The compound $[Re_2(CO)_8\{\mu\text{-}InRe(CO)_5\}_2]$, which contains a similar planar four-membered ring [Re—In—Re 71·07 (3)°, Re—Re 3·232 (1) Å] (Preut & Haupt, 1975), in which Sn is replaced by In, an atom of comparable size, has significantly larger acute ring angles at the In atoms and a longer Re—Re bond length across the ring. The variation of the homonuclear bond length and of the ring angle could be caused by the higher valence state of Sn compared with In in such clusters.

Both Sn atoms in the title compound are bonded to iodine and $Re(C_{18}H_{15}P)(CO)_4$ ligands. The ligand pairs are in the *trans* position with respect to the ring plane. The bond length Sn(1)—Re(2) is markedly shorter than the Sn—Re bond lengths in the ring and the bond lengths in $[SnBr_2\{Re(C_{18}H_{15}P)(CO)_4\}_2]$ [Sn—Re: 2·741 (2), 2·730 (2) Å] (Preut & Haupt, 1983). Such differences have not been observed between the Sn—Mn bonds in $[Mn_2(CO)_8\{\mu\text{-}Sn(X)Mn(CO)_5\}_2]$ (X = Cl, Br).

Intermolecular distances do not indicate interactions exceeding van der Waals forces.

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Dimeric *tert*-Butoxymagnesium Bromide–Diethyl Ether Adduct,* $[Mg_2Br_2(C_4H_9O)_2(C_4H_{10}O)_2]$: the Addition Product of a Grignard Reagent with Acetone

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Abstract. $M_r = 502\cdot9$, monoclinic, $P2_1/c$, $a = 9\cdot68\ (2)$, $b = 11\cdot10\ (2)$, $c = 15\cdot10\ (2)$ Å, $\beta = 129\cdot1\ (2)°$, $U = 1259\cdot1$ Å^3, $Z = 2$ (dimer units), $D_m = 1\cdot30\ (2)$, $D_x = 1\cdot33$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 3\cdot5$ mm^{-1}, $F(000) = 520$, $T = 293$ K. Final R is 0·0986 for 672 observed photographic data. The molecule is a dimer, as in solution, with a four-membered Mg_2O_2 ring linking the two halves of the dimer round a centre of symmetry. Whereas the Mg atoms are four-coordinate by virtue of the two short bridging *tert*-butoxy O atoms, a longer terminal ether O and a terminal Br atom, the two kinds of O atom are three-coordinate and trigonal, with the central O and its three neighbours lying very accurately in a plane. Thus there is some degree of d_π–p_π interaction between the metal and *tert*-butoxy O atoms.

Introduction. Though organic chemists often consider the Grignard reagent to behave as simply 'RMgX' and consider reaction mechanisms in terms of such a formulation, considerable effort has been devoted to the study of the true constitution of solutions of Grignard reagents and also to the kinetics and mechanism of their reactions with carbonyls (Ashby, 1980; Ashby & Yu, 1971). Crystallographic studies have shown that Grignard reagents RMgBr.2Et$_2$O (R = Et, Ph), isolated from diethyl ether solutions, contain monomeric units, with Mg in an approximately tetrahedral environment (Stucky & Rundle, 1964; Guggenberger & Rundle, 1968), but there is little information about the nature of the products of the reactions of Grignard reagents with ketones before the usual hydrolysis is performed. Only rarely have these products been isolated and such

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compounds have been shown to be dimeric in solution (Coates, Heslop, Redwood & Ridley, 1968). The present study was undertaken to provide structural information about this phase of the reaction. A preliminary report of this structure, the product from the reaction of methylmagnesium bromide with acetone, has been published (Moseley & Shearer, 1968).

Experimental. The title compound is obtained when a diethyl ether solution of acetone is slowly added to methylmagnesium bromide in ether at 195 K and the reaction mixture allowed to warm to room temperature (Coates *et al.*, 1968). Recrystallization from ether, colourless parallelepipedal plates, well developed [110] faces; crystal with *a* and *b* axes in the plane of the plate of cross-section 0·4 × 0·2 mm sealed in a thin-walled capillary tube under dry N_2; D_m by flotation in 2-bromopropane/bromoethane; intensity data from precession photographs, Zr-filtered Mo radiation, *hkn* ($n = 0$–5) and *hnl* ($n = 0$–4), intensities estimated visually using a calibrated scale, different nets placed on a common scale using a least-squares method (Monahan, Schiffer & Schiffer, 1967), intensities corrected for Lorentz and polarization factors, no absorption corrections made; 672 observed reflections, index range h −10/9, k 0/11, l 0/14. Mg and Br located from Patterson function, C and O atoms from successive Fourier syntheses; refinement by least squares, block-diagonal approximation minimizing $\sum w\Delta^2$ ($\Delta = F_o - F_c$), anisotropic temperature factors for Mg, Br, O and C; R converged to 0·0986, weighting scheme $w = [1-\exp(-15)(\sin\theta/\lambda)^2]/(1{\cdot}0 + 0{\cdot}1667|F_o| + 0{\cdot}0037|F_o|^2)$, max. Δ/σ in final LS cycle = 0·40, max. and min. electron densities in final difference map 3·5 and −0·4 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). Computer programs were supplied by Professor D. W. J. Cruickshank and Dr J. G. Sime of Glasgow University.

