Cooperative 1,1-Addition Reactions of Vicinal Phosphane/Borane Frustrated Lewis Pairs

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Keywords: frustrated Lewis pairs, nitric oxide, carbon monoxide, isonitriles, cooperative addition

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Abstract

The unsaturated vicinal phosphane/borane frustrated Lewis pairs (P/B FLPs) $\text{Ph}_2\text{PC}(p\text{-tolyl})=\text{C}(\text{R})\text{B}(\text{C}_6\text{F}_5)_2$ ($\text{R} = \text{C}_6\text{F}_5$ or CH_3) react with *tert*-butyl isocyanide to give an equilibrium mixture of the starting materials, the borane/isonitrile adduct and the P/B addition product to the isonitrile carbon atom. These cooperative 1,1-adducts were exclusively formed upon treatment of these FLPs with *n*-butyl isocyanide. The saturated vicinal FLP $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$ reacts analogously with carbon monoxide yielding the respective five-membered zwitterionic carbonyl heterocycle. Similarly cooperative CO addition was observed starting from a norbornane based vicinal P/B FLP. These saturated vicinal P/B FLPs (and several related systems) undergo analogous cooperative 1,1-addition reactions to nitric oxide (NO) to give the corresponding persistent five-membered heterocyclic FLP-NO nitroxide radicals. They were characterized spectroscopically and by X-ray diffraction and shown to undergo typical *N*-oxyl radical reactions. Some vicinal P/B FLPs also undergo 1,1-addition reactions to mesityl azide. Anomalous Staudinger reactions were observed to take place upon subsequent thermolysis or (in one case) photolysis.

1. Introduction

Attachment of sterically bulky substituents may effectively hinder Lewis acids and bases from undergoing the usual LA · LB adduct formation. Such frustrated Lewis pairs (FLPs) [1-4] then contain both the active Lewis acid and Lewis base compounds at the same time in solution. This creates the situation where both the Lewis acid and the Lewis base can separately exhibit their typical reaction pattern, but in addition it offers the interesting possibility to have both compounds of the frustrated Lewis pairs react cooperatively with added substrates. This offers the chance to achieve some unprecedented reaction behavior and to actually find new reactions. The heterolytic splitting of dihydrogen [5-8] by the main group element derived FLPs under mild conditions is a typical example, a reaction that requires transition metals or metal complexes. This reaction has become the basis for developing a variety of main group element catalyzed hydrogenation reactions [9-26]. Some intramolecular vicinal phosphane/borane FLPs such as **1** have shown rather high reactivities in this hydrogen activation [7] and consequently in some metal-free catalytic transformation processes. The intramolecular FLP **1** and its congeners undergo to a great variety of typical 1,2- (or 1,4-) addition reactions to unsaturated

molecules. Addition to carbon dioxide or sulfur dioxide are typical examples, but these FLP systems also add to organic carbonyl compounds, to alkenes, to enynes and diynes and even to α,β -unsaturated ynones (see Scheme 1) [27-30].

Scheme 1. FLP reactions of compound **1** [2,3,4].

With a few donor ligands $\text{X}\equiv\text{Y}$, e.g. isonitriles or carbon monoxide and similar systems, there is an interesting option for competing bonding situations conceivable. These strong σ -donors might just form adducts with the Lewis acid component [31] of the FLP which leads to typical products (**7**, Scheme 2) of Lewis acid chemistry. There might, however, be in some cases the possibility that the adjacent phosphane Lewis base might become involved in the overall bonding situation. Its attack on the Lewis acid activated ligand would then result in the formation of a zwitterionic five-membered heterocyclic product (**8** in Scheme 2). In this case the intramolecular P/B FLP would have undergone a 1,1-addition reaction to the incoming small molecule $\text{X}\equiv\text{Y}$. We have actually found a few such examples upon investigating typical intramolecular vicinal P/B FLP chemistry recently and we have investigated the chemistry of some examples. This will be illustrated and discussed in this account.

Dewar-Chatt-Duncanson model

Scheme 2. Cooperative FLP bonding of CO and other small donor/acceptor ligands [31,42].

2. Reaction of Vicinal P/B FLPs with Isonitriles

For this study we have used the unsaturated vicinal P/B FLPs **13** as substrates. This class of FLPs was conveniently prepared by means of the 1,1-carboboration reaction [32-36] of the respective diarylphosphino-acetylenes **11**. The reaction of a variety of diarylphosphino-acetylenes with e.g. $\text{B}(\text{C}_6\text{F}_5)_3$ resulted in a clean and usually rapid 1,1-carboboration reaction [37,38]. From separate studies using bis(diphenylphosphino)-acetylene (**9**) we knew that the PAr_2 group in these systems was a good migrating group. In a few cases we were even able to observe and isolate the respective phosphirenium borate zwitterions **12** [39-41] which might possibly be considered as intermediates of these specific 1,1-carboboration reactions (see Scheme 3).

Scheme 3. 1,1-Carboboration reactions of phosphino-acetylenes [37,39].

For this study we selected the diphenylphosphino-substituted systems, namely the FLPs **15** and **16** [42]. Both were prepared starting from the *p*-tolyl substituted diphenylphosphino-acetylene **14** (see Scheme 4). Its treatment with $\text{B}(\text{C}_6\text{F}_5)_3$ gave the FLP **15**. The 1,1-carbaboration reaction of **14** with the borane $(\text{C}_6\text{F}_5)_2\text{BCH}_3$ proceeded selectively by methyl group migrating from boron to carbon to give the unsaturated vicinal FLP **16**.

Scheme 4. 1,1-Carbaboration reactions of compound **14** [42].

