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Nitrous Oxide Detection

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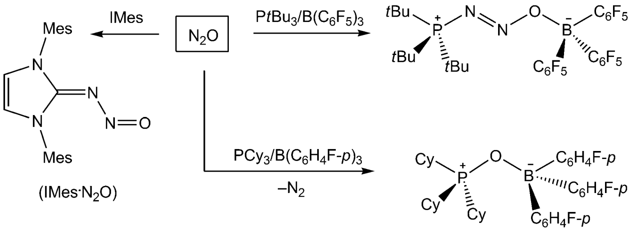
Frustrated Lewis Pairs as Molecular Receptors: Colorimetric and Electrochemical Detection of Nitrous Oxide**

*Michael J. Kelly, Jessica Gilbert, Remi Tirfoin, and Simon Aldridge**

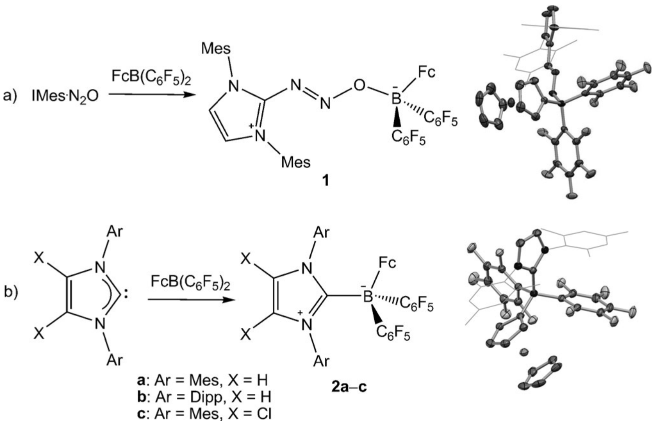
While the idea of sterically enforced Lewis acid/base frustration dates back as far as 1942,[1] exploitation of the latent reactivity of such systems constitutes a significant recent development in small-molecule activation.[2] Synergistic reactivity involving both donor and acceptor components has led to the trapping of molecules such as CO_2 and N_2O,[3,4] and to the cleavage of relatively inert bonds, such as that in H_2 for catalytic processes.[5,6] Given that the Lewis acidic component of many "frustrated Lewis pairs" (FLPs) is a halogenated triarylborane, and that related ferrocene-containing systems are accessible,[7] we hypothesized that electrochemical or colorimetric detection, even of relatively unreactive molecules, might be possible by employing an FLP approach. The conversion of a three-coordinate ferrocenyl borane to a four-coordinate borate is typically accompanied by a change in both the $Fe^{II/III}$ redox potential and the electronic absorption maxima of the ferrocenyl chromophore, and such systems have previously been shown to be effective in detecting anionic analytes.[8]

In particular, given the trapping of nitrous oxide by the $tBu_3P/B(C_6F_5)_3$ FLP reported by Stephan and co-workers,[4] and the reactivity of N_2O toward IMes described by Severin and co-workers (see Scheme 1),[9] we hypothesized that the combination of a bulky Lewis base (e.g. a tertiary phosphine or N-heterocyclic carbene) and an electron-deficient ferrocenyl borane (for example, of the type $FcB(C_6(Hal)_5)_2$; Fc = ferrocenyl = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) might constitute a viable colorimetric/electrochemical protocol for the detection of the potent environmental pollutant N_2O.[10] The selective detection of N_2O in general is problematic because 1) it is an intrinsically poor ligand for transition metal centers;[11] and 2) its reactivity as an oxygen atom transfer reagent is common to a number of other species. While the synergistic reactivity of the Lewis acid and base components in an FLP provides a solution to the former problem, careful choice of FLP components is required to develop a system which not only signals the presence of N_2O, but also gives a null response to exposure to other O-atom sources (including O_2).



Scheme 1. Previously reported ambiphilic N_2O binding (or degradation) by FLP systems, and of N_2O fixation by an N-heterocyclic carbene.[4,9] Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl.

