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Sterically congested phosphonium borate acids as effective Brønsted acid catalysts

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Dedicated to Martin Bennett on the occasion of his 80th birthday.

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ABSTRACT

Phosphonium borate acids $[HPPh_2(C_6F_5)][B(C_6F_5)_4]$ (**2**), $[HPMes_2(C_6F_5)][B(C_6F_5)_4]$ (**3**) and $[HPMes(C_6F_5)_2][B(C_6F_5)_4]$ (**4**) were synthesized via heterolytic dihydrogen cleavage in the presence of triisopropylsilylium and characterized by spectroscopic and crystallographic methods. Brønsted acid catalysis using compounds **2**–**4** proved to be efficient for a number of challenging reactions (namely ionic hydrogenation, hydroamination and hydroarylation), owing to the restrained nucleophilicity of the sterically hindered conjugate bases. Reactivity of compounds **2**–**4** suggests that their pK_a values are similar to that of diethyl oxonium acid.

1. Introduction

Brønsted acid catalysis has undergone tremendous advancement over the previous 20 years. Intrinsic to the mechanism of Brønsted acid catalysis, the role of the conjugate base must be considered. In the field of Brønsted acid asymmetric catalysis, the role of the conjugate base is pivotal to enantiomeric selectivity [1–3], whereas interaction with the conjugate base has been minimalized in the field of 'super-acidity'[4]. Essential to the development of 'super-acids', conjugate bases that are of very low basicity but stable in highly acidic environments have been developed [5–9]. However, such acids are widely incompatible with most organic reaction conditions, with their ability to protonate even weakly basic solvents, the electrochemical potential of the proton quickly adopts that of protonated solvent [10–12]. We sought to decouple the potential interaction between protonated reaction substrates and conjugate bases in Brønsted acid catalyzed reactions, so that our conjugate bases are reduced in role to 'proton carriers'. Additionally, we hoped to develop relatively strong Brønsted acids, allowing a wide range of challenging transformations to be catalysed. To achieve this, we looked for inspiration in developments in Frustrated Lewis Pair chemistry, where interaction between Lewis acids and bases is reduced using steric interactions. Thus our target acids are designed to act as proton sources, readily donating a coordinated proton, but having minimal interaction with larger acids after deprotonation occurs.

The unique unquenched reactivity of FLPs has been successfully utilized for the activation of small molecules, most notable being the reversible heterolytic cleavage of dihydrogen into protic and hydridic components. Such systems have shown tremendous application in the catalytic hydrogenation of imines, silyl enol ethers and olefins (inter alia) [13–16]. Generally, the use of electron rich Lewis bases to stabilise the evolved proton has limited the ability of FLP systems to catalyse the reduction of less basic substrates. However, Grimme and Paradies recently reported a phosphine-borane based FLP catalyst system employing the Lewis acid $B(C_6F_5)_3$ and electron poor phosphines {viz. $PPh_2(C_6F_5)$, $P(2,6\text{-}C_6H_3Cl_2)_3$ and $P(C_{10}H_7)_3$} capable of hydrogenating olefins using molecular hydrogen [17]. The high acidity of the intermediate phosphium acids, generated from H_2 cleavage, was key to the reactivity observed. However, instability of the intermediate phosphonium acids (in respect to recombination with $[HB(C_6F_5)_3]^-$) did not allow their isolation.

We reasoned that if such phosphonium acids were able to protonate olefins, and not bind bulky Lewis acids strongly, their isolation and modification to be even more hindered may provide convenient catalysts for a range of Brønsted acid catalyzed reactions. Herein we report the synthesis of new triaryl phosphine based Brønsted acids with their applications in catalyzing several organic transformations.

