Polyoxometalate Catalysts

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Lanthanide Complexes of the Monovacant Dawson Polyoxotungstate $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ as Selective and Recoverable Lewis Acid Catalysts**

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Polyoxometalates (POMs) are a large family of metal–oxygen clusters of the early transition metals in high oxidation states, most commonly V^{V}, Mo^{VI}, and W^{VI}.[1] Their intrinsic chemical properties as electron acceptors or as very strong Brønsted acids (in their protonated form) makes them catalysts in organic transformations,[2] and their ability to form peroxo complexes or to serve as a support for catalytically active metal ions in a high oxidation state is particularly useful in oxidation reactions.[3] Organometallic derivatives of POMs have proven to be effective catalysts in hydrogenation reactions.[4]

To the best of our knowledge, however, no Lewis acid catalysis involving POMs has been reported so far, despite the wide array of transformations that could be addressed. We imagined that lanthanide complexes of monovacant POMs—often called Peacock–Weakley type[5,6]—and in particular of $[\alpha_1\text{-P2W17O61}]^{10-}$[7–18] would be good candidates for such a task. Some of these compounds have already been studied for their luminescence and magnetic properties provided by the lanthanide ions.[19–21] Hill and co-workers have used the oxidant properties of cerium(IV) in the Keggin derivative $NaH_3[SiW_{11}CeO_{39}]$ as the active site for the aerobic oxidation of formaldehyde.[22] Because lanthanide(III) salts are extremely efficient, water-tolerant Lewis acids, their use in organic reactions has soared over the past ten years.[23–26] However, the quest for more selective and recoverable catalysts remains a challenging task.

The reactivity of lanthanide ions is still present when anionic ligands, such as binaphthyl derivatives, are used to tune the catalytic activity.[27] The use of inorganic polyanionic POMs as ligands should thus also be possible. Indeed, lanthanide complexes with monovacant POMs can be prepared with free coordination sites on the lanthanide ion, which are required to maintain Lewis acid activity. POMs would also bring an additional property: their solubility depends on the counterions. Group 1 metal ions lead to water-soluble complexes that can be used in biphasic catalyst systems,[28] whereas lipophilic ammonium ions solubilize the polyanions in organic solvents. Thus, POMs can be separated easily from small organic molecules by precipitation with diethyl ether or by nanofiltration.[29] Both methods have been applied for the recycling of POM-based oxidation catalysts, and could be extended to the Lewis acidic POM–Ln complexes.

We have chosen to evaluate the lanthanide complexes of the monolacunary Dawson polyoxotungstate $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$. The complexes $(TBA)_5H_2[\alpha_1\text{-Ln}(H_2O)_4\text{-}P_2W_{17}O_{61}]$ (Ln = La, Sm, Eu, Yb; TBA = tetrabutylammonium; Figure 1) are soluble in organic solvents, and the water molecules on the lanthanide ions are labile, thus providing the metal centers with available coordination sites for other ligands.[11,20,30–34] We surveyed catalysts including early, mid, and late lanthanides.

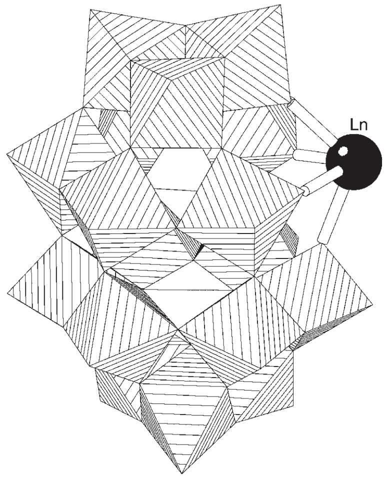

Figure 1. Lanthanide complexes of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$: the Ln^{3+} ions are coordinated to the vacant site in the lacunary Dawson structure and have four or five open coordination sites.

