The Preparation of Beryllium Diaryls by Exchange Reactions: Diarylberyllium Co-ordination Complexes

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Diphenylberyllium is formed in high yield by exchange between diethylberyllium and either triphenylborane or diphenylmercury. Other diaryls R_2Be (R = *o*-tolyl, *m*-tolyl, *p*-xylyl, *p*-chlorophenyl, and 1-naphthyl) have been prepared by exchange with appropriate triarylboranes. The first three listed are dimeric in benzene, the others being practically insoluble. The diethylberyllium–R_3B exchange procedure did not yield the desired beryllium compounds when R was benzyl, mesityl, isopropyl, cyclopentyl, cyclohexyl, or pentafluorophenyl.

Co-ordination complexes described include the *N,N,N',N'*-tetramethylethylenediamine complexes of di-*o*-tolyl-, di-*m*-tolyl-, di-*p*-xylyl-, and bispentafluorophenyl-beryllium, the bispyridine complexes of di-*o*-tolyl-, di-*m*-tolyl-, di-1-naphthyl-, and bispentafluorophenyl-beryllium, dibenzylberyllium–diethyl ether, di-*o*-tolylberyllium–trimethylamine, dimesitylberyllium–trimethylamine, and di-m-tolylberyllium–1,2-dimethoxyethane. Lithium tri-*o*-tolylberyllate has been prepared.

BERYLLIUM diaryls (R_2Be; R = Ph, *p*-tolyl) have been known since 1927,[1] having been prepared by heating beryllium with the appropriate diarylmercury. The preparation of diphenylberyllium by this method has been described independently in three other laboratories.[2-4] Recently it has been stated that this method yields a grossly impure product, and the reaction of phenyl-lithium with beryllium chloride in diethyl ether was recommended as the method of choice.[5] However, the latter reaction gives the ether complex of diphenylberyllium, not the base-free diaryl.

Since we had occasion to prepare certain base-free beryllium dialkyls by exchange reactions between diethylberyllium and trialkylboranes,[6] we have studied the extension of this method to the preparation of base-free beryllium diaryls. Diphenylberyllium was obtained in high yield from diethylberyllium and triphenylborane,

$$3Et_2Be + 2Ph_3B \longrightarrow 2Et_3B + 3Ph_2Be$$

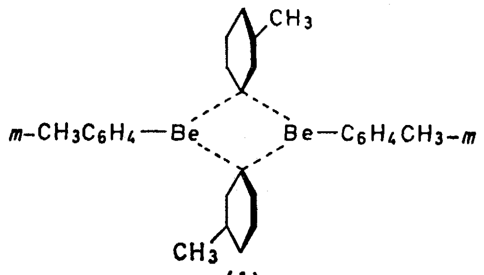
and also from diethylberyllium and diphenylmercury:

$$Et_2Be + Ph_2Hg \longrightarrow Et_2Hg + Ph_2Be$$

The products had i.r. spectra identical to that of diphenylberyllium prepared from beryllium and diphenylmercury.

No structural information is available about diphenylberyllium, whose sparing solubility in benzene may be due to a polymeric constitution in the crystalline state or to very good crystal packing of an oligomer of high symmetry. Having applied the diethylberyllium–triarylborane procedure to the preparation of R_2Be (R = *p*-C_6H_4Cl, *o*-C_6H_4Me, *m*-C_6H_4Me, 2,5-$C_6H_3Me_2$, and 1-naphthyl), we found that the *ortho*- and *meta*-tolyls and the xylyl are sufficiently soluble in benzene to allow their molecular weights to be determined cryoscopically. They are all dimeric in benzene and thus are formulated (I; *m*-tolyl$_2$Be).

Di-*p*-chlorophenylberyllium is insoluble in benzene, but dissolves slowly in diethyl ether, whereas di-1-naphthylberyllium dissolves neither in benzene nor in ether nor in a mixture of benzene and *N,N,N',N'*-tetramethylethylenediamine. However, it reacts with pyridine forming a yellow complex, $(1\text{-}C_{10}H_7)_2Be(py)_2$.



