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Journal of Organometallic Chemistry 691 (2006) 3060–3064
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Oxidative addition of an imidazolium cation to an anionic gallium(I) *N*-heterocyclic carbene analogue: Synthesis and characterisation of novel gallium hydride complexes

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Received 24 February 2006; accepted 10 March 2006
Available online 20 March 2006

Abstract

The reactions of *N*-heterocyclic carbenes and imidazolium salts towards an anionic gallium(I) heterocycle, $[:Ga\{[N(Ar)C(H)]_2\}]^-$, $Ar = C_6H_3Pr^i_2$-2, 6, have been studied. No reactions with *N*-heterocyclic carbenes were observed, though the reaction of the gallium heterocycle with the imidazolium salt, $[HC\{N(Mes)C(H)\}_2]Cl$, IMesHCl, $Mes = C_6H_2Me_3$-2,4,6, led to oxidative insertion of the Ga(I) centre into the imidazolium C–H bond and formation of the gallium hydride complex, $[HGa\{[N(Ar)C(H)]_2\}(IMes)]$. When this reaction was carried out in the presence of traces of water, partial hydrolysis of $[HGa\{[N(Ar)C(H)]_2\}(IMes)]$ resulted in the formation of the hydroxy-bridged, anionic gallium hydride complex, $[\{HGa[N(Ar)C(H)]_2\}_2OH][(IMes)_2H]$. Both compounds have been spectroscopically and structurally characterised.

Keywords: Gallium; Hydride; Heterocycle; Low oxidation state; Crystal structure

1. Introduction

In recent years we have been systematically studying the main group and transition metal coordination chemistry of the anionic gallium(I) heterocycle, $[:Ga\{[N(Ar)C(H)]_2\}]^-$, $Ar = C_6H_3Pr^i_2$-2, 6, which is a valence isoelectronic analogue of the *N*-heterocyclic carbene (NHC) class of ligand [1,2]. This has proved to be very fruitful and has shown that the nucleophilic gallium heterocycle has much in common with NHCs, especially with respect to its ability to stabilise thermally labile and/or low oxidation state metal fragments. However, whereas it is now widely accepted that the carbene centres of NHCs are very nucleophilic but poorly electrophilic due to significant overlap of both nitrogen p-orbital lone pairs with the carbene p-orbital [3], the gallium centre of $[:Ga\{[N(Ar)C(H)]_2\}]^-$ has the potential to act as both a Lewis base and a Lewis acid. The reasoning behind this comes from theoretical studies which have shown that the electronegativity difference between Ga and N leads to little orbital overlap between these centres in a model of the heterocycle and that, to some extent, it can be regarded as a diamido-complex of a Ga^+ centre [4]. As a result, we were interested in investigating the reactivity of the gallium centre of $[:Ga\{[N(Ar)C(H)]_2\}]^-$ towards strong nucleophiles, in particular NHCs. In this respect, it is noteworthy that NHCs have previously been shown to form adducts with some heavier group 14 analogues of NHCs, e.g. $[:E\{N(CH_2Bu^t)\}_2C_6H_4]$, E = Si, Ge, Sn or Pb [5]. In addition, there is one example of an NHC reacting with a neutral six-membered aluminium(I) heterocycle, $[:Al\{[N(Ar)C(Me)]_2CH\}]$ to give the aluminium hydride complexes, $[Al(H)(L)\{[N(Ar)C(Me)][N(Ar)C{=}CH_2]CH\}]$, $L = :C\{N(R)C(Me)\}_2$, R = Me or Pr^i, via a methyl to aluminium hydrogen migration [6]. The only other reports of reactions of NHCs with group 13 metal(I) fragments are those with the halides InBr [7] and "GaI" [8]

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0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.03.018

