Synthesis and characterisation of tetramethylpiperidinyloxide (TEMPO) complexes of group 13 metal hydrides

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Attempts have been made to prepare low oxidation state group 13 hydride complexes by reacting the metal trihydride–Lewis base adducts, $[MH_3(quin)]$ (quin = quinuclidine, M = Al, Ga or In), with reducing or hydrogen abstraction reagents. The 1 : 1 reactions with 2,2′,6,6′-tetramethylpiperidinyl oxide (TEMPO) yield the first structurally characterised nitroxide–group 13 hydride complexes, $[MH_2(quin)(TEMPO)]$ (M = Al or Ga). The 2 : 1 reaction with $[AlH_3(quin)]$ affords $[AlH(quin)(TEMPO)_2]$ which has also been structurally authenticated. The mechanisms of these reactions are discussed.

Introduction

The chemistry of aluminium and gallium trihydrides and their Lewis base adducts ($L \cdot MH_3$, M = Al or Ga, L = Lewis base) has been extensively explored.[1] These compounds have found numerous applications as, for example, chemo- and stereoselective reductants in organic synthesis,[2] and as precursors for materials (*e.g.* metal films and III/V semiconductors) important to the microelectronics industry.[3] In recent years, we have been examining an extension of this field to the stabilisation and further reactivity of indium trihydride complexes, with marked success.[4] We have found that the chemistry of indium trihydride adducts can significantly differ from that of their aluminium and gallium counterparts. This is perhaps best illustrated by our recent report of the controlled decomposition of $[InH_3(quin)]$ (quin = quinuclidine) in the presence of LiBr, which led to the first mixed oxidation state indium subhalide complex, $[In_5Br_8(quin)_4][(quin)_2H]$.[5]

In contrast, the fascinating chemistry of aluminium and gallium sub-halide complexes and clusters (*e.g.* $[Al_{22}Cl_{20}(THF)_{12}]$) has been well developed, largely by the group of Schnöckel.[6] Such complexes have been mainly accessed through the controlled decomposition of metastable metal(I) halide complexes, $[\{MX(L)\}_n]$ (M = Al or Ga, X = halide, L = amine, phosphine or ether). It occurred to us that there are no examples of sub-valent group 13 hydride complexes, $[M_xH_y(L)_z]$, but if these could be isolated their chemistry would be of great interest. It is of note that, to the best of our knowledge, there are only two structurally characterised complexes that could be considered to contain formally low oxidation state group 13 metal hydride fragments, *viz.* $[\{(DAB)Ga\}_2GaH_2][K(tmeda)_2]$ (DAB = $\{(2,6\text{-}C_6H_3Pr^i_2)NCH\}_2$)[7] and $[(Ar'Ga)(\mu\text{-}GaH)(\mu\text{-}PH_2)_2(GaAr')]$ (Ar′ = $2,6\text{-}C_6H_3(2,4,6\text{-}C_6H_2Pr^i_3)_2$).[8]

One potential route to low oxidation state group 13 metal hydride complexes is *via* the reactions of metal trihydride complexes with reductants or radical hydrogen abstraction reagents. Of the latter, 2,2′,6,6′-tetramethylpiperidinyl oxide (TEMPO) offered promise as it has been shown to homolytically cleave other p-block metal–hydrogen bonds (*e.g.* as in Bu^n_3SnH or Ph_3GeH) *via* hydrogen transfer to give metal–metal bonded species (*e.g.* $Bu^n_3SnSnBu^n_3$).[9] In addition, its reactivity towards low oxidation state p-block complexes has been previously examined.[10] In this report, we detail the reactivity of group 13 metal trihydride adducts towards TEMPO and other reagents. The reactions with TEMPO did not lead to low oxidation state metal hydride complexes, but instead to the first examples of nitroxide-group 13 metal hydride species.

Results and discussion

The metal trihydride adducts chosen for this study were $[MH_3(quin)]$, M = Al, Ga and In, which all possess good thermal stability relative to other Lewis base adducts. A number of methods for the preparation of low oxidation state metal hydride complexes were attempted. First, reductions of diethyl ether solutions of each adduct at −20 °C with sodium naphthalenide in 1 : 1 stoichiometries led only to complete decomposition of the adducts. Similarly, UV irradiation (λ = 254 nm) of a mixture of each complex with $Re_2(CO)_{10}$ (generating $^{\bullet}Re(CO)_5$ radicals) in toluene at −60 °C afforded intractable mixtures of products, free of M–H bonds (as determined by IR spectroscopy). These decomposition processes are not due solely to UV irradiation of the solutions, as repeating the irradiations in the absence of $Re_2(CO)_{10}$ under identical conditions led to no reactions.

