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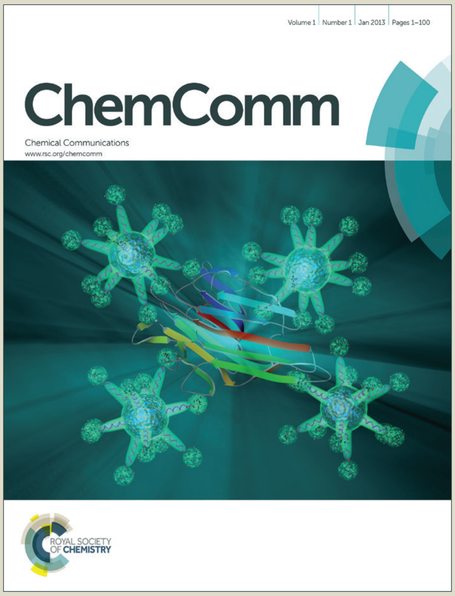

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Metal-free Lewis Acid Mediated Dehydrocoupling of Phosphines and Concurrent Hydrogenation†

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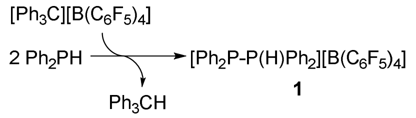
Abstract: The stoichiometric reaction of trityl cation with two equivalents of Ph_2PH affords the phosphine stabilized phosphenium salt $[Ph_2(H)PPPh_2][B(C_6F_5)_4]$ via hydride abstraction, while catalytic amounts of $B(p\text{-}HC_6F_4)_3$ effects catalytic phosphine dehydrocoupling with the liberation of H_2. This reaction is accelerated by the presence of olefin or imine, effecting concurrent hydrogenation.

Phosphorus coordination chemistry is dominated by the donor behaviour of trivalent, tricoordinate phosphines. However, very recently the Lewis acidity of P(V) phosphonium cations has garnered much attention as these species can be employed in a variety of catalytic reactions.[1] In a related sense, the donor-acceptor properties of low-coordinate phosphenium cations, $R_2P{:}^+$ has also drawn attention in recent years.[2] These species provide an interesting isolobal analogy to carbenes.[3] Phosphenium cations are typically readily prepared by halide abstraction or displacement from a suitable precursor using either weakly-coordinating anion or a suitable Lewis base.[2b, 4, 5]

P-H bond activation typically involves treatment with a strong base resulting in proton abstraction and generation of a phosphide anion[6] although Wright and coworkers have described the stannocene, mediated dehydrocoupling of a range of primary phosphines.However, the similarities of the Pauling electronegativities of hydrogen and phosphorus (2.20 and 2.19, respectively),[7] suggest that it should also be possible to generate a hydride and phosphenium cation from a phosphine. Nonetheless, attempts to abstract hydride[8] with trityl borate to generate a phosphenium cation failed.[9] Herein, we report the first hydride abstraction from secondary and primary arylphosphines by the concurrent action of a Lewis acid and excess phosphine, affording a route to a phosphine-stabilized phosphenium salt. Moreover, this reactivity is extended to effect the catalytic dehydrocoupling of phosphines and even concurrent transfer hydrogenation using the Lewis acid as a catalyst.

The reaction of Ph_2PH with $[Ph_3C][B(C_6F_5)_3]$ in 2:1 ratio in C_6H_5Br for 3 hours at 130 °C afforded Ph_3CH and $[Ph_2(H)PPPh_2]$ $[B(C_6F_5)_4]$ (**1**) [Eq. (1)]. The concurrent formation of Ph_3CH was clearly indicated by the ^1H NMR signal at 5.4 ppm. Compound **1** was separated and isolated as oil and its formulation confirmed by the observation of the two signals in ^{31}P NMR spectrum, a doublet at 4.5 ppm ($J(PH)$ = 417 Hz) and singlet at δ = -25.4 ppm. Interestingly, this stands in contrast to a previous report of a 1:1 reaction of Ph_2PH with $[Ph_3C][B(C_6F_5)_4]$ which afforded the adduct $[Ph_2(H)PCPh_3][B(C_6F_5)_4]$.[9]



$$2\ Ph_2PH \xrightarrow[Ph_3CH]{[Ph_3C][B(C_6F_5)_4]} \underset{\mathbf{1}}{[Ph_2P\text{-}P(H)Ph_2][B(C_6F_5)_4]} \quad (1)$$

