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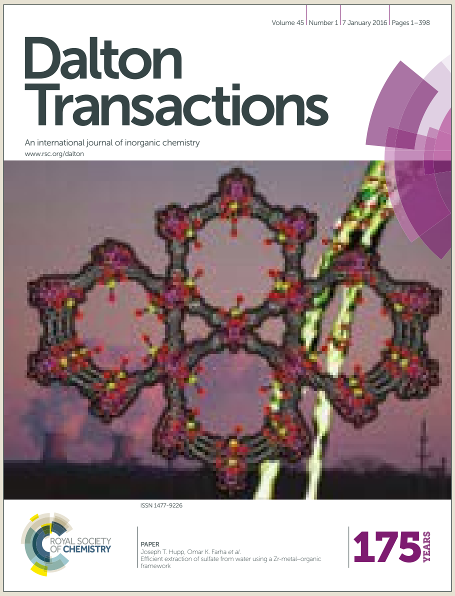

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COMMUNICATION

FLP reactivity of $[Ph_3C]^+$ and (*o*-tolyl)$_3$P and the capture of a Staudinger reaction intermediate

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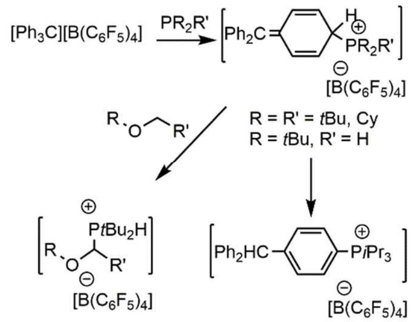
The frustrated Lewis pair (FLP) derived from trityl cation and (*o*-tolyl)$_3$P effects activation of 1,4-cyclohexadiene and 1-bromo-4-ethynylbenzene and heterolytically cleaves the S–S bond of diphenyl disulfide. The FLP also captures pentafluorophenyl azide as the Staudinger reaction intermediate; a species that reacts with Ph_3SiH to give the silyl analog.

The notion of a “frustrated Lewis pair” (FLP) has emerged in the last decade from the observation that the combination of a sterically encumbered Lewis acid and base could activate H_2.[1] While initially this allowed the development of metal-free catalysts for hydrogenations,[2-4] the concept has since been applied to activate an ever-broadening range of substrates and to rationalize phenomena that span enzymatic systems, material chemistry and surface science.[5-7]

In exploring the breadth of systems capable of acting as FLPs, a number of groups have used a wide range of Lewis bases and a smaller variety of Lewis acids.[8, 9] Indeed, the Lewis acid $B(C_6F_5)_3$ or its close structural relatives are ubiquitous in FLP chemistry. Fewer studies have probed other Lewis acidic systems.[10] In the case of carbon-based Lewis acids, use in FLP chemistry is comparatively rare. In 2010, Alcarazo and coworkers[11, 12] demonstrated an electron-poor bis(fluorenyl)allene could serve as the Lewis acid partner for the heterolytic S-S bond cleavage of disulfides when paired with the carbene, IDipp. In 2011, Arduengo and coworkers[13] described an all-carbon FLP that was capable of H_2 activation employing the trityl cation and the NHC *It*Bu at -60 °C. We have previously reported[14, 15] the cationic Ru–η^6–arene complex, $[((Ph_2PC_6H_4)_2B(\eta^6\text{-}Ph))RuCl][B(C_6F_5)_4]$ acts as a carbon-based Lewis acid at the *ortho*- and *para*-positions of the η^6-arene. More recently, Ingleson *et al.*[16] described an acridine-stabilized borenium cation system capable of acting as either a carbon- or boron-based Lewis acid. Structurally related *N*-methylacridinium cations[17] effected the heterolytic cleavage of H_2 when paired with 2,6-lutidine and allowed the catalytic hydrogenation of PhCH=NtBu.



Scheme 1 Reactions of $[Ph_3C]^+$ with phosphines.

