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Facile Reversibility by Design: Tuning Small Molecule Capture and Activation by Single Component Frustrated Lewis Pairs

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Supporting Information

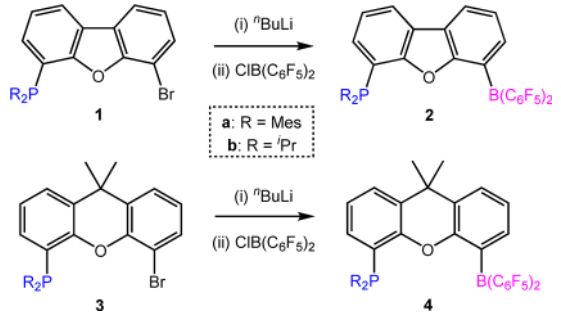
ABSTRACT: A series of single component FLPs has been investigated for small molecule capture, with the finding that through tuning of both the thermodynamics of binding/activation and the degree of preorganization (i.e., $\Delta S^{\ddagger}$) reversibility can be brought about at (or close to) room temperature. Thus, the dimethylxanthene system $\{(C_6H_4)_2(O)CMe_2\}(PMes_2)(B(C_6F_5)_2)$: (i) heterolytically cleaves dihydrogen to give an equilibrium mixture of FLP and H_2 activation product in solution at room temperature and (ii) reversibly captures nitrous oxide (uptake at room temperature, 1 atm; release at 323 K).

Although introduced as a concept as long ago as 1942,[1] the exploitation of frustrated Lewis pairs (FLPs) as a new paradigm for small molecule capture and activation stems from a landmark report by Stephan et al. in 2006.[2,3] The ability of such systems to activate strong nonpolar bonds (such as that in H_2) requires—in addition to putative Lewis frustration—that the acid and base components must together exceed a combined "threshold" strength.[4] Thermodynamically, this relates primarily to the strengths of the bonds (e.g., B−H and P−H) required to offset both breaking the strong H−H bond (436 kJ mol^{-1}) and the unfavorable entropic term associated with small molecule capture. Conformationally rigid single component FLPs in which the Lewis acid and base are installed onto a common backbone scaffold alter the thermodynamic balance, as the entropic penalty for small molecule capture is intrinsically smaller. In theory, this enables the use of weaker Lewis acid/base combinations, since a less negative ΔS° implies that a less favorable ΔH° is required to drive $\Delta G^{\circ} < 0$.[5]

Reversibility in small molecule capture and release is a key requirement in potential applications of FLPs such as chemical sensing and catalysis.[6] Such behavior requires not only that ΔG° is relatively close to zero but also that the barriers to activation in both directions ($\Delta G^{\ddagger}$) are also low. One approach to accomplishing the latter is to geometrically constrain the system, preorganizing the FLP such that the magnitude of $\Delta S^{\ddagger}$ is lowered.[5] In the case of dihydrogen activation by phosphine/borane FLPs, e.g., a number of theoretical studies have advanced the idea of a precursor "complex" featuring a P···B separation of 4.2−4.8 Å into which the H_2 guest molecule is introduced, polarized, and ultimately activated.[7,8] We perceived that the construction of a conformationally restricted, single-component FLP featuring a P···B separation within this range might therefore offer extremely facile H_2 activation. Moreover, if the resulting H^+/H^- components were confined to a molecular pocket within a relatively rigid FLP host, the kinetics of recombination might also be facile. As such, provided the thermodynamics of activation were appropriate, reversible capture/activation might be possible at (or close to) room temperature.[9,10]

Single component phosphine/boranes of types **2** and **4** featuring dibenzofuran and dimethylxanthene backbones[11] can readily be synthesized from the corresponding bromo/phosphine precursors (**1** and **3**) via lithiation and quenching with $ClB(C_6F_5)_2$ (Scheme 1). Mes_2P-containing systems were

Scheme 1. Syntheses of Dibenzofuran and Dimethylxanthene-Based FLPs 2 and 4



targeted, given the (known) inability of $ArPMes_2/ArB(C_6F_5)_2$ Lewis pairs to form classical donor/acceptor adducts, and **2a**/**4a** could be synthesized in yields of 56 and 60%, respectively. In a similar fashion, the more strongly σ-donating but less sterically encumbered $^iPr_2P$ function could be incorporated by employing a similar methodology and the related precursor **3b** (Scheme 1).

