on an Enraf-Nonius CAD4 diffractometer with $Cu_{K\alpha}$ radiation, 6856 of which were independent and used for all calculations. The structure was solved by direct methods (SHELXS-86[11]) and refined to F^2 anisotropically, the H atoms were refined with a riding model (SHELXL-93[12]). The final quality coefficient $wR2(F^2)$ was 0.2540, with a conventional $R(F) = 0.0780$ for 545 parameters and 91 restraints. One *p*-*t*Bu group and the triflate are disordered. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132812 (**2**), CCDC-132813 (**3** · Br^-), and CCDC-132814 (**4** · TfO^-). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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$(2,6\text{-}Mes_2H_3C_6)_2BiH$, a Stable, Molecular Hydride of a Main Group Element of the Sixth Period, and Its Conversion to the Dibismuthene $(2,6\text{-}Mes_2H_3C_6)BiBi(2,6\text{-}Mes_2C_6H_3)$**

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Philip P. Power*

Element derivatives of hydrogen are an important and fundamental compound class.[1] This is especially true for main group element hydrides, which are widely used as reducing agents. However, many such hydrides are currently unknown as stable species. For example, there are no stable hydride derivatives of members of the sixth period of the p-block (e.g., Tl, Pb, or Bi[2]). It is doubtful that their lack of stability is due to inherent weakness in the element–hydrogen bonds since these are comparable in strength to element–carbon bonds[3] and alkyl and aryl derivatives of these elements are already well-known. It is more probable that coordinative unsaturation in the hydrides provides a relatively low-energy decomposition pathway unavailable in the alkyl or aryl derivatives. If this hypothesis is correct it should be possible to synthesize stable hydrides of these metals by using sterically encumbering groups to hinder decomposition. It is now shown that the use of the sterically encumbering properties of terphenyl substituents enables the first stable hydride of bismuth to be prepared and characterized.

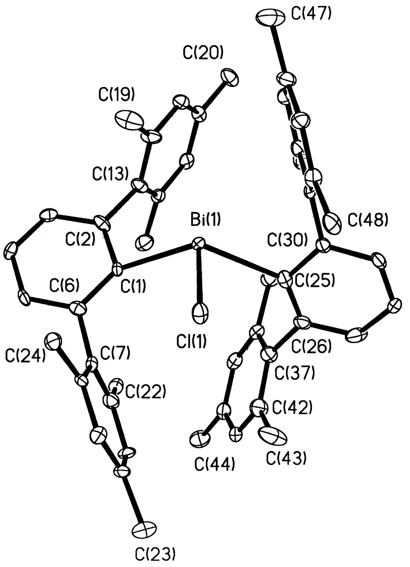

Figure 1. Structure of **1** (H atoms not shown). Selected bond lengths [Å] and angles [°]: Bi(1)-C(1) 2.337(7), Bi(1)-C(25) 2.418(8), Bi(1)-Cl(1) 2.483(3); C(1)-Bi(1)-C(25) 123.9(3), C(1)-Bi(1)-Cl(1) 98.43(19), C(25)-Bi(1)-Cl(1) 86.93(17).

Treatment of the very crowded diarylbismuth halide $(2,6\text{-}Mes_2H_3C_6)_2BiCl$ (**1**) with $LiAlH_4$ in Et_2O/PhMe solution affords the hydride derivative $(2,6\text{-}Mes_2H_3C_6)_2BiH$ (**2**) in about 30% yield. The corresponding reaction using $LiAlD_4$ gave the deuteride $(2,6\text{-}Mes_2H_3C_6)_2BiD$ (**3**). The compounds **1**–**3** were characterized by C,H elemental analysis, ^1H NMR, ^2H NMR (**3** only), ^{13}C NMR, and IR spectroscopy and by X-ray crystallography in the case of **1** and **2**.[4] The structure of **1** (Figure 1) provides evidence of high steric congestion at the bismuth center. Although the bismuth center remains pyramidally coordinated (sum of angles at Bi 309.26°), there are very large distortions in the geometry at the C(*ipso*) carbon atoms bound to bismuth. Thus, the Bi-C(*ipso*)-C(*ortho*) angles in the C(1) and C(25) terphenyl groups differ by 28.6 and 34.8°, respectively. In addition, the C(1) and C(25) aromatic ring planes deviate by 27 and 10° from the extended line of the Bi(1)–C(1) and Bi(1)–C(25) bonds. The Bi–C bond lengths of 2.337(7) and 2.418(8) Å are also quite long (cf. ca. 2.28, 2.328(13), and 2.357(14) Å in the crowded molecules $BiMes_3$[5], $Bi[CH(SiMe_3)_2]_3$[6] and $Bi[2,4,6\text{-}Ph_3C_6H_2]_3$[7]) and the C(1)-Bi-C(25) angle (123.9(3)°) is very wide in comparison to the usual angles seen in trivalent bismuth com-

