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PAPER

Low valent and hydride complexes of NHC coordinated gallium and indium†

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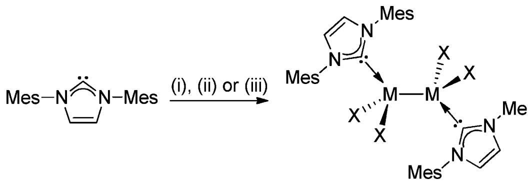
The reactions of the N-heterocyclic carbene 1,3-dimesitylimidazol-2-ylidene (IMes) with Ga[$GaCl_4$], "GaI", $InCl_2$ and $GaBr_3$ have been examined. All reactions using a low valent gallium or indium starting material led to species of the form [{MX_2(IMes)}$_2$], where M = Ga, X = Cl (**1**), I (**2**); M = In, X = Cl (**3**), with disproportionation and loss of gallium metal in the case of **2**. Reaction of IMes with gallium tribromide yields the air and moisture stable complex [$GaBr_3$(IMes)] (**4**), which has been used as a precursor to the mixed bromohydrides [$GaBrH_2$(IMes)] (**5**) and [$GaBr_2H$(IMes)] (**6**) by (i) ligand redistribution with [GaH_3(IMes)], (ii) hydride–bromide exchange with triethylsilane, and (iii) alkylation with ^{n}butyllithium followed by β-hydride elimination (**6** only). Attempts to prepare **1**, or monovalent analogues such as [{GaCl(IMes)}$_n$], by thermally induced reductive elimination of dihydrogen from the chlorohydride congeners of **5** and **6** resulted in isolation of the known compounds [IMesCl][Cl] (IMesCl = 1,3-dimesityl-2-chloroimidazolium), and/or 1,3-dimesityl-2-dihydroimidazole, and gallium metal. Preliminary photochemical NMR spectroscopy and catalytic studies of **5** and **6** aimed at reductive dehydrogenation under milder conditions are reported. Compounds **1** and **4** have been characterised by single crystal X-ray structure determination.

Introduction

Arduengo's report of the first main group element NHC complex; [AlH_3(IMes)] (IMes = 1,3-dimesitylimidazol-2-ylidene),[1] began a two decade period of sustained interest in the stabilisation of group 13 hydride and low valent complexes by NHCs.[2] In this vein, notable achievements include Robinson and Schleyer's isolation of a neutral [Ga_6Mes_4(IPrMe)$_2$] octahedron (Mes = 2,4,6-trimethylphenyl, IPrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene),[2d] Jones and Stasch's isolation of the first ambient temperature stable dialane [{AlH_2(IDipp)}$_2$] (IDipp = 1,3-di(diisopropylphenyl)imidazol-2-ylidene),[2e] and Jones' isolation of the first indium trihydride complexes.[2a,3] As part of a broad research program focusing on methods for the stabilisation of heavy group 13 hydrides, we have reported extensively on the use of sterically hindered ligands to stabilise aluminium and gallium hydrides.[4] This includes the NHC complexes [MX_2H(IMes)], M = Al[5,6] and Ga,[6,7] X = Cl and Br, which have exceptionally high decomposition temperatures for molecular alumino- and gallohydrides, and are entirely air stable. Herein we report the preparation of IMes adducts of tetrachloro and tetraiodo digallane; [{GaX_2(IMes)}$_2$] (X = Cl (**1**) and I (**2**)), and tetrachloro diindane; [{$InCl_2$(IMes)}$_2$] (**3**) (Scheme 1), the air-stable gallium tribromide complex [$GaBr_3$(IMes)] (**4**) and its use as a precursor to [$GaBrH_2$(IMes)] (**5**) and [$GaBr_2H$(IMes)][6] (**6**) by three synthetic pathways (Scheme 4). We also report on preliminary studies of the reductive elimination of H_2 from **5**, **6** and their chloride analogues.



Scheme 1 Preparation of compounds **1–3**. Reagents and conditions (i) M = Ga, X = Cl, 1.0 eq. Ga[$GaCl_4$], −78 °C to RT, toluene; (ii) M = Ga, X = I, 1.0 eq. "GaI", -Ga(s), −78 °C to RT, toluene; (iii) M = In, X = Cl, 1.0 eq. $InCl_2$, RT, 16 h, toluene.

Results and discussion

NHC supported tetrahalo dimetallanes

Jones and co-workers have reported the disproportionation reaction of monovalent indium bromide with IMes to afford [{$InBr_2$(IMes)}$_2$] and elemental indium,[2b] and the reaction of IDipp with *in situ* generated "GaI"[8] to yield the mono-NHC, iodide adduct of tetraiodo digallane; [HIDipp][I_3GaGaI_2(IDipp)], which exhibits an unusual eclipsed structure.[9]

As illustrated in Scheme 1, reaction of the IMes with Ga[$GaCl_4$] or "GaI" at −78 °C followed by gradual warming to room temperature, or $InCl_2$ at ambient temperature, affords colourless complexes **1–3** in moderate to good yield. For the preparations of **1** and **2**, addition of IMes initially affords bright orange reaction mixtures that fade to pale yellow, with deposition of gallium for **2**

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(solid with m.p. 30 °C), upon slow warming to room temperature. All three compounds are air and moisture sensitive, particularly **1** and **2** for which satisfactory elemental analyses could not be acquired. Compound **1** has been characterised by single crystal X-ray structure determination (Fig. 1, Table 1).

