

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

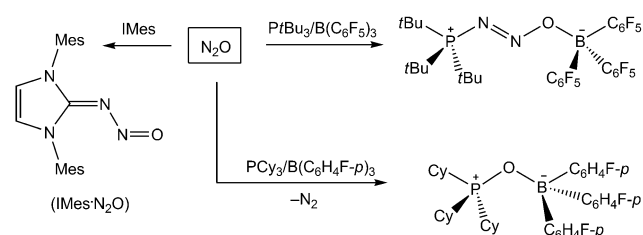
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While the idea of sterically enforced Lewis acid/base frustration dates back as far as 1942,^[1] exploitation of the latent reactivity of such systems constitutes a significant recent development in small-molecule activation.^[2] Synergistic reactivity involving both donor and acceptor components has led to the trapping of molecules such as CO₂ and N₂O,^[3,4] and to the cleavage of relatively inert bonds, such as that in H₂ 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]

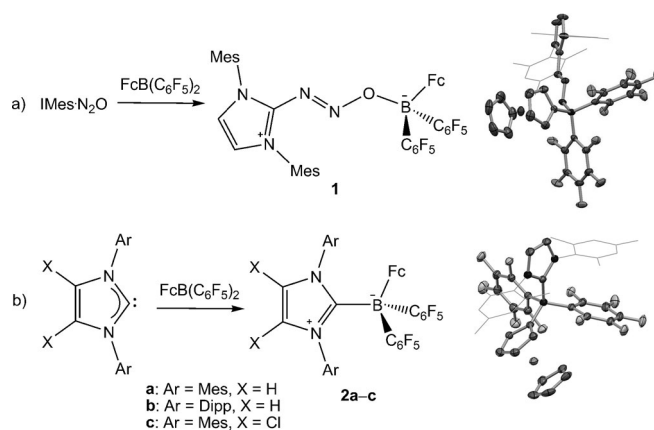
In particular, given the trapping of nitrous oxide by the *t*Bu₃P/B(C₆F₅)₃ FLP reported by Stephan and co-workers,^[4] and the reactivity of N₂O toward IMes described by Severin and co-workers (see Scheme 1),^[9] we hypothesized that the combination of a bulky Lewis base (e.g. a tertiary phosphine or N-heterocyclic carbene) and an electron-deficient ferrocenyl borane (for example, of the type FcB(C₆(Hal)₅)₂; Fc = ferrocenyl = (η⁵-C₅H₅)Fe(η⁵-C₅H₄)) might constitute a viable

colorimetric/electrochemical protocol for the detection of the potent environmental pollutant N₂O.^[10] The selective detection of N₂O 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 N₂O, but also gives a null response to exposure to other O-atom sources (including O₂).

Initial studies focused on the interaction of the known adduct IMes·N₂O (Scheme 1) with FcB(C₆F₅)₂ (Scheme 2a).^[7,9] In the event, the formation of the simple 1:1 complex IMes·N₂O·BFc(C₆F₅)₂ (**1**) in solution was confirmed



Scheme 1. Previously reported ambiphilic N₂O binding (or degradation) by FLP systems, and of N₂O fixation by an N-heterocyclic carbene.^[4,9] Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl.



Scheme 2. a) Complexation of IMes·N₂O by FcB(C₆F₅)₂; b) adduct formation between NHCs and FcB(C₆F₅)₂. Right: molecular structures of IMes·N₂O·BFc(C₆F₅)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 NMR spectroscopy, mass spectrometry, and X-ray crystallography. While this observation demonstrates the viability of binding an adduct of the type L·N₂O to a ferrocenyl borane, attempts to use Lewis pairs comprising FcB(C₆F₅)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(C₆F₅)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 N₂O.

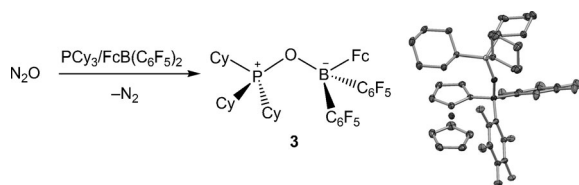
By contrast, combinations of FcB(C₆F₅)₂ and bulky tertiary phosphines, such as *t*Bu₃P, Cy₃P, or Ph₃P, do constitute

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[**] EPSRC (studentship to M.J.K.; NMSF, Swansea University).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201308475>.

