Group-transfer chemistry at transition metal centers in bulky alkoxide ligand environments

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Abstract

Emerging research in the field of organometallic chemistry is centered on the development of new efficient catalysts for the production of useful organic products via group (nitrene, carbene, oxo) transfer chemistry. Nitrene, carbene and oxo transfer with 3d (base) metals allows for economically viable and sustainable alternatives to generate new C-C, C-X, and X-X (X = N, O) bonds, as compared with precious metal catalysis or lengthy organic synthesis. This review specifically focuses on the evolving group transfer chemistry using mononuclear middle and late transition metal complexes in bulky alkoxide ligand environments. Bulky alkoxides are attractive ligand candidates for this chemistry because their steric and electronic properties generally lead to high-spin electrophilic reactive metal centers. Design and synthesis of well-defined alkoxide complexes are discussed first, with the focus on "non-symmetric" alkoxides [OCR_2R'] developed mostly during the last decade. Variation of the size and the electronic nature of substituents in [OCR_2R'] allows for the selective formation of bis- or tris(alkoxide) ligand platforms. Next, the reactivity of these complexes in oxo, nitrene, and carbene transfer is described. The electronic structures and reactivity of discrete mononuclear oxo-alkoxide complexes $M(OR)_n(O)$ are discussed in the context of bioinorganic (photosystem II) and heterogeneous (zeolites) catalysis. In the chapters describing nitrene and carbene chemistry, the major emphasis is on the electronic structure and reactivity of novel $M^{III}(OR)_2(Y\bullet)$ species (Y = NR, CR_2, N_3R, N_2CR_2), which enables a multitude of coupling reactions including catalytic nitrene homocoupling, catalytic coupling of nitrenes and carbenes with isocyanides, as well as rare or unprecedented reductive coupling of azides and diazoalkanes.

Keywords

Alkoxide ligands

Group transfer chemistry

Reductive coupling

Azoarenes

Carbene ligands

1. Introduction

One of the major foci of contemporary organometallic chemistry is on the development of new transition metal complexes for group-transfer catalysis, including carbene, nitrene, and oxo transfer. Base (3d) transition-metal nitrene, carbene, and oxo complexes are attractive functionalities in this regard, serving as vehicles for the sustainable formation of new C-N, C-O, C-C, and N-N bonds[1,2,3]. The sustainability of these transformations can be attributed to several factors: (1) the ability to carry out a relatively complex transformation in one step, minimizing the amount of by-products, (2) the use of diazoalkane/organoazide starting materials whose only by-product upon carbene/nitrene formation is dinitrogen, and (3) the use of base transition metals that offer low cost and (typically) low toxicity, yet are available in high abundance. Examples of the reactions mediated by carbene complexes[4] include C-H bond activation[5,6,7,8,9], cyclopropanation[10], and formation of heteroallenes (ketenes[11,12], ketenimines[13,14,15]) via direct coupling with CO/CNR and isocyanides (**Fig. 1**). Similarly, nitrenes serve as reactive intermediates in C-H bond amination [16,17], aziridination,[18,19,20] and formation of carbodiimides[21], isocyanates[22], and azoarenes[23,24,25,26] (**Fig. 2**). Reactive metal-oxo complexes have been a subject of long-standing interest in the inorganic community, linking the organometallic and bioinorganic perspectives.[27,28] Several "Holy Grail" reactions observed in bioinorganic chemistry, particularly selective mono-oxygenation[29], and efficient O-O bond formation in water oxidation to dioxygen[30], inspire significant interest in the design of homogeneous[31,32,33] or heterogeneous[34,35] metal-oxo catalysts capable of similar transformations.

Insert Fig. 1

Fig. 1. Formation of metallocarbenes from diazoalkanes and selected carbene transfer reactions.

Insert Fig. 2

Fig. 2. Formation of metallonitrenes (metal-imidos) from diazoalkanes and selected nitrene transfer reactions.

The reactivity of transition metal oxo[36,37], nitrene,[38,39,40] and carbene[41] complexes is determined by their electronic nature, which is regulated, in part, by the ancillary ligand type. A significant number of studies during the last decade demonstrated that strong-field ligands, that combine strong σ-donation and some degree of π-acceptance (e. g. N-heterocyclic carbenes[42,43,44,45] or phosphines[46,47]) form remarkably stable high-valent late metal imido, nitrido, and related complexes. In sharp contrast, relatively weak-field nitrogen-based ligands (e.g. dipyrromethene) were found to lead to reactive electrophilic nitrenes[48,49,50,51,52,53], carbenes[54,55], and related functionalities[56].

Alkoxides are among the simplest, oldest, and most easily synthesizable ligands for the transition metals[57,58,59]. Until relatively recently, however, the major focus of alkoxide chemistry was on oxophilic early transition metals, for which alkoxides were considered to be a natural fit[60,61,62,63,64]. Recent years have witnessed an increase in the use of alkoxides as supporting ligands for later transition metals, particularly 3d, due to several considerations presented below[65,66,67,68]. Alkoxides generally form relatively strong bonds with 3d metals, including middle and late, which makes them viable ligands for such elements. The higher electronegativity of oxygen (compared with nitrogen and carbon), however, should result in alkoxide being a weaker σ-donor than amide and alkyl. The presence of the occupied π-symmetry orbitals on the oxygen leads to π-donor character of the alkoxide. Due to the combination of weak σ-donation and π-donation, alkoxides could be considered among the weakest-field ligands; this weak-field nature could subsequently lead to reactive nitrene, carbene, and oxo functionalities due to the anticipated high-spin configurations at the metal centers in these complexes (**Fig. 3**).

Insert Fig. 3

Fig. 3. Steric and electronic aspects of alkoxide coordination in $M(OR)_2(=X)$ complexes (X = oxo, nitrene, carbene)

The steric aspect of the alkoxide ligation also merits consideration, as it has a significant effect on the design of alkoxide-based group-transfer catalysts. Unlike related amido ligands [NR_2], alkoxides [OR] feature a single substituent[60,69]. The lack of steric protection and the presence of the lone pairs on the oxygen often results in cluster formation, particularly for the π-basic later metals. Extreme bulk at the R group constitutes one of the solutions to this problem. Several bulky [OCR_3] ligands were designed in the recent decade, allowing formation of well-defined mononuclear platforms for the installation of a reactive functionality. Furthermore, the steric bulk of the alkoxide can be carefully modified to allow selective formation of bis(alkoxide) [$M(OR)_2$] and tris(alkoxide) [$M(OR)_3$] platforms. This review will examine these relatively recent developments, particularly concentrating on the design and synthesis of bulky systems developed for [CR_2], [NR], and [O] groups transfer, their stereoelectronic properties, and their reactivity. The focus will be on the alkoxide in its narrow definition (OCR_3), although related aryloxides and siloxides will be described and compared with alkoxides when appropriate.

The review will start with the description of [$M(OCR_3)_n$] (n = 2,3) complexes which can serve as precursors for group-transfer chemistry (**chapter 2**). The focus will be on how the choice of different R groups in the [OCR_3] ligand framework affects the overall shape and composition of the metal complex. Next, the reactivity of alkoxide-ligated complexes in oxo-transfer reactions (**chapter 3**) will be presented. The electronic structure of metal-oxo complexes in alkoxide ligand environments, and the relevance of these systems to the reactivity of PSII and heterogeneous metal-oxides, will be discussed. Following the description of oxo-transfer chemistry, nitrene-transfer chemistry at [$M(OCR_3)_n$] systems will be surveyed, with particular attention on the electronic structures and subsequent stoichiometric and catalytic reactivity (**chapter 4**). Finally, emerging late metal-carbene chemistry in the alkoxide ligand environments will be presented, again with emphasis on the unique electronic structure and reactivity of such species (**chapter 5**). In conclusion, we will summarize these recent developments and endeavor to forecast how this field will develop.

