Platinum Oxo Complexes

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# What Does it Really Take to Stabilize Complexes of Late Transition Metals with Terminal Oxo Ligands?

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density functional calculations · oxidation · oxo compounds · pincer ligands · platinum

The metal-mediated oxygenation of organic and inorganic substrates is of fundamental importance, not only in nature but also in academic and industrial laboratories. Representative examples of biological systems are the cytochromes P450 and the numerous molybdenum-based enzymes. In industry, the SOHIO process and $SO_2$ oxidation catalyzed by vanadium oxide are of particular importance, and the daily life of academic laboratories is hardly imaginable without simple stoichiometric reagents like permanganate salts or metal salen catalysts. Many of these systems act through terminal oxo ligands, that is, through M=O units, which consequently receive special attention. In this context, a recent groundbreaking study of a novel Pt=O complex[1] deserves to be highlighted against a more general background.

In the transition-metal block of the periodic system, certain trends regarding the occurrence of terminal oxo ligands emerge as a result of the balance between the effects of d-electron configuration and oxidation-state stabilities.[2] For early transition metals (e.g. Groups 4 and 5), a very rich oxo chemistry is found (with $O^{2-}$ in all common binding modes), and the corresponding compounds are very unreactive. One reason is that the central atoms (apart from vanadium) are comparatively redox-inert and therefore do not transfer bound oxo ligands readily; hence $TiO_2$ und $ZrO_2$, for instance, can be employed as support materials for catalysts.[3] Vanadium, however, can adopt a multitude of oxidation states, and its oxo chemistry is more comparable to the Group 6 elements molybdenum and tungsten, of which numerous compounds with terminal oxo ligands are known. Nonetheless, $Mo^{VI}$=O units can carry out oxo transfer reactions at low redox potentials, which is utilized by certain natural systems,[4] while $V^{V}$=O units are relatively stable and often effect oxidations only at higher temperatures; vanadium is thus a popular metal in heterogeneous catalysis.[5] Chromium is also in Group 6, but $Cr^{VI}$=O compounds are far more reactive than $M^{VI}$=O complexes of Mo and W. Like $Mn^{VII}$=O compounds, which they resemble far more distinctly, they belong to the strongest oxidants.[6,7] As in Group 6, reactivity in Group 7 also decreases from manganese to the higher homologues, and the same trend is found in Group 8, which already belongs to the late transition metals. While the heavier Group 8 elements still occur in the highest conceivable oxidation states and can be employed in those as oxides containing four M=O functionalities ($OsO_4$ and $RuO_4$) for oxidation ractions,[8] iron even in the oxidation state +IV is considered highly oxidizing, and many $O_2$-activating oxygenases utilize such $Fe^{IV}$=O moieties.[9] Until recently, complexes with terminal oxo ligands bound to noble metals such as Ag, Au, Pd, and Pt, located at the outer border of the late transition metals, were unknown. So why, upon moving from left to right across the transition-metal block, do M=O units become increasingly rare and strongly oxidizing even in comparatively low oxidation states? (The reactions of iron and copper oxidases, for instance, proceed at a much higher redox potential than those of molybdenum-based enzymes.[4])

Terminal oxo ligands are both comparatively hard Lewis bases and strong π donors; accordingly, they form particularly strong bonds to high-valent early (hard) transition-metal ions. In corresponding complexes, electrons can be delocalized from oxygen to the empty metal d orbitals. As we move from the early to the late transition metals, the d orbitals fill with valence electrons, which repulse the oxo ligands. When the known M=O compounds are aligned according to their d electron counts, it can therefore be noted that complexes with 0–2 d electrons are ubiquitous, while in complexes with more than 2 d electrons (as for oxidation states smaller than +IV) oxo ligands are usually found in bridging positions between two or more metal centers.[10] Consequently, only a few stable (isolable) $d^4$ M=O complexes exist. The first example with a metal from the platinum group was $[(mesityl)_3Ir{=}O]$ (**1**),[11] in which interaction between the d electrons and the oxo ligand is minimized by the tetrahedral coordination sphere (Scheme 1);[12] in the more recent past, the first structural characterization of an $Fe^{IV}$=O complex has attracted a lot of attention.[13] Borovik and co-workers reported a $d^5$ metal oxo species (**2**, Scheme 1)[14] that is formally a $Fe^{III}$=O complex; however, the oxo ligand is involved in several hydrogen bonds, and the complex should be regarded as a special case.

