

Dioxygen Activation by Organometallics of Early Transition Metals

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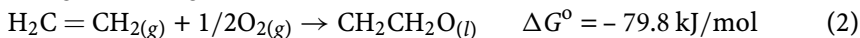
Abstract Organometallic compounds of the early transition metals (i.e., groups 3–6) react readily with oxygen (O₂). The different reaction pathways governing these reactions are distinguished and relevant examples from the recent organometallic literature are described. Catalytic aerobic oxidations are rare for these metals. However, the investigations of individual reaction steps contribute to the fundamental knowledge of organometallic chemistry, and they are valuable for the design of catalytic oxidations.

Keywords Organometallics · Dioxygen · Early transition metals · Oxygen atom transfer

1 Introduction

The utilization of dioxygen (O₂) in all manner of catalytic oxidation reactions is a highly attractive option for the preparation of oxygenated molecules. O₂ is a readily available, nontoxic reagent, and a common byproduct of aerobic oxidations is the innocuous substance water (H₂O). Thus, chemical processes using dioxygen are a goal of “green” or “sustainable” chemistry.

The reactions of O₂ with organic molecules are generally strongly favored in a thermodynamic sense (see Eqs. 1–3 for some prototypical examples).



However, they face substantial kinetic barriers, and none of the reactions shown above proceed with appreciable rate under mild conditions. Hence there arises the need for catalysts to facilitate the reactions. Besides, the desired reaction products—i.e., methanol, ethylene oxide, and phenol—are of course just kinetic products. The thermodynamic products for the three reactions shown, i.e., CO₂ and H₂O, are the same undesirable two in each case. Thus selectivity is called for, and once again catalysis will be the answer. Based on these fundamental considerations, much effort has already been expended on the search for selective catalysts for O₂-driven oxidations [1], and the need for future innovation remains strong.

Commercially practiced oxidation catalysis employing O₂ as terminal oxidant comprises examples of both heterogeneous and homogeneous catalysis; herein we are mostly concerned with the latter. In further narrowing the scope of this volume, we are considering only those reactions that involve “organometallic” species—i.e., molecules containing a direct metal–carbon bond—either as reactants, products, or intermediates. As both O₂ and hydrocarbon substrates can interact with and bind to metal complexes, there exist at least two general approaches to catalyzing oxidations. The more common approach involves the so-called “activation” of O₂ via coordination to a metal center [2] and its subsequent transformation into a reactive species (e.g., a high-valent metal oxo complex, such as the ferryl moiety commonly considered the reactive oxidant of the cytochrome P450 family of enzymes [3]). A second conceivable strategy relies upon “activation” of the hydrocarbon substrate by coordination to a metal, i.e., forming an organometallic species, which is subject to reaction with free O₂. Actually, even the “O₂-activation” approach may involve organometallic compounds, if the ancillary ligands of the catalyst include carbon-based ones.

This chapter is dedicated to a review of the recent organometallic chemistry of early transition metals (i.e., groups 3–6) with O₂. The oxophilic nature of these electropositive metals might suggest that they will resist complete the transfer of oxygen atoms to carbon, up to and including release of oxygenated products. Nevertheless, there are some examples of catalysis as well as many stoichiometric reactions, which shed light upon the mechanistic details of individual reaction steps comprising catalytic cycles of catalytic oxidations.

2 Reactions with O₂

The number of reactions of organometallic molecules with O₂ yielding well-characterized products in good yield is notably small. It is no accident that the typical synthetic organometallic laboratory is equipped with inert atmosphere glove boxes and Schlenk lines, and that rigorous exclusion of air by means of inert gas techniques and scrupulously dried and deoxygenated solvents pervade our daily routine [4]. Indeed, one's colleagues may receive the report of a reaction with O₂ with a thinly veiled contempt for sloppy laboratory technique.

Considering the potential utility of catalytic oxidations, and the need for a better understanding of the fundamental reaction steps involved, this relative paucity of systematic studies is unfortunate. It is an area that needs more work, and the scientific payoff warrants the occasional—if deplorable—transformation of a perfectly good organometallic compound into a black, smoldering tar.

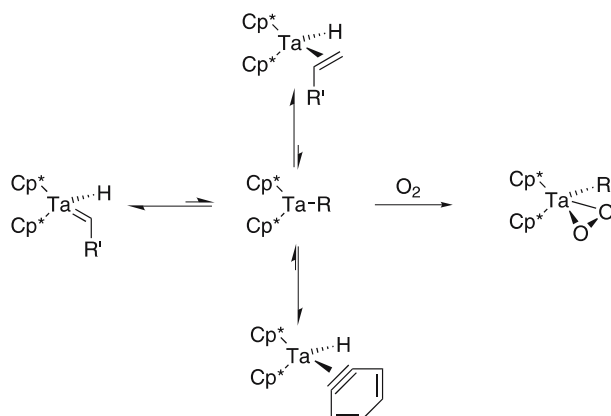
Any reaction of the type to be considered here begins with the interaction of an organometallic compound with O₂. This may lead to the formation of a dioxygen complex, however fleeting its existence. Further reactions may ensue. In the following sections we summarize the available results, organized by type of transformation. We begin with the evidence for coordination of O₂.

2.1 Binding of O₂

The reaction of organometallic compounds with O₂ may produce more or less stable dioxygen complexes. An early and unambiguous example of this kind of transformation was provided in the report by van Asselt et al. of the isolation of a series of stable peroxy alkyl complexes of the type Cp₂*Ta(η²-O₂)R (R = Me, Et, Pr, Bn, Ph) [5]. As shown in Scheme 1, O₂ presumably oxidatively adds to the 16-electron fragments Cp₂*TaR, which are in rapid equilibrium with the 18-electron olefin hydrides or alkylidene hydrides.

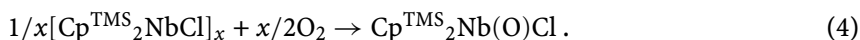
The benzyl derivative Cp₂*Ta(η²-O₂)Bn was structurally characterized by X-ray diffraction; the O₂-ligand is side-on coordinated and lies in the equatorial plane of the bent metallocene fragment. The O – O distance of 1.477(8) Å and the O – O stretching frequency (ν_{O-O} = 863 cm⁻¹) are consistent with a peroxy ligand (O₂²⁻) coordinated to tantalum in its highest possible formal oxidation state (+V). Notably, base appears to stabilize these complexes; i.e., in the presence of triethylamine Cp₂*Ta(η²-O₂)Me did not decompose even when heated to 80 °C.