Attention then shifted to the use of TEMPO, a stable nitroxide radical, which we proposed could effect controlled hydrogen radical abstraction from the metal hydride adducts. This seemed reasonable in light of the aforementioned report on hydrogen abstraction from Bu^n_3SnH by TEMPO.[9] However, the 1 : 1 reactions of $[MH_3(quin)]$ (M = Al or Ga) with TEMPO in toluene at −78 °C followed by slow warming to 20 °C gave low to moderate isolated yields of the nitroxide anion–metal hydride complexes, **1** and **2** (Scheme 1). The

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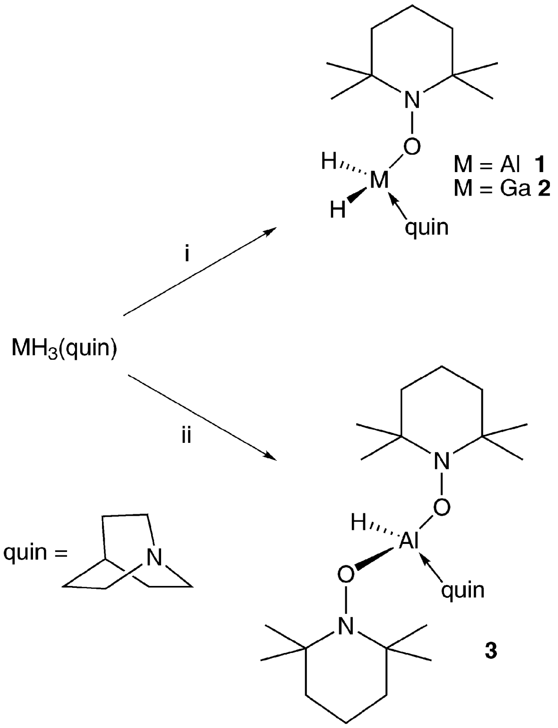

Scheme 1 *Reagents and conditions*: (i) TEMPO, toluene, $-1/2$ H_2; (ii) 2 TEMPO, toluene, $-H_2$.

related reaction with [InH_3(quin)] led to indium metal deposition above −15 °C, probably because the In analogue of **1** and **2** is thermally unstable above that temperature. The only other isolated product from this reaction was free quinuclidine. When the reaction with [AlH_3(quin)] was repeated with 2 equivalents of TEMPO, a moderate yield of the bis(nitroxide) complex, **3**, resulted. The corresponding reaction with [GaH_3(quin)] gave the 1 : 1 complex, **2**, and unreacted TEMPO as the only identifiable products, whilst the reaction with [InH_3(quin)] led, again, to indium metal deposition.

It seems likely that the mechanisms of the 1 : 1 reactions do not involve direct hydrogen transfer from the metal hydride to TEMPO, as this would generate TEMPOH (as in its reaction with $Bu^n{}_3SnH$) and would require a second equivalent of TEMPO to form the observed products. Another possibility exists, whereby one molecule of [MH_3(quin)] reacts with TEMPO to generate TEMPOH and this, in effect, acts as an acid in a subsequent reaction with a second molecule of [MH_3(quin)] to give **1** or **2** and dihydrogen. This would, however, necessitate the formation of M(II) hydrides, and/or their decomposition products (*e.g.* elemental M), in the primary step, no evidence for which was observed. Instead, we believe TEMPO acts as a Lewis base and attacks the metal centres, leading to homolytic cleavage of one M–H bond and subsequent dihydrogen formation (that these M–H cleavages occur *via* a bimolecular process involving M–H–M bridged intermediates[1] cannot be ruled out). Indeed, gas evolution from all reaction mixtures was observed in the temperature range −50 to −20 °C. This can be directly compared to the reaction of TEMPO with $Sm(C_5Me_5)_3$ which has been reported to yield a dimeric form of $Sm(TEMPO)_3$ and $(C_5Me_5)_2$ by initial attack of TEMPO at the metal centre of $Sm(C_5Me_5)_3$.[11] It is of note that reactions of TEMPO with group 13 trihalides do not proceed similarly and yield paramagnetic adducts of the type [MX_3(TEMPO)].[12]

