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Phenanthroline Decorated by a Crown Ether as a Module for Metallorganic−Polyoxometalate Hybrid Catalysts: The Wacker Type Oxidation of Alkenes with Nitrous Oxide as Terminal Oxidant

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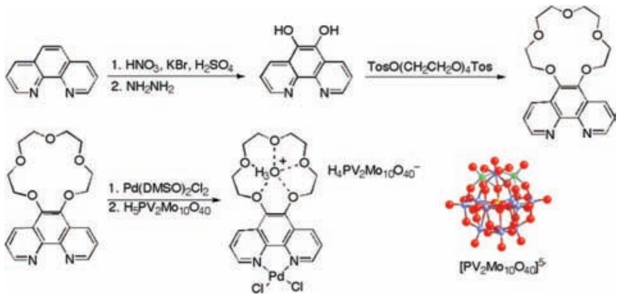
Polyoxometalates have been used in both acid and oxidation catalysis. Brønsted acidity in heteropoly acids[1] and Lewis acidity in Ln and similarly substituted polyoxometalates[2] have led to acid catalysis. Polyoxometalates with favorable oxidation potentials and reactive transition metal centers are useful for electron transfer oxidation reactions and activation of oxygen donors.[3] Another interesting area of polyoxometalate chemistry has been their use in hybrid catalytic systems wherein a metalloorganic catalytic center is coupled with a polyoxometalate. In this way the electronic, steric, or solubility properties of a metallorganic catalyst may be modified leading to improved reactivity or a cascade of reactions. Examples include $[(PPh_3)_2Rh(CO)]_3[XW_{12}O_{40}]$ for a combined hydroformylation−oxidation reaction,[4] a Rh(I) phosphine−polyoxometalate complex for aqueous biphasic hydrogenation,[5] a Pt(II)pyridinium−polyoxometalate complex for the aqueous phase aerobic oxidation of methane,[6] a Pt(II) imine−polyoxometalate complex for tandem pinacol coupling and rearrangement with hydrogen,[7] and a chiral amine−polyoxometalate for asymmetric enamine catalysis.[8] As is typical for hybrid polyoxometalate complexes,[9] these hybrid catalysts are assembled either by electrostatic interactions between a cationic metallorganic species and the polyanion[4,6−8] or through a covalent linker between the polyoxometalate and organic ligand.[5]

From our point of view the preparation of hybrid metallorganic-polyoxometalate assemblies via electrostatic interactions, although general for a large variety of polyoxometalates, is often complicated by a difficulty in attaining a 1:1 stoichiometry due to the polyanionic nature of the polyoxometalate. Higher ratio complexes are often quite insoluble and thus not amenable to homogeneous catalysis applications. On the other hand the preparation of hybrid complexes via use of covalent linkers is synthetically challenging, but perhaps more critically, is limited mostly to Lindqvist anions ($M_6O_{19}^{2-}$, M = Mo, W) and Keggin and Wells−Dawson type polyoxotungstates.[9] Important redox active polyoxometalates such as $H_5PV_2Mo_{10}O_{40}$ have not and probably cannot be covalently modified due to its propensity to undergo electron transfer rather than substitution reactions.

It is known that diethylether and polyethylene glycols bind to acidic polyoxometalates (heteropolyacids) via the induced dipole interactions of the ether and the hydronium cation of the polyoxometalate.[10] To utilize these induced dipole interactions for the preparation of a new type of metallorganic-polyoxometalate hybrid catalyst, we have used a phenanthroline ligand decorated with a 15-crown-5 ether moiety. A first example of the utility of the phenanthroline-crown ether module was via coordination of Pd(II) by the phenanthroline ligand and complexation of $H_5PV_2Mo_{10}O_{40}$ by the crown ether moiety that led to a hybrid catalyst active for the Wacker type oxidation of terminal alkenes to methyl ketones. The synthetic pathway is summarized in Scheme 1. Although the Wacker reaction typically utilizes molecular oxygen as a terminal oxidant, the use of this hybrid catalyst also allows, for the first time, the use of nitrous oxide as an effective terminal oxidant for this reaction.

