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REACTIONS OF DIMETHYLBERYLLIUM AND METHYL- AND ETHYLBERYLLIUM HYDRIDES WITH SOME NITROGEN, OXYGEN AND PHOSPHORUS SYSTEMS

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Summary

The reaction of dimethylberyllium with octamethylcyclotetrasiloxane produces methyl(trimethylsilanato)beryllium which is tetrameric in solution. Dimethylberyllium reacts with 2-(β-methylaminoethyl)pyridine or dimethylphosphine liberating methane and while in the former case a pure complex was isolated, for the latter, a beryllium-phosphine complex could not be obtained. Equimolar quantities of methylberyllium hydride and 4-dimethylaminopyridine form a sparingly soluble 1:1 complex but addition of Be-H occurs when EtBeH reacts with excess ligand, as is also the case when methylberyllium hydride reacts with benzonitrile to form the tetramer $(MeBeN{=}CHPh)_4$.

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Introduction

Reaction of dimethylberyllium with donor molecules containing acidic hydrogen atoms such as amines, alcohols and thiols to form associated products[1-6] in which association occurs via the coordinatively unsaturated donor atom, have been widely studied but reactions of primary or secondary phosphines with R_2Be have hitherto not been reported. Complexes of RBeH have been reported,[7-11] particularly with nitrogen donors, in which association occurs via BeH_2Be bridges and the addition of Be-H across multiple bonds is known.[12-14] Herein we report the results of some further studies in this area.

Results and Discussion

Dimethylberyllium reacts with $(Me_2SiO)_4$ on prolonged heating in toluene resulting in cleavage of the silicon-oxygen bond as found for the reactions of Grignard and organolithium reagents with the dimethylsiloxane tetramer.[15] The product, methyl(trimethylsilanato)beryllium which is tetrameric in benzene solution, has previously been prepared from Me_2Be and Me_3SiOH.[16] Though analytical data was not reported for this compound, it was shown to be tetrameric in the solid state having the slightly distorted cubane structure,[17] proposed for several compounds of the type $(RMOR')_4$[4] and earlier confirmed by crystallographic studies on $(MeZnOMe)_4$[18].

With 2-(β-methylaminoethyl)pyridine, dimethylberyllium reacts with the liberation of methane at room temperature forming colourless crystalline $MeBe(N(Me)C_2H_4(C_5H_4N))$, which was too insoluble for molecular mass determination but which was probably dimeric like $(MeBeN(Me)C_2H_4NMe_2)_2$[1] and $(HZnN(Me)C_2H_4NMe_2)_2$, the latter being dimeric in solution[12] and the solid state[19] with the metal 4-coordinate by virtue of the formation of 4- and 5-membered chelate rings with the diamine. Though dimethylberyllium and dimethylphosphine react with the liberation of methane, it was not found possible to isolate a beryllium-phosphine complex.

Methylberyllium hydride reacts with an equimolar amount of pyridine at low temperature to form a 1:1 complex which is dimeric in solution, association occurring via a double hydrogen bridge between beryllium atoms. Addition of an excess of pyridine to methylberyllium hydride at room temperature results in the formation of an orange dihydropyridine derivative, $C_5H_6N(Me)Bepy_2$ (py = pyridine), containing no beryllium-hydrogen bonds.[13] Similarly, methylberyllium hydride forms a 1:1 complex with 4-dimethylaminopyridine which was too insoluble for its molecular mass to be determined but which is probably dimeric since it showed an infrared absorption at 1333 cm^{-1}, characteristic of νBeH_2Be.[7] Ethylberyllium hydride reacts with excess 4-dimethylaminopyridine, forming initially a white precipitate and an orange solution which on warming results in the loss of hydrogen bound to beryllium as shown by the decrease in the hydrolysable $H:C_2H_5$ ratio in solution over a period of time. After boiling the solution overnight, the hydrolysable hydrogen content of the solution was negligible. Removal of the solvent resulted in the formation of an orange-brown oil which could not be purified by crystallisation or distillation and this was probably a hydropyridine derivative by analogy with the reaction of methylberyllium hydride with excess pyridine.[13]

