Addition of Organoberyllium Hydrides to Some Cyanides

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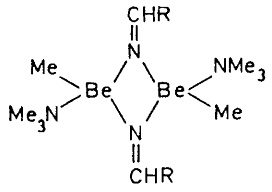
Methylberyllium hydride in trimethylamine rapidly adds to organic cyanides yielding dimeric methyleneamino-complexes [Me(RCH=N)Be,NMe$_3$]$_2$ (R = Bu^t, Ph, *o*-MeC$_6$H$_4$, or *m*-MeC$_6$H$_4$). Pyridine replaces trimethylamine in benzylideneamino(methyl)beryllium without cleaving the Be$_2$N$_2$ ring, giving (MeBeN=CHPh,py)$_2$. t-Butylberyllium hydride behaves similarly giving [Bu^t(RCH=N)Be,py]$_2$. With the latter further addition does not occur. Di-t-butylberyllium forms 2:1 co-ordination complexes with PhCN, rather than reducing the carbon–nitrogen triple bond.

Reduction of methyl cyanide with dimethylaluminium hydride gives ethylideneaminodimethylaluminium, (MeCH=NAlMe$_2$)$_2$, formulated with an Al$_2$N$_2$ ring, and many examples of this type of complex have been studied.[1] Beryllium compounds of the types (R$_2$C=NBeCl)$_2$ and [(R$_2$C=N)$_2$Be]$_2$ have also been prepared, and usually they are dimeric. However, (Ph$_2$C=N)$_2$Be is insoluble and may be polymeric; in general they were formulated with Be$_2$N$_2$ rings.[2] The *p*-tolyl compound is exceptional in being trimeric, [(*p*-tolyl$_2$C=N)$_2$Be]$_3$.[3] We now report briefly on the products resulting from addition of methyl- and t-butyl-beryllium hydrides (as diethyl ether or trimethylamine complexes) to some cyanides. When an alkylberyllium hydride is used in the form of its ether complex, no products were obtained that could be purified. Ether can in many instances be removed easily from beryllium complexes, *e.g.* by heating under reduced pressure, and in the case of the addition of methylberyllium hydride to phenyl cyanide an oily product was obtained whose molecular weight (cryoscopically in benzene) after heating the oil was a little over 2000. Though the beryllium content of this material was correct for the addition product, (MeBeN=CHPh)$_n$, whose i.r. spectrum contained four absorptions in the 1630—1650 cm^{-1} region appropriate for ν(C=N), and acid hydrolysis yielded benzaldehyde, the hydrolysable methyl content was less than half that expected, suggesting that some CH$_3$—Be addition to C=N bonds had occurred. No amine, however, could be detected in the hydrolysate, only beryllium sulphate, methane, and benzaldehyde.

The i.r. absorptions in the complexes we report due to ν(C=N) are comparable with those found earlier[3] for bridging as opposed to terminal ν(C=N).

In contrast, addition of an excess of trimethylamine gives yellow crystalline benzylideneamino(methyl)beryllium trimethylamine dimer, a result of Be—H addition to the cyanide group (I; R = Ph). This is the first example of an N=CHR group (as opposed to an N=CR$_2$ group) bridging two beryllium atoms. Four different types of *cis–trans* isomers are possible for (I); however we have no evidence that more than one was ever isolated. The alkylberyllium amide evolves trimethylamine, 1·75 mol per mole (I), when heated, and the resulting oil must contain 0·25 molecules of trimethylamine per dimer unit, possibly as a chain-ending oligomer. We were unable to remove all of the base.



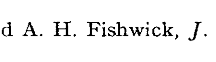
(I)

o- and *m*-Toluonitrile react similarly, giving [Me(RCH=N)Be,NMe$_3$]$_2$ where R = *o*-tolyl or *m*-tolyl, respectively. Neither the *ortho*- nor the *meta*-substituents would increase the steric congestion about the MeBe or aryl groups sufficiently to prevent association, nor did the solubility increase appreciably.

