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Structural aspects of Grignard reagents

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CONTENTS

ABSTRACT

Structures of Grignard reagents determined by X-ray diffraction, as of the end of August 1992, have been reviewed. There are two preparative procedures reported for the 24 structures, which include monomers, dimers and oligomers. The hard Mg(II) atom is found in a tetra-, penta- and hexacoordinate environment with ligands ranging from soft, through borderline to hard. The most common halogen associated with these Grignard structures is bromine. The carbon donor ligands are uni-, bi- or pentadentate. Relationships between structural parameters, covalent radii of coordinated atoms and the geometry of the coordination sphere are discussed.

ABBREVIATIONS

al	allyl
Bu^t	*tert*-butyl
C_6H_{11}	cyclohexyl
C_8H_8	cyclooctatetraenyl
$C_{12}H_{14}P$	phospholide

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$C_{14}H_{19}O_4$	1,3-xylyl-[15] crown-4
$C_{15}H_{26}N_2$	sparteine
$C_{22}H_{32}N_2$	6-benzylsparteine
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
Et	ethyl
Et_3N	triethylamine
Et_4en	*N*,*N*,*N*′,*N*′-tetraethylethylenediamine
Me	methyl
Me_4en	*N*,*N*,*N*,*N*-tetramethylethylenediamine
$(Me_3Si)C$	tris(trimethylsilyl)methyl
$(Me_3Si)_3$cp	tris(trimethylsilyl)cyclopentadienyl
np	neopentyl
Ph	phenyl
Ph_3C	triphenylmethyl
Pr^i	isopropyl
thf	tetrahydrofuran
thiq	*N*-pivaloyl-tetrahydroisoquinoline

1. INTRODUCTION

Magnesium chemistry has been an active field of study for a considerable time, and the relationships between the structure, reactivity and catalytic activity (particularly the Grignard reagents) have proven of major importance. Some aspects of the coordination chemistry of alkali and alkali-earth cations, together with some crystallographic data on Grignard reagents and other magnesium compounds, were briefly reviewed earlier [1]. Until the early 1960s, the primary questions concerning the physical nature of the Grignard reagents was whether the unsymmetrical RMgX species had anything other than a transitory existence in solution. The nature of the Grignard reagents has long been a subject of speculation and investigation, and it has become clear that the structure of a Grignard compound is dependent on the nature of the organic groups coordinated to the magnesium(II) atom.

There are some 24 Grignard reagents for which X-ray diffraction data are available, but to date they have not been systematically compared and classified. This, therefore, is the object of this review. The structures have been classified according to the coordination number of the magnesium atom, and subdivided into monomers, dimers and oligomers. The compounds have been listed and referenced in order of nuclearity, and within each type according to increasing coordination number, increasing complexity of the coordination sphere and increasing covalent radius of the principle coordinating atom.

2. PREPARATION OF THE GRIGNARD REAGENTS

In general, there are two preparative procedures for Grignard reagents. One involves the direct interaction of the alkyl or aryl halide and magnesium metal in a non-polar solvent such as diethylether or tetrahydrofuran. The other involves mixing a non-polar solution of the required ligand and a solution of RMgX, usually under an inert nitrogen atmosphere. The solvents most commonly used are toluene, diethylether or tetrahydrofuran.

3. MONOMERIC GRIGNARD COMPOUNDS

Structural data for these derivatives are given in Table 1. Under a variety of conditions, magnesium in Grignard reagents has been found with coordination number from four to eight. Two limiting configurations are generally observed for coordination number four, these being tetrahedral and square planar. Only the former has been found in the chemistry of the Grignard reagents, and there are seven such examples with the chromophores MgO_2CBr [2–4], MgN_2CCl [5] and MgN_2CBr [6–8], respectively. Hetero ligands tend to cause varying amounts of distortion about the magnesium(II) atom. Angular distortions from regular tetrahedral geometry occur in compounds where only unidentate ligands are present, with angles ranging from 101 to 125° [2–4]. For the examples which contain bidentate ligands [5–8], even larger distortions are observed, with angles ranging from 83 to 129°.

The mean Mg–L bond distance increases with the covalent radius of the coordinated atom in the sequence: 216.5(15,15) pm (N, 75 pm) $<$ 223(8,11) pm (C, 77 pm) $<$ 233.2 pm (Cl, 99 pm) $<$ 248(4,2) pm (Br, 114 pm). The first number in parentheses is the difference between the mean and the shortest distance, and the second is the difference between the mean and the longest distance. The covalent radius is given with the coordinating atom.