Each of **2a**, **4a**, and **4b** could be characterized by standard spectroscopic and analytical techniques, and their molecular structures determined in the solid state by X-ray crystallography. Diagnostic was ^{11}B NMR shifts in the range 60−65 ppm, indicative of a 3-coordinate unquenched borane, and ^{31}P resonances at δ_P = −38.1/−38.0 and −9.9 for **2a**/**4a** and **4b**, which are characteristic of $ArPMes_2$ and ArP^iPr_2 systems, respectively.[12] Structurally, a key observation is that the nonbonded P···B contacts for the two xanthene-based systems [4.243(3) and 4.487(3) Å for **4a**/**b**, respectively] are markedly shorter than that measured for di-benzofuran derived **2a** [5.669(1) Å, see SI]. Such differences mirror those observed for the related bis(PPh_2) derivatives [d(P···P) = 4.045(1) and 5.741(1) Å, respectively].[13]

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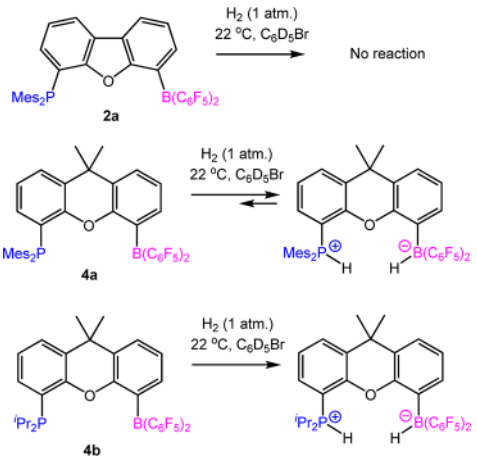
The heterolytic cleavage of dihydrogen by FLPs has been used as a benchmark for comparative discussions of reactivity.[4] Accordingly, the reactivity of **2a** and **4a**/**b** toward H_2 was investigated at 295 K and 1 atm pressure (Scheme 2). Under such

Scheme 2. Contrasting Reactivity of FLPs 2a, 4a, and 4b Towards H_2; Solution-Phase Equilibrium Between 4a-H_2 and 4a + H_2 at Room Temperature



conditions, **2a** is unreactive toward H_2, showing no evidence for the formation of the corresponding phosphonium borate after 12 h.[14] **4a**, by contrast, allows for very rapid cleavage of dihydrogen (<5 min at 295 K and 1 atm), with the marked contrast from **2a** conceivably underpinned by both kinetic and thermodynamic factors.[15] The molecular structure of **4a** features a P···B separation [4.243(3) Å] which is very similar to that predicted for the phosphine/borane "encounter pair" postulated in some models to precede H_2 activation.[7] Thus, the kinetics of activation by **4a** are likely to be enhanced by the inherent degree of preorganization and less unfavorable magnitude of $\Delta S^{\ddagger}$. DFT calculations suggest, in addition, that the dimethylxanthene backbone offers a more thermodynamically favorable basis for H_2 splitting (by ca. 30 kJ mol^{-1}).[15]

Characterization of the product of H_2 activation, i.e., **4a**-H_2 was achieved in solution by multinuclear NMR (PH unit: δ_H = 9.83, δ_P = −21.5 ppm, $^1J_{PH}$ = 526 Hz; BH unit: δ_H = 3.98, δ_B = −21.4 ppm, $^1J_{BH}$ = 94 Hz) and in the solid state by both elemental microanalysis and X-ray crystallography (Figure 1). H(1) and H(11) could be located in the difference Fourier map, and the heavy atom skeleton additionally confirms the expected quaternization at B(18) implied by the assimilation of H^-

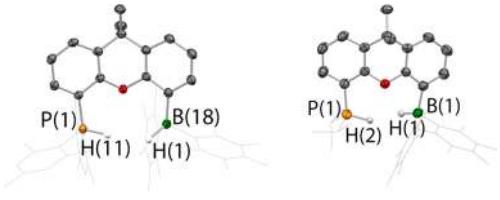


Figure 1. Molecular structures of **4a**-H_2 (left) and one component of the asymmetric unit of **4b**-H_2 (right) as determined by X-ray crystallography. Most H atoms omitted and Mes/C_6F_5 groups shown in wireframe format for clarity; thermal ellipsoids drawn at the 40% probability level. Key distances (Å) and angles (°): (for **4a**-H_2) P(1)···B(18) 4.293(3); (for **4b**-H_2) P(1)···B(1) 4.104(3), P(1)−H(2) 1.37(4), H(1)···H(2) 2.07(5), B(1)−H(1) 1.14(5).

