

IV.I.2 Activation of Hydrogen Under Ambient Conditions by Main Group Molecules

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Activation of Hydrogen Under Ambient
Conditions by Main Group Molecules
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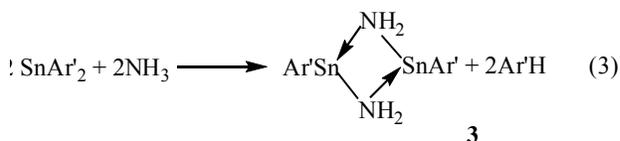
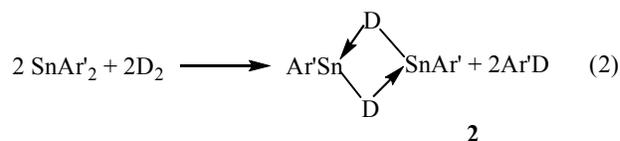
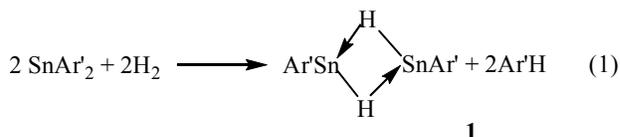
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Accomplishments:

A full paper describing the synthesis and characterization of a series of tin(II) hydrides by "chemical" reducing agents was published [1]. These have symmetrically bridged structures of formula $[(4-X-Ar')Sn(\mu-H)]_2$ ($4-X-Ar' = C_6H_2-4-X-2,6-(C_6H_3-2,6-Pr^i)_2$; $X = H, MeO, Bu^t$ and $SiMe_3$) or an unsymmetric hydride structure for the more hindered species $3,5-Pr^i-Ar^*SnSn(H)_2Ar^*-3,5-Pr^i_2$ ($3,5-Pr^i-Ar^* = C_6H_3-2,6-(C_6H_3-2,4,6-Pr^i)_2-3,5-Pr^i_2$). The compounds were prepared either by direct reduction of the corresponding aryl tin(II) chloride precursors $ArSnCl$ with $LiBH_4$, Bu^i_2AlH (DIBAL) or via the reaction of $ArSnNMe_2$ with $BH_3 \cdot THF$. They were characterized by 1H , ^{13}C and ^{119}Sn NMR and Mössbauer spectroscopy. Calculations showed that the more hindering aryl groups favored the unsymmetric structure. It was also shown that the hydride Ar^*SnH which is an orange colored, symmetric dimer in the solid phase has mostly an unsaturated structure and an intense blue color in solution owing to a change to the unsymmetric hydride structure and the existence of an equilibrium between the two forms.

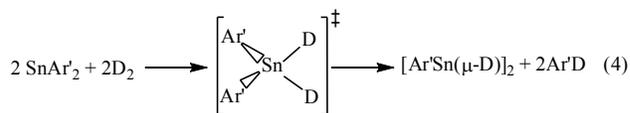
Armed with the spectroscopic and structural data for a range of such hydrides we tested a different synthetic approach involving the direct reaction of H_2 with unsaturated tin precursors to see if the tin(II) hydrides could be produced by this approach. In addition, we decided to conduct parallel investigations

involving the direct reaction of NH_3 with the same compounds. The results are summarized in equations 1-3 [2].



25°C, 1 Atmosphere, $Ar' = C_6H_2-2,6-(C_6H_3-2,6-Pr^i)_2$

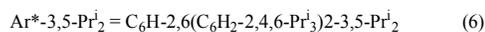
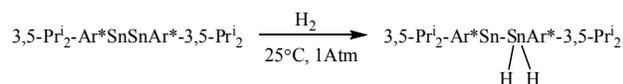
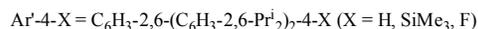
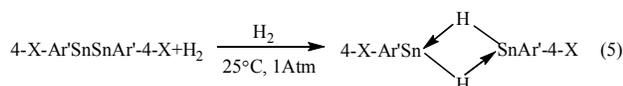
It can be seen that the reactions proceed under very mild conditions and the products 1-3 were isolated and essentially quantitative yield. They are the first examples of the direct reaction of the main group metals species with H_2 or NH_3 at 25°C and 1 atmosphere. The hydride and deuteride products 1 and 2 have symmetrically bridged structures. The reaction is remarkable in that $Ar'H$ or $Ar'D$ are also eliminated. Moreover, the reaction with deuterium (eq 2) shows that the deuterium is incorporated in the eliminated arene suggesting that the reaction proceeds through an $Sn(IV)$ intermediate in which H_2 or D_2 oxidatively adds to $SnAr'_2$ as shown by equation 4.



The reaction with ammonia (eqn 3) affords the amido bridged dimer 3 in quantitative yield also with arene ($Ar'H$) elimination. This reaction occurs below room temperature. The reactions are related to the addition of hydrogen or ammonia to stable carbenes reported recently by Bertrand [3].

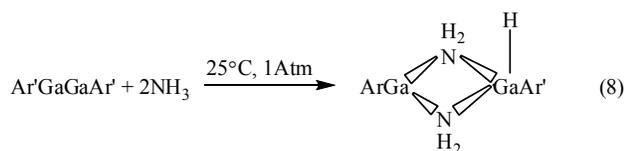
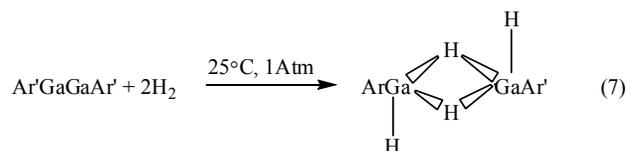
The reaction of H_2 with a range of distannynes as shown in equations 5 and 6 was also investigated.

The reactions proceeded very smoothly to afford the products cleanly and essentially quantitative yield [4]



the reactions may be contrasted with our earlier results on the corresponding germanium species Ar'GeGeAr' with hydrogen which afforded a mixture of products $\text{Ar'(H)}_2\text{GeGe(H)}_2\text{Ar'}$ and Ar'GeH_3 in an approximately 2:1 ratio [5].

The direct reaction of hydrogen and ammonia with unsaturated group 13 metals was also investigated [6] the reaction of hydrogen or ammonia with the digallene Ar'GaGaAr' afforded the product shown in equations 7 and 8.



The yields in each case were quantitative and the products were characterized by ^1H and ^{13}C NMR and IR spectroscopy as well as by X-ray crystallography. The compounds were the first instance of hydrogen or ammonia addition to a main group 13 metal species.

The reactions described in equations 1-8 together with the earlier results suggest that the insertion of unsaturated main group molecules into N-N or N-H bonds is a general phenomenon. The exploration of the mechanisms and extent of such reactions will be investigated over the next year as outlined in Section 7.

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Personnel Supported

Hoppe, Elke	25% commitment through 4/30/09
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Wang, Xinping	100% commitment through 8/31/09