In monoclinic $Mg(Me)(thf)_3Br$ [9], the five-coordinate magnesium(II) atom is at the centre of a trigonal bipyramid. The methyl group and the bromine atom are in axial sites, with the tetrahydrofuran ligands occupying the equatorial sites. This structure is the only example of a methyl Grignard reagent for which an X-ray structure is available.

The molecular structure of $Mg(thiq)(thf)_3Br$ [10] shows the Mg(II) atom to be in a pseudo-equatorial position of the (thiq) ring system, and to be sigma-bonded to its carbon atom (Mg–C = 224.5(11) pm). Intramolecular complexation of the carbonyl oxygen (Mg–O = 204.9(8) pm) gives a planar five-membered ring (C–Mg–O = 76.8(3)°). The magnesium atom is further coordinated by a bromine atom (Mg–Br = 262.2(4) pm and three thf molecules (Mg–O = 217.3(8,63) pm). The bromine atom occupies the position trans to the most electronegative ligand (carbonyl oxygen) on the Mg(II) atom, as expected.

TABLE 1

Structural data for monomeric Grignard compounds^a

Compound	Chromophore	Mg–L (pm)		L′–Mg–L (degree)		Ref.
$Mg(Et)(Et_2O)_2Br$	MgO_2CBr	O^b	204(2,1)	O,O^b	101.2(6)	2
		C	215(2)	O,C	110.7(8,1.1)	
		Br	248(1)	O,Br	103.4(5,4)	
				C,Br	125.0(5)	
$Mg(Ph)(Et_2O)_2Br$	MgO_2CBr	O	204(–,3)	O,O	Not given	3
		C	220	O,C	Not given	
		Br	244	O,Br	107(–,4)	
$Mg(Ph_3C)(Et_2O)_2Br$	MgO_2CBr	O	203(1,1)	O,O	101.5(4)	4
		C	225(1)	O,C	114.5(6,1.4)	
		Br	246.5(1)	O,Br	104.1(3,1.6)	
				C,Br	116.4(3)	
$Mg(Bu^t)(C_{15}H_{26}N_2)Cl$	MgN_2CCl	N	217.3(12,2)	N,N	83.9(5)	5
		C	219(2)	N,C	117.9(6,1.7)	
		Cl	233.2(7)	N,Cl	109.1(4,8.3)	
				C,Cl	114.7(5)	
$Mg(Et)(C_{15}H_{26}N_2)Br$	MgN_2CBr	N	215(3,1)	N,N	84.0(8)	6
		C	224(3)	N,C	120.5(9,1)	
		Br	248.2(9)	N,Br	105.9(7,2.5)	
				C,Br	115.1(8)	
$Mg(Et)(i\text{-}C_{15}H_{26}N_2)Br$	MgN_2CBr	N	218.0(3,15)	N,N	83.9(5)	7
		C	222.4(15)	N,C	117.9(6,11.6)	
		Br	250.6(6)	N,Br	112.2(4,10.6)	
				C,Br	112.1(5)	

Mg(Et)($C_{22}H_{32}N_2$)Br	MgN_2CBr	N	216(4,3)	N,N	83.1(1)	8
		C	234(5)	N,C	114.6(1,6.6)	
		Br	250.6(16)	N,Br	115.8(1,10.9)	
				C,Br	111.4(1)	
Mg(Me)(thf)$_3$Br	MgO_3CBr	O(eq)	213(–,15)	O,C/Br	92–122	9
		C(ap)	241 [Br(ap)]			
		Br(ap)	253 [C(ap)]	C/Br, Br/C	126	
Mg(thiq)(thf)$_3$Br	MgO_4CBr	O	204.9(8)	O,O	86.5(3,4.4)	10
		C	224.5(11)	O,C	88.3(4,11.5)	
		O(thf)	217.3(8,63)	O,Br	92.3(2,3.7)	
		Br	262.2(4)	C,Br	104.3(3)	
Mg($C_{14}H_{19}O_4$)Br	MgO_4CBr	O(eq)	213(1,1)	O,O	73.9(4)	11
		O(eq)	241(1,8)	O,C	122.1(4,2.4)	
		C(eq)	210(1)	O,Br	98.1(3,7)	
		Br(ap)	251.7(4)	C,Br	128.2(4)	
Mg{Me$_3$Si$_3$cp}(Me$_4$en)Br[c]	MgC_5N_2Br	C[d]	216.5	N,N	82.6(2)	12
		N	225.0(5,20)	N,Br	96.5(1,2.5)	
		Br	252.3(2)	N,C	123.0(–,3)	
				Br,C	124.9	
		C[d]	216.9	N,N	83.0(2)	
		N	223.9(5,21)	N,Br	96.6(1,1.2)	
		Br	251.0(2)	N,C	121.9(–,3)	
				Br,C	126.3	
Mg(cp(Et$_4$en)Br	MgC_5N_2Br	C	255(5)	N,N	82.5(5)	13
		N	226(–, 9)	N,Br	94.9(–,3.5)	
		Br	263(1)			

