NOT SOLELY A SPECTATOR: EXPLORING THE CHEMISTRY OF THE C—O BOND IN ALKOXIDE AND RELATED LIGANDS

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Abstract—The chemistry of the C—O bond in alkoxide ligands is reviewed, including various systems from the literature and from the author's laboratory. Related chemistry of hydroxide, aryloxide, and allyloxide ligands is also discussed. Cleavage or formation of the alkoxide C—O bond can occur in a homolytic or heterolytic fashion, for instance by addition of R^+ or $R^.$ to a metal oxo group. C—O cleavage or formation can also occur by exchange of R with the metal oxo group. C—O cleavage or formation can also occur by exchange of R with the metal center or another ligand. In general, a C—O or O—H bond should be considered activated in systems where a related metal–oxo complex is accessible.

Alkoxides and related ligands are widely used as ancillary or supporting ligands, but only recently has the reaction chemistry of alkoxide ligands received significant attention.[1] Our interest in the organometallic chemistry of metal-oxo complexes has led us in multiple ways to alkoxide, aryloxide, and hydroxide ligands, and to a particular interest in the chemistry of the alkoxide C—O bond and the hydroxide O—H bond. This review provides an overview of the reactions of these bonds, including chemistry studied in our labs and elsewhere.

The reaction chemistry of alkoxide ligands is important as organometallic chemistry increasingly deals with transformation of non-hydrocarbon ligands. Oxygenated organic compounds are an important class of feedstocks and products so an ability to manipulate oxygenated ligands such as alkoxides is needed. For instance, the ability of metal centers to mediate and catalyze oxidation reactions has been known and practiced for over a century, but our level of understanding of these processes and our ability to develop new oxidation reactions is just beginning.[2]

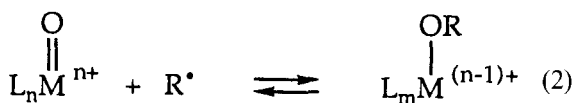The most common reactions of alkoxides and related ligands occur at oxygen or at the α-carbon.[1] Alkoxide ligands are most often introduced using alcohols or M′OR reagents in which the RO⁻ unit is already intact, by metathesis, alcoholysis, deprotonation reaction with a reducing metal center to make H_2,[1] oxidative addition,[3] and other routes. Small molecules can insert into the M—OR bond.[4] Aldehydes and ketones can insert into metal–carbon and metal–hydrogen bonds to give alkoxides, as widely practiced in synthetic organic chemistry (e.g. RMgX and $LiAlH_4$[5]). Such insertions are also often observed for transition metal hydride, alkyl, alkene, ketone, and other complexes, particularly of the early transition metals.[6] The reverse of this reaction, β-hydrogen elimination from an alkoxide, is well established especially for later transition metal complexes,[7] although to our knowledge β-alkyl elimination has not been documented.[8]

Reactions that form or cleave alkoxide C—O bonds are still sufficiently few in number that a clear systematization is not visible. For this review, with its focus on the relationship between oxo and alkoxide ligands, classification is based on the fate or origin of the carbon fragment. The next section describes reactions involving external attack of an alkyl group at a metal oxo and loss of an alkyl group from an alkoxide. Both heterolytic and homolytic processes are described. The transfer of an alkyl

group between an alkoxide and another ligand on the metal is also discussed later on in this paper and the final section describes the migration of an alkyl group between an alkoxide ligand and the metal center.

C—O CLEAVAGE OR FORMATION BY GAIN OR LOSS OF AN ALKYL GROUP

Alkoxides can be formed by attack of an alkyl group at an oxo ligand. The alkyl could be added as a carbocation, a radical, or conceivably as a carbanion [R^+, $R^.$, R^-; eqs (1)–(3)]. In the reverse direction, this corresponds to homolytic or heterolytic cleavage of the alkoxide C—O bond. Formally, eqs (2) and (3) in the forward direction involve reduction of the metal center by one and two electrons, respectively, as the alkyl group is oxidized to R^+ on forming the alkoxide.

$$L_n\overset{\overset{O}{\|}}{M}{}^{n+} + R^+ \rightleftharpoons L_m\overset{\overset{OR}{|}}{M}{}^{n+} \quad (1)$$

$$L_n\overset{\overset{O}{\|}}{M}{}^{n+} + R^. \rightleftharpoons L_m\overset{\overset{OR}{|}}{M}{}^{(n-1)+} \quad (2)$$

$$L_n\overset{\overset{O}{\|}}{M}{}^{n+} + R^- \rightleftharpoons L_m\overset{\overset{OR}{|}}{M}{}^{(n-2)+} \quad (3)$$

Heterolytic C—O bond cleavage/formation [eqs (1), (3)]

Loss of R^+ from an alkoxide ligand to give a metal-oxo complex and addition of R^+ to an oxo ligand to give an alkoxide complex [eq.(1)] are both known reactions, though not common. There are more examples of protonation of oxo complexes and deprotonation of hydroxide species and these therefore provide a better view of this area. In addition, proton transfer is kinetically more facile
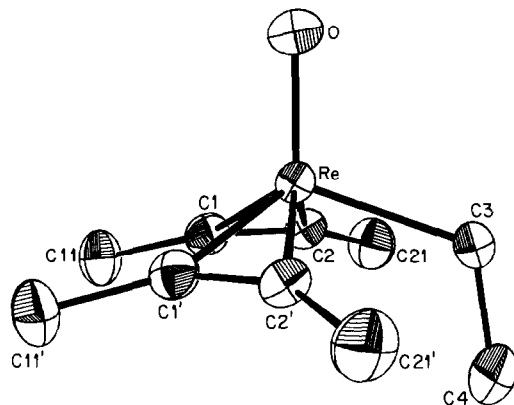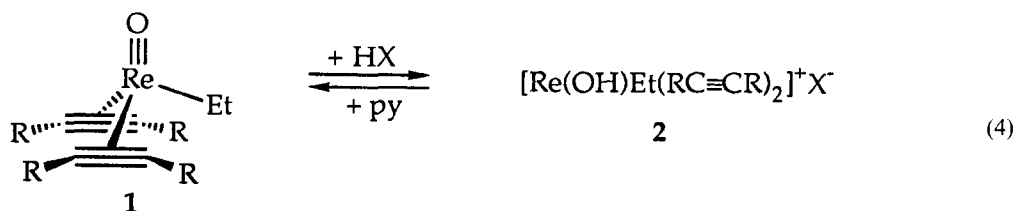

Fig. 1. ORTEP drawing of Re(O)Et(MeC≡CMe)₂ (1). (From ref. 10.)

than alkyl transfer and is easier to quantify (e.g. with pK_a values).

To summarize the current literature, almost all isolated metal hydroxide complexes are poor acids, being quite resistant to deprotonation, and the large majority of metal-oxo complexes are weak bases, protonated only with strong acids, if at all. Since there are no huge kinetic barriers to proton transfer, these characteristics are mutually inconsistent— they just reflect the limited range of hydroxide and oxo complexes that have been examined. Most isolated hydroxide complexes are in systems where the corresponding terminal oxo complex is not stable— for instance, in systems with d electron counts greater than two.[9] Similarly, most mono-oxo complexes are stable by virtue of the strong π donation from oxygen to the metal, which is significantly attenuated by protonation, making the oxo complex a weak base.

The chemistry of rhenium-oxo-bis(acetylene) compounds illustrates some of these principles. Re(O)Et(MeC≡CMe)₂ (1; Fig. 1) and related complexes can be reversibly protonated at oxygen to give highly reactive hydroxide complexes [Re(OH)Et(MeC≡CMe)₂]⁺ [2, eq. (4)].[10] [The rhenium-oxo bond is written as a triple bond because this is the best molecular orbital description, as in most mono-oxo complexes.[9,11]]

$$\underset{1}{\overset{\overset{O}{\underset{|}{\overset{\|\|}{Re}}}}{\overset{}{\underset{R\equiv R}{\overset{R\cdots\cdots R}{\diagdownEt}}}}} \underset{+\,py}{\overset{+\,HX}{\rightleftharpoons}} [Re(OH)Et(RC\equiv CR)_2]^+X^-$$

2

$$(4)$$

Only strong acids such as triflic acid and tri-fluoroacetic acid protonate the oxo group of 1, indicating that the hydroxide 2 is a strong acid. Complex 2 is characterized by NMR and IR, with $v_{Re-OH} = 595$ cm^{-1}, $v_{ReO-H} = 3200$ cm^{-1} (br), and the absence of a rhenium–oxo stretch.[10] While the NMR spectra of 1 indicate a rigid molecule, with inequivalent ends of the alkyne ligands, protonation disrupts the Re≡O bonding such that 2 is fluxional, with facile alkyne rotation.

The high acidity of 2 contrasts with the much

mixtures are observed within 2–3 min of adding CH_3CH_2OH to an acetonitrile solution of $Re(O)(OD)(MeC≡CMe)_2$.[12] The intramolecular proton transfer chemistry of 3 is described in the next section on C—O cleavage or formation by transfer to or from another ligand.

One more example will illustrate the range of basicity of rhenium-oxo-bis(acetylene) complexes. The formally rhenium(I)-oxo anion [Re(O)(MeC≡CMe)$_2$]$^-$ (4) deprotonates stoichiometric water and even acetone in acetonitrile solution [eq.

$$(6)$$
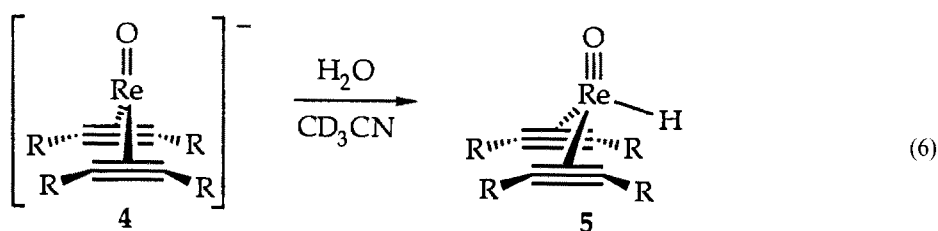
lower acidity of the closely related rhenium-oxo-hydroxide $Re(O)(OH)(MeC≡CMe)_2$ (3).[12] Complex 3 is unreactive with methylamine and "proton sponge" [1,8-bis(dimethylamino)-naphthalene] and decomposes when deprotonated by stronger bases such as LiO^{t}Bu and MeLi [eq. (5)].[13]

(6)], but protonation occurs at the metal to give the rhenium(III)-oxo-hydride 5, not a rhenium(I) hydroxide.

