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Small-Molecule Trapping **Hot Paper**

Frustrated Lewis Pair Activation of an *N*-Sulfinylamine: A Source of Sulfur Monoxide**

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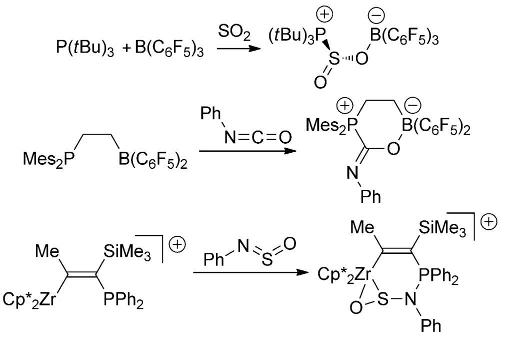
Abstract: *Inter- and intramolecular P/B frustrated Lewis pairs are shown to react with an N-sulfinylamine to form PNSOB linakages. These species can be regarded as phosphinimine–borane-stabilized sulfur monoxide complexes, and indeed these species act as sources of SO, effecting the oxidation of PPh_3 and delivering SO to $[RhCl(PPh_3)_3]$ and an N-heterocyclic carbene.*

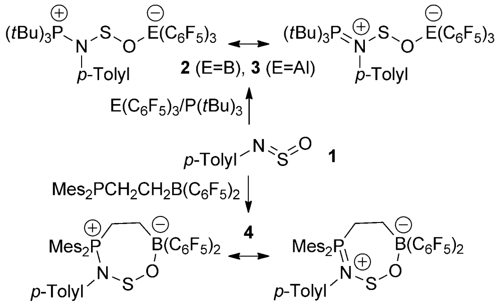
Reactive intermediates are integral to a variety of commonly used reactions, yet their fleeting existence is often difficult to confirm.[1] Sulfur monoxide has been detected in the atmospheres of planets and comets in outer space[2] but is an unstable compound on earth.[3] Early reports describe the trapping and characterization of SO in an argon matrix[4] but it was only first observed only in the early 1930s.[5] Since then, chemists have exploited transition metal complexes to stabilize this reactive diatomic molecule, although few examples are known.[6] The most common strategy for delivering SO has been extrusion from episulfoxides or trisulfide oxides, although most methods require elevated temperatures or suffer from low yields of the SO-trapped products.[7]

More recently, the advent of frustrated Lewis pairs (FLPs)[8] has prompted the exploration of main group compounds as reagents for activating small molecules. Indeed, sterically demanding combinations of Lewis acids and bases have been shown to activate H_2,[9] CO_2,[10] CO,[11] N_2O,[12] and more recently, SO_2.[13,14] The groups of Erker and Stephan reported that the combination of $P(tBu)_3$ and $B(C_6F_5)_3$ under an atmosphere of SO_2 add across one of the S=O bonds to yield zwitterionic $[(tBu)_3P{-}(S{=}O){-}O{-}B(C_6F_5)_3]$ (Scheme 1). In related work, Erker and co-workers explored the reactivity of isocyanates with their linked FLP system, in which P/B was found to add across the C=O bond, leaving the C=N double bond intact (Scheme 1). Based on these findings, we were inspired to investigate the chemistry of analogous systems with *N*-sulfinylamines (R-N=S=O), because they are isoelectronic with SO_2, easily prepared in high yields from the corresponding amine and $SOCl_2$,[15] and have been shown to be versatile building blocks for a variety of more complex products.[16] Very recently, Erker et al. reported that their Zr^+/P FLP system reacts with *N*-sulfinylamines, whereby the phosphine undergoes addition at N, and the Zr^+ is shown to coordinate both the S and O centers (Scheme 1).[17]



Scheme 1. Reactions of FLPs with SO_2, PhNCO, and PhNSO.

Initially, a combination of $P(tBu)_3$ and $B(C_6F_5)_3$ with one equivalent of *p*-Tolyl−N=S=O (**1**; *p*-Tolyl = 4-methylphenyl) resulted in the formation of a new species **2** (Scheme 2). A sharp singlet in the ^{11}B NMR spectrum at $\delta = -2.1$ ppm and a singlet at $\delta = 83.8$ ppm in the $^{31}P\{^1H\}$ NMR spectrum led us to tentatively formulate product **2** as the FLP adduct, however the nature of the binding could not be unambiguously determined from spectroscopy. X-Ray diffraction analysis revealed the structural formulation of **2** to be the



Scheme 2. Synthesis of **2–4**.

