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9-Triptycenyl complexes of group 13 and 15 halides and hydrides

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Abstract

The reactions of 9-lithiotriptycene with $AlCl_3$, $GaCl_3$ and $InBr_3$ have been carried out and have yielded the complexes, [(tript)$AlCl_2(OEt_2)$], [(tript)$GaCl_2$(THF)] and [(tript)$InBr(\mu\text{-}Br)_2Li(OEt_2)_2$], tript = 9-triptycenyl. The latter two complexes have been structurally characterised. The corresponding reactions of 9-lithiotriptycene with ECl_3 (E = P, As, Sb or Bi) afforded the complexes, [(tript)ECl_2], of which all but the phosphorus compound have been crystallographically authenticated. In addition, the high yield syntheses of the thermally stable primary pnictanes [(tript)EH_2] (E = As, Sb) have been achieved by reaction of the relevant halide complex with $LiAlH_4$. The X-ray crystal structure of the antimony hydride complex is reported.

Keywords: Antimony; Arsenic; Triptycene; Hydride; Group 13; Group 15

1. Introduction

The development of sterically bulky alkyl and aryl ligands has facilitated the renaissance of interest in main group chemistry that has occurred over the past 20 years. In group 15 this interest has largely revolved around the kinetic stabilisation of novel low coordination and/or low oxidation state organo-pnicogen compounds and their complexes, e.g., heteroalkynes, E≡CR; heteroalkenes, RE=CR_2 [1], dipnictenes, RE=ER [2] and pnictinidene complexes, L_nM=ER [3] (E = group 15 element). In group 13, sterically demanding ligands have most notably been employed to stabilise low oxidation state compounds, e.g., metal(I) diyls RM^I: (M = group 13 metal), which are finding wide use as strong σ-donor ligands in the formation of transition metal complexes [4], the nature of the metal–metal bonding in which is often a controversial issue [5].

We have a strong interest in low coordination and low oxidation state group 13 [6] and 15 chemistry [2b] and are keen to investigate the stabilising properties of new ligand systems in these areas. We have recently demonstrated the potential of the bulky triptycene moiety in this respect, with the synthesis of the first diphosphaalkyne, P≡$CC(C_6H_4)_3$CC≡P [7]. The remarkable thermal robustness of this air stable compound has prompted us to investigate the use of the 9-triptycenyl ligand (tript) in the preparation of, for example, group 13 diyl compounds, [(tript)M^I:] and transition metal terminal pnictinidene complexes, [L_nM=E(tript)]. The most convenient precursors to such compound types are the triptycenyl element dihalide or dihydride complexes, [(tript)EX_2], E = group 13 or 15 element, X = halide or hydride.

The synthesis and structural characterisation of the primary phosphane member of this series, [(tript)PH_2], has previously been reported [8]. Very recently, this work was extended to the low yield synthesis of the corresponding arsane, [(tript)AsH_2], though the stibane, [(tript)SbH_2], could not be prepared using the same methodology [9]. It is noteworthy that the triptycenyl ligand has also been employed in the preparation of several group 14 complexes, e.g. [(tript)EH_3] (E = Si or Ge) and [(tript)$_3$GeCl] [10], the former of which are air stable, whilst the steric properties of the 3-fold symmetric tript ligand in the latter has led to it being classed as a molecular "gear". To the best of our knowledge there have been no reports of triptycenyl complexes of group 13 metals. Herein, we describe the synthesis and structural characterisation of a series of such

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compounds, in addition to the preparation of several triptycenyl-group 15 complexes. These include a rare example of a structurally characterised primary stibane.

