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# Pd-containing Organopolyoxometalates Derived from Dawson Polyoxometalate $[P_2W_{15}V_3O_{62}]^{9-}$ : Lewis Acidity and Dual Site Catalysis

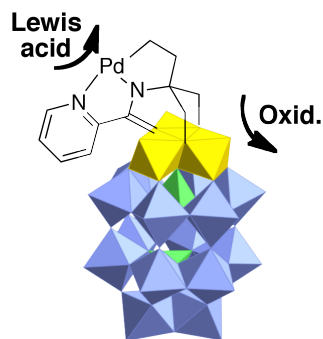
Benoît Riffled,† David Lachkar,‡ Julie Oble,†,§ Joaquim Li,† Serge Thorimbert,†,§,\* Bernold Hasenknopf,†,§,\* Emmanuel Lacôte,†,§,\*,\*

† Sorbonne Universités, UPMC Univ Paris 06, Institut Parisien de Chimie Moléculaire, 4 place Jussieu, 75005 Paris, France  
CNRS, UMR 8232, IPCM, 4 place Jussieu, 75005 Paris, France

§ ICSN-CNRS, Bâtiment 27, 1 avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France

‡ Université de Lyon, Institut de chimie de Lyon, UMR 5265 CNRS-Université Lyon I-ESCPE Lyon, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France

Supporting Information Placeholder



**ABSTRACT:** Grafting of a palladium complex to the Dawson vanadotungstate polyanion  $[P_2W_{15}V_3O_{62}]^{9-}$  via an organic ligand generates a large family of pincer-type hybrid polyoxometalates. The palladium-POM derivatives have dual catalytic properties. Unlike their parent inorganic polyanions, they catalyze allylations while retaining their oxidant character, which leads to single-pot dual site catalysis. This opens a new route for multicatalytic reactions.

Lewis acidic polyoxometalates (POMs) have emerged recently as a family of POMs with new catalytic properties.<sup>1</sup> Generally, POMs are nano-sized polyanionic clusters of highly oxidized early transition metals (most often  $V^V$ ,  $Mo^{VI}$  and/or  $W^{VI}$ ) and oxido ligands,<sup>2</sup> thus not Lewis acid candidates. To overcome this problem one can insert one (or several) Lewis acidic cation(s) into a lacunary framework;<sup>1a-j</sup> or tether it<sup>1k</sup> via a suitable ligand in an organopolyoxometalate.<sup>3</sup>

The Dawson POM  $[P_2W_{15}V_3O_{62}]^{9-}$  is an oxidation catalyst (as are its organo-hybrids).<sup>4,5</sup> Yet it is not Lewis acidic. Its oxo ligands can support transition metal ions in structures that are stable in organic solution,<sup>5a,6</sup> however with no open coordination sites for catalysis. Unfortunately, no  $[P_2W_{15}V_3O_{62}]^{9-}$ -derived mono-lacunary species exists, where one could insert a "naked" Lewis acidic cation, so another strategy had to be pursued to give Lewis acidity to  $[P_2W_{15}V_3O_{62}]^{9-}$ .

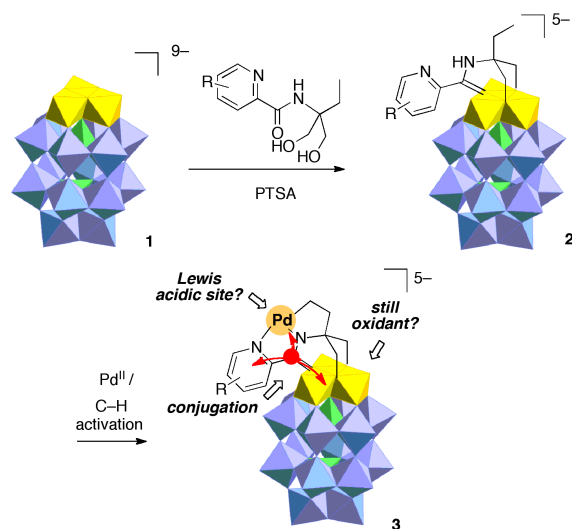
We recently showed that Pd-pincer POMs such **3** could be prepared via capping of the 3-vanadium triad of  $[P_2W_{15}V_3O_{62}]^{9-}$  (**1**) with picolinamide-diols, followed by pincer-complex formation via

palladation/C–H activation (Figure 1).<sup>7</sup> The C=O insertion into the POM framework ensures that the palladium is electronically conjugated to the POM, and not simply tethered to the inorganic moiety. One might envisage the use of this POM-Pd in Mizoroki-Heck couplings. However, the base required led to POM degradation under those reaction conditions.