(I)

The ether complex of dibenzylberyllium may be prepared from benzylmagnesium chloride and beryllium chloride, and the ether is retained even after several distillations at *ca.* 10^{-3} mmHg. The ^1H n.m.r. spectrum (100 MHz, with benzene as solvent and internal reference) of this complex is unusual since the single Be–CH_2 resonance at τ 8·25 is the lowest recorded for protons bound to carbon itself bound to beryllium. The resonances of the ethyl groups are normal. Attempts to prepare ether-free dibenzylberyllium failed, *e.g.* unchanged tribenzylborane was recovered from an attempted exchange with diethylberyllium, and bibenzyl was obtained in high yield when dibenzylmercury was heated with beryllium. There was no evidence of exchange when diethylberyllium was warmed either with dibenzylmercury or with dibenzylborinic anhydride, $(Bz_2B)_2O$.

Whereas tri-*o*-tolylborane undergoes exchange with diethylberyllium, trimesitylborane does not, presumably on account of the greater steric hindrance in the latter case. We also assume that steric hindrance prevents exchange between diethylberyllium and tri-isopropyl-, tricyclopentyl-, and tricyclohexyl-borane. In none of these instances was any triethylborane detected.

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The bistrimethylamine complex of diphenylberyllium has an appreciable dissociation pressure of the amine even at 0°, and the usual procedure for isolating the complex gives a product in which the Be : amine ratio is between 1 and 2. The relative instability of the bisamine complex is due to steric hindrance, but diphenylberyllium forms complexes with chelating ligands such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[4] As expected, the more sterically hindered di-*o*-tolyl- and dimesityl-beryllium formed 1 : 1 complexes with trimethylamine, with no indication of the formation of bisamine complexes when the amine was present in excess.

N,*N*,*N*′,*N*′-Tetramethylethylenediamine complexes of R_2Be (R = *o*-tolyl, *m*-tolyl, and 2,5-dimethylphenyl) are described in the Experimental section, as are the pyridine complexes $R_2Be(py)_2$ (R = *o*-tolyl, *m*-tolyl, 1-naphthyl). We also prepared one 1,2-dimethoxyethane complex, that of di-*m*-tolylberyllium, and one lithium derivative, $Li(o\text{-tolyl})_3Be$, analogous to the phenyl compound, $LiPh_3Be$.[7]

EXPERIMENTAL

All manipulations were carried out with careful exclusion of air and moisture by use of Schlenck tube, vacuum-line, and glove-box techniques. M.p.s were taken in sealed tubes under argon. Compounds were analysed by cautious hydrolysis followed by volumetric determination of beryllium by the fluoride method[8] under standardised conditions. The hydrocarbon product was evaporated under reduced pressure, separated from water by passage through a tube containing magnesium perchlorate, and weighed. Most of the compounds described below are sensitive to air and water, and to minimise the number of transfers from one vessel to another, *e.g.* for weighing, yields were in general not recorded. Yields appeared to be nearly quantitative apart from transfer losses, and similar to those quoted for the preparations of diphenylberyllium.

Diethylberyllium was prepared by a modification of Ashby and Arnott's method,[5] in that better yields were obtained (with less decomposition) if the reaction mixture of diethylmercury and beryllium was heated at 80—90° for 60 h.

Diphenylberyllium.—(a) *from beryllium and diphenylmercury*. Beryllium metal powder (0·30 g, previously activated by stirring with a dilute solution of diethylberyllium in ether) was stirred magnetically with diphenylmercury (10·2 g) in xylene (25 ml) in an evacuated sealed tube for 180 h at 140°. Separation of mercury was apparent after *ca*. 15 h. After the tube had cooled, it was opened (glove-box) and the contents were transferred to a double Schlenck tube. Solvent was then filtered off from the grey solid, and the latter was then extracted with benzene (100 ml) yielding crystalline diphenylberyllium (3·8 g, 82%), m.p. 249—251° (lit.,[4] 248—250°) (Found: Be, 5·5. Calc. for $C_{12}H_{10}Be$: Be, 5·5%).

(b) *From diethylberyllium and diphenylmercury*. Diphenylmercury (2·6 g, 7·3 mmol) and diethylberyllium (0·49 g, 7·3 mmol) in xylene (5 ml) were stirred at 90°. A white precipitate slowly formed. After 15 h the xylene was evaporated and the residue was washed with hexane. The product (0·94 g, 78%) had an i.r. spectrum identical with that of the previous preparation. Diethylmercury was recovered from the filtrate.