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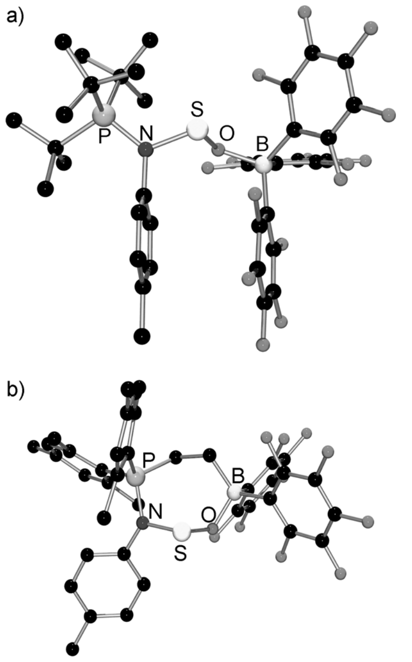


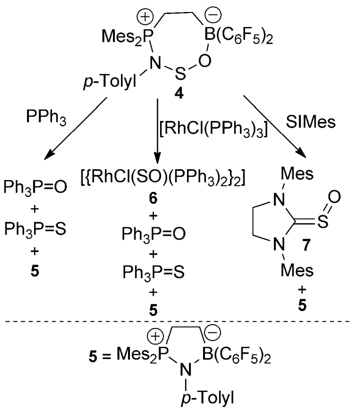
Figure 1. POV-ray depictions of **2** (a) and **4** (b). H atoms omitted for clarity.

adduct [(tBu)$_3$P−N(p-Tolyl)−S−O−B(C_6F_5)$_3$] (Figure 1a). The phosphine is bound to the nitrogen center with concomitant donation from the oxygen center to the borane, in contrast to the chemistry of isoelectronic SO_2. The N-S-O functionality has a resulting bond angle of 100.46(6)°. Based on a P−N bond length of 1.685(1) Å, a B−O bond length of 1.509(2) Å, and an S−O bond length of 1.625(1) Å, compound **2** can be more appropriately viewed as a phosphinimine–borane FLP[18] complex that is stabilizing SO. While redox-neutral, this FLP addition results in oxidation of the phosphorus center and reduction of the sulfur center.

This mode of binding was also found to occur in the reaction of a combination of P(tBu)$_3$ and Al(C_6F_5)$_3$ with **1**. The resulting species **3** exhibited similar spectroscopic and structural properties (Scheme 2, see the Supporting Information). The notable features of **3** are a similar P−N bond length of 1.686(1) Å, an elongated O−Al(C_6F_5)$_3$ bond length of 1.767(1) Å, and an N-S-O bond angle of 101.87(6)°.

In a similar fashion, Erker's prototypical ethylene-linked P/B species $Mes_2PCH_2CH_2B(C_6F_5)_2$[19] (Mes = 2,4,6-trimethylphenyl) was shown to react with **1** to afford product **4** (Scheme 2), which was confirmed crystallographically (Figure 1b). This unusual 7-membered heterocycle is a rare if not the only example in which six different atom types are linked contiguously. The P−N and B−O bond lengths are 1.673(2) and 1.528(3) Å, respectively, with a N-S-O bond angle of 104.94(8)°.

The formulation of **2**–**4** as phosphinimine–borane and phosphinimine–alane adducts of SO prompted us to investigate the possibility that these species could act as a source of SO. To this end, compound **4** was treated with 2 equivalents of PPh_3 at 110 °C. This resulted in clean conversion of the 7-membered ring to a 1:1:1 mixture of $Ph_3P{=}O$, $Ph_3P{=}S$, and a new product **5** (Scheme 3, Figure 2). The latter species gave rise to a ^{31}P NMR chemical shift at $\delta = 54.0$ ppm and was isolated by column chromatography in 81 % yield. The ^{11}B NMR spectrum of **5** shows a singlet at $\delta = -1.28$ ppm, with ^{19}F NMR peaks at $\delta = -131$, -161, and -166 ppm. The corresponding ^{1}H NMR spectrum shows the diagnostic peaks for a p-Tolyl group as well as a $Mes_2PCH_2CH_2B(C_6F_5)_2$ fragment. Together, the data suggest the formation of a 5-membered ring consisting of a phosphinimine–borane adduct. Crystals suitable for X-ray diffraction studies were obtained, which confirmed our structural prediction for **5** (Figure 2). Further investigation showed that the oxidation of PPh_3 with **4** is kinetically favorable at room temperature, albeit with an extended reaction time of 72 h. Regardless of reaction temperature, the same products were obtained in similar yields, with complete consumption of **4**. It is worth noting that an analogous oxidation is not observed when **1** is treated with 2 equivalents of PPh_3 and heated for several hours.