[Σ(∠C−B−C) = 333.2(6)°]. Additionally, it is notable that the P···B separation in **4a**-H_2 [4.293(3) Å] is essentially identical to that in **4a**, consistent with the idea that the free FLP is preorganized for the assimilation of H_2.

Remarkably, solutions obtained by redissolving crystalline samples of **4a**-H_2 in d_5-bromobenzene show not only resonances characteristic of the hydrogen activation product but also those due to the parent FLP **4a** and H_2 (at δ_H = 4.5 ppm). At 295 K the reversion to **4a** + H_2 accounts for ca. 5% of total composition, and by monitoring the position of equilibrium as a function of temperature, the thermodynamic parameters ΔH^o = 38 kJ mol^{-1} and ΔS^o = 102 J mol^{-1} K^{-1} (for H_2 loss) can be obtained from a Van't Hoff plot (Figure 2). The position of equilibrium can be

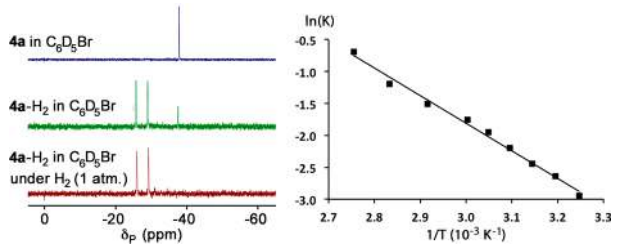


Figure 2. Van't Hoff plot based on the response to temperature (in the range 298−363 K) of the equilibrium between **4a**-H_2 and **4a** + H_2 in C_6D_5Br solution. From the linear fit (R^2 = 0.992) of ln(K) vs $1/T$ are obtained the values ΔH^o = 38 kJ mol^{-1} and ΔS^o = 102 J mol^{-1} K^{-1} for the loss of H_2 from **4a**-H_2.

manipulated in favor of **4a**-H_2 by the use of an overpressure of H_2, with the application of 1 atm pressure being sufficient to cause the complete disappearance of NMR signals due to the "free" FLP **4a**.

To our knowledge this represents the first example of an FLP system existing in solution-phase equilibrium with its dihydrogen activation product at room temperature.[9,10] The P^oTol_3/$B(C_6F_4H\text{-}4)_3$ system is reported to activate H_2 at 298 K and to lose dihydrogen slowly under vacuum at the same temperature (85% compete after 9 days);[9d] a number of other systems exhibit similar behavior in the solid state at more elevated temperatures.[2,9] Low temperatures and/or high pressures have also been employed to effect activation by FLPs of lower intrinsic reactivity, with quantitative H_2 release occurring on return to ambient conditions.[9k−m]

In the case of Stephan's landmark system, *para*-(Mes_2PH)-$C_6F_4\{B(C_6F_5)_2H\}$, dihydrogen release occurs at temperatures in excess of 373 K, with this process being characterized thermodynamically by values of ΔH^o = 90 kJ mol^{-1} and ΔS^o = 96 J mol^{-1} K^{-1}.[2] By comparison, the enthalpic term is much smaller in magnitude for **4a** (presumably reflecting the lower combined Lewis acidity/basicity of the borane/phosphine components), and since ΔS^o is—not unexpectedly—similar in the two cases, this facilitates the loss of H_2 at much lower temperatures.

From a kinetic perspective, the ease of H_2 release from **4a**-H_2 is presumably enhanced by the geometry enforced by the bulky P- and B-bound aryl substituents (Figure 1), which confine the hydridic/protic components to the central cavity. While the H···H contact (>2 Å in the solid state, as determined from the difference Fourier map) is not especially short (cf. 1.6−1.8 Å for the NH···HB contact in a tetramethylpiperidine-based single component system),[16] the lack of conformational flexibility in **4a**-H_2 is presumably a factor in the ease of H_2 release. Much in the same way as **4a** is itself configured for H_2 uptake, **4a**-H_2 is

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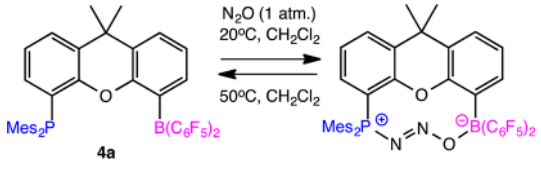
preorganized for H_2 loss, and low free energies of activation are rationalized for both the forward and reverse reactions.