The trityl cation ($[Ph_3C]^+$), first reported by Henderson in 1887[18], has been used as a protective reagent[19, 20] and catalyst[21-24] in organic transformations. The trityl cation has been exploited to abstract hydride or methyl anions to generate highly Lewis acidic species like borenium[25-27], silylium[28-31] and cationic metal centers.[32-36] Most recently, Berionni *et al* [37] have probed the nucleophilicities of sterically hindered phosphines, by determining the rates and equilibrium constants of their associations with trityl cations. In considering the use of the trityl cation in FLP chemistry, we note that we previously described the formation of classical donor-acceptor adducts with donors including PMe_3, PPh_3 and pyridines.[38] On the other hand, bulkier donors effected nucleophilic attack at the *para*-position of an aryl ring to give cyclohexadienyl-phosphonium cations $[R_3P(C_6H_5)CPh_2]^+$ (R = Cy, tBu) some of which rearomatized via proton migration to give $[iPr_3P(C_6H_4)CHPh_2]^+$. Nonetheless, we have reported the use of the intermediate cyclohexadienyl-phosphonium cations in FLP reactions with ethers to activate α-C-H bond affording $[tBu_2PH(CH(OR)R')][B(C_6F_5)_4]$ (Scheme 1).[39] Herein, we demonstrate that the trityl cation and (*o*-tolyl)$_3$P behaves as an

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†Electronic Supplementary Information (ESI) available: Experimental and analytical details are given. See DOI: 10.1039/x0xx00000x. Crystallographic details for **1**-**3**, **5** and **6** have been deposited in CCDC 1541632-1541636, respectively.

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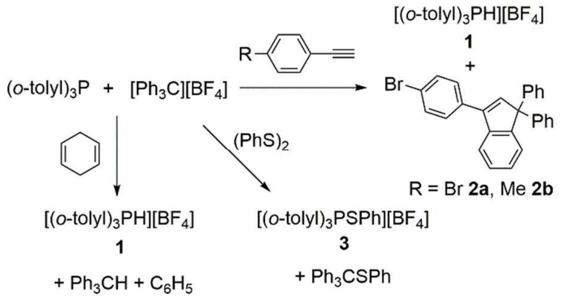
FLP to activate small molecules and intercept a Staudinger reaction intermediate.



Scheme 2 Reactions of the FLP derived from $[Ph_3C]^+$ and (*o*-tolyl)$_3$P with C_6H_8, BrC_6H_4CCH and $(PhS)_2$.

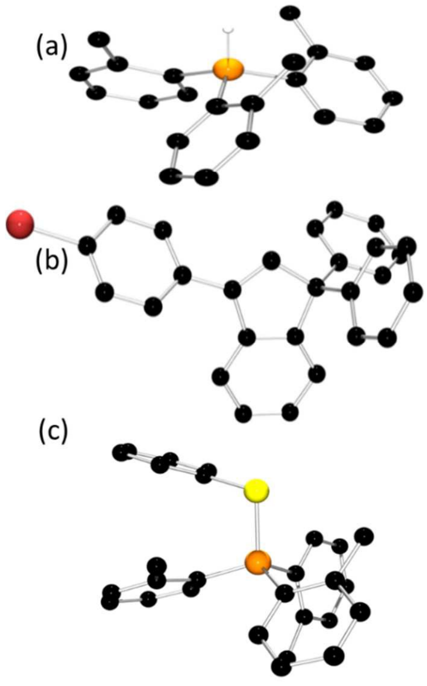


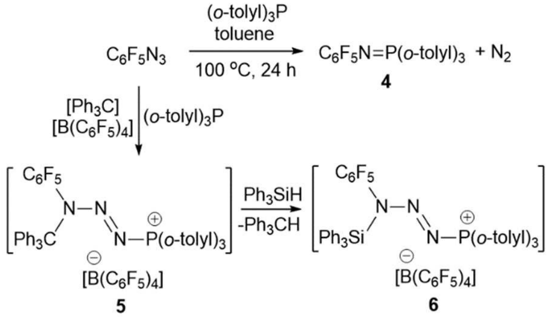
Fig. 1 POV-ray depiction of (a) the cation of **1**, (b) **2** and (c) the cation of **3**, C: black, H: white, P: orange Br: dark red. Hydrogen atoms (except P–*H*) and $[BF_4]^-$ anion are omitted for clarity.

