Review

Some highlights from the development and use of bulky monodentate ligands

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Dedicated to the memory of Colin Eaborn and Ian Rothwell – two colleagues who played key roles in the development of bulky ligands

Abstract

The development of bulky monodentate alkoxide, chalcogenolate (ER, E = S, Se or Te), amide, pnictide (ER$_2$ = N, P, As), alkyl, aryl and silyl ligands is briefly surveyed. These ligands have played a key role in the advancement of the modern organometallic and inorganic chemistry of all the major blocks (s, p, d, and f) of the periodic table. Most importantly, they have permitted numerous new classes of compounds to be isolated and studied. The investigation of steric effects induced by these ligands has led to, inter alia, transition metal alkylidene and alkylidyne complexes, room temperature cleavage of dinitrogen, and a wide range of transition metal and lanthanide complexes with two or three coordination. In addition, their use has sparked a revolution in main group chemistry which has led to the isolation of stable species with bonds and/or oxidation states hitherto unknown in stable compounds.
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1. Introduction

Of the various factors that influence the physical and chemical properties of compounds, those pertaining to the size of the atoms or groups of atoms involved in bonding are, perhaps, the easiest to appreciate. The concept of steric size arose from the necessity to account for chemical behavior and reactivity in terms of the structures of molecules. This need had its origins in the major advances which occurred in organic chemistry in the second half of the 19th century. The connection between steric effects and reactivity was made by several chemists, including Hofmann [1], Kehrmann [2] and Meyer [3] who ascribed difficulties in alkylating triarylamines, changes in the reactivity of substituted quinones, and esterification reactions to steric effects. The term "steric

hindrance" was used by Wegscheider [4] when examining related esterification reactions. Although the idea that steric factors affected chemical reactions and bond dissociation was realized (Conant) [5], it was not until the 1930s and 1940s that a greater knowledge of reaction mechanisms emerged through the work of several groups [6] which led simultaneously to a more detailed understanding of how the course of such reactions are governed by steric factors.

Investigation of the influence of steric factors on inorganic reactions of transition metal complexes developed somewhat later, but it was recognized in the early 1950s by Basolo, Pearson and coworkers and is now widely accepted as a major factor in such transformations [7]. However, this short review will not be concerned with the effects of steric factors on reaction rates and mechanisms. Instead, the focus will be on their influence on structure and bonding as well as the development and use of bulky ligands in inorganic and organometallic

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chemistry. This brief survey is limited to bulky monodentate, uninegative ligands and, for the most part, their homoleptic derivatives. Thus, many important studies involving sterically demanding neutral or chelating ligands such as phosphines, tris(pyrazolyl)borates [8], trisamidoamines [9], bis(phosphine)amides [10], numerous chelating alkyl or aryls, which have led to key advances, will not be discussed. In addition, the often multihapto bulky cyclopentadienyl ligands [11], which have played a central role in the development of transition metal chemistry and low valent main group chemistry, are not treated. Only what appear to be the most prominent developments can be outlined, with an emphasis on the original introduction of the ligands, since a comprehensive treatment would require a series of several volumes to deal with this vast area. No account of the numerous approaches to the quantification of steric effects will be given [12].

2. Bulky alkoxide and aryloxide ligands

The late 1940s and 1950s marked the beginning of a renaissance in inorganic and organometallic chemistry. In transition metal chemistry the ligand field theory was used to account for the bonding in classical transition metal complexes as well as their spectroscopic and magnetic behavior. In most of these complexes there was a preferred coordination number (usually six or four) as well as primary valence (most commonly +2 or +3), which distinguished them from organic and related species. Valence bond theory, as it was then developed, became less widely used, mainly because it did not handle the bonding and magnetic properties of the complexes in a convenient way. As a result, Crystal Field Theory, Ligand Field Theory, and subsequently Molecular Orbital Theory, were developed to rationalize their bonding. However, there did exist many classes of transition metal compounds where the number of ligands and the valence of the metal (if not always the coordination number) did coincide. Examples of these compounds included simple uncomplexed halides and, more importantly for this review, a small number of alkoxide derivatives of first row and early transition metals [13]. The early transition elements, e.g., those of Group 4, were of particular interest because of their stoichiometric relationship to the corresponding main group 14 element derivatives, for example the orthoesters of silicon, germanium or tin, i.e. $E(OR)_4$ (E = Si, Ge or Sn). Thus a comparison of the chemical and physical properties of each class of compound might offer insights to their behavior. Partly for such reasons during the 1950s, the groups of Bradley, Mehrotra, Wardlaw and others investigated the steric and electronic effects of alkoxide ligands in Ti, Zr and Hf derivatives. They reached conclusions that have since been shown to have wide applicability not only for alkoxides of transition metals but for metal alkoxides throughout the periodic table [14]. The dominant feature of metal alkoxides is their tendency to form oligomeric species through alkoxo bridges between two or three metals. Aggregation increases as the metal atom becomes more electron deficient as in the earlier transition metals or in main groups 1, 2 and 13. Aggregation is also increased with increasing size of the metal which permits more bridging. Increasing the size of the alkyl substituent decreases the extent of aggregation, and the steric properties of the R group are of greater importance than its electronic properties in preventing bridging by the OR group. These conclusions were based on extensive studies with a variety of common substituents, for example, OMe, OEt, OPr^n, OPr^i, OBu^i, OBu^s, OBu^t, OAm^n, OAm^i, OAm^t, etc. Bradley further proposed, on the basis of physical measurements, that the preferred structure of $M(OR)_x$ is generally one that allows the metal to retain its preferred coordination number (usually six) with the minimum degree of oligomerization involving the formation μ_2 or μ_3 alkoxo bridges. In this way, the structure of $\{Ti(OEt)_4\}_4$ was predicted correctly [15] prior to its determination by single crystal X-ray diffraction by Ibers [16].

Except in a few cases the 'normal' alkoxo substituents listed above do not permit the isolation of metal alkoxides with metal coordination numbers less than four. Thus, alkoxides of mono, di and trivalent (and many tetravalent) metals necessarily exist as associated species. This is due to the availability of oxygen lone pairs and the fact that alkoxy ligands carry only one organic substituent and are not very crowded. Moreover, the metal is separated from the organic substituent by the interposition of the oxygen atom so that the amount of steric hindrance at the metal is necessarily limited. It is possible to prevent association by introducing donor coligands (although this is difficult with the more associated, less hindered alkoxides) or by modifying the alkoxo ligand to include an electron acceptor in its structure. Nonetheless, for monodentate alkoxides very much larger substituents are required to achieve lower coordination numbers. With few exceptions, the use of very hindered –OR ligands did not occur until the 1980s. Instead, attention focused more on the use of more crowding amide and alkyl or aryl ligands (see below) to obtain low-coordinate or multiply bonded main group and transition metal species. These ligands carry two or three organic groups and are accordingly bulkier than alkoxides. Ironically, the first use of –OR ligands with sufficient bulk to induce low-coordination numbers did not involve alkoxides but commercially available, substituted aryloxides that carry two Bu^t substituents in the 2,6 positions on the aryl rings. Although aryloxides of metals had been known since the 19th century [13b,c] the steric effectiveness of the simplest aryloxo ligand –OPh does not differ greatly from the smaller

alkoxo ligands. In the late 1960s and early 1970s, however, Brown [17] and Corey [18] showed that alkali metal salts of these bulky phenoxides were powerful hindered Brønsted bases. Similarly, in 1972, Andersen and Coates showed that $Be(OC_6H_3-2,6-Bu^t_2)_2$ was monomeric (and by implication had two-coordinate Be) in benzene [19] and a monomeric structure was reported by Mehrotra for $Mg(OC_6H_2-2,6-Bu^i-4-Me)_2$ in THF [20]. Monomeric structures were also reported for the aluminum compounds R_2AlOAr ($R = Me$ or Bu^i, $Ar = C_6H_2-2,6-Bu^t-4-Me$) and $Bu^iAl(OAr)_2$ by Pasynkiewicz and coworkers [21]. In 1980, Lappert and Atwood described the X-ray crystal structures of the dimeric lithium transfer agent $(Et_2OLiOC_6H_2-2,6-Bu^t-4-Me)_2$ [22] and the monomeric derivatives $M(OC_6H_2-2,6-Bu^t_2-4-Me)_2$ ($M = Ge$ or Sn) featuring three coordinate Li and two coordinate Ge or Sn [23]. The same class of ligands was also applied to the early and mid transition metals by Horvath [24], Rothwell [25], Chisholm [26] and to the later transition metals by several other groups [27]. Numerous other examples of low coordinate main group element compounds stabilized by aryloxide, alkoxide and related ligands are provided in [13b,c].

