Azomethine Derivatives. Part 19.[1] Di-t-butylmethyleneamino-derivatives of Beryllium

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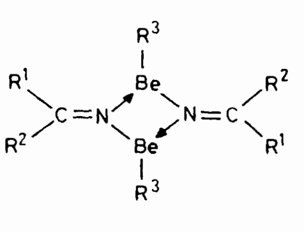
The synthesis of the new methyleneaminoberyllium compounds $[\mathrm{BeCl(N{=}CBu^t_2)}]_2$, $\mathrm{Li[Be(N{=}CBu^t_2)_3]}$, $[\mathrm{Be(N{=}CBu^t_2)_2}]_2$, $[\mathrm{BeBu^t(N{=}CBu^t_2)}]_2$, $\mathrm{Be(N{=}CBu^t_2)[N(SiMe_3)_2]}$, $[\mathrm{BeBu^t(N{=}CPh_2)}]_2$, and $[\mathrm{BeBu^t(N{=}CPh_2)}]_2$ is described. Features of their i.r., ^{1}H n.m.r., and mass spectra, and an *X*-ray crystallographic study of $[\mathrm{Be(N{=}CBu^t_2)_2}]_2$, are reported and discussed, with particular reference to indications of $\mathrm{N} \Rightarrow \mathrm{Be}$ ($p \rightarrow p$) dative π bonding in these compounds. The metal–nitrogen bond lengths and angles in $[\mathrm{Be(N{=}CBu^t_2)_2}]_2$ are compared with those in related beryllium compounds to illustrate the way that Be–N bond lengths reflect the co-ordination numbers of the metal and nitrogen atoms, and to illustrate the factors that influence the geometry of $(\mathrm{BeX})_2$ four-membered ring systems.

COMPOUNDS containing beryllium–nitrogen multiple bonds have attracted much interest.[2-4] This paper describes some new compounds containing such bonds linking methyleneamino-groups $\mathrm{R_2C{=}N}$ to co-ordinatively unsaturated beryllium atoms, which were prepared in order to resolve some problems in the methyleneamino-chemistry of beryllium left by an earlier study.[5]



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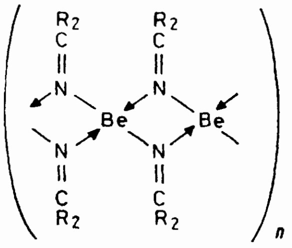

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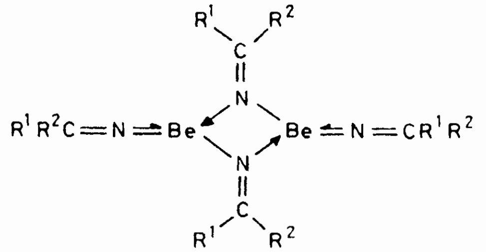

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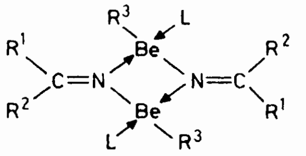

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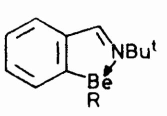

(4)

In that earlier study,[5] compounds of the formula types $[\mathrm{BeCl(X)}]_2$ (1) and $(\mathrm{BeX_2})_n$ (2) [$\mathrm{X = N{=}CPh_2}$, $\mathrm{N{=}C(C_6H_4Me\text{-}}p)_2$, or $\mathrm{N{=}CBu^t(C_6H_4Me\text{-}}p)$] were prepared. Whereas the former type were dimers, presumed to have structure (1; $\mathrm{R^3 = Cl}$), the latter had degrees of association, *n*, that depended on the substituents R. For example, whereas the diphenylmethyleneamino-compound $[\mathrm{Be(N{=}CPh_2)_2}]_n$ was apparently polymeric [structure (2a)], the bulkier substituents of the t-butyl(*p*-tolyl) analogue, $\{\mathrm{Be[N{=}CBu^t(C_6H_4Me\text{-}}p)]_2\}_2$, restricted its degree of association to 2, and the structure (2b) was suggested for this compound on the basis of its i.r. spectrum. Other structural types in beryllium–azomethine chemistry that do not afford scope for $\mathrm{N} \Rightarrow \mathrm{Be}$ dative π bonding [*e.g.* (3) and (4)] have been obtained in subsequent studies of beryllium–imine systems.[6,7]

Judging from molecular models, we considered that the di-t-butylmethyleneamino-ligand, $\mathrm{Bu^t_2C{=}N}$, should be bulky enough to stabilize three-co-ordinate beryllium, possibly even two-co-ordinate beryllium, and thus provide systems suitable for ^{1}H n.m.r. and crystallographic study, so we embarked on the present investigation of compounds containing this ligand. A brief preliminary account of some of this work has already been published.[8] The present account also includes some work on two new di*phenyl*methyleneamino-derivatives, prepared for comparison with their di-t-butylmethyleneamino-analogues.

RESULTS AND DISCUSSION

Synthesis of the New Di-t-butylmethyleneamino-derivatives.—Preparation of the new derivatives, which are listed in Table 1, was less straightforward than had been expected. Although the yellow, moisture-sensitive, crystalline solid di-t-butylmethyleneaminoberyllium chloride, $[\mathrm{BeCl(N{=}CBu^t_2)}]_2$, was readily prepared from equimolar proportions of beryllium chloride and the lithioketimine, $\mathrm{Li(N{=}CBu^t_2)}$, in a mixture of hexane and diethyl ether, attempts to prepare the bis(di-t-butylmethyleneamino)-derivative, $\mathrm{Be(N{=}CBu^t_2)_2}$, from a 1 : 2 mol ratio of the same reagents failed. The products isolated were $[\mathrm{BeCl(N{=}CBu^t_2)}]_2$ and the beryllate $\mathrm{Li[Be(N{=}CBu^t_2)_3]}$, which could be separated from the former by extraction with hexane [equations (1) and (2)]. The same lithium tris(di-t-butylmethyleneamino)beryllate was the only product (apart from lithium chloride) of reactions between $\mathrm{BeCl_2}$ and 3 mol equivalents of $\mathrm{Li(N{=}CBu^t_2)}$. This tendency for the metal chloride to form the ' ate ' complex in reactions with $\mathrm{Li(N{=}CBu^t_2)}$ is similar to the behaviour of aluminium chloride, which with 3 mol equivalents of $\mathrm{Li(N{=}CBu^t_2)}$ forms significant proportions of $\mathrm{Li[Al(N{=}CBu^t{}_2)_4]}$ in addition to the expected $\mathrm{Al(N{=}CBu^t{}_2)_3}$.[9,10]