Initial studies focused on the interaction of the known adduct IMes·N_2O (Scheme 1) with $FcB(C_6F_5)_2$ (Scheme 2a).[7,9] In the event, the formation of the simple 1:1 complex IMes·N_2O·$BFc(C_6F_5)_2$ (**1**) in solution was confirmed by NMR spectroscopy, mass spectrometry, and X-ray crystallography. While this observation demonstrates the viability of binding an adduct of the type L·N_2O to a ferrocenyl borane, attempts to use Lewis pairs comprising $FcB(C_6F_5)_2$ and an N-heterocyclic carbene to detect free nitrous oxide were thwarted by the ready formation of the corresponding carbene–borane adduct.[12] Thus, the adducts formed from $FcB(C_6F_5)_2$ and IMes (**2a**; Scheme 2b), or related NHCs featuring either enhanced steric bulk or a less electron-rich carbene donor (e.g. **2b** or **2c**), are unreactive toward N_2O.



Scheme 2. a) Complexation of IMes·N_2O by $FcB(C_6F_5)_2$; b) adduct formation between NHCs and $FcB(C_6F_5)_2$. Right: molecular structures of IMes·N_2O·$BFc(C_6F_5)_2$ (**1**; top) and **2a** (bottom) as determined by X-ray crystallography; H atoms omitted and mesityl groups shown in wire-frame format for clarity, and displacement ellipsoids shown at the 40% probability level. Dipp = 2,6-diisopropylphenyl.

By contrast, combinations of $FcB(C_6F_5)_2$ and bulky tertiary phosphines, such as tBu_3P, Cy_3P, or Ph_3P, do constitute

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[*] M. J. Kelly, J. Gilbert, R. Tirfoin, Prof. S. Aldridge
Inorganic Chemistry Laboratory
Department of Chemistry, University of Oxford
South Parks Road, Oxford, OX1 3QR (UK)
E-mail: Simon.Aldridge@chem.ox.ac.uk

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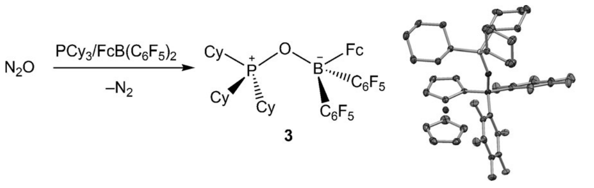
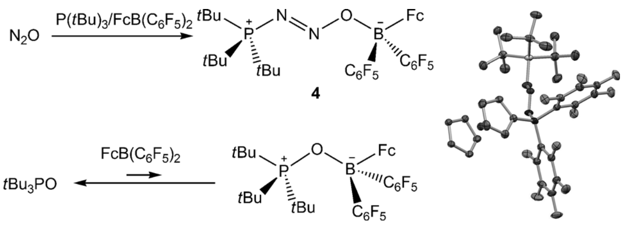
FLPs, as judged by solution-phase NMR and UV/Vis measurements.[13] Moreover, the $Cy_3P/FcB(C_6F_5)_2$ system undergoes a maroon-to-amber color change on exposure to N_2O in benzene. However, spectroscopic, analytical, and crystallographic data obtained for the product of this reaction suggest that it is the phosphine oxide adduct $Cy_3PO{\cdot}BFc(C_6F_5)_2$ (**3**; Scheme 3). Similar degradation chemistry resulting in the formation of a borane/phosphine oxide complex via N_2 extrusion has been reported by Stephan and co-workers for $Cy_3P/B(C_6H_4F\text{-}p)_3$ (Scheme 1).[4c] On the other hand, trapping of an essentially intact N_2O moiety is thought to depend on 1) maximizing the strength (and resulting irreversibility) of the binding of the R_3PNNO fragment at the borane Lewis acid, and 2) on the kinetics of trapping being faster than phosphine oxidation. Clearly, the formation of **3** from $Cy_3P/FcB(C_6F_5)_2$ and N_2O is problematic for applications in detection, insofar as the reactions of Cy_3P with a range of oxidizing agents are known to generate Cy_3PO.[14] As such, this particular FLP system is not likely to be selective for N_2O, merely signaling the presence of a broader class of oxygen atom transfer reagent.