Both the compounds **15** and **16** were characterized by X-ray diffraction. The molecular structure of compound **15** is depicted in Figure 1. It shows the substitution pattern at the central carbon-carbon double bond that is typical of a 1,1-carbaboration product. The *p*-tolyl group and the diphenylphosphino-substituent (both originating from the acetylene starting material **14**) are now found in geminal position attached at the former acetylene carbon atom C1, whereas the C_6F_5 and $\text{B}(\text{C}_6\text{F}_5)_2$ substituents, which were both introduced by means of the borane reagent, are found geminally positioned at C2. The tetra-coordinated $\text{C}=\text{C}$ double bond is *E*-configured. That brings the bulky $\text{B}(\text{C}_6\text{F}_5)_2$ Lewis acid and the PPh_2 Lewis base in syn-position and we notice a marked $\text{B}\cdots\text{P}$ bonding interaction (d 2.018(2) Å, $\angle \text{B1}^{\text{CCC}} 350.7^\circ$, $\angle \text{P1}^{\text{CCC}} 335.6^\circ$). Compound **16** shows similar structural features [d B1–P1: 2.033(3) Å].

Figure 1. Molecular structure of the vicinal P/B FLP **15** (thermal ellipsoids are shown with 30% probability) [42].

In solution compound **15** shows heteronuclear NMR signals at δ 13.1 [^{31}P] and δ -6.6 [^{11}B], respectively. (**16**: δ 12.3 [^{31}P] and δ -7.6 [^{11}B]). We note that in both compounds the coupling between the P and B centers ($^1J_{\text{PB}}$; $^3J_{\text{PB}}$) is negligible. We then treated the FLP **15** with *tert*-butyl isocyanide and isolated product **17** as a crystalline solid (see Scheme 5). Compound **17** was characterized by X-ray diffraction (see Figure 2). This gave the rather unspectacular result showing that we had simply isolated the adduct of the isonitrile donor to the borane Lewis acid functionality of the FLP **15**. Its phosphane Lewis base function was not involved in the binding of the isonitrile ligand (P1...C3 separation: 3.112 Å). It was left untouched. Consequently, compound **17** featured a pseudo-tetrahedrally coordinated boron center with the newly formed B1–C3 [1.610(6) Å] boron-isonitrile linkage. The B1...P1 separation is quite large at 3.213 Å and the P1 atom shows the typical trigonal-pyramidal coordination geometry ($\Sigma\text{P1}^{\text{CCC}} = 308.1^\circ$). The isonitrile C3–N4 bond length is found at 1.147(5) Å, the B1–C3–N4–C5 unit is practically linear [B1–C3–N4 = 177.9(4)°, C3–N4–C5 = 173.3(4)°].

Figure 2. A projection of the molecular structure of the isonitrile FLP adduct **17** (thermal ellipsoids are shown with 30% probability) [42].

However, when a sample of the adduct **17** was dissolved and the NMR spectra monitored, this revealed the surprising observation that in solution a mixture of **17** with the starting materials **15** and *tert*-butyl isocyanide was observed at room temperature (299 K) (see Figure 3).

Actually, the NMR spectra show a strong temperature dependence. Lowering the measuring temperature we observed a decrease of the concentration first of the starting material **15** and then also the adduct **17** in favor of the NMR resonances of a new species. The newly observed compound showed a prominent ^{31}P NMR signal at δ 10.2 and a ^{11}B NMR signal at δ -13.3 at 213 K. In this compound (**18**) we observed coupling between the pair of hetero atoms. The ^{31}P NMR signal appears as a 1:1:1:1 quartet showing a $^2J_{\text{PB}}$ coupling constant of ca. 45 Hz and, consequently, the ^{11}B NMR signal is a corresponding doublet. At 299 K the ratio of the three components was found as **15:17:18** = 37:63:0. It changed with decreasing temperature to mixtures having compound **18** markedly populated (213 K: **15:17:18** = 11:72:17).

Figure 3. Temperature dependent $^{11}\text{B}\{^1\text{H}\}$ NMR (left) and $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2) (192 MHz, CD_2Cl_2) (right) NMR spectra of the **15:17:18** mixture [42,43].

Scheme 5. Reaction of **15** and **16** with *tert*-butyl isocyanide [42].

The reaction between the FLP **16** and *tert*-butyl isocyanide proceeds similarly. We have isolated the pure isonitrile adduct **19** to the boron Lewis acid (see Scheme 5). Again, the system equilibrated with the starting material and the P/B bonded product **20** when brought back into solution. In this case the situation was quite extreme. At 299 K in solution we have only observed the starting compound **16**/isonitrile and the cooperative P/B addition product **20** in a ratio of 55:45. The latter shows a pair of coupled NMR signals of the PPh_2 ($\delta^{31}\text{P}$: +9.6) and the $\text{B}(\text{C}_6\text{F}_5)_2$ units ($\delta^{11}\text{B}$: -13.7). The **16:20** ratio changed slightly upon

lowering the temperature. At 193 K it amounted to 33:67 (with a trace of the simple isonitrile/borane Lewis acid adduct visible [42].

The equilibrium situation was changed drastically in favor of the cooperative P/B FLP 1,1-addition products when we employed the less sterically encumbered *n*-butyl isocyanide reagent instead of the much more bulky *tert*-butyl analogue. Reaction of the P/B FLP **15** with *n*-butyl-NC gave a solution that contained almost completely the five-membered heterocyclic 1,1-addition product **21**. It showed the typical ^{11}B NMR doublet at $\delta -13.6$ and its corresponding ^{31}P NMR 1:1:1:1 intensity quartet with $^2J_{\text{PB}} \sim 40$ Hz. There was a very minor component with very similar NMR features. We assigned the structures of the *E*-**21** and *Z*-**21** to this pair of products of the cooperative P/B FLP addition reactions. The *E*-**21** product was characterized by X-ray diffraction (see Figure 4). It showed the presence of the newly formed central heterocyclic five-membered ring. Carbon atoms C1 and C2 have the pair of aromatic substituents attached. The nitrogen atom of the newly formed imine moiety bears the *n*-butyl substituent, which is found in a largely extended conformation. The bonding angle at nitrogen is $118.4(4)^\circ$. The imine carbon atom shows a planar-tricoordinate bonding geometry as expected. However, two of its individual bonding angles differ markedly from the typical $\text{C}(\text{sp}^2)$ angle. Actually the new $\text{C}=\text{N}^n\text{Bu}$ moiety is substantially leaning over toward the phosphorus side [$\text{B1-C3-N4 } 136.5(4)^\circ$, $\text{P1-C3-N4 } 114.0(3)^\circ$, $\text{B1-C3-P1 } 109.5(3)^\circ$] as if the phosphane nucleophile might first have attacked the borane activated isonitrile unit. The P1-C3 bond of compound *E*-**21** is rather long at $1.818(5)$ Å, whereas the B1-C3 linkage is [$1.652(7)$ Å]. The C3-N4 bond [$1.283(6)$ Å] is as expected for an imine type $\text{C}=\text{N}$ double bond [42].