The synthesis of complexes with $d^6$ M=O units have, to date, only succeeded with strongly electron-withdrawing ligands. Accordingly, in 1989 the compound $Na[Re^{I}(O)(PhCCPh)_2]$ (**3**) was reported (Scheme 1),[10] in which the

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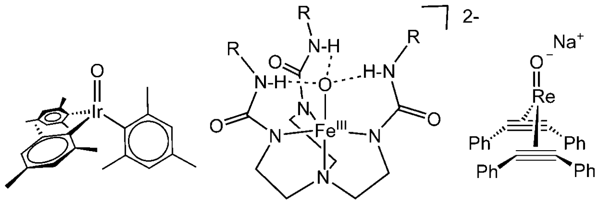


**1** **2** **3**

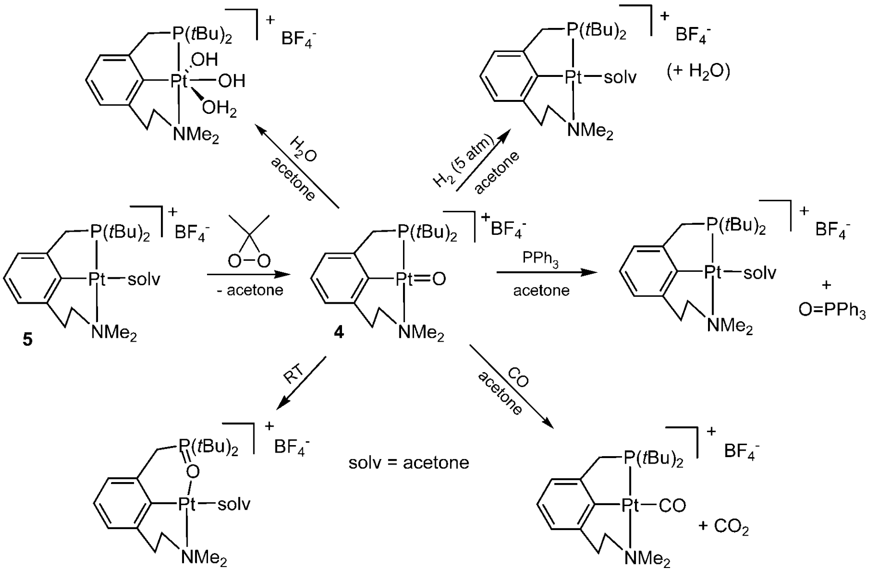
***Scheme 1.*** Isolable M=O compounds with $d^4$, $d^5$, and $d^6$ electron configurations.

alkyne ligands afford efficient back-bonding from the electron-rich metal center.

A few years ago, the use of polyoxometalate ligands (POM), which are strong π-acceptors, permitted the isolation of the first complexes of the noble metals Pt,[15] Pd,[16] and Au[17] with terminal oxo ligands. The platinum(IV) complex $[O{=}Pt(H_2O)L_2]^{16-}$ (Figure 1, $L = [PW_9O_{34}]^{9-}$) described by Hill and coworkers[15a] received special attention, on the one hand because this compound represented a breakthrough with the late transition metals, and on the other hand because intermediate oxoplatinum units are thought to play a major role in a multitude of oxidative processes occurring at platinum surfaces, such as in fuel-cell cathodes or in industrial oxidations that use supported platinum (automobile catalytic converters also use platinum).[18] Molecular oxoplatinum compounds may serve as models for such surface intermediates, and their investigation leads to valuable insights. Furthermore, platinum compounds are also employed in homogeneous oxidation catalysis,[19] and gas-phase studies have shown that $Pt^I$ is capable of catalyzing the oxidation of methane with dioxygen, in which intermediate $PtO^+$ cations occur.[20]

There is thus great interest in molecular Pt=O compounds from various fields. The fact that the first such species was isolated with the help of POM ligands can be understood on the basis of MO theory.[15a] The energy order of the d orbitals in a typical metal oxo complex with a distorted octahedral coordination sphere (as for the $O{=}PdO_4(O_{OH_2})$ unit with local $C_{4v}$ symmetry) is $d_{z^2}$ (σ) < $d_{xz}$,$d_{yz}$ (π) < $d_{xy}$ (nonbonding) < $d_{xz}$,$d_{yz}$ (π*) < $d_{x^2-y^2}$ (nonbonding) < $d_{z^2}$ (σ*). In the case of $d^2$ systems, the lowest four orbitals are doubly occupied, and the bond order is three, as the $d_{xy}$ orbital is nonbonding. However, with each additional electron the bond order is reduced by 0.5 through the occupation of the antibonding $d_{xz,yz}$ orbital pair, and thus the M=O bond is weakened (activated). Finally, in the case of a $d^6$ configuration, four electrons are located in these π* orbitals; in the absence of any additional effects, the bond from the O atom to the metal atom possesses hardly any conventional π character and must be regarded as single bond. Such an oxometal functionality should behave as a nucleophile—in contrast to, for instance, $Cr^{VI}{=}O$ and $Fe^{IV}{=}O$ units, which react electrophilically. Indeed, the compound $[O{=}Pt(H_2O)L_2]^{16-}$ discussed above is a $d^6$ system, but the POM ligands L permit (through their oxo ligands) $Pt\,d_{xz,yz} \rightarrow W\,d_{xz,yz}$ backbonding,[21] that is, the empty $W^{VI}$ orbitals function as π acceptors and reduce the antibonding character of the Pt $d_{xz,yz}$ orbitals by lowering them energetically. In consequence, the π-bonding character is increased and the PtO bond strengthened.