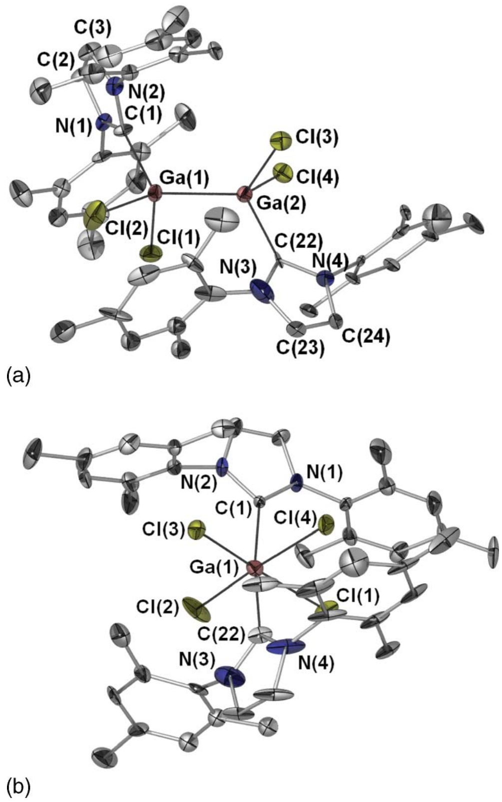


Fig. 1 (a) Molecular structure of **1**, and (b) view down Ga(1)–Ga(2) axis showing staggered arrangement of ligands (POV-Ray illustrations, 50% thermal elipsoids). All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ga(1)–Ga(2) 2.4243(17), Ga(1)–C(1) 2.047(11), Ga(2)–C(22) 2.062(13), Ga(1)–Cl(1) 2.241(4), Ga(1)–Cl(2) 2.212(4), Ga(2)–Cl(3) 2.237(3), Ga(2)–Cl(4) 2.248(3), C(1)–Ga(1)–Ga(2) 120.3(3), C(1)–Ga(1)–Cl(1) 104.7(3), C(1)–Ga(1)–Cl(2) 101.7(3), Cl(1)–Ga(1)–Ga(2) 102.07(11), Cl(1)–Ga(1)–Cl(2) 103.57(17), Cl(2)–Ga(1)–Ga(2) 122.17(11), N(1)–C(1)–N(2) 104.3(9), C(22)–Ga(2)–Ga(1) 121.3(3), C(22)–Ga(2)–Cl(3) 97.5(4), C(22)–Ga(2)–Cl(4) 105.8(4), Cl(3)–Ga(2)–Ga(1) 124.45(11), Cl(3)–Ga(2)–Cl(4) 102.33(12), Cl(4)–Ga(2)–Ga(1) 103.01(10), N(3)–C(22)–N(4) 104.4(12).

The ^{1}H NMR spectra of compounds **1** and **2** exhibit sharp signals, are near identical, and possess a unique feature relative to IMes adducts of trivalent hydrido and halo gallium species such as [GaH_3(IMes)],[3] [$GaCl_3$(IMes)][2c] and [$GaCl_2H$(IMes)],[7] wherein the mesityl methyl resonances are markedly shifted downfield (Table 2). This is particularly pronounced for the ^{1}H *ortho*-methyl resonances of **1** and **2**. For example, the ^{1}H *ortho*-methyl resonance of **2** is 0.19 ppm downfield of the analogous resonance of [$GaCl_3$(IMes)] (both C_6D_6), and the ^{1}H *para*-methyl resonance is 0.08 ppm downfield of that for the same complex.[10] An analogous shift is not observed for compound **3**, which exhibits similar chemical shifts to those of [$InClH_2$(IMes)] (2.13 and 2.17 ppm[3], respectively, **3**; 2.11 and 2.13 ppm) and those of [{$InBr_2$(IMes)}$_2$] (single broad resonance at 2.14 ppm) (Table 2).[2b]

Table 1 Summary of crystal measurement and refinement data for compounds **1** and **4**

	[{$GaCl_2$(IMes)}$_2$] (**1**)	[$GaBr_3$(IMes)] (**4**)
Mol. formula moiety	$C_{42}H_{48}Cl_4Ga_2N_4$	$C_{21}H_{24}Br_3GaN_2$
Mol. weight	890.08	613.87
T/K	173(2)	150(2)
Space group	$P2_1$	$Pca2_1$
a/Å	10.345(2)	16.4429(5)
b/Å	14.917(3)	16.6293(5)
c/Å	14.442(3)	17.4316
α (°)	90	90
β (°)	104.27(3)	90
γ (°)	90	90
Volume/Å^3	2160.0(8)	4766.4(3)
Z	2	8
D_c/g cm^{-3}	1.369	1.711
μ/mm^{-1}	1.528	6.193
Reflections collected	18728	75609
Unique reflections	9453	13580
Parameters varied	501	499
Flack parameter	0.00(3)	0.283(16)
R(int)	0.1327	0.1644
R_1	0.0906	0.0595
wR_2 (all data)	0.2289	0.1201

Table 2 Spectroscopic (^{1}H NMR and IR) and physical data for the complexes reported herein and related literature compounds

Compound	[a]o-CH_3	p-CH_3	4,5-C_2H_2	M-H	IR M-H	dec. (°C)
[{$GaCl_2$(IMes)}$_2$] (**1**)	2.17	2.13	5.76	—	—	230
[{GaI_2(IMes)}$_2$] (**2**)	2.19	2.13	5.70	—	—	216
[{$InCl_2$(IMes)}$_2$] (**3**)	2.11	2.17	5.76	—	—	234
[{$InBr_2$(IMes)}$_2$][2b]	2.14	2.14	5.74	—	—	n/a
[GaH_3(IMes)][3]	2.02	2.05	6.04	3.96	1780	214
[$GaClH_2$(IMes)][7]	2.03	2.05	5.95	4.72	1870	263
[$GaBrH_2$(IMes)] (**5**)	2.04	2.05	5.94	4.51	1874	270
[$GaCl_2H$(IMes)][7]	2.02	2.04	5.84	n/a	1917	274
[$GaBr_2H$(IMes)] (**6**)[6]	2.03	2.05	5.88	5.30	1925	286
[$GaBr_3$(IMes)] (**4**)	2.02	2.06	5.79	—	—	327
[$GaCl_3$(IMes)][2c]	2.00	2.05	5.77	—	—	176
[InH_3(IMes)][3]	2.29	2.38	6.35	5.20	1650	115
[$InClH_2$(IMes)][3]	2.13	2.17	6.09	6.84	1737	119

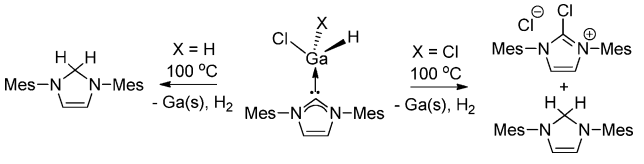
[a] All ^{1}H NMR spectroscopic data in C_6D_6.