In contrast to other phosphines, (*o*-tolyl)$_3$P does not form Lewis acid–base adduct nor does it effect nucleophilic aromatic substitution at a *para*-position of $[Ph_3C][BF_4]$ in dichloromethane at room temperature. This infers the formation of an FLP. While this mixture does not react with HD, treatment with 1,4-cyclohexadiene led to the rapid Csp^3–H activation and formation of salt [(*o*-tolyl)$_3$PH][BF_4] (**1**) with the release of benzene and triphenylmethane (Scheme 2). This was evident from the ^1H NMR spectrum which showed a characteristic P–*H* signal at 9.41 ppm with a coupling constant of 524 Hz, corresponding to the doublet at -14.2 ppm in ^{31}P NMR spectrum.[40, 41] Compound **1** was further characterized by single crystal X-ray diffraction analysis confirming its formulation (Fig. 1).

The FLP $[Ph_3C][BF_4]$/P(*o*-tolyl)$_3$ also activates C(sp)–H bond of 1-bromo-4-ethynylbenzene at room temperature to afford [(*o*-tolyl)$_3$PH][BF_4] (**1**) quantitatively. To our surprise, the expected product $(4\text{-}BrC_6H_4)C{\equiv}CCPh_3$ was not formed. Instead, an indene derivative $(4\text{-}BrC_6H_4)C{=}CHCPh_2C_6H_4$ **2a** was generated (Scheme 2)[41, 42] as evidenced by the vinylic hydrogen signal at 6.83 ppm in the ^1H NMR spectrum and the absence of a C(sp) signal in $^{13}C\{^1H\}$ NMR spectrum. The structure of **2** was unambiguously confirmed by X-ray crystallography (Fig. 1). The analogous reaction using 1-methyl-4-ethynylbenzene afforded $(4\text{-}MeC_6H_4)C{=}CHCPh_2C_6H_4$ **2b** (see SI).

Besides C–H bond activation, cleavage of S–S bond of diphenyl disulfide by the FLP $[Ph_3C][BF_4]$/P(*o*-tolyl)$_3$ proceeded at room temperature to give [(*o*-tolyl)$_3$PSPh][BF_4] (**3**) in 80% yield and Ph_3CSPh. Compound **3** gives a diagnostic signal at 51.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum,[43] and the formulation of **3** was further confirmed by X-ray crystallography (Fig. 1).

In seeking a further application, we probed the possibility that this FLP could intercept intermediates in the Staudinger oxidation of phosphine to phosphinimines.[44-46] Mechanistically, the first step involves the interaction of the phosphine with terminal nitrogen of the azide.[47-50] Although several phosphazide derivatives[51-53] have been isolated in the oxidation of sterically demanding phosphines, the polar nature of such intermediates typically prompts loss of N_2 affording the phosphinimine. Nonetheless, this polar nature seemed ideal for interception by an FLP.



Scheme 3 The reactions of (*o*-tolyl)$_3$P and FLP derived from (*o*-tolyl)$_3$P and $[Ph_3C]^+$ with $C_6F_5N_3$.

As an initial control experiment, the combination of pentafluorophenyl azide $C_6F_5N_3$ with (*o*-tolyl)$_3$P was shown to undergo the expected Staudinger reaction to provide the ensuing phosphinimine (*o*-tolyl)$_3PNC_6F_5$ **4** (^{31}P NMR: 15.1 ppm) with the loss of a N_2 molecule (Scheme 3). However, the reaction of FLP derived from $[Ph_3C][B(C_6F_5)_4]$ and (*o*-tolyl)$_3$P with an equal equivalent of pentafluorophenyl azide $C_6F_5N_3$ at room temperature gave a new phosphorus-containing species. The ^{31}P NMR spectrum showed a singlet at 44.2 ppm. Single crystals of **5** suitable for an X-ray diffraction study were grown by slow vapor diffusion of pentane into a CH_2Cl_2 solution. The molecular structure reveals the formulation of **5** as [(*o*-tolyl)$_3$PNNN(C_6F_5)(CPh_3)][$B(C_6F_5)_4$] that the trityl cation and (*o*-tolyl)$_3$P are bonded to N1 and N3, respectively (Fig. 2). The X-ray data reveal that the N1–N2 bond (1.371(4) Å) and N2–N3

