Oxidation reactions of an anionic gallium(I) N-heterocyclic carbene analogue with group 16 compounds

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Received 12th April 2005, Accepted 11th May 2005
First published as an Advance Article on the web 23rd May 2005

The reactivity of an anionic gallium(I) heterocycle, [K(tmeda)]{[N(Ar)C(Me)]2CH]}, R = C6H4,Pr′, towards elemental chalcogenes and diorgano-dichalcogenides has been investigated and comparisons drawn with the reactivity of the valence isoelectronic N-heterocyclic carbene class of ligand. The reactions of the heterocycle with N2O or (Te)PEt3 yielded the dimeric, dianionic gallium(III) complexes, [K(L)2][{(N(Ar)C(Me))2CH}]2, in a low isolated yield (Scheme 1). In addition, acyclic gallium(III) diyls, :GaR, are known to react with sources of elemental chalcogenes to give higher nuclearity complexes, for example the tetrameric heterocycle species, [EGa(C(SiMe3))2]12, where E = S, Se or Te.11 Herein, we report the outcomes of the reactions of 1 with sources of the non-radioactive chalcogenes and several dialkyl and diaryl-dichalcogenides.

Introduction

Our group1 and that of Schmidbaur2 have reported the syntheses of the anionic gallium(I) heterocycles, [Ga{(N(R)C(R′))2CH}]2, R = 2,6-disopropylphenyl or Bu′, which are valence isoelectronic analogues of the important N-heterocyclic carbene (NHC) class of ligand, viz.: C{(N(R)C(R′))2}. R′ = H, alkyl etc. In the past 10 years, the coordination chemistry of NHCs has been exhaustively studied and complexes with the majority of the non-radioactive metals are now known.3 Many of these have displayed activity as homogeneous catalysts in a number of synthetic processes, and some complexes are now commercially available for this purpose. Considering the importance of NHCs as ligands, we have embarked on a study to investigate the coordination chemistry of 1 toward s-, p- and d-block metals.4 In its early stages this has shown that there are parallels between the two ligand classes, and that like NHCs, 1 can stabilise metal fragments that are thermally labile and/or contain the metal in a low oxidation state.5 The stabilising ability of 1 is derived from its steric bulk and the very nucleophilic nature of the essentially sp-hybridised metal lone pair at its gallium centre.

The reactivity of NHCs towards the non-metallic or metalloid elements, and compounds containing these elements, has not been studied in great detail but a number of important results have been forthcoming. For example, the reactions of NHCs with elemental sulfur, selenium or tellurium have been documented, and the properties and further chemistry of the resulting monomeric cyclic chalcogenoureas, [(E)(C{(N(R)C(R′))2})], E = S, Se or Te, have been investigated.4 Of particular note here is the excellent thermal stability of cyclic tellurolurea derived from NHCs.6 This can be compared with that of most other tellurocarbonyl compounds, which are normally only isolated as metal complexes. It should also be mentioned that a silicon analogue of NHCs, Si{(N(R)C(Me))2CH}], has recently been shown to react with sulfur or selenium to give the chalcogen bridged dimers, [(µ-E)Si{(N(R)C(Me))2CH}]2, E = S, Se or Te.7 In light of the stability of complexes derived from the reactions of NHCs with group 16 precursors, it would be of interest to investigate the reactivity of 1 towards similar precursors. Although a variety of complexes between gallium and heavier chalcogenes are known,8 it was thought that the nucleophilicity and steric bulk of 1 could lead to stable complexes of low nuclearity. In this respect, it is worthy of mention that neutral gallium(I) heterocycles related to 1 have been successfully utilised to prepare the terminal chalcogenide complexes, [Te(H)(µ=(N(Ar)C(Me))2CH)]28 and [Te(H)(µ=(N(Ar)C(Me))2CH)]29 with the chalcogenide bridged dimers, [(µ-E)Ga{(N(Ar)C(Me))2CH}], E = O or S.10 In addition, acyclic gallium(II) diyls, :GaR, are known to react with sources of elemental chalcogenes to give higher nuclearity complexes, for example the tetrameric heterocycle species, [EGa(C(SiMe3))2], E = S, Se or Te.11 Herein, we report the outcomes of the reactions of 1 with sources of the non-radioactive chalcogenes and several dialkyl and diaryl-dichalcogenides.

