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Journal of Organometallic Chemistry 500 (1995) 289–297

Journal of Organometallic Chemistry

Invited review

Main Group and Group 11, 12, 2-pyridyl-(trimethylsilyl)methyl and -bis(trimethylsilyl)-methyl chemistry

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Received 20 February 1995

Abstract

Developments in the Main Group 1, 2, 13–15 and Groups 11 and 12 alkyl metal or metalloid chemistry of $CH(SiMe_3)$(2-pyridyl) (= r) and $C(SiMe_3)_2$(2-pyridyl) (= R) is reviewed along with observations on the closely related ligands, $CH(SiMe_3)$(6-methyl-2-pyridyl) (= rMe) and $C(SiMe_3)_2$(6-methyl-2-pyridyl) (= RMe).

Keywords: Alkyl metal; Main Group; Group 1, 2, 11–15; N-pyridylalkyl; N-functionalised alkyl; Trimethylsilylmethyl

1. Introduction

Bulky alkyl and aryl ligands have featured extensively in the development of novel Main Group chemistry where kinetic protection at the element in question is required. The most commonly used ligands are those devoid of β-hydrogen atoms. This approach has its origins in transition metal alkyl chemistry where such ligands are used to circumvent the potentially low energy β-hydrogen elimination process, and the ligands are sterically demanding in consequence of incorporating substituents at the β-carbon atoms. The most extensively studied ligands in Main Group chemistry are those based on trimethylsilyl-substituted groups, CH_2SiMe_3, $CH(SiMe_3)_2$, $C(SiMes)_3$ and related ligands developed mainly by Lappert and by Eaborn at the University of Sussex, and CH_2Bu^t, CH_2Ph, and mesityl and other *o*-substituted aryl ligands [e.g. 1–5]. We have developed alkyl chemistry for the bulky ligands, $CH(SiMe_3)$(2-pyridyl) (= r) and $C(SiMe_3)_2$(2-pyridyl) (= R), which incorporate the features of the foregoing ligands but also possess an N-donor functionality. This has yielded some unusual and unexpected chemistry [6–17] which is reviewed in this article along with that of the closely related ligands, $CH(SiMe_3)$(6-methyl-2-pyridyl) (= rMe) and $C(SiMe_3)_2$(6-methyl-2-pyridyl) (= RMe) which were initially used by Thornton and Izod [18]. N-functionalised aryl metal/metalloid chemistry has also recently gained prominence but is beyond the scope of this review [19]. The limited transition metal chemistry involving the above ligands is also reviewed.

2. Group 1 and 11

Initial developments in the case of Group 1 elements centred on preparing transfer reagents of r and R ligands; only in the case of the solvent-free lithium reagent $[(LiR)_2]$ was an alkyl species authenticated, **1**, Scheme 1 [6, 7], the others being associated with other types of bonding. Compound **1** can be prepared in high yield as a high purity crystalline solid by metallation with $LiBu^n$, and has been used to prepare a range of other Main Group derivatives. Overall, the nature of the species generated on metallation of rH and RH depends on the choice of solvent, and steric and electronic effects including the solvation of the lithium and the concentration of charge on carbon by polarisation of adjacent silicon atoms [20]. X-ray structure determinations have demonstrated that a range of products are possible, as summarised in Scheme 1, and in the absence of such structural studies the nature of the products would be oversimplified.

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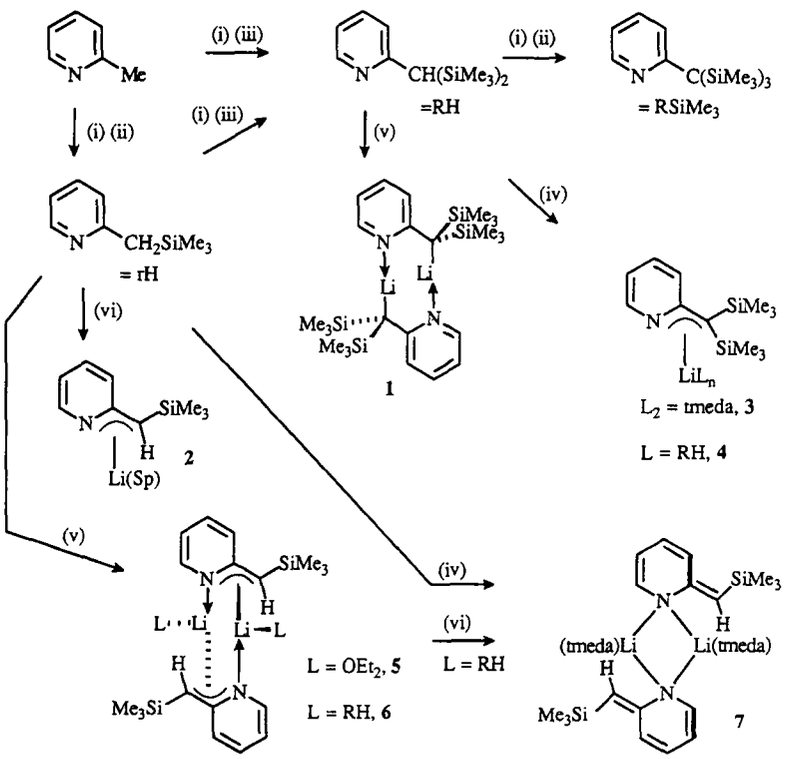
Elsevier Science S.A.
SSDI 0022-328X(95)00527-7