PCP and related pincer Pd(II) complexes are electrophilic enough to catalyze the allylation of imines.<sup>8</sup> Our Pd-POMs have a different geometry, but we surmised that they would also be electrophilic. We thus decided to investigate them as potential Lewis acids. We also hoped that the oxidative properties of the vanadotungstic framework might be retained in this new type of Lewis acidic POMs, that the general solubility of POMs would allow easy catalyst-recycling and that the ligand on the POM would allow a tuning of the catalytic activity not achievable with purely inorganic structures.

Our first task was to extend the scope of the palladation with regard to the pyridine and the carbon undergoing the C–H insertion. We previously evidenced that an aryl group in the 2-position of the

pyridine could lead to pincer complexes on this substituent, rather than onto the substituent on the diol.<sup>7</sup> So we focused on pyridines with no aryl substituent at the 2-position in order to limit the structural space to the former type of pincers (see **3**, Figure 1).



**Figure 1.** General strategy for installing Lewis acidity onto **1**.

The hybrid ligands **2a-j** were prepared in good yields from (TBA)<sub>5</sub>H<sub>4</sub>[P<sub>2</sub>W<sub>15</sub>V<sub>3</sub>O<sub>62</sub>] (**1**) and various amido-diols, under microwave heating at 80 °C for 35 min in the presence of 30 mol % of *para*-toluenesulfonic acid (PTSA) in dimethylacetamide (DMAc).<sup>9</sup>

A typical POM ligand (**2a**) was isolated in 82% yield after two successive precipitations in diethylether and ethanol and centrifugation. No trace of protonation of the pyridine was detected. POMs **2a-j** were obtained as TBA salts with varying amount of dimethylammonium cations. The ratio was determined by NMR and elemental analysis. Full analytical data can be found in the SI.

The palladations were carried out as described.<sup>7a</sup> In a typical experiment (Table 1, Entry 1), one equivalent of Pd(OAc)<sub>2</sub> was added to **2a** in acetonitrile at room temperature. After 5 minutes all the palladium acetate was solubilized. The two <sup>31</sup>P signals of the Dawson POM structure moved only slightly from δ = -5.7, -11.9 ppm in **2a** to δ = -6.0, -12.0 ppm in **3a**. The <sup>1</sup>H NMR signal of the amide proton at δ = 10.41 ppm in **2a** disappeared. In addition, the AB system corresponding to the two CH<sub>2</sub>OV (δ ~ 5.5 ppm in **2a**) turned into a broad singlet (δ = 5.48 ppm in **3a**). The <sup>13</sup>C spectra indicated that the methyl of the organic ligand in **2a** (δ = 7.6 ppm) had been turned into a methylene group (δ = 25.3 ppm in **3a**). Thus a 5-membered palladacycle was formed (see **3a** in Figure 2). ESI-MS confirmed the presence of the functional polyanion **3a**. Major signals are at m/z 1131.3 (calc. 1131.5 for {TBA(CH<sub>3</sub>CN)[P<sub>2</sub>V<sub>3</sub>W<sub>15</sub>O<sub>62</sub>C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>Pd]}<sup>4-</sup>) and m/z 1067.7 (calc. 1066.4 {TBA(CH<sub>3</sub>CN)[P<sub>2</sub>V<sub>3</sub>W<sub>15</sub>O<sub>62</sub>C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>Pd]}<sup>4-</sup>). For full spectrum, see SI.

Preparative experiments were carried out with the POMs ligands **2b-j** (Table 1, see Figure 2 for the structures and the SI for full description). All POMs **3a-g** were isolated and purified by successive precipitations in diethylether/ethanol and centrifugations, and fully characterized by IR, multinuclear NMR, ESI-MS and elemental analysis.