Scheme 3. Formation of the Cy_3PO adduct of $FcB(C_6F_5)_2$ (**3**) through the reaction of N_2O with the $Cy_3P/FcB(C_6F_5)_2$ FLP. Inset: molecular structure of **3** as determined by X-ray crystallography; H atoms and benzene solvate molecule omitted for clarity, and displacement ellipsoids shown at the 40% probability level.

By contrast, NMR experiments carried out with $FcB(C_6F_5)_2$ and the (independently synthesized and much bulkier) phosphine oxide tBu$_3$PO in either benzene or fluorobenzene, show that this combination forms only a very weakly bound Lewis acid/base adduct, presumably on steric grounds. The major compound in solution at ambient temperature remain the non-coordinated Lewis acid and base components,[15] and the maroon color (and UV/Vis bands at 231, 371, and 495 nm), associated with $FcB(C_6F_5)_2$, remain essentially unquenched. As such, the tBu$_3$P/FcB(C$_6$F$_5$)$_2$ system offers the potential for selective colorimetric detection of nitrous oxide, free from false positives arising from other oxidants, such as O_2.

Critically, the reaction of the tBu$_3$P/FcB(C$_6$F$_5$)$_2$ FLP with N_2O generates the ambiphilic adduct tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$ (**4**), the identity of which is suggested by NMR spectroscopy and mass spectrometry, and confirmed by X-ray crystallography (Scheme 4).[16] Presumably, the differential reactivity of the tBu$_3$P/FcB(C$_6$F$_5$)$_2$ and $Cy_3P/FcB(C_6F_5)_2$ FLPs toward N_2O stems from the stronger O-donor capabilities of tBu$_3$PNNO over Cy_3PNNO and the consequently diminished reversibility of binding of the former at $FcB(C_6F_5)_2$.[4c] The formation of **4** is accompanied by a maroon-to-amber color change, with the product being characterized by a very weak ($\varepsilon = 60\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) band at $\lambda_{max} = 434$ nm. Structurally, both the bond lengths within the PNNOB chain (d(PN) = 1.692(3), d(NN) = 1.251(3), d(NO) = 1.329(3), d(OB) = 1.543(4) Å) and the overall 'W'-shaped coordination motif closely match those reported by Stephan and co-workers for the related adduct tBu$_3$P·N$_2$O·B(C$_6$F$_5$)$_3$,[4a] and are therefore consistent with a dominant resonance contribution featuring an N=N double bond and P–N, N–O, and O–B single bonds (Scheme 4).



Scheme 4. Reaction of the tBu$_3$P/FcB(C$_6$F$_5$)$_2$ FLP with N_2O; weak binding of tBu$_3$PO to the borane $FcB(C_6F_5)_2$. Inset: molecular structure of **4** as determined by X-ray crystallography; H atoms and benzene solvate molecules omitted for clarity, and displacement ellipsoids shown at the 40% probability level.

Although tBu$_3$P is known to react with O_2 (or with H_2O_2) to generate tBu$_3$PO, the low affinity of the Lewis acid $FcB(C_6F_5)_2$ for this phosphine oxide means that no significant quenching of the UV signal (or indeed a visible color change) is observed for the tBu$_3$P/FcB(C$_6$F$_5$)$_2$ FLP in tetrahydrofuran on exposure to dry O_2 over a period of 6 hours. By contrast, the formation of adduct **4** on exposure to nitrous oxide is signaled by a maroon-to-amber color change, consistent with simple quenching of the Lewis acidic character of the pendant borane (Figure 1). Consistently, Piers has established that the yellow color observed on addition of the sterically unencumbered base PMe_3 to $FcB(C_6F_5)_2$ is due to the formation of the corresponding adduct $Me_3P{\cdot}BFc(C_6F_5)_2$.[7]

Alternatively, the formation of **4** can be signaled electrochemically, with a cathodic shift of greater than 300 mV (from +450 mV, with respect to FcH/FcH$^+$, to +150 mV) accompanying the formation of the adduct in α,α,α-trifluorotoluene.[7] Essentially no shift is observed in the presence of O_2 under analogous conditions. For detection applications,