2. Design of mononuclear precursors in alkoxide ligands environments

This review focuses specifically on the reactivity of well-defined mononuclear 3d metal complexes bearing monodentate alkoxide ligand environments. The steric profile of an alkoxide ligand can be used to control both complex nuclearity and the number of alkoxide ligands coordinated to the metal. Generally, tert-butoxo [$OCMe_3$] (or smaller) ligands have insufficient steric profile to prevent cluster formation, which is why well-defined mononuclear complexes required bulkier ligands [60,65]. Bulkier alkoxides can be constructed by installing larger R groups as part of the [OCR_3] skeleton. A large variety of alkoxide ligands [OCR_3] featuring identical or different R groups can be easily accessed by a nucleophilic attack of an organometallic reagent on the corresponding ketone/ester (**Fig. 4**). Other properties (e.g. crystallinity or solubility) can be controlled by the choice of a specific R group. Throughout the years, many different [OCR_3] featuring identical or different R groups were synthesized. The focus here is on the recent systems that allow subsequent group-transfer chemistry at mononuclear platforms (**Fig. 3**); the reader is referred to the previous, more general, accounts describing the design and synthesis of bulky alkoxides cited above.

Insert Fig. 4

Fig. 4. Typical synthetic routes to the alkoxide ligands.

[OC^tBu_3] ("tritox") is a prototypical bulky alkoxide ligand, whose transition metal chemistry was studied primarily by the groups of Wolczanski[70,71] and Power[72,73,74,75]. Tritox was postulated to be a steric (similar cone angle and symmetrical shape) and electronic (potentially one σ and two π orbitals donor) analogue of the ubiquitous cyclopentadienyl (Cp) ligand[60]. Due to its more electron σ-withdrawing nature, tritox could be expected to lead to more electrophilic and reactive metal centers[60]. The steric bulk of [OC^tBu_3] led to the selective formation of the bis(alkoxide) [$M(OC^tBu_3)_2$] complexes with transition metals. However, the utilization of tritox as an ancillary ligand in group-transfer chemistry was hampered by several notable deficiencies. When part of an early transition metal complex, tritox underwent facile decomposition, resulting in the formation of a metal-oxo functionality and organic products indicative of heterolytic O-CR_3 bond cleavage[60]. This decomposition was particularly pronounced for the heavier early transition metals (Zr, Ta), likely due to the strength of the ensuing metal-oxo bonds. Furthermore, tritox complexes often exhibited poor crystallinity, making their characterization by X-ray crystallography difficult. As a result, Wolczanski and coworkers shifted their focus to the related [OSi^tBu_3] ligand ("silox")[76], which exhibited similar stereoelectronic properties but with a more stable O-Si bond and higher crystallinity. It should be noted that 3d transition metals, particularly middle and late ones, demonstrated much higher stability as [$M(OC^tBu_3)_2$] complexes, because formation of metal-oxo bonds at these metals is less favorable[72,73,75]. Similarly, other bulky symmetrical alkoxides, such as [$OCPh_3$] and [$OCCy_3$] (Cy = cyclohexyl, **Fig. 5**) formed stable bis(alkoxide) complexes with later 3d transition metals[77,78].

Insert Fig. 5

Fig. 5. Commonly used bulky symmetric alkoxides (siloxides) forming mononuclear 3d complexes

The promise of bulky alkoxides as weak-field ancillary ligands for designing electrophilic metal centers prompted other groups to explore additional ligand candidates during the last decade, with a particular focus on non-symmetric alkoxides [OCR_2R'] (**Fig. 6**). The motivation behind breaking the perfect "conical symmetry" of [OCR_3] species by installing one significantly different R' group was to improve their conformational adaptivity, as a means to achieve more robust and less labile structures. It was postulated that the non-symmetric shape of [OCR_2R'] ligands would lock them in a preferred orientation in the respective complex, leading to tighter packing, more stable complexes, and higher crystallinity[65]. Furthermore, permutation of different R/R’ groups creates a larger number of new ligand candidates [OCR_2R'] as opposed to a limited number of [OCR_3]. Most of the recent efforts (and a bulk of this review) focused on two kinds of non-symmetric bulky alkoxides, [OC^tBu_2Me] and [OC^tBu_2Ph] (or its derivative [$OC^tBu_2(3,5\text{-}Ph_2Ph)$], **Fig. 6**). In both cases, two *tert*-butyl substituents were retained to keep the ligand sufficiently bulky and soluble in low-polarity solvents, while creating a steric gradient accessible through the third substituent.

Insert Fig. 6

Fig. 6. Recently designed bulky non-symmetric alkoxides forming mononuclear 3d complexes

Replacement of one of the *tert*-butyl groups in [OC^tBu_3] (tritox) by a methyl group led to a new ligand [OC^tBu_2Me], accordingly termed “ditox”[79,80,81,82]. Consistent with the expectations, ditox demonstrated selectivity for tris(alkoxide) ligation across the first-row transition series, featuring either trigonal planar, trigonal monopyramidal, or tetrahedral structures, depending on whether the solvent coordinated to the metal. Ditox complexes exhibited high crystallinity due, in part, to the preferred “head-to-tail” circular arrangement of [OC^tBu_2Me] that positioned the smaller methyl group next to the *tert*-butyl group of the adjacent ligand (see below, **Fig. 17**). Tris(ditox) platforms were found to support a wide range of oxidations states, including M(II) (Cr, Mn, Fe, Co), M(III) (V, Cr, Fe), M(IV)-oxo (V, Cr, Mn, Fe), and M(V)-oxo (V, Cr, Mn) (see below).

The synthesis of [$M^{II}(OC^tBu_2Me)_3]^-$ (M= Mn-Co) and [$M^{III}(OC^tBu_2Me)_3$] (M = V, Cr, Fe) complexes was accomplished by the addition of three equivalents of $LiOC^tBu_2Me$ (or

KOC^tBu_2Me) to MX_2 and MX_3 precursors[79,81,82]. M(II) tris(ditox) complexes were initially isolated as distorted trigonal planar "ate" species $[M^{II}(OC^tBu_2Me)(\mu^2\text{-}OC^tBu_2Me)_2M'(THF)_n]$ (M = Mn, Fe; M' = Li, K; n = 2, 1) (**Fig. 7**)[81,82]. Due to the intercalation of the alkali metal, these complexes exhibit two wide and one contracted RO-M-OR angles, resulting in a Y-shaped geometry. Intercalated alkali metal can be removed by application of the suitable crown ether, leading to the isolation of well-defined mononuclear anions $[M^{II}(OC^tBu_2Me)_3]^-$ (M = Mn, Fe), that exhibit trigonal planar geometries with nearly identical RO-M-OR angles[81,82]. Magnetic susceptibility measurements indicate high-spin states in all cases, which are close to spin-only values. The reactions of MCl_3 (M = V, Cr, Fe) with three equivalents of ditox forms $[M^{III}(OC^tBu_2Me)_3L]$ complexes (L = THF, absent; **Fig. 8**)[79,81]. For M = V and Fe, the complexes exhibited distorted trigonal monopyramidal structures, with a THF ligand occupying the axial position. For Cr, the geometry was trigonal planar. As with M(II) species, M(III) tris(alkoxide) complexes all exhibit high-spin configurations. Electrochemical measurements performed on the iron complexes demonstrate two irreversible oxidation events, Fe(II)/Fe(III) and Fe(III)/Fe(IV)[81] (**Fig. 9**), demonstrating the feasibility of two-electron group-transfer chemistry. The irreversibility of the Fe(II)/Fe(III) couple likely results from the different (trigonal planar vs. trigonal pyramidal) structures of Fe(II) and Fe(III) complexes.

Insert Fig. 7

Fig. 7. Synthesis of $[M^{II}(OC^tBu_2Me)_3]^-$ species.

Insert Fig. 8

Fig. 8. Synthesis of [$M^{III}(OC^tBu_2Me)_3$]L species.

Insert Fig. 9

Fig. 9. Irreversible Fe(II)/Fe(III) and Fe(III)/Fe(IV) oxidations demonstrated by the [$Fe(OC^tBu_2Me)_3$]$^-$ system.

