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Review

The stability of organometallic ligands in oxidation catalysis

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ABSTRACT

Organometallic precatalysts are increasingly applied to oxidation catalysis, where the spectator character of such ligands as Cp and Cp* is often assumed without definite proof. A number of reports of ligand lability under oxidative conditions have now appeared in the literature, raising concerns in reactions where primary oxidants are present. In such a case, partial or complete degradative loss of the organometallic ligand from the metal may need to be considered. This loss can sometimes deactivate a catalyst but it may also activate it by opening up labile sites at the metal. The highest risk applies to oxidation of the least reactive substrates, such as alkanes, since the catalyst may then also oxidize the CH bonds of its own ligands. More reactive substrates such as alkenes are likely to provide greater stabilization to the catalysts by providing a pathway for faster reaction of the substrate with the oxidized form of the catalyst. We therefore look at these and some related reactions to probe organometallic ligand loss under oxidative conditions, a topic that has received too little attention considering its important implications. Ligand loss can also affect applications to asymmetric catalysis and heterogenized homogeneous catalysts where the organometallic ligand is functionalized with a homochiral substituent or a tether to a surface. Ligands covered include CO, alkyls, aryls, alkenes, arenes, NHCs, cyclopentadienyls and other soft ligands.

Contents

1. Introduction 174
2. Carbonyls 175
3. Alkyls and aryls 175
4. Alkenes and arenes 176
5. *N*-Heterocyclic carbenes (NHCs) 177
6. Cyclopentadienyls 177
7. Other soft ligands 179
8. Conclusion 179
Acknowledgments 179
References 179

1. Introduction

Ligand robustness is a general problem in organometallic chemistry [1,2] but one that has attracted relatively little attention, given its importance in homogeneous catalysis. Fast ligand degradation can seriously limit catalyst lifetime and in practical applications, a limited lifetime translates to a higher loading of catalyst; this is a severe penalty for a precious metal catalyst, but even for the cheaper metals, the cost of the ligand itself can be considerable. Green chemistry aspirations [3] call for increased emphasis on catalysis, but the difference between a typical turnover number of 10^2 before deactivation and a TON of 10^6 or higher makes a very substantial difference to the shade of green achieved. Indeed, in industrial applications, the comparatively higher robustness of heterogeneous catalysts makes them a preferred resource, so to increase the penetration of homogeneous catalysis in industry we need to improve our understanding of catalyst degradation and of

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ways to counter it. In a classic early study, Collins identified the ligand decomposition pathways of an Fe-based oxidation catalyst and refined the ligand design to render the system robust and of great practical use [4].

Transition metal organometallic complexes have long shown their versatility in reductive and redox-neutral catalysis but are much less often seen in oxidative reactions. The reason is clear—many organometallics are air sensitive and decompose in the presence of oxidizing agents. For this reason, many of the reported cases of organometallic oxidation catalysis proceed by dehydrogenation, so that the catalyst is never exposed to any primary oxidant; these cases are not considered here.

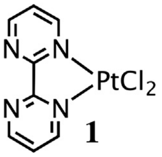
Numerous oxidation catalysts are simple salts or coordination complexes. The field goes right back to the 1890s with Fenton's reagent ($FeSO_4 + H_2O_2$) for alkane hydroxylation. The Fenton mechanism is believed to involve production of OH radicals that abstract H atoms from the substrate in the key step, so no organometallic intermediates are involved. Likewise, the P450 dependent enzymes and their model compounds also oxidize R_3CH to R_3COH, but this time the metal plays a more direct role. A formally Fe(V) oxo intermediate abstracts a hydrogen atom from R_3CH to give $R_3C^\bullet + Fe^{IV}{-}OH$. The subsequent OH transfer from iron to $R_3C^\bullet$ provides the product carbinol, R_3COH. Again, no organometallic intermediates are invoked, however [5].

Even where a coordination compound is the catalyst, it can be clear that an organometallic intermediate does play a key role. Such is the case for Shilov chemistry, where the conversion of alkanes, RH, to ROH and RCl, is mediated by aqueous $[PtCl_4]^{2-}$ as catalyst and $[PtCl_6]^{2-}$ as primary oxidant [6,7]. In one early case involving CH_4 as substrate, an organometallic intermediate, $[CH_3PtCl_5]^{2-}$, could even be detected. Periana's Pt dipyrimidine catalyst (**1**, Scheme 1) that converts CH_4 in c.H_2SO_4 to CH_3OSO_3H, is mechanistically similar to the Shilov system but has a much higher efficiency [8]. In these catalysts, the lability of the M—C bonds by reaction with oxidants is not a disadvantage but an essential part of the catalytic mechanism.

