Interaction of metal oxido compounds with $\text{B}(\text{C}_6\text{F}_5)_3$

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Abstract

Lewis acid base pair chemistry has been placed on a new level with the discovery that adduct formation between electron donor (Lewis base) and electron acceptor (Lewis acid) can be inhibited by the introduction of steric demand, thus preserving the reactivity of both Lewis centers, resulting in highly unusual chemistry. Some of these highly versatile *Frustrated Lewis Pairs* (FLP) are capable of splitting a variety of small molecules such as dihydrogen in a heterolytic and even catalytic manner. This is in sharp contrast to classical reactions where the inert substrate must be activated by a metal based catalyst. Very recently, research has emerged combining the two concepts, namely the formation of FLPs in which a metal compound represents the Lewis base, allowing for novel chemistry using the heterolytic splitting power of both together with the redox reactivity of the metal. Such reactivity is not restricted to the metal center itself being a Lewis acid or base, also ancillary ligands can be used as part of the Lewis pair, still with the benefit of the redox-active metal center nearby.

This minireview is designed to highlight the novel reactions arising from the combination of metal oxido transition metal or rare earth metal compounds with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. It covers a wide area in chemistry including small molecule activation, hydrogenation and hydrosilylation catalysis, and olefin metathesis substantiating the broad influence of the novel concept. Future goals of this young and exciting area are briefly discussed.

1. Introduction

Lewis' concept of an acid and a base is central in coordination chemistry where a strong bond is usually formed between the ligand (electron pair donor, Lewis base) and the central atom (electron pair acceptor, Lewis acid). This allows the development of stable coordination complexes, both with main group and transition metal elements. Also, the presence of Lewis acids in organic transformations is well-known to influence and enhance the reactivity. One among many examples is the activation of silanes in borane catalyzed hydrosilylation reactions, first reported by Piers and coworkers.^[1] While known since the beginning of last century, Lewis' concept was revolutionized in recent years after the discovery of the exceptional reactivity of Lewis acid base pairs which form no or a poor bond between them by deliberately introducing steric hindrance (Scheme 1). Compounds with such spatially separated Lewis acid and base functionalities, referred to as *Frustrated Lewis Pairs* (FLP), exhibit ambiphilic behavior.^[2–4] This led to many interesting applications in small molecule activations (e.g. H_2 ,^[5] CO_2 ,^[6,7] N_2 ^[8,9]) and catalysis, with the metal free hydrogenation of imines discovered by Stephan and coworkers in 2007 being a most prominent example.^[3–5,7,10,11] Piers' abovementioned seminal work on borane mediated hydrosilylation reactions was certainly influential for the discovery of FLPs.^[1,12]

Scheme 1. Top: Lewis adduct formation and frustrated Lewis pair; bottom: Lewis adduct formation between $\text{M}=\text{O}$ and $\text{B}(\text{C}_6\text{F}_5)_3$.

While initial research was dedicated to FLPs based on main group elements, over time Lewis pairs in which a transition metal compound acts directly as the

Lewis base attracted considerable attention.^[5,13,14,15] This allows for further reactivity in small molecule activation not observed with main group frustrated Lewis pairs alone, and easy screening by ligand modifications.^[5,13,16]

Metal oxides are of central importance in chemistry ranging from biological to material science applications. For example, molecular high-valent oxido species are believed to be crucial in oxidations reactions of non-heme enzymes leading to the development of a large scope of bioinspired model complexes.^[17] Molybdenum oxido species are found in the active site of oxygen atom transfer enzymes.^[18,19] In bulk materials metal oxides are omnipresent, ranging from ceramics and glass to more recent developments such as nanoparticles^[20] and energy storage materials.^[21]

The molecular metal oxido fragment usually reacts as electrophile,^[22] as for example observed in oxygen atom transfer reactions to Lewis basic phosphanes.^[19,23] However, an increasing number of recent reports reveal metal oxides exhibiting ambiphilic reactivity.^{[24][25].[26]} Despite the abundance of metal oxides, FLPs utilizing the M=O moiety as Lewis base remain scarce.^[11]

This minireview is focused on the reactivity of metal oxido complexes with the highly electrophilic and sterically encumbered Lewis acid B(C₆F₅)₃. The interaction with the strong Lewis acid alters the nature of the oxido functionality and the adjacent metal center leading to diverse reactivity exceeding the expected enhancement of reaction rates upon Lewis acid coordination. The focus herein is centered on reactivity, while summaries of ¹¹B NMR shifts of B(C₆F₅)₃ coordinated to oxido moieties were collected by Piers,^[27] and structural parameters of transition metal oxido borane adducts by Timoshkin and colleagues.^[28]