Addition of Be-H across the C≡N bond occurs readily. Methylberyllium hydride reacts with benzonitrile producing an oily product whose molecular mass was greater than 2000 and while the beryllium content was correct for the addition product, MeBeN=CHPh, and hydrolysis yielded benzaldehyde, the hydrolysable methyl content was much less than expected, suggesting that Me-Be addition had occurred across the C≡N link, though amine could not be detected in the hydrolysate. The trimethylamine complex of methylberyllium hydride adds to RCN to form the dimer species $(RCH{=}N(Me)BeNMe_3)_2$ (R = Ph, o-$CH_3C_6H_4$, m-$CH_3C_6H_4$).[20] We have found that slow reaction of MeBeH in ether with PhCN results in the formation of the glassy solid MeBeN=CHPh which *is tetrameric in benzene solution*. Attempts to add more than one mole of Be-H across the C≡N bond by reaction of two moles MeBeH with one mole of PhCN were unsuccessful.

Experimental

The compounds were prepared in double Schlenk tubes and transferred for infrared study and analysis in a glove-box equipped with a re-circulatory nitrogen purification system. Samples were hydrolysed in a vacuum line, initially at low temperature with 2-methoxyethanol, followed by degassed water and then dilute sulphuric acid. Methane and hydrogen were collected by a Töpler pump. If both gases were present, the mixture was burnt with excess of dry oxygen and the combustion products measured. Ethane was collected in a cold trap and measured in a standard bulb. Beryllium analyses were carried out using the tartrate-fluoride procedure.[21] Dimethylberyllium[22] and methyl- and ethylberyllium hydrides[13] were prepared by previously described methods.

Methyl(trimethylsilanato)beryllium. Dimethylberyllium (0.58 g, 15 mmol) was covered with toluene (20 cm^3) followed by the addition of octamethylcyclotetrasiloxane (0.89 g, 3 mmol) in toluene (10 cm^3) and the mixture heated under reflux for 40 hours. After cooling, the solution was filtered from excess dimethylberyllium and the solvent removed under reduced pressure leaving a white solid which was recrystallised from toluene/hexane (1:4) at -40 °C and dried *in vacuo*. m.p. 131-133 °C.

[Found: Be, 7.92; hydrolysable methyl, 13.31%; M (cryoscopically 0.77, 1.54 wt % in benzene) 451, 465. $C_{16}H_{48}Be_4O_4Si_4$ calcd.: Be, 7.98; hydrolysable methyl 13.27%; M, 452].

Methyl(2-pyridylethyl(β-methylamino)beryllium). 2-(β-methylaminoethyl)pyridine (1.36 g, 10.0 mmol) in ether (20 cm^3) was added to dimethylberyllium (0.42 g, 10.7 mmol) in ether (10 cm^3) at liquid air temperature. The solution was allowed to warm to room temperature slowly, with stirring, during which time methane was evolved and a pale yellow precipitate formed. The solution was stirred at room temperature for half an hour and then the precipitate extracted with ether yielding colourless crystals which were filtered off and dried *in vacuo*. On heating, the crystals started to turn yellow at 155 °C and melted to a red liquid at 177 °C. [Found: Be, 5.62; hydrolysable methyl, 9.51%. $C_9H_{14}BeN_2$ calcd.: Be, 5.65; hydrolysable methyl, 9.43%].