The bulky alkoxide $-OCHBu^t_2$ [28] and the related $-O(1\text{-}Ad)$ and $-O(2\text{-}Ad)$ [29] ligands were employed by Wilkinson and coworkers in 1980 to synthesize four coordinate or unassociated $Cr^{3+,4+}$, Mn^{2+}, Fe^{3+} and Co^{2+} complexes. The even bulkier $-OCBu^t_3$ ligand was used in 1983 to obtain the dimer $[Li(THF)OCBu^t_3]_2$, the three-coordinate Cr^{2+} species $[(THF)_2LiCl\cdot Cr(OCBu^t_3)_2]$ [30] (Fig. 1), and later, three coordinate Mn^{2+} alkoxides [31]. The $HOCBu^t_3$ alcohol precursor to the bulky alkoxide ligand $-OCBu^t_3$ was originally synthesized by Bartlett [32] and modified by Syper [33]. Its size and electronic properties were compared with those of the cyclo-

pentadienyl ligand by Wolczanski, and a number of early transition metal derivatives were prepared [34,35]. Its complexes are, however, subject to decomposition involving dealkylation to organic products accompanied by metal oxide production. This problem was overcome with use of the analogous silicon substituted ligand $-OSiBu^t_3$ (see below) [34]. The $-OCBu^t_3$ ligand was also shown to be effective in stabilizing two-coordinate monomeric Ge^{2+} and Sn^{2+} derivatives [36]. In addition, bulky alkoxide ligands such as $-OCPh_3$ or $-OCCy_3$ have been employed to stabilize three coordinate transition metal ions such as Co^{2+} [37]. Nonetheless, large as these ligands are, no aryloxy or alkoxy ligand has been shown to be effective in stabilizing two coordination in the transition metals with open shell (d^1–d^9) configurations. Perhaps, the recently reported terphenoxy ligands $-OC_6H_3-2,6\text{-}Trip_2$ (OAr^*) and $-OC_6H_3-2,6\text{-}Dipp_2$ (OAr'; $Dipp = C_6H_3-2,6\text{-}Pr^i_2$; $Trip = C_6H_2-2,4,6\text{-}Pr^i_3$) will be sufficiently bulky for this purpose [38].

There has also been considerable use of bulky alkoxide and aryloxide in Sc, Y, lanthanide and actinide chemistry. Although the first lanthanide [39] and actinide [40] alkoxides were reported in the 1950s by Bradley, Wardlaw and coworkers, it was not until the 1980s that interest in these types of complexes began to expand. In 1983 Lappert reported the use of the $-OC_6H_2-2,6\text{-}Bu^t_2-4\text{-}Me$ (Ar) aryloxide to synthesize $M(OAr)_3$, $M(OAr)_3L$ (L = Lewis base) and related anionic derivatives as well as the approximately trigonal planar complex structure of $Sc(OAr)_3$ (Fig. 2) was described [41]. Further work by Sen, with use of $OCBu^t_3$ [42], Lappert (also with $OCBu^t_3$) [43], and the groups of Clark [44], Deacon [45], and Sattelberger [46] (arylox-
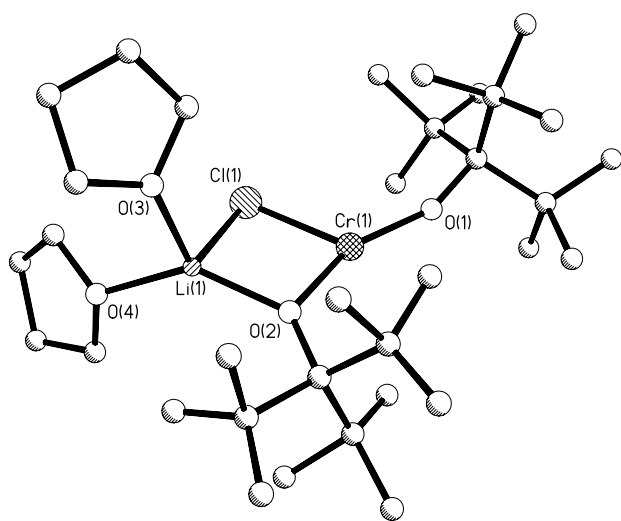

Fig. 1. Schematic drawing of $[(THF)_2LiCl\cdot Cr(OCBu^t_3)_2]$ illustrating the almost T-shaped coordination of Cr^{2+} [30].

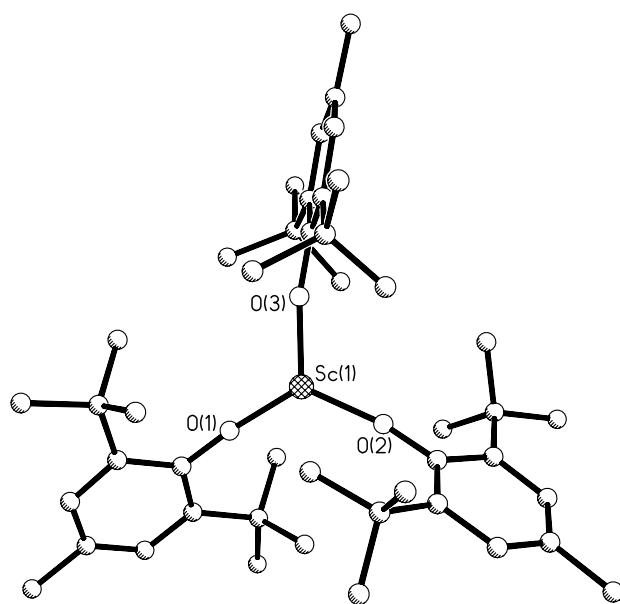Fig. 2. Schematic drawing of $Sc(OC_6H_3-2,6\text{-}Bu^t-4\text{-}Me)_3$ which has three coordinate, virtually planar, scandium [41].

ide) has greatly expanded the knowledge of these and related crowded species. The pre-1990 work on actinide alkoxide chemistry has been summarized in a review [46]. A prominent example of the use of the bulky aryloxide ligand (OC_6H_3-2,6-Pr^i_2) was in the stabilization of the homoleptic dimer $\{U(OC_6H_3$-2,6-$Pr^i_2)_3\}_2$ (Fig. 3) [47].

It is noteworthy that alkoxide and aryloxide ligands have been used extensively in olefin and metathesis catalytic systems [48]. Schrock and coworkers have shown that the use of several bulky alkoxo and aryloxo ligands (many of them fluorinated, e.g. $OCH(CF_3)_2$) is crucial to the effectiveness of well-defined Ta, Mo, W and Re metathesis catalysts [49].

Bulky siloxide ligands of the type $-OSiR_3$ have also been extensively investigated. A major reason for their use in preference to bulky alkoxides has been their lower tendency to undergo Si–O bond cleavage in comparison to the C–O bond. The early transition element derivatives of the bulky $-OSiBu^t_3$ ligand [50] have been the most investigated (Wolczanski) [34]. The ligand can stabilize three coordination in transition metal complexes, and the most noteworthy of these is $Ta(OSiBu^t_3)_3$ whose chemistry has proven of great interest as it undergoes a wide variety of reactions including the activation of E–H bonds (E = H, C, N, P or As and small molecules such as CO) (Fig. 4) [34]. The properties of these and other siloxides of transition metals including the bulky $-OSi(O-SiBu^t_3)_3$ [51], $-OSi(SiMe_3)_3$ [52], $-OSiCy_3$, and $-OSiPh_3$ have been reviewed [53]. In addition, Lickiss has reviewed the synthesis and structure of the ligand precursor organosilanols [54].

