Lessons from Isolable Nickel(I) Precursor Complexes for Small Molecule Activation

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CONSPECTUS

Small-molecule activation by transition metals is essential to numerous organic transformations, both biological and industrial. Creating useful metal-mediated activation systems often depends on stabilizing the metal with uncommon low oxidation states and low coordination numbers. This provides a redox-active metal center with vacant coordination sites well suited for interacting with small molecules.


Monovalent nickel species, with their d^9 electronic configuration, are moderately strong one-electron reducing agents that are synthetically attractive if they can be isolated. They represent suitable reagents for closing the knowledge gap in nickel-mediated activation of small molecules. Recently, the first strikingly stable dinuclear β-diketiminate nickel(I) precursor complexes were synthesized, proving to be suitable promoters for small-molecule binding and activation. They have led to many unprecedented nickel complexes bearing activated small molecules in different reduction stages.

In this Account, we describe selected achievements in the activation of nitrous oxide (N_2O), O_2, the heavier chalcogens (S, Se, and Te), and white phosphorus (P_4) through this β-diketiminatonickel(I) precursor species. We emphasize the reductive activation of O_2, owing to its promise in oxidation processes. The one-electron-reduced O_2 activation product, that is, the corresponding β-diketiminato-supported Ni–O_2 complex, is a genuine superoxonickel(II) complex, representing an important intermediate in the early stages of O_2 activation. It selectively acts as an oxygen-atom transfer agent, hydrogen-atom scavenger, or both towards exogenous organic substrates to yield oxidation products.

The one-electron reduction of the superoxonickel(II) moiety was examined by using elemental potassium, β-diketiminatozinc-(II) chloride, and β-diketiminatoiron(I) complexes, affording the first heterobimetallic complexes featuring a [NiO_2M] subunit (M is K, Zn, or Fe). Through density functional theory (DFT) calculations, the geometric and electronic structures of these complexes were established and their distinctive reactivity, including the unprecedented monooxygenase-like activity of a bis(μ-oxo)nickel–iron complex, was studied. The studies have further led to other heterobimetallic complexes containing a [NiO_2M] core, which are useful for understanding the influence of the heterometal on structure–reactivity relationships. The activation of N_2O led directly to the hydrogen-atom abstraction product bis(μ-hydroxo)nickel(II) species and prevented isolation of any intermediate. In contrast, the activation of elemental S, Se, and Te with the same nickel(I) reagent furnished activation products with superchalcogenido $E_2{}^-$ (E is S, Se, or Te) and dichalcogenido $E_2{}^{2-}$ ligand in different activation stages. The isolable supersulfidonickel(II) subunit may serve as a versatile building block for the synthesis of heterobimetallic disulfidonickel(II) complexes with a [NiS_2M] core.

In the case of white phosphorus, the P_4 molecule has been coordinated to the nickel(I) center of dinuclear β-diketiminatonickel-(I) precursor complexes; however, the whole P_4 subunit is a weaker electron acceptor than the dichalcogen ligands E_2, thus remaining unreduced. This P_4 binding mode is rare and could open new doors for subsequent functionalization of P_4.

Our advances in understanding how these small molecules are bound to a nickel(I) center and are activated for further transformation offer promise for designing new catalysts. These nickel-containing complexes offer exceptional potential for nickel-mediated transformations of organic molecules and as model compounds for mimicking active sites of nickel-containing metalloenzymes.
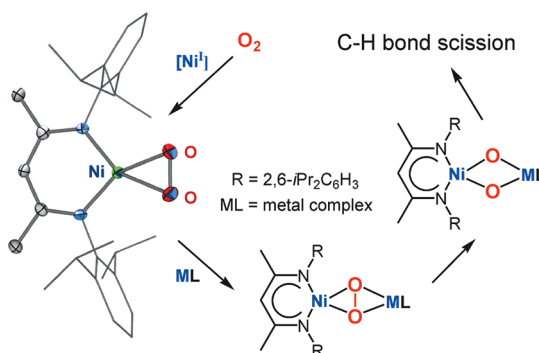
1. Introduction

The activation of small molecules mediated by transition-metal centers is of paramount importance in numerous stoichiometric and catalytic transformations of organic substrates in biological and industrial processes. Of particular relevance for coordination chemistry in this context is the identification and isolation of the initial adducts and subsequent reaction intermediates for unraveling the mechanism of electron transfer during the activation process. The realization of specific metal-mediated activation often depends critically on the design of systems capable of stabilizing a metal in uncommon low oxidation states and low coordination numbers, providing a redox-active metal center with vacant coordination sites that is well suited to interact with small molecules.

The nickel system, the light congener of extensively used palladium and platinum systems as catalysts in many important industrial processes, has garnered significant interest in recent years because nickel is much cheaper and more environmentally benign versus its heavier analogues. In particular, the chemistry of monovalent nickel systems deserves considerable attention owing to its role in several Ni-mediated catalytic transformations of organic molecules *inter alia* in $C(sp^3)$—$C(sp^3)$ coupling reactions.[1,2] Generally, a monovalent nickel center has a $3d^9$ valence electron configuration and can act as a moderately strong one-electron reducing reagent. In biological systems, monovalent nickel species have been considered to play a key role in several nickel-containing enzymes for small molecule activation, among hydrogenases,[3] carbon oxide dehydroganases (CODHs),[4] and methyl-*S*-coenzyme M reductases.[5]

Particularly designed ligand systems are needed to synthesize metastable monovalent nickel complexes for the elucidation of structure−reactivity relationships. Notable examples include the tripodal thioether-supported nickel(I) and nickel(I)-tetraazamacrocyclic systems developed recently by Riordan and co-workers,[6] which are capable of activating dioxygen at low temperature to give two different types of superoxonickel(II) complexes. However, both types of Ni−O_2 complexes could only be characterized spectroscopically at low temperature and were prevented from any isolation and further investigation of their reactivity.