TABLE 1

Analytical data for the new methyleneaminoberyllium compounds

Compound	Analysis (%) C	H	Be	N	M	Appearance, m.p. (θ_c/°C)	Solvents [a]	Structure type
$\mathrm{[BeCl(N{=}CBu^t{}_2)]_2}$ [b]	56.6	9.3	4.9	7.4	343	Pale yellow crystals, 88—90	t *, b	(1)
$\mathrm{C_{18}H_{36}Be_2Cl_2N_2}$ requires	58.5	9.8	4.9	7.6	369			
$\mathrm{Li[Be(N{=}CBu^t{}_2)_3]}$ [c]	74.6	12.6	2.1	9.4	453	Pale yellow crystals, 141—142	h *,t,b	(6)
$\mathrm{C_{27}H_{54}BeLiN_3}$ requires	74.3	12.4	2.1	9.6	436			
$\mathrm{[Be(N{=}CBu^t{}_2)_2]_2}$	74.5	12.3	3.2	10.0	548	Pale yellow needles, 220—230	d,h *,t,b	(2b)
$\mathrm{C_{36}H_{72}Be_2N_4}$ requires	74.8	12.4	3.1	9.7	578			
$\mathrm{[BeBu^i(N{=}CBu^t{}_2)]_2}$	75.7	12.5	4.4	6.9	395	Pale yellow crystals, 139—141	d,h *,b	(1)
$\mathrm{C_{26}H_{54}Be_2N_2}$ requires	75.7	13.1	4.4	6.8	412			
$\mathrm{[BeBu^i(N{=}CPh_2)]_2}$	83.0	7.8	3.6	5.5	480	Deep red crystals, 133—135	d,h *,b	(1)
$\mathrm{C_{34}H_{38}Be_2N_2}$ requires	82.9	7.7	3.7	5.7	492			
$\mathrm{[BeBu^t(N{=}CPh_2)]_2}$	82.9	7.4	3.5	5.7	472	Orange crystals, 185—187	b *, d	(1)
$\mathrm{C_{34}H_{38}Be_2N_2}$ requires	82.9	7.7	3.7	5.7	492			
$\mathrm{Be(N{=}CBu^t{}_2)[N(SiMe_3)_2]}$	58.5	11.8	8.9	8.9	307	Pale yellow oil, b.p. 120 °C *ca.* 0.1 mmHg	t,b	(5)
$\mathrm{C_{15}H_{36}BeN_2Si_2}$ requires	58.3	11.7	9.1	9.1	309			

Molecular weights were obtained cryoscopically using benzene solutions. [a] This column lists the solvents in which the compound is known to dissolve (b = benzene, d = diethyl ether, h = hexane, t = toluene); that used for recrystallization of analytical samples is marked with an asterisk. [b] Cl, 19.0 (requires 19.2%). [c] Li, 1.6 (requires 1.6%).

The bis(t-butylmethyleneamino)beryllium compound[8] $\mathrm{[Be(N{=}CBu^t{}_2)_2]_2}$ could, however, be prepared by the action of the ketimine, $\mathrm{Bu^t{}_2C{=}NH}$, on ethereal di-isobutylberyllium [equation (3)]. This reaction is of a

$$\mathrm{BeBu^i{}_2 + 2Bu^t{}_2C{=}NH \longrightarrow \tfrac{1}{2}[Be(N{=}CBu^t{}_2)_2]_2 + 2Bu^iH} \quad (3)$$

type that has been used[11] to prepare various aminoberyllium compounds $\mathrm{BeX(NR_2)}$ and $\mathrm{Be(NR_2)_2}$. It was smooth and complete by the time the reagents, mixed at −78 °C, had warmed to room temperature.

$$\mathrm{2BeCl_2 + 4Li(N{=}CBu^t{}_2)} \xrightarrow{(1)} \mathrm{\tfrac{1}{2}[BeCl(N{=}CBu^t{}_2)]_2 + Li[Be(N{=}CBu^t)_3] + 3LiCl}$$

$$\mathrm{2BeCl_2 + 4Li(N{=}CBu^t{}_2)} \xrightarrow{(2)} \mathrm{[Be(N{=}CBu^t{}_2)_2]_2 + 4LiCl}$$

The ready formation of the beryllate complex $\mathrm{Li[Be(N{=}CBu^t{}_2)_3]}$ from $\mathrm{BeCl_2}$ and $\mathrm{2Li(N{=}CBu^t{}_2)}$, and the existence of the *di*lithium beryllate complexes $\mathrm{Li_2[Be(C{\equiv}CPh)_4]}$[12] and $\mathrm{Li_2[BeMe_4]}$,[13] prompted us to attempt the synthesis of the tetrakis(t-butylmethyleneamino)beryllate $\mathrm{Li_2[Be(N{=}CBu^t{}_2)_4]}$ from $\mathrm{[Be(N{=}CBu^t{}_2)_2]_2}$ and 4 mol equivalents of $\mathrm{Li(N{=}CBu^t{}_2)}$ in hexane, also from $\mathrm{Li[Be(N{=}CBu^t{}_2)_3]}$ and $\mathrm{Li(N{=}CBu^t{}_2)}$ in the same solvent. The colourless precipitates that resulted were found to be deficient in lithioketimine, analysing as $\mathrm{Li_{1.7-1.8}Be(N{=}CBu^t{}_2)_{3.7-3.8}}$. Attempts were therefore made to detect the formation of $\mathrm{Li_2[Be(N{=}CBu^t{}_2)_4]}$ in solution by conductimetric titration of $\mathrm{Li(N{=}CBu^t{}_2)}$ against $\mathrm{[Be(N{=}CBu^t{}_2)_2]_2}$, but the results were inconclusive. Difficulties were encountered with the reactivity of these compounds towards commonly used solvents such as nitrobenzene and benzonitrile, and also with obtaining reproducible behaviour using ether solvents, in which crystalline $\mathrm{Li(N{=}CBu^t{}_2)}$ has apparently only very low solubility, although relatively concentrated solutions in mixed ether–hydrocarbon solvents can be prepared by adding ethers to the hydrocarbon solutions (pentane or hexane) in which $\mathrm{Li(N{=}CBu^t{}_2)}$ is normally prepared. When the conductimetric titration was carried out using hexane as the solvent the conductivity certainly increased as aliquots of $\mathrm{Li(N{=}CBu^t{}_2)}$ were added to the solution of $\mathrm{[Be(N{=}CBu^t{}_2)_2]_2}$, although apparently without significant discontinuities (see Figure 1).

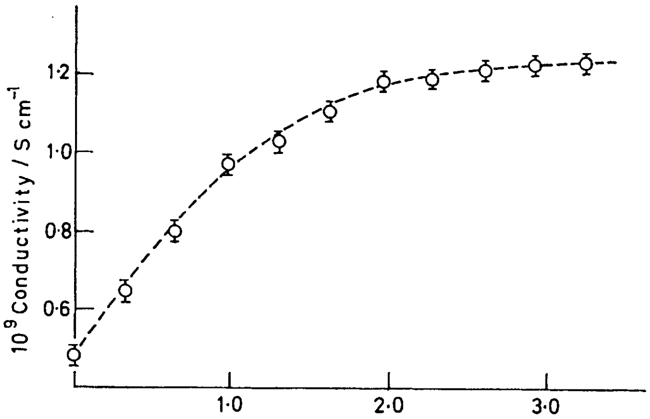

FIGURE 1 Conductimetric titration of $\mathrm{[Be(N{=}CBu^t{}_2)_2]_2}$ with $\mathrm{Li(N{=}CBu^t{}_2)}$

The methyleneaminoberyllium alkyls $\mathrm{[BeBu^i(N{=}CR_2)]_2}$ (R = Ph or $\mathrm{Bu^t}$) and $\mathrm{[BeBu^t(N{=}CPh_2)]_2}$ were prepared from equimolar proportions of the dialkyl $\mathrm{BeR_2}$ (R = $\mathrm{Bu^i}$ or $\mathrm{Bu^t}$) and the ketimine $\mathrm{R_2C{=}NH}$ (R = Ph or $\mathrm{Bu^t}$) in ethereal solution. Attempts to prepare the t-butyl compound $\mathrm{BeBu^t(N{=}CBu^t{}_2)}$ by this method were unsuccessful, affording powders or gums of variable composition. We accordingly tried three other routes to this compound, using as reagents (*i*) $BeBu^t_2 + Bu^tCN$, (*ii*) $[BeCl(N{=}CBu^t_2)]_2 + 2LiBu^t$, and (*iii*) $[BeCl(Bu^t)]_n + nLi(N{=}CBu^t_2)$, with the following results.