Finally, bulky diorganoboryl ($-BR_2$) groups have also been used to generate modified alkoxide ligands of the type $-OBR_2$ where R = Mes or $CH(SiMe_3)_2$. Several metal salts (e.g. Li, Co or W) have been synthesized. They display short B–O bonds due to B–O, p–p π overlap which tends to reduce the bridging properties of the oxygen [55].
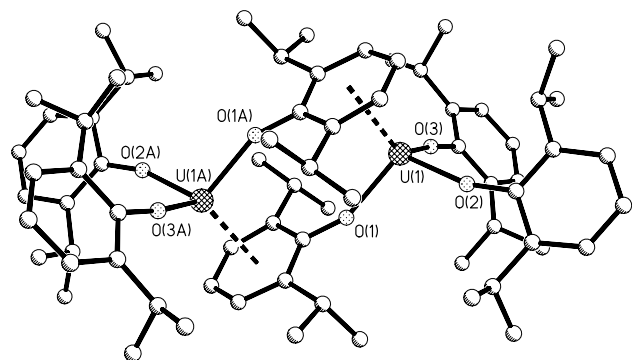

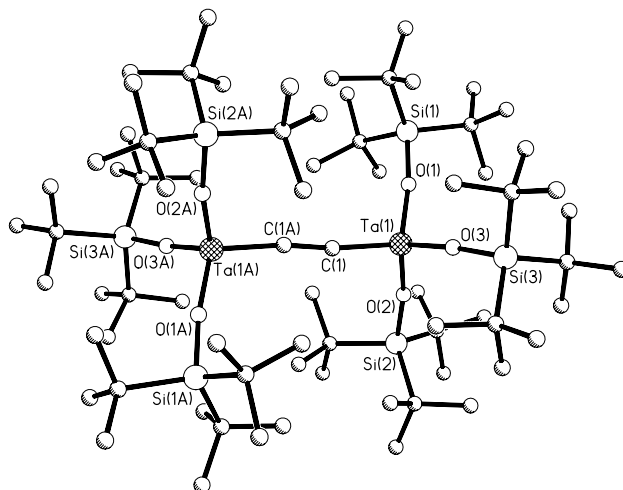Fig. 3. Illustration of the dimerization in $\{U(OC_6H_3$-2,6-$Pr^i_2)_3\}_2$ [47].

Fig. 4. Illustration of the large size of the silox ligand $-OSiBu^t_3$ in $\{=C=Ta(OSiBu^t_3)_3\}_2$ [34b].

3. Bulky heavier chalcogenolate ligands

Of the heavier chalcogen analogues of the oxygen derivatives the majority are alkyl or aryl thiolates with a small but significant number of selenolate and tellurolates. There is a vast chemistry of transition metal thiolates and derivatives. Their importance owes much to their relevance to biological systems for which very bulky thiolates have a limited but not negligible relevance. Complexes of sterically hindered thiolate ligands were reviewed by Dilworth and Hu in 1993 [56] and the selenolate and tellurolate complexes were reviewed by Arnold in 1995 [57]. More recent reviews by Ruhlandt-Senge and coworkers have surveyed the s-block element chemistry of these and related ligands [58,59]. Sulfur, selenium and tellurium are of course much larger elements than oxygen. Consequently, significantly larger substituents are required at the heavier chalcogen to produce a similar steric effect. A feature of the heavier chalcogenolate literature is its focus on aryl, and, in the heaviest elements, silyl groups to provide steric hindrance. The reasons for this are due in part to synthetic considerations but also, as in the case of the aryl thiolates, to electronic factors where the tendency for C–S bond cleavage and decomposition is minimized. In spite of this, the first structurally characterized molecular alkali metal thiolate salt concerned the alkyl, rather than aryl, thiolates $\{(THF)_2LiS-CH(SiMe_3)_2\}_2$ and $\{(THF)_{3.5}Li_2\{SC(SiMe_3)_3\}_2$ [60]. The most prominent bulky thiolate ligands to be employed in the chemistry of transition metals were the $-STrip$, $-SDipp$, $-SC_6H_3$-2,6-Ph_2, and $-SMes^*$ (Temp = C_6H_2-2,4,6-Pr^i_3; Dipp = C_6H_3-2,6-Pr^i_2; $Mes^* = C_6H_2$-2,4,6-Bu^t_3). Many of the early investigations of these hindered complexes were carried out by Dilworth and his group [56]. The $-STrip$ ligand is readily available as the thiol by the reduction of the $TripSO_3Cl$ salt with $LiAlH_4$.
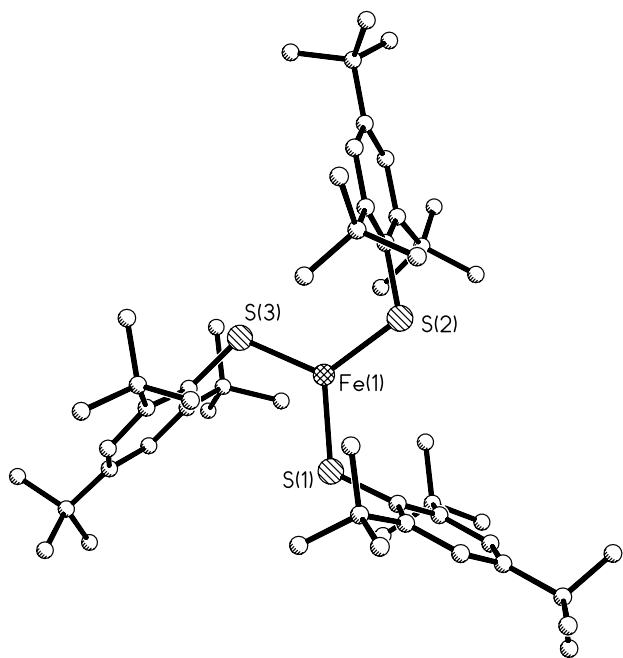
Fig. 5. Illustration of the three coordination in the anion [Fe(SMes*$_3$)]$^-$ [64].

Fig. 6. Illustration of {FeN(SiMe$_3$)$_2$}$_3$ which afforded the first structural proof of stable three coordination in an open shell transition metal complex [75].

The original syntheses of the other aryl thiolates involved more lengthy routes. However, if the lithium salt of the aryl group can be synthesized, conversion to the thiol via reaction with sulfur and hydrolysis can usually be accomplished in good yield. The –EMes* (E = S or Se) ligands have been shown to be effective in the stabilization of two and three coordination throughout the periodic table. Examples are given by Sn(SMes*)$_2$ [61], Al(SMes*)$_3$ [62], {M(SMes*)$_2$}$_2$ [63] (M = Mn, Fe, Co), [Fe(SMes*)$_3$]$^-$ (Fig. 5) [64], and {Cd(SMes*$_2$)$_2$}$_2$ [65]. The 1990s witnessed rapid developments in the chemistry of bulky selenolate and tellurolate ligands various aspects of which have been detailed in a 1995 review by Arnold [57]. The use of the silyl selenolate and tellurolate ligands –E{Si(SiMe$_3$)$_3$} [57], in particular, have allowed a rich chemistry of main group and transition metal derivatives of these ligands with low association numbers to be explored. More recently, the extremely crowding terphenyl thiolate ligands –SC$_6$H$_3$-2,6-Ar$_2$ (Ar = Mes or Trip) have been reported and several of their alkali and alkaline earth metal salts have been structurally characterized [58]. In addition, their use in transition metal chemistry has allowed the isolation of quasi two coordinate, open shell thiolate complexes such as Fe(SC$_6$H$_3$-2,6-Mes$_2$)$_2$ [66].

4. Bulky diorganoamide (–NR$_2$) and disilylamide ligands

Diorganoamide ligands (–NR$_2$) [67] occupy a position between alkoxides and alkyl ligands. They are in-