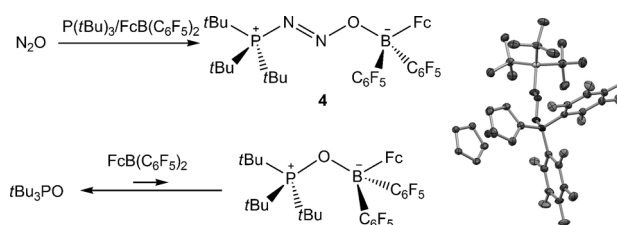
FLPs, as judged by solution-phase NMR and UV/Vis measurements.^[13] Moreover, the $\text{Cy}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ system undergoes a maroon-to-amber color change on exposure to N_2O in benzene. However, spectroscopic, analytical, and crystallographic data obtained for the product of this reaction suggest that it is the phosphine oxide adduct $\text{Cy}_3\text{PO}\cdot\text{BFc}(\text{C}_6\text{F}_5)_2$ (**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 $\text{Cy}_3\text{P}/\text{B}(\text{C}_6\text{H}_4\text{F}-p)_3$ (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 $\text{Cy}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ 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 $\text{FcB}(\text{C}_6\text{F}_5)_2$ (**3**) through the reaction of N_2O with the $\text{Cy}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ 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 $\text{FcB}(\text{C}_6\text{F}_5)_2$ and the (independently synthesized and much bulkier) phosphine oxide $t\text{Bu}_3\text{PO}$ 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 $\text{FcB}(\text{C}_6\text{F}_5)_2$, remain essentially unquenched. As such, the $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ 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 $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ FLP with N_2O generates the ambiphilic adduct $t\text{Bu}_3\text{P}\cdot\text{N}_2\text{O}\cdot\text{BFc}(\text{C}_6\text{F}_5)_2$ (**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 $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ and $\text{Cy}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ FLPs toward N_2O stems from the stronger O-donor capabilities of $t\text{Bu}_3\text{PNNO}$ over Cy_3PNNO and the consequently diminished reversibility of binding of the former at $\text{FcB}(\text{C}_6\text{F}_5)_2$.^[4c] The formation of **4** is accompanied by a maroon-to-amber color change, with the product being characterized by a very weak ($\epsilon =$



Scheme 4. Reaction of the $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ FLP with N_2O ; weak binding of $t\text{Bu}_3\text{PO}$ to the borane $\text{FcB}(\text{C}_6\text{F}_5)_2$. 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.

$60 \text{ L mol}^{-1} \text{ cm}^{-1}$) band at $\lambda_{\text{max}} = 434 \text{ nm}$. Structurally, both the bond lengths within the PNNOB chain ($d(\text{PN}) = 1.692(3)$, $d(\text{NN}) = 1.251(3)$, $d(\text{NO}) = 1.329(3)$, $d(\text{OB}) = 1.543(4) \text{ \AA}$) and the overall 'W'-shaped coordination motif closely match those reported by Stephan and co-workers for the related adduct $t\text{Bu}_3\text{P}\cdot\text{N}_2\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3$,^[4a] and are therefore consistent with a dominant resonance contribution featuring an $\text{N}=\text{N}$ double bond and $\text{P}-\text{N}$, $\text{N}-\text{O}$, and $\text{O}-\text{B}$ single bonds (Scheme 4).

Although $t\text{Bu}_3\text{P}$ is known to react with O_2 (or with H_2O_2) to generate $t\text{Bu}_3\text{PO}$, the low affinity of the Lewis acid $\text{FcB}(\text{C}_6\text{F}_5)_2$ for this phosphine oxide means that no significant quenching of the UV signal (or indeed a visible color change) is observed for the $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ 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 $\text{FcB}(\text{C}_6\text{F}_5)_2$ is due to the formation of the corresponding adduct $\text{Me}_3\text{P}\cdot\text{BFc}(\text{C}_6\text{F}_5)_2$.^[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,