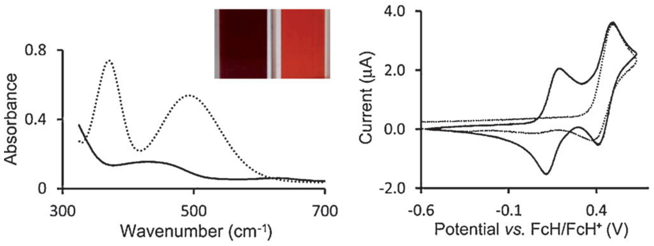


Figure 1. Effects of exposure of the tBu$_3$P/FcB(C$_6$F$_5$)$_2$ FLP to N_2O, monitored by (left) UV/Vis spectroscopy (dashed line tBu$_3$P/FcB(C$_6$F$_5$)$_2$, solid line tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$) and (right) cyclic voltammetry (dashed line tBu$_3$P/FcB(C$_6$F$_5$)$_2$, solid line equimolar mixture of tBu$_3$P/FcB(C$_6$F$_5$)$_2$ and tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$). Inset photograph: solutions of tBu$_3$P/FcB(C$_6$F$_5$)$_2$ (left) and tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$ (right) in benzene (ca. 70 mM concentration, housed in UV cuvettes).

electrochemical rather than colorimetric reporting represents a more viable option: the large binding-induced shift in $E_{1/2}$ enables the detection of small quantities of **4** (in the < 100 μM concentration range) even in the presence of a large excess of unreacted $FcB(C_6F_5)_2$ (see the Supporting Information). Conversely, the much larger extinction coefficient associated with $FcB(C_6F_5)_2$ (compared to that for its tBu$_3$PN$_2$O adduct) means that visible detection of **4** can only really be achieved once near-quantitative consumption of the free ferrocenyl Lewis acid has been effected.

In conclusion, the tBu$_3$P/$FcB(C_6F_5)_2$ system establishes a proof-of-principle for the detection of N_2O by an FLP, or at least a means for discriminating from other O-atom sources, such as O_2. The underpinning chemistry hinges on the differential ability of $FcB(C_6F_5)_2$ to coordinate tBu$_3$PO and tBu$_3$PNNO, which in turn is due to the smaller steric demand of the latter structure in the immediate vicinity of the O-donor.

Experimental Section

Included here are the synthetic, spectroscopic, and crystallographic data for $Cy_3PO{\cdot}BFc(C_6F_5)_2$ (**3**) and tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$ (**4**). Analogous data for **1**, **2a–c**, and $FcB(F)(C_6F_5)_2(C_6F_4)PCy_3$ and crystallographic information are included in the Supporting Information.