Another organometallic dioxygen complex was found to be the first-formed intermediate in the transformation shown in Eq. 4 (Cp^{TMS} = η⁵-



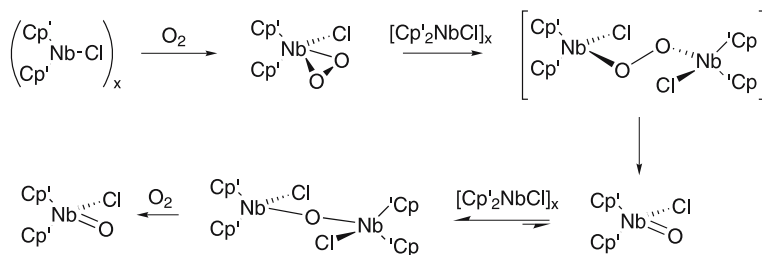
Scheme 1 Formation of a tantalum peroxo complex

$C_5H_4SiMe_3$), which is obviously a multi-step reaction [6].



The oxo complex was the final product of prolonged exposure of $[Cp^{TMS}_2NbCl]_x$ to air. However, rapid reaction with pure O_2 yielded the peroxo complex $Cp^{TMS}_2Nb(\eta^2-O_2)Cl$ as the major product. Its identity was confirmed by independent synthesis following literature precedent. Thus, the analogous $Cp_2Nb(\eta^2-O_2)Cl$ had been prepared earlier by reaction of Cp_2NbCl_2 with hydrogen peroxide [7]. The proposed series of events leading to the formation of $Cp^{TMS}_2Nb(O)Cl$ is shown in Scheme 2; note that the direct reaction of $Cp_2^{TMS}Nb(\eta^2-O_2)Cl$ with $[Cp^{TMS}_2NbCl]_x$ immediately gave $Cp^{TMS}_2Nb(O)Cl$, and that the bridging oxo complex $[Cp^{TMS}_2NbCl]_2(\mu-O)$ has also been isolated. This series of reaction steps must be considered a probable scenario for any reaction producing oxo complexes from O_2 , even when the intermediates shown here are not directly observable.

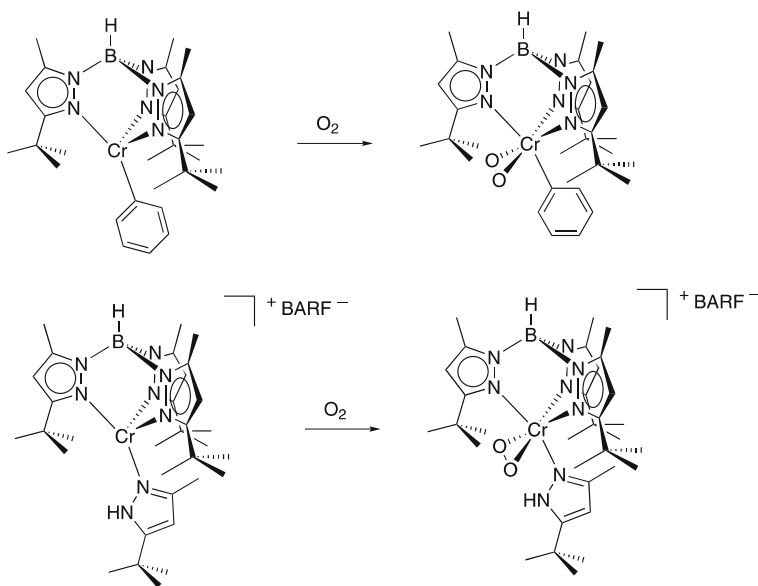
An organometallic dioxygen adduct of an even more fleeting kind was observed in the reaction of the divalent chromium phenyl complex $Tp^{tBu,Me}Cr-$



Scheme 2 Formation of a niobium peroxo intermediate and subsequent reactions

Ph ($\text{Tp}^{t\text{Bu},\text{Me}} = \text{hydrotris}(3\text{-tert-butyl-5-methylpyrazolyl})\text{borate}$) with O_2 [8]. While the ultimate product of the reaction is the product of an O_2 insertion into the Cr – C bond (Sect. 3.1), the first identifiable step is the binding of O_2 to chromium. At -45°C , a color change of the solution from the brilliant blue of $\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr-Ph}$ to a dark red indicated the formation of a new compound, which is stable at this low temperature. Monitoring the reaction by in-situ IR spectroscopy revealed the appearance of a new band at 1027 cm^{-1} , which shifted to 969 cm^{-1} when $^{18}\text{O}_2$ was used. These vibrational data are consistent with the formation of a chromium(III) superoxide complex, namely $\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}(\text{O}_2)\text{Ph}$ (Scheme 3, top).

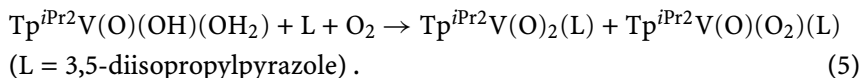
While most superoxo complexes—in contrast to peroxo compounds—have been assigned a “bent, end-on” coordination mode [9], the superoxide ligand of $\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}(\text{O}_2)\text{Ph}$ was suggested to exhibit the more unusual “side-on” (η^2) coordination [10]. The reactivity of the complex did not allow for the determination of its molecular structure; however, close analogs could be isolated, crystallized and structurally characterized by X-ray diffraction. For example, the reaction of $[\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}(\text{pz}'\text{H})]\text{BARF}$ ($\text{pz}'\text{H} = 3\text{-tert-butyl-5-methylpyrazole}$, $\text{BARF} = \text{tetrakis}(3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl})\text{borate}$) with O_2 produced the stable dioxygen complex $[\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}(\text{pz}'\text{H})(\eta^2\text{-O}_2)]\text{BARF}$ (Scheme 3, bottom), which featured a side-on bound superoxide ligand ($d_{\text{O-O}} = 1.327(5)\text{ \AA}$, $\nu_{\text{O-O}} = 1072\text{ cm}^{-1}$) [11]. Other structurally characterized



Scheme 3 Formation of a chromium phenyl superoxo intermediate and a stable analog thereof

representatives of this class of molecules include $\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}(\eta^2\text{-O}_2)\text{Cl}$ and $\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}(\text{pz}')(\eta^2\text{-O}_2)$ [12].