Scheme 6. Reaction of **15** and **16** with *n*-butyl isocyanide [42].

Figure 4. A view of the molecular structure of compound *E*-**21** (thermal ellipsoids are shown with 30% probability) [42].

The methyl substituted analogue **16** reacted similarly with *n*-butyl isocyanide. In solution we monitored the very typical heteronuclear magnetic resonance signals of only the *E*- and *Z*-**22** isomers. (see Scheme 6 and Figure 5)

The major isomer showed ^{11}B and ^{31}P NMR signals at $\delta -13.9$ (d, $^2J_{\text{PB}} \sim 45$ Hz) and $\delta 11.7$ (1:1:1:1 quartet), respectively. Compound *E*-**22** was also characterized by X-ray diffraction [B1–C3 1.653(4) Å, C3–P1 1.273(3) Å, C3–N4 1.273(3) Å, angles B1–C3–P1 107.81(16)°, P1–C3–N4 112.81(19)°, B1–C3–N4 139.3(2)°].

Figure 5. $^{11}\text{B}\{^1\text{H}\}$ (192 MHz, CD_2Cl_2) (left) and $^{31}\text{P}\{^1\text{H}\}$ (243 MHz, CD_2Cl_2) (right) NMR spectra of *E*-/*Z*-**22** product mixture [42,43].

These systems are remarkable with regard to several issues. The 1,1-addition products (**18**, **20-22**) require a combined coordinated action of both the phosphane Lewis base and the borane Lewis acid. Phosphane nucleophiles usually do not add to isonitrile donors but borane electrophiles do [44,45]. Therefore, these systems may be regarded as the products of a cooperative reaction of the compounds of the P/B FLP with the added isonitrile reagents. We do not know at this time about the mechanistic pathway of the formation of these products, but in the case of the *tert*-butyl isocyanide adducts we have observed the equilibrium of the heterocyclic FLP 1,1-addition product to the isonitrile carbon atom with the conventional borane/isonitrile addition product and even with the free isonitrile/P/B FLP mixture. In the systems **17** and **19** both the borane and the phosphane seem to follow their usual separate reactivities with an isonitrile, so one may classify their reaction pattern as *additive* in contrast to the *cooperative* product formation of e.g. their heterocyclic isomers **18** and **20**. In a (very) formal sense one might drive this classification in the **15** + isonitrile $\rightleftharpoons$ **17** $\rightleftharpoons$ **18** (resp. **16** + isonitrile $\rightleftharpoons$ **19** $\rightleftharpoons$ **20**) equilibrium further and determine that the borane in **15/16** is hindered from isonitrile addition because of the internal phosphane coordination; this would then characterize an *anti-cooperative* behavior of the FLP components in these remarkable systems [46-48]. We also recognize that the FLP/isonitrile coordination behavior seems markedly

dependent on the steric bulk of the alkyl substituent of the isonitrile reagent: with *n*-butyl isocyanide we have only observed the cooperative 1,1-addition of the phosphane/borane Lewis pair to the isonitrile carbon atom.

3. Reaction of Selected Vicinal P/B FLPs with Carbon Monoxide

We do not want to overstress the notion of a metal reminiscent coordination behavior of vicinal P/B frustrated Lewis pairs, although there is a remote similarity of the bonding features of e.g. the metal ligand interaction in e.g. a metal carbonyl (as it is described by the Dewar-Chatt-Duncanson model) [49,50] with the cooperative P/B isonitrile bonding features observed in the compounds **18** and **20** - **22**. (see above)

Isonitriles are very reactive systems, however, which may not necessarily serve as good carbon monoxide analogues. Indeed the unsaturated vicinal P/B FLPs **15** and **16** used in this study did not react with carbon monoxide under our typical reaction conditions. We observed neither cooperative P/B CO bonding nor simple borane Lewis acid CO coordination.

This changed when we employed several saturated vicinal P/B FLP systems and exposed them to CO under carefully controlled reaction conditions. Our parent saturated ethylene-bridged P/B FLP **1** reacted with carbon monoxide (2 bar) in pentane solution [51]. The carbonylation product **23** precipitated over a period of 5 d at $-40\text{ }^{\circ}\text{C}$. It was isolated as a yellow crystalline solid in 74% yield. Compound **23** showed an intense IR carbonyl stretching band at $\tilde{\nu} = 1757\text{ cm}^{-1}$. It featured heteronuclear magnetic resonance features at $\delta -13.3$ (^{11}B) and $\delta -2.3$ (^{31}P), respectively, and a carbonyl ^{13}C NMR resonance signal at $\delta 228.9$ with a $^1J_{\text{PC}}$ coupling constant of 98 Hz.