Key features of this systematic study include (i) observation that the ligands r and R can interact with lithium in a variety of ways, as η^1-alkyls, **1**, four and six electron species as η^3-aza-allyl ligands, **2–4**, and η^3-aza-allyl:σ-donor ligands, **5** and **6**, and four electron species as a bridging amido entity with an exocyclic double bond, **7**; (ii) the formation of two coordinate lithiums as in **1**, albeit with additional agostic Li....H contacts; (iii) the finding that η^3-aza-allyl systems can be associated with lithium attached to one donor group, as in **4** where the donor group is RH, or two donor groups, tmeda, as in **5**, or (−)-sparteine, as in **2**; (iv) observation of the formation of η^3-aza-allyl or bridging amido species for r for two different bidentate co-ligands, tmeda or (−)-sparteine, **2** and **7** respectively, the more hindered bidentate favouring the monomeric η^3-aza-allyl species; (v) the finding that in the absence of an external LiBu^n activating agent such as tmeda, mixed metallated/unmetallated species, **4** and **6** are formed, which has mechanistic implications in respect of complexation of lithium by the N-hetero atom being the primary process en route to metallation; (vi) the finding that OEt_2 catalyses the formation of **1** from LiBu^n and RH, the product arising from competitive complexation between diethyl ether and intermolecular N-donation, the steric hindrance at the *ispo*-C centre and design characteristics of the N-centre relative to the *ispo*-C centre favouring the dimeric species even when the product is recrystallised from the stronger O-donor THF, although THF complexation persists in solution; (vii) related to (vi) is the observation of the absence of multicentre bonding in **1** for a highly electron deficient species, which presumably arises from buttressing effects of the trimethylsilyl groups, and the incorporation of OEt_2 in the product for the less silyl-substituted 2-methylpyridine, **5**; and (viii) the observation that except for the formation of compound **6** the reactions can be explained in terms of expected thermodynamic acidities, including the formation of RH in a single metallation reaction from 2-methylpyridine since the methyl group in 2-methylpyridine and methylene group in rH would favour metallation of preformed rH by metallated 2-methylpyridine. Compound **6** is formed by treating a 1:1 mixture of rH and RH, establishing the reverse acidity rH > RH, which can be accounted for in terms of negative hyperconjugation in rH which over-rides the extra polarisation by the two silicon centres in RH [8]. Compound rH can be prepared according to Scheme 1 or by treating 2-methylpyridine with $LiNPr^i_2$ in THF then with $SiMe_3Cl$ [21].

Analogous to the formation of RH in a single metallation step is the formation of 2-methyl-6-bis(trimethyl-



Scheme 1. Organolithium reagents derived from metallation of 2-trimethylsilylmethylpyridine and 2-bis(trimethylsilyl)methylpyridine: (i) Li(tmeda)Bu^n/hexane; (ii) $SiMe_3Cl$, hexane; (iii) $SiMe_3Cl$, OEt_2; (iv) LiBu^n/hexane or Li(tmeda)Bu^n/hexane; (v) LiBu^n/hexane — OEt_2 or RH; (vi) Li[(-)sparteine]Bu^n/hexane — OEt_2; and (vi) tmeda/hexane.

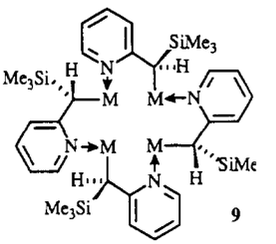
silyl)methylpyridine, MeRH, via lithiation of 2,6-dimethylpyridine using $LiBu^n$ as its tmeda complex [18,22]. Metallation of MeRH using $LiBu^n$(tmeda) yields the methine-abstracted product, as expected on acidity grounds, although on quenching with $SiMe_3Cl$, 2-trimethylsilyl-6-bis(trimethylsilyl)pyridine is formed, a result that has been ascribed to tautomerisation of the carbanion [18]. Metallation of this tris-trimethylsilyl derivative is at the methylene carbon, consistent with the formation of **6** in lithiation of a mixture of rH and RH, Scheme 1 [8]. Lithium complexes of rMe and RMe ligands have also been prepared by treating the corresponding substituted pyridine with $LiBu^n$ in hexane/OEt_2, and they are useful in preparing a range of other Main Group derivatives [22]. Related to these studies is the direct dilithiation of 2,6-bis(trimethylsilylmethyl)-pyridine at the methylene positions, the product was characterised as the tmeda adduct with each $Li(tmeda)^+$ unit bound η^3-aza-allyl, as in **2–4**, on opposite sides of the plane defined by the heterocycle and adjacent *ipso*-C-centres [23].

Monovalent Group 11 species, $[(MR)_2]$, **8**, X = H, M = Cu [7,10], Ag [9,10] and Au [10], have been prepared from **1** in THF. The copper compound has remarkable thermal stability, subliming at 160°C in vacuo, whereas the gold compound decomposes at 120°C, and the silver compound is even less stable, decomposing above 0°C. The copper compound is also unusual in showing a two electron oxidation, thus yielding the first example of a formally Cu(II) alkyl species. Analogous compounds based on RMe, $[M(RMe)_2]$, **8**, X = Me, M = Cu, Ag and Au, are similarly prepared [22] and are more thermally stable, especially the silver compound which melts without decomposition at 151°C. The increased stability is a result of the extra kinetic protection at the metal centre associated with the presence of the methyl group in the 6-position of the pyridine.