We first examined Mannich-type reactions of silyl enol ethers with imines[35,36] and found that no reaction occurred with the potassium salts of the POM–Ln complexes, possibly due to solubility issues. We thus switched to complexes that are soluble in organic solvents,[30] especially acetonitrile, and

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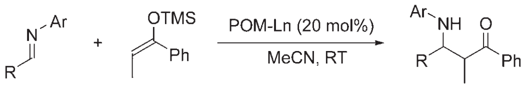
were able to isolate β-amino ketones **1a**–**e**, thus proving the catalytic activity of the POM–Ln complexes, although the reaction times were generally longer than those observed with the corresponding lanthanide triflates (two days vs. a few hours). This was expected considering the decreased Lewis acidity of the lanthanides when complexed to the monovacant POM ligand. Nonetheless, the products **1a**–**e** were isolated in good to excellent yields (Table 1). No reaction occurred when the substrates were mixed in the presence of lacunary $(TBA)_6H_4[\alpha_1\text{-}P_2W_{17}O_{61}]$, which allowed us to exclude a Brønsted acid catalysis for the reaction. Formation of **1a** worked best with the Yb complex as catalyst (Table 1, entry 1), followed by the Sm complex (Table 1, entry 2). La and Eu derivatives were also acceptable (Table 1, entries 3 and 4), although the reactions were slower and the conversion was not optimal. The aldolization is not stereoselective, but neither is it stereoselective with the corresponding triflates.

Table 1: POM–Ln-catalyzed aldol reactions of imines.



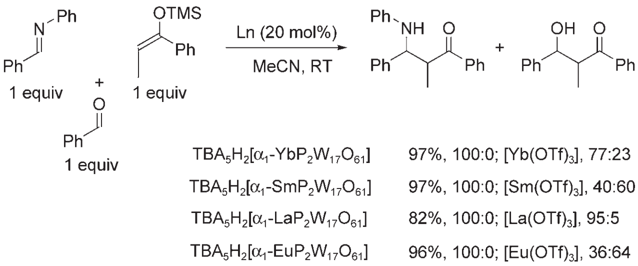
1a–e

Entry	R	Ar	Catalyst	Product	Yield [%]	d.r.
1	Ph	Ph	$(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$	**1a**	96	50:50
2	Ph	Ph	$(TBA)_5H_2[\alpha_1\text{-}SmP_2W_{17}O_{61}]$	**1a**	91	50:50
3	Ph	Ph	$(TBA)_5H_2[\alpha_1\text{-}LaP_2W_{17}O_{61}]$	**1a**	81[a]	50:50
4	Ph	Ph	$(TBA)_5H_2[\alpha_1\text{-}EuP_2W_{17}O_{61}]$	**1a**	71[b]	50:50
5	Ph	*o*-HOC_6H_4	$(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$	**1b**	84	50:50
6	Ph	*p*-$MeOC_6H_4$	$(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$	**1c**	81[c]	60:40
7	*o*-HOC_6H_4	Ph	$(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$	–[d]	–	–
8	CO_2Et	Ph	$(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$	**1d**	70	68:32
9	CO_2Et	*p*-$MeOC_6H_4$	$(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$	**1e**	77	65:35

[a] Yield of isolated product. Conversion was approx. 90%. See Supporting Information for experimental details. [b] Yield of isolated product. Conversion was approx. 80%. [c] Reaction took six days. [d] No conversion was observed.

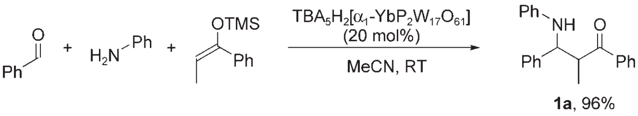
Except where noted, we decided to proceed with the Yb complex to evaluate the influence of substituents on the imine. Introduction of a hydroxy substituent in the *ortho* position of the aromatic ring attached to the imine carbon totally shut down the reaction, and only the hydrolyzed products were isolated (Table 1, entry 7). We suppose that such a substitution diminishes the electrophilicity of the carbon atom to such an extent that our compounds, which have lower Lewis acidity, are now inactive. On the contrary, the glyoxaldehyde-derived imines reacted much faster, and the reactions were finished in less than an hour (Table 1, entries 8 and 9).