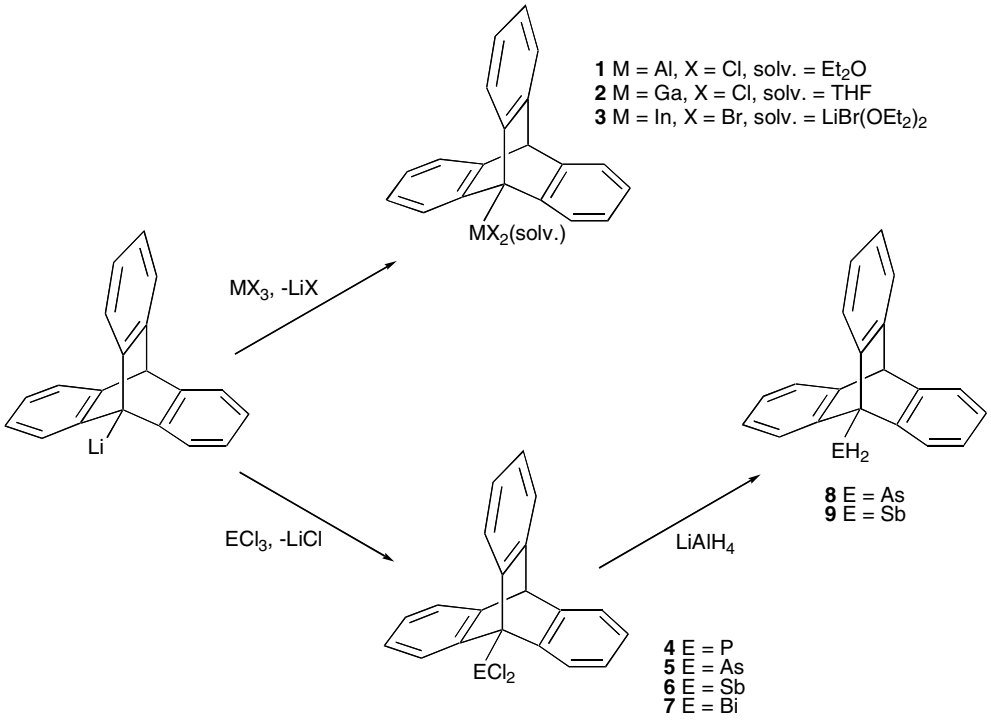
2. Results and discussion

2.1. Triptycenyl group 13 halide complexes

The reactions of 9-lithiotriptycene with $AlCl_3$, $GaCl_3$ or $InBr_3$ in either diethyl ether or THF afforded the first group 13-triptycenyl complexes, **1**–**3**, in good yields (Scheme 1). All three complexes appear to be indefinitely stable in the air and are thermally robust. The spectroscopic data for each are consistent with their proposed formulations, though a resonance for the carbon bearing the aluminium centre in **1** was not observed in its ^{13}C NMR spectrum, probably due to the quadrupolar nature of the metal. Both compounds **2** and **3** were shown to be monomeric in the solid state by X-ray crystallography (vide infra) but unfortunately X-ray quality crystals of **1** could not be grown. Therefore, its degree of association in the solid state cannot be certain and both monomeric 4-coordinate or a dimeric 5-coordinate, chloride-bridged complexes are possible. The low solubility of this compound in non-coordinating organic solvents prevented its solution molecular weight determination by normal methods. It is noteworthy, however, that related, solvated aluminium complexes employing moderately bulky aryl ligands, e.g., $[(Mes)AlCl_2(THF)]$, $Mes = C_6H_2Me_3$-2,4,6 [11], are monomeric in the solid state, whilst bulkier ligands can lead to unsolvated 3-coordinate monomers, e.g., $[(Mes^*)AlCl_2]$, $Mes^* = C_6H_2Bu^t_3$-2,4,6 [12].

The molecular structure of complex **2** is depicted in Fig. 1 and confirms it is monomeric. The gallium centre has a distorted tetrahedral environment with Ga–Cl bond lengths in the normal range [13]. Similarly, the Ga–C distance of 1.978(7) Å is very close to those observed in related 3- and 4-coordinate, monomeric complexes, e.g., 1.935(4) Å in $[(Mes^*)GaCl_2]$ [14] and 1.946(4) Å in $[(Ar')GaCl_2(THF)]$, $Ar' = C_6H_2Pr^i_3$-2,4,6 [11]. Interestingly, however, the Ga–O bond length in **2** [1.940(5) Å] is significantly shorter than that in $[(Ar')GaCl_2(THF)]$ [2.011(4) Å], which is the only previously structurally characterised alkyl gallium dihalide complex coordinated by an ether. This is especially surprising as, intuitively, the tript ligand would be expected to be more sterically demanding than the Ar′ ligand and, therefore, should probably lead to a longer Ga–O bond in **2**. No explanation can be offered for this observation at present.

The structure of **3** (Fig. 2) is related to that of **2** but it exits as an "-ate" complex with a distorted tetrahedral indium centre with one terminal bromide and two bromides that bridge to the lithium centre. This can be compared to $[\{(Me_3Si)_3C\}InCl_2(\mu\text{-}Cl)Li(THF)_3]$ [15], though in that case there is only one bridging halide. The In–C bond length of 2.176(6) Å in **3** is similar to those in related 4-coordinate complexes, e.g., 2.17(2) Å



Scheme 1.

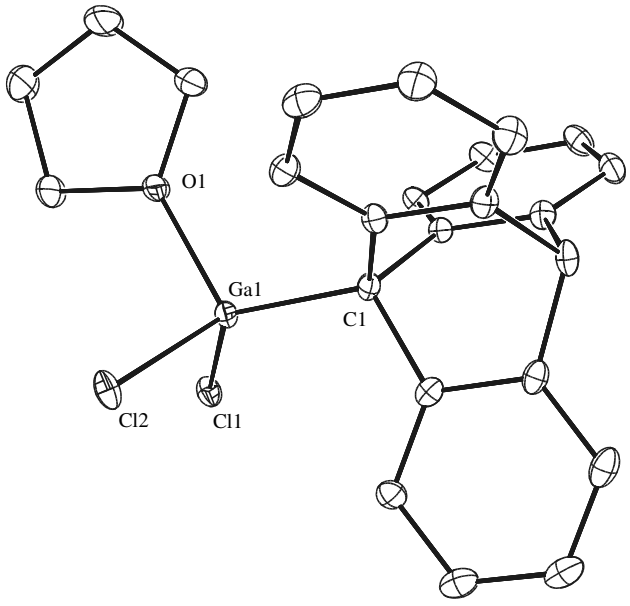


Fig. 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ga(1)–C(1) 1.978(7), Ga(1)–O(1) 1.940(5), Ga(1)–Cl(1) 2.1994(19), Ga(1)–Cl(2) 2.1917(19), C(1)–Ga(1)–Cl(1) 116.0(2), C(1)–Ga(1)–Cl(2) 120.8(2), C(1)–Ga(1)–O(1) 111.8(2), Cl(1)–Ga(1)–Cl(2) 105.59(7), Cl(1)–Ga(1)–O(1) 101.15(18), Cl(2)–Ga(1)–O(1) 98.56(18).

in [{$(Me_3Si)_3C$}$InCl_2$(μ-Cl)Li$(THF)_3$], but significantly longer than in 3-coordinate complexes with trigonal planar indium centres, e.g., 2.116(5) Å in [(Mes*)$InBr_2$] [14]. Not surprisingly, the bridging In–Br bonds are markedly longer than the terminal In–Br bond.

2.2. Triptycenyl group 15 halide complexes

The complexes [(tript)ECl_2], E = P **4**, As **5**, have been previously prepared as in situ intermediates for the preparation of [(tript)EH_2] though no data were given in those reports [8,9] and the complexes were not isolated. In this study, **4**, **5** and the heavier pnicogen analogues, [(tript)ECl_2], E = Sb **6**, Bi **7**, were prepared in moderate to good yields from the reactions of ECl_3 (E = P, As, Sb and Bi) with one equivalent of 9-lithiotriptycene in THF (Scheme 1). All complexes are thermally very robust and appear to be indefinitely stable in air in the solid state. The spectroscopic data for the complexes are consistent with their proposed structures which in the cases of **5**–**7** were confirmed by X-ray crystallographic analyses.