The three compounds $[(MR)_2]$, **8**, X = H, M = Cu [7,10], Ag [9,10], and Au [10], are centrosymmetric species with close M....M contacts, and N–M–C angles close to 180°, 2.214(1) Å, 178.0(5)°, M = Cu, 2.656(1) Å, 174.5(1)°, M = Ag, 2.672(1) Å, 176.3(5)°, M = Au, and the hydrocarbyl group acting as an A-frame [10]. Interestingly, in the case of **1** the structure is highly distorted relative to the others, showing agostic Li.....H contacts with N–Li–C 146.(4) Å [7]. While none of the compounds based on RMe have been structurally authenticated, steric hindrance would dictate a dimeric structure with the pyridine ring methyl group of one ligand astride two trimethylsilyl groups of the other ligand.

For the less hindered ligand, r, only the copper compound **9** could be prepared; reactions involving lithium reagents with the silver and gold substrates rapidly yielding metallic mirrors [10]; unlike **8**, compound **9** is a tetramer rather than a dimer with the ligands bridging successive metal centres, alternating above and below the Cu_4 plane, M.....M much longer than in **8**, X = H, M = Cu, at 2.668(2) Å. The corresponding Cu(I) alkyl based on CH_2SiMe_3 is also a tetramer, but with multicentre bonding [24]. We note that for compounds of rMe that the silver derivative is isolable [22], but the corresponding r compound spontaneously decomposes at room temperature to give a silver mirror.

8, X = H or Me, M = Cu, Ag, Au

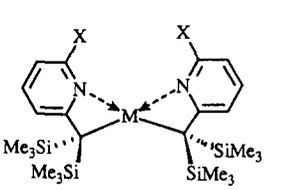


9

3. Group 2 and 12

Mononuclear complexes $[MR_2]$, **10**, X = H, M = Mg, Zn, Cd and Hg [11], are accessible via metallation of RH with $MgBu^nBu^s$ in heptane, M = Mg, or $Cl^-/-R$ exchange involving $LiR(THF)_n$ and MCl_2, M = Zn, Cd and Hg; rH is also metallated by $MgBu^nBu^s$ [11]. Compounds **10** have high thermal stability, but a slightly greater reactivity than the related compounds $[M\{C(SiMe_3)_3\}_2]$, M = Zn, Cd and Hg [25].

Developments involving the 6-methylsubstituted ligands RMe and rMe include (i) the synthesis of $[M(RMe)_2]$, M = Zn, Cd, Hg, from the appropriate metal chloride and lithium reagent [22], all structurally authenticated [26] and of comparable stability to the $[MR_2]$ analogues; (ii) similar synthesis of $[Cd(rMe)_2$(tmeda)] [22], structurally authenticated [26]; and (iii) synthesis of [M(RMe)Cl], M = Zn, Hg, structurally authenticated in the case of M = Hg along with [HgRCl] [26]. The latter compounds are prepared by the reaction of one equivalent of a lithium reagent with a metal chloride or *via* redistribution of preformed dialkyl compound with the metal chloride, although for zinc excess



10, X = H or Me, M = Zn, Cd, Hg

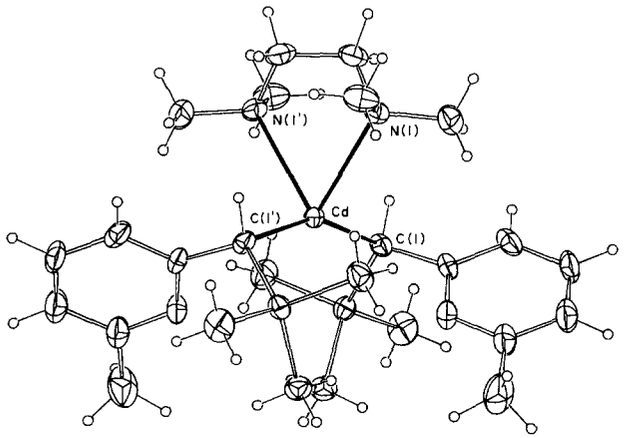


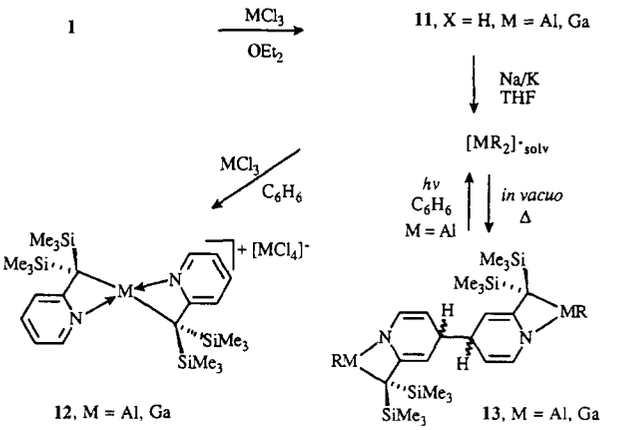
Fig. 1. Projection of the molecular structure of $[Cd(rMe)_2(tmeda)]$ which has crystallographically imposed C_2 symmetry; Cd–C(1) 2.217(7); Cd–N(1) 2.606(5); C(1)–Cd–C(1') 152.5(2)° [26].

of the dialkyl is required, a 1:1 mixture resulting in only 34% conversion into the alkyl chloride [22, 27].