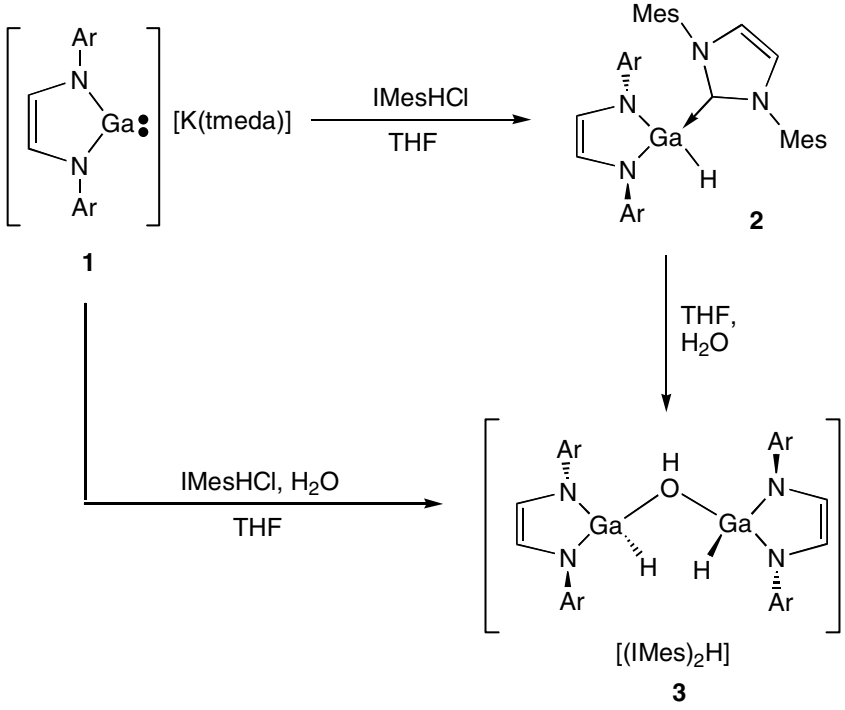
which led to disproportionation reactions and the formation of NHC-metal(II) complexes.

The Ga(I) centre of $[:Ga\{[N(Ar)C(H)]_2\}]^-$ is relatively strongly reducing and has the ability to oxidatively insert into several E–E bonds (E = P, Se, Te) [2a,2c]. In light of this, it was thought worthwhile to investigate the reactivity of $[:Ga\{[N(Ar)C(H)]_2\}]^-$ towards imidazolium cations, $[HC\{N(R)C(R')\}_2]^+$ (the protonated forms of NHCs), with the expectation that the metal centre would oxidatively insert into the imidazolium C–H bond to form NHC-gallium hydride complexes. There is recent precedent for this in transition metal chemistry where Ni(0) and Pd(0) complexes have C–H activated imidazolium cations to give unusually stable NHC-metal hydride complexes [9]. The results of our studies into the reactivity of $[:Ga\{[N(Ar)C(H)]_2\}]^-$ toward NHCs and imidazolium cations are reported herein.

2. Results and discussion

The reactions of $[K(tmeda)][:Ga\{[N(Ar)C(H)]_2\}]^-$, **1**, with either a hindered or an unhindered NHC, $:C\{N(R)C(R')\}_2$, R = R′ = Me or R = mesityl, R′ = H, were attempted in toluene. In both cases only the starting materials were recovered from the reaction mixture. Despite earlier theoretical studies which suggested the heterocycle's gallium centre should be electrophilic [4], this result is perhaps not surprising considering the overall anionic nature of the ring. Similarly, attempts to form complexes of $[:Ga\{[N(Ar)C(H)]_2\}]^-$ with a range of unhindered strong Lewis bases, e.g. quinuclidine, also met with failure.

