Chem. Rev. 1995, 95, 2405–2456

Intramolecular Coordination in Organometallic Compounds of Groups 2, 12, and 13

Gert-Jan M. Gruter, Gerard P. M. van Klink, Otto S. Akkerman, and Friedrich Bickelhaupt*

Department of Chemistry, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

Received January 19, 1995 (Revised Manuscript Received June 16, 1995)

Contents

I. Introduction

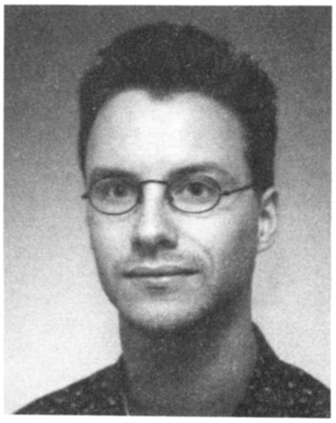
Nearly 40 years have elapsed since the synthesis of the first stable organometallic derivatives with intramolecular coordinate (dative) bonding. The term intramolecular coordination (IC) has been used to indicate that the donor atom is linked to the metal by one or more atoms, connected by *two* or more covalent bonds ("a chain"). At their discovery in 1955, these compounds were called "inner complexes" by Bähr and Müller.[1] Since then, only two reviews on "intramolecular coordination in organic derivatives of non-transition elements" have appeared. Both were published by Prokof'ev in 1970[2] and in 1976,[3] respectively, and treated IC of *all* non-transition elements. The present review will be confined to IC of the elements of groups 2, 12, and 13. IC Compounds of lithium require separate treatment, as their structures differ significantly from those of groups 2, 12, and 13 due to extensive aggregation. We excluded IC in compounds of the elements of group 14–16 as well as organotransition metal intramolecular coordination compounds because these have received extensive coverage by Omae,[4–9] who, on the other hand, included only few non-transition metal compounds.

The reason for the comparatively slow development of this field and the relatively limited number of review articles on this subject is 2-fold. First, and most important, is the fact that compared to the long history of synthetic applications of group 2, 12, and 13 organometallic compounds, the investigation of their structure and bonding in general covers a much shorter period. Physical and physicochemical methods for the determination of the structure of a chemical substance, which is often required in the detection and demonstration of IC, became only available relatively recently. The second reason is the difficulty to track down the literature in which IC compounds are discussed. When we performed a computer search on IC, only part of the known IC compounds emerged. Therefore, in order to find as many IC compounds as possible, all chapters on organometallic chemistry of *Chemical Abstracts* were screened by hand from 1976 (appearance of the last review) until March 1995, in order to cover the literature up to 1994. However, it must be emphasized that even with this method, it is very difficult to achieve completeness, and we may have missed compounds in which IC does occur. We would very much like to receive from the readers of this review article any references to compounds we have not included.

The aim of this review is to survey data on the structural, physical, and chemical properties of in-

0009-2665/95/0795-2405$15.50/0

Gert-Jan M. Gruter was born in Amsterdam in 1963. He received his M.Sc. degree from the Vrije Universiteit in Amsterdam in 1990 with a synthetic study on [1.1]metacyclophane in the group of F. Bickelhaupt, and his Ph.D. with F. Bickelhaupt and O. S. Akkerman on topics combining organometallic and macrocyclic (crown ether) chemistry in 1994. In the same year, he joined DSM Research and is currently working in the field of homogeneous Ziegler–Natta catalysis. His research interests are intramolecular coordination, macrocyclic chemistry, chemical topology (rotaxanes, catenanes), and, more recently, metallocenes and polyolefin chemistry.



Gerard P. M. van Klink was born in Heemskerk, The Netherlands, in 1966. He obtained his M.Sc. from the Vrije Universiteit in Amsterdam in 1992 with an investigation of the activation of organomagnesium compounds by crown ethers. Presently, he is engaged in research for a Ph.D. thesis with O. S. Akkerman and F. Bickelhaupt, working on the mechanism of formation of the Grignard reagent and on the synthesis of new organometallic rings, rotaxanes, and catenanes.

Otto S. Akkerman, born in 1932 in Apeldoorn, The Netherlands, obtained his Ph.D. in organic chemistry at the Vrije Universiteit of Amsterdam with Professor Dr. J. Coops. Since 1978 he has worked with F. Bickelhaupt in the field of organometallic chemistry. Current research interests are the thermochemistry of organomagnesium and other organometallic compounds (reaction enthalpies, enthalpies of formation, and bond dissociation energies) and organometallic compounds of groups 2 and 12 containing macrocycles capable of intramolecular coordination.

Friedrich Bickelhaupt obtained his Ph.D. in organic chemistry at the University of Tübingen with G. Wittig in 1957. After a postdoctoral period with K. Wiesner (University of New Brunswick at Fredericton, Canada, alkaloid chemistry) and R. B. Woodward (Harvard University, chlorophyl synthesis), he joined in 1960 the research laboratories of Boehringer Mannheim (Germany, psychopharmaca). In 1964, he was appointed Professor of Organic Chemistry at the Vrije Universiteit in Amsterdam. Current research interests are in the fields of organometallic chemistry, of low coordination chemistry in groups 14 and 15, and in valence isomers of benzene and small cyclophanes.

tramolecularly coordinated main group organometallic compounds.

II. General Aspects

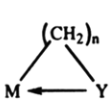
A. Definitions

In 1955 IC was defined for the first time as "The compounds are cyclic, having a methylene chain and a coordinative bond between the metal (M) and ligand atoms (Y)" [1] (Scheme 1).

In 1976, IC was defined again in Prokof'ev's review:[3] "Compounds are intramolecularly coordinated if the chain containing the donor atom (Y) is linked to the acceptor element (M) via *carbon* atoms" (Scheme 2).

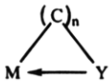
In this review, we will use a slightly adapted version of this definition. Prokof'ev used C_n instead of $(CH_2)_n$, because the connecting carbon atoms are often part of an aromatic ring or part of a C=C or C=O group. Both Prokof'ev[3] and Omae[9] explicitly exclude compounds with a *non*-carbon atom in the chain. However, we will include these compounds, as long as the atom connected to the metal is a carbon atom, because in fact these compounds do exhibit the phenomenon of IC. An illustrative example of this category is given in Scheme 3.[10-12]

Scheme 1



M = metal
Y = coordinating atom
n = preferably 3 or 4

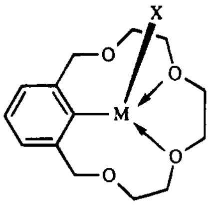
Scheme 2



M = metal
Y = coordinating atom or group
$n \geq 1$

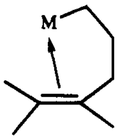
Compounds in which the donor group of Scheme 1 is a carbon–carbon double bond will also be considered (Scheme 4).

Scheme 3



M = Mg; X = Ph, Br
M = Zn; X = I

Scheme 4



IC has been successfully applied in the synthesis of reactive and unstable species such as carbenes and arynes, species often not readily available by other methods. Reactions of this kind were reviewed by Prokof'ev *et al.* in 1977.[13]

As shown above, IC can be described as a donor−acceptor interaction with partial charge transfer taking place within a single molecule, leading to the formation of a new dative M−Y single bond. The distinction between a dative and a covalent bond has been extensively evaluated by Haaland.[14] In the context of our review, Haaland's conclusions are of conceptual importance; they may be briefly summarized as follows. A chemical bond is dative, if bond cleavage (by the lowest energy pathway) occurs heterolytically; a chemical bond is "normal" (either covalent or ionic) if this cleavage occurs homolytically. Comparison of the physicochemical properties of both bond types for certain pairs of atoms M−Y (M is main group metal; Y is a donor atom of groups 15−17) showed the following trends:[14]

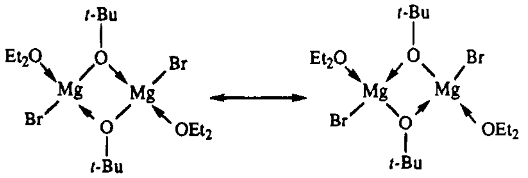
(1) The strength of a dative bond is very much dependent on the groups bonded to the acceptor atom. These different bond strengths are clearly reflected by differences in bond lengths.

(2) From data of the metals of groups 12−14, the strength of a dative bond is presumed to be less than half of that of a covalent bond between the same (or an isoelectronic) pair of atoms. Again, the distinction is also revealed in the bond lengths.

(3) The coordination geometry around the acceptor atom can be predicted by the VSEPR (*V*alence *S*hell *E*lectron *P*air *R*epulsion) model: e.g. electron donors in pentacoordinated trigonal-pyramidal adducts occupy equatorial positions. The VSEPR model also predicts that coordinative bonding to an(other) electron donor lengthens the metal−acceptor atom bonds and decreases their bond angle. Both effects are amplified by steric repulsion between the donor molecule and substituents at the acceptor atom.

(4) Some molecules show equal bond lengths due to delocalization of bonds (resonance). In these cases the bond lengths lie usually between the length of a fully covalent bond and of a fully dative bond and increase with growing dative character. In symmetrical fragments like $M_2(\mu_2\text{-}NR_2)$, $M_2(\mu_2\text{-}OR)$, or $M_2(\mu_2\text{-}X)$ (where X = halogen) every M−N/O/X bond is half covalent and half dative. An illustrative example is given in Scheme 5.

Scheme 5



The strength of a coordinative IC bond is in principle the same as that of an intermolecular bond between the same metal center and a coordinating (solvent) molecule and has been suggested to be energetically close to hydrogen bonding.[3] The extremes, however, are rather far apart: from structures in which IC occurs only in the transition state on the one side, to nearly complete charge transfer as in γ-aminopropyl compounds of boron on the other. However, there are some specific aspects in which IC differs from "normal" *inter*molecular coordination. IC involves the formation of rings. Upon ring formation, ring strain may be introduced, which may weaken the IC bond. Furthermore, IC can often be sterically less demanding than intermolecular coordination. This may be illustrated by organomagnesium chemistry (cf. section III.B.3). While *inter*molecularly coordinated Grignard reagents seldom have coordination numbers higher than 4, *intra*molecularly coordinated ones can obtain coordination numbers as high as 5 or even 6. The difference is clearly related to steric factors: while in the intermolecular case, steric hindrance between the substituents at magnesium and/or between the solvating (ether) molecules prevents the coordination of more than two Lewis bases, IC replaces the van der Waals repulsion of independent groups by favorable bonding interactions.

The data reviewed are arranged systematically on the basis of group number of the periodic table in the order 2, 12, and 13; subdivisions have been made for individual metals (for group 2 only), for donating atoms, and for ring-size. The donating atoms are treated in the (arbitrary) order N, P, (As), O, S, Hal, and C=C; each type of ligand is discussed in the order of increasing size of the rings formed in IC. As in the review of Prokof'ev,[3] particular attention is given to X-ray crystal and gas phase electron diffraction studies, since the geometric criterion—the donor−acceptor bond distance—is one of the most clear-cut pieces of evidence for the presence or absence of coordination.

B. Coordination

The lone pairs in ethers can be described in two different ways. The oxygen is considered to be either (approximately) sp^3 hybridized which makes the two lone pairs degenerate and places them in a plane perpendicular to the C−O−C plane, or it is considered sp^2−p hybridized involving a sp^2 lone pair along the bisector of C−O−C and one in a p_z orbital perpendicular to the C−O−C plane. Chakrabarti and Dunitz have investigated the spacial orientation of alkali and alkaline earth cations toward ethers by analyzing a large number of crystal structures.[15] In a similar fashion, we have analyzed the geometric relation between carbon-bonded magnesium[16] or zinc[17] and the ether oxygen. From these investigations, it can be concluded that there seems to be no particular tendency for magnesium or zinc to be located on or near the bisector, which is the direction of the sp^2 lone pair and/or the ether dipole axis: magnesium and zinc are located in a rather flat ellipsoid along the plane of the lone pairs. In this regard, IC compounds do not differ markedly from *inter*molecular complexes.

C. Synthesis

Like normal organometallic compounds, intramolecularly coordinated organometallic compounds are usually synthesized by transmetalation (mostly by lithium− or magnesium−metal exchange), by direct reaction from a halogen precursor compound, or by metalation. The use of regioselective *ortho*-metalation reactions of aromatic substrates has become widespread in organic and organometallic synthesis, since many of those proceed easily with high selectivity and good yields. Several effects are believed to account for the ease of such reactions. In most cases, the heteroatom renders the adjacent proton more acidic by inductive effects and thus favors metalation. Coordination of the organometallic reagent to the heteroatom(s) of the substrate brings the reactants together in an initial complex and makes subsequent conversion a favored "intramolecular" process. In the transition state, the coordinating heteroatoms will assist in minimizing the energy barrier for the reaction. Finally, thermodynamic stabilization of the product drives the reaction to completion; the formation of IC bonds and/or dipolar interactions is energetically favorable, mainly because the congestion around the metal is reduced and because the entropy of coordination is less negative.

D. Characterization

X-ray crystal structure determination and gas-phase electron diffraction furnish by far the most convincing evidence for the occurrence of intramolecular coordination. However, crystals suitable for an X-ray crystal structure determination often cannot be obtained, and in many cases gas-phase electron diffraction is not possible due to low vapor pressures or the complexity resulting from the presence of too many different bonds. Other valuable tools for the demonstration of IC are NMR and IR spectroscopy. The latter is especially useful if a carbonyl group is involved in IC. This functional group is very common in organotransition metal chemistry, but it is usually not stable in the presence of group 2 and 12 (Zn and Cd) compounds because addition of the metal−carbon bond across the carbonyl group or reduction occur. Another valuable tool in the determination of IC is thermochemistry which, moreover, is one of the few methods to quantify the strength of an IC bond. Unfortunately, this technique has not often been applied, as the experimental setup for air- and moisture-sensitive organometallic compounds is difficult. In our laboratory, equipment has been developed for the measurement of heats of reaction in fully sealed glass systems (cf. section III.B.3).

In special cases, specific properties of IC compounds can be used for their identification. Characteristic features of IC are the relatively low and sharp melting points and relatively low boiling points. The monomeric nature of IC compounds has been demonstrated by molecular weight determinations; in combination with elemental analyses of the assumed IC compound and analyses of its hydrolysis products, further evidence for its constitution may be obtained. As a test for the presence of a gap in the coordination of a metal, "Ätherabblasversuche" (ether blow off experiments) were important. An accurately weighed sample of a compound subjected to this test is mixed with a certain donor solvent, for instance diethyl ether. Normally, the metal center of the organometallic compound strongly coordinates to the solvent and thus prevents its evaporation. If, however, the donor solvent is evaporated rapidly and quantitatively, it is assumed that the metal atom is coordinatively saturated by IC to such a degree that coordination to an external donor solvent is not required.

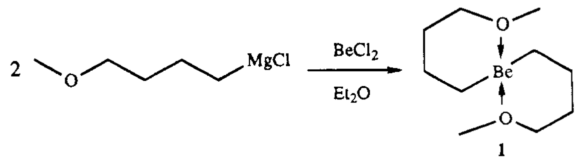
III. Group 2 Metals

A. Beryllium

The organometallic chemistry of beryllium is not developed as much as that of lithium or of beryllium's heavier brother magnesium. As a result, very few IC compounds of beryllium are known to date. The IC chemistry of beryllium is therefore treated in chronological order and not by ligand and ring size.

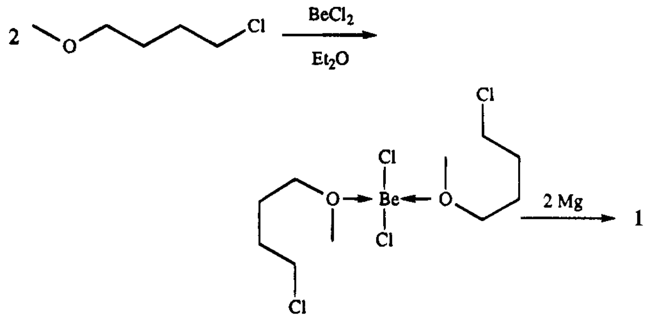
The electron deficiency of beryllium is evident from a distinctive tendency toward coordination with nucleophilic ligands (ethers, amines) or—in their absence—toward aggregation; however, there are no compounds known with a coordination number greater than four, presumably because the atomic orbitals of beryllium required to accomodate additional bonds would have the principal quantum number of three and are thus too high in energy to participate in bond formation.[18] Illustrative for the characteristic competition between coordination and association is the difficulty to obtain absolutely ether-free diethylberyllium from a diethyl ether solution. By incorporation of a donor atom (O, S) at a suitable position in the alkyl chain, Bähr and Thiele[19] succeeded in diminishing the coordinative unsaturation of beryllium and thus in reducing self-association. This strategy was successful for bis(4-methoxybutyl)beryllium (**1**) and for bis[3-(ethylthio)propyl]beryllium (**2**). Compound **1** was synthesized by two routes: from the Grignard reagent of 4-chloro-1-methoxybutane and anhydrous beryllium chloride in diethyl ether (Scheme 6), or from the reaction of a precom-

Scheme 6



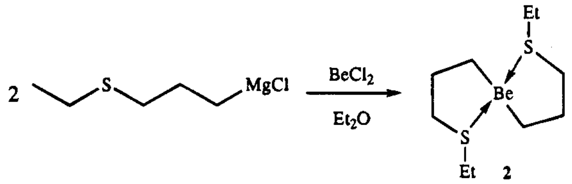
plex, formed in a highly exothermic reaction from 2 mol of 4-chloro-1-methoxybutane and 1 mol of beryllium chloride, by reaction with magnesium in diethyl ether (Scheme 7).

Scheme 7



Compound **2** could only be synthesized by the first approach (Scheme 8). It is a remarkable compound, because it is known that dimethyl- and diethylberyllium associate rather than form (*inter*molecular!) adducts in dimethyl sulfide.[20] In **2**, coordination goes along with ring formation. The compound, which is monomeric and has the tetracoordination characteristic for beryllium, does not form adducts with the stronger Lewis base diethyl ether. Similarly **1** is also monomeric and does not form adducts with diethyl ether.

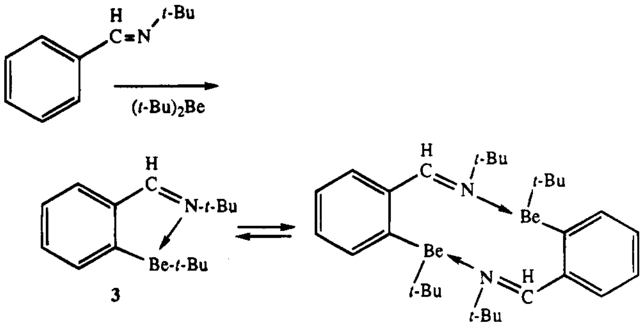
Scheme 8



The properties of the intramolecularly coordinated organoberyllium species **1** and **2** were found to be markedly different from those of the known (associated) organoberyllium compounds such as diethylberyllium. Very characteristic are the low melting points (**1**, 7.5–7.8 °C; **2**, 7–8 °C) and boiling points [**1**, 108 °C (4 Torr); **2**, 122–123 °C (2 Torr)]. Although the molecular weights of **1** and **2** are roughly 3 times higher than that of diethylberyllium, the boiling points fall in the same range. Both compounds show a remarkable thermal stability and a decreased reactivity toward oxygen. Compound **2** underwent no decomposition during prolonged heating at its boiling point [220–225 °C (1 bar)]. Elemental analysis, molecular weight determination (cryoscopy in benzene), hydrolysis, and "Ätherabblasversuche" at room temperature showed the presence of intramolecular coordination in compounds **1** and **2**.

In contrast to the rapid reduction of aldehydes and ketones by beryllium alkyls, only a few azomethines and no alkyl cyanides were reduced. Instead, addition and complex formation was observed. Complex formation between *tert*-butylated azomethines (PhCH=N-*t*-Bu) and dialkylberyllium leads to *ortho*-metalation. With $(t\text{-Bu})_2Be$, the degree of association of the resulting product **3** in benzene is 1.55–1.66, which was taken to indicate the presence of the equilibrium depicted in Scheme 9.[21]

Scheme 9



B. Magnesium

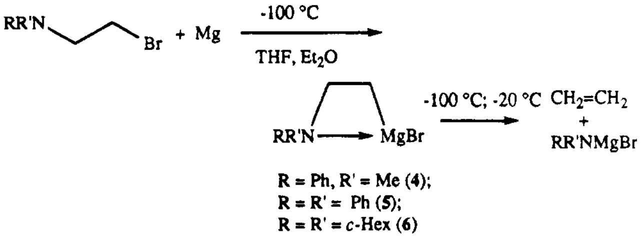
About 90 crystal structures of organomagnesium compounds containing an Mg–C bond are known to date;[16] 17 of these show IC. In order to be able to compare the structural data of IC organomagnesium compounds with "normal" *inter*molecularly coordinated organomagnesium compounds, the structural chemistry of the latter is briefly outlined.

In intermolecular alkyl and aryl complexes, the Mg–C bond lengths range from 2.15 to 2.30 Å; the covalent bond length of a typical magnesium–carbon bond is 2.15 Å.[16] In Grignard reagents, the terminal Mg–Br lengths are 2.44–2.48 Å; in dimeric μ-Br species, they are increased to 2.58 Å. Mg–O coordinative bond distances fall in the range of 2.05–2.20 Å; relatively short Mg–O bonds (2.0 Å) imply strongly coordinating ether groups (e.g. 2.026 Å in $EtMgBr\cdot(Et_2O)_2$ and 2.020(5) Å in $[(p\text{-tolyl})_2Mg\cdot THF]_2$), while weak Mg–O interactions result in long Mg–O bonds (up to 2.8 Å; e.g. 2.767–2.792 Å in the complex of diethylmagnesium threaded in 18-crown-6[22]). The variation of coordination number and association of the magnesium has been attributed to the steric requirements of the solvating ether or amine;[23] the effective volume follows the order $NEt_3 > OEt_2 >$ THF, but the inherent basicity of such ligands must also play an important role. It is of interest that in the solid state, diorganylmagnesium compounds MgR_2 and most Mg(R)X centers are involved in tetracoordination only (if IC donors are absent). One way to increase coordination numbers of magnesium is the use of IC ligands which normally require less space around the metal center.

1. Magnesium Complexes with Nitrogen Donor Atoms

a. Four-Membered Rings. The chemical manifestations of IC are rather varied and sometimes even involve anomalous elimination reactions and rearrangements. When alkyl halides containing a heteroatom in the β-position are reacted with metals, extremely unstable organometallic compounds are formed which decompose by β-elimination resembling an E1cB process.[24] From the beginning of this century, contradictory reports appeared about the existence of the β-amino Grignard reagent $PhMeNCH_2CH_2MgBr$ (**4**).[25-28] In 1979, the first reliable proof for the existence of compounds of this type at very low temperature was provided.[29] Several halides $RR'NCH_2CH_2Br$ were reacted with highly activated magnesium between −75 and −100 °C in THF and diethyl ether to furnish the Grignard

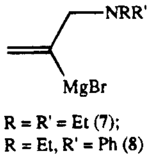
Scheme 10



compounds $RR'NCH_2CH_2MgBr$ [R = Ph, R′ = Me (**4**); R = R′ = Ph (**5**); R = R′ = cyclohexyl (**6**); Scheme 10]. These compounds decompose between −90 and −20 °C under formation of ethylene. Originally, this facile elimination was assumed to be accelerated by intramolecular coordination; however, Steinborn suggested that elimination occurs already at intermediate radical stages.[29] The thermal stabilities increase in the series **4** < **5** < **6**. This order apparently reflects the different nucleophilicities and steric bulk of the R_2N groups.

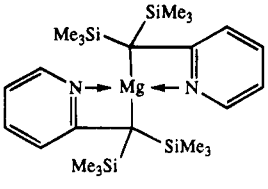
There are only two other examples of successful formation of Grignard compounds containing a β-nitrogen atom. Ficini *et al.*[28] reported β-nitrogen substituted vinylic Grignard compounds $RR'NCH_2CH(MgBr){=}CH_2$ [R = R′ = Et (**7**); R = Et, R′ = Ph (**8**); Scheme 11]. Their stability at room temperature was attributed to the higher electronegativity of the sp^2-carbon atom and to the reduced tendency to form an allene by β-elimination.[28,30]

Scheme 11



In the second example, β-elimination is not possible (Scheme 12). Compound **9** was synthesized by rapid metalation of $2\text{-}CH(SiMe_3)_2C_5H_4N$ with (n-Bu)(s-Bu)Mg,[31] a reaction which is presumably assisted by the pyridine nitrogen,[32] as $o\text{-}(Me_3SiCH_2)_2C_6H_4$ is not metalated at all under the conditions where $2\text{-}Me_3SiCH_2C_5H_4N$ is metalated.[31]

Scheme 12



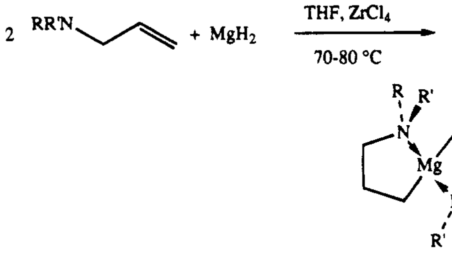
9

The IC was demonstrated by an X-ray crystal structure.[31] The Mg−C and Mg−N distances are 2.219 and 2.131 Å, respectively. The C−Mg−C and N−Mg−N angles are 157.07 and 117.49°, respectively. In the four-membered rings, the C−Mg−N, C−C−Mg and Mg−N−C angles are 67.32, 84.54 and 91.17°. The large C−Mg−C angle suggests that the normally linear coordination (sp) of a dialkylmagnesium[16] is only slightly disturbed toward tetrahedral by the two pyridine nitrogens; the observed C−N−Mg angle is 91.17°, while the orientation of the lone pair of the pyridine nitrogen would ideally be 120°. However, the authors conclude from the fact that two highly strained four-membered rings are formed that IC in **9** is strong, which is also in line with the remarkably small C−C−Mg angle.

b. Five- and Six-Membered Rings. Haloalkylamines $R_2N(CH_2)_nX$ generally form stable organomagnesium compounds in THF when $n \geq 3$.[33-35] The first reaction of magnesium with a γ-halo tertiary amine was reported by von Braun *et al.* as early as 1919;[36] it gave $PhMeNCH_2CH_2CH_2MgBr$ (**10**). This work was confirmed by Gilman and Heck,[26] but the most important contributions to this series of Grignard reagents was made by Marxer.[37] Later, modified experimental procedures were published by Perrine and Sargent,[38] but the reaction remains difficult and not always gives satisfactory results. Solvent, temperature, and reaction time dependence of the formation of the Grignard reagents from γ-chloropropylamines were investigated by Sadet and Rumpf in 1973.[34] The occurrence of IC in γ-aminoorganomagnesium compounds has been confirmed spectroscopically by ^1H NMR spectroscopy (*vide infra*), but it is difficult to estimate the extent of IC in these compounds.

Recently, a series of magnesium inner complexes has been prepared by reacting MgH_2 (prepared by homogeneous catalysis from Mg and H_2) as a THF suspension with dialkylallylamines, dialkyl-3-butenylamines, and alkyl-3-butenyl ethers in the presence of catalytic amounts of transition metal derivatives.[39] The first reaction studied was that with allyldimethylamine. A smooth reaction was observed at 70 °C, and the addition product $Mg[(CH_2)_3NMe_2]_2$ (**11**) (Scheme 13) was isolated by vacuum sublimation as long white needles.

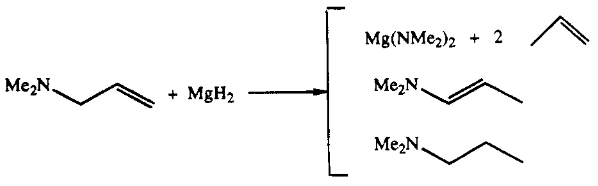
Scheme 13



11	R = R' =	Me	**16**	R =	Me	R' =	Et
12		Et	**17**		Me		Bu
13		Pr	**18**		Me		c-Hex
14		i-Pr	**19**		Me		Ph
15		Bu					

In side reactions (Scheme 14) propene (≤17%) was formed, isomerization of the allylic group occurred to give *trans*-1-propenyldimethylamine (15%), and hydrogenation yielded propyldimethylamine (8.5%).

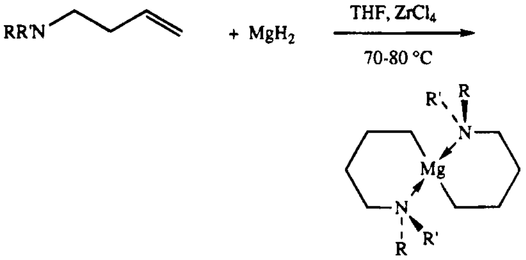
Scheme 14



The reactions of the many other tertiary allylamines shown in Scheme 13 yielded in all cases minor amounts of the above-described side products besides unreacted starting material (30–50%). The yields of the organomagnesium compounds were 35–50% with the exception of those of the amines with bulky substituents: **14** (11%) and **18** (5%). All products were obtained in pure form by vacuum distillation as yellow liquids which solidified upon standing at room temperature. In principle, inter- and intramolecular coordination could both lead to tetra-coordinated magnesium. However, the results of cryoscopic molecular weight determinations and mass spectrometry suggested that monomeric structures were present both in solution and in the gas phase.

The 3-butenylamines reacted analogously with MgH_2 to give $Mg[(CH_2)_4NRR']_2$ (**20-26**) in 10–50% yield, depending on the size of R (Scheme 15).

Scheme 15

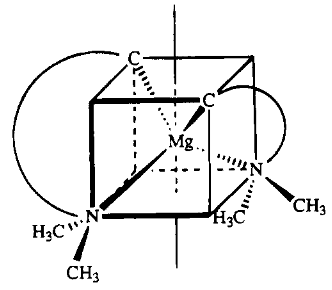


20	R = R' =	Me	**24**	R = Me R' =	Et
21		Et	**25**	Me	Bu
22		Pr	**26**	Me	*c*-Hex
23		Bu			

Again, side reactions were hydrogenation (4–20%) and isomerization of the double bond (10–25%), but with these compounds, the formation of butene and $Mg(NRR')_2$ was not observed. ^1H NMR spectroscopy of $Mg(s\text{-}Bu)_2$ showed that the signals of the α-protons shifted from the normal value of $\delta = +0.2$ to $\delta = -0.15$ to -0.35 ppm upon complexation of magnesium with nitrogen or oxygen. The chemical shifts of the α-protons of the described inner complexes were found in the same region (−0.14 to −0.35 ppm) indicating the presence of heteroatom-coordinated magnesium.

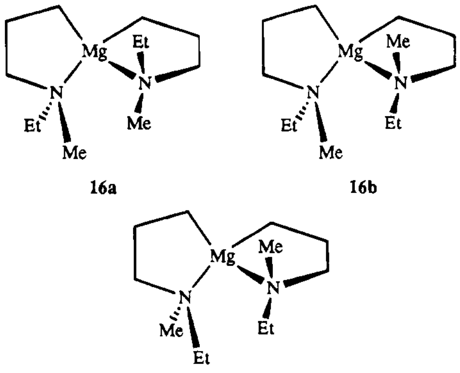
The tetrahedral compounds **11-26** are chiral and the two alkyl groups at nitrogen in the symmetrically substituted amino Grignards are diastereotopic. Scheme 16 illustrates the different environments.

Scheme 16



The ^{13}C NMR spectrum of $Mg[(CH_2)_4NMe_2]_2$ (**20**), measured at −80 °C, shows the two expected signals (43.27 and 47.35 ppm) for the methyl substituents. At room temperature, only one signal is observed (45.72 ppm). Apparently exchange between the *N*-methyl groups occurs at this temperature, probably via dissociation of the nitrogen–magnesium IC bonds.

Scheme 17



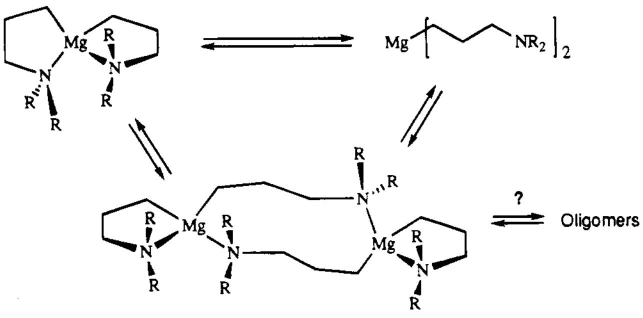
16a **16b**

16c

For the compounds with two different alkyl substituents on nitrogen, three different stereoisomers are conceivable; in Scheme 17, the three possibilities for $Mg[(CH_2)_3NMeEt]_2$ (**16**) are shown. However, only two isomers were observed (^{13}C NMR), the major component being **16a** as it has the least steric hinderance of the nitrogen alkyl groups, while **16c** is absent because of strong repulsion between the neighboring ethyl groups.

The ^{13}C NMR spectra of the symmetrically substituted five-membered ring chelates $Mg((CH_2)_3NR_2)_2$ are strongly temperature and concentration dependent. The dependence on concentration is an indication for association to dimers and oligomers (Scheme 18). ^{13}C NMR spectra indicate that with larger substituents on nitrogen, the tendency of intramolecular coordination decreases while intermolecular association increases.

Scheme 18



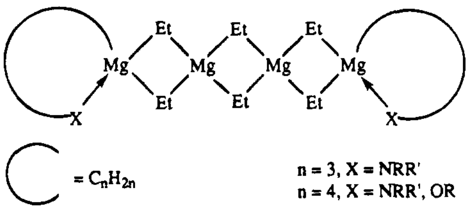
It is known, that dialkylmagnesium compounds as well as Grignard reagents readily exchange alkyl groups in solution.[40] Accordingly, the reaction of diethylmagnesium with $Mg[(CH_2)_nNRR']_2$ ($n = 3, 4$; R, R′ = Me, Et, *n*-Pr, *n*-Bu, *c*-Hex) and with $Mg[(CH_2)_4OR]_2$ (R = Me, Et, *n*-Pr, *n*-Bu, *n*-Pe, *n*-Hex) resulted in mixed ethyl[(dialkylamino)alkyl]- (**27-36**; Scheme 19) and ethyl(4-alkoxybutyl)magnesium compounds (*vide infra*; **55-60**; Scheme 37).[41]

Scheme 19

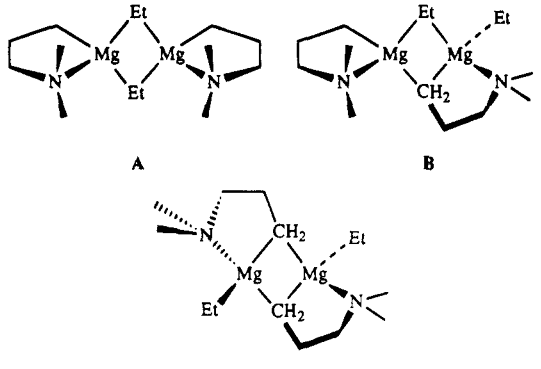
$$MgEt_2 + Mg(C_nH_{2n}NRR')_2 \longrightarrow [Et\text{-}Mg\text{-}C_nH_{2n}NRR']_2$$

n = 3; R = R' = Me (**27**), Et (**28**), *n*-Pr (**29**);
R = Me, R' = Et (**30**), *n*-Bu (**31**), *c*-Hex (**32**)
n = 4; R = R' = Me (**33**), Et (**34**);
R = Me, R' = Et (**35**), *n*-Bu (**36**)

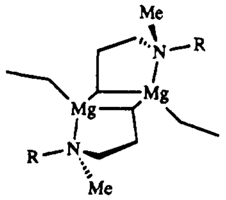
Scheme 20



Scheme 21



Scheme 22



R = Me (**27**), *c*-Hex (**32**)

Even when diethylmagnesium and bis[(dialkylamino)alkyl]magnesium were mixed in ratios up to 5:1, chelates were formed which were soluble in apolar solvents. This indicates the formation of Et_2Mg oligomers with (dialkylamino)alkyl end groups. In Scheme 20, the 3:1 complex is shown.[41]

Molecular weight determinations of the 1:1 mixture showed dimeric species $(EtMgC_nH_{2n}X)_2$ to be present in solution (Scheme 21). None of the products gave a M^+ signal in the mass spectrum, but the most characteristic signal resulted (in all cases) from a M_2–Et species. In general, as a result of a decreased electron density, the ^1H NMR chemical shift of an α-proton of a carbon μ-bridging between two magnesium centers is deshielded relative to the α-proton of a carbon which is η^1-bonded to magnesium. The α-proton signals of the (dialkylamino)alkyl and alkoxybutyl moieties ($CH_2{}^1$) appear at lower field than the α-protons of the ethyl groups ($CH_2{}^2$), which indicates bridging of the *chelating ligand* as in structure **C** (Scheme 21). Furthermore, **A**, **B**, and **C** show a different number of (N-bonded) methyl signals in the ^{13}C NMR spectrum (1, 4, and 2, respectively); by this criterium, structure **C** could be confirmed by ^{13}C NMR spectroscopy.

The structural type of **C** occurs in the oxygen analogues, too, but $\Delta\delta(CH_2{}^1 - CH_2{}^2)$ is 0.1–0.2 ppm for the Et–Mg–C_4H_8OR compounds, which is larger than the 0.05–0.06 ppm observed for the corresponding Et–Mg–$C_3H_6NR_2$ and Et–Mg–$C_4H_8NR_2$ compounds. This was explained as resulting from the stronger complexation of oxygen.

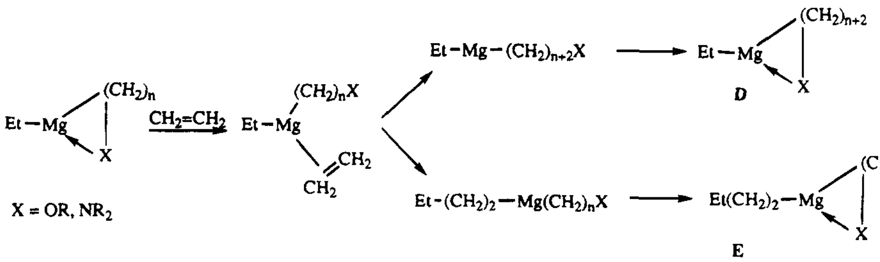
The IR spectra show an intense, characteristic band at 500 cm^{-1} in the Mg–C region, assigned to the alkyl-bridged structure of the mixed ethyl IC complex. As for the monomeric chelates $Mg[(CH_2)_nX]_2$ (X = NR′R″, OR), bands at 550–570 or at 580–600 cm^{-1} are characteristic for the six-membered ring $Mg(CH_2)_4X$ (X = NR′R″, OR) or the five-membered ring $Mg(CH_2)_3NR'R''$, respectively. These results are also in accordance with the assigned structure **C**. The alkyl-bridging structures were definitely confirmed by the crystal structures of ethyl[3-(*N*,*N*-dimethylamino)propyl]magnesium (**27**) and ethyl[3-(*N*-cyclohexyl-*N*-methylamino)propyl]magnesium (**32**) (Scheme 22).

Both structures have C_i symmetry and a Mg_2C_2 four-membered ring. At the bridging carbon, there is a small angle of 74°, typical for a two-electron three-center bond. The C–Mg–C angle in the four-membered ring is 106°. The intramolecular metal–metal distance is 2.75 Å, which is shorter than in oxygen bridged four-membered rings (3.04–3.12 Å)[42] and also significantly shorter than the Mg–Mg distance in magnesium metal (3.2 Å). The intraannular Mg–C distances (2.27–2.29 Å) correspond with those in the bridges of polymeric Me_2Mg and Et_2Mg.[43] The terminal Mg–C distances of the Mg–Et bonds are 2.142 (**27**) and 2.129 Å (**32**) and the Mg–N distances are 2.181 (**27**) and 2.195 Å (**32**).

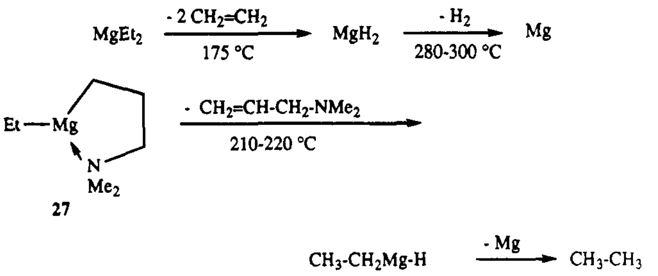
The presence of two different Mg–C bonds, exocyclic and endocyclic, may entail different chemical reactivities. This was investigated by means of insertion reactions of ethylene or reactions with CO_2, benzaldehyde and isobutyl methyl ketone.[41] The reactions with ethylene are shown in Scheme 23. Generally, the Mg–Et bond was slightly more reactive (more products of type **E** than of type **D**), especially when the donor atom was oxygen. A rationalization of these results was not provided.

