Frustrated Lewis pairs: reactivities of TMS protected amines and phosphines in the presence of $B(C_6F_5)_3$†

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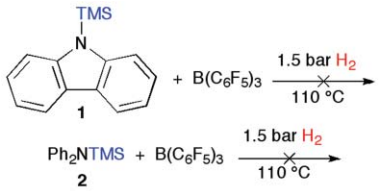
TMS protected amines in combination with $B(C_6F_5)_3$ were found to activate H_2 and this is followed by a cleavage of the N–Si bond and the generation of TMSH. A TMS protected phosphine on the other hand reacts rapidly with $B(C_6F_5)_3$ to give the known compound $tBu_2P(C_6F_4)B(C_6F_5)_2$ by a facile and efficient route.

Since the first publication on hydrogen activation by "frustrated" pairs of Lewis acids and bases appeared,[1] there has been considerable interest in exploring this exciting field. This is because on the one hand these main group element systems have the potential to become efficient green hydrogenation catalysts and on the other hand they can be used as models for the research on non-metal hydrogen storage materials.[2]

Not only has there been the introduction and study of a wide variety of frustrated Lewis pairs (FLPs) which can cleave dihydrogen,[3-9] or activate C–C multiple bonds,[7,9,10] but also their successful use in hydrogenation catalysis under mild conditions has been demonstrated on numerous substrates.[11-14] Those included the reduction of imines, enamines, silyl enol ethers, protected nitriles, aziridines and also an asymmetric hydrogenation of an imine.[15]

In continuation of our own work on the facile heterolytic cleavage of dihydrogen by simple and bulky amines in combination with $B(C_6F_5)_3$,[3] we became interested in the behaviour of trimethylsilyl (TMS) protected amines under equal conditions. There are two properties of this group which should influence the performance of the amine in the process of activating hydrogen: the TMS group is (i) very bulky which means that most TMS protected amines should not form a stable adduct together with $B(C_6F_5)_3$, and (ii) it reduces the Lewis basicity at the nitrogen center in comparison with the analogous *t*-butyl substituted amine.[16]

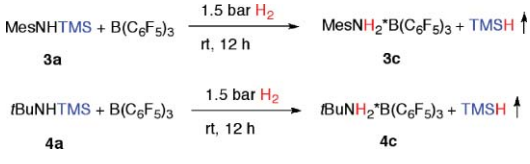
We started our investigations with the TMS protected carbazole **1** and diphenylamine **2**. Mixing of the two compounds separately with $B(C_6F_5)_3$ in toluene afforded colourless solutions. Multinuclear NMR studies (^1H, ^{11}B, ^{13}C, ^{19}F) showed no changes in the spectra in comparison with the pure substances which indicates that a stable Lewis acid (LA)/Lewis base (LB) adduct formation did not appear in both cases. After exposing the solutions to a hydrogen atmosphere (1.5 bar) for 24 h at room temperature or at 110 °C no reaction could be detected by NMR (Scheme 1).



Scheme 1 Weak Lewis bases cannot activate H_2 in combination with $B(C_6F_5)_3$ under mild conditions.

Because of the low basicity of the TMS protected amines with aromatic substituents the combined LA/LB strength is evidently not strong enough to cleave the H_2 bond heterolytically under such mild conditions.

We continued our studies by mixing the more basic TMS-amine **3a** which has an electron donating mesityl group with $B(C_6F_5)_3$. The toluene solution turned bright yellow, but by NMR spectroscopy (^1H, ^{11}B, ^{13}C, ^{19}F), no LA/LB adduct or any other reaction was detected. By exposing this solution to 1.5 bar H_2 for 12 h at room temperature a white precipitate formed.[17] The isolated product dissolved well only in very polar solvents like DMSO. In the ^1H and ^{13}C spectra no signals can be detected that refer to the three methyl groups at Si. In addition ^{11}B NMR exhibits a single resonance at –0.98 ppm and the chemical shift difference $\Delta\delta_{p,m}$ between the F atoms in *meta* and *para* position of the C_6F_5 fragments is 6.59 ppm. These values are characteristic of a four coordinate neutral adduct of $B(C_6F_5)_3$.[18,19] In fact the ^1H spectrum is identical with the spectrum of pure 2,4,6-trimethylaniline in DMSO and the ^{11}B and ^{19}F spectra are identical with the corresponding spectra of $B(C_6F_5)_3$ in DMSO. Therefore it can be assumed that the adduct **3c** is formed during the reaction (Scheme 2). By the subsequent dissolution in DMSO the coordinative B–N bond is cleaved in favour of the more stable DMSO–$B(C_6F_5)_3$ complex.