In previous studies we have shown that the imidazol-2-ylidene 4,5-C_2H_2 ^{1}H NMR resonance provides a useful handle for the Lewis acidity of the coordinated group 13 metal.[4a,5–7] Based on this measure, comparison of the 4,5-C_2H_2 resonances of compounds **1–3** with that of [$GaCl_3$(IMes)] (Table 2),[2c,10] and the likely trend in [InH_nCl_m(IMes)] resonances (Table 2),[3] indicates that tetrahalo digallane and diindane possess similar Lewis acidities to those of their trivalent analogues. It is noteworthy that the ^{1}H and ^{13}C NMR spectra of **2** do not contain more than one set of IMes resonances nor an imidazolium-2-CH resonance, as would be consistent with the ionic formulation of the species reported by Jones and co-workers.[9] All three compounds exhibit carbenic carbon resonances in the expected region (**1**; 139.5, **2**; 139.8, **3**; 140.2 ppm, [$GaCl_2H$(IMes)]; 140.3 ppm, also C_6D_6).[7]

Cooling of a saturated toluene solution of **1** to −25 °C afforded colourless prisms suitable for single crystal X-ray structure determination. Compound **1** crystallises in the monoclinic space group $P2_1$ with one staggered molecule in the asymmetric unit (Fig. 1). The bonds of **1** are expectedly longer than those of its trivalent analogue [GaCl$_3$(IMes)] (**1**; Ga–C 2.047(11) and 2.062(13) Å, Ga–Cl 2.212(4)–2.248(3) Å, [GaCl$_3$(IMes)]; 1.954(4) Å and 2.1674(8)–2.1910(8) Å, respectively).[2c] Surprisingly, its bonding exhibits marked differences relative to the eight known structurally characterised tetrachloro digallanes [{GaCl$_2$(L)}$_2$] (L = Lewis base),[11] of which seven exhibit a staggered conformation. For instance, the Cl–Ga–Cl angles of **1** (103.57(17) and 102.33(12)°) are below the range described by the aforementioned complexes (104.8–110.2 Å),[11] the Ga–Cl bonds are extended (2.212(4)–2.248(3) Å *versus* mean average of 2.20 Å), and the Cl–Ga–Ga bonding evidences two distinct chloride environments at each gallium (Cl(1)–Ga(1)–Ga(2) 102.33(12)° and Cl(4)–Ga(2)–Ga(1) 103.01(10)°, Cl(2)–Ga(1)–Ga(2) 122.17(11)° and Cl(3)–Ga(2)–Ga(1) 124.45(11)°, range of observed Cl–Ga–Ga angles for literature [{GaCl$_2$(L)}$_2$] species 111.6–118.0°).[11] Comparison of **1** with the IDippGaI$_2$ fragment of the eclipsed anion of [HIDipp][Ga$_2$I$_5$(IDipp)][9] also indicates greater distortion despite the decreased size of the NHC herein. This can be seen in the Ga–Ga–I, I–Ga–I and C–Ga–I angles about the IDippGaI$_2$ of the anion, which range from 103.24(4)–109.81(19)°, while the analogous Ga–Ga–Cl, Cl–Ga–Cl and C–Ga–Cl angles of **1** lie between 101.7(3) and 122.17(11)°.

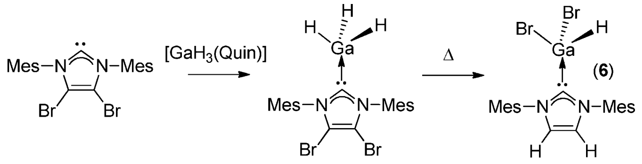
The thermally induced reductive dehydrogenation of group 13 halometallanes (MXH$_n$, M = Ga or In, X = Cl or Br)[12,13] is an under utilised pathway to low valent group 13 species. This is most likely as the reactions are complicated by the competing requirements of adduct stabilisation (good ligand donation) and dihydrogen elimination (weak ligand donation). A further consideration is the thermal stability of the low valent generated, which may decompose at the temperatures employed. With complex **1** fully characterised, we attempted to prepare **1** or its monovalent congener *via* the NMR scale dehydrogenation of [GaClH$_2$(IMes)] and [GaCl$_2$H(IMes)], which we have reported previously.[7] The successes of Jones and Stasch,[2e] and Robinson and Schleyer[2d] in isolating low valent aluminium and gallium species, respectively, provides evidence that NHCs can stabilise low valent group 13 compounds.

Unlike their alane counterparts, which are stable for extended periods in toluene at reflux,[5] the chlorohydrides [GaClH$_2$(IMes)] and [GaCl$_2$H(IMes)], which represent chloride analogues of **5** and **6** *vide infra*, decompose above 100 °C (d_8-toluene, ^{1}H NMR spectroscopy) to afford gallium metal and, for [GaClH$_2$(IMes)]; 1,3-dimesityl-2-dihydroimidazole,[14] or, for [GaCl$_2$H(IMes)], a mixture of 1,3-dimesityl-2-dihydroimidazole and 2-chloro-1,3-dimesitylimidazolium chloride (Scheme 2).[15] The identity of these products was confirmed by preparative scale reactions and ^{1}H NMR spectroscopic and melting point analysis on the species formed.[15] In view of the typical high coloration of low valent gallium cluster compounds,[2d,16] it is noteworthy that heated solutions remained pale yellow or colourless while being heated. Moreover, at no time were resonances attributable to **1** observed when heating either chlorohydride at lower temperatures (d_8-toluene, ^{1}H NMR spectroscopy). The formation of 2-halo-1,3-dimesitylimidazolium halides has been observed before when heating [TlX$_3$(IMes)] (X = Cl or Br) compounds to reflux in 1,3,5-mesitylene.[17]



Scheme 2 Thermal decomposition of [GaClH$_2$(IMes)] and [GaCl$_2$H(IMes)] in toluene.