Alkoxide complexes analogous to the hydroxide species above have also been prepared. The oxo-alkoxide species $Re(O)OR'(RC≡CR)_2$ analogous

$$(5)$$
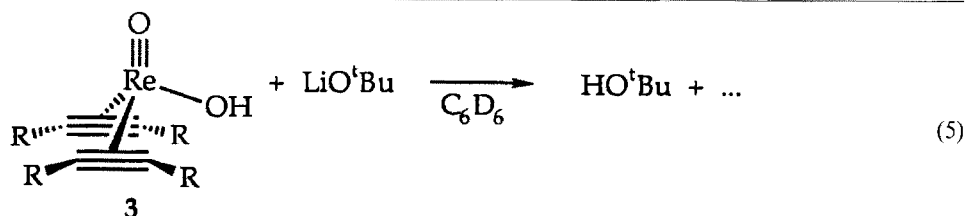
The lower acidity is in large part due to the instability of the dioxo product. Rhenium(III)-mono-oxo compounds such as 1 and 3 have the right combination of orbitals to make one multiple bond, but deprotonation to a dioxo species would place an oxygen lone pair in contact with a filled rhenium d orbital.[11] Such filled-filled π-antibonding interaction can be quite important in metal-oxo and metal-alkoxide chemistry.[9b,14,15] The low lability of the hydroxyl proton is also indicated by slow hydrogen exchange on the NMR time-scale: a sharp hydroxyl resonance is observed in the NMR of 3 in CD$_3$CN, which is unaffected by addition of 10 equivalents of water.[12] Exchange is still rapid on the chemical time-scale, however, since statistical

to the hydroxide 3—rhenium "esters" in the old nomenclature—are typical mid-transition metal alkoxides. They exchange with added protic reagents, H_2O, HOR', H_2NR, and H_2S, they undergo β-elimination (ethoxy to acetaldehyde) as well as other decomposition pathways, and they insert CO to give alkoxycarbonyl complexes such as $Re(O)[C(O)OEt](MeC≡CMe)_2$.[14] A much more reactive alkoxide appears to be formed on alkylation of 1 by $Me_3O^+BF_4^-$ [eq. (7)]. The product of eq. (7) is tentatively assigned as a methoxide complex on the basis of NMR spectra with fluxional acetylenes, similar to those of 2 [eq. (4)].[16] No reaction is observed between 1 and methyl triflate (MeOTf), suggesting that the cationic methoxide

complex is a more powerful methylating agent than MeOTf.

the decomposition products are not usually characterized.[19]

$$\text{1} \xrightarrow{+ \ Me_3O^+ BF_4^-} [Re(OMe)Et(RC{\equiv}CR)_2]^+ \qquad (7)$$
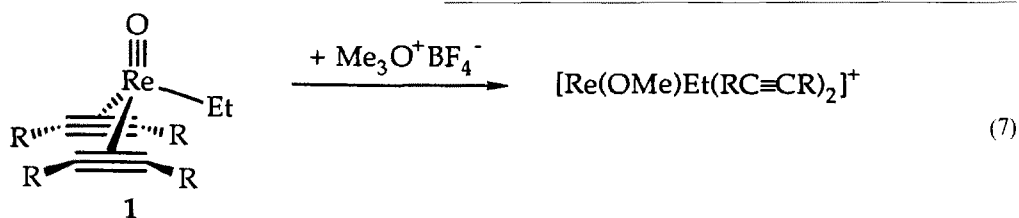
The tungsten(VI) fluoride-alkoxides $F_5W(OR)$ were shown by Noble and Winfield, 25 years ago, to be very potent alkylating agents.[17] The methoxy and ethoxy complexes decompose at ambient temperature to the oxo compound $F_4W(O)$ and the alkyl fluoride, while the phenoxide derivative is much more stable. The methoxy complex converts benzene to toluene in half an hour at 25°C! [eq. (8)]. These reactions appear to proceed by mechanisms with S_N1 character since the ethoxy decomposes faster than the methoxide.
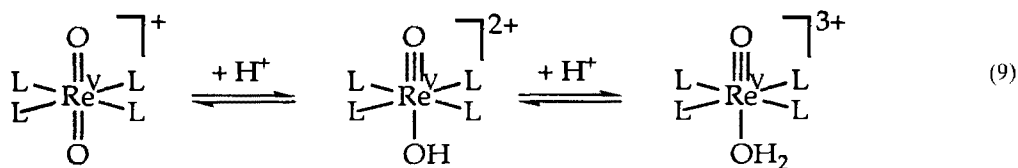
The nucleophilicity and basicity of mono-oxo complexes is typically quite low. The vanadyl ion, VO^{2+}, is not protonated in aqueous strong acid, although it can be protonated and alkylated in nonaqueous media. VO(salen), for instance, reacts with $Ph_3C^+BF_4^-$ in acetonitrile to give Ph_3COCPh_3 and V(salen)$[BF_4]_2$ (salen = N,N'-ethylenebis[salicylideneamine]).[20] $Cp_2M{=}O$ (M = Mo, W) and (tmtaa)Ti${=}O$ are rare examples of nucleophilic mono-oxo compounds (tmtaa is a dianionic tetraaza macrocycle).[21] In these cases, attack at oxy-

$$F_4W(OCH_3) + C_6H_6 \xrightarrow{25°C} F_4W(O) + C_6H_5CH_3 + HF \qquad (8)$$
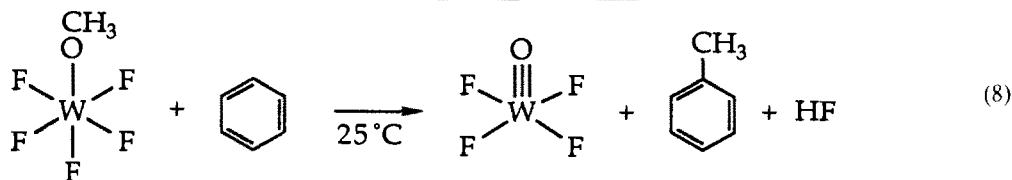
This is an extreme case of an alkoxide as an alkylating agent, with a tungsten center that can make a very strong metal-oxo multiple bond and five electron withdrawing fluoride ligands. In other cases, loss of carbocations from alkoxides (S_N1 chemistry) is observed only with quite stable carbocations. As an example, Wolczanski and co-workers[18] have concluded that the tri-tert-butylmethoxide ligand, OC^tBu_3, is not a great spectator ligand because of the ready dissociation of tri-tert-butylmethyl cation (presumably both for electronic and steric reasons). tert-Butoxide complexes are often more labile than other alkoxides, although
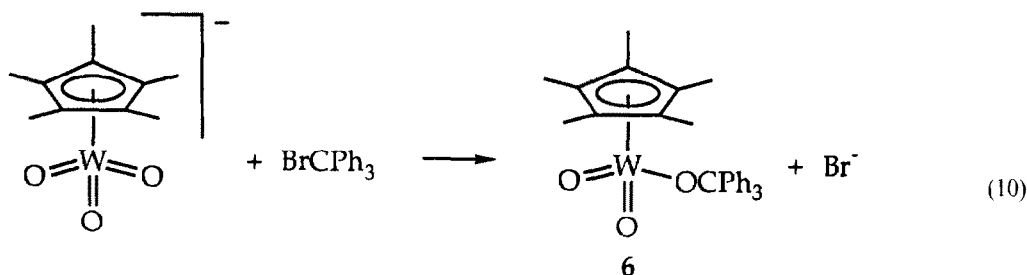
gen is accompanied by coordination of another ligand to make up for the loss of oxygen-to-metal π donation.

Alkylation and protonation of metal-oxo complexes to give alkoxides are much more common for polyoxo complexes, in which conversion of one oxo to an alkoxide is compensated by more π-donation from the remaining oxo group(s). Rhenium(V)-trans-dioxo complexes are a good example of this ability of a "spectator" oxo group to accommodate changes in the bonding of another oxo, as illustrated in eq. (9) (L = py, NH_2Me, 1/2 en, CN^-, etc).[22] The last oxo group (like most

$$\left[\begin{array}{c} O \\ L{-}Re{-}L \\ L{-}Re{-}L \\ O \end{array}\right]^+ \xrightarrow{+ H^+} \left[\begin{array}{c} O \\ L{-}Re{-}L \\ L{-}Re{-}L \\ OH \end{array}\right]^{2+} \xrightarrow{+ H^+} \left[\begin{array}{c} O \\ L{-}Re{-}L \\ L{-}Re{-}L \\ OH_2 \end{array}\right]^{3+} \qquad (9)$$
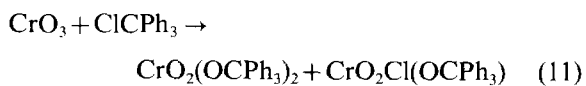
mono-oxo complexes) is very difficult to protonate, so the second protonation occurs to give an oxo-aquo species, not a bis(hydroxide).[22]

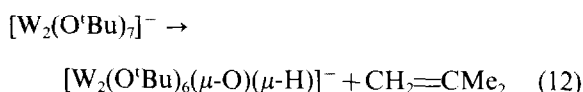Geoffroy and co-workers[23] have provided excellent examples of nucleophilic polyoxo complexes: $Cp*MO_3^-$ (M = Mo, W), which alkylate and metallate at oxygen quite readily [e.g. eq (10)]. $Cp*MO_3^-$ are not strong bases, being stable to $^iBuNH_3^+$. Still, the trityloxy product $Cp*W(O)_2(OCPh_3)$ (6) does not appear to lose Ph_3C^+ readily as it is recrystallized from THF/Et_2O (free Ph_3C^+ is quite reactive with THF).