Accordingly, attention was shifted to an examination of the reactivity of **1** towards imidazolium salts. Although a reaction was observed with $[HC\{N(Me)C(Me)\}_2]Cl$, only an intractable mixture of products was obtained. In contrast, the 1:1 reaction of the bulkier imidazolium salt, $[HC\{N(Mes)C(H)\}_2]Cl$, IMesHCl, Mes = $C_6H_2Me_3$-2,4,6, with **1** in THF led to a mixture of the gallium hydride complexes, **2** and **3**, in low (5%) and moderate yields (41%), respectively (Scheme 1). It seems likely that **2** was formed via the oxidative insertion of the Ga(I) centre of **1** into the imidazolium C–H bond. To the best of our knowledge this represents the first example of such a reaction, though a number of related C–H, C–C, Si–H and M–Cl activation reactions have been recently reported for transition metal complexes of the metal(I) diyls, $:M(C_5Me_5)$, M = Al or Ga [10]. It is apparent that **3** arose from the partial hydrolysis of **2** with 0.5 equivalents of water which preferentially attacks the coordinated IMes ligand of **2** over its hydride ligand. A recent paper [11] has shown that the earlier patent preparation of IMesHCl [12] can lead to a product contaminated with significant amounts of its monohydrate, $IMesHCl \cdot H_2O$, which is difficult to dry due to strong Cl···HO hydrogen bonding in the crystal lattice. When IMesHCl was recrystallised from dichloromethane and dried in vacuo for 24 h at 130 °C it was sufficiently water free to repeat the reaction with **1**. This led to a moderate isolated yield (44%) of **2** with no evidence for the concomitant formation of **3**. When a pure sample of **2** was treated with trace amounts of water in THF, the characteristic Ga–H stretching absorption of **3** (vide infra) was observed in the infrared spectrum of the product mixture.



Scheme 1.

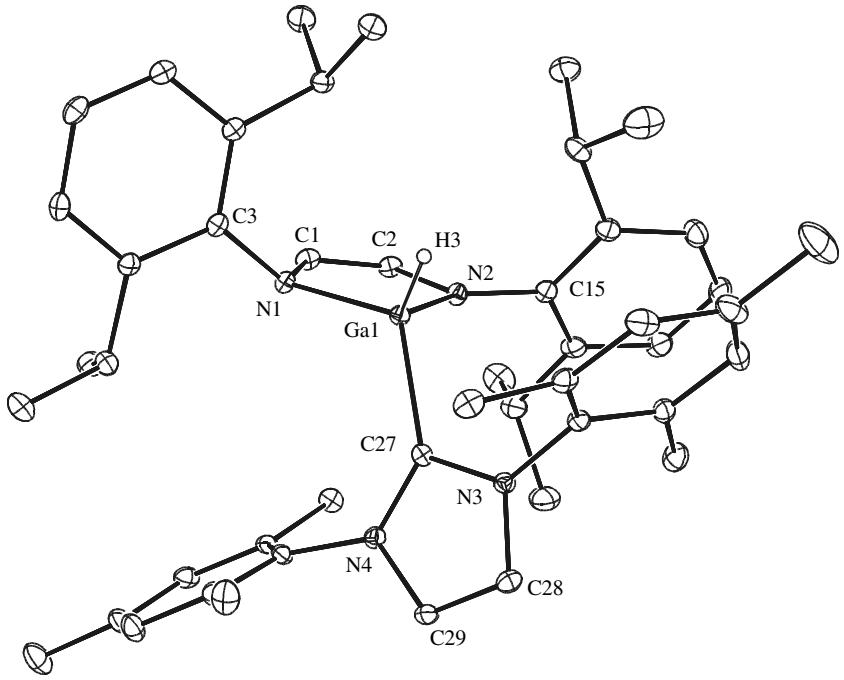


Fig. 1. Molecular structure of **2** (non-hydride hydrogen atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°): Ga(1)–N(1) 1.923(3), Ga(1)–N(2) 1.924(3), Ga(1)–C(27) 2.095(3), Ga(1)–H(3) 1.498(16), N(1)–C(1) 1.418(4), N(2)–C(2) 1.405(4), N(3)–C(27) 1.358(4), N(3)–C(28) 1.379(4), N(4)–C(27) 1.369(4), N(4)–C(29) 1.378(4), C(1)–C(2) 1.337(4), C(28)–C(29) 1.342(4) and N(1)–Ga(1)–N(2) 89.40(11), N(1)–Ga(1)–H(3) 112.8(10), N(2)–Ga(1)–H(3) 121.2(10), C(27)–Ga(1)–H(3) 104.9(10), N(3)–C(27)–N(4) 103.3(2).