2. Formation of classical Lewis adducts between B(C₆F₅)₃ and M=O moieties

The first metal oxido moiety coordinated by a Lewis acid was described by Osborn and coworkers in 1981 for complexes of the type [WO(CH₂R)₃X] and [WO(CH₂R)(CHR)X] in the course of their investigation of the interaction of tungsten oxido alkylidene catalysts with the Lewis acid AlBr₃ in olefin metathesis.^[29] Structural evidence for such a coordination was provided in 1987 with the report of the adduct [W{OAlBr₃}(CH₂tBu)₃Br] (**1**) (Figure 1).^[30] Beside the structural novelty this also represents the first clear evidence for an activating effect of a coordinated Lewis acid

in metal oxido chemistry. Research in this direction was limited, was limited, and it only recently became the focus of interest again, possibly parallel with the seminal discovery of frustrated Lewis pairs (FLP).^[5,11]

The first Lewis adduct featuring a M-O-B(C₆F₅)₃ unit was reported by Siedle et al. in the course of their investigations on Ziegler Natta type catalyst systems.^[31] In the search for aluminum-free catalysts, [Cp*₂ZrMe₂] was reacted with [NEt₃H][HOB(C₆F₅)₃] to form [Cp*₂Zr{OB(C₆F₅)₃}] (**2**) in which the otherwise rare Zr=O moiety^[32] is stabilized by the borane and by an additional Zr-F interaction (Figure 1).

Figure 1. Molecular structures of the oxido Lewis adducts [W{OAlBr₃}(CH₂*t*Bu)₃Br]^[30] (**1**, left) and [Cp*₂Zr^{IV}{OB(C₆F₅)₃}]^[31] (**2**, right).

Thereafter, a systematic study on the formation of Lewis adducts of various transition metal oxido complexes and B(C₆F₅)₃ by Green and coworkers led to a variety of examples as depicted in Figure 2.^[33–36]

Figure 2. Selected examples of transition metal oxido based Lewis adducts synthesized by Green and coworkers.^[33–36]

It is noteworthy, that most complexes coordinate only one equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, even in the presence of additional oxido groups and of excess Lewis acid. This can be attributed to steric hindrance (especially in *cis*-dioxido complexes) and to the electronic situation. The latter is highlighted by a study with dianionic tungstate $[\text{WO}_4]^{2-}$ which leads upon addition of borane to a rare compound containing multiple $\text{M}=\text{O}-\text{B}$ bonds.^[37] In contrast, the neutral compound $[\text{LWO}_3]$ ($\text{L} = 1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane}$) is only capable to coordinate one molecule of $\text{B}(\text{C}_6\text{F}_5)_3$.^[37] Also the monoanionic perrhenate ion $[\text{ReO}_4]^-$, exhibiting lower electron density, coordinates only one borane (Figure 3).

Figure 3. Multiple adduct formation in dianionic tungstate compared to neutral tungsten trioxide and monoanionic perrhenate.^[37]

This is in agreement with similar observations made in uranium dioxide chemistry where in U(VI) compounds (electron poor) one oxido moiety was coordinated by a borane, whereas in U(V) and U(IV) species both oxido groups were able to coordinate one molecule of B(C₆F₅)₃ (see chapter 5, Figure 7).^[38–40]

A common feature of the Lewis adducts is the expected elongation of the metal oxido bond length by approximately 0.1 Å compared to the parent compound. This elongation is often accompanied by a shortening of the bonds to the other ligands to compensate the electron withdrawing effect of the M-O-B unit.^[33–37] However, it seems that in lower valent complexes the influence is smaller as in the rhenium(III) compound [Re^{III}{OB(C₆F₅)₃}(2,7-nonadiyne)] (**15**) only an Re=O elongation from 1.692(4) to 1.724(3) Å occurs upon borane coordination.^[41]

3. Non-conventional metal oxido borane adduct formation

The obvious way to prepare the adduct is by reacting an appropriate metal oxido Lewis base with the Lewis acid B(C₆F₅)₃. However, several other paths were followed, especially in cases where the metal oxido compound is not stable without Lewis acid. For example, [Ti{OB(C₆F₅)₃}(acac)₂] (**3**) can be isolated as a monomeric species while the borane-free parent compound forms the dimer [{TiO(acac)₂}]₂.^[33,42]

The aqua adduct H₂O·B(C₆F₅)₃ generally acts as a Brønsted acid (H[HOB(C₆F₅)₃])^[43] exhibiting rich reactivity towards transition metal complexes, albeit without the formation of a metal oxido moiety.^[27,44] Additionally, H₂O·B(C₆F₅)₃, first discovered by Roesky and coworkers, may also be used as an oxido transfer agent. They were able to prepare a hitherto unknown monoalumoxane species, in which the Al=O moiety is stabilized by coordinated B(C₆F₅)₃.^[45]