In compounds **10**, X = H, the ligand R acts as a chelate with the dative M–N interaction progressively weakening down Group 12, as reflected in elongation of the distances, 2.30, 2.49, 2.78 Å, cf. 2.13 Å, for M = Mg, and an opening of the C–M–C angle, 164, 174, 180°, cf. 157° for M = Mg. (For related $[M[C(SiMe_3)_3]]$, M = Mg, Zn or Hg, the angle is restricted to 180° [1b].) The formation of chelate ring systems is not observed in lithium complexes based on the same ligand. A similar structural trend is also observed for compounds **10**, X = Me, M = Zn. Cd, Hg [26], although there are considerable differences in angles, most noteworthy is the decrease in the N–M–N angle for M = Zn and Cd by 20.8 and 22.8°, respectively. This can be traced to the fact that the pyridine ring methyl group would otherwise clash with the trimethylsilyl substituent of the other ligand.

Compound $[Cd(rMe)_2(tmeda)]$ crystallises as the *rac*-isomer with the *ipso*-protons directed towards the tmeda, Fig. 1. Here the pyridyl-N groups are remote from the metal centres, as in the case of **10**, X = H, Me, M = Hg, and presumably complexation of tmeda is favoured over intra-molecular complexation within strained four membered chelate ring systems, despite the fact that the Cd–N distances, 2.605(5) Å are longer than the Cd–N distances in the aforementioned homoleptic compounds based on R and RMe which possess such ring systems in which the distances are 2.49 and 2.517 Å respectively. Overall, the geometry is grossly distorted tetrahedral with a large C–Cd–C angle typical of compounds of this type, and also for N-donor adducts of dialkylzinc species [28].

The structure of [HgRCl] [26] shows a near linear 2-coordination which is due to relativistic effects [29]. There is a weak secondary Hg.....Cl interaction across a centre of symmetry, at 3.588(4) Å, consistent with



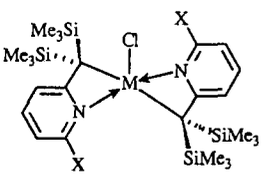
Scheme 2.

theoretical studies on $HgCl_2$ [29]; the same structural motif has also been established for [Hg(RMe)Cl (Hg–C 2.12(1) Å, Hg–Cl 2.329(5) Å, C–Hg–Cl 175.0(3)°, Hg .... Cl 3.559(7) Å [22, 26], and related systems [1d, 30]. More pronounced secondary metal .... halogen interaction is expected for [Zn(RMe)Cl], as has been observed for $[Zn(CPh_2SiMe_3)(\mu\text{-}Cl)]_2$ [1d].

4. Group 13

Chelate ring formation is also prevalent in Group 13 chemistry. Two types of M(III) compounds based on R have been structurally authenticated, the five coordinate species, **11**, X = H, M = Ga, In, Scheme 2, derived from $Cl^-/-R$ exchange, and the four coordinate cationic species isolated as the tetrachloroaluminates **12**, M = Al, Ga, on treatment of **11**, X = H with MCl_3 [12,13]. These form liquid clathrates in benzene with the overall composition 1:12 and 1:6 complex:solvent for M = Al and Ga respectively It is noteworthy that cationic aluminium alkyls are uncommon [31, 32], unlike those of the heavier Group 13 elements.

Other Group 13 chemistry includes: (i) the synthesis of $[M(RMe)_2Cl]$, M = Al, Ga, In, and $[InR_2Cl]$, via $Cl^-/-R$ exchange, and (ii) the synthesis of $[M(RMe)Cl_2]$, M = Al, In, made exclusively by the $Cl^-/-R$ exchange route except for M = In for which the dichloride was also prepared by redistribution involving $InCl_3$ and $[In(RMe)_2Cl]$ [22]. Compound



11, X = H or Me, M = Al, Ga, In

$[Al(RMe)Cl_2]$ does not form a liquid clathrate in benzene, unlike the corresponding R analogue, which is in fact ionic, characterised as $[AlR_2]^+[AlCl_4]^-$ [12]. This suggests that $[Al(RMe)Cl_2]$ is stabilised as a four coordinate neutral species, the extra methyl substituent on the pyridine ring disfavouring ligand redistribution to a species with two alkyl groups on the same metal centre. For $[InRCl_2]$ a covalent oligomeric structure is likely in the solid, and in solution (nitromethane) unlike the aluminium and gallium ionic species [12, 13]. Indeed the related compounds $[In(CH_2SiMe_3)_2Cl]$ and $[In(CH_2SiMe_3)Cl_2]$ and dimeric and polymeric respectively, with the halides bridging two metal centres [4].