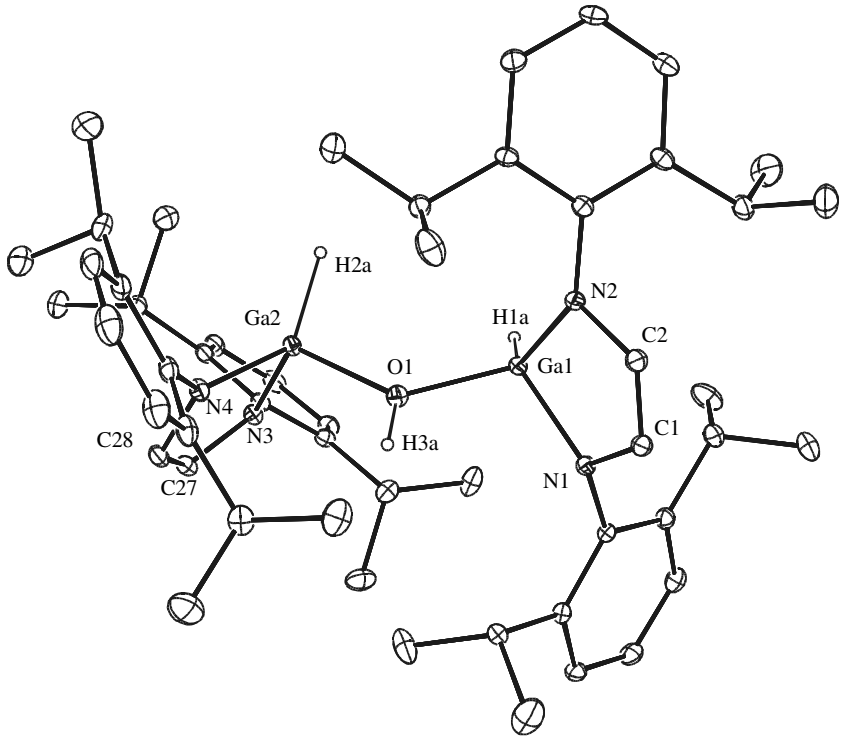


Fig. 2. Structure of the anionic component of **3**. (non-hydride hydrogen atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°): Ga(1)–N(1) 1.884(3), Ga(1)–N(2) 1.904(3), Ga(1)–O(1) 1.928(2), Ga(1)–H(1A) 1.492(16), Ga(2)–N(3) 1.887(3), Ga(2)–N(4) 1.888(3), Ga(2)–O(1) 1.955(2), Ga(2)–H(2A) 1.527(17), N(1)–C(1) 1.400(4), N(2)–C(2) 1.408(4), N(3)–C(27) 1.404(4), N(4)–C(28) 1.402(4), C(1)–C(2) 1.347(4), C(27)–C(28) 1.333(5) and N(1)–Ga(1)–N(2) 88.95(11), N(1)–Ga(1)–O(1) 106.31(10), N(2)–Ga(1)–O(1) 114.21(11), N(1)–Ga(1)–H(1A) 119.9(10), N(2)–Ga(1)–H(1A) 124.8(10), O(1)–Ga(1)–H(1A) 102.0(10), N(3)–Ga(2)–N(4) 88.49(11), N(3)–Ga(2)–O(1) 110.67(11), N(4)–Ga(2)–O(1) 103.20(11), N(3)–Ga(2)–H(2A) 123.8(11), N(4)–Ga(2)–H(2A) 128.3(11), O(1)–Ga(2)–H(2A) 100.9(11), Ga(1)–O(1)–Ga(2) 130.32(12).

The molecular structure of **2** and the structure of the anionic component of **3** are depicted in Figs. 1 and 2, respectively. In both, the hydride ligands were located from difference maps and refined isotropically, thus confirming that the coordination geometries of all gallium centres are distorted tetrahedral. In monomeric **2**, the carbene–Ga distance is similar to those in other NHC-gallium hydride complexes [13] and the geometry of the GaN_2C_2 ring is suggestive of the presence of a localised C–C double bond. Of note is the fact that one of the Ar substituents of that ring (that attached to N(1)) is bent out of the least squares plane of the heterocycle by 34.8°. This most likely arises from steric buttressing between it and one of the mesityl substituents of the NHC ligand. As far as we are aware, the only gallium heterocycle related to that in **2** can be found in the complex, $[HGa\{[N(Bu^t)C(H)]_2\}]_2$, which is dimeric through N–Ga interactions [14]. The anion of **3** contains a bent Ga–O(H)–Ga moiety with Ga–O bond lengths that are in the normal range for such fragments [15], though with a significant difference between the two. The cation of **3** has been previously structurally characterised [16] and shows the imidazolium proton to bridge the two IMes carbene centres. The sterically protected nature of this proton may provide an explanation for why it is stable to reaction with either Ga–H fragment.