The same method was employed in the pursuit of tantalum oxido complexes.^[46,47] The reaction of H₂O·B(C₆F₅)₃ with suitable precursors allowed for the isolation of stabilized oxido compounds of the type [Cp*Ta{OB(C₆F₅)₃}R₂] (**18^{Me}** R= Me, **18^{Bn}** R= Bn) which showed interesting organometallic transformations (Scheme 2).^[48]

Scheme 2. Synthesis and reactivity of Ta=O borane adducts.^[46,48]

Upon use of $[NEt_3H][HOB(C_6F_5)_3]$ methane is displaced from $[Cp^*_2ZrMe_2]$ forming $[Cp^*_2Zr\{OB(C_6F_5)_3\}]$ (**2**) as mentioned above (Figure 1),^[31] while use of $[BMIM][HOB(C_6F_5)_3]$ (BMIM = 1-n-butyl-3-methylimidazolium) allows the isolation of the anionic complex $[Cp_2Zr\{OB(C_6F_5)_3\}Me]^-$ (**23**) under retention of one methyl group (Figure 4).^[49] Both zirconium compounds containing a Zr=O-B moiety remain tetrahedral, realized by an additional Zr-F interaction in the former and a methyl group in the latter (Figure 4). More recently, similar reactivity was also found for related hafnocene compounds.^[50]

Figure 4. Zirconium oxido borane adducts $[Cp^*_2Zr\{OB(C_6F_5)_3\}]$ ^[31] (**2**, left) and $[Cp_2Zr\{OB(C_6F_5)_3\}Me]^-$ ^[49] (**23**, right).

A very different approach was followed by Mindiola and coworkers who reported the titanium complex **25** exhibiting a Ti=O-B bond in which the oxygen atom is derived from CO₂ (Scheme 3).^[51] The Lewis acid initially acts as a methyl abstractor from a bulky titanium methyl imido compound forming an ion pair. Subsequently metathesis-like reaction of the imido group with CO₂ leads to isocyanate and the titanium oxido borane adduct.

Scheme 3. Reactivity of a titanium methyl imido complex towards B(C₆F₅)₃ and CO₂ under formation of isocyanate and a titanium oxido borane adduct.^[51]

Comparable reactivity was disclosed by Cummins and coworker, who reacted the borane-capped terminal niobium phosphide **26** with CO₂ generating a phosphathynolate salt and the corresponding niobium oxido borane adduct **27** (Scheme 4).^[52]

Scheme 4. Metathesis reaction of an anionic niobium phosphide with CO₂, reported by Cummins and coworkers.^[52]

4. Influence of Lewis acid coordination on electronic situation and reactivity

Interesting ambiphilic reactivity of a metal oxido moiety was recently reported by Ison and coworkers.^[25] They found that the oxido group in the rhenium(V) compound [ReO(Cl)(L)] (L = DAP = 2,6-bis(mesitylamino)methyl)pyridine or DAAM = N,N-bis(2-arylaminoethyl)methylamine) is capable to coordinate to B(C₆F₅)₃ in a nucleophilic manner and, in contrast, it can be cleaved by triphenyl phosphine forming OPPh₃ where the oxygen atom acts as an electrophile towards phosphorous. This is an

important finding in view of the preference for an electrophilic behavior of high valent metal oxido moieties.

In complexes $[\text{ReO}(\text{Ac})(\text{L})]$ with two nucleophilic sites (oxido and acetyl) $\text{B}(\text{C}_6\text{F}_5)_3$ coordinates exclusively to the oxido group while BF_3 is found at the acetyl oxygen atom despite the comparable Lewis acidity (Scheme 5).^[25] This suggests higher nucleophilicity of the acetyl oxygen but steric preference of oxido coordination in the case of $\text{B}(\text{C}_6\text{F}_5)_3$.