The Tp ligands (i.e., tris(pyrazolyl)borates or scorpionates [13]) are close analogs to the Cp ligands (i.e., η^5 -cyclopentadienyl), and in connection with the chemistry of the $\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}$ complexes mentioned above, a recent example of O_2 -binding from vanadium chemistry is of interest, even though it is formally not organometallic chemistry. Reaction of the V(IV) complex $\text{Tp}^{i\text{Pr}_2}\text{V}(\text{O})(\text{OH})(\text{OH}_2)$ with oxygen yields two products in a 1 : 1 ratio as shown in Eq. 5 [14].



The crystal structure of the dioxygen complex $\text{Tp}^{i\text{Pr}_2}\text{V}(\text{O})(\text{O}_2)(\text{L})$ has been determined, and revealed a side-on bonded O_2 ligand. Based on the O – O distance of 1.379(6) Å and $\nu_{\text{O-O}}$ of 960 cm^{-1} it was formulated as a V(V) peroxo complex, even though these values are on the borderline between the peroxo and superoxo designations. The mechanism of this reaction is curious. Reaction with $^{18}\text{O}_2$ showed incorporation of ^{18}O solely in the O_2 ligand and not in the oxo groups. It appears that the O_2 binding step must be preceded by a disproportionation ($2 \text{V}(\text{IV}) \rightarrow \text{V}(\text{III}) + \text{V}(\text{V})$) followed by reaction of V(III) with O_2 .

The examples summarized above demonstrate that organometallic derivatives of early transition metals can and will form dioxygen complexes, even though the stability of these adducts varies widely. The availability of some d-electrons is required; i.e., d^0 -complexes do not show this mode of reactivity, presumably because binding of O_2 requires some degree of electron transfer (oxidation of the metal).

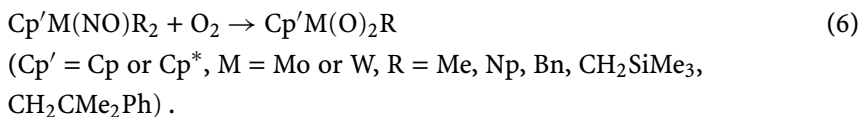
2.2

Formation of Oxo Complexes

The exposure of organometallic compounds to O_2 frequently results in the formation of metal oxo complexes. The oxygen atom may be bound as a terminal ligand or bridging several metals. The oxide ion (O^{2-}) is a good π -donor and interacts strongly with early metals in high oxidation states, due to the availability of empty d-orbitals of appropriate symmetry [15]. As shown in Sect. 2.1, the formation of oxo complexes may be mechanistically complex (Scheme 2), but the large thermodynamic driving force for the formation of the final product [16] often renders intermediates so short-lived as to evade detection. Nevertheless, the intervention of dioxygen complexes must be considered probable unless the organometallic reagent has a d^0 -configuration.

There are many examples of organometallic compounds containing oxygen atoms as ligands; an appreciable number of these resulted from reactions with O_2 . Early work has been reviewed by Bottomley and Sutin [17]. Thus we concentrate on more recent reports, and those of particular interest.

Legzdins et al. have reported the formation of oxo alkyls of tungsten and molybdenum in moderate yields (45–60%) according to Eq. 6 [18, 19].

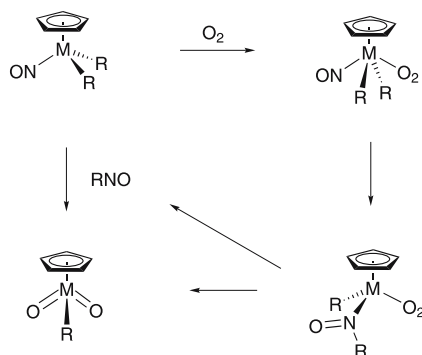


An interesting, albeit unexplained, observation was the beneficial effect of adventitious water upon the reaction yield (10–15% increase in yield). When the oxygenation of Cp*W(NO)(CH₂SiMe₃)₂ was carried out with ¹⁸O₂, the products were a mixture of Cp*W(¹⁶O)₂(CH₂SiMe₃) (12%), Cp*W(¹⁶O)(¹⁸O)(CH₂SiMe₃) (35%), and Cp*W(¹⁸O)₂(CH₂SiMe₃) (53%). Thus the majority of the oxo ligands were derived from O₂. The formation of the ¹⁶O isotopologs is consistent with the suggested reaction mechanism, shown in Scheme 4.

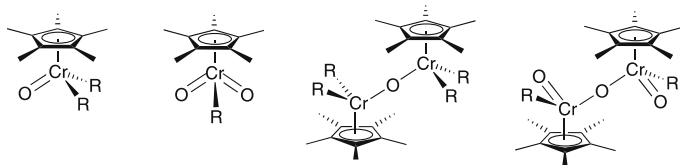
Insertion of coordinated NO into one of the metal alkyls would yield a nitrosoalkane, which could dissociate and in turn react with the starting material via O-atom transfer. The independent observation that PhNO reacted with Cp*W(NO)(CH₂SiMe₃)₂ to form Cp*W(O)₂(CH₂SiMe₃) in low yield supports the role of the nitrosoalkane as an alternative oxidant.

An unusual Mo(IV) dioxo complex was formed in the reaction of (Cp^{TMS})₂Ti(CCSiMe₃)₂ with Mo(CO)₃(NCMe)₃, followed by air oxidation. {(Cp^{TMS})₂Ti(CCSiMe₃)₂}Mo(CO)₄ is a likely intermediate; its reaction with O₂ yields the dioxo species {(Cp^{TMS})₂Ti(CCSiMe₃)₂}Mo(O)₂ [20].

Paramagnetic chromium alkyls in the +II and +III oxidation states have been reacted with O₂. For example, treatment of Cp*Cr(py)Me₂ [21] or



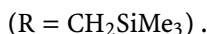
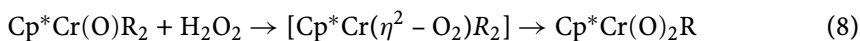
Scheme 4 Formation of high-valent oxo alkyls



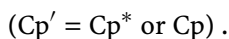
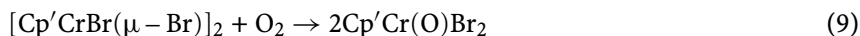
Scheme 5 Various chromium oxo alkyls

$[\text{Cp}^*\text{Cr}(\mu\text{-Me})]_2$ [22] yielded a set of oxo alkyls ranging in oxidation state from +IV to +VI. Scheme 5 summarizes the structural types, most of which have been confirmed by X-ray crystallography.

