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# Increased Lewis Acidity in Hafnium-Substituted Polyoxotungstates

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**Abstract:** Monolacunary polyoxotungstates $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ react with $HfCl_4$ to yield $[\alpha_1\text{-}HfP_2W_{17}O_{61}]^{6-}$ and $[\alpha\text{-}Hf(OH)PW_{11}O_{39}]^{4-}$, isolated as organo-soluble tetrabutylammonium (TBA) salts. Subsequent analyses, including mass spectrometry, show that they are stronger Lewis acids than $(TBA)_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$. The new polyoxotungstates catalyze Lewis acid mediated organic reactions, such as Mukaiyama aldol and Mannich-type additions. In particular, reactions with aldehydes, which were impossible with lanthanide polyoxotungstates, are made possible. Thus these modifications of the polyoxometalate composition allowed fine tuning of the Lewis acidity. The catalysts could be easily recovered and reused.

**Keywords:** aldol reaction · hafnium · imines · Lewis acids · polyoxometalates

## Introduction

Catalysis by polyoxometalates (POMs), which are clusters of early transition metals in high oxidation states ($W^{VI}$, $Mo^{VI}$, $V^{V}$) and oxo ligands, has been greatly expanding these last years.[1] Part of the attraction POMs exert on the chemical community stems from the rich array of structures and compositions that can be easily prepared and handled, because this allows fine-tuning of chemical properties such as redox potentials, acidities, and reactivities. Traditionally, POM-based catalysis has focused on Brønsted catalyzed reactions,[2] and oxidations.[3] We have introduced recyclable organo-soluble Lewis acidic lanthanide(III) complexes of the monovacant $\alpha_1$-Dawson polyoxotungstate $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$,[4] which opened a new field of catalytic applications to polyoxometalates: Lewis acid mediated organic reactions.[5] In our previous study, we observed that the lacunary ligand significantly decreased the Lewis acidity of the lanthanide ions. Yet, Lewis acid properties were retained, though only the reactions of imines with silyl enol ethers were catalyzed. Aldehydes were left unchanged. It appeared to us that increased Lewis acidity of the polyoxometallic complexes, and thus C=O bond activation, might be obtained by introducing smaller and/or more charged cations into the polyoxotungstic framework. At the same time, the coordination number of the new cation should remain large enough to leave open coordination sites even when it is incorporated in the monolacunary polyoxometalate. The $Hf^{4+}$ ion meets these requirements. The ionic radius for the more charged $Hf^{4+}$ (as compared to $Yb^{3+}$) is 71 pm for a coordination number of six (86.8 pm for $Yb^{3+}$), representing a 18% reduction in size.[6] It also accommodates seven or eight ligands.[7]

Hafnium-containing POMs are rare.[8] Most recent results show the possibility to sandwich a $Hf^{IV}$ ion between two monolacunary Keggin or $\alpha_2$-Dawson polyoxotungstates.[8d]

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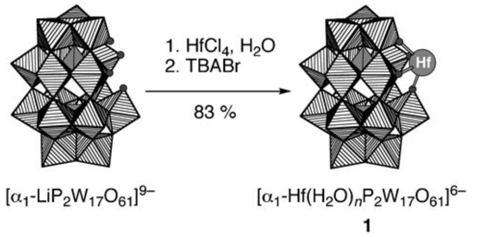
Whereas this confirms our initial assumption of possible eight-coordination for $Hf^{4+}$, these compounds are not suitable as catalysts, because no sites are available on the hafnium atom.[9] We report herein the syntheses of an unprecedented organo-soluble hafnium-substituted chiral $\alpha_1$-Dawson phosphotungstate and a Keggin phosphotungstate, both with 1:1 Hf/POM stoichiometry, and the evaluation of their Lewis acidity in solution, as well as their gas-phase behavior under electrospray desorption conditions.

## Results and Discussion

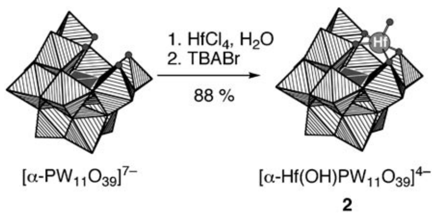
**Preparation and characterization**: The desired $\alpha_1$-Dawson complex was prepared by slowly reacting $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ with $HfCl_4$ in water (Scheme 1). The pH of the solution decreased from 5.5 to ≈3, and a white precipitate was obtained upon addition of tetrabutylammonium bromide (TBABr). Subsequent analysis showed that it corresponded to the new compound $(TBA)_5K[\alpha_1\text{-}Hf(H_2O)_4P_2W_{17}O_{61}]$ (**1**) isolated in 83 % yield.[10] IR spectra of **1** proved the intact Dawson framework. The P–O vibrational band was no longer split as in the vacant polyoxometalate, which follows the trend established in analogous lanthanide complexes. The third $\nu_{P-O}$ band decreases in energy and intensity with decreasing size of the inserted Ln ion.[11] The corresponding complex thus behaves similarly to the parent Dawson ion $[P_2W_{18}O_{62}]^{6-}$. The $^{31}P$ NMR spectrum showed two peaks, and the $^{183}W$ NMR spectrum showed 17 peaks, in accordance with the $\alpha_1$ isomer of the substituted Dawson structure, in which both phosphorus and all 17 tungsten sites are different. The chemical shifts were in the normal range of diamagnetic polyoxotungstates. Elemental analysis was consistent with the proposed formula.