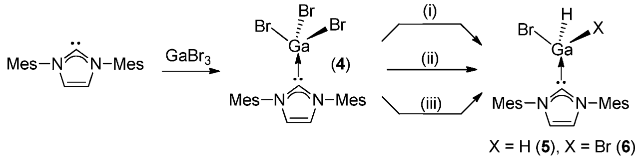
NHC supported gallium tribromide and bromohydrides



Scheme 3 Original preparation of compound **6** *via* hydride–bromide exchange at an NHC.[6]

In previous studies we have reported the preparation of [GaBr$_2$H(IMes)] (**6**) from the reaction of quinuclidine coordinated gallane and 4,5-dibrominated IMes (IMesBr) (Scheme 3).[6] This reaction is selective for the dibromogallane (GaBr$_2$H) and requires heating of the intermediate complex [GaH$_3$(IMesBr)] to 50 °C in toluene. This path differs from the conventional syntheses of halogallanes,[4b] introduced independently by Greenwood[18] and Schmidbaur,[19] wherein redistribution of halide and hydride ligands about gallium or hydride-bromide exchange with a silane is used respectively. Seeking a larger scale preparation of **6** for reactivity studies, we attempted the preparation of [GaBrH$_2$(IMes)] (**5**) and **6** utilising both Greenwood and Schmidbaur's routes from a common [GaBr$_3$(IMes)] (**4**) precursor, as-well-as attempting β-hydride elimination from a [GaBr$_2$(^{n}Bu)(IMes)] intermediate prepared from **4** (Scheme 4).

The stoichiometric reaction of gallium tribromide with IMes in diethyl ether affords [GaBr$_3$(IMes)] (**4**) (Scheme 4) as a white precipitate that may be recrystallised from toluene to afford colourless square plates suitable for single crystal X-ray structure determination (Fig. 2). Like [GaCl$_3$(IMes)],[2c] compound **4** is air and moisture stable. Spectroscopic data for **4** are also in accordance with those expected based on the aforementioned trend in 4,5-C$_2$H$_2$ ^{1}H NMR resonances of the coordinated IMes (Table 2).[5–7]



Scheme 4 Preparation of compounds **4–6**. Reagents and conditions (i) 0.5 (**6**) or 2.0 (**5**) eq. [GaH$_3$(IMes)], 50 °C, 36h, toluene; (ii) 1.0 (**6**) or 2.0 (**5**) eq. HSiEt$_3$, -BrSiEt$_3$, –20 °C to RT, toluene; (iii) 1.0 eq. ^{n}BuLi (**6** only), -LiBr, -^{n}butene, RT to 70 °C, 6 h, toluene.

Compound **4** crystallises in the orthorhombic space group *Pca*2$_1$ with two unique molecules in the asymmetric unit. The two distinct molecules exhibit comparable bonding parameters (Fig. 2). Accordingly, only one molecule is discussed here. It is noteworthy that **4** is isomorphous with [AlCl$_2$H(IMes)][5] and [GaCl$_2$H(IMes)],[7] and crystallises in the same space group as [GaCl$_3$(IMes)].[2c] Despite the considerable bulk of its NHC ligand, the molecular structure of **4** (Fig. 2) exhibits remarkably regular bond angles about gallium, and gallium to bromine contacts that are comparable to the mean of those for [GaBr$_3$(L)] (L = Lewis base) adducts (2.3103(12)–2.3226(12) Å *versus* 2.32 Å).[11] For instance, the Br–Ga–Br angles range from 107.22(5)–108.96(5)°

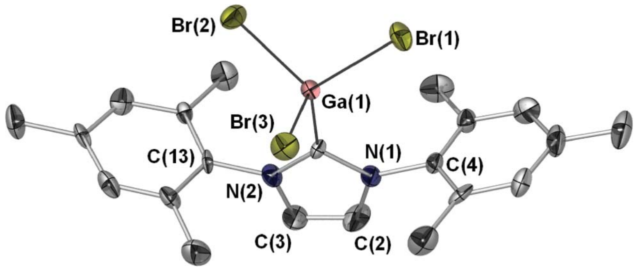


Fig. 2 Molecular structure of **4** (POV-Ray illustration, 50% thermal ellipsoids). All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ga(1)–C(1) 2.006(8), Ga(1)–Br(1) 2.3103(12), Ga(1)–Br(2) 2.3226(12), Ga(1)–Br(3) 2.3162(14), C(1)–Ga(1)–Br(1) 112.6(2), C(1)–Ga(1)–Br(2) 112.2(2), C(1)–Ga(1)–Br(3) 107.3(2), Br(1)–Ga(1)–Br(2) 107.22(5), Br(1)–Ga(1)–Br(3) 108.96(5), Br(2)–Ga(1)–Br(3) 108.37(5), N(1)–C(2)–N(2) 104.6(7).

and the C–Ga–Br angles range from 107.3(2)–112.6(2)°. These are the reverse of most structural authenticated [$GaBr_3$(L)] species (mean literature values; Br–Ga–Br 111.4°, L–Ga–Br 107.4°),[11] and indicate considerable pyramidalisation of the gallium that is only rivalled by the related $P(SiMe_3)_3$,[20] $PH({}^tBu)_2$[21] and $N(SnMe_3)_2$[22] adducts (mean Br–Ga–Br 108.5° and mean L–Ga–Br 110.5°).

Reaction of **4** with two or one half equivalent(s) of [GaH_3(IMes)][3] in toluene, with heating to 50 °C for one and a half days, yields **5** and **6**, respectively, in good to moderate yield without further purification (Scheme 4). Likewise, reaction of **4** with one or two equivalents of triethylsilane at low temperature yields **6** and **5**, respectively, in good to excellent yield after extraction into toluene and washing with diethyl ether (**6**), or simply washing with diethyl ether (**5**) (Scheme 4). The infrared Ga–H stretches of **5** and **6** (1874 and 1925 cm^{-1}, Table 2) are comparable to those of their chloride relatives (1870 and 1917 cm^{-1}, Nujol),[7] but contrast the stretch listed in our original report of **6** (1880 cm^{-1}), which may have been due to contamination of samples with **5**.[6] These demonstrate inductive strengthening of the Ga–H bond relative to [GaH_3(IMes)] (Ga–H, 1780 cm^{-1}).[3] The ^1H NMR spectra of **5** and **6** (C_6D_6) exhibit the expected resonances (Table 2) and are consistent with the trend in Lewis acidity $GaBr_3 > GaBr_2H > GaBrH_2 > GaH_3$ as denoted by the 4,5-C_2H_2 resonances, which shift downfield with increasing acidity (5.79 > 5.88 > 5.94 > 6.04 ppm).[3,4a] The ^1H NMR spectra of **5** and **6** exhibit broad Ga–H resonances due to the quadrupole moment of gallium. The chemical shift of these (Table 2) is consistent with increased deshielding of the hydride(s) upon going from **5** to **6** (4.51 and 5.30 ppm, [GaH_3(IMes)] 3.96 ppm)[3] and is consistent with the chemical shift of related hydrides like [$GaClH_2$(Quin)] (Quin = quinuclidine, 4.72 ppm).[23] The solid state decomposition temperatures (Table 2) of **5** and **6** are remarkable (270 and 286 °C, respectively) and are accompanied by appreciable tolerance to air and moisture, making **5** and **6** two of the most stable molecular gallium hydrides prepared.