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bond (1.244(4) Å) are in the range of N–N single bond and double bond respectively. The P1–N3 distance (1.722(3) Å) is typical of P–N single bond lengths of bulky secondary phosphinoamines (1.71~1.79 Å)[54], while the C7–N1 bond (1.547(5) Å) is clearly longer than C1–N1 bond (1.427(5) Å). The formation of **5** can be viewed as an FLP interception of an intermediate in the Staudinger reaction of (*o*-tolyl)$_3$P with $C_6F_5N_3$ (Scheme 3). In is noteworthy that heating **5** afforded no evidence of phosphinimine, rather a complex mixture of unidentified products was observed.

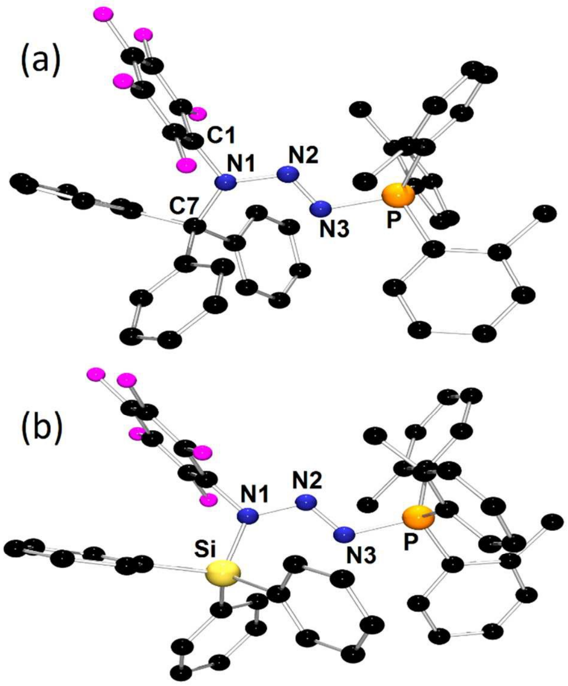

Fig. 2 POV-ray depiction of the cation of (a) **5**, (b) **6**. C: black, N: navy-blue, F: pink, Si: golden, P: orange. Hydrogen atoms and $[B(C_6F_5)_4]^-$ anions are omitted for clarity. Selected bond distances [Å] of **5**: C1–N1, 1.427(5); C7–N1, 1.547(5); N1–N2, 1.371(4); N2–N3, 1.244(4); N3–P, 1.722(3). **6**: Si–N1, 1.834(4); N1–N2, 1.359(5); N2–N3, 1.275(5); N3–P, 1.710(4).

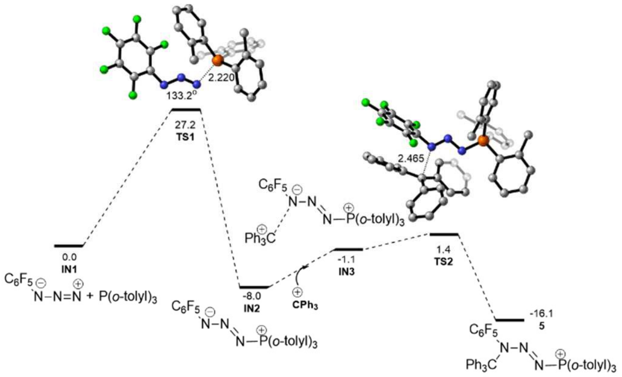

Fig. 3 Free energy profile for the reaction of $[Ph_3C]/P(o\text{-tolyl})_3$ FLP with $C_6F_5N_3$. Energies are given in kcal mol^{-1}.