The reaction of 2,2′-bipyridyl with the dimeric methyl-(*m*-methylbenzylideneamino)beryllium–trimethylamine complex yields bipyridyldimethylberyllium, which resembles the disproportionation of methylberyllium dimethylamide upon addition of the base, yielding Me$_2$Be,bipy.[4]

Not surprisingly, trimethylamine in (I; R = Ph) may be replaced by pyridine giving the pyridine dimer, which is thermally stable to at least 165 °C in contrast to the trimethylamine and ether complexes. Isolation of the pyridine dimer suggests that the lone pair of electrons on the azomethine-nitrogen atom is a better base to beryllium than that of the pyridine nitrogen atom.

Pivalonitrile (2,2-dimethylpropanenitrile) reacts with methylberyllium hydride to yield methyl(neopentylideneamino)beryllium which was isolated as the pyridine-containing dimer (II; L = py, R = Me). The dimer fails to react with another molar equivalent of hydride, perhaps on account of steric hindrance about the



(II)

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[2] C. Summerford, K. Wade, and B. K. Wyatt, *J. Chem. Soc.* (*A*), 1970, 2016.

[3] C. Summerford, K. Wade, and B. K. Wyatt, *Chem. Comm.*, 1969, 61.

[4] G. E. Coates and A. H. Fishwick, *J. Chem. Soc.* (*A*), 1967, 1199.

carbon–nitrogen double bond as MeBeH readily reduces PhCH=NPh in ether giving [PhCH$_2$(Ph)NBeMe]$_2$.[5]

The Be—H bond of t-butylberyllium hydride adds to the carbon–nitrogen triple bond in pivalonitrile in diethyl ether to give a liquid. Addition of trimethylamine gives dimeric (II; L = NMe$_3$, R = Bu^t). Trimethylamine is replaced by pyridine, yielding (II; L = py, R = Bu^t). The hydride also adds to benzonitrile giving benzylideneamino(t-butyl)beryllium as the pyridine complex, and this is dimeric in benzene solution.

In view of the existence of 1 : 1 co-ordination complexes of di-t-butylberyllium and t-butylberyllium chloride with pivalonitrile [6] it is noteworthy that dimethylberyllium dissolves in a toluene solution of pivalonitrile, though upon removal of volatile matter under reduced pressure dimethylberyllium is recovered. The heat of depolymerization of dimethylberyllium (heat of vaporization 98·3 kJ mol^{-1} of monomer) [7] is therefore similar to the heat of complexation. That this result is not entirely due to steric congestion about the beryllium atom in a hypothetical 2 : 1 complex, *viz.* Me$_2$Be(NCBu^t)$_2$ is shown by way of example, by isolation of the red monomeric Bu$^t_2$Be(NCPh)$_2$.

Though we could not isolate a crystalline product, addition of Be—C bonds in Me$_2$Be to benzonitrile is indicated by our isolation of acetophenone upon hydrolysis. This is the only instance we have noted of addition of a Be—C bond to a cyanide.

EXPERIMENTAL

All manipulations were carried out with careful exclusion of air and moisture by use of Schlenk tube, vacuum-line, and glove-box techniques. Compounds were analysed by cautious hydrolysis, beginning with 2-methoxyethanol at low temperature, followed by quantitative separation and measurement of volatile materials and volumetric determination of beryllium by the fluoride method [8] under standardized conditions. Molecular weights were determined cryoscopically in benzene. The compounds described below are very sensitive to air and water, and to minimize the number of transfers from one vessel to another, *e.g.* for weighing, yields were not recorded. Except for transfer and recrystallization losses, yields appeared to be nearly quantitative. 2,4-Dinitrophenylhydrazone derivatives of the aldehyde obtained by hydrolysis of the iminoberyllium compounds were made in all cases, and were identified by their melting points.[9] I.r. data were collected (Nujol mulls) on Beckman IR 10 and Perkin-Elmer 621 spectrophotometers. I.r. data are reported only when the compound does not melt without decomposition and such data are thus needed for identification, or when the bands are significant in the context of this study; *i.e.* ν(C=N).

