Previous Page

It is important to note that the chlorin macrocycle is "ruffled" rather than completely planar and the Mg atom is ~30–50 pm above the plane of the 4 N atoms. In fact the Mg is not 4-coordinate but carries one (or sometimes two) other ligands, notably water molecules, which play a crucial role in interconnecting the basic chlorophyll units into stacks by H bonding to the cyclopentanone ring V of an adjacent chlorophyll molecule (see structure 5).

The function of the chlorophyll in the chloroplast is to absorb photons in the red part of the visible spectrum (near 680–700 nm) and to pass this energy of excitation on to other chemical intermediates in the complex reaction scheme. At least two photosystems are involved: the initiating photosystem II (P680) which absorbs at 680 nm and the subsequent photosystem I (P700). The detailed redox processes occurring, and the enzyme-catalysed synthetic pathways (dark reactions) in-so-far as they have yet been elucidated, are described in biochemical texts and fall outside our present scope. The Mg ion apparently serves several purposes: (a) it keeps the macrocycles fairly rigid so that energy is not so readily dissipated by thermal vibrations; (b) it coordinates the H_2O molecules which mediate in the H bonding between adjacent molecules in the stack; and (c) it thereby enhances the rate at which the short-lived singlet excited state formed initially by absorption of a photon by the macrocycle is transformed to the corresponding longer-lived triplet state which is involved in the redox chain (since this involves the H bonded system between several individual chlorophyll units over a distance of some 1500–2000 pm). However, it is by no means clear why, of all metals, Mg is uniquely suited for this purpose.

5.3.5 Organometallic compounds[29-31]

Compounds containing M–C bonds are well established for Be and Mg but, as with the alkali metals, reactivity within the group increases with increasing electropositivity, and relatively few organometallic compounds of Ca, Sr or Ba have been isolated.

Beryllium[30]

Beryllium dialkyls (BeR_2, R = Me, Et, Pr^n, Pr^i, Bu^i etc.) can be made by reacting lithium alkyls or Grignard reagents with $BeCl_2$ in ethereal solution, but the products are difficult to free from ether and, when pure compounds rather than solutions are required, a better route is by heating Be metal with the appropriate mercury dialkyl:

$$BeCl_2 + 2LiMe \xrightarrow{Et_2O} BeMe_2.nEt_2O + 2LiCl$$

$$BeCl_2 + 2MeMgCl \xrightarrow{Et_2O} BeMe_2.nEt_2O + 2MgCl_2$$

$$Be + HgMe_2 \xrightarrow{110^\circ} BeMe_2 + Hg$$

$BePh_2$ (mp 245°) can be prepared similarly, using LiPh or $HgPh_2$; an excess of the former reagent yields $Li[BePh_3]$. Beryllium dialkyls are colourless solids or viscous liquids which are spontaneously flammable in air and explosively hydrolysed by water. $BeMe_2$ (like $MgMe_2$, p. 131) has been shown by X-ray analysis to have a chain structure analogous to that found in $BeCl_2$ (p. 116) though the bonding is probably best described in terms of 2-electron 3-centre bridge bonds involving $\cdot CH_3$ groups rather than that adopted by bridging Cl atoms which each form two 2-electron 2-centre bonds involving a total of 4 electrons per Be–Cl–Be bridge (Fig. 5.8). Each C atom has a coordination number of 5 (cf. bonding in boranes, carbaboranes, etc., p. 157). Higher alkyls are progressively less highly polymerized and the sterically crowded $BeBu^t_2$ is monomeric. As with polymeric $BeCl_2$, addition of strong ligands results in depolymerization and the eventual formation of monomeric adducts, e.g. $[BeMe_2(PMe_3)_2]$, $[BeMe_2(Me_2NCH_2CH_2NMe_2)]$, etc. Pyrolysis eliminates alkenes and leads to mixed hydrido species of variable composition (see also p. 115).

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[29] G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. 1, *The Main Group Elements*, 3rd edn., Chap. II, Group II, pp. 71–121, Methuen, London, 1967.

[30] N. A. Bell, Chap. 3, Beryllium in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, pp. 121–53.

[31] W. E. Lindsell, Chap. 4, Mg, Ca, Sr and Ba, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, pp. 155–252.

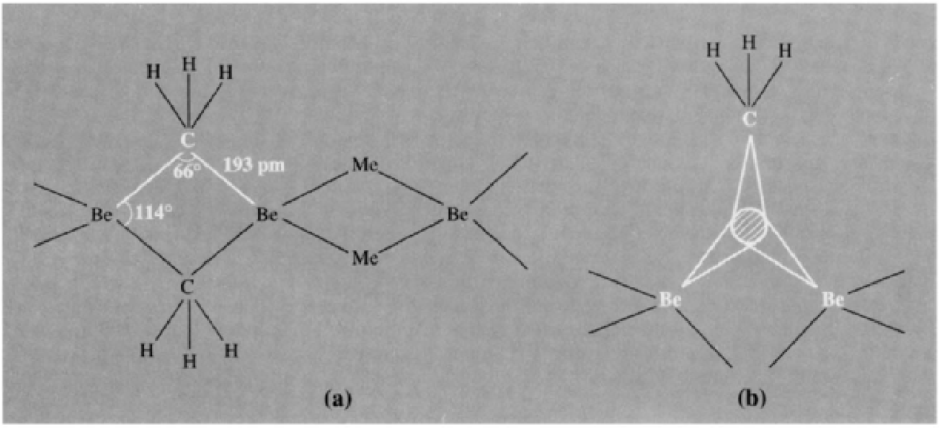
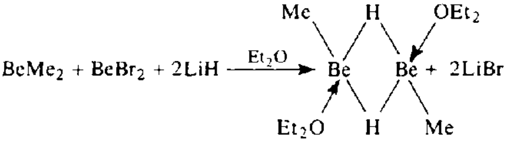
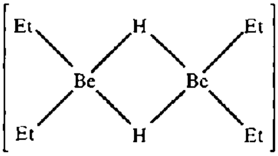


Figure 5.8 (a) Chain structure of $BeMe_2$ showing the acute angle at the bridging methyl group; the Be···Be distance is 209 pm and the distance between the 2 C atoms across the bridge is 315 pm. (b) Pictorial representation of the 3 approximately sp^3 orbitals used to form one 3-centre bridge bond; this description of the bonding is consistent with the acute bridging angle at C and the close approach of adjacent Be atoms noted in (a).