Overall, the environment about the metal in $[MR_2]^+$ is a distorted tetrahedron [13], similar to the isoelectronic $[MgR_2]$ [11], the distortion arising from the strained four membered chelate ring systems. Surprisingly the compound $[InR_2Cl]$ [26] is not isostructural with the gallium analogue, Fig. 2 [13], crystallising in $Pn2_1a$ (Z = 4) cf. $C_{2/c}$, (Z = 12). Nevertheless the coordination environment is very similar, being a distorted trigonal bipyramidal with N-donors in apical positions. The structure is similar to the closely related intramolecularly co-ordinated species $[In(C_6H_4\text{-}o\text{-}CH_2NMe_2)_2Cl]$ [33]. The compound $[InR_2Cl]$ is fluxional in solution, with equivalent trimethylsilyl groups on the ^1H NMR time scale, as for the gallium analogue [13]; in the solid there are two different types of trimethylsilyl groups. The aluminium analogue however, has non-equivalent groups on the ^1H NMR time

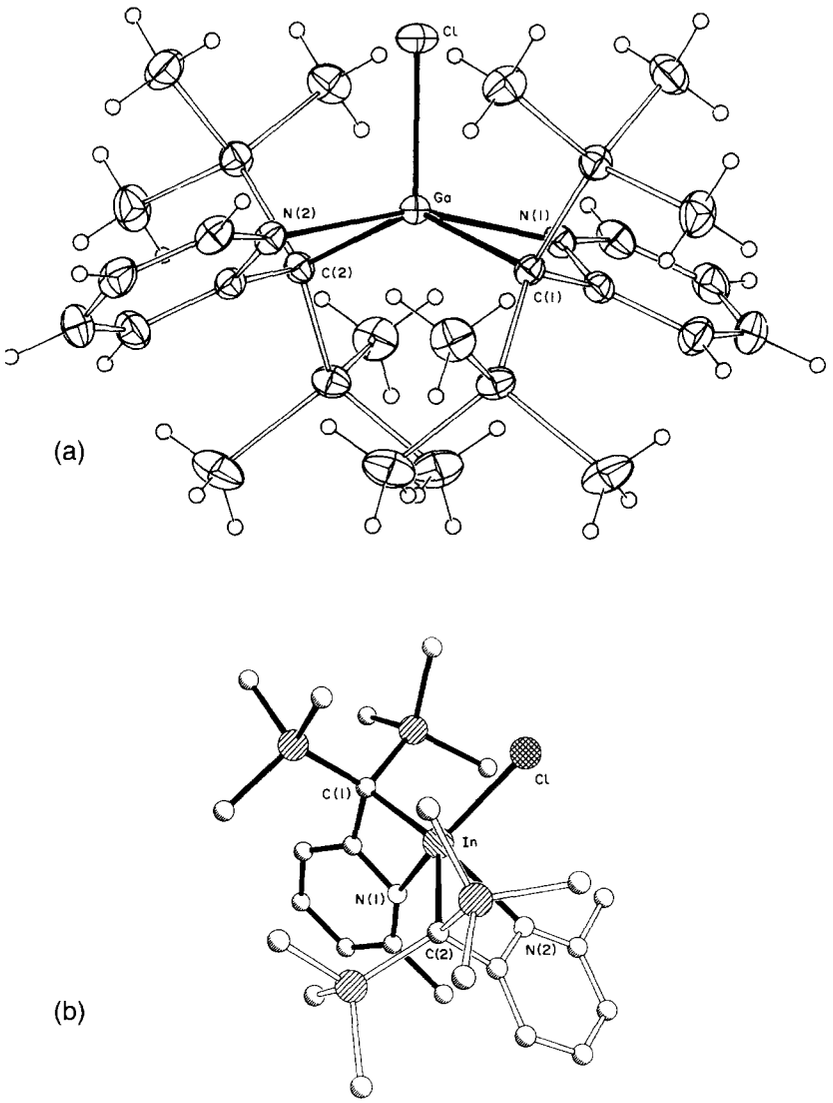


Fig. 2. Crystal structures of (a) $[GaR_2Cl]$ [13] and (b) $[In(RMe)_2Cl]$ [26]; Ga, In–Cl 2.218, 2.452(2) Å, Ga, In–C 2.065, 2.267 Å, Ga, In–N 2.223, 2.336(6) and 2.514(6) Å, Cl–Ga, In–C 105.2(1) to 111.7(1), 103.6(2) and 110.1(2)°, Cl–In, Ga–N 96.5(1) to 100.1(1)°, 90.6(2) and 84.4(2)°, C(1)–Ga, In–C(2) 132.7(2) to 149.5(2), 138.9(2)°, N–Ga, In–N 159.8(1) to 167.1(1), 84.4(2)°, C(1)–Ga, In–N(1) 65.6(2) to 67.2(2), 67.5(4)°, C(1)–Ga, In–N(2) 104.8(2) to 110.7(2) (includes C(2)–Ga–N(1)), 140.8(2)°, C(2)–In–N(1) 105.9(2).

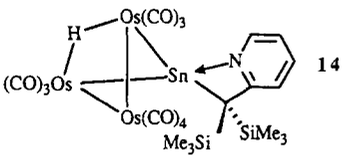
scale, consitent with rigid chelate rings being maintained in solution for a five coordinate species, possibly of similar geometry to the gallium analogue in the solid.