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[**] This work was supported by the National Science Foundation. The Bruker SMART 1000 difractometer was funded in part by NSF Instrumentation Grant CHE-9808259. Mes = $2,4,6\text{-}Me_3C_6H_2$.

pounds.[5–7] The Bi–Cl distance (2.483(3) Å) is not greatly lengthened in comparison to that in $[2,4,6\text{-}(CF_3)_3H_2C_6]_2BiCl$ (2.463(3) Å).[8] Another interesting feature of the structure is the large difference of about 11.5° between the two C-Bi-Cl angles which is almost identical to that in $[2,4,6\text{-}(CF_3)_3H_2C_6]_2$-BiCl.[8]

Replacement of the chlorine atom by a hydrogen atom results in **2** whose structural parameters suggest that it is significantly less crowded than **1**. The molecule is characterized by the presence of a twofold rotational axis of symmetry through the bismuth atom which bisects the C-Bi-C angle (Figure 2). The C-Bi-C angle is 114.9(3)° which is 9° less than the corresponding angle in **1**. In addition, the Bi–C bond (2.314(7) Å) is slightly shorter than those in **1**. Moreover, the difference between the Bi-C(*ipso*)-C(*ortho*) angles is just 6.5° and the deviation of the Bi–C(*ipso*) vector from the plane of the C(*ipso*) ring is 12.4°. Peaks which correspond to the disordered hydrogen atom could be located at two disordered positions with respect to the axis 1.94 Å distant from bismuth. Although this distance is comparable to the 1.865 Å calculated for BiH_3[9], the difference in the scattering power of bismuth and hydrogen is such that the reliability of such assignments is limited.[10]

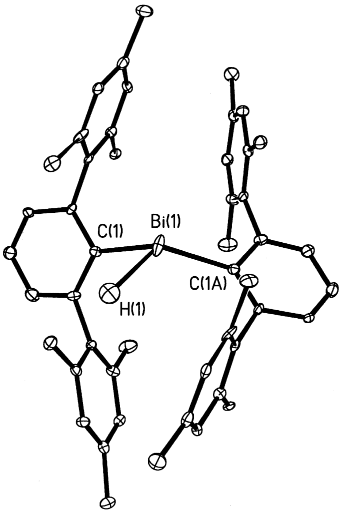
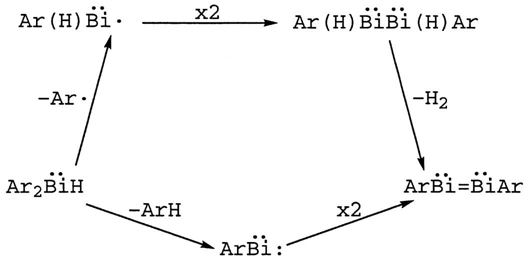


Figure 2. Structure of **2** (only H attached to Bi is shown). Selected bond lengths [Å] and angles [°]: Bi(1)-C(1) 2.314(7), Bi(1)-H(1) 1.94(2); C(1)-Bi-C(1A) 114.9(3).

The presence of a Bi–H moiety in **2** is proven by a strong IR absorption band at 1759 cm^{-1} which is in remarkably good agreement with the theoretically predicted value (1760 cm^{-1}) for BiH_3.[11] In contrast, the IR spectrum of **3** displayed no absorbance at this frequency. Instead, a strong peak was observed at 1260 cm^{-1} which is close to the value predicted (1248 cm^{-1}) on the basis of the difference in reduced mass between **2** (Bi–H) and **3** (Bi–D). Unfortunately, ^1H or ^2H NMR spectra of **2** or **3** did not display signals that could be assigned to the hydrogen or deuterium attached to bismuth. Possibly, the large quadrupole moment of the ^{209}Bi nucleus (100 %, $I = 9/2$, quadrupole moment -0.4×10^{-28} m^{-2}) and the low local symmetry at the bismuth center broaden these peaks to such an extent that they are not observable under these conditions.