Alkyl and aryl N and P donor functionalities, which are prevalent in organometallic and coordination chemistry, do not allow for such stabilization. Nevertheless, Milstein and coworkers very recently used a PCN pincer ligand to generate a platinum(IV) complex with a terminal oxo ligand, which was isolated, characterized, and investigated with respect to its reactivity (**4** in Scheme 2).[1]



***Scheme 2.*** Synthesis and reactivity of the $Pt^{IV}{=}O$ complex **4**.

The synthesis was accomplished starting from the cationic complex **5** through treatment with dimethyloxirane, and although in the absence of suitable crystals it was not possible to perform single crystal X-ray and neutron diffraction studies, the identity of **4** could be revealed by a multitude of methods, including DFT studies. Accordingly, a band at 783 $cm^{-1}$ in the IR spectrum could be assigned to a $\nu_{Pt=O}$ vibration, and the shift observed in the $^{195}Pt$ NMR spectrum provides evidence for the platinum(IV) oxidation state, which was further confirmed by the results of XANES investigations. The constitution of **4** deduced this way served as the input for a geometry optimization of its molecular structure after the chosen DFT method had been verified by calculations on comparable complexes for which the molecular structures had been determined by X-ray diffraction studies. It turned out that the platinum center develops a distorted square-planar coordination environment, so that—in contrast to the tetrahedrally coordinated Ir complex **1**[11,12]—d electrons and oxo ligand interfere with each other and Pt−O $\pi^*$ orbitals are occupied. Admittedly, the oxo ligand bends out of the C-Pt-P plane by 35.3°, thereby reducing unfavorable overlap of metal and ligand orbitals.[1] The EXAFS data are also in good qualitative agreement with the structure ascertained theoretically. While the DFT calculations show that the residues at the ligand prohibit dimerization of the compound, it also becomes obvious that they do not completely shield the oxo ligand. It is exposed, repulsed by d electrons, and the aryl ligand in *trans* position is not capable of relieving the situation by accepting electron density; from these characteristics, a rather high reactivity and tendency to decomposition would be expected, which should render the isolation of **4** almost impossible. However, **4** in powder form or in solution is stable enough to allow for characterization with the methods described above at room temperature without further precautions; even though decomposition gradually occurs by intramolecular transfer of the oxo ligand to the coordinated phosphane unit, this reaction needs three days to reach completion. Furthermore, the oxidative reactivity corresponds to what is known for "normal" metal complexes with terminal oxo ligands (Scheme 2). $PPh_3$ is converted into $O{=}PPh_3$, and it is not surprising that CO is oxidized to $CO_2$ and $H_2$ to $H_2O$. The reaction with water, however, led to an interesting finding: $H_2O$ adds to the Pt=O moiety, which leads to a well-defined $Pt(OH)_2$ compound that could be isolated and characterized. The lucidity of this reaction sequence is surely unique, and it could play an important role, for example as a potential elementary step during the $O_2$ oxidation of $Pt^{II}$ complexes in aqueous medium to give $Pt^{IV}$ compounds, which is of great interest for the development of catalytic cycles for alkane oxidation.[19,22]

The contribution of Milstein and co-workers shatters the established model for the explanation of the lack of late-transition-metal complexes with terminal oxo ligands. While the stability of compounds like the one in Figure 1 can still be explained on the basis of the special acceptor properties of the coordinated ligands, **4** represents an organoplatinum compound in which the ligands have essentially σ-donor character. Thus it can be argued that perhaps Pt=O units occur more frequently on surfaces and in molecular compounds than previously assumed and that maybe a larger number of such compounds would already exist if their synthesis had been pursued in a more direct and unreserved manner. The publication discussed herein encourages the scientific community to do just that, and maybe then we can give a more satisfactory answer to the title question.

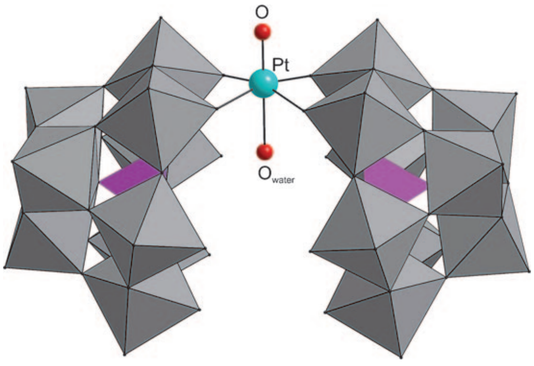


***Figure 1.*** Crystal structure of $[O{=}Pt(H_2O)L_2]^{16-}$.[15a]

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