The thermolysis reaction of the ethyl[(dialkylamino)alkyl]- and ethyl(4-alkoxybutyl)magnesium IC complexes was compared to that of diethylmagnesium.[41] The thermolysis of Et_2Mg proceeds in two

Scheme 23



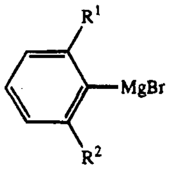
Scheme 24



steps. At approximately 175 °C, ethylene is released and, in a second step, H_2 is eliminated at 280−300 °C (Scheme 24). With the IC compounds, a different process is operating: at 190−200 °C (oxygen compounds) or at 210−220 °C (nitrogen compounds), thermolysis occurred, the gas produced being ethane instead of ethylene. Apparently, a β-hydrogen transfer from the aminoalkyl group to magnesium and subsequent elimination of ethane is the predominant process. In Scheme 24 the decomposition process of $EtMg(CH_2)_3NMe_2$ (**27**) is shown.

The [(dimethylamino)methyl]phenyl ligand and the 1,3-bis[(dimethylamino)methyl]phenyl ligand have been used extensively during the last decade as intramolecular coordinating ligands for many different (transition) metals.[44] From 1-bromo-2-[(dimethylamino)methyl]benzene, the corresponding Grignard reagent **37** (Scheme 25) was formed readily and in quantitative yield, while the *meta* and *para* derivative did not react under analogous conditions.[45]

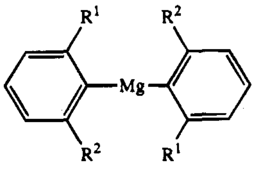
Scheme 25



$R^1 = CH_2NMe_2, R^2 = H$ (37)
$R^1 = R^2 = CH_2NMe_2$ (38)

In our group, the Grignard reagents **37** and **38** (Scheme 25) were prepared to determine the effects of IC upon the position of the Schlenk equilibrium with the corresponding diarylmagnesium compounds (Scheme 26).[46]

Scheme 26

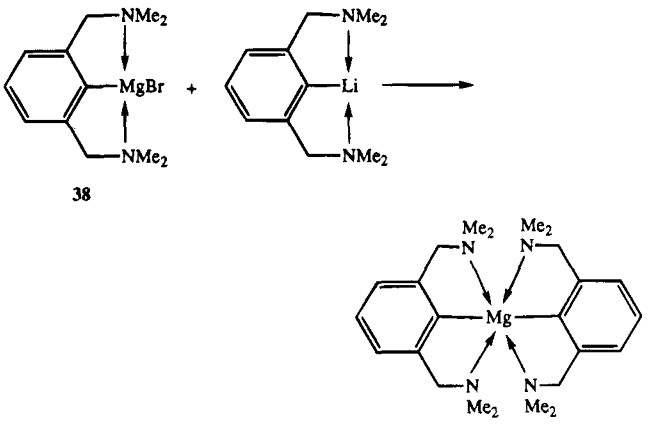


$R^1 = CH_2NMe_2, R^2 = H$ (39)
$R^1 = R^2 = CH_2NMe_2$ (40)

Both compounds were formed from the reactions of the corresponding bromides with magnesium in THF in quantitative yield. The diarylmagnesium compound **39** was obtained from the exchange reaction of the corresponding diorganylmercury compound with magnesium in THF.

With bis[2,6-bis[(dimethylamino)methyl]phenyl]mercury, the corresponding exchange reaction did not take place (not even at 60 °C), probably because of steric reasons. Therefore, **40** was prepared from the Grignard compound **38** and the corresponding organolithium compound (Scheme 27).

Scheme 27



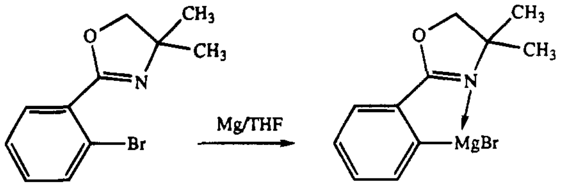
As most of the compounds investigated in this context were IC compounds with oxygen donors, the effects of IC upon the position of the Schlenk equilibrium for the nitrogen compounds **37** and **38** will be discussed in section III.B.3.

Usually Grignard reagents add to imines as shown in Scheme 28. However, an oxazoline system can be used as a protecting group for the carboxyl function during Grignard formation.[47] In compound **41**, neither intramolecular nor intermolecular addition to the C=N bond is observed (Scheme 29).

Scheme 28

$$R\text{-}N{=}CR^1R^2 + R^3MgX \longrightarrow R(MgX)N\text{-}CR^1R^2R^3$$

Scheme 29



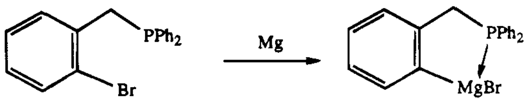
41

c. Seven-Membered and Larger Rings. One intramolecular nitrogen-coordinated anthrylenemagnesium compound with seven- and 10-membered chelate rings was synthesized; this compound is described in section III.B.3 as it is the only nitrogen donor compound in a series of five IC complexes with oxygen donors.

2. Magnesium Complexes with Phosphorus Donor Atoms

From (*o*-bromobenzyl)diphenylphosphine and magnesium the deep red Grignard reagent **42** was obtained in quantitative yield (Scheme 30).[48] Although the occurrence of IC in this compound was not investigated (**42** was used as a precursor for intramolecularly coordinated tin(II) compounds), it

Scheme 30



42

Scheme 31

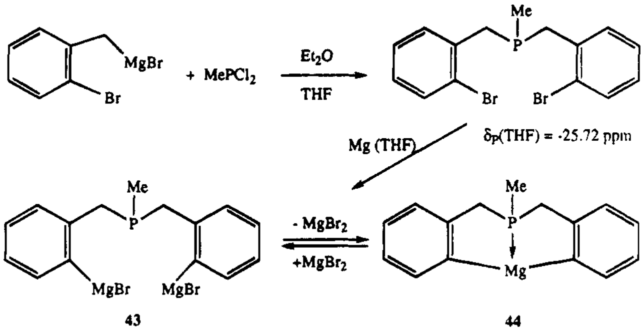


Table 1. The Temperature Dependence of the ^{31}P NMR Spectrum of 43 and 44 (in THF)

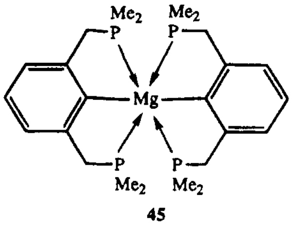
	δ(^{31}P) (ppm)		
T, (°C)	43	44	43:44
32	−26.82 (s)	−32.40 (s)	1:2
63	−27.05 (s)	−31.85 (s)	1:3

is quite likely, as the donor atom and the electrophilic metal may interact to form a five-membered ring.

The reaction of (*o*-bromobenzyl)magnesium bromide with methyldichlorophosphine resulted in the formation of the bis(*o*-bromobenzyl)methylphosphine.[49] When this compound was reacted with 2 equiv of magnesium in THF, the metal was completely consumed and a deep red solution was obtained. ^{31}P NMR spectroscopy, a simple tool for the analysis of such compounds in solution, was used for identification. The ^{31}P NMR spectrum of the reaction mixture at room temperature showed two major signals with different intensities. The chemical shift of one of them (δ = −26.82 ppm) does not differ much from that of the starting material (δ = −25.72 ppm) and was ascribed to the di-Grignard reagent **43**, while the second signal (−32.40 pm) was believed to stem from the cyclic diarylmagnesium **44** (Scheme 31); note that **43** and **44** are related by the Schlenk equilibrium. The high-field shift of the latter signal was explained by the transannular interaction between phosphorus and magnesium. The temperature dependence of the ^{31}P NMR spectrum (Table 1) was taken as a measure for the shift of the Schlenk equilibrium between **43** and **44** as shown in Scheme 31.

The tetraphosphorus analogue (L_2MgP_4) of **40** (L_2MgN_4) and of **71** (L_2MgO_4; *vide infra*) was reported very recently.[50] The reaction of Li{2,6-($Me_2PCH_2)_2$-C_6H_3} with $MgCl_2$ in Et_2O/THF at −70 °C yielded the hexacoordinated diarylmagnesium compound bis[2,6-bis[(dimethylphosphano)methyl]phenyl]magnesium (**45**) in 90% yield (Scheme 32).

Scheme 32



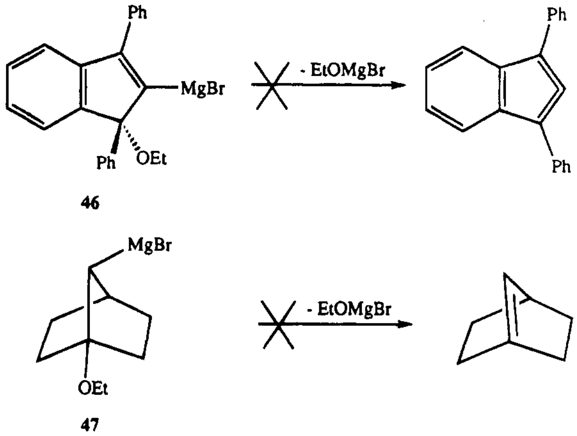
45

The X-ray crystal structure shows a distorted octahedral coordination of magnesium and the molecule has C_2 symmetry. The distortions from octahedral result from the formation of five-membered chelate rings. The trans P−Mg−P angles are only 148.98(1)°. The Mg−P distances, for which no references are available, are 2.761(1) and 2.770(1) Å. The Mg−C bond distances of 2.216(1) Å are quite long. The corresponding values for **71** were 2.093(4) and 2.105(4) Å. By analyzing the complicated multiplet ($AX_2X'_2$ spin system) of the *ipso*-carbon atom in the ^{13}C NMR spectrum, it was concluded that hexacoordination was maintained in toluene solution. Finally, the authors promise us analogous complexes of other main group metals (for which **45** can serve as a precursor) in the future!

3. Magnesium Complexes with Oxygen Donor Atoms

a. Four-Membered Rings. As in the case of the corresponding nitrogen compounds (see section III.B.1), the synthesis of β-alkoxyalkyl Grignard reagents from the corresponding halides leads to very unstable organometallic compounds, which normally decompose more or less at the instant of their formation under the formation of alkenes as a result of easy β-elimination. In 1969, the first example of a stable β-alkoxyalkyl Grignard compound was reported. In (1-ethoxy-1,3-diphenyl-2-indenyl)magnesium bromide (**46**), the normal β-elimination could not take place because the strain in the five-membered ring allene would be too high (Scheme 33).[30]

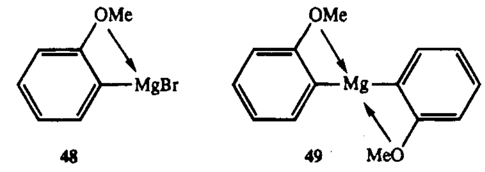
Scheme 33



Two years later, our group reported another example of a β-alkoxy-substituted Grignard compound, 1-ethoxy-7-(bromomagnesio)norbornane (**47**), which is stable because β-elimination is prohibited by Bredt's rule (Scheme 33).[51] The remarkable stability of **47** was proven by heating the Grignard solution in THF for 2 days at 80 °C: no change was observed in the NMR spectrum. In **47**, there probably is no IC because the magnesium and oxygen centers are too far apart.

The synthesis of β-alkoxy-substituted Grignard compounds, in which the α- and β-carbon atoms are incorporated into an aromatic ring, gives stable products because β-elimination to the highly energetic aryne is too unfavorable. Thermochemical investigation of the Grignard reagent (*o*-methoxyphenyl)magnesium bromide (**48**; Scheme 34) in THF solution showed a $\Delta H_{para} - \Delta H_{ortho}$ of −11.5(2.8) kJ (mol Mg−C)$^{-1}$ for the reaction with acetic acid;[52] the

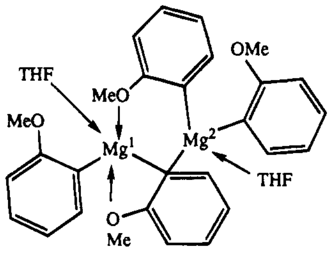
Scheme 34



corresponding bis(*o*-methoxyphenyl)magnesium (**49**) showed $\Delta\Delta H_{para-ortho} = -11.2(2.3)$ kJ (mol Mg−C)$^{-1}$.[53] While these thermochemical data clearly underline the enthalpic effect of interaction between the metal and ether functions, the assignment to IC in the sense of direct O→Mg coordination is ambiguous because the benzene ring separates the two functions considerably, and a dipolar interaction between the Mg−C(aryl) and O−C(aryl) dipoles is certainly, at least in part, involved.

Pure **49**, prepared from bis(*o*-methoxyphenyl)mercury and magnesium,[54] was monomeric in THF solution in the concentration range of 3.9−11.8 mmol L^{-1}, as established by association measurements using the isothermal stationary distillation technique.[55] All attempts at isolating crystals of **49** from a pure THF solution, either by cooling or concentrating, were unsuccessful. However, a dimeric species was isolated by crystallization of **49** from an *n*-hexane solution containing a relatively small amount (<10%) of THF (Scheme 35).[54]

Scheme 35

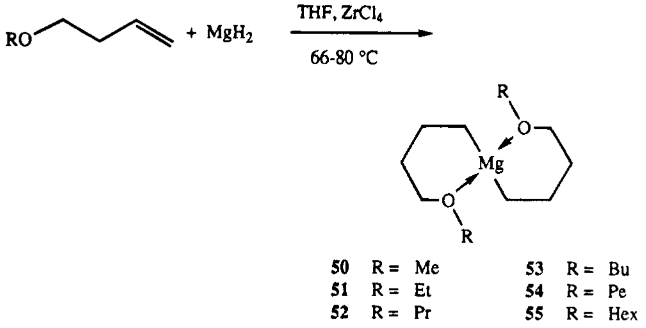


(**49**)$_2$

The structure contains one pentacoordinate (Mg^1) and one tetrahedral magnesium (Mg^2). The remarkable feature of the structure of **49** is the way in which the two magnesium atoms are connected by two bridging aryl groups. One of the methoxyphenyl groups bridges the two metal atoms through the *ipso*-carbon in a normal μ_2 fashion (C_{ipso}−Mg^1, 2.327(6) Å; C_{ipso}−Mg^2, 2.305(6) Å), but the angle between the plane of this aryl group and the plane through the *ipso*-carbon and both magnesium atoms is diminished (from ideally 90 to 59°) in order to facilitate the formation of an IC bond (Mg^1−O = 2.166(4) Å). The resulting four-membered ring is not planar. The other aryl group bridges in a completely different way between the two magnesiums: it is σ-bonded to one of the magnesiums through its *ipso*-carbon (Mg^2−C, 2.199(7) Å) and to the other magnesium through its oxygen (Mg^1−O, 2.056(5) Å). The two magnesium atoms do not have the same number of bonds to carbon. Thus, Mg^2 gains partial magnesiate character, while, in turn, Mg^1 formally carries a (partial) positive charge, which is compensated by coordination to three oxygens (Mg^1−O(THF), 2.064(5) Å). In the ^{13}C NMR spectrum in toluene-d_8 of **49**, only six aryl carbon signals and one methoxy signal were discernable. This suggests a fast interchange between the two nonidentical aryl groups.

b. Five- and Six-Membered Rings. The method for the formation of nitrogen−magnesium five- and six-membered rings by addition of MgH_2 to ω-dialkylamino-substituted 1-alkenes (cf. section III.B.1) was also successful for ω-oxygen-substituted 1-alkenes.[39] In the reaction of 3-butenyl ethers with MgH_2, the products **50-55** were formed (Scheme 36).

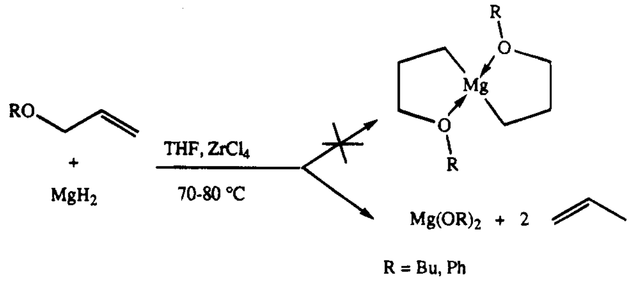
Scheme 36



The only side reaction was hydrogenation of the starting material to give the saturated ether. The reactions depend on the size of the group R at oxygen: longer alkyls impede MgH_2 addition. All alkoxy magnesium IC complexes were isolated by vacuum distillation. Compounds **50** and **51** are white solids; **52−55** are viscous liquids.

Reactions of MgH_2 with allyl−alkyl ethers did not yield the expected organomagnesium compounds, but reductive cleavage of the oxygen−allyl bond was observed instead (Scheme 37). Addition of MgH_2 to the methyl-substituted allyl ethers 1-alkoxy-*trans*-2-butene and 3-alkoxy-1-butene was equally unsuccessful.

Scheme 37



Cryoscopic molecular weight determinations showed the structures of **50-55** to be monomeric, which is indicative for the occurrence of IC. An upfield shift (−0.14 to −0.35 ppm) of the α-protons is indicative of heteroatom coordination to magnesium. The tetrahedral compounds **50-55** are chiral.

The IR "fingerprint" region of oxygen IC complexes contains C−O−C bands at approximately 1050 and 1090 cm^{-1} (bands of uncomplexed ethers appear at approximately 1125 cm^{-1}). While the IR spectrum of **50** (R = Me) shows only the bands of complexed ethers at 1050 and 1090 cm^{-1} and a shoulder at 1125 cm^{-1}, for larger R the intensity of the band at 1125 cm^{-1} increases, while those at 1050 and 1090 cm^{-1} decrease. With **55** (R = Hex), the band of the uncomplexed ether at 1120 cm^{-1} dominates. Definite proof for IC in bis(4-methoxybutyl)magnesium (**50**; melting point 32–33 °C) was obtained from its crystal structure. The structure has a C_2 axis with the magnesium atom centered in a distorted tetrahedron. The Mg–O and Mg–C distances are 2.071 and 2.144 Å, respectively; the C–Mg–C and O–Mg–O angles are 140.2 and 96.4°, respectively.

The reaction of IC complexes **50-55** with $MgEt_2$ lead to the formation of ethyl(4-alkoxybutyl)magnesium compounds **56-61** (Scheme 38).[41]

Scheme 38

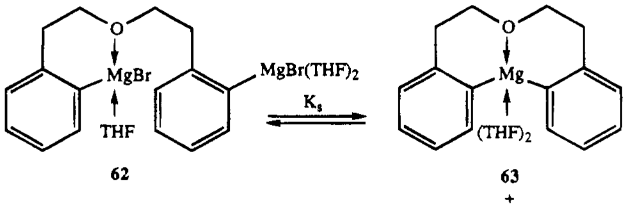
$$MgEt_2 + Mg((CH_2)_4OR)_2 \longrightarrow [Et\text{-}Mg\text{-}(CH_2)_4OR]_2$$

R = Me (**56**), Et (**57**), *n*-Pr (**58**); *n*-Bu (**59**), *n*-Pe (**60**), *n*-Hex (**61**)

The difference in reactivity of the Mg–Et and Mg–C_4H_8OR bonds follows from the reaction of these complexes with ethylene (Scheme 23), benzaldehyde, isobutyl methyl ketone and CO_2. With ethylene, up to six ethylene molecules were inserted; insertion occurred preferentially into the Mg–Et bond (whereas in the case of the ethyl[(dialkylamino)alkyl]magnesium compounds, both bonds were about equally reactive; cf. section III.B.1). Complexes **50-55** were not very reactive toward ethylene: only 10% mono insertion was observed, compared to 80% mono or bis insertion for the bis[(dimethylamino)alkyl]magnesium compounds **11-26**. When comparing the ^{1}H NMR spectra of $Mg(C_4H_8OR)_2$ compounds with that of $MgEt_2$·2THF, deshielding of the signals of the ethyl Mg–CH_2 protons of 0.05–0.13 ppm is observed. The oxygen coordination in the alkoxybutyl inner complexes is apparently stronger than in the THF adduct. Thermolysis of ethyl(4-alkoxybutyl)magnesium inner complexes showed similar features as observed for the ethyl[(dialkylamino)alkyl]magnesium complexes (cf. section III.B.1, Scheme 24).

Substitution of the aromatic ring of phenylmagnesium bromide with groups capable of IC is of interest for many reasons. For instance, it will change the Schlenk equilibrium, since the complexation modes of the Grignard reagent and of the corresponding diarylmagnesium compound will be influenced differently. Clear indications of this effect were found in our studies of the di-Grignard reagent 1,5-bis[2-(bromomagnesio)phenyl]-3-oxapentane (**62**, Scheme 39):[56] the position of the Schlenk equilibrium (in THF solution) was found to lie completely on the side of the diarylmagnesium species **63**. Stabilization of **63** through an intramolecular coordinative bond was postulated to account for the stability of **63** relative to that of **62**.

Scheme 39



62

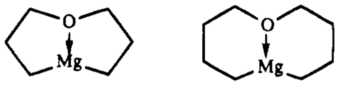
63
+
$MgBr_2(THF)_4$

According to the crystal structures of the two magnesium species on the right side of the Schlenk equilibrium they possess a total of seven Mg–O bonds [three in **63**[46] (*vide infra*) and four in $MgBr_2$[57,58]]. Coordination in **62** is probably less efficient; the two magnesiums will be tetracoordinated involving three molecules of THF plus an intramolecular ether oxygen; at most, the intramolecularly coordinated magnesium may be pentacoordinate (involving two THF molecules). Therefore, by conversion of **62** to **63**, the total number of Mg–O bonds increases by three; this makes ΔH_s negative. The value of ΔS_s is difficult to estimate, as the number of particles in solution is doubled ($\Delta S_s > 0$), but conformational freedom is lost and the number of coordinated molecules of THF increases ($\Delta S_s < 0$). Nevertheless, the thermodynamics is apparently favorable enough to drive the equilibrium completely to the right.

While **63** is thermodynamically more stable than **62**, it is not stabilized relative to diphenylmagnesium as was concluded later from thermochemical protolysis experiments (ΔH_R for **63** is 9.0 kJ mol^{-1} more exothermic than ΔH_R for Ph_2Mg). The crystal structure of **63**[46] revealed a pseudo-trigonal-bipyramidal (TBP) coordination geometry of magnesium, which is rarely found in organomagnesium compounds. Without IC, the ether oxygen of **63** and the magnesium would be part of a 10-membered ring; this unfavorable situation is improved by formation of an IC bond. Surprisingly, two molecules of THF are also coordinated to the magnesium atom, which is possible because of the small intraannular C_{ipso}–Mg–O_{intra} angles of the two six-membered chelate rings (88.2 and 88.7°) relative to that for a tetrahedral geometry (109°). The bond distances in **63** reflect a normal TBP geometry: the axial ligands have relatively long bonds to magnesium (Mg–O(1), 2.242 (IC); Mg–O(3), 2.221 Å) while in the equatorial plane, bond lengths have normal values (Mg–C(1), 2.165; Mg–C(16), 2.155; Mg–O(2), 2.095 Å); this may result from two opposite effects: bond extension due to a higher coordination number and bond contraction due to tighter bonding of the equatorial ligands. It is assumed that the coordination of magnesium of **63** in solution is analogous to that in the solid state.

Two other cyclic organomagnesium compounds with IC were prepared in our group (Scheme 40).[56]

Scheme 40

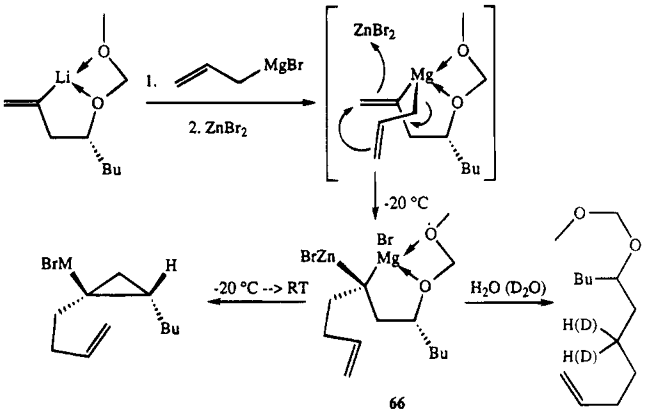


64 65

Most likely, in 1-oxa-5-magnesacyclooctane (**64**), two five-membered chelate rings are formed, while two six-membered rings are present in 1-oxa-6-magnesacyclodecane (**65**). The compounds were synthesized by transmetalation with metallic magnesium from the corresponding mercury compound, which in turn was prepared by ring-closure reaction of the corresponding di-Grignard reagent with 1 equiv of $HgBr_2$. Crystal structures of **64** and **65** are not available, but association measurements by stationary isothermal distillation[55] showed the compounds to be monomeric in THF solution. Association measurements of the di-Grignard solutions showed that the Schlenk equilibria were completely shifted toward the cyclic compounds and $MgBr_2$; this was attributed to IC stabilization of the monomeric compounds.

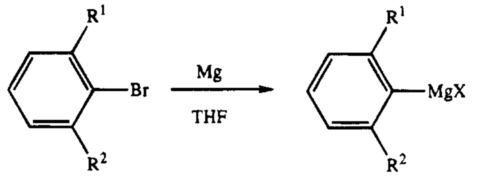
Addition of an ethereal solution of allylmagnesium bromide and zinc dibromide to an ethereal solution of a functionalized vinyllithium compound at −20 °C lead to the formation of the stable organobimetallic compound **66**, as evidenced by the fact that quenching of the reaction mixture with HCl (or DCl) afforded the expected dideuterated alkene (Scheme 41).[59] On warming the reaction mixture very slowly to room temperature, **66** underwent a diastereoselective 1,3-elimination to give a single isomer of a metalated cyclopropane.

Scheme 41



A series of phenylmagnesium bromides **67-69**, **37**, and **38** with *ortho* substituents capable of forming IC bonds were used to study the effects of IC on the Schlenk equilibrium, while PhMgBr and **F** served as models without IC; the Grignard reagents were obtained from the corresponding aryl bromides (Scheme 42).[46]

Scheme 42

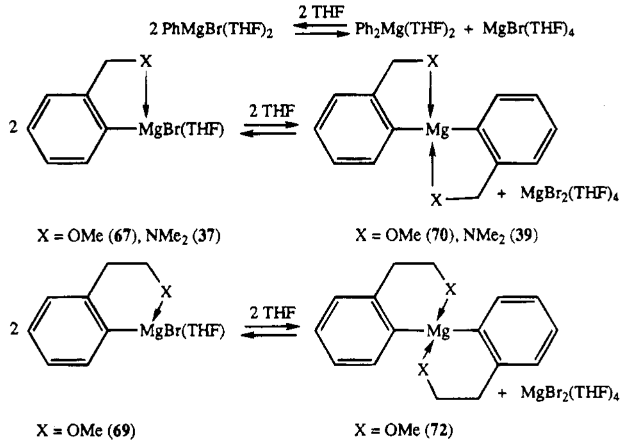


ArBr	X = Br	(X = Ar)
$R^1 = R^2 = H$	PhMgBr	Ph_2Mg
$R^1 = CH_2OMe$; $R^2 = H$	**67**	**70**
$R^1 = R^2 = CH_2OMe$	**68**	**71**
$R^1 = CH_2CH_2OMe$; $R^2 = H$	**69**	**72**
$R^1 = CH_2NMe_2$; $R^2 = H$	**37**	**39**
$R^1 = R^2 = CH_2NMe_2$	**38**	**40**
$R^1 = R^2 = H$; *p* -CH_2OMe	**F**	**G**

For comparison, the results with the nitrogen-donor-containing compounds **37** and **39** (cf. section III.B.1) are included in the discussion here. Identification of the Grignard and the diorganomagnesium compounds is normally not feasible because of rapid exchange between the different species in solution; in the present case, however, it was possible both by ^1H and ^{13}C NMR spectroscopy between 200 and 298 K. Analyses of the Schlenk equilibria ($2ArMgX \rightleftharpoons Ar_2Mg + MgX_2$) were achieved by using variable-temperature NMR spectroscopy. The values for ΔH_s and ΔS_s, together with the composition of the equilibrium mixture at 298 K, are presented in Table 2.[46]

The parameters of PhMgBr, **67**, **69**, **37**, and **F** show similar values. The closest analogy is that between PhMgBr and **F**: neither can form intramolecular coordinative bonds. For **67**, **69**, and **37**, one must assume that IC occurs as indicated in Scheme 43.

Scheme 43



The number of chelate rings remains the same since **70**, **72**, and **39** have two IC bonds which completely satisfy the tendency toward tetracoordination of magnesium. The resulting overall change is the binding of two additional molecules of THF, just as in the case of Ph_2Mg and **F**; the thermodynamic parameters reflect this analogy.

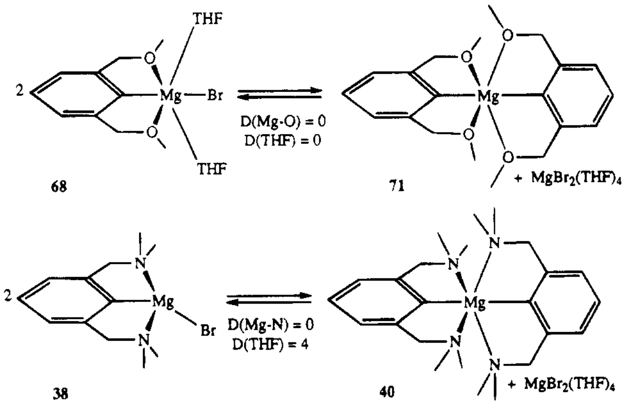
The parameters of **68** and **38**, and therefore presumably their complexation behavior, deviate considerably from those of the other compounds investigated. From the IC point of view this is most intriguing. Since both compounds belong to the same category of 2,6-disubstituted aryl Grignard compounds, it is remarkable that the deviation of both

Table 2. Parameters ΔH_s and ΔS_s for the Schlenk Equilibria: $2ArMgBr \rightleftharpoons Ar_2Mg + MgBr_2$

				Grignard composition at 298 K		
compound	*T* range (K)	ΔH_s (kJ mol^{-1})	ΔS_s (J mol^{-1} K^{-1})	K	ArMgBr (%)	Ar_2Mg (%)
$PhMgBr/Ph_2Mg$	209−236	−18.7	−79.3	0.134	73	27
67/70	234−292	−13.7	−83.9	0.010	91	9
68/71	208−238	+6.8	+23.0	1.061	49	51
69/72	227−279	−20.8	−89.1	0.100	76	24
	199−213	+8	+36			
37/39	249−311	−14.1	−86.9	8.57×10^{-3}	92	8
	227−246	+10	+10			
38/40	224−287	−33.9	−175.4	6.06×10^{-4}	98	2
F/G	203−241	−16.5	−64.0	0.352	63	37

ΔH_s and ΔS_s is slightly positive for **68** and strongly negative for **38** as compared to e.g. **67** (Table 2). This trend was explained as follows. A crystal structure of **71** showed that its magnesium is hexacoordinated and does not contain external solvent molecules. This coordination number is unusually high for organomagnesium compounds. The four ether oxygens are part of an intramolecular arrangement, in which both aryl groups are perpendicular, which reduces to a considerable extent the steric hindrance that prevents coordination of four separate ether molecules. It is plausible that in **68**, like in **71**, the magnesium center is hexacoordinate. This perfectly explains the deviating thermodynamic parameters for the equilibrium **68**/**71** as elaborated in Scheme 44. In this equilibrium, neither the number of coordinated molecules of THF nor the number of Mg−O bonds change because the four THF present in two molecules of **68** are needed to solvate the product magnesium bromide. Consequently, the values of ΔH_s and ΔS_s are expected to be close to zero and indeed, small values were found experimentally (Table 2).

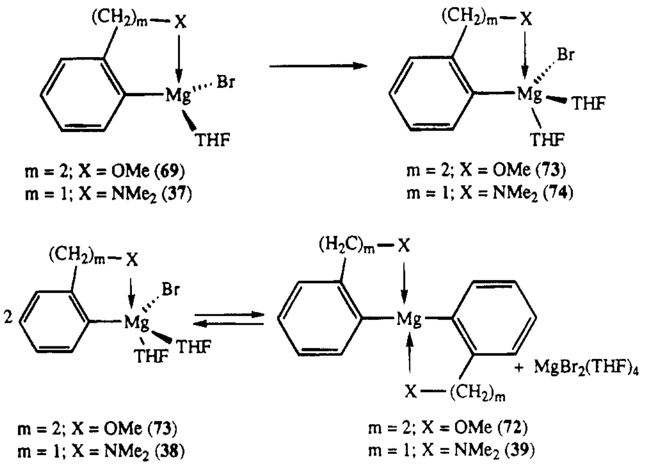
Scheme 44



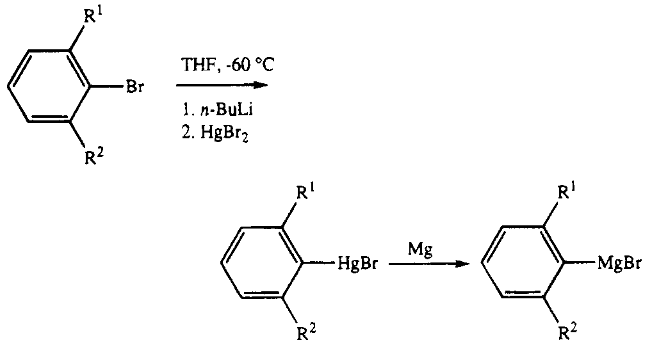
The situation is completely different for the couple **38**/**40** (Scheme 44). Both for electronic reasons (stronger Lewis base nitrogen) and for steric reasons (bulkier Lewis base), the magnesium center in **38** is postulated to be tetracoordinate, in contrast to **68**; on the other hand, the magnesium center in **40** is probably hexacoordinate like in **71** since all the ligands are intramolecular. Four molecules of THF are required to solvate the magnesium bromide, formed in the Schlenk equilibrium, which will be accompanied by a large negative entropy change. From the Schlenk parameters of phenylmagnesium bromide, one can estimate that for the binding of 1 mol of THF in either an organomagnesium compound or magnesium bromide the thermodynamic parameters are $\Delta S = -40$ J mol^{-1} K^{-1} and $\Delta H = -9$ kJ mol^{-1}. For the conversion of **38** to **40**, four molecules of THF will be bound, yielding four new Mg−O bonds. For this process, ΔS_s and ΔH_s are estimated to be $4 \times (-40) = -160$ J mol^{-1} K^{-1} and $4 \times (-9) = -36$ kJ mol^{-1}, respectively. These theoretical values are in surprisingly good agreement with the experimental values of −175.4 J mol^{-1} K^{-1} and −33.9 kJ mol^{-1}, respectively.

The van't Hoff plots of the equilibria of **69** and **37** show that at low temperature, these compounds have a slight bias toward higher coordination numbers. One of their ligands is intramolecular and hence less crowded, which makes additional coordination by one molecule of THF possible (Scheme 45); addition of a second molecule of THF (i.e. the transformation to **73** or **74**, respectively) is favored by enthalpy (ΔH(Mg−O) = −9 kJ mol^{-1}), but disfavored by entropy (ΔS(THF) = −40 J mol^{-1} K^{-1}). Therefore, the transformation is favored at lower temperatures (second entries in Table 2). For **73** and **74**, the Schlenk equilibrium involves Δ(THF) = 0 and Δ(Mg−O) = 0 just as for **68**, and the $\Delta H/\Delta S$ values are similar.[46]

Scheme 45



Scheme 46

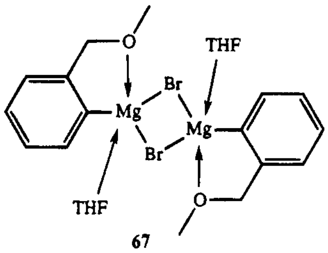


	ArMgBr
$R^1 = CH_2OMe$; $R^2 = H$	67
$R^1 = CH_2OCH_2CH_2OMe$; $R^2 = H$	75
$R^1 = CH_2(OCH_2CH_2)_2OMe$; $R^2 = H$	76
$R^1 = CH_2(OCH_2CH_2)_3OMe$; $R^2 = H$	77
$R^1 = CH_2(OCH_2CH_2)_4OMe$; $R^2 = H$	78
$R^1 = R^2 = CH_2OMe$	68
$R^1 = R^2 = CH_2OCH_2CH_2OMe$	79
$R^1 = R^2 = CH_2(OCH_2CH_2)_2OMe$	80

A series of phenylmagnesium bromides with IC substituents $CH_2(OCH_2CH_2)_nOCH_3$ at one [n = 0−4 (**67**, **75-78**)] or both [n = 0−2 (**68**, **79**, **80**)] *ortho* positions (Scheme 46) has been investigated in our group.[60] The pure Grignard reagents with more than two oxygens in the side chain had to be prepared by the exchange reaction of the corresponding arylmercury bromides with magnesium, since their synthesis from the corresponding bromides and magnesium was accompanied by extensive ether cleavage in the substituents if $n > 1$; this phenomenon is ascribed to the occurrence of a highly reactive carbanion during the process of formation of the Grignard reagent (*vide infra*).

The Grignard reagents exhibit IC both in solution and in the crystalline state, as was concluded from ^{1}H NMR spectroscopy and from X-ray crystal structure determinations. The structures of four complexes with one *ortho* substituent (n = 0–3) were determined. They show higher than usual coordination numbers. The structure of **67** can be related to those of normal, halogen-bridged, dimeric Grignard reagents, but its magnesium is pentacoordinated (Scheme 47).

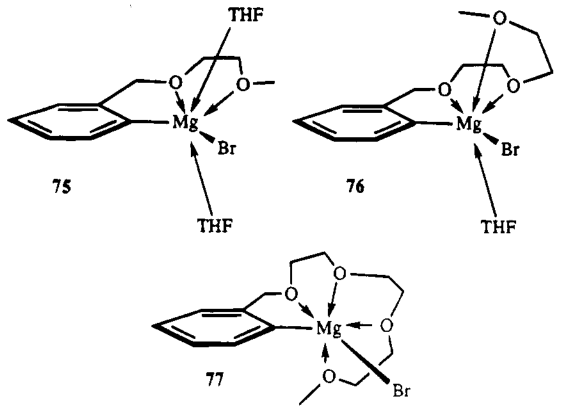
Scheme 47



67

It is not clear why **67** is the only dimer in this series; possibly crystallization from a more concentrated solution is responsible. The dimer is centrosymmetrical, consisting of two relatively weakly associated monomers, resulting in two sets of relatively short (2.509 Å) and long (2.705 Å) Mg–Br distances. The central four-membered ring is a planar rectangle. Each magnesium atom has not only two μ-Mg–Br bonds, one Mg–C bond (2.110(8) Å), and a coordinating THF (Mg–O = 2.037(6) Å), but also interaction with the intramolecular ether group (Mg–O = 2.105(7) Å). It is remarkable that, in spite of the higher coordination number of magnesium, this latter bond is only slightly elongated; this elongation may be caused by ring strain involved in the formation of the five-membered ring chelate which has an unfavorable small bite angle C–Mg–O of 79.3° at magnesium, and by the apical position of the ligand. The length of the Mg–C bond is short to normal and not strongly affected by the unusual coordination geometry. The coordination of the Mg atoms is distorted trigonal bipyramidal. The IC oxygen and the weakly bonded bromine occupy the axial positions (Br–Mg–O = 175.3(2)°).