That reactions between nitriles and beryllium dialkyls [method (*i*)] can afford ketiminoberyllium alkyls has been demonstrated by Giacomelli and Lardicci,[14] who isolated the ketone Bu^iPhCO after hydrolyzing the products of the reaction between $BeBu^i_2$ and PhCN. [The simultaneous formation of some *ald*iminoberyllium alkyl, $BeBu^i(N{=}CHPh)$, was indicated by the presence of benzaldehyde among the hydrolysis products.] Subsequently, Coates and Smith [7] obtained acetophenone on hydrolyzing the products of reactions between $BeMe_2$ and PhCN. However, they found that $BeBu^t_2$ does not add across the triple bond of PhCN, although they were able to isolate the nitrile adduct $BeBu^t_2(NCPh)_2$. We found a similar lack of reactivity of $BeBu^t_2$ towards Bu^tCN. No insertion of Bu^tCN into the beryllium–carbon bonds of $BeBu^t_2$ occurred, although adduct formation was indicated by the nitrile stretching frequency (2 272 cm^{-1}) of the oil of composition $BeBu^t_2{\cdot}Bu^tCN$ [*cf.*[15] $\nu(C{\equiv}N)$ at 2 235 cm^{-1} for unco-ordinated Bu^tCN].

There was similarly no reaction when $[BeCl(N{=}CBu^t_2)]_2$ and $LiBu^t$ [method (*ii*)] were held for 16 h in toluene at 70 °C (at higher temperatures, $LiBu^t$ loses 2-methylpropene and deposits LiH); the $[BeCl(N{=}CBu^t_2)]_2$ was recovered unchanged. Reaction did occur when $[BeCl(Bu^t)]_2$ and $2Li(N{=}CBu^t_2)$ [method (*iii*)] were heated together in toluene at 70 °C, although the products were oils of variable composition having strong absorptions in the azomethine stretching region at *ca.* 1 700 and 1 620 cm^{-1}, the former indicative of methyleneamino-groups attached to co-ordinatively unsaturated beryllium, the latter indicative of bridging methyleneamino-groups. The intended product, $BeBu^t(N{=}CBu^t_2)$, may have been a component of these oils but we were unable to isolate it.

The last compound in Table 1, $Be(N{=}CBu^t_2)[N(SiMe_3)_2]$, was prepared by the reaction of $BeCl_2$ successively with equimolar proportions of $Li(N{=}CBu^t_2)$ and $Li[N(SiMe_3)_2]$, equation (4). It was isolated as an oil, b.p. 120 °C at

$$BeCl_2 \xrightarrow[-\,LiCl]{+\,Li{=}N(CBu^t_2)} \tfrac{1}{2}[BeCl(N{=}CBu^t_2)]_2 \xrightarrow[-LiCl]{+\,Li[N(SiMe_3)_2]} Be(N{=}CBu^t_2)[N(SiMe_3)_2] \quad (4)$$

ca. 0.1 mmHg pressure,* which set to a waxy solid on standing at room temperature and dissolved as the monomer (by cryoscopy and osmometry) in benzene.

With the exception of $Li[Be(N{=}CBu^t_2)_3]$, which also apparently dissolved in benzene as the monomer (by cryoscopy), the remaining compounds prepared were dimeric in benzene. The structural type listed in the final column of Table 1 can be inferred from the state of association, and is supported by our spectroscopic studies of these compounds as outlined below. Before these are discussed, however, we consider the structure of $[Be(N{=}CBu^t_2)_2]_2$ which has been established by an *X*-ray crystallographic investigation [8] and which is central to a discussion of the spectra and structures of the other compounds.

The Structure of Bis[bis(di-t-butylmethyleneamino)-beryllium], $[Be(N{=}CBu^t_2)_2]_2$.—From molecular models, we had expected that the bulk of the di-t-butylmethyleneamino-groups would be sufficient to prevent dimerization of the compound $Be(N{=}CBu^t_2)_2$, containing two such groups attached to the same beryllium atom. However, cryoscopic measurements showed that the compound dissolved in benzene as the dimer, and an *X*-ray crystallographic study (a preliminary report of which has already been published [8]) has revealed the presence of dimeric molecules, $[Be(N{=}CBu^t_2)_2]_2$, in the crystal. Experimental details of the *X*-ray study, and the manner in which the structure was determined and refined, are given at the end of this paper. Table 2 gives the atomic co-ordinates, and Table 3 lists interatomic distances and bond angles and the equations of some weighted least-squares mean planes.

TABLE 2

Atomic co-ordinates and their estimated standard deviations for $[Be(N{=}CBu^t_2)_2]_2$

	x	*y*	*z*
N(1)	0.016 5(4)	0.164 5(5)	0.039 7(4)
N(2)	0.074 6(4)	−0.000 8(4)	0.009 4(4)
C(1)	0.010 4(5)	0.244 9(6)	0.018 7(7)
C(2)	0.041 2(7)	0.314 0(6)	0.095 8(8)
C(3)	0.113 2(8)	0.374 0(8)	0.097 1(9)
C(4)	−0.035 1(9)	0.375 2(10)	0.084 0(12)
C(5)	0.082 4(9)	0.265 4(9)	0.192 6(9)
C(6)	−0.028 6(8)	0.269 9(8)	−0.083 3(8)
C(71) *	0.000 2(53)	0.195 3(33)	−0.129 8(27)
C(81) *	−0.132 1(20)	0.264 9(45)	−0.123 1(27)
C(91) *	−0.014 8(41)	0.360 6(26)	−0.108 7(24)
C(72) *	−0.090 1(44)	0.198 7(32)	−0.135 2(20)
C(82) *	−0.081 3(35)	0.359 4(31)	−0.101 1(23)
C(92) *	0.049 7(22)	0.281 8(64)	−0.097 2(20)
C(10)	0.151 3(6)	−0.001 7(5)	0.021 4(5)
C(11)	0.223 3(5)	0.041 8(6)	0.104 5(5)
C(12)	0.198 2(6)	0.043 2(7)	0.181 8(6)
C(13)	0.237 2(6)	0.139 5(6)	0.083 7(6)
C(14)	0.310 1(6)	−0.011 9(7)	0.143 3(6)
C(15)	0.166 8(6)	−0.044 2(6)	−0.055 3(6)
C(16)	0.199 3(6)	−0.142 6(6)	−0.026 2(7)
C(17)	0.079 9(6)	−0.050 0(7)	−0.144 5(6)
C(18)	0.228 3(6)	0.009 7(7)	−0.076 1(6)
Be	0.011 3(7)	0.066 5(7)	0.030 6(7)

* Occupation factor 0.5, all others 1.0.