Another non-symmetric alkoxide ligand system investigated in the context of group-transfer chemistry is [OC^tBu_2Ph][83,84]. The design of [OC^tBu_2Ph] can be traced to similar arguments as for [OC^tBu_2Me]: the replacement of one of the *tert*-butyl groups by a phenyl group should afford a conformationally adaptive ligand capable of forming stable and crystalline complexes. There are, however, notable differences between [OC^tBu_2Me] and [OC^tBu_2Ph]. Most importantly, phenyl is significantly larger than methyl. Both [OC^tBu_3] and [$OCPh_3$] formed preferentially [$M(OR)_2$]-type complexes, so [OC^tBu_2Ph] is expected to prefer bis(alkoxide) ligation, vs. the selective tris(alkoxide) ligation observed for [OC^tBu_2Me]. Second, the phenyl group can be easily modified via substitution in various positions, if additional steric intervention is required. Substitution in the *meta* positions produced a slightly bulkier variant of [OC^tBu_2Ph], [$OC^tBu_2(3,5\text{-}Ph_2Ph)$][85]; *meta* substituents are not pointing towards the metal and therefore are not expected to undergo intramolecular C-H activation. Studies conducted so far demonstrated selectivity of [OC^tBu_2Ph] towards formation of bis(alkoxide) platforms, albeit tris(alkoxide) ligation for [OC^tBu_2Ph] was shown to be possible under forcing conditions. In contrast, [$OC^tBu_2(3,5\text{-}Ph_2Ph)$] was shown to exclusively form $M(OC^tBu_2(3,5\text{-}Ph_2Ph))_2$ complexes.

Two synthetic routes were found to lead reliably to $M(OR)_2(THF)_2$ complexes (M = Cr-Co; OR = OC^tBu_2Ph, $OC^tBu_2(3,5\text{-}Me_2Ph)$). The reaction of MCl_2 (M = Cr-Co) with $LiOC^tBu_2Ph$

initially formed small clusters of [$M_2Li_2Cl_2(OC^tBu_2Ph)_4$] topology featuring seesaw geometry at the transition metals[83]. The reaction likely proceeded via [$MLiCl_2(OC^tBu_2Ph)_2(THF)_2$] intermediates (observed directly only for iron) (**Fig. 10**). For nickel, the reaction stopped at the [$NiLiCl(OC^tBu_2Ph)_2(THF)_2$] (or [$NiLiBr(OC^tBu_2Ph)_2(THF)_2$]) intermediates, and did not proceed further[84]. Subsequent treatment of seesaw clusters [$M_2Li_2Cl_2(OC^tBu_2Ph)_4$] with $TlPF_6$ precipitated TlCl and $LiPF_6$, and formed the desired mononuclear species $M(OR)_2(THF)_2$[84] (M = Mn, Fe, Co), except for [$Cr_2Li_2Cl_2(OC^tBu_2Ph)_4$] that failed to produce an isolable product. The second route involved the reaction of $M(N(SiMe_3)_2)_2(THF)_n$ precursors with two equivalents of HOC^tBu_2Ph or $HOC^tBu_2(3,5\text{-}Ph_2Ph)$ (**Fig. 11**). Treatment of $Fe(N(SiMe_3)_2)_2(THF)_n$ with $HOC^tBu_2(3,5\text{-}Ph_2Ph)$ yielded $Fe(OC^tBu_2(3,5\text{-}Ph_2Ph))_2(THF)_2$[86]. For Cr, the reaction with HOC^tBu_2Ph produced a $Cr_2(OR)_4$ dimer[87]; bulkier alkoxide $HOC^tBu_2(3,5\text{-}Ph_2Ph)$ formed the monomeric product $M(OC^tBu_2(3,5\text{-}Ph_2Ph))_2(THF)_2$[85].

Insert Fig. 10

Fig. 10. Reactions of MCl_2 (M = Cr-Ni) with two equivalents of $LiOC^tBu_2Ph$ leading to the formation of $M(OC^tBu_2Ph)_2(THF)_2$ for M = Mn-Co.

Insert Fig. 11

Fig. 11. Reactions of metal-amide precursors with HOC^tBu_2Ph and $HOC^tBu_2(3,5\text{-}Ph_2Ph)$.

The $M(OC^tBu_2Ph)_2(THF)_2$ and $M(OC^tBu_2(3,5\text{-}Ph_2Ph))_2(THF)_2$ species exhibited coordination geometries intermediate between seesaw and tetrahedral. The RO-M-OR angles were between 130-139 ° for $[OC^tBu_2Ph]$; slightly wider angles of 142 ° (Fe) and 147 ° (Cr) were observed for the complexes of bulkier $[OC^tBu_2(3,5\text{-}Ph_2Ph]$. THF-M-THF angles were in the 85-95 ° range.

One of the notable drawbacks of an alkoxide ligand is its kinetic lability. While it is possible to control coordination geometry of an alkoxide ligand by its size, it still may undergo dissociation from the metal. To improve the overall stability of bis(alkoxide) ligand platforms (of $M(OR)_2$ species), Groysman, Lord and coworkers have very recently designed and synthesized chelating bis(alkoxide) $H_2[OO]^{Ph}$ (**Fig. 12**)[88]. $H_2[OO]^{Ph}$ combines two $[OCPh_3]$ motifs linked through a 4,4'terphenyl bridge. The reaction of $Fe(N(SiMe_3)_2)_2(THF)_n$ with $H_2[OO]^{Ph}$ yields $Fe[OO]^{Ph}(THF)_2$ complex that is structurally related to $Fe(OC^tBu_2Ph)_2(THF)_2$ and $Fe(OC^tBu_2(3,5\text{-}Ph_2Ph))_2(THF)_2$ described above, but with the major difference of a wider intra-alkoxide (RO-Fe-OR) angle of 156 ° suggestive of the more sterically congested reactive site. We attribute the more sterically congested nature of "$Fe[OO]^{Ph}$" to the geometry and the rigidity of terphenyl-bridged bis(alkoxide) ligand.

Insert Fig. 12

Fig. 12. Synthesis of iron complex $Fe[OO]^{Ph}(THF)_2$ bearing chelating bis(alkoxide) ligand.

An alternative strategy to the design of well-defined mononuclear middle and late 3d complexes involves alkoxide ligands featuring electron-withdrawing, generally heavily fluorinated, substituents[89,90,91,92]. Electron-deficient alkoxides display lower basicity, which decreases bridging and stabilizes mononuclear species. In addition, perfluorination leads to more robust ancillary ligands in oxidizing environments. The coordination geometry and ligand field strengths of selected electron-deficient alkoxide ligands (**Fig. 13**) were explored by Doerrer and coworkers. Thus, [OC(CF_3)$_3$] formed tris(alkoxide) and tetra(alkoxide) complexes for middle and late metals in M(II) oxidations state (Fe(II)-Zn(II))[90,91]. For Cu(I), a variety of bis(alkoxide) $[Cu(OR^F)_2]^-$ complexes were obtained, to be investigated as models for Cu sites in zeolites (see **chapter 3** for the reactivity studies)[93]. $[Cu^I(OR^F)_2]^-$ precursors were generally synthesized using a $[CuMes]_n$ precursor and the combination of HOR^F and KOR^F (or $TlOR^F$) (**Fig. 14**)[94,95]. Structural and conductivity studies suggest extensive K---F/O interactions, which were proposed to stabilize the $[Cu(OR^F)_2]^-$ skeleton toward disproportionation reactions.

Insert Fig. 13

Fig. 13. Examples of fluorinated alkoxides investigated by the Doerrer group.

Insert Fig. 14

Fig. 14. Synthesis of mononuclear copper(I) complexes bearing fluorinated alkoxides.