Scheme 48

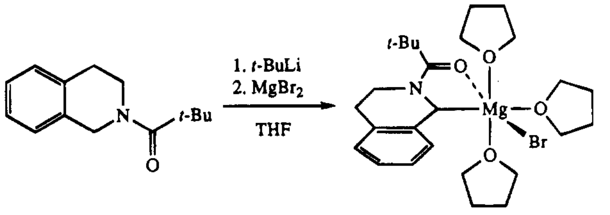


75 **76** **77**

From **75** on, hexacoordination of the magnesium occurs: additional THF molecules serve to complete the pseudooctahedral surrounding in the case of **75** (+2THF) and **76** (+1THF), until a completely solvent free, but "supersolvated" species is obtained in **77** (Scheme 48). The octahedral coordination state in **75**-**77** is quite unusual for a Grignard compound, the only previous example being **81** (*vide infra*). The small intraannular angles within the connected five-membered rings (about 75°) can be better accommodated in higher coordination states; the octahedral geometry (ideal angles 90°) is much more favorable than tetrahedral (angles 109°) or trigonal pyramidal (angles 90°/120°). IC diminishes the steric crowding which normally is a consequence of higher coordination; moreover, IC will be favored entropically over bonding of independent solvent molecules. The THF molecules in **75** and **76** are bound relatively weakly; dissociation occurs in an apolar solvent (toluene-d_8) and a solvent-free complex (probably an insoluble dimer or oligomer) precipitates.[60]

Lithiation of *N*-pivaloyl-1,2,3,4-tetrahydroisoquinoline (THIQ) with *tert*-butyllithium yields the lithiated pivaloylamide, which can be transmetalated to the magnesium derivative **81** by addition of magnesium bromide etherate (Scheme 49).[61] Compound **81** shows high stereospecificity in the reaction with acetophenone.

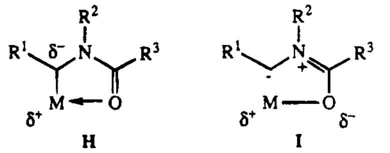
Scheme 49



81

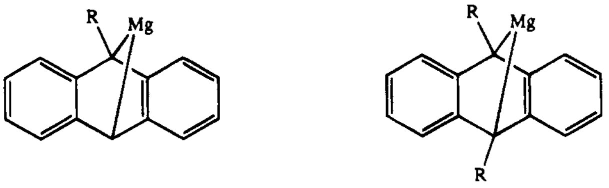
The molecular structure of **81**·3THF (Scheme 49) shows the metal to be in a pseudoequatorial position of the THIQ ring system (as is often found in magnesium halides and their complexes), with IC by the carbonyl oxygen (2.049 Å) to give a planar five-membered ring. Magnesium has a σ-bond to carbon (2.245 Å) and is further coordinated by a bromide (*trans* to the carbonyl oxygen; Mg–Br = 2.622(4) Å, C–Mg–Br = 173.4°) and three THF molecules (Mg–O = 2.146, 2.136, and 2.236 Å). The longest Mg–O distance is located in the "*exo*" position, which is also the most favorable position for bonding and subsequent reaction of the electrophile. In connection with the much higher diastereoselectivity of the reaction of **81** as opposed to the lithiated pivaloylamide, the coordination spheres, 4-fold (tetrahedral) for lithium and octahedral for magnesium, are relevant. The octahedral geometry in **81** brings the ligands closer together (angles of 90 vs ca. 109°), while the bond lengths Mg–O/Mg–C vs Li–O/Li–C do not differ significantly. Therefore in **81**, the complex is more crowded, the electrophile undergoing steric repulsions more strongly and earlier on the way to the transition state; this may render the reaction more selective than in the case of the corresponding lithium compound. Bond distances show that compounds of this type cannot be considered as a dipole-stabilized carbanion **I** which has been proposed on several occasions,[62-65] but rather as intramolecularly coordinated α-metalated amides **H** (Scheme 50).

Scheme 50



Very recently, the synthesis of anthrylenemagnesium compounds with IC substituents was reported (Scheme 51).[66]

Scheme 51



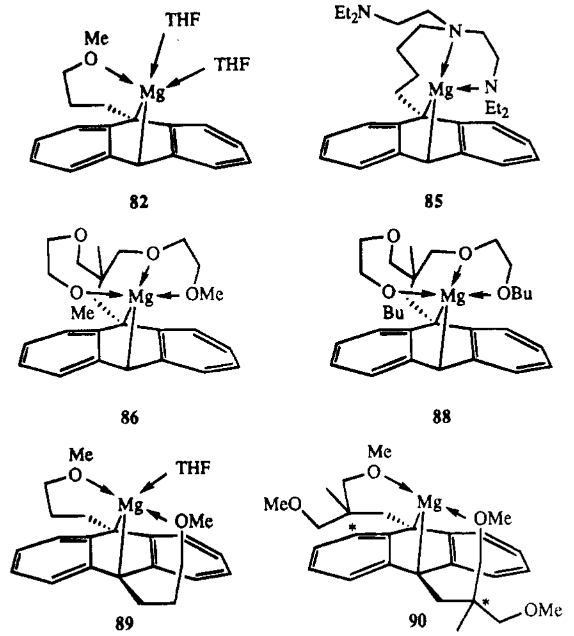
R = $(CH_2)_3OMe$ (**82**)
$(CH_2)_4OMe$ (**83**)
$(CH_2)_4NEt_2$ (**84**)
$(CH_2)_4N((CH_2)_2NEt_2)_2$ (**85**)
$CH_2C(Me)(CH_2O(CH_2)_2OMe)_2$ (**86**)
$CH_2C(Me)(CH_2O(CH_2)_2OEt)_2$ (**87**)
$CH_2C(Me)(CH_2O(CH_2)_2OBu)_2$ (**88**)

R = $(CH_2)_3OEt$ (**89**)
$CH_2C(Me)(CH_2OMe)_2$ (**90**)
$CH_2C(Me)(CH_2OEt)_2$ (**91**)

It was difficult to establish the existence of IC in these compounds, as X-ray analysis and ^1H NMR in solution was not possible in all cases. As the parent compound anthrylene magnesium is coordinated by three molecules of THF,[67,68] substituents with one or two donor atoms were connected to the 9-position or to the 9- and 10-positions, to give compounds in which the number of donor atoms ranges from 1 to 4. With the exception of **88** and **89**, all anthrylenemagnesium inner complexes were insoluble precipitates, which were analyzed after filtration and drying. The corresponding dihydroanthracenes were obtained on hydrolysis; the amount of magnesium incorporation was determined by titration with EDTA, while the amount of coordinated THF was determined by gas chromatography.

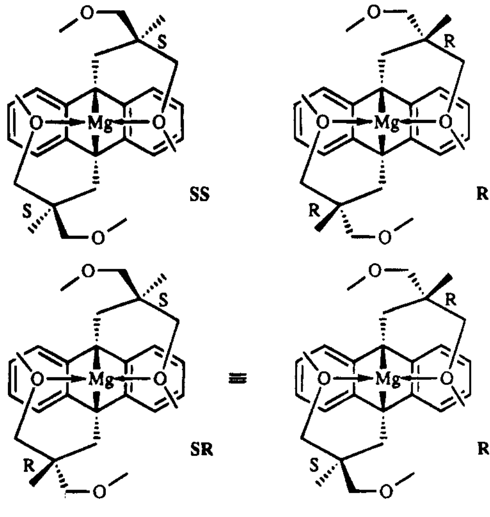
The microcrystalline solids were spectroscopically investigated by infrared and CP/MAS-NMR spectroscopy. In compounds **86**–**91**, both free and coordinated ether groups were identified, while the IR spectra of **82**, **85**, and **89** showed the simultaneous presence of coordinated THF and coordinated ether groups. The complexes **82**, **85**, **86**, and **88**–**90** (Scheme 52) were investigated by ^{13}C CP/MAS solid-state NMR spectroscopy. The number of coordinated THF molecules and IC ether groups per anthrylene moiety were determined from the shifts of the α- and β-ether carbon atoms (*vide supra*); for THF, these correlated well with the GC data.[66]

Scheme 52

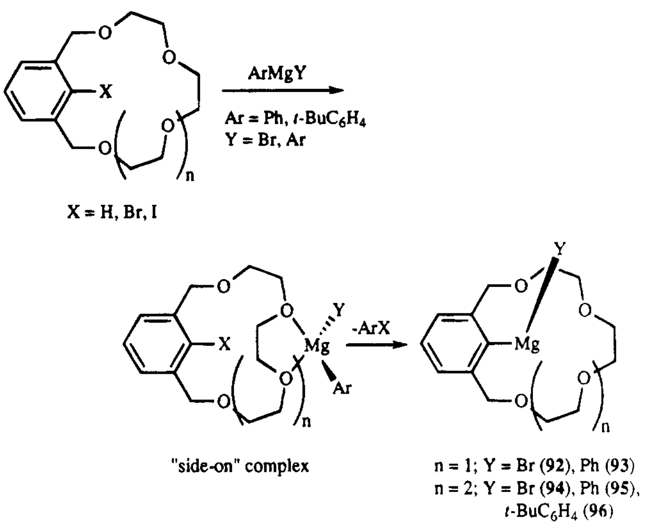


The conclusions from these analyses are represented in the structures drawn in Scheme 52. In compounds **82**, **86**, **88**, and **89**, the magnesium center is pentacoordinated. Diastereomers, although possible, were not observed for **82** and **86**, while for **89** a second component (possibly a coordination isomer) was observed with 20% abundance. As **88** has the same donor configuration as **86**, similar behavior was expected. Instead, the number and intensities of the signals in the CP/ MAS spectrum of **88** indicated the presence of two nonequivalent asymmetrical molecules in a 1:1 ratio. Furthermore, a third isomer (±25%) was observed. CP/MAS spectroscopy of compound **90** showed the compound to be tetracoordinated. When magnesium is coordinated by only one of the two ether oxygen atoms of one substituent, both quaternary carbon atoms of these substituents become chiral and adopt either the *R* or *S* configuration. For quasitetrahedral coordination of the magnesium center, four diastereoisomers are possible (Scheme 53). The *RR* and *SS* isomers have C_2 symmetry, while the asymmetrical *SR* and *RS* isomers are identical. The signals in the CP/MAS spectrum indicated that either both *SS* and *RR* isomers were present in a 1:1 ratio, or only the nonsymmetrical isomer *SR* (= *RS*). CP/MAS spectroscopy of compound **85** (which has three nitrogen donor atoms) showed that the magnesium is tetracoordinate. This is probably due to the larger sterical requirements of the dimethylamino groups as compared to that of ethers.

Scheme 53



Scheme 54



c. Seven-Membered and Larger Rings. Intriguing possibilities for IC are offered by 1,3-xylylene crown ethers, which at the aromatic 2-position have an intraannular anchoring site for covalent binding of metals inside the cavity of the crown ether. The synthesis of 1,3-xylylene crown Grignard compounds by reaction of the bromides **N** and **O** with magnesium was accompanied by extensive ether cleavage (again ascribed to the occurrence of a highly reactive carbanion during Grignard reagent formation; *vide supra*).[69] Therefore, these compounds [[2-(bromomagnesio)-1,3-xylylene]-15-crown-4 (**92**) and −18-crown-5 (**94**)] were prepared in pure form by reacting the corresponding bromides with *n*-butyllithium at low temperature, followed by addition of 1 equiv of magnesium bromide.[70] The corresponding arylmagnesio compounds (**93**, **95**, and **96**) were prepared via exchange reactions with diarylmagnesiums, the principle of which is presented in Scheme 54; the results are summarized in Table 3.

The following reactivity trends in the exchange reactions were found: X = I > Br > H ≫ Cl = 0 and 15-crown-4 > 18-crown-5 > 21-crown-6 = 0. Four different intraannular magnesium substituted crown compounds, **92**,[69] **93**,[10] **94**,[70] and **96**[11] have been structurally investigated by X-ray crystallography. Compound **92** was the first example of a Grignard reagent engaged in an intramolecular crown ether coordination. The oxygens O(1) and O(4) are farther removed from Mg than in intermolecular coordinated "normal" Grignard reagents, but both their distance [2.33(1) and 2.49(1) Å, respectively] and their orientation suggest a weak interaction. Surprisingly, the coordination to O(2) and O(3) (eight-membered chelates!) in **92** is stronger [2.13(1) and 2.12(1) Å, respectively] than that to O(1) and O(4) (five-membered chelates!); this is probably due to conformational restraints of the metacyclophane skeleton of the crown ether ligand. The coordination sphere of magnesium can be described as a pentagonal pyramid with bromine in the apex [Mg−Br = 2.517(4) Å]; the basal plane is formed by the four oxygen atoms, which are in an almost planar arrangement, and C(1), which is 1.06(2) Å below the plane of the oxygens [Mg−C(1) = 2.10(1) Å]. The crystal structure of **93** is practically identical to that of **92**. Again, O(2) and O(3) have shorter bonds to Mg (2.183(3) and 2.209(3) Å) than O(1) and O(4) (2.619(3) and 2.335(3) Å), the xylylene−magnesium bond being shorter [Mg−C(1) = 2.127(2) Å) than the phenyl−magnesium bond Mg−C(Ph) = 2.154(4) Å]. The angle C(1)−Mg−C(Ar) has the rather normal value of 131.2°. Note that **93** is one of the few examples of a diorganylmagnesium compound with two different, nonexchanging organic groups.

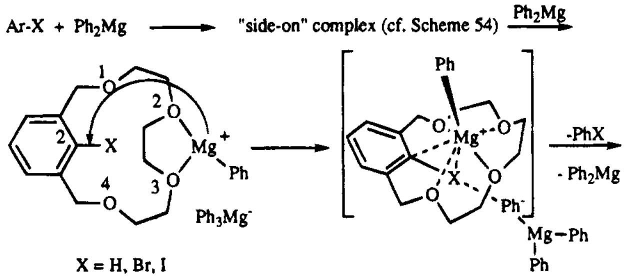
The crystal structure of **94** contains two independent structural units, which are rather irregular (low symmetry), and the conformation of its crown ether ring appears to be strained.[70] The central magnesium atom is coordinated by four of the five available oxygen atoms in a distorted octahedral fashion [Mg−O(2) = 2.170(4), Mg−O(3) = 2.235(4), Mg−O(4) = 2.331(4) and Mg−O(5) = 2.126(4) Å, respectively]. The low symmetry of the structure and the presence of a noncoordinating oxygen atom indicates that the size of the crown ether ring is too large and therefore unfavorable. However, the Mg−C and Mg−Br bonds have quite normal lengths [2.176(5) and 2.597(23) Å, respectively]. Compound **96** is a diarylmagnesium compound completely analogous to its phenyl analogue **95**; of the latter, an X-ray crystal structure has not been obtained. The structure of **96** differs markedly from that of **94**, which is the Grignard reagent corresponding to **95**, and is also rather irregular. Because of its distance to magnesium (2.713 Å), O(1) must be regarded as virtually nonbonding, as is O(4). Actually, only three of the five oxygens are coordinating and the geometry can be regarded as distorted trigonal bipyramidal. In the equatorial plane, the C−Mg−C angle is enlarged [139.2(2)°], which leads to smaller C−Mg−O angles. Like in **93**, the Mg−C

Table 3. Interactions between 1,3-Xylylene Crown Ethers and Organomagnesium Reagents

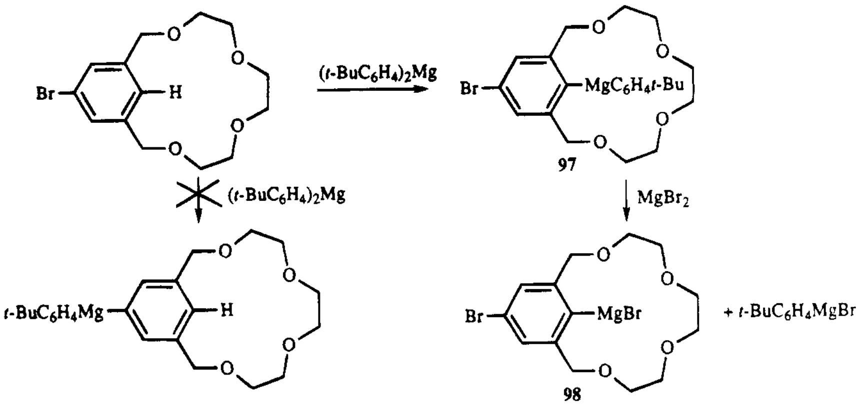
			Ar_2Mg (Ar = Ph, *p*-*t*-BuC_6H_4)		PhMgBr		
compd	X	*n*	type of reaction	product	type of reaction	product	ref(s)
J	H	1	metalation (slow)	**93**	metalation (slow)	**92**	10,11,69
K	H	2	complexation	side-on/rotaxane	complexation	complex[a]	71
L	Cl	1	complexation	side-on complex			72
M	Cl	2	complexation	side-on complex			72
N	Br	1	Br/Mg exchange	**93**	Br/Mg exchange	**92**	10,11,69
O	Br	2	Br/Mg exchange	**95**, **96**	Br/Mg exchange	**94**	10,11,70
P	Br	3	complexation	complex[a]			72
Q	I	1	I/Mg exchange	**93**	I/Mg exchange	**92**	72
R	I	2	I/Mg exchange	**95**	I/Mg exchange	**94**	72

[a] This undefined complex is probably also a side-on complex, but in the absence of a crystal structure, its identity could not be established.

Scheme 55



Scheme 56



bonds are different, the xylylene–Mg bond being shorter [Mg–C(1) = 2.128(4) Å] than the aryl–Mg bond [Mg–C(2) = 2.154(4) Å]. The equatorial Mg–O(3) bond is much shorter [2.146(4) Å] than the axial ones [Mg–O(2) = 2.337(4) and Mg–O(5) = 2.317(3) Å, respectively].

The mechanism of the reactions of organometallics with 1,3-xylylene crown ethers has been extensively investigated;[10–12,74–76] it is illustrated for the formation of **93** in Scheme 55. After the formation of an initial side-on complex, in which the organomagnesium species is coordinated to oxygens 2 and 3, the reactions proceed via an intermediate magnesiate species Ph_3Mg^-, which attacks the intraannular substituent X (H/Br/I) in a nucleophilic substitution process. The cationic magnesium atom is simultaneously involved in an electrophilic attack on the aryl carbon atom C(2), which is facilitated by the symmetrical coordination to the crown ether ring.

None of these reactions were found to occur in THF, as this donor solvent is stronger coordinating than the crown ether and thus prevents the formation of the side-on complex. The dramatic influence of IC by a 1,3-xylylene-15-crown-4 ligand is illustrated by the extreme reversal of the "natural" reactivity order, which is halogen–metal exchange ≫ metalation in (5-bromo-1,3-xylylene)-15-crown-4: the reaction with bis(*p-tert*-butylphenyl)magnesium in diethyl ether yielded [5-bromo-2-(*p-tert*-butylphenylmagnesio)-1,3-xylylene]-15-crown-4 (**97**) in nearly quantitative yield (Scheme 56).[11] Halogen–metal exchange (the only reaction expected and actually observed with *n*-butyllithium) does not occur at all. Addition of a THF solution of magnesium bromide to **97** converted the latter completely to the Grignard compounds [5-bromo-2-(bromomagnesio)-1,3-xylylene]-15-crown-4 (**98**) and *p-tert*-butylphenylmagnesium bromide.

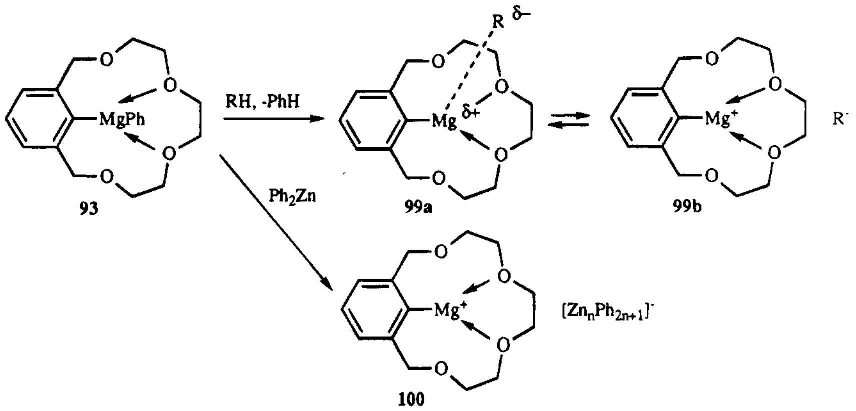
Replacement of the phenyl group in **93** by a group which is a more stable anion because of charge delocalization, results in dissociation to form a species which presumably contains crown ether-coordinated cationic magnesium.[76] Thus, reaction of **93** with 9-phenylfluorene gave the orange-red crystalline product [(2-magnesio-1,3-xylylene)-15-crown-4] [9-phenylfluorenide] (**99**), in almost quantitative yield (Scheme 57).

The ^1H NMR signals of the crown ether ethylene groups show large upfield shifts. The xylylene CH_2 signals are singlets, which supports either a planar ion **99b** or rapid exchange of the 9-phenylfluorenidyl anion in **99a**. In another attempt to obtain the solvent separated cation, (2-magnesio-1,3-xylylene)-15-crown-4, the reaction of **93** and diphenylzinc was investigated.[76] Analyses of the resulting solution by ^1H NMR spectroscopy suggested the formation of a complex [(2-magnesio-1,3-xylylene)-15-crown-4]·[triphenylzincate] (**100**), in addition to some residual **93** (Scheme 57). The phenyl groups in **100** are equivalent, with a phenyl/crown ether ratio of 3:1. The characteristic AB pattern of the xylylene CH_2 hydrogens of **93** is changed to a singlet in **100**. Upon addition of an excess of diphenylzinc, the signals of **93** in the ^1H NMR spectrum disappeared completely and the ratio of phenyl/crown ether signal integral increased, suggesting the formation of higher zincate anions like $Ph_5Zn_2^-$.

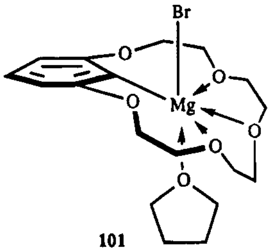
Very recently, the crown ether Grignard reagent [2-(bromomagnesio)-1,3-phenylene]-16-crown-5 (**101**) was characterized by its crystal structure. The structure appeared to be exceptional in a number of ways (Scheme 58).[77]

The magnesium center is hexacoordinated in a strongly distorted octahedron, with three crown ether oxygens (Mg–O 2.081, 2.136, and 2.096 Å, respectively) and the *ipso*-carbon (Mg–C 2.193 Å) in the

Scheme 57



Scheme 58

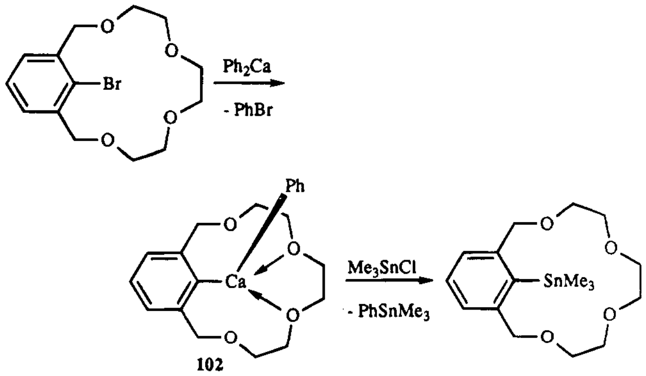


equatorial plane and with the bromine (Mg−Br 2.660 Å) and THF oxygen (Mg−O 2.315 Å) in axial positions. Furthermore, the C_{ipso}−Mg vector forms an angle of 27° with the plane of the aromatic ring. Besides having a unique structure, **101** is remarkable as the first example of an intraannular functionalized 1,3-phenylene crown ether and of an organometallic crown ether in which the metal is additionally coordinated to an intermolecular donor molecule.

C. Calcium

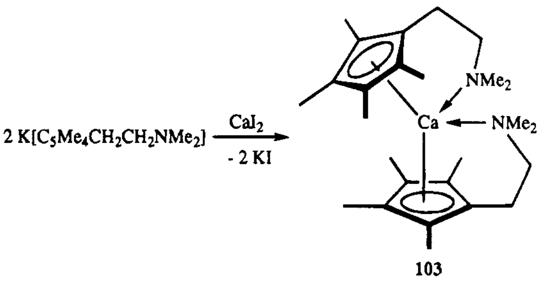
Metalation of (2-bromo-1,3-xylylene)-18-crown-5 with diphenylcalcium yields the expected products [2-(phenylcalcio)-1,3-xylylene]-18-crown-5 (**102**) and bromobenzene in almost quantitative yield[76] (Scheme 59; cf. section III.B.3 for similar exchange reactions of magnesium).[11] The identity of **102** was proven by reaction with trimethyltin chloride which yielded [2-(trimethylstannio)-1,3-xylylene]-18-crown-5 and phenyltrimethyltin. Crystals suitable for a structure determination were not obtained, but the occurrence of IC in **102** is highly probable in view of the X-ray crystal structure of its magnesium analogue **93**.

Scheme 59



Several examples concerning the incorporation of bifunctional 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl systems in metal complexes were reported in 1993.[78] The anion of 1-[2-(dimethylamino)ethyl]-2,3,4,5-teramethylcyclopentadiene reacts smoothly with CaI_2 to yield the metallocene (η^5: η^1-$C_5Me_4CH_2CH_2NMe_2)_2Ca$ (**103**, Scheme 60).

Scheme 60



The intramolecular nitrogen coordination was proven by NMR spectroscopy and by an X-ray crystal structure (although the structure was not completely solved, IC could be proven). Furthermore, adduct formation with THF was not observed, which is contrary to the behavior of the decamethylmetallocene of calcium.

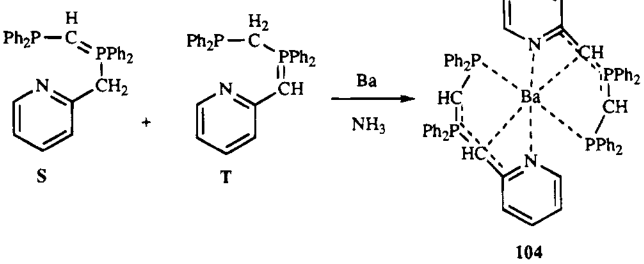
D. Strontium

To our knowledge, examples of IC in organostrontium chemistry are not known.

E. Barium

From the ylide mixture **S**, **T** (Scheme 61) with barium metal in liquid ammonia, the solvent-free barium complex **104** was obtained under formation of H_2;[79] **104** is an orange solid which is very sensitive

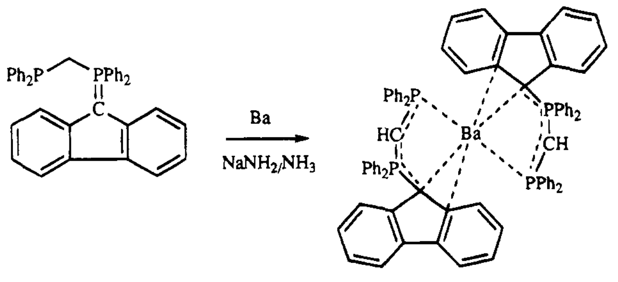
Scheme 61



to air and water, but under inert gas it is stable up to its melting point of 127 °C. The structure of **104** was confirmed by IR and by ^1H, ^{13}C, and ^{31}P NMR spectroscopy in dioxane. Of the corresponding sodium compound, an X-ray crystal structure was determined. This structure is analogous to that for **104**.

A second barium compound (**105**), having features similar to **104**, was obtained from the reaction of the fluorenylylide precursor with $NaNH_2$ and barium metal as shown in Scheme 62.[80] ^1H and ^{31}P NMR spectra showed the formation of **105**, an orange solid with a melting point of 137 °C.

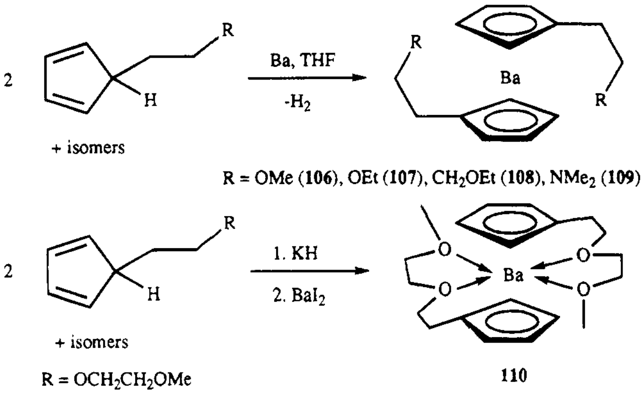
Scheme 62



105

Recently, a series of bariocenes was synthesized (Scheme 63).[81,82] Compounds **106**–**109** were particularly insoluble in typical organic solvents. This resulted in poor solution ^{13}C NMR data and likewise, solution cryoscopic molar mass determinations were not feasible. For bariocene **110**, the presence of IC was indicated by ^{13}C NMR measurements.

Scheme 63



IV. Group 12 Metals

Diorganozinc compounds interact with electron donors like ethers or tertiary amines, but the donor–acceptor bonds are obviously weaker than in complexes of triorganoaluminum or -gallium compounds.[83,84] Interactions of diorganozinc compounds with cyclic ethers are stronger than with dialkyl ethers, but even the complexes with THF are at least 80% dissociated in the gas phase at 140 °C.[85] Electron–donor acceptor zinc–nitrogen bonds are generally stronger than zinc–oxygen analogues, but the electron diffraction pattern of the vapor formed from (the liquid) 1:1 complex $Me_2Zn{\cdot}NMe_3$ indicated quantitative dissociation at 30 °C.[83] As was discussed in section III.B.3, the corresponding IC donor–acceptor bonds are generally stronger because on complexation, the enthalpy is more negative due to less steric crowding while the entropy is less negative due to the intramolecular nature of the process.

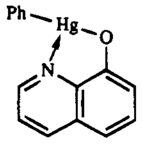
As bond lengths are important in discussing the nature and strength of dative bonds, it is helpful to establish the standard value for the Zn–D bond length and its range of variation. This analysis was first performed by Boersma *et al.*[83] A representative value for a covalent Zn–O bond distance was taken from $(ArO)_2Zn{\cdot}2THF$ (Ar = 2,6-di-*tert*-butylphenyl) in which the Zn–O(Ar) distance is 1.89 Å, 0.19 Å shorter than the dative Zn–O(THF) distance in the same molecule (2.08 Å).[86] The Zn–O distance in the IC compounds $Zn[(CH_2)_nOMe]_2$ (2.37 and 2.38 Å for n = 3 (**155**) and n = 4 (**157**), respectively) is about 0.5 Å longer than the covalent Zn–O distance.[87] A reasonable value for a covalent Zn–N bond is provided by the monomeric amide $Zn[N(SiMe_3)_2]_2$,[88] Zn–N = 1.82 Å, 0.25 Å shorter than the dative Zn–N bond distance in the Cl_2ZnN_2 complexes $ZnCl_2{\cdot}$[1,10-phenanthroline][89] and $ZnCl_2{\cdot}$[2,9-dimethylphenanthroline][90] (2.06 and 2.07 Å, respectively) and 0.5 Å shorter than the IC bond distance in $Zn[(CH_2)_3NMe_2]_2$ (2.31 Å).[83] In the complex of $ZnCl_2$ with thiourea,[91] where the metal coordination is Cl_2ZnS_2, the mean Zn–S distance is 2.35 Å, 0.38 Å shorter than that in $Zn[(CH_2)_3SMe]_2$ (2.73 Å).[83]

Exchange of one alkyl group of R_2ZnD_2 (R = alkyl and D = N, O, S, *vide infra*) for a more electronegative group like chlorine or a transition-metal containing group leads to a shortening of the IC bond by about 0.1 Å. Exchange of the second alkyl group by an electronegative group leads to additional shortening of the Zn–D bonds, again by about 0.1 Å.[83]

The four Zn–N bond distances in the central four-membered ring of $Me_2Zn_2(\mu\text{-}NPh_2)_2$[92] (in which each NPh_2 is bridging over the two MeZn moieties) are 2.07 Å. Each bond may be regarded as a 50:50 resonance form between a covalent and a dative bond because the bond distance is close to the mean value of the covalent Zn–N distance in $Zn[N(SiMe_3)_2]_2$ (1.82 Å) and the dative bond distance in $Zn[(CH_2)_3NMe_2]_2$ (2.31 Å).

The structural chemistry of mercury compounds is a special case within the structural chemistry of metals; this is largely due to the fact that the mercury atom does not form regular coordination polyhedra. In the review by Kuz'mina and Struchkov[93] on the structural chemistry of organomercury compounds, the role of inter- and intramolecular secondary interactions was studied systematically. These interactions (bonds), although rather labile, exert a definite influence on the (crystal) structure, which is manifested in a peculiar, rather irregular, coordination around the mercury atom. In all cases where a distortion of the characteristic linear coordination of the Hg atom (sp hybridization) is observed, it is in fact due to secondary bonds. The upper limit of the distances within the coordination polyhedron cannot be defined sharply, as even distances larger than the sum of the van der Waals radii may influence the structure as a whole as well as the stability of the other bonds. This can be illustrated by the crystal

Scheme 64



111A, 111B, 111'

Table 4. Relevant Bond Lengths (Å) and Angles (deg) for 111

compd	Hg−N	Hg−O	Hg−Ph	O−Hg−Ph
111A	2.29	2.19	2.18	142
111B	2.40	2.15	2.14	154
111′	2.57	2.06	2.05	175

structure of phenylmercury 8-hydroxyquinolinate (**111**, Scheme 64), which is not an IC compound according to the definition in section II.A because the metal−carbon bond is not part of the chelate ring.[94] Compound **111** occurs in two modifications, **111** and **111′**. In **111**, there are two crystallographically independent molecules (**111A** and **111B**). The geometrical parameters of the three molecules **111A**, **111B**, and **111′** are quite different (Table 4).

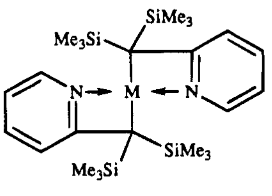
This example clearly illustrates that the dative Hg−N bonds are weak, as the difference in the geometrical parameters of molecules **111A**, **111B**, and **111′** results only from the different molecular environments in the crystal and are thus strongly influenced by crystal packing forces; nevertheless, the influence of the Hg−N interaction on the Hg−C and Hg−O is considerable.

A. Group 12 Metal Complexes with Nitrogen Donor Atoms

1. Four-Membered Rings

The highly hindered alkyl−ligand $NC_5H_4[2\text{-}C(SiMe_3)_2]$, which was already encountered in section III.B.3 as an IC ligand for magnesium, has also been used to prepare the corresponding complexes of zinc, cadmium, and mercury.[31] Reaction of the corresponding lithium compound $LiR(THF)_n$ with MCl_2 gave **112-114**. All three compounds are mononuclear metal(II) alkyls in which the dative metal−nitrogen interactions progressively weaken and the C−M−C angles become larger in the sequence **112-114** (Scheme 65, Table 5). It is noteworthy that R is capable of chelate ring formation, despite the fact that the four-membered ring is strained. Compared to the related compounds MR'_2 [M = Zn, Cd, Hg; R′ = $C[(SiMe_3)_3]$],[95] **112-114** were reported to have a similarly high thermal stability, but a slightly higher reactivity.

Scheme 65



M = Zn (**112**), Cd (**113**), Hg (**114**)

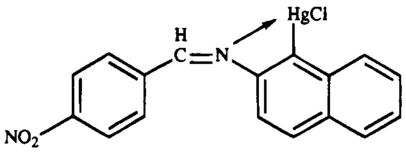
Table 5. Relevant Bond Distances (Å), Angles (deg), and Melting Points (°C) for 112-114

compd	M	M−C	M−N	C−M−C	mp
112	Zn	2.07_0	2.29_4	164.4_0	123
113	Cd	2.2_7	2.4_9	$174._3$	127
114	Hg	2.1_6	2.7_8	179.5_3	114

In general, the dative Hg−X interaction is more favorable if the heteroatom X is located in the plane through the mercury atom which is perpendicular to its two covalent bonds. A larger distance between the heteroatom and this plane results in a less effective overlap of the interacting orbitals of Hg and X, i.e. a weaker IC bond.[93] The dative Hg−N bond in molecules with four-membered chelate rings is weaker than in molecules with five-membered chelate rings. This is illustrated by the very weak dative interaction in **114** (see Table 5).

As part of an effort to investigate substituent effects on the intramolecular coordination between N and Hg, the mercuration of 36 substituted benzylideneanilines has been studied.[96] The position of the HgCl group in the mercuration product **115** of *N*-(4-nitrobenzylidene)-*β*-naphthylamine was confirmed by a single-crystal X-ray structure determination, which also provided circumstantial evidence for the existence of a N→Hg IC with a four-membered ring (Scheme 66).

Scheme 66

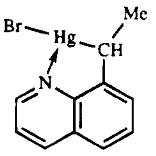


115

2. Five- and Six-Membered Rings

The structure of 8-[α-(bromomercurio)ethyl]quinoline (**116**, Scheme 67) is a true IC analogue of **111** as the Hg−C bond is included in the chelate.[94] The mercury atom in **116** has a planar "T-shaped" coordination. The Hg−N distance of 2.92 is close to the sum of the van der Waals radii (3.15 Å) and corresponds to a very weak dative bond. The Hg−C bond length is 2.453 Å and the C−Hg−Br angle is 174.6°.

Scheme 67

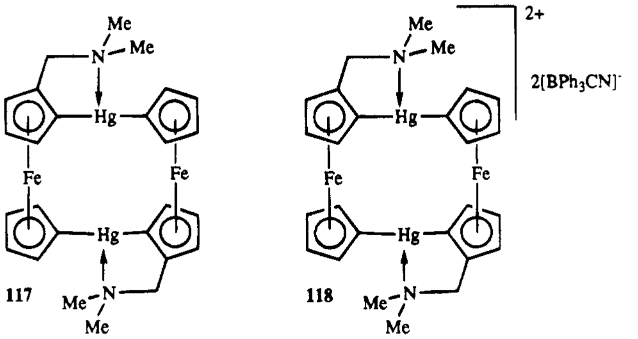


116

The structures of some [[(dimethylamino)methyl]ferrocenyl]mercury derivatives are shown in Scheme 68. The Hg−N distances in the two crystallographically independent centrosymmetric molecules of the bis[(dimethylamino)methyl] derivative of 1,1-dimercurioferrocenophane **117**[97] are 2.92 and 3.05 Å, respectively, i.e. close to the sum of the van der Waals radii. The five-membered chelate ring is not planar, but the NMe_2 groups are oriented in such a way that the nitrogen lone pairs are directed toward the mercury atom.

In the corresponding dication of the salt **118** (Scheme 68), the IC Hg−N bond is stronger because

Scheme 68

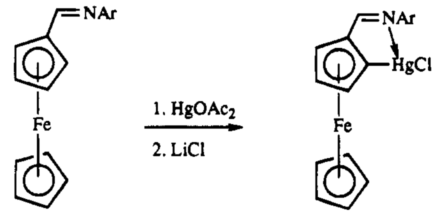


117 118

the electron density at mercury is decreased due to the positive charges. The chelate rings in **118** are planar, and the Hg−N distances are decreased to 2.83 Å.

Very recently, the mercuration of a series of [(arylimino)methyl]ferrocenes was reported to occur predominantly at the *ortho* position of the substituted ferrocenyl ring to yield the 2-mercurated ferrocenylimines **119-129** (Scheme 69).[98]

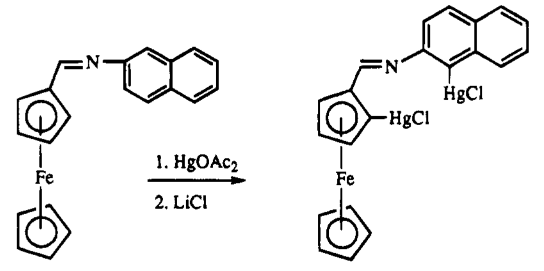
Scheme 69



Ar = p-OCH$_3$C$_6$H$_4$ (119), p-CH$_3$C$_6$H$_4$ (120), C$_6$H$_5$ (121), p-ClC$_6$H$_4$ (122), p-BrC$_6$H$_4$ (123), p-IC$_6$H$_4$ (124), p-NO$_2$C$_6$H$_4$ (125), m-ClC$_6$H$_4$ (126), m-BrC$_6$H$_4$ (127), m-NO$_2$C$_6$H$_4$ (128), 1-naphthyl (129)

In the mercuration of [(2-naphthylimino)methyl]ferrocene, the result was different: the dimercurated product **130** was obtained in high yield (Scheme 70).