In view of the high formal oxidation state of some of these molecules, their pronounced stability was quite surprising. Notably, these reactions do not produce alkoxide derivatives, i.e., an insertion of oxygen in the Cr – C bond was not observed. The mechanism of formation of the compounds shown in Scheme 4 probably involves the kinds of steps shown in Scheme 2. The direct reaction of $[\text{Cp}^*\text{Cr}(\mu\text{-Me})]_2$ to yield $\text{Cp}^*\text{Cr}(\text{O})_2\text{Me}$ may represent an unusual example of the 4-electron oxidative addition of O_2 to a single metal center. The formation of the same Cr(VI) alkyl from $\text{Cp}^*\text{Cr}(\text{py})\text{Me}_2$ presumably follows the same pathway, but results in homolytic cleavage of a Cr – Me bond, so as to not exceed the highest possible oxidation state of chromium. Corroborating evidence comes from the transformations shown in Eqs. 7 and 8; the reaction of a metal oxo group with H_2O_2 frequently results in the formation of a metal peroxo moiety (here a Cr(V) peroxo alkyl). In this case, the peroxo dialkyl intermediate is not observed; however, it is reminiscent of the tantalum complexes $\text{Cp}^*_2\text{Ta}(\eta^2\text{-O}_2)\text{R}$ (Scheme 1). The weak Cr – C bond of the first row transition metal presumably confers little protection against further oxidation to Cr(VI).



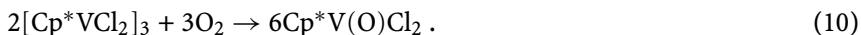
The alkyl complexes mentioned above are very electron rich, and thus their susceptibility to reaction with O_2 is not a great surprise, though the formation of stable organometallic oxidation products may be. Somewhat more unusual is the reaction of metal(III) halides with O_2 . Relatively recent results in this area begin with the report by Morse et al. of the oxidative addition of O_2 to $[\text{Cp}^*\text{CrBr}(\mu\text{-Br})]_2$, see Eq. 9 [23].



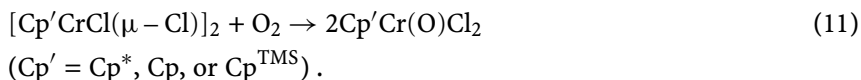
The reaction proceeds within minutes in CH_2Cl_2 , although coordinating solvents (e.g., THF, CH_3CN) inhibit the reaction rate. The authors also noted that

“concentrated solutions of $[\text{Cp}^*\text{CrBr}(\mu - \text{Br})]_2$ (> 100 mM) are not noticeably O_2 sensitive”. These observations are probably best explained by an obligatory dissociation of the dinuclear complex into coordinatively unsaturated Cp^*CrBr_2 fragments, which can bind O_2 .

A very similar set of reactions producing the analogous vanadium compound $\text{Cp}^*\text{V}(\text{O})\text{Cl}_2$ was published independently and contemporaneously by the groups of Bottomley [24] and Doherty [25], see Eq. 10.



Finally, we have reported the analogous syntheses of $\text{Cp}^*\text{Cr}(\text{O})\text{Cl}_2$ and $\text{CpCr}(\text{O})\text{Cl}_2$ via reaction of the corresponding cyclopentadienyl chromium(III) chlorides with O_2 (Eq. 11) [26]. While these reactions are slow (days at room temperature) they produce the oxo complexes in high yield.



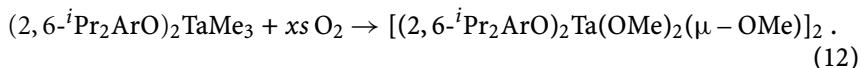
The facile activation of dioxygen by these simple organometallic complexes generates high-valent ($\text{V}(\text{V})$, $\text{Cr}(\text{V})$) metal oxo complexes, which may undergo oxygen atom transfer reaction with organic substrates, and thus serve as catalysts for aerobic oxidations (Sect. 3.3).

2.3

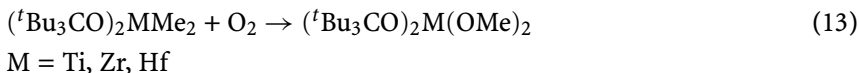
Radical Chain Reactions

When the organometallic reactant has a d^0 -configuration, the formation of a dioxygen adduct of significant stability or lifetime does not appear possible. Dioxygen complexes invariably feature some degree of charge transfer to O_2 (falling either into the superoxo or peroxy rubric), and a d^0 -metal center cannot easily give up another electron. However, this does not preclude a reaction between O_2 and an electron-rich alkyl from taking place. Removal of an electron from a metal-carbon bonding MO weakens the metal alkyl bond and induces homolytic cleavage. Thus reactions of early metal alkyls in high oxidation states often involve radical processes.

Early examples of this kind of reactivity include reports about the oxygenation of alkylzirconium(IV) complexes of the type $\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$, yielding the corresponding alkoxides $\text{Cp}_2\text{Zr}(\text{OR})\text{Cl}$, which can be hydrolyzed to the alcohols [27], and similar autoxidation reactions of Cp_2ZrR_2 [28]. A more recent case is the formation of a tantalum(V) alkoxide by the reaction shown in Eq. 12 [29].



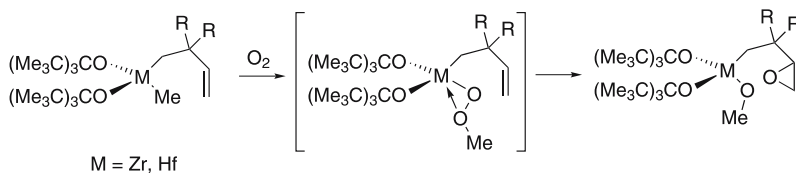
A detailed mechanistic study of this type of reaction was carried out by Lubben and Wolczanski, who investigated the reactions of a series of alkoxy alkyls of group 4 ($M = \text{Ti, Zr, Hf}$) with O_2 [30]. Thus, exposure to O_2 of the methyl complexes, shown in Eqs. 13 and 14, rapidly generated methoxide derivatives.



