The Diphenylmethyleneaminomagnesium Bromide Tetrahydrofuran Adduct $Mg_2Br_2(THF)_2(\mu\text{-}N{:}CPh_2)_2(\mu\text{-}THF)$; *X*-Ray Crystal Structure

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Summary Two tetrahydrofuran (THF) adducts of diphenylmethyleneaminomagnesium bromide have been isolated, of formulae $Mg_2Br_2(N{:}CPh_2)_2(THF)_3$ and $Mg_2Br_2(N{:}CPh_2)_2(THF)_2$: an *X*-ray crystallographic study of the former has shown it to contain bridging THF molecules, attached to the magnesium atoms by unusually long bonds.

DIPHENYLMETHYLENEAMINOMAGNESIUM BROMIDE, MgBr(N:CPh_2), prepared in ether solution either from PhCN and PhMgBr, or from Ph_2CNH and Pr^iMgBr, reacts with an excess of tetrahydrofuran (THF) to afford a pale yellow crystalline adduct of composition $Mg_2Br_2(N{:}CPh_2)_2(THF)_3$ (I), an *X*-ray crystallographic study of which has revealed some unusual features.

Crystals of (I) are monoclinic, with $a = 17{\cdot}819$, $b = 10{\cdot}647$, $c = 22{\cdot}051$ Å, $\beta = 112{\cdot}86°$, space group $C2/c$, $Z = 4$. The intensity data were collected on a Hilger and Watts four-circle diffractometer, using Zr-filtered Mo radiation, to a limit of $\theta = 23°$. The structure was solved by means of the Patterson function and refined by full-matrix least-squares methods to $R = 0{\cdot}06$ for the 2029 reflections with net counts $\geqslant 2\sigma$.

The molecules of (I) (see Figure) contain two MgBr(THF) units bridged not only by two N:CPh_2 units, but also by one tetrahydrofuran molecule linked symmetrically (on the molecular 2-fold axis, which coincides with a crystal 2-fold axis) to both metal atoms by unusually long bonds (2·45 Å; *cf.* 2·07 Å for the bonds to the terminal THF molecules, and *cf.* 3·25 Å, the minimum distance expected[1] for nonbonded magnesium and oxygen atoms). The length of these bonds suggests that they fall into the 'secondary' classification of Alcock,[2] and it appears significant that they are virtually co-linear with the terminal Mg–O bonds ($\angle O_tMgO_b = 173°$) The remaining bonds are of normal length, similar to those reported for related organomagnesium compounds.[3–6]

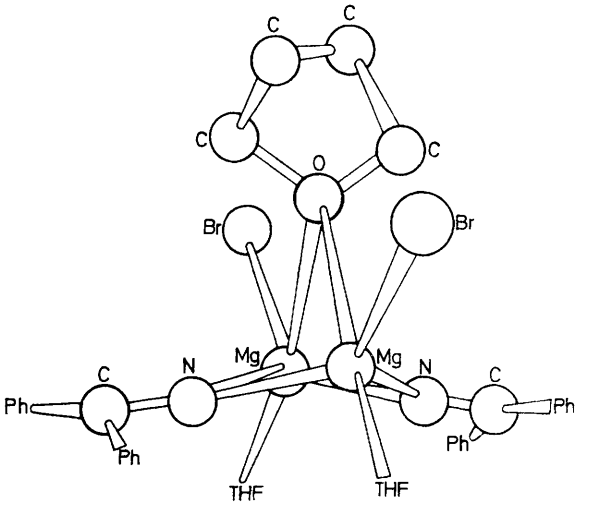
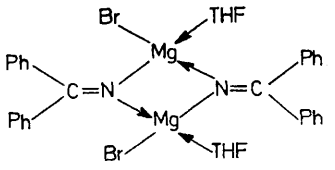


FIGURE. Molecular structure of $Mg_2Br_2(THF)_2(\mu\text{-}N{:}CPh_2)_2(\mu\text{-}THF)$. Interatomic distances: Mg–N, 2·078(4); Mg–Br, 2·474(2); Mg–O_t, 2·066(5); Mg–O_b, 2·453(5); C=N, 1·259(9); Mg–Mg, 2·886(3) Å; bond angles: Mg–N–Mg, 88·0(2); N–Mg–N, 89·0(2); Mg–O_b–Mg, 72·1(1); Br–Mg–O_t, 96·6(2); Br–Mg–O_b, 87·4(1); O_t–Mg–O_b, 173·1(2)°.

One of the tetrahydrofuran molecules of (I), presumably the bridging one, can be removed under reduced pressure, and also evidently separates when (I) is dissolved in benzene,



(II)

in which M (by cryoscopy) is 380 [(I) requires M, 785]. The residual $Mg_2Br_2(N:CPh_2)_2(THF)_2$ (II), which can also be prepared directly from equimolar proportions of MgBr(N:CPh_2) and THF, gives a different X-ray powder diffraction pattern, and presumably has the structure shown. Recrystallisation of (II) from THF regenerates (I).

In (I), the $(MgN)_2$ ring is nonplanar; the $Ph_2C:N$ groups are folded slightly away from the bridging THF molecule (the dihedral angle between the MgNMg planes is 154°). The $BrMgO_t$ angle of 97° also reflects the presence of the bridging THF molecule; a larger $BrMgO_t$ angle would be expected in (II).

The cross-ring Mg – – – Mg distance of 2·89 Å in (I) may be compared with Mg – – – Mg distances of 2·67 Å in $(Et_2Mg)_n$,[7] 2·72 Å in $(Me_2Mg)_n$,[8] 2·85 Å in $(Bu^tOMgBr,OEt_2)_2$,[9] 2·94 Å in $[Me_2NC_2H_4N(Me)MgMe]_2$,[4] 3·20 Å in $Mg_4Br_6O(OEt_2)_4$,[10] 3·53 Å in $(EtMgBrNEt_3)_2$,[3] and 3·73 Å in $[EtMg_2Cl_3(THF)_3]_2$.[6] Short metal–metal distances (< 3 Å) are thus a feature of compounds with small bridging atoms like carbon,[7,8] nitrogen,[4] or oxygen,[9] even though metal–metal bonding interactions are likely to be significant only in the case of electron-deficient alkyl bridges,[11] which appropriately have the shortest Mg – – – Mg distances.[7,8] Bridging through bromine[3,10] or chlorine[6] allows a longer metal–metal distance.

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