Scheme 1. Preparation of Hf-substituted Dawson ion **1**. The drawing is not based on structure determination. The coordination sphere of Hf should be completed by solvent molecules.

The first reduction potential of **1** was determined by polarography on a rotating disk, glassy carbon electrode in acetonitrile. We measured this reduction at −0.51 V versus SCE, compared to −0.59 V for $[\alpha_1\text{-}YbP_2W_{17}O_{61}]^{7-}$. The slight increase of $E_{red}$ can be related to the decrease in negative charge. The Hf compound **1** is thus not significantly more oxidizing than the lanthanide complex, a fact to be taken into account in the interpretation of the mass spectra (see below). As a consequence, the same organic reactions as those catalyzed before by $[\alpha_1\text{-}YbP_2W_{17}O_{61}]^{7-}$ should be accessible to **1** without oxidative side reactions.

A similar synthesis starting from the monolacunary Keggin polyoxotungstate $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ delivered $(TBA)_{3.7}K_{0.3}[\alpha\text{-}Hf(OH)PW_{11}O_{39}]$ (**2**) in 88 % yield after recrystallization (Scheme 2). The intact Keggin structure was confirmed by IR and $^{31}P$ NMR spectroscopy. The presence of a hydroxo ligand was established by elemental analysis, and confirmed by mass spectrometry (see below).



Scheme 2. Preparation of Hf-substituted Keggin ion **2**. The hydroxy ligand is represented, but not the solvent molecules that are potentially part of the coordination sphere of Hf.

Based on the spectroscopic evidence, binding of $Hf^{IV}$ to the lacunary oxygen atoms must be admitted for **1** and **2**. We therefore represent the compounds as drawn in Schemes 1 and 2. Coordination of further ligands is possible, as can be seen in related compounds $[Hf(F)SiW_{11}O_{39}]^{5-}$[8c] and $[Zr(OH)PW_{11}O_{39}]^{4-}$.[12] Also, as mentioned above, the Hf-ion attains eight-coordination in the sandwich compounds $[Hf(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ and $[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$.[8d] Therefore, available coordination sites on the Hf ion should be considered for **1** and **2**. We provide below evidence for such coordination by ESI-MS.

In both syntheses of **1** and **2**, $HfCl_4$ is completely hydrolyzed. This contrasts with the behavior of $HfF_4$. In the synthesis of $[Hf(F)SiW_{11}O_{39}]^{5-}$[8c] under similar conditions, one halide ion remains bound to Hf.

We did not observe any evidence for dimerization of **1** (or **2**) into structures similar to the 2:2 complexes of the analogous lanthanide compounds under identical conditions.[4] This should not come as a surprise for **1**: as stated before, the hafnium ion is much smaller than the smallest lanthanide we examined (Yb). Dimerization into the 2:2 complexes would thus develop considerably higher strain and electronic repulsion between the two polyoxometallic subunits. It is reasonable to assume that polyoxotungstate **2** should have a structure close to that of the slightly more charged hafnium-substituted silicotungstate.

**Mass spectrometric analysis—evidence for coordination to the polyanions**: To gain additional insight into the stoichiometry and reactivity of the POMs, we analyzed them by negative ESI mass spectrometry, using the same parameters as with our analogous lanthanide complexes.[4] The mass spectrum from $MeCN/H_2O$ (Figure 1b) displays three series of peaks that characterize the anion of **1**. Each series corresponds to a different charge state (3−, 4−, and 5−), and

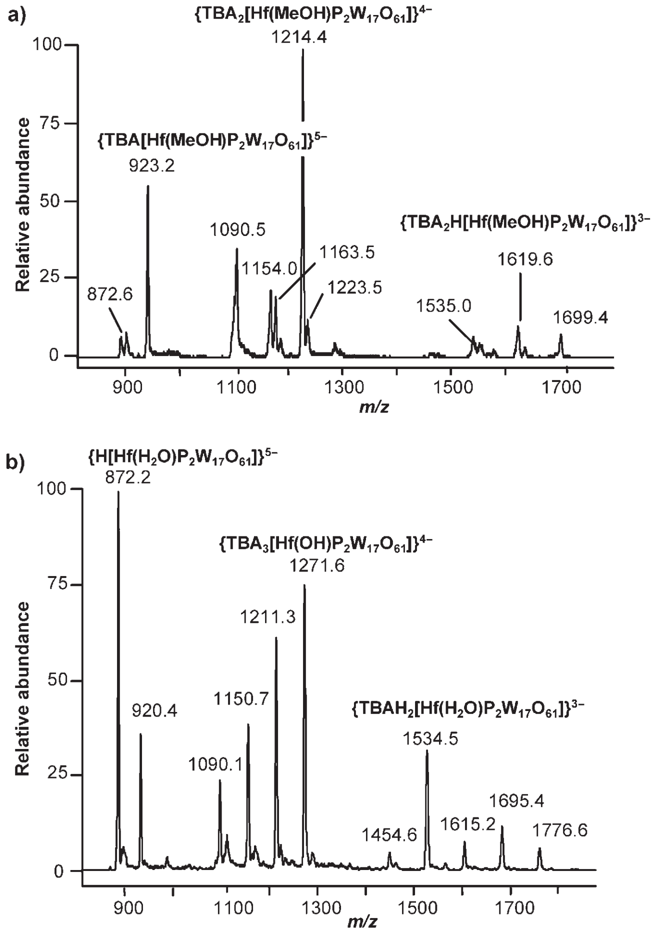


Figure 1. ESI-MS analysis of **1** (50 μmol L$^{-1}$). a) MeCN/MeOH; b) MeCN/$H_2O$. See the Supporting Information for full assignment.