This prompted further efforts to employ Lewis acids to effect P-P dehydrocoupling. To that end, the Lewis acid $B(p\text{-}C_6F_4H)_3$ **2** [10] was employed as the common electrophilic borane. $B(C_6F_5)_3$ is known to undergo reaction with phosphines to give *para*-attack products of the form $R_2P(H)(C_6F_4)BF(C_6F_5)_2$.[11] In an initial stoichiometric reaction **2** was added to two equivalents of Ph_2PH and heated to 130 °C. This resulted in slow formation of $(Ph_2P)_2$ as evidenced by the ^{31}P NMR signal -15 ppm. The concurrent formation of H_2 was evident from the ^1H NMR peak at 4.5 ppm. Under catalytic conditions, reaction of 10 mol % of the borane **2** with Ph_2PH was heated to 130 °C for 12 h in a closed vessel. This afforded a 38% conversion to $(Ph_2P)_2$ **3**. Prolonged heating of the reaction mixture did not increase conversion, however, removal of H_2 from the reaction vessel, furthered conversion to 54%. Subsequent and continuous removal of H_2 led to quantitative formation of **3**. This observation infers that the Lewis acid mediated hydrogenation of the biphosphine regenerates

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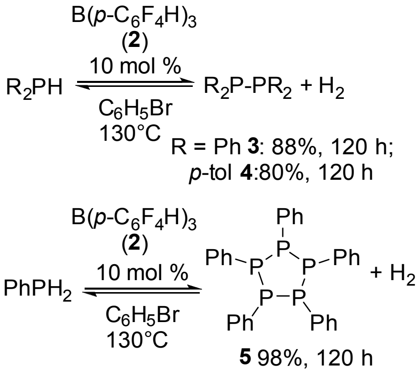
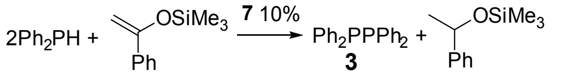
Ph_2PH. While the reduction of P-P bonds has been previously reported,[12] the present result is the first to describe the reverse reaction, namely the Lewis acid mediated dehydrocoupling of phosphines.



Scheme 1. Catalytic dehydrocoupling of phosphines

Analogous dehydrocoupling of $(p\text{-tol})_2PH$ at 130 °C for 120 h proceeds in a similar fashion to give $((p\text{-tol})_2P)_2$ **4** in 80% while $PhPH_2$ undergo dehydrocoupling to give $(PhP)_5$ **5** in 98% yield (Scheme 1). Interestingly, the sterically demanding phosphines $(o\text{-tol})_2PH$ or Mes_2PH groups did not lead to P-P coupling, rather only the phosphine-borane adducts were observed. Similarly efforts to dehydrocouple secondary alkylphosphines gave only the phosphine-borane adducts. These latter observations indicated the steric and electronic limits for this Lewis acid mediated P-P dehydrocoupling.



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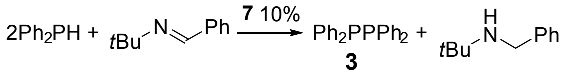

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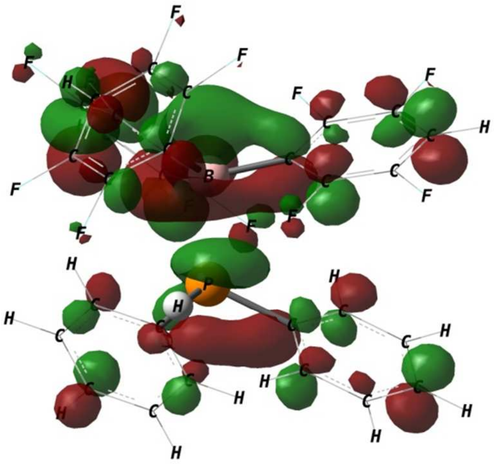
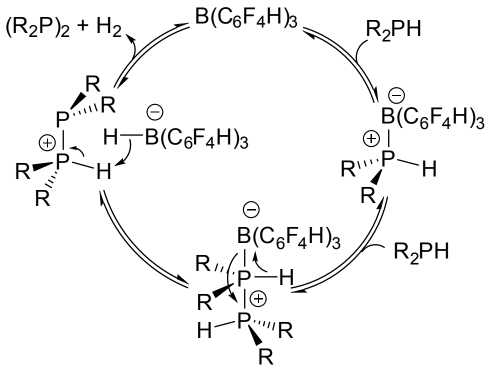


Figure 2. LUMO of $(p\text{-}C_6F_4H)_3B(PHR_2)$ (isovalue = 0.033)