To our knowledge, there are no clear examples of the loss of R^- from an alkoxide or the addition of R^- to an oxo to give an alkoxide ligand. However, the distinction between R^+ and R^- loss can be blurred when the R group winds up on the metal or on another ligand (see the following sections). The interesting report of C—O cleavage in a tert-butoxide ligand by Budzichowski et al.[29] provides an illustration of this issue. $[W_2(O^tBu)_7]^-$ decomposes readily to give isobutylene and a ditungsten μ-oxo μ-hydrido complex [eq. (12)].

$$O=\overset{\displaystyle |}{\underset{\displaystyle O}{W}}=O \quad + \quad BrCPh_3 \quad \longrightarrow \quad O=\overset{\displaystyle |}{\underset{\displaystyle O}{W}}-OCPh_3 \quad + \quad Br^- \qquad (10)$$

6

Most classical inorganic oxyanions are basic to some degree, ranging from the quite basic vanadate and ferrate ions to perrhenate which is almost inert, like perchlorate. The aqueous pK_a values of these species are well known,[24] although it should be noted that nucleophilicity does not always correlate with basicity for these species.[25] The oxyanions are formally related to oxo-alkoxide complexes (inorganic "esters"), although the alkoxide complexes are usually formed by other synthetic routes. For instance, alkylation of inorganic vanadate VO_4^{3-} formally gives the well known and fairly inert vanadate "esters" $V(O)(OR)_3$, which are typically prepared from alcohols and $V(O)Cl_3$. [The vanadium chemistry is not grossly different from the chemistry of organic and inorganic phosphates, $P(O)(OR)_3$ and PO_4^{3-}.] Similarly, the perrhenate "esters" $ROReO_3$ are formed from ReO_3Cl and Me_3SiOMe.[26] $ROReO_3$ complexes are not very stable, apparently related to heterolyis of the C—O bond as the tert-butoxy derivative is less stable than the methoxy complex ($Me_3SiOReO_3$ is a useful source of Me_3Si^+).[26,27] Chromate "esters" (chromyl alkoxides) can be prepared by alkylation [eq. (11)], although the high reactivity of chromium(VI) limits the generality of this reaction.[28]

$$CrO_3 + ClCPh_3 \rightarrow$$

$$CrO_2(OCPh_3)_2 + CrO_2Cl(OCPh_3) \quad (11)$$

$$[W_2(O^tBu)_7]^- \rightarrow$$

$$[W_2(O^tBu)_6(\mu\text{-O})(\mu\text{-H})]^- + CH_2{=}CMe_2 \quad (12)$$

The authors describe this reaction as proceeding in a manner similar to a retro-ene reaction wherein isobutylene is liberated concomitantly with W=O and W—H bond formation. To force this interesting reaction into the classification scheme of this review, it could be seen as an E2 elimination, similar to the carbocation (E1) elimination discussed above, facilitated by simultaneous H^+ transfer to the W_2 unit. However, the hydrogen that is transferred to the metal is formally bound as a hydride ligand, not H^+. Thus the reaction could also be viewed as cleavage of the alkoxide to tert-butyl carbanion, synchronous with loss of H^- to the Lewis acidic ditungsten center. This description makes the redox nature of eq. (12) more evident ($W_2^{III} \rightarrow W_2^{IV}$), as loss of R^- from an alkoxide is a two-electron oxidation of the metal center(s) [eq. (3)].

The closest analog to the addition of R^- to an oxo group is the reversible addition of hydride to an imido ligand reported by Templeton and co-workers.[30] $NaBH_4$ effects H^- addition to the cationic imido complex $[Tp*(CO)_2W{=}NPh]^+$ and the hydride can be removed from the amide nitrogen by Ph_3C^+ [eq. (13); $Tp* =$ hydrido tris[3,5-dimethylpyrazolyl]borate, $HB[Me_2pz]_3$].

$$(13)$$
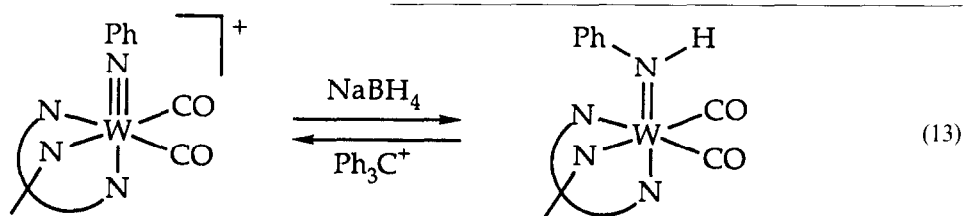
Surprisingly, the reaction does not occur by direct hydride addition to nitrogen, but by initial hydride attack at a carbonyl ligand to give a formyl as the kinetic product [eq. (14)]. Intramolecular transfer of the hydride from the formyl to the imido forms the amide.[30]

ligand has been studied by kinetic and radiolytic techniques in a few systems. For instance, trapping of alkyl radicals by permanganate and chromate both occur at close to diffusion-limited rates.[33] We have found that radical additions to Cr=O bonds are key steps in the oxidation of alkanes by chromyl


$$(14)$$
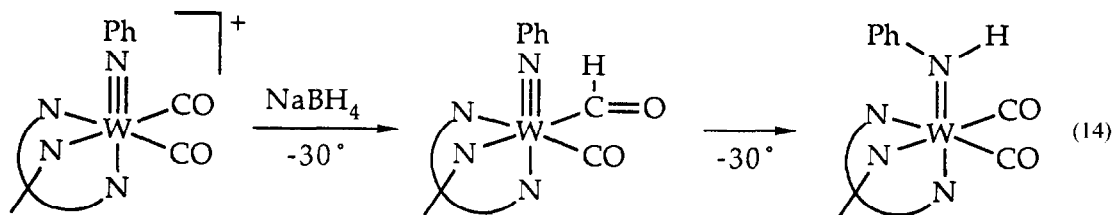
It remains to be seen whether such pathways are possible for oxo/alkoxide and oxo/hydroxide interconversions. It should be noted, however, that addition and loss of other nucleophiles from oxygen are quite common [eq. (15)], including alkene/epoxide, pyridine/pyridine N-oxide, Me$_2$S/Me$_2$SO, Ph$_3$P/Ph$_3$PO interconversions.[31] And glycolates can be formed from olefins or decompose to olefins, as in eq. (16) (to select one of many examples).[32]

Homolytic C—O bond cleavage/formation [eq (2)]

The addition of an organic radical to an oxo

chloride, CrO$_2$Cl$_2$. The initial alkane-activating step in these reactions is hydrogen atom transfer from the alkane to a chromium-oxo group, forming a chromium(V) hydroxide, Cr(OH)(O)Cl$_2$ (Scheme 1).[34] The evidence for this step includes a simple second-order rate law, a primary isotope effect, and trapping of the alkyl radical with CBrCl$_3$.[34] The hydroxide complex is not observed, however, because it is unstable to further reduction and/or disproportionation.

Formation of Cr(OH)(O)Cl$_2$ is an example of radical addition to a metal-oxo group [eq. (2)],

$$M\text{=}O + :Nu \rightleftarrows M\text{--}ONu \qquad (15)$$

$$+ \ CH_2\text{=}CH_2 \qquad (16)$$
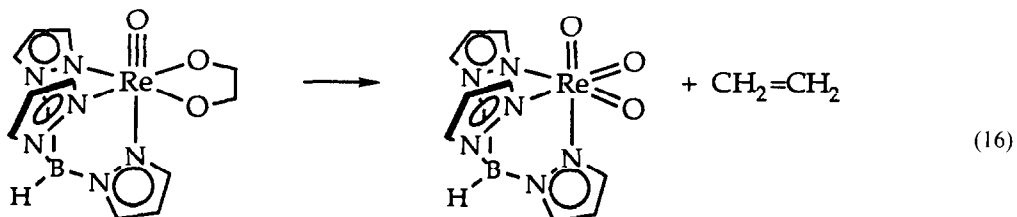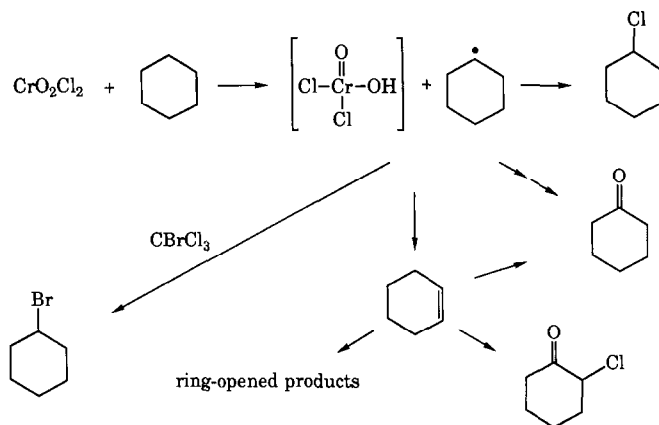
Scheme 1. Mechanism of CrO_2Cl_2 oxidation of cyclohexane.[34a]

although free H· is not involved. CrO_2Cl_2 is able to remove H· from alkanes such as cyclohexane because it makes a strong bond to a hydrogen atom, the O—H bond in $Cr(OH)(O)Cl_2$.[34] The strength of this O—H bond is estimated to be similar to the 83 kcal mol^{-1} O—H bond in $[O_3MnO—H]^-$, formed by H· addition to permanganate. This bond strength is calculated using a thermochemical cycle based on the redox potential of permanganate and the pK_a of $HMnO_4^-$.[34a]