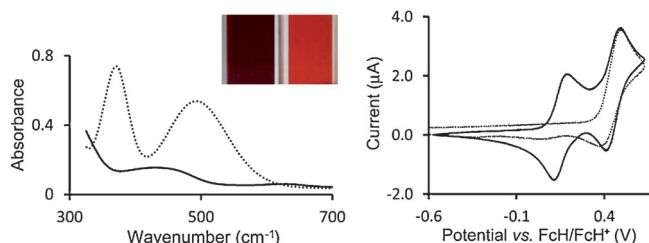


Figure 1. Effects of exposure of the $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ FLP to N_2O , monitored by (left) UV/Vis spectroscopy (dashed line $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$, solid line $t\text{Bu}_3\text{P}\cdot\text{N}_2\text{O}\cdot\text{BFc}(\text{C}_6\text{F}_5)_2$) and (right) cyclic voltammetry (dashed line $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$, solid line equimolar mixture of $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ and $t\text{Bu}_3\text{P}\cdot\text{N}_2\text{O}\cdot\text{BFc}(\text{C}_6\text{F}_5)_2$). Inset photograph: solutions of $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ (left) and $t\text{Bu}_3\text{P}\cdot\text{N}_2\text{O}\cdot\text{BFc}(\text{C}_6\text{F}_5)_2$ (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 $< 100 \mu\text{M}$ concentration range) even in the presence of a large excess of unreacted $\text{FcB}(\text{C}_6\text{F}_5)_2$ (see the Supporting Information). Conversely, the much larger extinction coefficient associated with $\text{FcB}(\text{C}_6\text{F}_5)_2$ (compared to that for its $t\text{Bu}_3\text{P-N}_2\text{O}$ 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 $t\text{Bu}_3\text{P}/\text{FcB}(\text{C}_6\text{F}_5)_2$ 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 $\text{FcB}(\text{C}_6\text{F}_5)_2$ to coordinate $t\text{Bu}_3\text{PO}$ and $t\text{Bu}_3\text{PNNO}$, 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 $\text{Cy}_3\text{PO-BFc}(\text{C}_6\text{F}_5)_2$ (**3**) and $t\text{Bu}_3\text{P-N}_2\text{O-BFc}(\text{C}_6\text{F}_5)_2$ (**4**). Analogous data for **1**, **2a-c**, and $\text{FcB}(\text{F})(\text{C}_6\text{F}_5)_2(\text{C}_6\text{F}_4)\text{PCy}_3$ and crystallographic information are included in the Supporting Information.

3: $\text{FcB}(\text{C}_6\text{F}_5)_2$ (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 ($3 \times 10 \text{ mL}$), and dried in vacuo. Yield: 343 mg, 43 % (purity: $> 95\%$). Single crystals of $\text{Cy}_3\text{PO-BFc}(\text{C}_6\text{F}_5)_2 \cdot 1/2 (\text{C}_6\text{H}_6)$ 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 ^1H NMR spectroscopy. ^1H (300 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{H}} = 7.30$ (s, 2H, C_6H_6), 4.26, 4.00 (s, each 2H, $\text{C}_5\text{H}_4\text{B}$), 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). $^{11}\text{B}\{^1\text{H}\}$ (96 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{B}} = 6$ ppm (br). $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{C}} = 149.8$, 146.5, 139.4, 136.1 (C_6F_5), 128.8 (C_6H_6), 110.8, 74.8, 70.0 ($\text{C}_5\text{H}_4\text{B}$), 68.8 (C_5H_5), 35.2 (d, $^1J_{\text{PC}} = 58.7 \text{ Hz}$, Cy), 27.1 (d, $^3J_{\text{PC}} = 12.7 \text{ Hz}$, Cy), 26.6 ppm (d, $^2J_{\text{PC}} = 17.8 \text{ Hz}$, Cy). ^{19}F (282 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{F}} = -127.9$ (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). $^{31}\text{P}\{^1\text{H}\}$ (121 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{P}} = 68.3$. UV/Vis ($\text{C}_6\text{H}_5\text{F}$) λ_{max} , nm (ϵ): 450 (60 $\text{L mol}^{-1} \text{ cm}^{-1}$). MS(EI) m/z (%): 530.0 (11) $[\text{FcB}(\text{C}_6\text{F}_5)_2]^+$. Elemental microanalysis: calcd for $\text{C}_{42}\text{H}_{44}\text{BF}_{10}\text{Fe OP}$, C 59.18%, H 5.20%; found C 58.97, 58.82%, H 5.38, 5.47%. Crystallographic data for $\text{Cy}_3\text{PO-BFc}(\text{C}_6\text{F}_5)_2 \cdot 1/2 (\text{C}_6\text{H}_6)$: $\text{C}_{43}\text{H}_{45}\text{BF}_{10}\text{FeOP}$, $M_r = 865.44$, triclinic, $P\bar{1}$, $a = 9.8771(1)$, $b = 12.501(1)$, $c = 17.2452(3) \text{ \AA}$, $\alpha = 72.9492(6)^\circ$, $\beta = 79.1339(6)^\circ$, $\gamma = 75.3271(8)^\circ$, $V = 1954.20(5) \text{ \AA}^3$, $Z = 2$, $\rho_c = 1.471 \text{ Mg m}^{-3}$, $T = 150 \text{ K}$, $\lambda = 0.71073 \text{ \AA}$. 8842 independent reflections [$R(\text{int}) = 0.000$] 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 $-0.50 \text{ e \AA}^{-3}$.

