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1,1-Phosphinoboration of diazomethanes†

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The reactions of the phosphinoboranes Ph_2PBMes_2 , Ph_2PBpin , and Ph_2PBcat with the diazomethanes Ph_2CN_2 , $C_{12}H_8CN_2$, and EtO_2CCHN_2 are shown to give products of 1,1-phosphinoboration. The products (1–6) are shown to have PNB linkages with three-coordinate boron centers, whereas the products (EtOOC)CNN(PR₂)(Bpin) (R = Ph 7, tBu 8) form zwitterionic heterocycles resulting from chelation of the ester carbonyl to boron. DFT calculations show that the reactions are initiated by N-to-B addition followed by 1,2-phosphinyl shift.

The reaction of B–H, B–C, or B–X (X = halide) bonds has widespread applications in chemistry. While B–H bonds in boranes give rise to classic applications of 1,2-hydroborations, 1,1- and 1,2-carboborations have also emerged as powerful synthetic tools for the derivatization of boranes. In recent years, Ingelson¹ has described avenues to 1,2-haloborations of alkynes, whereas Melen and co-workers² have described unique examples of 1,3-haloborations.

Targeting the expanded utility of boron reagents, we have focused our interest on the reactivity of B–P bonds. While the phosphinoborane $Et_2PB(NMe_2)_2$ was first prepared in the 1960s by Nöth and coworkers,³ the chemistry of these species did not garner much attention until the early 2000s. In 2006, Scheer *et al.* examined the reactivity of H_2PBH_2 stabilized by NMe₃,⁴ while in 2008, we reported the cleavage of H_2 by $R_2PB(C_6F_5)_2$ (R = *t*Bu, Cy, Mes) as well as the dehydrogenation of ammonia borane.^{5,6} In 2015, Su⁷ reported 1,2-phosphinoboration of benzophenone, dimethylbutadiene, and acetonitrile using tBu_2PB (biphenyl). In the same year, Westcott^{8–11} demonstrated the broad applicability of these phosphinoboration reactions, reporting such 1,2-additions to aldehydes, ketones, imines, pyridines, and heteroallenes using the readily accessible phosphinoboranes, R₂PBpin (R = Ph, Cy) and Ph₂PBcat. More recently, we have collaborated with the Westcott group to report the 1,2-phosphinoboration of carbodiimides, isocyanates, isothiocyanates, and CO₂. In addition, we have reported the 1,2-phosphinoboration of diazobenzene affording N₂-linked frustrated Lewis pairs which act as FLP synthons for unusual main group heterocycles.¹² Finally, we also described the double 1,2-phosphaaddition to CO₂ affording an unprecedented route to diphospha-ureas (Scheme 1).¹³

While examples of 1,1-phosphinoboration reactions are rare, being generally limited to the addition of chalcogen atoms,¹⁴⁻¹⁶ Westcott *et al.* did achieve the 1,1-phosphinoboration of terminal allenes and alkynes using a rhodium catalyst.⁸ In this communication, we report the uncatalyzed 1,1-phosphinoboration of diazomethanes. The nature of the resulting PNB derivatives are dependent on the substituents on the diazomethane and boron center.



Scheme 1 Examples of uncatalyzed phosphinoboration reactions.

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The reaction of Ph₂PBMes₂ and diphenyldiazomethane in CH₂Cl₂ took place at ambient temperature over a 3 h period. Removal of the solvent and recrystallization of the residue from hot Et₂O afforded a white solid of 1 in 82% isolated yield (Scheme 2). The ${}^{11}B{}^{1}H{}$ and ${}^{31}P{}^{1}H{}$ NMR spectra gave rise to single resonances at 45.8 and 57.2 ppm, respectively. The ¹H and ¹³C¹₁H NMR spectra as well as the HRMS data were consistent with 1 being derived from the equimolar combination of the two reagents. An X-ray diffraction study of 1 revealed the formulation as Ph₂CNN(PPh₂)(BMes₂) in which the phosphinoboration of the diazomethane occurs in a 1,1-fashion. The resulting N-P and N-B bond distances were determined to be 1.752(2) Å and 1.428(3) Å, respectively, with a P-N-B angle of 120.2(2)°. The N-N distance in 1 is 1.433(2) Å, while the C-N distance is 1.282(3) Å. These latter distances are consistent with single and double bonds, respectively. This BNP linkage is reminiscent of that seen in the product of the 1,1-addition reaction of an intramolecular P/B FLP with mesitylazide.¹⁷