Benzylideneamino(methyl)beryllium–Trimethylamine, [PhCH=N(Me)Be,NMe$_3$]$_2$.—A solution of the methylberyllium hydride–diethyl ether complex [10] (10 mmol) in toluene was placed in a Schlenk tube. Trimethylamine (2 ml) was condensed onto it, and the mixture was allowed to warm to room temperature and was stirred for 2 h. This mixture was then cooled in liquid nitrogen and benzonitrile (10 mmol) was added. This was allowed to warm to room temperature with stirring (2 h). After evaporation of all volatile material under vacuum, the residue was crystallized from benzene as a yellow crystalline *dimer*, m.p. 127—131° (decomp. with gas evolution) [Found: Be, 4·85; hydrolysable methyl, 8·15%; *M* (0·49 and 0·74 wt. %), 384 and 386. C$_{22}$H$_{36}$Be$_2$N$_4$ requires Be, 4·82; hydrolysable methyl, 8·03%; *M*, 374]. The i.r. spectrum contained absorptions at 2728m, 1966w, 1890w, 1822w, 1690m, 1653s, 1648s, 1618m, 1593m, 1577s, 1488m, 1474s, 1308m, 1284m, 1244s, 1228m, 1180s, 1105m, 1100m, 1070m, 1021w, 1005s, 1000s, 960m, 910w, 856s, 827m, 772s, 720s, and 692s cm^{-1}. Hydrolysis with dilute acid gave benzaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 237° (lit.,[9] 239°).

Methyl(m-*methylbenzylideneamino*)*beryllium–Trimethylamine*, [Me(*m*-C$_6$H$_4$CH=N)Be,NMe$_3$]$_2$.—This was similarly prepared, from *m*-toluonitrile, and crystallized from benzene as yellow *prisms*, m.p. 133—136° (decomp. with gas evolution) [Found: Be, 4·45; hydrolysable methyl, 7·50%; *M* (1·18 and 1·77 wt. %), 416 and 403. C$_{24}$H$_{40}$Be$_2$N$_4$ requires Be, 4·48; hydrolysable methyl, 7·47%; *M*, 402]. The i.r. spectrum contained absorptions at 2710m, 1900w, 1825,w 1750w, 1647s, 1600w, 1580m, 1278s, 1238s, 1225sh, 1171s, 1148s, 1092s, 1080sh, 990s, 956m, 900m, 870m, 830m, 760m, 700m, and 680w cm^{-1}. Hydrolysis with dilute acid gave 3-methylbenzaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 194° (lit.,[9] 195°).

Methyl(o-*methylbenzylideneamino*)*beryllium–Trimethylamine*, [Me(*o*-MeC$_6$H$_4$CH=N)Be,NMe$_3$]$_2$.—This was similarly prepared, from *o*-toluonitrile, and crystallized from benzene as yellow *prisms*, m.p. 137—139° (decomp. with gas evolution) [Found: Be, 4·45; hydrolysable methyl, 7·30%; *M* (0·95 and 1·43 wt. %), 410 and 409. C$_{24}$H$_{40}$Be$_2$N$_4$ requires Be, 4·48; hydrolysable methyl, 7·47%; *M*, 402]. The i.r. spectrum contained absorptions at 2798m, 2770w, 1970w, 1926w, 1952w, 1837w, 1693w, 1655sh, 1640s, 1649s, 1478s, 1406m, 1375s, 1282m, 1244m, 1230w, 1208m, 1174s, 1151m, 1108sh, 1101m, 1048w, 1031w, 1004s, 967m, 871m, 855s, 830m, 818s, 783s, 758s, 728s, and 710m cm^{-1}. Hydrolysis with dilute acid gave 2-methylbenzaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 193° (lit.,[9] 194°).