In the past decade, chelating monoanionic β-diketiminate ligands have been successfully utilized for stabilizing main-group elements and transition metals in unusual low oxidation states.[7] Among low-valent transition-metal systems, isolable β-diketiminato-nickel(I) complexes bearing

sterically demanding aryl substituents at the nitrogen atoms have also been reported and turned out to be suitable candidates for a more extensive investigation on the reactivity of Ni(I) species.[8−12] The striking reactivity of the β-diketiminatonickel(I) species is highlighted by its capability to even bind dinitrogen to form isolable Ni−N_2 complexes and to activate dihydrogen to give dinuclear hydridonickel(II) complexes in the absence of arenes or donor solvents.[12,13] The aforementioned approach to generate metastable Ni−O_2 species described by Riordan and co-workers prompted us to investigated the binding and activation of dioxygen and related small molecules employing the dinuclear β-diketiminatonickel(I) precursor $[(L^{iPr}Ni)_2(\mu-\eta^3:\eta^3-C_6H_5Me]$ **1a** $[L^{iPr} = HC(CMeNC_6H_3{}^iPr_2)_2]$, which has been synthesized by Stephan and co-workers.[10] Surprisingly, exposure of the latter to dry dioxygen led to the first isolable superoxonickel(II) complex, whereas reaction with the elemental heavier chalocogens E (E = S, Se, Te) furnished the unprecedented $[(L^{iPr}Ni)_2E_2]$ butterfly-like complexes, which undergo facile dissociation in arene solutions to form superchalcogenidonickel(II) complexes $L^{iPr}NiE_2$ and $L^{iPr}Ni(I)$. In this Account, we wish to demonstrate that the synthesis and striking reactivity of two β-diketiminato-nickel(I) precursors toward N_2O, O_2, elemental sulfur, selenium, and tellurium, and P_4 is a fruitful and inspiring basis for closing the knowledge gap in low-valent Ni-mediated activation of small molecules.

2. Synthetic Routes to Toluene-Masked β-Diketiminato-Nickel(I) Precursors

In 2005, Stephan and co-workers first reported the successful synthesis of the dinuclear β-diketiminate-toluene−nickel complex $[(L^{iPr}Ni)_2(\mu-\eta^3:\eta^3-C_6H_5Me]$ (**1a**) $[L^{iPr} = HC(CMeNC_6H_3{}^iPr_2)_2]$, which has been isolated as dark-red crystals, by reduction of $L^{iPr}NiBr_2Li(THF)_2$ with K/Na alloy or MeMgBr in toluene.[10] Recently, we developed a simpler route to the latter complex by using potassium graphite as a mild reducing reagent (Scheme 1). Accordingly, the overnight reduction in toluene at room temperature furnishes solely **1a**, affording **1a** in 75% isolated yield.

Similarly, the analogous β-diketiminato-toluene−nickel complex $[(L^{Et}Ni)_2(\mu-\eta^3:\eta^3-C_6H_5Me]$ (**1b**) $[L^{Et} = HC(CMeN-C_6H_3Et_2)_2]$, bearing a sterically less demanding β-diketiminate ligand, is also easily accessible using the same protocol.[13] Complex **1b** adopts a similar conformation as that observed for **1a** in solid state (Figure 1). In solution, both complexes **1a** and **1b** show diamagnetic behavior according
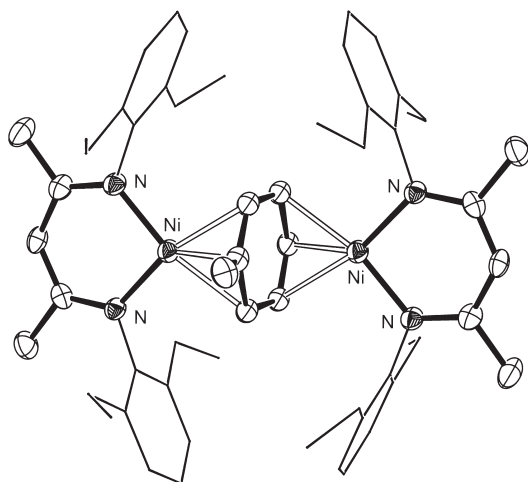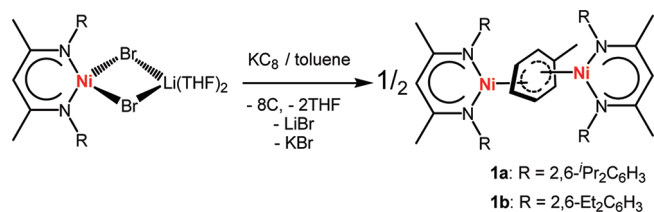
FIGURE 1. Molecular structure of the dinuclear β-diketiminato-toluene−nickel(I) precursor complex **1b**.

SCHEME 1. Synthesis of **1a** and **1b** by Mild Reduction with KC_8

**1a**: R = 2,6-^{i}Pr$_2$C$_6$H$_3$
1b: R = 2,6-Et$_2$C$_6$H$_3$

to the ^{1}H and ^{13}C NMR spectra recorded in C_6D_6 and exhibit sharp resonance signals with chemical shifts in the normal range for the respective β-diketiminate ligands.

As proposed by Stephan et al.,[10] both complexes represent Ni(II) species bearing a Birch-like reduced toluene ligand. Astonishingly, the electron transfer from Ni to toluene within the complexes is reversible in solution. Accordingly, in arene solutions the presence of a L^{iPr}Ni(I) species can be detected by electron paramagnetic resonance (EPR) spectroscopy. The suitability of **1a** to serve as a facile source of L^{iPr}Ni(I) in solution has been further supported by the formation of corresponding Ni(I) complexes with a variety of σ and π donors under release of the toluene molecule.[10] Thus the nickel complexes **1a** and **1b** may also be described as toluene-masked nickel(I) species.

3. Activation of N$_2$O

Activation of nitrous oxide (N$_2$O) is relevant both to the removal of N$_2$O as a green-house gas and to the selective oxidation of organic substrates by N$_2$O. An oxygen-atom transfer from N$_2$O to a nickel−diphenylcarbene complex to afford a nickel−benzophenone species was recently reported by Hillhouse, Cundari, and co-workers.[14]

SCHEME 2. Activation of N$_2$O with **1a**
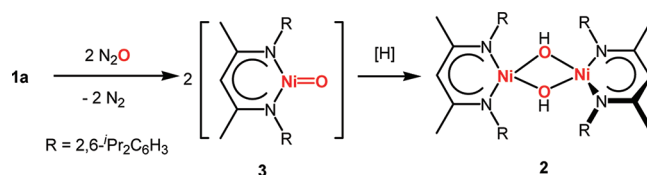
The reactivity of **1a** toward N$_2$O has been examined with the hope of isolating L^{iPr}Ni=O under O-atom transfer from N$_2$O to the respective nickel center. Such a (β-diketiminato)-Ni=O species was recently suggested by Cundari and co-workers as a potential reagent for activation of methane through a hydrogen-atom abstraction according to their calculations.[15] Exposure of **1a** in toluene to dry N$_2$O gas at −20 °C led solely to the isolation of dinuclear β-diketiminato-hydroxonickel(II) **2** bearing two μ-hydroxo bridged ligands (Scheme 2).[16] Presumably, transient L^{iPr}Ni=O **3** was produced initially by the monooxygenation of **1a** by N$_2$O under release of N$_2$, which acted as a hydrogen scavenger and subsequently underwent dimerization to yield **2** as the final product. DFT calculations revealed a short Ni−O distance for the two alternative spin states of **3** (1.64 Å for $S = ^1/_2$ and 1.67 Å for $S = ^3/_2$). Moreover, high spin density was found at the terminal oxygen atom in **3**. Both features are reminiscent of those for a {Fe^{IV}=O} group in heme and non-heme iron complexes.[17,18]