Scheme 5. Reactivity of rhenium oxido acetyl complexes towards boron Lewis acids.^[25,53]

Furthermore, the borane in $[\text{Re}\{\text{OB}(\text{C}_6\text{F}_5)_3\}(\text{Ph})(\text{DAP})]$ (**28^{Ph}**) was found to be reversibly coordinated to the rhenium oxido group which leads to highly interesting reactivity towards dihydrogen.^[54] Upon addition of a mixture of H_2/D_2 scrambling to HD was observed suggesting heterolytic cleavage of dihydrogen. This is likely to occur via hydridoborate formation and protonation of the metal oxido group, a behavior reminiscent of a frustrated Lewis pair (FLP). Although such an ion pair was not observed, its formation is highly probable in view of the found reactivity towards olefin hydrogenation. $[\text{ReO}(\text{Ph})(\text{DAP})]$ in presence of 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ (3.5 bar H_2 , 100 °C) allowed reduction under full conversion of several terminal and internal as well as cyclic olefins.^[54]

Subsequent substitution studies by introducing more steric bulk into the DAP ligand as well as using other Lewis acids ($\text{Al}(\text{C}_6\text{F}_5)_3$ or $\text{HB}(\text{C}_6\text{F}_5)_2$) support the suggested mechanistic cycle in which the initial activation of the olefin occurs at the Lewis acid forming an alkyl aluminate or borate, respectively, thereby generating a carbocation

at the olefin which binds to the nucleophilic metal oxido group (Scheme 6). Only thereafter heterolytic cleavage of H₂ occurs under intermediate protonation of the metal oxido group and subsequent product formation. This mechanistic view is supported by DFT calculations and also explains the observed isomerized side products.^[55]

The related hydrido complex [ReO(H)(DAP)] was furthermore used in a fundamental study on olefin insertion into the Re-H bond.^[56] Coordination of the Lewis acids B(C₆F₅)₃ or Al(C₆F₅)₃ to the terminal oxido group has a pronounced impact on the electronic situation at the metal center thereby significantly increasing the rate of olefin insertion (rate constant increased by a factor of 10⁷ to 10¹¹).

Scheme 6. Proposed FLP-type mechanism for oxidorhenium catalyzed olefin hydrogenation (bold) and additionally observed reactivity.^[54,55]

Very recently, we synthesized the Lewis adduct [Mo{OB(C₆F₅)₃}(NtBu)(L)₂] (L = 2,4-di-tert-butyl-6-((phenylimino)methyl)phenolate) (**30**) based on a molybdenum oxido

imido species which was found forming a reactive Lewis pair in solution (Scheme 7).^[57] The coordination of the Lewis acid was confirmed by a new set of signals corresponding to the meta, ortho and para fluorines of $\text{B}(\text{C}_6\text{F}_5)_3$, respectively, observable by ^{19}F NMR spectroscopy. This might become a useful measure for the interaction within the Lewis pair similar to the Gutmann-Beckett method where the shift of the ^{31}P NMR signal of OPEt_3 allows the determination of the Lewis acidity in a given pair.^[58] Reaction with silanes led to heterolytic cleavage of Si-H bonds at ambient conditions under formation of the ion pairs $[\text{Mo}\{\text{OSiR}_3\}(\text{NtBu})(\text{L})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**31^{Et}** R= Et, **31^{Ph}** R= Ph), comprised of a cationic Mo(VI) silanolate complex and the borohydride anion. Similar ion pairs, albeit not isolated, were postulated in Ison's rhenium system to be responsible for H/D scrambling.^[54] Further interesting reactivity of the molybdenum-based ion pairs included anion fluorination (forming $[\text{Mo}\{\text{OSiR}_3\}(\text{NtBu})(\text{L})_2][\text{FB}(\text{C}_6\text{F}_5)_3]$, **32^{Et}** and **32^{Ph}**) or exchange of the silyl group upon reaction with trimethylsilyl chloride forming $[\text{Mo}\{\text{OSiMe}_3\}(\text{NtBu})(\text{L})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**31^{Me}**).^[57] The latter reaction was somewhat surprising since Me_3SiCl reacted as an electrophile while no Mo-O scission was observed.

Scheme 7. Heterolytic cleavage of Si-H bonds at an Mo=O-B unit yielding isolable ion pairs.^[57]

UV/vis spectroscopy and electrochemistry allowed assessment of the electronic situation within the ion pairs.^[57] In the UV/vis spectra, a pronounced red-shift of the vis maximum was observed going from the parent compound $[\text{MoO}(\text{NtBu})(\text{L})_2]$ to the Lewis adduct **29** and the ion pairs **30**, indicative of an energetically lower transition and thus more accessible unoccupied molecular orbitals (Figure 5). Cyclovoltammetric experiments revealed an irreversible Mo(VI)/Mo(V) couple for the Lewis adduct, reversible Mo(VI)/Mo(V) couples for all ion pairs, while no redox

feature was found for the uncoordinated oxido imido molybdenum complex (Figure 5). Again, this clearly corroborates that increased electrophilicity of the molybdenum metal center facilitates one electron reduction of Mo(VI) to Mo(V).