Discussion. Final atomic parameters are given in Table 1.*

The molecular arrangement is shown in Fig. 1 and bond lengths and angles in Table 2. The compound is dimeric in the solid state, as in solution (Coates *et al.*, 1968), by virtue of a centrosymmetric four-membered Mg_2O_2 ring which allows the bridging *tert*-butoxy O atoms to become three-coordinate and the Mg atoms to become four-coordinate by also bonding to a terminal Br atom and forming a coordinate bond to an ether molecule. The Mg—Br bond length, 2·435 (7) Å, is in

Table 1. *Fractional positional parameters* (×10^4) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

B_{eq} values calculated by reference to Willis & Pryor (1975).

	x	y	z	B_{eq}(Å^2)
Br(1)	2456 (3)	2697 (2)	526 (2)	4·07 (6)
Mg(1)	128 (8)	1279 (6)	0 (6)	2·31 (17)
O(1)	561 (17)	30 (11)	1019 (11)	2·39 (37)
O(2)	−2035 (17)	2256 (14)	−560 (12)	3·45 (39)
C(1)	1180 (27)	90 (18)	2177 (16)	2·50 (53)
C(2)	3106 (53)	−328 (41)	2975 (25)	7·78 (140)
C(3)	1095 (76)	1437 (33)	2368 (40)	8·18 (167)*
C(4)	−171 (73)	−596 (58)	2218 (33)	9·59 (215)*
C(5)	−2613 (47)	3951 (27)	−1720 (34)	5·23 (105)
C(6)	−2146 (39)	3561 (24)	−615 (28)	4·90 (95)
C(7)	−3719 (37)	1636 (34)	−1032 (31)	6·25 (113)
C(8)	−4263 (57)	1729 (55)	−315 (43)	8·94 (184)

* Anisotropic temperature factors non-positive definite.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code: (i) −*x*, −*y*, −*z*.

Mg—Br	2·435 (7)	O(2)—C(7)	1·47 (3)
Mg—O(1)	1·91 (1)	C(1)—C(2)	1·52 (4)
Mg—O(1^{i})	1·91 (1)	C(1)—C(3)	1·53 (4)
Mg—O(2)	2·01 (1)	C(1)—C(4)	1·55 (6)
O(1)—C(1)	1·45 (2)	C(5)—C(6)	1·49 (6)
O(2)—C(6)	1·45 (3)	C(7)—C(8)	1·48 (6)

O(1)—Mg—O(2)	111·8 (7)	Mg—O(2)—C(7)	120 (2)
O(1)—Mg—Br	121·2 (5)	C(6)—O(2)—C(7)	115 (2)
O(2)—Mg—Br	107·0 (5)	O(1)—C(1)—C(2)	108 (2)
O(1^{i})—Mg—Br	122·5 (5)	O(1)—C(1)—C(3)	104 (2)
O(1^{i})—Mg—O(2)	109·3 (7)	O(1)—C(1)—C(4)	108 (2)
O(1^{i})—Mg—O(1)	83·3 (7)	C(2)—C(1)—C(3)	110 (3)
Mg—O(1)—Mg^{i}	96·7 (6)	C(2)—C(1)—C(4)	118 (3)
Mg—O(1)—C(1)	131 (1)	C(3)—C(1)—C(4)	109 (3)
Mg^{i}—O(1)—C(1)	133 (1)	O(2)—C(6)—C(5)	108 (3)
Mg—O(2)—C(6)	126 (2)	O(2)—C(7)—C(8)	114 (3)

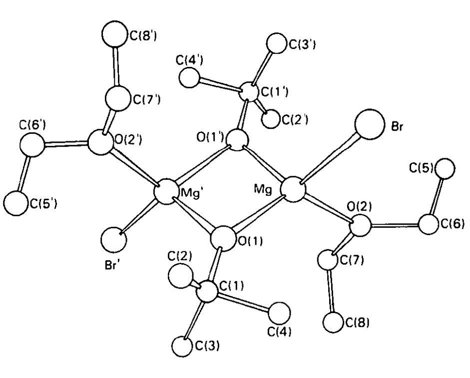

Fig. 1. Structure of $(\mathrm{Bu^tOMgBr.OEt_2})_2$.