Scheme 70

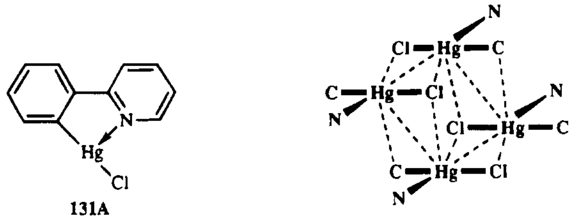


130

The regiospecificity in this case also results from coordination of the mercury to the imino nitrogen prior to electrophilic substitution. The chromatographic and spectral properties of the 2-mercurated products show the presence of intramolecular N−Hg coordination in a five-membered ring. TLC bands of very small amounts of products mercurated at other positions move more slowly than those of the 2-mercurated analogues. The "anomalous" sequence of elution observed for the isomeric (chloromercurio)(imino)ferrocenes can be explained by postulating coordination between the imino and the 2-chloromercurio groups, thereby decreasing the electron density in the C=N bond. This could cause a decrease in the affinity of the 2-chloromercurio isomers for the chromatographic material. The IR spectra of compounds **119-130** showed C=N absorptions which were shifted to lower energy by 4−15 cm^{-1}; this can also be explained by the occurrence of IC. The ^{1}H NMR spectra of compounds **119-130** were completely consistent with the proposed structures (1,2-substitution). The occurrence of IC was further confirmed by the single-crystal structure analysis of 2-(chloromercurio)-1-[[(4-methoxyphenyl)imino]methyl]ferrocene **119**. The Hg−N distance [although rather long at 2.897(2) Å] and the decrease of the Hg−C−C and C−C−C angles within the five-membered ring (from the normal angle of 126° to 120.7 and 123.4°, respectively) is an indication for the Hg−N interaction. The Hg−Cl distance (2.295(9) Å) is similar to those found for typical organic derivatives of mercury, but the Hg−C distance [2.016(3) Å] is somewhat shorter.[93] The C−Hg−Cl angle is 176.84°. The Cp rings are almost parallel (dihedral angle 2.01°) and the chelate ring HgCCCN is nearly planar. The dihedral angle between the substituted Cp ring and the chelate ring is 2.29°, and that between the Cp ring and the phenyl ring is 38.58°.

The reaction of mercury(II) acetate with 2-phenylpyridine, followed by metathesis with lithium chloride, yielded the complex (2-pyridylphenyl)mercury chloride (**131A**; Scheme 71).[99]

Scheme 71



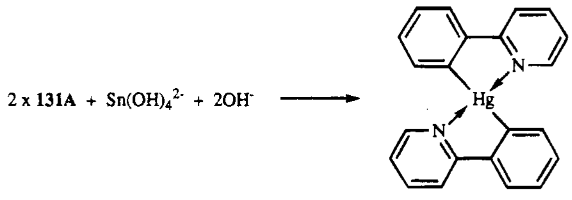
131A

The crystal and molecular structure of this complex reveals the presence of a tetranuclear [Hg$_4$L$_4$Cl$_4$] aggregate (Scheme 71) with two similar, but crystallographically different types of [HgLCl] units. Each mercury is linearly coordinated to a chloride (2.314 and 2.335 Å) and a carbon atom [2.07(1) Å], and exhibits a surprisingly long contact only with the pyridyl nitrogen atom [2.63(1) and 2.67(1) Å]. Furthermore, an unusual semibridging Hg−C−Hg interaction is observed to give an unexpected tetrameric arrangement reminiscent of the "ladder" structures observed in organolithium derivatives.[99] The compound was investigated by ^{1}H and ^{13}C NMR spectroscopy ([$^1J_{\mathrm{C1-Hg}}$ = 2767 Hz; $^2J_{\mathrm{C2-Hg}}$ = 105 Hz; $^2J_{\mathrm{C6-Hg}}$ = 120 Hz; $^3J_{\mathrm{C3-Hg}}$ = 165 Hz; $^3J_{\mathrm{C5-Hg}}$ = 214 Hz; $^4J_{\mathrm{C4-Hg}}$ = 214 Hz]).

Symmetrization of **131A** with alkaline sodium stannite in a two-phase system gave bis[2-(pyridin-2′-yl)phenyl]mercury (**131B**; Scheme 72).[100] Compound **131B** was also prepared from 2-(2′-aminophenyl)pyridine by the diazo method.

The ^{1}H NMR spectrum was fully assigned with the aid of decoupling experiments. $J_{\mathrm{Hg-H6}}$ and $J_{\mathrm{Hg-H3}}$ were half those of **131A** as expected for a diorganomercurial. A parent ion was observed in the mass spectrum and heterocyclic nitrogen−mercury inter-

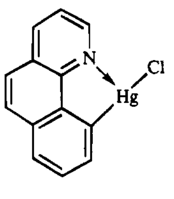
Scheme 72



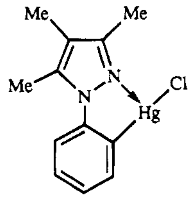
131B

action was proven by X-ray crystallography. The molecule is centrosymmetric with linear C−Hg−C bonding, a linear N−Hg−N arrangement, and C−Hg−N angles of 70.3(3)°, giving a distorted square planar stereochemistry. The Hg−C distance is 2.098(8) Å and the Hg−N distance [2.798(7) Å] implies significant Hg−N IC. Lengthening of Hg−N from the distance in **131A** can be attributed to the weaker acceptor properties of diorgano than of monoorgano mercurials. Mercuration of benzo[*h*]quinoline and 3,4,5-trimethyl-1-phenylpyrazole (mercuric acetate/LiCl) yielded benzo[*h*]quinolin-10-ylmercuric chloride (**132**) and [2-(3′,4′,5′-trimethylpyrazol-1′-yl)phenyl]mercuric chloride (**133**), respectively (Scheme 73).[100]

Scheme 73



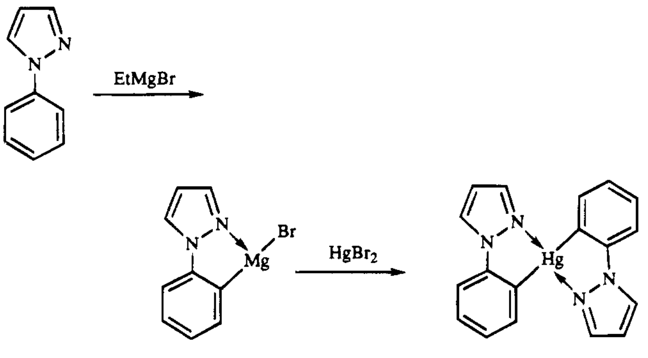
132



133

Reaction of [2-(pyrazol-1′-yl)phenyl]magnesium bromide (which is probably an IC compound itself) with mercuric bromide yielded bis[2-(pyrazol-1′-yl)phenyl]mercury[100] (**134**, Scheme 74). The substantial downfield ^{199}Hg NMR chemical shifts of **131A**−**133** were attributed to (weak) IC by the heterocyclic nitrogen donor atoms.[100]

Scheme 74

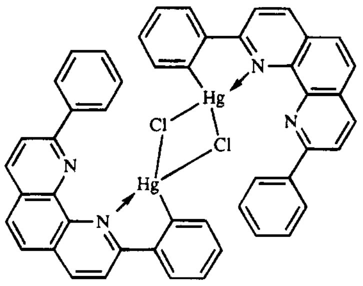


134

The reaction of mercury(II) acetate with 2,9-diphenyl-1,10-phenanthroline (dpp) in refluxing ethanol and in the presence of lithium chloride gave the ortho-cyclometalated complex **135** (Scheme 75).[101]

X-ray crystal structure analysis revealed two structural units (type A and B) of the dimer **135** in the crystal lattice. The two types of structural units are distinguished by their different conformations around the interannular bonds between the phenyl group and phenanthroline ring. The Hg−N distances 2.60 Å (five-membered ring; significant IC) and 3.85 Å (eight-membered ring; no IC) and proton chemical shifts of the metalated dpp suggest that the 1,10-phenanthroline ring is weakly coordinated to the Hg−phenyl moiety with one of its nitrogen atoms. Unlike **131**, which has a tetrameric structure, the degree of aggregation for the mercurated dpp is apparently reduced by the steric bulkiness of the ligand. The coordination around Hg approximates that of an elongated tetrahedron with one of the two Hg−Cl distances [3.240(8) Å] substantially longer than the other [Hg−Cl (2.317(8) Å]. The Hg−C distances (2.113 Å) are similar to those of e.g. **131A** and **131B**. In the monomeric subunit of **135**, the nonmetalated phenyl ring forms larger dihedral angles with the phenanthroline unit (type A = 28.6°, type B = 38.6°) than those of the metalated one (type A = 23°, type B = 16.2°). Furthermore, the mass spectrometric and NMR characterization, as well as the spectroscopic (UV−vis) and photochemical properties are discussed.

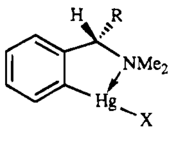
Scheme 75



135

To investigate the occurrence of IC in organomercury compounds, 2-$Me_2NCH_2C_6H_4HgX$ [ArHgX; X = Cl (**136**), OAc (**137**)], (2-$Me_2NCH_2C_6H_4)_2Hg$ (Ar_2Hg; **138**), and (*S*)-2-$Me_2NCH(Me)C_6H_4HgX$ [(*S*)-ArHgX; X = Cl (**139**), OAc (**140**)] were synthesized (Scheme 76).[102]

Scheme 76

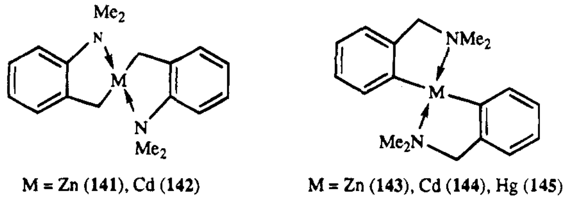


	X	R
136	Cl	H
137	OAc	H
138	Ar	H
139	Cl	Me
140	OAc	Me

Ar_2Hg, ArHgCl, and (*S*)-ArHgCl were obtained from the corresponding ArCu, ArLi, or (*S*)-ArCu derivatives, respectively; ArHgOAc, ArHgCl, and (*S*)-ArHgOAc were obtained via the ligand exchange reactions between Ar_2Hg and the respective HgX_2 or between (*S*)-ArHgCl and AgOAc. They were identified by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy; molecular weight determinations indicated that they are monomeric in chloroform. IC in **136**−**138** could not be demonstrated by ^{1}H and ^{13}C NMR spectroscopy, but the observation of anisochronous NMe resonances in **139** and **140** at low temperature indicated that in solution, the mercury center is tricoordinate as a result of stable intramolecular Hg−N coordination. Because in this situation, the nitrogen atom is in a stable tetrahedral array, the inversion at nitrogen is slowed down. The coalescence temperatures and the chemical shift differences for the NMe_2 protons in **139** and **140** are almost equal (212 and 209 K; 18 and 20 Hz at 60 MHz, respectively) which might be an indication that the *a priori* conceivable chelation of mercury by the acetate group does not interfere with the dynamic Hg−N interaction.

In the early 1980s, a study was undertaken with the objective to compare, by X-ray crystallography, an appropriate trio of homoleptic Zn, Cd, and Hg derivatives.[103] By reacting [*o*-(dimethylamino)benzyl]lithium or [*o*-[(dimethylamino)methyl]phenyl]lithium with MX_2 (M = Zn, Cd, Hg), compounds **141-145** were synthesized (Scheme 77).

Scheme 77

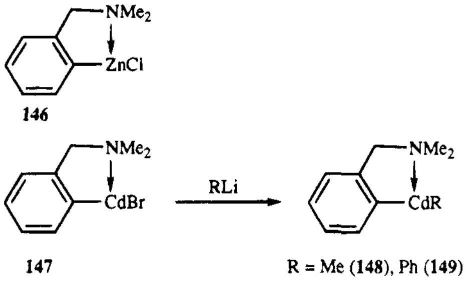


However, the yields and crystal quality were consistently poor except for the diarylmercury compound **145**, and although compounds **141-144** showed enhanced thermal stability compared to simple dicoordinated diorganometallic species, they were rather air and light sensitive. Compound **145** has a centrosymmetric arrangement in which the geometry about the mercury atom is planar and also nearly coplanar to both coordinating phenyl ring systems. The C−Hg−C axis is constrained to exact linearity by crystallographic symmetry with Hg−C = 2.10 Å. Other bond lengths in the structure are unexceptional, but the orientation of the dimethylamino groups is remarkable in bringing the nitrogen atom in close vicinity to mercury at 2.89 Å. Like the C−Hg−C vector, the N−Hg−N linkage is strictly linear; the two intersect at an angle of 71°. Interpretation of the structure adopted by **145** (and comparable compounds) seems to require either (a) d−s mixing at mercury, which has hitherto been regarded as unlikely, or (b) donation into a single empty acceptor orbital ($6p_x$ or $6p_y$) by two donor lone pair hybrids, necessitating an orbital description based on three-center delocalized bonding and, coincidentally, predicting a long Hg−N distance, as is observed. The d−s mixing is held to be unlikely in diorganomercurials; rather, their feeble acceptor properties have been related to low charge on the metal, while sp hybridization is predominating.[104,105]

The spectroscopic data for **141−145**, particularly those from NMR spectra, provide disappointingly little additional insight concerning the structure. The lack of any conspicuous changes in the series **143−145** suggests that the three molecules adopt a common geometry in solution, and this geometry may correspond to the chelated arrangement found for **145** by the X-ray study. One unusual feature encountered for **145** is the spin coupling of ^{199}Hg with both nuclei of the methylene group: both are rather large at $^3J_{Hg-C}$ = 63 and $^4J_{Hg-H}$ = 18 Hz, respectively. Each compound proved to be sufficiently volatile for characterization by mass spectrometry; by CH_4 chemical ionization (GCMS), molecular ions were observed in all cases.

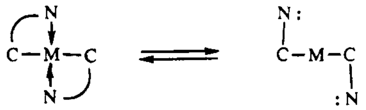
Compounds **143** and **144** were simultaneously and independently synthesized by another group, again by reacting MCl_2 (M = Zn, Cd) with ArLi (Ar = 2-[(dimethylamino)methyl]phenyl).[106] Furthermore, the organometallic halides ArZnCl (**146**; via ArLi) and ArCdBr (**147**; via the electrochemical oxidation of cadmium metal in the presence of ArBr) were prepared. The latter was converted to ArCdMe (**148**) and to ArCdPh (**149**) with MeLi and PhLi, respectively (Scheme 78).

Scheme 78



Again, the nature of the coordination in **143** and **144** (which may occur as di-, tri-, or tetracoordinate species) was investigated by ^{1}H NMR spectroscopy. For **143** at ambient temperatures and for **144** at 25 and −50 °C, both the NCH_2 and NCH_3 sets of protons give rise to singlets ($CDCl_3$ solution). The tetracoordinate Ar_2M complex would lack a molecular symmetry plane, and therefore anisochronous resonances should be observed. Therefore, Cd−N bond dissociation which is fast on the NMR time scale (even at −50 °C) must occur, as pyramidal inversion can only take place when the nitrogen is not coordinated to the metal. It was concluded that the equilibrium shown in Scheme 79 lies well to the right as a result of the considerable strain involved in the formation of a pseudotetrahedral MC_2N_2 unit.

Scheme 79

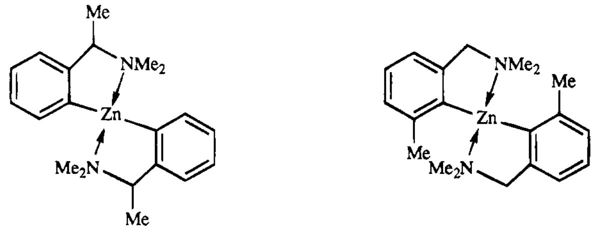


The bite angle N−M−C in related ArM complexes has been shown to be close to 75° (e.g., 75.3° in $Ph_2ArSnBr$,[107] 73° in CpArTi,[108] and 77° in Ar_2InCl[109]). Note that in contrast, five-membered Hg−N chelate rings were shown to be stable on the NMR time scale for **139** and **140** at −70 °C.[102] However, as X-ray diffraction studies of the corresponding mercury compound **145** showed the presence of IC and because it has been shown that with the *o*-$(CSiMe_3)_2C_5H_4N$ ligand, IC decreases from Zn (**103**) via Cd (**104**) to Hg (**105**), IC in **143** and **144** cannot be excluded.

Additionally, EI and FD mass spectra of **144** and, for comparison, the EI spectrum of ArBr were investigated. The EI-induced decomposition of **144** and that of ArBr differ significantly. For **144**, no molecular ion or organocadmium fragments were observed; its FD spectrum showed *m/z* values up to ~800, resulting from ionized aggregates. Furthermore, the molecular ion cluster of Ar_2Cd^+ was clearly observed. These data, however, do not furnish information on the occurrence of IC.

Compounds related to **143** were prepared more recently. Bis[2-[1-(dimethylamino)ethyl]phenyl]zinc (**150**) and bis[6-methyl-2-[(dimethylamino)methyl]-phenyl]zinc (**151**) were reported without further investigation concerning the presence of IC (Scheme 80).[110,111]

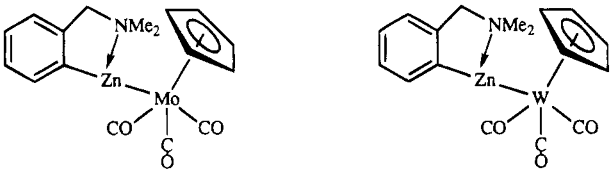
Scheme 80



150 **151**

Two bimetallic derivatives of **146** have been reported. From the reaction of bis[[(dimethylamino)-methyl]phenyl]zinc (**143**) with Zn[CpMo(CO)$_3$]$_2$ or Zn[CpW(CO)$_3$]$_2$, compounds **152** and **153** were obtained, respectively (Scheme 81).[112] The presence of IC in these compounds was indicated by microwave titration results. Furthermore, a crystal structure of another bimetallic zinc compound was determined (**160**, *vide infra*).

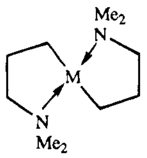
Scheme 81



152 **153**

Reaction of ZnCl$_2$ with the Grignard reagents X(CH$_2$)$_n$MgCl (n = 3, X = OMe, SMe, NMe$_2$; and n = 4, X = OMe) in Et$_2$O/THF yielded Zn[(CH$_2$)$_n$X]$_2$ [n = 3, X = NMe$_2$ (**154**, Scheme 82), OMe (**155**, Scheme 101), SMe (**156**, Scheme 108); n = 4, X = OMe (**157**, Scheme 101)].[113] For reasons of comparison, some of the properties of compounds **155**−**157**, (which contain oxygen and sulfur donating groups) are discussed here. The IR spectra did not unambiguously indicate the presence or absence of coordinative zinc−heteroatom interactions. The compounds easily lose coordinating solvents such as Et$_2$O and THF, suggesting that zinc has attained tetracoordination intramolecularly. Ebulliometric molecular weight determinations showed the compounds to be monomeric in benzene, the molecular weight being concentration independent. Therefore, the tetracoordination of Zn cannot be due to intermolecular association.

Scheme 82



M = Zn (**154**), Cd(**164**), Hg(**165**)

Table 6. Carbon 13 Shifts [Δ = δ(R$_2$Zn) − δ(RH)] of the γ-Carbon Atoms in Zn[(CH$_2$)$_n$X]$_2$

compd	n	X	δ(R$_2$Zn)	δ(RH)	Δ[a]	Scheme
154	3	NMe$_2$	74.59	75.62	−1.03[114,115]	82
155	3	OMe	36.64	40.07	−3.43	101
156	3	SMe	62.08	63.86	−1.78	108
157	4	OMe	32.21	34.51	−2.30	101
Bu$_2$Zn			29.73	24.90	+4.83	

[a] Relative shift Δ = δ(R$_2$Zn) − δ(RH).

^{13}C NMR spectroscopy gave conclusive evidence on the existence of IC. In the ^{13}C NMR spectra, the absorptions of the α-carbon atoms [Zn−C$_\alpha$−C$_\beta$−C$_\gamma$−(C$_\delta$)−X−C$_\epsilon$] are shielded relative to those in dibutylzinc. Similar shielding is observed if dibutylzinc is complexed with 2,2′-bipyridine or TMEDA. Comparison of the relative shifts [Δ = δ(R$_2$Zn) − δ(RH)] of the γ-carbon atoms for **154-157** with the relative shift [Δ = δ(Bu$_2$Zn) − δ(BuH)] of the γ-carbon atoms of dibutylzinc, reveals that the γ-carbon signals of the former are more shielded (Table 6). These high-field shifts can only be explained by the so-called γ-effect which is quite general in saturated ring systems,[116−118] demonstrating the presence of fixed five- and six-membered ring systems.

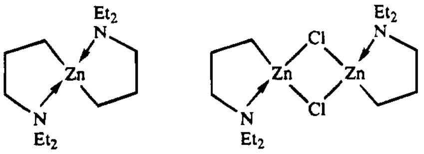
By reacting **154**−**157** with 2,2′-bipyridine (bipy), the dissociation constants of the resulting 1:1 complexes were calculated using the ^{13}C(1)-chemical shifts of the quaternary carbon of the bipy species, since these shifts are particularly sensitive to coordination. It appears that the dissociation constants of the bipy complexes increase in the order K_D(**157**) ≪ K_D(**156**) < K_D(**155**) < K_D(**154**), indicating that the strengths of the IC bonds increase in the same order. These data also show a five-membered ring (**155**) to be more stable than a six-membered ring (**157**), other factors being equal. With TMEDA, which is a better σ-donor, stronger complexes are formed than with bipy. Only the TMEDA complex of **154** is strongly dissociated, which means that TMEDA cannot compete with IC in this compound. The ^{13}C NMR spectra of **155-157** indicate that IC is lost in the presence of TMEDA, which is manifested by the disappearance of the γ-effect.

About 10 years after the publication of these results, the molecular structure of **154** (mp: 37 °C) was determined by X-ray crystallography and by gas-phase electron diffraction.[83] In the crystalline phase, the molecular symmetry of **154** is C_2, with a pseudo-two-fold axis going through zinc and the center of the C(β)−C(γ) bond. The Zn−N bond distance is 2.307-(4) Å, the Zn−C bond distance is 1.984 Å and the coordination around zinc is considerably distorted from tetrahedral: the angle C−Zn−C is 156.4(2)° and N−Zn−N is 109(7)°. The five-membered chelate ring is significantly puckered, resulting in a half-chair conformation, with one of the methyl groups in an axial and the other in an equatorial position. The same conformation appears to persist in the gas phase, but the presence of other conformers could not be ruled out.

A rough estimate was made of the strength of zinc–heteroatom dative bonds.[83] The monodentate ligand complex $Me_2Zn{\cdot}NMe_3$ is completely dissociated in the gas phase,[83] which means that the entropy increase upon dissociation apparently outweighs the loss of complexation enthalpy. Since in IC compounds, dissociation of the donor atom will result in a smaller increase in entropy, even very small complexation enthalpies (as low as a few kilojoules per mole) are sufficient to keep the internal donor groups coordinated to the metal. As weak interactions generally result in flat potential energy surfaces, large distortions can occur in response to small steric or electronic effects. The weakness of the IC bond in **154** [2.307(4) Å in the solid state and 2.392 Å in the gas phase] becomes apparent upon comparison with the value calculated from Pauling's "covalent tetrahedral radii":[119] Zn–N = 2.01 Å. In diorganozinc compounds, both the steric interactions between the organic groups and the electronic energy will be insensitive to small variations in the C–Zn–C angle caused by introduction of additional ligands. If these ligands are very weak donors, there will be no electronic preference for donation in one of the two different p orbitals. Small donations into the same orbital are—to a first approximation—additive, but with increasing strength of electronic interaction, the additivity relation breaks down because of saturation effects. Two weak ligands can donate to the same p orbital [resulting in a near linear D–Zn–D orientation (**156**)] or to different p orbitals, but stronger donors will have a definite preference for donation into different p orbitals, resulting in angles close to 90° (because of steric factors and the unfavorable arrangement of the bond dipoles, the actual angle will be slightly larger, as in **155**). However, in the NMe_2 complex **154**, steric factors become important. Given a linear C–Zn–C skeleton and a ligand "bite angle" of about 90°, it follows as a natural consequence that the NMe_2 group of one ligand and the α-CH_2 group of the other ligand are also oriented with a span angle of 90° at zinc, but experience a particularly strong repulsive interaction.

In 1980, the NEt_2 analogue of **154**, $[Et_2N(CH_2)_3]_2Zn$ (**158**), was synthesized by reacting the corresponding Grignard with 0.5 equiv of $ZnCl_2$. The dimeric compound $[Et_2N(CH_2)_3ZnCl]_2$ (**159**) was obtained when the Grignard reagent was reacted with 1 equiv of $ZnCl_2$ (Scheme 83).[120] Compound **158** is a distillable liquid. Crystals obtained at low-temperature melt between −30 and −16 °C. As the spectroscopic data of **158** correspond to those of **154**, the same spiranoid chelate structure was postulated.

Scheme 83

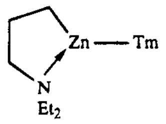


158 159

Alkylzinc halides are often tetrameric (EtZnCl or EtZnBr[121]) or polymeric (EtZnI[122]), but cryoscopy of **159** in benzene showed this compound to be dimeric, independent of concentration. It melts between 120 and 125 °C under decomposition, and its properties differ markedly from those of the corresponding R_2Zn derivatives and of simple alkylzinc halides. Compound **159** is not volatile, not very air sensitive, reacts only slowly with water, is unreactive toward Et_2O and MeI, and is only slightly soluble in nonpolar solvents. These findings were taken as evidence for coordinatively saturated Zn atoms.[120]

The stabilities of simple and internally coordinated organozinc–transition metal compounds toward disproportionation have been investigated by the microwave titration technique.[112] Simple alkyl and aryl derivatives disproportionate to such an extent as to preclude isolation. IC was found to stabilize the asymmetric compounds (cf. **152**, **153**), and several derivatives (**160-163**) containing the (dimethylamino)propyl group were isolated (Scheme 84).

Scheme 84



Tm = $Mn(CO)_5$ (160), $Co(CO)_4$ (161), $CpMo(CO)_3$ (162), $CpW(CO)_3$ (163)

The crystal structure of one of them, $Me_2N(CH_2)_3ZnW(Cp)(CO)_3$ (**163**), was determined by a single-crystal X-ray study. The molecule contains a central tungsten atom, surrounded in a tetragonal pyramidal fashion with the cyclopentadienyl group in the apical position and three carbon monoxide molecules and a zinc atom occupying the basal positions. The zinc atom is tricoordinate, being surrounded by the tungsten atom and the chelating (dimethylamino)propyl group; there is, however, a short intermolecular contact of 2.61(3) Å between zinc and a carbonyl oxygen atom, which is rather short for a normal nearest neighbor contact in such a crowded molecule. The intramolecular Zn–N bond length is 2.19(3) Å, the Zn–C distance is 1.99(3) Å and the Zn–W distance is 2.685(3) Å. The chelate ring is puckered in an envelope fashion.

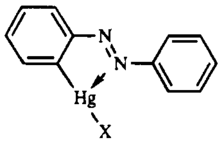
In 1985, bis[3-(dimethylamino)propyl]cadmium (**164**) and its mercury analogue (**165**) were reported (Scheme 82).[115] Both compounds were prepared by reacting the corresponding organolithium or -magnesium chloride derivatives with $CdCl_2$ or $HgCl_2$. Compound **164** is a colorless distillable compound, which is sensitive to air and water (yielding dimethylpropylamine) and to light (yielding 1,6-bis(dimethylamino)hexane). In the IR spectrum, the Cd–C vibrations occurred at 519 and 435 cm^{-1}, while for Me_2Cd these bands were found at 538 and 468 cm^{-1}.[123] In the EI mass spectrum, the molecular ion peak as well as characteristic fragment peaks were observed. The ^{13}C NMR spectrum of **164** is very similar to that of the zinc analogue **154**, with shielding of C_α and C_β and a characteristic deshielding of $C\gamma$ ($\Delta = \delta(R_2Cd) - \delta(RH) = -1.75$ ppm), which indicates clearly the formation of a spiranoide IC compound.

Bis[3-(dimethylamino)propyl]mercury (**165**) was synthesized analogously to the cadmium compound **164**.[115] It is a colorless distillable compound. In the

EI mass spectrum, the molecular ion peak and characteristic fragment peaks are present. In the IR spectrum, the same bands were observed as for unsubstituted dialkylmercury compounds: 600 and 527 cm^{-1} (cf. 602 and 519 cm^{-1} for n-Bu$_2$Hg). From the ^{13}C NMR spectrum in CDCl$_3$, it is not clear whether IC occurs. The only remarkable feature was a concentration-dependent $^{1}J_{^{13}\mathrm{C}-^{199}\mathrm{Hg}}$ coupling constant. As it is known that $^{1}J_{^{13}\mathrm{C}-^{199}\mathrm{Hg}}$ coupling constants for organomercury compounds increase with increasing donor capacity of the solvent, this concentration dependence may arise from *inter*molecular donation by the dimethylamino groups.

A considerable number of IC mercury compounds have been obtained from indirect or direct *ortho*-metalation reactions of azobenzenes. The ready and specific cleavage of the mercury–carbon bond makes these compounds useful intermediates in synthetic reactions involving arylazo groups. The first representatives were prepared by indirect *ortho*-mercuration. Ustynyuk and co-workers isolated [2-(phenylazo)phenyl]mercuric chloride (**166**) and [2-(phenylazo)phenyl]mercuric acetate (**167**) from the cleavage of cyclopentadienyl[2-(phenylazo)phenyl]nickel by HgCl$_2$ and Hg(OAc)$_2$, respectively (Scheme 85).[124]

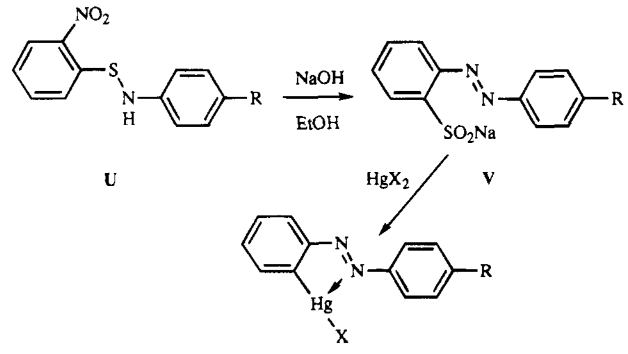
Scheme 85



X = Cl (**166**), OAc (**167**)

A different indirect route involved the base-promoted rearrangement of a 2-nitrobenzenesulfenanilide (**U**; Scheme 86) to the sodium azobenzene-2-sulfinate (**V**), and its subsequent treatment with HgX$_2$ to give the halomercuri derivatives **166** and **168**–**172**.[125]

Scheme 86

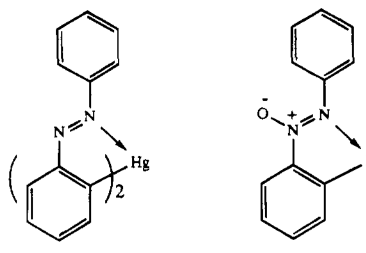


R = H; X = Cl (**166**), X = Br (**168**), X = I (**169**)
X = Cl; R = OMe (**170**), R = Me (**171**), R = Cl (**172**)

[2-(Phenylazo)phenyl]mercuric chloride (**166**) was symmetrized to bis[2-(phenylazo)phenyl]mercury (**173**; Scheme 87) by refluxing in an acetone solution of triphenylphosphine.

The first report of a direct mercuration concerned the reaction of mercuric acetate with azoxybenzene and subsequent treatment with sodium chloride to produce **174** (Scheme 87).[126]

Scheme 87

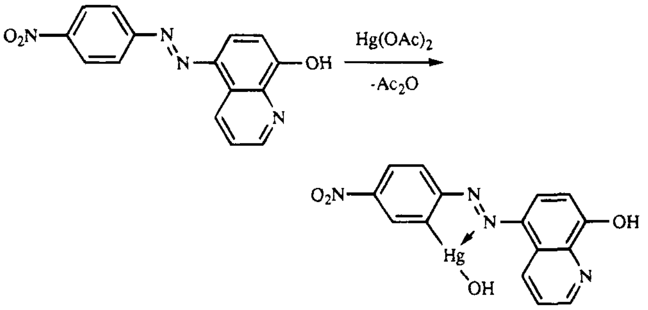


173 **174**

Twenty years later, the first successful direct *ortho*-mercuration of azobenzenes was reported.[127] Reaction of azobenzene and mercuric acetate in refluxing methanol, followed by treatment with an excess of lithium chloride, yielded [2-(phenylazo)phenyl]mercuric chloride (**166**) as the only monosubstituted product (40%; mp = 202–204 °C; Scheme 85). Subsequently, 10 *ortho*-substituted azobenzenes were mercurated and mercuration was found to occur predominantly at the *ortho* position.[128] The regiospecificity of these reactions suggests that the mercury is directed into the *ortho* position by coordination of the mercury to an azo nitrogen, followed by an electrophilic substitution reaction. NMR and UV data show mercury–nitrogen coordination in the mercurials, but not in the initial coordination complexes. A kinetic study of the *ortho*-mercuration of 2-methylazobenzene provided evidence for complex formation before and during the rate determining step of the electrophilic substitution.[129]

The mercuration of 1-(4-nitrophenyl)-2-(8-hydroxyquinolin-5-yl)diazene with mercuric acetate in boiling toluene occurred under elimination of acetic anhydride to form **175** (Scheme 88).[130]

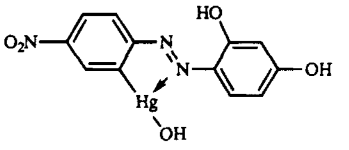
Scheme 88



175

IR, UV, NMR and microchemical analysis were in good agreement with the suggested structure (mp = 255–256 °C). Additionally, three other (8-hydroxyquinolinyl)diazene derivatives with IC mercury were reported. Analogously, 4-[(*p*-nitrophenyl)azo]resorcinol reacted with mercuric acetate to give 4-[[(*p*-nitro-*o*-(hydroxymercurio)phenyl]azo]resorcinol (**176**; mp = 260 °C; Scheme 89).[131] In the UV–vis spec-

Scheme 89



176

trum of **176**, the 550 nm band of the parent compound has disappeared because the nitrogen lone pair is blocked by donation to mercury. The mercuration of other substituted aryl-, trihydroxyphenyl-, and hydroxynaphthyl diazines was also reported.[131]

Ethyl[ω-(dimethylamino)-1-alkynyl]zinc compounds (Scheme 90) and bis[ω-(dimethylamino)-1-alkynyl]zinc compounds (Scheme 91) were prepared by metallation of the (dimethylamino)alkynes $HC{\equiv}C(CH_2)_nNMe_2$ (n = 1−4) with diethylzinc or diphenylzinc to give **177**−**184**, respectively.[132]

Scheme 90

$$Me_2N(CH_2)_nC{\equiv}CH + Et_2Zn \xrightarrow[50\ h]{C_6H_6,\ 60\ °C} EtZnC{\equiv}C(CH_2)_nNMe_2 + EtH$$

n = 1 (**177**), 2 (**178**), 3 (**179**), 4 (**180**)

Scheme 91

$$2Me_2NCH_2C{\equiv}CH + Et_2Zn \xrightarrow[50\ h]{C_6H_6,\ 60\ °C} \underset{\mathbf{181}}{Zn[C{\equiv}CCH_2NMe_2]_2} + 2EtH$$

$$2Me_2N(CH_2)_nC{\equiv}CH + Ph_2Zn \xrightarrow[50\ h]{C_6H_6,\ 60\ °C} Zn[C{\equiv}C(CH_2)_nNMe_2]_2 + 2C_6H_6$$

n = 2 (**182**), 3 (**183**), 4 (**184**)

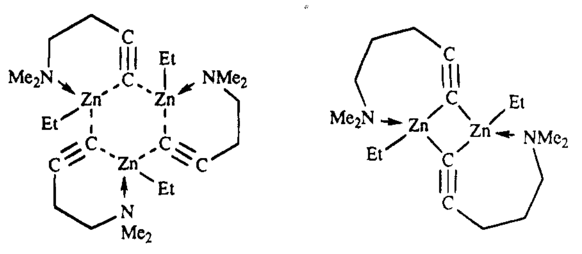
The ethyl groups in **178-180** are unreactive toward the parent alkynes so that it is impossible to prepare the dialkylzinc compounds from diethylzinc and 2 equiv of the (dimethylamino)alkyne. However, *N,N*-dimethylpropargylamine is acidic enough to react with both ethyl groups of diethylzinc to give $Zn[C{\equiv}CCH_2NMe_2]_2$ (**181**; Scheme 91). The remaining dialkynylzinc compounds (**182-184**) were synthesized by treatment of the appropriate alkynes in a 2:1 ratio with diphenylzinc, which is a stronger metallating agent (Scheme 91).[133]

The question arose whether zinc was engaged in coordinative bonding with carbon−carbon multiple bonds, in normal σ-type coordinating bonds with the dimethylamino groups, or in a combination of both. The decomposition temperatures of **177-180** are lower than those of **181-184**, which may indicate insufficient coordinative saturation in **177-180**. The degrees of association in benzene (ebulliometry) decrease with increasing value of n for all compounds. This phenomenon may be correlated to the increasing flexibility of the alkyl chains linking the zinc and nitrogen atoms; as a result, the interaction between zinc and nitrogen will become stronger, thus increasing the stability of smaller units (*vide infra*). In pyridine, all compounds are monomeric.

The IR spectra (in pyridine, in benzene, or in the solid state) show characteristic shifts of the carbon−carbon triple bond stretching vibrations. On the basis of these data, the presence of bridging alkynyl groups in the monoalkynylzinc compounds was assumed. Data for the dialkynylzinc compounds (ratio zinc/nitrogen = 1:2) suggested the absence of alkynyl bridges for **181** and the presence of bridging and nonbridging alkynyl groups for **182-184**. The results of NMR measurements were in full accord with those of the IR spectra. Again, in solution the presence of two types of (dimethylamino)alkynyl groups (ratio 1:1) in **182-184** was confirmed, one with bridging and one with nonbridging alkynyl groups. Furthermore, in the ^{13}C NMR spectra of **182-184** below −30 °C, two different types of dimethylamino groups (ratio 1:1) were discernible; in one of these, nitrogen−zinc coordination occurs, which immobilizes the dimethylamino groups and leads to nonequivalence of the methyl groups.

On the basis of the degrees of association in benzene and the spectroscopic data, plausible structures were assigned. It was suggested that in **177**, tetracoordination of zinc is attained by alkynyl bridging and *inter*molecular Zn−N coordination to give a polymeric structure. Structural proposals for the trimeric **178** and the dimeric **179** are given in Scheme 92. The different degrees of association may be related with the size of the chelate ring formed and with the rigidity of the carbon chain. The molecular weight of **180** could not be measured due to insufficient solubility, but in view of the spectroscopic data, a structure involving Zn−N coordination and alkynyl bridges was proposed by analogy.

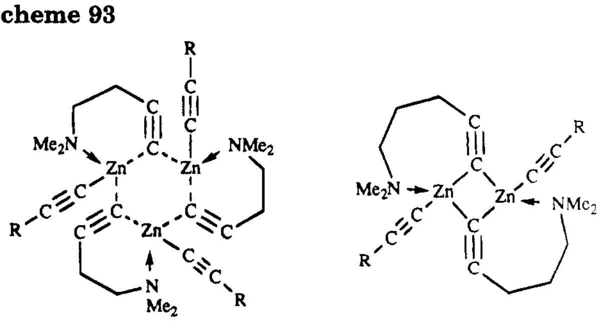
Scheme 92



178 **179**

In all dialkynylzinc compounds (in which the N/Zn ratio is 2), the tetracoordination could in principle be attained by zinc−nitrogen coordination only. In polymeric **181**, bridging alkynyl groups are absent and Zn−N coordination is suggested to be *inter*molecular. For trimeric **182** and dimeric **183**, structures analogous to those of the monoalkynylzinc derivatives were proposed in which two different NMe_2 groups can be distinguished (Scheme 93): one is chelating, while the other one essentially plays a role analogous to that of the ethyl groups in **178** or **179**. For **184** too, a structure can be envisaged in which both types of coordination occur.