Results and discussion

In the initial stages of this study it was observed that exposure of [K(tmeda)][1] to an excess of either dry air or O2 resulted in decomposition of the heterocycle and the recovery of the diazaabutadiene, [N(Ar)=C(CH3)], as the only isolable product. As a result, a more controllable route to the oxidation of the gallium(I) heterocycle was sought. To this end, its treatment with a stoichiometric amount of N2O gave rise to the dimeric, dianionic gallium(III) complexes, [K(L)2][{(N(Ar)C(Me))2CH}], E = O or S.10 In addition, acyclic gallium(III) diyls, :GaR, are known to react with sources of elemental chalcogenes to give higher nuclearity complexes, for example the tetrameric heterocycle species, [EGa(C(SiMe3))2], E = S, Se or Te.11 Herein, we report the outcomes of the reactions of 1 with sources of the non-radioactive chalcogenes and several dialkyl and diaryl-dichalcogenides.

Scheme 1

(i) N2O, Et2O; (ii) (Te)PEt3, THF; (iii) Ph2Se2, Et2O; (iv) Ph2Te2, Et2O.

To overcome this lack of reactivity, [K(tmeda)][1] was reacted with soluble sources of the atomic chalcogenes. In the case of sulfur, the gallium heterocycle was treated with 1 equiv.
of either propylene sulfide or (SP)PPb, but both reactions led to intractable mixtures of products. Similarly, the reaction of [K(tmeda)][I] with (Se)PcEt, yielded an inseparable mixture of products, no components of which could be identified. More success was had in the reaction of (Te)PcEt, with the gallium heterocycle. This proceeded, in good yield, to the extremely sensitive, yet thermally robust dimeric complex, which is closely related to 2.

The NMR spectra of 2 and 3 are consistent with their empirical formulae but shed little light on their degree of association. In the solid state this was determined by obtaining the X-ray crystal structures of the compounds (Figs. 1 and 2 respectively, Table 1). Complex 2 is dimeric and sits on a centre of inversion. The bridging oxide ligands have asymmetric interactions with the two gallium centres, giving rise to short [1.814(3) Å] and long [1.905(3) Å] Ga–O bond lengths. The shortness of the former interactions could suggest they possess some Ga–O double bond character involving π-donation from the oxygen centre to the empty Ga p-orbital. Indeed, they are the shortest Ga–O interactions within Ga2O4, four-membered rings by some margin and can be compared to the Ga–O distances in the related, more symmetric dimers, e.g. [Na(Al(C6H11)2)] [Na(Al(C6H11)2)] 1.8583(10) and 1.8485(9) Å and [THF][Li(μ-O)GaMe2]], (Mes = mesityl) [1.897(3) and 1.898(3) Å]. Moreover, the Ga–O bonds in 2 are significantly shorter than that in the monomeric complex, [Mes*O)GaBu]2, the [Mes*O)GaBu]2, (Mes* = C6H4Bu2–2,4,6)] [1.821(3) Å] for which a small degree of Ga–O x-bonding has been suggested.14 In addition, although the heterocycle centroid–Ga(1)–O(1) angle is more acute than the ideal angle for Ga–O x-bonding (180°), it is much more obtuse (148.5°) than the heterocycle centroid–Ga(1)–O(1) angle (126.2°). It must be said, however, that due to the electronegativity differences between Ga and O, the bonding between these two centres in 2 is probably largely ionic in character. Furthermore, the asymmetric nature of its Ga2O4 ring could arise from a disturbing effect of the O–K interaction [2.584(3) Å], which is well within the established range of coordinate bonds of this type.15 The K-centres in 2 are additionally η1-coordinated to the gallium heterocycle and chelated by a molecule of tmeda, as is the case in the dimeric solid state structure of [K(tmeda)][I]. The K–Ga distances in the former [3.1338(16) Å] are, however, considerably shorter than those in the latter [3.5318(18) Å].11 Another notable feature of the structure of 2 is the Ga···K separation of 2.608 Å, which is at the upper end of the range for Ga–K single bonds and very close to that in the related compound, [μ-O)Ga{Na(Al(C6H11)2)}2] [2.5989(3) Å].16 As was proposed for that compound, the shortness of the Ga···K distance in 2 probably does not constitute an interaction, and arises from the fact that the ligation of the Ga centres by electronegative N- and O-atoms increases their relative ionic nature and, thus, decreases their effective radii.