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[a] Where more than one chemically equivalent distance or angle is present, the mean value is specified. The first number in parentheses is the e.s.d., and the second is the maximum deviation from mean.

[b] The coordinated atom or ligand is specified in these columns.

[c] There are two crystallographically independent molecules present.

[d] The ring centroid.

In another example [11] magnesium is hexacoordinated in a strongly distorted pentagonal pyramidal configuration. The apex of the pyramid is occupied by a bromine atom, while the distorted basal plane contains a carbon atom and four oxygen atoms from the pentadentate 1,3-xylyl-15-crown-4 ligand. The oxygen atoms form "pairs", one having a mean Mg–O distance of 213(1,11) pm, and the other of 241(1,8) pm. This suggests that the eight-membered ring chelation is more stable than the five-membered [11].

In the remaining two examples [12,13], the magnesium(II) atom is semi-sandwiched between a cyclopentadienyl ring and a bidentate N-donor ligand plus a bromine atom. In one of these [12], two essentially identical but otherwise crystallographically independent molecules are present, differing in the angular arrangement of the cyclopentadienyl ring, bond distances and angles (Table 1). This is an example of distortion isomerism [14] in which two species, differing only by degree of distortion, coexist.

The data in Table 1 indicate the variability of the coordination sphere about the "hard" magnesium(II) atom. In each example, the coordination sphere is built up of a mixture of soft, borderline and hard donor ligands, which range from unidentate to bidentate and pentadentate. The most common coordinated halogen is bromine, and of the carbon donors the predominant species is the ethyl group. The mean Mg–L bond distance increases with covalent radius of the coordinating atom, and with increasing coordination number. For example, one observes the following sequences, for O-donor ligands: 204 pm (tetra-) < 213 pm (penta-) < 217 pm (hexa-coordinate); for Br atom ligand: 248 pm (tetra-) < 253 pm (penta-) < 257 pm (hexa-coordinate); for unidentate C-donor ligands: 223 pm (tetra-) < 241 pm (penta-coordinate).

It is noted that the orthorhombic crystal class is by far the most common in this series of Grignard reagents [3–8,10,13], with three monoclinic examples [2,9,11] and one triclinic [12].

4. DIMERIC AND OLIGOMERIC GRIGNARD COMPOUNDS

Structural data for the dimeric and oligomeric Grignard reagents are summarised in Table 2. There are three dimeric examples [15–17]. In $[Mg(al)(Me_4en)Cl]_2$ [15], two $Mg(al)(Me_4en)$ moieties are bridged by a pair of chlorine atoms with markedly different Mg–Cl distances of 240.0(1) and 269.4(1) pm, and Mg–Cl–Mg bridge angles of 95.32(3)°. A similar structure was found for the other two dimeric species [16,17], in which two Mg(Et)L units ($L = Et_3N$ [16] or Pr^i_2O [17]) are held together by a pair of bromine atoms with almost equivalent Mg–Br distances of 256.7 and 257.9 pm, respectively.