The fact that no gallium counterpart of **3** is formed in the 2 : 1 reaction of TEMPO with [GaH_3(quin)] can be explained by the lower Lewis acidity of gallium hydride complexes relative to aluminium hydrides.[1] This would make attack of TEMPO at the hindered gallium centre of **2** less likely than attack at the aluminium centre of **1**, which ultimately gives **3**. It is noteworthy that **3** does not react with excess TEMPO at ambient temperature.

The ambient temperature NMR spectra of the diamagnetic complexes **1–3** all display significant peak broadening. This could be due to a combination of processes including rotation of the TEMPO ligand about the N–O and/or M–O bonds of the complexes, and/or inversion about the N-centre of the TEMPO ligand(s). Whatever the process in operation is, variable temperature NMR studies on **1–3** did not lead to any significant resolution of their spectra. In addition, no hydride resonances were observed in the ^1H NMR spectra of the aluminium complexes due to quadrupolar broadening of these signals by the metal (^{27}Al, 100%, $I = 5/2$). In contrast, the ^1H NMR spectrum of **2** does exhibit a hydride resonance (δ 5.22 ppm) in the normal range,[1] but this is very broad due to the quadrupolar nature of both naturally occurring gallium isotopes (^{69}Ga, 60.1%, $I = 3/2$; ^{71}Ga, 39.9%, $I = 3/2$). The M–H stretching absorptions for **1** (1782 cm^{-1}), **2** (1850 cm^{-1}) and **3** (1819 cm^{-1}) are all broad and all occur at higher frequencies than their metal trihydride precursors, [MH_3(quin)] M = Al (1720 cm^{-1})[13] or Ga (1810 cm^{-1})[14] (for comparison: M = In, 1642 cm^{-1})[4]. This can be explained by the greater electron withdrawing ability of the TEMPO anion than the hydride ligand, which leads to a reduction in the polarity of the M–H bonds of the complexes with increasing TEMPO substitution.

The X-ray crystal structures of **1–3** (Fig. 1 and 2) were determined and represent the first for nitroxide complexes of group 13 metal hydrides. Moreover, there has been only one previously structurally characterised TEMPO–group 13 complex, *viz*. [$B(TEMPO)_3$].[15] The structure of **2** is isomorphous with that of **1** (both compounds sit on a mirror plane) so only the molecular structure of the latter is depicted in Fig. 1 (relevant metrical data for **2** are included in the caption). The hydride ligands of all complexes were located from difference maps and refined isotropically without restraints. This allowed the coordination geometry of each to be assigned as distorted tetrahedral with surprisingly acute O–M–N angles (**1** 94.04(13)°, **2** 90.8(2)°, **3** 97.5° (mean)). The M–O, M–N and M–H distances are all in the normal ranges,[16] whilst the N–O distances and pyramidal TEMPO N-centres ($\sum$angles: **1** 330.4°, **2** 326.6°, **3** 332.6° (mean)) are indicative of fully reduced nitroxide ligands.

Conclusion

In summary, the first examples of nitroxide–group 13 hydride complexes have been prepared in the reactions of TEMPO with quinuclidine adducts of aluminium trihydride or gallium