Figure 5. Left: UV/vis spectra of complex [MoO(NtBu)(L)₂] (yellow), Lewis adduct **30** and silanolate complexes **31**; Right: Corresponding cyclic voltammograms of **30** and **31**.

These spectral and electrochemical changes are in good agreement with the structural data obtained by single-crystal X-ray diffraction analysis, showing a Mo-O bond elongation from 1.7198(18) in [MoO(NtBu)(L)₂] (double bond) to 1.8975(19) in the ion pair [Mo(OSiPh₃)(NtBu)(L)₂][FB(C₆F₅)₃] (**32**^{Ph}).^[57]

Figure 6. From left to right: Molecular structures of [MoO(NtBu)(L)₂], Mo=O bond length 1.7198(18)^[59], Lewis adduct **30**, Mo=O bond length 1.8221(9)^[57] and ion pair **32**^{Ph}^[57], Mo-O bond length 1.8975(19).

Furthermore, the reported silanolate/borohydride ion pairs reacted with carbonyl substrate, regenerating the initially formed Lewis adduct via an unusual mechanism featuring an insertion into the B-H bond of the anion (Scheme 8).

Scheme 8. Observed reaction sequence after addition of benzaldehyde to ion pairs **31^{Et}** and **31^{Ph}**.

The finding, that metal oxido-based Lewis adducts can exhibit FLP-like reactivity,^[5,11,15] is very interesting in view of the high abundance of the metal oxido functionality.^[5,11] It is therefore very likely that more systems exhibiting diverse FLP-like reactivity will be described in the future.

Careful choice of the metal system is however crucial, as undesired further reactivities may occur, such as complete scission of the metal oxido moiety or cleavage of the B-C bond in B(C₆F₅)₃. For example, complete removal of the oxido group upon addition of the Lewis acid was observed in an oxidorhenium(V) hydride complex, where reaction with B(C₆F₅)₃ under CO atmosphere led to a reduction resulting in a cationic tris-carbonyl rhenium(I) complex.^[53] Also in a cerium(IV) aqua oxido compound complete scission of a M=O bond occurred upon addition of B(C₆F₅)₃ forming the dicationic cerium(IV) compound **33** with hydroxyborate anions (Scheme 9).^[60,61]

Scheme 9. Oxido abstraction from a Ce=O moiety with B(C₆F₅).^[61]

Carbon boron bond cleavage was observed in the reaction of vanadium oxido dimers of the type $[\{VO(L)_3\}_2]$ with $B(C_6F_5)_3$. While $[\{VO(NEt_2)_3\}_2]$ gave the expected borane adduct **34**, with the more electrophilic $[\{VO(OCH_2CF_3)_3\}_2]$ substitution of one $F_3CCH_2O^-$ ligand by $C_6F_5^-$ occurred to form the dimeric compound **35**, as displayed in Scheme 10.^[62]

Scheme 10. Reactivity of vanadium oxido complexes towards $B(C_6F_5)_3$.^[62]

5. Reactivity of the uranyl moiety $[UO_2]^{2+}$ towards $B(C_6F_5)_3$

The uranium-oxygen bonds in the linear uranyl(VI) dication $[UO_2]^{2+}$ are very strong; the average bond dissociation energy (BDE) of 604 kJ/mol is higher than for the carbon-oxygen bonds in CO_2 (532 kJ/mol).^[63,64] It is therefore the prevalent form of natural uranium in aqueous environment. Functionalization of the oxido ligand is of importance for various reasons such as in uranium ore mining or in spent nuclear fuels. However, chemistry of this highly stable moiety became only recently accessible, aided by an increased understanding of the bonding situation in the uranyl moiety^[63], the use of non-aqueous media as well as the discovery of Lewis acid activation.

The first uranyl compound with a direct coordination of $B(C_6F_5)_3$ was described 2004 by Sarsfield and coworkers where the borane is coordinated to one of the two oxygen atoms $[UO(OB\{C_6F_5\}_3)(NCN)_2(THF)]$ ($NCN = \{(Me_3SiN)CPh(NSiMe_3)\}$, **36**).^[65] This discovery sparked research leading to interesting functionalization chemistry.^[66]

A detailed investigation of the effect of Lewis acid coordination on the uranyl moiety has been carried out by Hayton and coworkers with uranyl complexes supported by two bulky acnac ligands (Scheme 11). Variation of the steric bulk of the ligand, allowed or prevented coordination of $B(C_6F_5)_3$ on the oxido groups.^[38] In contrast to the uranyl(VI) compounds, where only coordination of maximum one borane was observed, addition of two equiv of $B(C_6F_5)_3$ to the reduced uranyl(V) compound