The molecular structures of each (Figs. 3–5) show them to be monomeric and isostructural, though none are isomorphous. In all, the pnicogen centre is significantly distorted from a trigonal geometry with the degree of pyramidalisation increasing in the series (Σ angles about E (°): **5**, 296.65; **6**, 292.32 and **7** 285.61) in line with the expected increase in s-character of the lone pair at E. The E–C bond lengths are similar to those recorded for related monomeric complexes employing sterically demanding ligands, e.g. [{2,6-$(Ar')_2C_6H_3$}-$AsCl_2$] 2.005 Å avge.; [{2,6-$(Ar')_2C_6H_3$}$SbCl_2$] 2.187(5) Å; [{2,6-$(Mes)_2C_6H_3$}$BiCl_2$] 2.267(5) Å [16], though the As–C distance in **5** is significantly shorter than that in the analogous primary arsane [(tript)AsH_2] 2.170(18) Å [9]. It is noteworthy that **7** is only the second structurally

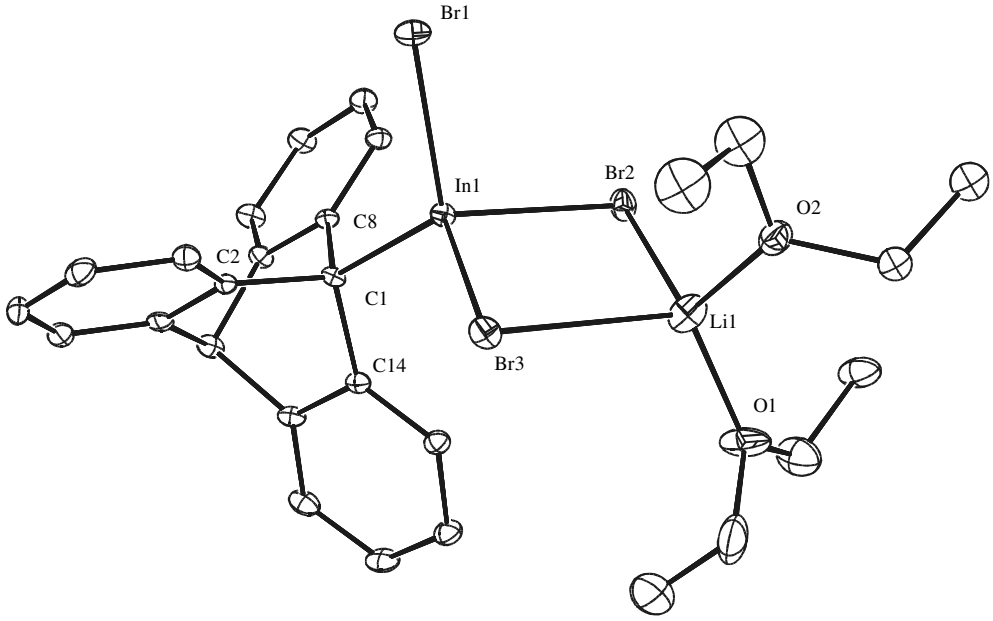


Fig. 2. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): In(1)–C(1) 2.176(6), In(1)–Br(1) 2.5090(9), In(1)–Br(2) 2.5706(9), In(1)–Br(3) 2.5644(9), Li(1)–Br(2) 2.628(15), Li(1)–Br(3) 2.705(17), Li(1)–O(1) 1.897(16), Li(1)–O(2) 1.889(18), C(1)–In(1)–Br(1) 118.29(16), C(1)–In(1)–Br(2) 115.41(17), C(1)–In(1)–Br(3) 114.87(16), Br(1)–In(1)–Br(2) 102.96(3), Br(1)–In(1)–Br(3) 105.55(3), Br(2)–In(1)–Br(3) 97.02(3), In(1)–Br(2)–Li(1) 86.0(4), In(1)–Br(3)–Li(1) 84.5(3), O(1)–Li(1)–O(2) 114.0(9), O(1)–Li(1)–Br(2) 111.7(7), O(1)–Li(1)–Br(3) 113.3(8), O(2)–Li(1)–Br(2) 115.4(7), O(2)–Li(1)–Br(3) 108.2(6), Br(2)–Li(1)–Br(3) 92.3(5).

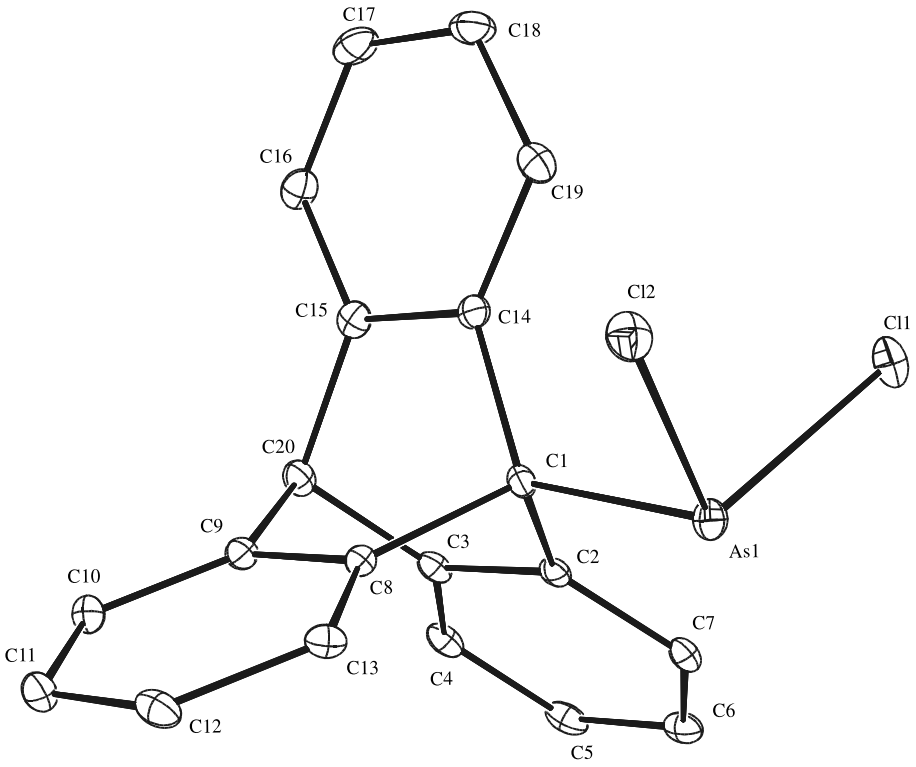


Fig. 3. Molecular structure of **5**. Selected bond lengths (Å) and angles (°): As(1)–C(1) 1.980(3), As(1)–Cl(1) 2.1932(10), As(1)–Cl(2) 2.1945(9), C(1)–As(1)–Cl(1) 98.77(9), C(1)–As(1)–Cl(2) 98.04(9), Cl(1)–As(1)–Cl(2) 99.84(4).