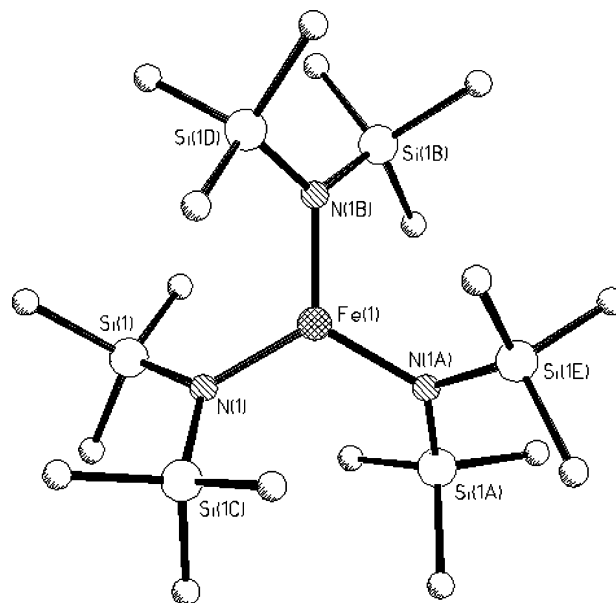herently more crowding than alkoxides, and even the smallest dialkyl amide ligand, –NMe$_2$, can stabilize four coordination as in monomeric Ti(NMe$_2$)$_4$ or Mo(NMe$_2$)$_4$. Metal dialkyl amides of alkali metals and zinc have been known since the 19th century. The first transition metal diorganoamide, Ti(NPh$_2$)$_4$, was reported by Fernelius and Dermer in 1935 [68] and Gilman and coworkers reported the first actinide amide U(NEt$_2$)$_4$ in 1956 [69]. However, it was not until the early 1960s that the first systematic investigations of the chemistry of transition metal amides occurred. As with the alkoxides, investigations by Bradley and coworkers focused initially on the earlier groups 4, 5, and 6 [70]. The presence of two substituents at nitrogen ensured that most of these were monomeric and soluble in hydrocarbon solvents. These results paved the way for the investigation of bulkier ligands and it was shown that the –NPr^i$_2$ ligand stabilized three coordination at chromium in Cr(NPr^i$_2$)$_3$ [71]. However, at about the same time Bürger and Wannagat introduced the very important –N(SiMe$_3$)$_2$ ligand in several publications in 1963 and 1964. Silylamido derivatives of the transition metal ions Cr(III) [72], Mn(II) [73], Fe(III) [74], Co(II) [73], Ni(II) [72], and Cu(I) [72] were described. With the exception of the copper derivative, it was shown that the compounds were monomeric in hydrocarbon solution thereby implying the presence of three and even two-coordinate metals. Bradley and coworkers showed that the –N(SiMe$_3$)$_2$ ligand stabilized three-coordination in Sc(III), Ti(III), V(III) [74], and, with use of PPh$_3$ coligands, in Co(II) and Ni(I) [75,76] complexes. X-ray crystallographic studies of the M(III) species afforded

the first structural proof [74] (Fig. 6) of three coordination in open shell transition metal complexes [77–79], and showed that they possessed a trigonal planar M(III) center as well as –N(SiMe₃)₂ ligands that were planar at nitrogen (like almost all metal amides) with angles near 50° between the M(III) and nitrogen coordination planes. The series of transition metal M(III) species was later extended to include Mn(III) and Co(III) [80]. In addition, Al{N(SiMe₃)₂}₃ [81] and later M{N(SiMe₃)₂}₃ (M = Ga–Tl) [76c] were found to have very similar structures. Bradley and coworkers also expanded the use of the ligand to lanthanide elements where monomeric, three coordinate pyramidal structures were observed [82]. Andersen and coworkers extended the range of known three coordinate silylamides to actinides such as U{N(SiMe₃)₂}₃ [83]. The M(II) species M{N(SiMe₃)₂}₂ (M = Mn, Fe or Co) were found to have weakly dimerized, amide bridged structures as crystals [84–86]. In solution and in the vapor phase [87], they are monomeric with two-coordinate metals and readily form complexes with a variety of Lewis base donors [88]. Gambarotta and coworkers showed that {Cr(NPr$^i_2$)₂}₂ was dimerized in a similar way [89]. Dimerization of the silylamides can be prevented by use of the bulkier –N(SiMe₂Ph)₂ and –N(SiMePh₂)₂ ligands, which afford two coordinate metals in the solid state [90,91] (Fig. 7) although the metals also exhibit weak π-interactions to the aryl rings. It was also found that boryl amide ligands, for example –NMesBMes₂, were effective at stabilizing two coordination [92]. Fröhlich and coworkers also used the –NPh₂ ligand to synthesize a number of low coordinate species [93] which were later shown to have dimeric amide bridged structures like the silylamides [94].

In the 1990s, Cummins and his group introduced amide ligands of the type –N(R)Ar (R = t-Bu, –C(CD₃)₂CH₃, 1-Adamantyl(1-Ad), Ar = Ph, C₆H₄-3-

F, C₆H₃-3,5-Me₂) [95,96]. Crystallization of a number of M{N(R)Ar}₃ complexes show that they have structures in which the three aryl groups are directed to the same side of the MN₃ coordination plane which gives the MN₃ plane two different 'faces'. The use of such ligands allowed reactions not hitherto seen in complexes of other monodentate amide ligands to be observed. The most spectacular of these involved the reaction of Mo(N(R)Ar)₃ (itself a relatively rare example of an open shell, three coordinate 2nd or 3rd row transition metal) with N₂ which occurs at room temperature to give the nitride N{MoN(R)Ar}₃ (Fig. 8) or at low temperature (−35 °C) to give the N₂ bridged complex (μ-N₂){Mo(N-(R)Ar)₃}₂ [97]. A reaction under similar conditions with white phosphorus afforded the phosphide PMo(N-(R)Ar)₃ [98]. No reference to this chemistry would be adequate without mention of the corresponding work of Schrock and coworkers with triamideamine ligands [9]. These amines are of the type N(CH₂CH₂N(R)H)₃ (R = SiMe₃, SiEt₃, SiMe₂Bu^t, C₆H₅) which, when deprotonated, react with transition metal halides, to form, inter alia, complexes of formula M{N(R)CH₂CH₂}₃N (e.g., M = Ti–Fe) which have trigonal monopyramidal metal coordination. In other words, they possess an MN₃ coordination plane that has two different sides and are thus related to the already mentioned amides of Cummins. These tetradentate ligands confer on their transition metal complexes a spectacular chemistry related to that of the –N(R)Ar complexes but these results cannot be elaborated here [9].

As has been shown, the steric effects of bulky amide ligands on transition metal amide chemistry was first investigated in the late 1960s and early 1970s. Regarding
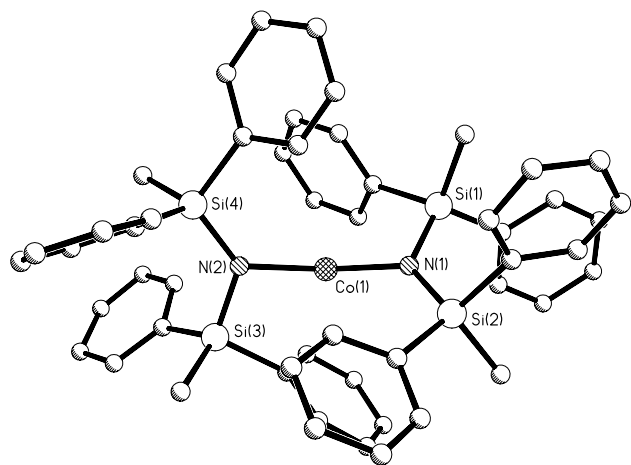

Fig. 7. Illustration of the almost linear structure Co{N(SiMePh₂)₂} which has two coordination in the crystalline phase [90].
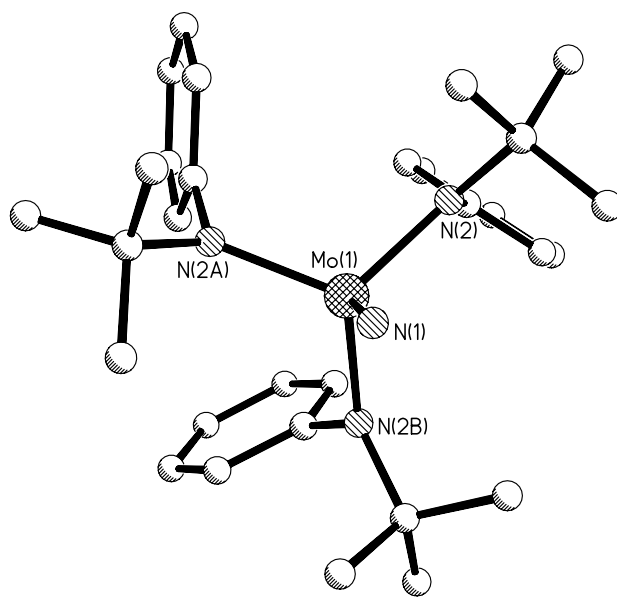

Fig. 8. Illustration of the structure of the molybdenum nitride NMo(N(Bu^t)Ph)₃ [97b].

