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Addition of Ethylene or Hydrogen to a Main Group Metal Cluster under Mild Conditions

Petra Vasko,[a] Shuai Wang,[b] Heikki M. Tuononen,*[a] and Philip P. Power*[b]

Abstract: Reaction the tin cluster Sn8(ArH3)8 (ArH3 = C6H5-2,6-(C6H3-2,4,6-Me3)3) with excess ethylene or dihydrogen at 25 °C / 1 atmosphere yielded two new clusters that incorporated ethylene or hydrogen. The reaction with ethylene yielded Sn8(AH8)8(C6H3)2 that contained five ethylene moieties bridging four aryl substituted tin atoms and one tin-tin bond. Reaction with H2 produced a cyclic tin species of formula (Sn8H8)2, which could also be synthesized by the reaction of [(ArH3)Sn(μ-Cl)]2 with DIBAL-H. These reactions represent the first instances of direct reactions of isolable main group clusters with ethylene or hydrogen under mild conditions. The products were characterized in the solid state by X-ray diffraction and IR spectroscopy and by multinuclear NMR spectroscopy. Density functional theory calculations were performed to explain the reactivity of the cluster.

In 2005 it was shown that a main group molecule could react with dihydrogen at room temperature and atmospheric pressure.[1] Since then a wide variety of main group compounds have been investigated for their reactions with small molecules under mild conditions.[2-5] Such reactions are dependent on the existence of donor and acceptor orbitals of suitable symmetry and modest energy separation.[6] Thus, multiply bonded or unsaturated main group species have commonly been used. For example, heavier group 14 alkynes, ArP3=EEArP3, and carbene, :E(Ar=CH)2, analogues (E = Ge or Sn; ArP3=CH = C6H5-2,6-(C6H3-2,4,6-Me3)3) react readily with hydrogen, ethylene and other small molecules under mild conditions.[7-10] Activation of small molecules can also be effected by stable carbenes such as :C(Bu)2(IPr)2N(11) or frustrated Lewis pairs using a phosphine or related electron donor and B(C6F5)3 as the acceptor.[12] Several reactions have been shown to be reversible, which also has generated widespread interest.[13-15] The reactivity of these main group compounds toward small molecules can resemble that of transition metal complexes, and thus, may have use in catalytic applications.[16]

The reactivity of main group clusters toward small molecules under ambient conditions has remained virtually unexplored.[17] There have been a few theoretical studies on dihydrogen activation by aluminum clusters[18] and the activation of ammonia-borane by a gallium nitrogen cage compound.[19] Main group molecular clusters are also of interest because the coordination of their constrained atoms may resemble that of atoms at elemental surfaces.[20-29] Herein we report the reactions of the tin cluster Sn8(AH8)8 (ArH3 = C6H5-2,6-(C6H3-2,4,6-Me3)3) with excess ethylene or dihydrogen to afford the products 1 and 2 as depicted in Scheme 1. The product 1 shows that the initial cluster has absorbed five ethylene molecules. A reaction between the tin cluster and dihydrogen yields the tin hydride 2. Significantly, both reactions involve the loss of the unsubstituted tin atoms in the cluster. The syntheses of 1 and 2 are described as well as their characterization by NMR spectroscopy and X-ray crystallography. Computational investigations of model systems for 1 and 2 are also described.

Compound 1 was synthesized by treating Sn8(AH8)8 in THF with ethylene under ambient conditions (Scheme 1). The initially dark purple mixture was stirred for 2.5 days at 25 °C to afford a dark red solution and a metallic precipitate, assumed to be elemental tin. After work-up, compound 1 was isolated in 14 % yield. Colorless crystals were grown from diethyl ether at 6 °C overnight. Compound 1 crystallizes in a triclinic P1 space group with two diethyl ether solvent molecules.[24] Figure 1 depicts the solid state structure of 1 and it can be seen that the initial tin cluster, Sn8(AH8)8, has incorporated five ethylene molecules and the four unsubstituted tin atoms have been eliminated. One C6Me2 moiety is disordered over two positions, each with 50 % occupancy and only one of these sites (C7A and C8A) is shown.

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Values Sn(4) and 1.1 ppm Sn(1) and Sn(2), indicating two tin elemental tin. Hence, the tin hydride decompose the majority of the starting cluster with deposition of more sterically encumbered hydrogen bridged dimer (ArP4Sn(μ-H)).[26] or that of the asymmetric stannylstannylene ArP4SnSnH2ArP4[29] and related species.[30] The orientation of the hydrogens alternate on either side of the SnH. The Sn-Sn bond lengths (2.8433(4) and 2.8050(3) Å) are slightly shorter than the Sn-Sn single bonds in the other terminal tin hydrides,[29,30] but within the range of typical Sn-Sn single bonds. There are a few structures in the literature that incorporate a SnH ring, but none have Sn-H bonds. The known species have formulas SnL8 (L = alkyl ligand) or SnL’4 (L’ = bidentate ligand).[31–33] The 1H NMR spectrum of 2 shows a hydride signal at 3.97 ppm, and the 119Sn NMR spectrum at ~24.3 ppm, JSn-H = 1590 Hz.[34]