three pathways: the radical can abstract Cl· from chromium, it can donate a second hydrogen to give an alkene, and it can add to an oxo group to form a cyclohexyl alkoxide ligand (which is subsequently oxidized). In the reactions we have studied, the reaction of isobutane provides the clearest example of alkoxide formation by radical addition. Addition of t-butyl radical to CrO_2Cl_2 forms (among other products) a t-butoxide ligand which is observed as t-butanol on hydrolysis [eq. (17)].[34b,c]
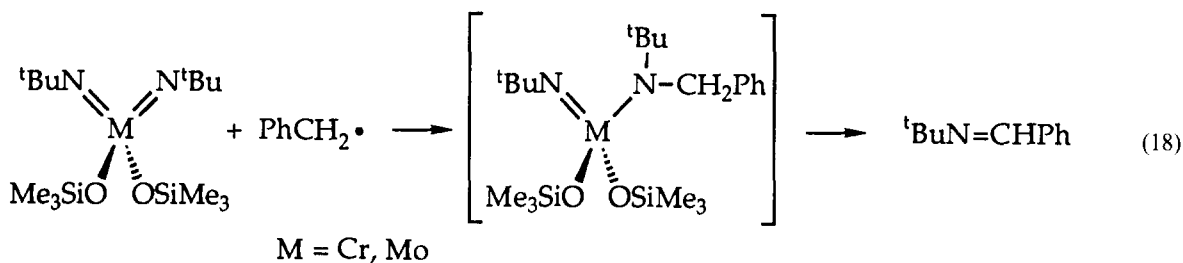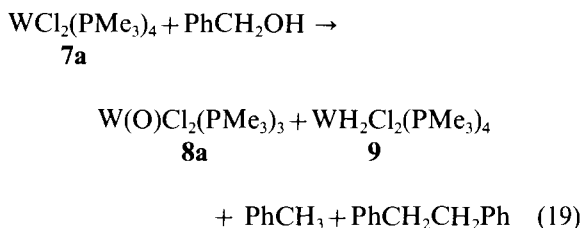
$$CrO_2Cl_2 + Me_3CH \longrightarrow Me_3C\bullet \xrightarrow{CrO_2Cl_2} [Cr(O)(O^tBu)Cl_2]$$

$$\downarrow H_2O \qquad\qquad (17)$$

$$^tBuOH + ...$$
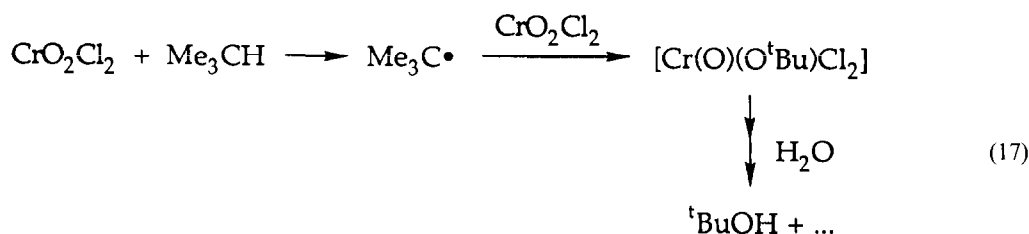
Hydrogen atom transfer from cyclohexane to CrO_2Cl_2 is slow (4×10^{-6} M^{-1} s^{-1} at 75°C) because the abstraction step is thermodynamically uphill, with $\Delta H \cong +13$ kcal mol^{-1}. The relative rates of hydrogen atom abstraction from different hydrocarbons correlate with the C—H bond strengths: cyclohexane > cyclooctane $\cong$ isobutane > toluene, with toluene 5×10^3 more reactive than cyclohexane on a per hydrogen basis. This is as expected for a hydrogen atom transfer process.[34b,c]

The cyclohexyl radical formed on hydrogen atom abstraction from cyclohexane is then rapidly trapped by CrO_2Cl_2 (Scheme 1). Based on competition with trapping by $CBrCl_3$, the rate of reaction of CrO_2Cl_2 with cyclohexyl radical is calculated to be 3×10^9 M^{-1} s^{-1}, close to the diffusion limit.[34a] As shown in Scheme 1, trapping of cyclohexyl radicals occurs by

This is another example of eq. (2), radical addition to a metal-oxo group. The facility of C—O bond formation is due to its being very exothermic (note that formation of an O—H bond in this system is ca 83 kcal mol^{-1} downhill). From another perspective, addition of R· to an oxo ligand occurs with one-electron reduction of the metal center, a result strongly favored by the highly oxidizing chromium(VI) center. The CrO_2Cl_2 chemistry is similar to the proposed mechanism of alkane oxidation by cytochrome P-450 enzymes and model systems; initial hydrogen atom transfer to a ferryl oxygen (Fe=O), followed by very rapid trapping of the alkyl radical to give the alcohol product.[35]

There are a few other examples of related reactions. Aqueous TiO^{2+} reacts with ·CMe_2OH at 10^6 M^{-1} s^{-1} with the formation of Ti^{3+} and acetone, a

reaction that could occur by C—O bond formation or, as suggested by Espenson and co-workers,[36] by electron transfer. In a related example, Chan and Nugent[37] showed that benzyl radicals are trapped by the imido complexes $M(N^tBu)_2(OSiMe_3)_2$ (M = Cr, Mo), most likely via the benzyl t-butyl amide [eq. (18)].

$$WCl_2(PMe_3)_4 + PhCH_2OH \rightarrow$$
$$\mathbf{7a}$$

$$W(O)Cl_2(PMe_3)_3 + WH_2Cl_2(PMe_3)_4$$
$$\mathbf{8a} \qquad\qquad \mathbf{9}$$

$$+ PhCH_3 + PhCH_2CH_2Ph \quad (19)$$

$$M = Cr, Mo$$

These reactions may be closely related to reactions at metal oxide surfaces. The oxidation of propylene to acrylonitrile over molybdenum oxide catalysts proceeds via intermediate allyl radicals, which have been suggested to add to surface imido groups.[38] The oxidation of methane to methanol over metal oxide catalysts has been shown to involve gas phase methyl radicals which add to oxo groups of the oxide surface.[39]

Homolytic cleavage of the C—O bond in an alkoxide ligand—the reverse of eq. (2)—is a rare process because of the strength of the C—O bond. For instance, the C—O bond in benzyl alcohol is 81 kcal mol^{-1} [this is the ΔH for $PhCH_2OH \rightarrow PhCH_2^. + ^.OH$].[40] But there is evidence that radicals can be formed on thermolysis of metal alkoxide complexes, which may have some relevance to the use of alkoxides as precursors to metal oxides by pyrolysis or chemical vapor deposition.[41] Sen and co-workers[41] have analyzed the products from the thermolysis of titanium tetra-alkoxides to TiO_2 at 550°C and found evidence for homolytic, as well as other paths.
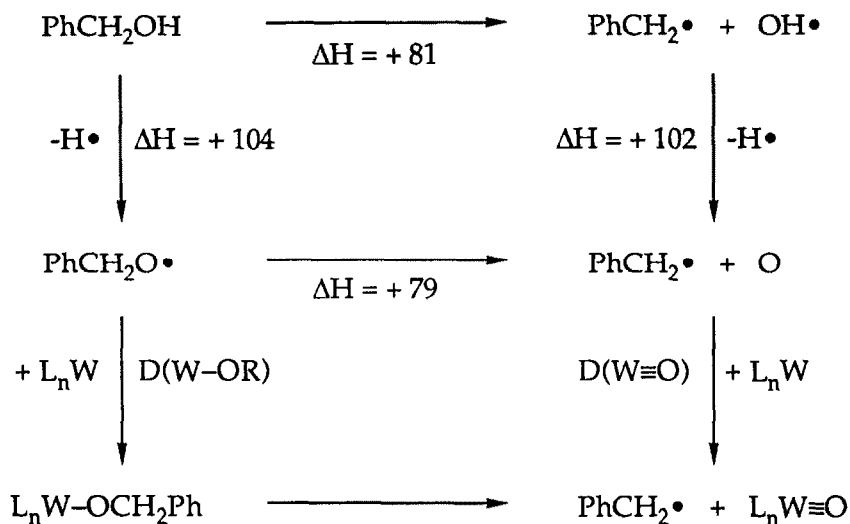
We have recently found evidence for C—O bond homolysis in the reaction of alcohols with WCl_2L_4 (L = PMe_3, $\mathbf{7a}$; $PMePh_2$, $\mathbf{7b}$). Heating a benzene solution of $\mathbf{7a}$ with benzyl alcohol at 80°C forms the tungsten oxo-trisphosphine complex $W(O)Cl_2(PMe_3)_3$ ($\mathbf{8a}$), the tungsten dihydride $WH_2Cl_2(PMe_3)_4$ ($\mathbf{9}$), toluene, and bibenzyl [eq. (19)].[42] The presence of bibenzyl is strongly suggestive of the intermediacy of benzyl radicals. Preliminary indications are that these radicals can be trapped by added $\mathbf{9}$ or dihydroanthracene.

The analogous reaction of cyclopropyl methanol yields only butenes, presumably via the rapid ring opening of the cyclopropylcarbinyl radical.

While the mechanisms of these reactions have not yet been fully worked out, it seems likely that the radicals are formed by homolysis of the C—O bond in a tungsten-alkoxide intermediate. While this is likely an uphill step, it is much less unfavorable than in the alcohol because of the formation of a very strong tungsten-oxo bond. The tungsten-oxygen triple bond in $\mathbf{8a}$ has been estimated to be $\geqslant 138 \pm 5$ kcal mol^{-1}, based on the exoergic reaction of $\mathbf{7a}$ with CO_2.[43] If the W≡O bond formed on homolysis is 60 kcal mol^{-1} stronger than the W—OCH_2Ph single bond, which is not unreasonable with the bond strength quoted above, then homolysis of the O—CH_2Ph bond would be uphill by only 20 kcal mol^{-1}. This value is derived from the thermochemical cycle in Scheme 2. Thus, when a very strong metal-oxo bond can be formed, the MO—R and MO—H bonds can be quite weak.