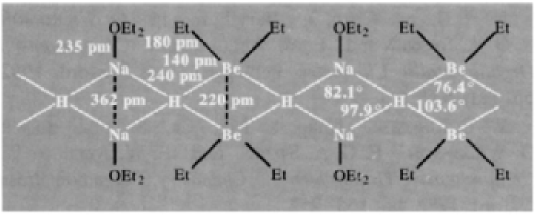
Alkylberyllium hydrides of more precise stoichiometry can be prepared by reducing $BeBr_2$ with LiH in the presence of BeR_2, e.g.:



The coordinated ether molecules can be replaced by tertiary amines. Use of NaH in the absence of halide produces the related compound $Na_2[Me_2BeH_2BeMe_2]$; the corresponding ethyl derivative crystallizes with 1 mole of Et_2O per Na but this can readily be removed under reduced pressure. The crystal structure of the etherate is shown in Fig. 5.9[32] and is important in illustrating once more (cf. p. 103) how misleading it can be to differentiate too sharply between different kinds of bonding in solids, for example: ionic $[Na(OEt_2)]_2{}^+[Et_2BeH_2BeEt_2]^{2-}$ or polymeric $[Et_2ONaHBeEt_2]_n$. Thus in the structure shown in Fig. 5.9 each Be is surrounded tetrahedrally by 2 Et and 2 bridging H to form a subunit



In addition, each H is coordinated tetrahedrally by 2 Be and 2 Na, and each Na is directly bonded to 1 Et_2O. Be–C is 180 pm and Be–H is 140 pm, close to expected values; Na–H is 240 pm, equal to that in NaH. The distance Na···Na is 362 pm which is less than in Na metal (372 pm) but greater than in NaH (345 pm), where each Na is surrounded by 6H; Be···Be is 220 pm as in Be metal. It is therefore misleading to consider the structure as being built up from the isolated ions $[Na(OEt_2)]^+$ and $[Et_2BeH_2BeEt_2]^{2-}$ and it is perhaps better to regard it as a chain polymer $[Et_2ONaHBeEt_2]_n$ which in plane projection can be written as:



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[32] G. W. Adamson and H. M. M. Shearer, *J. Chem. Soc., Chem. Commun.*, 240 (1965).

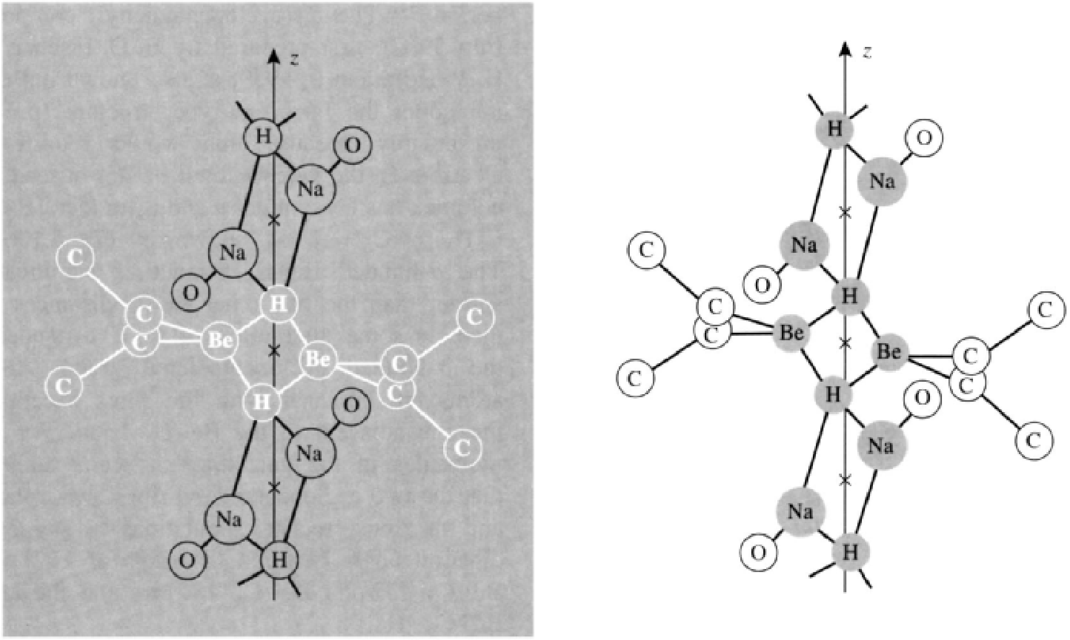
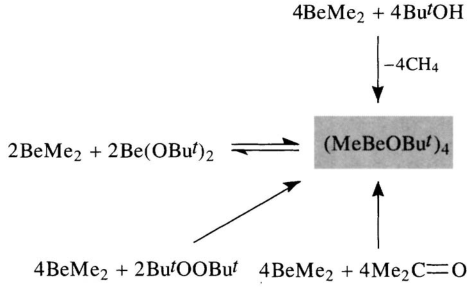
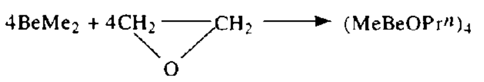


Figure 5.9 Crystal structure of the etherate of polymeric sodium hydridodiethylberyllate $(Et_2ONaHBeEt_2)_n$ emphasizing two features of the structure (see text).

Alkylberyllium alkoxides (RBeOR′) can be prepared from BeR_2 by a variety of routes such as alcoholysis with R′OH, addition to carbonyls, cleavage of peroxides R′OOR′ or redistribution with the appropriate dialkoxide $Be(OR')_2$, e.g.:

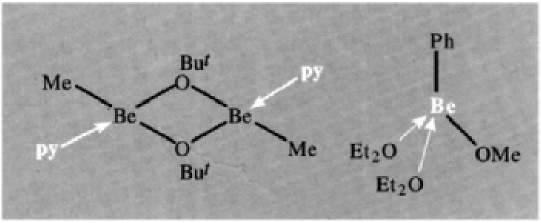


Ring opening of ethylene oxide has also been used:

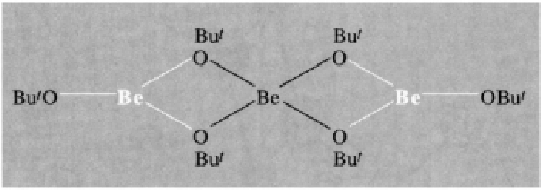


$$4BeMe_2 + 4CH_2\!-\!CH_2\ (\text{O}) \longrightarrow (MeBeOPr^n)_4$$

The compounds are frequently tetrameric and probably have the "cubane-like" structure established for the zinc analogue $(MeZnOMe)_4$. The methylberyllium alkoxides $(MeBeOR')_4$ are reactive, low-melting solids (mp for R′ = Me 25°, Et 30°, Pr^n 40°, Pr^i 136°, Bu^t 93°). Bulky substituents may reduce the degree of oligomerization, e.g. trimeric $(EtBeOCEt_3)_3$, and reaction with coordinating solvents or strong ligands can also lead to depolymerization, e.g. dimeric $(MeBeOBu^t.py)_2$ and monomeric $PhBeOMe.2Et_2O$:



Reaction of beryllium dialkyls with an excess of alcohol yields the alkoxides $Be(OR)_2$. The methoxide and ethoxide are insoluble and probably polymeric, whereas the *t*-butoxide (mp 112°) is readily soluble as a trimer in benzene or hexane; the proposed structure:



involves both 3- and 4-coordinate Be and is consistent with the observation of 2 proton nmr signals at τ 8.60 and 8.75 with intensities in the ratio 2:1. (A precisely analogous structure has been established by X-ray diffraction analysis for the "isoelectronic" linear trimer $[Be(NMe_2)_2]_3$.)(33)

Beryllium forms a series of cyclopentadienyl complexes $[Be(\eta^5\text{-}C_5H_5Y]$ with Y = H, Cl, Br, Me, $-C{\equiv}CH$ and BH_4, all of which show the expected C_{5v} symmetry (Fig. 5.10a). If the *pentahapto*-cyclopentadienyl group (p. 937) contributes 5 electrons to the bonding, then these are all 8-electron Be complexes consistent with the octet rule for elements of the first short period.(34) The bis(cyclopentadienyl) compound (mp 59°C), first prepared by E. O. Fischer and H. P. Hofmann in 1959, is also known but does not adopt the ferrocene-type structure (p. 937) presumably because this would require 12 electrons in the valence shell of Be. Instead, the complex has C_s symmetry and is, in fact, $[Be(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$, as shown in Fig. 5.10b.(35) The σ-bonded Be–C distance is significantly shorter than the five other Be–C distances and there is some alternation of C–C distances in the σ-bonded cyclopentadienyl group. All H atoms are coplanar with the rings except for the one adjacent to the $Be-C_\sigma$ bond. For free molecules in the gas phase it seems unlikely that the two cyclopentadienyl rings are coplanar, and the most recent calculations(36) suggest a dihedral angle between the rings of 117° with $Be-C_\sigma$ 172 pm, $Be-C_\pi$ 187 pm, and the angle $Be-C_\sigma-H$ 108°.

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(33) J. L. Atwood and G. D. Stucky, *Chem. Comm.* 1967, 1169–70.

(34) E. D. Jemmis, S. Alexandratos, P. v. R. Schleyer, A. Streitwieser and H. F. Schaeffer, *J. Am. Chem. Soc.* **100**, 5695–700 (1978).

(35) C.-H. Wong, T.-Y. Lee, K.-J. Chao and S. Lee, *Acta Cryst.* **B28**, 1662–5 (1972); C. Wong, T. Y. Lee, T. J. Lee, T. W. Chang and C. S. Liu, *Inorg. Nucl. Chem. Lett.* **9**, 667–73 (1973).

(36) D. S. Marynick, *J. Am. Chem. Soc.* **99**, 1436–41 (1977). See also J. B. Collins and P. v. R. Schleyer, *Inorg. Chem.* **16**, 152–5 (1977).

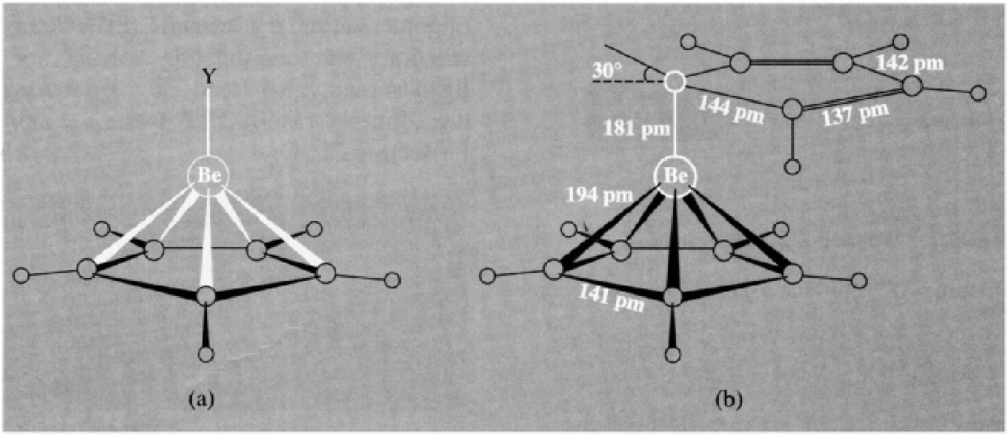


Figure 5.10 Cyclopentadienyl derivatives of beryllium showing (a) the C_{5v} structure of $[Be(\eta^5\text{-}C_5H_5)Y]$ and (b) the structure of crystalline $[Be(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$ at −120° (see text).

Pentamethylcyclopentadienyl derivatives are also known, e.g. $[(\eta^5\text{-C}_5\text{Me}_5)\text{BeCl}]$; this reacts with LiPBu^t_2 in Et_2O at −78° to give colourless crystals of $[(\eta^5\text{-C}_5\text{Me}_5)\text{BePBu}^t_2]$ in high yield.(37) Here the dibutylphosphido group is acting as a 1-electron ligand to Be to form a covalent bond of length 208.3 pm almost perpendicular to the C_5 plane: angle P–Be–C_5(centroid) 168.3° Interestingly, the Be–C_5(centroid) distance (148 pm) is notably shorter than that found in $[(\eta^5\text{-C}_5\text{H}_5\text{BeMe}]$ (190.7 pm), implying stronger bonding in the pentamethyl derivative. Because the Be nucleus has a spin of 3/2, the $^{31}\text{P}\{^1\text{H}\}$ nmr signal consists of a 1:1:1:1 quartet with a coupling constant $^1J_{\text{Be-P}}$ of 50.0 Hz; this is an order of magnitude greater than for Lewis-base (2-electron) tertiary phosphine adducts of Be.