In an analogous fashion, the stoichiometric reaction of Ph_2PBMes_2 with fluorenyldiazomethane afforded the isolation of a yellow solid 2 in 95% isolated yield (Scheme 2). Similar to 1, the ${}^{11}B{}^{1}H$ NMR signal for 2 is seen at 52.7 ppm, while the ${}^{31}P{}^{1}H$ NMR resonance occurs at 64.3 ppm. The ${}^{1}H$, ${}^{13}C{}^{1}H$ NMR, and HRMS data suggested a formulation of 2 as $C_{12}H_8NN(PPh_2)(BMes_2)$, similar to 1, a postulate that was confirmed by an X-ray diffraction study (Fig. 1b). The metric parameters of 2 were also similar to 1, with the N–P, N–B, N–N, and C–N distances being 1.758(1) Å, 1.441(2) Å, 1.433(2) Å, and 1.285(2) Å, respectively.

Such phosphinoborations could be extended to reactions of Ph_2PBcat and Ph_2PBpin with diphenyldiazomethane. Following an analogous protocol, the species $Ph_2CNN(PPh_2)(Bcat)$ 3, $Ph_2CN_2(PPh_2)(Bpin)$ 4, and $C_{12}H_8CNN(PPh_2)(Bpin)$ 5 were isolated in 91%, 95%, and 96% yields, respectively (Scheme 2). These species exhibited ¹¹B{¹H} NMR resonances at 25.6, 24.3, and 24.5 ppm, while the ³¹P{¹H} NMR signals were seen at 49.8, 48.5, and 48.4 ppm, respectively. In addition, the formulations of compounds 3 and 4 were also unambiguously confirmed *via* crystallography characterization further demonstrating the 1,1-phosphinoborations of the diphenyldiazomethanes. Both compounds crystallized with two molecules in the asymmetric unit (Fig. 2). Compound 3 gave rise to average P–N, N–B, N–N, and C–N bond



Fig. 1 POV-ray depictions of molecular structure of (a) 1, (b) 2. Hydrogen atoms are omitted for clarity. C: black, N: blue, B: yellow-green, P: orange.

metric parameters of 1.730(1) Å, 1.412(2) Å, 1.444(2) Å, and 1.281(2) Å, respectively, while the corresponding distances in **4** average 1.722(2) Å, 1.427(3) Å, 1.436(2) Å, and 1.286(2) Å. The slightly longer B–N distance in **4** is consistent with a more electron rich boron center.



Fig. 2 POV-ray depictions of molecular structure of (a) **3**, (b) **4**. Hydrogen atoms are omitted for clarity. C: black, N: blue, O: red, B: yellow-green, P: orange.



This phosphinoboration protocol could also be extended to reactions of Ph_2PBMes_2 with ethyl 2-diazoacetate. The resulting product, (EtOOC)CHNN(PPh_2)(BMes_2) **6** was isolated as a yellow solid in 89% yield. Similar to the products discussed above, the ¹B{¹H} NMR and ³¹P{¹H} NMR resonances were observed at 46.4 and 57.9 ppm, respectively (Scheme 3). HRMS data affirmed the molecular weight derived from the combination of the two reagents and X-ray crystallographic study confirmed **6** to be the analogous 1,1-phosphinoboration product (Fig. 3) with a geometry and metric parameters (P–N 1.762(1) Å, N–B 1.439(2) Å, N–N 1.423(2) Å, N–C 1.274(2) Å) similar to those seen in **1**.