## C—O CLEAVAGE OR FORMATION BY TRANSFER TO OR FROM ANOTHER LIGAND

Reactions in which a group is transferred between an oxo and another ligand are closely related to the heterolytic and homolytic alkoxide reactions discussed above. However, new possibilities arise from the prospect of concomitant bond making and bond breaking. Perhaps the most intriguing of these reactions is the migration of an
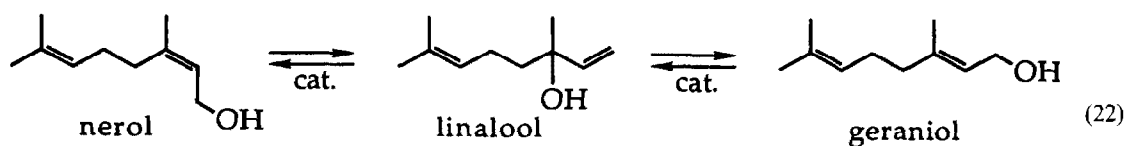
$$PhCH_2OH \xrightarrow{\Delta H = +81} PhCH_2\bullet + OH\bullet$$

$$-H\bullet \;\bigg| \; \Delta H = +104 \qquad\qquad \Delta H = +102 \; \bigg| \; -H\bullet$$

$$PhCH_2O\bullet \xrightarrow{\Delta H = +79} PhCH_2\bullet + O$$

$$+ L_nW \;\bigg| \; D(W-OR) \qquad\qquad D(W\equiv O) \; \bigg| \; + L_nW$$

$$L_nW-OCH_2Ph \longrightarrow PhCH_2\bullet + L_nW\equiv O$$

$$\boxed{\Delta H \text{ for the lowest reaction is } 79 - D(W\equiv O) + D(W-OR) \text{ kcal/mol.}}$$

Scheme 2. Thermochemical cycle for WO—R dissociation. Based on data from ref. 40. All values are in kcal mol^{-1}. D(PhCH$_2$O—H) is taken as a typical RO—H bond strength, from ref. 40(c).

allyl group to or from a multiply bonded ligand [eq. (20)], a process which closely resembles a Claisen rearrangement [eq. (21)].[44]

$$(20)$$

$$(21)$$
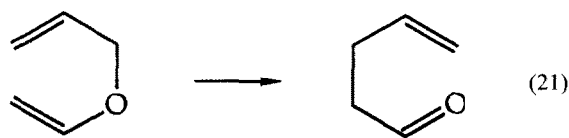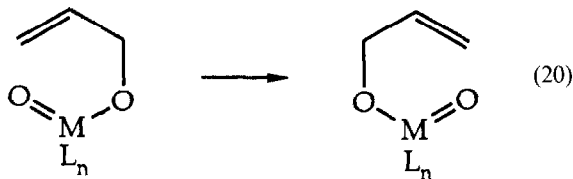
In a substituted allylic alcohol, eq. (20) results in allylic transposition of the oxygen. This chemistry is practiced commercially in variants of eq. (22),

the isomerization of linalool to geraniol and nerol using vanadium (or tungsten) oxo complexes as catalysts at 160°C.[45]

Osborn and co-workers[46] have found that this type of reaction proceeds readily at a molybdenum-oxo center at ambient temperatures [eq. (23), adapted from ref. 46(c)]. ^{17}O labeling and kinetic experiments support the proposed pericyclic transition state (A). Allyl groups are also transferred from alkoxide to imido groups, and from amide to imido groups, although these are less facile than eq. (23). Such conversion of allylic alcohols to allylic amines has been suggested to be occurring in propylene ammoxidation over molybdenum oxide catalysts.[38,46c] The reactions occur more rapidly with more electron deficient molybdenum centers, which suggests that the metal acquires electron density in the transition state.[46]

Chan and Nugent[37] were among the first to report the conversion of allylic alcohols to allylic amines, using W(N^{t}Bu)$_2$(NH^{t}Bu)$_2$ (10) [eq. (24)].

$$(22)$$

catalyst = VO(OR)$_3$, WO(OR)$_4$, WO(OR)$_4$L

(23)

(24)
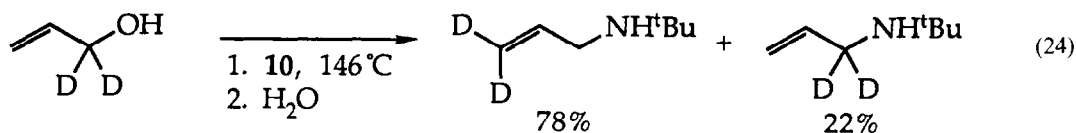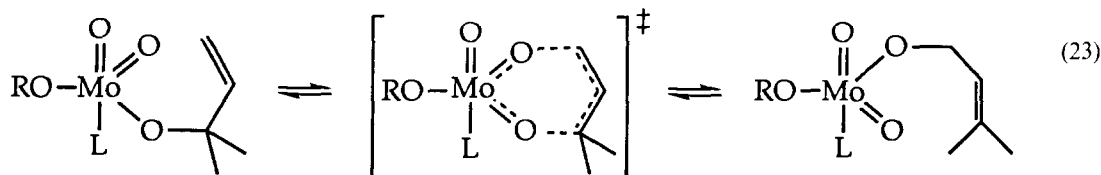
The observation of only partial transposition in eq. (24) and related reactions could result from double allyl migrations,[46c] or it could indicate that the reactions are not completely proceeding by a pericyclic transition state as in eq. (23).[37] A second pathway could involve a biradical intermediate or transition state (**B**), generated by C—O bond homolysis and


B
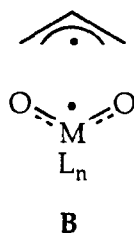
consumed by trapping of the allyl radical, similar to the chemistry described in the section on homolytic C—O bond cleavage/formation. Biradical tran-

examples—can also be viewed as a pericyclic reaction.

We have not seen allyl transfer in the rhenium-oxo-bis(acetylene) system. The isomeric methyl-substituted allyloxide complexes in eq. (25) do not interconvert over a week at 70°C, prior to decomposition.[13,14]

It is not surprising that eq. (25) is slow since the analogous transfer of a proton is quite slow.[12] The oxo-hydroxide **3** can be prepared with ^{18}O enrichment primarily in the hydroxide, by hydrolysis of $Re(O)OEt(MeC\equiv CMe)_2$ by $H_2^{18}O$. Tautomerization to the equilibrium isotopic distribution requires roughly 1.5 days at ambient temperature in benzene solution [eq. (26)].[12]

Kinetic data on the isomerization of $3\text{-}^{18}OH$ in benzene are consistent with a first order approach to equilibrium.[12] The rate is unaffected by the presence of ethanol, dimethylamine, and 0.1 equivalent of benzoic acid. These data are consistent with

70 °C

(25)
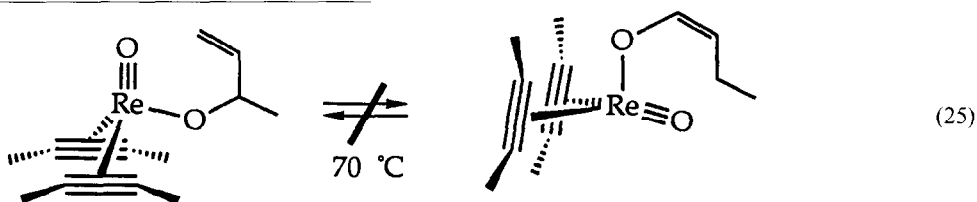
sition states have been much discussed for organic Cope and Claisen rearrangements, and the current consensus seems to be that their energies are only slightly above the energies of the pericyclic transition states.[47] A few related examples of pericyclic-looking reactions involving metal–ligand multiple bonds have been discussed, but their mechanisms have not been established.[48] The migration of an allyl group between an oxo group and a metal center [see eq. (29)]—of which there are as yet no

intramolecular proton transfer from the hydroxide to the oxo group but do not rule out other pathways.

Proton transfer between oxygens is usually fast because the addition of a proton to an oxygen lone pair does not cause a substantial change in structure.[49] The unusually slow tautomerization of **3** is due to the fact that the proton is added not to an oxygen lone pair but rather to a rhenium–oxygen π-bonding orbital. Proton motion is therefore

$$3\text{-}^{18}OH \quad \xrightleftharpoons[\;]{\;} \quad t_{1/2} \cong 11 \text{ hr} \quad 3\text{-Re}{\equiv}^{18}O \tag{26}$$
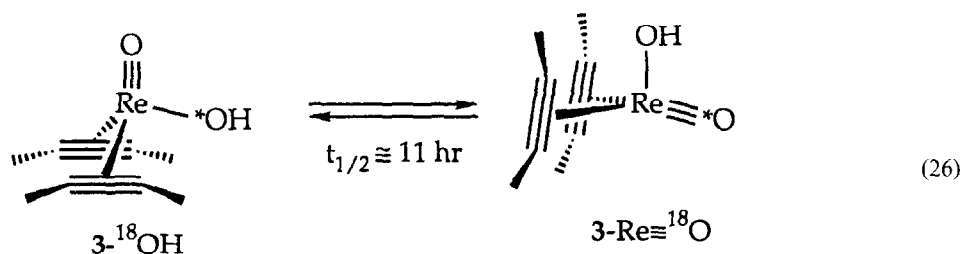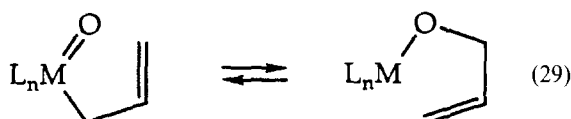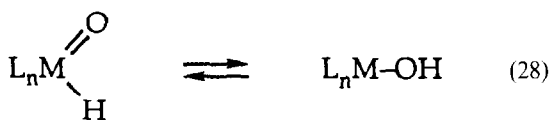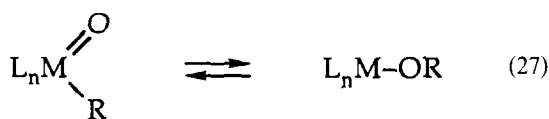
coupled with significant changes in bonding and structure. For instance, the alkyne ligands must rearrange on proton transfer [as illustrated in eq. (26)] since the alkynes are constrained to lie in a plane perpendicular to the rhenium-oxo bond (and there is a large barrier to alkyne rotation).[11a]

Slow proton transfer between oxygen or nitrogen atoms has been observed in other systems where a π-bonding orbital is the proton-accepting site.[50] Studies of exchange between $H_2^{18}O$ and the aqueous vanadyl ion show that exchange of the oxo group is much less facile than the other bound oxygen ligands (water or hydroxide). For $V(O)(H_2O)_5^{2+}$, the half-life for exchange of the oxo group with solvent water is 6.7 h at $0°C$.[51] In more basic solution deprotonation occurs to give the oxo-hydroxide $V(O)(OH)(H_2O)_4^+$, which undergoes more facile oxo exchange—a half-life of 0.5 s at $0°C$—but still slow for a proton exchange reaction. In contrast, proton transfer in d^0 oxyacids such as vanadates ($HVO_4^{2-}, H_2VO_4^-$), bichromate ($HCrO_4^-$), etc., is extremely rapid, such that a selectively isotopically labeled isomer would be scrambled essentially instantaneously. Only one ^{17}O NMR signal is observed for partially enriched HVO_4^{2-} and $H_2VO_4^-$.[52] The origin of this difference may be in the electron count, that proton transfer to an oxo ligand is slow in complexes with d electrons, when electronic and structural rearrangements occur.