Magnesium(31)

Magnesium dialkyls and diaryls, though well established, have been relatively little studied by comparison with the vast amount of work which has been published on the Grignard reagents RMgX. The dialkyls (and diaryls) can be conveniently made by the reaction of LiR (LiAr) on Grignard reagents, or by the reaction of HgR_2 (HgAr_2) on Mg metal (sometimes in the presence of ether). On an industrial scale, alkenes can be reacted at 100° under pressure with MgH_2 or with Mg in the presence of H_2:

$$\text{LiR} + \text{RMgX} \xrightarrow{\text{Et}_2\text{O}} \text{MgR}_2 + \text{LiX}$$

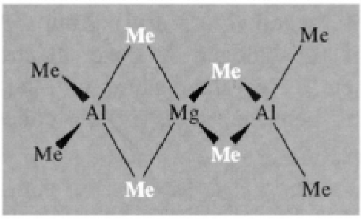
$$\text{HgR}_2 + \text{Mg} \xrightarrow{\text{Et}_2\text{O}} \text{MgR}_2 + \text{Hg}$$

$$2\text{C}_2\text{H}_4 + \text{H}_2 + \text{Mg} \xrightarrow[100^\circ]{\text{pressure}} \text{MgEt}_2$$

A suitable laboratory method is to shift the Schlenk equilibrium in a Grignard solution (p. 132) by adding dioxan to precipitate the complex MgX_2.diox; this enables MgR_2 to be isolated by careful removal of solvent under reduced pressure:

$$2\text{RMgX} \rightleftharpoons \text{MgR}_2 + \text{MgX}_2 \xrightarrow{\text{C}_4\text{H}_8\text{O}_2} \text{MgR}_2 + \text{MgX}_2.\text{C}_4\text{H}_8\text{O}_2$$

MgMe_2 is a white involatile polymeric solid which is insoluble in hydrocarbons and only slightly soluble in ether. Its structure is very similar to that of BeMe_2 (p. 128) the corresponding dimensions for MgMe_2 being: Mg–C 224 pm, Mg–C–Mg 75°, C–Mg–C 105°, Mg···Mg 272 pm and C···C (across the bridge) 357 pm. Precisely analogous bridging Me groups are found in dimeric Al_2Me_6 (p. 259) and in the monomeric compound $\text{Mg(AlMe}_4)_2$ which can be formed by direct reaction of MgMe_2 and Al_2Me_6:



MgEt_2 and higher homologues are very similar to MgMe_2 except that they decompose at a lower temperature (175–200° instead of ~250°C) to give the corresponding alkene and MgH_2 in a reaction which reverses their preparation. MgPh_2 is similar: it is insoluble in benzene dissolves in ether to give the monomeric complex $\text{MgPh}_2.2\text{Et}_2\text{O}$ and pyrolyses at 280° to give Ph_2 and Mg metal. Like BePh_2 it reacts with an excess of LiPh to give the colourless complex $\text{Li[MgPh}_3]$.

The first organosilylmagnesium compound $[\text{Mg(SiMe}_3)_2].(\text{-CH}_2\text{OMe})_2$, was isolated in 1977;(38) it was obtained as colourless, spontaneously flammable crystals by reaction of bis(trimethylsilyl)mercury with Mg powder in

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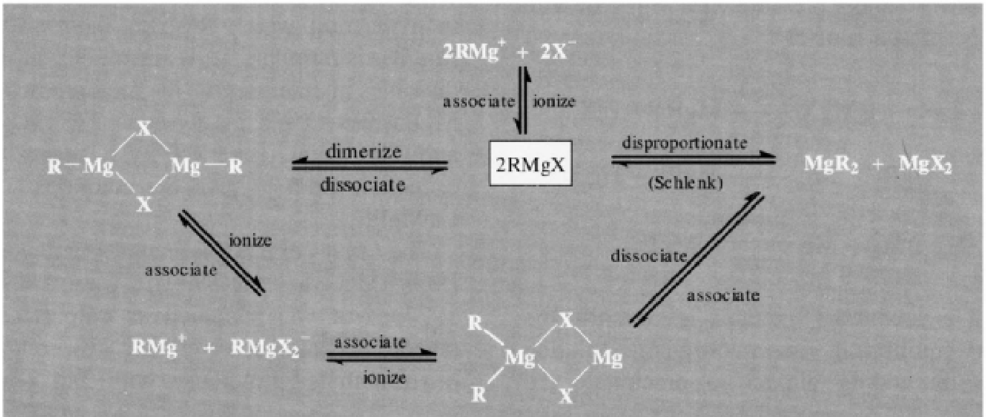
[37] J. L. Atwood, S. G. Bott, R. A. Jones and S. U. Koschmieder, *J. Chem. Soc., Chem. Commun.*, 692–3 (1990).

[38] L. Rösch, *Angew. Chem. Int. Edn. Engl.* **16**, 247–8 (1977).

1,2-dimethoxyethane. More recently[39] the bulkier bis{tris(trimethylsilyl)methyl} derivative, [Mg{C(SiMe$_3$)$_3$}$_2$], was obtained as an unsolvated crystalline monomer; this was the first example of 2-coordinate (linear) Mg in the solid state, though this geometry had been established earlier by electron diffraction in the gas phase for bis(neopentyl)magnesium.[40]

Grignard reagents are the most important organometallic compounds of Mg and are probably the most extensively used of all organometallic reagents because of their easy preparation and synthetic versatility. Despite this, their constitution in solution has been a source of considerable uncertainty until recent times.[41] It now seems well established that solutions of Grignard reagents can contain a variety of chemical species interlinked by mobile equilibria whose position depends critically on at least five factors: (i) the steric and electronic nature of the alkyl (or aryl) group R, (ii) the nature of the halogen X (size, electron-donor power, etc.), (iii) the nature of the solvent (Et$_2$O, thf, benzene, etc.), (iv) the concentration and (v) the temperature. The species present may also depend on the presence of trace impurities such as H$_2$O or O$_2$. Neglecting solvation in the first instance, the general scheme of equilibria can be set out as shown below. Thus "monomeric" (solvated) RMgX can disproportionate to MgR$_2$ and MgX$_2$ by the Schlenk equilibrium or can dimerize to RMgX$_2$MgR. Both the monomer and the dimer can ionize, and reassociation can give the alternative dimer R$_2$MgX$_2$Mg. Note that only halogen atoms X are involved in the bridging of these species.