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2. Experimental

2.1. General information

All reactions, unless stated otherwise, were carried out in an inert atmosphere using standard Schlenk and high vacuum techniques. All common reagents used were obtained from commercial suppliers without further purification. Ether free $Li[B(C_6F_5)_4]$ [18], $[Ph_3C][B(C_6F_5)_4]$ [19], $PBr(C_6F_5)_2$ [20] and $PBrMes_2$ [21] were synthesized using previously reported procedures. All solvents used for reactions were either obtained from a Pure Solv MD-7 solvent purification system or dried following literature methods [22]. All deuterated solvents used were obtained from commercial sources and dried using calcium hydride followed by vacuum distillation. NMR spectra were recorded using Bruker Avance 500 (AV500) and Bruker Avance 400 (DRX400) NMR spectrometers. Gas Chromatography-Mass Spectrometry (GC–MS) results were recorded using an Agilent 5975 GCMSD with a HP-5 column (low resolution quadrupole benchtop mass spectrometer), coupled to an Agilent 7890A Gas Chromatograph. Known compounds were identified using the NIST Mass Spectra Library available in the GC–MS and by their reported ^{1}H NMR data.

2.2. X-ray crystallography

Single crystal data were measured on a four circles goniometer Kappa geometry Bruker AXS D8 Venture equipped with a Photon 100 CMOS active pixel sensor detector using a molybdenum (λ = 0.71073 Å) or copper (λ = 1.54180 Å) monochromatized X-ray radiation source.

Frames were integrated with the Bruker SAINT [23] software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method implanted in the software (Twinabs) [24]. The structures were solved by the direct method using the SHELXT program or SIR92 program [25]. Refinement of the structure was carried out by least squares procedures on weighted F^2 values using the SHELXL-version 2014/6 or using CRYSTALS [26,27]. All heavy atoms were assigned anisotropic displacement parameters, hydrogens atoms were located on difference Fourier maps then introduced as fixed or located geometrically. Compound **2** was found to be twinned, two distinct domains were depicted using the software Cell_now integrated in package software: APEX v2014.11.0. [28] The structure although twinned could be solved and fully refined.

2.3. Synthesis of phosphines

2.3.1. Dimesityl(pentafluorophenyl)phosphine

A freshly prepared ethereal solution (50 mL) of bromo(pentafluorophenyl)magnesium (prepared from 58 mmol of magnesium and 7.2 mL of bromopentafluorobenzene) was added dropwise to an ethereal solution (50 mL) of equimolar amount of bromodimesitylphosphine (13.32 g, 58 mmol) maintained in an ice-salt bath. After complete addition the reaction mixture was allowed to warm to room temperature and stirred overnight. $MgBr_2$ was separated by cannula filtration and the reaction was quenched with water (20 mL). The organic components were extracted with ether (3 × 30 mL) and combined extracts were reduced under vacuum. The crude mixture was purified by column chromatography to afford the title phosphine as a white solid. Yield: 12.0 g, 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, J = 4.0 Hz, 4H), 2.27 (s, 6H), 2.17 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): ^{13}C NMR (100.6 MHz, C_6D_6): δ 147.77 (dm, $^1J_{C-F}$ = 249.9 Hz, *C*F), 143.02 (d, $^1J_{C-}$P = 18.6 Hz, *C*P), 141.55 (dm, $^1J_{C-F}$ = 254.4 Hz, *C*F), 137.79 (dm, $^1J_{C-F}$ = 252.5 Hz, *C*F), 131.62 (d, J = 7 Hz), 130.65 (d, J = 4 Hz), 130.32 (d, J = 7 Hz), 114.10–113.45 (m, *ipso*-C), 22.80 (d, J = 17 Hz, *o*-*C*H$_3$), 20.89 (s, *p*-*C*H$_3$); ^{31}P NMR (162 MHz, $CDCl_3$): δ −47.91 (t, J = 37.0 Hz, 1P); ^{19}F NMR (376 MHz, $CDCl_3$): δ −129.46 to −129.78 (m, 2F), −153.03 (t, J = 20.5, 1F), −161.47 (td, J = 23.9, 8.9, 2F).