Benzylideneamino(methyl)beryllium–Pyridine, PhCH=N-(Me)Be,py.—A solution of the methylberyllium hydride–diethylether complex (15·76 mmol) in toluene was placed in a Schlenk tube. Benzonitrile (15·76 mmol) was added to the cooled (−78°) toluene solution, which was allowed to warm to room temperature and was then stirred for 2 h. The solution was cooled to −78° and pyridine (15·76 mmol) was added. After 2 h with stirring at room temperature, evaporation of all volatile material under vacuum yielded a residue which was crystallized from a large amount of benzene as cream coloured crystals, m.p. 162—163° (Found: Be, 4·35; hydrolysable methyl, 7·20%. C$_{26}$H$_{28}$Be$_2$N$_4$ requires Be, 4·35; hydrolysable methyl, 7·25%). The i.r. spectrum contained absorptions at 1688m, 1653s, and 1603s cm^{-1}. Hydrolysis with dilute acid gave benzaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 237° (lit.,[9] 239°).

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[7] G. E. Coates, F. Glockling, and N. D. Huck, *J. Chem. Soc.*, 1952, 4496.

[8] D. A. Everest, 'The Chemistry of Beryllium,' Elsevier, Amsterdam, 1964, p. 120.

[9] N. D. Cheronis, J. B. Entrikin, and E. M. Hodnett, 'Semimicro Qualitative Organic Analysis,' Interscience, New York, 1965.

[10] N. A. Bell and G. E. Coates, *Proc. Chem. Soc.*, 1964, 59; *J. Chem. Soc.*, 1964, 692.

Methyl(neopentylideneamino)beryllium–Pyridine, [Me(Bu^{t}CH=N)Be,py]$_2$.—This was similarly prepared from pivalonitrile and crystallized from benzene as yellow *prisms*, m.p. 127—129° [Found: Be, 4·90; hydrolysable methyl, 8·00%; *M* (1·06 and 1·59 wt. %), 344 and 369. $C_{22}H_{36}Be_2N_4$ requires Be, 4·82; hydrolysable methyl, 8·02%; *M*, 374]. The i.r. spectrum contained absorptions at 1682s, 1650sh, and 1603s cm^{-1}. Hydrolysis with dilute acid gave pivaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 208° (lit.,[9] 209°).

Benzylideneamino(t-butyl)beryllium–Pyridine, [PhCH=N(Bu^t)Be,py]$_2$.—This was similarly prepared from t-butylberyllium hydride [11] and benzonitrile, and crystallized from benzene as yellow *prisms*, m.p. 177—179° (decomp.) [Found: Be, 3·65; hydrolysable butyl, 26·3%; *M* (0·61 and 0·92 wt. %), 442 and 499. $C_{32}H_{40}Be_2N_4$ requires Be, 3·61; hydrolysable butyl 26·9%; *M*, 498]. The i.r. spectrum contained absorptions at 2738m, 1640s, 1601m, 1590w, 1575m, 1482m, 1441s, 1302w, 1208m, 1190m, 1150w, 1063m, 1046m, 1024w, 1011w, 1001w, 992w, 981w, 955w, 948w, 838m, 809m, 764w, 741s, 718s, 700s, 690s, 677m, 644w, 630w, 610w, and 595m cm^{-1}. Hydrolysis with dilute acid gave benzaldehyde: 2,4-dinitrophenylhydrazone derivative, m.p. 235° (lit.,[9] 239°).

t-Butyl(neopentylideneamino)beryllium–Pyridine, [Bu^t(Bu^{t}CH=N)Be,py]$_2$.—This was similarly prepared, from t-butylberyllium hydride and pivalonitrile, and crystallized from hexane as yellow *prisms*, m.p. 124—126° [Found: Be, 4·00; hydrolysable butyl, 25·3%; *M* (0·71 and 1·06 wt. %), 436 and 442. $C_{28}H_{48}Be_2N_4$ requires Be, 3·94; hydrolysable butyl, 24·9%; *M*, 458]. The i.r. spectrum contained absorptions at 1670s, 1655s, and 1610s cm^{-1}. Hydrolysis with dilute acid gave pivaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 208° (lit.,[9] 209°).