C—O CLEAVAGE OR FORMATION BY TRANSFER TO OR FROM THE METAL CENTER

The migration of an alkyl or aryl ligand to an oxo ligand is a particularly interesting way to generate a new C—O bond and to selectively oxidize a metal-alkyl or -aryl [eq. (27)]. The interconversion of hydroxide and oxo-hydride complexes [eq. (28)] is of interest because of the ubiquity of hydroxide ligands in aqueous media and on oxide surfaces. And analogous allyl migrations [eq. (29)] are metallaclaisen rearrangements and could be pericyclic in nature (see previous section).

$$L_nM{\overset{O}{\diagdown}}_R \quad \xrightleftharpoons[\;]{\;} \quad L_nM\text{-}OR \tag{27}$$

$$L_nM{\overset{O}{\diagdown}}_H \quad \xrightleftharpoons[\;]{\;} \quad L_nM\text{-}OH \tag{28}$$

$$L_nM \quad \xrightleftharpoons[\;]{\;} \quad L_nM \tag{29}$$

Oxo-alkyl/alkoxide rearrangements

Attention was first drawn to alkoxide/oxo-alkyl rearrangements [eq. (27)] by Sharpless and co-workers[53] in their 1977 proposal of a new mechanism for the oxidation of alkenes by metal-oxo complexes such as OsO_4 and CrO_2Cl_2. The proposed mechanism for oxidation of alkenes to diols by OsO_4 is outlined in eq. (30) (not shown are ligands such as pyridine which are typically added to facilitate the reaction and stabilize the product).[53,54]

The oxo-alkene intermediate is proposed to

$$O{=}\overset{O}{\underset{O}{\overset{\|}{Os}}}{=}O \;+\; \quad \xrightleftharpoons[\;]{\;} \quad \xrightleftharpoons[\;]{\;} \quad \longrightarrow \tag{30}$$
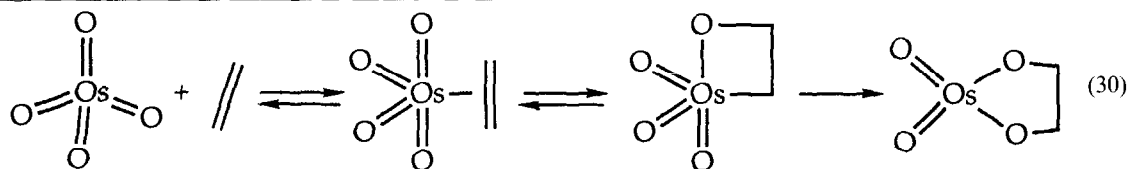
rearrange to an oxametallacyclobutane, forming the first carbon–oxygen bond, and then the second alkoxide is formed by 1,2-migration of the coordinated alkyl to an oxo group. This mechanism continues to inspire debate[54] and has stimulated a number of studies, particularly on the formation and cleavage of oxametallacycles and nitrogen analogues.[55] The last step, however—an example of eq. (27)—has received much less attention.
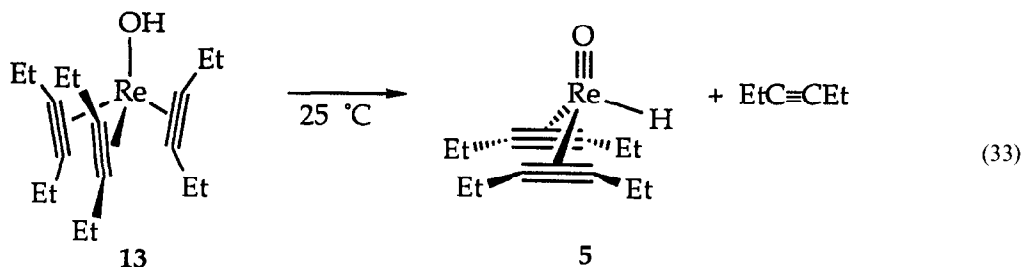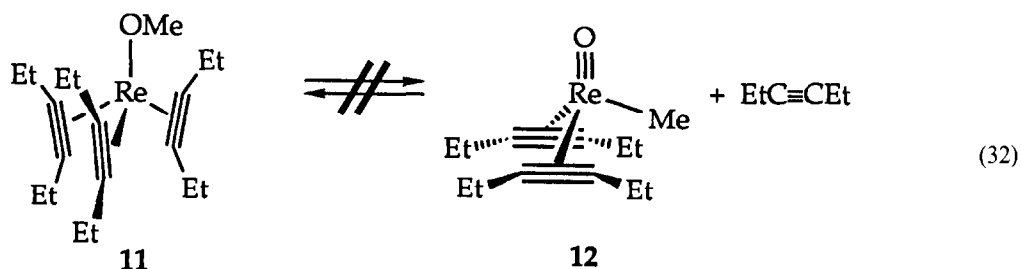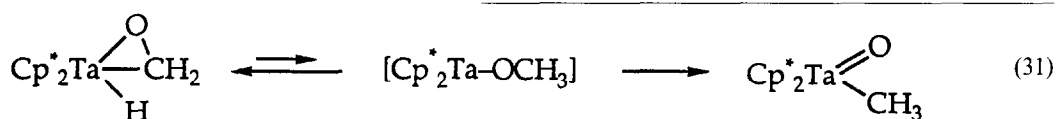
There are few examples of interconversions of alkoxide or aryloxide ligands with oxo-alkyl and oxo-aryl compounds [eq. (27)], and some of these have only been inferred from indirect evidence.[56] The classic example of this rearrangement is the study by Bercaw and co-workers[57] of the conversion of $[Cp_2^*Ta(OCH_3)]$ to $Cp_2^*Ta(O)CH_3$ [eq. (31)], along with the analogous sulfur, nitrogen, and carbene ($=CH_2$) reactions. The methoxide complex is formed reversibly from the formaldehyde hydride complex by β-hydrogen insertion/elimination at 60°C, as inferred from NMR magnetization transfer studies.

methoxide complex and the barrier to methoxide rearrangement; the latter could not be separately determined because the methoxide complex was not directly observed. But it is clear that α-methyl elimination is much less facile than β-hydrogen elimination, by a factor of 10^9 in rate, 16 kcal mol^{-1} in $\Delta G^{\ddagger}$.[57]

A significant barrier to alkoxide/oxo-alkyl exchange has been observed in two rhenium systems where we have isolated closely related alkoxide and oxo-alkyl complexes. The rhenium(I)-tris (acetylene)-methoxide (11) and the rhenium(III)-bis (acetylene)-oxo-methyl complex (12) do not interconvert up to their decomposition temperatures [90°C for 11, 120°C for 12; eq. (32)].[58]

The 3-hexyne ligands in 11 are liable, so this is not the cause of the barrier to rearrangement. A similar lack of rearrangement is observed for the phenoxide/oxo-phenyl and acetate/oxo-acyl derivatives, although these have less liable alkyne ligands.[58]

The rhenium(I)-tris(acetylene)-hydroxide complex 13, however, does rearrange at ambient tem-

$$Cp_2^*Ta\underset{H}{\overset{O}{<}}CH_2 \;\rightleftarrows\; [Cp_2^*Ta-OCH_3] \;\longrightarrow\; Cp_2^*Ta\overset{O}{\underset{CH_3}{<}} \qquad (31)$$

$$(32)$$

$$\xrightarrow{25\ °C}$$

$$+ \; EtC\equiv CEt \qquad (33)$$

13   **5**

The formation of the oxo-methyl product requires heating to 140°C, and occurs with a barrier of 34.9(2) kcal mol^{-1} at 140°C ($\Delta G^{\ddagger}$) starting from the formaldehyde complex. This barrier includes both the $\Delta G°$ for pre-equilibrium formation of the

peratures to the oxo-hydride 5 [eq. (33)].[59] The hydroxide complex has been isolated and fully characterized (Fig. 2).