The analogous reactions of ethyl 2-diazoacetate with Ph₂PBpin and tBu_2PBpin also proceeded to give compounds 7 and 8 as yellow solids in 86 and 90% yields, respectively (Scheme 3). In contrast to the species above, the ${}^{11}B{}^{1}H{}$ NMR spectra of 7 and 8 gave resonances at 11.9 and 8.8 ppm, respectively. These data suggest the generation of four-coordinate boron centers. The corresponding ³¹P{¹H} NMR resonances were seen at 52.9 and 89.0 ppm, respectively. The nature of these species were crystallographically confirmed to be of the formulation (EtOOC)CHNN- $(PR_2)(Bpin)$ (R = Ph 7, tBu 8). In these species, 1,1-phosphinoboration of the diazomethane proceeds in addition to the chelation of the borane fragment with the carbonyl of the ester functionality (Fig. 3). This quaternization of the boron centers in 7 and 8 is attributed to the lesser steric demands of the pinacolate ligand, making the boron accessible for chelation. The resulting BOC₂N₂ heterocyclic rings are planar with B-O, B-N, C-N, C-C, and N-N distances of 1.592(1) Å, 1.551(1) Å, 1.311(1) Å, 1.428(2) Å, and 1.334(1) Å in 7 while the corresponding distances in 8 were 1.589(2) Å, 1.561(2) Å, 1.314(3) Å, 1.416(3) Å, and 1.332(2) Å. These distances are consistent with conjugation over the OCCNN portion of these heterocycles, consistent with the observed planarity. The exocyclic N-P distances in 7 and 8 were found to be 1.7484(9) Å and 1.760(2) Å, respectively. It is interesting to note that related BNNCCO heterocycles have been previously reported to make near infrared photoluminescent copolymers¹⁸ and fluorescent dves.19

Conceptually, the observed 1,1-phosphinoboration could be initiated by addition of terminal N of the diazomethane to either the B or P center of the B–P reagent.^{20,21} Extensive DFT



Fig. 3 POV-ray depictions of molecular structure of (a) **6**, (b) **7**, (c) **8**. Hydrogen atoms are omitted for clarity. C: black, N: blue, O: red, B: yellow-green, P: orange.

calculations, at the PW6B95-D3/def2-QZVP+COSMO-RS(CH2Cl2)// TPSS-D3/def2-TZVP+COSMO (CH₂Cl₂) level of theory²² were performed to probe the mechanism. Computations show that the 1,1-phosphinoboration reaction of diazomethane Ph₂CNN with Ph2PBcat proceeds via addition of the terminal N-atom of Ph₂CNN to the Lewis-acidic B-center from the side opposite to the electron lone pair on P-atom (Fig. 4). This affords the unstable adduct **A** that is 14.7 kcal mol^{-1} higher in free energy with a long B-N bond of 1.60 Å. The B-N bond becomes shortened through π -electron conjugation over the BNNC backbone accompanied by the 1,2-phosphinyl shift from B to N atom (via transition structure TSP). The reaction is -26.9 kcal mol⁻¹ exergonic over a barrier of only 17.8 kcal mol⁻¹, yielding the product 3. This is consistent with the observed rapid 1,1-phosphinoboration reactions at room temperature. Similar reaction from the opposite side of 3 encounters a 4.7 kcal mol⁻¹ higher free energy barrier while other conceivable reaction pathways involving terminal N-to-P addition or direct additions of N=N to either P-B or B-P showed even higher barriers of 29.7, 36.5, and 32.5 kcal mol^{-1} , respectively (see ESI[†]).



Fig. 4 DFT computed reaction free energy path in CH₂Cl₂ solution (in kcal mol⁻¹, at 298 K and 1 mol L⁻¹ reference concentration) for the phosphinoboration of diazomethane Ph₂CNN using Ph₂PBcat.

In conclusion, the above reactions of phosphinoboranes with diazomethanes demonstrate rare examples of uncatalyzed 1,1-phosphinoborations. Moreover, while all of the resulting products include PNB linkages, the sterically demanding systems yield three-coordinate boron centers. In contrast, the sterically less encumbered boron centers of 7 and 8 chelate to the ester substituent on the diazomethane fragment affording four-coordinate boron centers and unique planar heterocycles. The utility of such 1,1-phosphinoboration in the development of new FLP systems is the subject of current study.

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Conflicts of interest

The authors declare no conflict of interest.

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