Heating of **2** or **3** led to an interesting elimination reaction. In contrast to the precursor **1**, which melts without noticeable decomposition at 203–204 °C, **2** and **3** undergo a rapid color change at 135–136 °C for **1**, and at 138–139° for **2**. In both cases a purple solid is produced which has identical spectroscopic properties to those previously described for the dibismuthene $(2,6\text{-}Mes_2C_6H_3)BiBi(2,6\text{-}Mes_2C_6H_3)$. X-ray data also afforded cell constants and a structure that were essentially the same as those previously observed.[12] The yield of the dibismuthene in this reaction is quite high (80 %) so that this elimination reaction represents an alternative synthetic route to dibismuthenes.[12, 13] At least two plausible mechanisms for the decomposition of **2** and **3** to the dibismuthene product may be envisaged as shown in Scheme 1. One (top pathway) involves initial cleavage of the bismuth–aryl bond, followed by dimerization of the bismuth fragments to form a dibismuthane, which then eliminates hydrogen to form the dibismuthene. The second (bottom pathway) involves the concerted elimination of the arene followed by rapid dimerization of the bismuthenes to give the product. However the obervation of a deuterated arene coproduct upon heating a solution of **2** or **3**, combined with the lack of visually observable H_2 evolution, favors the pathway involving the initial elimination of ArH (ArD).



Scheme 1. Two possible mechanisms for the transformation of Ar_2BiH to ArBi=BiAr (Ar = $2,6\text{-}Mes_2C_6H_3$).

Experimental Section

All work was carried out under anaerobic and anhydrous conditions.

1: A solution of $Li(2,6\text{-}Mes_2C_6H_3)$ (1.35 g, 4.21 mmol)[14] in toluene (20 mL) was added dropwise to a suspension of $BiCl_3$ (0.66 g, 2.1 mmol) in toluene (10 mL) at about 0 °C. The mixture was warmed to room temperature and stirred overnight. The mixture was filtered through celite and the solvent was removed under reduced pressure. The residue was extracted with hexane (80 mL) and the pale yellow solution was warmed to dissolve the precipitates. Cooling to room temperature over a period of 2 h afforded X-ray diffraction quality, pale yellow crystals of **1**. Yield 0.69 g, 36 %. M.p. 203–204 °C (decomp); IR: $\tilde{\nu} = 288$ cm^{-1} (Bi–Cl); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.74$ (s, 12H; *o*-CH_3), 1.82 (s, 12H; *o*-CH_3), 2.33 (s, 12H; *p*-CH_3), 6.82 (s, 8H; *m*-Mes), 7.17 (d, $^3J_{H,H} = 7.8$ Hz, 4H; *m*-C_6H_3), 7.33 (t, $^3J_{H,H} = 6.9$ Hz, 2H; *p*-C_6H_3); ^{13}C {^1H} NMR (75 MHz, C_6D_6): $\delta = 21.47$ (*p*-CH_3), 22.48 (*o*-CH_3), 22.50 (*o*-CH_3), 128.6 (*m*-Mes), 129.1 (*p*-C_6H_3), 134.0 (*m*-C_6H_3), 136.5 (*o*-C_6H_3), 137.0 (*o*-Mes), 137.4 (*o*-Mes), 140.2 (*i*-Mes), 149.6 (*p*-Mes), 201.5 (*i*-C_6H_3); satisfactory C,H analysis.

2: A solution of $LiAlH_4$ (1.5 g, 39.5 mmol) in Et_2O (30 mL) was added to a rapidly stirred solution of **1** (3.41 g, 3.75 mmol) in toluene (40 mL) with cooling to about 0 °C. The solution immediately became black on addition of $LiAlH_4$. Stirring was continued overnight at room temperature, whereupon the solvent was removed under reduced pressure. The residue was extracted with C_6H_6 (50 mL), and the resultant red supernatant liquid was decanted. The red solution was concentrated to about 5 mL at which point a colorless solid precipitated. Hexane (50 mL) was added and the solution was heated to dissolve the majority of the precipitates. The solution was then decanted (60 °C) and allowed to cool slowly to room temperature affording X-ray diffraction quality, colorless crystals of **2**. Yield 0.96 g, 29.3 %. M.p.: on heating the crystals became red at 130 °C and purple at 139 °C (decomp); IR: $\tilde{\nu} = 1759\ \text{cm}^{-1}$ (s, Bi–H); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.85$ (s, 12 H; *o*-CH_3), 1.88 (s, 12 H; *o*-CH_3), 2.24 (s, 12 H; *p*-CH_3), 6.81, 6.82 (8 H; *m*-Mes), 6.84 (d, $^3J_{H,H} = 7.2$ Hz, 4 H; *m*-C_6H_3), 7.01 (t, $^3J_{H,H} = 7.6$ Hz, 2 H; *p*-C_6H_3); $^{13}C\{^1H\}$ NMR (100 MHz, C_6H_6): $\delta = 21.29$ (*p*-CH_3), 21.87 (*o*-CH_3), 126.396 (*m*-C_6H_3), 128.306 (*p*-C_6H_3), 129.09 (*m*-Mes), 135.79 (*o*-Mes), 136.62 (*o*-C_6H_3), 144.3 (*i*-Mes), 150.9 (*p*-Mes), 153.2 (*i*-C_6H_3); satisfactory C,H analysis.