The stereochemistry around the metal centre in $[Al(RMe)_2Cl]$ is similar to that of $[MR_2Cl]$, M = Ga [13], In, for example, a distorted trigonal bipyramid with the N-centres in apical positions, 158.9(4)° [26]. This further supports the view that the structure of $[AlR_2Cl]$ possesses the same stereochemistry about the metal centre. Seemingly the incorporation of the methyl groups in the six position of the pyridine rings has little effect on the arrangement of the ligands. However, for the indium compound a different stereochemistry is evident, the most obtuse angle being associated with an N-centre and a C-centre, 140.8(2)°, Fig. 2 [26]. The origin of this is unlikely to be in the steric requirements of the ring methyl groups since the metal centre is larger. Rather it reflects a flat potential energy surface for the five coordinate species, which is consistent with the fluxional process for this compound and that based on R (see above). Thus the solid state structures of both these compounds represent isomers for time averaging of the trimethylsilyl groups in solution. The metal ligand distances in both are similar and similar to those in $[In(C_6H_4\text{-}o\text{-}CH_2NMe_2)_2Cl]$ [33].

Reduction/halide abstraction for **11**, X = H, M = Al, Ga is effected using Na/K alloy in THF, affording highly coloured solutions containing the paramagnetic, ligand centred $[MR_2]\cdot$, which reversibly associates in the solid to a diamagnetic material, Scheme 2 [13]. This is reminiscent of the formation of the Gomberg dimer, $(trityl)_2$, in solutions containing the trityl radical, $CPh_3\cdot$ [34], although here there is head-to-tail association, **13**, in contrast to tail-to-tail association in the cream or pale green solid Al and Ga containing species. Bulky alkyl ligands lacking an N-functionality undergo association via weak M–M bonding as $R_2M\text{–}MR_2$, formally Al(II) and Ga(II) species, R = $CH(SiMe_3)_2$ [3].

5. Group 14

Interest in the Group 14 elements concerns the stabilisation of hypervalent Si(IV) species, and divalent metal species. Compounds of the latter type have been prepared for tin, notably $[SnR_2]$ (from **1**), [SnRCl] (from **1** or redistribution involving $[SnR_2]$ and $SnCl_2$), and $[SnR\{N(SiMe_3)_2\}]$ (from **1** and $[Sn\{N(SiMe_3)_2\}]$) [15, 16]. In all structures in the solid state R acts as chelate ring to the metal centres which all possess a stereochemically active lone pair of electrons. Surprisingly $[SnR_2]$ is isostructural with **11**, M = Ga, with the latter having the chloride in place of a pair of electrons. Sn–N–donor dissociation is evident in solution for [SnRCl], ΔG 43.5(8) kJmol^{-1}, and $[SnR\{N(SiMe_3)_2\}]$, ΔG 42.7(8) kJmol^{-1}, with an additional fluxion for the



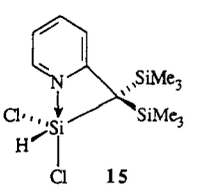
14

latter compound attributed to rotation about the Sn-amide nitrogen bond, ΔG 76.1(8) kJmol^{-1}. The related compound, $Sn\{CH(SiMe_3)_2\}_2$ is associated in the solid, with a short Sn–Sn bond of 2.768 Å, but exists as an equilibrium mixture of this dimer and the monomer in solution [2]. No substantiated Ge(II) or Pb(II) compounds have been prepared. $[SnR_2]$ reacts with $[Os_3(H)_2(CO)_{10}]$ to afford a stannyne complex, $[Os_3(\eta\text{-}H)SnR(CO)_{10}]$, **14** [35].

Reaction of $[SiCl_3X]$ (X = H or Me) or $[SiCl_2Me_2]$ with **1** yields five coordinate species $[SiRCl_2X]$ or $[SiRClMe_2]$, which show strong intramolecular Si–N interactions in the solid (X-ray structure of X = H, **15**) and in solution with a rapid equilibrium between four and five coordinate species, ΔG = 51(4) kJmol^{-1} [14, 22]. The analogous compounds based on the related ligand 2-Ph_2-2-pyridyl, seemingly showing similar steric hindrance and ligand bite, are devoid of Si–N interactions, and it appears the Si–N interaction in $[SiRCl_2X]$ arises from minimisation of steric buttressing between the proton attached to C(2) of the pyridyl ring and the trimethylsilyl groups in R. In general less strained ring systems are required for stabilising hypervalent species involving N-donation [36].

Other Group 14 chemistry focuses on silicon(IV) species based on RMe, rMe and r [23], and includes (i) the synthesis of the five coordinate species $[Si(RMe)XCl_2]$, X = Me or H, structurally authenticated for X = H [26], and $[Si(RMe)Me_2Cl]$ (^{29}Si NMR), whereas the trimethylsilyl derivative of RMe, $[Si(RMe)Me_3]$, is four coordinate (^{29}Si NMR); and (ii) the synthesis of four coordinate *rac*-$[Si(r)_2MeX]$, X = Me, Cl (both structurally authenticated [26]), and $[Si(rMe)_2MeX]$, X = Me, Cl, all generated from a lithium reagent and the appropriate chlorosilane.

