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Palladium(II) Phosphotungstate Derivatives: Synthesis and Characterization of the $[Pd_x\{WO(H_2O)\}_{3-x}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{(6+2x)-}$ Anions

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A series of Pd^{II} derivatives of the $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ heteropolytungstate with the general formula $[Pd_x\{WO(H_2O)\}_{3-x}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{(6+2x)-}$ (x = 1–3) is described. These compounds are obtained by the reaction between $[Pd^{II}(NO_3)_2]\cdot H_2O$ and the corresponding vacant polyoxometalates in water. They are characterized by IR and multinuclear NMR (^{31}P and ^{183}W) spectroscopy. Compound $K_{10}[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ was characterized by XRD: it crystallized in the orthorhombic space group *Pcmn* with parameters a = 18.119(3) Å, b = 19.729(3) Å, c = 24.856(5) Å, V = 8886(3) Å^3.

Introduction

The coordination chemistry of polyoxometalates (POMs) with “noble” transition metal cations (NTMCs) has grown in interest over the last decade. The formation of such derivatives has been attractive from the start in the field of catalysis.[1–9] Considering the potential importance of these NTMCs in oxidation catalysis on the one hand, and the well-known robustness of heteropolytungstate ligands toward thermal and oxidative conditions on the other hand, the synthesis of such systems appears to be a worthwhile goal for chemists. However, although a few reports of well-described syntheses of platinum-group derivatives of polyoxometalates have been published before 1990,[10–13] most studies came out after the description of the phosphotungstoruthenate heteropolyanions $[PW_{11}O_{39}\{RuL\}]^{n-}$ in 1992 by Rong and Pope:[14] the porphyrin-like $[PW_{11}O_{39}]^{7-}$ ligand was shown to accommodate ruthenium cations with different oxidation states (in the range +II to +V), thus proving that polyoxometalates are a versatile class of π-donor and π-acceptor ligands capable of stabilizing both high- and low-valent cations.[9] Since this date, an increasing number of studies that deal with ruthenium-incorporated derivatives emerged in the literature from our[15–19] and other groups.[20–29] Nevertheless, with regard to the other noble elements, few studies have been done,[30,31] except for the grafting of some organometallic moieties like $\{RhCp^*\}^{2+}$ and $\{M^I(COD)\}^+$, (M = Ir, Rh).[32–39] Recently, the groups of both Kortz and Hill described the formation and the characterization of several palladium derivatives of heteropolytungstates in which the metallic cations are bound to four oxygen atoms of two $[A,\alpha\text{-}XW_9O_{34}]^{n-}$ units (X = P, n = 9 or X = Si, n = 10)[40–43] or of two $[B,\alpha\text{-}X^{III}W_9O_{33}]^{9-}$ units (X = As, Sb).[44,45] Besides their interest as structural models of oxide-supported palladium catalysts,[46–49] the compounds reported by Hill are remarkable for their stabilization of Pd^{IV}=O,[41] Pt^{IV}=O[42] and very recently Au^{III}=O functions.[50] It should be noted here that the Pd^{IV} and Pt^{IV} complexes have both been obtained by aerobic oxidation of Pd^{II}- and Pt^{II}-containing POM intermediates. These last reactions, which have been carried out in water, may be considered as potential steps in the catalytic oxidation of organic substrates. It is therefore valuable to isolate potential palladium catalysts in different oxidation states and to characterize their molecular features. We thus present here a detailed study of the reactivity of Pd^{II} cations towards some phosphotungstates deriving from $[A,\alpha\text{-}PW_9O_{34}]^{9-}$.