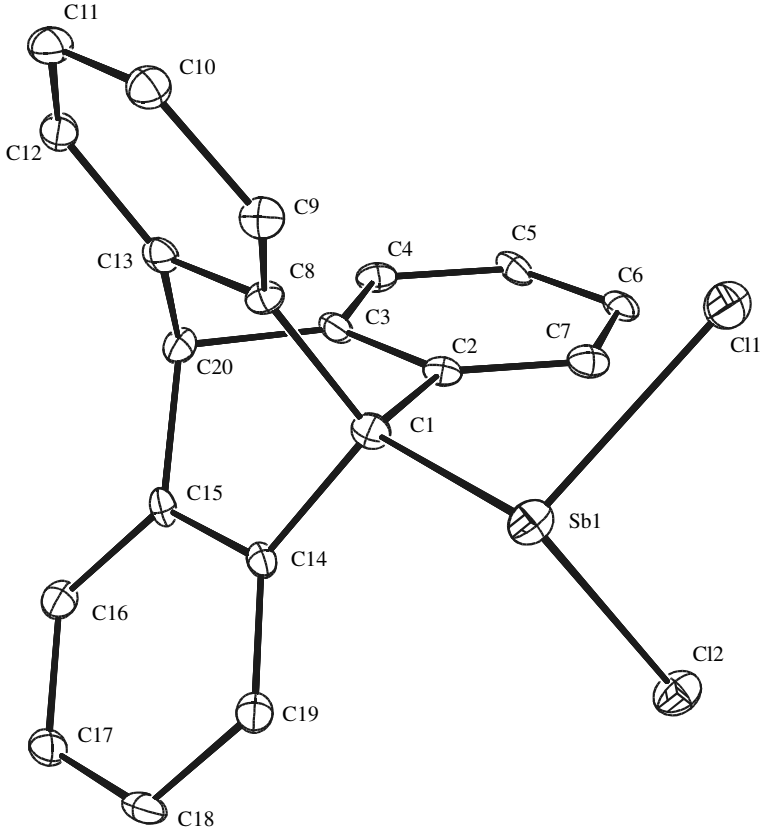


Fig. 4. Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Sb(1)–C(1) 2.226(8), Sb(1)–Cl(1) 2.368(2), Sb(1)–Cl(2) 2.363(2), C(1)–Sb(1)–Cl(1) 99.1(2), C(1)–Sb(1)–Cl(2) 97.1(2), Cl(1)–Sb(1)–Cl(2) 96.12(8).

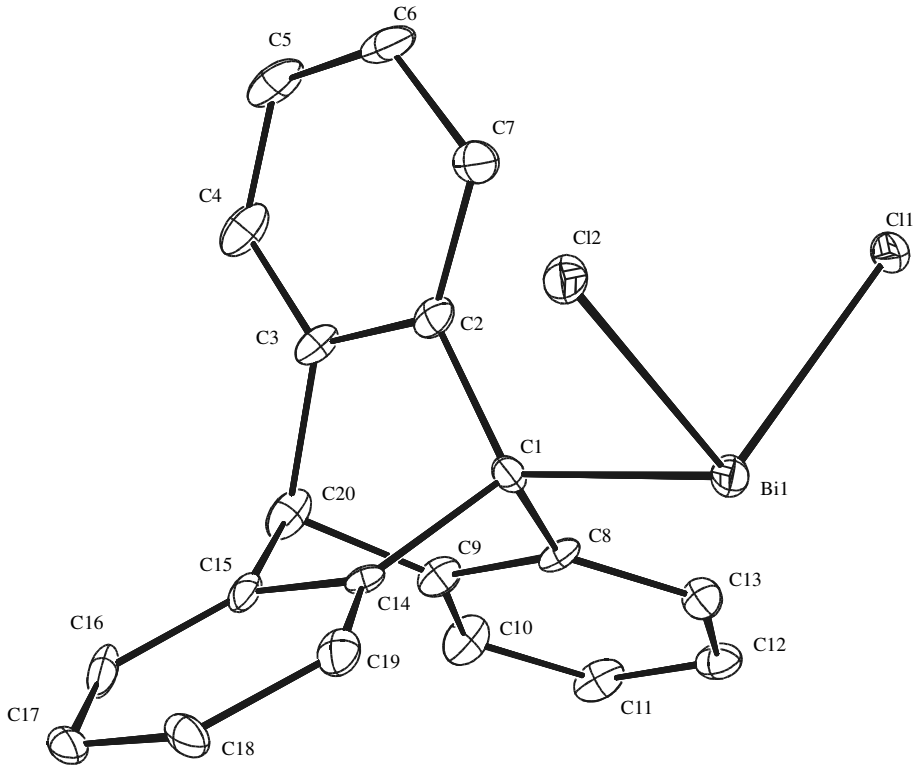


Fig. 5. Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Bi(1)–C(1) 2.299(11), Bi(1)–Cl(1) 2.523(3), Bi(1)–Cl(2) 2.468(3), C(1)–Bi(1)–Cl(1) 96.6(3), C(1)–Bi(1)–Cl(2) 91.0(3), Cl(1)–Bi(1)–Cl(2) 98.01(10).

characterised example of a monomeric, uncoordinated alkyl or aryl bismuth dihalide complex, the other being [{2,6-$(Mes)_2C_6H_3$}$BiCl_2$].