The structure of $[Si(RMe)HCl_2]$ is the same as that of $[SiRHCl_2]$, **15** [14], with the unique silicon in a trigonal bipyramidal environment, the N-donor and one of the chlorides in apical positions. Molecules of $[Si(r)_2MeX]$, X = Me or Cl, are present as the *rac*-iso-



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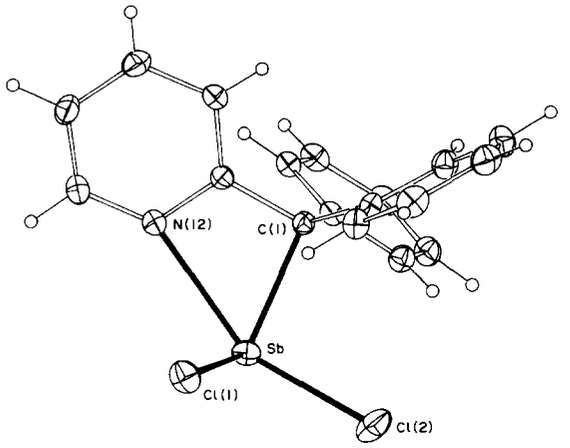


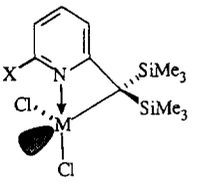
Fig. 3. Crystal structures of [Sb(CPh$_2$-2-pyridyl)Cl$_2$] [39]: Sb–Cl(1) 2.370(2), Sb–Cl(2) 2.421(2), Sb–C(1) 2.253(4), Sb–N(12) 2.521(3) Å, Cl(1)–Sb–Cl(2) 90.84(4)°, Cl(1)–Sb–C(1) 104.81(8)°, Cl(1)–Sb–N(12) 80.70(7)°, Cl(2)–Sb–C(1) 93.97(9)°, Cl(2)–Sb–N(12) 148.16(7)°, C(1)–Sb–N(12) 59.44(9)°.

mers in the solid, with a C_2 symmetry axis imposed, such that for X = Cl, the chloride and methyl group attached to the same silicon centre are disordered. Spectroscopic data on the related compounds [Si(rMe)$_2$MeX], X = Me, Cl, are also consistent with a *rac*-isomer and four coordination for the unique silicon centre.

6. Group 15

Attempts to extend the methodology to Group 15 chemistry have been thwarted by decomposition and competing reactions [17]. The compounds [MRCl$_2$], **16**, X = H, can be prepared from **1** and MCl$_3$, M = As, Sb and Bi, the arsenic compound being thermally unstable (dec. 20 °C) with respect to elimination of SiMe$_3$Cl; facile elimination of the same species also occurs on attempts to prepare the analogous phosphorus compound, as is the case for the related P(III) compound [P{C(SiMe$_3$)$_3$}Cl$_2$] [37]. Another related ligand, CPh$_2$-2-pyridyl, devoid of trimethylsilyl groups but with similar steric hindrance, yields a stable dichloro species, [P(CPh$_2$-2-pyridyl)Cl$_2$] [38]; the antimony analogue has also been prepared and structurally authenticated showing a chelate ring and the environment around the metal greatly affected by a stereochemically active lone pair of electrons [39], Fig. 3, similar to that established for **16**, X = H, M = Sb [17], and the corresponding RMe derivative, (see below). The potential for novel chemistry for [P(CPh$_2$-2-pyridyl)Cl$_2$] alone is demonstrated by its reaction with M(COT), M = Ca, Sr and Ba, to yield a stable phosphacyclopropane, [P(η^2-COT)(CPh$_2$-2-pyridyl)] (COT = cyclooctatetraene) with no P.....N interaction [38].

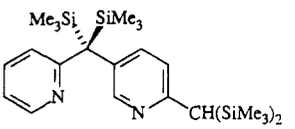
Treatment of BiCl$_3$ with 1.5 equivalents of **1** results in a head-to-tail coupling, **17**, which presumably arises



16, X = H or Me, M = As, Sb, Bi

from reductive coupling and/or nucleophilic attack of a coordinated R followed by rearrangement. Radical intermediates are unlikely in view of the tail-to-tail coupling for MR$_2$ · species, M = Al, Ga [13]. The reaction of NiCl$_2$ with Li(r) in THF yields the head-to-head coupled product, **18**, along with elemental nickel, possibly via a reductive-elimination process [40], whereas the reaction of NiCl$_2$ with **1** gave the head-to-tail product, **17**, along with some [NiR$_2$] [40]. Here and in the bismuth case head-to-head coupling is impossible because of steric buttressing in linking two heavily substituted carbons, cf. the Gomberg dimer [34]. Attempts to prepare [MR$_2$Cl] species, M = As and Sb results in elimination of SiMe$_3$Cl, but for bismuth a red solid is obtained which rapidly decomposes at 0°C yielding a novel 'C_2' insertion product, **19**, which most likely arises from loss of CH$_2$ = C(H)-OSiMe$_3$ possibly from a Bi(V) intermediate, for example, one derived from oxidative addition to Bi(III) of a C–O bond of THF.

The first Group 15 compound based on a mono-silyl substituted alkyl, rMe, viz. [Sb(rMe)Cl$_2$]$_2$ is dimeric with bridging chlorides in the solid state, Fig. 4 [26] (cf. monomeric for [SbRCl$_2$] [17], and [Sb(RMe)Cl$_2$] [26]). Phosphorus, arsenic, antimony and bismuth(III) compounds of the type [M(RMe)Cl$_2$] are readily accessible via lithium/halogen exchange reactions; the phosphorus compound is significantly more stable than the corresponding R analogue (dec. > −78 °C), slowly de-



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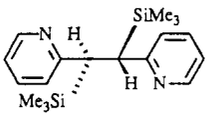

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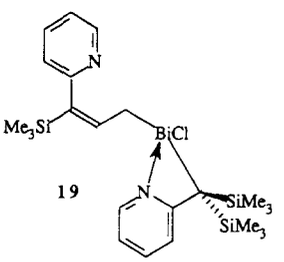