Evidence for these species and the associated equilibria comes from a variety of techniques such as vibration spectroscopy, nmr spectroscopy, molecular-weight determinations, radioisotopic exchange using ^{28}Mg, electrical conductivity, etc. In some cases equilibria can be displaced by crystallization or by the addition of complexing agents such as dioxan (p. 131) or NEt$_3$. The crystal structures of several pertinent adducts have recently been determined (Fig. 5.11). None call for special comment except the curious solvated dimer [EtMg$_2$Cl$_3$(OC$_4$H$_8$)$_3$]$_2$ which features both 5-coordinate trigonal bipyramidal and 6-coordinate octahedral Mg groups; note also that, whilst 4 of the Cl atoms each bridge 2 Mg atoms, the remaining 2 Cl atoms are triply bridging.



Schematic representation of the principal equilibria in Grignard solutions; solvation of the various species has been omitted for clarity.

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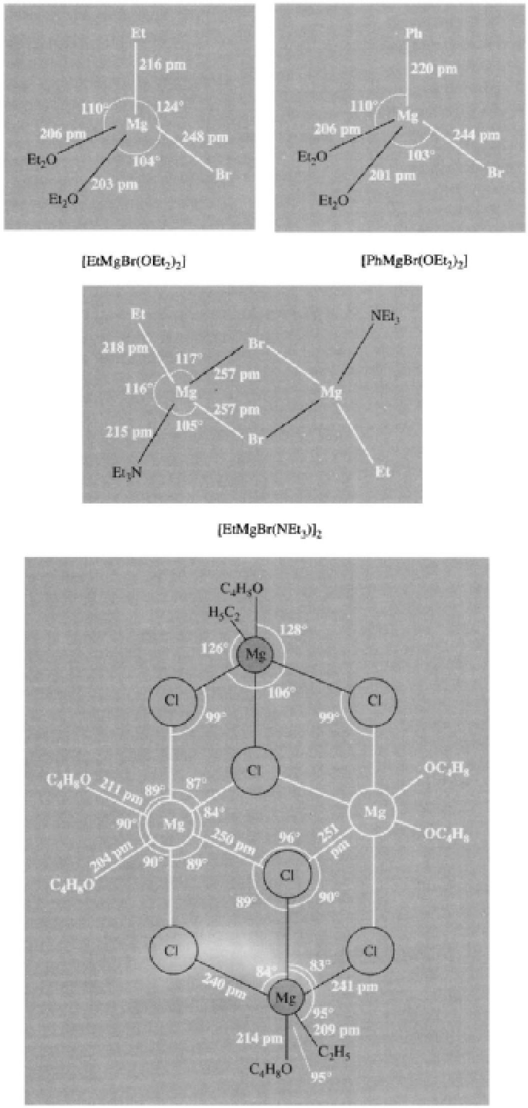
[39] S. S. Al-Juaid, C. Eaborn, P. B. Hitchcock, C. A. McGeary and J. D. Smith, *J. Chem. Soc., Chem. Commun.*, 273–4 (1989).

[40] E. C. Ashby, L. Fernholt, A. Haaland, R. Seip and R. C. Smith, *Acta Chem. Scand., Ser. A* **34**, 213–7 (1980).

[41] E. C. Ashby, *Qt. Rev.* **21**, 259–85 (1967).



$[EtMgBr(OEt_2)_2]$

$[PhMgBr(OEt_2)_2]$

$[EtMgBr(NEt_3)]_2$

Figure 5.11 Crystal structures of adducts of Grignard reagents.

Grignard reagents are normally prepared by the slow addition of the organic halide to a stirred suspension of magnesium turnings in the appropriate solvent and with rigorous exclusion of air and moisture. The reaction, which usually begins slowly after an induction period, can be initiated by addition of a small crystal of iodine; this penetrates the protective layer of oxide (hydroxide) on the surface of the metal. The order of reactivity of RX is $I > Br > Cl$ and alkyl > aryl. The mechanism has been much studied but is not fully understood.(42) The fluorides RMgF (R = Me, Et, Bu, Ph) can be prepared by reacting MgR_2 with mild fluorinating agents such as $BF_3.OEt_2$, Bu_3SnF or SiF_4.(43) The scope of Grignard reagents in syntheses has been greatly extended by a recently developed method for preparing very reactive Mg (by reduction of MgX_2 with K in the presence of KI).(44) Grignard reagents have a wide range of application in the synthesis of alcohols, aldehydes, ketones, carboxylic acids, esters and amides, and are probably the most versatile reagents for constructing C–C bonds by carbanion (or occasionally(45) free-radical) mechanisms. Standard Grignard methods are also available for constructing C–N, C–O, C–S (Se, Te) and C–X bonds (see Panel on pp. 134–5).

A related class of compounds are the alkylmagnesium alkoxides: these can be prepared by reaction of MgR_2 with an alcohol or ketone or by reaction of Mg metal with the appropriate alcohol and alkyl chloride in methylcyclohexane solvent, e.g.:

$$4MgEt_2 + 4Bu^tOH \longrightarrow (EtMgOBu^t)_4 + 4C_2H_6$$

$$2MgMe_2 + 2Ph_2CO \xrightarrow{Et_2O} (MeMgOCMePh_2.Et_2O)_2$$

$$6Mg + 6Bu^nCl + 3Pr^iOH \longrightarrow (Bu^nMgOPr^i)_3 + 3MgCl_2 + 3C_4H_{10}$$

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[42] H. R. Rogers, C. L. Hill, Y. Fujiwara, R. J. Rogers, H. L. Mitchell and G. M. Whitesides, *J. Am. Chem. Soc.* **102**, 217–26 (1980), and the three following papers, pp. 226–43.

[43] E. C. Ashby and J. Nackashi, *J. Organometall. Chem.* **72**, 203–11 (1974).

[44] R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.* **96**, 1775–81 (1974).

[45] C. Walling, *J. Am. Chem. Soc.* **110**, 6846–50 (1988).

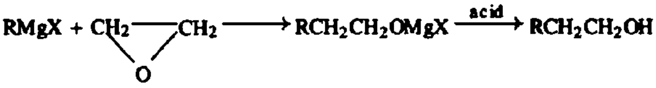
Synthetic Uses of Grignard Reagents

Victor Grignard (1871–1935) showed in 1900 that Mg reacts with alkyl halides in dry ether at room temperature to give ether-soluble organomagnesium compounds; the use of these reagents to synthesize acids, alcohols, and hydrocarbons formed the substance of his doctorate thesis at the University of Lyon in 1901, and further studies on the synthetic utility of Grignard reagents won him the Nobel Prize for Chemistry in 1912. The range of applications is now enormous and some indication of the extraordinary versatility of organomagnesium compounds can be gauged from the following brief summary.