The dinuclear homovalent complex **2** is paramagnetic due to the structurally distinct L^{iPr}Ni(II) moieties with one Ni(II) in square planar (low-spin) and the other in tetrahedral (high-spin) geometry (Figure 2). This astonishing structure is possibly attributed to the bulkiness of the β-diketiminate ligand. In contrast, an analogous dimeric hydroxo nickel complex with a less sterically encumbered β-diketiminato ligand contains two almost planar tetracoordinate d^8-Ni(II) centers in the molecular structure (see also below).[19]

4. Activation of O$_2$

Dioxygen activation mediated by the nickel-group metals (Ni, Pd, Pt) has attracted much attention owing in large part to the importance of palladium and platinum reagents as oxidation catalysts for aerobic oxidation of organic substrates.[20−22] However, the development of nickel analogues for stoichiometric and catalytic aerobic oxidation is particularly desirable due to the larger natural abundance of Ni vs Pd and Pt. Generally, dioxygen does not react directly with nickel(II) species to form superoxo or peroxo Ni−O$_2$ complexes. The known isolable hydroperoxo- and peroxonickel complexes
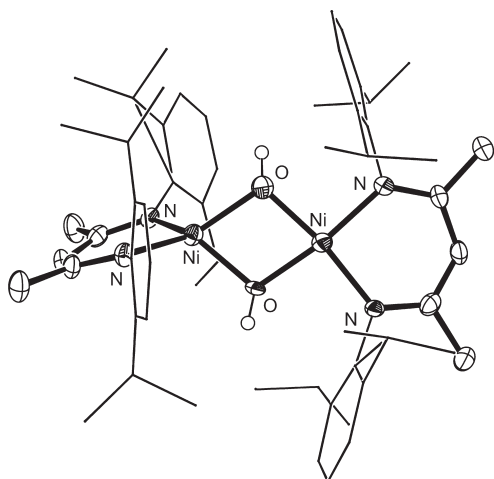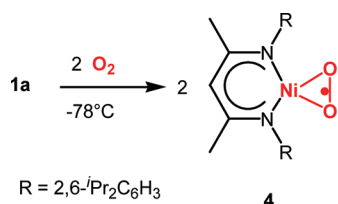
FIGURE 2. Molecular structure of di-β-diketiminato-bis(μ-hydroxo)-nickel(II) **2**.

SCHEME 3. Activation of O_2 with **1a**

R = 2,6-^{i}Pr$_2$C$_6$H$_3$

that can serve as suitable oxygenation reagents for organic substrates were prepared by treatment of Ni^{II} precursors with H_2O_2.[23−28] A single exception is the isolation of the side-on peroxonickel(II) complex Ni(O_2)(^{t}BuNC)$_2$ resulting from two-electron reduction of O_2 by the respective *tert*-butylisocyano-nickel(0) precursor.[29,30] As mentioned already, Riordan et al. first examined the direct reduction of O_2 using nickel(I) systems.[6] However, the thus-formed Ni−O_2 complexes are highly unstable and decompose at ambient temperature. By choosing the toluene-masked β-diketiminatonickel(I) complex **1a** as reducing toward O_2, we fortunately encountered the facile formation of an isolable Ni−O_2 complex.[16]

Thus, the activation of O_2 with **1a** is fast yet controllable. Exposure of a toluene solution of **1a** to dry O_2 at −78 °C led to the formation of **4** as indicated by the color change from red-brown to green (Scheme 3), and the desired product could be isolated as dark green crystals in 84% yield.

The molecular structure of **4** established by single-crystal X-ray diffraction analysis features an O_2^- ligand, which coordinates to the nickel center in a side-on manner and coplanar with the six-membered C_3N_2Ni ring (Figure 3). The O−O distance of 1.347(2) Å is shorter than the typical O−O bond length (>1.40 Å) reported for peroxo complex,[31]
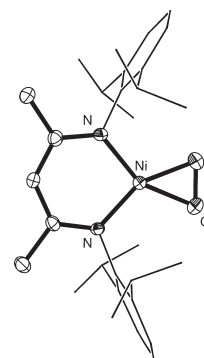

FIGURE 3. Molecular structure of β-diketiminato-superoxonickel **4**.

implying superoxo character of the O_2 ligand of **4**. The superoxo nature of **4** is also supported by the ^{16}O—^{16}O stretching vibration mode of $\nu = 971$ cm^{-1} ($\nu(^{18}$O—^{18}O) = 919 cm^{-1}) determined by IR spectroscopy.

Complex **4** is paramagnetic both in solution and in the solid state. Acordingly, X-band EPR measurements of **4** in a frozen toluene solution at 50 K revealed a paramagnetic ground state with spin $S = {}^1/_2$. The rhombic spectrum has principal g values of 2.138, 2.116, and 2.067. The aniso-tropic g values are consistent with those of ionic O_2^- dissolved in water.[32] In line with that, the DFT calculations showed that the coordinated dioxygen ligand is one-electron reduced and the unpaired electron is completely lo-cated at the O_2 moiety (in the π^* orbital) (Figure 4). Thus complex **4** represents a genuine superoxonickel(II) complex.

As expected, the superoxide **4** is a gentle oxygenation reagent, which may transfer one of the oxygen atoms to the proper reaction partner. Acordingly, it reacted with triphe-nylphosphine to give O=PPh$_3$ and **2** (Scheme 4). Moreover, treatment of **4** with half an equivalent of the starting material **1a** at room temperature led to the same product, presumably also via intermediate **3**.

The reaction of **1b** with O_2 at low temperature has also been examined. However, the corresponding nickel super-oxide L^{Et}NiO$_2$ does not survive at ambient temperature in the reaction solution, probably due to the lower protection of the NiO$_2$ moiety provided by the less sterically encum-bered β-diketiminato ligand.[13] Instead the dinuclear and homovalent bis(μ-OH)-bridged β-diketiminate nickel(II) com-plex L^{Et}Ni(OH)$_2$NiL^{Et} was isolated as a hydrogen-atom ab-straction product. Unlike the molecular structure of the analogue **2**, L^{Et}Ni(OH)$_2$NiL^{Et} features two Ni(II) centers in a square planar coordination environment.