the main group elements, Wannagat and coworkers had used $NaN(SiMe_3)_2$ as a transfer agent for the synthesis of the already described transition metal complexes [72,73]. It was also shown that treatment of $HN(SiMe_3)_2$ with an iodo Grignard reagent in Et_2O give the product $\{(Me_3Si)_2N\}_2Mg \cdot MgI_2 \cdot 4Et_2O$ which when treated with 1,4-dioxane gave $(diox)_3 \cdot Mg\{N(SiMe_3)_2\}_2$ or with $NaN(SiMe_3)_2$ to give $Mg\{N(SiMe_3)_2\}_2 \cdot Et_2O$ which could be converted to $Mg\{N(SiMe_3)_2\}_2$ by sublimation [99]. The latter has an amide bridged dimeric structure [100] very similar to the one described for $Mn\{N(SiMe_3)_2\}_2$ [84,85]. The use of a variety of bulky amido ligands (including silylamides) has allowed the bonding characteristics of both the alkali metal and alkaline early derivatives to be explored [101]. However, application of the $-N(SiMe_3)_2$ and related bulky silyl amide ligands to other main group element members led to compounds with unusual structures and bonding. For example, in 1973 Niecke and coworkers showed that the reaction of two equivalents of $LiN(SiMe_3)(Bu^t)$ with PF_3 afforded $FP\{N(SiMe_3)Bu^t\}_2$ [102]. This product eliminated Me_3SiF during distillation at low pressure to give the first stable iminophosphane $Bu^tN{=}PN(SiMe_3)Bu^t$. In 1974 the groups of Lappert [103] and Zuckerman [104] showed that reaction of two equivalents of $LiN(SiMe_3)_2$ with $SnCl_2$ in Et_2O gave the two coordinate, orange tin(II) species: $Sn\{N(SiMe_3)_2\}_2$ which remains two-coordinate in the solid (at that time a rarity for divalent group 14 elements). It is freely soluble in hydrocarbons such as hexane and behaves as a two electron donor analogous to carbenes. These results were extended to include the corresponding Ge(II) and Pb(II) derivatives. It was found that photolysis of solutions of $M\{N(SiMe_3)_2\}_2$ (M = Ge or Sn) in hydrocarbons afforded solutions that contained the persistent free radicals. $M\{N(SiMe_3)_2\}_3$ whose EPR parameters indicated that they had pyramidal coordination at the group 14 element [105]. The half-lives of these radicals were remarkably long, and under anaerobic and anhydrous conditions, ranged from 3 to 5 months. Reduction of the diamidochlorophosphane or arsane $ClE\{N(SiMe_3)_2\}_2$ (E = P or As) by an electron rich olefin with photolysis afforded the persistent radicals: $\dot{E}\{N(SiMe_3)_2\}_2$ which have half lives of several days at room temperature [106]. In the group 16 elements the use of the $-N(SiMe_3)_2$ ligand has also afforded unusual odd electron species. Among these is the stable radical cation salt: $[Te\{N(SiMe_3)_2\}_2]^+[AsF_6]^-$ synthesized by Roesky and coworkers which has been structurally characterized and displays shorter Te–N bonds than those in the neutral $Te\{N(SiMe_3)_2\}_2$ consistent with the higher Te^{3+} oxidation state [107]. Several other investigations in the 1990s focused on monomeric amides of the metals Al–Tl of formula $R_2MNR'_2$, R = Bu^t, Trip, Mes^*, R' = $SiMe_3$, $-Bu^t$, Pr^i or mixture of groups, in order to study M–N π-bonding. These bonds were found

to be significantly weaker than the corresponding B–N π-bonds and are generally have an energy of ca. 10 $kcal\,mol^{-1}$ or less [108]. A notable recent use of the $-N(SiMe_3)_2$ ligand has been in the synthesis of extremely interesting metalloid clusters of the main group 13 elements by Schnockel and coworkers. Examples of these include $[Al_7\{N(SiMe_3)_2\}_6]^-$, $[Al_{12}\{N(SiMe_3)_2\}_8]^-$, $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ or $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$. These and related compounds have been reviewed [109].

Other bulky diorganoamide groups have been used to induce low coordination members; these include the commercially available 2,2,6,6-tetramethylpiperidido group [110] and the dimesitylamide $-NMes_2$ [111].

5. Bulky diorganophosphides and arsenide ligands

The use of heavier pnictogen groups analogous to the amides as sterically crowding species has been much less extensive. There are several reasons for this, but the main ones involve the greater sizes of P, As, Sb or Bi, the generally more elaborate syntheses required for $-\ddot{E}R_2$ (E = P–Bi) and the fact that the pnictogen remains pyramidal owing to the much greater inversion barrier at E in comparison to N. The E lone pair thus remains more stereochemically active and there is a much greater bridging tendency. Planar pnictogen geometries are observed only in cases where strong multiple bonds can be formed with use of the pnictogen lone pair. This is the case in species such as $(\eta^5\text{-}C_5H_5)_2M(PR_2)_2$ (M = Zr or Hf, R = Et, $c\text{-}C_6H_{11}$, Ph) which contain both single and double M–P bonds which interconvert near room temperature [112]. Well characterized homoleptic diorganopnictide complexes of the transition elements are quite rare. Among these are compounds such as $[Li(DME)][M(PR_2)_5]$ (M = Zr, Hf; R = $c\text{-}C_6H_{11}$), $[Li(DME)][M(PR_2)_4]$ (M = Ti, V, Re), $[Li(DME)_2][Nb(PR_2)_4]$ $[Li(DME)_3][M_2(PR_2)_5]$ (M = Cr, W) of Baker and coworkers [112] or the unusual neutral Mo(II) dimer $Mo_2(PBu^t_2)_4$ of Jones and coworkers which was synthesized from the reaction of $Mo_2(OAc)_4$ with 4 equivalents of $LiPBu^t_2$. It features two bridging and two terminal $-PBu^t_2$ groups [113]. Several homoleptic phosphido derivatives of transition metals Ti, V, Cr, Mn, Fe, Ni, and Pd were reported in the early 1960s by Issleib and coworkers but none was structurally characterized [114]. These reports included $V\{P(c\text{-}C_6H_{11})_2\}_3$ and $Cr\{P(c\text{-}C_6H_{11})_2\}_3$ which were reported to be monomeric (and presumably three coordinate) in benzene. No low coordinate (three or less) open shell homoleptic transition metal diorganopnictide complexes have been structurally characterized.

In the main group elements, there has been considerable interest in the structures of the lithium salts of diorganopnictides, several of which have been characterized by X-ray crystallography. The most sterically crowded are $[LiP\{CH(SiMe_3)_2\}_2]_2$ [115], which has a dimeric

structure with two lithiums bridging the two phosphides, and M(18-crown-6)PHMes* (Mes* = C_6H_2-2,4,6-Bu^t_3; M = Na or K) which are monomers with the alkali metal solvated by 18-crown-6 [116]. Group 1 complexes of P and As donor ligands have been reviewed [117]. Sterically crowded diorganopnictides ligands have also been used in the study of multiple bonding between boron, aluminum or gallium and phosphorus or arsenic, for example R'_2MER_2 (R, R' = alkyl or aryl, M = B, Al or Ga, E = P or As). Such compounds are normally associated and have strong M–E bridging. The use of combinations of substituents such as t-Bu, Mes, Trip and silyl groups has enabled a variety of such compounds to be synthesized and the multiple character of the M–E bond to be experimentally measured [118]. Sterically crowded lithium salts of the type LiE(R)BMes$_2$ (E = P or As, R = Ph, c-C_6H_{11}, Mes) feature essentially planar geometries at phosphorus or arsenic owing to π-bonding between the pnictogen lone pair and the boron p-orbital. Their use as ligands for other metals has not been explored, however. Finally, it is notable that the use of combinations of bulky substituents on boron and phosphorus allowed the first examples of compounds of formula (RBPR')$_3$ (e.g., with R = Mes, R' = Ph, c-C_6H_{11}) which are B–P analogues of borazine to be synthesized [119].