(c) *From diethylberyllium and triphenylborane*. Diethylberyllium (1·45 g, 21·6 mmol) and triphenylborane (3·50 g, 14·5 mmol) were mixed and after 36 h at room temperature triethylborane (1·10 g, 77·5%) was evaporated. Benzene (5 ml) was added to the residue and the mixture was stirred for 10 h while boiling at atmospheric pressure under reflux. When the mixture had cooled, the solid product was separated by filtration, and washed with benzene (2 × 5 ml) giving diphenylberyllium (3·10 g, 88%), m.p. 248—250°. The i.r. spectrum was identical to that of the other preparations.

Di-p-*chlorophenylberyllium*.—This compound was prepared by method (c), from tri-*p*-chlorophenylborane.[9] The *product* did not melt, but decomposed above 300° [Found: Be, 4·0; chlorophenyl (as chlorobenzene), 95·7%. $C_{12}H_8BeCl_2$ requires Be, 3·9; chlorophenyl, 96·1%].

Di-m-*tolylberyllium*.—Tri-*m*-tolylborane[10] (2·48 g) was mixed with diethylberyllium (0·88 g). After 72 h at 25° 70% of the theoretical amount of triethylborane had been collected. The residue was then stirred with toluene (5 ml) for 10 h at 90°. After evaporation of all volatile material the residue was washed with hexane and recrystallised from benzene–hexane. The product had m.p. 168—170° [Found: Be, 4·8; tolyl, 94·5%; *M* (cryoscopic, 0·83 and 1·18 wt. % in benzene), 384 and 374. $C_{28}H_{28}Be_2$ requires Be, 4·7; tolyl, 95·3; *M*, 382].

Di-o-*tolylberyllium*.—This compound was similarly prepared from tri-*o*-tolylborane,[10] and had m.p. 215—217° [Found: Be, 4·75; tolyl, 94·0%; *M* (cryoscopic, 0·56 and 0·84 wt. % in benzene), 380 and 388. $C_{28}H_{28}Be_2$ requires Be, 4·7; tolyl, 95·3; *M*, 382].

Di-p-*xylylberyllium*.—This compound was similarly prepared from tri-*p*-xylylborane,[11] and had m.p. 158—160° (it solidified to a glass) [Found: Be, 4·3; xylyl, 95·0%; *M* (cryoscopic, 0·72 and 1·08 wt. % in benzene), 417 and 424. $C_{32}H_{36}Be_2$ requires Be, 4·1; xylyl, 95·9%; *M*, 438].

*Di-*1*-naphthylberyllium*.—Diethylberyllium (0·59 g), tri-1-naphthylborane[12] (2·3 g), and toluene (5 ml) were stirred for 48 h at 100°. After removal of all volatile material the residual product was washed with warm benzene, and had m.p. 255—258° (decomp.) (Found: Be, 3·5; naphthyl, 95·2%. $C_{20}H_{14}Be$ requires Be, 3·4; naphthyl, 96·6%).

Co-ordination Complexes of Beryllium Diaryls.—*Dimesitylberyllium–trimethylamine*. Mesitylmagnesium bromide (from mesityl bromide, 18·5 g) in diethyl ether (200 ml) was added dropwise to the diethyl ether complex of beryllium chloride (10·0 g) in ether (50 ml). After the addition was completed, the mixture was boiled with reflux for 5 h. The solution was then decanted from solid matter and solvent was removed by evaporation. The white residue was sublimed at 140—150° (10^{-3} mmHg). The sublimate had m.p. 175—178°, and the ratio Be : Et_2O was 1 : 0·70. In an attempt to remove ether from the product, it was heated at 90° for 3 days *in vacuo* but the Be : Et_2O ratio was then 1 : 0·68.

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The product (0·70 g) was dissolved in benzene (5 ml), trimethylamine in excess was added, and the mixture was stirred for ½ h; volatile material was then removed. The residue crystallised from benzene–hexane as *needles*, m.p. 130—132° (the melt then solidified to a glass) [Found: Be, 3·1; Me_3N, 18·9%; *M* (cryoscopic, 0·85 and 1·28 wt. % in benzene), 304 and 313. $C_{21}H_{31}BeN$ requires Be, 2·94; Me_3N, 19·3%; *M*, 306].