within a series, the attribution was obtained by exchanging $TBA^+$ counterions with $H^+$. More interestingly, all peaks correspond to complexes with solvent molecules (i.e., $CH_3OH$ and $H_2O$). These molecules are most likely coordinated to the $Hf^{IV}$ atom. Under the same desolvation conditions, $[\alpha_1\text{-}Ln(H_2O)_4P_2W_{17}O_{61}]^{7-}$ loses all its coordinated solvent.[4] This indicates an increased ability of ligand binding in the gas phase of **1** compared to the analogous lanthanide complexes, a property that should be directly related to their Lewis acidity in solution. Furthermore, two signals in Figure 1b at *m/z* 1271.6 and *m/z* 1776.6 indicate one more TBA cation than the number expected from the charge balance of $Hf^{4+}$ and $[P_2W_{17}O_{61}]^{10-}$ in the presence of water. More precisely, by considering the *m/z* ratio difference between two consecutive peaks of a chosen series (e.g., 1090.1–1150.7, 1150.7–1211.3, and 1211.3–1271.6), the variations correspond to a $H^+$–$TBA^+$ exchange for a quadruply charged species. This allows us to elucidate the structure corresponding to a peak, and especially that corresponding to the signal at *m/z* 1271.6, which should be either $\{TBA_3[Hf(H_2O)P_2W_{17}O_{61}]\}^{4-}$ or $\{TBA_3[Hf(OH)P_2W_{17}O_{61}]\}^{4-}$. The resolution and accuracy of the ion-trap mass spectrometer used limit the precision of mass determination. If the former assignment was correct, the negative charge of the $[P_2W_{17}O_{61}]$ polyoxometalate framework would be eleven, that is, a reduction by one electron. Such reductions of polyoxotungstates under ESI conditions have been reported.[13] However, they were concentration dependent and occurred only at higher concentrations than those used in this study. Also (see above), the reduction potential of **1** is not significantly different than that of $[\alpha_1\text{-}YbP_2W_{17}O_{61}]^{7-}$, for which we never observed any reduction during our numerous ESI studies. Therefore, in the present case the hypothesis of reduction under ESI conditions must be ruled out. As a consequence, the signal at *m/z* 1271.6 should be unambiguously assigned to the second composition $\{TBA_3[Hf(OH)P_2W_{17}O_{61}]\}^{4-}$, in which the additional negative charge results from the deprotonation of the bound water molecule. Possibly, all the other observed anions might be formulated as $\{TBA_{3-x}H_x[Hf(OH)P_2W_{17}O_{61}]\}^{4-}$, that is, maintaining a hydroxo ligand. Likewise, the signal at *m/z* 1776.6 should be assigned to $\{TBA_4[Hf(OH)P_2W_{17}O_{61}]\}^{3-}$. The same anion bearing a hydroxo ligand is present in $TBA_7[\alpha_1\text{-}Hf(OH)P_2W_{17}O_{61}]$ (**3**), which has been isolated from solution after filtration of **1** through a weakly basic $TBA^+$-loaded cationic resin. The composition of (**3**) was established by elemental analysis. This further confirms the coordination abilities of **1**, since the ease of deprotonation of a water molecule (in solution and in the gas phase) is a good proof of binding and thus Lewis acidity.[14]

When the ESI analysis was performed in the presence of MeOH, this solvent coordinated to the complex (Figure 1a). This illustrates the possibility of ligand exchange. Also, signals assigned to two bound MeOH molecules are observed (*m/z* 1163.5, 881.9), illustrating the possibility of higher coordination number on the $Hf^{IV}$.

The outcome for Keggin derivative **2** is even simpler: peaks including a hydroxo ligand (*m/z* 718.3 ($[\alpha\text{-}Hf(OH)PW_{11}O_{39}]^{4-}$), *m/z* 1038.8 ($\{TBA[\alpha\text{-}Hf(OH)PW_{11}O_{39}]\}^{3-}$), *m/z* 1679.3 ($\{TBA_2[\alpha\text{-}Hf(OH)PW_{11}O_{39}]\}^{2-}$)) are preponderant in the spectrum from MeCN/$H_2O$ (Figure 2b). The remaining minor signals cannot be explained by protonation of these species. The ESI mass spectrum recorded from MeCN/MeOH is remarkably simple (Figure 2a). It shows only three signals, all resulting from $[Hf(OMe)P_2W_{17}O_{61}]^{4-}$, with 0–2 TBA cations. Hence, deprotonation of the bound ligand ($H_2O$, MeOH) is more favorable in the Keggin derivative, and a hydroxo ligand is exchangeable for a methoxo one. This parallels the solution properties, as we observed the formation of a hydroxo ligand on **2** during its synthesis, whereas in the case of **1**, the hydroxo ligand was generated only in the presence of base (formation of **3**). These observations seem to indicate a higher Lewis acidity of the Keggin structure **2** than the Dawson structure **1**.