Compound **23** was characterized by X-ray diffraction (see Scheme 7, Figure 6). It shows a central heterocyclic five-membered ring that was formed by bond formation of the carbonyl carbon atom with both the borane Lewis acid and the phosphane Lewis base of the FLP starting material **1**. The B1–C3 bond length [1.662(3) Å] is in the typical boron-carbon single bond range [*cf.* B1–C2 in **23** is 1.624(3) Å]. The C3–O1 carbonyl linkage is 1.191(2) Å, a value between a C $\equiv$ O double and triple bond, which is a bit reminiscent of a metal carbonyl feature. The coordination geometry of the carbonyl carbon atom C3 is trigonal planar (sum of bond angles $\Sigma\text{C3}^{\text{POB}} = 360.1^{\circ}$, but with two of the bond angles deviating markedly from the typical 120° value: the internal B1-C3-P1 angle is enforced by

the five-membered ring structure. However, marked leaning over of the C=O unit toward the phosphane side [angles B1-C3-O1 135.7(2)°, P1-C3-O1 119.2(1)°] probably represents a typical CO/FLP coordination features. It seems as if a CO molecule added to the boron Lewis acid had been captured by the adjacent phosphane Lewis base similarly as it was depicted for compound **21** in Figure 4 for the cooperative bonding case.

Scheme 7. Carbonylation of the FLP **1** [51].

Figure 6. Molecular structure of the FLP/CO addition product **23** (thermal ellipsoids are shown with 30% probability) [51].

We have also treated the FLP **24** with carbon monoxide [51]. It formed the cooperative P/B CO adduct **25** in pentane solution. The reaction is reversible above ca. 240 K, so the product was isolated by crystallization at low temperature. It was obtained as a crystalline solid in 63% yield. It shows a CO stretch in the IR spectrum at 1791 cm⁻¹ and NMR signals at δ -12.8 (¹¹B), δ -6.4 (³¹P) and δ 224.7 (¹³C of the C=O group with ¹J_{PC} ≈ 111 Hz).

The X-ray crystal structure analysis of compound **25** shows similar structural features as compound **23** (see Scheme 8, Figure 7), only that the carbonyl C≡O

bond length in **25** is even shorter at 1.174(2) Å (C8–O1) (*cf.* free CO: 1.128 Å) [52] which seems to support the notion of the FLP-CO/metal-carbonyl coordination resemblance. The B1–C8 bond length in **25** is in the usual range [1.684(2) Å], whereas the P1–C8 distance of 2.104(2) Å is even longer than the respective P1–C3 bond in **23**. In **25** the coordination geometry of the trigonal planar carbonyl carbon atom is again quite unsymmetrical [angle B1–C8–O1 135.3(2)°, B1–C8–P1 106.4(1)°].

Scheme 8. Carbonylation of compound **24** [51].

Figure 7. Molecular structure of compound **25** (thermal ellipsoids are shown with 30% probability) [51].

Stephan *et al.* reported a related case of a cooperative CO binding in the intramolecular N/B FLP systems **26** (R = *i*Pr or *t*Bu). Its reaction with carbon monoxide cleanly gave the heterocyclic addition products **27** (R = *i*Pr or *t*Bu; see Scheme 9, IR (R = *i*Pr): $\tilde{\nu}$ = 1714 cm⁻¹) [53].

Scheme 9. Carbonylation of compound **26** [53].

In solution we have not obtained any sign of the formation of the respective simple borane carbonyl isomers of the compounds **23** or **25**. However, these systems were detected in matrix isolation experiments. We had found that the hydrogen addition product **28** showed a remarkable dependency of its stability on the aggregation state. The phosphonium/hydrido borate system was stable in solution, almost regardless of the solvent polarity. A DFT study had confirmed that, but also revealed that such systems were much less stable with regard to the reverse reaction, i.e. the liberation of dihydrogen in the gas phase [54]. We used this remarkable feature to transport the sensitive P/B FLP **24** through the gas phase into a CO doped argon matrix [51]. For this purpose e.g. the FLP hydrogen cleavage product **28** was sublimed at 120 - 150 °C and trapped in an argon matrix at 10 K. We observed the IR spectrum of the hydrogen-free FLP product **24** and separately of free CO in the matrix ($\tilde{\nu} = 2138 \text{ cm}^{-1}$). Warming the matrix to 35 K resulted in the observation of a new strong IR feature at ($\tilde{\nu} \approx 2196 \text{ cm}^{-1}$) which we have assigned to the formation of the FLP-borane carbonyl compound **29** (see Scheme 10). The IR (C=O stretch) of **29** is above that of free CO. This indicates strengthening of the CO carbon-oxygen bond in the product as it is typically observed in many Lewis acid CO adducts or “non-classical” metal carbonyls, respectively [55-58].

Scheme 10. Reaction of compound **24** with CO at low temperature [51].

Since 1937 it is known by work of Schlesinger *et al.* [31] that diborane reacts with CO to form borane carbonyl (**30**). No further reaction of the borane bonded

carbon monoxide molecules was observed. Borane carbonyl is a gas (b.p. $\approx -64\text{ }^{\circ}\text{C}$, IR: $\tilde{\nu}(\text{CO}) \approx 2151\text{ cm}^{-1}$) [59].

We have recently found a similar behavior upon treatment of Piers' borane $[\text{HB}(\text{C}_6\text{F}_5)_2]$ [60,61] with carbon monoxide, which simply gave "Piers' borane-carbonyl" **32**. It was isolated by crystallization at low temperature ($-40\text{ }^{\circ}\text{C}$) and characterized by X-ray diffraction (see Scheme 11 and Figure 8) [62]. It shows a CO bond length of $\text{C1-O1} = 1.107(2)\text{ \AA}$ ($\text{B1-C1} 1.601(2)\text{ \AA}$, angle $\text{B1-C1-O1 } 174.7(2)^{\circ}$). In solution Piers' borane-carbonyl exhibits a ^{13}C NMR carbonyl resonance at $\delta 169.2$ (223 K) and ^{11}B NMR signal at $\delta -30.6$ ($^1J_{\text{BH}} = 95\text{ Hz}$) at 253 K. Again, no subsequent reduction of CO was observed in this $[\text{B}]\text{H}$ borane/CO system.

Scheme 11. Borane carbonyl formation [31,62].

Figure 8. Molecular structure of the borane carbonyl **32** (thermal ellipsoids are shown with 30% probability) [62].