The room temperature elimination of isobutene from sterically hindered *t*-butylgallium compounds has been reported by Power[24] and Gillan.[25] Impure **6** was isolated after heating a solution of *in situ* generated [$GaBr_2({}^nBu)$(IMes)] to 70 °C in toluene (*n*-butene loss). This occurs with deposition of a grey solid that melts just above room temperature (gallium m.p. 29.8 °C). Attempts to isolate the intermediate alkylgallium compounds (*cf* the use of *n*-butyl group relative to the aforementioned elimination of isobutene at room temperature *t*-butyl studies)[24,25] and study *n*-butene elimination at varying temperatures, or simple use of lower conversion temperatures, resulted in Ga–H free intractable mixtures. A ^1H NMR spectrum of the impure material displays 4,5-C_2H_2 resonances at 5.79 and 5.88 in a 1 : 3 ratio. These resonances can be attributed to compounds **4** and **6**, respectively. The deposition of gallium metal during this reaction, and subsequent isolation of **4** and **6**, indicates a mixture of compounds **4–6** and [GaH_3(IMes)] is generated, and that this mixture exists as a series of equilibria at elevated temperatures. These are most likely perturbed by solution phase decomposition of **5** and [GaH_3(IMes)] at the temperatures used.

Preliminary dehydrogenation studies of 5 and 6

The poor success of thermal methods in generating low valent compounds from chloride analogues of **5** and **6** led us to consider alternative methods for reductive dehydrogenation. To this end, d_8-toluene solutions of **5** and **6** were irradiated *in situ* during ^1H NMR spectroscopy experiments using broadband light output from a 100 W mercury arc lamp at a range of temperatures with spectra collected after irradiation periods of up to twenty two minutes. Initial experiments using **6** at 188 K led to a loss of signal intensity without new signals. This is indicative of the formation of an insoluble or paramagnetic product, the latter being inconsistent with diamagnetic compounds **1** and **2**, *cf* sharp ^1H NMR resonances. To enable observation of low solubility products, repeat ^1H NMR experiments on **5** and **6** were conducted at 273 K, wherein irradiation resulted in loss of 4,5-C_2H_2 singlets (**5**; 5.88 ppm, **6**; 5.76 ppm in d_8-toluene) and broad hydride singlet resonances (**5**; 4.38 ppm, **6**; 5.18 ppm in d_8-toluene) and formation of new resonances in the 4,5-C_2H_2 region of the spectrum (5.77 ppm and 5.69 ppm respectively) as-well-as a new singlet resonance at 4.52 ppm. The chemical shift of the latter resonance corresponds exactly to that of dissolved dihydrogen in d_8-toluene, as confirmed by a separate control experiment. Equilibration of both systems after irradiation (15 min) results in a stable set of 4,5-C_2H_2 ^1H NMR resonances (**5**; 5.74 ppm, **6**; 5.65 ppm, shifts of 14.41 Hz and 21.03 Hz respectively) that are accompanied by singlets attributable to the methyl and *meta*-aryl protons of IMes (**5**; 1.86 (12H), 2.05 (6H), 6.65 (4H) ppm, **6**; 1.85 (12H), 2.07 (6H), 6.66 (4H) ppm). It is noteworthy that overall no loss of signal intensity was observed throughout the experiment or after equilibration, as confirmed by post irradiation monitoring. Furthermore, no gallium metal was generated, and resonances attributable to 'free' IMes, [GaH_3(IMes)], **4**, 1,3-dimesityl-2-dihydroimidazole, or a 2-haloimidazolium (*cf* thermal studies of [$GaCl_2H$(IMes)] and [$GaClH_2$(IMes)]) were not observed. From these data it is clear that **5** and **6** generate different species upon irradiation, and that these do not exhibit the downfield shift of methyl resonances noted for **1** and **2** in d_6-benzene. Line broadening, compound insolubility and solvent melting point precluded the use of d_6-benzene for analogous experiments.

Baker and co-workers have reported the catalytic dehydrogenation of aminoborane [$BH_3(NH_3)$] (2.8 equivalents of H_2 per molecule) using the catalyst [$Ni(N_3NHC)_2$], where N_3NHC = 1,3,4-triphenyl-1,2,4-triazol-5-ylidene.[26] Himmel and co-workers have reported a thermally induced catalytic dehydrogenation of the guanidinate supported gallium hydride [{GaCl(hpp)H}$_2$] (hppH = 1,4,6-triazabicyclo[3.3.0]oct-4-ene) using [$TiCl_2Cp_2$]/^{n}BuLi and

[{RhCl(COD)}$_2$] precatalysts.[27] In an effort to further explore the catalytic dehydrogenation of our NHC supported bromogallanes, the dehydrogenation of **5** and **6** on an NMR scale using [Ni(IMes)$_2$][28] (5 mol%) was attempted, wherein each species was heated to 50 °C (*cf* thermal catalytic studies of Himmel)[27] with acquisition of ^{1}H NMR spectra over a period of twelve hours (d_8-toluene). During this time signals attributable to the parent species reduced in intensity with the growth of new singlets at 1.85, 2.07 and 6.66 ppm. The new resonances are in accordance with those generated during the photochemical study with the exception of signals attributable to the 4,5-C_2H_2 moiety, which are absent. This could indicate nickel catalysed hydrogen–deuterium exchange with the solvent. 4,5-Deuterium labelling of 'free' 1,3-disubstituted imidazol-2-ylidenes is well established using weakly acidic solvents such as d_6-DMSO, d_3-acetonitrile and d_6-acetone.[15,29] However, to our knowledge, deuteration using a nickel catalyst with d_8-toluene, as per that suggested here, is unprecedented. It is noteworthy that [Ni(IMes)$_2$] can be characterised in d_8-toluene without loss of 4,5-C_2H_2 resonance intensity, and the limited literature concerning this compound makes no mention of deuterium-hydrogen exchange. Moreover, the literature pertaining to bis(imidazol-2-ylidene) or bis(triazol-5-ylidene) complexes of nickel contains a single report of H/D exchange, this being at an activated benzylic carbon using D_2O as a deuterium source.[30]