Standard procedures convert RMgX into ROH, RCH_2OH, RCH_2CH_2OH and an almost unlimited range of secondary and tertiary alcohols:

$$RMgX + O_2 \longrightarrow ROOMgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{acid} 2ROH$$

$$RMgX + HCHO \longrightarrow RCH_2OMgX \xrightarrow{acid} RCH_2OH$$



$$RMgX + R'CHO \longrightarrow RR'CHOMgX \xrightarrow{acid} RR'CHOH$$

$$RMgX + R'COR'' \longrightarrow RR'R''COMgX \xrightarrow{acid} RR'R''COH$$

Aldehydes and carboxylic acids having 1 C atom more than R, as well as ketones, amides and esters can be prepared similarly, the reaction always proceeding in the direction predicted for potential carbanion attack on the unsaturated C atom:

$$RMgX + HC(OEt)_3 \xrightarrow{acid} RCH(OEt)_2 \xrightarrow{acid} RCHO$$

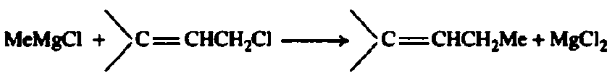
$$RMgX + CO_2 \longrightarrow RCO_2MgX \xrightarrow{acid} RCO_2H$$

$$RMgX + R'CN \longrightarrow [RR'C{=}NMgX] \xrightarrow{acid} RR'C{=}O$$

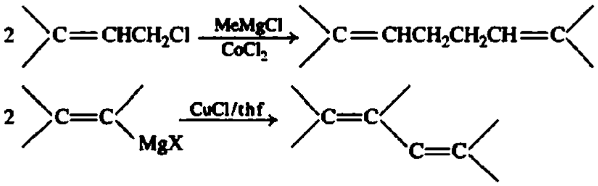
$$RMgX + R'NCO \longrightarrow [RCNR'(OMgX)] \xrightarrow{acid} RC(O)NHR'$$

$$RMgX + EtOCOCl \longrightarrow [RC(OEt)Cl(OMgX)] \xrightarrow{acid} RCO_2Et$$

Grignard reagents are rapidly hydrolysed by water or acid to give the parent hydrocarbon, RH, but this reaction is rarely of synthetic importance. Hydrocarbons can also be synthesized by nucleophilic displacement of halide ion from a reactive alkyl halide, e.g.

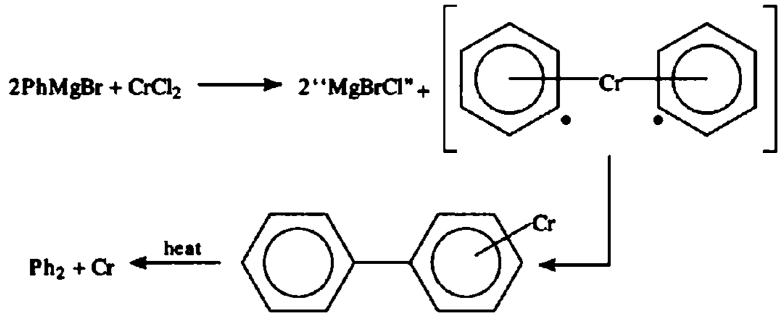


However, other products may be formed simultaneously by a free-radical process, especially in the presence of catalytic amounts of $CoCl_2$ or CuCl:

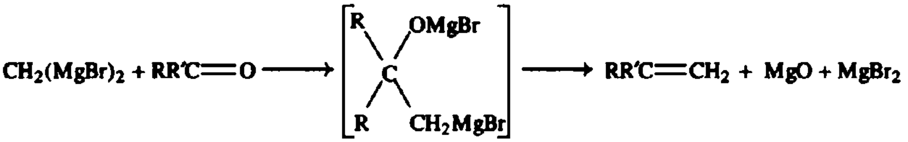


Panel continues

Similarly, aromatic Grignard reagents undergo free-radical self-coupling reactions when treated with MCl_2 (M=Cr, Mn, Fe, Co, Ni), e.g.:



Alkenes can be synthesized from aldehydes or ketones using the Grignard reagent derived from CH_2Br_2:



$$CH_2(MgBr)_2 + RR'C{=}O \longrightarrow \left[\begin{matrix} R & & OMgBr \\ & C & \\ R & & CH_2MgBr \end{matrix}\right] \longrightarrow RR'C{=}CH_2 + MgO + MgBr_2$$

The formation of C–N bonds can be achieved by using chloramine or *O*-methylhydroxylamine to yield primary amines; aryl diazonium salts yield azo-compounds:

$$RMgX + ClNH_2 \longrightarrow RNH_2 + \text{“}MgClX\text{”}$$

$$RMgX + MeONH_2 \longrightarrow RNH_2 + MeOMgX$$

$$RMgX + [ArN_2]X \longrightarrow RN{=}NAr + MgX_2$$

Carbon-oxygen bonds can be made using the synthetically uninteresting conversion of RMgX into ROH (shown as the first reaction listed above); direct acid hydrolysis of the peroxo compound ROOMgX yields the hydroperoxide ROOH. Carbon-sulfur bonds can be constructed using S_8 to make thiols or thioethers, and similar reactions are known for Se and Te:

$$RMgX + S_8 \longrightarrow RS_xMgX \xrightarrow{RMgX} RSMgX$$

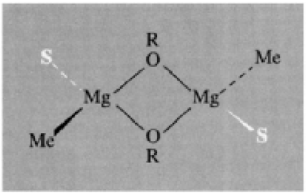
$$\begin{tikzcd}
 & RSH + MgX_2 \\
RSMgX \arrow[ur, "acid"] \arrow[r, "RMgX"] \arrow[dr, "R'I"'] & R_2S + MgX_2 + Mg \\
 & RSR' + \text{“}MgIX\text{”}
\end{tikzcd}$$

Formation of C–X bonds is not normally a problem but the Grignard route can occasionally be useful when normal halogen exchange fails. Thus iodination of Me_3CCH_2Cl cannot be achieved by reaction with NaI or similar reagents but direct iodination of the corresponding Grignard effects a smooth conversion:

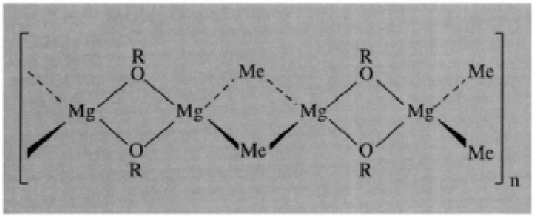
$$Me_3CCH_2MgCl + I_2 \longrightarrow Me_3CCH_2I + \text{“}MgClI\text{”}$$

Further examples of the ingenious use of Grignard reagents will be found in many books on synthetic organic chemistry and much recent work in this area was reviewed in a special edition of *Bull. Soc. Chim. France*, 1972, 2127–86, which commemorated the centenary of Victor Grignard's birth.