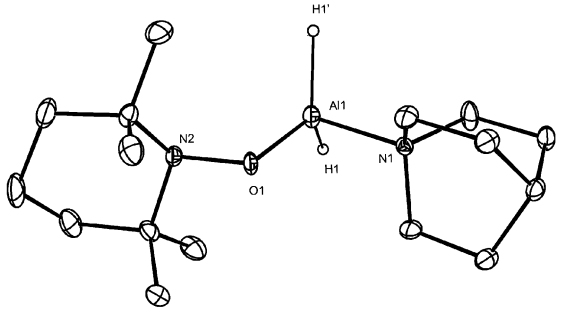

Fig. 1 Molecular structure of **1** (ellipsoids shown at the 25% probability level). Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.754(3), Al(1)–N(1) 2.003(3), Al(1)–H(1) 1.59(3), O(1)–N(2) 1.456(4); O(1)–Al(1)–N(1) 94.04(13), O(1)–Al(1)–H(1) 117.7(10), N(1)–Al(1)–H(1) 103.2(11), N(2)–O(1)–Al(1) 113.4(2), H(1)–Al(1)–H(1)′ 115.4(9); Selected bond lengths (Å) and angles (°) for **2**: Ga(1)–O(1) 1.850(5), Ga(1)–N(1) 2.078(7), Ga(1)–H(1) 1.43(6), O(1)–N(2) 1.447(8); O(1)–Ga(1)–N(1) 90.8(2), O(1)–Ga(1)–H(1) 117(2), N(1)–Ga(1)–H(1) 103(2), N(2)–O(1)–Ga(1) 112.7(4), H(1)–Ga(1)–H(1)′ 118.6(9). Symmetry operation: ′*x*, −*y* + 1/2, *z*.

trihydride. The mechanisms of these reactions probably involve nucleophilic attack of TEMPO at the metal centre and subsequent cleavage of M–H bonds. We are continuing our efforts to prepare low oxidation state group 13 hydride complexes and will report on this in due course.

Experimental

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Hexane and toluene were distilled over potassium then freeze–thaw degassed prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either a Bruker DXP400 or a Jeol Eclipse 300 plus spectrometer and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used. Mass spectra were obtained from the EPSRC National Mass Spectrometry Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Reproducible microanalyses on all compounds could not be obtained due to their extreme air and moisture sensitivity. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. [AlH_3(quin)][13] and [GaH_3(quin)][14] were synthesised by literature procedures, whilst all other chemicals were obtained from commercial sources and used as supplied.

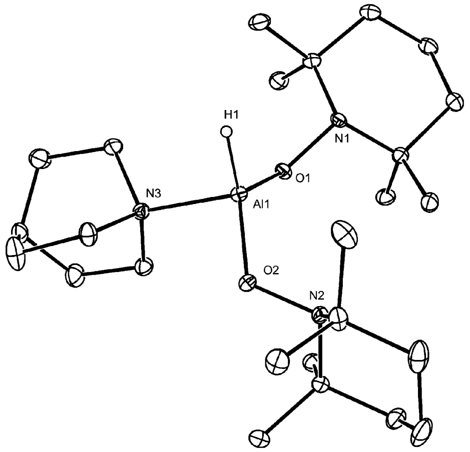

Fig. 2 Molecular structure of **3** (ellipsoids shown at the 25% probability level). Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.7423(15), Al(1)–O(2) 1.7535(15), Al(1)–N(3) 2.0215(17), Al(1)–H(1) 1.55(2), O(1)–N(1) 1.4602(19), O(2)–N(2) 1.453(2); O(1)–Al(1)–O(2) 119.89(7), O(1)–Al(1)–N(3) 101.38(7), O(2)–Al(1)–N(3) 93.68(7), O(1)–Al(1)–H(1) 116.5(8), O(2)–Al(1)–H(1) 115.8(8), N(3)– Al(1)– H(1) 103.1(8), N(1)–O(1)–Al(1) 121.37(11), N(2)–O(2)–Al(1) 120.48(10).

Preparation of [AlH_2(quin)(TEMPO)] 1

To a solution of [AlH_3(quin)] (0.17 g, 1.25 mmol) in toluene (15 cm^3) at −78 °C was added a solution of TEMPO (0.19 g, 1.25 mmol) in toluene (15 cm^3) over 5 min. The resultant solution was slowly warmed to room temperature and stirred overnight to yield a pale yellow solution. Volatiles were removed *in vacuo* and the residue extracted with hexane (10 cm^3). Filtration, concentration and cooling of the extract to −30 °C overnight yielded colourless crystals of **1** (0.05 g, 15%) Mp 97–100 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.92 (br s, 12H, CH_3), 1.26–1.53 (br m, 6H, TEMPO CH_2), 1.58 (br, 6H, quin CH_2), 1.78 (br, 1H, quin CH), 2.47 (br, 6H, quin NCH_2), AlH_2 resonance not observed; ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 18.3 (TEMPO CH_2), 20.0 (CH), 22.3 (CH_3), 24.5 (quin CH_2), 40.6 (TEMPO CH_2), 46.9 (NCH_2), 59.7 (N*C*Me_2); IR ν/cm^{-1} (Nujol): 1782 (AlH); MS/EI *m*/*z*: 157 [TEMPOH$^+$, 78%], 141 [TEMPOH$^+$ − O, 100%].