The molecules $[Be(N{=}CBu^t_2)_2]_2$ are centrosymmetric [structural type (2b); Figures 2 and 3] with two alkylideneamino-groups bridging the two beryllium atoms by means of a planar four-membered $(BeN)_2$ ring, the remaining two alkylideneamino-groups being terminally attached, one to each beryllium atom. The effect of the bulk of the t-butyl groups can be seen in the orientation of both the terminal and bridging alkylideneamino-groups, which differ markedly from what might have been expected. For a structure of type (2b), to maximize $N{\rightleftharpoons}Be$ dative π bonding, the terminal alkylideneamino-groups would be expected to be attached to the beryllium atoms by linear $C{=}N{\rightleftharpoons}Be$ units lying on the Be–Be axis;

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

moreover, the skeletal atoms of the bridging alkylideneamino-groups would be expected to lie in the $(\mathrm{BeN})_2$ ring plane. In fact, the terminal alkylideneamino-groups are bent out of the ring plane, *i.e.* the mean plane of Be, N(2), and C(10) and the atoms related to these by the centre of symmetry (Tables 2 and 3, Figures 2 and 3), so that N(1) is 0.50 Å and C(1) 1.29 Å from that plane, the Be$^{\mathrm{I}}\cdots$Be–N(1) angle being 160.7(8)° and the Be–N(1)–C(1) angle being 160.5(9)°. The bridging methyleneamino-groups are twisted (with respect to this same plane) about the N(2)–C(10) axes, giving a dihedral angle of 37.0° between the ring plane and the plane of N(2), C(10), C(11), and C(15). Atoms C(11) and C(15) are respectively 0.78 Å below and 0.86 Å above the ring plane. This twisting of the bridging groups allows the bulky t-butyl substituents to be accommodated, otherwise dimerization would not have been possible without drastic bond lengthening or other distortion. [The C(sp^3)–C(sp^3) and C(sp^2)–C(sp^3) bonds are slightly longer than expected but none differs significantly from its mean.] In turn, the twisting of the bridging groups can be seen as the cause of the bending of the terminal groups, which significantly are bent away from that side of the molecule on which the bridging groups are closer. While close distances of approach are found between methyl carbon atoms in the same methyleneamino-group, these distortions result in only two contacts of <4 Å between methyl carbon atoms in *different* methyleneamino-groups in the same molecule. Of the

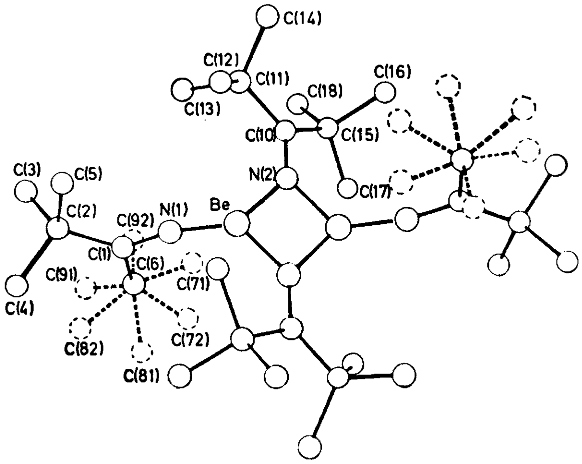


FIGURE 2 Molecular structure of $[\mathrm{Be(N{=}CBu^t_2)_2}]_2$ showing the atom numbering and the two sets of sites [C(71), C(81), and C(91) and C(72), C(82) and C(92)] of the disordered butyl group centred on C(6)

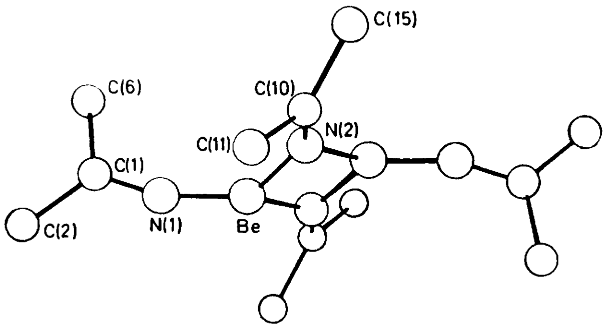


FIGURE 3 Molecular skeleton of $[\mathrm{Be(N{=}CBu^t_2)_2}]_2$ showing the orientations of the methyleneamino-groups with respect to the $(\mathrm{BeN})_2$ ring

TABLE 3

Structural data for $[\mathrm{Be(N{=}CBu^t_2)_2}]_2$

(*a*) Bond lengths (Å) and their estimated standard deviations.

Be–N(1)	1.502(13)	C(6)–C(91)	1.504(45)
Be–N(2)	1.682(15)	C(6)–C(72)	1.493(54)
Be–N(2$^{\mathrm{I}}$)	1.674(14)	C(6)–C(82)	1.601(53)
N(1)–C(1)	1.269(12)	C(6)–C(92)	1.528(46)
N(2)–C(10)	1.279(14)	C(10)–C(11)	1.528(12)
C(1)–C(2)	1.559(15)	C(10)–C(15)	1.588(13)
C(1)–C(6)	1.568(16)	C(11)–C(12)	1.570(14)
C(2)–C(3)	1.563(19)	C(11)–C(13)	1.578(13)
C(2)–C(4)	1.578(21)	C(11)–C(14)	1.585(14)
C(2)–C(5)	1.619(17)	C(15)–C(16)	1.600(13)
C(6)–C(71)	1.600(68)	C(15)–C(17)	1.563(13)
C(6)–C(81)	1.630(44)	C(15)–C(18)	1.537(16)

(*b*) Bond angles (°) and their estimated deviations.

N(2)–Be–N(2$^{\mathrm{I}}$)	96.9(7)	Be–N(1)–C(1)	160.5(9)
N(1)–Be–N(2)	127.9(8)	N(1)–C(1)–C(2)	118.1(9)
N(1)–Be–N(2$^{\mathrm{I}}$)	129.6(9)	N(1)–C(1)–C(6)	118.5(9)
Be$^{\mathrm{I}}$–Be–N(1)	160.7(8)	C(2)–C(1)–C(6)	123.4(9)
Be–N(2)–Be$^{\mathrm{I}}$	83.1(7)	N(2)–C(10)–C(11)	120.1(8)
Be–N(2)–C(10)	138.1(8)	N(2)–C(10)–(C15)	117.6(8)
Be$^{\mathrm{I}}$–N(2)–C(10)	138.8(8)	C(11)–C(10)–C(15)	122.2(8)

C–C–C angles in ordered t-butyl groups: 105.6(7)—112.9(8)
in disordered t-butyl group: 103(3)—120(2)

(*c*) Some intramolecular non-bonding contracts (Å)

Be $\cdots$ Be$^{\mathrm{I}}$	2.23(2)	C(3) $\cdots$ C(92)	3.24(5)
N(2) $\cdots$ N(2$^{\mathrm{I}}$)	2.51(1)	C(4) $\cdots$ C(81)	3.51(5)
Be $\cdots$ C(2)	3.90(1)	C(4) $\cdots$ C(91)	3.45(4)
Be $\cdots$ C(6)	3.54(2)	C(4) $\cdots$ C(82)	2.84(4)
Be $\cdots$ C(12)	3.10(2)	C(81) $\cdots$ C(16$^{\mathrm{I}}$)	3.76(5)
Be $\cdots$ C(17$^{\mathrm{I}}$)	3.06(2)	C(13) $\cdots$ C(18)	3.29(1)
Be $\cdots$ C(71)	3.28(5)	C(13) $\cdots$ C(92)	3.93(6)
Be $\cdots$ C(72)	3.22(4)		
C(3) $\cdots$ C(91)	3.13(4)	C(14) $\cdots$ C(16)	3.27(1)
C(3) $\cdots$ C(82)	3.49(5)	C(14) $\cdots$ C(18)	3.29(1)

(*d*) Intermolecular contacts <4.0 Å

C(3) $\cdots$ C(18$^{\mathrm{IV}}$)	3.49	C(13) $\cdots$ C(92$^{\mathrm{IV}}$)	3.87
C(4) $\cdots$ C(14$^{\mathrm{VI}}$)	3.77	C(16) $\cdots$ C(16$^{\mathrm{V}}$)	3.64
C(12) . . . C(18$^{\mathrm{III}}$)	3.95	C(17) $\cdots$ C(17$^{\mathrm{II}}$)	3.34

Roman numeral superscripts refer to the following equivalent positions with respect to the molecule at x, y, z:

I	$-x, -y, -z$	IV	$\frac{1}{2} - x, \frac{1}{2} - y, -z$
II	$-x, y, -\frac{1}{2} - z$	V	$\frac{1}{2} - x, -\frac{1}{2} - y, -z$
III	$x, -y, \frac{1}{2} + z$	VI	$-\frac{1}{2} + x, \frac{1}{2} + y, z$

(*e*) Equations of some weighted least-squares mean planes where X, Y, Z are in Å with respect to the orthogonal axes a, b, c^*. Deviations (Å) of atoms from the mean plane are given in square brackets

Plane (1): Be, N(2), C(10)

$$0.1147X + 0.4113Y - 0.9042Z = 0$$

[Be 0.001, N(2) 0.012, C(10) −0.010, N(1) 0.496, C(1) 1.291, C(11) −0.784, C(15) 0.857]

Plane (2): N(2), C(10), C(11), C(15)

$$0.0613X + 0.8766Y - 0.4773Z = 0$$

[N(2) −0.001, C(10) −0.021, C(11) 0.009, C(15) 0.010]

Plane (3): Be, N(1), C(1), C(2), C(6)

$$-0.9960X + 0.0140Y - 0.0879Z = 0$$

[Be 0.021, N(1) 0.011, C(1) −0.007, C(2) −0.017, C(6) 0.003] short intramolecular contacts observed between methyl carbon atoms of the *same* methyleneamino-group, most involve carbon atoms of the disordered t-butyl group centred on C(6). Each of the two sets of sites for the carbon atoms of this disordered group gives rise to very similar intramolecular contacts, so there is understandably no one preferred set of sites.

The terminal Be–N(1) bond length (1.50 Å), the shortest beryllium–nitrogen bond yet reported, is appropriate for a bond involving atoms of low co-ordination number with a substantial degree of ($p\rightarrow p$) $N\rightleftharpoons Be$ dative π bonding (see Table 4, which gives data for a series of beryllium–nitrogen compounds,[16-21] showing the relation of the Be–N bond lengths to the co-ordination numbers of the beryllium and nitrogen atoms). From Table 4, it is also apparent that the bridging Be–N distances [1.682(15) and 1.674(14) Å] in $[Be(N{=}CBu^t{}_2)_2]_2$ are appropriate for single bonds between three-co-ordinate nitrogen atoms. The N=C bond lengths [N(1)–C(1) 1.269(12) and N(2)–C(10) 1.279(14) Å] are in line with the values found for such related compounds as $P(N{=}CPh_2)_3$ (1.28 Å),[1] $Li[Al(N{=}CBu^t{}_2)_4]$,[10] $[AlMe_2(N{=}CMeBu^t)]_2$,[22] $[BMe_2(N{=}CHMe)]_2$,[22] $M(N{=}CPh_2)_4$ (M=Si or Ge) [23] (all 1.27 Å), and $[Mo(\eta\text{-}C_5H_5)(CO)_2(N{=}CBu^t{}_2)]$ (1.26 Å).[24]

TABLE 4

The relation between beryllium–nitrogen bond lengths and the co-ordination numbers of the atoms involved

Compound	Be–N bond length (Å)	Co-ordination numbers		Ref.
		Be	N	
$BeMe_2(quinuclidine)_2$	1.91	4	4	16
$[BeMe(C{\equiv}CMe)(NMe_3)]_2$	1.81	4	4	17
$[Be(NMe_2)_2]_3$	1.78	4	4	18
$[BeH(NMeCH_2CH_2NMe_2)]_2$	1.75	4	4	19
$[Be(N{=}CBu^t{}_2)_2]_2$	1.68	3	3	This work
$[Be(NMe_2)_2]_3$	1.65	3	4	18
$K[Be(NH_2)_3]$; $Rb[Be(NH_2)_3]$	1.59	3	3	20
$[Be(NMe_2)_2]_3$	1.57	3	3	18
$Be[N(SiMe_3)_2]_2$	1.56	2	3	21
$[Be(N{=}CBu^t{}_2)_2]_2$	1.50	3	2	This work

TABLE 5

Interatomic distances and bond angles in $(BeX)_2$ rings

Compound	X	Co-ordination number		Distance/Å			BeXBe angle (°)	Ref.
		Be	X	r(Be–X)	r(Be · · · Be)	r(X · · · X)		
$[\{Na(OEt_2)\}_2(Et_2BeH)_2]$	H	4	4	1.40	2.20	1.73	104	29
$(BeMe_2)_n$	C	4	5	1.93	2.09	3.24	66	28
$[BeMe(C{\equiv}CMe)(NMe_3)]_2$	C	4	3	1.85, 1.89	2.33	2.93	77	17
$[Be(C{\equiv}CMe)_2(NMe_3)]_2$	C	4	3	1.84, 1.90	2.32	2.94	77	30
	C	4	3	1.76, 2.04	2.55	2.83	84	30
$[Be(N{=}CBu^t{}_2)_2]_2$	N	3	3	1.68	2.23	2.52	83	This work
$[Be(NMe_2)_2]_3$	N	3,4	4	1.65, 1.78	2.30	2.55	84	18
$[BeH(NMeCH_2CH_2NMe_2)]_2$	N	4	4	1.75, 1.76	2.32	2.62	83	19
$Be_3Cl_2(OBu^t)_4$	O	3,4	3	1.54, 1.64	2.23	2.23	89	*a*
$[BeBr(OBu^t)(OEt_2)]_2$	O	4	3	1.62	2.30	2.29	91	*a*
$[BeMe(OSiMe_3)]_4$	O	4	4	1.73	2.43	2.47	89	*b*
$(BeCl_2)_n$	Cl	4	2	2.02	2.63	3.05	82	*c*

[a] H. M. M. Shearer, unpublished work. [b] D. Mootz, A. Zinnius, and B. Böttcher, *Angew. Chem. Internat. Edn.*, 1969, **8**, 378. [c] R. E. Rundle and P. H. Lewis, *J. Chem. Phys.*, 1952, **20**, 132.

Despite the bent $C{=}N\rightleftharpoons M$ structure of the terminal alkylideneamino-groups {which is itself not unprecedented: $Li[Al(N{=}CBu^t{}_2)_4]$ [10] contains similarly slightly bent $C{=}N\rightleftharpoons Al$ units} it is worth noting that the plane in which atoms C(1), C(2), and C(6) lie is inclined at an angle of 88.3° to the $(BeN)_2$ ring plane, reflecting the allene-like structure, $R_2C{=}N\rightleftharpoons BeX_2$ (*cf.* $R_2C{=}C{=}CR'_2$) of this part of the molecule (the two ligands X, the bridging alkylideneamino-groups, formally contribute a total of three electrons to the beryllium atom).

The shape of the $(BeN)_2$ ring in $[Be(N{=}CBu^t{}_2)_2]_2$ is a further interesting feature of the structure. Although the two crystallographically distinct edges, Be–N(2) and Be–N(2^I), do not differ significantly in length [1.682(15) and 1.674(14) Å respectively], the ring angles at beryllium (97°) and nitrogen (83°) do differ in a manner and to an extent that deserves comment. In the ring, the metal and nitrogen atoms are in very similar states of co-ordination: both are three-co-ordinate, and both are involved in exocyclic double bonds (N=C and $Be\rightleftharpoons N$). In view of this similarity, a greater ring angle at the more electronegative atom, nitrogen, might have been expected on electron-pair repulsion grounds, since the bond pairs in the Be–N ring bonds are expected to be centred nearer to nitrogen than to beryllium. However, reference to Table 5, which gives interatomic distances and bond angles for this and other $(BeX)_2$ ring systems, shows that the ring angles at nitrogen in $[Be(N{=}CBu^t{}_2)_2]_2$, $[Be(NMe_2)_2]_3$,[18] and $[BeH(NMeCH_2CH_2NMe_2)]_2$ [19] are virtually identical (83—84°), despite the different metal and nitrogen co-ordination numbers in these compounds. Indeed, the data in Table 5 show that the most important factor affecting the shapes of these $(BeX)_2$ rings is the identity of the bridging atom X. The BeXBe angle lies in the range 66—84° when X = C, 83—84° when X = N, and 89—91° when X = O. This increase in the MXM angle in the sequence $X = C < N < O$ confirms the earlier observation by Magnuson and Stucky [25] about such ring systems.