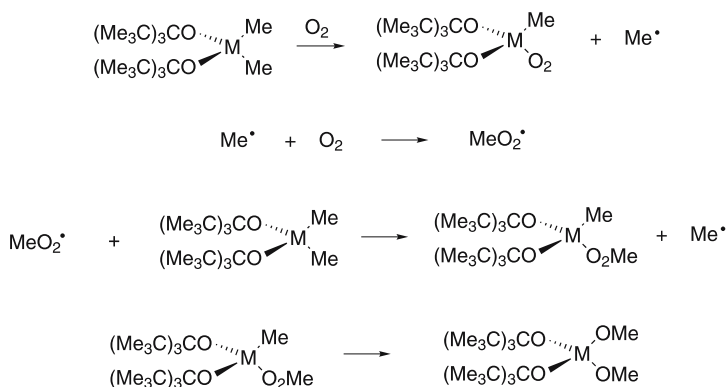
The formation of methylperoxy intermediates—i.e., the product of a formal insertion of O_2 into the metal–methyl bond—was substantiated by the observation of epoxidation of allylic alkoxydes (Scheme 6), in analogy to the proposed mechanism for the Sharpless epoxidation utilizing *tert*-butylhydroperoxide (TBHP). A similar oxygen atom transfer from a coordinated alkylperoxide to olefin was also postulated for the epoxidation of olefins with TBHP catalyzed by $\text{Cp}^*\text{Mo}(\text{O})_2\text{Cl}$ [31]. The use of organomolybdenum oxides in olefin epoxidation catalysis (albeit not with O_2) has recently been reviewed [32].

A crossover experiment demonstrated scrambling of the methyl groups between metal atoms during the oxygenation, and various other observations indicated the occurrence of a radical chain process. The conclusion regarding the mechanism of this O_2 insertion was that it parallels the autoxidation of main group alkyls (e.g., BR_3 , AlR_3 , ZnR_2) and proceeds by an $\text{S}_{\text{H}}2$ homolytic substitution process [33]. As shown in Scheme 7, interaction with O_2 results in homolysis of a metal–carbon bond and provides the initiation step. The methyl radical is trapped by O_2 in a diffusion controlled reaction, and the resulting methylperoxy radical attacks another metal alkyl under displacement of its methyl group (the propagation step of the chain reaction). The methylperoxy ligand delivers an oxygen atom to another alkyl (or an alkene), and scrambling of alkoxy ligands between metal atoms ensures complete oxidation of all alkyl ligands.

An informative recent case study from magnesium chemistry highlights the parallels of the group 4 chemistry described above to the behavior of



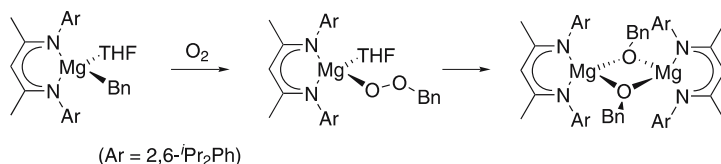
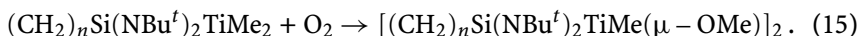
Scheme 6 Intramolecular oxygen transfer from methylperoxo ligand to an olefin



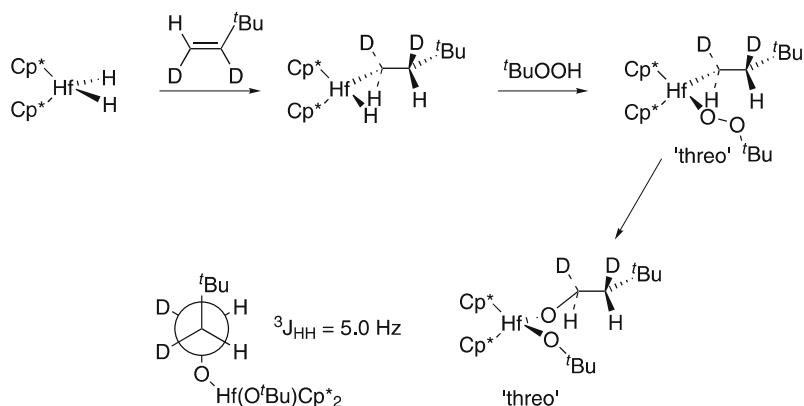
Scheme 7 Radical chain mechanism for the autoxidation of Zr(IV) alkyls

representative elements. The reaction of a β -diketiminate magnesium benzyl compound with O_2 led, for the first time, to the isolation and structural characterization of an alkylperoxy compound, which crystallized as a dimer with $\mu - \eta^2 : \eta^1$ benzylperoxy groups. The proposed mechanism for the overall transformation involves dioxygen insertion into the Mg – C bond followed by oxygen atom transfer to a further magnesium alkyl to ultimately form benzylperoxy derivatives, see Scheme 8 [34]. On the basis of several lines of evidence, the mechanism of this O_2 insertion was assigned to be a radical chain process much like the one outlined in Scheme 7. In particular, the relative stability of the benzyl radical was held responsible for the rapid initiation step and thus the unprecedented isolation of the benzylperoxy intermediate.

Despite the radical character of these autoxidations, they may exhibit some selectivity. This can, for example, be seen in a recent report by Kim et al., which notes the selective transformation of a titanium(IV) diamido dimethyl complex into a mixed alkoxide alkyl (Eq. 15) and the complete lack of reactivity of the corresponding dibenzyl complex with O_2 [35]. Both of these observations are probably the result of steric protection. When the metal complex becomes too hindered to allow close interaction with O_2 , the oxidation can no longer be initiated.



Scheme 8 Autoxidation of a magnesium alkyl



Scheme 9 Retention of configuration in oxygen transfer to an alkyl

Regarding the delivery of an oxygen atom from an alkylperoxy ligand to a neighboring alkyl group, there arises the question of stereochemistry. In the early work on zirconium alkyls, a mixture of 50% racemization and 50% retention of stereochemistry of the α -carbon was observed [36]; this was interpreted as the result of complete racemization in the formation of the alkylperoxide (by a radical chain mechanisms), coupled with retention of configuration in the O-atom transfer step. The latter step has been probed directly by the indirect synthesis of a hafnium alkyl alkylperoxide, and the monitoring of the stereochemical result of the oxygen transfer [37]. Scheme 9 shows the synthesis and stereochemical outcome of the compounds. These experiments confirm the suggestion that the insertion of the oxygen atom into the alkyl proceeds with retention of configuration at the migrating carbon center.

There would appear to be two distinct modes of reactivity of early transition metal alkyls with O_2 . When the metal is not in its highest oxidation state, an O_2 complex of variable stability may form, and its subsequent reactivity may or may not involve the metal-carbon bond. The formation of remarkable stable oxo alkyls is an example of this pathway. In contrast, d^0 -alkyls react with O_2 by a radical chain mechanism that invariably leads to formation of alkoxide complexes; labile alkylperoxy ligands are clearly implicated as intermediates in these reactions.