It is noted that the mean Mg–C bond distances in the tetra- and penta-coordinated Mg(II) dimer derivatives (214 and 217 pm) are shorter than those found in the monomer species (223 and 241 pm, respectively). The mean Mg–Br(bridge)

TABLE 2

Structural data for dimeric and oligomeric Grignard compounds[a]

Compound	Chromophore	Mg–L (pm)		M–M (pm) M–L–M (degree) μL–M–μL (degree)		L′–Mg–L (degree)		Ref.
$[Mg(al)(Me_4en)Cl]_2$ at 150 K	MgN_2Cl_2C	N[b]	224.8(2,37)		Not given	N,N[b]	80.20(7)	15
		(al)C	217.9(3)	Cl[b]	95.32(3)	N,C	99.26(8)	
		μCl	240.0(1)		84.69(3)	N,Cl	97.51(5,9.62)	
			269.4(1)			C,Cl	125.29(7)	
$[Mg(Et)(Et_3N)Br]_2$	$MgBr_2NC$	N	215		Not given	N,Br	105.3	16
		C	218			C, Br	117	
		μBr	256.7(–,1)			N, C	116.2	
$[Mg(Et)\{(Pr^i)_2O\}Br]_2$	$MgBr_2OC$	O	201.9(6)		Not given	O,C	120.7(3)	17
		C	209.4(11)	Br	86.8(1)	O,Br	117.0(3,3)	
		μBr	257.9(3,3)		93.2(1)	C,Br	102.2(2,3)	
$[Mg_2(Et)(thf)_3(\mu_3\text{-}Cl)\cdot(\mu\text{-}Cl)_2]_2$	$MgCl_3OC$	C(eq)	219(3)		Not given	C,μCl	125.9(12)	18
		μCl(eq)	240.1(11,6)			C,O	95.4(16)	
		O(ap)	214(2)		c_1	C_1,μ_3Cl	95.4(10)	
		μ_3Cl	279.1(9)					
	$MgCl_4O_2$	O	208(2,4)					
		μCl	248.9(9,17)			μ_3Cl,μ_3Cl	83.6(3)	
		μ_3Cl	250.2(10,7)			$\mu_3Cl, \mu Cl$	90.9(3,3.8) c_2	
$[(Mgnp_2)_2(npMgBr)_2]_n$	MgC_4	μC	234(2,11)		Not given 74.5(6,4)	C,C	108.7(7,19.0)	19
	MgC_2Br_2	μC	227(2,7)			C,Br	115.0(5,14.4)	
		μBr	281.3(5,5)	Br	86.4(2)	Br,Br	93.6(2)	

TABLE 2 (*continued*)

Structural data for dimeric and oligomeric Grignard compounds[a]

Compound	Chromophore	Mg–L (pm)		M–M (pm) M–L–M (degree) μL–M–μL (degree)		L′–Mg–L (degree)		Ref.
$[(C_8H_8)(\eta^5\text{-cp}^*)Th(Cl)_2\cdot Mg(Me_3CCH_2)(thf)]\cdot 0.5$ toluene[d]	$MgCl_2OC$	O	205(2)		Not given		Not given	20
		C	210(3)	Cl	95.9(3,2)			
		μCl	241(1,0)		92.8(4)			
	ThC_8Cl_2	cp*C	254					
		μCl	289.0(7,6)					
		(C_8H_8)C	202		74.4(2)			
$[(thf)_2LiBr_2Mg\cdot\{(Me_3Si)_3C\}(thf)]$	$MgBr_2OC$	O	206.1(13)		Not given	O,Br	98.2(4,6)	21
		C	219(2)	Br	80.4(9,1)	C,Br	119.4(5,6)	
		μBr	253.3(6,18)		98.0(2)	O,C	118.9(6)	
	LiO_2Br_2	O	195(5,0)			O,O	107(2)	
		μBr	247(4,2)			Br,Br	101(1)	
						O,Br	112(2,6)	
$[\{(cp^*)U(\mu\text{-}O)\cdot(\mu\text{-}C_{12}H_{14}P)\}_2Mg\cdot(C_{12}H_{15}P)_2(\mu_3\text{-}O)(\mu Cl)_2]$	MgC_2Cl_2O	C(eq)	223(4,0)		Not given	C,C	120(2)	22
		μCl(ap)	279(1,0)		[e]	C,Cl	86(1)	
		μ_3O(eq)	194(4)			C,O	128(1)	
						Cl,O	78.9(4)	
	UC_7O_2Cl	cp*C	285(2,3)		343.7(3)	C,C	151(1)	
		μC	264(2,4)	O	106(1,2)	C,O	79.9(6,12.9)	
		μO	213(2)			C,Cl	80.4(6,7)	
		μCl	292.8(9)			O,Cl	72.3(6)	
		μ_3O	218(2)				146.4(8)	
$[Me_2Si(Bu^tN)_2AlMe_2MgI]_2$	MgN_2I_2C	μC	261(1)		261.2(4)	N,I	103.7(2,1)	23
		μN	227.9(6,20)	I	92.9(1)		165.9(2,4)	
		μI	283.0(3,19)		87.1(1)	C,I	106.2(4,1.1)	
	AlN_2C_2	C	196(1)		[f]	C,C	108.9(5)	
		μC	201(1)			C,N	116.1(5,9)	
		μN	188.2(6,5)			N,N	Not given	