Results and Discussion

Synthesis

Rational Synthesis of the $[Pd_x\{WO(H_2O)\}_{3-x}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{(6+2x)-}$ Complexes (x = 1, 2, 3)

The synthesis of the tripalladium derivative $[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]^{12-}$ (**3**) (Figure 1) was first reported by Knoth et al., together with that of other $[M_3\{A,\alpha\text{-}PW_9O_{34}\}_2]^{12-}$ complexes (M = Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, $\{Ce^{IV}O\}^{2+}$).[11] However, in that work, the synthesis of the tripalladium species has been simply described as a variation of that of the nickel derivative. Hill et al. also mentioned its use as an

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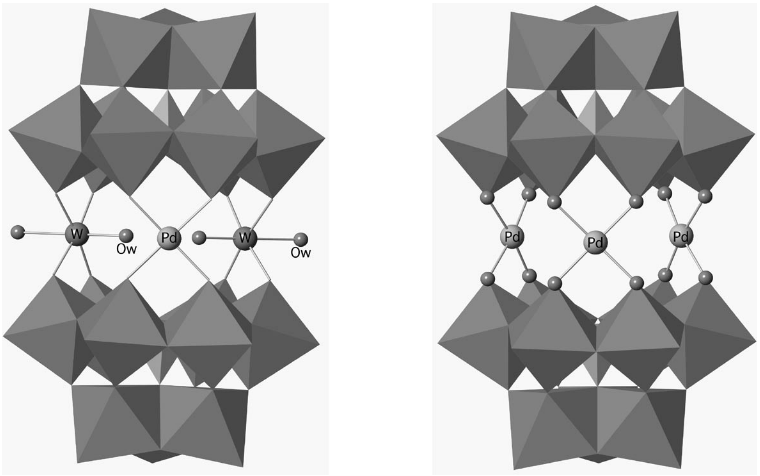


a b

Figure 1. Schematic representation of the anions of **1** (a) and **3** (b).

intermediate in the synthesis of a $\{Pd^{IV}{=}O\}^{2+}$ derivative, namely $[\{Pd^{IV}{=}O(OH)\}\{WO(H_2O)\}P_2W_{18}O_{68}]^{13-}$.[41] Nevertheless, in both works no characterization of this complex is available, except its chemical analysis, but two XRD structural characterizations have been very recently announced (see Structural Characterization section). In the present work, we report on the detailed description of its synthesis and a complete characterization in solution. As proposed by Knoth et al.,[11] we used $[Pd(NO_3)_2]\cdot H_2O$ as the starting material, since this precursor is soluble in water at room temperature and because it contains no halides, which are known to form very stable complexes with Pd^{2+}. Thus, reacting $[Pd(NO_3)_2]\cdot H_2O$ with $K_9[A,\alpha\text{-}PW_9O_{34}]\cdot xH_2O$ at room temperature led to the quantitative formation of **3** (as observed from the ^{31}P NMR spectrum of the mother solution), which can be precipitated as its potassium salt by adding KCl, with a yield of 45%. The crystals used for the X-ray diffraction study were obtained after a few days by slow evaporation of the mother liquor at room temperature. Note that the use of the potassium salt of $[A,\alpha\text{-}PW_9O_{34}]^{9-}$ instead of the sodium salt is required. Indeed, according to ^{31}P NMR spectroscopy the sodium salt led to a mixture of mostly unidentified compounds, among which **3** remained the major species. In this case, addition of KCl did not allow the isolation of a pure product.