Although superoxonickel complex **4** is inert toward sub-strates bearing weak C−H bonds such as 9,10-dihydroan-thracene, which can be activated by a Cr(III)−superoxo
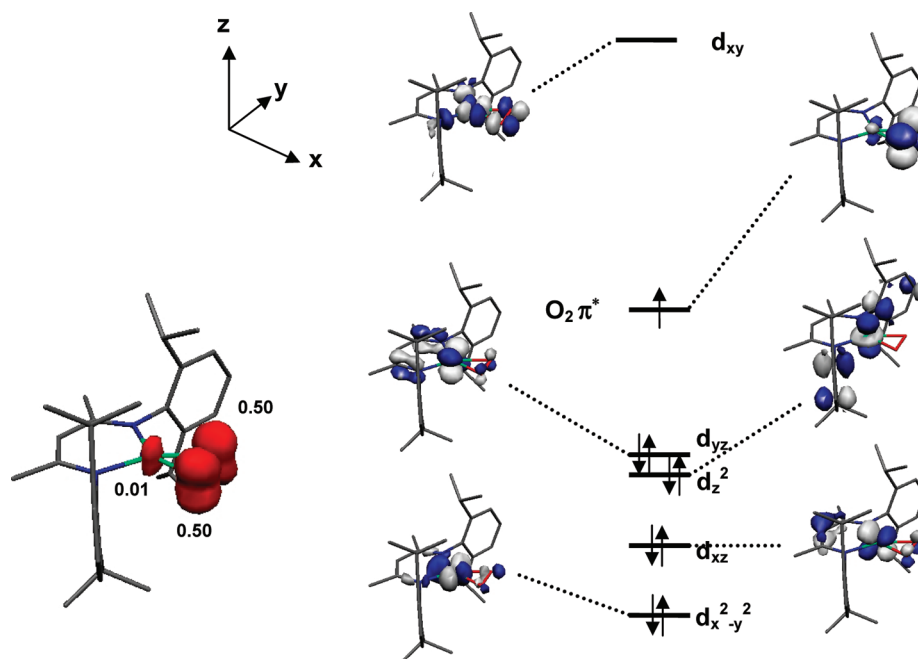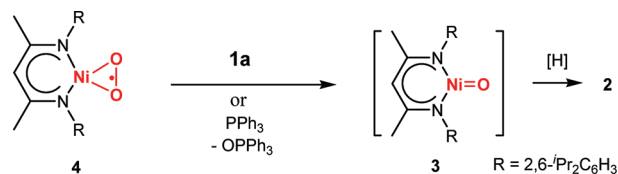
FIGURE 4. DFT-calculated Mulliken spin density of β-diketiminato-superoxonickel(II) **4** (left) and its frontier orbitals (right).

SCHEME 4. Conversion of **4** to **2**

complex as reported by Nam recently,[33] it showed interesting reactivity in the oxidation of O−H and N−H groups from exogenous organic substrates (Scheme 5).[34] It reacted readily with cyclohexanol and 1-phenylethanol to give the corresponding ketones, respectively. Moreover, the reaction with 2,6-di-*tert*-butylphenol afforded 2,6-di-*tert*-butyl-1,4-benzoquinone with an O-atom transferred from the super-oxo ligand to the *para*-position of the phenol species. This observation is reminiscent of the oxidation process reported for selected superoxocobalt systems.[35,36]

The reactivity of superoxide **4** toward N−H bonds has also been investigated.[34] For instance, it reacted with 1,2-diphenylhydrazine to give the expected azobenzene as sole oxidized product. Presumably, these oxidation reactions took place through an initial hydrogen-atom abstraction from the O−H or N−H group in the substrates. Strikingly, **4** showed dioxygenase-like activity when treated with *para*-substituted-2,6-di-*tert*-butylphenols, yielding the unprecedented oxidation product **5** that incorporates two separated oxygen atoms from a single O_2^- subunit. Overall, such reactivity

SCHEME 5. Reactivity of **4** toward Exogenous Subtracts (R = 2,6-^{i}Pr$_2$C$_6$H$_3$)
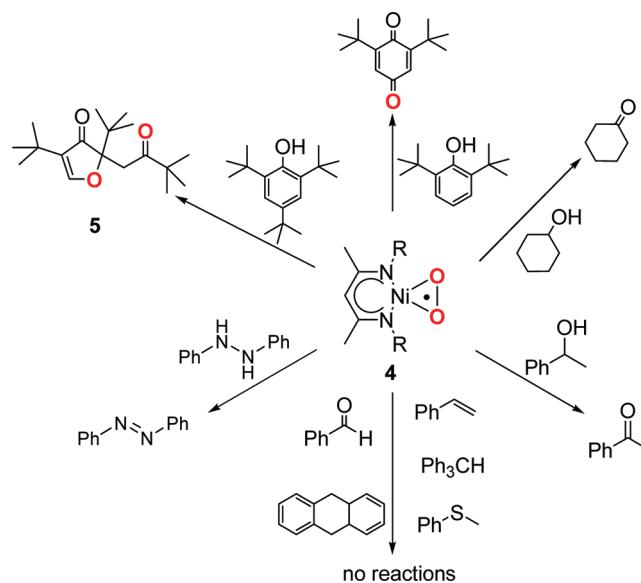
studies on nickel species derived from the interaction with O_2 offer novel and interesting perspectives in understanding and designing metal-mediated dioxygen activation and selective oxygenation of organic substrates.

Furthermore, the superoxo ligand O_2^- of **4** can be further converted into a peroxo ligand O_2^{2-} by one-electron reduction.[37] Accordingly, the reduction of a solution of **4** in THF with elemental potassium at room temperature led to a
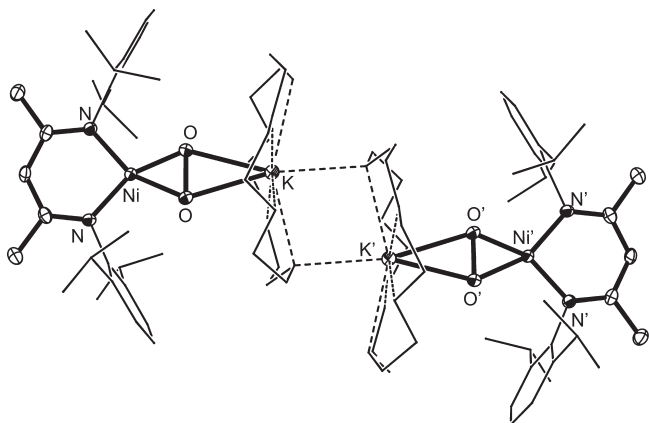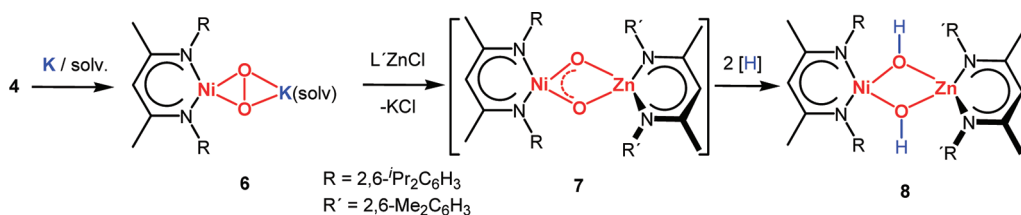
SCHEME 6. Formation of the Heterobimetallic Peroxo Species **6** and Its Reactivity

R = 2,6-^{i}Pr$_2$C$_6$H$_3$
R′ = 2,6-Me$_2$C$_6$H$_3$

FIGURE 5. Molecular structure of β-diketiminatonickel superoxide **6**·[18]crown-6.