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' data and a crystal-packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39070 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

good agreement with the values found in PhMgBr.2Et$_2$O, 2·44 (2) Å (Stucky & Rundle, 1964), and in EtMgBr.2Et$_2$O, 2·48 (1) Å (Guggenberger & Rundle, 1968). The bond angles at Mg are considerably removed from their normal tetrahedral value and probably at least two factors contribute to this situation. Participation in the four-membered ring requires that the angle in the ring, 83·3 (7)°, be much less than the others round Mg. Also the discrepancy in size between the atoms bonded to the metal is probably responsible for the remaining two O—Mg—O angles [O(1)—Mg—O(2), 111·8 (7)° and O(1^i)—Mg—O(2), 109·3 (7)°] being less than the mean value [116·9 (5)°] of the O—Mg—Br angles.

In the Mg$_2$O$_2$ ring the angle at O, 96·7 (6)°, is larger than that at Mg, the shape of the ring being consistent with both the state of hybridization of the constituent atoms and also with their relative sizes. Although three-coordinate, all the O atoms are coplanar with their three attached atoms within the limits of experimental error and this arrangement may be dictated by packing considerations. Crystal structures of Grignard reagents provide examples of both trigonally, EtMgBr.2Et$_2$O (Guggenberger & Rundle, 1968), and tetrahedrally coordinated, PhMgBr.2Et$_2$O (Stucky & Rundle, 1964), ether O atoms. The ring O atom, the Mg atoms and the tertiary C atom of the *tert*-butyl groups all deviate by less than 0·01 Å from their mean plane and the situation with respect to the O and C atoms of the ether molecule is scarcely less precise. Clearly, the second lone pair of electrons on both types of O atom is sterically insignificant. The equations of the mean planes and the deviations from these planes have been deposited.*

The two Mg—O distances differ significantly. While the Mg—O distance, 2·01 (1) Å, involving the ether O atoms compares well with the values found in crystalline PhMgBr.2Et$_2$O, 2·01 (4), 2·06 (4) Å (Stucky & Rundle, 1964), and in EtMgBr.2Et$_2$O, 2·03 (2), 2·05 (2) Å (Guggenberger & Rundle, 1968), the Mg—O distances, 1·91 (1), 1·91 (1) Å, in the ring are significantly shorter. Although the 3*d* orbitals for Mg are normally regarded as relatively diffuse and of high energy, appreciable d_π–p_π interaction, as suggested in connection with the trimer (Bu^{n}MgOPr^i)$_3$ (Bryce-Smith & Graham, 1966) may possibly contribute to the bond shortening in the Mg$_2$O$_2$ ring and would require trigonal O atoms as found here. In order to clarify this suggestion, we have examined the structure of (Bu^{t}OBeBr.OEt$_2$)$_2$ which is also dimeric in the solid phase (Bell, Shearer & Twiss, 1984) and for which d_π–p_π interactions can be precluded. The Be—O bonds in the ring, 1·60 (4), 1·63 (3) Å, are not significantly shorter than the Be bond to ether O atoms, 1·65 (3) Å. Other features of this structure parallel those found in the Mg compound and the coplanarity of the three-coordinate O atoms is true to the same degree.

Thus it appears that the steric effects alone are important enough to impose an unusual electronic situation on the O atoms and although these effects will be more pronounced in the case of the molecule based on the small central ring, it is quite possible that the molecular shape of both Be and Mg compounds arises from such considerations, and that any extra bonding in the Mg compound occurs as a secondary consequence of the relevant atoms finding themselves with a suitable geometry.

The thermal vibrations of the three terminal C atoms of the *tert*-butyl group are high (Table 1) and there may be disorder of the *tert*-butyl group arising from two or more orientations about O(1)—C(1) co-existing in the crystal. The packing arrangement* of the dimeric units shows that the only non-bonding intermolecular contact less than 4 Å is between C(3) at x, y, z and C(4) at $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

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* See deposition footnote.

* A diagram illustrating the crystal packing has been deposited. See deposition footnote.

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