$[\text{Cp}^*_2\text{Co}][\text{UO}_2(\text{Aracnac})_2]$ led to coordination of borane to both oxido groups (**37**), and addition of another equiv of Cp^*_2Co led to the uranium(IV) compound $[\text{Cp}^*_2\text{Co}]_2[\text{U}\{\text{OB}(\text{C}_6\text{F}_5)_3\}_2(\text{Aracnac})_2]$ (**38**).^[39] Furthermore, $[\text{UO}_2(\text{Aracnac})_2]$ underwent facile hydrosilylation of the oxido moiety with HSiR_3 mediated by $\text{B}(\text{C}_6\text{F}_5)_3$ forming the reduced $[\text{U}^{\text{V}}\{\text{OSiR}_3\}\{\text{OB}(\text{C}_6\text{F}_5)_3\}(\text{Aracnac})_2]$ (**41**) and H_2 .^[67] Upon addition of two equiv of Et_3SiH , silylation of both oxido groups occurred to $[\text{U}^{\text{V}}\{\text{O}-\text{SiR}_3\}_2(\text{Aracnac})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**40**).^[68] Both **40** and **41** can be reduced further to uranium(IV) by cobaltocene forming $[\text{Cp}_2\text{Co}][\text{U}^{\text{IV}}\{\text{OSiR}_3\}\{\text{OB}(\text{C}_6\text{F}_5)_3\}(\text{Aracnac})_2]$ (**42**) or $[\text{U}^{\text{IV}}\{\text{OSiR}_3\}_2(\text{Aracnac})_2]$ (**43**), respectively.^[67,68]

Scheme 11. Reactivity of an uranyl(VI) complex supported by bulky acnac ligands towards $\text{B}(\text{C}_6\text{F}_5)_3$ and reducing agents, reported by Hayton and coworkers.^[38,39,67,68]

The formation of ion pairs upon reaction of the uranyl moiety in presence of the borane is reminiscent of our molybdenum-based system^[57] (Scheme 7), however with lower chemoselectivity, presumably caused by the rich redox-chemistry of the

uranium center. The reduction from U(VI) to U(V) represents a comparable behavior to the molybdenum system supported by our observed drastic shift in the redox-potential (Figure 5).^[57] In reactions employing analogous complexes featuring the less donating ligand dibenzoylmethanate (dbm), complete cleavage of one U-O bond was achieved forming $[U^V\{OB(C_6F_5)\}(dbm)_3]$ (**44**).^[69]

Arnold and coworkers reported the well-behaved uranyl(VI) complex $[U^{VI}O_2Cl(dp)]$ coordinated by the monoanionic tetradentate dipyrin ligand (dp), which upon reduction to the dinuclear species $[U^VO_2(dp)]_2$, is capable to coordinate one or two molecules of $B(C_6F_5)_3$ per uranium center, respectively under by cleavage of the intermediately formed dimer (Figure 7).^[40]

The influence of $B(C_6F_5)_3$ coordination at the uranyl oxido groups was also investigated by means of electrochemistry revealing an increase of the U^V/U^{IV} reduction potential upon addition of borane.

Figure 7. Molecular structures of uranyl(V) complexes with $B(C_6F_5)_3$ molecules coordinated to one (**45**, left) or two (**46**, right) oxido moieties.^[40]

Electrochemical investigation revealed a significant positive shift from -2.2 V (vs Fc/Fc^+) found for the U(VI) chloride complex to -0.49 V for the bis-borane compound $[U^V\{OB(C_6F_5)_3\}_2(dp)]$ (**46**), so that the generated U^{IV} species in the latter may be considered a mild reducing agent.^[40] Such a pronounced shift of the redox potential

upon borane coordination has also been observed in the molybdenum system described above (Figure 5).^[57]

6. Lewis acid-induced valence tautomerism

As mentioned in the introduction, metal oxido species play an important role in biological oxidation reactions. For this reason, a long-standing goal in bioinorganic model chemistry has been to generate high-valent metal oxido species. Stabilization of the terminal oxido group in these often difficult to access compounds by a Lewis acid has been considered. Particular attention attracted the report of a crystal structure showing the coordination of the Lewis acidic Sc^{3+} ion to a high-valent iron oxido moiety.^[70,71]