2.3.2. Mesityl-bis(pentafluorphenyl)phosphine

A freshly prepared tetrahydrofuran solution (50 mL) of bromomesitylmagnesium (prepared from 13.3 mmol of magnesium and 2.04 mL of bromomesitylene) was added dropwise to an ethereal solution (50 mL) of $PBr(C_6F_5)_2$ (2 mL, 13.3 mmol) maintained at below 0 °C. The resulting cloudy mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue stirred vigorously with dry methanol for five minutes before evaporation. The cycle of methanol addition and solvent removal was performed three times. The resulting solid residue was dissolved in dry diethyl ether (50 mL) and separated from $MgBr_2$ by cannula filtration. The solvent was evaporated and the residue dried under vacuum for 12 h at room temperature. The crude mixture was purified by recrystallization from dry methanol. Yield: 3.5 g, 55%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (d, J = 4.0 Hz, 2H), 2.40 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.10 (dm, $^1J_{C-F}$ = 246.8 Hz, *C*F), 145.05 (d, $^1J_{C-}$P = 20.8 Hz, *C*P), 141.96 (d, J = 1.4 Hz), 141.79 (dm, $^1J_{C-F}$ = 254.6 Hz, *C*F), 137.67 (dm, $^1J_{C-F}$ = 255.7 Hz, *C*F), 130.12 (d, J = 6 Hz), 122.76 (d, J = 14 Hz), 109.45–108.61 (m, *ipso*-C), 22.86 (d, J = 19 Hz, *o*-*C*H$_3$), 21.28 (s, *p*-*C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −54.71 (q, J = 29 Hz, 1P); ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.28 to −131.52 (m, 4H), −151.71 (td, J = 20.5, 1.0, 2H), −160.73 (m, 4H).

2.4. Synthesis of phosphonium salts

2.4.1. Method I

Ether free $Li[B(C_6F_5)_4]$ (0.69 g, 1.0 mmol) and phosphine (1.0 mmol) were dissolved in dichloromethane. The solution was saturated with hydrogen chloride by passing HCl gas through the solution for five minutes. The reaction vessel was sealed and the mixture was allowed to stir for 24 h. Resulting mixture was filtered and the colourless filtrate was concentrated under reduced pressure. Hexane was added to induce precipitation. The resulting white solid was washed with hexane and dried in vacuo.

2.4.2. Method II

A flame dried Teflon capped Schlenk tube was charged with 0.92 g of $[Ph_3C][B(C_6F_5)_4]$ (1.0 mmol) and 2.0 mL of chlorobenzene. An excess amount of triisopropylsilane (0.25 mL, 1.22 mmol) was added to the solution which was stirred at room temperature for 10 min. A chlorobenzene solution of triaryl phosphine (1.0 mmol) was added to the mixture. After 10 min, an aliquot was taken to confirm the formation of **1** {^{31}P NMR (202 MHz): δ −9.95 (s, 1P). ^{29}Si NMR (99 MHz): δ 38.61 (d, Si, J = 22 Hz).}. In the cases of $PMes_2(C_6F_5)$ and $PMes(C_6F_5)_2$, NMR data showed the silylium/phosphine mixture to be a Frustrated Lewis Pair. The reaction tube was immersed into liquid nitrogen to freeze the solution. The tube was exposed to vacuum and refilled with hydrogen gas. The reaction vessel was sealed and the mixture was heated overnight at 60 °C. The resulting pale brown solution was concentrated under reduced pressure. The remaining solution was triturated with hexane, yielding a pale brown precipitate which was isolated and thoroughly washed with hexane before being dried under vacuum.

2.4.3. Diphenyl(pentafluorophenyl)phosphonium tetrakis (perfluorophenyl)borate (*2*)

Off white solid. Yield: 0.72 g (70%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.27 (d, 1H, J = 528 Hz, P–*H*), 7.41–7.36 (m, 2H, C_{Ar}-*H*), 7.24–8.19 (m, 4H, C_{Ar}-*H*), 7.13–7.07 (dd, 4H, J = 16, 7.6 Hz, C_{Ar}-*H*); ^{31}P NMR