The molecular structure of 3 shows it to be dimeric, but in contrast to 2, the telluride ligands are essentially symmetrically bridging. The lengths of the Ga–Te bonds (2.618 Å avg.) are close to the mean for all previously structurally characterised examples (2.66 Å)13 and comparable to those in related complexes, e.g. [Te2(C2H4)], (CPh3)3Te and (C6H5)3Te [2.570(9) Å].18 They are, however, significantly longer than in terminal tellurido complexes, e.g. 2.422(3) Å in the familiar [Te2(C2H4)]2. In addition, the planar GaTe core of the complex possesses Te–Ga–Te and Ga–Te–Ga angles of 98.77(2) and 81.23(2)° respectively, which are consistent with the larger covalent radius of Te over Ga. The size of the Te centres can also be used to explain why the Ga···Te separation in 3 (3.408 Å) is much larger than that in 2 (2.608 Å). Each potassium cation of 3 is coordinated by a molecule of THF, a Te lone pair and η1- and η1′-interactions from the arene substituents of opposing gallium heterocycles. Finally, the geometries of these essentially planar heterocycles are similar to those in 2, and contain distorted tetrahedral gallium centres.

Considering the success had oxidising the gallium centre of 1 with sources of elemental chalcogens, it was deemed appropriate to investigate similar reactions with dialkyl or diaryl dichalcogenides, REER. These were thought likely to oxidatively add to the Ga(t)centre of the gallium heterocycle. In this respect, it is somewhat surprising that, to the best of our knowledge, there are no examples of related reactions between REER and NHCs. Mixed success was had in this phase of the study, as treating [K(tmeda)][I] with 1 equiv. of either Bu'OBOBu or PhSeSePh led to intractable mixtures of products, the identity of which could not be determined. In contrast, the oxidative addition reactions of [K(tmeda)][I] with PhEePh (E = Se or Te) proceeded cleanly to give the related complexes, 4 and 5, which differ only in the degree of solvation of their potassium cations (Scheme 1). These differences are derived from the
The molecular structures of 4 and 5 are depicted in Figs. 3 and 4, respectively. The geometries of the heterocycles in the anionic fragments of each, [(PhE)Ga(\([N(Ar)C(H)])\)]\(^+\), are similar and both possess distorted tetrahedral gallium centres. As was the case with the structures of 2 and 3, the Ga–N distances and N–Ga–N angles of 4 and 5 are, respectively, considerably shorter and more obtuse that those in the free gallium(III) heterocycle [Ga–N avg. = 1.970 Å; N–Ga–N = 83.02(11)°].\(^1\) There are, however, significant differences between the structures of 4 and 5. For instance, the potassium cation in 4 is coordinated by lone pairs of two SePh fragments from different heterocycles. This leads to short and long K–Se interactions [K(1)–Se(2) 3.4903(11) Å; K(1)–Se(1) 3.4903(11) Å] that lie in the normal range.\(^2\) In addition, η^- and η'^-interactions (K–C < 3.45 Å) with two heterocycle aren substituents lead to an infinite 1-dimensional polymeric structure for this complex. Although the Ga–Se bond lengths [Ga(1)–Se(1) 2.4026(6) Å; Ga(1)–Se(2) 2.4301(7) Å], both are close to the mean for all crystallographically characterised examples (2.41 Å).\(^11\)

![Fig. 3 Molecular structure of 4 (isopropyl groups removed for sake of clarity). Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.912(3), Ga(1)–N(2) 1.898(3), Ga(1)–Se(1) 2.4026(6), Ga(1)–Se(2) 2.4301(7), Se(1)–C(27) 1.923(4), C(1)–C(2) 1.336(4), Se(2)–K(1) 3.3241(10), Se(2)–K(1) 3.4903(11), N(1)–Ga(1)–N(2) 87.9(2), N(1)–Ga(1)–Te(1) 121.56(18), N(1)–Ga(1)–Te(2) 118.63(18), N(2)–Ga(1)–Te(1) 119.27(19), N(2)–Ga(1)–Te(2) 115.90(18), Te(1)–Ga(1)–Te(2) 96.06(3), Ga(1)–Te(1)–C(27) 103.9(2), Ga(1)–Te(1)–K(1) 82.57(5), K(1)–Te(1)–C(27) 127.5(2), Ga(1)–Te(2)–C(33) 94.77(18), Ga(1)–Te(2)–K(1) 85.12(5), K(1)–Te(2)–C(33) 102.3(2), Te(1)–K(1)–Te(2) 61.62(4).