3. Middle and Late 3d Metal-Oxo Complexes in Alkoxide Ligand Environments

There is a growing interest in the design and reactivity of 3d middle and late metal-oxo complexes in the oxygen-donor ligand environments. This interest is motivated by several relatively recent discoveries of the important roles that manganese, iron, cobalt, or nickel oxo functionalities play in biological and heterogeneous catalysis. Some of the most prominent examples include highly efficient O-O bond formation by the active site of Photosystem II (PSII) or metal-oxide catalysts[96,97] and selective methane hydroxylation by iron and copper zeolites or enzymes[98,99]. The active sites of the aforementioned catalysts feature primarily oxo or hydroxo (or carboxylate) ancillary ligation. The active site of Photosystem II, which is responsible for the formation of dioxygen from two waters, comprised the [Mn_4CaO_5] cluster[100]. In addition to the oxo ligands making up the core of the cluster, it contains carboxylate (Asp and Glu) and water/hydroxo ligands. A possible mechanism for the O-O bond formation step involves coupling of a Mn(IV) terminal oxyl radical with a nearby μ^2-oxo bridging two additional Mn(IV) centers (**Fig. 15**). Oxygen-producing cobalt-oxide materials feature reactive surface sites with Co(IV) in all-oxygenic environments[101]. The O-O bond formation is proposed to operate via two nearby cobalt(IV) oxyl radicals[102,103].The active site of methane hydroxylation by iron-zeolites contains square-pyramidal high-spin iron(IV)-oxo, coordinated by surface aluminosilicate oxygens. The formation of Fe(IV)-oxo takes place via oxidation of the mononuclear α-Fe(II) site with an O atom donor N_2O (**Fig. 15**)[99]. Highly reactive high-spin ($S = 2$) iron(IV)-oxo abstracts H atom from methane to form iron(III)-hydroxo and methyl radical, which is followed by radicals recombination to yield methanol. Similar selective formation of methanol from methane takes place at the active site of methane monooxygenase (MMO), with O_2 as an oxygen atom donor[104]. MMOs feature a di-iron site displaying mostly monodentate carboxylate ligation, in addition to water and histidine.

Insert Fig. 15

Fig. 15. Active sites of metalloenzymes or heterogeneous catalysts featuring reactive metal-oxos in oxygen-rich ligand environment.

What is the role of oxygen-donor ligand environment in the formation and reactivity of metal-oxo functionalities? How do specific coordination geometries around metal-oxo influence their reactivity[36,37]? Well-defined low-dimensional models mimicking postulated coordination environments of biological or heterogeneous sites can provide mechanistic tools to answer these questions. Alkoxides are the most convenient synthetic instrument for mimicking anionic oxygen donors (i.e. oxo/siloxo/hydroxo/carboxylate) found in heterogeneous or biological catalysis; the well-defined low-nuclearity structure of such models is enabled by the steric control provided by the OR substituent. Furthermore, as discussed above, the shape of the R group on the alkoxide can potentially form oxo complexes in specific geometries, which could control their electronic structure and reactivity. The coverage of this chapter will focus on recent chemistry of mononuclear oxo-alkoxide complexes. We note there has also been a significant amount of work on well-defined multinuclear mimicks of the OEC featuring alkoxide ligation[105].

As described above, the ditox [OC^tBu_2Me] ligand enabled formation of trigonal tris(alkoxide) $[M(OR)_3(L)]^{0/1-}$ complexes selectively. Subsequent oxo-transfer yielded pseudotetrahedral $[M(OR)_3(=O)]^{0/1-}$ species, whose electronic structure and reactivity were studied by Nocera and coworkers. The initial investigation focused on the effect of tris(alkoxide) ancillary ligation on the electronic structure of d^0-d^2 early transition metal-oxo complexes (M =V(V), Cr(V), and Cr(IV))[79]. It should be noted that d^0-d^2 systems typically demonstrate triple metal-oxo bonds and accordingly electrophilic oxo functionalities in stronger-field ligand environments[36,37]. $V^{V}(OC^{t}Bu_2Me)_3(O)$ (d^0) and $Cr^{V}(OC^{t}Bu_2Me)_3(O)$ (d^1) were obtained via treatment of the corresponding precursors with NMe_3O and PhIO, respectively (**Fig. 16**). The d^2 complex $[Cr^{IV}(OC^{t}Bu_2Me)_3(O)](CoCp_2)$ was synthesized via the reduction of $Cr^{V}(OC^{t}Bu_2Me)_3(O)$ with cobaltocene. All $[M(OR)_3(=O)]^{0/1-}$ exhibit an approximate C_3 symmetry with the head-to-tail circular arrangement of $[OC^{t}Bu_2Me]$ (**Fig. 17**). Combined structural, spectroscopic, computational, and reactivity study suggested that the d electrons populate orbitals with significant antibonding metal-oxo character, thereby decreasing metal-oxo bond order. For the d^0 V(V) system, structural and spectroscopic studies were consistent with the triple V≡O bond: vanadium-oxo distance of 1.605(1) Å, V-O stretching frequency of 981 cm^{-1}. For the d^1 system (Cr(V)), Cr-oxo bond distance was longer (1.649(2) Å), and the Cr-O stretching frequency was lower, 946 cm^{-1}. A further decrease in the Cr-oxo stretching frequency (to 870 cm^{-1}) was observed for the d^2 system $[Cr^{IV}(OC^{t}Bu_2Me)_3(O)]^-$; magnetic measurements demonstrated two unpaired electrons for this system. DFT calculations suggested that strongly donating alkoxides destabilize the d_{xy}/d_{x2-y2} orbitals, thereby causing the d_{xz}/d_{yz} orbitals to be lower in energy (**Fig. 17**); d_{xz}/d_{yz} orbitals are of π-antibonding character with respect to the metal-oxo bond. Accordingly, introduction of one d electron (Cr(V)) led to the lowering of the metal-oxo bond order to 2.5; two d electrons ($d_{xz}^1d_{yz}^1$ configuration, Cr(IV)) gave a double bond (**Fig. 16**).

Insert Fig. 16

Fig. 16. Top: Synthesis of $[M(OR)_3(=O)]^{0/1-}$ complexes

Insert Fig. 17

Fig. 17. Left: X-ray structure of the pseudotetrahedral $Cr(OR)_3(O)$ complexes (OR = OC^tBu_2Me) highlighting the "head-to-tail" arrangement of [OC^tBu_2Me]. Right: d orbital splitting diagram for [$Cr^V(OC^tBu_2Me)_3(O)$].

Reactivity studies supported the electronic structures proposed above. Cr(V) demonstrated electrophilic character of the metal-oxo, consistent with the bond order of 2.5. Treatment of [$Cr^V(OC^tBu_2Me)_3(O)$] with PPh_3 resulted in oxo transfer to triphenylphosphine to form PPh_3O[79] (**Fig. 18**). In contrast, no reaction was observed with electrophilic reagents BPh_3 or Me_3SiCl. The partial radical character of the oxo function (due to the oxo participation in the SOMO) was probed by the reaction with Bu_3SnH or $Bu_3SnSnBu_3$, which can serve as precursors for Bu_3Sn radicals. Both reagents formed [$Cr^{IV}(OC^tBu_2Me)_3(OSnBu_3)$][79], which could be expected upon metal-oxo coupling with an alkyltin radical. In contrast, the Cr(IV)-oxo (bond order of 2) demonstrated nucleophilic character at the metal-oxo. Whereas no oxo-transfer reactivity with phosphine was observed, [$Cr^{IV}(OC^tBu_2Me)_3(=O)$] reacted readily with Me_3SiCl to form [$Cr^{IV}(OC^tBu_2Me)_3(OSiMe_3)$]. The divergent reactivity of Cr(V) vs. Cr(IV) is presented in **Fig. 18**.

Insert Fig. 18

Fig. 18. Divergent reactivity of Cr(V) and Cr(IV) ditox complexes.