3: $FcB(C_6F_5)_2$ (500 mg, 0.94 mmol) and Cy_3P (264 mg, 0.94 mmol) were dissolved in benzene (20 mL), and the solution subjected to three freeze-pump-thaw cycles before backfilling with N_2O (ca. 4 atm). After standing at room temperature for 24 hours, orange crystals formed, which were isolated by filtration, washed with pentane (3×10 mL), and dried in vacuo. Yield: 343 mg, 43% (purity: >95%). Single crystals of $Cy_3PO{\cdot}BFc(C_6F_5)_2{\cdot}{}^1/_2(C_6H_6)$ were grown from a solution in benzene; after exposure of the crystalline samples to continuous vacuum, 0.33 equivalents of benzene solvate remained, as judged by ^{1}H NMR spectroscopy. ^{1}H (300 MHz, [D$_8$]THF, 20°C): $\delta_H = 7.30$ (s, 2H, C_6H_6), 4.26, 4.00 (s, each 2H, C_5H_4B), 3.91 (s, 5H, C_5H_5), 2.11 (br m, 3H, Cy), 1.94 (br m, 6H, Cy), 1.77 (br m, 12H, Cy), 1.26 ppm (br m, 12H, Cy). ^{11}B{^{1}H} (96 MHz, [D$_8$]THF, 20°C): $\delta_B =$ 6 ppm (br). ^{13}C{^{1}H} (75 MHz, [D$_8$]THF, 20°C): $\delta_C = 149.8$, 146.5, 139.4, 136.1 (C_6F_5), 128.8 (C_6H_6), 110.8, 74.8, 70.0 (C_5H_4B), 68.8 (C_5H_5), 35.2 (d, $^1J_{PC} = 58.7$ Hz, Cy), 27.1 (d, $^3J_{PC} = 12.7$ Hz, Cy), 26.6 ppm (d, $^2J_{PC} = 17.8$ Hz, Cy). ^{19}F (282 MHz, [D$_8$]THF, 20°C): $\delta_F =$ -127.9 (4F, *ortho*-CF of C_6F_5), -160.1 (2F, *para*-CF of C_6F_5), -164.5 ppm (4F, *meta*-CF of C_6F_5). ^{31}P{^{1}H} (121 MHz, [D$_8$]THF, 20°C): $\delta_P = 68.3$. UV/Vis (C_6H_5F) λ_{max}, nm (ε): 450 (60 L mol^{-1} cm^{-1}). MS(EI) m/z (%): 530.0 (11) $[FcB(C_6F_5)_2]^+$. Elemental microanalysis: calcd for $C_{42}H_{44}BF_{10}Fe\ OP$, C 59.18%, H 5.20%; found C 58.97, 58.82%, H 5.38, 5.47%. Crystallographic data for $Cy_3PO{\cdot}BFc(C_6F_5)_2{\cdot}{}^1/_2(C_6H_6)$: $C_{43}H_{45}BF_{10}FeOP$, $M_r = 865.44$, triclinic, $P\bar{1}$, $a =$ 9.8771(1), $b = 12.501(1)$, $c = 17.2452(3)$ Å, $\alpha = 72.9492(6)$, $\beta =$ 79.1339(6), $\gamma = 75.3271(8)°$, $V = 1954.20(5)$ Å^3, $Z = 2$, $\rho_c =$ 1.471 Mg m^{-3}, $T = 150$ K, $\lambda = 0.71073$ Å. 8842 independent reflections [R(int) = 0.000] used in all calculations. $R_1 = 0.0348$, $wR_2 = 0.0738$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.0515$, $wR_2 = 0.0900$ for all unique reflections. Max./min. residual electron densities 0.49 and -0.50 e Å^3.