The situation changed in the presence of a vicinal FLP. Treatment of **24** with CO and Piers' borane resulted in the clean reduction of CO to the formyl borane stage [63].

We isolated the formyl borane product **33**, stabilized at the FLP template. The systems **1** and **35** reacted analogously and we isolated the respective FLP template substituted η^2 -formyl borane systems **34** and **37**. A detailed DFT study by S. Grimme *et al.* has revealed that the formation of Piers' borane carbonyl **32** from its components is exergonic by $\Delta G \approx -7 \text{ kcal mol}^{-1}$ in toluene solution, whereas the subsequent CO reduction to the formyl borane product would be endergonic by ca. $+13 \text{ kcal mol}^{-1}$. This thermodynamic restriction was apparently overcome by attaching the system to the FLP template. Formation of the adduct **36** is exergonic by ca. -6 kcal mol^{-1} and by additional ca. $-17 \text{ kcal mol}^{-1}$ in the actual CO reduction step giving the FLP template coordinated formyl borane product **37** (see Scheme 12) [63].

Scheme 12. CO reduction at FLP templates [63].

The (η^2 -formyl)borane product **33** was characterized by X-ray diffraction (see Figure 9). It liberated the genuine formyl borane product **38** upon treatment with excess pyridine (see Scheme 13). The pyridine stabilized formyl borane **38** was also characterized by X-ray diffraction [$d(\text{C}=\text{O}) = 1.210(2) \text{ \AA}$]. It shows typical spectroscopic carbaldehyde features ($^1\text{H}/^{13}\text{C}$ NMR of the CHO group: δ 11.24/233.1) and it behaves chemically as a reactive aldehyde.

Figure 9. Molecular structure of the FLP template stabilized (η^2 -formyl)borane product **33** (thermal ellipsoids are shown with 30% probability) [63].

Scheme 13. Formation of a stabilized formyl borane [62].

4. FLP Reactions with Nitric oxide: Formation of the Persistent P/B FLP-NO Nitroxide Radicals.

In organometallic chemistry, nitric oxide (NO) serves as one of the most interesting ligands due to the variability of its binding mode as well as reactivity patterns. Depending on the nature of the transition metal, the reactivity properties of NO can vary from being electrophilic, nucleophilic or radical in nature depending on the extent of backbonding [64,65]. Nonetheless, NO has relatively limited direct synthetic applications, especially considering its high degree of unsaturation [66], despite its massive scale of industrial production as an intermediate in nitric acid production.

Scheme 14. Organic NO reactions [67,72].

Nitric oxide can be also captured by metal-free scaffolds. Highly reactive o-quinodimethanes such as **40** result in the formation of an organic nitroxide **41** upon closure of a 5-membered heterocycle by captured NO (see Scheme 14) [67,68]. The resulting nitroxide bears resemblance to perhaps the most ubiquitous stable nitroxide (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO **42**) [69-71]. The radical character of TEMPO makes it useful in a variety of chemical and biochemical applications such as an initiator for radical polymerization and as a spin-probe [70,71]. Alternatively, radical cations based on 1,2-diarylethenes such as **43** or calix[4]arenes bind NO via electron transfer where NO is formally oxidized to NO^+ that has a high affinity for arenes; electrophilic NO reactivity results for captured NO in the resulting nitrosonium arene complexes such as **44** (see Scheme 14) [72-74].

Initial attempts at capture of NO by the frustrated Lewis pair approach employed the intermolecular FLP system ${}^t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ which resulted in a 40% conversion to a 1:1 mixture of the species ${}^t\text{Bu}_3\text{P}-\text{N}_2\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$ (**45**) and ${}^t\text{Bu}_3\text{P}-\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$ (**46**) (see Scheme 15) [75]. These observations reflect the long known reaction of 2 equiv. NO with phosphanes R_3P that gives the phosphane oxide $\text{R}_3\text{P}=\text{O}$ along with N_2O . Accordingly, the product ${}^t\text{Bu}_3\text{P}-\text{N}_2\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$ (**45**) can be also synthesized by stirring a solution of “open” FLP system under an atmosphere of N_2O for a day [76].

Scheme 15. Reaction of intermolecular FLP with NO [75].

Successful FLP capture of NO [77] takes place with the intramolecular P/B FLP $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B(C}_6\text{F}_5)_2$ (**1**) [7] developed by the Erker group. The FLP-NO compound **47** can be easily prepared *in situ* by exposure of a solution of FLP **1** either in fluorobenzene or pentane to NO_g by bubbling directly to the solution or stirring it under an NO atmosphere (see Scheme 16) [75,78].

Scheme 16. Formation of the FLP-NO nitroxide radical **47** [75,77].

X-ray crystallography reveals that 1,1-addition of NO to the FLP **1** occurred to give both P–N [1.712(14) Å] and B–N [1.592(2) Å] bonds in the five membered heterocycle **47** (see Figure 10). The exocyclic N–O bond dramatically lengthened to 1.296(17) Å as compared to 1.15 Å in free NO. The IR spectrum of **47** supports this reduction in NO bond order with $\tilde{\nu}_{\text{NO}} = 1474 \text{ cm}^{-1}$ ($\tilde{\nu}_{15\text{NO}} = 1457 \text{ cm}^{-1}$) as compared to free NO ($\tilde{\nu}_{\text{NO}} = 1875 \text{ cm}^{-1}$). Optical spectroscopy gives a weak band at 705 nm ($\epsilon = 6.7 \text{ M}^{-1}\text{cm}^{-1}$) due to the NO $n \rightarrow \pi^*$ transition that results in further reduction of the N–O bond order in the excited state as revealed through vibrational fine structure with an average spacing of 1109(11) cm^{-1} [75].

Figure 10. X-ray crystal structure of FLP-NO adduct **47** (thermal ellipsoids are shown with 15% probability) [75].