FIGURE 6. DFT-calculated spin density of intermediate **7** ($S = 1$).

color change from green to brown-red and formation of a single diamagnetic product, indicating the formation of the heterobimetallic peroxo species **6** (Scheme 6).

The latter complex has been isolated in the form of brown-red crystals and fully characterized. It crystallized as a dimer with a crown ether coordinated to the K-ion ,which features a planar {Ni(μ,η^2:η^2-O$_2$)K} core (Figure 5). The Ni(II) center also adopts a square-planar geometry as that in **4**. As expected, the O−O distance of 1.468(2) Å is significantly longer than that observed in precursor **4** and similar to the distances observed for other metal peroxo complexes (1.4−1.5 Å).[31]

The peroxo species **6** is much more stable than **4** and shows no reaction with the aforementioned organic substrates tested for **4**. Surprisingly, replacement of the potassium cation in **6** by the non-redox-active β-diketiminatozinc(II) ion,[38] resulted in the O−O bond scission and subsequent H-atom abstraction to give the heterobimetallic bis(μ-OH)-bridged complex **8** (Scheme 6). As suggested by DFT calculations, the latter reaction occurred via the reactive intermediate **7** featuring two cleaved oxygen atoms (Figure 6). With the redox-inert Zn(II) center, both oxygen atoms in **7** mainly preserve their radical character and carry 60% of the unpaired spin density. The oxygen-centered
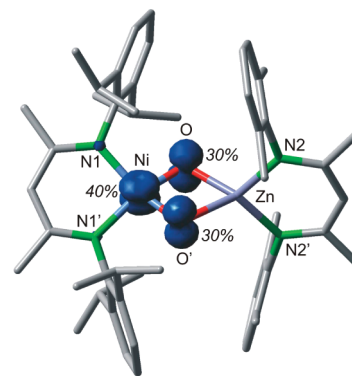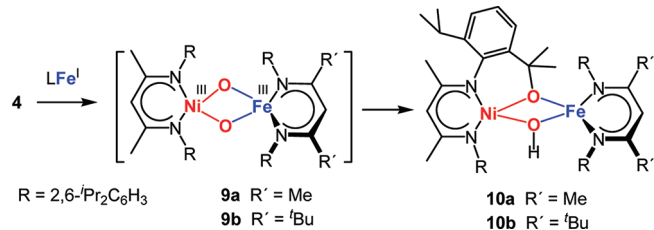
diradical character is, however, somewhat diluted by withdrawing electron density from the Ni(II) site, which carries 40% of the unpaired spin density. Such Ni−O spin polarization in **7** may account for the H-atom abstraction from the surrounding to give **8**. This finding underlines the importance of subtle electronic changes for the reactivity of heterobimetallic peroxo complexes.

The oxidative addition of iron(I) precursors to superoxo complex **4** in the hope of synthesizing a {FeO$_2$Ni} complex has also been investigated. Two β-diketiminatoiron dinitrogen complexes were chosen as Fe(I) sources.[39] Remarkably, the assembly of the first heterobimetallic {FeO$_2$Ni} complexes led to selective C−H activation and the isolation of the first μ-alkoxo-μ-hydroxo bridged NiFe complexes **10a** and **10b** (Scheme 7). Obviously, the latter resulted from an unexpected oxygenation of a C−H bond in one of the isopropyl groups at the β-diketiminato ligand coordinated to nickel.

This monooxygenase-like reactivity has been rationalized by DFT calculations. Again, the C−H bond activation is mediated by the [Ni(μ-O)$_2$Fe] core in **9a** and **9b**. In the optimized structure of **9a**, both metal centers adopt a distorted square planar coordination geometry. In sharp contrast to the oxygen-centered diradical **7** with a [Ni(μ-O)$_2$Zn] subunit,[37] the unpaired spin density in **9a** is mainly distributed on both metals. Accordingly, the nickel center has 0.8
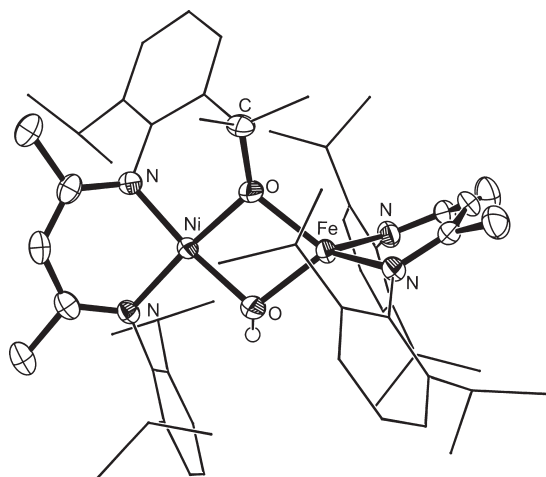
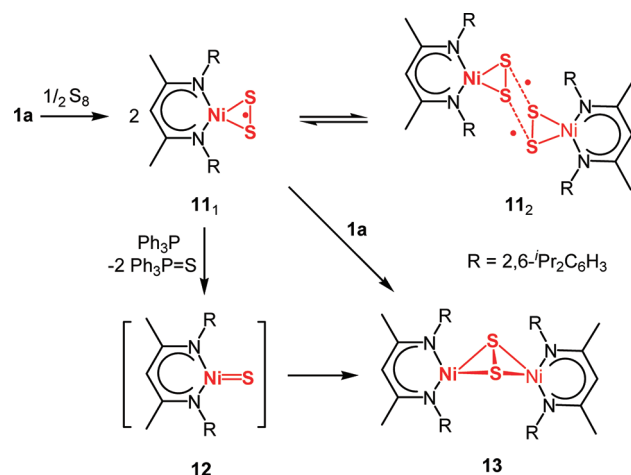**FIGURE 7.** Molecular structure of **10a**.
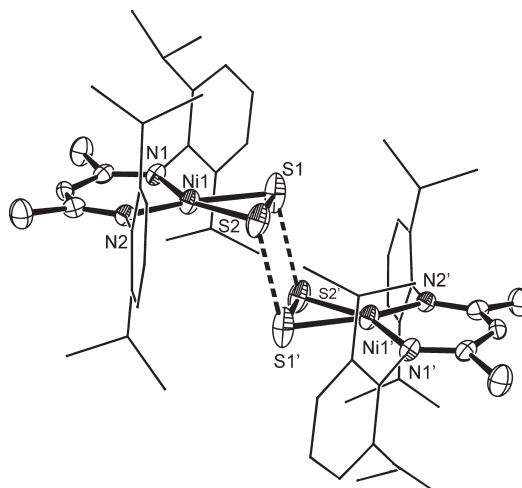
FIGURE 8. Molecular structure of **11₂**.