2.3. Triptycenyl group 15 hydride complexes

The primary pnictanes, [(tript)EH_2], E = P or As **8**, have previously been synthesised using a one-pot procedure involving the reaction of 9-lithiotriptycene with either PCl_3 or $AsCl_3$ followed by in situ reduction with $LiAlH_4$ [8,9]. In the latter case the arsane could only be isolated in an 11% yield. Moreover, attempts to extend this methodology to the synthesis of the primary stibane, [(tript)SbH_2] **9**, failed. Independently, we have examined the reactions of the isolated and recrystallised halide complexes, **5** and **6**, with $LiAlH_4$ in diethyl ether which lead smoothly to the primary pnictanes, **8** and **9**, in good yields (67% and 65%, respectively). Unfortunately, the related reaction of **7** with $LiAlH_4$ did not lead to the bismuthane, [(tript)BiH_2], but to decomposition and the deposition of elemental bismuth. This is not surprising as to date there are no known thermally stable primary bismuthanes and only one structurally characterised secondary bismuthane, [{2,6-$(Mes)_2C_6H_3$}$_2$BiH] [17].

The spectroscopic data for **8** are identical to those in the previous report. The infrared spectrum of **9** exhibits a broad Sb–H stretching absorption at 1865 cm^{-1}, whilst its ^1H NMR spectrum displays a resonance at δ 3.16 ppm which was assigned to its hydride ligands. These data are consistent with those for related primary stibanes, e.g. [{$(Me_3Si)_2HC$}SbH_2] [18] and [{2,6-$(Ar')_2C_6H_3$}SbH_2] [19] which show Sb–H stretches at 1860 and 1875 cm^{-1} in their infrared spectra and hydride resonances at δ 2.12 and 2.66 ppm in their ^1H NMR spectra. Finally, comment should be made about the high thermal stability of **9** (dec. 170 °C) which presumably arises from the kinetic protection afforded by the 9-triptycenyl ligand and is comparable to the stability of the bulky terphenyl substituted stibane [{2,6-$(Ar')_2C_6H_3$}SbH_2] (dec. 195 °C).

The X-ray crystal structure of **8** was obtained and found to be isomorphous to that recently described. Therefore, details of this structure will not be included here. Crystals of **9** suitable for X-ray diffraction were obtained from diethyl ether. Its molecular structure (Fig. 6) shows it to be monomeric, as is the case for the only other structurally characterised uncoordinated primary stibane, [{2,6-$(Ar')_2C_6H_3$}SbH_2] [19]. Unfortunately, its hydride ligands could not be located from difference maps but the Sb–C bond length of 2.206(6) Å is not significantly different (within 3 e.s.ds) to those in both **6** and [{2,6-$(Ar')_2C_6H_3$}SbH_2] (2.17 Å avg.).

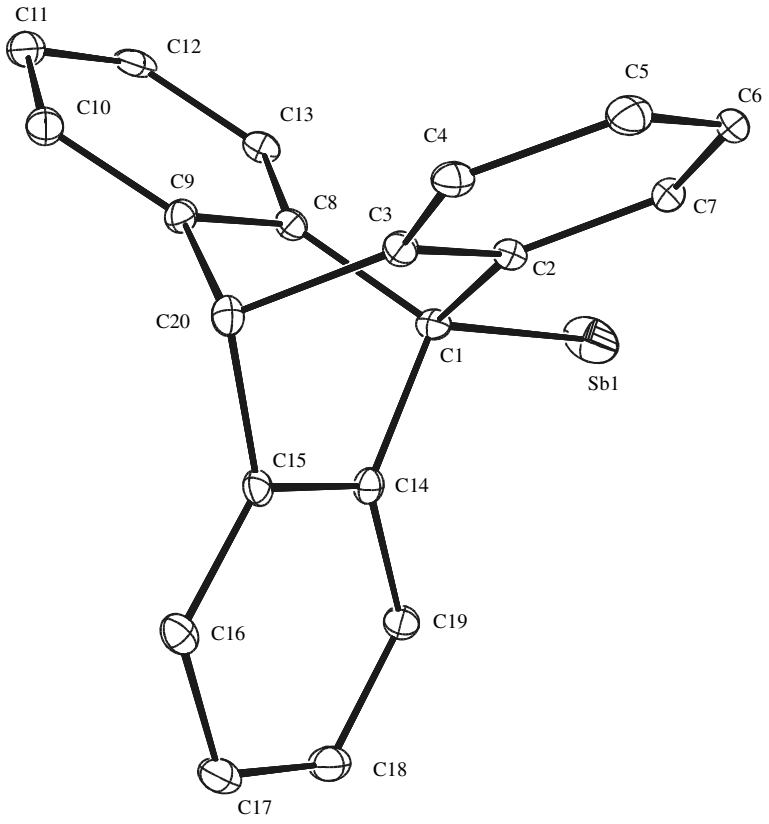


Fig. 6. Molecular structure of **9**. Selected bond lengths (Å): Sb(1)–C(1) 2.206(6), Sb(1)–C(1)–C(14) 111.9(4), Sb(1)–C(1)–C(8) 116.2(4), Sb(1)–C(1)–C(2) 112.8(4).