6. Bulky alkyl and aryl ligands

Element derivatives of both alkyl and aryl ligands are of great importance for several reasons that range from theoretical, biological, catalytic as well as their extensive use as synthetic reagents [120]. Alkyl ligands are more flexible in their steric properties than either alkoxides or amides since the α-carbon can carry up to three substituents. It is interesting to observe that homoleptic alkyl or aryl derivatives of all the main group elements (except noble gases or highly radioactive elements) were known by the middle of the last century whereas the corresponding homoleptic alkyl or aryl derivatives of the d and f block metals with open shell configurations were quite scarce. Numerous heteroleptic alkyl and aryl compounds with stabilizing coligands were known for almost all the transition elements [121]. But homoleptic compounds were limited to scattered examples across the series, examples of which are TiMe$_4$ (unstable above −80 °C), MnR$_2$ (R = Me or Ph), anionic species such as, Li$_4$VPh$_6$, Li$_3$CrR$_6$ (R = Me or Ph) and the group 10 metals [121]. For a long time it was widely thought that homoleptic, open shell transition alkyls or aryls were inherently unstable owing to weak metal–carbon bonds. There is thermochemical evidence to show that metal–carbon bonds are indeed weaker than metal–nitrogen or metal–oxygen bonds in related alkoxide and amide derivatives of Ti, Zr and Hf, but the M–C bonds are not inherently weak and have energies in the approximate range 40–80 kcal mol^{-1} for the alkyls M(CH$_2$X) (M = Ti, Zr, Hf; X = Bu^t, Ph or SiMe$_3$) [122]. In 1970, the view of transition metal–carbon bonds began to change at a rapid pace when it was shown almost simultaneously by Lappert [123] and Wilkinson [124] that the key to isolating stable homoleptic transition metal alkyls lay in their kinetic stabilization, i.e. by blocking low-energy decomposition pathways with use of steric hindrance to protect the metal center or alkyl groups that lacked β-hydrogens. The –CH$_2$SiMe$_3$ ligand was the most prominent to be employed in the early investigations and was found to be most useful in the stabilization of four coordinate complexes such as MR$_4$ (M = Ti, Zr, Hf, V, Cr and Mo). Other ligands of a similar type, lacking β-hydrogens such as –CH$_2$Bu^t (neopentyl), –CH$_2$CMe$_2$Ph (neophyl), –CH$_2$Ph (benzyl) were also explored [18,120]. In addition, "bridgehead" ligands such as 1-norbornyl [125] or 1-adamantyl [126], which contain β-hydrogens, but do not readily undergo elimination (mainly for reasons of geometrical strain at an unsaturated bridgehead carbon of the decomposition product), also afforded generally very stable four coordinate complexes [127]. These involved an expanded variety of transition metals in both common and unusual oxidation states. Thus, in addition to TiR$_4$, VR$_4$ and CrR$_4$ complexes (R = 1-norbornyl), MnR$_4$, FeR$_4$, CoR$_4$ species could also be stabilized [127].

Apart from the isolation of the transition metal compounds themselves, the most interesting development arising from the investigation of the alkyl ligands lacking β-hydrogen occurred in 1974 when Schrock reported the synthesis of the alkylidene (Me$_3$CH$_2$C)$_3$TaC(H)CMe$_3$ upon reaction of Cl$_2$Ta(CH$_2$CMe$_3$)$_3$ with two equivalents of LiCH$_2$CMe$_3$ [128]. The more stable pentaalkyl Ta(CH$_2$-SiMe$_3$)$_5$, which could be isolated at low temperature has had its decomposition, which occurs by α-hydrogen abstraction to (Me$_3$SiCH$_2$)$_3$TaC(H)SiMe$_3$, quantified. The driving force for decomposition in both complexes is the relief of steric hindrance in the very crowded pentaalkyl TaR$_5$. These original results were developed into a spectacularly fruitful field of investigation involving not only alkylidenes, but also alkylidyne complexes and their rôle in catalytic metatheses reactions [129].

In spite of isolated use of bulkier ligands such as –CPh$_3$ [130], initial investigations of bulky alkyl groups likely to stabilize low coordination number focused primarily on the –CH(SiMe$_3$)$_2$ ligand. It is isoelectronic with –N(SiMe$_3$)$_2$ and has a similar steric requirement. The use of this ligand dates from 1970 and was developed by Lappert and coworkers who employed its very useful steric properties throughout the periodic table [131]. The list of new compound classes stabilized by this ligand is arguably greater than that of any bulky alkyl group especially in its main group derivatives. Among these are: the first well characterized homoleptic three coordinate alkyl derivatives of transition metals (CrR$_3$, R = CH(SiMe$_3$)$_2$)

[132] (Fig. 9) lanthanides LaR_3 [133], or actinides, UR_3 (Sattelberger) [134], the first stable germanium, tin or lead compounds analogous to alkenes R_2MMR_2 (M = Ge, Sn or Pb), Lappert [135] (Fig. 10) the first persistent or stable radical derivatives of germanium tin (·MR_3) [136], phosphorus or arsenic: ·MR_2 [106], and the first structurally authenticated Al–Al bond in a stable molecular compound in R_2AlAlR_2 by Uhl [137] (Fig. 11). The results obtained in the group 13 and 14 elements in particular played a founding rôle in the study of multiple bonding between heavier main group 14 elements and metal–metal bonding between the heavier group 13 elements.

The bulkier –$C(SiMe_3)_3$ and related ligand derivatives, which were originated and primarily developed by Eaborn, Smith and coworkers, can also point to an extensive list of achievements in the stabilization of low coordination numbers [138]. Among these are: two coordinate dialkyl metal anions of $[Li(THF)_4][RMR]$ (M = Li, Cu or Ag; R=$C(SiMe_3)_3$) [139], the first structure of an unsolvated dimeric organolithium species $(LiR)_2$ [140]; the first two coordinate magnesium and dialkyl MgR_2 [141]; the first open shell transition metal alkyl that is two coordinate in the solid state (Fig. 12) [142]; the divalent alkyls CaR_2, YbR_2 and EuR_2 in which the metal is formally two coordinate but has bent geometry with relatively close approaches by ligand CH_3 groups to the metal center [143]. The –$C(SiMe_3)_3$ ligand also proved itself in heavier main group multiple bonding where Cowley and coworkers employed it in the synthesis of the first stable AsP and AsAs double bonded species [144]. The organometallic compounds of –$C(SiMe_3)_3$ and related groups has been reviewed recently [138].

In sterically encumbered aryl groups, crowding is generally induced by the introduction of substituents at the ortho positions. The use of the mesityl substituent to obtain the landmark first stable disilene $Mes_2Si=SiMes_2$ (West) is well known [145]. Mesityl groups were

Fig. 10. Illustrations of $Sn_2\{CH(SiMe_3)_2\}_4$ – the first structure of a heavier group 14 element analogue of an alkene that was stable in the solid state [135].
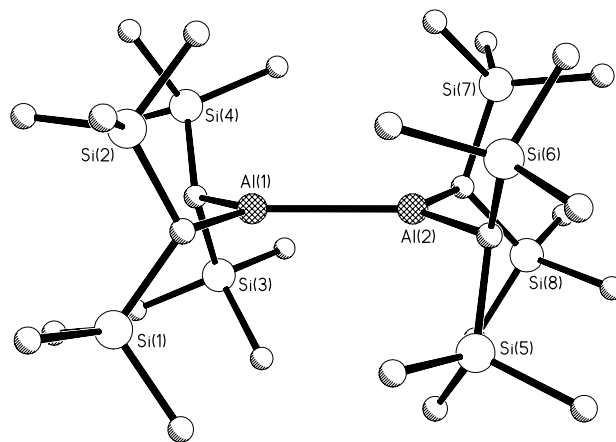
Fig. 11. The structure of the first stable tetraorganodialane $Al_2\{CH(SiMe_3)_2\}_4$. It was also the first stable, well characterized molecular species with an Al–Al bond [137].
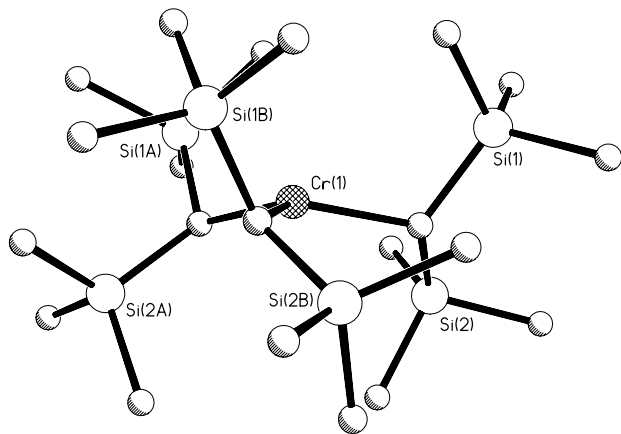