Most indicative of the radical nature of **47** is the multi-line solution X-band EPR spectrum (see Figure 11) at room temperature that results from coupling of the electron spin to the ^{14}N , ^{31}P and $^{11/10}\text{B}$ nuclei [75]. Simulation of the signal centered at $g = 2.0089$ gives $A(^{14}\text{N}) = 18.5$ MHz, $A(^{31}\text{P}) = 48.5$ MHz, and $A(^{11}\text{B}) = 9.1$ MHz. Substitution of ^{15}NO in the synthesis of FLP-NO **47** changes the appearance of the EPR spectrum and allows $A(^{15}\text{N}) = 25.5$ MHz to be extracted through simulation, essentially identical to the expected value of 26.0 MHz based on the gyromagnetic ratios of ^{15}N and ^{14}N ($|\gamma_{15\text{N}}| / |\gamma_{14\text{N}}| = 1.4$). Notably, the $A(^{14}\text{N})$ hyperfine coupling observed in **47** is significantly depressed from that found in TEMPO ($A(^{14}\text{N}) = 43.5$ MHz) [79].

Figure 11. Experimental and simulated X-band EPR spectra of FLP-NO **47** (6.5 mM in fluorobenzene, RT) illustrating the effect of isotopic substitution at N [75].

The electronic structure of **47** was further elucidated through high level DFT calculations by S. Grimme *et al.* at the dispersion corrected (DFT-D3 [80,81] method) TPSS [82] level. A spin density “Umpolung” of NO upon FLP capture occurs giving N and O spin densities of 0.34 and 0.54 e^- (see Figure 12), respectively as compared to 0.71 and 0.29 e^- for free NO. While the electronic structure of **47** bears similarity to the nitroxide TEMPO, the spin density in the FLP-NO adduct **47** is more polarized towards O (TEMPO: 0.44 and 0.50 e^- at N and O, respectively).

Figure 12. Spin density plot of FLP-NO **47** from DFT (TPSS/def2-TZVP) [75].

A family of FLP-NO species **48** - **52** may be prepared by the addition of NO to the corresponding intramolecular frustrated Lewis pairs with saturated P-B linkers (see Figure 13) [75,78,83]. These *N*-oxyl products all featured a

five-membered heterocyclic ring with the N-O moiety oriented very similar to common organic *N*-oxyl radicals such as TEMPO. The N–O distances range from 1.291(3) to 1.325(3) Å with similar P–N and B–N distances seen in **47**. EPR spectra of **47** - **52** all exhibit multi-line X-band EPR spectra centered at $g = 2.0078 - 2.0089$ with similar values of $A(^{14}\text{N})$ [18.5 - 20.7 MHz], $A(^{31}\text{P})$ [47.0 - 51.0 MHz], and $A(^{11}\text{B})$ [8.9 - 9.5 MHz].

Figure13. Family of P/B FLP-NO adducts [78,83].

In the case of systems with unsaturated backbones linking the phosphane and borane moieties such as **53** - **55**, direct reaction with NO does not typically lead to the FLP-NO adduct as the initial product (see Scheme 17) [84]. The tighter P···B interaction enforced by the shorter, more rigid backbone discourages FLP capture of NO. Initial reaction of 2 equiv. NO with the pendant PMes_2 groups in **54** and **55** results in formation of the corresponding phosphane oxide species **56** and **57**. Coordination of the pendant $\text{P}(=\text{O})\text{Mes}_2$ group in **56** and **57** to the borane center loosens the P···B interaction and allows for NO capture leading to FLP-NO adducts **58** and **59** [84]. Accordingly, addition of excess NO to FLPs **54** and **55** each bearing a pendant PMes_2 group leads to phosphane oxide/FLP-NO adducts **58** and **59** in 81% and 87% yield, respectively.

Scheme 17. Reactions of unsaturated FLPs with NO [84].

NO capture appears to be more sensitive to the FLP structure than heterolytic cleavage of H_2 . For instance, addition of excess NO (1.5 bar) to FLP **60** with a 3 carbon linker leads only to oxidation to the phosphane oxide **61** whereas H_2 addition readily occurs at room temperature (1.5 bar) to give the phosphonium borate **62** (see Scheme 18) [84].

Scheme 18. Reactions of the FLP **60** with NO and with H_2 [84].

Capture of NO by most intramolecular phosphane-borane FLPs is irreversible as suggested for the significant free energy change associated with NO binding. For instance, capture of NO by FLP **1** to give FLP-NO **47** results in a calculated $\Delta G = -11.9 \text{ kcal mol}^{-1}$ [75]. Accordingly, crossover experiments between FLP **1** and FLP-NO **51** as well as the complementary FLP **63** / FLP-NO **47** pair show no evidence of exchange after standing 16 h in solution (see Scheme 19) [78].

Scheme 19. Crossover experiments with FLPs and FLP-NO radicals [78].

To gain insight into the mechanism of NO capture, the reaction between the bicyclic FLP **24** with NO has been kinetically examined [85]. Addition of NO to FLP **24** is a second order reaction with an overall rate law $v = k[\text{NO}][\text{FLP}]$. The second order rate constant was found highly solvent dependent, with a larger rate constant in lower polarity solvents ($k = 0.51(5)$ and $48.9(1.8) \text{ M}^{-1}\text{s}^{-1}$ in dichloromethane and toluene at 293 K, respectively). Eyring analysis provided activation parameters of $\Delta H^\ddagger = 13.1(3) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -6.1(10) \text{ cal K}^{-1} \text{ mol}^{-1}$ in toluene to give $\Delta G^\ddagger = 14.9(3) \text{ kcal mol}^{-1}$ at 298 K. Computational analysis favored the formation of a weakly bound $\text{B}\cdots\text{NO}$ adduct **64** over a $\text{P}\cdots\text{NO}$ intermediate **65** prior to ring closure to give FLP-NO **52** which gives an overall calculated activation barrier $\Delta G^\ddagger = 11.8 \text{ kcal mol}^{-1}$ at 298 K (see Scheme 20). Concerted addition of NO to FLP **24** was also considered that requires a conformational change involving rotation about one of the P-Mes vectors ($\Delta G^\ddagger \approx 10 - 11 \text{ kcal mol}^{-1}$) and would proceed by nearly barrierless NO addition. This concerted mechanism predicts an overall first order reaction ($\text{rate} = k[\text{PB}]$), inconsistent with the experimentally observed second order overall kinetics.