Scheme 93



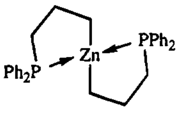
182 **183**

B. Group 12 Metal Complexes with Phosphorus Donor Atoms

From the reaction of the Grignard reagent $Ph_2P(CH_2)_3MgCl$ and 0.5 equiv of $ZnCl_2$ in diethyl ether,

$[Ph_2P(CH_2)_3]_2Zn$ (**185**) was obtained.[134] Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from toluene. The zinc atom is tetracoordinate, both phosphorus atoms being involved in IC (Scheme 94).

Scheme 94



185

The C−Zn−C angle is 147.1°, which is intermediate between that of a linear and a tetrahedral bond arrangement; the P−Zn−P angle is 105.7°. The coordinative Zn−P bonds (2.598 and 2.572 Å) are only 0.15 Å longer than the sum of the covalent radii of these elements.[119] In the corresponding OMe, SMe, and NMe_2 derivatives, the coordinative bond lengths were about 0.35 Å longer than the sum of the covalent radii of the elements involved (*vide supra*). This indicates that the Zn−P interaction is stronger than that between zinc and other heteroatoms, which is even more remarkable when one takes into account that the phosphorus carries electron-withdrawing phenyl groups, whereas the other heteroatoms are methyl substituted. The Zn−C bond lengths in **185** are normal (2.00 and 2.02 Å).

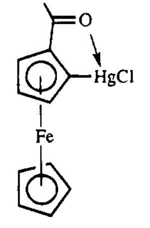
Ebulliometry showed **185** to be monomeric in benzene solution. The γ-^{13}C shows an upfield shift $\Delta\delta$ of 2.84 ppm in C_6D_6 and of 3.36 ppm in CD_2Cl_2 relative to the corresponding carbon in diphenylpropylphosphine, which indicates that **185** occurs as the internally coordinated complex in both solvents. The presence of IC in solution also follows from the nature and magnitude of the P−C coupling constants. The coupling pattern of the α-C signals is strongly indicative for an AXX′ spin system (A = ^{13}C; X, X′ = ^{31}P) in which both the AX (AX′) and XX′ couplings necessarily occur across zinc.

C. Group 12 Metal Complexes with Oxygen Donor Atoms

1. Four-Membered Rings

Acetoxymercuration of a variety of substituted ferrocenes (methoxycarbonyl-, acetyl-, and formylferrocene) and subsequent treatment of the resulting products with lithium chloride produced appreciable amounts of 2-chloromercurated acylferrocenes **186-188** (Scheme 95), as well as their 1′-substituted isomers.[135] The inductive effect of the carbonyl group would be expected to deactivate the ring toward further electrophilic substitution. The fact that a substantial amount of substitution at the 2-position is observed can be explained by coordination of the carbonyl group with the incoming electrophile which directs substitution into the neighboring position.

Scheme 95

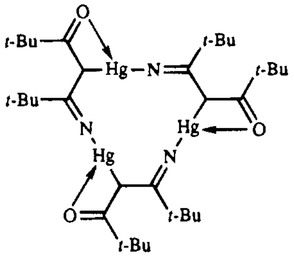


R = OMe (**186**), Me (**187**), H (**188**)

Preparative thin-layer chromatography was utilized to resolve the mixture of mercurated products. In each separation, the band possessing the highest R_f value contained the 2-(chloromercurio)-1-acylferrocenes **186-188**. The sequence of elution observed for the isomeric (chloromercurio)(acyl)ferrocenes can again be explained by the fact that coordination between the carbonyl and the 2-chloromercurio groups decreases the affinity of the 2-chloromercurio isomers for the chromatographic material (cf. **119-130**). IR spectra of **186** and **187** show that the carbonyl absorptions are shifted to lower energy by 30 and 10 cm^{-1}, respectively, when compared with the unmercurated parent compounds. The 1′-mercurated products exhibit carbonyl stretching frequencies very close to those of the parent compounds.

The reaction of mercury(II) perchlorate trihydrate with 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one in a 1:1 ratio in methanol yielded a colorless crystalline complex (mp = 225 °C under decomposition).[136] The cationic and anionic FAB mass spectra indicated the complex to be a trimer. An X-ray analysis revealed that the structure of **189** was that of a cyclic trimer (Scheme 96). The mercury atoms are σ-bonded to C-4 of the ligand with distances of 2.106, 2.109, and 2.096 Å; the second bond, formed with nitrogen atoms of another ligand, shows short Hg−N distances (2.087, 2.090, and 2.073 Å). The C−Hg−N moiety is almost linear (175.1, 175.5, and 171.8°). The intramolecularly coordinating oxygen atoms of the three acyl groups are located at one side with long distances to mercury (2.519, 2.532, and 2.549 Å). The small distortions are probably caused by the unsymmetrically located perchlorate anions and one molecule of THF (not shown).

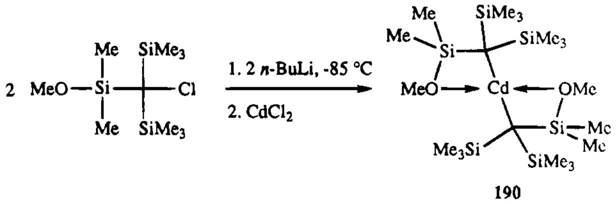
Scheme 96



189

In 1992 the crystal structure of $Cd[C(SiMe_3)_2SiMe_2OMe]_2$ (**190**) was reported (Scheme 97).[137]

Scheme 97



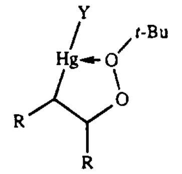
190

The lone pairs of the methoxy oxygens point toward the metal, rather than outward, as in the corresponding mercury compound. The Cd−O distance (3.09 Å) is only slightly less than the sum of the van der Waals radii (3.10 Å). Apparently, intramolecular O→Cd coordination is very weak.

2. Five- and Six-Membered Rings

Investigation of the stereochemistry of the peroxymercuration of acyclic alkenes suggested that a determining factor is the presence of Hg→O IC.[138] Compounds RCH(OO-*t*-Bu)CH(HgY)R (**191-194**) were prepared and on the basis of ^{1}H NMR spectroscopy, *threo*-1-(bromomercurio)-2-(*tert*-butylperoxy)-1,2-diphenylethane (**191**) was regarded as being least likely to be involved in IC. However, this compound was the only one available for X-ray crystal structure determination which revealed the existence of an IC Hg−O bond between mercury and the *tert*-butylperoxy group (Scheme 98). For this reason, IC in **192-194** was assumed to be present as well. The Hg−O distance in **191** is 2.68 Å, which is considerably longer than the covalent distance (2.10 Å), but significantly less than the sum of the van der Waals radii (2.90 Å). The Hg−C bond is 2.13 Å and the C−Hg−Br angle is 177°.

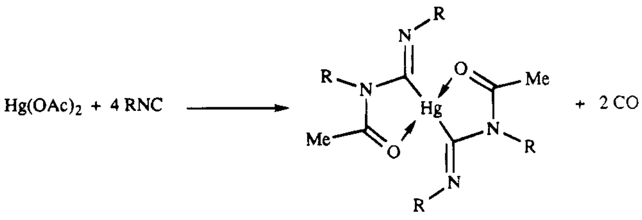
Scheme 98



R = Ph; Y = Br (191), CF_3CO_2 (192)
R = Me; Y = Br (193), CF_3CO_2 (194)

Mercuric acetate reacted with aromatic isocyanides to form spiranoid IC organomercury compounds **195** and **196** (Scheme 99).[139] *tert*-Butyl and cyclohexyl isocyanide reacted in an analogous manner with mercuric acetate, but the products **197** and **198** were not stable and only the corresponding N−R acetamides were isolated.

Scheme 99

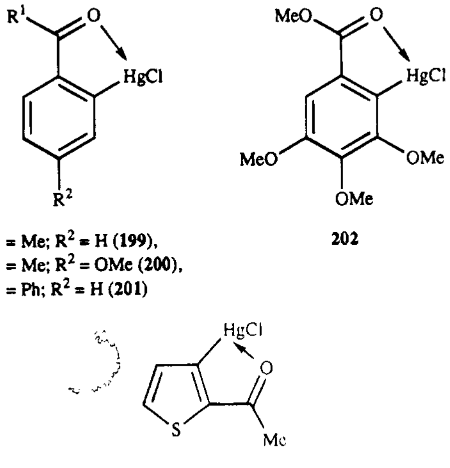


R = 2,6-$Me_2C_6H_3$ (195), Ph (196), t-Bu (197), c-Hex (198)

Compounds **195** and **196** are crystalline solids (mp 224−5 and 195−8 °C, respectively). The crystal structure of **195** was determined by X-ray diffraction. The molecule has C_2 symmetry around the central mercury atom. The Hg−C bond distances are 2.109 Å, which is common for covalent Hg−C bonds. The Hg−O bond distances are 2.629 Å, which suggests a weak interaction (the sum of the van der Waals radii is 3.1 Å, but a typical covalent Hg−O bond is 2.1 Å). The geometry around the mercury is that of an extremely distorted tetrahedron; the C−Hg−C moiety is slightly bent (170.75°) and the O−Hg−O angle is 105.31°.

Two common routes to arylmercury derivatives are direct mercuration or reaction of mercury(II) salts with aryllithium or aryl−Grignard reagents. Both methods are usually unsuited for the introduction of mercury *ortho* to a ketone or ester function. The transmetalation of readily available *ortho*-manganated precursors proved to be a new method giving high yields;[140] with $HgCl_2$, five white crystalline air stable compounds (**199-203**) were obtained (Scheme 100).

Scheme 100



R^1 = Me; R^2 = H (199),
R^1 = Me; R^2 = OMe (200),
R^1 = Ph; R^2 = H (201)

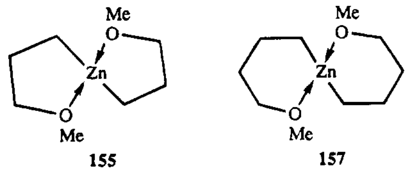
202

203

The products were characterized by microanalysis and NMR and mass spectrometry. The X-ray crystal structure of **199** revealed that the molecule is essentially planar, although the acetyl group is slightly twisted so that the oxygen atom is 0.17 Å above the mean plane and the CH_3 carbon is 0.16 Å below. The oxygen atom is directing toward the mercury atom with a Hg−O distance of 2.71 Å, which is even longer than in **195**. The interaction must be weak since the Cl−Hg−C angle deviates only 4° from linearity and the C=O bond length is equal to that in free acetophenone.[141] The Hg−C and Hg−Cl distances (2.07 and 2.323 Å, respectively) are in the expected range.

In the reaction of 4-methoxybutyl iodide with zinc, the desired bis(4-methoxybutyl)zinc (**157**) was not obtained; instead the starting material was cleaved to form tetrahydrofuran, Me_2Zn, and ZnI_2.[142] By reaction of 4-(methoxybutyl)magnesium chloride with $ZnCl_2$, **157** was smoothly obtained[143] (Scheme 101). Bis(3-methoxypropyl)zinc (**155**) was prepared analogously.[113]

Scheme 101



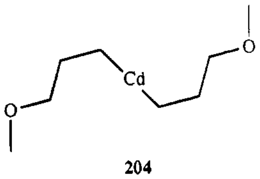
155 157

Compounds **155** and **157** are colorless, slightly viscous, distillable liquids (for **155**: mp = −36 °C).[143] Both compounds are monomeric in benzene (cryoscopy and ebulliometry). In the EI mass spectrum of **157**, the most significant peaks are M^+, $[M-(CH_2-CH_2)]^+$, and $[M-(CH_2-CH_2-CH_2-CH_2)]^+$, of which the last two are indicative for an interaction between zinc and oxygen. Addition of 2.5 mL of diethyl ether to 1 g of **155** or **157**, followed by bubbling through of dry nitrogen for 60 min at room temperature, resulted in quantitative removal of the ether (Ätherabblasversuch), in contrast to unsubstituted dialkylzinc compounds which can be separated from Et_2O or THF only by repeated fractional distillation.[144] From the ^1H NMR spectrum, it was not clear whether or not IC occurs in this compound. The position of the α-CH_2 group ($\delta = 0.15$ ppm) differs markedly from that of organozinc compounds of the type $Zn(CH_2R)_2$ (~1.5 ppm). However, the chemical shift of the CH_3O protons is equal to those of methyl *n*-butyl ether and of methyl 4-chlorobutyl ether. From the IR spectrum, it was concluded, that the "open" form was predominant, but that a weak interaction between zinc and oxygen occurred.[143] In contrast, from the γ-effect in the ^{13}C NMR spectra, it was concluded that IC in **155** and **157** did occur.[113]

Seven years later, in 1984, IC was proven to be present in **155** and in **157** by gas-phase electron diffraction studies.[87] The Zn–O bond distances are 2.37(3) (**155**) and 2.38(5) Å (**157**). The O–Zn interaction is not sufficiently strong to reduce the C–Zn–C angle to a tetrahedral value; it is, in fact, only slightly distorted from linear [175(20)° and 158(13)°, respectively]. While the five-membered chelate rings in **155** are fairly flat, the six-membered chelate rings in **157** are strongly buckled and the valence angles Zn–C–C, C–C–C, and C–C–O are larger. Because of the large number of structural parameters that had to be refined, the error limits are wide.

The preparation of the cadmium compound $[CH_3O(CH_2)_3]_2Cd$ **204** (the cadmium analogue of **155**) was reported only recently.[145] A thorough vibrational and multinuclear magnetic resonance study suggests strongly that there is no internal coordination of the oxygen atoms to the cadmium atom (Scheme 102).

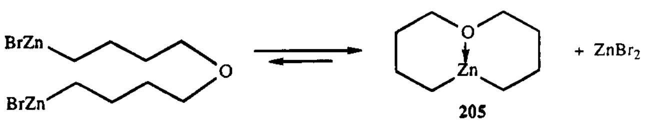
Scheme 102



204

The compound 1-oxa-6-zincacyclodecane (**205**) has a monomeric structure as a result of IC.[53] It was prepared from the reaction of bis(4-bromo-*n*-butyl) ether with Rieke zinc.[146] The equilibrium between the resulting bifunctional organozinc bromide and the cyclic compound **205** (and $ZnBr_2$) is shifted completely to the side of **205** because of the favorable IC (Scheme 103).

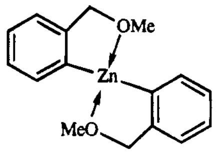
Scheme 103



205

Bis[2-(methoxymethyl)phenyl]zinc (**206**, Scheme 104), the zinc analogue of the corresponding magnesium compound **70** (Scheme 43) was prepared from the 2:1 reaction of [2-(methoxymethyl)phenyl]lithium and $ZnCl_2$.[110] Although the presence of IC was not investigated, its occurrence is likely.

Scheme 104

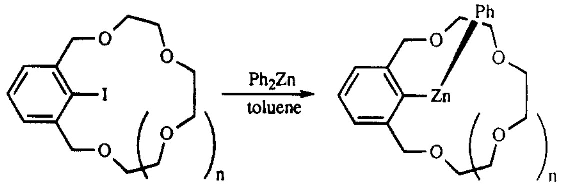


206

3. Seven-Membered and Larger Rings

The surprising metalations and halogen–metal exchange reactions between 1,3-xylylene crown ethers and diphenylmagnesium or phenylmagnesium bromide were discussed in section III.B.3. The reactions between diphenylzinc and the hydrogen- and bromine-substituted 1,3-xylylene crown ethers (see Table 3) did not proceed beyond the stage of side-on complex formation. Obviously, the activating power of the crown ether moieties was not sufficient for halogen–metal exchange reactions to take place. Crystal structures of the stable side-on complexes formed from **K**, **N**, and **O** with diphenylzinc were determined.[71] Because iodine is usually more reactive than bromine in exchange reactions, (2-iodo-1,3-xylylene)-15-crown-4 (**Q**) and -18-crown-5 (**R**) were heated with diphenylzinc in a 1:1 ratio at 60 °C for several weeks; this resulted in iodine–zinc exchange, a reaction which eventually went to completion. The products [2-(phenylzincio)-1,3-xylylene]-15-crown-4 (**207**) and -18-crown-5 (**208**) were identified by ^1H NMR spectroscopy (Scheme 105).[147]

Scheme 105



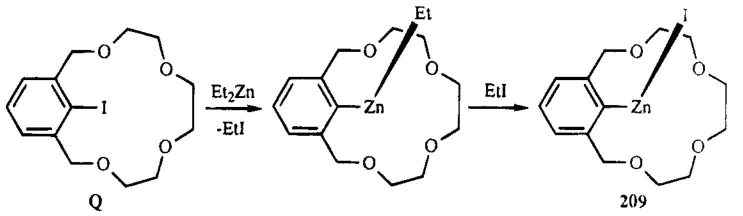
n = 1 (**Q**), 2 (**R**)

n = 1 (**207**), 2 (**208**)

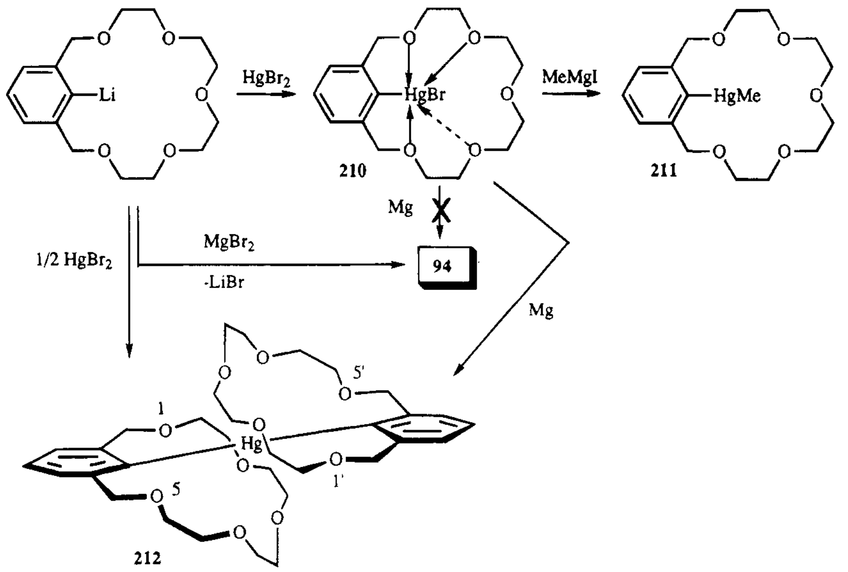
When diethylzinc was used as the solvent and as the organometallic reagent in the reaction with **Q**, NMR spectroscopy showed that a reaction had taken place. Surprisingly, an X-ray crystal structure determination revealed the resulting crystalline product to be [2-(iodozincio)-1,3-xylylene]-15-crown-4 (**209**),[12] instead of the expected [2-(ethylzincio)-1,3-xylylene]-15-crown-4, i.e. the ethyl group on zinc had been replaced by iodine; this was ascribed to a Wurtz-type reaction which—apparently due to activation by the crown ether system—occurs with an ease which is unusual for an organozinc reagent (Scheme 106).

The molecular structure of **209** bears some resemblance to that of [2-(bromomagnesio)-1,3-xylylene]-15-crown-4 (**92** cf. section III.B.3, Table 3).[10] The structure appears to be that of a rather normal tetracoordinated organozinc compound with zinc in

Scheme 106



Scheme 107



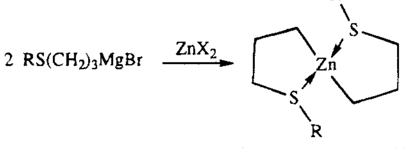
the center of a distorted tetrahedron surrounded by C(1), I, O(2), and O(3). The bond lengths and angles are close to those of *inter*molecularly coordinated organozinc reagents;[71,148] the Zn−C bond (1.982 Å) is slightly longer than normal, while the bonds to O(2) and O(3) are slightly shorter (2.171 and 2.242 Å, respectively). The Zn−I bond distance is 2.563 Å. The distances and orientation of O(1) and O(4) (2.596 and 2.673 Å, respectively) suggest a weak coordination,[149] which makes the zinc in fact hexacoordinated in a strongly distorted pentagonal pyramid with C(2) and the four oxygens in the distorted basal plane and iodine at the apex.

The 1:1 reaction of (2-lithio-1,3-xylylene)-18-crown-5 (which was also used to prepare the pure magnesium compound **94**) with $HgBr_2$ yielded the corresponding organomercury compound [2-(bromomercurio)-1,3-xylylene]-18-crown-5 (**210**), which crystallizes without solvent (Scheme 107).[70] Its crystal structure reveals that intramolecular Hg−O coordination occurs with two of the five oxygens (Hg−O(1) 2.754(6) Å and Hg−O(5) 2.855(6) Å), and only weak interaction with a third crown ether oxygen (Hg−O(4) 3.060(6) Å). Probably because of these mercury-oxygen interactions, the C1−Hg−Br bond angle, 175.0(2)°, deviates slightly from linearity. The C1−Hg−O angles in the two five-membered rings, resulting from IC, are 72.5(3)° and 71.9(3)°, respectively. Reaction of **210** with methylmagnesium iodide gave **211**, a stable compound that disproportionated to dimethylmercury and the diarylmercury compound bis[(1,3-xylylene-18-crown-5)-2-yl]mercury (**212**) only very slowly (<5% after 1 month in the solid state). Attempted synthesis of the Grignard reagent **94** yielded, under rather drastic conditions (10 days, 50 °C), compound **212**, which was also formed in the 2:1 reaction of (2-lithio-1,3-xylylene)-18-crown-5 and $HgBr_2$. It is noteworthy that **212** does not undergo the expected consecutive reaction with magnesium to give the magnesium analogue of **212**, but the crystal structure of **212** shows that the mercury is completely encapsulated by both crown ether rings. The structure is centrosymmetric around the mercury, which means that the oxygens O(1), O(5), O(1′), and O(5′) lie in one plane on the corners of a parallelogram with mercury in its center; for these oxygens weak coordination is apparent: Hg−O(1) [= Hg−O(1′)] 3.064(3) Å and Hg−O(5) [= Hg−O(5′)] 2.984(3) Å. These bond lengths are slightly larger than those found in the HgBr compound **210**. The Hg−C bond is slightly elongated [2.070(4) Å] and the C−Hg−C angle is 180°.

D. Group 12 Metal Complexes with Sulfur Donor Atoms

Like many of the IC compounds of zinc, bis(3-(ethylthio)propyl)zinc (**213**) was synthesized from the corresponding Grignard reagent (Scheme 108).[83,143]

Scheme 108



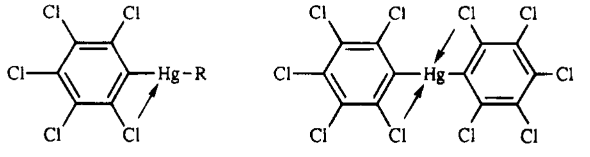
R = Me (**156**); Et (**213**)

Compound **213** is a colorless, viscous, air and moisture sensitive compound. The decomposition temperature lies above 200 °C, which is about 50 °C higher than that of dialkylzinc compounds with comparable chain lengths. In the EI mass spectrum, the most important peaks are M^+ and $[M-(CH_2-CH_2-CH_2)]^+$; the latter is taken as an indication for an intramolecular coordinative interaction between zinc and sulfur. As the NMR and IR spectra were not indicative for the presence of IC in **156** and **213**, Thiele and co-workers[143] concluded that in solution the "open-chain" structures were predominant and that IC was essentially absent. However, at the same time, van der Kerk and co-workers[113] published the results of their structural investigations on **154**–**157** (Schemes 82, 101, and 108), and on the basis of chemical properties, degrees of association, dipole moments, and ^{13}C NMR spectroscopy, they concluded that *exclusive* IC between Zn and the heteroatoms occurs in solution. Ten years later, the chelate bonding of the ligands (in the gas-phase) was confirmed for **156** (as well as for **154**) by gas phase electron diffraction.[83] The Zn–S bond distance in **156** is 2.73 Å, which is about 0.3–0.4 Å longer than the sum of the tetrahedral covalent radii; the Zn–C bond distance is normal at 1.991 Å. The C–Zn–C angle is 163° and the S–Zn–S angle is very large with 173°. The coordination geometry around zinc is consequently nearly square planar (see also the discussion in section IV.A).

E. Group 12 Metal Complexes with Halogen Donor Atoms

In 1965, C_6Cl_5HgCl (**214**), $(C_6Cl_5)_2Hg$ (**215**), C_6Cl_5HgPh (**216**), and C_6Cl_5HgMe (**217**) were reported "in the hope that they would stimulate further work on the investigation of the possible intramolecular Hg–Cl coordination".[150] Only 2 years later, Bregadze concluded from ^{35}Cl nuclear quadrupole resonance (NQR) spectra of **214-217** that an intramolecular Cl–Hg coordinative interaction between mercury and *ortho* chlorine atoms is indeed present; in **217**, a Cl–Hg–Cl "bent bond" was postulated (Scheme 109).[151]

Scheme 109

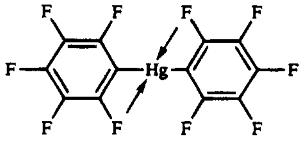


R = Cl (214), Ph (216), Me (217)

215

The crystal structure of bis(pentafluorophenyl)mercury (**218**) was determined[152] and the C–Hg–C angle appeared to be nearly linear (176.2°), which was in contradiction with the calculations of Sipos and co-workers[153] who proposed (in 1955!) that the angle C–Hg–C should be 130–150°. The angle between the planes of the two phenyl rings is 59.4°, which increases the distance between the *ortho*-fluorine atoms of the two rings and thus reduces the electrostatic repulsions. In the molecule, there are four Hg–F interactions with distances of 3.14, 3.22, 3.25, and 3.32 Å (Scheme 110).

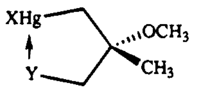
Scheme 110



218

Intramolecular mercury–halogen coordination in several (3-halopropyl)mercury compounds (**219-226**) (Scheme 111) was investigated by ^1H NMR spectroscopy.[154] It was concluded that γ-chlorine and γ-bromine atoms are coordinated to mercury, although rather weakly. The mercury–chlorine bond is clearly weaker than that with bromine, yet it is still well above the limit of detectability. The temperature dependence of chemical shifts and coupling constants established the existence of a conformational energy difference and allowed a rough estimate of its magnitude as ΔH(Hg–Br) ≈ 1 kcal/mol. A "conformational titration" was described, in which the magnetic nonequivalence of the methylene group is monitored as a function of concentration of an added base which can displace the intramolecular donor.

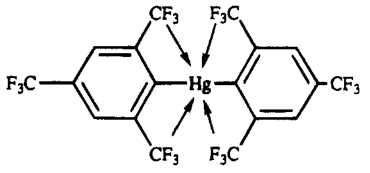
Scheme 111



X = Cl; Y = Cl (219), Br (220), NMe₂ (221), H (222), Me (223), *t*-Bu (224)
X = Br; Y = Br (225) and X = I; Y = OH (226)

Lithiation of 1,3,5-tris(trifluoromethyl)benzene, followed by reaction with mercury(II) chloride yielded bis[2,4,6-tris(trifluoromethyl)phenyl]mercury (**227**) (Scheme 112).[155] The compound was a white solid (mp = 78–80 °C). The presence of IC was suggested because the mercury compound was thermally very stable and because the X-ray crystal structures of the analogous tin and lead compounds revealed IC.

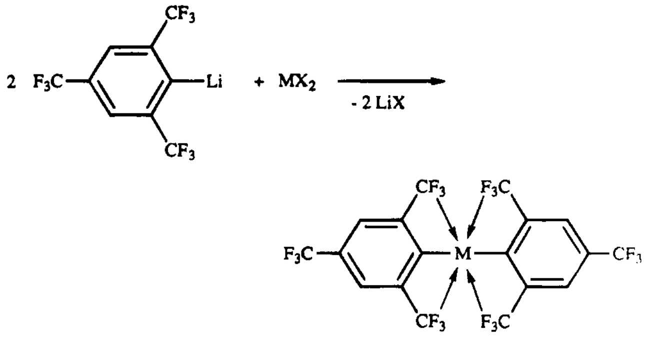
Scheme 112



227

Five years later, in 1992, the molecular structures of $[2,4,6-(CF_3)_3C_6H_2]_2Hg$ (**227**), $[2,4,6-(CF_3)_3C_6H_2]_2Zn$ (**228**), and $[2,4,6-(CF_3)_3C_6H_2]_2Cd(MeCN)$ (**229**) were determined by X-ray crystallography (Scheme 113).[156]

Scheme 113



M = Hg (227)
Zn (228)
Cd (229)

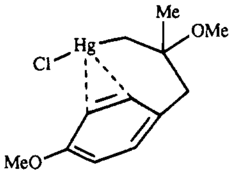
Compounds **228** and **229** are the first examples of structurally characterized di- and tricoordinate monomeric diarylzinc and -cadmium compounds, respectively. Characteristic structural features of all three derivatives are weak M−F interactions. For **228**, the short Zn−F interactions are 2.544(6), 2.532(6), 2.609(6), and 2.561 Å; for **229** short Cd−F distances are 2.892(6), 2.797(6), and 2.931(8) Å and for **227** the short Hg−F distances are 3.23(3), 3.12(3), 3.28(3), and 3.12(3) Å.

F. Group 12 Metal Complexes with π-Donors

Donor properties are exhibited not only by heteroatoms, but also by π-systems. The interactions of π-electron systems with transition metals involving vacant low-energy d orbitals of the metal are commonly known. With nontransition metals, this interaction is considerably less typical as in this case, outer orbitals of the metal atoms with a higher energy are involved. Stable mercury π-complexes do not exist, but the existence of secondary bonds between Hg and π-systems has been established beyond doubt.[93]

The existence of weak IC involving mercury by π-donation from one of the C−C units of an aryl benzene ring was first recognized in 1968 by a preliminary X-ray structure analysis and an NMR study of [3-(4-methoxyphenyl)-2-methyl-2-methoxypropyl]mercury chloride (**230**) (Scheme 114).[157] The X-ray crystal structure revealed that the mercury atom is located 3.05 Å above one of the phenyl C−C π-bonds. The C−Hg−Cl bonds are only slightly distorted from linearity. Interpretation of the ^{1}H NMR spectra furnished evidence for the occurrence of IC in solution. Methylene group magnetic nonequivalence, long-range mercury−proton coupling data and perturbation of the aromatic proton pattern all supported the proposed chelate effect.

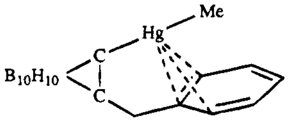
Scheme 114



230

Contrary to **230**, where the π-interaction of the mercury atom is realized with one C−C unit of the aromatic ring, the IC bond in 1-(methylmercurio)-2-benzyl-*o*-carborane (**231**) may be considered as a π-allyl type of coordination (Scheme 115).[158] The average Hg−C distances in two crystallographically independent molecules are 3.14, 3.28, and 3.38 Å.

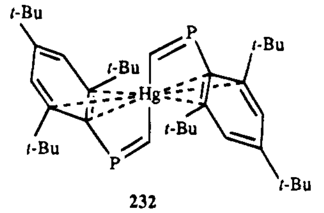
Scheme 115



231

A similar type of interaction occurs in the (phosphaalkenyl)mercury compound (*Z,Z*)-(Mes*P═CH)$_2$Hg (**232**; Mes* = 2,4,6-tri-*tert*-butylphenyl) which was prepared from *Z*-Mes*P═CHLi and HgCl$_2$.[159] The X-ray crystal structure of **232** exhibits two crystallographically independent molecules A and B, which are nearly identical. The structure shows a double *Z* configuration at the P═C bond with the mercury atom sandwiched between the two aromatic rings; the aryl rings are slightly bent toward the mercury atom, indicating a stabilizing interaction between them (Scheme 116).

Scheme 116

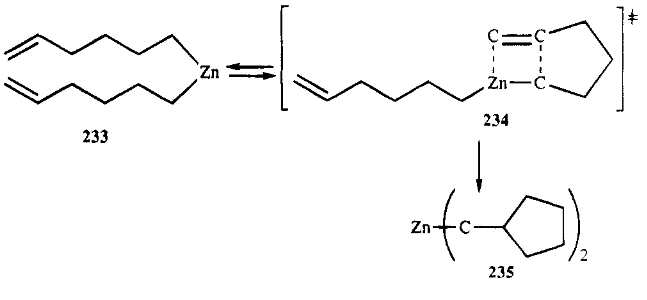


232

The mercury atom in **232** resides on an inversion center and has a normal linear coordination geometry (C−Hg−C = 180°). The Hg−C single bond lengths are rather short (2.042 and 2.079 Å in molecules A and B, respectively). The mean planes of the two (bent!) benzene rings are parallel and the distances between the mercury atoms and the centers of the aryl rings are 3.571 and 3.470 Å. The mercury atom is located asymmetrially above the Mes* ring, with the shortest distance to C-*ipso* (3.252 Å) and its neighboring carbons (3.549 and 3.710 Å) for molecule A and C-*ipso* (3.170 Å) and both neighboring carbons (3.604 and 3.442 Å) for molecule B.

In the synthesis of di-5-hexenylzinc (**233**) from di-5-hexenylmercury and zinc by metal exchange, bis(cyclopentylmethyl)zinc (**235**) was obtained as a byproduct. When the reaction mixture was kept at 120 °C for 3.5 days, **235** was formed in approximately 90% yield.[160] The cyclization reaction was suggested to proceed through a four-center transition state (**234**; Scheme 117).

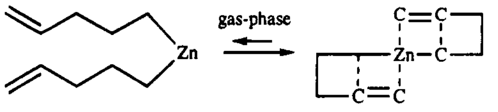
Scheme 117



Di-4-pentenylzinc (**236**) was found to be stable under the same conditions, probably because an analogous cyclization reaction would yield a strained cyclobutane ring. The ^{1}H NMR spectrum of **236** shows an anomalous downfield shift of one of the vinyl protons relative to that of the parent hydrocarbon. This shift has been interpreted as evidence for IC between Zn and the double bonds.[160]

Haaland and co-workers have investigated **236** by gas-phase electron diffraction.[161] Both chains were

Scheme 118



236

found to be coiled back to bring the C=C bonds close to the zinc center (Zn−C ≈ 2.20 Å; Scheme 118).

V. Group 13 Metals

As was previously mentioned at the beginning of section IV, the donor−acceptor bonds of organoaluminum and -gallium compounds with electron donors like ethers or tertiary amines are markedly stronger than in complexes of diorganozinc compounds.[83,84] A typical Al−N dative bond distance is 2.06(1) Å as in $N(CH_2CH_2)_3Al$[162] and some typical Al−O dative bond distances are: 2.03(4) Å in $AlMe_3[O(CH_2)_3]$[163] and 2.02(2) Å in $AlMe_3[dioxane]AlMe_3$.[164] The bond distance in $AlMe_3(SMe_2)$ is 2.55(2) Å.[163] Terminal Al−C distances are typically just below 2.0 Å: the Al−C distance in $[Al(2,4,6\text{-}Me_3C_6H_2)_3]$ is 1.995(8) Å[165] and in $[Al(CH_2C_6H_5)_3]$ 1.982(6)−1.997(6) Å.[166]

The sum of the covalent radii of gallium and nitrogen is 1.95 Å.[167] The distances in pure donor-acceptor complexes like $Me_3Ga{\cdot}NMe_3$ and $Me_3Ga{\cdot}$[urotropine] are 2.20(3)[168] and 2.14 Å,[169] respectively.

It is known that InL_3 (L = monodentate organic or inorganic ligand) forms stable adducts with Lewis bases like Et_2O, NR_3, HNR_2, and H_2NR.[170] The distances of inter- and intramolecular dative In−N bonds are longer than the sum of their covalent radii (2.19 Å) but significantly shorter than the sum of their van der Waals radii (3.45 Å). Some representative values are 2.33(1) and 2.44(1) Å in $EtInI_2{\cdot}$[TMEDA];[171] 2.30(1) and 2.49(1) Å in $EtInBr_2{\cdot}$[TMEDA][171] and 2.21(1) Å in $[MeInCl_2]{\cdot}[t\text{-}BuNH_2]$.[172] Some representative values of covalent In−N bond distances are 2.138(5) Å in $CH_3In[CH_3NC(CH)_4N]_2$;[173] 2.183(5) Å in $[(CH_3)_2In]_2C_2(NCH_3)_4$;[174] 2.187(13) Å in $CH_3In\{[CH_3N(CH_2)_2NCH_3]In(CH_3)_2\}_2$;[173] 2.20(1) Å in methyl(tetraphenylporphinato)indium(III).[175]

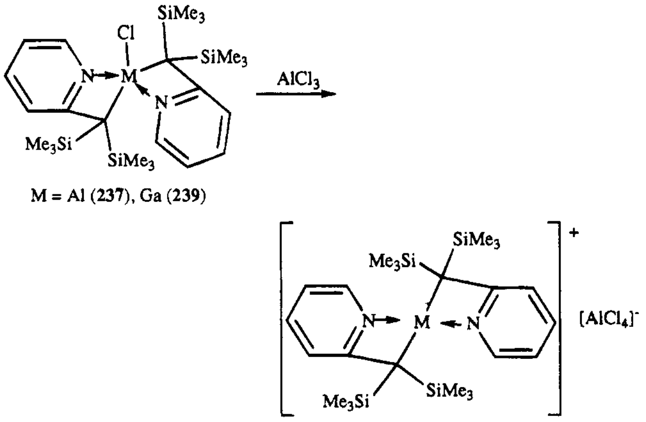
A. Group 13 Metal Complexes with Nitrogen Donor Atoms

1. Four-Membered Rings

A solution of $2\text{-}[(Me_3Si)_2CLi]C_5H_4N$ (LiL) reacts with $AlCl_3$ to give L_2AlCl (**237**) in moderate yield.[176] Four-membered chelate rings are formed (Scheme 119); this is analogous to the complex with Mg (cf. **9**, Scheme 12), Zn (cf. **112**), and Cd (cf. **113**), but different from that with Hg (cf. **114**, Scheme 65).

In the complex, the aluminum center is probably pentacoordinated. This coordination was unknown for nonbridging alkylaluminum compounds. The nonequivalence of the $SiMe_3$ groups in the ^1H NMR spectrum is an indication that the same structure is maintained in solution. When 1 equiv of $AlCl_3$ was added to **237** in benzene, $[L_2Al^+][AlCl_4^-]$ (**238**) was formed (Scheme 119). In the crystal structure of **238**, two kinds of Me_3Si groups can be discerned, but according to the ^1H NMR spectrum, they are equivalent in solution as a result of fast exchange on the NMR time scale. In the crystal structure of **238**, the cation has a distorted tetrahedral geometry due to steric hindrance between the ligands. The Al−C distance (1.99 Å) is typical for a terminal Al−C bond. The Al−N distances (1.92 Å) are significantly shorter than those found in other adducts between nitrogen Lewis bases and organoaluminum complexes [e.g. 2.02 Å in $Me_2AlI(NMe_3)$[177]]. It was suggested that this difference is probably a result both of the cationic nature of the aluminum center and of the reference bond lengths, as the latter were taken from amine adducts where the N-donor atoms are sp^3 hybridized, whereas in **238**, the nitrogen has sp^2 hybridization. The mean N−Al−C angle in the bidentate ligand is 73°, while the C−Al−C and N−Al−N angles are 152.2 and 114.6°, respectively.