Following the initial study on pseudotetrahedral d^0-d^2 [$M(OR)_3(O)$] complexes, Nocera and coworkers investigated related d^3 (Mn(IV)) and d^4 (Fe(IV)) systems. Synthesis of pseudotetrahedral dark-green Mn^{IV}-oxo complex [$Mn^{IV}(OC^tBu_2Me)_3(=O)$][$K(15\text{-crown-}5)_2$] was accomplished via treatment of $[Mn^{II}(OC^{t}Bu_2Me)_3][K(15\text{-crown-}5)_2]$ with PhIO (**Fig. 19**)[82]. The C_3-symmetrical structure of the $[Mn^{IV}(OC^{t}Bu_2Me)_3(=O)]^-$ anion is nearly isomorphic with the structures of corresponding V/Cr complexes described above, exhibiting similar disposition of the ditox ligands. The Mn^{IV}-oxo bond distance is 1.628(2) Å, significantly longer than a typical Mn(V)-oxo[106,107,108], but is in line with (or slightly shorter than) previously reported Mn(IV)-oxo bond lengths[109,110]. The Mn-oxo stretch was observed at 845 cm^{-1}. Magnetic measurements confirmed the high-spin configuration of the d^3 system anticipated for weak-field alkoxide ligands. Structural and spectroscopic similarity of $[Mn^{IV}(OC^{t}Bu_2Me)_3(=O)]^-$ with the corresponding chromium and vanadium complexes suggests similar occupancy of the π-antibonding d_{xz}/d_{yz} set. $[Mn^{IV}(OC^{t}Bu_2Me)_3(=O)]^-$ underwent reversible oxidation to form postulated $[Mn^{V}(OC^{t}Bu_2Me)_3(=O)]$ (**Fig. 19**), a d^2 system isoelectronic with $[Cr^{IV}(OC^{t}Bu_2Me)_3(=O)]^-$. $[Mn^{IV}(OC^{t}Bu_2Me)_3(=O)]^-$ was found to react with weak C-H bonds (9,10-dihydroanthracene and 1,4-cyclohexadiene); no reaction with stronger C-H bonds was observed. Furthermore, no oxo-transfer with PPh_3 (ten-fold access) was observed. As $[Mn^{IV}(OC^{t}Bu_2Me)_3(=O)]^-$ constitutes a model of the S3 state of the OEC (Mn(IV) in the all anionic oxygen-ligand environment), it was hypothesized that the diminished electrophilic character of such species helps to attenuate reactivity in the pre-catalytic resting state[82].

Insert Fig. 19

Fig. 19. Formation and reactivity of $[Mn^{IV}(OC^{t}Bu_2Me)_3(O)][K(15\text{-crown-}5)_2]$.

The high-valent d^4 complex “$[Fe^{IV}(OC^{t}Bu_2Me)_3(O)]^-$“ was accessed via the oxidation of $[Fe^{II}(OC^{t}Bu_2Me)_3Li(THF)]$ or ion-separated $[Fe^{II}(OC^{t}Bu_2Me)_3][K(15\text{-crown-}5)_2]$ with PhIO[81].

This reaction led to the isolation of several different iron(III)-hydroxo products all featuring pseudotetrahedral $[Fe^{III}(OC^{t}Bu_2Me)_3(OH)]^-$ core (**Figs. 20, 21**). It is likely that this product originates from solvent H-atom abstraction by the highly electrophilic transient “$[Fe^{IV}(OC^{t}Bu_2Me)_3(O)]^{-}$“. This hypothesis was supported by the isolation and structural characterization of the peculiar “bis-THF” ligand, featuring a new C-C bond in place of C-H bonds (**Fig. 20**). Furthermore, the reaction in THF-d_8 formed significant quantities of $[Fe^{III}(OC^{t}Bu_2Me)_3(OD)]^-$, consistent with deuterium abstraction from the solvent[81]. The oxidative potency of “$[Fe^{IV}(OC^{t}Bu_2Me)_3(O)]^{-}$“ is further indicated by the immediate formation of $[Fe^{III}(OC^{t}Bu_2Me)_3(OH)]^-$ at reaction temperatures down to -78 ºC and in hydrocarbon solvents possessing strong C-H bonds (benzene or pentane), in contrast to only weak C-H bonds activation by Mn. The oxo-transfer reaction in CH_3CN resulted in the formation of the mixture of $[Fe^{III}(OC^{t}Bu_2Me)_3(CH_2CN)]^-$ and $[Fe^{III}(OC^{t}Bu_2Me)_3(OH)]^-$, again consistent with C-H activation of the solvent. The use of the fluorinated solvents enabled oxo-transfer catalysis from Me_3NO to PPh_3. Computational studies on the postulated “$[Fe^{IV}(OC^{t}Bu_2Me)_3(O)]^{-}$“ intermediate suggested a similar electronic structure to the pseudotetrahedral V/Cr/Mn oxo analogues. The high-spin nature of the intermediate (S=2), the steric accessibility of the exposed oxo function in pseudotetrahedral geometry, and significant oxo participation in the SOMOs all contribute to the unparalleled C-H activation reactivity of “$[Fe^{IV}(OC^{t}Bu_2Me)_3(O)]^{-}$“species. The attempt to form “$Fe^{V}(OC^{t}Bu_2Me)_3(O)$” by the oxidation of $Fe^{III}(OC^{t}Bu_2Me)_3(THF)$ with NMe_3O led instead to the isolation and structural characterization of the $[Fe^{III}(OC^{t}Bu_2Me)_3(ONMe_3)]$ adduct.

Insert Fig. 20

Fig. 20. Oxo-transfer reactivity of $[Fe^{II}(OR)_3Li(THF)]$ ($OR = OC^tBu_2Me$) to yield iron-hydroxo products via postulated iron(IV)-oxo intermediate.

Insert Fig. 21

Fig. 21. Oxo-transfer reactivity of ion-separated $[Fe^{II}(OR)_3][K(15\text{-crown-}5)_2]$ ($OR = OC^tBu_2Me$) in various solvents to yield iron(III)-hydroxo (and iron-alkyl) products.

Using a bis(alkoxide) platform $[M(OC^tBu_2Ph)_2]$, that has formed mononuclear nitrene and carbene complexes of the general $M(OR)_2(=X)$ form (see below), Groysman and coworkers attempted to synthesize a related oxo complex $[Fe^{IV}(OC^tBu_2Ph)_2(O)]$. Treatment of $Fe^{II}(OC^tBu_2Ph)_2(THF)_2$ with PhIO led instead to the formation of an Fe(III) μ-oxo complex $Fe_2(OC^tBu_2Ph)_4(\mu^2\text{-}O)(THF)_2$ (**Fig. 22**)[84]. Similarly, treatment of $Fe^{II}(OC^tBu_2Ph)_2(THF)_2$ with a sulfide-transfer reagent formed $Fe_2(OC^tBu_2Ph)_4(\mu^2\text{-}S)(THF)_2$. No oxo/sulfide-transfer reactivity to PPh_3 was observed for these products.

Insert Fig. 22

Fig. 22. Formation of bridging oxo/sulfide complexes with $[Fe(OC^tBu_2Ph)_2]$ precursors.

Doerrer and coworkers investigated oxygenase reactivity of copper-alkoxide complexes as models for copper sites in zeolites[93]. Various copper(I) bis(alkoxide) precursors

$[Cu(OR^F)_2]^-$ ($OR^F = OC(CF_3)_3$, $OC(CF_3)_2Ph$, $OC(CF_3)_2Me$ and pin^F) reacted with dioxygen to form trinuclear ("T") reactive intermediates featuring a $[Cu_3(\mu^3\text{-}O)_2]^{3-}$ ($Cu^{III}/Cu^{II}/Cu^{II}$) core (**Fig. 23**)[94]. The formation of the T intermediates was likely preceded by a dimeric $[Cu_2(\mu^2\text{-}O)_2]^{2+}$ ("O") intermediate with a (Cu^{III}/Cu^{III}) core; additional fast intermediates were proposed as well. It is possible that potassium encapsulation by F atoms, which forms effective $\{[Cu(OR^F)_2]^-\}K_2$ dimers in solution, is responsible for the formation of dimeric "O" species. The T intermediates demonstrated ligand-dependent limited stability under -40 ºC and were characterized by cryospray-ionization mass spectrometry and Raman spectroscopy; their structure was supported by DFT calculations. Upon warming to room temperature, intra- and intermolecular hydroxylation was observed[94]. Complexes featuring partially fluorinated ligands ($OC(CF_3)_2Ph$ and $OC(CF_3)_2Me$) underwent ligand hydroxylations, whereas fully fluorinated ligands ($OC(CF_3)_3$ and pin^F) demonstrated intermolecular monooxygenase reactivity, forming 3,5-di-tert-butylcatecholate from 2,4-di-tert-butylphenolate (**Fig. 23**)[93].