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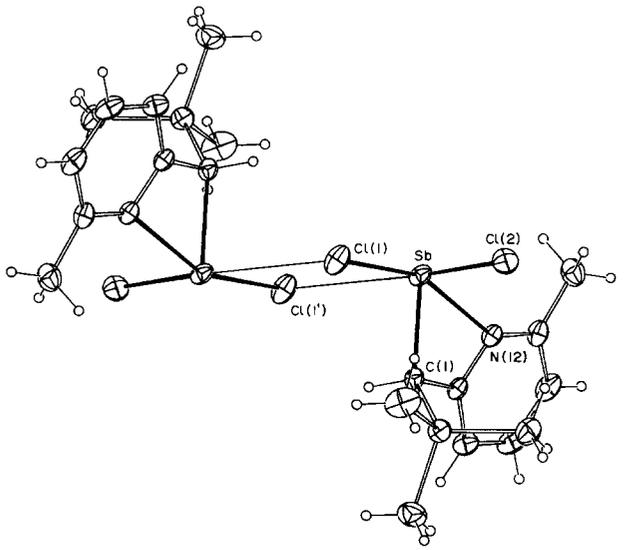

Fig. 4. Projection of centrosymmetric, dimeric $[Sb(rMe)Cl_2]_2$; selected bond distances (Å): Sb–Cl(1) 2.494(1), Sb–Cl(2) 2.393(1), Sb–C(1) 2.177(4), Sb–N(12) 2.418(3), Sb–Cl(1') 3.352(1) [26].

composing at 0°C. The first dialkyl based on R or RMe, has also been prepared, viz. $[Sb(RMe)_2Cl]$. The structures of $[Sb(RMe)Cl_2]$ [26] and the R analogue [17] have the same stereochemistry about the metalloid centre, viz. a distorted trigonal bipyramid with the Cl, chelating C, Sb and the lone pair of electrons approximating to a trigonal plane. The formation of a dimeric structure in the case of rMe demonstrates the need to use bulky ligands to circumvent bridging halide species, and oligomeric and polymeric species [17]. The overall stereochemistry is a distorted octahedron with a stereochemically active lone pair of electrons in a plane containing Sb, N(12), Cl(1), and C(1), Fig. 4 [26].

7. Transition metal chemistry

Developments for r and R, other than for Group 11 and 12 elements and the osmium cluster stannyne complex, **14**, discussed above, include (i) formation of monocyclopentadienylnickel(II) derivatives for both ligands, as thermally stable species, the compound $[NiR(\eta^5\text{-}C_5H_5)]$ being structurally authenticated and showing a chelate ring system for the hydrocarbyl group [41]; (ii) the synthesis of the thermally stable Co(II) alkyl species, *trans*-$[CoR_2]$, derived from **1** and $CoCl_2$, the chelate rings here being associated with a *trans*-square planar metal centre [41]; (iii) the low yield synthesis of the air stable, square planar $[NiR_2]$ [18]; and (iv) the synthesis of $[(\eta^5\text{-}C_5H_5)_2ZrCl(r)]$ from **7** (Scheme 1) and zirconocene dichloride, the N-donor attached to the metal centre in the solid, while in solution there is a temperature dependant equilibrium between this species and the N-free metal centre species [42]. Reduction to the Zr(III) species results in metal–halogen cleavage, possible with the zirconocene moiety attached to r in a chelate ring or as an η^3-aza-allyl linkage, cf. lithium complexes in Scheme 1.

8. Conclusions

The use of bulky alkyl ligands bearing 2-pyridyl substituents offers scope for gaining access to new classes of compounds across a wide spectrum of the Periodic Table, stabilised in part by N-donor interaction to the metal or metalloid centres. Compounds isolated thus far include monomeric, hypervalent, subvalent, electron deficient and low coordinate species. Clearly the ligands bearing two trimethylsilyl groups on the *ipso*-carbon in R and RMe are preferred over those bearing one such group, r and rMe. However, a possible complication for these types of pyridyl/trimethylsilyl substituted alkyl ligands is the tendency towards coupling reactions, 'head-to-tail' and 'tail-to-tail', identified from reactions aimed at preparing novel species directly by metal halogen exchange, or of gaining access to unusual oxidation states via reduction routes. Thus further developments in this area would be the incorporation of N-donor groups, or other donor types, not associated with aromatic ring systems and/or facilitating electron transfer away from the metal/metalloid centres. Another complication is the tendency to eliminate trimethylsilyl chloride in the case of Group 15 derivatives, although the use of RMe rather than R lowers the case of this decomposition pathway, at the same time imparting greater kinetic protection at the metal/metalloid centre in consequence of the extra steric hindrance associated with the pyridine ring methyl substituent.

Acknowledgements

The authors gratefully acknowledge contributions to the research from Professor Allan White, Dr. Lutz Engelhardt, Dr. Ulrich Kynast, Dr. Rocco Papasergio, and Dr. Brian Skelton (University of Western Australia), Professor Michael Lappert and Dr. Brian Jolly (University of Sussex), Alexander Sobolev (L. Karpov Institute of Physical Chemistry), and Dr. Mark Henderson and Dr. Cameron Jones (Griffith University). Financial support from the Australian Research Council is also acknowledged.

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