For the preparation of the complex with two Pd^{2+} cations we used the corresponding bis-lacunary anion, i.e. $[P_2W_{19}O_{69}(H_2O)]^{14-}$. This anion, whose structure was described a few decades ago,[51] is known to form adducts with divalent cations.[52] Thus, the reaction, at room temperature, between $[P_2W_{19}O_{69}(H_2O)]^{14-}$ and two equivalents of Pd^{II} should lead to the quantitative formation of $[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{10-}$ (complex **2**, Figure 5). However, the ^{31}P NMR spectrum of the mother liquor essentially exhibits two signals, in a roughly 1:1 ratio (δ = –11.6 and –14.2 ppm), that can not be reconciled with the expected symmetrical structure of $[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{10-}$ (at least C_{2v}). Moreover, the sample obtained by rapid precipitation by addition of KCl to the mother liquor also exhibits two signals in its ^{31}P MAS NMR spectrum, but with unequal intensity: the signal at high frequency (δ = –11.85 ppm) is more intense than that at low frequency (δ = –14.6 ppm, see Figure S1 in the Supporting Information). This argues for the presence of two different species formed by the addition of Pd^{II} to the bis-lacunary anion. The formation of these compounds appears to be rapid, since the immediate addition of potassium chloride in the reaction mixture led to the instantaneous appearance of a precipitate that contains only these two compounds. It is worth noting that redissolving the solid precipitate in pure water leads back to a ^{31}P NMR solution spectrum with two signals of equal intensity. All these observations led us to consider that two species are in equilibrium in aqueous solution. Allowing the crystallization to occur slowly enabled us to grow large crystals. Two types of crystals with different shapes were then obtained, among which red plate crystals suitable for an X-ray diffraction study were found to contain the expected $[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{10-}$ complex anion (**2**). The ^{31}P NMR spectrum recorded immediately after dissolution of a few red plate crystals initially presents a single resonance at –14.2 ppm, thus assigned to **2**. It evolves rapidly by the appearance of the signal at –11.6 ppm (assigned to another species **2′**), which grows progressively to reach a final 1:1 ratio. This confirms the hypothesis of a rapid equilibrium between two different complexes **2** and **2′**.

Accordingly, the chemical analysis indicated that the W/Pd composition of the solid mixture of **2** and **2′** obtained after addition of KCl remains equal to 19:2, confirming that both compounds are possible isomers.[53]

The complex $[Pd\{WO(H_2O)\}_2\{A,\alpha\text{-}PW_9O_{34}\}_2]^{8-}$ (**1**), has been obtained by the direct reaction of the monovacant $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ with an excess of $[Pd(NO_3)_2]\cdot H_2O$ at room temperature in water. As for the previous complexes, the formation of **1** is somewhat fast since checking the mother liquor by ^{31}P NMR spectroscopy showed the absence of the starting anion $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ after only half an hour. As for the two other compounds, the potassium salt of **1** can be obtained by precipitation with KCl in 70% yield. All three complexes are sufficiently soluble in water for their characterization in solution.

Reaction between $K_{10}[P_2W_{20}O_{69}(H_2O)_2]$ and $[Pd(OAc)_2]$

We have also checked the reactivity of the poorly water-soluble palladium precursor $[Pd(OAc)_2]$. This complex, which should in fact be described as a trimer $[Pd_3(OAc)_6]$, is known to be poorly reactive at room temperature except in concentrated HNO_3.[54]

The reaction of the potassium salt of the monovacant $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ anion with an excess of $[Pd(OAc)_2]$ (3 equiv.) has been carried out in refluxing water for half an hour. In these conditions the final pH is equal to 4.6, while the pH was equal to 3.1 when we treated $K_{10}[P_2W_{20}O_{70}(H_2O)_2]\cdot 24H_2O$ with palladium nitrate. The former reaction led to the formation of a mixture of four major species as observed by ^{31}P NMR spectroscopy [δ = –11.6 ppm (22%); δ = –11.8 ppm (16%); δ = –12.85 ppm (33%); δ = –14.2 ppm (22%), see Figure S2 in the Supporting Information]. Among these resonances, those of equal intensity at δ = –14.2 and –11.6 ppm can be confidently assigned to compound **2** in equilibrium with **2′**, because of their chemical shift values and also because of their close relative abundance in the mixture. In the same way, we can also assign the peak at δ = –12.85 ppm to the expected $[PdP_2W_{20}O_{70}(H_2O)_2]^{8-}$ anion (**1**). The last signal (at δ = –11.8 ppm) may be tentatively assigned to the Pd^{IV} derivative $[\{Pd^{IV}{=}O(OH)\}\{WO(H_2O)\}P_2W_{18}O_{68}]^{13-}$ reported by Hill.[41] Unfortunately, all our attempts at isolating and characterizing this compound remained unsuccessful. In addition, two minor signals are observed at δ = –12.3 and –12.7 ppm, whose intensities increased while prolonging the heating. Signals with the same chemical shifts were observed from the reaction between $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot xH_2O$ and $[Pd(NO_3)_2]\cdot H_2O$ at room temperature. From a comparison with the latter experiment, the lines at δ = –12.3 and –12.7 ppm were thus finally attributed to palladium derivatives of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion. Furthermore we have found that addition of $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot xH_2O$ in the reaction mixture led to an enhancement of both peaks.