Neither for the Dawson, nor for the Keggin derivative were any significant peaks in the mass spectra assignable to dimeric forms, even when operating under the softer desolvation conditions specifically used to observe dimers in the lanthanide series.[4] Only the peak at *m/z* 1142.5 (Figure 2b)

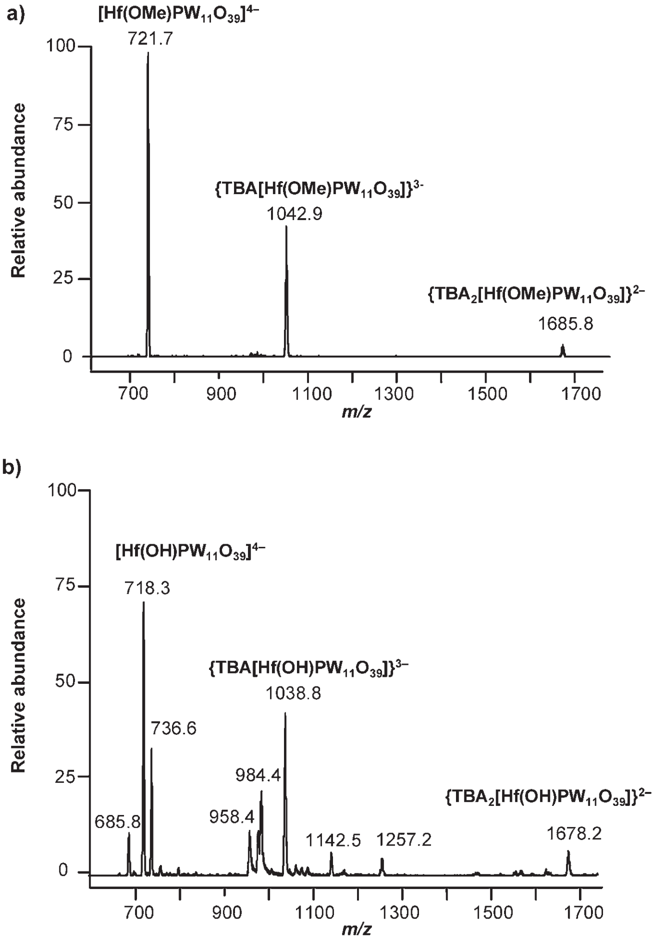
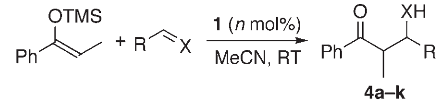


Figure 2. ESI-MS analysis of **2** (50 μmol L$^{-1}$). a) MeCN/MeOH; b) MeCN/H$_2$O. See the Supporting Information for full assignment.

Table 1. Catalytic activity of **1**.



| | X | R | *n* | Product | Yield [%][a] | ds |
|---|---|---|---|---|---|---|
| 1 | NPh | Ph | 20 | **4a** | 85 | 60:40 |
| 2 | NPh | Ph | 5 | **4a** | 86[b] | 55:45 |
| 3 | NPh | Ph | 2 | **4a** | 81[c] | 55:45 |
| 4 | N(*p*-OMe)Ph | Ph | 20 | **4b** | 40 | 50:50 |
| 5 | N(*o*-OH)Ph | Ph | 20 | **4c** | 52 | 55:45 |
| 6 | NPh | CO$_2$Et | 20 | **4d** | 96[d] | 60:40 |
| 7 | N(*p*-OMe)Ph | CO$_2$Et | 20 | **4e** | 99 | 50:50 |
| 8 | O | Ph | 20 | **4f** | 85 | ≈50:50 |
| 9 | O | (*p*-NO$_2$)Ph | 20 | **4g** | 74[e] | 55:45 |
| 10 | O | (*p*-Cl)Ph | 20 | **4h** | 65[e] | 60:40 |
| 11 | O | furyl | 20 | **4i** | 40[f] | 55:45 |
| 12 | O | (*p*-OMe)Ph | 20 | – | – | – |
| 13 | O | *n*Et | 20 | **4j** | 45[f] | 65:35 |
| 14 | O | *i*Pr | 20 | **4k** | 11[g] | n.d.[h] |

[a] See the Supporting Information for full experimental details. [b] Reaction took 24 h. [c] Reaction took 72 h. [d] Reaction required three equivalents of imine. [e] Conversion was 85 %. [f] Conversion was approx. 50 %. [g] Conversion was <20 %. [h] n.d. = not determined.

might correspond to {[HfPW$_{11}$O$_{39}$]$_2$H}$^{5-}$, but such an isolated and weak signal is not sufficient to establish the presence of dimers in solution.

**Use in catalysis**: Encouraged by the increased Lewis acidity in Hf-containing POMs, we focused on Lewis acid catalysis of Mukaiyama aldol and Mannich-type reactions. Brønsted catalysis by protonated POMs has recently been reported for these reactions,[2] but, apart from our previous report (see above), not POM-based Lewis acid catalysis. We focused first on **1** (Table 1).