24 → **52**: $\Delta G = -22.6 \text{ kcal mol}^{-1}$; $\Delta G^\ddagger = 11.8 \text{ kcal mol}^{-1}$
(overall via B...NO intermediate)

Scheme 20. Capture of NO by FLP **24** favors weakly bound B...NO intermediate. (All free energies by DFT calculated at 298 K) [85].

The O-centered radical nature of FLP-NO species leads to relatively strong O-H bonds in the reduced hydroxylamine species FLP-NOH [75,78]. For instance, in FLP-NOH **66** derived from FLP-NO **47**, the calculated O-H bond strength is $77.3 \text{ kcal mol}^{-1}$ [75]. This is approximately 10 kcal mol^{-1} higher than the reduced hydroxylamine derived from TEMPO calculated at $67.2 \text{ kcal mol}^{-1}$ that compares well with experimental values in benzene [86]. Therefore, FLP-NO species possess significant driving force for H-atom abstraction reactions. FLP-NO species **47** – **52** rapidly react with 1,4-cyclohexadiene (doubly allylic C-H bond strength = 77 kcal mol^{-1}) [87] to give the corresponding FLP-NOH species and benzene (see Schemes 13 and 21).

Scheme 21. Hydrogen abstraction reaction of the persistent FLP-NO radical **47** [75,78].

The N–O bond length of 1.422(2) Å in FLP-NOH **66** is increased from 1.296(2) Å in the corresponding FLP-NO adduct **47** [75]. IR spectroscopy further supports a reduction of the N-O bond order. While $\tilde{\nu}({}^{14}\text{NO}) = 1474\text{ cm}^{-1}$ ($\tilde{\nu}({}^{15}\text{NO}) = 1457\text{ cm}^{-1}$) for FLP-NO **47**, a lower energy vibration $\tilde{\nu}({}^{14}\text{NO}) = 1110\text{ cm}^{-1}$ ($\tilde{\nu}({}^{15}\text{NO}) = 1082\text{ cm}^{-1}$) is observed for FLP-NOH **66**. Curiously, the low energy N-O stretch observed for the reduced species **66** is nearly identical to the average vibronic spacing observed in the optical spectrum of FLP-NO **47** that is due to N-O vibrational modes excited state of FLP-NO **47**.

This H-atom abstraction behavior can be utilized to create new O–C bonds derived from nitric oxide. While TEMPO sluggishly reacts with benzylic C–H bonds, requiring heating at 120 – 130 °C in neat ethylbenzene, [88,89] prototypical FLP-NO **47** reacts with cyclohexene or ethylbenzene at room temperature to give an equivalent of FLP-NOH **66** and the corresponding O-bound allylic or benzylic products **67** and **68** (see Scheme 22) [75]. Heating FLP-NO in neat toluene (C–H BDE = 90 kcal mol⁻¹) at ca. 80 °C for 1 h also results in formation of FLP-NO-CH₂Ph species **69** [75,78]. These reactions are general for this family of phosphino-borane FLP-NO species.

Scheme 22. Radical reactions of **47** [75,78].

FLP-NO **47** abstracts hydrogen atoms from mildly activated C–H bonds in substrates R–H to produce FLP-NOH **66** and the corresponding O-alkyl hydroxylamine FLP-NOR via second order overall kinetics with rate law: rate $v =$

[FLP-NO][RH] [75]. The rate of the reaction is heavily dependent on the C–H bond strength of the substrate R–H. Reaction with cyclohexene (C–H BDE = 82 kcal mol⁻¹) [87] is swift with excess substrate ($k_{298\text{K}} = 4.1(3) \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$) while reaction with ethylbenzene (C–H BDE = 87 kcal mol⁻¹) [87] requires longer reaction times at the same temperature ($k_{298\text{K}} = 5.6(2) \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$) [75]. Reactions in neat toluene (C–H BDE = 90 kcal mol⁻¹) [87] required heating for 1-2 hours at 80 °C [78]. Considering the primary kinetic isotope effect observed in the reaction of FLP-NO **47** with ethylbenzene ($k_{\text{H}} / k_{\text{D}} = 3.8(3)$ at 298 K), these reactions likely proceed via initial H-atom abstraction of R–H by FLP-NO to give FLP-NOH along with R• that is rapidly captured by a second equivalent of FLP-NO to give FLP-NOR.

The O-centered radical reactivity of FLP-NO species can also be employed in nitroxide mediated styrene polymerization (see Scheme 23) [78]. As with related O-alkylated hydroxylamines, the C–O bond of the 2° benzyl species FLP-NO-CH(Me)Ph **70** can be cleaved at higher temperatures to release the ethylbenzene radical Ph(Me)CH• (**71**) with formation of FLP-NO **51**. The activation energy of 34.9 kcal mol⁻¹ for release of this benzylic radical is similar to that of TEMPO-styryl system (31.8 kcal mol⁻¹) [90,91]. The released benzylic radical may add to styrene to form a new benzylic radical that may be transiently captured by the FLP-NO species **51** generated upon expulsion of the benzylic radical **71** from **70**. Carrying out the polymerization reaction in neat styrene at 120 – 130 °C gave polystyrene with a narrow polydispersity index of 1.30 when controlled by a small amount of added FLP-NO radical **51** [78].

Scheme 23. NMP reaction of styrene with compound **70** [78].