Compound 2 crystallizes in an orthorhombic Fdd2 space group. The asymmetric unit consists of a Sn(H)(ArMe6) moiety and 0.5 Et2O, with the rest of the molecule generated by symmetry. It consists of a puckered ring of four tin atoms each 7-bonded to a hydrogen and an ArMe6 ligand in addition to the neighboring tins. The tin atoms are tetrahedrally coordinated. The overall tetrameric structure may be contrasted with that of the more sterically encumbered hydrogen bridged dimer (ArP4Sn(μ-H)).[26] or that of the asymmetric stannylstannylene ArP4SnSnH2ArP4[29] and related species.[30] The orientation of the hydrogens alternate on either side of the SnH. The Sn-Sn bond lengths (2.8433(4) and 2.8050(3) Å) are slightly shorter than the Sn-Sn single bonds in the other terminal tin hydrides,[29,30] but within the range of typical Sn-Sn single bonds. There are a few structures in the literature that incorporate a SnH ring, but none have Sn-H bonds. The known species have formulas SnL8 (L = alkyl ligand) or SnL’4 (L’ = bidentate ligand).[31–33] The 1H NMR spectrum of 2 shows a hydride signal at 3.97 ppm, and the 119Sn NMR spectrum at ~24.3 ppm, JSn-H = 1590 Hz.[34]

The reactivity of the tin cluster towards H2 and ethylene was investigated computationally using the PBE0 hybrid functional[35–38] with def2-TZVP basis sets.[38] A model compound Sn9H4 was used to lower computational cost. The calculations show that the reaction of dihydrogen with the Sn9H4 cluster yields an addition product Sn9H8Ph2 (Figure 3) initially, whose formation is thermodynamically disfavored in the gas phase (ΔH = 4 kJ mol−1; ΔG = 39 kJ mol−1). The Gibbs energy or activation was found to be 134 kJ mol−1, consistent with the fact that the reaction with H2 required mild heating and an excess of hydrogen gas to proceed. A similar addition product was located for the reaction of Sn9H4 with ethylene (see Figure 3). However, the gas phase reaction is exothermic and only slightly disfavored by entropy (ΔH = -33 kJ mol−1; ΔG = 22 kJ mol−1). The Gibbs energy of activation is also significantly smaller, 86 kJ mol−1, consistent with experimental observations.
The frontier orbitals of Sn₄Ph₄ have both electron donating and acceptor features (see SI), which rationalizes the relatively facile formation of Sn₄H₂Ph₄ and Sn₄(C₂H₅)₂Ph₄. The modelling of mechanisms for the formation of [Sn(H)Ph₄]⁺, Sn₄Ph₄(C₂H₅), and elemental tin is beyond the scope of this work. However, the peculiar structure of 1 with an unreacted Sn-Sn bond prompted us to investigate the possible insertion of a sixth ethylene to Sn₄Ph₄(C₂H₅)₂ to form Sn₄Ph₄(C₂H₅)₂. The structures of ethylene, Sn₄Ph₄(C₂H₅)₂ and Sn₄Ph₄(C₂H₅)₆ were optimized (see SI) and their energies compared, which revealed that the addition of a sixth equivalent of ethylene is thermodynamically favored (ΔG = -12 kJ mol⁻¹) though the reaction could be prevented by kinetic factors. Unfortunately, we could not locate a transition state for the addition of the sixth ethylene molecule, thus the magnitude of the activation barrier remains unknown.

Figure 3. Optimized structures for the addition products of Sn₄Ph₄ with H₂ (left) and ethylene (right).

In summary, we have described the syntheses and characterization data for two new insertion products of small molecules to a tin cluster under mild conditions. Further studies on the reactivity of Sn₄{(Ar₆Me₆)₂} towards other small molecules and attempts to prepare Sn₄{(Ar₆Me₆)₃}(C₂H₅)₆ are on-going.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions by using modified Schlenk line techniques under a dinitrogen atmosphere or in a Vacuum Atmospheres HE-43 drybox. Solvents were dried and stored over sodium. Physical measurements were performed under anaerobic and anhydrous conditions. ¹H, ¹³C[¹H] and ¹¹⁹Sn[¹H] NMR spectra were obtained on a Varian 400 or 600 MHz spectrometers and referenced to known standards. IR spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 1430 Infrared Spectrophotometer. Melting points were determined on a Meltemp II apparatus using glass capillaries sealed with vacuum grease, and are uncorrected. All starting materials were obtained from commercial sources and used as received. Sn₄{(Ar₆Me₆)₃}(C₂H₅)₆ and ([Ar₆Me₆]Snμ-Cl)₂[Cl] were prepared by literature procedures.