Conclusions

In conclusion, we have prepared a catalogue of new di- and trivalent gallium N-heterocyclic carbene species (**1**, **2**, **4–6**) and a related bis(NHC) complex of tetrachloro diindane (**3**). The divalent gallium complexes **1** and **2** exhibit diagnostic downfield shifted ^{1}H NMR methyl signals in d_6-benzene that differentiate them from trivalent species such as **4**, and exhibit ^{1}H NMR 4,5-C_2H_2 signals that are indicative of similar Lewis acidity to their GaX_3 analogues. The first air stable NHC adduct of gallium tribromide has been prepared (**4**) and used as a precursor to mono- and dibromogallium hydride species **5** and **6**. Several methods have been employed in this regard, with the greatest success (as judged by yield) achieved using triethylsilane (Scheme 4). Attempts to generate low valent species such as **1** by thermal dehydrogenation of [GaClH$_2$(IMes)] and [GaCl$_2$H(IMes)] led to decomposition and isolation of 1,3-dimesityl-2-dihydroimidazole, and 1,3-dimesityl-2-dihydroimidazole and 1,3-dimesityl-2-chloroimidazolium chloride, respectively. Preliminary NMR spectroscopic studies of the photochemical and catalytic dehydrogenation of **5** and **6** under milder conditions than those applied to [GaClH$_2$(IMes)] and [GaCl$_2$H(IMes)] led to stable gallium compounds with the generation of dihydrogen in solution (photochemical studies) or the loss of 4,5-C_2H_2 resonances (nickel catalysed studies). The latter is consistent with nickel catalysed H/D exchange at the gallium coordinated NHC. These preliminary studies show promise. Further catalytic and photochemical studies of group 13 halohydrides and their synthetic application are ongoing in our laboratory.

Experimental

All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of ultra high purity argon in flame-dried glassware. Diethyl ether and toluene were collected from an Innovative Technology MD-7 solvent purification system and freeze-thaw degassed prior to use. 'GaI',[8] [GaH$_3$(IMes)],[3] IMes,[31] [GaCl$_2$H(IMes)][7], [GaClH$_2$(IMes)][7] and [Ni(IMes)$_2$][28] were prepared according to literature procedures, all other reagents were purchased from Sigma-Aldrich and used as received. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Avatar 320 FTIR spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectroscopic characterisations were recorded on Bruker spectrometers (see below for MHz) at 298 K unless otherwise stated, with chemical shifts referenced to the residual ^{1}H and ^{13}C resonances of d_6-benzene (δ 7.16 and 128.06 ppm, respectively). See separate section below for ^{1}H NMR spectroscopic studies of reductive dehydrogenation. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were conducted at the University of Otago, P.O. Box 56, Dunedin, New Zealand. Single crystal X-ray diffraction data collections were undertaken at UNSW using a Bruker Apex II CCD diffractometer.†

[{GaCl$_2$(IMes)}$_2$] (1)

A solution of Ga[GaCl$_4$] (209 mg, 0.74 mmol) in toluene (15 mL) was treated dropwise with a solution of IMes (434 mg, 1.43 mmol) in toluene (40 mL) at −78 °C with stirring. The resultant orange solution was allowed to warm to ambient temperature over several hours, during which the colour faded to pale yellow. Filtration and concentration *in vacuo* (~ 30 mL), followed by slow cooling to −25 °C afforded colourless prisms (110 mg, 26%) after one week, m.p. 182–184 °C, dec. 230–234 °C. ^{1}H NMR (400.13 MHz, C_6D_6); δ 2.13 (s, 12 H, *p*-C*H*$_3$), 2.17 (s, 24 H, *o*-C*H*$_3$), 5.76 (s, 4 H, NC*H*), 6.75 (s, 8 H, *m*-C_6H_2). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6); δ 18.6 (*o*-CH_3), 21.2 (*p*-CH_3), 123.6 (NCH), 129.3 (*m*-C_6H_2), 129.9 (*p*-C_6H_2), 134.5 (*o*-C_6H_2), 135.5 (*ipso*-C_6H_2), 139.5 (NCN). IR (Nujol) ν/cm^{-1}; 1608 (*w*), 1539 (*w*), 1261 (*w*), 1230 (*w*), 1097 (*br*, *m*), 1031 (*br*, *m*), 854 (*w*), 800 (*br*, *m*), 727 (*w*), 665 (*w*).

[{GaI$_2$(IMes)}$_2$] (2)

A solution of IMes (257 mg, 0.84 mmol) in toluene (40 mL) was added dropwise to a stirred slurry of 'GaI' (0.84 mmol) in toluene (20 mL) at −78 °C. The resultant orange mixture was allowed to warm to ambient temperature over several hours, during which the colour of the solution faded to pale yellow with a grey deposit. Filtration, followed by solvent removal *in vacuo*, afforded a brown powder. Washing with diethyl ether (30 mL) gave **2** as an off white powder (180 mg, 34%), m.p. 216–220 °C, dec. 300–320 °C. ^{1}H NMR (300.30 MHz, C_6D_6); δ 2.13 (s, 12 H, *p*-C*H*$_3$), 2.19 (s, 24 H, *o*-C*H*$_3$), 5.70 (s, 4 H, NC*H*), 6.75 (s, 8 H, *m*-C_6H_2). ^{13}C{^{1}H} NMR (75.51 MHz, C_6D_6); δ 18.1 (*o*-CH_3), 21.2 (*p*-CH_3), 124.4 (NCH), 129.3 (*m*-C_6H_2), 130.5 (*p*-C_6H_2), 135.0 (*o*-C_6H_2), 136.1 (*ipso*-C_6H_2), 139.8 (NCN). IR (Nujol) ν/cm^{-1}: 1608 (*w*), 1261 (*w*), 1223 (*w*), 1112 (*w*), 1032 (*m*, *br*), 929 (*w*), 857 (*w*), 800 (*m*, *br*), 761 (*w*), 727 (*w*, *br*).