3. Conclusion

The preparations of a range of thermally stable group 13 and 15 halide complexes incorporating the sterically demanding 9-triptycenyl ligand have been discussed. The arsenic and antimony halide complexes, **5** and **6**, have been used as precursors for the high yield syntheses of their analogous primary pnictanes, **8** and **9**. We are currently examining the use of the triptycenyl group 13 halide complexes as precursors to group 13 diyls, [(tript)M^{I}:], via their reduction. In addition, the use of the primary pnictanes as precursors to transition metal terminal pnictinidene complexes, [$L_nM=E$(tript)], is being examined and will be reported on in future publications.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Toluene, DME and THF were distilled over potassium. Diethyl ether and hexane were distilled over Na/K, whilst CH_2Cl_2 was distilled over CaH_2 then freeze/thaw degassed prior to use. ^1H and ^{13}C NMR spectra were recorded on either a Bruker DXP400 spectrometer operating at 400.13 and 100 MHz, respectively, or a Jeol Eclipse 300 spectrometer operating at 300.52 and 75.57 MHz, respectively, and were referenced to the residual ^1H or ^{13}C resonances of the solvent used. The numbering scheme for NMR assignments (Fig. 7) is based on IUPAC guidelines [20]. Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions, or obtained from the EPSRC National Mass Spectrometric Service at Swansea University (ESI). IR spectra were recorded

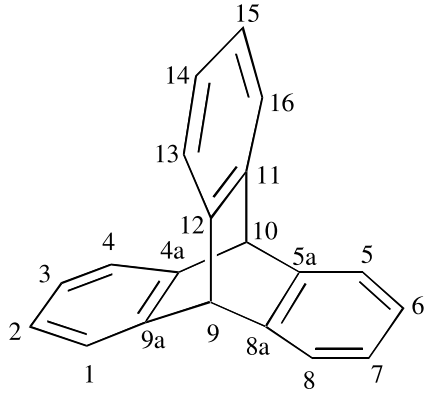


Fig. 7. Numbering scheme for NMR assignments.

using a Nicolet 510 FT-IR spectrometer as a Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under argon and are uncorrected. 9-Bromotriptycene [21] and 9-lithiotriptycene [8] were prepared by modifications of the literature procedures. All other starting materials were obtained commercially. PCl_3 and $AsCl_3$ were distilled immediately prior to use, whilst $AlCl_3$, $GaCl_3$ and $InBr_3$ were sublimed prior use. $LiAlH_4$ was recrystallised from Et_2O.

4.1. [(tript)$AlCl_2$(OEt_2)] (1)

To a solution of $AlCl_3$ (0.15 g, 0.15 mmol) in Et_2O (10 cm^3) held at −78 °C was added a solution of Li(tript) (0.30 g, 0.15 mmol) in toluene (10 cm^3) over 5 min. The resultant solution was allowed to warm to room temperature and stirred for 12 h whereupon volatiles were removed in vacuo. The white residue was extracted with CH_2Cl_2 (10 cm^3) and hexane added to the onset of crystallisation. Placement at −30 °C for 18 h yielded **1** as a white powder (0.30 g, 63%); m.p. 218–221 °C (dec.); ^{1}H NMR (300 MHz, CD_2Cl_2, 300 K): δ 1.39 (t, 6H, $^3J_{HH} = 7.1$ Hz, CH_3), 4.09 (q, 4H, $^3J_{HH} = 7.1$ Hz, OCH_2), 5.55 (s, 1 H, C10H), 7.08 (m, 6H, Ar–CH), 7.51 (m, 6H, Ar–CH); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 14.0 (CH_3), 54.0 (C10), 69.6 (OCH_2), 119.1 (C2, C7, C14), 123.4 (C4, C5, C16), 123.7 (C3, C6, C15), 125.3 (C1, C8, C13), 143.9 (C9a, C8a, C12), 145.9 (C4a, C5a, C11); IR(Nujol, cm^{-1}): ν 1455(s), 1376(s), 1260(s), 1095(s), 801(s), 742(m); MS APCI: m/z (%) 351 [$M - OEt_2^+$, 10], 254 [triptH$^+$, 100].

4.2. [(tript)$GaCl_2$(THF)] (2)

To a solution of $GaCl_3$ (0.32 g, 1.81 mmol) in THF (10 cm^3) held at −78 °C was added a solution of Li(tript) (0.50 g, 1.92 mmol) in toluene (10 cm^3) over 5 min. The resultant solution was warmed to room temperature and stirred for 12 h. Volatiles were then removed in vacuo and the white residue extracted with CH_2Cl_2 (10 cm^3). Hexane was added to the solution until the onset of crystallisation. Placement at −30 °C for 12 h yielded **2** as colourless crystals (0.83 g, 96%); m.p. 238–242 °C (dec.); ^{1}H NMR (300 MHz, CD_2Cl_2, 300 K): δ 2.09 (m, 4H, CH_2), 4.39 (m, 4H, OCH_2), 5.55 (s, 1 H, C10H), 7.42 (m, 6H, Ar–CH), 7.62 (m, 6H, Ar–CH); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 25.2 (CH_2), 57.1 (C10), 73.6 (OCH_2), 124.1 (C2, C7, C14), 125.1 (C4, C5, C16), 125.9 (C3, C6, C15), 128.6 (C1, C8, C13), 146.4 (C9a, C8a, C12), 147.4 (C4a, C5a, C11); IR(Nujol, cm^{-1}): ν 1453(s), 1377(s), 1342(s), 1262(m), 1197(m), 1132(w), 1112(m), 1076(m), 838(s); MS EI: m/z (%) 393 [M − THF$^+$, 20], 254 [triptH$^+$, 100]; Accurate Mass MS (EI) Calc. for M^+ − THF: $C_{20}H_{13}Cl_2Ga$: 391.9645. Found 391.9636.

4.3. [(tript)InBr(μ-Br)$_2$Li(OEt_2)$_2$] (3)

To a solution of $InBr_3$ (0.68 g, 1.91 mmol) in Et_2O (10 cm^3) at −78 °C was added a solution of Li(tript) (0.50 g, 1.92 mmol) in toluene (10 cm^3) over 5 min. The solution was allowed to warm to room temperature and stirred for 12 h whereupon volatiles were removed in vacuo and the resultant white residue extracted with CH_2Cl_2 (10 cm^3). Hexane was added to the extract until the onset of crystallisation. Placement at −30 °C for 20 h yielded **3** as colourless crystals (0.40 g, 28%); m.p. 102–104 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 1.27 (t, 12H, $^3J_{HH} = 7.1$ Hz, CH_3), 3.77 (q, 8H, $^3J_{HH} = 7.1$ Hz, OCH_2), 5.47 (s, 1H, C10H), 7.41 (m, 6H, Ar–CH), 7.87 (m, 6H, Ar–CH); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 14.6 (CH_3), 53.8 (C10), 66.1 (OCH_2), 124.8 (C2, C7, C14), 125.0 (C4, C5, C16), 125.4 (C3, C6, C15), 125.7 (C1, C8, C13), 147.2 (C9a, C8a, C12), 147.8 (C4a, C5a, C11); IR(Nujol, cm^{-1}): ν 1457(s), 1277(m), 1260(s), 1192(w), 1152(w), 1091(s), 1019(br), 800(s); MS APCI: m/z (%) 528 [M^+ − LiBr(OEt_2)$_2$, 15], 448 [triptInBr$^+$, 100], 254 [triptH$^+$, 40].