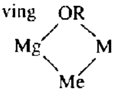
As with the Grignard reagents, the structure and degree of association of the product depend on the bulk of the organic groups, the coordinating ability of the solvent, etc. This is well illustrated by MeMgOR (R = Pr^n, Pr^i, Bu^t, $CMePh_2$) in thf, Et_2O and benzene:[(46)] the strongly coordinating solvent thf favours solvated dimers (A) but prevents the formation both of oligomers (B) involving the relatively weak Me bridges and of cubane structures (C) involving the relatively weak triply bonding oxygen bridges.



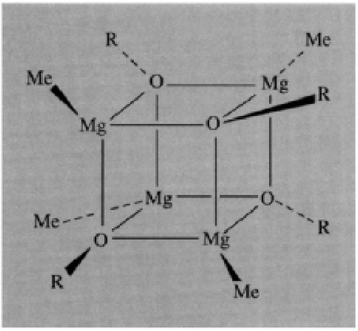
A, solvated dimer



B, linear oligomer (various isomers are possible e.g. involving



Mg bridges, etc.)



C, cubane tetramer (unsolvated)

By contrast, in the more weakly coordinating solvent Et_2O, Me bridges and μ_3-OR bridges can form, leading to linear oligomers and cubanes, provided OR is not too bulky. Thus when R = $CMePh_2$, oligomerization and cubane formation are blocked and $MeMgOCMePh_2$ exists only as a solvated dimer even in Et_2O. In benzene, R = Bu^t and Pr^i form cubane tetramers but Pr^n can form an oligomer of 7–9 monomer units. The sensitive dependence of the structure of a compound on solvation energy, lattice energy and the relative coordinating abilities of its component atoms and groups will be a recurring theme in many subsequent chapters.

Dicyclopentadienylmagnesium $[Mg(\eta^5\text{-}C_5H_5)_2]$, mp 176°, can be made in good yield by direct reaction of Mg and cyclopentadiene at 500–600°; it is very reactive towards air, moisture, CO_2 and CS_2, and reacts with transition-metal halides to give transition-element cyclopentadienyls. It has the staggered (D_{5d}) "sandwich" structure (cf. ferrocene p. 1109) with Mg–C 230 pm and C–C 139 pm;[(47)] the bonding is thought to be intermediate between ionic and covalent but the actual extent of the charge separation between the central atom and the rings is still being discussed.

Calcium, strontium and barium[(31,48)]

Organometallic compounds of Ca, Sr and Ba are far more reactive than those of Mg and have been much less studied until recently. For example, although about 50 000 papers have been published on organomagnesium compounds and reagents, less than 1% of this number have appeared for the heavier triad of elements. Many of the differences in reactivity can be traced to the larger radii of the cations (Ca^{2+} 100, Sr^{2+} 118, Ba^{2+} 135 pm) when compared to Mg^{2+} (72 pm) — i.e the lower (charge/size) ratio enhances still further the ionic character of the bonding and thus increases the kinetic lability of the ligands. Coordinative unsaturation also plays a rôle and, indeed, the organometallic behaviour of the heavier alkali metals often resembles

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[46] E. C. ASHBY, J. NACKASHI and G. E. PARRIS, *J. Am. Chem. Soc.* **97**, 3162–71 (1975).

[47] W. BÜNDER and E. WEISS, $[Mg(\eta^5\text{-}C_5H_5)_2]$, *J. Organometall. Chem.* **92**, 1–6 (1975).

[48] T. P. HANUSA, *Polyhedron* **9**, 1345–62 (1990)

that of the similarly-sized divalent lanthanide elements (Yb^{2+} 102, Eu^{2+} 117, Sm^{2+} 122 pm) rather than that of Mg. In these circumstances it became clear that stability would be enhanced by the use of bulky ligands. Early work showed that the reactive compounds MR_2 (M = Ca, Sr, Ba; R = Me, Et, allyl, Ph, $PhCH_2$, etc.) can be prepared using HgR_2 under appropriate conditions, often at low temperature. Compounds of the type RCaI (R = Bu, Ph, tolyl) have also been known for some time and can now be isolated as crystals.

Calcium (and Sr) dicyclopentadienyl can be made by direct reaction of the metal with either $[Hg(C_5H_5)_2]$ or with cyclo-C_5H_6 itself; cyclopentadiene also reacts with CaC_2 in liquid NH_3 to form $[Ca(C_5H_5)_2]$ and HC≡CH. The barium analogue $[Ba(C_5H_5)_2]$ is best made (though still in small yield) by treating cyclo-C_5H_6 with BaH_2. The structure of $[Ca(C_5H_5)_2]$ is unique.(49) Each Ca is surrounded by 4 planar cyclopentadienyl rings and the overall structure involves a complex sharing of rings which bridge the various Ca atoms. The coordination geometry about a given Ca atom is shown in Fig. 5.12: two of the rings (A, C) are η^5, with all Ca–C distances 275 pm. A third ring (B) is η^3 with one Ca–C distance 270, two at 279, and two longer distances at 295 pm. These three polyhapto rings (A, B, C) are arranged so that their centroids are disposed approximately trigonally about the Ca atom. The fourth ring (A′) is η^1, with only 1 Ca–C within bonding distance (310 pm) and this bond is approximately perpendicular to the plane formed by the centroids of the other 3 rings. The structure is the first example in which η^5-, η^3- and η^1-C_5H_5 groups are all present. Indeed, the structure is even more complex than this implies because of the ring-bridging between adjacent Ca atoms; for example ring A (and A′) is simultaneously bonded η^5 to 1 Ca (248 pm from the ring centre) and η^1 to another on the opposite side of the ring, whereas ring C is equally associated in *pentahapto* mode with 2 Ca atoms each 260 pm from the plane of the ring.

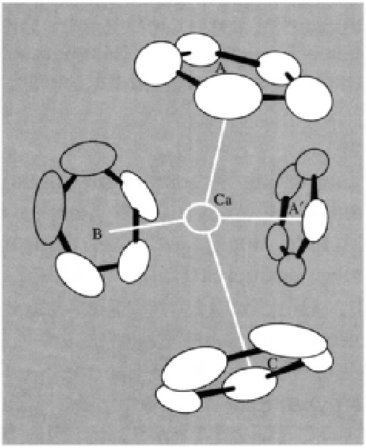

Figure 5.12 Coordination geometry about Ca in polymeric $[Ca(C_5H_5)_2]$ showing $2\times\eta^5$-, η^3- and η^1- bonding (see text).