*Di-*o*-tolylberyllium–trimethylamine.* The amine in excess was condensed at −197° on di-*o*-tolylberyllium (0·46 g) which had been dissolved in benzene (5 ml). The mixture was allowed to warm to room temperature and was then stirred ½ h. After the evaporation of all volatile material the residue crystallised from benzene–hexane as small *needles*, m.p. 198—200° [Found: Be, 3·65; tolyl, 72·0%; *M*(cryoscopic, 0·57 and 0·86 wt. % in benzene), 236 and 241. $C_{17}H_{23}BeN$ requires Be, 3·6; tolyl, 72·8%; *M*, 250].

Dibenzylberyllium–diethyl ether complex (*Preparation by* DR. B. R. FRANCIS). Benzylmagnesium chloride (2 molar proportions) in ether (250 ml) was added to beryllium chloride (22·8 g of bisdiethyl ether complex, 0·1 mol) in ether (500 ml). The supernatant liquid was decanted from magnesium chloride, and was concentrated by evaporation, finally by successive additions of 20—30 ml portions of methylcyclohexane and evaporation of volatile matter. After a final separation from magnesium chloride, evaporation yielded a viscous liquid which was transferred to a short-path distillation apparatus. At 10^{-3} mmHg and a bath temperature of 120—150° colourless *needles* collected in the receiver (−10°). There was evidence of much decomposition in the distillation vessel. The product had m.p. 50—51° [Found: Be, 3·4; diethyl ether, 27·5%; *M* (cryoscopic, 1·00 and 1·51 wt. % in benzene), 245 and 259. $C_{18}H_{24}BeO$ requires Be, 3·4; ether, 27·9%; *M*, 265].

N,N,N′,N′-*Tetramethylethylenediamine Complexes*.—(a) *With di-*o*-tolylberyllium.* Addition of the diamine in slight excess to di-*o*-tolylberyllium (0·51 g) in benzene (5 ml) resulted in perceptible heat evolution. After the solution had been stirred ½ h, volatile matter was removed and the residue was crystallised from benzene–hexane, m.p. 178—180° [Found: Be, 3·0; tolyl, 58·9% *M* (cryoscopic, 0·73 and 1·10 wt. % in benzene), 285 and 294. $C_{20}H_{30}BeN_2$ requires Be, 2·9; tolyl, 59·3%; *M*, 307].

(b) *With di-*m*-tolylberyllium.* This complex was similarly prepared and had m.p. 145—147° [Found: Be, 2·9; tolyl, 59·0%; *M* (cryoscopic, 0·59 and 0·88 wt. % in benzene), 282 and 296. $C_{20}H_{30}BeN_2$ requires Be, 2·9; tolyl, 59·3%; *M*, 307].

(c) *With di-*p*-xylylberyllium.* This complex was similarly prepared, and had m.p. 177—179° [Found: Be, 2·7; xylyl, 62·3%; *M* (cryoscopic, 0·60 and 0·90 wt. % in benzene), 317 and 325. $C_{22}H_{34}BeN_2$ requires Be, 2·7; xylyl, 62·7%; *M*, 335].

(d) *With bispentafluorophenylberyllium.* Beryllium chloride–bisdiethyl ether (7·3 g) was added to a stirred suspension of pentafluorophenyl-lithium [13] in benzene (50 ml) and ether (200 ml) at −78°. The mixture was allowed slowly to warm to room temperature, stirring being continued a further 2 h. After decantation from solids, the solution was concentrated by distillation, finally under reduced pressure, giving a light brown product which solidified in *ca.* ½ h [Found: ratio Be : Et_2O : C_6F_5, 1 : 0·70 : 1·89]. An attempt to purify a small amount of this product by short-path distillation resulted in melting at *ca.* 90° and a mild explosion at 130° (both bath temperatures).