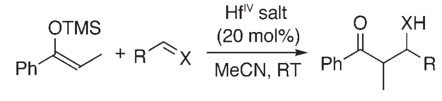
All reactions were carried out using standard organic techniques. The POM ligand renders the Hf complex more stable toward water than HfCl$_4$.[16] Reactions with imines worked smoothly (entries 1–7). The loading could be reduced to 2 % (entries 2–3), albeit this resulted in longer reaction times (72 versus 6 h). An excess of imine was required in the case of the simple pyruvate derivative (entry 6), as that substrate tends to react with itself. A similar—if less marked—trend was observed in the lanthanide case. Yet, *para*-substitution on the aniline end of the imine with an electron-donating group stabilized the imine, and excellent yield was reached with only one equivalent of *para*-methoxyphenylimine (entry 7). The results reported in entries 4 and 5 are puzzling, since the yields are rather low when compared to the other cases.

We next turned our attention to aldehydes. Gratifyingly, aldol products were obtained (entries 8–14). Good yields were reached with aromatic aldehydes, provided the aromatic groups were not too electron-rich (compare entries 8–10 to entries 11–12). In those cases, the POM ligand reduces the Lewis acidity of $Hf^{IV}$ relative to HfCl$_4$ or Hf(OTf)$_4$ (see Table 2). Reactions with aliphatic aldehydes were very sluggish (entries 13 and 14). Mostly starting materials were recovered along with some aldol products.

We wished to get an idea on how the polyoxometallic framework affected Lewis acidity. Table 2 presents the outcome of the reactions with the standard hafnium(IV) salts used as Lewis acid catalysts.[9]

HfCl$_4$ is an excellent Lewis acid for simple Mukaiyama aldol reactions of aldehydes. Hf(OTf)$_4$ has proven detrimen-

Table 2. Catalysis with HfCl$_4$ and Hf(OTf)$_4$.



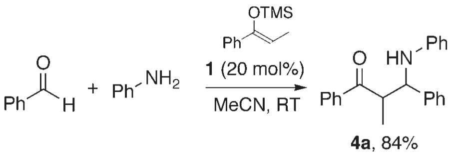
| | X | R | $Hf^{IV}$ salt | *t* [h][a] | Product | Yield [%] |
|---|---|---|---|---|---|---|
| 1 | NPh | Ph | HfCl$_4$[b,c] | 6 | **4a** | 75 |
| 2 | NPh | Ph | Hf(OTf)$_4$[b] | 6 | **4a** | 81 |
| 3 | O | Ph | HfCl$_4$ | 0.25 | **4f** | 98 |
| 4 | O | Ph | Hf(OTf)$_4$ | 0.25 | decomp | – |
| 5 | O | (*p*-NO$_2$)Ph | HfCl$_4$ | 0.25 | **4g** | 88 |
| 6 | O | (*p*-NO$_2$)Ph | Hf(OTf)$_4$ | 0.25 | **4g** | 44 |
| 7 | O | furyl | HfCl$_4$ | 0.25 | decomp[d] | – |

[a] Reaction time. [b] Reaction was run at 0 °C. [c] When run at RT, the reaction delivered byproducts issued from competing imino Diels–Alder reactions. [d] Low yield of diaddition product was observed.

tal to the substrates and low yield (entry 6) or no product at all (entry 4) were observed. The POM complex is less Lewis acidic than both $HfCl_4$ and $Hf(OTf)_4$. The weaker activity is an advantage that is already evident when comparing **1** with $Hf(OTf)_4$. When the substrates are too fragile, even $HfCl_4$ has limitations: contrary to what was observed with less active catalyst **1** (Table 1, entry 11), reaction of furfuraldehyde with $HfCl_4$ did not stop at the aldol level (entry 7). It delivered low yields of diaddition products. Those originated from the intermediate aldol product that underwent dehydration in the reaction conditions. The less-active complex **1** suppressed this problem.

For imines (entries 1 and 2), the POM complex has a similar reactivity as both $HfCl_4$ and $Hf(OTf)_4$. Overall, the two oxophilic $Hf^{IV}$ salts are much less reactive toward imines than they are toward aldehydes, which offsets the advantage there is in working with a weaker Lewis acidic POM complex. Yet, running the reactions with $HfCl_4$ above 0°C was detrimental, as byproducts arising from a competitive imino Diels–Alder reaction appeared (entry 1).

In both cases, though, the main advantage of our POM complexes is that they are air and water stable, and can easily be recycled. Indeed, we could set up a one-pot procedure in which aniline and benzaldehyde were pre-mixed prior addition of the silylenol ether and **1** (Scheme 3). No loss in yield was observed, even though one full equivalent (five relative to the catalyst) of water was released upon formation of the imine. Kobayashi has recently introduced a similar stabilization of Lewis acids by basic ligands in water,[16] and has identified this property as a "door to new applications of Lewis acids in synthesis".[16c]

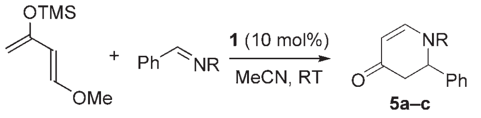


Scheme 3. One-pot procedure.

Recycling of the catalyst was possible. The precipitation/centrifugation protocol we developed for the POM–lanthanide complexes was used to isolate **1** with no modification of its structure, or activity.[5] In the reaction of diphenylimine with the silylenol ether (Table 1, entry 1), catalyst **1** was recycled four times without leaching (as evidenced by NMR spectroscopy), and each time the yield in **4a** was excellent (85, 85, 80, and 95%).

As was anticipated, the reactions were not limited to aldol-type ones. Imino Diels–Alder reactions with Danishefsky's diene were also catalyzed by **1** (Table 3).