The C-H activation worked with both electron-withdrawing and electron-donating substituents on the pyridine, independently of

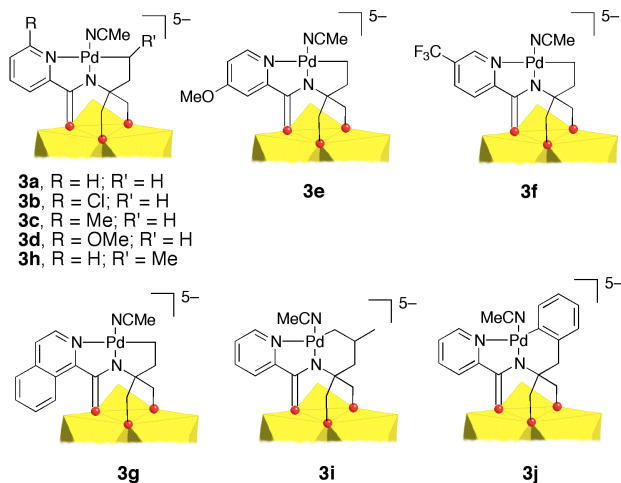
the position of the substituents (compare Table 1, entries 2, 6 and 3-5, see Figure 2 for structures). An isoquinoline derivative also led to the cyclopalladated POM derivative (see **3g**, 84%, Entry 7).

The steric hindrance at the C-H site was gradually increased to evaluate the preference for 5 or 6-membered ring formation. The propyl derivative **3h** led to 5-membered palladacycle **3h** in 90% yield (entry 8). However, an additional methyl group, as in **3i**, redirected the C-H insertion to the primary methyl moiety, likely because the tertiary carbon of the isobutyl group is not accessible for steric reasons (Entry 9, 95%). A 6-membered palladacycle was also isolated in 98% yield from benzyl derivative **2j** via an aromatic C-H insertion (Entry 10).

**Table 1.** Preparation of the Pd-containing POMs: scope

Entry	POM	Pyridine	R	Product, Yield (%)
1	<b>2a</b>	2-pyridyl	Et	<b>3a</b> , 87
2	<b>2b</b>	(6-Cl)-2-pyridyl	Et	<b>3b</b> , 75
3	<b>2c</b>	(6-Me)-2-pyridyl	Et	<b>3c</b> , 82
4	<b>2d</b>	(6-OMe)-2-pyridyl	Et	<b>3d</b> , 90
5	<b>2e</b>	(4-OMe)-2-pyridyl	Et	<b>3e</b> , 93
6	<b>2f</b>	(5-CF <sub>3</sub> )-2-pyridyl	Et	<b>3f</b> , 99
7	<b>2g</b>	1-isoquinolyl	Et	<b>3g</b> , 84
8	<b>2h</b>	2-pyridyl	<i>n</i> -Pr	<b>3h</b> , 90
9	<b>2i</b>	2-pyridyl	<i>i</i> -Bu	<b>3i</b> , 95
10	<b>2j</b>	2-pyridyl	CH <sub>2</sub> Ph	<b>3j</b> , 98

**Figure 2.** Structures of the POM-palladacycles obtained.



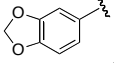
Thus, the grafting strategy to build Pd-containing organohybrids of **1** is highly versatile. Interestingly, the mass spectra of **3a-j** indicated that one molecule of the solvent used for the synthesis (MeCN) was present. Thus, the compounds have one coordination site at the Pd center potentially available for catalytic purposes.

The palladium center on the POM might complex Lewis bases, such as imines or aldehydes, as a traditional Lewis acid through exchange of the solvent. Or it could undergo nucleophilic attack from allylmetal reagents at the electrophilic Pd site to generate  $\eta^1$ -allyl-Pd(II) POMs, which could allylate imines and/or aldehydes. In both cases, the reactivity would derive from the presence of the accessible electrophilic center. The allylation of imines thus appeared to be an excellent benchmark to determine whether the Pd embedding approach can bring new properties to tungstovanadate ion **1** without POM degradation.

In a typical experiment, *N*-(phenylmethylene)-benzenesulfonamide **4a** was heated at 40°C in a micro-wave oven with two equivalents of allyltributylstannane in the presence of 4 mol % of **3a** in DMF (Table 2, Entry 1).