5. 1,1-FLP Addition Reactions to Mesityl Azide

We had prepared the geminal P/B FLP **73** by treatment of the alkenyl phosphane **72** with $[\text{HB}(\text{C}_6\text{F}_5)_2]$. The very electron poor $(\text{C}_6\text{F}_5)_2\text{P}$ -substituent directed the hydroboration reaction toward the formation of the unusual C₁-bridged FLP **73**. The system **73** added mesityl azide in a 1,3-fashion yielding the six-membered heterocyclic product **74** (see Scheme 24) [92]. It turned out that the regioselectivity of the hydroboration reaction of this electron-deficient type of alkenyl phosphanes bearing the $(\text{C}_6\text{F}_5)_2\text{P}$ moiety was very dependent on the alkenyl substitution pattern. The alkenyl phosphane isomer **75** added Piers' borane $[\text{HB}(\text{C}_6\text{F}_5)_2]$ to cleanly yield the vicinal P/B FLP **76**. Compound **76** also underwent a cooperative mesityl azide addition reaction; in this case a clean 1,1-P/B addition to the terminal azide nitrogen atom was observed yielding the five-membered heterocyclic product **77** (see Scheme 24 and Figure 14) [45,93].

Figure 14. Molecular structure of the mesityl azide 1,1-P/B FLP addition product **77** (thermal ellipsoids are shown with 15% probability) [93].

Scheme 24. Anomalous Staudinger reaction of a FLP/mesityl azide system [92,93].

Figure 15. A view of the molecular structure of anomalous Staudinger product **78** (thermal ellipsoids are shown with 15% probability) [93].

Compound **77** can be regarded as a trapping product along the way of a Staudinger reaction [94-97]. It may have been formed by azide attachment to the phosphane, but then trapping of the azide unit by the electrophilic borane might have prevented this system to follow the usual Staudinger reaction pathway and we have isolated the 1,1-P/B FLP addition product instead. However, thermolysis of **77** resulted in a competing reaction pathway, namely in an anomalous Staudinger reaction [45,93,98-101]. This resulted in N–N bond cleavage and formation of the respective [P]=NH phosphinimine **78** that was internally N-coordinated to the adjacent boron Lewis acid (see Scheme 24 and Figure 15) The N–N cleavage finally liberated a N₂-Mes fragment which was found stabilized as the respective dimethylindazole derivative **79**. Compound **79** was isolated by sublimation and structurally identified by formation of its B(C₆F₅)₃ adduct **80** by X-ray diffraction (see Scheme 24 and Figure 16) [45,93].

Figure 16. Molecular structure of the dimethylimidazole/ $\text{B}(\text{C}_6\text{F}_5)_3$ adduct **80** (thermal ellipsoids are shown with 30% probability) [93].

Our parent vicinal P/B FLP **1** also underwent a 1,1-addition to mesityl azide to form the product **81** (see Scheme 25). In this case the five-membered heterocyclic azide addition product underwent an anomalous Staudinger reaction upon photolysis to give a mixture of the internal phosphinimine/borane adduct **82** and the dimethylimidazole derivative **79** [93].

Scheme 25. Photolytic anomalous Staudinger reaction of compound **81** [93].

6. Conclusions

The unsaturated vicinal P/B FLPs are quite unique that they show three different reaction modes upon exposure to the sterically somewhat bulky *tert*-butyl isocyanide reagent under equilibrium conditions. We have found the mixture of the starting materials equilibrating on a “chemical” time scale with the conventional isonitrile addition product (**17** or **19**) to the borane Lewis acid and with the unconventional P/B isonitrile addition product, the five-membered heterocycles **18** or **20** respectively. In a formal sense these three reaction modes

may be classified as cooperative (**18** or **20**), additive (**17** or **19**) and anti-cooperative (**15** or **16** + ^tBuNC), respectively. Toward the less sterically demanding *n*-butyl isocyanide reagent the systems **15** or **16** showed only cooperative behavior giving rise to the sole formation of the zwitterionic heterocycles **18** or **20** respectively (found as various *E*-/*Z*- mixtures). The formation of the cooperative products of these (and related) vicinal P/B FLPs is in a way reminiscent to the isonitrile coordination behavior to transition metals. This notion is apparently supported by the fact that we have even observed a few similar cooperative reactions of FLPs with carbon monoxide. It seems that the saturated vicinal P/B FLP **1** and **24** (and a few related systems) form the respective five-membered heterocyclic carbonyl products by a combination of a dative bond from the CO nucleophile to the boron Lewis acid which becomes supported by a back-bonding feature by interaction of the phosphane donor with the carbonyl π^* -acceptor orbital, a situation which is not identical with but reminiscent of the bonding situation in a transition metal carbonyl complex as it is commonly described by the Dewar-Chatt-Duncanson model. Main group element containing FLPs have been shown to exhibit quite some reactions that were previously considered typical for reagents in a metal containing regime, H₂-activation being the most prominent feature. Now it seems that this similarity might extend into coordination chemistry as well.

In view of these observations in FLP/isonitrile or CO chemistry it is not too surprising that many saturated vicinal P/B FLPs undergo clean 1,1-addition reactions to nitric oxide (NO) to yield the persistent five-membered heterocyclic FLP-NO nitroxide radicals, which show a behavior closely related to the organic nitroxyls such as TEMPO and PINO.

Cooperative reactivity is a trademark of many frustrated Lewis pairs, be they intra- or intermolecular systems. This has first been shown for heterolytic cleavage of dihydrogen and later for a great variety of 1,2- (and some 1,4-) addition reactions of FLPs to unsaturated substrates, among them CO₂, SO₂, alkenes, alkynes etc. Now it has become apparent that 1,1-addition reactions such as shown for the examples presented and discussed in this account represent another important feature of frustrated Lewis pair chemistry

Acknowledgement

Gerhard Erker and Timothy H. Warren cordially thank their coworkers for their contributions to the chemistry described in this article. G.E. thanks the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt-Stiftung and the European Research Council for financial support. T.H.W. thanks the US National Science Foundation (CHE-0957606) and the American Chemical Society Petroleum Research Fund (PRF#51971-ND3) for financial support as well as W.R. Grace for gifts of $\text{B}(\text{C}_6\text{F}_5)_3$.

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