Fig. 9. Illustration of $Cr\{CH(SiMe_3)_2\}_3$ the first structurally characterized monomeric transition metal trialkyl [132].
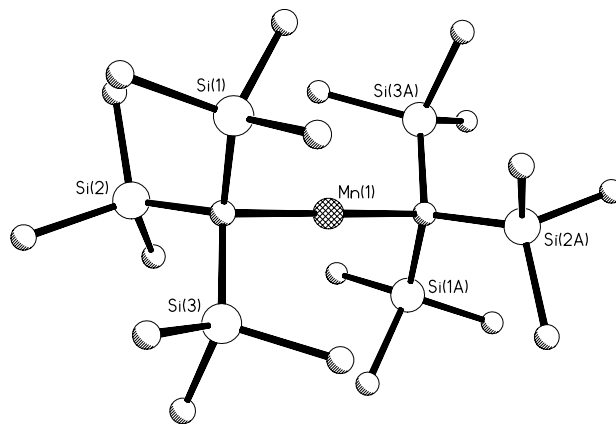
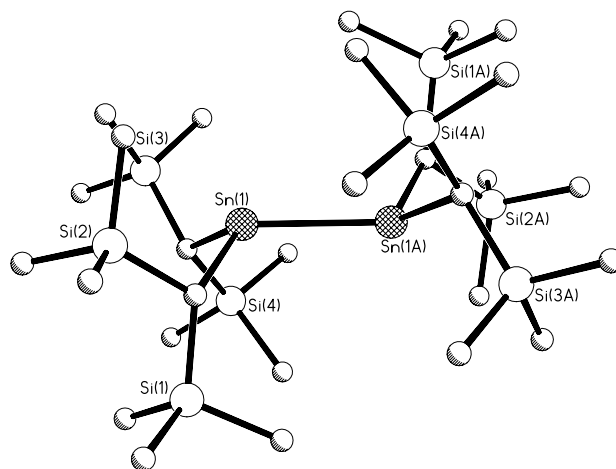Fig. 12. Illustration of $Mn\{C(SiMe_3)_2\}_2$ the first structural characterization of a stable, open shell two coordinate transition metal dialkyl in the crystal phase [142].

also used to stabilize the first B–B double bonds [146]. In an extensive series of papers, beginning in the 1970s, Seidel and coworkers showed that the mesityl ligand (C_6H_2-2,4,6-Me_3) could stabilize a range of homoleptic transition metal derivatives [147a–d] such as $MMes_4$ (M = Ti, V, Cr, Mo) [147a–c] ($FeMes_2)_2$ [147d]. The trimeric and dimeric structures of ($MnMes_2)_3$ (Floriani) [148] and ($CoMes_2)_2$ (Theopold) [149] have been demonstrated as well as the existence of a variety of association numbers for Cu(I), Ag(I) and Au(I) aryls (Floriani) [150]. Wilkinson and coworkers employed mesityl and related aryl ligands to synthesize several new types of heavier transition metal species, the most notable of which are the M(o-tolyl)$_4$ (M = Cr, Mo, W), M(o-tolyl)$_4$ (M = Re, Ru, Os), and $MMes_3$ (M = Rh or Ir) [141]. There is also an extensive range of homoleptic, anionic transition metal aryls (usually phenyls or mesityls) in which alkali metal counter cations are often associated with the anion through complexation with the attached aryl rings with solvation by ethers [151]. More limited use has been made of the bulkier –C_6H_2-2,4,6-Pr^i_3 (Trip) ligand in transition elements although it has been used extensively in group 13 and group 14 element chemistry as exemplified by the derivative $Trip_2GeGeTrip_2$ (Weidenbruch) [152], ($SnTrip_2)_3$ (Sita and Masamune) [153] and $Trip_2PbPbTrip_2$ (Weidenbruch) [154], and the group 13 metal–metal bonded species $Trip_2MMTrip_2$ (M = Al, Ga or In) [108]. In combination with other ligands, it has been used to stabilize species with Si=P double bonds (Driess) [155]. The even more crowded –C_6H_2-2,4,6-Bu^t_3 (Mes* or supermesityl) has been shown to stabilize linear two coordination in open shell transition metal species as exemplified by $MMes^*_2$ (M = Mn or Fe) [156,157] as well as $MgMes^*_2$ [157].

In contrast to transition metals, the important Mes* (supermesityl) ligand has been widely used in main group chemistry. The key bromo derivative was synthesized in good yield by Pearson in 1976 [158]. In 1979 Yoshifuji, Shima and Inamoto synthesized the lithium salt LiMes* and used it to form Cl(O)PMes*$_2$ [159]. This proved to be a very crowded species to the extent that the aryl rings were deformed to a boat configuration due to the high steric congestion [160]. More spectacular evidence of the steric protection afforded by this group came from the reduction of PCl_2Mes^* with magnesium which produced the first compound with a stable phosphorus-phosphorus double bond, i.e. Mes*PPMes* (Fig. 13) [161] Subsequently, the Mes* group has been widely used in main group for steric protection in the stabilization of low coordination numbers, radicals [162], multiple bonding [163] and hydride species [164]. In some instances where congestion is high and bonds are sufficiently reactive activation of a C–H bond of an ortho Bu^t group can occur [165].

Another bulky aryl group that has proven sterically effective in stabilizing unusual compounds is C_6H_2-
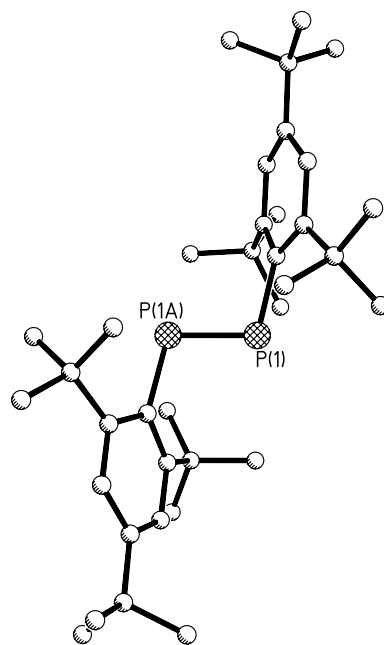
Fig. 13. Illustration of Mes*PPMes* the first stable species with a P=P double bond [161].

2,4,6-$(CH(SiMe_3)_2)_3$ (Tbt) which uses the already encountered –$CH(SiMe_3)_2$ substituent at the ortho and para positions of the aryl ring. Tokitoh and Okazaki have made considerable use of Tbt to induce stability in several interesting new types of stable species. The most notable of these are compounds with multiple bonds between heavier group 14 elements and the chalcogens [166]. These compounds are heavier element analogues of ketones such as Tbt(Trip)M=E (M = Si; E = S, Ge; E = S, Si or Te), Tbt(C_6H_3-2,6-(2-Pr^i-$C_6H_4)_2$)Sn=Se (Fig. 14) and have considerably shortened ME distances in comparison to single bonds. In addition, use of the

Fig. 14. Illustration of the structure of Tbt(C_6H_3-2,6-(2-Pr^i-$C_6H_4)_2$)Sn=Se that has a stable Sn=Se double bond [b].

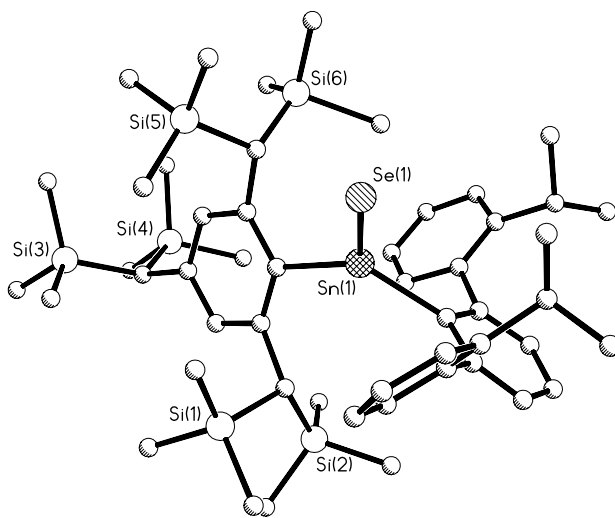Tbt substituent led to the first stable distibenes and dibismuthenes which contain authentic Sb–Sb [167a] and Bi–Bi [167b] double bonds that have lengths 7–8% shorter than single bonds. The dibismuthene is the heaviest element doubly bonded compound synthesized to date. These, and related bulky aryl ligands, have been used extensively to stabilize aromatic rings containing heavier group 14 elements [168].