**Table 2. Catalytic allylation of sulfonylimines and aldehydes**

$\text{Ar}-\text{CH}=\text{X} + \text{CH}_2=\text{CH}-\text{CH}_2-\text{SnBu}_3 \xrightarrow[\text{DMF, 40 } ^\circ\text{C (MW)}]{\text{3 (4 mol\%)}} \text{Ar}-\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_3)-\text{CH}=\text{X}$ <p><b>4a-f</b> (X = NR)  <b>5a-h</b> (X = O)</p> <p><b>6a-f</b> (X = NR)  <b>7a-h</b> (X = O)</p>			
Entry	Ar, X	Cat.	Prod., Yield (%)
1	Ph, NSO <sub>2</sub> Ph	<b>3a</b>	<b>6a</b> , 89
2	Ph, NTs	<b>3a</b>	<b>6b</b> , 90
3	<i>p</i> Cl-C <sub>6</sub> H <sub>4</sub> , NTs	<b>3a</b>	<b>6c</b> , 88
4	<i>p</i> Me-C <sub>6</sub> H <sub>4</sub> , NTs	<b>3a</b>	<b>6d</b> , 94
5	<i>p</i> MeOC <sub>6</sub> H <sub>4</sub> , NTs	<b>3a</b>	<b>6e</b> , 86
6	Ph, <i>N</i> - <i>t</i> Bu	<b>3a</b>	— <sup>a</sup>
7	Ph, NSO <sub>2</sub> Ph	<b>3e</b>	<b>6a</b> , 53 <sup>b</sup>
8	Ph, NSO <sub>2</sub> Ph	<b>3f</b>	<b>6a</b> , 66 <sup>b</sup>
9	Ph, NSO <sub>2</sub> Ph	<b>3g</b>	<b>6a</b> , 77
10	Ph, NSO <sub>2</sub> Ph	<b>3a</b> <sup>c</sup>	<b>6a</b> , 19 <sup>d</sup>
11	Ph, O	<b>3a</b>	<b>7a</b> , 69
12	<i>o</i> Br-C <sub>6</sub> H <sub>4</sub> , O	<b>3a</b>	<b>7b</b> , 77

13	<i>p</i> Cl-C <sub>6</sub> H <sub>4</sub> , O	<b>3a</b>	<b>7c</b> , 71
14	<i>p</i> NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> , O	<b>3a</b>	<b>7d</b> , 95
15	<i>o</i> Me-C <sub>6</sub> H <sub>4</sub> , O	<b>3a</b>	<b>7e</b> , 77 <sup>e</sup>
16	2,4(MeO) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> , O	<b>3a</b>	<b>7f</b> , 95 <sup>e</sup>
17	 , O	<b>3a</b>	<b>7g</b> , 94 <sup>e</sup>
18	MeS-C <sub>6</sub> H <sub>4</sub> , O	<b>3a</b>	<b>7h</b> , 83 <sup>f</sup>

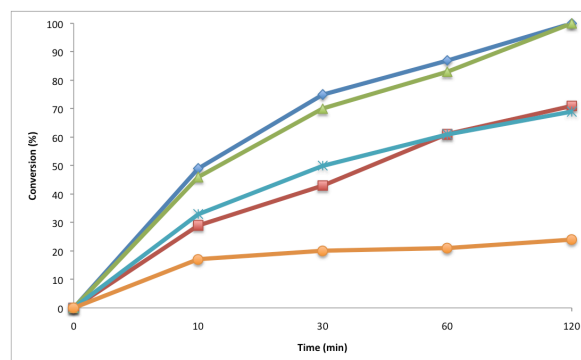
All yields are isolated yields. Unless otherwise noted, conversion into product was 100% after 2h. <sup>a</sup> Starting material was recovered intact. <sup>b</sup> Conversion was 70% after two hours. <sup>c</sup> 0.4 mol% of **3a** was used. <sup>d</sup> Conversion was 24% after two hours. <sup>e</sup> The reaction was heated at 80 °C. <sup>f</sup> The reaction was heated at 120 °C.

The sulfonylimines with either electron withdrawing (Table 2, Entry 3) or electron donating groups (Entries 4-5, 7-10) delivered the expected products. The allylamines were obtained in good to excellent yields in all cases but one. Only the allylation of phenyl-*t*-butylimine failed (Entry 6). The reaction did not proceed in that case, which may be a consequence of both the steric hindrance and the electron-donating character of the bulky *t*-butyl substituent on the nitrogen. When the loading of **3a** was lowered to 0.4 mol%, the reaction proceeded but stopped at about 24% conversion (see below). Isoquinolyl POM-Pd **3g** behaved exactly as **3a** (Entry 9), while **3e-f** were less reactive (70% conversion after 2h, entries 7-8).

Aromatic aldehydes were examined next. Again, those were allylated without problem (Entries 11-18). An electron-withdrawing nitro substituent on the aromatic ring helped the reaction (entry 14), while strong electron-donating substituents required us to heat the reaction more (entries 15-17). Finally, POM **2a** which has the same structure as **3a** except for the absence of any Pd atom left the imine unchanged.

The Pd-POMs thus catalyze allylations of imine and aldehyde electrophiles at the Pd centers in the hybrid POM structure. The trends observed with the substituents are consistent with an increased or lowered reactivity of the electrophiles toward the allylmetal intermediates.