3 Reactions of Oxygenated Complexes

As outlined above, the initial reaction of early transition metal organometallics with O_2 may produce a variety of complexes containing oxygen atoms—in the form of superoxo (O_2^-), peroxo (O_2^{2-}), oxo (O^{2-}), or alkylperoxo (RO_2^-)

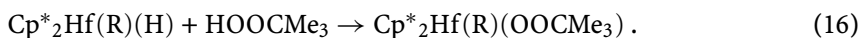
ligands. These functional groups may give rise to further transformations, such as insertion reactions or oxygen atom transfer. This section is dedicated to a review of these follow-up reactions.

3.1

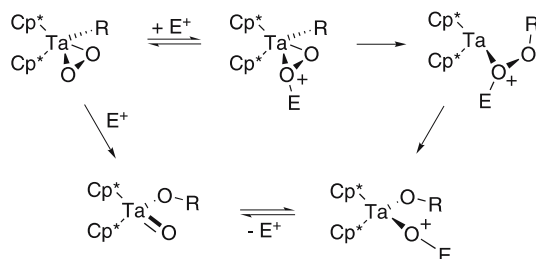
Dioxygen Insertion

Leaving aside the autoxidations of d^0 -alkyls, which only formally yield O_2 insertion products, there are a very few examples of reactions where migratory insertion of a coordinated O_2 into a metal alkyl bond seems indicated. Thus, heating of $Cp^*_2Ta(\eta^2-O_2)Me$ (Sect. 2.1) in solution in the absence of any base results in its transformation into $Cp^*_2Ta(O)OMe$ [1]. Lewis acids were noted to catalyze the reaction. While there is no direct evidence for the formation of an alkylperoxo intermediate, the final product could easily be rationalized as resulting from an α -alkoxide elimination (Scheme 10).

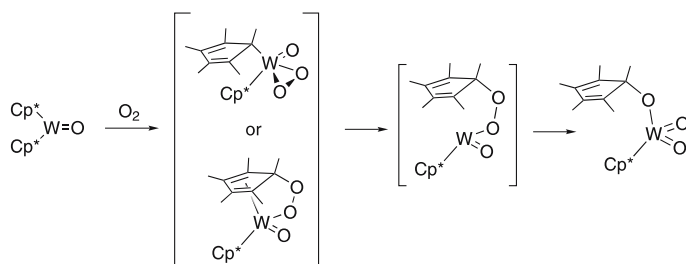
The parallel to the mechanism of the reaction of $Cp^*_2Hf(OOCMe_3)(R)$ to $Cp^*_2Hf(OCMe_3)(OR)$ was noted, with CMe_3^+ serving as the electrophile, implying the formation of the peroxyalkyl, aided by coordination of an electrophile at the exo-oxygen atom during the migration. It is worth noting that in none of the cases described in this section was the peroxyalkyl stable enough to be isolated or even spectroscopically observed. Apparently, such compounds of the early transition metals are stable only in the d^0 -configuration—see e.g., $Cp^*_2Hf(OOCMe_3)(R)$ above, which was prepared not by a reaction with O_2 , but rather according to Eq. 16 [38].



Another probable candidate for an O_2 insertion is the reaction of $Cp^*_2W = O$ with O_2 . The product of this reaction was the structurally characterized $Cp^*_2W(O)_2(OC_5Me_5)$ [39, 40]. In this case, neither an O_2 -complex nor the peroxyalkyl intermediate was detected, leading the authors to equivocate on the exact mode of product formation (Scheme 11). However, the d^2 -configuration of the starting material makes the initial formation of an O_2 adduct reasonably likely, even though this might require an $\eta^5 \rightarrow \eta^1$ shift of one Cp^*



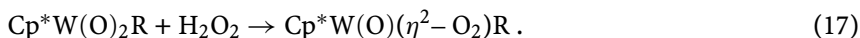
Scheme 10 Electrophile assisted O_2 insertion into tantalum alkyl



Scheme 11 O_2 insertion into a tungsten cyclopentadienyl

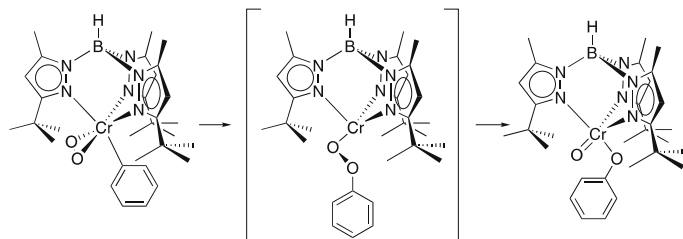
ligand so as to not exceed an 18-electron configuration. This adduct could then undergo an insertion of O_2 into the metal–carbon bond, followed by an α -alkoxide elimination to produce the final product.

The related alkyl complexes $Cp^*W(O)(O_2)R$ ($R = Me, CH_2SiMe_3$), which have been prepared according to Eq. 17 [10], provide precedent for the existence of the postulated dioxygen complex. However, neither of these two alkyls undergo the subsequent O_2 insertion, leaving in some ambiguity the mechanism of the transformation shown in Scheme 10.



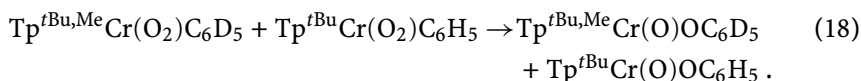
Finally, a well-characterized O_2 -insertion transforms $Tp^{tBu,Me}Cr(O_2)Ph$ into the paramagnetic oxo alkoxide $Tp^{tBu,Me}Cr(O)OPh$, see Scheme 12 [4]. This reaction proceeds below room temperature, and the starting material has only been characterized by in-situ IR spectroscopy. However, analogous O_2 complexes were isolated and characterized by X-ray crystallography, so there can be little doubt about its assignment as a side-on bonded Cr(III) superoxo complex.

In order to rule out a radical chain process akin to those described in Sect. 2.3, a crossover experiment was carried out. The result, shown in Eq. 18, establishes the intramolecular nature of the transformation. While this does not strictly rule out homolytic events along the reaction pathway (Cr–Ph or O–O bond cleavage), any resulting radicals must be very short-lived and



Scheme 12 Intramolecular O_2 insertion into chromium phenyl bond yield oxo alkoxide

cannot escape the solvent cage in which they are generated.



Another possible mechanism for this transformation would be oxidative addition of the O_2 to chromium, yielding $\text{Tp}^{t\text{Bu,Me}}\text{Cr}(\text{O})_2\text{Ph}$, followed by an insertion of an oxo ligand. However, as we shall show in the next section, such insertions are exceedingly rare. Accordingly, $\text{Cp}^*\text{Cr}(\text{O})_2\text{Me}$ (Scheme 5)—a close analog of the hypothetical $\text{Tp}^{t\text{Bu,Me}}\text{Cr}(\text{O})_2\text{Ph}$ —shows no tendency to insert an oxygen ligand into the methyl group.