Reaction of dimethylberyllium and dimethylphosphine. Dimethylphosphine (171 Ncc, 7.6 mmol) was condensed on to dimethylberyllium (0.34 g, 8.6 mmol) and ether (1 cm^3) in a glass tube at -183 °C. The tube was sealed before allowing it to warm slowly to room temperature when all the material had dissolved. On warming to 65 °C, the solid bubbled and slowly turned liquid and the tube was maintained at this temperature for 12 hours after which time bubbling had ceased and the contents of the tube were liquid. The tube was opened and methane (140 Ncc, 6.25 mmol), identified by its infrared spectrum, was collected. It was not found possible to crystallise the product and attempts to sublime it by heating at 65 °C in a vacuum resulted in decomposition, producing dimethylberyllium as sublimate.

Methylberyllium hydride-4-dimethylaminopyridine. 4-dimethylaminopyridine (0.75 g, 6.15 mmol) in ether (50 cm^3) was added slowly to methylberyllium hydride in ether (20 cm^3 of a 0.307 mol.dm^{-3} solution, 6.15 mmol) at -78 °C. The immediate white precipitate which formed, did not dissolve either when the solution was warmed to room temperature or in benzene and so it was filtered off and dried *in vacuo*. The solid was shown to be crystalline by its X-ray powder photograph and darkened in the range 140-150 °C before melting at 152 °C to a red liquid on heating in a sealed tube under vacuum.

[Found: hydrolysable methyl, 9.94; hydrolysable H, 0.67; Be, 6.00%. $C_8H_{14}BeN_2$ calcd.: hydrolysable methyl, 10.20; hydrolysable H, 0.68; Be, 6.13%].

Reaction of ethylberyllium hydride and excess 4-dimethylaminopyridine. Ethylberyllium hydride in ether (10 cm^3 of a 0.499 $mol.dm^{-3}$ solution, 4.99 mmol) was added to 4-dimethylaminopyridine (1.98 g, 16.2 mmol) in benzene (25 cm^3) with stirring. An orange-yellow solution formed together with a white precipitate. The solution was boiled for a few minutes and then allowed to cool. The hydrolysable $H:C_2H_5$ ratio in solution was shown to be 1:2.65; after boiling for a further two hours the ratio had increased to 1:3.56 and after boiling overnight no hydrolysable hydrogen could be detected in the orange-brown solution. Removal of solvent under reduced pressure left an orange-brown oil which also separated from ether-hexane mixture at low temperature but would not crystallise. The compound did not distil in vacuum up to 100 °C and darkened at higher temperatures.

Benzylideneamino(methyl)beryllium. Benzonitrile (1.03 g, 10 mmol) in ether (20 cm^3) was slowly added to ethereal methylberyllium hydride (40 cm^3 of a 0.250 $mol.dm^{-3}$ solution, 10 mmol) at -96 °C and the mixture allowed to warm to room temperature with stirring. All the hydrolysable hydrogen had disappeared from solution after about one hour and the CH_3:Be ratio was 1:1.02. Solvent was removed under reduced pressure and the product recrystallised from benzene/hexane mixture at -30 °C as a glassy solid which was filtered off and dried *in vacuo*. The product was amorphous (X-ray powder photograph) and shrank from 80 °C before melting in the range 90-130 °C.

[Found: hydrolysable methyl, 11.6; Be, 7.11%; M (cryoscopically

1.92, 1.28, 0.96 wt % in benzene) 549, 540, 537. $C_{32}H_{36}Be_4N_4$ calcd.: hydrolysable methyl 11.7; Be, 7.19%; M, 512].

Reaction of 2MeBeH and C_6H_5CN. Benzonitrile (0.500 g, 4.86 mmol) in ether (20 cm^3) was added to ethereal methylberyllium hydride (39 cm^3 of a 0.25 $mol.dm^{-3}$ solution, 9.75 mmol) at -78 °C and the mixture allowed to warm to room temperature with stirring. Aliquots (2 cm^3) of the solution were analysed for hydrolysable CH_3 and H at various time intervals. Even after boiling the solution under refluxing conditions for two days, then removing the solvent and heating the viscous residue at 80 °C for 8 hours before replacing the ether, the hydrolysable CH_3:H ratio in solution remained at 1.99:1.

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