Scheme 2 Activation of H_2, cleavage of the N–Si bond and formation of a LA/LB adduct.

A solution (C_6D_6) of the even more basic *N*-trimethylsilyl-*t*-butylamine (**4a**) with $B(C_6F_5)_3$ remained colourless and showed also by NMR no sign of adduct formation. Interestingly this frustrated pair clearly reacted over 12 h with hydrogen (1.5 bar)

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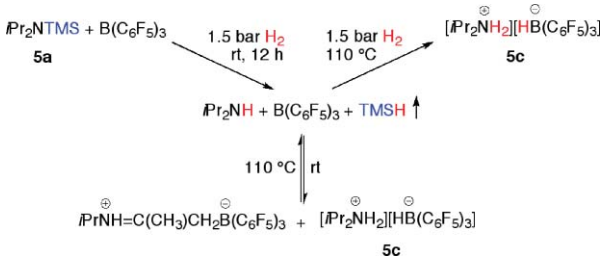
at room temperature (Scheme 2)[17] and yielded the known adduct **4c**[20] which could be identified by multinuclear NMR. When the sample was transferred directly out of the reaction vessel into the NMR tube without evaporation of the solvent, in addition to the signals for product **4c** there appeared a clear multiplet at 4.15 ppm and a doublet at 0.02 ppm in the proton NMR spectrum and also one signal at −2.75 ppm in the carbon spectrum. They could be assigned to trimethylsilane (TMSH)[21] which has a low boiling point of 6.7 °C.[22] Therefore only a small amount of TMSH compared to **4c** could be detected in solution. After evaporation of the volatile compounds these signals disappeared completely.

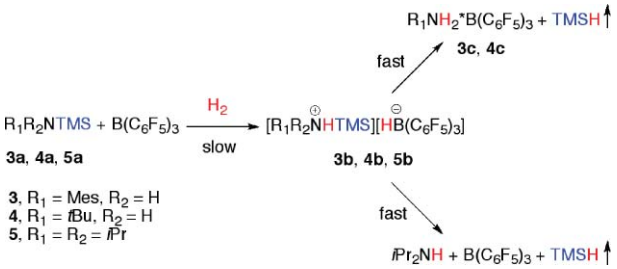
As expected no LA/LB adduct could be detected by ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR in the pale yellow solution of the extremely bulky *N*-trimethylsilyldiisopropylamine (**5a**) and $B(C_6F_5)_3$ in toluene-D_8. In contrast to previous literature,[23] there is also no sign of any other side reactions induced by a hydride abstraction in α position to nitrogen. We assume that this unreactivity is caused by the steric congestion of **5a**. After stirring this mixture at room temperature under 1.5 bar pressure of H_2 for 12 h, NMR data showed the expected 1 : 1 mixture of the salt **5c** and the zwitterion iPrNH=C(CH$_3$)CH$_2$B(C$_6$F$_5$)$_3$ plus the additional side product TMSH (Scheme 3). As described earlier by us,[3] the former two compounds are in an equilibrium with free diisopropylamine and $B(C_6F_5)_3$ at 110 °C. Thus, when exposing a solution of **5a** and $B(C_6F_5)_3$ at 110 °C to a hydrogen atmosphere (1.5 bar), two equivalents of H_2 were consumed and after evaporation the pure product **5c** was obtained.



Scheme 3 Activation of a second equivalent of H_2 after cleavage of the N–Si bond.

We conclude from these observations that H_2 activation by TMS protected amines in combination with $B(C_6F_5)_3$ is in principle possible if the Lewis basicity of the amine is strong enough and if the amine is bulky enough to form a frustrated pair. The proposed mechanism of the activation is shown in Scheme 4. Dihydrogen is split heterolytically by **3a**, **4a** and **5a** in combination with $B(C_6F_5)_3$ and the salts **3b**, **4b** and **5b** are formed. One additional experimental observation supports this assumption: after 10 h of reacting **4a** and $B(C_6F_5)_3$ with H_2, ^{19}F NMR showed two sets of signals comprising of 3 peaks. One set can be attributed to the product **4c** and the other one is consistent with the anion $[HB(C_6F_5)_3]^-$.[24]