$[Mg_2(Pr^i)(Et_2O)Br_2 \cdot MoH(cp)_2]_2$	$MgBr_2C$	C	Not given	276(3)			Br,Br	94(3)	24
		μBr	255(3,4)				Br,Mo	119(2,1)	
	$MgBr_2O$	O	Not given	281(3)			Br,Br	91(3)	
		μBr	260(3,1)		Br	87(1,1)	Br,Mo	116(2,3)	
	$MoC_{10}H$		Not given				Mg,Mg	104(2)	
$[Mg_2(C_6H_{11})(Et_2O)Br_2 \cdot MoH(cp)_2]_2$	$MgBr_2C$	C	222(2)	285.3(7)			Br,Br	89.4(2)	24
		μBr	267.0(5,0)				Br,C	110.5(1)	
	$MgBr_2O$	O	208(2)	273.7(6)			Br,Br	94.4(6)	
		μBR	255.9(4)		Br	87.7(2)	Br,O	100.3(2)	
	$MoC_{10}H$	H	Not given				Mg,Mg	108.7(4)	
		cpC	231(2,4)						

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[a] Where more than one chemically equivalent distance or angle is present, the mean value is specified. The first number in parentheses is the e.s.d., and the second is the maximum deviation from mean.

[b] The coordinated atom or ligand is specified in these columns.

[c1] μ_3Cl–Mg–μCl = 83.3(3,3)°, μCl–Mg–μCl = 106.1(4)°; μ_3Cl–Mg–O = 169.2(7)°; μCl–Mg–O = 90.3(7,4)°; μ_3Cl–Mg–C = 95.4(10)°; μCl–Mg–C = 126.3(12,4)°; Mg–μ_3Cl–Mg = 89.2(3,7)°; Mg–μCl–Mg = 99.2(4,4)°.

[c2] μ_3Cl–Mg–O = 93.6(6,7) and 175.5(7,1)°; μCl–Mg–O = 89.1(6,6)°; O–Mg–O = 89.6(8)°; Mg–μ_3Cl–Mg = 96.4(3)°.

[d] There are two crystallographically independent molecules present.

[e] Mg–O–U = 128.0(6)°; Mg–Cl–U = 80.8(5)°.

[f] Al–C–Mg = 67.5(3)°; Al–N–Mg = 77.1(2,4)°.

distance of 257.3 pm for tetra-coordinate Mg(II) is longer than that of the Mg–Br (terminal) distance in the tetrahedral monomeric species, as might be expected.

The structure of monoclinic $[Mg_2(Et)(thf)_3Cl_3]_2$ [18] is shown in Fig. 1. The molecule lies on a crystallographic inversion centre, and contains a total of five four-membered bridging units consisting of magnesium and chlorine atoms. There are two pairs of independent magnesium(II) atoms which are penta- and hexa-coordinated, respectively. Two triple bridged and four double bridged chlorine atoms are present in the molecule (Table 2). This is the only tetrameric Grignard reagent for which X-ray data are available.

The structure of triclinic $[(Mgnp_2)_2(npMgBr)_2]_n$ [19] consists of a polymeric chain, involving an alternating pattern of two $Mgnp_2$ and two npMgBr fragments connected by bridging neopentyl and bromide ligands, with all Mg(II) atoms in a tetrahedral environment.