Table 3. Imino Diels–Alder reactions catalyzed by **1**.

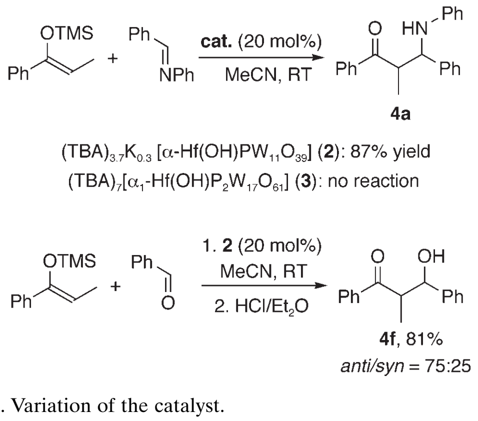


| | R | Product | Yield [%] |
|---|---|---|---|
| 1 | Ph | **5a** | 84 |
| 2 | (*p*-MeO)Ph | **5b** | 90 |
| 3 | (*p*-Cl)Ph | **5c** | 69 |

We could exclude a Lewis-type catalysis by decomplexed $Hf^{4+}$ for the previous reactions. Indeed, no trace of lacunary POM has been observed by any technique we used. Besides, the complexation constants for lanthanides in the $\alpha_1$ series are extremely high,[15b] and we can assume the one for $Hf^{4+}$ to be similar, or even stronger given the increased charge/size ratio, which is a leading factor for the complexation equilibrium. Acid catalysis with POMs generally arises from proton counterions (as in $H_3[PW_{12}O_{40}]$), but we could exclude such direct Brønsted catalysis, because **1** has no proton as counterion. Alternatively, protons can be generated through water activation by metal counterions.[17] In this latter case, the POM itself plays no catalytic role. To the best of our knowledge, no POM-based Brønsted catalysis directly involving a Lewis acidic substituent in the POM framework has been reported,[18] but we clearly observed the deprotonation of coordinated solvent molecules by MS, and with weakly basic resins. It would therefore be possible to imagine that **1** deprotonates a water molecule from the coordination sphere of hafnium, resulting in an indirect and unprecendented Brønsted catalysis. A second evident mechanism would see the hafnium atom in the POM act as a catalytic cornerstone directly binding the substrate. The fact that our complexes catalyze imino Diels–Alder reactions is a point in favor of the latter mechanism.

To discriminate between the two possibilities, we ran the reaction of diphenylimine and the standard silylenol ether with **2** and **3**, which bear hydroxo ligands (Scheme 4).

Good yields in **4a** (87%) and **4f** (81%) were obtained with **2**. A possible explanation would be a stronger Lewis acidity of the Hf ion in the Keggin structure compared to the $\alpha_1$-Dawson structure. This acidity would be decreased by the hydroxo ligand to such an extent that **2** had roughly the same activity as **1**. Coordination of a hydroxo ligand to **1** (giving **3**) would withdraw any significant Lewis acidity.



Scheme 4. Variation of the catalyst.

Indeed **3** does not catalyze the formation of **4a**. The fact that the Keggin ion was obtained with a hydroxo ligand during the synthesis, (contrary to the Dawson ion), and also the preponderant presence of deprotonated coordinated solvent molecules in the mass spectra of **2**, further point to a difference in the Lewis acidity of the Hf ion in these two structures. The lacuna in the $\alpha_1$-Dawson structure was described in the literature as more basic.[15] We think this is in favor of a direct Lewis acid catalysis. Yet, we cannot entirely rule out alternative indirect Brønsted catalysis for **1**, the key feature of which to explain the differences between **2** and **3** would be the relative facility of accessing oxo ligands from hydroxo ones.[12] However, as we never observed double deprotonation (a bis-hydroxo species by deprotonation of a second water molecule on the hafnium ion, or formation of an oxo ligand on Hf), both of these compounds should rather act as direct Lewis acids (coordination of substrate), than as water activating agents. Our attempts to evidence complexation of benzaldehyde and diphenylimine to **1** or **2** either by MS or NMR spectroscopy has so far not been successful. This is probably due to the weak binding constant and fast ligand exchange. Under such conditions, the increase in the chemical shift of the sp$^2$ carbon of the ligand (or the modification of that of the diamagnetic POM) is below 0.2 ppm, which we considered insignificant. Also, the accessible concentrations of substrate and POM together in MS are not high enough to form significant amounts of complexes.

## Conclusion

We have prepared the new compounds $(TBA)_5K[\alpha_1\text{-Hf}(H_2O)_4P_2W_{17}O_{61}]$ and $(TBA)_{3.7}K_{0.3}[\alpha\text{-Hf(OH)}PW_{11}O_{39}]$. They have been characterized thoroughly, in particular by IR, and $^{31}$P and $^{183}$W NMR spectroscopy, and mass spectrometry. Their 1:1 stoichiometry leaves available coordination sites on the Hf ion that govern their reactivity. A noticeable increase in Lewis acidity compared to analogous lanthanide complexes makes them possible catalysts for additions of silyl enol ethers to aromatic aldehydes. This illustrates how Lewis acidity can be fine-tuned by changes in the POM composition. Although the exact mechanism has yet to be determined, we have shown that the reaction was catalyzed directly by the POM complex. Whether the POM framework is directly binding the substrate, or is activating a solvent molecule, its inherent Lewis acid properties are crucial for the catalysis. This is an important achievement in catalysis by POMs. The air and water stability of the catalyst, and the ease of their recycling, are valuable properties compared to hafnium salts as catalysts. Work aiming at fully understanding the role of the POM framework in this new type of catalysis, examining its full scope and assessing the potentialities of these new systems for asymmetric transformations—in particular the $\alpha_1$-lacunary ligand is chiral—is underway. We will report on it in due course.