Scheme 119

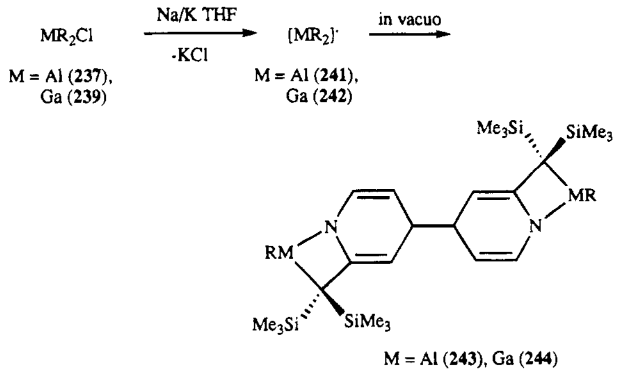


M = Al (**237**), Ga (**239**)

M = Al (**238**), Ga (**240**)

A few years later, the structure of the analogous L_2GaCl compound **239** (Scheme 119) was reported by the same group.[178] There are three independent molecules of **239** present in the unit cell; these molecules lie on crystallographic 2-fold axes, the metal centers have highly distorted trigonal-bipyramidal geometries with the N centers in the apical positions and a mean N−Ga−N angle of 162.6°. For molecules 1, 2, and 3, the Ga−C bond distances are 2.080(4), 2.059(4), and 2.056(4) Å, the Ga−N distances 2.268(4), 2.186(3), and 2.214(4) Å, and the Ga−Cl distances 2.211(2), 2.212(2), and 2.231(2) Å, respectively. The mean N−Ga−C angle in the bidentate ligand is 66.7°, while the mean C−Ga−C and N−Ga−N angles are 139.6 and 162.6°, respectively. Conditions for the synthesis of **239** from LiR must be precisely controlled to avoid the formation of the ionic compound $[GaR_2]^+[GaCl_4]^-$ (**240**), which is isostructural with **238**. Nonequivalence of the trimethylsilyl groups of **237** is consistent with the structure of **239**. However, the gallium compound showed dynamic equivalence of these groups, possibly because weaker M−N interactions allow rotation about the M−C bonds. Reduction of MR_2Cl in THF yields the paramagnetic dialkyl species $[MR_2]^{\bullet}$ (**241**, **242**), which are stable in solution. Upon removal of the solvent the diamagnetic compounds **243** and **244** are formed in which the pyridyl groups are reductively coupled (Scheme 120).[178]

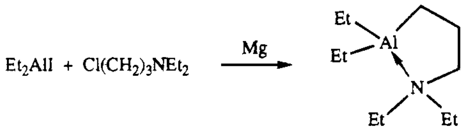
Scheme 120



2. Five- and Six-Membered Rings

In 1955, Bähr and Müller published the first paper dealing with the concept of IC. One of the two IC compounds reported was [3-(diethylamino)propyl]-diethylaluminum [**245**; Scheme 121; see introduction (section I)].[1] Compound **245** was synthesized from the "precomplex", which was formed from diethylaluminum iodide and 3-(chloropropyl)diethylamine, by reaction with magnesium. At room temperature, **245** is a colorless liquid (mp −2 °C) which could be distilled at 97 °C at 3 mbar and is air and moisture sensitive. The compound was monomeric in benzene according to cryoscopy, and added diethyl ether and methyl iodide were removed quantitatively without difficulty ("Ätherabblasversuche"), whereas methyl iodide reacts instantaneously in a strongly exothermic reaction with the starting material (3-chloropropyl)diethylamine to furnish the white crystalline quaternary ammonium salt. Therefore it was concluded that **245** is completely intramolecularly coordinated.

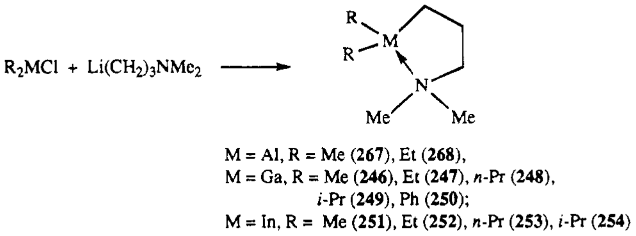
Scheme 121



245

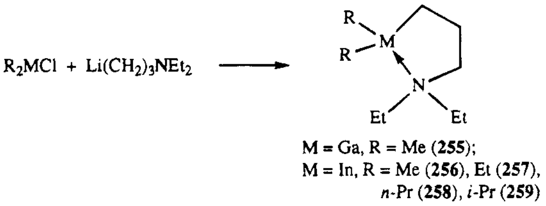
Twenty-five years after the publication of compound **245**, similar gallium and indium compounds were prepared by Schumann and co-workers for application in optoelectronic devices grown by the technique of MOVPE (metal organic vapor phase epitaxy).[179] The reaction of Me_2GaCl, Et_2GaCl, $(n\text{-}Pr)_2GaCl$, $(i\text{-}Pr)_2GaCl$, Ph_2GaCl, and the corresponding diorganoindium chlorides with [(dimethylamino)propyl]lithium in pentane resulted in the formation of the intramolecularly coordinatively saturated triorganogallium and triorganoindium compounds $R_2M(CH_2)_3NMe_2$ [M = Ga, R = Me (**246**), Et (**247**), *n*-Pr (**248**), *i*-Pr (**249**), Ph (**250**); M = In, R = Me (**251**), Et (**252**), *n*-Pr (**253**), *i*-Pr (**254**); Scheme 122], in high yields as liquids or low-melting solids.

Scheme 122



The use of [(diethylamino)propyl]lithium resulted in the formation of the corresponding diorgano-[(diethylamino)propyl] derivatives $R_2M(CH_2)_3NEt_2$ [M = Ga, R = Me (**255**); M = In, R = Me (**256**), Et (**257**), *n*-Pr (**258**), *i*-Pr (**259**); Scheme 123].

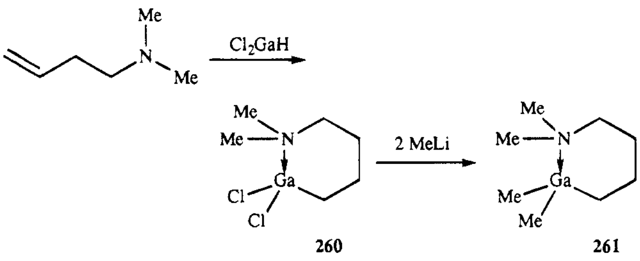
Scheme 123



These compounds were fairly stable in air and showed only slow decomposition in contact with water or alcohol. They were readily soluble in organic solvents like diethyl ether, benzene, or hexane. Cryoscopic molecular weight determinations in benzene for **246** and **251** revealed their monomeric constitution in solution, indicating that the compounds are stabilized by IC via five-membered ring formation. Six-membered rings formed by this type of IC were expected to be even more stable against oxygen and moisture because of reduced ring strain.

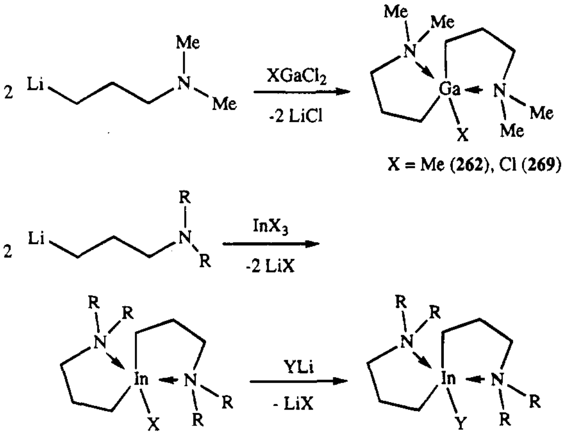
An example for this kind of compounds is [4-(dimethylamino)butyl]dimethylgallium (**261**); it was synthesized from its dichlorogallium analogue **260** as shown in Scheme 124. Compound **261** has similar properties as **246**, yet it is a liquid at room temperature.[179]

Scheme 124



In triorganogallium or -indium derivatives containing two 3-(dialkylamino)propyl ligands, two five-membered chelate rings may be formed involving pentacoordinated gallium and indium. $MeGaCl_2$ reacted with 2 equiv of $Me_2N(CH_2)_3Li$ to yield bis[3-(dimethylamino)propyl]methylgallium (**262**, Scheme 125). Bis[3-(dimethylamino)propyl]methylindium (**265**) and bis[3-(diethylamino)propyl]methylindium (**266**) were prepared by the reaction of $InCl_3$ with 2 equiv of the corresponding (aminopropyl)lithium compound to give bis[3-(dimethylamino)propyl]indium chloride **263** and its diethylamino analogue **264**, which by reaction with methyllithium were converted to the corresponding bis[3-(dialkylamino)-propyl]methylindium derivatives **265** and **266** (Scheme 125).[179]

Scheme 125



X = Me (**262**), Cl (**269**)

R = Me, X = Cl (**263**), Br (**270**)
R = Et, X = Cl (**264**),

R = Me, Y = Me (**265**), I (**271**), CN (**272**), SCN (**273**), CCCF$_3$ (**274**), CCCMe (**275**), CCSiMe$_3$ (**276**), OC$_6$F$_5$ (**277**), O$_2$CCF$_3$ (**278**),
R = Et, Y = Me (**266**), I (**279**), CN (**280**), SCN (**281**), CCCF$_3$ (**282**), CCCMe (**283**), CCSiMe$_3$ (**284**), OC$_6$F$_5$ (**285**), O$_2$CCF$_3$ (**286**)

Compounds **250**, **263**, and **264** were purified by crystallization (colorless crystals; mp 137, 92 and 94 °C, respectively); **255** and **262** were sublimed [45 °C (0.01 mbar) and 40 °C (0.01 mbar); colorless crystals; mp 56 and 52 °C, respectively]; all other compounds are distillable liquids.

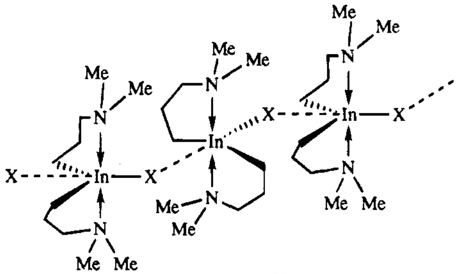
The occurrence of IC in **246-259** was confirmed by variable-temperature ^{1}H NMR studies. As an example the results for **249** are discussed. Two sets of doublets were observed at room temperature for the methyl groups of the two isopropyl groups. At the coalescence temperature of 56 °C, only one broad doublet was detected indicating dissociation of the metal–nitrogen bond which is a prerequisite for free rotation in the 3-(dimethylamino)propyl ligand and/or inversion at nitrogen. Furthermore, the signal of the $(CH_3)_2N$ group is shifted to lower field with increasing temperature, which was also ascribed to a dissociation of the metal–nitrogen coordination. The presence of one signal for the protons in the $N(CH_3)_2$ moiety in the spectra of **262** and **265**, even at low temperature, is according to the authors an indication that both dimethylamino groups are coordinated to the metal.[179]

In a separate study, the physical properties of these compounds were further elaborated, and in addition, two new aluminum derivatives $R_2Al(CH_2)_3NMe_2$ [R = Me (**267**), Et (**268**); Scheme 122] were reported.[180]

From the reaction of $GaCl_3$ with 2 equiv of [3-(dimethylamino)propyl]lithium (RLi), R_2GaCl (**269**) was obtained (Scheme 125).[181] The crystal structure revealed (*vide infra*) that both N atoms are coordinated to the metal to yield a pentacoordination which is exceptionally rare for organogallium compounds. $InBr_3$ reacts with RLi (Scheme 125) to the corresponding R_2InBr (**270**). From **263** and **264** the corresponding iodides **271** and **279** were obtained by reaction with LiI in THF. The tendency of indium to obtain pentacoordination results in the formation of R_2InCl only, even when MCl_3 is reacted with 1 equiv of RLi. The ^{1}H NMR spectra of these organogallium halides and organoindium halides and the X-ray crystal structure analysis of **269**,[181] **270**,[182] and **271**[181] show that the metal centers in these compounds are pentacoordinated. The metal atoms are located in the center of distorted trigonal bipyramids in which both coordinating nitrogen atoms occupy the axial positions. Two carbon atoms and the halogen are located in the equatorial positions. The GaC_2Cl moiety of **269** is almost planar. The C–Ga–C′ angle has widened to 138.7(2)° (ideally 120°), with C–Ga–Cl and C′–Ga–Cl angles of only 110.6(2)° as a result of sterical crowding of both (dimethylamino)propyl ligands. The N–Ga–N′ angle is almost linear with 177.8°.

The Ga–N, Ga–C, and Ga–Cl distances are 2.344(3), 1.979(4), and 2.273(1) Å, respectively. The indium bromide and iodide analogues **270** and **271** also show distortions of the indium angles from the ideal value of 120° for a trigonal bipyramid: C–In–C′, C–In–X, and C′–In–X angles are 150.4(6), 104.5(4), and 105.0(4)° for **270** and 144.8(2), 105.5(2), and 109.7(2)° for **271**, respectively. These strong distortions result from "long-range" coordination of the halogen atom to the indium center of a neighboring molecule. The *intra*molecular indium–halogen distances are relatively long with 2.644(2) and 2.841(0) Å for **270** and **271**, respectively, while the *inter*molecular indium–halogen distances for both compounds are 3.975 and 4.481 Å. Although the latter distances are rather large, this interaction influences the coordination situation at the metal to a large extent. Therefore, the coordination can be described as borderline between 5-fold and 6-fold. Scheme 126 shows the chain of halogen and indium atoms with an almost linear coordination at indium. For **270** the Br–In–Br′ and In–Br–In′ angles are 179.39 and 142.92° respectively.

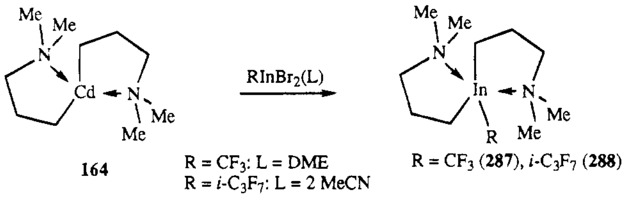
Scheme 126



X = Br (**270**), I (**271**)

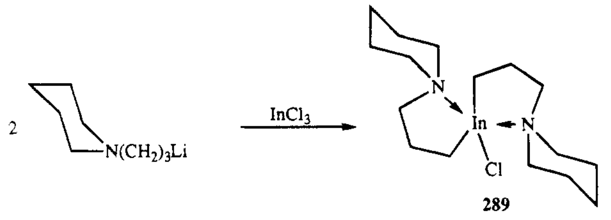
Complexes **263** and **264** were used as starting materials for the synthesis of a variety of organoindium IC compounds. In this way, compounds **271-286** were obtained by reaction with the appropriate lithium (or sodium for **278** and **286**) compounds (Scheme 125). This method was not successful for the synthesis of perfluoroalkylindium derivatives R_2InR^F. The reaction of R_2InCl with $Cd(CF_3)_2$, an approved CF_3 transfer reagent, did not yield the expected product. However, when R_2Cd was reacted with $CF_3InBr(DME)$ and i-$C_3F_7InBr(MeCN)_2$, CF_3InR_2 (**287**) and i-$C_3F_7InR_2$ (**288**) were obtained (Scheme 127).

Scheme 127



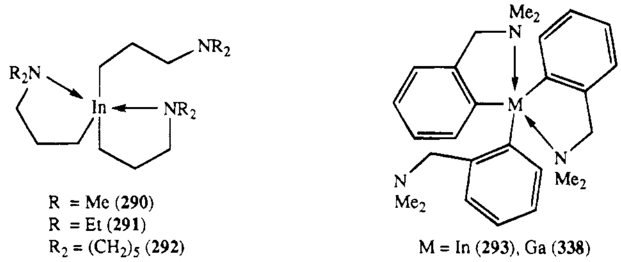
From $InCl_3$ and 2 equiv of (3-*N*-piperidinopropyl)lithium the colorless bis(3-*N*-piperidinopropyl)indium chloride (**289**) was synthesized (Scheme 128).[181]

Scheme 128



In 1992, Schumann succeeded in synthesizing four R_3In compounds $In[CH_2CH_2CH_2NMe_2]_3$ (**290**), $In[CH_2CH_2CH_2NEt_2]_3$ (**291**), $In[CH_2CH_2CH_2N(CH_2)_5]_3$ (**292**), and $In[2\text{-}(Me_2NCH_2C_6H_4]_3$ (**293**) for use in MOVPE (Scheme 129).[183]

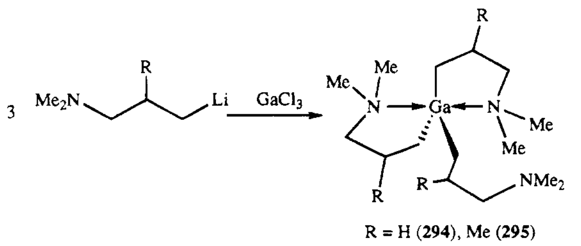
Scheme 129



All compounds were characterized by elemental analysis and NMR and mass spectra. The X-ray analysis showed the indium atom of **293** to be pentacoordinated, with two coordinating and one noncoordinating 2-[dimethylamino)methyl]phenyl ligand.

The same phenomenon was observed for the homoleptic gallium analogues.[181] Gallium trichloride reacts with 3 molar quiv of [3-(dimethylamino)propyl]lithium and [3-(dimethylamino)-2-methylpropyl]lithium under formation of the colorless liquids tris[3-(dimethylamino)propyl]gallium (**294**) and tris[3-(dimethylamino)-2-methylpropyl]gallium (**295**) (Scheme 130).

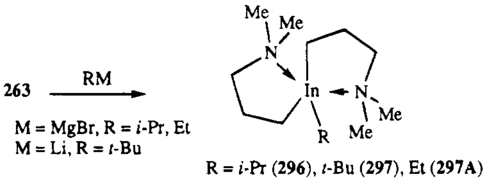
Scheme 130



Because of the large steric requirements of the third organic ligand in **294**, the gallium atom is only pentacoordinated and the coordination geometry has shifted (compared to **269**, Scheme 125) toward ideal trigonal bipyramidal. Like in **269**, the equatorial plane (GaC_3) is nearly planar and the three C–Ga–C angles are 116.0(1)°, 121.4(1), and 122.3(1)°. The N–Ga–N′ angle is more distorted with 168.9(1)°. The Ga–C distances are 1.993(3) Å (coordinating ligands) and 2.000(3) Å, while the Ga–N distances are rather long with 2.402(2) and 2.562(3) Å.

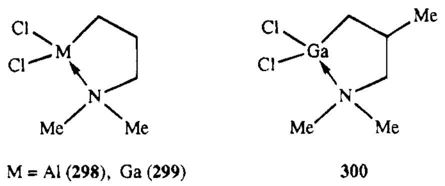
The alkylation of **263** (Scheme 125) with *i*-PrMgBr and *t*-BuLi in diethyl ether yielded the triorganoindium compounds **296**, **297**, and **297A** as colorless liquids (Scheme 131).[182]

Scheme 131



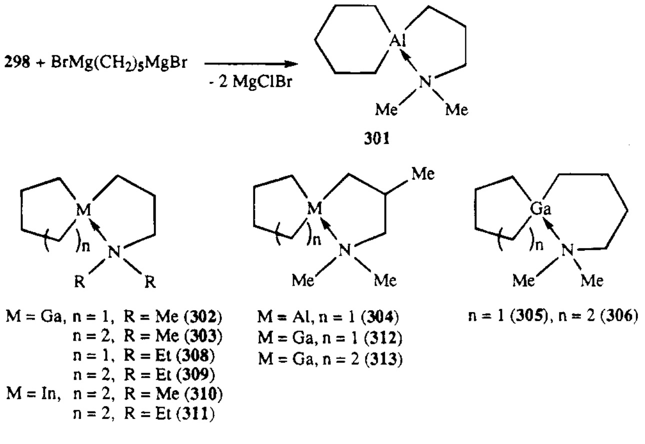
Schumann and co-workers extended their studies on metallacyclic IC compounds of aluminum, gallium, and indium.[184] [3-(Dimethylamino)propyl]lithium and [3-(dimethylamino)-2-methylpropyl]lithium reacted with equimolar amounts of $AlCl_3$ or $GaCl_3$ to yield the monoorganometal dichlorides $Me_2N(CH_2)_3MCl_2$ [M = Al [**298**; bp 200 °C (0.2 mbar)], M = Ga (**299**)] and $Me_2NCH_2CH(Me)CH_2GaCl_2$ (**300**) as colorless viscous oils (Scheme 132).

Scheme 132



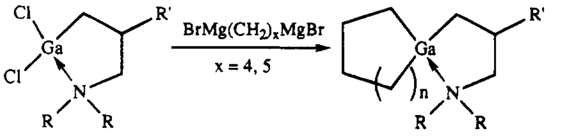
The subsequent reaction of **298**, **299**, or **300** with the di-Grignard reagents 1,4-bis(bromomagnesio)butane or 1,5-bis(bromomagnesio)pentane afforded the metallacycles **301-304** in high yields as colorless, almost air stable, distillable liquids (Scheme 133).[184] The reaction of [4-(dimethylamino)butyl]gallium dichloride (**260**, Scheme 124) with the 1,4- and 1,5-di-Grignard reagents resulted in the formation of the distillable compounds 1-[4-(dimethylamino)butyl]gallacyclopentane (**305**) and -cyclohexane (**306**), respectively (Scheme 133).

Scheme 133



In a later paper by the same group, the X-ray crystal structure of **303** was reported together with several other members of this class of compounds.[185] [3-(Diethylamino)propyl]gallium dichloride (**307**) was synthesized as a starting material for several gallacycloalkanes (Scheme 134). With the di-Grignard reagents 1,4-bis(bromomagnesio)butane and 1,5-bis(bromomagnesio)pentane, the metallacycloalkanes **308** and **309** were obtained. Complex **308** is a colorless solid, while **309** is a distillable colorless liquid (at room temperature) like **302** and **303**.[184] The latter compounds are monomeric when freshly prepared, as was shown by the X-ray crystal structure of **303** after crystallization at low temperature. After storage of **309**, **302**, and **303** the viscosity increased significantly, while the vapor pressure decreased from 30 Pa (15 °C) to 0.2 Pa (20 °C), which may be explained by association.

Scheme 134



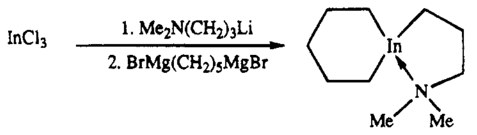
R' = H, R = Et (**307**)
R' = R = Me (**300**)

R' = H, R = Et, n = 1 (**308**), n = 2 (**309**)
R' = R = Me, n = 1 (**312**), n = 2 (**313**)

When compound **300**[184] (Scheme 132) was reacted with the di-Grignard reagents, the chiral gallacycloalkanes 1-[3-(dimethylamino)-2-methylpropyl]-1-gallacyclopentane (**312**) and -hexane (**313**) were obtained as racemates (Scheme 134).[185] These compounds are also colorless liquids, but they are rather viscous. Nevertheless, **313** has a high vapor pressure (220 Pa at 15 °C) and crystals were obtained by sublimation to a finger cooled to −78 °C. The melting point of the crystals appeared to be −20 °C, and a crystal structure was obtained by low-temperature X-ray diffraction. The structure of **313** is similar to that of **303** (Scheme 133). The gallium atom is located in the center of a distorted tetrahedron. Both gallacyclohexane rings are present in the chair conformation, while the nonplanar five-membered rings show the "envelope-like" conformation. Normal sp^3-hybrid angles are observed for $C_{(c\text{-Hex})}$−Ga−N [107.3(1) and 105.3(1)° for **303** and 107.9(1) and 106.1(1)° for **313**], but not for the C−Ga−N angles within the five-membered ring [87.3(1)° for **303** and 87.7(1)° for **313**]. The Ga−N distances are not exceptional with 2.148(2) and 2.154(2) Å, for **303** and **313**, respectively. The Ga−C distances range from 1.967 to 1.993 Å.

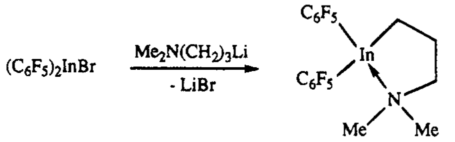
Analogous indium compounds could not be obtained by the routes that were successful for gallium: the stoichiometric reaction of $InCl_3$ with [3-(dimethylamino)propyl]lithium or -magnesium chloride only yielded the dialkylated **263** (Scheme 125).[185] Furthermore, disproportionation of **263** with $InCl_3$ was not observed. The desired 1-[3-(dimethylamino)propyl]-1-indacyclohexane (**311**) was only obtained (in low yield) when $InCl_3$ was reacted with [3-(dimethylamino)propyl]lithium and 1,5-bis(bromomagnesium)pentane in a one pot procedure (Scheme 135).

Scheme 135



Bis(pentafluorophenyl)indium bromide reacts with [3-(dimethylamino)propyl]lithium to form [3-(dimethylamino)propyl]bis(pentafluorophenyl)indium (**314**), an air-stable solid (Scheme 136).[185] The crystal structure, determined from crystals obtained after sublimation, shows the expected *intra*molecular coordination of the amine nitrogen and an *inter*molecular coordination of one fluorine atom of a neighboring molecule. The resulting pentacoordination explains the stability of the compound. The X-ray crystal structure shows **314** to be a dimer in the solid state. Indium is coordinated in a distorted trigonal bipyramid with three carbon atoms in equatorial and nitrogen and fluorine in axial positions. The structural geometry of the (dimethylamino)propyl ligand resembles that of **303** (Scheme 134) and **313** (Scheme 135) with a puckered envelope-like configuration. The In−F' distance in **314** (3.180 Å) is less than the sum of the van der Waals radii (3.50 Å)[167] which makes it a real (coordinative) bond. The N−In−F angle [160.21(17)°] is distorted from the ideal angle for a trigonal bipyramid. The In−N distance is 2.310(5) Å and the In−C distances are 2.151(6) Å for the (dimethylamino)propyl ligand and 2.196(8) and 2.194(9) Å for the aryl groups.

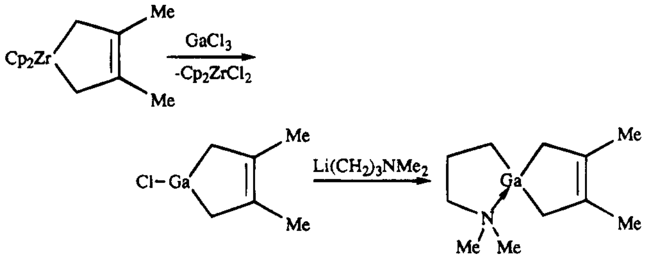
Scheme 136



314

Reaction of bis(cyclopentadienyl)-3,4-dimethylzirconacyclopent-3-ene with $GaCl_3$ yielded 1-chloro-3,4-dimethylgallacyclopent-3-ene which was converted with [3-(dimethylamino)propyl]lithium to 1-[3-(dimethylamino)propyl]-3,4-dimethylgallacyclopent-3-ene (**315**) in low yield (Scheme 137).[185] The corresponding aluminum and indium compounds could not be obtained in pure form.

Scheme 137

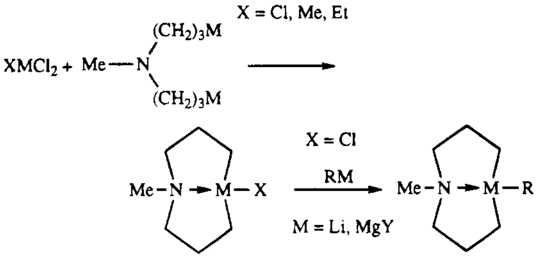


315

The treatment of the metal trichloride or several alkylmetal dichlorides with bis[3-(chloromagnesio)propyl]methylamine in a 1:1 molar ratio resulted in the formation of the corresponding 1-metalla-5-azacyclooctanes **316-319** (Scheme 138). In contrast to the ethyl compounds **316** and **318**, which are liquids at room temperature, the methyl compounds **317** (mp 34 °C) and **319** (mp not given) are solids.[184]

In search for better gallium and indium precursors for gas-phase epitaxy, more members of the 1-metalla-5-azacyclooctane family were synthesized and spectroscopically investigated.[186] Gallium trichloride reacts at −78 °C in a THF/ether solvent mixture with an equivalent amount of the di-Grignard reagent bis[3-(chloromagnesio)propyl]methylamine to 1-chloro-5-methyl-1-galla-5-azacyclooctane (**320**), a starting material for the alkylated derivatives **317**, **318**, and **321-330** (Scheme 138). All these compounds are colorless distillable liquids, in which intermolecular interactions are negligible. The compounds are stable toward oxygen and water. At low temperature, crystals of **320** and **329**, suitable for X-ray crystal structure determination were obtained. In **320**, the gallium atom is located 0.1631(6) Å above the plane through the two gallium-bonded carbon atoms and the chlorine atom. The ideally planar Cl−Ga−N−C(H_3) orientation is distorted by a torsion angle of 10.3(5)°. Additionally, the Cl−Ga−N angle is enlarged to 105.2(1)°, while the C−Ga−N angles approach the ideal bonding angle of 90° with 90.5(2) and 89.5(2)°. The Ga−C bonds [1.969(7) and 1.957(7) Å] and the Ga−Cl bond [2.232(2) Å] are not exceptional. The Ga−N bond distance is 2.112(5) Å.

Scheme 138



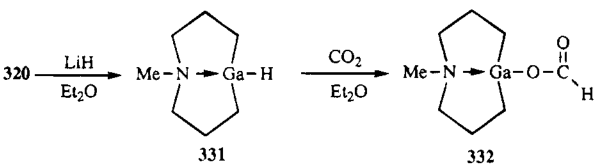
M = Al, R = Et (**316**)
M = Ga, X = Me (**317**), Et (**318**), Cl (**320**)
M = In, R = Me (**319**)

M = Ga, R = Pr (**321**), *i*-Pr (**322**), *n*-Bu (**323**), *t*-Bu (**324**), Ph (**325**), Me_3SiCH_2 (**326**), $Me_2N(CH_2)_3$ (**327**), $Et_2N(CH_2)_3$ (**328**), $Me_2NCH_2CH(Me)CH_2$ (**329**), 2-$Me_2NCH_2C_6H_4$ (**330**)

By substitution of the chlorine atom of **320** by the additionally intramolecular coordinating 3-(dimethylamino)-2-methylpropyl ligand, the coordination number at gallium was raised to five.[186] In the monomeric **329**, the newly introduced nitrogen atom coordinates to gallium at the basis of the original trigonal pyramid, forming a trigonal bipyramid, with three carbon atoms in the equatorial plane and the two nitrogens in axial positions. The geometry of the 1-galla-5-azacyclooctane ring is almost identical to that of **320**. The three C−Ga−C angles in the equatorial plane are almost ideal with 119.9(1), 119.5(1), and 120.0(1)°, respectively. The three Ga−C distances (each 2.00 Å) and the Ga−N distances [2.392(1) Å (ring-N) and 2.37(5) Å (side-arm-N)] are slightly longer than in **320**, resulting from the increase of the coordination number from 4 to 5. The N−Ga−N angle is almost linear with 178.8(1)°.

When **320** is reacted with LiH at 0 °C in ether, 5-methyl-1-galla-5-azacyclooctane (**331**) is formed in low yield (Scheme 139).[186] The compound is thermally not stable above 50 °C and hydrolyzes rapidly when exposed to air. The X-ray crystal structure was determined. With CO_2, insertion of C=O into the Ga−H bond is observed (Scheme 139). The resulting 5-methyl-1-galla-5-azacyclooctyl 1-formiate (**332**) crystallizes as a coordination polymer chain in which pentacoordinated gallium is coordinated in a trigonal-bipyramidal fashion.

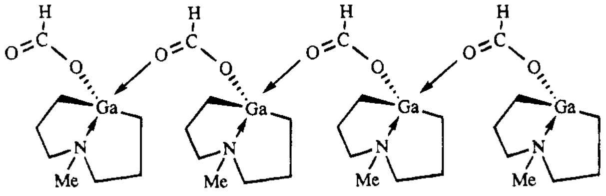
Scheme 139



331 **332**

The monomeric structure of **331** resembles that of **320**. The hydrogen atom occupies one of the base positions of a strongly distorted trigonal pyramid. The gallium atom is located 0.1438(1) Å above the plane through the gallium-bonded carbons and the hydrogen. The conformation of the cyclooctane ring as well as the Ga−N distance (2.117(3) Å) are equal to those in **320**. Thus, the corresponding angles are C−Ga−C 120.2(1)°, C−Ga−H 114.6(9) and 123.2(9)°. The Ga−H bond [1.47(2) Å] is significantly shorter as was found for corresponding base-stabilized organogallium hydrides. For $(Me_2NCH_2CH_2OGaH_2)_2$, Ga−H distances of 1.55(7) and 1.73(5) Å were reported[187] and in the diazabutadiene complex [$\{H_2Ga\}_2\{\mu$-N(*t*-Bu)CH$\}_2$] distances between 1.54(12) and 1.57(8) Å were found.[188] In **332** pentacoordination results from additional *inter*molecular coordination with an oxygen atom of a formiate group of a neighboring molecule, leading to chains of molecules in the crystal (Scheme 140).

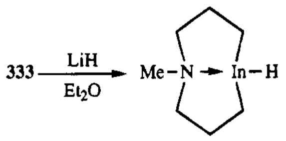
Scheme 140



332

In a single molecule, gallium is pentacoordinated (like in **329**), in a distorted trigonal bipyramidal fashion with the oxygen and two carbons in the equatorial plane with angles of 133.7(3)° (C−Ga−C) and 118.4(3) and 107.4(2)° (C−Ga−O). The distance to the axial nitrogen and oxygen are 2.291(5) and 2.182(4) Å, respectively, while the N−Ga−O angle is 178.1(2)°. The intramolecular Ga−O distance is 1.951(4) Å, a normal value for organogallium alkoxides. While the Ga−N distance is significantly larger than that found for **320** and **331**, it is shorter than those found for the doubly intramolecularly nitrogen-coordinated **329**. Corresponding indium compounds were also investigated.[186] $InCl_3$ reacts with MeN[$(CH_2)_3Li$]$_2$ to form 1-chloro-5-methyl-1-inda-5-azacyclooctane (**333**), which in turn reacts with LiH to form 5-methyl-1-inda-5-azacyclooctane (**334**) which decomposes above −30 °C (Scheme 141).

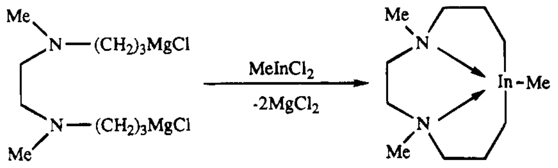
Scheme 141



334

The reaction between $MeInCl_2$ and *N,N'*-bis[3-(chloromagnesio)propyl]-*N,N'*-(dimethylethylene)diamine gave **335** as a colorless liquid (Scheme 142).[184]

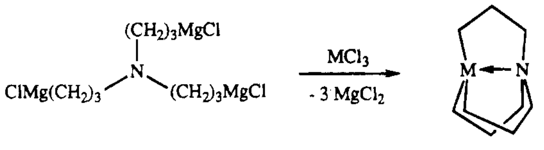
Scheme 142



335

The bicyclic compounds **336** (mp not given) and **337** (mp 54 °C) were prepared from the metal trichlorides and tris[3-(chloromagnesio)propyl]amine in high yields as low melting solids (Scheme 143).

Scheme 143



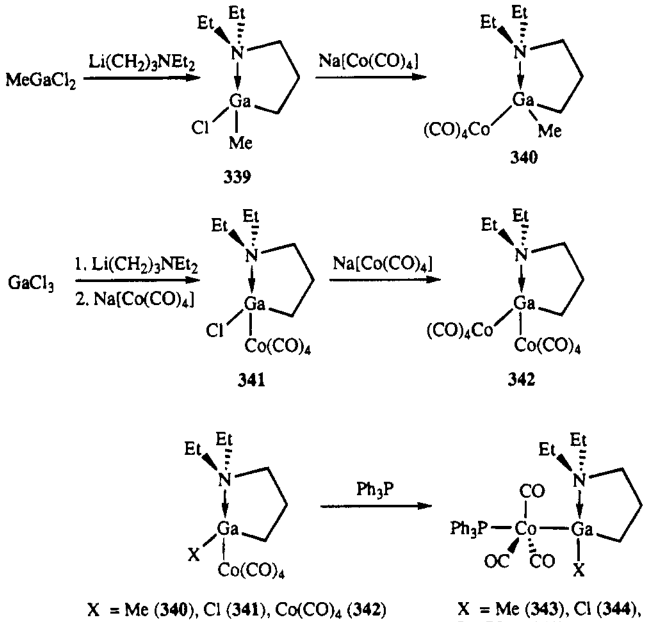
M = Al (**336**), Ga (**337**)

Compounds **298-337** were identified by their ^1H and ^{13}C NMR and mass spectra. All compounds showed the expected signals for monomeric IC structures. The molecular structure of **337** was determined by X-ray diffraction. In the monomeric units, the gallium atom is surrounded in a trigonal-pyramidal fashion by the three methylene groups and the amine nitrogen. It is very remarkable that the gallium atom lies in the plane formed by the three gallium-bonded methylene groups, because so far, gallium has been found to be coordinated in a distorted tetrahedral fashion. The electron deficiency of the metal is balanced by IC bonding to the nitrogen atom situated at the apex of the pyramid. The Ga–N distance (2.095 Å) is only slightly longer than the sum of the covalent radii of gallium and nitrogen (1.95 Å)[167] and markedly shorter than in pure donor–acceptor complexes like $Me_3Ga{\cdot}NMe_3$ (2.20 Å)[168] or $Me_3Ga{\cdot}$[urotropine] (2.14 Å).[169] The Ga–C bonds are not exceptional with 1.998 Å; the C1–Ga–C1', C1–Ga–N, and C2–C1–Ga angles are 120, 89.2, and 103.7° respectively. In spite of the presence of a sterically unprotected site of the pyramid, the compound is rather stable against moisture and air.[184]

Tris[2-[(dimethylamino)methyl]phenyl]gallium (**338**, Scheme 129) the gallium analogue of **293**, was also reported.[181] The crystal structure shows an almost ideal trigonal bipyramid with the three aryl carbon atoms in equatorial and two of the three nitrogens in axial positions. The X-ray crystal structure of **338** was independently reported by a second group.[189]

Carefully purified starting materials and precisely controlled stoichiometries guarantee high-yield "one-pot syntheses" of the volatile organogalliocobalt complexes **339-345** (Scheme 144).[190] These compounds are stabilized by IC at the gallium center. The compounds were identified by ^1H, ^{13}C, and ^{31}P NMR, infrared υ(CO), and MS data.

Scheme 144



X = Me (**340**), Cl (**341**), Co(CO)₄ (**342**) X = Me (**343**), Cl (**344**), Co(CO)₄ (**345**)

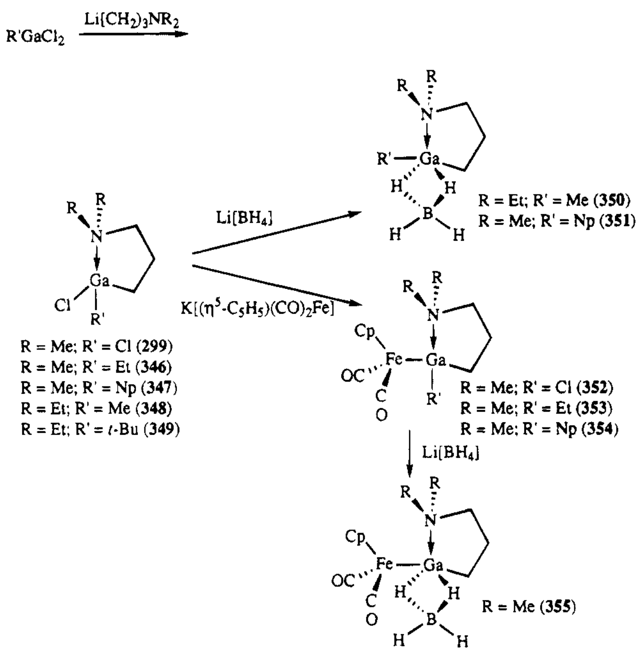
From $MeGaCl_2$ and $Et_2N(CH_2)_3Li$, the mixed alkylated isolable $Et_2N(CH_2)_3Ga(Me)Cl$ (**339**) was obtained. Compound **340** was obtained from **339** by nucleophilic substitution at the remaining chloride at gallium by sodium tetracarbonylcobaltate. Compounds **341** and **342** were prepared from $GaCl_3$, following the same procedure. Thermal decarbonylation of **340-342** at 80 °C, in the presence of 1 equiv of phosphines, e.g. $P(C_6H_5)_3$, yielded quantitatively the *trans*-phosphine-substituted complexes **343-345**. A single-crystal X-ray analysis of [μ-[3-(diethylamino)propyl]gallio][bis(tetracarbonylcobalt)] (**342**) reveals cobalt–gallium bond distances averaging to 2.543 Å. The Ga–N bond distance is 2.225(4) Å.

Similar organogallium compounds (**346-355**) with mixed substitution patterns of the type $(R_1)(R_2)Ga[(CH_2)_3NR_2]$ have been synthesized and fully characterized (Scheme 145).[191]

All these compounds are stabilized by IC at the gallium center. The solid-state structures of **352** and **355** exhibit Fe–Ga bond lengths of 2.4565(4) and 2.375(1) Å, respectively. The Ga–N distances in both compounds are 2.185(3) Å, while the Ga–B distance in **355** amounts to 2.374(3) Å. Remarkably pure Fe/Ga thin films were grown from **355** by low-pressure MOVPE. The BH_4 group lowers both the decomposition temperature of the single source precursor and the degree of contamination of the mixed-metal thin films by carbon.