The critical influence on reversibility of the thermodynamics of H_2 activation/release is emphasized by considering the reaction of the $^{i}Pr_2P$-containing system **4b**. This FLP features a similar P···B separation to **4a** [4.487(4) Å] and also activates H_2 readily at 295 K and 1 atm pressure. In addition, the corresponding H_2 activation product, **4b**-H_2, features a geometry for the phosphonium/borate entity closely related to its Mes_2P-substituted counterpart [d(P···B) = 4.104(3), d(H···H) = 2.07(5) Å]. However, no observable hydrogen evolution is observed from **4b**-H_2 in d_5-bromobenzene solution at temperatures up to 353 K. Thus, while it could be argued that **4b**-H_2, like **4a**-H_2, is preconfigured for H_2 loss, the presence of the more strongly donating alkyl-substituted phosphine component is presumably responsible for the back reaction being energetically unfeasible at low temperatures.

Reversibility appears to have significant influence on the ease of isotopic exchange in **4a**/**4b**.[17] **4a**-D_2 (synthesized independently from **4a** and D_2) undergoes facile exchange (<1 h at 295 K) with H_2 to give an equilibrium gas-phase mixture containing statistical amounts of HD; the corresponding reaction of **4a**-H_2 with D_2 similarly generates HD (together with H_2/D_2). *In situ* ^{1}H NMR monitoring of the latter reaction reveals two PH signals, consistent with the formation of both PH/BH and PH/BD phosphonium borate isotopologue (SI). By contrast, analogous experiments with **4b**-H_2/D_2 do not yield any observable HD even after 12 h. This, together with a similar lack of reactivity toward D_2 by $[PMes_3H]^+[B(C_6F_5)_3H]^-$ (e.g.), argues against a mechanism in this case involving direct exchange of D_2 with PH or BH bonds.[17b] A potential alternative route involves exchange of H^+ (or H^-) between zwitterionic **4a**-H_2 and the free FLP **4a** to give separate cationic phosphonium borane, and anionic phosphine borate entities (i.e., $[\mathbf{4a}\text{-H}]^+$ and $[\mathbf{4a}\text{-H}]^-$). With the same "shuttling" of D^+/D^- available to the deuteriated analogue **4a**-D_2, H/D scrambling could be initiated for **4a**, but not for **4b**, due to the dearth of free FLP in equilibrium with **4b**-H_2. Notably, the $Et_2O/B(C_6F_5)_3$ system, for which an equilibrium with the H_2 activation product has been proposed (but not spectroscopically observed), also mediates H/D scrambling when exposed to HD.[17a]

While **4a** can therefore be used to activate/release H_2 at ambient temperature, we wondered whether such reversibility could also be applied to capture other small molecules.[18] The intramolecular P···B separations determined for FLPs **4a** and **4b** are not dissimilar to those measured crystallographically for two-component FLPs which have been employed to capture and/or detect nitrous oxide, N_2O (ca. 4.9 Å for $^{t}Bu_3P{\cdot}N_2O{\cdot}B(C_6F_5)_2R$, where R = C_6F_5 or Fc).[19] As such, we hypothesized that xanthene-based FLP systems might also act as single component receptors for N_2O. Consistent with this idea, the reaction of **4a** with nitrous oxide at 1 atm pressure in dichloromethane solution leads to the formation of the adduct **4a**·N_2O (Scheme 3), which has been characterized by standard spectroscopic and analytical means and has been shown crystallographically to feature a single molecule of N_2O bound cooperatively between P(1) and B(5) (Figure 3).