4.4. [(tript)PCl_2] (4)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to −78 °C and Bu^{n}Li (2.00 cm^3 of a 1.6M solution in hexane, 3.20 mmol) added over 5 min. The resultant suspension was warmed to room temperature and stirred for 1 h. The suspension was then cooled to −78 °C and PCl_3 (0.40 cm^3, 4.5 mmol) added dropwise over 5 min. Warming to room temperature gave an orange solution which was subsequently heated at reflux for 90 min. Volatiles were then removed in vacuo and the residue extracted into toluene (30 cm^3). The extract was filtered, concentrated to ca. 10 cm^3 placed at −30 °C for 15 h to yield **4** as an off-white microcrystalline powder (0.67 g, 63%); m.p. 222–227 C; ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 5.02 (s, 1H, C10H), 6.67–7.76 (m, 12H, Ar–CH); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 54.6 (C10), 59.3 (d, $^1J_{PC} = 63.4$ Hz, C9), 124.8 (d, $^4J_{PC} = 2.3$ Hz, C2, C7, C14), 123.9 (C4, C5, C16), 125.7 (C3, C6, C15), 126.1 (d, $^3J_{PC} = 4.6$ Hz, C1, C8, C13), 142.9 (d, $^2J_{PC} = 17.3$ Hz, C9a, C8a, C12), 147.7 (d, $^3J_{PC} = 5.8$ Hz, C4a, C5a, C11); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 182.1 (s); IR(Nujol) ν/cm^{-1} 1287(m), 1257(m), 1197(m), 1132(m), 1036(m), 730(s); MS EI: m/z (%) 355 [M^+, 35], 253 [tript$^+$, 100]; Accurate mass MS (EI) Calc. for $C_{20}H_{13}PCl_2$: 354.0126. Found: 354.0128.

4.5. [(tript)$AsCl_2$] (5)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to −78 °C and Bu^{n}Li (2.00 cm^3 of a 1.6 M

solution in hexane, 3.20 mmol) added over 5 min. The resultant suspension was warmed to room temperature and stirred for 1 h. It was then cooled to −78 °C and $AsCl_3$ (0.40 cm^3, 4.5 mmol) added dropwise over 5 min. Warming to room temperature gave an orange solution which was subsequently heated at reflux for 90 min. Volatiles were removed in vacuo and the residue extracted into toluene (30 cm^3). Concentration and placement at −30 °C overnight gave colorless crystals of **5** (0.70 g, 58%); m.p. 198–200 °C, ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ 5.40 (s, 1H, C10H), 6.99–7.39 (m, 12H, Ar–H); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 54.1 (C10), 54.4 (C9), 124.3 (C2, C7, C14), 125.2 (C4, C5, C16), 125.7 (C3, C6, C15), 126.0 (C1, C8, C13), 145.3 (C9a, C8a, C12), 147.3 (C4a, C5a, C11); IR(Nujol) ν/cm^{-1}: 1285(m), 1262(m), 1189(m), 1132(m), 730(s), 479 (m, As–Cl); MS APCI m/z (%): 309 [M^+, 100].

4.6. [(tript)$SbCl_2$] (6)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to −78 °C and Bu^{n}Li (2.00 cm^3 of a 1.6 M solution in hexane, 3.20 mmol) added. The resultant suspension was warmed to room temperature and stirred for 1 h. The suspension was then cooled to −78 °C and a solution of $SbCl_3$ (1.03 g, 4.5 mmol) in THF (10 cm^3) added dropwise over 10 min. Warming the mixture to room temperature afforded an orange solution which was heated at reflux for 30 min. Volatiles were removed in vacuo and the residue extracted into toluene (30 cm^3). Hexane was added to the extract to the point of crystallisation and the solution was placed at −30 °C for 15 h to give colourless crystals of **6** (0.70 g, 52%); m.p. 246–247 °C, ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 5.41 (s, 1H, C10H), 7.03–7.54 (m, 12H, Ar–H); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 300 K): δ 54.3 (C10), 54.4 (C9), 122.5 (C2, C7, C14), 124.9 (C4, C5, C16), 126.1 (C3, C6, C15), 126.4 (C1, C8, C13), 145.4 (C9a, C8a, C12), 147.9 (C4a, C5a, C11); IR(Nujol) ν/cm^{-1}: 1289(m), 1259(m), 1189(m), 1137(m), 545(m), 465(m, Sb–Cl); MS APCI m/z (%): 445 [M^+, 100]; Accurate mass MS (CI) Calc. mass for $C_{20}H_{13}^{121}SbCl_2$: 444.9505. Found: 444.9518.