4: $FcB(C_6F_5)_2$ (220 mg, 0.42 mmol) and tBu$_3$P (81 mg, 0.40 mmol) were dissolved in benzene (6 mL), and the solution subjected to three freeze-pump-thaw cycles before backfilling with N_2O (ca. 4 atm). The solution was allowed to stand at room temperature for 12 hours, giving orange crystals, which were isolated by filtration, washed with pentane (3×10 mL) and dried in vacuo to afford tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$ as an orange powder. If stirred the reaction proceeds to completion significantly more quickly (<1 h), although not to the formation of single crystals. Yield: 267 mg, 86% (contaminated with trace tBu$_3$PO). Single crystals of tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$·(C$_6$H$_6$) suitable for X-ray crystallography were grown from a solution in benzene; after exposure of crystalline samples to continuous vacuum, 0.67 equivalents of benzene solvate remained, as judged by ^{1}H NMR spectroscopy. ^{1}H (300 MHz, [D$_8$]THF, 20°C): $\delta_H = 7.29$ (s, 4H, C_6H_6), 4.10 (s, 2H, C_5H_4B), 4.01 (s, 2H, C_5H_4B), 3.86 (s, 5H, C_5H_5), 1.53 ppm (d, 27H, $^3J_{PH} = 14.7$ Hz, P(CMe$_3$)$_3$). ^{11}B{^{1}H} (96 MHz, [D$_8$]THF, 20°C): $\delta_B = 3$ ppm (br). ^{13}C{^{1}H} (125 MHz, [D$_8$]THF, 20°C): $\delta_C = 149.2$, 147.3, 138.3, 136.4 (C_6F_5), 128.8 (C_6H_6), 73.8, 69.4 (C_5H_4B), 68.4 (C_5H_5), 41.7 (d, $^1J_{PC} = 30.0$ Hz, quaternary C of PtBu$_3$), 29.3 ppm (Me of PtBu$_3$). B-bound carbon of C_5H_4B not observed. ^{19}F (282 MHz, [D$_8$]THF, 20°C): $\delta_F = -131.0$ (d, 4F, $^3J_{FF} =$ 14.9 Hz, *ortho*-CF of C_6F_5), -163.4 (d, 2F, $^3J_{FF} = 19.7$ Hz, *para*-CF of C_6F_5), -167.4 ppm (dd, 4F, $^3J_{FF} = 14.9$ Hz, $^3J_{FF} = 19.7$ Hz, *meta*-CF of C_6F_5). ^{31}P{^{1}H} (121 MHz, [D$_8$]THF, 20°C): $\delta_P = 65.3$ (s). UV/Vis (C_6H_5F) λ_{max}, nm (ε): 434 (120 L mol^{-1} cm^{-1}). MS(EI) m/z (%): 530.0 (11) $[FcB(C_6F_5)_2]^+$, 776.2 (100) [tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$]$^+$. HRMS(EI) (m/z): calcd for [M^+] (^{10}B, ^{54}Fe isotopomer), 774.1895; found 774.1887. $E_{1/2}$ (0.05 M [nBu$_4$N][B(C$_6$F$_5$)$_4$] electrolyte in $C_6H_5CF_3$) = +150 mV, relative to FcH/FcH$^+$. Crystallographic data for tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$·(C$_6$H$_6$): $C_{40}H_{42}BF_{10}FeN_2OP$, $M_r = 854.40$, monoclinic, $P2_1$, $a =$ 11.0548(4), $b = 15.1745(7)$, $c = 11.6859(5)$ Å, $\beta = 92.794(2)°$, $V =$ 1957.99(14) Å^3, $Z = 2$, $\rho_c = 1.449$ Mg m^{-3}, $T = 150$ K, $\lambda = 0.71073$ Å. 6191 independent reflections [R(int) = 0.000] used in all calculations. $R_1 = 0.0452$, $wR_2 = 0.1059$ for observed unique reflections [$I > 2\sigma(I)$] and $R_1 = 0.0488$, $wR_2 = 0.1093$ for all unique reflections. Max./min. residual electron densities 0.25 and -0.48 e Å^3.

CCDC 945600 (**3**) and 945599 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] For a wide-ranging recent study of NHC/borane FLPs, see: S. Kronig, E. Theuergarten, D. Holschumacher, T. Bannenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Inorg. Chem.* **2011**, *50*, 7344 – 7359.

[13] The $Cy_3P/FcB(C_6F_5)_2$ system, but crucially not the tBu$_3$P/FcB($C_6F_5)_2$ FLP, shows evidence for the formation (over ca. 10 d) of a very small amount of a zwitterionic product derived from nucleophilic attack by the phosphine at the *para* position of one pentafluorophenyl ring. The identity of this product, FcB(F)-$(C_6F_5)(C_6F_4)PCy_3$, was confirmed crystallographically (see the Supporting Information).

[14] The oxidation of tertiary phosphines to the corresponding phosphine oxide by N_2O has been reported previously: S. Poh, R. Hernandez, M. Inagaki, P. G. Jessop, *Org. Lett.* **1999**, *1*, 583 – 584.

[15] Multinuclear NMR studies carried out on an equimolar mixture of $FcB(C_6F_5)_2$ and tBu$_3$PO (such as might be formed from the tBu$_3$P/FcB$(C_6F_5)_2$ FLP in the presence of a compatible O-atom transfer agent) at about 50 mM concentrations showed an approximately 3:1 mixture of the free acid/base and adduct at room temperature (ca. 1:1 at 218 K).

[16] On a preparative scale (100–500 mg), this reaction proceeds quantitatively on exposure of a solution of tBu$_3$P/FcB$(C_6F_5)_2$ (ca. 70 mM) to N_2O (about 4 atm). No reaction is observed on exposure of this FLP to CO_2.