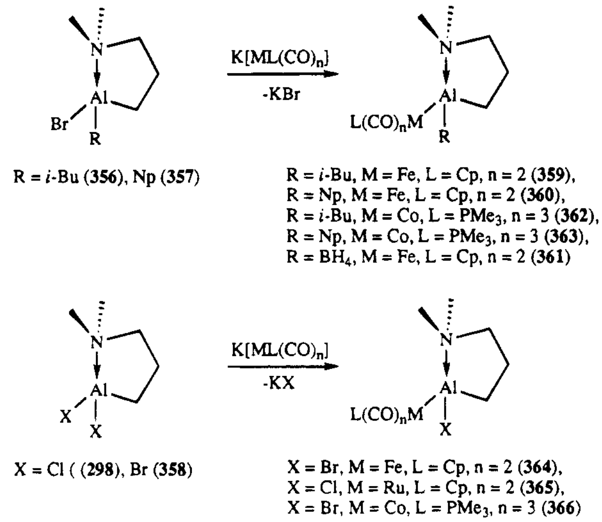
Similar aluminum compounds were reported by the same group.[192] When equimolar quantities of the intramolecular base-stabilized aluminum halides **356**, **357**, **298**, and **358** were combined with transition metal carbonylates $[L(CO)_nM][K]$ (M = Fe, Ru, Co; L = CO, PMe_3, Cp; $n = 1-3$) in THF solution, one halide group at the aluminum center was selec-

Scheme 145



tively and almost instantaneously substituted by the transition metal fragment to yield the new IC compounds **359-366** (Scheme 146).

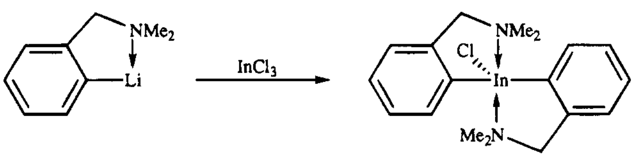
Scheme 146



The remaining halide functionalities of **364-366** were exchanged in subsequent steps by various residues. In contrast to the related Fe–Ga chemistry, quantitative introduction of the [BH_4^-] substituent to yield **361** failed. The presence of chelating alkyl substituents at the aluminum is not a necessary requirement; however, it adds some stability against the influence of air and moisture. Dinuclear systems such as **359-366**, which contain an organoaluminum moiety linked to a transition-metal fragment by a *nonbridged* metal–metal bond are extremely rare. The presence of a σ-bond for **359** was confirmed by an X-ray crystal structure [Fe–Al 2.456(1) Å]. The aluminum atom resides in the center of a distorted tetrahedral coordination sphere. The Al–N distance of 2.094(3) Å is not exceptional.

In 1980, the neutral complex bis[2-[(dimethylamino)methyl]phenyl]indium chloride (**367**) was reported to be the only product isolated from the reaction of the corresponding organolithium compound with $InCl_3$.[109] The X-ray crystal structure of **367** was the first example of an organoindium compound with a trigonal-bipyramidal (TBP) geometry as a result of IC (Scheme 147).

Scheme 147

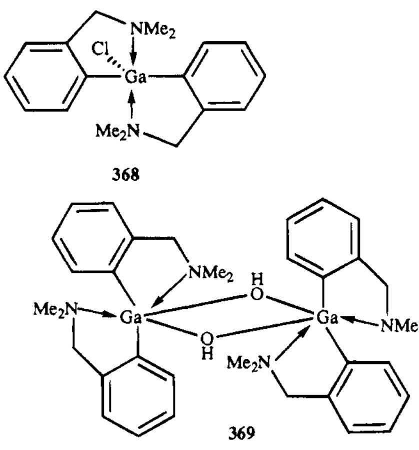


367

The geometry of the molecule is essentially TBP with the two nitrogen atoms in the apical positions and the chlorine and two carbon atoms in equatorial positions, which is the arrangement generally observed for TBP molecules containing two organic ligands.[193] The N_2InCl part of the molecule approaches ideal TBP geometry with N–In–N and two Cl–In–N angles of 178.4, 89.4, and 89.9°, respectively. The main distortion arises from the displacement of aryl carbon atoms from the equatorial plane due to the geometric constraints of the NC_3In five-membered chelate ring. The bite angles C(aryl)–In–N (77.0 and 76.1°) are close to those observed in other [2-[(dimethylamino)methyl]phenyl]metal complexes. In the equatorial plane, the C–In–C angle (153.3°) is quite large and the C–In–Cl angles are rather small (102.9 and 103.7°). The In–Cl distance (2.465 Å) and the In–C bond lengths (2.144 and 2.154 Å) fall within the normal range. The In–N bond distances of 2.442 and 2.482 Å are substantially longer than the "normal" value for an In–N single bond (~2.28 Å). In five-membered chelate rings, several factors will contribute to the weakening of the In–N bond: the apical bonds in TBP complexes are generally weaker than those in the equatorial plane,[193] a R_2InCl compound will have weaker acceptor properties than $InCl_3$, and finally, skeletal strain is induced by ring formation.

Together with **338** (Scheme 129) two bis[2-[(dimethylamino)methyl]phenyl] compounds of gallium, $(2\text{-}Me_2NCH_2C_6H_4)_2GaCl$ (**368**) and $[(2\text{-}Me_2NCH_2C_6H_4)_2GaOH]_2$ (**369**) were reported (Scheme 148).[189]

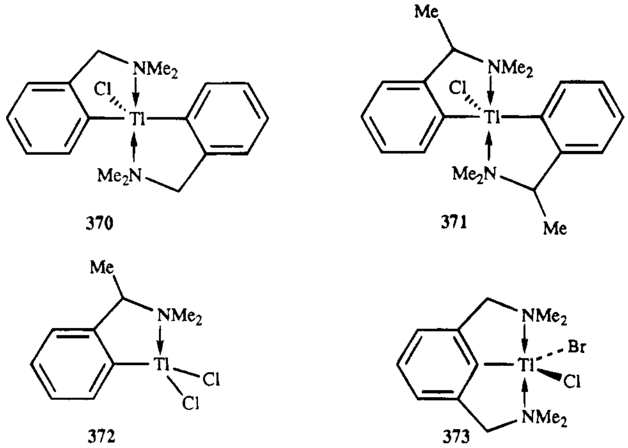
Scheme 148



The structure of **368** is similar to that of **367**. The N−Ga−N angle is 178.6(2)°, while the Cl−Ga−N angles average 90.2(2)°. The Ga−N distances are 2.304(6) and 2.385(6) Å. The Ga−C and Ga−Cl distances are 1.975(6) and 1.977(7) and 2.269(2) Å, respectively. Trialkyl and triaryl complexes of gallium(III) are normally hydrolyzed rapidly by water. In wet $CDCl_3$ **338** reacts with water to form free ligand (LH) and, presumably, the L_2GaOH or $[L_2GaOH_2]^+$ analogues of **368**. The ^1H NMR spectrum of the new gallium species exhibits somewhat broadened peaks, but is otherwise identical to that of **369**, crystals of which were obtained while recrystallizing a crude mixture of **338** and **368** in $CHCl_3−Et_2O$. Again, the gallium atom has a distorted trigonal bipyramidal coordination geometry. The bridging hydroxide oxygen atom occupies an axial position on Ga, and an equatorial site on Ga′. The other axial position on Ga is taken by a nitrogen and two aryl carbons occupy the remaining equatorial sites. The length of the Ga−N bond is 2.576(3) Å, Ga−O 1.8929(4) and 2.0216(4) Å, and Ga−C 1.973(4) and 1.979(4) Å.

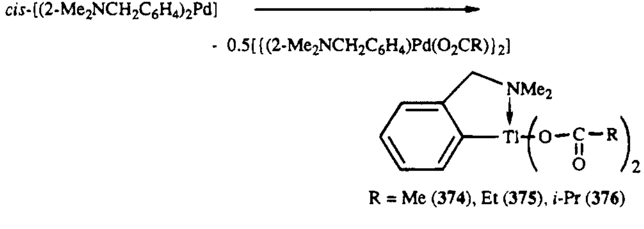
The IC thallium compounds $[(2\text{-}Me_2NCH_2C_6H_4)_2TlCl]$ (**370**), $[[(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4]_2TlCl]$ (**371**), $[[(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4]TlCl_2]$ (**372**), and $[[2,6\text{-}(Me_2NCH_2)_2C_6H_3]TlClBr]$ (**373**) were synthesized by reaction of $TlCl_3$ with the corresponding lithium compounds in a 1:1 or 1:2 ratio (Scheme 149).[194]

Scheme 149



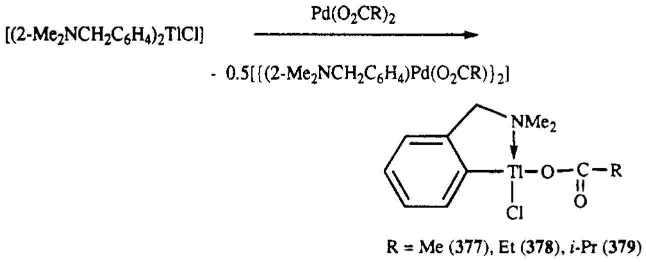
Reaction of *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$ with $Tl(O_2CR)_3$ (R = Me, Et, and *i*-Pr) yielded the tetracoordinated organothallium carboxylates $[(2\text{-}Me_2NCH_2C_6H_4)Tl(OCR)_2]$ [R = Me (**374**), Et (**375**) and *i*-Pr (**376**)] as shown in Scheme 150.[194]

Scheme 150



The reverse reactions of **370** with $Pd(O_2CR)_2$ (R = Me, Et, and *i*-Pr) resulted in the formation of monoorganometallic compounds $[(2\text{-}Me_2NCH_2C_6H_4)Tl(OCR)Cl]$ [R = Me (**377**), Et (**378**) and *i*-Pr (**379**)] according to Scheme 151.

Scheme 151

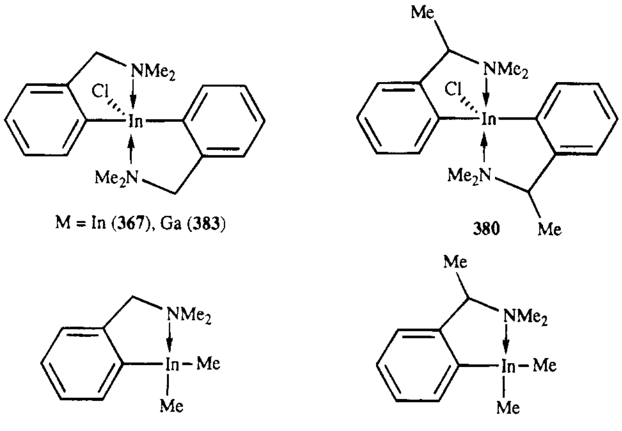


The formation of the bromide-containing product **373** is due to chloride−bromide exchange with LiBr which is present from the synthesis of the lithium compound. Even the use of excess of the lithium reagent gave only the bis-substituted compound **370**; the tris-substituted compound $(2\text{-}Me_2NCH_2C_6H_4)_3Tl$ was not isolated. Compound **371** was obtained by a similar procedure from the corresponding lithium compound and $TlCl_3$, while **372** was synthesized via ligand exchange reaction between **371** and $TlCl_3$. The compounds were identified by elemental analysis, molecular weight determinations (all monomeric in $CHCl_3$), and ^1H and ^{13}C NMR spectroscopy. The presence of a direct aryl−thallium bond was derived from the coupling constants of the various H and C atoms with Tl. The observed coupling of thallium with the carbon and hydrogen atoms of the NMe_2 groups in **372** must be due to the long-range couplings which are quite normal in thallium compounds[195] (e.g. 114 Hz for a ${}^5J_{^{203,205}Tl-^{13}C}$ and 66 Hz for a ${}^6J_{^{203,205}Tl-^{1}H}$ in $p\text{-}MeC_6H_4Tl(O_2CCF_3)_2$).[196] In contrast, the variable temperature ^{13}C NMR spectra of **371** and **372**, which contain a stable chiral carbon center, provided unambiguous evidence for Tl−N coordination. The inversion at nitrogen is blocked on the NMR time scale, resulting in two anisochronous resonances for the carbon nuclei of the NMe_2 group, both with thallium coupling. At ambient temperature, the methyl groups become homotopic and the two signals start to coalesce. Furthermore, it is noteworthy that **371**, having a bipyramidal structure with a five-coordinate thallium, can exist in two diastereoisomeric forms. However, the low-temperature NMR spectra indicate that only one isomer is present.

Arylindium compounds $(2\text{-}Me_2NCH_2C_6H_4)_2InCl$ (**367**), $[(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4]_2InCl$ (**380**), $(2\text{-}Me_2NCH_2C_6H_4)InMe_2$ (**381**), and $[(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4]InMe_2$ (**382**) were synthesized via the organolithium route and characterized by ^1H and ^{13}C NMR spectroscopy (Scheme 152).[197]

The NMR spectra clearly revealed that intramolecular In−N coordination occurs in solution, resulting in pentacoordinate Ar_2InCl (**367** and **380**) and tetracoordinate $ArMe_2In$ (**381** and **382**) structures. The CH_2 and NMe_2 ^1H resonances, as well as the NMe_2 ^{13}C resonance of **381** are isochronous in the temperature range studied (−80 to +100 °C); this does not distinguish between a tri- or tetracoordinate structure. However, introduction of a methyl group at the benzylic carbon atom to give **382** allows a choice to be made. The ^{13}C NMR spectra of **382** at or below room temperature reveal anisochronous

Scheme 152



M = In (**367**), Ga (**383**)

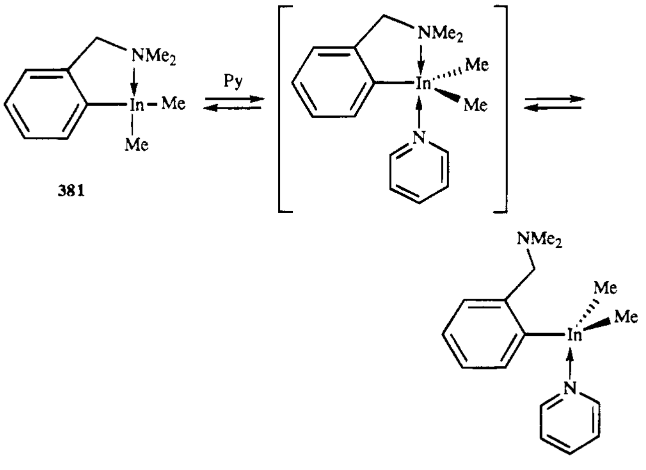
380

381

382

$(CH_3)_2N$ ^{13}C resonances which indicate that nitrogen has a stable tetrahedral configuration as a result of In−N coordination. The prochiral $InMe_2$ assembly likewise becomes diastereotopic as a result of In−N coordination as evidenced by two singlets for the two In-bonded methyl groups at −50 °C. Coalescence of the latter two singlets at room temperature points to the occurrence of a dynamic process involving In−N bond dissociation. The geometry around indium in **382** (and by inference in **381**) will cause a distortion from a tetrahedral coordination because the bite angle will be close to 75°. The observation that nevertheless IC does occur points to relatively strong acceptor behavior of indium. In contrast to **367** and **380** which are white crystalline solids (mp 191 and 179 °C, respectively), the dimethylarylindium compounds **381** and **382** are distillable liquids; molecular weight determinations showed that these compounds exist as monomers in benzene. In pyridine solution, the In−N bond in the tetracoordinate $ArMe_2In$ compounds weakens as the result of formation of a pentacoordinate intermediate in which the NMe_2 and pyridine ligand are in axial positions (Scheme 153). Such a TBP structure has actually been observed for $(2\text{-}Me_2NCH_2C_6H_4)_2InCl$ (**367**) in the solid state (*vide supra*).[109]

Scheme 153

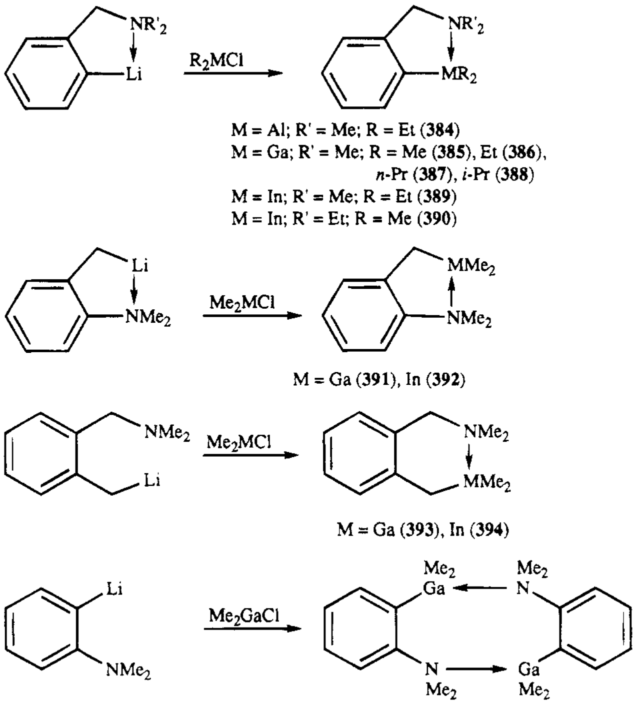


381

The synthesis of **367** was reported again,[181] this time together with the synthesis of its gallium analogue **383** (Scheme 152). The X-ray crystal structure of the latter shows a distorted trigonal bipyramid in which the coordinating nitrogen atoms occupy axial positions. The N−Ga−N angle is near to ideal with 179.2(1)°, while the Ga−N distances are 2.301(2) and 2.394(2) Å.

Intramolecularly stabilized tetracoordinated organoaluminum, -gallium, and -indium compounds $2\text{-}R'_2NCH_2C_6H_4MR_2$ **384-395** (Scheme 154) have been

Scheme 154



M = Al; R' = Me; R = Et (**384**)
M = Ga; R' = Me; R = Me (**385**), Et (**386**), *n*-Pr (**387**), *i*-Pr (**388**)
M = In; R' = Me; R = Et (**389**)
M = In; R' = Et; R = Me (**390**)

M = Ga (**391**), In (**392**)

M = Ga (**393**), In (**394**)

395

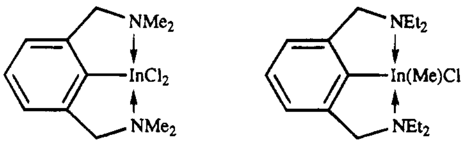
synthesized in pentane from the dialkylmetal chlorides and the appropriate organolithium compounds.[198] The stabilization in compounds **384-392** is due to the formation of a five-membered chelate ring, while in **393** and **394**, a six-membered ring is formed. Starting from $o\text{-}Me_2NC_6H_4Li$, a compound containing a four-membered chelate ring was not observed. Instead, in **395** an eight-membered ring system was formed via *inter*molecular coordination, as indicated by cryoscopy in benzene. All compounds are moderately stable in air and show only slow decomposition in contact with moisture, except for the dimeric **395**. Compound **395** was purified by crystallization (colorless crystals; mp 68 °C); **385**, **390**, and **393** were sublimed (colorless crystals, mp 34, 31, and 35 °C, respectively); the other compounds (**384**, **386-389**, **391**, **392**, and **394**) were distillable liquids.

The ^1H and ^{13}C NMR spectra show the expected pattern and shifts with the exception of **388**, where two sets of doublets are observed at room temperature for the methyls of the two isopropyl groups. Broadening of the signals occurs at higher temperatures (coalescence temperature > 80 °C). The mass spectra of **384-394** show no peaks at m/z values higher than those of the monomeric molecular ions. The most dominant feature observed is the loss of CH_3, C_2H_5, or C_3H_7, respectively. Other significant fragments are $C_7H_7^+$ (m/z 91) and Me_2NCH_2 (m/z 58).[198]

The molecular structures of **385** and **390** have been determined by X-ray diffraction. The crystal structure of **385** showed a discrete monomer, with the gallium atom in a distorted tetrahedral environment. The GaC_3 moiety is close to planarity, with gallium 0.28 Å above the C_3 plane. The angles around gallium do not deviate much from tetrahedral, with the exception of the C−Ga−N angle within the five-membered ring which is 84.4°. This also influences the geometry around the phenyl ring: the C−C−Ga angle within the five-membered ring is smaller (110.7°) than the expected 120°. The Ga−N distance of 2.133 Å is in agreement with the corresponding values observed in adducts formed between R_3Ga and NR'_3;[168,169,199] all are longer than the sum of the covalent radii for gallium and nitrogen (1.95 Å).[167] Surprisingly, the aromatic C−Ga bond (1.991 Å) is slightly longer than the two methyl C−Ga distances (1.977 and 1.978 Å).[198] The geometry of **390** is similarly distorted as that of **385** by intramolecular metal−nitrogen coordination. The C−In−N angle in the ring is only 78.9° and the increase in radii in going from gallium (in **385**) to indium (in **390**) results in a larger displacement of the benzylic carbon out of the plane of the phenyl ring by 0.94 Å (0.12 Å in **385**) with a (sensational!) torsion angle In−C−C−C in the five-membered ring of 46.1° compared to only 5.4° for the corresponding Ga−C−C−C in **385**. In the five-membered ring, the C−C−In angle is 108.9° and the C−C−C angle within the ring, 107.3°, is also significantly distorted from 120°. The In−N distance (2.38 Å) is longer than the sum of the covalent radii (2.19 Å[109]), but significantly shorter than the sum of the van der Waals radii (3.45 Å). Again, the aromatic C−In bond length (2.205 Å) is longer than the other two methyl−indium distances (2.150 and 2.140 Å).[198]

In their continuous effort to enhance the stability of group 13 compounds toward water and oxygen, Schumann *et al.* prepared $2,6\text{-}(Me_2NCH_2)_2C_6H_3InCl_2$ (**396**) and $2,6\text{-}(Et_2NCH_2)_2C_6H_3In(Me)Cl$ (**397**) from the corresponding lithium compounds and $InCl_3$ and $MeInCl_2$, respectively (Scheme 155).[199]

Scheme 155



396 **397**

Both compounds are colorless solids, melting at 108−110 °C (**396**) and 52−54 °C (**397**). In these molecules, indium is pentacoordinated as demonstrated by an X-ray crystal structure analysis of **397**. Nucleophilic attack of water or oxygen at the metal center is significantly impeded due to the steric demand of the bulky ligand, as both nitrogen atoms coordinate to the metal center, which was also confirmed in solution by ^1H and ^{13}C NMR spectroscopy. The molecule exhibits a distorted trigonal-bipyramidal geometry with the chlorine and the two carbon atoms bound to indium in equatorial and the nitrogen atoms in axial positions. The indium atom lies 0.027 Å out of the equatorial plane. The distortion from the ideal trigonal-bipyramidal symmetry is caused by the geometry of the ligand. The bond N1−In−N2 angle (144.9°) is significantly smaller than the respective angle 178.4° in $[2\text{-}(Me_2NCH_2)C_6H_4]_2InCl$ (**367**, Schemes 147 and 152). The In−N distances are 2.603 and 2.607 Å, which is longer than the sum of their covalent radii (2.19 Å) but significantly shorter than the sum of their van der Waals radii (3.45 Å). The ligand constraint prevents the nitrogens from moving closer to the metal center. One of the nitrogens resides 0.756 Å below, and the other 0.606 Å above the phenyl plane. The C−In−C angle is significantly increased to 130.1°. The bite angles of C(aryl)−In−N (72.7 and 72.3°) belong to the smallest ones known. The In−Cl distance of 2.377 Å is normal as are the In−C(alkyl) and In−C(aryl) bond lengths of 2.160 and 2.156 Å, respectively.[200]

The reactions of [2,6-bis[(dimethylamino)methyl]phenyl]lithium (NCNLi) with Me_2GaCl, Me_2InCl, Et_2InCl, and $n\text{-}Pr_2InCl$ resulted in the formation of the triorganometal compounds **398-401** which were isolated in high yields after distillation or sublimation as a colorless liquid (**401**) or low melting solids with mp 34, 53, and 41 °C for **398**, **399**, and **400**, respectively (Scheme 156).[201]

Scheme 156

M = Ga; R = Me (**398**)
M = In; R = Me (**399**), Et (**400**), *n*-Pr (**401**)

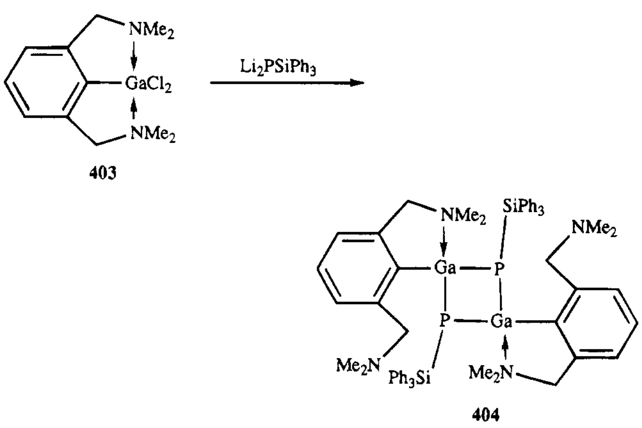
402

Et_2InCl reacts with [2,6-bis[(diethylamino)methyl]phenyl]lithium to yield [2,6-bis[(diethylamino)methyl]phenyl]diethylindium (**402**, Scheme 156). Compounds **398-402** are readily soluble in aliphatic or aromatic hydrocarbons and ethers. Decomposition of these compounds has not been observed, not even by water or oxygen after prolonged exposure to air. They were identified by ^1H and ^{13}C NMR spectroscopy and mass spectrometry, and showed the signals expected for monomeric IC structures. The characteristic fragmentation pattern of the 2,6-bis[(dimethylamino)methyl]phenyl ligand is the dominant feature in the mass spectra of these compounds.[201]

In 1990, $[[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(PSiPh_3)]_2$ (**404**), the first compound of the type RMER′ in which M and E are members of groups 13 and 15 other than boron, aluminum, and nitrogen, was synthesized.[202] The NCN ligand was used because of its ability to stabilize Lewis acidic metal centers. The reaction of NCN−Li with 1 equiv of $GaCl_3$ resulted in the formation of $NCNGaCl_2$ (**403**) which was characterized by ^1H and ^{13}C NMR spectroscopy and by its crystal structure (Scheme 157). The gallium atom in **403** is involved in trigonal-bipyramidal coordination. Both nitrogen atoms occupy axial positions, but all angles are significantly distorted: the N−Ga−N and Cl−Ga−Cl angles are 158.2(1) and 110.01(8)° respectively. Furthermore, both Ga−Cl bond lengths are 2.189(2) Å; the Ga−N distances are 2.359(4) and 2.351(4) Å and Ga−C is 1.924(4) Å.

When **403** was reacted with Li_2PSiPh_3, **404** (mp 234−237 °C) was obtained (Scheme 157); it was

Scheme 157

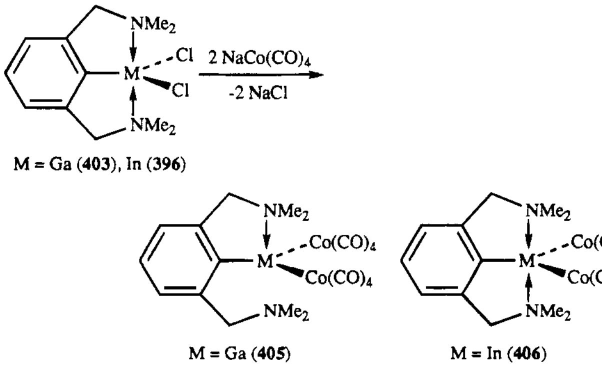


identified by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and its crystal structure, which showed the compound to be a dimer with a center of symmetry. In the central planar Ga_2P_2 moiety, the P−Ga−P angle is 94.25(5)° and the Ga−P−Ga angle is 85.75(5)°. The Ga−P bond length is with 2.338(1) Å more than 0.1 Å shorter than in other dimeric or trimeric RR′GaPR″R‴ compounds; it was suggested that this results from a small contribution of dative P−Ga π-bonding.[202]

Each gallium atom is tetracoordinated, as only one of the dimethylamino groups of each ligand is coordinating. The Ga−N and Ga−C distances are 2.139(4) and 1.982(4) Å and the P−Ga−C and P−Ga−N and C−Ga−N angles are 129.4(1), 119.1(1), and 84.2(2)°, respectively. From the ^{1}H and ^{13}C NMR spectra, it was concluded that rapid exchange occurs between coordinating and free NMe_2 groups. In EI and CI mass spectra above 130 °C, **404** was observed as a monomeric species.

Compounds **396** and **403** were used to synthesize the intermetallic derivatives $[\{(2,6\text{-}Me_2NCH_2)_2C_6H_3\}M\{Co(CO)_4\}_2]$ [M = Ga (**405**); M = In (**406**); Scheme 158].[203] The metathetical reaction of **403** with $NaCo(CO)_4$ in Et_2O afforded the corresponding bis(tetracarbonyl) cobalt derivative **405**. The CI-MS of **405** exhibits a molecular ion at m/z 603 $[M + 1]^{\bullet +}$. X-ray analysis revealed that only one of the dimethylamine groups is coordinated to gallium and as a consequence the $CGaCo_2$ moiety is trigonal pyramidal. The gallium positions are disordered and there are two isomers in the unit cell. The Ga−N bond distances [2.405(10) and 2.394(17) Å in the major (67%) and minor (33%) isomers] are considerably larger than those in other amine−gallane adducts. The Ga−C distance is 1.983(14) Å and the Ga−Co distances are 2.602(16) and 2.536(19) Å.

Scheme 158

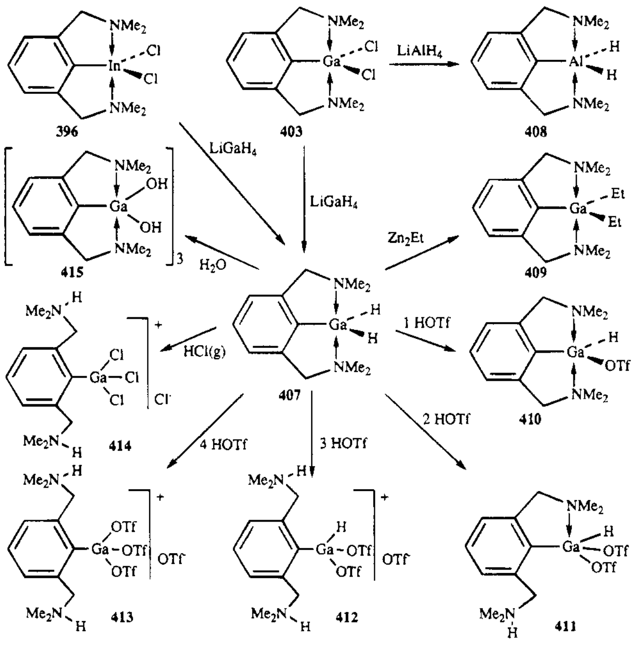


Treatment of the analogous organoindium dichloride **396** with 2 equiv of $NaCo(CO)_4$ in Et_2O afforded the intermetallic derivative **406**.[203] The special properties of **406** are very similar to those of **405**. However, interestingly, the X-ray crystal structure revealed that in contrast to **405**, the group 13 element is pentacoordinate in a distorted trigonal bipyramid. Although the $ClInCo_2$ unit is planar, the axial N−In−N angle [143.1(2)°] departs considerably from the ideal trigonal bipyramidal value of 180°. The In−N bond distances are unusually long [2.702(5) and 2.711(5) Å], implying a weak In−N dative interaction. The In−C distance is 2.158(6) Å and the In-Co distances are 2.674(1) and 2.679(1) Å. As there is no vacant 5p orbital available on indium, significant Co−In multiple bonding is precluded.

In an added note it is reported that the compound $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}In\{Mn(CO)_5\}_2]$ has been prepared and characterized by X-ray crystallography.[203] One of the dimethylamine groups is coordinated to indium, with a pyramidal $ClInMn_2$ moiety which shows an average In−Mn bond distance of 2.761(4) Å.

Gallium dihydride **407** was prepared via the reaction of the corresponding gallium dichloride **403** with $LiGaH_4$ (Scheme 159).[204] Interestingly, the reaction of **403** with $LiAlH_4$ results in transmetalation with formation of the corresponding aluminum dihydride (**408**). Moreover, treatment of the indium analogue **396** with $LiGaH_4$ gave **407**.

Scheme 159

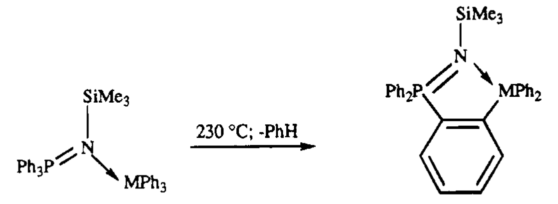


An X-ray analysis revealed that **407** is monomeric in the solid state and that there are no unusually short intermolecular contacts. The coordination sphere of gallium comprises a distorted trigonal bipyramid in which the axial sites are occupied by two nitrogen atoms and the equatorial sites by the aryl carbon and two hydride ligands. The hydride ligands were detected in the final difference map.

Compound **407** is remarkably stable and survives attempted photolysis (254 nm, Et_2O) and vapor-phase heating (350 °C). Nevertheless, **407** exhibits a diverse reactivity. Thus, reaction with Et_2Zn converts **407** quantitatively into the diethyl analogue [2,6-$(Me_2NCH_2)C_6H_3$]$GaEt_2$ (**409**), which was characterized by NMR and mass spectrometry. The hydride reactivity of **407** was explored further by treatment with four successive equivalents of trifluoroacetic acid (HOTf, Scheme 159). Interestingly, the first equivalent of HOTf attacks a Ga−H bond to produce **410** in preference to quaternizing a Me_2N group. As a result of the introduction of an electron-withdrawing substituent into the coordination sphere, the hydridic character of the remaining Ga−H bond is severely reduced. Accordingly, the second equivalent of HOTf quaternizes one of the Me_2N groups, leaving the Ga−H bond intact (**411**). Likewise, the third equivalent of HOTf quaternizes the remaining Me_2N moiety to form **412** and it is only the fourth equivalent of HOTf that protonates the final Ga−H and affords **413** (Scheme 159). The analogous tetrachloro compound **414** was obtained by reaction of **407** with excess of HCl. The X-ray crystal structures of **412** and **414** show that there is no intramolecular coordination occurring by the quaternized nitrogen atoms. Finally, aqueous hydrolysis of **407** affords **415**, the first example of a bis(hydroxide) gallium. Compound **415** was characterized on the basis of spectroscopic data and by X-ray analysis. The solid state of **415** consists of an extensively hydrogen-bonded network which features layers of gallium bis(hydroxide) complexes sandwiching a layer of water molecules. Both nitrogens are coordinated to gallium, but details about distances or angles are not available.[204]

Exactly one equivalent of benzene is eliminated during the thermolysis of triphenylaluminum and -gallium adducts of [(trimethylsilyl)imino]triphenylphosphorane at 230 °C (**416A** and **417A** respectively, Scheme 160).[205]

Scheme 160

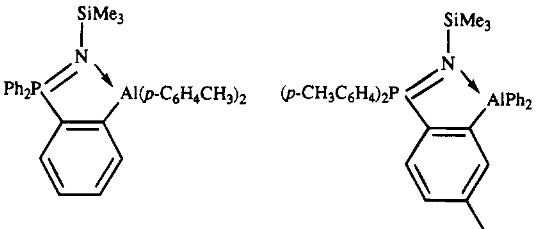


M = Al (**416A**), Ga (**417A**)

M = Al (**416**), Ga (**417**)

From the compositions and the properties of the products **416** and **417**, it was concluded that IC occurs by formation of heterocyclic five-membered chelate rings. When the phenyl groups in **416A** were replaced by tolyl groups, either at aluminum or at phosphorus, it was observed that toluene or benzene was eliminated, respectively, to form **418** or **419** (Scheme 161). This means that the eliminated aromatic group stems from the metal and that the reaction can be considered to be an orthometalation of a phosphorus-bound aryl group.

Scheme 161

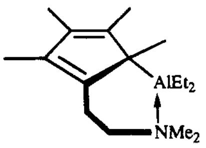


418

419

Lithiation of 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadiene and subsequent reaction with a stoichiometric amount of Et_2AlCl in THF yielded (η^1:η^1-$C_5Me_4CH_2CH_2NMe_2$)$AlEt_2$ (**420**, Scheme 162).[78] As a result of intramolecular nitrogen coordination **420** is monomeric in solution as well as in the solid state as was determined by cryoscopy and X-ray crystallography, respectively.

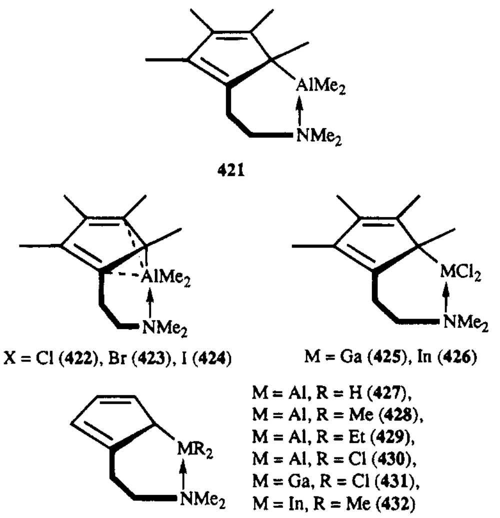
Scheme 162



420

In a recent preliminary communication, the syntheses of cyclopentadienyl complexes containing the polydentate $C_5R_4CH_2CH_2NMe_2$ ligands (R = H, Me) and group 13 elements (Al, Ga, In) were described (Scheme 163).[206]

Scheme 163



421

X = Cl (**422**), Br (**423**), I (**424**)

M = Ga (**425**), In (**426**)

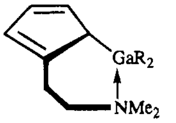
M = Al, R = H (**427**),
M = Al, R = Me (**428**),
M = Al, R = Et (**429**),
M = Al, R = Cl (**430**),
M = Ga, R = Cl (**431**),
M = In, R = Me (**432**)

By reacting the lithium salt $LiC_5Me_4(CH_2)_2NMe_2$ with a stoichiometric amount of Me_2AlCl or AlX_3 (X = Cl, Br, I) in Et_2O, the compounds (η^1:η^1-$C_5Me_4(CH_2)_2$-NMe_2)$AlMe_2$ (**421**) and ($\eta^{2/3}$:η^1-$C_5Me_4(CH_2)_2NMe_2$)-AlX_2 [X = Cl (**422**), Br (**423**), I (**424**)] were obtained in high yield. In **421-424** the presence of intramolecular nitrogen coordination was proven by NMR, X-ray diffraction (**421** and **423**; no specific information given), and by their behavior toward donor solvents. Reaction of $LiC_5Me_4(CH_2)_2NMe_2$ with MCl_3 (M = Ga, In) yields the compounds (η^1:η^1-$C_5Me_4(CH_2)_2$-NMe_2)MCl_2 [M = Ga (**425**), In (**426**)]. Their structures are comparable to those of **421**. The X-ray crystal structure of **426** was determined, but again no details were given. All compounds **421-426** are solids, which show a remarkable stability toward air.

Similar results were reported for the nonmethylated $C_5H_4(CH_2)_2NMe_2$ ligand. Reaction of $C_5H_5(CH_2)_2NMe_2$ with $H_3Al{\cdot}(Et_2O)_n$ leads to an adduct of both reagents which, after heating for several hours in n-hexane, yields the first cyclopentadienyl aluminane (η^1:η^1-$C_5H_4(CH_2)_2NMe_2$)AlH_2 (**427**) under H_2 elimination and C−C coupling. Reaction of $LiC_5H_4(CH_2)_2NMe_2$ with R_2AlCl (M = Al, Ga) yields the compounds (η^1:η^1-$C_5H_4(CH_2)_2NMe_2$)AlR_2 [R = Me (**428**), Et (**429**)] and (η^1:η^1-$C_5H_4(CH_2)_2NMe_2$)MCl_2 [M = Al (**430**), Ga (**431**)]. Reaction of the free $C_5H_5(CH_2)_2NMe_2$ with Me_3In in toluene yields (η^1:η^1-$C_5H_4(CH_2)_2NMe_2$)$InMe_2$ (**432**) under formation of methane. Crystal structures of the air and moisture-sensitive compounds **427-431** revealed the presence of intramolecular coordination (no additional details given). For compounds **421-431**, the chemical shifts of the N-bound methyl and methylene protons show a significant downfield shift ($\Delta\delta$ = 0.14 − 0.59 ppm) in the ^1H NMR spectrum, indicating the presence of IC in solution.