## Experimental Section

**General remarks**: Reagents and chemicals were purchased from commercial sources and used as received. The lacunary polyoxometalates, $K_9[\alpha_1\text{-}LiP_2W_{17}O_{61}]$[19] and $K_7[\alpha\text{-}PW_{11}O_{39}]$[20] were prepared as reported in the literature. Reactions were carried out under argon, with magnetic stirring. $CH_3CN$ was dried and distilled from $CaH_2$. Thin-layer chromatography (TLC) was performed on Merck 60F254 silica gel. Merck Geduran SI 60 Å silica gel (40–63 μm) was used for column chromatography. IR spectra were recorded from a Bruker Tensor 27 ATR diamond PIKE spectrophotometer and in KBr disk from a Biorad FTS 165 FT-IR spectrometer. $^1$H NMR [$^{13}$C NMR] spectra were recorded at room temperature with a 400 MHz [100 MHz] Bruker AVANCE 400 spectrometer. Chemical shifts are given in ppm, referenced to the residual resonances of the solvents ($\delta = 7.26$ or 77.2 ppm, for $CDCl_3$). Coupling constants ($J$) are given in Hertz (Hz). $^{31}$P NMR spectra were obtained at 298 K in 5 mm o.d. tube at 162 MHz, by use of a Bruker AVANCE 400 at a concentration of 100 mg 0.5 mL$^{-1}$. External 85 % $H_3PO_4$ in coaxial tube was used as reference.$^{183}$W NMR spectrum was recorded at 298 K in 10 mm o.d. tubes at 12.5 MHz on a Bruker AVANCE II 300 spectrometer equipped with a low-frequency special VSP probehead. Chemical shifts are referenced to $WO_4^{2-}$ ($\delta = 0$ ppm) according to the IUPAC recommendation. They were measured by the substitution method, using a saturated aqueous solution (in $D_2O$) of dodecatungstosilicic acid ($H_4SiW_{12}O_{40}$) as a secondary standard ($\delta = -103.8$ ppm). pH was measured with Hanna Instrument HI 221 pH meter. Polarograms were recorded in MeCN with $TBABF_4$ as supporting electrolyte on a Radiometer POL150 using a glassy carbon rotating disk electrode, a Pt electrode and a saturated calomel electrode linked by a salt bridge. Mass spectrometry experiments have been carried out on an electrospray-ion trap instrument (Bruker, Esquire 3000). The 50 pmol μL$^{-1}$ solutions of POMs were infused using a syringe pump (160 μLmin$^{-1}$). The negative ion mode was used with capillary high voltage 3500 V. The orifice/skimmer voltage difference was set to 40 V to avoid decomposition of the POMs. The low-mass-cutoff (LMCO) of the ion trap was set to 100 Th. Elemental analysis were carried out by the "Service Central d'Analyse", CNRS, Vernaison, France or by the ICSN, CNRS, Gif, France.

**$(TBA)_5K[\alpha_1\text{-Hf}(H_2O)_4P_2W_{17}O_{61}]$ (1)**: The lacunary $K_9[Li(\alpha_1\text{-}P_2W_{17}O_{61})]$ (5.0 g, 1.0 mmol) was dissolved in distilled water (125 mL) at 25 °C. The suspension was stirred until a clear solution was obtained. $HfCl_4$ (321 mg, 1.0 mmol) was dissolved in water (10 mL) and added dropwise to the stirring solution. The pH of the solution decreased from 5.5 to $3.0 \pm 0.1$. After 2 min, a solution of TBABr (3.75 g, 11.5 mmol) in water (50 mL) was added dropwise. After complete addition (pH $4.0 \pm 0.1$), the solution was allowed to stir for an additional 2 min. The precipitate was then collected by filtration. The crude product was dissolved in $CH_3CN$ (4 mL) and a solution of $Et_2O$/EtOH/Acetone (9:1:1) was added. The white precipitate was then collected by centrifugation. Yield: 4.81 g (83 %); $^{31}$P NMR (162 MHz, $c = 0.036$ mol L$^{-1}$, $CD_3CN$ + 10 % $D_2O$): $\delta = -10.7$ (s, 1P, $PW_8Hf$), $-11.5$ ppm (s, 1P, $PW_9$); $^{183}$W NMR (12.5 MHz, $c = 0.036$ mol L$^{-1}$, $CD_3CN$ + 10 % $D_2O$): $\delta = -114.1, -119.9, -123.9, -126.2, -130.5, -140.5, -142.3, -147.8, -165.0, -167.6, -171.1, -174.0, -174.8, -175.0, -176.7, -177.2, -187.6$ ppm; IR $\tilde{\nu} = 2963$ (m), 2936 (m), 2875 (m), 1485 (m), 1459 (m), 1382 (w), 1153 (w), 1083 (s), 1015 (w), 954 (s), 904 (s), 777 cm$^{-1}$ (vs); elemental analysis calcd (%) for the product dried for 12 h at $4 \times 10^{-2}$ Torr, $C_{86}H_{197}N_8KHfO_{65}P_2W_{17}$ (5788.31): C 17.84, H 3.40, N 1.71, K 0.67, P 1.078, W 53.99, Hf 3.08; found: C 17.54, H 3.33, N 1.24, K 0.40, P 1.16, W 54.12, Hf 3.24. The number of solvent molecules is difficult to determine with precision; assuming eight-coordination of $Hf^{4+}$, four solvent molecules should be included, most likely $H_2O$ because $Hf^{4+}$ is oxophilic. Elemental analysis and TGA are consistent with a further three molecules MeCN from recrystallization (see Supporting Information, Figure S1).