Elemental analyses for compounds **1** and **2** were routinely high in carbon and hydrogen due to decomposition in transit. Example analysis for **1**: Anal. Calc. for $C_{42}H_{48}N_4Ga_2Cl_4$: C, 56.67; H, 5.44; N, 6.29. Found: C, 57.85 (+1.18%); H, 6.06 (+0.60%); N, 5.90%.

[{InCl$_2$(IMes)}$_2$] (3)

InCl$_2$ (302 mg, 1.63 mmol) was added to a solution of IMes (520 mg, 1.71 mmol) in toluene (30 mL) with stirring at room temperature. The reaction mixture was stirred for 16 h, whereupon a white precipitate was isolated by filtration and dried *in vacuo* to afford **3** as an analytically pure white powder (620 mg, 64%), m.p. 234–238 °C (dec.). ^{1}H NMR (500.13 MHz, C_6D_6); δ 2.11 (s, 24 H, *o*-C*H*$_3$), 2.17 (s, 12 H, *p*-C*H*$_3$), 5.76 (s, 4 H, NC*H*), 6.80 (s, 8 H, *m*-C_6*H*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 273 K); 18.3 (*o*-*C*H_3), 21.4 (*p*-*C*H_3), 123.5 (N*C*H), 129.9 (*m*-C_6H_2), 130.2 (*p*-*C*$_6H_2$), 133.7 (*o*-*C*$_6H_2$), 135.1 (*ipso*-*C*$_6H_2$), 140.2 (N*C*N). IR (Nujol) ν/cm^{-1}: 2277 (*w*, *br*), 1608 (*w*), 1541 (*w*), 1231 (*m*), 1109 (*w*), 1035 (*w*, *br*), 931 (*w*), 850 (*m*), 768 (*m*), 728 (*w*). Anal. Calc. for $C_{22}H_{48}Cl_4In_2N_4$: C, 51.46; H, 4.94; N, 5.72. Found: C, 51.51; H, 5.11; N, 5.82%.

[$GaBr_3$(IMes)] (4)

A solution of IMes (840 mg, 2.76 mmol) in diethyl ether (30 mL) was added dropwise with stirring to a solution of gallium tribromide (844 mg, 2.73 mmol) in diethyl ether (30 mL) at −40 °C. The reaction was allowed to warm to ambient temperature with stirring overnight. An off white precipitate (880 mg, 53%) was isolated by filtration. Recrystallisation (saturated toluene solution) at −25 °C afforded colourless square plates suitable for X-ray diffraction studies, m.p. 278 °C, dec. 327 °C. ^{1}H NMR (300.13 MHz, C_6D_6); δ 2.02 (s, 12 H, *o*-C*H*$_3$), 2.06 (s, 6 H, *p*-C*H*$_3$), 5.79 (s, 2 H, NC*H*), 6.71 (s, 4 H, *m*-C_6*H*$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6); 18.2 (*o*-*C*H_3), 21.1 (*p*-*C*H_3), 124.4 (N*C*H), 128.9 (*m*-*C*$_6H_2$), 129.9 (*p*-*C*$_6H_2$), 133.1 (*o*-*C*$_6H_2$), 135.5 (*ipso*-*C*$_6H_2$), 140.9 (N*C*N). IR (Nujol) ν/cm^{-1}; 3137 (*w*), 2727 (*w*), 2670 (*br*, *w*), 2411 (*br*, *w*), 1605 (*m*), 1230 (*m*), 1168 (*br*, *w*), 1128 (*w*), 1031 (*br*, *m*), 932 (*m*), 856 (*sh*, *s*), 722 (*w*), 703 (*w*). Anal. Calc. for $C_{21}H_{24}Br_3GaN_2$: C, 41.09; H, 3.94; N, 4.56. Found: C, 41.28; H, 3.93; N, 4.41%.

[$GaBrH_2$(IMes)] (5)

(i) A solution of **4** (258 mg, 0.42 mmol) in toluene (15 mL) was added dropwise with stirring to a solution of [GaH_3(IMes)] (320 mg, 0.85 mmol) in toluene (35 mL). The stirred reaction mixture was heated to 50 °C for 36 h, filtered, and the volatiles removed *in vacuo* to afford **5** as an off-white powder (260 mg, 45%); (ii) Triethylsilane (0.40 mL, 2.53 mmol) was added with stirring to a solution of **4** (775 mg, 1.26 mmol) in toluene (30 mL) at −20 °C. The stirred reaction mixture was allowed to warm to ambient temperature overnight. Drying *in vacuo* and washing with diethyl ether (3 × 5 mL) afforded analytically pure **5** as a white powder (165 mg, 86%), m.p. 194 °C, dec. 270 °C. ^{1}H NMR (500.13 MHz, C_6D_6); δ 2.04 (s, 12 H, *o*-C*H*$_3$), 2.05 (s, 6 H, *p*-C*H*$_3$), 4.51 (br s, 2 H, Ga-*H*), 5.94 (s, 2 H, NC*H*), 6.71 (s, 4 H, *m*-C_6*H*$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6); 17.9 (*o*-*C*H_3), 21.1 (*p*-*C*H_3), 122.8 (N*C*H), 127.9 (*m*-*C*$_6H_2$), 129.6 (*p*-*C*$_6H_2$), 134.4 (*o*-*C*$_6H_2$), 135.0 (*ipso*-*C*$_6H_2$), 140.0 (N*C*N). IR (Nujol) ν/cm^{-1}; 1874 (*br*, *m*, *Ga-H*). Anal. Calc. for $C_{21}H_{26}BrGaN_2$: C, 55.30; H, 5.75; N, 6.14. Found: C, 55.88; H, 5.92; N, 6.45%.