The compounds ($C_5H_4CH_2CH_2NMe_2$)GaR_2 [R = Br (**433**), Me (**434**), H (**435**)] were obtained in good yields from $GaBr_3$, Me_2GaCl, H_2GaCl, and the lithium or potassium salt of the cyclopentadiene (Scheme 164).[207]

Scheme 164



R = Br (**433**), Me (**434**), H (**435**)

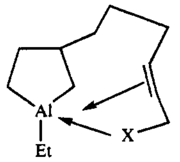
They show intramolecular coordination by the nitrogen atom in the side chain.

Compounds **434** and **435** were characterized by X-ray crystallography, but no details about the structures are given. The chemical shifts of the methyl and methylene protons neighboring the nitrogen center, show a significant low-field shift ($\Delta\delta$ = 0.22 − 0.55 ppm), caused by intramolecular coordination. Their monomeric structures, sufficiently high volatilities and well-behaved fragmentation make them potential candidates for MOCVD.

3. Seven-Membered and Larger Rings

Cyclometalation of 2,7-octadiene derivatives $CH_2{=}CH(CH_2)_3CH{=}CHCH_2X$ (X = NEt_2, OMe, OH, SBu) with $AlEt_3$ in the presence of catalytic amounts of Cp_2ZrCl_2, was reported (Scheme 165).[208] IC in aluminacyclopentanes **436-439** was inferred from ^{13}C NMR data. In situ reactions of **436-439** with S_8 afforded the corresponding tetrahydrothiophenes, in which aluminum had been replaced by sulfur, in 31−68% yield.

Scheme 165

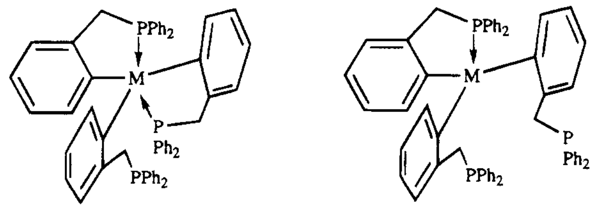


X = NEt_2 (**436**), OMe (**437**), OH (**438**), SBu (**439**)

B. Group 13 Metal Complexes with Phosphorus Donor Atoms

To our knowledge one example of a group 13 IC compound with phosphorus donor atoms for each of the elements Al, Ga, In, and Tl has been reported. The Al, Ga, and In complexes $M[o\text{-}(Ph_2PCH_2)C_6H_4]_3$ [M = Al (**440**), Ga (**441**), In (**442**)], were obtained from MCl_3 and the lithiated ligand in diethyl ether (Scheme 166) in 63−80% yield.[209,210] $Tl[o\text{-}(Ph_2PCH_2)C_6H_4]_3$ (**443**) was prepared from TlCl by a disproportionation reaction. Tl(I) species containing the P ligand were not detected.

Scheme 166



M = Al (**440**), In (**442**) M = Ga (**441**), Tl (**443**)

$Al[o\text{-}(Ph_2PCH_2)C_6H_4]_3$ (**440**) is the first triorganoaluminum bis(phosphine) adduct where C_3P_2 pentacoordination was definitely proven for both the solution and the solid state. ^{27}Al NMR spectroscopy reveals a pentacoordinated aluminum center (at T = 368 K; $\delta(^{27}Al)$ = 131 ppm, $\omega_{1/2}$ = 12 kHz). In the ^{31}P NMR spectrum a single line is observed, the chemical shift of which is temperature dependent; it shifts from −13.5 ppm at 310 K to −14.2 ppm at 243 K. At T = 193 K this resonance signal splits into two groups of signals with an integral ratio of 1:2, which is indicative of the presence of two different types of phosphorus atoms in **440**. An X-ray structure analysis revealed a trigonal-bipyramidal coordination at aluminum with a donor set comprised of three carbon atoms in the equatorial plane and two of the three phosphino functions in axial positions. The Al−P bonds [2.676(3) and 2.782(2) Å] are exceedingly long for which no precedent is found in the literature; normally Al−P bond lengths in phosphine adducts of aluminum alkyls with coordination number 4 typically range between 2.4 and 2.6 Å. The third phosphine is hanging free. Slight deviations from an ideal trigonal-bipyramidal geometry may be accounted for by the five-membered ring formation, in particular the P−Al−C_{ipso} intraring angles [79.2(2)/76.8(2)°] and also the P−Al−P angle which deviates noticeably from linearity [164.8(1)°].

Like **440**, the heavier congeners **441-443** are stereochemically nonrigid molecules in solution. Surprisingly, in the solid state only the indium compound **442** resembles the aluminum complex [C_3P_2 pentacoordination; In−P1 2.845(1) Å; In−P2 2.925(1) Å; P1−In−P2 163.6(1)°] while the gallium compound **441** and the thallium compound **443** contain tetracoordinate metal centers [C_3P; Ga−P1 2.553(2) Å; Tl−P1 2.795(1) Å]. This may be rationalized by the noticeably less polar Ga−P bonds as compared to Al−P and In−P bonds, while in **443** the span of the ligand is not sufficient to allow for chelating coordination at a penta- (or hexa-) coordinate thallium center.

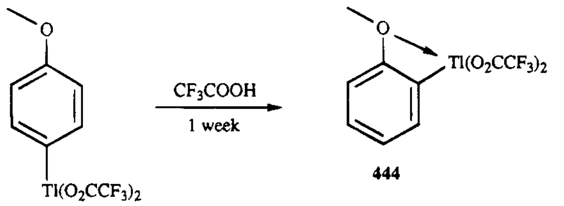
The geometry around gallium and thallium is remarkable. In both cases, the metal and the three C-atoms bound to it are almost in one plane (sum of the three C−Ga−C angles is 355.7° and of the three C−Tl−C angles is 354.8°). With the coordinated phosphorus atom, the coordination around gallium and thallium is nearly trigonal pyramidal. Apparently, the rehybridization from sp^2 to sp^3 upon coordination is hardly developed.

C. Group 13 Metal Complexes with Oxygen Donor Atoms

Although many group 13 organometallic complexes with intermolecularly coordinating oxygen donors are known, only two IC compounds of group 13 elements with oxygen donor atoms have been reported. Very recently a third example was prepared in our group.

Reaction of an equimolar amount of $Tl(O_2CCF_3)_3$ and anisole in trifluoroacetic acid for a week at room temperature, followed by a quench with iodine, resulted in the formation of monoiodoanisole (59%; *ortho*/*meta*/*para* = 79:0:21) and 2,4-diiodoanisole (13%). Thallation at −25 °C over 15 min and subsequent quench resulted in the formation of monoiodoanisole (75%; *ortho*/*meta*/*para* = 7:0:93).[211] Obviously, the initially formed *para* isomer rearranges to the IC stabilized *ortho* isomer (**444**; Scheme 167).

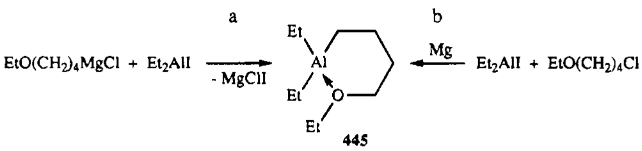
Scheme 167



444

(4-Ethoxybutyl)diethylaluminum (**445**) was synthesized via two different routes: (a) the Grignard compound 1-(chloromagnesio)-4-ethoxybutane was reacted with Et_2AlI, and (b) magnesium was added to a precomplex which is formed in the exothermic reaction of Et_2AlI with 1-chloro-4-ethoxybutane (Scheme 168).[1]

Scheme 168

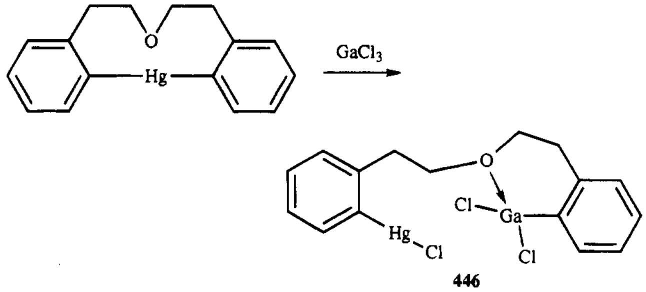


445

Cryoscopy revealed **445** to be monomeric in benzene. “Ätherabblasversuche” indicated **445** to be coordinatively saturated; it is a colorless, strong smelling liquid.

Very recently, the 3-oxa-1,5-diphenylpentane ligand was used in our laboratory in an attempt to synthesize an intramolecularly coordinated diarylgallium compound from the corresponding cyclic diarylmercury. However, the reaction stopped “half-way”: the gallium center reacted at one aromatic ring, while mercury stayed bound to the other. The X-ray crystal structure determination showed the product to be **446** (Scheme 169).[212]

Scheme 169

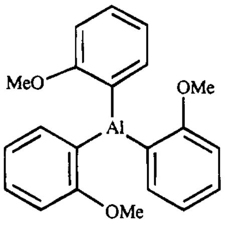


446

The gallium center is coordinated in a distorted tetrahedral fashion, with a small O−Ga−C angle (96.7°) due to the formation of a six-membered chelate ring. The IC bond between oxygen and gallium (2.038 Å) is the first of its kind. The Ga−C bond distance of 1.931 Å and the Ga−Cl distances of 2.180 and 2.160 Å are normal.

The presence of IC in tri-2-anisylaluminum (**447**)[213] has not been investigated (Scheme 170).

Scheme 170

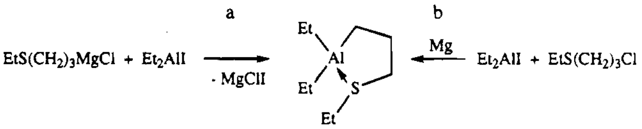


447

D. Group 13 Metal Complexes with Sulfur Donor Atoms

Only one example of a group 13 organometallic compound with sulfur IC has been reported. [3-(Ethylthio)propyl]diethylaluminum (**448**; Scheme 171)

Scheme 171



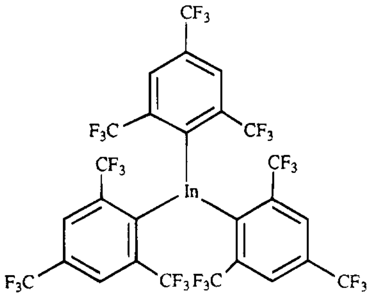
448

was also synthesized via the routes described for **445** (cf. Scheme 168), using dimethyl sulfide as the solvent.[214] Even at −80 °C, **448** is a liquid. “Ätherabblasversuche” indicated **448** to be coordinatively saturated (facile and complete removal of Me_2S).

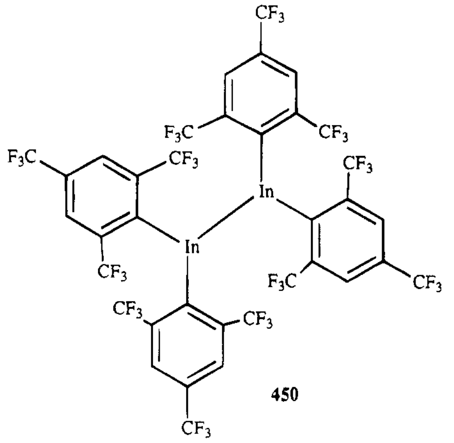
E. Group 13 Metal Complexes with Halogen Donor Atoms

Two indium compounds $[2,4,6\text{-}(CF_3)_3C_6H_2]_3In$ (**449**) and $\{[2,4,6\text{-}(CF_3)_3C_6H_2]_2In\}_2$ (**450**) showing weak In−F interactions were reported (Scheme 172).[215] The short In−F interactions in **449** are 2.772(7), 2.775(6), 2.776(6), 2.798(5), 2.734(7), and 2.727(7) Å; in **450**, they are 2.885(10), 2.801(10), 2.837(10), 2.840(11), 2.848(8), 2.866(8), 2.957(13), and 2.816(10) Å.

Scheme 172



M = In (**449**), Ga (**451**)



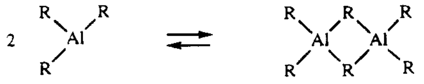
450

Recently, the gallium analogue of **449**, tris[2,4,6-tris(trifluoromethyl)phenyl]gallium (**451**) was reported (Scheme 172).[216] Compound **451** crystallizes as a monomer with two molecules in the unit cell. There are no short intermolecular contacts. The structure is isomorphous with that of **449**. The R_F ligands are arranged in a propeller-like fashion around the gallium center with twist angles of 54.7, 47.4, and 47.0° for the three ligands. In this conformation one o-CF_3 group of an aryl ring is placed above and one below the gallium atom in an overall trigonal-prismatic fashion. The Ga−F contacts in the secondary coordination sphere render the Ga atom nonacoordinate. Six intramolecular Ga−F contacts (one for each CF_3 group) fall in the range 2.665(19)−2.844(16) and thus are shorter than the sum of the van der Waals radii (3.45 Å).[217] The average Ga−C bond length of 2.001(5) Å is slightly longer than in the unfluorinated tris(aryl) compounds $(Mes)_3Ga$ [1.968(4) Å][218] and $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3Ga$ [1.972(11) Å],[219] probably due to the larger steric demands of the R_F substituent. Attempts to observe $^{19}F-^{71}Ga$ couplings in the ^{19}F NMR spectra were not successful.

F. Group 13 Metal Complexes with π-Donors

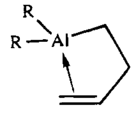
It is well known that organoaluminum compounds AlR_3 have a high tendency to dimerize;[220] in this way, the electron deficiency of the metal is reduced through the formation of two-electron three-center bonds involving μ-bridging R groups (Scheme 173).

Scheme 173

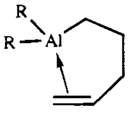


The molecular weights of tri-n-butyl-, tri-n-pentyl-, tri-1-but-3-enyl- (**452**), and tri-1-pent-4-enylaluminum (**453**) were determined by cryoscopy in cyclohexane.[221]

Scheme 174



452



453

The equilibrium represented in Scheme 173 shifts to the monomeric side when an olefinic functionality is incorporated in the alkyl chain as in **452** and **453**, which can be explained by the occurrence of IC as indicated in Scheme 174: the π-electrons compete with the μ-bridging R groups for the Lewis acidic metal center.

VI. References

(1) Bähr, G.; Müller, G. E. *Chem. Ber.* **1955**, *88*, 251.
(2) Prokof'ev, A. K.; Bregadze, V. I.; Ohklobystin, O. Yu. *Uspekhi Khimii* **1970**, *39*, 412; *Russ. Chem. Rev.* **1970**, *39*, 197.
(3) Prokof'ev, A. K. *Uspekhi Khimii* **1976**, *45*, 1028; *Russ. Chem. Rev.* **1976**, *45*, 519.
(4) Omae, I. *Chem. Rev.* **1979**, *79*, 287.
(5) Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235.
(6) Omae, I. *Coord. Chem. Rev.* **1979**, *28*, 97.
(7) Omae, I. *Coord. Chem. Rev.* **1982**, *42*, 245.
(8) Omae, I. *Angew. Chem.* **1982**, *94*, 902.
(9) Omae, I. In *Organometallic Intramolecular-coordination Compounds*; Elsevier: Amsterdam, 1986.
(10) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Angew. Chem.* **1988**, *100*, 1143.
(11) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1991**, *10*, 3826.
(12) Gruter, G. J. M.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 425.
(13) Nefedov, O. M.; D'yachenko, A. I.; Prokov'ef, A. K. *Uspekhi Khimii* **1977**, *46*, 1787; *Russ. Chem. Rev.* **1977**, *46*, 941.
(14) Haaland, A. *Angew. Chem.* **1989**, *101*, 1017.
(15) Chakrabarti, P.; Dunitz, J. D. *Helv. Chim. Acta* **1982**, *65*, 1482.
(16) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem.* **1991**, *32*, 147.
(17) Gruter, G. J. M. To be published.
(18) Bell, N. A. In *Comprehensive organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 3, p 122.
(19) Bähr, G.; Thiele, K.-H. *Chem. Ber.* **1957**, *90*, 1578.
(20) Coates, G. E.; Huck, N. D. *J. Chem. Soc.* **1952**, 4501.
(21) Andersen, R. A.; Coates, G. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1171.
(22) Pajerski, A. D.; BergStresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4844.
(23) Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1971**, *28*, 5.
(24) Cockerill; Harrison. In *The Chemistry of Functional groups, Supplement A*; Patai, Ed.; Wiley: New York, 1977; Part 1, pp 158−178.
(25) von Braun, J.; Heider, K.; Müller, E. *Chem. Ber.* **1917**, *50*, 1637.
(26) Gilman, H.; Heck, L. L. *Chem. Ber.* **1929**, *62*, 1379.
(27) Nesmeyanov, A. N.; Freidlina, R. Kh.; Kan, E. I. *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1950**, 531.
(28) Ficini, J.; Sarrade-Loucheur, G.; Normant, H. *Bull. Soc. Chim. Fr.* **1962**, 1219.
(29) Steinborn, D. *J. Organomet. Chem.* **1979**, *182*, 313.
(30) Ficini, J.; Depezay, J. C. *Tetrahedron Lett.* **1969**, 4795.
(31) Henderson, M. J.; Papasergio, R. I.; Raston, C. L.; White, A. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1986**, 672.
(32) Lindsell, W. E. In *Comprehensive organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 4, pp 163−164.
(33) Normant, H. *Pure Appl. Chem.* **1972**, 30.
(34) Sadet, J.; Rumpf, P. *Bull. Soc. Chim. Fr.* **1973**, 2016.
(35) Rumpf, P. *C. R. Acad. Sci.* **1962**, *254*, 3105.
(36) von Braun, J.; Kirschbaum, G. *Ber.* **1919**, *52*, 1725.
(37) Marxer, A. *Helv. Chim. Acta* **1941**, *24*, 209; E; U. S. P., 2.411, 664, 1946.
(38) Perrine, T. D.; Sargent, L. *J. Org. Chem.* **1949**, *14*, 583.
(39) Angermund, J.; Bogdanovic, B.; Koppetsch, G.; Krüger, C.; Mynott, R.; Schwickardi, M.; Tsay, Y.-H. *Z. Naturforsch.* **1986**, *41B*, 455.

(40) Schlenk, W.; Schlenk, W., Jr. *Chem. Ber.* **1929**, *62*, 920.
(41) Bogdanovic, B.; Koppetsch, G.; Krüger, C.; Mynott, R. *Z. Naturforsch.* **1986**, *41B*, 617.
(42) Moseley, P. T.; Shearer, H. M. M. *J. Am. Chem. Soc.* **1968**, *97*, 3162.
(43) Weiss, E. *J. Organomet. Chem.* **1964**, *2*, 314; *J. Organomet. Chem.* **1965**, *4*, 101.
(44) Some representative references are: (a) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Verhoeckx, G. J.; Spek, A. L.; Kroon, J. *J. Chem. Soc., Dalton Trans.* **1980**, 1352. (b) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; Zoutberg, M. C.; Heijdenrijk, D. *Organometallics* **1989**, *8*, 1373.
(45) Jones, F. N.; Hauser, C. R. *J. Org. Chem.* **1962**, *27*, 701.
(46) Markies, P. R.; Altink, R. M.; Villena, A.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1991**, *402*, 289.
(47) Luckenbach, R.; Lorenz, K. *Z. Naturforsch.* **1977**, *32B*, 1038.
(48) Jurkschat, K.; Abicht, H.-P.; Tzschach, A.; Mahieu, B. *J. Organomet. Chem.* **1986**, *309*, C47.
(49) Jurkschat, K.; Abicht, H.-P. *Z. Anorg. Allg. Chem.* **1985**, *25*, 338.
(50) Pape, A; Lutz, M; Müller, G. *Angew. Chem.* **1994**, *106*, 2375.
(51) Grootveld, H. H.; Blomberg, C.; Bickelhaupt, F. *Tetrahedron Lett.* **1971**, *22*, 1999.
(52) Villena, A. Thesis, Free University, Amsterdam, The Netherlands, 1982.
(53) Freijee, F. M. J. Thesis, Free University, Amsterdam, The Netherlands, 1981.
(54) Markies, P. R.; Schat, G.; Villena, A.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1991**, *411*, 291.
(55) van Vulpen, A.; Coops, J. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 203.
(56) Freijee, F. J. M.; van der Wal, G.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1982**, *240*, 229.
(57) Schröder, F. A. *Chem. Ber.* **1969**, *102*, 2035.
(58) Sarma, R.; Ramirez, F.; McKeefer, B.; Chaw, Y. F.; Marecek, J. F.; Nierman, D.; McCaffrey, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 5289.
(59) Beruben, D.; Marek, I.; Labaudinière, L.; Normant, J. F. *Tetrahedron Lett.* **1993**, *34*, 2303.
(60) Markies, P. R.; Schat, G.; Griffioen, S.; Villena, A.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1991**, *10*, 1531.
(61) Seebach, D.; Hansen, J.; Seiler, P.; Gromek, J. M. *J. Organomet. Chem.* **1985**, *285*, 1.
(62) Beak, P.; Brubaker, G. R.; Farney, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 3621.
(63) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275.
(64) Reitz, D. B.; Beak, P.; Tse, A. *J. Org. Chem.* **1981**, *46*, 4317.
(65) Beak, P.; Zaidel, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 1010.
(66) Benn, R.; Bogdanovic, B.; Brüning, M.; Grondey, H.; Herrmann, W.; Kinzelmann, H.-G.; Seevogel, K. *Chem. Ber.* **1993**, *126*, 225.
(67) Bogdanovic, B.; Liao, S.; Mynott, R.; Schlichte, K.; Westeppe, U. *Chem. Ber.* **1984**, *117*, 1378.
(68) Bartmann, E.; Bogdanovic, B.; Janke, N.; Liao, S.; Schlichte, K.; Spliethoff, B.; Treber, J.; Westeppe, U.; Wilczok, U. *Chem. Ber.* **1990**, *123*, 1517.
(69) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4284.
(70) Markies, P. R.; Villena A.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1993**, *463*, 7.
(71) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4845.
(72) Gruter, G. J. M. To be published.
(73) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1991**, *10*, 3538.
(74) Gruter, G. J. M.; van Klink, G. P. M.; Heropoulos, G. A.; Akkerman, O. S.; Bickelhaupt, F. *Organometallics* **1991**, *10*, 2535.
(75) Gruter, G. J. M.; van Klink, G. P. M.; Akkerman, O. S.; Bickelhaupt, F. *Organometallics* **1993**, *12*, 1180.
(76) Markies, P. R. Thesis, Free University, Amsterdam, The Netherlands, 1990.
(77) Gruter, G. J. M. To be published.
(78) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, *450*, C1.
(79) Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B. *Chem. Ber.* **1982**, *115*, 3290.
(80) Schmidbaur, H.; Deschler, U.; Seyferth, D. *Z. Naturforsch.* **1982**, *37B*, 950.
(81) Rees, W. S., Jr.; Dippel, K. A. In *Chemical Processing of advanced materials*; Hench, L. L., West, J. K., Eds.; Wiley: New York, 1992; p 327.
(82) Rees, W. S., Jr.; Lay, U. W.; Dippel, K. A. *J. Organomet. Chem.* **1994**, *483*, 27.
(83) Dekker, J.; Boersma, J.; Fernholt, L.; Haaland, A.; Spek, A. L. *Organometallics* **1987**, *6*, 1202.
(84) Boersma, J. In *Comprehensive organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol, 2, p 830.
(85) Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1962**, *319*, 183.
(86) Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 1803.
(87) Boersma, J.; Fernholt, L.; Haaland, A. *Acta Chem. Scand.* **1984**, *A38*, 523.
(88) Haaland, A.; Hedberg, K.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 1972.
(89) Reimann, C. W.; Block, S.; Perloff, A. *Inorg. Chem.* **1966**, *5*, 1185.
(90) Preston, H. S.; Kennard, C. H. L. *J. Chem. Soc., Chem. Commun.* **1967**, 708.
(91) Kunchur, N. R.; Truter, M. R. *J. Chem. Soc.* **1958**, 3478.
(92) Bell, N. A.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1182.
(93) Kuz'mina, L. G.; Struchkov, Y. T. *Croat. Chem. Acta* **1984**, *57*, 701.
(94) Raston, C. L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 537.
(95) Eaborn, C.; Retta, N.; Smith, J. D. *J. Organomet. Chem.* **1980**, *190*, 101.
(96) Ding, K.; Yangjie, W.; Hongwen, H.; Lianfang, S.; Xin, W. *Organometallics* **1992**, *11*, 3849.
(97) Kuz'mina, L. G.; Struchkov, Y. T.; Lemenovsky, D. A.; Urasovsky, I. F.; Nifant'ev, I. E.; Perevalova, E. G. *Koord. Khim.* **1983**, *9*, 1212.
(98) Huo, S. Q.; Wu, Y. J.; Zhu, Y.; Yang, L. *J. Organomet. Chem.* **1994**, *470*, 17.
(99) Constable, E. C.; Leese, T. A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1989**, 570.
(100) Black, D. St. C.; Deacon, G. B.; Edwards, G. L.; Gatehouse, B. M. *Aust. J. Chem.* **1993**, *46*, 1323.
(101) Chan, C. W.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **1994**, *33*, 3656.
(102) van der Ploeg, A. F. M. J.; van der Kolk, C. E. M.; van Koten, G. *J. Organomet. Chem.* **1981**, *212*, 283.
(103) Atwood, J. L.; Berry, D. E.; Stobart, S. R.; Zaworotko, M. J. *Inorg. Chem.* **1983**, *22*, 3480.
(104) Grdenic, D. *Q. Rev., Chem. Soc.* **1965**, *19*, 303.
(105) Dean, P. A. W. *Prog. Inorg. Chem.* **1978**, *24*, 109.
(106) Osman, A.; Steevensz, R. G.; Tuck, D. G.; Meinema, H. A.; Noltes, J. G. *Can. J. Chem.* **1984**, *62*, 1698.
(107) van Koten, G.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1976**, *118*, 183.
(108) van der Wal, W. F. J.; van der Wal, H. R. *J. Organomet. Chem.* **1978**, *153*, 335.
(109) Khan, M.; Steevensz, R. C.; Tuck, D. G.; Noltes, J. G.; Corfield, P. W. R. *Inorg. Chem.* **1980**, *19*, 3407.
(110) van der Schaaf, P. A.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 4334.
(111) Abbenhuis, H. C. L.; van Belzen R.; Grove, D. M.; Klomp, A. J. A.; van Mier, G. P. M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 210.
(112) Budzelaar, P. H. M.; Alberts-Jansen, H. J.; Mollema, K.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *J. Organomet. Chem.* **1983**, *243*, 137.
(113) Hofstee, H. K.; Boersma, J.; van der Meulen, J. D.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *153*, 245.
(114) Thiele *et al.* report a Δ value of +1.94 for **154**.
(115) Langguth, E.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1985**, *530*, 69.
(116) Lippmaa, E.; Pehk, T.; Past, J. *Eesti NSV Tead Akad. Toim Fuus. Mat.* **1967**, *16*, 345.
(117) Lippmaa, E.; Pehk, T. *Kem. Teollisuus* **1967**, *24*, 1001.
(118) Stothers, J. B. In *Carbon-13 NMR spectroscopy*; Academic Press: New York, 1972; p 60.
(119) Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaka Press, NY, 1960; p 246.
(120) Thiele, K.-H.; Langguth, E.; Müller, G. E. *Z. Anorg. Allg. Chem.* **1980**, *462*, 152.
(121) Boersma, J.; Noltes, J. G. In *Organozinc coordination Chemistry*; Grafisch Bedrigf Schotarius u. Jens: Utrecht, 1968.
(122) Moseley, P. T.; Shearer, H. M. M. *J. Chem. Soc., Chem. Commun.* **1966**, 876.
(123) Butler, I. S.; Newburg, N. L. *Spectrochim. Acta* **1977**, *33A*, 669.
(124) Ustynyuk, Y. A.; Barinov, I. V.; Sirotkina, E. I. *Dokl. Akad. Nauk SSSR* **1969**, *187*, 112.
(125) Cross, R. J.; Tennent, N. H. *J. Organomet. Chem.* **1973**, *61*, 33.
(126) Ukai, T.; Ito, Y. *J. Pharm. Soc. Jpn.* **1953**, *73*, 821; *Chem. Abstr.* **1954**, *48*, 9945*i*.
(127) Roling, P. V.; Dill, J. L.; Rausch, M. D. *J. Organomet. Chem.* **1974**, *69*, C33.
(128) Roling, P. V.; Kirt, D. D.; Dill, J. L.; Hall, S.; Hollstrom, C. *J. Organomet. Chem.* **1976**, *116*, 39.
(129) Roling, P. V.; Pickering, R. A. *J. Organomet. Chem.* **1976**, *122*, 289.
(130) El-Sawi, E.; Moti, F. A.; El-Messary, S. *Bull. Soc. Chim. Belg.* **1985**, *94*, 69.
(131) El-Sawi, E. A.; Ahmed, M. A. *Acta Chim. Hung.* **1987**, *124*, 657.

(132) de Koning, A. J.; van Rijn, P. E.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1979**, *174*, 129.
(133) Okhlobystin, O. Y.; Zakharkin, L. I. *J. Organomet. Chem.* **1965**, *3*, 257.
(134) Dekker, J.; Münninghoff, J. W.; Boersma, J.; Spek, A. L. *Organometallics* **1987**, *6*, 1236.
(135) Kovar, R. F.; Rausch M. D. *J. Organomet. Chem.* **1972**, *35*, 351.
(136) Dietrich, K.; König, K.; Mattern, G.; Musso, H. *Chem. Ber.* **1988**, *121*, 1277.
(137) Al-Juaid, S. S.; Eaborn, C.; Habtemariam, A.; Hitchcock, P. B.; Smith, J. D *J. Organomet. Chem.* **1992**, *437*, 41.
(138) Halfpenny, J.; Small, R. W. H. *J. Chem. Soc., Chem. Commun.* **1979**, 879.
(139) Sawai, H.; Takizawa, T.; Iitaka, Y. *J. Organomet. Chem.* **1976**, *120*, 161.
(140) Cooney, J. M.; Gommans, L. H. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1987**, *336*, 293.
(141) Tanimoto, Y.; Kobayashi, H.; Nagakura, S.; Saito, Y. *Acta Crystallogr. B* **1973**, *29*, 1822.
(142) Thiele, K.-H. *Angew. Chem.* **1959**, *71*, 650.
(143) Thiele, K.-H.; Heinrich, M.; Brüser, W.; Schröder, S. *Z. Anorg. Allg. Chem.* **1977**, *432*, 221.
(144) Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1965**, *337*, 14.
(145) Almond, M. J.; Beer, M. P.; Heath, P.; Heyburn, C. A.; Rice, D. A.; Sheridan, L. A. *J. Organomet. Chem.* **1994**, *469*, 11.
(146) Rieke, R. D. *Top. Curr. Chem.* **1975**, *59*, 1.
(147) Gruter, G. J. M. To be published.
(148) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Spek, A. L *J. Organomet. Chem.* **1992**, *430*, 1.
(149) The longest coordinative bond between zinc and oxygen is 2.88 Å; it was found in the threaded compound formed from diethylzinc and 15-crown-5 and is the average value of coordination to five oxygens![22]
(150) Paulik, F. E.; Green, S. I. E.; Dessy, R. E. *J. Organomet. Chem.* **1965**, *3*, 229.
(151) Bregadze, V. I.; Babushkina, T. A.; Okhlobystin, O. Y.; Semin, G. K. *Teor. Eksp. Khim.* **1967**, *3*, 547; *Chem Abstr.* **1968**, *68*, 100521t.
(152) Kunchur, N. R.; Mathew, M. *J. Chem. Soc., Chem. Commun.* **1966**, 71.
(153) Sipos, J.; Sawatzky, H.; Wright, C. F. *J. Am. Chem. Soc.* **1955**, *77*, 9759.
(154) Kiefer, E. F.; Gericke, W. *J. Am. Chem. Soc.* **1968**, *90*, 5131.
(155) Carr, G. E.; Chambers, R. D.; Holmes, T. F.; Parker, D. G. *J. Organomet. Chem.* **1987**, *325*, 13.
(156) Brooker, S.; Bertel, N.; Stalke, D.; Noltermeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edelmann, F. T. *Organometallics* **1992**, *11*, 192.
(157) Kiefer, E. F.; Waters, W. L.; Carlson, D. A. *J. Am. Chem. Soc.* **1968**, *90*, 5127.
(158) Furmanova, N. G.; Struchkov, Y. T.; Kalinin, V. N.; Ya, B.; Finkelshtein, B. Y.; Zakharkin, L. I. *Zh. Strukt. Khim.* **1980**, *21*, 96.
(159) Goede, S. J.; van Schaik, H.-P.; Bickelhaupt, F. *Organometallics* **1992**, *11*, 3844.
(160) Denis, J. S.; Oliver, J. P.; Dolzine, T. W.; Smart, J. B. *J. Organomet. Chem.* **1974**, *71*, 315.
(161) Almenningen, A.; Helgaker, T. U.; Haaland, A.; Samdal, S. *Acta Chem. Scand.* **1982**, *A 36*, 159.
(162) Whitt, C. D.; Parker, L. M.; Atwood, J. L. *J. Organomet. Chem.* **1971**, *32*, 291.
(163) Fernholt, L.; Haaland, A.; Hargittai, M.; Seip, R.; Weidlein, J. *Acta Chem. Scand.* **1981**, A *35*, 529.
(164) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5362.
(165) Jerius, J. J.; Hahn, J. M.; Rahman, A. F. M. M.; Mols, O.; Ilsley, Oliver, J. P. *Organometallics* **1986**, *5*, 1812.
(166) Rahman, A. F. M. M.; Siddiqui, K. F.; Oliver, J. P. *Organometallics* **1982**, *1*, 881.
(167) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(168) Golubinskaya, L. M.; Golubinskii, A. V.; Mastryukov, V. S.; Vilkov, L. V.; Bregadze, V. I. *J. Organomet. Chem.* **1976**, *117*, C4.
(169) Krause, H.; Sille, K.; Hausen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1982**, *235*, 253.
(170) Tuck, D. G. In *Comprehensive organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 683.
(171) Khan, M. A.; Peppe, C.; Tuck, D. G. *J. Organomet. Chem.* **1985**, *280*, 17.
(172) Veith, M.; Recktenwald, O. *J. Organomet. Chem.* **1984**, *264*, 19.
(173) Arif, A. M.; Bradley, D. C.; Dawes, H.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1987**, 2159.
(174) Gerstner, W.; Schwarz, W.; Hausen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1979**, *175*, 33.
(175) Lecomte, C.; Protas, J.; Cocolios, P.; Guilard, R. *Acta. Crystallogr., B* **1980**, *36*, 2769.
(176) Engelhardt, L. M.; Kynast, U.; Raston, C. L.; White, A. H. *Angew. Chem.* **1987**, *99*, 702.
(177) Atwood, J. L.; Milton, P. A. *J. Organomet. Chem.* **1973**, *52*, 275.
(178) Kynast, U; Skelton, B. W.; White, A. H.; Henderson, M. J.; Raston, C. L. *J. Organomet. Chem.* **1990**, *384*, C1.
(179) Schumann, H.; Hartmann, U.; Wassermann, W. *Polyhedron* **1990**, *9*, 353.
(180) Pohl, L; Hostalek, M.; Schumann, H.; Hartmann, U.; Wassermann, W.; Brauers, A.; Regel, G. K.; Hövel, R.; Balk, P. *J. Cryst. Growth* **1991**, *107*, 309.
(181) Schumann, H.; Seuss, T. D.; Just, O.; Weimann, R.; Hemling, H.; Görlitz, F. H. *J. Organomet. Chem.* **1994**, *479*, 171.
(182) Schumann, H.; Görlitz, F. H.; Seuss, T. D.; Wassermann W. *Chem. Ber.* **1992**, *125*, 3.
(183) Schumann, H.; Seuss, T. D.; Hemling, H. *Eur. J. Solid State Inorg. Chem.* **1992**, *29* (Suppl.), 81.
(184) Schumann, H.; Hartmann, U.; Wassermann, W.; Just, O.; Dietrich, A.; Pohl, L.; Hostalek, M.; Lokai, M. *Chem. Ber.* **1991**, *124*, 1113.
(185) Schumann, H.; Just, O.; Seuss, T. D.; Görlitz, F. H.; Weimann, R. *J. Organomet. Chem.* **1994**, *466*, 5.
(186) Schumann, H.; Just, O.; Seuss, T. D.; Weimann, R. *J. Organomet. Chem.* **1994**, *472*, 15.
(187) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1975**, *53*, 58.
(188) Henderson M. J.; Kennard, C. H. L.; Raston, C. L.; Smith, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1203.
(189) Coggin, D. K.; Fanwick, P. E.; Green, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1127.
(190) Fischer R. A.; Behm, J.; Priermeier, T. *J. Organomet. Chem.* **1992**, *429*, 275.
(191) Fischer, R. A.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *459*, 65.
(192) Fischer, R. A.; Priermeier, T. *Organometallics* **1994**, *13*, 4306.
(193) Gillespie, R. J. *J. Chem. Educ.* **1970**, *47*, 18.
(194) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155.
(195) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1980**, *39*, 253.
(196) Ernst, L. *J. Organomet. Chem.* **1974**, *82*, 319.
(197) Jastrzebski, J. T. B. H.; van Koten, G.; Tuck, D. G.; Meinema, H. A.; Noltes, J. G. *Organometallics* **1982**, *1*, 1492.
(198) Schumann, H.; Hartmann, U.; Wassermann, W.; Dietrich, A.; Görlitz, F. H.; Pohl, L.; Hostalek, M. *Chem. Ber.* **1990**, *123*, 2093.
(199) Schumann, H.; Hartmann, U.; Dietrich, A.; Pickardt, J. *Angew. Chem.* **1988**, *100*, 1119; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1077.
(200) Schumann, H.; Wassermann, W.; Dietrich, A. *J. Organomet. Chem.* **1989**, *365*, 11.
(201) Schumann, H.; Hartmann, U.; Wassermann, W. *Chem. Ber.* **1991**, *124*, 1567.
(202) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Ruiz, J.; Atwood, J. L.; Bott, S. G. *Angew. Chem.* **1990**, *102*, 1169.
(203) Olazábal C. A.; Gabbaï, F. P.; Cowley, A. H.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *Organometallics*, **1994**, *13*, 421.
(204) Cowley, A. H.; Gabbaï, F. P.; Atwood, D. A.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 1559.
(205) Schmidbaur, H.; Wolfsberger, W. *J. Organomet. Chem.* **1969**, *16*, 188.
(206) Jutzi, P.; Dahlhaus, J.; Bangel, M. *J. Organomet. Chem.* **1993**, *460*, C13.
(207) Jutzi, P.; Bangel, M. *J. Organomet. Chem.* **1994**, *480*, C18.
(208) Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P.; Muslukhov, R. R.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 2831; *Chem Abstr.* **1991**, *114*, 164318h.
(209) Müller, G.; Lachmann, J.; Rufinska, A. *Organometallics* **1992**, *11*, 2970.
(210) Müller, G.; Lachmann, J. *Z. Naturforsch.* **1993**, *48 B*, 1544.
(211) Deacon, G. B.; Smith, R. N. M.; Tunaley, D. *J. Organomet. Chem.* **1976**, *114*, C1.
(212) van Klink, G. P. M. To be published.
(213) Nesmeyanov, A. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1942**, 372.
(214) Bähr, G.; Müller, G. E. *Chem. Ber.* **1955**, *88*, 1765.
(215) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070.
(216) Schluter, R. D.; Isom, H. S.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Olbrich, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1994**, *13*, 4058.
(217) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993; p 292.
(218) Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* **1986**, *5*, 1814.
(219) Petrie, M. A.; Power, P. P.; Rasika Dias, H. V.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.
(220) Eisch, J. J. In *Comprehensive organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 6, p 555.
(221) Dolzine, T. W.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 1737.

CR940256L