The spectroscopic data for **2** and **3** are consistent with their formulations. Of most note are their infra-red spectra which exhibit strong, broad Ga–H stretching absorptions (**2**: 1854 cm^{-1}; **3**: 1902 cm^{-1}) in the normal range [17]. In addition, a broad O–H stretching absorption (3510 cm^{-1}) was observed in the spectrum of **3**. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** are more symmetrical than might be expected if its solid state structure is retained in solution and are suggestive of a fluxional process occurring. Although, cooling solutions of **2** to the point of precipitation in D_8-toluene (ca. −30 °C) led to no visible change in the spectrum, it is likely that the fluxional process involves a bending of the gallium heterocycle's N-substituents in and out of the heterocycle plane, with concomitant rotation or partial rotation of the IMes ligand about the Ga–C bond. If so, this process must be rapid on the NMR timescale. It is also of note that resonances corresponding to the hydride ligands of both complexes were not observed in their respective ^1H NMR spectra, as is often the case for gallium hydride complexes [17], a result of the quadrupolar nature of gallium.

3. Conclusion

In summary, the first oxidative addition of an imidazolium C–H bond to a gallium(I) centre has given rise to an NHC complex of a gallium hydride heterocycle. The partial hydrolysis of this complex has afforded an unusual hydroxide bridged gallium hydride complex. This work again highlights the synthetic versatility of the anionic gallium(I) heterocyclic complex, **1**, studies of which are ongoing in our laboratory.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. THF and hexane were distilled over potassium, whilst diethyl ether was distilled over Na/K then freeze/thaw degassed prior to use. ^1H, and $^{13}C\{^1H\}$ spectra were recorded on either a Bruker DXP400 or Jeol Eclipse 300 spectrometer, and were referenced to the residual ^1H 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. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Compound **1** [18], IMes [19] and IMesHCl [11,12] were synthesised by literature methods. All other chemicals were obtained commercially and used as received.

4.1. *[HGa{[N(Ar)C(H)]$_2$}(IMes)] (2)*

[K(tmeda)][:Ga{[N(Ar)C(H)$_2$}] (0.15 g, 0.25 mmol) in THF (10 cm^3) was added over 5 min to a suspension of rigorously dried IMesHCl (0.08 g, 0.25 mmol) in THF (30 cm^3) at −78 °C. The mixture was warmed to room temperature overnight to yield a red solution. Volatiles were removed in vacuo and the residue extracted with hexane (20 cm^3). Filtration, concentration and cooling to −30 °C overnight yielded red crystals of **2** (0.08 g, 44%). M.p. = 95–100 °C; ^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.87 (d, $^3J_{HH} = 5$ Hz, 12H, $CHCH_3$), 0.94 (d, $^3J_{HH} = 5$ Hz, 12H, $CHCH_3$), 1.51 (s, 12H, *o*-CH_3), 1.83 (s, 6H, *p*-CH_3), 3.29 (sept, $^3J_{HH} = 5$ Hz, 4H, $CHCH_3$), 5.39 (s, 2H, $GaN_2C_2H_2$), 5.58 (s, 2H, $CN_2C_2H_2$), 6.36–6.91 (m, 10H, ArH); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 17.5 (*o*-CH_3), 20.7 (*p*-CH_3), 24.8 ($CHCH_3$), 25.7 ($CHCH_3$), 31.7 ($CHCH_3$), 122.5 ($CN_2C_2H_2$), 122.8 ($GaN_2C_2H_2$), 123.6, 124.0, 129.6, 134.6, 135.0, 139.2, 146.9, 149.7 (ArC), 171.8 (NCN); IR ν/cm^{-1} (Nujol): 1854(s, Ga–H), 1251(s), 1091(s), 1033(s), 804(s); *m/z* (EI): 303 [$IMesH^+$, 100%], 378 [$(ArNCH)_2H^+$, 35%], 447 [$Ga(ArNCH)_2$, 16%], 750 [M^+, 3%]; Accurate Mass MS (EI^+) Calc. for M^+: $C_{47}H_{61}N_4Ga$: 750.4147. Found: 750.4141%.