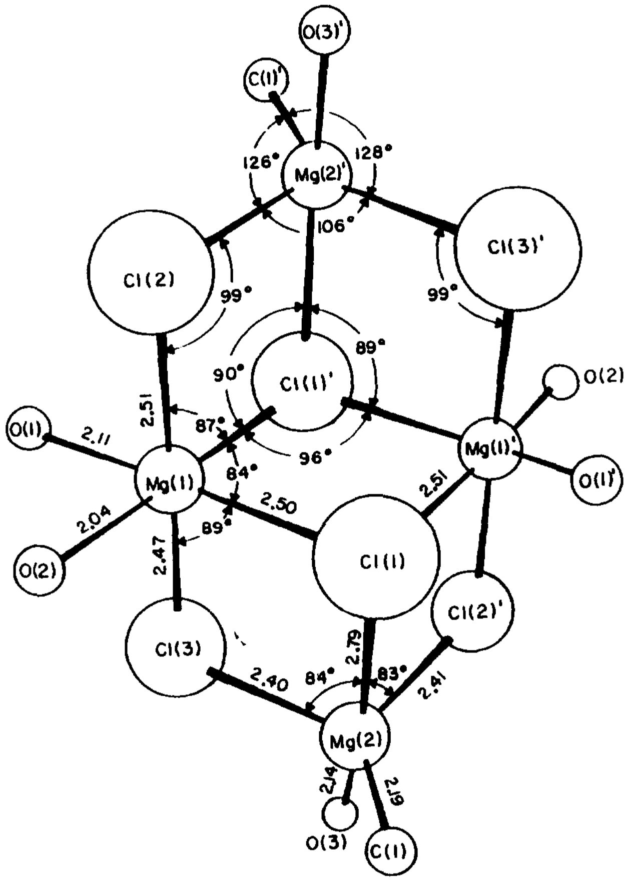

Fig. 1. Molecular structure of $[Mg_2(Et)(thf)_3Cl_3]_2$ [18].

There are two Grignard adduct derivatives in which the Grignard is connected to another heterometallic unit to form heterometallic species [20,21]. In the white monoclinic crystals of [$(C_8H_8)(\eta^5\text{-cp}^*)Th(Cl)_2Mg(Me_3CCH_2)(thf)$] [20], two of the chlorine atoms serve to bridge between the $Mg(Me_3CCH_2)(thf)$ and $Th(cp^*)(C_8H_8)$ moieties. While the Mg(II) atom is in a tetrahedral environment, thorium is formally deca-coordinate ThC_8Cl_2 (Table 2).

In the lithium–magnesium derivative [21] two bromine atoms serve to bridge the $Mg\{(Me_3Si)_3C\}(thf)$ and $Li(thf)_2$ units, completing a tetrahedral environment about both the Mg(II) and Li(I) atoms. A structural view of the heterotrimetallic Grignard adduct is shown in Fig. 2. The molecule contains a crystallographic twofold axis that passes through the three unique atoms O_1, O_2 and Mg. The basic structural feature is an oxo-centred trimetal cluster composed of two uranium and one magnesium atom. The U_2MgO unit, the two chlorides and the oxide bridging the triangular edges, together with the centroids of the two pentamethylcyclopentadienyl groups all lie in a plane [22]. The geometry about the Mg(II) atom is distorted trigonal-bipyramidal (Table 2).