Scheme 1. Pathway for the Preparation of Pd(II)Phenanthroline−Crown Ether $H_5PV_2Mo_{10}O_{40}$ Complex



The phenanthroline ligand decorated with the 15-crown-5 ether group, 15-crown-5-phen, was prepared by modification of a literature reported technique.[11] Further reaction of 15-crown-5-phen with $Pd^{II}(DMSO)_2Cl_2$ led to the formation of the expected square planar Pd(II) compound, Pd^{II}(15-crown-5-phen)Cl_2, Figure S1. Addition of 1 equiv of $H_5PV_2Mo_{10}O_{40}$ to 1 equiv of Pd^{II}(15-crown-5-phen)Cl_2 each dissolved in acetonitrile led to the immediate formation of a yellow-orange precipitate. Elemental analysis suggests the formation of a hybrid complex of a 1:1 ratio, Pd^{II}(15-crown-5-phen)Cl_2−$H_5PV_2Mo_{10}O_{40}$. UV−vis, Figure 1 left, and IR spectra, Figure 1 right, of the hybrid complex clearly show that they are both additive combinations of the spectra of Pd^{II}(15-crown-5-phen)Cl_2 plus $H_5PV_2Mo_{10}O_{40}$.

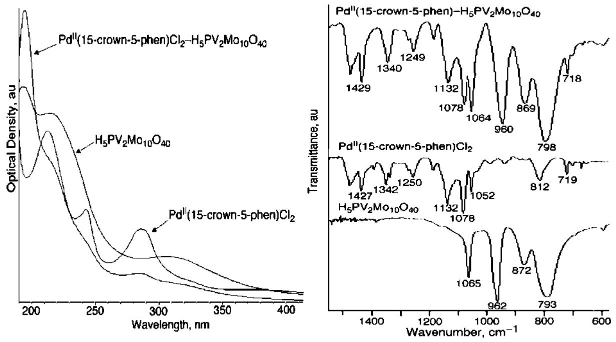


Figure 1. UV−vis spectra of 5 μM solutions in acetonitrile (left) and IR (right) spectra of the hybrid complex, Pd^{II}(15-crown-5-phen)Cl_2−$H_5PV_2Mo_{10}O_{40}$, and its component parts.

Similarly, the ESI-mass spectra, Figure S2, of Pd^{II}(15-crown-5-phen)Cl_2−$H_5PV_2Mo_{10}O_{40}$ also showed both component parts of the complex. Although the parent peak was not observable, the positive ion mass spectrum had major peaks at m/z = 571.48 and 589.49 associated with the molecular mass of the Pd^{II}(15-crown-5-phen)Cl_2 fragment plus Na and K, respectively, while the negative ion mass spectrum showed a fragmentation pattern identical to that of $H_5PV_2Mo_{10}O_{40}$. NMR identification of the complex is presented in the Supporting Information.

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In the past, $H_5PV_2Mo_{10}O_{40}$ has been used as a co-oxidant instead of Cu^{2+} for the aerobic Wacker oxidation of ethylene to acetaldehyde.[12] It has also been recently reported that in water/dimethylacetamide (DMA) the Wacker oxidation of alkenes was catalyzed by $PdCl_2/O_2$ without need for a cocatalyst.[13] Oxidation of 1-octene with O_2 catalyzed by Pd^{II}(15-crown-5-phen)Cl_2−$H_5PV_2Mo_{10}O_{40}$ dissolved in water/DMA showed somewhat higher activity, Table S1, than use of $PdCl_2$ alone. The hybrid catalyst was significantly more active and selective to oxidation than Pd^{II}(phen)Cl_2 or Pd^{II}(phen)Cl_2 plus $H_5PV_2Mo_{10}O_{40}$; the latter catalysts led to considerable alkene isomerization. Various alkenes were oxidized by Pd^{II}(15-crown-5-phen)Cl_2−$H_5PV_2Mo_{10}O_{40}/O_2$, Table S2.

In the novel use of N_2O as an environmentally benign, terminal oxidant, we have found, Table 1, that Pd^{II}(15-crown-5-phen)-Cl_2−$H_5PV_2Mo_{10}O_{40}$ is uniquely active for the oxidation of a model terminal alkene, 1-octene, to selectively yield the corresponding 2-octanone. No anti-Markovnikov addition product, *n*-octanal, was observed. The use of a simple mixture of Pd^{II}(phen)Cl_2 and $H_5PV_2Mo_{10}O_{40}$ yielded significantly lower yields and also reduced reaction selectivity, an observation that emphasizes the advantage of the use of hybrid complexes over simple mixtures. The reaction is general for linear alkenes, Table 2, although yields are lower (1-dodecene) as the solubility of the substrate decreases in the solvent.