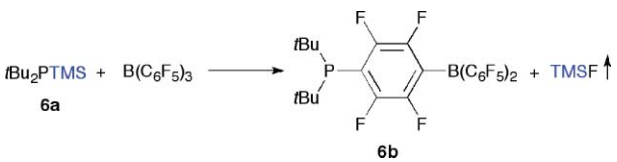
The resulting salts **3b**, **4b**, and **5b** are not stable in contrast to the salts of unprotected amines reported earlier[3,13,14] and decompose. TMSH is released and stable LA/LB adducts are formed in the case of **3** and **4** which cannot activate H_2 even at elevated temperatures (110 °C). When **5** is employed the bulky diisopropylamine and $B(C_6F_5)_3$ are formed which react further as described before (Scheme 3).[3] Although the TMS group is



Scheme 4 Proposed mechanism for the activation of H_2 by TMS protected amines in combination with $B(C_6F_5)_3$.

often referred to as a "bulky proton",[25] its behaviour differs significantly from that of a real proton in the examined systems: there are only a few examples of FLPs known where H_2 can evolve after activation.[1,2,3,8,12] Even in those cases it has never been reported to be fast and quantitative at room temperature. Our investigations basically lead to the reverse reaction of the previously reported $B(C_6F_5)_3$ catalyzed dehydrogenative silation of alcohols with tertiary silanes: the authors report that H_2 evolves while a Si–O bond is formed and in our case H_2 is consumed while a Si–N bond is broken followed by the formation of a tertiary silane.[26]

Since it is well-known in the literature that bulky phosphines can also cleave dihydrogen in combination with $B(C_6F_5)_3$[4-9] the question arose whether this is also feasible with TMS protected phosphines. By mixing trimethylsilyldi-*t*-butylphosphine **6a** with $B(C_6F_5)_3$ in benzene at room temperature, the solution turned bright orange, and after subsequent evaporation it was found by NMR spectroscopy that it converts cleanly into the previously reported intramolecular boron–phosphorus compound **6b**[5] (Scheme 5), which is able to activate hydrogen and catalyzes the hydrogenation of imines. This finding is in agreement with previous results on the reaction of TMS protected phosphines with polyfluoroarenes.[27-29] After the nucleophilic attack of the phosphorous at the carbon atom in *para* position on the electron deficient C_6F_5-ring a strong Si–F bond (561 kJ mol^{-1})[30] forms and fluorotrimethylsilane (TMSF) with a low boiling point of 16.4 °C[31] evolves. The mechanistic study of the reaction of $(CH_3)_2$PTMS with polyfluorarenes suggested a S_NAr pathway.[28]



Scheme 5 Reaction of a TMS protected bulky phosphine with $B(C_6F_5)_3$.

Accordingly, the TMS-phosphine shows a different behaviour than secondary phosphines. If R_2PH is heated together with $B(C_6F_5)_3$ in a 1 : 1 stoichiometry, nucleophilic attack at the same C atom also takes place, but then a rearrangement occurs and the corresponding zwitterion $R_2PH(C_6F_4)BF(C_6F_5)_2$ is formed.[19]

As has been investigated earlier the TMS protected phosphines offer a much greater reactivity than the respective amines.[29] This is in accordance with our own studies: Even by heating TMS-amines with $B(C_6F_5)_3$ to 110 °C we could not find similar reactivity due to their lower nucleophilicity.

Conclusions

It is shown that various TMS protected amines with a high enough steric congestion and Lewis basicity can activate H_2 in combination with $B(C_6F_5)_3$ under mild conditions. By doing so the N–Si bond is quantitatively cleaved and the amines are deprotected.[32] This represents a new metal free hydrogen activation by *N*-TMS amines and $B(C_6F_5)_3$ with the simultaneous generation of TMSH which could be used in further hydrosilation reactions for example. In combination with the previously reported $B(C_6F_5)_3$ catalyzed hydrosilation of imines[33] a novel method for the reduction of imines could be developed. Another application could be the effective and clean deprotection of sensitive organometallic compounds since it was demonstrated earlier[14] that H_2 activation is feasible with these substances. In addition, the described reaction of TMS protected phosphines with $B(C_6F_5)_3$ offers an efficient access to the frustrated Lewis pair tBu$_2$P(C_6F_4)B$(C_6F_5)_2$. This route may also work for other $R_2P(C_6F_4)B(C_6F_5)_2$ species and thereby facilitate the ongoing investigation of their potential to activate small molecules.[1,5,6,9]

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