**Figure 3.** Conversion as a function of time for the allylation of diphenylimine catalyzed by a) **3a** (4 mol%, deep blue diamonds); b) **3a** (0.4 mol%, orange dots); **3e** (4 mol%, light blue stars); **3f** (4 mol%, red squares); **3g** (4 mol%, olive green triangles).



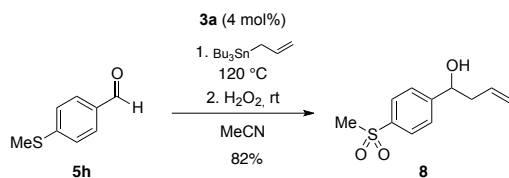
In order to learn more about the reaction and the possible influence of the pyridine substitution we selected four of the organo-Pd POMs with no (**3a**, **3g**), donating (**3e**) and withdrawing (**3f**) substituents for further examination. The conversion of the allyla-

tion of diphenylimine was followed over a period of two hours (Figure 3). After that time, the reaction was over with unsubstituted pyridine and isoquinoline POM-Pd **3a** and **3g**. The selectivity of the reaction is total, corresponding to a TON of 25 and a TOF of 12.5 h<sup>-1</sup>. For the POM-Pd containing polar substituents (**3e**, **3f**), the reaction was still selective, but did not reach completion within two hours (the catalyst was however still active (TON = 17.5; TOF = 8.75 h<sup>-1</sup>). Finally, decreasing the loading resulted in a less efficient reaction, which stopped at about 24% conversion (however, since conversion dropped less sharply than the loading, the TON improved to 60; TOF = 30 s<sup>-1</sup>). This confirms our hypothesis that the activity of the catalysts might be tuned via the substitution of the organic ligand of the organo-POM.

Finally, POM **3a** was precipitated after addition of diethyl ether at the end of the reaction. This led to its recycling by centrifugation. It could be reused up to eight times without loss of its catalytic activity (e. g. 89% yield at the seventh run, see Table S1 in the SI).

We next investigated whether **3a** retained the catalytic properties of the vanadotungstates in the presence of the palladium atom. Bifunctional substrate **5h** including both a sulfide and an aldehyde moiety was chosen as model substrate to probe this issue. It was placed in the presence of 4 mol% of **3a** and submitted to allylstannane at 120°C. Then H<sub>2</sub>O<sub>2</sub> was added in the same pot, and the reaction was left overnight at rt (Scheme 1). Sulfonol alcohol **8** was isolated in 82% yield with no trace of alcohol oxidation. No reaction took place when the same sequence was carried out without the POM. Similarly, alcohol **7h** was left mostly unchanged when reacted with H<sub>2</sub>O<sub>2</sub> in the absence of any POM. Only minor amounts of the corresponding sulfoxide and sulfone were obtained. Finally, benzyl alcohol was not oxidized in the reaction conditions.

**Scheme 1. Dual catalytic activity of 3a**



The combined observation prove that POM **3a** has dual catalytic properties. From what precedes the Pd center is responsible for the allylation since **2a** does not catalyze it, and it is not poisoned by the sulfide. As for other vanadotungstates,<sup>4a,j</sup> the vanadium triad is likely responsible for the chemoselective oxidation, although its exact mechanism is not known at this stage.

To conclude, a surface organometallic approach can be used to add new catalytic properties to the Dawson vanadotungstate polyanion [P<sub>2</sub>W<sub>15</sub>V<sub>3</sub>O<sub>62</sub>]<sup>9-</sup>. Pyridine-derived diol-amide ligands installed on the POM lead to electrophilic pincer-like POM-Pd(II) hybrids. The latter are recyclable catalysts for the allylation of imines and aldehydes, as well as oxidation catalysts. Both types of catalysis are compatible and a dual catalytic, one-pot process was devised. In addition, the coordination sphere of the Pd center can be easily modified, leading to reactivity tuning. Further work will focus on extending the concept of dual-site POM catalysts toward other structures and reactions, as well as to design a chiral environment for asymmetric versions of the reactions studied.

## ASSOCIATED CONTENT

### Supporting Information

Procedures for synthesis, full characterization of all new compounds described; recycling of the catalysts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\* serge.thorimbert@upmc.fr, bernold.hasenknopf@upmc.fr, emmanuel.lacote@univ-lyon1.fr

## ACKNOWLEDGMENT

Université Pierre et Marie Curie, CNRS, ICSN and the French National Research Agency (ANR, grant 08-PCVI-0005) are acknowledged for financial support. FR2769 is acknowledged for technical assistance.

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