SCHEME 7. Reaction of **4** with Iron(I) Precursors

R = 2,6-^{i}Pr$_2$C$_6$H$_3$ **9a** R′ = Me   **10a** R′ = Me
                  9b R′ = ^{t}Bu   **10b** R′ = ^{t}Bu

SCHEME 8. Activation of S$_8$ with **1a**

spins, and 2.9 spins are on the iron site, while the oxygen atoms carry an averaged unpaired spin density of only 0.08. Thus the latter species contains essentially a [Ni^{III}(μ-O)$_2$Fe^{III}] core, which may be less reactive than **7** but more selective and oxygenates one of the isopropyl groups in the supporting ligand to give **10a** (Figure 7).

As for why the oxygenation took place selectively on one of the C–H groups of the β-diketiminato ligand coordinated at Ni instead of that at Fe could not been rationalized by the results of DFT calculations. In fact, neither complex-induced proximity effects nor favorable interactions of the relevant orbitals of oxygen could be recognized. On the contrary, the C–H hydrogen atoms of the isopropyl groups belonging to the β-diketiminatoiron moiety in **9a** are found closer to the μ-oxo bridges. Further investigations on other heterobimetallic [NiO$_2$M] complexes (M = Mn, Cr, Co) are needed to answer this question.
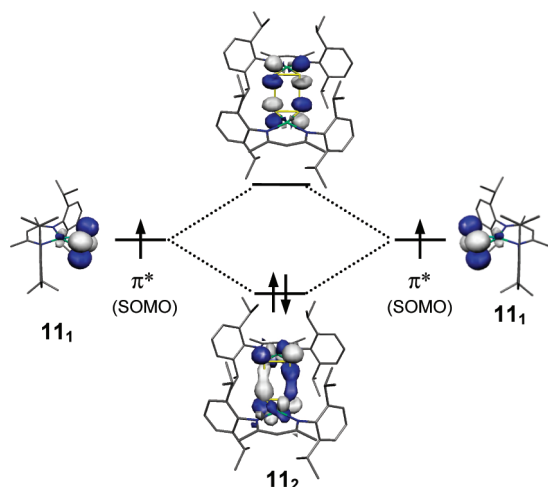
5. Activation of S$_8$

Similar to the O$_2$ activation, the reaction of **1a** in toluene with S$_8$ at −60 °C led readily to the first isolable "side-on" supersulfidonickel(II) complex **11** (Scheme 8).[40] The electronic structure of the monomer **11₁** suggested by DFT

calculations is similar to its oxygen homologue with the unpaired electron located at the S$_2^-$ ligand. In line with that, the ^{1}H NMR spectrum recorded in C$_6$D$_6$ showed paramagnetic shifted resonances. X-band EPR measurements in toluene solutions at room temperature revealed a paramagnetic ground state for **11₁** with a spin $S = {}^1/_2$. The spectrum in frozen solution at 50 K is rhombic and has principal g values of 2.148, 2.082, and 2.073.

In the solid state, complex **11₁** dimerizes and shows a structure featuring a four-membered, rectangular-shaped S$_4$ ring with two relatively short (S1−S2 and S1′−S2′, 1.944(2) Å) and two very long S−S distances (S1···S2′ and S1′···S2, 2.777(2) Å) (Figure 8). As rationalized by DFT calculations, the driving force for the dimerization arises from the formation of a four-sulfur−two-electron bond (Scheme 9). Since the SOMO of **11₁** is a singly occupied π^* orbital of the S$_2$ ligand,

11_1 π^* (SOMO) π^* (SOMO) 11_1

11_2

FIGURE 9. Molecular structure of **13**.

the dimerization of 11_1 leads to a stabilization by $\pi^*-\pi^*$ interaction between the sulfur atoms. Notably, such dimerization has not been observed for the oxygen homologue **4**, probably due to the smaller size of the oxygen atoms, which are well protected by the supporting β-diketiminato ligand.

As expected for a supersulfide, complex **11** can be further reduced simply by using the Ni(I) precursor **1a** in toluene at room temperature (Scheme 8). The reaction led to the formation of the genuine disulfide complex **13** having a $[\text{Ni}_2(\mu\text{-}(\eta^2{:}\eta^2\text{-S}_2)]$ core (Figure 9). Alternatively, complex **13** could be accessed by gentle sulfur transfer of 11_1 to Ph$_3$P. In the latter case, the hypothetical terminal sulfido nickel species **12** could be an intermediate for the reaction. In the butterfly structure of **13**, the S−S distance of 2.051(1) Å is significantly longer than that in 11_2, indicating that the supersulfide S$_2^-$ has been reduced to a normal disulfide S$_2^{2-}$. Consistently, complex **13** is diamagnetic both in solution and in the solid sate.

6. Activation of Elemental Selenium and Tellurium

In contrast to the ready activation of O$_2$ and S$_8$, the activation of elemental selenium and tellurium with **1a** is relatively slow even at room temperature, leading to complexes **14** and **15** with a $[\text{Ni}^{II}_2(\mu-\eta^2{:}\eta^2\text{-E}_2)]$ (E = Se, Te, respectively) core (Scheme 10b).[41] The latter species have been isolated in the form of crystals in high yields and fully characterized. Both complexes adopt a butterfly structure similar to **13** in the solid state with a two-electron reduced E$_2^{2-}$ subunit.