Scheme 3. Reaction of **4** with PPh_3, RhCl(PPh_3)$_3$, or SIMes.

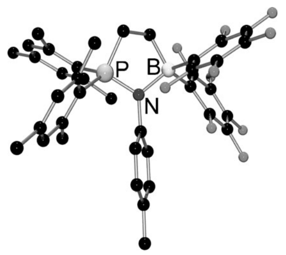


Figure 2. POV-ray depiction of **5**. H atoms omitted for clarity.

Additionally, **4** was shown to react with [RhCl(PPh_3)$_3$] in a 3:2 ratio at room temperature over 29 h, during which complete consumption of Wilkinson's complex and **4** was evidenced by ^{31}P NMR spectroscopy. In addition to compound **5**, $Ph_3P{=}O$, and $Ph_3P{=}S$, a new product **6** was isolated. This material precipitated from the reaction mixture as insoluble crystals and thus was not amenable to characterization by NMR spectroscopy. However, X-ray analysis of the resulting orange crystals of **6** confirmed the formulation as [{RhCl(μ-$\eta^1\eta^2$-SO)(PPh_3)$_2$}$_2$] (Scheme 3, Figure 3). In this

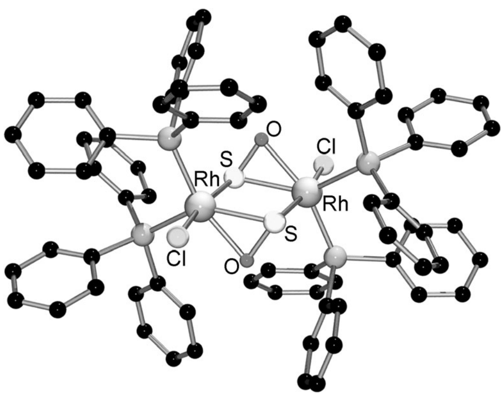


Figure 3. POV-ray depiction of **6**. H atoms omitted for clarity.

species, the two SO moieties are S-bound to one Rh center while the SO bond is η^2-bound to the adjacent metal center. The Rh–S distances were found to be 2.271(2) and 2.327(1) Å and the S–O and Rh–O distances were found to be 1.530(5) and 2.140(4) Å, respectively. In previous literature, based on IR data, the product derived from the reaction of stilbene episulfoxide and [RhCl(PPh$_3$)$_3$] was proposed to be the dimer [{RhCl(SO)(PPh$_3$)}$_2$], in which the SO ligands were terminal and Cl ligands bridged the Rh centers.[20] Compound **6** represents a rare example of a [Rh(SO)] complex[6c,20,21] and is only the second to be crystallographically characterized.[22]

In a similar fashion, compound **4** was found to react with an N-heterocyclic carbene. Treatment of **4** with one equivalent of SIMes (SIMes = 1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) in toluene resulted in an immediate reaction and precipitation of a new faint yellow product **7**, with quantitative formation of **5**. The ^{1}H NMR spectrum of **7** showed resonances attributable to an SIMes fragment, and the ^{13}C{^{1}H} NMR spectrum showed a resonance at $\delta =$ 183.2 ppm, characteristic of a C═S fragment. Crystals suitable for X-Ray diffraction analysis were used to confirm the identity of material **7** as the SO adduct of SIMes (Scheme 3, Figure 4). While related compounds, known as sulfines or thiourea S-oxides, have previously been prepared by methods including dehydrohalogenation of sulfinyl chlorides and oxidation of thiocarbonyl compounds,[23] the present route provides the first example of a synthesis of a sulfine in which a carbene acts as an SO trap.

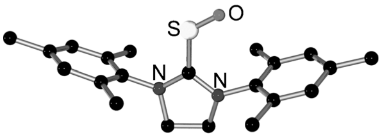


Figure 4. POV-ray depiction of **7** (one orientation of the twofold disordered O atom is shown). H atoms omitted for clarity. C═S: 1.697(3) Å, S═O: 1.303(5) Å.

In summary, we have shown that an *N*-sulfinylamine is captured by both inter- and intramolecular FLPs. In contrast to the binding of isoelectronic SO$_2$, this species binds via N and O to P and B, respectively, thereby generating stable, isolable products that are best viewed as phosphinimine–borane complexes of SO. The cyclic adduct **4** in the presence of PPh$_3$, Wilkinson's complex, or SIMes is shown to generate the corresponding oxidation or SO-trapped products with concomitant formation of the phosphinimine–borane adduct **5**. This stable, yet labile SO transfer agent presents a new avenue through which main group compounds can be used to deliver sulfur monoxide.

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