Reaction of Methyl(m-*methylbenzylideneamino*)*beryllium–Trimethylamine with* 2,2′-*Bipyridyl*.—2,2′-Bipyridyl (bipy) (2·5 g, 16 mmol) in toluene (10 ml) was added to [Me(*m*-MeC$_6$H$_4$CH=N)Be,NMe$_3$]$_2$ (8 mmol) in toluene (10 ml) which had previously been cooled in liquid nitrogen. This was allowed to warm to room temperature and was stirred for 1 h. Upon heating to *ca.* 60° the orange-red solution produced a yellow precipitate, which was recrystallized from benzene, in which it is sparingly soluble, m.p. 160—170° (decomp.) [Found: Be, 4·65; hydrolysable methyl, 14·9%; Calc. for Me$_2$Be(bipy) [12] ($C_{12}H_{14}$-BeN_2): Be, 4·62; hydrolysable methyl, 15·4%].

Pyrolysis of Benzylideneamino(methyl)beryllium Trimethylamine and Ether Complexes.—A sample of [Me(*o*-MeC$_6$H$_4$-CH=N)Be,NMe$_3$]$_2$ was heated to 150° for 30 min under vacuum and the evolved gas measured and analysed. Trimethylamine (1·75 mol per mole of starting compound) was evolved. The ether complex of PhCH=N(Me)Be (an oil) was heated to 100° for 1 h under vacuum (until no further gas evolution was observed). The residue was analysed [Found: Be, 6·0; hydrolysable methyl, 4·1%; *M* (0·98 and 3·96 wt. %), 2030 and 2100. Calc. for unsolvated benzylideneamino(methyl)beryllium, $C_9H_{11}BeN$: Be, 6·3, hydrolysable methyl, 10·0%. The i.r. spectrum of the pyrolysis product of the benzylideneamino(methyl)beryllium ether complex contained absorptions at 1654sh, 1648sh, 1640s, and 1628sh cm^{-1}. Hydrolysis of the oil with dilute acid gave benzaldehyde: 2,4-dinitrophenylhydrazone derivative, m.p. 233° (lit.,[8] 239°).

Reaction of Methylberyllium Hydride–Ether with Pivalonitrile.—Methylberyllium hydride (6·8 mmol) in benzene was cooled to −78°. Pivalonitrile (6·8 mmol) in benzene was added. This was warmed to room temperature and stirred for 2 h. All volatile materials were removed leaving a colourless oil. All attempts to crystallize the substance failed using benzene or hexane or mixtures of these. Hydrolysis of the oil with dilute acid gave pivaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 205° (lit.,[8] 209°).

Reaction of Methylberyllium Hydride–Ether with Benzonitrile.—Methylberyllium hydride (4·76 mmol) in toluene was cooled to −78°. Benzonitrile (0·49 ml, 4·76 mmol) was added. The mixture was allowed to warm to room temperature and was stirred for 2 h. All volatile materials were removed leaving a colourless oil. All attempts to crystallize the product failed using hexane, benzene, or mixtures of these. After 2 h at reduced pressure (10^{-3} mmHg) an oily cream-coloured solid was obtained. Hydrolysis of this solid with dilute acid gave benzaldehyde; 2,4-dinitrophenylhydrazone derivative, m.p. 237° (lit.,[8] 239°).