In a similar endeavor and encouraged by the occurrence of Ca^{2+} ions in the oxygen evolving complex (OEC),^[71,72] Goldberg and coworkers produced a corrolazine-based high valent manganese(V) oxido compound as presented in Scheme 12.^[73,74] Reactivity studies towards Lewis acids revealed an unexpected behavior, namely the formation of a valence tautomer upon addition of a strong Lewis acid: from Mn(V)=O to the Mn(IV)=O radical cation **47** in which one electron is transferred from the ligand to the metal site. The tautomer seems to be formed independent of the nature of the Lewis acid as similar reactivity has been observed with Zn^{2+} , $\text{B}(\text{C}_6\text{F}_5)_3$ and even with the Brønsted acid $\text{HB}(\text{C}_6\text{F}_5)_4$ (protonation).^[73,75,76]

Scheme 12. Lewis acid addition induced valence state change in a manganese oxido corrolazine compound (left, Goldberg)^[74] and a manganese oxido corrole compound (right, Abu-Omar).^[77,78]

Highly interesting, the tautomers behave very different with regard to electron transfer (ET), oxygen atom transfer (OAT) as well as hydrogen atom transfer (HAT) reactivity. The manganese(V) oxido starting material was found to be the poorer oxidant

compared to the Lewis acid coordinated species but only one-electron transfer is observed to Mn(IV)O in contrast to a two-electron process to Mn(III) in the former case. This is possibly the reason for the contradictory influence on OAT and HAT. The rate of the two-electron process OAT is dramatically decreased upon addition of the Lewis acid while the rate for the one-electron process HAT is increased by a factor of 100 with B(C₆F₅)₃.^[73–75,79]

A similar tautomerization triggered by Lewis or Brønsted acid coordination was observed in the corrole-based manganese(V) oxido compound recently reported by Abu-Omar and coworkers (Scheme 12).^[77,78] Also the corrole system showed accelerated HAT in the radical cation **48**, while oxygen atom transfer was only observed for the manganese(V) oxido state.^[77] The observed rate enhancements in HAT furthermore were found to depend on the nature of the added Lewis acid.^[78] A striking difference to Goldberg's reports is, however, that both valence states undergo HAT under formation of the same manganese(III) product, i.e. no difference in stoichiometry was observed for the two valence tautomers.^[77]

Again, the influence of the coordinated Lewis acid on the tendency for one- or two-electron processes may be compared to our oxido imido molybdenum(VI) complexes. While two-electron reduction upon OAT is readily occurring, a Mo(VI)/Mo(V) redox couple for a one-electron process was only observable upon coordination of B(C₆F₅)₃ (compound **30**, Scheme 7).^[57,59]

7. The role of Lewis acids in metathesis reactions

Alkylidene complexes of group 6 metals have found tremendous application as classical metathesis catalysts.^[80] Typically, as discovered by Richard Schrock, they represent high-oxidation state molybdenum(VI) and tungsten(VI) compounds coordinated by the alkylidene moiety, an imido group and two monoanionic, mainly alkoxido ligands.^[81] In particular, the steric bulk of the imido group leads to stable species preventing bimolecular deactivation. For this reason, related Mo and W oxido alkylidene complexes have been far less applied, although such species were discovered early on.^[82] However, as the oxido alkylidene moiety might be involved in heterogeneous catalytic systems, interest was revived in recent years. It was shown that upon using sterically demanding alkoxido, amido and other ligands bimolecular

deactivation may be prevented but such compounds tend to be less reactive in metathesis reaction.^[83–88]

The investigation of Lewis acid base interaction in olefin metathesis dates back to Osborn's description of a bridge between catalyst and cocatalyst as described above (2. chapter), however, $B(C_6F_5)_3$ was at that time not considered.^[29]

Significant reactivity enhancement of the oxido alkylidene catalysts used in metathesis reactions was achieved by addition of the borane Lewis acid. Schrock and coworkers have shown that $B(C_6F_5)_3$ coordinates to the oxido group forming borane adducts. In $[W\{OB(C_6F_5)_3\}(CHtBu)(OHMT)(Me_2Pyr)]$ (OHMT: 2,6-dimesitylphenoxide; Me_2Pyr : 2,5-dimethylpyrrolide, **49**), the B-O bond was found to be relatively weak indicated by dynamic behavior in solution demonstrated by broad NMR signals and the long B-O bond distance of 1.571(3) Å found in the molecular structure (Figure 8).^[83] Nevertheless, the influence on the reaction rate in the olefin metathesis reaction is significant as 90 % of 1-octene is converted to 7-tetradecene in 1 h at room temperature while the parent complex without borane reacted very slowly (hours).