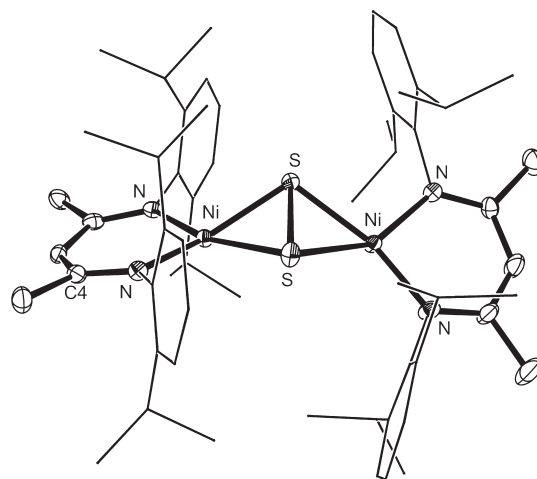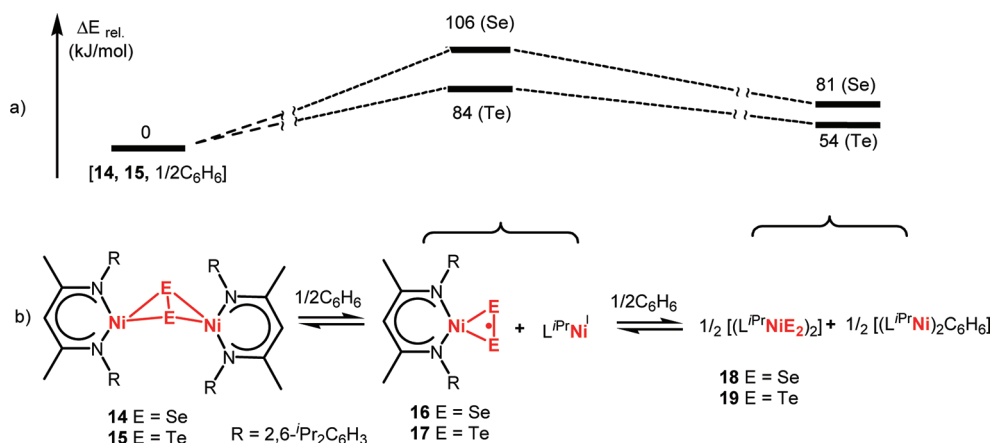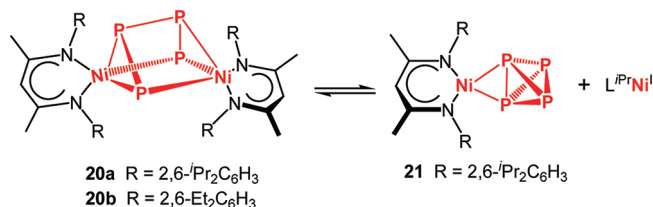The complexes are diamagnetic in the solid state but surprisingly exhibit paramagnetic behavior in solution as indicated by NMR spectroscopy and magnetic measurements. This phenomenon was rationalized by the unexpected dissociation of **14** and **15** to the corresponding superchalcogenido species **16** and **17** under concomitant reductive elimination of L^{iPr}Ni in solution. Similar to their sulfur homologue, the thus-formed nickel superselenido **16** and supertellurido **17** also dimerize in the solution to give **18** and **19**, respectively. The formation of the unique types of superchalcogenido complexes as well as their dimers has been proven by HR-ESI mass spectrometry and well supported by DFT calculations (Scheme 10a). The calculated reaction energies for the dissociation of **14** and **15** into **16** and **17** amount to 106 and 84 kJ mol^{-1}, respectively, revealing that the dissociation of **15** occurs more easily than that of **14**. In agreement with that, **15** showed greater effective magnetic moment (1.86 μ_B vs 1.06 μ_B for **14**) in C$_6$D$_6$ determined using Evans method.[42] The optimized structures of **16** and **17** are reminiscent of their oxygen and sulfur homologues. The unpaired electrons are also localized at the E$_2^{2-}$ (E = Se, Te) ligand.

Interestingly, the reaction of **14** or **15** with **11** resulted in the formation of disulfide complex **13** and the corresponding elemental chalcogen as precipitate. Treatment of **14** or **15** with dry dioxygen afforded the superoxonickel(II) **4** along with precipitation of elemental selenium and tellurium, respectively. This unusual reactivity additionally underlined the facile dissociation of **14** and **15**. Most notably is that the L^{iPr}Ni(I) species can act as a leaving group. In the case of disulfide species **13**, no similar dissociation has been detected.
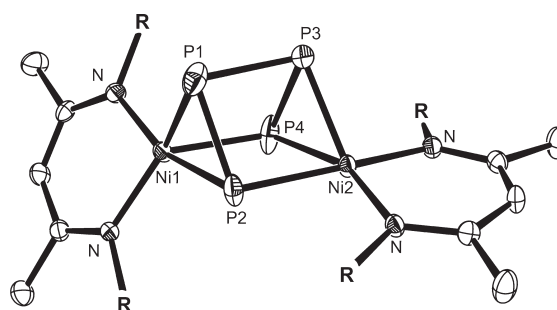
7. Activation of White Phosphorus (P$_4$)

Remarkably, even the relatively unreactive tetraphosphorus molecules can be activated with **1a**, affording the unique

SCHEME 10. (a) Simplified DFT-Derived Energy Profile and (b) a Representation of the Dissociation of **14** and **15** in the Presence of Benzene

SCHEME 11. White Phosphorus Activation Products **20a** and **20b**

FIGURE 10. Molecular structure of **20a** (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) and **20b** (R = 2,6-Et$_2$C$_6$H$_3$).

tetraphosphorus dinickel complex **20a** in high yield (Scheme 11).[43] In the solid state, **20a** adopts a structure with a Ni$_2$P$_4$ cluster featuring two β-diketiminato ligands each coordinated to a Ni center (Figure 10). While three of the P−P distances (P1−P2, 2.186(1) Å; P1−P3, 2.183(2) Å; P3−P4, 2.186(1) Å) show no significant change compared with those in a free P$_4$ molecule, the other three P−P bonds are elongated (ranging from 2.531(2) to 2.769(2) Å).

Unexpectedly, such P−P bond activation does not indicate any P$_4$ reduction because the nickel atoms remain as Ni(I) center according to the spectroscopic data and DFT calculations. In the solid state, **20a** is diamagnetic owing to the strong antiferromagnetic coupling between both Ni^I sites mediated via superexchange through the bridging P$_4$ ligand. In solution, **20a** performs partial dissociation to the mononuclear P$_4$−Ni(I) complex **21** and thus shows paramagnetic behavior (Scheme 11). According to DFT calculations, the dissociation product **21** in turn contains also a Ni^I center, which is coordinated by a neutral P$_4$ ligand in an η^2-fashion.

Interestingly, P$_4$−dinickel complex **20b** supported by the sterically less demanding β-diketiminato ligand and prepared by a similar route as for **20a** reveals geometric parameters comparable to those of **20a** in the molecular structure. However, it shows diamagnetic behavior both in

the solid state and in solution, indicating no dissociation similar to that of **20a** in solution. Thus the dissociation of **20a** observed in solution might be rationalized again by the presence of steric congestion. The distinct behavior of **20a** and **20b** in solution through subtle changes of the steric hindrance is also supported by DFT calculations, which showed different dissociation energy (−26.9 kJ mol^{-1} for **20a** vs +0.6 kJ mol^{-1} for **20b**).