Reaction of t-Butylberyllium Hydride–Ether with Pivalonitrile, then Trimethylamine.—Bu^{t}BeH,Et$_2$O (7·93 mmol) in hexane was cooled to −78°. Bu^{t}CN (7·93 mmol) in hexane was added and the mixture was allowed to warm to room temperature with stirring. As it warmed the clear colourless solution turned cloudy and light yellow. On gentle warming the solution became clear and colourless. All solvent was removed, leaving a colourless oil which was miscible with benzene. All attempts to crystallize the product from hexane failed. Trimethylamine (2 ml) was condensed onto the compound, but all attempts to obtain a crystalline product failed. {*Note:* Pyridine was subsequently added and [Bu^{t}CH=N(Bu^t)Be,py]$_2$ was obtained.}

Reaction of t-Butylberyllium Hydride–Ether with an Excess of Pivalonitrile.—Bu^{t}BeH,Et$_2$O (10·4 mmol) in hexane was cooled to −196°. Pivalonitrile (20·8 mmol) was added. This was allowed to warm to room temperature and was stirred for 2 h. The solvent was removed. All attempts to obtain crystals from the resulting colourless oil failed. Pyridine was added and crystalline [Bu^{t}CH=N(Bu^t)Be,py]$_2$ was then obtained.

Reaction of t-Butylberyllium Hydride–Ether with an Excess of Benzonitrile.—Bu^{t}BeH,Et$_2$O (10·4 mmol) in hexane was cooled to −196°. Benzonitrile (10% excess) was added. This was allowed to warm to room temperature and was stirred for 2 h. A yellow solid was obtained. Attempts were made to crystallize this from benzene but only an oil resulted. Pyridine was then added yielding crystalline [PhCH=N(Bu^t)Be,py]$_2$.

Reaction of Dimethylberyllium with Pivalonitrile.—Dimethylberyllium (10 mmol) was placed in a Schlenk tube and toluene (5 ml) was added. At −197° pivalonitrile (10 mmol) was added. The solution was allowed to warm to room temperature with stirring. The resulting solution was clear and colourless. The solvent was removed and a white insoluble product was obtained. This white solid could again be dissolved in toluene, benzene, or hexane containing pivalonitrile. Again the white solid could be obtained when the solvent (and pivalonitrile) was removed. The white solid was believed to be dimethylberyllium which formed a weak complex in solution with pivalonitrile.

Reaction of Dimethylberyllium with Benzonitrile.—Dimethylberyllium (17·2 mmol) was placed in a Schlenk tube, followed by toluene (5 ml). The tube was cooled to −78°

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[11] U. Blindheim, G. E. Coates, and R. C. Srivastava, *J.C.S. Dalton*, 1972, 2302.

[12] G. E. Coates and S. I. E. Green, *J. Chem. Soc.*, 1962, 3340.

and benzonitrile (17·2 mmol) was added. This was allowed to warm to room temperature and was stirred for 2 h. The solution was slightly yellow. All attempts to crystallize the substance failed. No crystals could be obtained in the presence of bases (NMe_3,py). Hydrolysis of the oil with dilute acid gave acetophenone; 2,4-dinitrophenylhydrazone derivative, m.p. 239° (lit.,[8] 238°).

Di-t-butylberyllium–Bisbenzonitrile, $Bu^t_2Be(NCPh)_2$.—To di-t-butylberyllium-ether (1·073 g, 5·45 mmol) in a Schlenk tube hexane (5 ml) was added, and the tube was cooled to −78°. Benzonitrile (1·12 ml, 10·90 mmol) was added. The solution was allowed to warm to room temperature and was stirred for 2 h. A yellow precipitate formed. The mixture was gently warmed until all the solid had dissolved. The solution was allowed to stand overnight while orange-red *crystals* formed, m.p. 64—65° [Found: Be, 2·90; hydrolysable butyl, 33·2%; *M* (2·02 and 3·02 wt. %), 310 and 300. $C_{22}H_{28}BeN_2$ requires Be, 2·74; hydrolysable butyl, 34·6%; *M*, 329]. The i.r. spectrum contained an absorption at 2278 cm^{-1}.

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