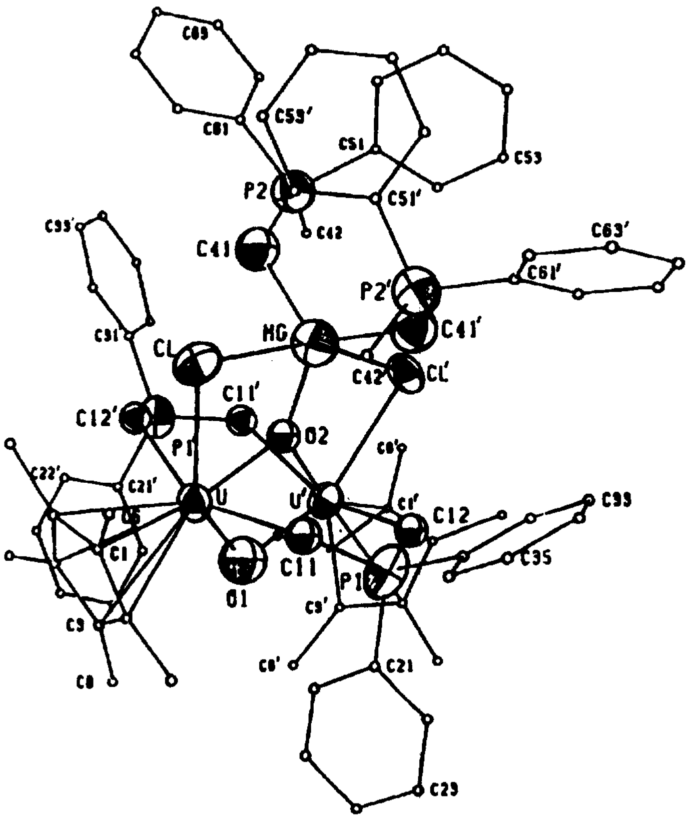

Fig. 2. View of [$\{cp^*U(O)(C_{12}H_{14}P)\}_2(O)(Cl)_2Mg(C_{12}H_{15}P)_2$] [22].

Another heterometallic Grignard adduct [23] contains a centrosymmetric Mg_2I_2 rectangle, as shown in Fig. 3. The magnesium atom is further coordinated by two N atoms of the Bu^{t}N ligands plus a methyl group. Each of the aluminium atoms is tetra-coordinate (Table 2). The Mg–Mg distance of 261.2(4) pm is the shortest found in the chemistry of the Grignard adducts.

The remaining two heterometallic Grignard adducts are isomorphous [24]. A schematic outline of the structure is shown in Fig. 4. It can be seen that there are two pairs of non-equivalent magnesium(II) atoms. The Mg–Mo distances of 276(3)

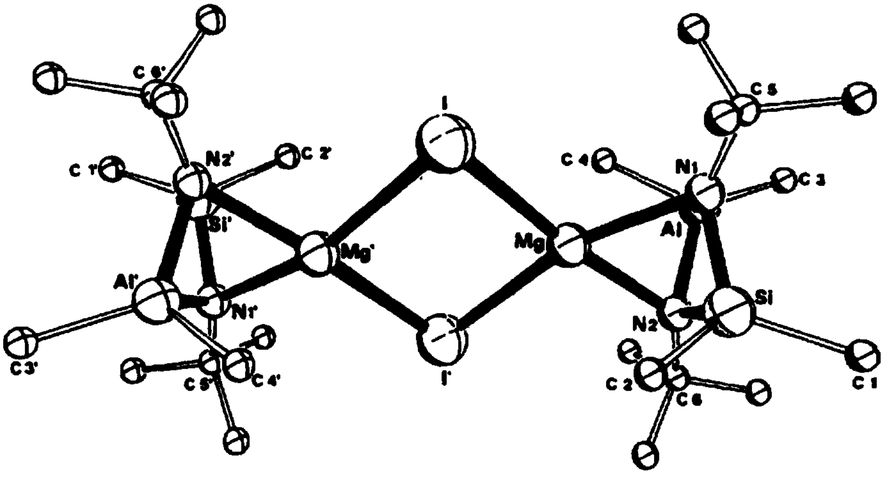

Fig. 3. Molecular structure of $[Me_2Si(NBu^t)_2AlMe_2MgI]_2$ [23].

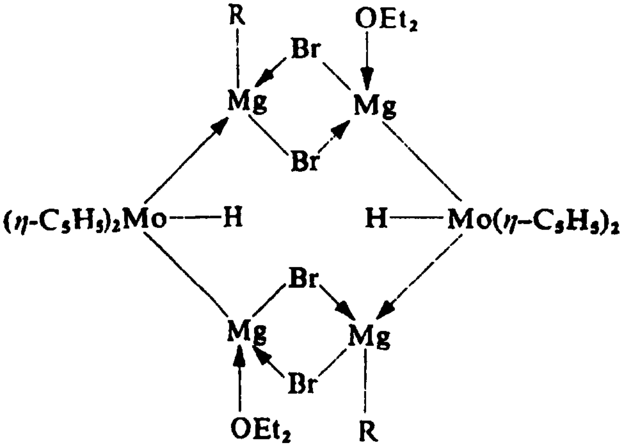

Fig. 4. Schematic outline of $[Mg_2R(Et_2O)Br_2MoH(cp)_2]_2$ [24].

and 281(3) pm (when R is isopropyl), 283.5(7) and 273.7(6) pm (when R is cyclohexyl) indicate a metal–metal bond.