To gain more insight into the electronic structure of **5**, natural bond orbital (NBO) calculations were carried out at M06-2X/TZVP//M06-2X/Def2SVP level of theory. It is noteworthy that this level of theory was recently established as an excellent method for describing main group systems.[55, 56] The results revealed that the NBO charges of N1 and N3 atoms are -0.21 and -0.61 a.u., respectively, while the P1 (1.79 a.u.), N2 (0.06 a.u.) and C7 (0.08 a.u.) atoms are positively charged. The calculated Wiberg bond indices (WBI) of N1-C1, N1-N2, N2-N3, N1-C7 and P-N3 are 0.98, 1.31, 1.65, 0.86 and 0.88, respectively, indicating the multiple bond characters of N1-N2 and N2-N3 bonds. The second-order perturbation theory of the NBO method demonstrated significantly high stabilization energy (101 kcal mol^{-1}) by two-electron donor–acceptor interactions from the lone pair of N1 into the N2-N3 π* antibonding orbital (Fig. **S1**)[57, 58], accounting for its air and moisture tolerance. Mechanistic insights regarding the formation of **5** was investigated at the SCRF-M06-2X/6-311++G(2d,p)//M06-2X/6-31G(d) level of theory. Initially, the approach of P(*o*-tolyl)$_3$ with terminal N atom of $C_6F_5N_3$ led to the distortion of the azide fragment. A transition state **TS1** featuring a bent N_3 fragment with the activation energy of 27.2 kcal mol^{-1} was located. Subsequently the formation of P1-N3 bond gave a stable intermediate **IN2** (-8.0 kcal mol^{-1}), which could be readily trapped by a trityl cation via **TS2** (1.4 kcal mol^{-1}). The final product **5** was formed in a reaction that is exothermic by -16.1 kcal mol^{-1}. The much lower activation barrier (9.4 kcal mol^{-1}, **IN2→TS2**) of the second step comparing with that (27.2 kcal mol-1, **IN1→TS1**) of the first step indicates the capture of the intermediate **IN2** by $[Ph_3C]^+$ is facile.

The low barrier to the formation of compound **5** prompted suggestions that ready access to **IN2** provides an avenue for the replacement the trityl fragment. To this end, compound **5** was reacted with an equivalent of Ph_3SiH at room temperature. This resulted in the production of the new species **6** in 93% yield with the release of triphenylmethane (Scheme 3). The spectral data for **6** were very similar to **5** suggesting the formulation of [(*o*-tolyl)$_3$PNNN(C_6F_5)($SiPh_3$)][$B(C_6F_5)_4$]. The replacement of triphenylmethyl group in **5** by the triphenylsilyl group in **6** was confirmed via X-ray diffraction data (Fig. 3). The structural parameters of **6** are analogous to those in **5** with a Si-N bond distance of 1.834(4) Å. The N1-N2, N2-N3 and N3-P bond distances were found to be 1.359(5) Å, 1.275(5) Å and 1.710(4) Å, respectively. This exchange of the trityl cation in **5** for the silylium cation in **6** is reminiscent of the borane exchange reported for *t*Bu$_3$P(N_2O)B(p-F-C_6H_4)$_3$ with more Lewis acidic boranes as well as with the $[Ph_3C]^+$ cation.[59]

In conclusion, we have demonstrated that combination of $[Ph_3C]^+$ and (*o*-tolyl)$_3$P acts as an FLP, effecting the dehydrogenation of hexadiene, the cycloaddition/ activation of alkyne to the trityl cation and the heterolytic cleavage of diphenyl disulfide. Moreover, this FLP reacts with pentafluorophenyl azide to trap an intermediate in the Staudinger reaction of (*o*-tolyl)$_3$P with the azide. This capture provided an avenue of exchange of the trityl fragment for a Ph_3Si unit via reaction of **5** and Ph_3SiH. This latter observation is in accord with DFT calculations that suggested the capture of the intermediate **IN2** by $[Ph_3C]^+$ is only mildly exothermic. We

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are continuing to examine the unique reactivity of FLP systems.

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TOC Graphic

Trityl cation and (*o*-tolyl)$_3$P is an FLP that effects C–H bonds and alkyne activation, heterolytically cleavage of S–S bonds and captures a Staudinger reaction intermediate.