Slow evaporation of the mother liquor at room temperature led to the crystallization of a mixture of two compounds. A ^{31}P MAS NMR spectroscopic study showed that this mixture contained only the compounds **2**[55] (δ = –14.6 ppm) and **1** (δ = –12.9 ppm) mentioned above (see Figure S3 in the Supporting Information).

In conclusion of this part, it appears that complexation reactions with the metastable $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ anion are strongly dependent on the experimental conditions. Indeed, at high temperature and/or if the pH is not controlled, rapid degradation of the anion may occur with the release of tungstate ions from the central belt of the anion. This behaviour has been evidenced here by the formation of the dipalladium derivatives of the $[P_2W_{19}O_{69}(H_2O)]^{14-}$ anion, **2** and **2′**. It is worth noting that in the case of the reaction with palladium nitrate (done at lower pH and room temperature) decomposition does not occur, since we do not observe the formation of highly-substituted complexes, even with a large excess of palladium or by a prolonged reaction time. The release of free tungstates may explain the formation of palladium derivatives of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion, since $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ is known to be unstable in the presence of tungstates and to evolve into $[\alpha\text{-}PW_{11}O_{39}]^{7-}$.[56]

Multinuclear NMR Spectroscopy

^{31}P NMR Spectroscopy

In solution the mono-, di- and tripalladium derivatives **1**, **2** and **3** exhibit one unique ^{31}P NMR signal at –12.9, –14.2 and –12.3 ppm, respectively. This agrees with the equivalence of the two $\{\alpha\text{-}PW_9\}$ moieties in each of these complexes. For both compounds **1** and **2** the ^{31}P NMR resonances are shifted to lower frequency with respect to the corresponding mono- and divacant anions $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ (–12.3 ppm) and $[P_2W_{19}O_{69}(H_2O)]^{14-}$ (–10.05 ppm), respectively, in agreement with the general trend observed for P-centred POMs, i.e. shielding of the ^{31}P nucleus increases (low-frequency shift) on going from the lacunary to the more saturated species.

A rationale for the influence of the number of palladium ions is, however, hard to infer from the experimental data: actually, starting from $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ (–13.2 ppm),[51] progressive substitution of palladium for tungsten in the central belt leads successively to deshielding, shielding and deshielding of the phosphorus nuclei.

^{183}W NMR Spectra

The ^{183}W NMR spectra of compound **1** (Figure 2) have been recorded at room temperature from the mother solu-

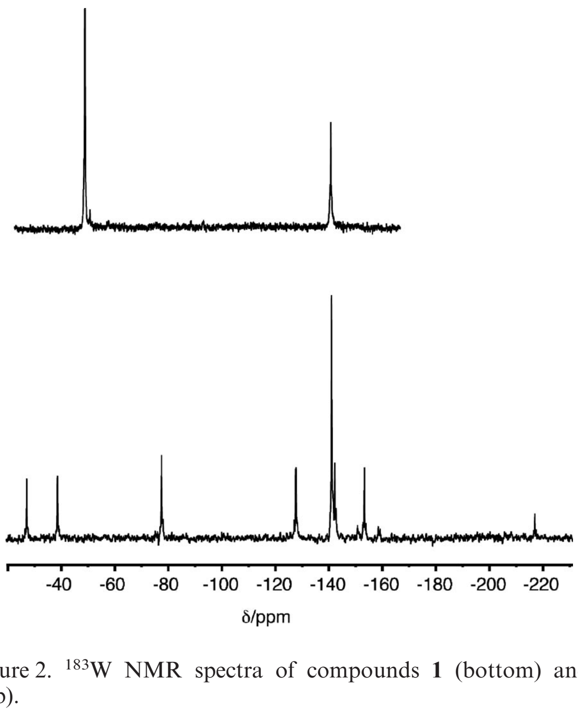


Figure 2. ^{183}W NMR spectra of compounds **1** (bottom) and **3** (top).