A consequence of the acute BeNBe angle in $[Be(N{=}CBu^t{}_2)_2]_2$ is that the cross-ring metal–metal distance is relatively short, only 2.23(2) Å. Since this is an electron-precise ring system [four electron pairs are available for bonding in the $(BeN)_2$ ring], there should be no cross-ring metal–metal bonding such as occurs in electron-deficient rings to reduce the metal–metal distance and make the angle at the bridging atom yet more acute.[26,27] The data in Table 5 show that the shortest metal–metal distances yet found in $(BeX)_2$ ring systems occur in the dimethyl derivative $(BeMe_2)_n$ [28] and in the hydride-bridged complex $[\{Na(OEt_2)\}_2(Et_2BeH_2BeEt_2)]$,[29] both of which have electron-deficient bridges and so significant cross-ring metal–metal bonding, although the acetylene-bridged species $[BeMe(C{\equiv}CMe)(NMe_3)]_2$ [17] and $[Be(C{\equiv}CMe)(NMe_3)]_2$,[30] also commonly regarded as having electron-deficient bridges, have much longer Be–Be distances. The electron-deficient or -precise nature of the bridge is by no means the dominant factor affecting the shape of these rings.

The Spectra of the New Methyleneaminoberyllium Compounds.—The frequencies of the azomethine stretching absorptions in the i.r. spectra of the new compounds are listed in Table 6, together with data for related compounds prepared previously.[5] These absorptions lie in two well defined regions, from 1 600—1 650 and from 1 720—1 750 cm^{-1}. Now that the structure of $[Be(N{=}CBu^t_2)_2]_2$ has been established, these can with confidence be assigned, as previously suggested,[5] to bridging and terminal groups respectively, and used to support structures of type (1), with bridging methyleneamino-groups, for the methyleneaminoberyllium alkyls $[BeR(N{=}CR'_2)]_2$ and chlorides $[BeCl(N{=}CR'_2)]_2$ (R = Bu^i or Bu^t, R' = Bu^t, C_6H_4Me-*p*, or Ph). Moreover, they indicate that the compounds $[Be(N{=}CR_2)_2]_n$ (R = Ph or C_6H_4Me-*p*), which were of too low solubility to obtain reliable molecular weights by cryoscopic measurements on benzene solutions,[5] are probably dimers or other relatively small oligomers rather than high polymers [structure (2a)] with exclusively bridging methyleneamino-groups. The one monomeric compound in Table 6, $Be(N{=}CBu^t_2)[N(SiMe_3)_2]$, significantly is the only one that does not absorb in the region appropriate for bridging methyleneamino-groups. Instead, its spectrum has a broad absorption centred at *ca.* 1 740 cm^{-1}, consistent with structure (5), in which the skeletal $C_2CNBeNSi_2$ unit would be expected to be planar, although flexible.

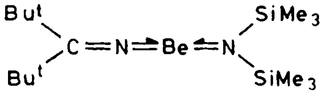
TABLE 6

Azomethine stretching bands (cm^{-1})

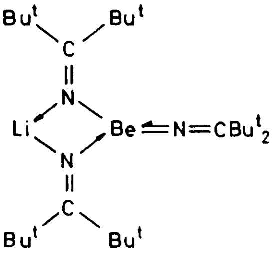
Compound	$\nu(C{=}N)_\mu$	$\nu(C{=}N)_t$
$[BeCl(N{=}CBu^t_2)]_2$ *	1 626	
$\{BeCl[N{=}CBu^t(C_6H_4Me\text{-}p)]\}_2$	1 614	
$[BeBu^i(N{=}CBu^t_2)_2]_2$ *	1 635	
$[Be(N{=}CBu^t_2)_2]_2$ *	1 631	1 721
$\{Be[N{=}CBu^t(C_6H_4Me\text{-}p)]_2\}_2$	1 637	1 739
$Be(N{=}CBu^t_2)[N(SiMe_3)_2]$ *		1 734 1 747br
$[BeCl(N{=}CPh_2)]_2$	1 608	
$\{BeCl[N{=}C(C_6H_4Me\text{-}p)_2]\}_2$	1 610	
$[BeBu^i(N{=}CPh_2)]_2$ *	1 610	
$[Be(N{=}CPh_2)_2]_n$	1 627	1 732
$\{Be[N{=}C(C_6H_4Me\text{-}p)_2]_2\}_3$	1 626	1 731
$[BeBu^t(N{=}CPh_2)]_2$ *	1 648	

* This work; remaining data from ref. 5; all relate to Nujol mulls.

Not listed in Table 6 are the frequencies of the azomethine stretching absorptions of the 'ate' complex $Li[Be(N{=}CBu^t_2)_3]$ and the material of composition $Li_{1.8}Be(N{=}CBu^t_2)_{3.8}$. The former absorbed at 1 663 cm^{-1}, the latter at 1 660 and 1 709 cm^{-1}. Absorptions at *ca.* 1 660—1 670 cm^{-1}, higher than expected for methyleneamino-groups bridging two beryllium atoms, might well be due to the unsymmetrical LiNBe bridges expected in such a derivative: $Li[Al(N{=}CBu^t_2)_4]$, which contains unsymmetrical LiNAl bridges as well as terminal methyleneamino-groups, absorbs at 1 642 [$\nu(C{=}N)_\mu$] and 1 700 cm^{-1} [$\nu(C{=}N)_t$].[10] The absence of an absorption in the 1 720—1 750 cm^{-1} region is a puzzling feature of the spectrum of $Li[Be(N{=}CBu^t_2)_3]$, which might be expected to have structure (6).



(5)



(6)

The ^1H n.m.r. spectra of several of the new methyleneamino-derivatives were recorded using toluene solutions. The chloride $[BeCl(N{=}CBu^t_2)]_2$ gave the expected singlet at τ 9.10, while $[Be(N{=}CBu^t_2)_2]_2$ gave a singlet (intensity 2) at τ 8.77 attributable to the butyl groups of the bridging ligands and an ill resolved doublet (maxima at τ 8.69 and 8.71, of overall intensity 2) attributable to the non-equivalent butyl groups on the apparently still bent terminal ligands. The peaks did not change significantly in form or chemical shift when the samples were cooled from 40 to −60 °C. The absorption due to the butyl protons of $[BeBu^t(N{=}CPh_2)]_2$ was a sharp singlet at τ 8.93.

The silylamino-derivative $Be(N{=}CBu^t_2)[N(SiMe_3)_2]$ gave a surprisingly complex n.m.r. spectrum, with a set of absorptions, of overall intensity 1, in the range τ 8.6—9.0, attributable to the t-butyl protons, and another set of absorptions, of the same overall intensity, in the range τ 9.65—9.95, attributable to the trimethylsilyl groups. In principle, a compound with structure (5) would be expected to give rise to a singlet for each of the two types of proton present. The beryllate $Li[Be(N{=}CBu^t_2)_3]$ gave a complex set of absorptions in the τ 8.65—9.00 region.