4.7. [(tript)$BiCl_2$] (7)

TriptBr (1.00 g, 3.00 mmol) in THF (30 cm^3) was cooled to −78 °C and Bu^{n}Li (2.00 cm^3 of a 1.6 M solution in hexane, 3.20 mmol) added. The resultant suspension was warmed to room temperature and stirred for 1 h. It was then cooled to −78 °C and a solution of $BiCl_3$ (1.42 g, 4.5 mmol) in THF (10 cm^3) added dropwise over 5 min. The suspension was warmed to room temperature and stirred for 16 h in the absence of light. Volatiles were removed in vacuo and the residue extracted into toluene (30 cm^3). Hexane was added to the point of crystallisation and the solution placed at −30 °C for 15 h to give colourless crystals of **7** (0.20 g, 13%); m.p. 155 °C, ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 5.10 (s, 1H, C10-H), 6.60–7.30 (m, 12H, Ar–H), ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 53.3 (C10), 53.2 (C9), 122.5 (C2, C7, C14), 124.0 (C4, C5, C16), 124.9 (C3, C6, C15), 127.9 (C1, C8, C13), 144.4 (C9a, C8a, C12), 146.9 (C4a, C5a, C11); IR(Nujol) ν/cm^{-1}: 1296(m), 1255(m), 1187(m), 1137(m), 475(m, Bi–Cl); MS CI m/z (%): 533 [M^+, 15], 253 [trip$^+$, 100]; Accurate mass MS (CI) Calc. mass for $C_{20}H_{13}Bi^{35}Cl_2$: 532.0193. Found: 532.0188.

4.8. [(tript)AsH_2] (8)

A suspension of (tript)$AsCl_2$ (0.65 g, 1.6 mmol) in diethyl ether (20 cm^3) was added to a solution of $LiAlH_4$ (0.08 g, 2.00 mmol) in diethyl ether (20 cm^3) at −78 °C over 5 min. The resultant suspension was warmed to room temperature and stirred in the absence of light for 60 h. The solution was filtered, concentrated to ca. 20 cm^3 at placed at −30 °C overnight to give colourless crystals of **8** (0.36 g, 67%). The spectroscopic data were found to be consistent with those previously reported for this compound [9].

4.9. [(tript)SbH_2] (9)

A suspension of (tript)$SbCl_2$ (0.50 g, 1.1 mmol) in diethyl ether (20 cm^3) was added to a solution of $LiAlH_4$ (0.08 g, 2.00 mmol) in diethyl ether (20 cm^3) at −78 °C over 5 min. The resultant suspension was warmed to room temperature and stirred in the absence of light for 60 h. The solution was then filtered, concentrated to ca. 20 cm^3 and placed at −30 °C overnight to give colourless crystals of **9** (0.36 g, 67%); m.p. 170–172 °C dec., ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 3.16 (s, 2H, SbH_2), 5.16 (s, 1H, C10-H), 6.82–6.75 (m, 6H, ArH), 7.20–7.49 (m, 6H, ArH); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 54.9 (C10), 55.1 (C9), 123.5 (C2, C7, C14), 124.9 (C4, C5, C16), 125.1 (C3, C6, C15), 126.1 (C1, C8, C13), 146.6 (C9a, C8a, C12), 148.7 (C4a, C5a, C11); IR(Nujol): ν/cm^{-1} 1865(m, Sb–H); MS CI m/z (%): 377 [M^+, 20], 253 [trip$^+$, 100]; Accurate mass MS (CI) Calc. mass for $C_{20}H_{15}^{121}Sb_2$: 376.0106, measured mass: 376.0200.

4.10. Crystallographic studies

Crystals of **2**, **3**, **5**, **6**, **7** and **9** 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 (SHELX 97) [22] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). The hydrogens attached to Sb(1) in the structure of **9**

Table 1
Summary of crystallographic data for complexes **2**·$(CH_2Cl_2)_{0.5}$, **3**, **5**·$(C_7H_8)_{0.5}$, **6**, **7**·$(C_6H_{14})_{0.5}$ and **9**

	2·$(CH_2Cl_2)_{0.5}$	**3**	**5**·$(C_7H_8)_{0.5}$	**6**	**7**·$(C_6H_{14})_{0.5}$	**9**
Chemical formula	$C_{24.5}H_{22}Cl_3GaO$	$C_{28}H_{33}Br_3InLiO_2$	$C_{23.5}H_{17}AsCl_2$	$C_{20}H_{13}Cl_2Sb$	$C_{23}H_{20}BiCl_2$	$C_{20}H_{15}Sb$
Formula weight	508.49	763.03	445.19	445.95	576.27	377.07
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$C2/c$	Cc	$P2_1/n$	$P2_1/n$
a (Å)	11.440(2)	10.565(6)	22.929(5)	15.769(3)	13.272(3)	11.975(2)
b (Å)	14.819(3)	14.212(3)	10.922(2)	11.103(2)	9.1190(18)	8.8310(18)
c (Å)	14.988(3)	20.028(4)	16.060(3)	20.103(4)	16.432(3)	15.044(3)
α (°)	90	90	90	90	90	90
β (°)	103.74(3)	90	107.11(3)	108.02(3)	96.65(3)	107.18(3)
γ (°)	90	90	90	90	90	90
V (Å^3)	2468.2(9)	3007.2(10)	3843.9(13)	3347.1(12)	1975.3(7)	1519.9(5)
Z	4	4	8	8	4	4
μ(Mo Kα) (mm^{-1})	1.452	4.794	2.051	1.963	9.200	1.805
Unique reflections	4293	5832	3519	5256	3424	3477
$R_1(I > 2\sigma(I))$	0.0724	0.0462	0.0371	0.0440	0.0505	0.0768
wR_2' (all data)	0.2269	0.0838	0.0858	0.1044	0.1271	0.1591

could not be located from difference maps and were not refined. The asymmetric unit of **6** contains two crystallographically independent molecules though no significant geometric differences were found between them. Therefore, the metric parameters for only one are discussed in the text. Compounds **3** and **6** crystallise in chiral space groups ($P2_12_12_1$ and Cc, respectively) and the absolute structures of each have been assigned based on the values of the Flack parameters after final refinements (0.021(12) and 0.01(3), respectively). Crystal data, details of data collections and refinement are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **2**, **3**, **5**–**7** and **9** have been deposited with the Cambridge Crystallographic Data Centre **2**: CCDC No. 222053; **3**: CCDC No. 222054; **5** CCDC No. 222055; **6**: CCDC No. 222056; **7**: CCDC No. 222057; **9**: CCDC No. 222058. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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