Insert Fig. 23

Fig. 23. Selected reactions of $[Cu(OR^F)_2]^-$ complexes with O_2.

4. Nitrene transfer chemistry

There has been significant interest in the design of low-coordinate nitrene (imido) complexes featuring alkoxide ligand environments. As discussed earlier, the weak-field π-donating nature of alkoxide ligands is expected to render such complexes highly reactive. Low coordination is desirable to enable substrate coordination prior to the N-substrate bond formation.

Groysman, Lord and coworkers investigated the reactivity of chromium complexes bearing bis(alkoxide) ligand environments, [Cr(OR)$_2$] (OR = OC^{t}Bu$_2$Ph and OC^{t}Bu$_2$(3,5-Ph$_2$Ph))[85,87]. Treatment of dimeric Cr$_2$(OC^{t}Bu$_2$Ph)$_4$ with bulky aryl or alkyl azides N$_3$R' (R = mesityl, 2,6-Et$_2$Ph, adamantyl) afforded mononuclear trigonal planar imido complexes Cr(OC^{t}Bu$_2$Ph)$_2$(NR')[87] (**Fig. 24**); the nature of the product did not change when excess N$_3$R' was used. Magnetic measurements demonstrated high-spin electron configuration ($S = 1$). In contrast, treatment of Cr$_2$(OC^{t}Bu$_2$Ph)$_4$ with less bulky *para*-substituted aryl azides (R' = 4-MePh, 4-MeOPh) produced diamagnetic Cr(VI) bis(imido) complexes Cr(OC^{t}Bu$_2$Ph)$_2$(NR')$_2$, again irrespective of the metal-to-azide ratio[87]. Related chromium-imido complexes in bis(siloxide) ligand environments were previously reported by Wolczanski and coworkers[111].

Insert Fig. 24

Fig. 24. Reactivity of Cr$_2$(OR)$_4$ dimer with bulky (right) and non-bulky organoazides.

Catalytic reactivity of Cr$_2$(OC^{t}Bu$_2$Ph)$_4$ in nitrene transfer to isocyanides to form carbodiimides was also explored[87]. A distinctive correlation between the structure of the intermediate (i.e. trigonal planar Cr^{IV}(OC^{t}Bu$_2$Ph)$_2$(NR') vs. tetrahedral Cr^{VI}(OC^{t}Bu$_2$Ph)$_2$(NR')$_2$) and nitrene-transfer reactivity was observed. Bulky aryl/alkyl azides, that formed Cr(IV) mono(imido) complexes, enabled catalytic performance with different isocyanides (**Fig. 25**). In contrast, no reactivity was observed for the *para*- or *meta*-substituted aryl azides, which formed Cr^{VI} bis(imido) complexes. DFT calculations rationalized this observation, suggesting that isocyanide has to bind to the metal center prior to N-C bond formation. Coordinatively unsaturated trigonal monoplanar $Cr^{IV}(OC^{t}Bu_2Ph)_2(NR')$ enabled such binding, as opposed to tetrahedral $Cr^{VI}(OC^{t}Bu_2Ph)_2(NR')_2$, emphasizing the importance of low coordination in group-transfer chemistry.

Insert Fig. 25

Fig. 25. Catalytic synthesis of carbodiimides by $[Cr(OR)_2]$ system.

Given the well-established activity of iron-nitrene in group transfer reactions, nitrene-transfer reactivity of iron complexes in alkoxide and related O-based ligand environments drew particularly close attention. Early on, Kawaguchi and coworkers described reactivity of two-coordinate $Fe(OAr)_2$ (Ar = 2,6-Ad-4-MePh or Ar = 2,6-Ad-4-^{i}PrPh) with adamantyl azide[112]. The reaction formed pale green Fe(II) products Fe(OAr)(OAr'-NHAd) (**Fig. 26**). It was hypothesized that the reaction proceeded via a reactive transient electrophilic Fe(IV)-imido complex $[Fe^{IV}(OAr)_2(NAd)]$ which inserts nitrene into the C-H bond of the neighboring adamantyl group.

Insert Fig. 26

Fig. 26. Insertion of nitrene into an aryloxide C-H bond demonstrated by Kawaguchi and coworkers.

Lord, Groysman and coworkers investigated the reactivity of various iron bis(alkoxide) systems with organoazides. Two distinctly different reactivity pathways were observed as a function of the R group on the azide, alkyl vs. aryl. Treatment of $Fe(OC^{t}Bu_2Ph)_2(THF)_2$ with an alkyl (adamantyl) azide led to the reductive coupling of the azide via the terminal nitrogens to yield an iron(III) hexazene complex $(RO)_2Fe(\mu\text{-}\kappa^2{:}\kappa^2\text{-}AdN_6Ad)Fe(OR)_2$ (OR = $OC^{t}Bu_2Ph$, **Fig. 27**)[113]. Remarkably, reductive coupling by $Fe(OC^{t}Bu_2Ph)_2(THF)_2$ did not require the reducing power of Fe(I)/Mg(I)/Zn(I) metalloradicals, as in the previous instances of this relatively rare transformation[114,115,116]. DFT calculations suggested that the initial azide coordination to mononuclear $[Fe^{II}(OC^{t}Bu_2Ph)_2]$ species may form an azide-bridged dimer **(Fig. 27**) with significant azide reduction; the dimerization event places azide radicals in near proximity and allows for the subsequent reductive coupling.

Insert Fig. 27

Fig. 27. Possible mechanism for the reductive coupling of adamantyl azide to give $Fe(OR)_2$-hexazene.

Treatment of $Fe(OC^{t}Bu_2Ph)_2(THF)_2$ with aryl azides N_3Ar led to the reductive splitting of N_3Ar and likely formation of nitrene intermediates[117]. For bulky aryl azides (e.g. mesityl, 2,6-diethylphenyl), the reaction yielded corresponding azoarenes quantitatively (**Fig. 28**)[117]. Mesityl nitrene coupling is selective for the $[Fe(OR)_2]$ system even in the presence of a large excess (solvent) of a weak C-H bond donor, cyclohexadiene. For aryl azides lacking *ortho* substituents (e.g. phenyl, 3,5-dimethylphenyl), the initial nitrene formation resulted in alkoxide disproportionation to give $Fe_2(\mu^2\text{-}NAr)_2(OC^{t}Bu_2Ph)_2(THF)_2$ and $Fe(OC^{t}Bu_2Ph)_3$. The resulting bridging imido complexes $Fe_2(\mu^2\text{-NAr})_2(OR)_2(THF)_2$ did not produce azoarene upon thermolysis; treatment with additional azide or isocyanide similarly produced no additional products, emphasizing the stability of the $[Fe_2(\mu^2\text{-NAr})]$ core.

Insert Fig. 28

Fig. 28. Reactivity of $Fe(OR)_2(THF)_2$ (OR = OC^tBu_2Ph) with aryl azides: formation of azoarenes for Ar = 2,4,6-Me_3PhN_3 and 2,6-Et_2PhN_3, and iron-imido dimers for Ar = Ph and 4-MePh.

