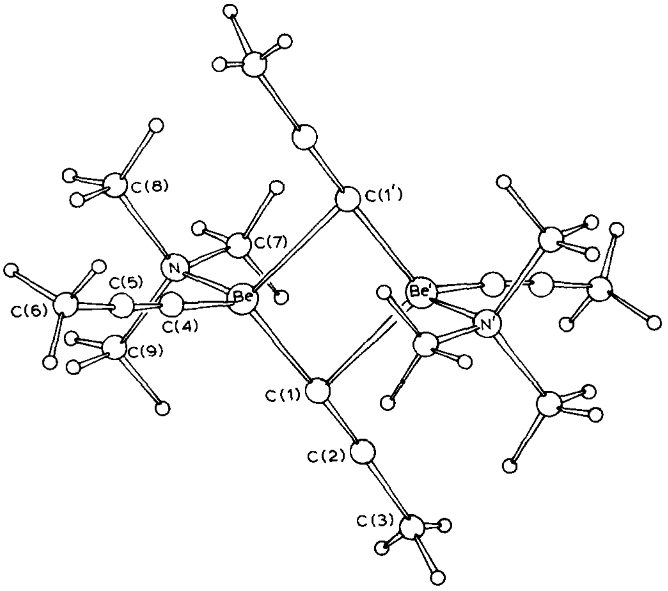


Fig. 2. Structure of $[(MeC{\equiv}C)_2BeNMe_3]_2$, Dimer **B** (Type II).

beryllium atoms, viz:

	Dimer **A**	Dimer **B**
Be–C(1)	1.836(6)	1.763(7) Å
Be–C(1′)	1.904(6)	2.042(6) A
Be–C(2′)	2.812(7)	2.538(7) A
Be–C(1)–C(2)	154.9(4)	168.6(4)°
Be′–C(1)–C(2)	128.5(3)	100.2(3)°

Thus in dimer **B**, not only does C(1) adopt a more asymmetric position with respect to the two metal atoms, but the Be–μ-(C)–CMe angles are highly asymmetric. The latter afford a closer "side-on" approach of the alkynyl grouping to the second beryllium, such that the bonding in **B** has a significantly higher contribution from Type II structure than does **A**. Support for this is afforded by comparing the distances in the Be–C (bridging) and Be–C (terminal) bonds. Thus, while in dimer **A** the Be–C(1) distance is significantly longer (1.836(6) compared with 1.719(6)), in **B** the values are very similar (1.763(7), 1.735(6) Å). In view of the significant differences in the Be–μ(alkynyl) interactions for the two dimers, one might have expected to find differences in the C≡C distances for the bridging propynyl ligands. However, it has been suggested that the C≡C bond length does not serve as an effective measure of metal–π interaction and we are unable to find any significant differences between the C(1)–C(2) bond distances in the two dimers [5].

The greater the type II character in the bonding the more electron-precise will the Be_2C_2 ring system become, thereby reducing the need for Be...Be interactions. The Be...Be distance in **B** (2.549(6) Å) is the longest known in $(BeX)_2$ bridged systems apart from that found (2.63 Å) for $(BeCl_2)_n$. This value is significantly longer than that in **A** (2.319(6) Å), further evidence that the Be_2C_2 ring system in **B** is the more electron-precise. The greater Be...Be interaction in **A** is facilitated by an opening up of the C(1)–Be–C(1′) angle from the value of 96.2(4)° found in **B** to 103.4(4)°. There is a less clear distinction between data for electron-deficient and electron-precise $(BeX)_2$ systems than for $(AlX)_2$ bridging systems and some beryllium compounds containing 1 electron or 3 electron bridging ligands have similar short metal...metal interactions, comparable with those found in **A** e.g. $(Me_2Be)_n$, 2.09(1) [8]; $(NaOEt_2)_2(Et_2BeH)_2$, 2.219(3) [9]; $[MeBe(C{\equiv}CMe)NMe_3]_2$, 2.335 [6] cf. $[(Me_2N)_2Be]_3$, 2.300(9) [10]; $[(Bu^t_2C{=}N)_2Be]_2$, 2.23(2) [11]; $[BrBe(OBu^t)OEt_2]_2$, 2.30(4) [12]; $[HBeN(Me)C_2H_4NMe_2]_2$, 2.316(3) Å [13]. However, it is felt that the overall geometry indicates that molecule **A** is predominantly an electron-deficient dimer of type I and molecule **B** is tending towards an electron-precise dimer of type II.

Examination of inter- and intra-molecular distances indicates that the difference in the geometry of the two Be_2C_2 ring systems cannot be attributed to packing effects. Rather they would appear to show that both forms have comparable energies. Recent MO calculations have confirmed the energetic equivalence of the two types of interactions and also that the Be′-C(2) bond index in **B** is greater than in **A** [14].

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