The mass spectra of the methyleneaminoberyllium compounds were useful aids to identification, although because beryllium is a light monoisotopic atom its presence in fragments was less obvious than many metals, and as with the spectra of methyleneamino-derivatives of other elements the spectra tended to be swamped by the methyleneamino-ligands and fragments of their breakdown. The most abundant fragments were generally R^+, $[RCNH]^+$, and $[R_2CN]^+$. Common features of the spectra of the di-t-butylmethyleneamino-compounds were peaks at *m/e* 29.5 and 38.7 attributable to metastable species, equations (5) and (6) respectively.

$$[Bu(vinyl)CN]^+ \longrightarrow Bu^+ + CH_2{=}CHCN \qquad (5)$$

$$[Bu(H)CN]^+ \longrightarrow Bu^+ + HCN \qquad (6)$$

The relative ease with which the butyl cation (*m/e* 57) separated from fragments, and its relative stability, was a dominant feature of the spectra, in which its peak was normally the most intense, some 10^2 or 10^3 times as intense as high-mass peaks attributable to parent ions or fragments derived from them by loss of methyl or butyl groups. Salient features of the spectra are given in the Experimental section.

Reactions of the New Methyleneamino-compounds.—**CAUTION**: All the compounds listed in Table 1 are moisture-sensitive, and decompose rapidly on exposure to air. For this reason as well as the health hazard posed by readily hydrolyzed, possibly flammable, beryllium compounds, they were kept under dry nitrogen or *in vacuo*. Hydrolysis afforded beryllium hydroxide and ketimine, readily detected by the development of new peaks in the O–H, N–H, and C=N stretching regions of the i.r. spectra, and apparent from the loss of colour and opaque surface acquired by crystals exposed to moist air.

The aldiminoberyllium alkyls $[BeR(N{=}CHR')]_2$ ($R =$ Me or Bu^t, $R' = Bu^t$, Ph, or C_6H_4Me) were already known to form adducts $[BeR(N{=}CHR')L]_2$ with $L = NMe_3$ or pyridine.[7] We therefore briefly explored the capacity of $[BeCl(N{=}CBu^t{}_2)]_2$ and $[Be(N{=}CBu^t{}_2)_2]_2$ to react with Lewis bases such as NMe_3 and $Me_2NCH_2CH_2NMe_2$. The starting materials were recovered unchanged, however, when the reagents were mixed either in toluene or neat at up to 80 °C. This lack of reactivity towards these amines, together with the fact that the compounds in Table 1 were isolated in an ether-free form when diethyl ether was a component of the solvent mixture used during their preparation, shows that these compounds have a negligible Lewis acidity towards such Lewis bases, a feature that can be attributed to the shielding of their three-co-ordinate beryllium atoms by the bulky methyleneamino-groups.

EXPERIMENTAL

Materials and Techniques.—Beryllium chloride was prepared by heating finely divided beryllium in a stream of chlorine gas followed by resublimation. Solutions of $BeBu^i{}_2$ and $BeBu^t{}_2$ in diethyl ether, prepared by reaction of $BeCl_2$ with the appropriate Grignard reagent, were gifts from Professor G. E. Coates. Their concentration was determined by titrating the alkaline solution formed by adding an excess of KF to the beryllium hydrolysate (organic matter having previously been destroyed by repeated evaporation to dryness with nitric acid) to a green end-point using Bromothymol Blue indicator. Other reagents were prepared as described in earlier parts of this series (see refs. 1 and 5 and refs. therein). Manipulations were carried out using standard vacuum-line or inert-atmosphere techniques.

Infrared spectra were recorded on a Grubb–Parsons Spectromaster, ^1H n.m.r. spectra at 60 MHz on Perkin-Elmer R10 or Varian A56/60D spectrometers, and mass spectra on an A.E.I. M.S.9 instrument at 70 eV and an accelerating potential of 8 kV, with a source temperature of 150—200 °C, direct insertion, and electromagnetic scanning. Carbon, hydrogen, and nitrogen were determined using a Perkin-Elmer 240 elemental analyser, chlorine by fusion with potassium prior to halide titration, lithium by flame photometry, and beryllium by the fluoroberyllate titration method.

Preparation of Di-t-butylmethyleneamino-derivatives.—Two examples suffice to illustrate the methods used.

Bis[chloro(di-t-butylmethyleneamino)beryllium]. A solution of $Li(N{=}CBu^t{}_2)$ was prepared by adding $LiBu^t$ (11.6 cm^3 of a 2.18 mol dm^{-3} solution in hexane, 25 mmol) by syringe to a frozen (−196 °C) solution of Bu^tCN (2.0 g, 25 mmol) in hexane (40 cm^3). The mixture was allowed to warm to room temperature and stirred for 40 min before being added to a frozen (−196 °C) solution of $BeCl_2$ (2.0 g, 25 mmol) in diethyl ether (40 cm^3). The solution was then stirred at room temperature for 4 h during which a white solid precipitated. Solvent was removed *in vacuo*, and replaced with toluene (20 cm^3) in which the residue was heated to boiling for 20 min. Solvent was again pumped off, and the residue was extracted with hot toluene, which afforded a yellow solution from which $[BeCl(N{=}CBu^t{}_2)]_2$, m.p. 88—90 °C (decomp.) crystallized on cooling.

Bis[bis(di-t-butylmethyleneamino)beryllium]. The compound $BeBu^i{}_2$ (3 cm^3 of a 3.66 mol dm^{-3} solution in diethyl ether, 10.8 mmol) was added by syringe to a frozen solution of $Bu^t{}_2CNH$ (3.1 g, 22 mmol) in diethyl ether (40 cm^3) at −196 °C. The initially colourless solution gradually turned yellow as it warmed to room temperature. The solution was heated under reflux for 2 d to ensure complete reaction, after which yellow crystals of $[Be(N{=}CBu^t{}_2)_2]_2$, m.p. 220—230 °C (decomp.), separated.

Conductimetric Titration of $[Be(N{=}CBu^t{}_2)_2]_2$ *with* $Li(N{=}CBu^t{}_2)$.—A solution of $Li(N{=}CBu^t{}_2)$ (0.2 mmol per cm^3 hexane) was added in 0.5 cm^3 aliquots to a solution of $[Be(N{=}CBu^t{}_2)_2]_2$ (0.306 mmol of monomer, $Be(N{=}CBu^t)_2$, *in* 5 cm^3 hexane) in a conductivity cell with platinum electrodes (1 cm^2 area each, 0.5 cm apart). The solutions were under dry nitrogen and held at 22 °C during the titration. Conductivities were measured using a Wayne–Kerr B224 Universal Bridge (for results see Figure 1).

Mass Spectra.—The main high-mass fragments (*m/e* values, relative intensities in parentheses, and assignments) in the mass spectra were as follows.

$[BeCl(N{=}CBu^t{}_2)]_2$: 232, 230, 228 (0.2) $[Be_2Cl_2(NCBu_2)]^+$; 207 (3) $[Be(NCBu_3)]^+$; 187, 185 (1) $[BeCl(HNCBu_2)]^+$; 171, 169 (0.5) $[BeCl(NCBu_2) - Me]^+$; 149 (0.2) $[Be(NCBu_2)]^+$; 141 (2) $[HNCBu_2]^+$; 126 (10) $[HNCBu_2 - Me]^+$; 84 (90) $[HNCBu]^+$; and 57 (100) Bu^+.