Equation (33) is one of the first examples of hydroxide/oxo-hydride interconversion, eq. (28). Re-
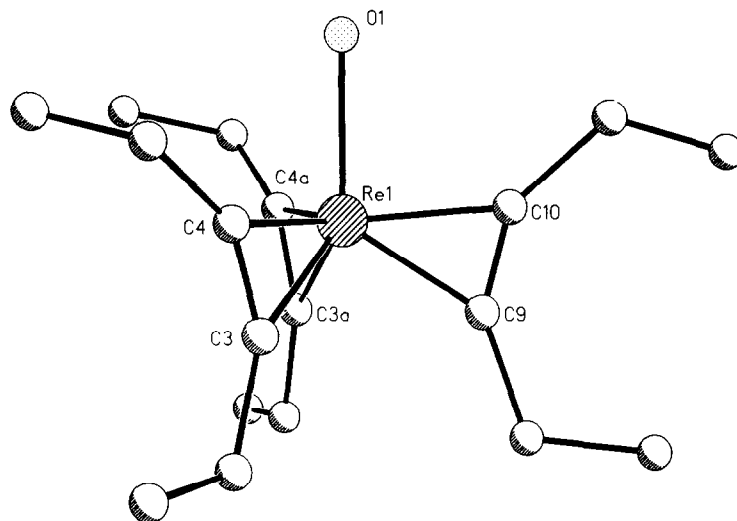
Fig. 2. ORTEP drawing of Re(OH)(EtC≡CEt)₃ (13). The hydroxide hydrogen was not located.
(From ref. 59.)

arrangement of the unobserved tantalum hydroxide [Cp*₂Ta(OH)] to the oxo-hydride Cp*₂Ta(O)H has been inferred from labeling studies.[60] The much larger barrier for alkyl vs. hydrogen elimination is typical of many rearrangements. Bercaw and co-workers[57b] have found that hydrogen migrates 10^6–10^{10} faster than a methyl group in α eliminations, and a similar rate difference is reported by Brookhart et al.[61] for β-elimination reactions. The lack of rearrangement of the methoxide complex 11 [eq. (32)] is consistent with methyl migration being at least ca 10^6 times slower than hydrogen migration [eq. (33)].
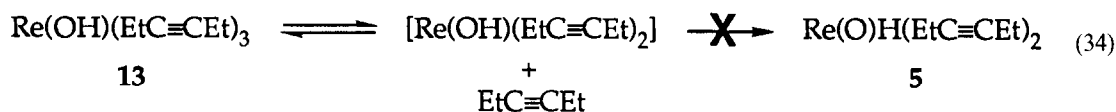
The hydroxide-to-oxo hydride rearrangement [eq. (33)] is first order in 13, is not inhibited by added 3-hexyne, and shows a primary isotope effect on deuteration of the hydroxide ($k_{OH}/k_{OD} = 5$). These data rule out the standard organometallic mechanism of initial ligand loss and rearrangement occurring via a coordinatively unsaturated rhenium(I)-bis(acetylene)-hydroxide intermediate, [Re(OH)(EtC≡CEt)₂] [eq. (34)]. The isotope effect

molecularly in the coordinatively saturated tris (acetylene) species 13, with hydrogen migration occurring either synchronously with or prior to the loss of ligand.[59]

Significant barriers to alkyl and aryl migration are also observed for interconversion of tris-pyrazolylborate rhenium compounds. The oxo-ethyl and ethoxy complexes TpRe(O)Et(Cl) (14) and TpRe(OEt)Cl(py) (15) do not thermally interconvert, nor do the oxo-phenyl and phenoxy complexes TpRe(O)Ph(Cl) (16) and TpRe(OPh) Cl(MeCN)(17; Tp = HBpz₃).[62] For instance, 16 may be heated at 160°C for a month in aceto-nitrile with less than 10% decomposition, and 17 decomposes over several days at 120°C to give unidentified diamagnetic products but no 16 is observed. X-ray crystal structures of TpRe(O)Ph₂ and TpRe(OPh)Cl(py) are shown in Fig. 3.

Compounds 14 and 16 do rearrange on photolysis however [eqs (35) and (36)].[62]

The photochemical oxo phenyl-to-phenoxide reaction [eq. (36)] is intramolecular, as shown by a

$$\text{Re(OH)(EtC≡CEt)}_3 \rightleftharpoons [\text{Re(OH)(EtC≡CEt)}_2] \xrightarrow{\quad X \quad} \text{Re(O)H(EtC≡CEt)}_2 \quad (34)$$
$$\textbf{13} \qquad\qquad\qquad + \qquad\qquad\qquad \textbf{5}$$
$$\text{EtC≡CEt}$$

would imply that the second step is rate limiting but this would require alkyne inhibition. The alkyne ligands in 13 are labile, however, as evidenced by alkyne exchange concurrent with formation of 5. Rearrangement apparently takes place intra-

cross-over experiment using TpRe(^{18}O)(C₆H₅)(Cl) and TpRe(^{16}O)(C₆D₅)(Cl).[62] Photolyses of sub-stituted aryl compounds show that the carbon bound to the metal becomes bound to oxygen in the aryloxide. Thus the phenyl migration is a simple

$$+ C_2H_4 + C_2H_6 + \ldots \tag{35}$$

14 → **15**

$$(36)$$

16 → **17**
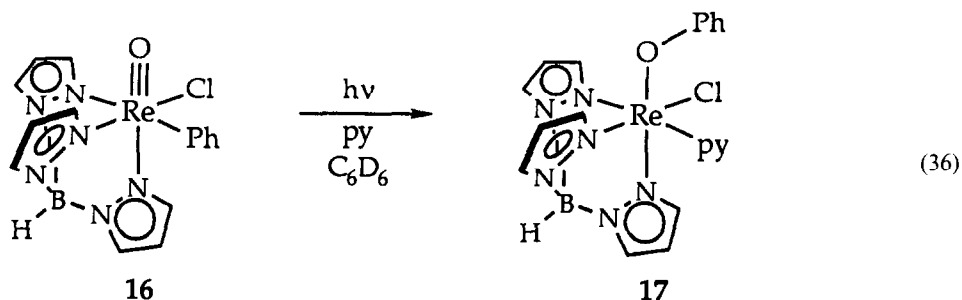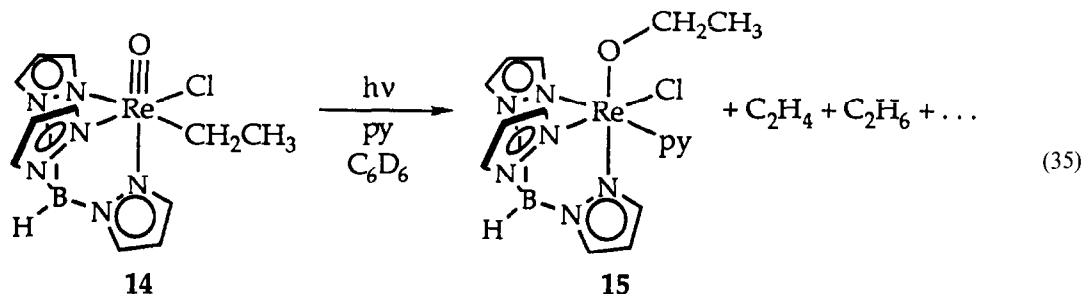
intramolecular [1,2]phenyl shift. Acetonitrile and Me$_2$SO can also be used as traps instead of pyridine, indicating that migration occurs prior to trapping of a coordinatively unsaturated aryloxide intermediate. In contrast, net ethyl migration occurs via free ethyl radicals, as indicated by the production of ethylene and ethane. The rearrangement is shut down in the presence of thiophenol, the ethyl group being converted to ethane by hydrogen atom abstraction.[62] The ethoxide complex is most likely formed by addition of ethyl radical to an intermediate rhenium oxo complex, another example of eq. (2).

The observation of significant thermal barriers to alkoxide/oxo-alkyl intervention is perhaps not surprising given the large number of stable alkoxide and oxo-alkyl complexes that have been synthesized. This should be contrasted with the relatively facile migration of alkyl groups to carbene ligands.[63] It should be noted that for most oxo-alkyl and -alkoxide complexes, rearrangement is likely to be thermodynamically unfavorable because of the redox properties of the metal or the instability of the product oxo complex. However, a number of oxidizing oxo-alkyl species are surprisingly resistant to rearrangement: examples include V(O)R$_3$,[56c] Cp*CrO$_2$(CH$_3$) and Cp*CrO(CH$_3$)$_2$,[64] (HB[3,5-Me$_2$pz]$_3$)MoO$_2$(R),[65] CpMoO$_2$(R)[66] and related oxo-sulfido complexes,[67] (HB[3,5-Me$_2$pz]$_3$)WO$_2$(R),[68] ReO$_2$(CH$_2$SiMe$_3$)$_3$,[69] CH$_3$Re(O)$_2$(O$_2$C$_6$H$_4$)(py),[70] and OsO$_2$(mesityl)$_2$.[71]

Brown[72a] has recently prepared an oxo-phenyl complex that undergoes facile rearrangement, at below 0°C, to a phenoxy complex (Scheme 3). The dioxorhenium(VII) complex [TpReO$_2$Ph]$^+$ (**18**) is generated from the rhenium (V)-oxo-phenyl-triflate TpRe(O)Ph(OTf) (**19**) using the oxygen atom transfer reagents pyridine N-oxide (pyO) or Me$_2$SO (OTf = triflate = O$_3$SCF$_3$). The triflate ligand in **19** is readily replaced by Me$_2$SO to form a fairly stable adduct, [TpRe(O)Ph(OSMe$_2$)]OTf, which reversibly loses Me$_2$S to give **18**, as indicated by magnetization transfer and kinetic studies. Reaction of pyO with **19** at low temperatures allows direct observation of **18**, and its rearrangement to the phenoxide product.