Replacement of the ligand C_5H_5 by the bulkier C_5Me_5 results in improved solubility, volatility and kinetic stability of the compound, and all three complexes $[M(\eta^5\text{-}C_5Me_5)_2]$ have been prepared in >65% yield by the reaction of NaC_5Me_5 (or KC_5Me_5) with the appropriate diiodide, MI_2, in diethyl ether or thf, followed by removal of the coordinated ether (or thf) by refluxing the product in toluene. $[Ca(C_5Me_5)_2(thf)_2]$ has also been prepared in 48% yield by the reaction of C_5HMe_5 and $Ca(NH_2)_2$ in liquid ammonia. The greater tractability of these complexes enabled the first (gas-phase) molecular structures of organo-Sr and organo-Ba compounds to be determined,(50) and also the first organo-Ba crystal structure.(51) Group comparisons show that the angle subtended by the two C_5Me_5 ring centroids at the metal atom in the gas phase is almost the same (to within 1 esd) for the three metals (154 ± 4°) but that this drops to 131.0° for crystalline $[Ba(C_5Me_5)_2]$. A theoretical rationalization for these angles, especially in the gas phase, is not obvious.(48)

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[49] R. Zerger and G. Stucky, *J. Organometall. Chem.* **80**, 7–17 (1974).

[50] R. A. Andersen, R. Blom, C. J. Burns and H. V. Volden, *J. Chem. Soc., Chem. Commun.*, 768–9 (1987).

[51] R. A. Williams, T. P. Hanusa and J. C. Huffman, *J. Chem. Soc., Chem. Commun.*, 1045–6 (1988).

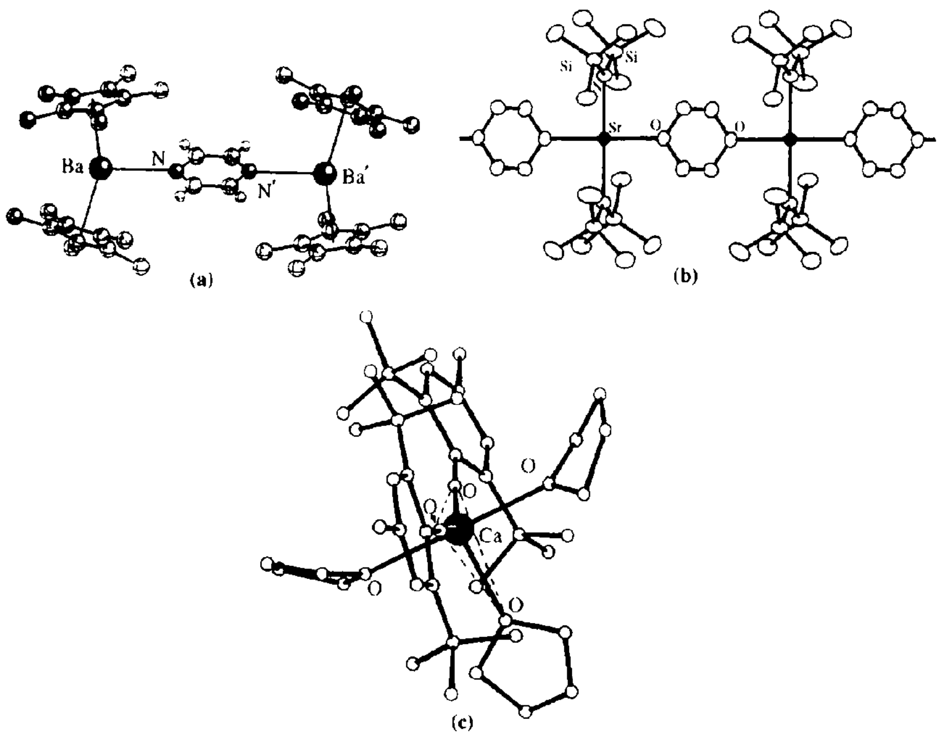

Figure 5.13 (a) Structure of $[\{Ba(\eta^5\text{-}C_5Me_5)_2\}_2(\mu\text{-}1,4\text{-}C_4H_4N_2)]$ in which the pyrazine ligand bridges two bent $\{BaCp^*{}_2\}$ units to give a centrosymmetric adduct with an essentially linear disposition of the four atoms BaNNBa. (b) The polymeric dioxane-bridged structure of $[\{trans\text{-}Sr(NR_2)_2(\mu\text{-}1,4C_4H_8O_2)]$ ($R = SiMe_3$) showing the 4-coordinate square-planar stereochemistry of the Sr atoms. (c) The 5-coordinate trigonal-bipyramidal structure of $[Ca(OAr)_2(thf)_3]$ ($Ar = C_6H_2\text{-}2,6\text{-}Bu^t{}_2\text{-}4\text{-}Me$) showing one equatorial and two axial thf ligands.

Attempts to prepare the mono(cyclopentadienyl) derivatives are sometimes frustrated by a Schlenk-type equilibrium (see p. 132), but judicious choice of ligands, solvent etc. occasionally permits the isolation of such compounds, e.g. the centrosymmetric halogen-bridged dimer $[\{(\eta^5\text{-}C_5Me_5)Ca(\mu\text{-}I)(thf)_2\}_2]$ which crystallizes from toluene solution. The complex is isostructural with the dimeric organosamarium(II) analogue.(52)

Other interesting structures of organometallic and related complexes of the heavier Group 2 metals include those of the centrosymmetric pyrazine adduct $[\{Ba(\eta^5\text{-}C_5Me_5)_2\}_2(\mu\text{-}1,4\text{-}C_4H_4N_2)]$, (Fig. 5.13a)(48), the square-planar Sr complex $[\{trans\text{-}Sr(NR_2)_2(\mu\text{-}1,4\text{-}C_4H_8O_2)\}]$ ($R = SiMe_3$), Fig. 5.13b(53) and the 5-coordinate trigonal-bipyramidal Ca complex $[Ca(OAr)_2\text{-}(thf)_3]$ ($Ar{=}C_6H_2\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}Me$), Fig. 5.13c.(54)

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[52] W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.* **107**, 941-6 (1985).

[53] F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 724-6 (1991).

[54] P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 1141-2 (1990).