A portion (5·5 g) of the light brown product which must in part have been $(C_6F_5)_2Be$–ether complex, was dissolved in benzene and the diamine in slight excess was added. After 15 min of stirring, volatile matter was evaporated under reduced pressure and the solid residue was crystallised from benzene–hexane to give small *needles*, which decomposed to a black tar between 123 and 126° [Found: Be, 2·1; C_6F_5, 71·9%; *M* (cryoscopic, 0·84 and 1·26 wt. % in benzene), 464 and 470. $C_{18}H_{16}BeF_{10}N_2$ requires Be, 1·96; C_6F_5, 72·8%; *M*, 459].

Pyridine Complexes.—(a) *With di-*o*-tolylberyllium.* Addition of pyridine (2 ml, an excess) to di-*o*-tolylberyllium (0·61 g) in benzene (4 ml) resulted in exothermic reaction. After removal of volatile matter the residue crystallised from benzene–hexane as *plates*, m.p. 171—173° (decomp.) [Found: Be, 2·6; tolyl, 51·9%; *M* (cryoscopic, 0·60 and 0·90 wt. % in benzene), 332 and 340. $C_{24}H_{24}BeN_2$ requires Be, 2·6; tolyl, $52{\cdot}1_5\%$; *M*, 349].

(b) *With di-*m*-tolylberyllium.* Similarly prepared, this complex had m.p. 177—179° (decomp.) [Found: Be, 2·6; tolyl, 51·7%; *M* (cryoscopic, 0·55 and 0·82 wt. % in benzene), 342 and 354. $C_{24}H_{24}BeN_2$ requires Be, 2·6; tolyl, $52{\cdot}1_5\%$, *M*, 349].

(c) *With di-*1*-naphthylberyllium.* Addition of pyridine in slight excess to a suspension of di-1-naphthylberyllium (0·48 g) in benzene (5 ml) resulted in a clear yellow solution. The *complex* crystallised when the solution was concentrated; it shrank at 115° and had m.p. 178—180° (decomp.) (Found: Be, 2·0; naphthyl, 59·1%. $C_{30}H_{24}BeN_2$ requires Be, 2·1; naphthyl, 60·4%).

(d) *With bispentafluorophenylberyllium.* A slight excess of pyridine was added to a solution of the impure bispentafluorophenylberyllium–ether complex (0·63 g) in benzene (5 ml), with slight heat evolution. The solution was concentrated until crystallisation began, warmed until all solid dissolved, and allowed to cool when the *pyridine complex* crystallised. The complex began to change colour at 150° and decomposed to a black liquid at 170° [Found: Be, 1·8; C_6F_5, 66·0%; *M* (cryoscopic, 0·76 and 1·1 wt. % in benzene), 515 and 492. $C_{22}H_{10}BeF_{10}N_2$ requires Be, 1·8; C_6F_5, 66·7%; *M*, 501].

*Di-*m*-tolylberyllium–*1,2-*Dimethoxyethane*.—The ether (0·50 g) was added to di-*m*-tolylberyllium (0·60 g) in benzene (5 ml). After evaporation of solvent, the complex crystallised from hexane as *needles*, m.p. 130—131° [Found: Be, 3·25; tolyl, 64·1% *M* (cryoscopic, 0·61 and 0·92 wt. % in benzene), 263 and 270. $C_{18}H_{24}BeO_2$ requires Be, 3·2; tolyl, 64·8%; *M*, 281].

*Lithium Tri-*o*-tolylberyllate.*—*o*-Tolyl-lithium (0·27 g, from n-butyl-lithium and *o*-bromotoluene) in diethyl ether (5 ml) was added to di-o-tolylberyllium (0·52 g) in ether (5 ml). The mixture was stirred 1 h and the ether was then removed under reduced pressure. The *complex* crystallised from ether–benzene, m.p. 210—213° (decomp.) (Found: Be, 3·0; tolyl, 94·0%. $C_{21}H_{21}BeLi$ requires Be, 3·1; tolyl, 94·5%).

Instances in which Beryllium–Boron Exchange was Not Observed.—No triethylborane was detected when diethylberyllium was heated with the following boranes for stated times and temperatures: (*a*) trimesitylborane [14] in toluene,

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110° for 48 h, (*b*) tricyclohexylborane [15] at 80—90° for 72 h, (*c*) tricyclopentylborane [16] at 60° for 80 h, (*d*) tri-isopropylborane at 80° for 48 h, (*e*) trispentafluorophenylborane [17] at 80° for 10 h.

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