Stahl's Pd 'oxidase' catalysts rely on *N*-donor spectator ligands but also involve substrate-derived organometallic intermediates that are labile under the reaction conditions, as in the aerobic conversion of cyclohexanones to phenols [9].

The present topic involves homogeneous catalysis of oxidative reactions in which both a reactive primary oxidant, such as H_2O_2, *t*BuOOH, oxone, Ce(IV) salts or $NaIO_4$, is present and in which the precatalyst has spectator ligand bound via an M—C bond. In such cases, several possibilities arise: a) the organometallic ligand may be retained by the metal throughout the catalytic cycle or b) this ligand may be lost to give a coordination complex that is the true catalyst. Alternatively, c) the complex may be entirely oxidized to produce a heterogeneous catalyst such as a metal oxide, either as a precipitate, deposit or nanoparticle suspension [10], or d) the catalyst may deactivate by oxidative degradation.

Ligand degradation may thus help or hinder catalysis: where an organometallic ligand is lost in this way, catalyst activation or deactivation may follow. Catalyst activation may require cleavage of an organometallic ligand to liberate the labile sites needed at the metal for catalysis. If the same catalyst is available in other ways, the organometallic precursor may have limited advantage, for example if $Mo(CO)_6$ gives a catalyst equally available from Na_2MoO_4. On the other hand, strong donor ligands such as Cp or Cp* may make the catalyst precursor more easily oxidized by the primary oxidant and facilitate access to a reactive coordination catalyst not otherwise easily available.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Scheme 1. Periana's Pt dipyrimidine catalyst.

Oxidative conditions are expected to provide a harsher environment for organometallics and the possibilities for ligand cleavage may therefore be of more frequent occurrence than in traditional reductive or redox-neutral chemistry. Distinguishing such cases is not easy, particularly where catalyst loadings are low, and as a result many studies omit mechanistic tests for survival of the organometallic ligand and for the presence or absence of catalytically active particles or deposits in the reaction. Some ligands, such as CO, alkenes and H, may be particularly sensitive but oxidation is very mechanism-dependent and different combinations of reagents and conditions may well alter the reactivity order, although there is still insufficient work reported in this area to make a meaningful attempt to cover that aspect.

2. Carbonyls

It has long been known that carbonyls can easily be removed by oxidation to give catalytically active homogeneous catalysts, as in the *t*BuOOH-driven epoxidation of alkenes with $Mo(CO)_6$ [11]. Such methods also have preparative value: Roy and Wieghardt found that $(tacn)M(CO)_3$ (Scheme 2. M = Mo and W; tacn = 1,4,7-triazacyclononane) cleanly reacts with H_2O_2 in thf to give $(tacn)MO_3$ (Scheme 2) [12]. Me_3NO gives partial decarbonylation and is thus a more selective preparative reagent [13] for oxidatively induced substitution of metal carbonyls by a variety of ligands; nucleophilic attack of the oxide oxygen on the CO carbon is believed to be the mechanism in this case.

As shown by Kühn and coworkers in 2003, the classic organometallic compound, $CpMo(CO)_3Cl$, acts as an epoxidation catalyst for alkenes. The primary oxidant, *t*BuOOH, first induces loss of the CO ligands to form isolable $CpMo(O)_2Cl$. In catalysis, the pentabenzyl-substituted Cp derivative showed even higher epoxidation activity than $MeReO_3$ itself, one of the best known catalysts [14].

In a related case, $CpMo(CO)_3Me$ and *t*BuOOH first give the dioxo complex, $CpMo(O)_2Me$, then the isolable peroxide, $CpMoO(\eta^2\text{-}O_2)Me$, both inactive for stoichiometric epoxidation (Scheme 3). The latter is converted by *t*BuOOH to a reactive species, probably $CpMo(OH)(OOtBu)(\eta^2\text{-}O_2)Me$, that transfers an O atom to the alkene [15]. Both the methyl group and the Cp survive the oxidative loss of the carbonyls as well as numerous catalytic cycles of epoxidation.

These examples are sufficient to show that CO is one of the easiest organometallic ligands to remove via oxidation. CO ligands require back bonding for stable binding to a metal, but oxidation of the metal greatly reduces the degree of back donation possible. This effect also enhances the partial positive charge on the CO carbon and so increases the tendency for nucleophilic attack at that carbon, either by the solvent or the oxidant.

3. Alkyls and aryls

The methyl group is widely recognized as having special stability; higher alkyls usually have β-H substituents which give them

$$(tacn)Mo(CO)_3 \xrightarrow{H_2O_2} (tacn)MoO_3$$

Scheme 2. $(tacn)MO_3$ synthesis.