The putative $[Fe(OC^tBu_2Ph)_2(NAr)]$ intermediate was modeled using full DFT calculations for $[Fe(OC^tBu_2Ph)_2(NMes)]$ and with QM/MM methods for $[Fe(OC^tBu_2(3,5\text{-}Ph_2Ph))_2(4\text{-MeOPh})]$[86,117] (see below). In both cases the quintet state is predicted to be lowest in energy with a variety of functionals due to the well-documented spin-state sensitivity of DFT, but the triplet state is computed to be close enough in energy that it may be involved in reactivity[118,119]. As **Fig. 29** shows for both $Fe(OR)_2(NPh)$ and $Fe[OO]^{Ph}(NPh)$, the spin density of this nitrene intermediate shows significant β spin on the NPh moiety consistent with its formulation as a high-spin Fe^{III} ion antiferromagnetically coupled to a nitrene radical, similar to what Betley and co-workers reported for their dipyrromethene-based nitrene[120].

Insert Fig. 29

Fig. 29. Spin density isosurface plots (iso = 0.002 au) for the quintet states of $[Fe(OC^tBu_2Ph)_2(NPh)]$ (left) and $[Fe[OO]^{Ph}(NPh)]$ (right) calculated at the B3LYP/def2-TZVP

level of theory[121,122,123,124,125,126,127]. Alpha and beta spin are represented with blue and gray, respectively.

To prevent alkoxide disproportionation, indicated by the formation of iron mono(alkoxide) and iron tris(alkoxide) species, two different approaches were pursued. The first approach involved design of bulkier monodentate alkoxide ligand, [$OC^tBu_2(3,5\text{-}Ph_2Ph)$], which precluded formation of the tris(alkoxide) by-product by virtue of the steric bulk[86]. The stability of the bis(alkoxide) ligation also prevented formation of the unreactive bis(μ-imido) dimers, and provided insight into the reaction mechanism. The reaction was found to proceed via structurally and spectroscopically characterized iron-tetrazene intermediates[86], which constitute a "dormant" form of the reactive imido: heating iron-tetrazene complexes formed azoarene products (**Fig. 30**). Combined field-dependent ^{57}Fe Mössbauer high-frequency and EPR spectroscopic data carried out on the tetrazene complexes $Fe(OR)_2(ArNNNNAr)$ (OR = $OC^tBu_2(3,5\text{-}Ph_2Ph)$) showed the system to contain a high spin Fe(III) (S=5/2) antiferromagnetically coupled with monoanionic tetrazene ligand (S=1/2)[86]. The Mössbauer isomer shift $\delta = 0.495$ mm/s was found to be similar to the isomer shift of another high spin Fe(III) tetrazene reported by Chirik and coworkers[128], but different from an Fe(II) tetrazene reported by Holland and coworkers[129,130] or an Fe(IV) tetrazene reported by Jenkins and coworkers[131]. A QM/MM study proposed that azoarene formation takes place via bimolecular coupling of iron-imidos. The second approach involved design of chelating bis(alkoxide) $[OO]^{Ph}$ which exhibited tighter binding to the metal[88], and thereby allowed reactivity studies with broader range of substrates. It should be also noted that the stability of both systems allowed reactivity studies under elevated temperatures.

Insert Fig. 30

Fig. 30. Formation and reactivity of iron-nitrene and iron-tetrazene complexes supported by [OR] (OR = $OC^tBu_2(3,5\text{-}Ph_2Ph)$).

Catalytic azoarene formation reactivity of different iron-alkoxide complexes was investigated for the $Fe(OC^tBu_2Ph)_2(THF)_2$[117], $Fe(OC^tBu_2(3,5\text{-}Ph_2Ph)_2(THF)_2$[86], and $Fe[OO]^{Ph}(THF)_2$[88] systems. Catalytic reactivity of the above systems exhibited a clear structure-activity relationship depending mostly on the overall steric hindrance at the active site, and generally agreed well with the stoichiometric reactivity. The steric effect of the alkoxide ligand can be approximated by the O-Fe-O angle in the precursor (**Fig. 31**). There is a small increase of the O-Fe-O angle in going from $[Fe(OC^tBu_2Ph)_2]$ to $[Fe(OC^tBu_2(3,5\text{-}Ph_2Ph)_2]$; a much more significant increase is observed for the chelating bis(alkoxide) $Fe[OO]^{Ph}$, making the catalytic position the most hindered. The most open and accessible position in $[Fe(OC^tBu_2Ph)_2]$ allows efficient coupling of bulky aryl nitrenes, however, the system is unstable towards disproportionation, particularly when heated. Wider interalkoxide angle in $[Fe(OC^tBu_2(3,5\text{-}Ph_2Ph)_2]$ precludes formation of "$Fe(OC^tBu_2(3,5\text{-}Ph_2Ph))_3$", which allows utilization of more pressing conditions. As a result, wider range of aryl nitrenes underwent coupling, albeit the yields for the *para*-substituted substrates were still low (**Fig. 32**). In contrast, the system with the most sterically hindered active site ($Fe[OO]^{Ph}$) demonstrated selectivity for the non-bulky substrates, enabling efficient coupling of *para*- and *meta*-substituted aryl nitrenes; no reactivity with *ortho*-substituted aryl azide was observed.

Insert Fig. 31

Fig. 31. Comparison of the interalkoxide O-Fe-O angle for various $Fe(OR)_2$ complexes.

Insert Fig. 32

Fig. 32. Divergent reactivity of iron-alkoxide complexes in nitrene coupling.

5. The chemistry of cobalt and iron bis(alkoxide)s with diazoalkanes: formation of cobalt carbenes vs. reductive coupling of diazoalkanes at iron

Groysman, Lord and coworkers reported the synthesis and characterization of the first high-valent cobalt-carbene complex in the bis(alkoxide) environment[132]. Treatment of $Co(OC^{t}Bu_2Ph)_2(THF)_2$ with N_2CPh_2 led to the isolation of $Co(OC^{t}Bu_2Ph)_2(=CPh_2)$ as brown crystals (**Fig. 33**). X-ray structure determination revealed a surprisingly short $Co\text{-}C_{carbene}$ bond (1.773 Å), suggesting increased $Co\text{-}C_{carbene}$ π-character exhibited by Schrock-type alkylidenes. The only other reported cobalt carbene complexes exhibiting such a short Co-carbene bonds are those containing electron-withdrawing fluorinated groups at the carbene carbon, $Co(PPh_3)Cp(=CFR^1)$ ($R^1 = F, CF_3$) of 1.7395(14) and 1.751(3) Å[133]. This is in contrast to most previously synthesized cobalt carbenes, which have significantly longer Co-C bonds (1.9 – 2.0 Å) and are formulated as Co(I)-Fischer carbene complexes[134,135,136,137,138]. One notable exception is highly reactive cobalt-carbenes in porphyrin ligand environments, which are proposed to form as low-spin Co(III)-carbene radical upon activation of the carbene precursors[139]. Interestingly, solution magnetic measurements showed $Co(OC^tBu_2Ph)_2(=CPh_2)$ to be low-spin (S = ½) species, in contrast to other alkoxide complexes which were high-spin. EPR analysis supports the ground state S = ½ species with $g_x = 3.04(1)$, $g_y = 2.17(1)$, and $g_z = 1.91(1)$[132]. The X-band EPR spectrum shows eight-line hyperfine splitting due to coupling of the unpaired electron with the cobalt center. Cyclic voltammetry shows three reduction events at −1.17 V, −2.46 V, and −3.16 V, with the first two being quasi-reversible, supporting a high-valent species. The reaction of $Co(OC^tBu_2Ph)_2(THF)_2$ with $N_2C(Ph)(CO_2Me)$ formed a similar brown intermediate, tentatively assigned as $[Co(OC^tBu_2Ph)_2(=C(Ph)(CO_2Me))]$ based on its UV-vis and NMR spectra[146]. Attempts to isolate and structurally characterize $[Co(OC^tBu_2Ph)_2(=C(Ph)(CO_2Me))]$ led instead to the isolation of the corresponding olefin, that is known to form from transient carbene complexes.

Insert Fig. 33

Fig. 33. Synthesis of high-valent cobalt-carbene complexes.