The decreased Lewis acidity of our compounds made them good candidates for chemoselective reactions. Lanthanides favor activation of aldimines over aldehydes, but selectivity is usually achieved only at −23 °C and is not always excellent, particularly with samarium derivatives.[37] We thus ran competition reactions between the benzimine of aniline and benzaldehyde (Scheme 1): only the aldimine reacted at room temperature in the presence of our POM–Ln complexes. The improved selectivities over $Ln(OTf)_3$ were particularly noticeable with $(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$ (selectivity changed from around 3:1 to 100:0), and, most interestingly, with $(TBA)_5H_2[\alpha_1\text{-}SmP_2W_{17}O_{61}]$ and $(TBA)_5H_2[\alpha_1\text{-}EuP_2W_{17}O_{61}]$, which actually brought about an inversion of selectivity. Improvement was still observed with $(TBA)_5H_2[\alpha_1\text{-}LaP_2W_{17}O_{61}]$, a derivative with a lanthanide, whose triflate already greatly favors additions to imines. Overall, the POM–Ln compounds are extremely selective catalysts that are slightly to much better than their parent triflates.



Scheme 1. Comparison of the chemoselectivity for POM–Ln catalysts and Ln triflates.

We also carried out a three-component reaction starting from aniline, benzaldehyde, and the same silyl enol ether as before (Scheme 2). Amine **1a** was isolated almost quantitatively, and the reaction proceeded without molecular sieves.



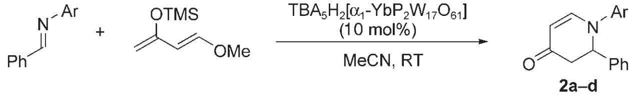
1a, 96%

Scheme 2. The three-component reaction.

We next turned our attention to the imino Diels–Alder reaction of various imines with the Danishefsky diene in the presence of $(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$.[38] Cyclic adducts **2a**–**d** were isolated in good yields and the reactions proceeded smoothly (Table 2, entries 1–3). Introduction of an *ortho*-hydroxy substituent on the aniline[39a] resulted in a lower yield (57%; Table 2, entry 4), and the use of imines derived from ethyl glyoxalate also proved detrimental (20–30% yield). In this latter case oligomers of the starting materials were also present.

Encouraged by the preceding results, we turned our attention to a variation of the imino Diels–Alder reaction that uses an imine as the aza-diene and an enol ether as the dienophile.[39] Reaction of diphenylimine with ethyl vinyl

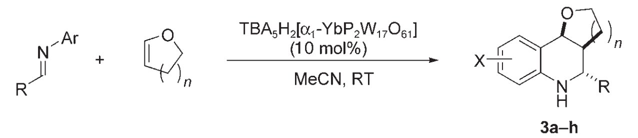
Table 2: POM–Yb-catalyzed imino Diels–Alder reaction with the Danishefsky diene.

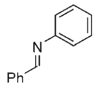
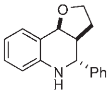
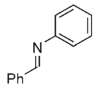
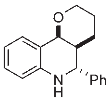
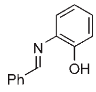
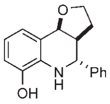
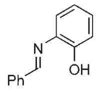
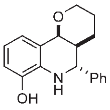
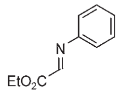
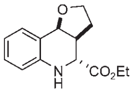
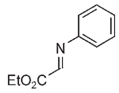
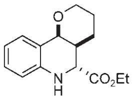
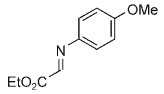
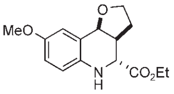
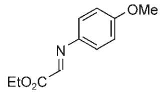
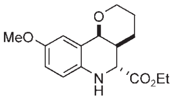


Entry	Ar	Product	Yield [%][a]
1	Ph	**2a**	89
2	*p*-MeOC$_6$H$_4$	**2b**	98
3	*p*-ClC$_6$H$_4$	**2c**	76
4	*o*-HOC$_6$H$_4$	**2d**	57

[a] See Supporting Information for experimental details.

Table 3: POM–Yb-catalyzed imino Diels-Alder using imines as azadienes.