The data in Table 2 show that the magnesium(II) atoms are tetra-, penta- and hexa-coordinated. The mean Mg–L bond distance of the tetra-coordinated derivatives increases with the covalent radius of the donor atom in the order 205 pm (OL, 73 pm) < 215 pm (NL, 75 pm) < 216 pm (CL, 77 pm). For the bridging ligands, the order is 231 pm (μCL, 77 pm) < 241 pm (μCl, 99 pm) < 261 pm (μBr, 114 pm). For the penta-coordinate adducts, the Mg–L distances increase in the order, for unidentate ligands 214 pm (OL) < 220 pm (CL); and for bridging ligands 194 pm (μ_3O, 73 pm) < 228 pm (μNL, 75 pm) < 258 pm (μCl, 99 pm) < 261 pm (μCL, 77 pm) < 283 pm (μI, 133 pm). The mean Mg–O bond distances in this series of adducts are shorter than those in the monomeric adducts. The most common crystal class in this series is monoclinic [15–18,20,23,24], the other two are triclinic [19] and hexagonal [22].

5. CONCLUSIONS

Grignard reagents are well established as powerful catalysts, and the first X-ray structure of a derivative was obtained in 1963 for Mg(ph)(Et$_2$O)$_2$Br [3]. From the subsequent structures collected in this review, it is evident that there is no "typical" Grignard structure, but rather a considerable dependence on the nature of the groups coordinated around the magnesium(II) atom. Relatively minor changes in the type of organic ligand, or coordinated solvent molecule, can give rise to a completely different type of structural arrangement. This does suggest that the structural arrangement observed in the solid state may not correspond exactly with the active structural arrangement in solution. Regarding the question of the existence of the unsymmetrical R–Mg–X species, there are several examples of such a species with coordination numbers from four to six (Table 1), the extra coordination sites involving either solvent molecules or other donor sites on the R ligand. The unsymmetrical species is thus not a transitory solution species, although it may not be safe to assume that the coordination number is just four, in view of the existence of the five-coordinate Mg(Me)(thf)$_3$Br [9]. In addition, there two other, higher coordination number, examples in which R is a π-donor and solvent is also incorporated. In the oligomeric derivatives (Table 2), it can be seen that bridging is not solely dependent on the halogen atoms present, as it is in the dimeric examples investigated to date.

There are two examples [12,20] in which two crystallographically independent molecules, differing by degree of distortion, coexist in the same crystal. The differences occur in both the Mg–L bond distances and the bond angles, which is typical for distortion isomerism [14].

From the nuclearity point of view, there are monomers, homo- and hetero-dimers, hetero-trimers, homo- and hetero-tetramers, and a homo-polymer. The magnesium(II) atoms are tetra-, penta- and hexa-coordinate, with tetra-coordinate being the most common. There is one example in which the Mg(II) atom is coordinated by an η^5-cyclopentadienyl ring, plus a bidentate Me_4en ligand and a bromine atom [12], giving a rather unique semi-sandwich type of structure.

From both Tables 1 and 2, it is seen that the mean Mg–L bond distance increases with the covalent radius of the coordinated atom, e.g. the tetra-coordinate derivatives Mg–L(terminal) distances in the order 205 pm (OL, 73 pm) < 215 pm (NL, 75 pm) < 220 pm (CL, 77 pm) < 233 pm (Cl, 99 pm) < 248 pm (Br, 114 pm). For the bridging ligands, the order is 231 pm (μ-CL) < 241 pm (μ-Cl) < 261 pm (μ-Br). As the coordination number increases, non-bonding repulsion forces between the ligands are greater and this causes the metal–ligand distances to increase. Thus, for example, the mean Mg–L distances for a C-donor ligand (CL) increase in the order 220 pm (tetra-) < 225 pm (penta-coordinate); for a bromine ligand the order is 248 pm (tetra-) < 253 pm (penta-) < 257 pm (hexa-coordinate); and for O-donor ligands (OL) the order is 205 pm (tetra-) < 213 pm (penta- and hexa-coordinate). This seems to suggest that, although the Grignard reagents can utilize a variety of ligand types, the central magnesium retains its essentially "hard" character.

Including the Grignard reagents, there are almost 400 magnesium compounds for which X-ray data are available [25], both coordination compounds and organometallic derivatives. The Grignard reagent structures include several of the types found in the general body of magnesium compound structures, rather than having a typical or characteristic structure, as noted above. However, given the variety of structural types clearly possible for the Grignard reagents, further crystallographic studies of these important compounds should be both interesting and useful.

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