4.2. *[{HGa[N(Ar)C(H)]$_2$}$_2$OH][(IMes)$_2$H] (3)*

[K(tmeda)][:Ga{[N(Ar)C(H)$_2$}] (0.25 g, 0.42 mmol) in THF (20 cm^3) was added to a suspension of IMesHCl (containing water of crystallisation) (0.14 g, 0.41 mmol) in THF (20 cm^3) at −78 °C over 5 min. The mixture was warmed to room temperature overnight to yield a brown/red solution. Volatiles were removed in vacuo and the residue washed with hexane (20 cm^3) and extracted with diethyl ether (30 cm^3). Filtration, concentration and cooling to −30 °C overnight yielded yellow crystals of **3** (0.13 g, 41%). M.p. = 118–126 °C; ^1H NMR (400 MHz, D_8-THF,

Table 1
Crystal data for compounds **2** · (hexane)$_{0.5}$ and **3** · (hexane)$_{0.25}$

	2 · (hexane)$_{0.5}$	**3** · (hexane)$_{0.25}$
Chemical formula	$C_{50}H_{68}GaN_4$	$C_{95.5}H_{127.5}Ga_2N_8O$
Formula weight	794.80	1543.00
T (K)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	13.207(3)	12.747(3)
b (Å)	12.992(3)	28.139(6)
c (Å)	27.036(5)	25.725(5)
β (°)	90.71(3)	100.28(3)
V (Å^3)	4638.6(16)	9079(3)
Z	4	4
μ (Mo Kα) (mm^{-1})	0.629	0.642
Reflections collected [R_{int}]	26 148 [0.0838]	74 008 [0.0901]
Unique reflections	9399	17 692
R_1 ($I > 2\sigma(I)$)	0.0589	0.0572
wR_2' (all data)	0.1421	0.1551

298 K): δ 0.93 (d, $^3J_{HH} = 6$ Hz, 24H, CHCH_3), 1.12 (d, $^3J_{HH} = 6$ Hz, 24H, CHCH_3), 1.85 (s, 24H, o-CH_3), 2.23 (s, 12H, p-CH_3), 3.40 (sept, $^3J_{HH} = 6$ Hz, 8H, CHCH$_3$), 4.80 (br s, 1H, OH), 5.55 (s, 2H, GaN$_2$C$_2H_2$), 6.89–7.60 (m, 24H, ArH and CN$_2$C$_2H_2$), 10.81 (br s, 1H, IMesH$^+$); ^{13}C NMR (125 MHz, D$_8$-THF, 298 K): δ 18.4 (o-CH_3), 20.5 (p-CH_3), 22.9, 23.8 (CHCH$_3$), 28.01 (CHCH$_3$), 118.5 (GaN$_2C_2$H$_2$), 122.2 (CN$_2C_2$H$_2$), 125.9, 126.7, 132.5, 138.2, 140.8, 142.0, 145.4, 146.8 (ArC), 172.8 (NCN); IR ν/cm^{-1} (Nujol): 3510(br, OH), 1902(s, Ga–H) 1258(s), 1101(s), 927(s), 761(s); m/z (−ve CI): 462 [H(OH)Ga(ArNCH)$_2^-$, 8%], 907 [{HGa(ArNCH)$_2$}$_2$OH$^-$, 15%]; Accurate Mass MS (CI$^-$) Calc. for {HGa(ArNCH)$_2$}$_2$OH$^-$: $C_{52}H_{73}ON_4Ga_2$: 907.4301. Found: 907.4333%.

4.3. Crystallographic studies

Crystals of **2** and **3** suitable for X-ray crystal structure 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) [20] using all unique data. Crystal data, details of data collections and refinement are given in Table 1.

Acknowledgements

We gratefully acknowledge financial support from the EPSRC (part funded studentship for R.P.R., studentship for D.P.M.). Thanks also go to the EPSRC Mass Spectrometry Service.

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre; **2** · (hexane)$_{0.5}$: CCDC No. 299517; **3** · (hexane)$_{0.25}$: CCDC No. 299518. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.018.

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