$Li[Be(N{=}CBu^t{}_2)_3]$: 429 (1) $[Be(NCBu_2)_3]^+$; 355 (3) $[Be_2Bu(NCBu_2)_2]^+$; 281 (2) $[H(NCBu_2)_2]^+$; 232 (0.5) $[Be(NCBu_2)_2 - Bu]^+$; 207 (0.5) $[BeBu(HNCBu_2)]^+$; 149 (0.8) $[Be(NCBu_2)]^+$; 147 (1) $[Li(NCBu_2)]^+$; 142 (2) $[H_2NCBu_2]^+$; 141 (3) $[HNCBu_2]^+$; 140 (1) $[NCBu_2]^+$; 134 (0.3) $[Be(NCBu_2) - Me]^+$; 84 (21) $[HNCBu]^+$; and 57 (100) Bu^+.

$[Be(N{=}CBu^t{}_2)_2]_2$: 464 (0.1) $[P - 2Bu]^+$; 355 (0.1) $[Be_2Bu(NCBu_2)_2]^+$; 316 (0.3) $[Be(NCBu_2)_2{\cdot}HCN]^+$; 288

(0.2) $[\mathrm{Be(NCBu_2)} - \mathrm{H}]^+$; 282 (0.4) $[\mathrm{(HNCBu_2)_2}]^+$; 273 (0.7) $[\mathrm{Be(NCBu_2)_2} - \mathrm{MeH}]^+$; 259 (0.2) $[\mathrm{Be(NCBu_2)_2} - \mathrm{2Me}]^+$; 232 (0.2) $[\mathrm{Be(NCBu_2)_2} - \mathrm{Bu}]^+$; 207 (0.4) $[\mathrm{BeBu(NCBu_2)H}]^+$; 191 (0.4) $[\mathrm{BeBu(NCBu_2)} - \mathrm{Me}]^+$; 176 (0.2) $[\mathrm{BeBu(NCBu_2)} - \mathrm{2Me}]^+$; 149 (0.7) $[\mathrm{Be(NCBu_2)}]^+$; 142 (1) $[\mathrm{H_2NCBu_2}]^+$; 141 (9) $[\mathrm{HNCBu_2}]^+$; 140 (1) $[\mathrm{NCBu_2}]^+$; 93 (2) $[\mathrm{Be(NCBu_2)} - \mathrm{C_4H_8}]^+$; 84 (90) $[\mathrm{HNCBu}]^+$; and 57 (100) Bu^+.

$[\mathrm{BeBu^i(N{=}CBu^t{}_2)}]_2$: 412 (0.1) P^+; 397 (0.1) $[P - \mathrm{Me}]^+$; 356 (6) $[P - \mathrm{C_4H_8}]^+$; 355 (19) $[P - \mathrm{Bu}]^+$; 300 (5) $[P - \mathrm{2C_4H_8}]^+$; 297 (4) $[\{\mathrm{Be(NCBu_2)}\}_2 - \mathrm{H}]^+$; 288 (0.2) $[\mathrm{Be(NCBu_2)_2} - \mathrm{H}]^+$; 281 (0.2) $[\mathrm{H(NCBu_2)_2}]^+$; 272 (2.5) $[P - \mathrm{NCBu_2}]^+$; 232 (1) $[\mathrm{Be(NCBu_2)_2} - \mathrm{Bu}]^+$; 191 (0.2) $[\mathrm{BeBu(NCBu_2)} - \mathrm{Me}]^+$; 176 (2) $[\mathrm{BeBu(NCBu_2)} - \mathrm{2Me}]^+$; 149 (9) $[\mathrm{Be(NCBu_2)}]^+$; 123 (0.2) $[\mathrm{BeBu_2}]^+$; 83 (90) $[\mathrm{NCBu}]^+$; and 57 (100) Bu^+.

$\mathrm{Be(N{=}CBu^t{}_2)[N(SiMe_3)_2]}$: 293 (0.2) $[P - \mathrm{Me}]^+$; 281 (0.2) $[\mathrm{H(NCBu_2)_2}]^+$; 222 (0.7) $[\mathrm{Be(NCBu_2)(SiMe_3)}]^+$; 161 (2) $[\mathrm{NH(SiMe_3)_2}]^+$; 160 (0.2) $[\mathrm{N(SiMe_3)_2}]^+$; 149 (2) $[\mathrm{Be(NCBu_2)}]^+$; 148 (4) $[\mathrm{Be(NCBu_2)} - \mathrm{H}]^+$; 146 (100) $[\mathrm{NH(SiMe_3)_2} - \mathrm{Me}]^+$; 141 (0.5) $[\mathrm{HNCBu_2}]^+$; 130 (6) $[\mathrm{N(SiMe_3)_2} - \mathrm{2Me}]^+$; 84 (11) $[\mathrm{HNCBu}]^+$; and 57 (13) Bu^+

Crystallographic Study of $[\mathrm{Be(N{=}CBu^t{}_2)_2}]_2$.—The compound crystallized from hexane solution as pale yellow crystals elongated along *c*. The crystal used for data collection had dimensions 0.4 × 0.35 × 0.6 mm and was sealed in a thin-walled capillary tube in an atmosphere of dry nitrogen.

Crystal data. $\mathrm{C_{36}H_{72}Be_2N_4}$, $M = 579.9$, Monoclinic, $a = 17.765(1)$, $b = 15.261(1)$, $c = 16.915(1)$ Å, $\beta = 118.52(1)°$, $U = 4\,032$ Å^3, $D_m = 0.94$—0.96, $Z = 4$, $D_c = 0.95$ g cm^{-3}, $\mu = 0.58$ cm^{-1} for Mo-K_α radiation, $\lambda = 0.710\,69$ Å, space group $C2/c$ or Cc, the centrosymmetric space group being chosen on the basis of the structure determination.

The intensity data were collected on a Hilger and Watts diffractometer using zirconium-filtered molybdenum radiation and a θ—2θ scan. Two sets of equivalent reflections were recorded to the limit of $\theta = 20°$. Some reflections in the range $20 < \theta \leqslant 22.5°$ were also recorded but the intensities were found to have decreased sharply and the data collection was terminated. The intensities were corrected for Lorentz and polarization effects and 1 351 independent reflections were classed as observed having net counts $>2\sigma$. The unit-cell dimensions were obtained by a least-squares treatment of the positions of 12 high-order reflections.

Structure determination and refinement. A partial interpretation of the Patterson function, on the basis of the centrosymmetric space group, yielded the positions of seven atoms, namely the beryllium, two nitrogen, and four carbon atoms. The positions of the remaining non-hydrogen atoms were found from successive difference-Fourier syntheses. One such map showed six peaks of similar height near the tertiary carbon atom C(16) indicating that the t-butyl group was disordered and this feature was represented by placing six carbon atoms at the peak sites, each with an occupation factor of 0.5. None of the hydrogen atoms was located, presumably due to the considerable thermal motion of the methyl carbon atoms. The atomic parameters were refined by full-matrix least-squares methods and with anisotropic thermal parameters for all the atoms the final value of R was 0.127 for the 1 351 observed reflections. In the final difference map the largest peak had a height of 0.4 e Å^{-3}.

Parameter shifts in the final cycle of refinement were all $<0.3\sigma$. The weighting scheme was given by $w^{\frac{1}{2}} = 2N/|F_o|[T + g^2B + (0.06N)^2]^{\frac{1}{2}}$, where N is the net count and g is the ratio of the time spent measuring the total count (T) to that spent measuring the two backgrounds whose sum is B. Unobserved reflections were given zero weight and the scattering factors were taken from ref. 31. The atomic positional parameters are shown in Table 2 and the thermal parameters and structure factors are listed in Supplementary Publication No. SUP 22370 (9 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.