**$(TBA)_{3.7}K_{0.3}[\alpha\text{-Hf(OH)}PW_{11}O_{39}]$ (2)**: The lacunary $K_7[\alpha\text{-}PW_{11}O_{39}]$ (2.0 g, 0.67 mmol) was dissolved in distilled water (8 mL) at 80–90 °C. The suspension was stirred until a clear solution was obtained. $HfCl_4$ (235 mg, 0.73 mmol, 1.1 equiv) was dissolved in hot water (1 mL) and added dropwise to the stirring solution. After 5 min, a solution of TBABr (1.83 g, 5.7 mmol, 8.5 equiv) in hot water (7 mL) was added dropwise. After complete addition, the solution was allowed to stir for an additional 2 min. The precipitate was then collected by filtration and washed successively with $H_2O$, EtOH, and $Et_2O$. The crude product was dissolved in $CH_3CN$ (10 mL) and the remaining solid was removed by centrifugation. A solution of Acetone/EtOH (v/v; 1:1, 12 mL) were added to the filtrate and then $Et_2O$ (50 mL). The white precipitate was collected by centrifugation. Yield: 2.27 g (88 %); $^{31}P$ NMR (162 MHz, $c = 0.036$ mol$L^{-1}$, $CD_3CN$): $\delta = -12.06$ ppm (s, 1 P); IR: $\tilde{\nu} = 2963$ (m), 2936 (m), 2875 (m), 1485 (m), 1459 (m), 1382 (w), 1152 (w), 1091 (m), 1059 (s), 956 (s), 886 $cm^{-1}$ (s); elemental analysis calcd (%) for $C_{59.2}H_{140.2}N_{3.7}K_{0.3}HfO_{43}PW_{11}$ including 3 $H_2O$ (3835.7): C 18.54, H 3.68, N 1.35, K 0.31, P 0.81, W 52.72, Hf 4.65; found: C 18.33, H 3.56, N 1.30, K 0.29, P 0.85, W 51.68, Hf 4.67.

**General procedure 1 (GP1)—Mannich-type reactions**: The imine (0.5 mmol, 1 equiv) and the silyl enol ether (0.5 mmol, 1 equiv) were added to a solution of $TBA_5K[\alpha_1\text{-}Hf(H_2O)_nP_2W_{17}O_{61}]$ or $TBA_{3.7}K_{0.3}[\alpha\text{-}Hf(OH)PW_{11}O_{39}]$ (20 mol %, 0.1 mmol) in $CH_3CN$ (3 mL). After completion of the reaction (unless otherwise noted), a solution of acetone/ethanol (1:1) (6 mL) was added, followed by diethyl ether (60 mL). The white precipitate (catalyst) was centrifuged and separated from the reaction products. The remaining organics were concentrated under reduced pressure. The residue was purified by flash column chromatography (pentane/ethyl acetate 95:5) to afford the desired β-amino ketones as unseparable mixtures of the two diastereomers.

**General procedure 2 (GP2)—aldol reactions**: The aldehyde (0.5 mmol, 1 equiv) and the silyl enol ether (0.75 mmol, 1.5 equiv) were added to a solution of $TBA_5K[\alpha_1\text{-}Hf(H_2O)_nP_2W_{17}O_{61}]$ or $TBA_{3.7}K_{0.3}[\alpha\text{-}Hf(OH)PW_{11}O_{39}]$ (20 mol %, 0.1 mmol) in $CH_3CN$ (3 mL). After completion of the reaction, a solution of acetone/ethanol (1:1; 6 mL) was added followed by diethyl ether (60 mL). The white precipitate (catalyst) was centrifuged and separated from the reaction products. The organics were concentrated in vacuo. The crude mixture was dissolved in dichloromethane (2 mL) and a 1 M solution of HCl in diethyl ether (0.2 mL) was added. After 10 min, the solvent was evaporated under reduced pressure. The crude mixture was dissolved in dichloromethane and washed with aqueous saturated sodium hydrogenocarbonate and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography to afford the desired products.

**General procedure 3 (GP3)—imino Diels–Alder reactions**: The imine (0.5 mmol, 1 equiv) and diene or enol ether (0.75 mmol, 1.5 equiv) were added to a solution of the catalyst $TBA_5K[\alpha_1\text{-}Hf(H_2O)_nP_2W_{17}O_{61}]$ (10 mol %, 0.05 mmol, 280 mg) in $CH_3CN$ (3 mL). After completion of the reaction, a solution of acetone/ethanol (v/v; 1:1, 6 mL) was added followed by diethyl ether (60 mL). The white precipitate (catalyst) was centrifuged and separated from the reaction products. The organics were concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired cyclic adducts.

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