Table 1. Oxidation of 1-Octene with N_2O Catalyzed by Pd Catalysts[a]

catalyst	conversion mol%	selectivity mol %
Pd^{II}(15-crown-5-phen)Cl_2−$H_5PV_2Mo_{10}O_{40}$	>99	>99
Pd^{II}(phen)Cl_2	<1	<1
Pd^{II}(phen)Cl_2 + $H_5PV_2Mo_{10}O_{40}$	25	86[b]
$PdCl_2$	0	0
$PdCl_2$ + $H_5PV_2Mo_{10}O_{40}$	0	0
$H_5PV_2Mo_{10}O_{40}$	0	0
none	0	0

[a] 100 μmol of 1-octene, 1 μmol of catalyst (each component where relevant), 0.5 mL of DMA, 0.5 mL of H_2O, 3 bar of N_2O, 150 °C, 18 h. [b] The remaining products were linear octene isomers.

Table 2. Oxidation of Alkenes with N_2O Catalyzed by Pd^{II}(15-crown-5-phen)Cl_2−$H_5PV_2Mo_{10}O_{40}$[a]

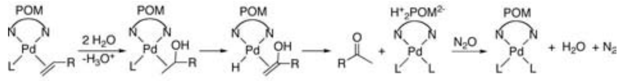
substrate	product	yield (selectivity), mol%
1-hexene	2-hexanone	>99 (>99)
1-heptene	2-heptanone	>99 (>99)
1-octene	2-octanone	>99 (>99)
1-nonene	2-nonanone	>99 (>99)
1-decene	2-decanone	90 (>99)
1-dodecene	2-dodecanone	10 (>99)
cyclooctene	cyclooctene	0
1,5-hexadiene	3-methylcyclopentanone	>99 (>99)

[a] 100 μmol of substrate, 1 μmol of Pd^{II}(15-crown-5-phen)-Cl_2−$H_5PV_2Mo_{10}O_{40}$, 0.5 mL of DMA, 0.5 mL of H_2O, 3 bar of N_2O, 150 °C, 18 h.

A question arises if the reaction proceeds via a typical Wacker type mechanism: oxidative addition of H_2O to the alkene to yield ketone and "Pd^0" followed by reoxidation of "Pd^0" by $H_5PV_2Mo_{10}O_{40}$ and N_2O. An alternative could be noncatalytic 1,3-dipolar addition of N_2O to the alkene to yield ketones;[14] such reactions are known to be selective for cyclic ketones but not for linear alkenes. The observations that there was no reaction without catalyst (Table 1) and cyclooctene did not react (Table 2) strongly tend to discount this possibility. A second possibility is that the catalyst decomposes N_2O to N_2 and O_2, the latter then acting as the *de facto* terminal oxidant. However, in an experiment where substrate was left out of the reaction mixture, a sampling of the gases after 18 h at 150 °C showed no formation of O_2 rendering such a scenario unlikely. Finally there is a possibility that the catalyst activates N_2O to yield an oxo species that reacts with the alkene to yield a ketone. Although this scenario cannot be excluded, reactions of metal-oxo species more typically lead to epoxide rather than ketone formation.[15] Further, one would expect that such a reaction would not be limited to terminal alkenes as observed here. In fact, reaction specificity toward terminal alkenes is a hallmark of the Wacker reaction.

Although it is premature to give a detailed description of the reaction mechanism, invoking the Stille mechanism[16] coupled with the known propensity of $H_5PV_2Mo_{10}O_{40}$ to oxidize hydrides[6,7] leads to the following reaction scheme, Scheme 2. Reoxidation of the polyoxometalate with N_2O is apparently relatively slow since oxidation of 1,5-hexadiene yielded the reductive cyclization product, 3-methylcyclopentanone, rather than 1-hexen-5-one or 2,5-hexadione as normally observed, Scheme S1.

Scheme 2. Proposed Reaction Mechanism



A Pd^{II}phenanathroline-$H_5PV_2Mo_{10}O_{40}$ catalyst prepared by utilizing an induced dipole interaction between a crown ether moiety and a polyoxometalate has been shown to catalyze the Wacker oxidation of alkenes using N_2O instead of O_2 as oxidant.

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Supporting Information Available: Full experimental details, additional catalyst characterization, and oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

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