3: $LiAlD_4$ (0.25 g, 5.95 mmol) was added by using a solids addition tube to a solution of **1** (5.27 g, 5.8 mmol) in toluene (40 mL) at about −78 °C. The solution was allowed to warm slowly to room temperature overnight and stirring was continued for 30 h by which time the supernatant liquid had become red. This solution was filtered and the supernatant liquid was pumped to dryness. The resulting solid was extracted with hexane/toluene (3/1) (3 × 80 mL). Colorless, X-ray diffraction quality, crystals of **3** were obtained from these solutions upon cooling to −20 °C. Yield 0.52 g, 10 %. M.p.: on heating the crystals became red at 132 °C and purple at 139 °C;. IR: $\tilde{\nu} = 1260\ \text{cm}^{-1}$ (s, Bi–D); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.85$ (s, 12 H; *o*-CH_3), 1.88 (s, 12 H; *o*-CH_3), 2.24 (s, 12 H; *p*-CH_3), 6.81, 6.82 (8 H; *m*-Mes), 6.84 (d, $^3J_{H,H} = 7.2$ Hz, 4 H; *m*-C_6H_3), 7.01 (t, $^3J_{H,H} = 7.6$ Hz, 2 H, *p*-C_6H_3); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): $\delta = 21.29$ (*p*-CH_3), 21.87 (*o*-CH_3), 126.396 (*m*-C_6H_3), 128.306 (*p*-C_6H_3), 129.09 (*m*-Mes), 135.79 (*o*-Mes), 136.62 (*o*-C_6H_3), 144.3 (*i*-Mes), 150.9 (*p*-Mes), 153.2 (*i*-C_6H_3); satisfactory C,H analysis.

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Synthesis of (*E*)-α,β-Unsaturated Esters and Amides with Total Selectivity Using Samarium Diiodide[**]

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The development of methods for the stereoselective formation of carbon–carbon double bonds could be considered one of the most important challenges in organic synthesis.[1] The synthesis of α,β-unsaturated esters[2] is generally achieved by C=C bond formation with Wittig,[3] Horner–Emmons,[4] Heck,[5] or Peterson[6] reactions, or with the Cope rearrangement,[7] from acetylenic compounds[8] or α-sulfanylester derivatives.[9] However, in most of these papers, total control of the stereoselectivity of the carbon–carbon double bond formation remained unresolved.[3a, b, d, 4–6c, 8a, 9b,c, 10] Some methodologies are limited by their poor generality,[7, 8b, 9a, 11] and other papers describe the preparation of α,β-unsaturated esters in which the substitution pattern of the olefin is quite simple (monosubstituted or 1,2-disubstituted).[3c, 6d] Only a few examples of the synthesis of α-substituted α,β-unsaturated esters in which the C=C bond is trisubstituted have been reported.[12]

Recently, we described a stereoselective synthesis of (*Z*)-vinyl halides by treatment of O-acetylated 1,1-dihaloalkan-2-ols with samarium diiodide; this was the first general stereoselective β-elimination reaction promoted by SmI_2.[13, 14] Here we report a new methodology to obtain α,β-unsaturated esters **2** with total stereoselectivity, by treatment of the easily available 2-halo-3-hydroxyesters **1** with samarium diiodide [Eq. (1)]. We also describe preliminary results of the synthesis of related α,β-unsaturated amides.

When a solution of SmI_2 in THF was added dropwise to several 2-halo-3-hydroxyesters **1** (prepared by reaction between the corresponding lithium enolates of α-haloesters and

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