Scheme 3. Reversible Capture of Nitrous Oxide by 4a



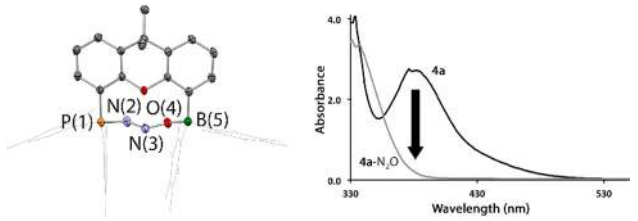


Figure 3. (left) Molecular structure **4a**-N_2O as determined by X-ray crystallography. H atoms and solvate molecule omitted, and Mes/C_6F_5 groups shown in wireframe format for clarity; thermal ellipsoids drawn at the 40% probability level. Key distances (Å) and angles (°): P(1)···B(5) 4.565(2), P(1)−N(2) 1.706(2), N(2)−N(3) 1.267(2), N(3)−O(4) 1.316(3), O(4)−B(5) 1.542(2), P(1)−N(2)−N(3) 104.0(1), N(2)−N(3)−O(4) 111.7(2), N(3)−O(4)−B(5) 109.4(2). (right) UV−vis spectra of **4a** (black) and **4a**-N_2O (gray) in fluorobenzene solution (1.0 mol dm^{-3}).

Metrical parameters for the bound NNO unit [notably N(2)−N(3) and N(3)−O(4) distances of 1.267(2) and 1.316(3) Å, respectively, and the N(2)−N(3)−O(4) angle of 111.7(2)°] are similar to those reported for related N_2O adducts formed with two-component FLPs.[19] The P(1)−N(2)−N(3) and N(3)−O(4)−B(5) angles [104.0(1) and 109.4(1)°], however, are more acute in **4a**-N_2O, and the P···B separation [4.565(2) Å] is therefore narrower than those determined for systems of the type $^{t}Bu_3P{\cdot}N_2O{\cdot}B(C_6F_5)_2R$.[19] It is, however, ca. 0.3 Å wider than that found in "free" **4a**. This observation may explain the relatively slow uptake of N_2O ($t_{1/2} \approx 12$ h) compared, e.g., to that of H_2 ($t_{1/2}$ < 5 min), and with this in mind we wondered whether the implied distortion of the xanthene backbone might be exploited to release the N_2O guest at elevated temperatures. Given the constraints of the binding pocket we also perceived that the trans-to-cis isomerization about the N═N double bond implicated in N-to-P oxygen atom-transfer processes (and hence in phosphine oxide formation)[20] ought not to be facile for **4a**-N_2O. Accordingly, warming a solution of the adduct in dichloromethane to 323 K for 2 h leads to quantitative reversion to **4a**, with no evidence obtained spectroscopically for competing P−O bond formation. To our knowledge, this represents the first reported example of the reversible sequestration of N_2O.

The regeneration of **4a** is even more facile in d_5-bromobenzene and can be followed *in situ* by ^{1}H NMR, allowing for the determination of the associated first order rate constant at a range of temperatures (see SI). An Eyring plot then yields the activation parameters $\Delta H^{\ddagger}$ = 104 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 38 J mol^{-1} K^{-1} for N_2O loss. Interestingly, the loss of N_2O is also accompanied by the regeneration of the yellow color of the free FLP **4a** (**4a**-N_2O being colorless; Figure 3), suggesting potential applications of such systems in the reversible sensing of nitrous oxide.

In conclusion, we show that a single-component frustrated Lewis pair with appropriately tuned binding/activation thermodynamics (ΔG° = −7.9 kJ mol^{-1} at 295 K) and a preorganized binding domain can reversibly activate dihydrogen in arene solution at room temperature to give an equilibrium mixture of H_2 bound/free FLP. This reversibility in small molecule capture/activation can also be exploited toward N_2O, leading to the development of reversible colorimetric detection protocol for nitrous oxide.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08614.

Synthetic and characterizing data for all new compounds (PDF)

Crystallographic data for all X-ray crystal structures (CIF)

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Notes

The authors declare no competing financial interest.

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(15) The intramolecular P···B separation in **2a** is 5.669(1) Å, implying that H_2 activation likely involves two molecules of the FLP. As such, differences in the degree of preorganization suggest that the kinetics of H_2 uptake will be less favorable than for **4a**. DFT calculations imply that the energy change accompanying H_2 activation by **2a** is ca. 30 kJ mol^{-1} less favorable than for **4a** (NB: the experimentally determined value of ΔG°_{295} for H_2 uptake by **4a** is −7.9 kJ mol^{-1}).

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(18) For an example of the reversible binding of other small molecules by single-component FLPs see, e.g.: Mömming, C.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643−6646.

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