The striking non-redox (innocent) character of P−P bonds of a P$_4$ moiety coordinated to a Ni(I) center was also demonstrated by using a silylene-activated P$_4$ species.[44] Starting from the latter furnished the novel heterobinuclear tetraphosphorus complexes **22a** and **22b**, which could be isolated in high yields (Scheme 12).[45] According to the X-ray diffraction analyses, both complexes possess a [Si($\mu,\eta^{2:2}$-P$_4$)Ni] core, in which the nickel center is coordinated to an η^2-P$_4$Si moiety and adopts a tetrahedral coordination geometry (Figure 11). Due to the coordination to the Ni center, the distances between P3 and P4 (ranging from 2.335(4) to 2.354(2) Å) are significantly longer than the other P−P distances (avg 2.245 Å) within the molecules. However, such
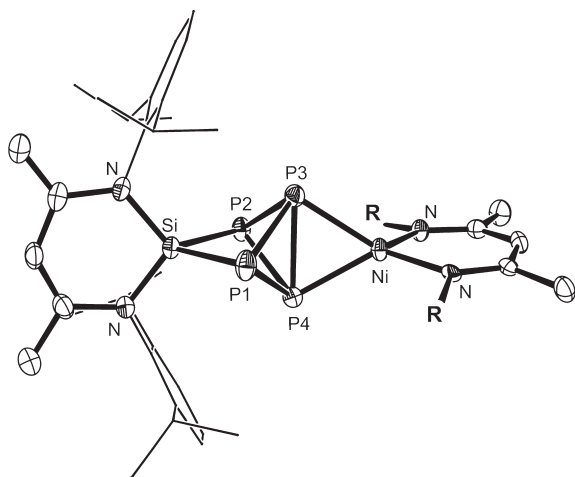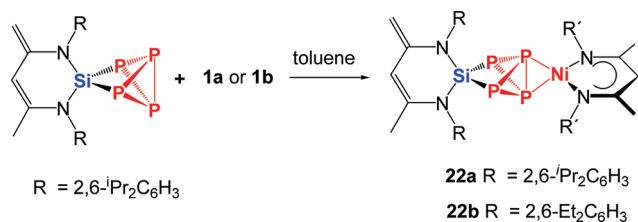
FIGURE 11. Molecular structure of **22a** (R = 2,6-^{i}Pr$_2$C$_6$H$_3$) and **22b** (R = 2,6-Et$_2$C$_6$H$_3$).

SCHEME 12. Reaction of Silylene-Activated White Phosphorus with **1a** and **1b**

R = 2,6-^{i}Pr$_2$C$_6$H$_3$

22a R = 2,6-^{i}Pr$_2$C$_6$H$_3$
22b R = 2,6-Et$_2$C$_6$H$_3$

elongation does not lead to a redox-driven P−P activation, and the Ni site remains as monovalent. In line with that, the latter complexes are paramagnetic both in the solid state and in solution. A spin doublet ground state of Ni(I) has been deduced from the electron paramagnetic resonance and magnetic measurement. The P$_4$ moieties in **22a** and **22b** with elongated P−P bonds owing to the coordination to nickel, together with those in Ni$_2$−P$_4$ complexes **20a** and **20b**, may allow selective activation and functionalization in the presence of additional reagents.

8. Summary and Outlook

The exploration of Ni(I) chemistry is still in its infancy. Advanced methods to synthesize isolable Ni(I) species opened new doorways to investigate the role of Ni(I) sites in numerous chemical and biological processes. Owing to their facile access and high stability, β-diketiminatonickel(I) precursor complexes have proven to be suitable species for the investigation of small molecule activation as exemplarily shown for nitrous oxide, elemental chalcogens, and white phosphorus (P$_4$). While the activation of N$_2$O led via oxygen transfer and hydrogen atom abstraction to a bis(μ-hydroxo)nickel(II)

product, the reactions with O$_2$ and its elemental heavier congeners furnished a series of isolable binding products with dichalcogen ligands in different reduction stages.

Thus the first isolable nickel superoxide L^{iPr}NiO$_2$ with a "side-on" O$_2$ ligand is accessible from a single-electron reduction of a dioxygen molecule by the nickel(I) promoter. The facile isolation of the latter superoxo nickel complex not only allowed us to investigate its intriguing activity toward exogenous substrates for O−H or N−H bond scission but also paved the way to unprecedented heterobimetallic complexes with unusual functioning cores using L^{iPr}NiO$_2$ as a building block. Accordingly, the step-by-step reduction of dioxygen has been described and the different behavior of the heterobimetallic species [NiO$_2$K], [NiO$_2$Zn], and [NiO$_2$Fe] has been experimentally examined and theoretically studied by DFT. Interestingly, the initially formed bis(μ-oxo)nickel−iron complex even exhibits unprecedented monooxygenase-like activity to activate a C−H bond within the supporting ligand.

Elemental sulfur, selenium, and tellurium can also be activated by utilizing the same nickel(I) precursor. Unexpectedly, the resulting dichalcogenido complexes with a butterfly-like shaped [NiE$_2$Ni] core undergo reversible dissociation in solution to form superchacogenido complexes L^{iPr}NiE$_2$ (E = S, Se, Te) and L^{iPr}Ni(I). In the case of white phosphorus, the binding products of two molar equivalents of L^{iPr}Ni(I) and P$_4$ led to (L^{iPr}Ni)$_2$P$_4$ species with different P−P bond distances, although the P$_4$ ligand remains unreduced. Similarly, the silylene-activated P$_4$ moiety also formed coordination adducts with the β-diketiminatonickel(I) species. The P$_4$ subunits may allow subsequent activation and functionalization in the presence of additional reagents. The current progress in synthesizing isolable β-diketiminatonickel(I) precursors and the wealth of activation products with different reduction stages is very encouraging to extract the mechanistic details involving Ni(I) sites in small molecule activation and as active sites in catalytic processes.

BIOGRAPHICAL INFORMATION

Shenglai Yao obtained his Ph.D. degree in 2005 at the Johannes Gutenberg University of Mainz. Afterwards he joined the Driess group at the Technische Universität at Berlin and continues to work in the group as a senior researcher. He has a strong interest in small molecule activation using low-valent main-group elements and transition metals.

Matthias Driess completed his Ph.D. degree in 1988 at the University of Heidelberg under the supervision of Professor Walter Siebert. He then worked from 1988 to 1989 as a postdoctoral fellow at the University of Wisconsin at Madison with Professor Robert West. He

returned to the University of Heidelberg and finished his Habilitation in 1993. In 1996, he accepted a position as a full professor of Inorganic Chemistry at the Ruhr Universität Bochum (Germany) before moving to a full professorship at the Institute of Chemistry (Metalorganic Chemistry and Inorganic Materials) of the Technische Universität Berlin (2004). Since 2007, he serves as chairman of the Cluster of Excellence "Unifying Concepts in Catalysis" (UniCat) in the Berlin—Potsdam area. He received several awards among the Chemistry Award of the Academy of Sciences at Göttingen (2000), the Otto Klung Award for Outstanding Chemistry (2000), and the Alfred Stock Memorial Award of the German Chemical Society (2010).

FOOTNOTES

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