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

Roman Dobrovetsky, Katsuhiko Takeuchi and Douglas W. Stephan

Abstract: The stoichiometric reaction of trityl cation with two equivalents of Ph₂PH affords the phosphine stabilized phosphonium salt [Ph₂(Ph)PPPPh₂][B(C₆F₅)₄] via hydride abstraction, while catalytic amounts of B(p-HC₆F₅)₃ effects catalytic phosphine dehydrocoupling with the liberation of H₂. 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. In a related sense, the donor-acceptor properties of low-coordinate phosphonium cations, R₂P⁺ has also drawn attention in recent years. These species provide an interesting isolobal analogy to carbenes. Phosphonium cations are typically readily prepared by halide abstraction or displacement from a suitable precursor using either weakly-coordinating anion or a suitable Lewis base.

P-H bond activation typically involves treatment with a strong base resulting in proton abstraction and generation of a phosphide anion 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), suggest that it should also be possible to generate a hydride and phosphonium cation from a phosphine. Nonetheless, attempts to abstract hydride with trityl borate to generate a phosphonium cation failed. 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 phosphonium 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 Ph₂PH with [Ph₂C][B(C₆F₅)₄] in 2:1 ratio in C₆H₄Br for 3 hours at 130 °C afforded Ph₂CH and [Ph₂(H)PPPPh₂][B(C₆F₅)₄] (1) [Eq. (1)]. The concurrent formation of Ph₂CH was clearly indicated by the ³H 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 ¹³P 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 Ph₂PH with [Ph₂C][B(C₆F₅)₄] which afforded the adduct [Ph₂(H)PCPh₂][B(C₆F₅)₄].

This prompted further efforts to employ Lewis acids to effect P-P dehydrocoupling. To that end, the Lewis acid B(p-HC₆F₅)₃ was employed as the common electrophilic borane. B(C₆F₅)₃ is known to undergo reaction with phosphines to give para-attack products of the form R₂P(H)(C₆F₅)BF(C₆F₅)₂. In an initial stoichiometric reaction 2 was added to two equivalents of Ph₂PH and heated to 130 °C. This resulted in slow formation of Ph₂P₂; as evidenced by the ¹³P NMR signal -15 ppm. The concurrent formation of H₂ was evident from the ¹H NMR peak at 4.5 ppm. Under catalytic conditions, reaction of 10 mol % of the borane 2 with Ph₂PH was heated to 130 °C for 12 h in a closed vessel. This afforded a 38% conversion to (Ph₂P)₂. Prolonged heating of the reaction mixture did not increase conversion, however, removal of H₂ from the reaction vessel, furthered conversion to 54%. Subsequent and continuous removal of H₂ led to quantitative formation of 3. This observation infers that the Lewis acid mediated hydrogenation of the biphosphine regenerates...
Ph₂PH. 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.

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 Ph₂PH in the presence of a stoichiometric amount of 1-phenyl-1-trimethylsiloxyethylene or N-benzylidene-tert-butylamine and a catalytic amount of B(p-C₆F₅H)₃ at 130 °C results in the complete transformation to (Ph₂P)₂ and hydrogenation of the organic species after 30 hours and 38 hours, respectively [Eq. (2 and 3)].

Scheme 1. Catalytic dehydrocoupling of phosphines

Analogous dehydrocoupling of (p-tol)₂PH at 130 °C for 120 h proceeds in a similar fashion to give ((p-tol)₂P)₂ 4 in 80% while PhPH₂ undergo dehydrocoupling to give (PhP)₂ 5 in 98% yield (Scheme 1). Interestingly, the sterically demanding phosphines (o-tol)₂PH or Mes₂PH groups did not lead to P-P coupling, rather only the phosphine-borate adducts were observed. Similarly efforts to dehydrocouple secondary alkylphosphines gave only the phosphine-borate adducts. These latter observations indicated the steric and electronic limits for this Lewis acid mediated P-P dehydrocoupling.

Scheme 2. Proposed mechanism of R₂PH 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 R₂PH. Coordination of a secondary phosphine to borane as in the adduct (Ph₂PH)B(p-C₆F₅H)₃ presumably generates an electrophilic P center due to low lying but unoccupied molecular orbital (LUMO) formed at P center¹⁴,¹⁵ prompting nucleophilic attack by free Ph₂PH. This view is supported by DFT calculations of the molecular orbitals of the adduct (Ph₂PH)B(p-C₆F₅H)₃ performed at WB97XD/def2TZV level of theory.¹⁴ The LUMO is concentrated on the B and P centers. Attack by Ph₂PH 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 [Ph₂(H)PPPPh₂][HB(C₆F₅H)₃]. This salt can either evolve H₂ 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 [Ph₂P-P(H)Ph₂]⁺ is the proton source and the anion [(H₃C₆F₅)₂BH]⁻ 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 ΔH = -5.2 kcal mol⁻¹ and ΔG = 0.6 kcal mol⁻¹. The subsequent generation of the intermediate salt [Ph₂H(H)PPPPh₂][HB(C₆F₅H)₃] is slightly endothermic and endergonic with ΔH = 1.3 kcal mol⁻¹ and ΔG = 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
type reduction of the phosphate halides, or dehydrohalogenation of R₃PX and R₃PH are well established. A variety of other stoichiometric methods have also been described. Metal catalyzed dehydrocoupling of phosphines has also been demonstrated employing Ti, Zr and Rh-based catalysts. Wright and coworkers 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 phosphate dehydrocoupling was described employing 1,1-azobis(cyclohexane-1-carbonitrile) (VAZO88) as the initiator. Thus the present work illustrates the first examples of metal-free, Lewis acid catalysed phosphate 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 P₂R₄ and R₂PH is a very rare case where both the incorporation and release of H₂ are catalysed by main group species.

In conclusion hydride abstraction from phosphines by Lewis acids is reported leading to phosphate stabilized phosphonium cation. This chemistry can be employed to effect the catalytic dehydrocoupling of phosphines by the borane B(p-C₆F₅H₃), a reaction that is accelerated in the presence of a hydrogen acceptor. In this fashion, this effects simultaneous metal-free hydrogenation catalysis. We are continuing to study and develop new strategies for metal-free catalysis.

Notes and references


10 mol% cat.
B(C₆F₄H)₃

R₂PH \xrightarrow{130 \degree C} (R₂P)₂ + H₂

R₂PH

B(C₆F₄H)₃

R'P \equiv H

R