7. Bulky terphenyl ligands

These are ligands of the type $–C_6H_3$-2,6-Ar_2 in which two aryl groups (meta to each other) are bonded to a central aryl ring. The attached or flanking aryl rings (Ar) usually carry substituents at their ortho (and often para) positions so that they are constrained to maintain an almost perpendicular orientation with respect to the central aryl ring. In this way a wedge shaped space, shielded by the flanking aryls, is generated. This arrangement is often sufficient to protect a reactive center from attack. Terphenyls, although synthesized earlier in 1942 [169], were investigated by Hart and coworkers in the 1980s as part of a general approach to the formation of aryl–aryl bonds and as building blocks for species that combine a concave shape with endofunctionality [170]. Later a one-pot synthetic route to these ligands was developed [171,172] and much bulkier substituted flanking rings such as C_6H_2-2,4,6-Pr^i_3 (Trip) and C_6H_3-2,6-Pr^i_2 (Dipp) introduced. The three most commonly used bulky terphenyl ligands are

Ar$^{\#}$ Ar′   Ar*
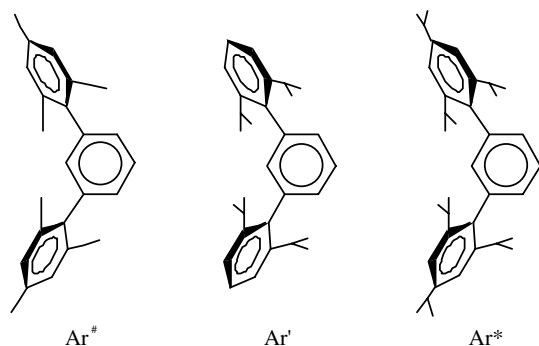
and in the ca. 10 years since their first use as metal ligands in 1993 [173], they have between them, permitted an impressive array of new compounds to be synthesized [174,175]. Among these are mononuclear lithium or sodium derivatives with low or zero solvation by Lewis bases [176], the first structural characterization of heavier group 14 element radicals [177], the first stable compound with a triple bond to a heavier group 14 element [178], the gallium species $Na_2Ar^*GaGaAr^*$ with its controversial bonding (Robinson) [179], one coordinate InAr* (Fig. 15) and TlAr* species [180], the first stable
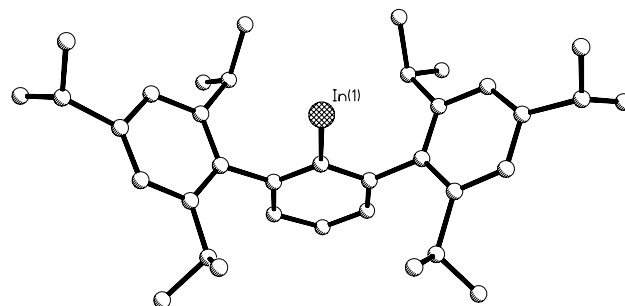

Fig. 15. Illustration of the structure of InAr* that features one coordinate In and underlines the shielding power of the Ar* terphenyl ligand [180].

divalent hydride of a group 14 element [181], the first stable alkyne analogues of heavier group 14 elements [182], a homologous series of heavier dipnictines with a common terphenyl substituent [183], first lanthanide (II) aryls [184]. At present it seems unlikely that the full stabilizing potential of these ligands has been exhausted.

8. Bulky silyl ligands

Bulky silyl ligands have played an increasingly prominent rôle over the last decade in the stabilization of compounds of unusual structure oxidation state and bonding. Silyls differ from alkyls in their electronic properties due to the effect of the heavier silicon atom and its ability to stabilize charge at an adjacent center. The two most widely used bulky silyls are the so-called supersilyl and hypersilyl ligands as shown by

supersilyl   hypersilyl
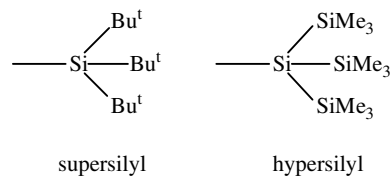
These and related ligands such as $–SiMeBu^t_2$ or $–SiPhBu^t_2$ have been applied with success to a wide range of problems [185,186]. A more recent addition to the bulky silyl ligand array is $–SiMe(SiBu^t_3)_2$ which was introduced in attempts to isolate a stable disilyne. The 1,2-dichlorodislene precursor to the disilyne, ${(Bu^t_3Si)_2MeSi}(Cl)Si{=}Si(Cl){SiMe(SiBu^t_3)_2}$, is stable to attack by H_2O, MeOH, HF and $NaSiBu^t_3$ [187].

The $–Si(SiMe_3)_3$ transfer agent $LiSi(SiMe_3)_3$ was introduced by Gilman and Smith in 1968 [188]. This ligand has been widely used in the stabilization of many low coordinate compounds including tetrahedral ${Ga-Si(SiMe_3)_3}_4$, which is monomeric as a vapor [189], a 2 center, 2 electron Tl–Tl bond in ${(Me_3Si)_3Si}_2TlTl{Si-(SiMe_3)_3}_2$ [190] and the low-coordinate transition
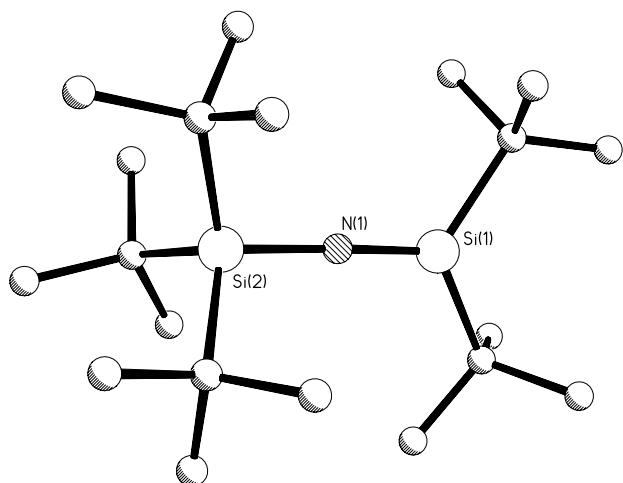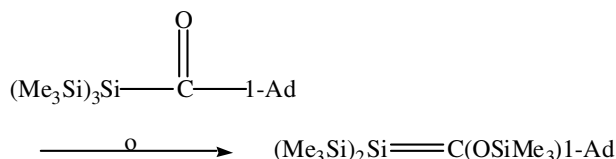
Fig. 16. Illustration of the structure of $Bu^t_2Si{=}N(SiBu^t_3)$; the first stable species with a silicon–nitrogen double bond.

metal silyls $[NEt_4][Fe(Cl)\{Si(SiMe_3)_3\}_2]$ [191] or $[Cu\{Si(SiMe_3)_3\}_2]^-$ [192]. Its most spectacular use, perhaps, has involved the 1982 synthesis of the first stable species having a silicon carbon double bond as shown by the rearrangement

involving transfer of $SiMe_3$ from silicon to oxygen (Brook) [193].

The supersilyl ligand $-SiBu^t_3$ was synthesized later than $-Si(SiMe_3)_3$ due to the experimental difficulty in adding more than two Bu^t groups to silicon. These difficulties were overcome with use of Si–F reagents independently by three different groups (Doyle [194], Spialter [195] and Weidenbruch [196]) in 1975. The use of the ligand has been heavily investigated, especially by Wiberg and his group. Its use has been responsible for a number of notable accomplishments. The earliest outstanding success was the synthesis of the first stable compound with a silicon–nitrogen double bond [197] (Fig. 16) in accordance with the scheme

$$Bu^t_2Si(Cl)N_3 + NaSiBu^t_3 \rightarrow Bu^t_2Si{=}NSiBu^t_3 + NaCl + N_2$$
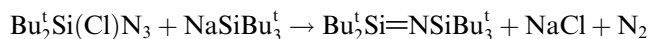
More recent achievements include the crystallization of the first stable neutral radical centered on a heavier group 13 element in the form of $(Bu^t_3Si)_2GaGaSiBu^t_3$ [198]. In addition several new clusters of heavier group 13 and 14 elements have been synthesized. A notable recent success has been the synthesis of a triplet silylene

[199]. Variants of the super and hypersilyl ligands are becoming increasingly important as illustrated by the use of the $-SiMeBu^t_2$ ligand in the isolation of the crystalline radicals $E(SiMeBu^t_2)_3$ (E = Si or Ge) [200].

9. Conclusions

Since the initial studies in the late 1950s the use of sterically crowded ligands has advanced to the extent that it is now a major research area in its own right. There has been a continuous development of the electronic and steric properties of such ligands over the past four decades which shows no sign of diminishing. The continued application of these ligands to synthetic problems throughout the periodic table may be anticipated.

Acknowledgement

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