[$GaBr_2H$(IMes)] (6)[6]

(i) A solution of **4** (516 mg, 0.84 mmol) in toluene (12 mL) was added dropwise, with stirring, to a room temperature solution of [GaH_3(IMes)] (160 mg, 0.42 mmol) in toluene (12 mL). The reaction mixture was then heated to 50 °C for 36 h with deposition of a small quantity of Ga metal. The mixture was filtered whilst hot and volatiles removed *in vacuo* to afford analytically pure **6** as an off-white powder (480 mg, 71%). (ii) Triethylsilane (0.16 mL, 1.01 mmol) was added with stirring to a solution of **4** (626 mg, 1.02 mmol) in toluene (10 mL) at −20 °C. The reaction mixture was allowed to warm to ambient temperature overnight and stirred for a further 48 h. Drying *in vacuo* afforded impure **6**. Washing with diethyl ether (15 mL) followed by extraction into toluene (30 mL) afforded analytically pure **6** as a white powder after removal of volatiles *in vacuo* (400 mg, 75%). (iii) ^{n}Butyllithium (0.10 mL, 1.6 M, 0.16 mmol) was added dropwise with vigorous stirring to a solution of **4** (95 mg, 0.15 mmol) in toluene (40 mL) at room temperature. The resultant mixture was heated to 70 °C for 6 h with deposition of a grey solid. This occurred with light effervescence. Volatiles were removed *in vacuo* to yield an off-white powder containing **6** contaminated with **4** as evidenced by ^{1}H NMR (28 mg, 29%, calculated as **6**). Updated data for **6**: m.p. 188 °C, dec. 286 °C. ^{1}H NMR (300.13 MHz, C_6D_6); δ 2.03 (s, 12 H, *o*-C*H*$_3$), 2.05 (s, 6 H, *p*-C*H*$_3$), 5.30 (br s, 1 H, Ga-*H*), 5.88 (s, 2 H, NC*H*), 6.70 (s, 4 H, *m*-C_6*H*$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6); 18.0 (*o*-*C*H_3), 21.1 (*p*-*C*H_3), 125.7 (N*C*H), 127.9 (*m*-*C*$_6H_2$), 129.7 (*p*-*C*$_6H_2$), 135.2 (*o*-*C*$_6H_2$), 135.4 (*ipso*-*C*$_6H_2$), 140.5 (N*C*N). IR (Nujol) ν/cm^{-1}; 1925 (*br*, *w*, *Ga-H*). Anal. Calc. for $C_{21}H_{25}Br_2GaN_2$: C, 47.15; H, 4.71; N, 5.24. Found: C, 47.59; H, 4.70; N, 5.36%.

NMR irradiation experiments

General procedure for preparation of NMR samples

All photolysis experiments were conducted using screw cap 5 mm NMR tubes and septa. NMR tubes were oven dried (120 °C) followed by flame drying under vacuum to remove residual water prior to use. d_8-Toluene stock solutions of **5** and **6** were prepared in a glovebox (1.0 mg mL^{-1}). A solution (0.6 mL) containing the hydride to be irradiated or catalytically dehydrogenated was added to the NMR tube *via* syringe using an inert UHP argon manifold followed by freeze-pump-thaw cycling.

Procedure for photochemical studies[32]

Photolysis of the solution was monitored using ^{1}H NMR spectroscopy on a Bruker DMX 600 instrument fitted with a ^{1}H/^{31}P/X TBI probe. Irradiation was achieved using an Oriel 100 W mercury-arc lamp, with light transmitted using a 2 m long, 1.5 mm diameter, silica core single fibre UV transmitting fibre optic cable. The ^{1}H NMR spectrum of the sample was collected prior to irradiation. During irradiation and equilibration spectra were collected at 65 s intervals (32 scans). Samples were irradiated for 22 min (**6** at 188 K), 17 min (**5** at 273 K), 18 min (**6** at 273 K) after which the lamp was turned off and spectra were collected for another 102, 33 or 29 min, respectively.

Photochemical control reaction – dissolved H_2 in d_8-toluene

d_8-Toluene (0.6 cm^3) was added to a 5 mm NMR tube. The solution was degassed by freeze-pump-thaw cycling and H_2 gas (500 cm^3) was bubbled through the solution over a period of five minutes. ^{1}H NMR (600.13 Hz, 273 K); δ 4.52 (s, 2 H, *H*$_2$).

Procedure for catalytic studies

Samples for catalytic dehydrogenation were prepared as follows; a stock solution of [Ni(IMes)$_2$] (50 μL, 0.5 mg mL^{-1}, d_8-toluene) was added to an NMR tube containing a stock solution of **5** or **6** (500 μL, 1.0 mg mL^{-1}, d_8-toluene). ^{1}H NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400.13 MHz).

X-ray structure determination

Crystalline samples of **1** and **4** were mounted on glass fibres in silicone oil at −100(2) °C and −123(2) °C, respectively. A summary of crystallographic data can be found in Table 1. Data were collected using graphite monochromated Mo-Kα X-ray radiation (λ = 0.71073 Å) on a Bruker Apex II CCD diffractometer, and data were corrected for absorption by empirical methods using SADABS. Structural solution and refinement was carried out using the SHELX[33] suite of programs and the interface X-Seed.[34] Hydrogen atoms were refined in calculated positions (riding model).

Variata

Data for compound **1** were poor. Compound **1** undergoes a destructive phase change at −123(2) °C leading to data collection at the higher temperature of −100(2) °C. Unlike the IMes ligand coordinated to Ga(1), the IMes ligand coordinated to Ga(2) (N(3), N(4), C(22)–C(42)) exhibits a significant number of prolate and oblate atoms across the two aryl rings and imidazole heterocycle. Attempts to model two separate occupancies for (i) each ring separately, (ii) rings in combination, or (iii) together as two separate IMes occupancies, resulted in unacceptable thermal parameters (non positive definite). Only one occupancy has been refined for the second IMes with the exception of *meta*-carbon C(27) and *ortho*-methyl C(31), which were successfully modelled over two sites with occupancies of 83 : 17% (a:b) (highest occupancy shown in Fig. 1). The remaining suspected 'disordered' atoms (C(22)–C(26), C(28)–C(30), C(32), C(33), N(1), N(2)) have been refined using ISOR 0.05 restraints (isotropic displacement parameters). The largest residual hole and peak of electron density (−2.18 e Å^{-3} and 1.33 e Å^{-3}) are located 0.17 Å and 0.70 Å from *meta*-carbon C(38). Attempts to model disorder of this atom failed repeatedly.

Compound **4** crystallises with two unique molecules in the asymmetric unit. No additional space group symmetry elements were identified. The bonding parameters for both molecules are comparable. Parameters for the lowest numbered molecule have been used in the discussion throughout this article and this molecule has been used in Fig. 2.

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