The phenyl-to-oxo migration in **18** is quite facile, with an extrapolated half-life of 4 min at 25°C [$\Delta H^{\ddagger} = 14.8(7)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -21(3)$ e.u.]. This is a remarkable contrast with the large barriers observed for interconversions of **11/12**, **14/15**, and **16/17**. We believe that the ease of phenyl migration in **18** is due to the oxo groups being electrophilic, as will be discussed in detail in an upcoming report.[72b] If the oxo groups have some electrophilic character then the migrations can resemble carbocation rearrangements, which are usually very rapid. Presumably this is also the origin of the facile alkyl and hydride migrations to metal carbenes, as Fischer carbene complexes typically behave as electrophiles.
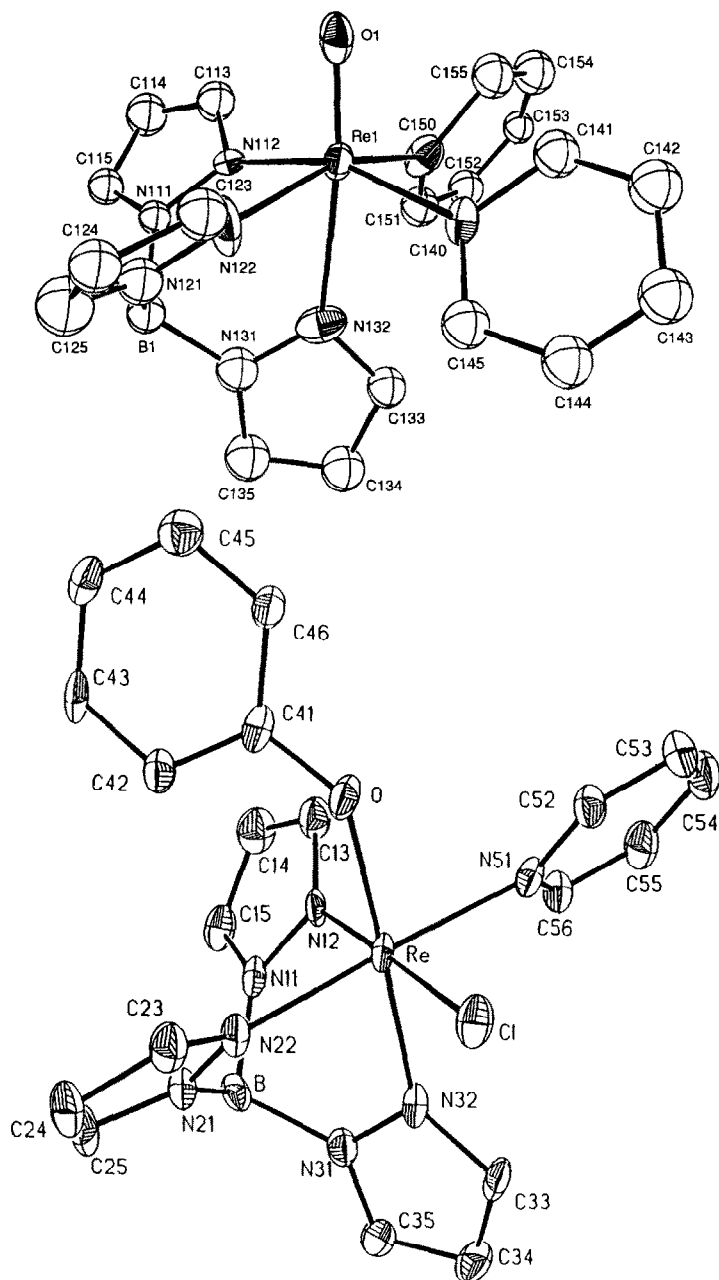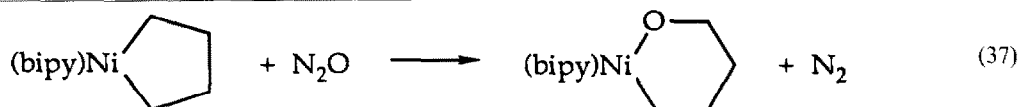
Fig. 3. ORTEP drawings of (a) TpRe(O)Ph$_2$ and (b) TpRe(OPh)Cl(py). (From ref. 72.)

Other metal-alkyl to metal-alkoxide reactions

Insertion of an oxygen atom into a metal-alkyl bond can be accomplished in a variety of ways, not just by migrations to a stable oxo ligand. For instance, Hillhouse and co-workers[73] have inserted an oxygen atom into a nickel metallacycle using N$_2$O [eq. (37)] and have recently reported related chemistry of aryl azides, NNNAr.

Similarly, van Koten and co-workers[74] have observed oxygen insertion into a palladium-aryl bond on treatment with ^{t}BuOOH [eq. (38)]. The

$$(\text{bipy})\text{Ni}\underset{\diagdown}{\diagup} \quad + \quad \text{N}_2\text{O} \quad \longrightarrow \quad (\text{bipy})\text{Ni}\underset{\diagdown}{\overset{\text{O}}{\diagup}} \quad + \quad \text{N}_2 \qquad (37)$$
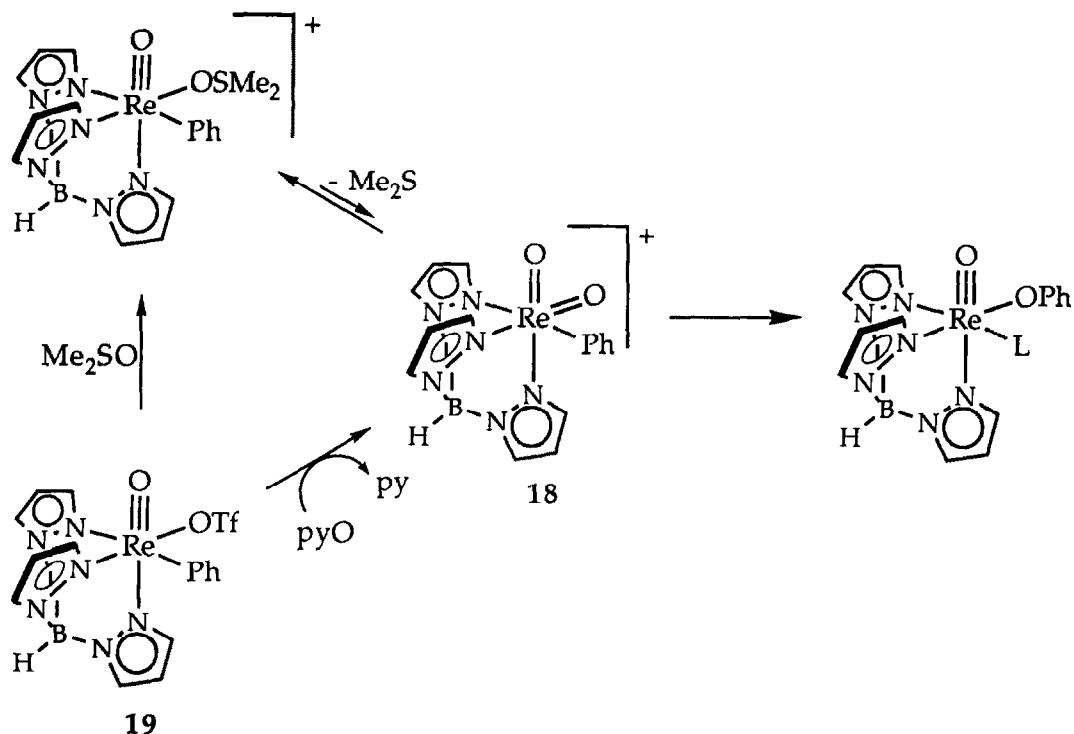
Scheme 3. Rearrangement of an oxo-phenyl complex to a phenoxy compound. (Adapted from ref. 72.)
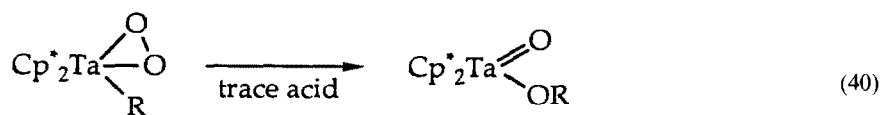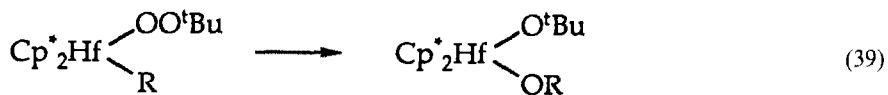
mechanisms of these processes have not as yet been well established.

Coordinated peroxides also can oxidize neighboring alkyl groups, as shown by Bercaw and co-workers[57] for both alkylperoxo and η^2-peroxo ligands [eqs (39) and (40) compare eq. (31)].

Since alkylperoxy complexes can be formed from dioxygen insertion into a metal alkyl, bis(alkoxide)

$$\tag{38}$$

$$\text{Cp}^*_2\text{Hf} \begin{array}{c} \text{OO}^t\text{Bu} \\ \text{R} \end{array} \longrightarrow \text{Cp}^*_2\text{Hf} \begin{array}{c} \text{O}^t\text{Bu} \\ \text{OR} \end{array} \tag{39}$$

$$\text{Cp}^*_2\text{Ta} \begin{array}{c} \text{O} \\ \text{O} \\ \text{R} \end{array} \xrightarrow{\text{trace acid}} \text{Cp}^*_2\text{Ta} \begin{array}{c} \text{O} \\ \text{OR} \end{array} \tag{40}$$

$$(^tBu_3CO)_2MMe_2 + O_2 \rightarrow (^tBu_3CO)_2M(OMe)_2 \tag{41}$$
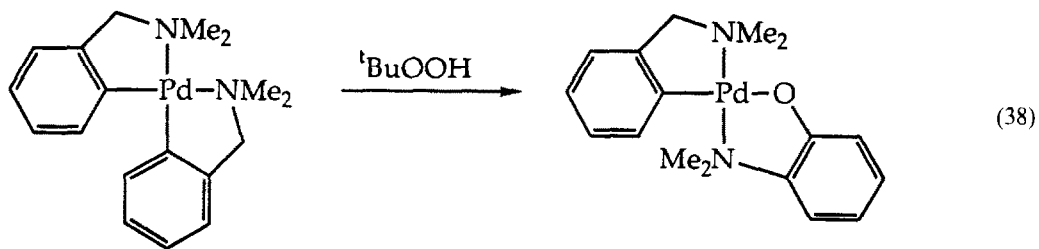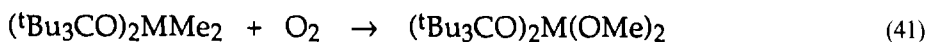
complexes can be formed from dialkyls, as illustrated by eq. (41) (M = Ti, Zr).[75] This type of reaction is also common for main group metal alkyl compounds.[76]

The last few reactions are somewhat outside the scope of this report since both M—O and C—O bonds are made, but they indicate that metal-alkyl complexes can be good precursors to alkoxides. It remains to be seen whether any of these reactions will prove to be general synthetic routes.

CONCLUDING COMMENT

Alkoxide ligands are often stable and fairly unreactive ancillary ligands. In particular, the C—O bond is not usually considered a site of reactivity. But in compounds where a related oxo complex is accessible, the C—O bond of an alkoxide ligand—and the O—H bond of a hydroxide—should be considered activated, and a range of interesting chemistry can result.

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