4: $\text{FcB}(\text{C}_6\text{F}_5)_2$ (220 mg, 0.42 mmol) and $t\text{Bu}_3\text{P}$ (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 ($3 \times 10 \text{ mL}$) and dried in vacuo to afford $t\text{Bu}_3\text{P-N}_2\text{O-BFc}(\text{C}_6\text{F}_5)_2$ as an orange powder. If stirred the reaction proceeds to

completion significantly more quickly ($< 1 \text{ h}$), although not to the formation of single crystals. Yield: 267 mg, 86 % (contaminated with trace $t\text{Bu}_3\text{PO}$). Single crystals of $t\text{Bu}_3\text{P-N}_2\text{O-BFc}(\text{C}_6\text{F}_5)_2 \cdot (\text{C}_6\text{H}_6)$ 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 ^1H NMR spectroscopy. ^1H (300 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{H}} = 7.29$ (s, 4H, C_6H_6), 4.10 (s, 2H, $\text{C}_5\text{H}_4\text{B}$), 4.01 (s, 2H, $\text{C}_5\text{H}_4\text{B}$), 3.86 (s, 5H, C_5H_5), 1.53 ppm (d, 27H, $^3J_{\text{PH}} = 14.7 \text{ Hz}$, $\text{P}(\text{CMe}_3)_3$). $^{11}\text{B}\{^1\text{H}\}$ (96 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{B}} = 3$ ppm (br). $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{C}} = 149.2$, 147.3, 138.3, 136.4 (C_6F_5), 128.8 (C_6H_6), 73.8, 69.4 ($\text{C}_5\text{H}_4\text{B}$), 68.4 (C_5H_5), 41.7 (d, $^1J_{\text{PC}} = 30.0 \text{ Hz}$, quaternary C of $\text{P}(\text{tBu})_3$), 29.3 ppm (Me of $\text{P}(\text{tBu})_3$). B-bound carbon of $\text{C}_5\text{H}_4\text{B}$ not observed. ^{19}F (282 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{F}} = -131.0$ (d, 4F, $^3J_{\text{FF}} = 14.9 \text{ Hz}$, *ortho*-CF of C_6F_5), -163.4 (d, 2F, $^3J_{\text{FF}} = 19.7 \text{ Hz}$, *para*-CF of C_6F_5), -167.4 ppm (dd, 4F, $^3J_{\text{FF}} = 14.9 \text{ Hz}$, $^3J_{\text{FF}} = 19.7 \text{ Hz}$, *meta*-CF of C_6F_5). $^{31}\text{P}\{^1\text{H}\}$ (121 MHz, $[\text{D}_8]\text{THF}$, 20°C): $\delta_{\text{P}} = 65.3$ (s). UV/Vis ($\text{C}_6\text{H}_5\text{F}$) λ_{max} , nm (ϵ): 434 (120 $\text{L mol}^{-1} \text{ cm}^{-1}$). MS(EI) m/z (%): 530.0 (11) $[\text{FcB}(\text{C}_6\text{F}_5)_2]^+$, 776.2 (100) $[t\text{Bu}_3\text{P-N}_2\text{O-BFc}(\text{C}_6\text{F}_5)_2]^+$. HRMS(EI) (m/z): calcd for $[M^+]$ (^{10}B , ^{54}Fe isotopomer), 774.1895; found 774.1887. $E_{1/2}$ (0.05 M $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ electrolyte in $\text{C}_6\text{H}_5\text{CF}_3$) = +150 mV, relative to FcH/FcH^+ . Crystallographic data for $t\text{Bu}_3\text{P-N}_2\text{O-BFc}(\text{C}_6\text{F}_5)_2 \cdot (\text{C}_6\text{H}_6)$: $\text{C}_{40}\text{H}_{42}\text{BF}_{10}\text{FeN}_2\text{OP}$, $M_r = 854.40$, monoclinic, $P2_1$, $a = 11.0548(4)$, $b = 15.1745(7)$, $c = 11.6859(5) \text{ \AA}$, $\beta = 92.794(2)^\circ$, $V = 1957.99(14) \text{ \AA}^3$, $Z = 2$, $\rho_c = 1.449 \text{ Mg m}^{-3}$, $T = 150 \text{ K}$, $\lambda = 0.71073 \text{ \AA}$. 6191 independent reflections [$R(\text{int}) = 0.000$] 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 $-0.48 \text{ e \AA}^{-3}$.

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.

Received: September 29, 2013

Published online: November 12, 2013

Keywords: boranes · ferrocene · frustrated Lewis pairs · nitrous oxide · phosphines

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