Synthesis of Sn₄{(Ar₆Me₆)₃}(C₂H₅)₆ (1). 0.700 g of Sn₄{(Ar₆Me₆)₃} was dissolved in ca. 40 mL of THF. The flask was flushed with ethylene gas for ca. 45 min at 25 °C and then stirred under an ethylene atmosphere for another 48 h. The initially dark purple solution became dark red with a grey precipitate (assumed to be elemental tin). The mixture was allowed to settle and filtered. The filtrate was evaporated and the residue was dissolved in ca. 20 mL of Et₂O. Filtration followed by reduction in volume to ca. 6 mL and storage at 6 °C overnight yielded colorless crystals of 1 which were dried under vacuum. Yield 0.080 g (14 %). ¹H NMR (25 °C, CD₂Cl₂, 600 MHz): δ = -0.10 (t, JHH = 8.0 Hz, 4H, Sn-Ch₂CH₃-C₆H₅), 0.11 (m, JHH = 8.0 Hz, 4H, Sn-Ch₂CH₃-C₆H₅), 0.52 (t, JHH = 24.0 Hz, 8H, Sn-Ch₂CH₃-C₆H₅), 0.74 (t, JHH = 8.0 Hz, 4H, Sn-Ch₂CH₃-C₆H₅), 2.04 (s, 24H, Mes-CH₂), 2.07 (s, 24H, Mes-CH₂), 2.29 (s, 12H, Mes-CH₂), 2.34 (s, 12H, Mes-CH₂). 6.83, 6.84, 6.87, 6.91, 7.19 ppm (aromatic H, 28H), ¹³C[¹H] NMR (25 °C, CD₂Cl₂, 151 MHz): δ = 6.5, 9.2, 9.5, 13.9, 14.4, 19.8 (CH₂-CH₃), 21.4, 21.6, 21.6, 21.3 (Mes-CH₃), 31.9 (CH₂-CH₃), 128.4, 128.6, 128.9, 129.0, 129.3, 132.6, 133.6, 141.9, 142.7, 147.2 and 150.2 ppm (aromatic C), three ipso-C signals were not observed, ¹¹⁹Sn[¹H] NMR (25 °C, CD₂Cl₂, 149 MHz): 336.0 (Sn-Sn) and 1.1 ppm (Sn=CH₂). Melting point: 152-155 °C (decomp.). IR in Nujol mull (cm⁻¹) with CsI plates: 650, 520, 475, 335 and 315 (Sn=C, stretching and bending). UV-Vis (toluene, nm): 307, 321 and 330.

Synthesis of Sn₄{H(Ar₆Me₆)}₂ (2). Method A. Sn₄{(Ar₆Me₆)₃} (0.661g) was dissolved in ca. 25 mL of toluene and warmed to 60 °C. The mixture was stirred using an H₂ atmosphere for 3.5 h and then cooled to room temperature. Stirring was continued overnight without any color change but a significant amount of grey precipitate (elemental tin) was formed. The precipitate was allowed to settle and the solution was filtered. The volume was reduced to ca. 10 mL and 5 mL of THF was added. The mixture was placed in a fridge. Crystals of compound 2 were collected from the mixture which contained mainly unreacted Sn₄{(Ar₆Me₆)₃}. Method B. A solution of disobutyl aluminum hydride in hexanes (3.2 mL, 1 M, 3.2 mmol, diluted with 2 mL of hexanes) was added dropwise to the diethyl ether solution of [[(Ar₆Me₆)Sn(μ-Cl)]₂] (0.708 g in ca. 30 mL of diethyl ether) at -78 °C. The solution became orange and was stirred for ca. 2 h. A green precipitate was formed and removed by filtration. Storage of the diethyl ether solution at -30 °C overnight yielded yellow crystals of 2. Yield 0.135 g (21 %). ¹H NMR (25 °C, CD₂Cl₂, 600 MHz): δ = 1.66 (s, 12H, Mes-CH₂), 1.80 (s, 12H, Mes-CH₂), 2.07 (s, 12H, Mes-CH₂), 2.15 (s, 12H, Mes-CH₂), 2.33 (s, 24H, Mes-CH₂), 3.97 (s, 4H, Sn-H), 6.73, 6.77, 6.82, 7.07, 7.10, 7.12 ppm (aromatic H, 28H), ¹³C[¹H] NMR (25 °C, CDCl₃, 151 MHz): δ = 21.5, 21.8, 22.0, 22.4 and 23.7 ppm (Mes-CH₃), 128.4, 128.5, 128.7, 128.8, 128.9, 129.0, 129.3, 131.5, 133.5, 134.6, 135.9, 136.0, 141.7, 142.0, 144.5, 150.0 and 150.2 ppm (aromatic C), ¹¹⁹Sn NMR (25 °C, CDCl₃, 149 MHz): δ = -324.3 (d, ¹HH = 1590 Hz, Sn-H) [3] Melting point: >300 °C. IR in Nujol mull (cm⁻¹) with CsI plates: 1845 (Sn-H stretching), 730 (Sn-H bending). UV-Vis (toluene, nm): 296 and 308.

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