The above examples indicate the feasibility of the insertion of coordinated O_2 into early transition metal alkyls. The resulting alkylperoxides apparently suffer rapid α -elimination to oxo-alkoxides. In all likelihood, this reflects the strong stabilization of the higher oxidation states of these oxophilic metals by oxygen π -donors. To actually isolate the insertion product requires a late transition metal or a d^0 -configuration (the α -elimination is formally a 2-electron oxidation). To wit, the insertion of coordinated O_2 into a rhodium alkyl gives rise to an isolable methylperoxo intermediate [41]. Peroxyalkyls of early transition metal in their highest oxidation states have been isolated as well. Their chemistry is dominated by oxygen atom transfer and or homolytic cleavage of the O – O bond [42].

3.2

Oxygen Insertion

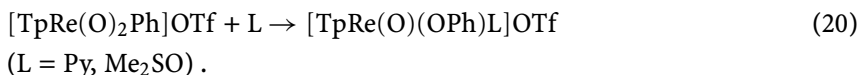
The insertion of a metal bound oxo group into a metal carbon σ -bond (Eq. 19), e.g., of an alkyl or aryl, has great appeal as an elementary step in the oxygenation of organic molecules.



However, the number of well-characterized examples of this transformation is inversely proportional to its desirability. Specifically, there is currently only one system that demonstrably follows this reaction pathway. The metal involved is rhenium and thus not really within the purview of this chapter. However, given the importance of this reaction, a quick summary is provided here.

Following earlier reports of a photochemically driven phenyl-to-oxo migration [43, 44], Brown and Mayer published a study of a related system that exhibits a thermal insertion of an oxo group into a rhenium phenyl bond [45]. The reaction is shown in Eq. 19; it exhibits clean first order kinetics, with activation parameters of $\Delta H^\ddagger = 14.8(7)$ kcal/mol and $\Delta S^\ddagger = -20.5(25)$ eu (half

life of 4 minutes at 25 °C!).

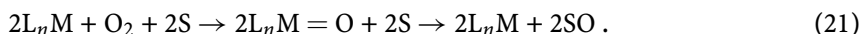


The key to this unique chemistry appears to be the high electrophilicity of the oxo ligands in the cationic Re(VII) precursor. While there are many examples of oxo alkyls of the early transition metals (Sect. 2.2), none of them show any indication of O-insertion chemistry. For example, Cp*Cr(O)₂Me might be expected to feature fairly electrophilic oxo ligands, and yet it does not produce any methoxide derivatives. In summary, the insertion of oxo ligands into metal alkyls must be considered a highly unusual transformation associated with a large kinetic barrier. It becomes viable only under very special circumstances. The discovery of further examples of this fundamental transformation would be a significant step forward in organometallic oxidation chemistry.

3.3

Oxygen Atom Transfer

Intermolecular oxygen atom transfer from a metal complex to an organic substrate is an archetypical reaction step in oxidation catalysis. As the transformation of O₂ into metal oxo groups by oxidative addition is a well-precedented process (Sect. 2.2), its combination with transfer of the oxygen atom to an oxidizable substrate (“S”) constitutes a catalytic cycle for aerobic oxidations (Eq. 21). Examples of such cycles exist in organometallic chemistry, by virtue of oxo complexes with carbon-based ancillary ligands.



Transfer of metal bound oxo ligands will be facilitated by high electrophilicity of the complex, and by weak metal–oxo bonds. For these reasons, electron-withdrawing ligands and first-row transition metals in high oxidation states would seem to be the obvious place to look for oxygen atom transfer chemistry. It is no accident that hexavalent chromium has a long history of use as a stoichiometric and catalytic oxidant [46]; hence electron deficient organometallic chromium oxo complexes—related to chromyl chloride [47]—should be a good place to look for oxygen atom transfer, especially when they can be formed by reaction of a low valent precursor with O₂.

Cp*Cr(O)Br₂ was an early example, but its potential as an oxidant was not explored extensively [14]. The complex was reported to catalyze the aerobic oxidation of PPh₃, but it does not react with Et₂S. According to a footnote, less electron rich CpCr(O)Br₂ did “oxygenate Et₂S”, but no further detail was given.

We have investigated the analogous chlorides and found them to be more reactive; there are issues that render them inefficient as catalysts, but the basic concept of Eq. 21 is realized. Cyclopentadienyl chromium(III) chlorides react with O_2 to form the corresponding Cr(V) oxo derivatives $Cp'Cr(O)Cl_2$ ($Cp' = Cp^*, Cp, Cp^{TMS}$). $Cp^*Cr(O)Cl_2$ transfers oxygen to a variety of substrates. Thus, it oxidizes PPh_3 and $AsPh_3$, but not $MeSPh$, or $MeS(O)Ph$. The oxidation of PPh_3 to $OPPh_3$ is catalytic, whereas the reaction with $AsPh_3$ is stoichiometric, generating the arsine oxide complex $Cp^*Cr(OAsPh_3)Cl_2$. The latter is apparently so stable ($OAsPh_3$ does not dissociate) that it cannot be reoxidized by O_2 . Product inhibition is one of the significant problems of this system, as many of the oxidation products form stable pseudooctahedral chromium(III) complexes of the oxidized substrates. Other molecules that react with $Cp^*Cr(O)Cl_2$ are 1,4-cyclohexadiene (\rightarrow benzene), 9,10-dihydroanthracene (\rightarrow anthracene) and 1,2-diphenylhydrazine (\rightarrow azobenzene). The dehydrogenation of 1,4-cyclohexadiene is catalytic and produces H_2O as byproduct. After several turnovers, the resting state of the catalyst becomes the water adduct $Cp^*Cr(OH_2)Cl_2$; this has been isolated and structurally characterized [48]. $Cp^*Cr(O)Cl_2$ does not react with ordinary olefins.

One of the interesting features of these oxygen atom transfer reactions is that they comprise an example of “two state reactivity” [49–52], i.e., the reactants and products have different spin states. $Cp'Cr(O)Cl_2$ contains a d^1 -ion and has a doublet ground state ($S = 3/2$), whereas the products feature Cr(III) (d^3 , $S = 3/2$) in a quartet ground state. Somewhere along the reaction coordinate the reaction must cross over from the doublet potential energy surface (PES) to the quartet PES. There has been much interest in the effects of spin state on chemical reactivity [51, 53–55], and this has motivated us to perform calculations on this system. Figure 1 shows the two intersecting reaction paths on the doublet and quartet PES, respectively, for the epoxidation of ethylene by $Cp'Cr(O)Cl_2$. It can be seen that the reaction on the doublet PES proceeds through an intermediate, in which one oxygen—carbon bond has been formed. However, instead of continuing on this surface, the reaction reaches a “minimum energy crossing point” (MECP) close to the intermediate, which obviates the traversing of the second (higher) barrier on the doublet surface and leads smoothly to the quartet product.