Furthermore, $[WO(CHCR)(OHMT)(Me_2Pyr)]$ ($R = tBu$ or $C(Me)_2Ph$) is a catalyst for the ring-opening metathesis polymerization (ROMP) of various norbornadiene monomers forming highly tactic polymers.^[86] While some of the monomers did not react at room temperature, upon addition of one equiv of $B(C_6F_5)_3$ smooth polymerization occurred. In contrast to the reactivity with 1-olefins, the presence of the borane did not influence the stereoselectivity of the polymerization reactions since in both, with and without borane, the same high degree of tacticity was observed.^[85] Possibly, acceleration is caused by binding of the borane to the oxido ligand but due to relative weak interaction relative rates within the polymerization reaction remain identical as in the non-borane catalyst leading, albeit faster, to the same tacticity. However, the exact nature of the influence of the borane remains elusive.

Figure 8. Molecular structures of the tungsten oxido alkylidene borane adduct $[W\{O-B(C_6F_5)_3\}(CHtBu)(OHMT)(Me_2Pyr)]^{[83]}$ (**49**, left) and the molybdenum alkylidene borane adduct $[Mo\{O-B(C_6F_5)_3\}(CHSiMe_3)(N=PtBu_3)_2]^{[87]}$ (**50**, right).

A further study revealed that $[WO(CH_2)(OHMT)_2]$ with two sterically demanding OHMT ligands reacts with ethylene to the propene coordinated $[WO(CH_2=CHCH_3)(OHMT)_2]$ via metathesis, β -H and reductive elimination. Upon addition of $B(C_6F_5)_3$ the olefin is substituted followed by oxidative coupling of two molecules of ethylene forming the metallocyclobutane complex $[WO(CH_2)_4(OHMT)_2]$. It is interesting to note that no spectroscopic evidence for adduct formation with the Lewis acid in this more sterically demanding complex was observed, suggesting only a small amount of a reactive species being formed. Although the coordination of borane to the oxido group is proposed further evidence remains to be found.^[84]

Also molybdenum oxido alkylidene compounds were reacted with $B(C_6F_5)_3$ and used as catalyst precursors in metathesis reactions. The adduct $[Mo\{O-B(C_6F_5)_3\}(CHSiMe_3)(N=PtBu_3)_2]$ (**50**) was easily accessible by reaction of the parent complex with the borane.^[87] The molecular structure, determined by single crystal X-ray diffraction analysis, reveals a significant elongation of the Mo-O bond in the adduct compared to the one in the parent oxido complex $[MoO(CHSiMe_3)(N=PtBu_3)_2]$ (0.15 Å longer, Figure 9). However, the phosphinimido ligands seem electronically deactivating as the parent complex is inactive towards 1-olefins and is a poor ROMP catalyst for norbornene. Nevertheless, the borane coordinated complex was found to

be a more efficient catalyst in the ROMP reaction using norbornene. A similar accelerating effect was recently found with the more well-behaved molybdenum oxido alkylidene complex $[\text{MoOCl}(\text{CHPhOMe})(\text{HIPT})]$ (Figure 9) under addition of $\text{B}(\text{C}_6\text{F}_5)_3$ capable of stereoselective ROMP reactions.

Figure 9. Molybdenum oxido alkylidene complex $[\text{MoOCl}(\text{CHPhOMe})(\text{HIPT})]$ exhibiting $\text{B}(\text{C}_6\text{F}_5)_3$ -enhanced ROMP reactivity.^[88]

8. Concluding remarks

The influence of the coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to various metal oxido moieties on reactivity is very diverse. Adducts may be formed with the typical early transition metal or rare earth metal oxido compounds either by direct reaction with the Lewis acid or by using an appropriate starting material, the Lewis acid and an additional oxygen donor such as e.g. H_2O or CO_2 . As expected, the stability depends on the steric and electronic situation within the adduct. By careful adjustment of the steric demand the $\text{M}-\text{O}-\text{B}$ bond strength may be decreased in such a way that weak adduct formation might or might not occur. Independent whether the adduct is actually observed in solution the reactivity of the Lewis acid base pair approaches that of classical FLPs. The most interesting aspect, however, is the influence on the electronic situation upon borane addition. Facile redox reactivity of the metal presents an additional aspect not observed in main group Lewis pairs. This gives rise to novel reactivities leading to compounds with unusual redox states. Especially the observation of the Lewis acid to promote one-electron redox switches that leaves the employed metal moiety, depending on its nature, in an uncommon oxidation state and therefore ready for unusual reactivity, is a promising novel concept.

More research towards the combination of frustrated Lewis pair reactivity with redox labile metal complexes is likely to emerge soon. As such, the activation of small molecules such as CO_2 , N_2 , H_2 and others as well as their catalytic conversion may

be enabled by non-classical pathways. The concept has already found first applications in N₂ activation^[8,9] and the future holds promise that it will be used to discover more unusual and novel chemistry.

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Conflict of interest

The authors declare no conflict of interest.

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