Entry	Imine	*n*	Product		Yield [%][a]	d.r.[a]
1		1		**3a**	67 (80)	60:40 (50:50)
2		2		**3b**	79 (89)	80:20 (50:50)
3		1		**3c**	63 (74)	90:10 (55:45)
4		2		**3d**	39[b] (64)	80:20 (50:50)
5		1		**3e**	39[b,c]	50:50
6		2		**3f**	< 40[b,c]	50:50
7		1		**3g**	67 (48)	50:50 (50:50)
8		2		**3h**	62 (<20[b])	50:50 (50:50)

[a] The value in brackets refers to the same reaction using Yb(OTf)$_3$. See Supporting Information for experimental details. [b] Aromatic degradation products were also observed. [c] The starting imine reacted with itself.

ether in the presence of our POM–Yb catalyst was hampered by aromatization of the desired compound into the corresponding quinoline; therefore, in order to limit this decomposition path, we switched to cyclic enol ethers. We selected the same two classes of imines we had used previously, namely the bis-aromatic compounds (Table 3, entries 1–4) and the derivatives of ethyl glyoxalate (Table 3, entries 5–8). The former reacted smoothly, although the yields were slightly lower than those we obtained with Yb(OTf)$_3$. The essential advantage of the POM–Ln catalysts over lanthanide triflates lies in the stereochemical outcome of the reactions: in all examples the diastereoselectivity of the reaction increased noticeably. Given that this increase is most pronounced with *ortho*-hydroxy substrates, we assume that H-bonding interactions between the reactants and the polyanionic ligand exist.[11,12,40] This change in selectivity when the POM–Yb complex is used further indicates that the catalytically active species is not free Yb^{3+}.

In our hands, no significant yields of the tricyclic products could be attained with Yb(OTf)$_3$ and ethyl glyoxalate derivatives (Table 3, entries 5–8) even though we observed rapid consumption of the starting material. We thus thought it might be interesting to use weaker Lewis acids. If our assumption that decomposition is due to an acceleration of the divergent reaction pathways by Yb(OTf)$_3$ was correct, then using the weaker POM–Yb Lewis acid should help. This turned out to be partially the case (Table 3, entries 7 and 8). The stereoselectivity did not vary in these cases, despite possible interactions of the substrates with the polyoxotungstic framework. These intriguing findings show that we need to know more about the POM–Ln–substrate interactions in order to rationalize and fully master their reactivity.

It remained to be shown that the catalysts can be recovered and reused.[29,41] As stated before, we wished to take advantage of the solubility properties of POMs to devise an operationally simple recovery procedure. The complexes we used are soluble in acetonitrile, but not in diethyl ether, in which the vast majority of the adducts are soluble. Indeed, addition of a diethyl ether/ethanol/acetone solution (20:1:1 by volume)[36] to the reaction mixture leading to **1a** (Table 1, entry 1) caused precipitation of a white solid, which was isolated by centrifugation. High-field NMR spectroscopic analysis showed that the solid was pure $(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$, which was isolated quantitatively. We were able to reuse the same catalyst up to ten times with no loss in yield. The following experimental facts made us confident that there had been no leaching of Yb^{3+}: 1) our initial work bears out the decomplexation of Yb^{3+} from the POM upon precipitation;[30] 2) Yb^{3+} is paramagnetic and would influence the NMR spectra of the filtrate, which was not the case (no paramagnetic shift or line broadening); 3) after removal of the POM–Ln complex, the supernatant showed no catalytic activity.

In conclusion, we have discovered a new class of reactions catalyzed by functionalized POMs. The complexation of lanthanide ions by a POM ligand confers essential features, among which a sharply increased chemoselectivity and an increase of the diastereoselectivity in some cases stand out. Furthermore, the catalysts can be easily recovered and reused with no drop in reactivity. Work aimed at further extending the array of possible reactions, understanding the POM–Ln–substrate interactions, which we think provide the basis of diastereoselectivity, as well as examining the enantioselective version of these reactions with additional chiral ligands is underway. The POM $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ itself is chiral and has been used as a racemate throughout this study. Provided an efficient optical resolution method becomes available, our POM–lanthanide complexes could be converted into chiral catalysts without the need for an additional ligand. Progress along these lines will be presented in due course.

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