Preparation of [GaH_2(quin)(TEMPO)] 2

To a solution of [GaH_3(quin)] (0.39 g, 2.15 mmol) in toluene (15 cm^3) at −78 °C was added a solution of TEMPO (0.34 g, 2.15 mmol) in toluene (15 cm^3) over 5 min. The resultant solution was warmed to room temperature and stirred overnight to yield a pale yellow solution. Volatiles were removed *in vacuo* and the residue extracted with hexane (10 cm^3). Filtration, concentration and cooling to −30 °C overnight yielded colourless crystals of **2** (0.17 g, 23%) Mp 110–112 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.72 (br s, 12H, CH_3), 1.23–1.77 (br m, 6H, TEMPO CH_2), 1.49 (br, 6H, quin CH_2), 1.78 (br, 1H, quin CH), 2.42 (br, 6H, quin NCH_2), 5.22 (br, 2H, GaH_2); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 17.8 (TEMPO CH_2), 20.0 (CH), 24.4 (CH_3), 25.2 (quin CH_2), 40.3 (TEMPO CH_2), 47.6 (NCH_2), 59.2 (N*C*Me_2); IR ν/cm^{-1} (Nujol): 1850 (GaH); MS/EI *m*/*z*: 338 [M$^+$ − H, 100%], 157 [TEMPOH$^+$, 71%].

Preparation of [AlH(quin)$(TEMPO)_2$] 3

To a solution of [AlH_3(quin)] (0.31 g, 2.16 mmol) in toluene (15 cm^3) at −78 °C was added a solution of TEMPO (0.68 g, 4.33 mmol) in toluene (15 cm^3) over 5 min. The resultant solution was slowly warmed to room temperature and stirred overnight to yield a pale yellow solution. Volatiles were removed *in vacuo* and the residue extracted with hexane (10 cm^3). Filtration, concentration and cooling of the extract

Table 1 Crystal data for compounds **1–3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{16}H_{33}AlN_2O$	$C_{16}H_{33}GaN_2O$	$C_{25}H_{50}AlN_3O_2$
M_r	296.42	339.16	451.66
T/K	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/c$
a/Å	6.3500(13)	6.3500(13)	12.707(3)
b/Å	10.747(2)	10.729(2)	11.963(2)
c/Å	13.239(3)	13.273(3)	17.660(4)
β/°	92.69(3)	92.61(3)	95.14(3)
V/Å^3	902.5(3)	903.3(3)	2673.8(9)
Z	2	2	4
D_c/Mg m^{-3}	1.091	1.247	1.122
μ(Mo-Kα)/mm^{-1}	0.112	1.522	0.100
F(000)	328	364	1000
No. reflns collected	6069	4659	18772
No. independent reflns	1674	1672	6103
R_{int}	0.0913	0.1353	0.0763
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0679$ $wR2 = 0.1507$	$R1 = 0.0897$ $wR2 = 0.2239$	$R1 = 0.0599$ $wR2 = 0.1197$

to −30 °C overnight yielded colourless crystals of **3** (0.38 g, 39%) Mp 159–162 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.69 (br s, 24H, CH_3), 1.30–1.61 (br. m, 12H, TEMPO CH_2), 1.51 (br, 6H, quin CH_2), 1.72 (br, 1H, quin CH), 2.48 (br, 6H, quin NCH_2), AlH resonance not observed; ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 18.4 (TEMPO CH_2), 20.4 (CH), 22.1 (CH_3), 24.6 (quin CH_2), 40.1 (TEMPO CH_2), 42.0 (NCH_2), 59.7 (N*C*Me_2); IR ν/cm^{-1} (Nujol): 1819 (AlH); MS/EI m/z: 157 [TEMPOH$^+$, 100%].

X-Ray crystallography

Crystals of **1–3** 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 F^2 by full matrix least squares (SHELX97)[17] using all unique data. All non-hydrogen atoms are anisotropic with non-hydridic H-atoms included in calculated positions (riding model). Hydride ligands were located from difference maps and refined isotropically. Crystal data, details of data collections and refinement are given in Table 1.

CCDC reference numbers 645534–645536.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702641b

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