DFT calculations at the B3LYP/6-31G(d) level of theory gave Mulliken spin densities of 1.77 and -0.68 on cobalt and carbene carbon atoms, respectively, which suggested two α spins on cobalt and one β spin on the carbene. This supported the interpretation of this species as intermediate-spin Co(III) antiferromagnetically coupled to a carbene radical, but was in between the ideal values of 2 and –1 for that state and 1 and 0 for a Co(IV) alkylidene. Furthermore, the $S_{\alpha\beta}$ value of 0.64 for the magnetically coupled orbitals suggested Co-C π bonding. While the Mulliken spins were not sensitive to basis set[140], the choice of functional gave a range of values from 1.42 and –0.44 on the low end (closer to Co(IV)/alkylidene) to 1.89 and –0.82 on the high end (near the ideal values for Co(III)/carbene radical). These varying spins correlated with the amount of exact exchange in the functional used[141]. Calculations on a hypothetical Rh bis-alkoxide alkylidene showed non-negligible β spin on the carbene carbon (up to –0.3 depending on the functional choice), which suggested this system has more carbene radical than alkylidene character but significant contributions from both to its electronic structure.

Carbene formation from diazoalkanes is well precedented for iron complexes[142,143]. However, an iron complex in the alkoxide ligand environment exhibited remarkably different behavior. The reaction of $Fe(OC^{t}Bu_2Ph)_2(THF)_2$ with diphenyldiazomethane led to the formation of benzophenone azine in high yield; no metal-based intermediates were observed or isolated in this transformation[132]. In contrast, treatment of $Fe(OC^{t}Bu_2Ph)_2(THF)_2$ with methyl diazo(phenyl)acetate (and several closely related diazoesters) resulted in the first example of the reductive coupling of diazoesters through the terminal nitrogens to afford the tetrazene-bridged bis(diazenylacetate) ligand $\{Fe_2[\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}MeO_2CC(Ph)NNNNC(Ph)\text{-}CO_2Me](OR)_4\}$ (OR = $OC^{t}Bu_2Ph$, **Fig. 34**)[144]. Mössbauer and DFT experiments suggest the reductively coupled has two HS Fe(III) centers. Reductive coupling of diazoesters through the terminal nitrogens is related to the reductive coupling of diphenyldiazomethane (previously reported by Stephan and coworkers using the highly reducing Mg(I)-nacnac complex)[145], as well as to the reductive coupling of azide to form hexazene complexes, which was also reported for $Fe(OR)_2(THF)_2$[113], as well for other strongly reducing complexes[114,115]. $\{Fe_2[\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}MeO_2CC(Ph)NNNNC(Ph)\text{-}CO_2Me](OR)_4\}$ undergoes relatively slow decomposition to yield methyl benzoylformate azine as one of the products.

Insert Fig. 34

Fig. 34. Reductive coupling reactivity mediated by an iron(II) bis(alkoxide) (OR = $OC^{t}Bu_2Ph$).

DFT calculations were performed to explain the contrasting reactivity observed for the diazoester with the cobalt and iron precursors[144]. The initial, κ^1, binding of diazoester to the metal was preferred for Co, whereas isomerization to a κ^2 form was found to be preferred for iron (**Fig. 35**). Bidentate (κ^2) coordination leads to the reduction of the diazoester, taking place at the N-N π^*, which (1) creates significant radical density on the terminal nitrogen and (2) stabilizes diazoester towards N_2 expulsion. Both factors facilitate exergonic reductive coupling through the terminal nitrogens. For Co, the κ^2 binding mode that reduces the diazoester is disfavored, which is consistent with its lower reduction potential; carbene formation is also thermodynamically favored over reductive coupling for the $[Co(OR)_2]$ system, however, barriers for reductive coupling were not located (but appeared barrierless for Fe based on relaxed scans of the coupling N–N distance).

Insert Fig. 35

Fig. 35. Summary of free energies for Fe vs Co, reductive splitting vs. reductive coupling.

The reactivity of $Co(OC^{t}Bu_2Ph)_2(=CPh_2)$ towards carbene group transfer was explored. Only sluggish cyclopropanation reactivity was observed with several different olefins[132]. In contrast, $Co(OC^{t}Bu_2Ph)_2(=CPh_2)$ exhibited facile and high-yielding ketenimine formation upon reaction with alkyl or aryl isocyanides[146]. Excess isocyanide was required in this transformation due to formation of bis(isocyanide) complexes $Co(OC^tBu_2Ph)_2(CNR^')_2$, which were isolated and characterized for $R^'$ = 2,6-$Me_2C_6H_3$, 4-$OMeC_6H_4$, adamantyl (**Fig. 36**). While ketenimine formation was not catalytic for diphenyldiazomethane, diazoesters methyl phenyl(diazo)acetate $N_2C(Ph)(CO_2Me)$ and ethyl diazoacetate $N_2C(H)(COOEt)$ led to full turnover of the system. Methyl phenyl(diazo)acetate led to moderate yields due to formation of byproducts (corresponding azine and olefin), while $N_2C(H)(COOEt)$ led to the improved yields and no by-product formation. DFT calculations suggested that the isocyanide coordination to the cobalt center of $Co(OC^tBu_2Ph)_2(=CPh_2)$ precedes C-C bond formation, in contrast to the more classical Fischer carbene systems (such as coordinatively saturated $Cr(CO)_5(=CROR')$), where the C-C bond formed by a direct attack of isocyanide on carbene carbon[147]. Subsequent addition of isocyanide forms the bis(isocyanide) complex and ketenimine. Reaction of the bis(isocyanide) complex with diazoalkane/ester restores cobalt-carbene intermediate (**Fig. 36**). Theoretical and mechanistic studies suggested that the lack of catalysis for N_2CPh_2 was due to the more favorable formation of the bis(isocyanide) complexes compared with the carbene complex.

Insert Fig. 36

Fig. 36. Stoichiometric and catalytic cycle for the ketenimine formation by cobalt-mediated carbene group transfer to isocyanides

6. Conclusions and outlook

This review focuses on the group-transfer reactivity of a novel reactive motif in organometallic chemistry: low-coordinate middle/late 3d metal complexes in exceedingly weak-field bulky alkoxide ligand environments. A variety of factors including the ionic character of the alkoxides, their relatively weak σ-donicity, and their π-donating capability all strongly favor the formation of high-spin M(III) centers in most cases. Thus, the reactions of $[M^{II}(OR)_2]$ precursors with oxidizing substrates all converge on the generalized $M^{III}(OR)_2(X\bullet)$ intermediate, where the radical is stabilized by coupling with high-spin metal centers. Trigonal iron and/or cobalt $M^{III}(OR)_2(X\bullet)$ complexes (X = azide, nitrene, diazoalkane, carbene) demonstrate rare or unprecedented reactivity, including metal-based homocoupling of nitrenes, coupling of carbenes with isocyanides, and reductive coupling of azides and diazoalkanes. Related high-valent tris(alkoxide) Fe-oxo complexes and bis(alkoxide) Cu-oxo complexes activate strong C-H bonds whereas $[Mn^{IV}(OR)_3(=O)]^-$ demonstrates attenuated reactivity of the oxo functionality, consistent with the proposed role of Mn(IV) oxidation state in the pre-catalytic state of the Oxygen Evolving Center.

The results presented in this review demonstrate the rich potential of the weak-field alkoxide ligand platforms in the design of reactive group-transfer catalysts, and call for further studies. One particularly attractive avenue for future studies involves designing chelating bis(alkoxide) or tris(alkoxide) ligands. Whereas monodentate alkoxides offer unmatched ease of design and synthesis, the labile nature of an alkoxide often leads to catalyst demise. Chelating alkoxide ligands can increase catalyst stability, enable evaluation of more challenging reaction conditions, and allow for more careful geometric control of substrate binding to the metal ion. Another avenue of potential interest in this chemistry involves chemistry of heavier mid- and late transition metal complexes with alkoxides. Alkoxide complexes of heavier late transition metals are rare, and are generally difficult to synthesize. It is possible that chelating alkoxides (perhaps, featuring additional donors) could lead to the sufficiently stable species, enabling the isolation and subsequent electronic structure and reactivity studies of unprecedented 4d/5d late metal-alkoxide complexes.

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