Fig. 4 Molecular structure of 5. Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 1.896(6), Ga(1)–N(2) 1.900(6), Ga(1)–Te(1) 2.5785(12), Ga(1)–Te(2) 2.6577(10), Te(1)–K(1) 3.886(3), Te(2)–K(1) 3.711(3), C(1)–C(2) 1.336(4), Se(1)–Ga(1)–N(2) 87.9(2), N(1)–Ga(1)–Te(1) 121.56(18), N(1)–Ga(1)–Te(2) 118.63(18), N(2)–Ga(1)–Te(1) 119.27(19), N(2)–Ga(1)–Te(2) 115.90(18), Te(1)–Ga(1)–Te(2) 96.06(3), Ga(1)–Te(1)–C(27) 103.9(2), Ga(1)–Te(1)–K(1) 82.57(5), K(1)–Te(1)–C(27) 127.5(2), Ga(1)–Te(2)–C(33) 94.77(18), Ga(1)–Te(2)–K(1) 85.12(5), K(1)–Te(2)–C(33) 102.3(2), Te(1)–K(1)–Te(2) 61.62(4).

In contrast to 4, complex 5 is monomeric with its potassium cation chelated by both tellurium centres and coordinated by three molecules of diethyl ether. An examination of the Ga–Te bond lengths [Ga(1)–Te(1) 2.5785(12) Å and Ga(1)–Te(2) 2.6577(10) Å] revealed them to be significantly different but, again, to lie within the normal range.\(^15\) This difference could allow 5 to be described as a ‘ate’ complex of [(PhE)TeGa(\([N(Ar)C(H)])\)] and KTePh. In line with this description is the difference in the two K–Te bond lengths [Te(1)–K(1) 3.386(3) Å and Te(2)–K(1) 3.711(3) Å], the shorter of which is associated with the longer Te–Ga interaction. Furthermore, the two C–Te–Ga angles in the complex are
considerably different [C(27)–Te(1)–Ga(1) 103.9(2); C(33)–Te(2)–Ga(1) 194.7(18°)]. Finally, the Te–Ga–Te angle [96.06(3°)] is markedly more acute than the corresponding Se–Ga–Se angle in 4 [103.96(3°)], though this may be due to chelation of the potassium cation by both Te-centres in the former.

**Conclusion**

In summary, the reactivity of an anionic gallium(l) NHC analogue, [K(tmeda)][Ga{N(Ar)C(H)}2], towards sources of elemental chalcogens and diorgano-dichalcogenides has been investigated. This has given rise to four crystallographically characterised complexes in which the gallium centres have been oxidised by the chalcogen precursor. Of these, the dimeric oxide and telluride complexes, 2 and 3, display significant structural differences, which in the former may suggest a small degree of Ga-O x-bonding. Similarly, differences were observed between the structures of the polymeric phenyl selenide and monomeric phenyl telluride complexes, 4 and 5, the latter of which can be described as an ‘ate’ complex. This study further highlights both similarities and differences between the reactivity of the gallium heterocycle, [Ga{N(Ar)C(H)}2]], and that of the valence isoelectronic N-heterocyclic carbene class of ligand.