In the course of the above-mentioned calculations, it became clear that the activation energy for the epoxidation reaction was predicted to be significantly lower for the unsubstituted complex $CpCr(O)Cl_2$. Indeed, $CpCr(O)Cl_2$ and its more soluble analogue $Cp^{TMS}Cr(O)Cl_2$ reacted with various olefins to yield products of oxygen atom transfer (Scheme 13) [56]. Among the olefins investigated, only norbornene and β -methylstyrene produced the corresponding epoxides, along with other oxygenates, whereas styrene and α -methylstyrene gave oxygenated products that can—in part—be rationalized as products of subsequent ring opening of the epoxide (Scheme 12). In support of this hypothesis, we have shown that the reaction of norbornene

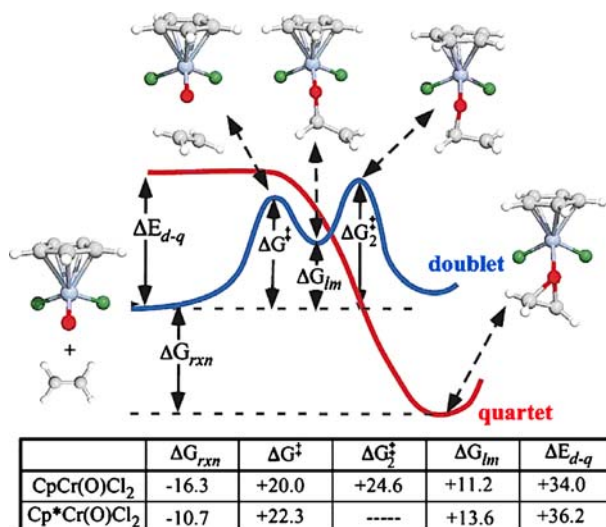
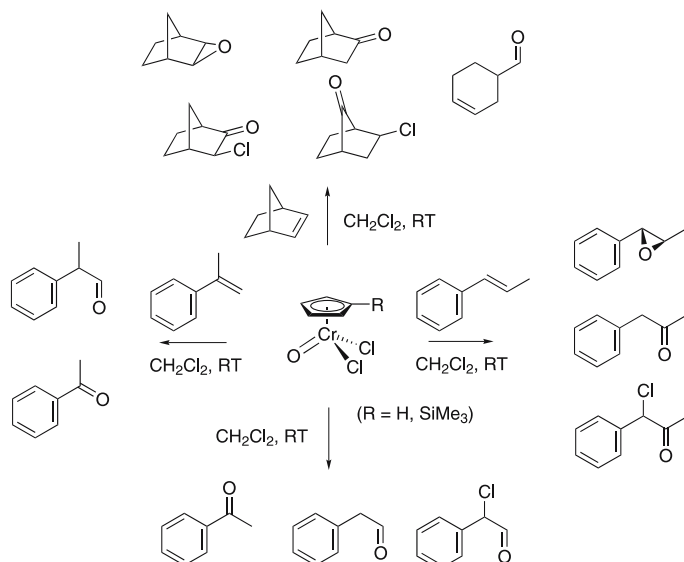


Fig. 1 Doublet and quartet potential energy surfaces for the epoxidation of ethylene with $\text{Cp}'\text{Cr}(\text{O})\text{Cl}_2$



Scheme 13 Oxygen atom transfer from chromium to olefins yields variety of products

oxide with $[\text{Cp}'\text{Cr}(\mu\text{-Cl})(\text{Cl})_2]$ produces all the same byproducts that are formed in the reaction of $\text{Cp}'\text{Cr}(\text{O})\text{Cl}_2$ with norbornene.

There are some surprises, such as the occurrence of chlorinated products. The chlorine derives from the metal complex and not from the chlo-

minated solvent, as the same products formed when the reactions were run in nitromethane. Their formation is consistent with a radical intermediate (Fig. 1) [57, 58], which can abstract a chlorine atom from the metal in an intramolecular fashion. Another curious observation is the formation of benzaldehyde in the oxidation of styrene; one wonders how the cleavage of the C = C double bond occurs.

These reactions are not catalytic, and the oxygenation of the Cr(III) precursors is very slow, presumably reflecting the lesser oxygen affinity of the less electron rich complexes. Nevertheless, they are proof of the concept that an organometallic complex can mediate the oxidation of organic substrates by O₂. The product distributions also point out some of the problems that must be addressed to make this chemistry synthetically useful. They include—inter alia—the ring opening of the primary epoxide products, the incorporation of coligands (here chloride), and the slow reaction rates. Furthermore, there is obviously a tradeoff between the rate of the reaction of the reduced form of the catalyst with O₂ and the reactivity of the oxidized form with organic substrates. However, appropriate ligand design may solve all of these problems. It is reasonable to suggest that a catalytic aerobic epoxidation of substituted olefins is possible.

4

Conclusions

Organometallic derivatives of the early transition metal react with O₂ in a variety of ways. While the formation of stable O₂ adducts is possible for these metals, the number of characterized examples of such complexes is small. The high oxophilicity of the electropositive metals, and the availability of empty d-orbital for L → M π-donation favor the formation of oxo complexes via cleavage of the O–O bond, most often in bimolecular reactions. However, under the right circumstances, high-valent metal oxo complexes can transfer oxygen atoms to organic substrates, thus offering a possible pathway for catalytic aerobic oxidations.

Early metal alkyls in the highest formal oxidation states (i.e., with d⁰-configurations) react with O₂ by a radical chain mechanism. The alkylperoxy intermediates thus formed are highly reactive; they can transfer oxygen to other alkyl groups (forming alkoxides), or to oxidizable organic functional groups (e.g., olefins). In the absence of O-acceptors they suffer facile O–O bond homolysis.

Early transition metals have a high affinity for oxygen. This is especially true for electron-rich organometallic compounds. Accordingly, the final products of reactions with O₂ will often feature metal oxygen bonds. In this neighborhood of the periodic table, complete transfer of oxygen to an organic

substrate is the exception rather than the rule. Knowing this is a valuable lesson to heed when looking for catalytic oxidations.

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