Interestingly, the present dehydrocoupling reactions can also be exploited to effect transfer hydrogenation of organic unsaturates. Moreover, the presence of a hydrogen atom acceptor serves to accelerate the dehydrocoupling reactions. Thus, reaction of Ph_2PH in the presence of a stoichiometric amount of 1-phenyl-1-trimethylsiloxyethylene or N-benzylidene-tert-butylamine and a catalytic amount of $B(p\text{-}C_6F_4H)_3$ at 130 °C results in the complete transformation to $(Ph_2P)_2$ and hydrogenation of the organic species after 30 hours and 38 hours, respectively [Eq. (2 and 3)].



Scheme 2. Proposed mechanism of R_2PH dehydrocoupling.

A radical mechanism for this dehydrocoupling was excluded as performance of the reaction in the presence of the radical trap reagent cyclohexadiene,[13] showed no formation of benzene; rather only **3** was formed. Thus, an ionic-polar mechanism is proposed in which both hydride and proton originate from R_2PH. Coordination of a secondary phosphine to borane as in the adduct $(Ph_2PH)B(p\text{-}C_6F_4H)_3$ presumably generates an electrophilic P center due to low lying but unoccupied molecular orbital (LUMO) formed at P centre[1b, 1e] prompting nucleophilic attack by free Ph_2PH. This view is supported by DFT calculations of the molecular orbitals of the adduct $(Ph_2PH)B(p\text{-}C_6F_4H)_3$ performed at WB97XD/def2TZV level of theory.[14] The LUMO is concentrated on the B and P centers. Attack by Ph_2PH at the boron center would result in replacement of one phosphine by the other. On the other hand, attack at phosphorus center generates the proposed pentacoordinate P center. The transient five coordinate phosphorus atom transfers hydride to borane generating $[Ph_2(H)PPPh_2][HB(C_6F_4H)_3]$. This salt can either evolve H_2 or sequentially deliver proton and hydride to an organic unsaturate (Scheme 2). Hydrogenation of olefin or imine is thought to proceed in a manner similar to FLP reductions however in the present case $[Ph_2P\text{-}P(H)Ph_2]^+$ is the proton source and the anion $[(HC_6F_4)_3BH]^-$ is the source of hydride. Calculations employing the conductor-like polarizable continuum solvation model (CPCM)[15] in bromobenzene were carried out. The reaction of **1** with **6** is slightly exothermic with $\Delta H = -5.2$ kcal mol^{-1} and $\Delta G = 0.6$ kcal mol^{-1}. The subsequent generation of the intermediate salt $[Ph_2(H)PPPh_2][HB(C_6F_4H)_3]$ is slightly endothermic and endergonic with $\Delta H = 1.3$ kcal mol^{-1} and $\Delta G = 15.4$ kcal mol^{-1} consistent with the thermal conditions required for dehydrocoupling.

To put this reactivity in context P-P dehydrocoupling is typically achieved by either stoichiometric or catalytic processes.[16] Würtz

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type reduction of the phosphine halides, or dehydrohalogenation of R_2PX and R_2PH are well established.[17] A variety of other stoichiometric methods have also been described.[18] Metal catalyzed dehydrocoupling of phosphines has also been demonstrated employing Ti,[19] Zr[20] and Rh[21]-based catalysts. Wright and coworkers[16c, 16f] have described the stannocene, mediated dehydrocoupling of a range of primary phosphines, providing the first main-group mediated P-P dehydrocoupling. Very recently a radical route to phosphine dehydrocoupling was described employing 1,1-azobis[cyclohexane-1-carbonitrile] (VAZO®88) as the initiator.[22] Thus the present work illustrates the first examples of metal-free, Lewis acid catalysed phosphine dehydrocoupling. It is also interesting to note that we have previously reported the reverse reaction that is the hydrogenation of P-P bonds. With the exception of frustrated Lewis pairs, the P_2R_4 and R_2PH is a very rare case where both the incorporation and release of H_2 are catalysed by main group species.

In conclusion hydride abstraction from phosphines by Lewis acids is reported leading to phosphine stabilized phosphenium cation. This chemistry can be employed to effect the catalytic dehydrocoupling of phosphines by the borane $B(p\text{-}C_6F_4H)_3$, a reaction that is accelerated in the presence of a hydrogen acceptor. In this fashion, this effects simultaneous metal-free hydrogenation catalysis. We are continiuing to study and develop new strategies for metal-free catalysis.

Notes and references

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