**Experimental**

**General considerations**

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. THF was distilled over potassium whilst diethyl ether (20 mL) at 78 °C was added a solution of Ph2Te2 (0.20 g, 0.46 mmol) in diethyl ether (10 mL) over 10 min. The resultant solution was warmed to room temperature and stirred for 24 h, whereupon volatiles were removed in vacuo and the residue extracted into hexane (30 mL). Filtration, concentration and placement at −35 °C overnight yielded orange–red crystals of 4 (0.22 g, 48%). Mp 168–174 °C (dec). 1H NMR (400 MHz, C6D6, 298 K): δ 1.13 (d, 12 H, JHH = 6.0 Hz, CH2), 1.24 (d, 12 H, JHH = 6.0 Hz, CH2), 3.45 (sept., 4 H, JHH = 6.0 Hz, CH2), 6.20 (2 H, NCH2), 7.07–7.64 (m, 16 H, ArH); 13C NMR (75.57 MHz, C6D6, 298 K): δ 24.1 (CH2CH), 24.4 (CH2CH), 28.0 (CH), 123.1 (CN), 123.7 (m-ArC), 123.7 (p-ArC), 124.7 (p-ArC), 127.4 (PhSe), 128.5 (PhSe), 130.7 (PhSe), 140.0 (p-ArC), 144.8 (ipso-ArC); IR (Nujol): 1666 w, 1573 m, 1459 ms, 1377 s, 1350 m, 1326 w, 1261 s, 1099 s, 1019 s, 810 w, 765 m, 733 m, 689 w, 668 m, 666 w cm−1; MS/ESI –ve: m/z (%): 681 [PhSe][Ga{N(Ar)C(H)}2]], 22, [156 [PhSe]2], 100.

[K(OE3)][(PhTe)2]Ga{N(Ar)C(H)}2]. 5. To a solution of [K(tmeda)][Ga{N(Ar)C(H)}2]] (0.35 g, 0.58 mmol) in diethyl ether (20 mL) at −78 °C was added a solution of Ph2TeC (0.24 g, 0.58 mmol) in Et2O (10 mL). The resultant solution was warmed to room temperature and stirred for 24 h, whereupon volatiles were removed in vacuo and the residue extracted into hexane (30 mL). Filtration, concentration and placement at −35 °C overnight yielded orange crystals of 5 (0.37 g, 57%). Mp 152–156 °C (dec). 1H NMR (400 MHz, C6D6, 298 K): δ 1.15 (d, 12 H, JHH = 6.5 Hz, CH2), 1.28 (d, 12 H, JHH = 6.5 Hz, CH2), 1.39 (t, 18H, JHH = 7.1 Hz, CH2CH), 4.09 (q, 12H, JHH = 7.1 Hz, CH2OCH3), 3.49 (sept., 4 H, JHH = 6.6 Hz, CH2), 6.25 (2 H, NCH2), 7.07–7.64 (m, 16 H, ArH); 13C NMR (75.57 MHz, C6D6, 298 K): δ 14.0 (CH0), 24.8 (CHCH), 25.3 (CHCH), 28.9 (CH), 69.8 (OCH2), 123.8 (CN), 124.2 (m-ArC), 124.5 (p-ArC), 128.4 (PhTe), 129.2 (PhTe), 132.5 (PhTe), 141.1 (PhTe), 143.8 (p-ArC), 144.2 (ipso-ArC); IR (Nujol): 1573 m, 1454 s, 1377 s, 1321 m, 1259 s, 1225 s, 1102 m, 1016 m, 997 w, 934 w, 799 s, 756 s, 728 s, 690 s, 650 w cm−1; MS/ESI +ve: m/z (%): 681 [PhSe][Ga{N(Ar)C(H)}2]], 22, [156 [PhSe]2], 100.

**X-Ray crystallography**

Crystals of 2, 3, 4 and 5 suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F2 by full matrix least squares (SHELX97) using all unique data. One molecule of potassium coordinated diethyl ether (that containing O3) in the structure of 5 was found to be disordered over two sites. This disorder was successfully modelled and the atoms of both disordered sets were subsequently refined isotropically. Only the atoms of the higher occupancy set are displayed in Fig. 4. All other non-hydrogen atoms in each structure were refined anisotropically with H-atoms included in calculated positions (riding model). Crystal data, details of data collections and refinement are given in Table 1.

CCDC reference numbers: 268537–268540.
See http://www.rsc.org/suppdata/dt/b5/b505085e/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC for financial support (partial studentship for MK and postdoctoral fellowship for RJB). The EPSRC mass spectrometry service at Swansea University is also thanked.

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15 As determined from a survey of the Cambridge Crystallographic Database, April, 2005.