tion in which 0.2 mL of D_2O was added, as well as from an aqueous solution of the isolated potassium salt, both at room temperature and at 343 K to increase the solubility. According to the symmetry (C_{2v}) of its monovacant precursor $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ the symmetry of the $[PdP_2W_{20}O_{70}(H_2O)_2]^{8-}$ anion might also be C_{2v}; this should lead to a six-line spectrum (four lines with intensity 4 and two with intensity 2). However, the experimental room-temperature spectra are much more complex as they both display nine lines with the relative approximate intensity 2:2:2:2:6:2:1:2:1 (see Table 1 for chemical shift data), a pattern that does not agree with either C_{2v} symmetry, or any lower symmetry (C_s, C_2, C_1); in fact, the most intense signal (at –140.7 ppm) appears to result from the overlap of different resonances, as shown by the spectrum recorded at 343 K (two signals with relative intensity 2:4), as well as by the room temperature ^{31}P–^{183}W INEPT spectrum (Figure 3).[57] With that in mind, the ^{183}W NMR spectrum displays nine resonances with intensity 2, and two resonances with intensity 1, a spectrum consistent with the C_s symmetry group (a subgroup of C_{2v}) only. The precursor anion $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ contains two symmetry planes, a vertical one that exchanges inter alia the tungsten atoms of the equatorial crown and a horizontal one that contains these W atoms (and Pd) and exchanges the two $\{PW_9\}$ moieties. As proven by the ^{31}P NMR spectrum of **1**, which exhibits a unique resonance, the two $\{PW_9\}$ subunits remain equivalent in $[PdP_2W_{20}O_{70}(H_2O)_2]^{8-}$; accordingly the unique symmetry plane of **1** is that containing Pd and the two nonequivalent tungsten atoms of the central belt (Scheme 1).

Why/how should/might the two *trans*-$\{WO(H_2O)\}^{4+}$ fragments from the equatorial crown be nonequivalent? While in $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ the water molecules of these fragments are both pointing outside the cavity,[51] one of these two fragments may be reverted in **1** with its water molecule pointing inside the cavity. Non-equivalence of the two equatorial W atoms in **1** could also be due to the presence of one five-coordinate equatorial tungsten atom, as observed in the $[As^{III}_2W_{21}O_{69}(H_2O)]^{6-}$ anion.[58] This last hypothesis can however be ruled out as the square-pyramidal tungsten atoms in such POM structures are generally strongly deshielded. Actually for **1** the two ^{183}W signals with an intensity of 1 are both in the low frequency part of the spectrum and their chemical shifts (–148.5 and

Table 1. ^{31}P NMR and ^{183}W NMR chemical shifts for derivatives of the $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ anion.

	^{31}P chemical shift [ppm]	^{183}W chemical shift [ppm]
$[P_2W_{21}O_{71}(H_2O)_3]^{6-}$	–13.20	–108.3 (2 W), –108.5 (4 W), –124.7 (4 W), –129.7 (4 W), –131.2 (4 W), –152.3 (2 W), –225.9 (1 W)
$[P_2W_{20}O_{70}(H_2O)_2]^{10-}$	–12.35 (–10.05)	–74.6 (2 W), –100.1 (4 W), –142.6 (4 W), –158.6 (4 W), –159.3 (4 W), –195.3 (2 W)[63]
$[P_2W_{19}O_{69}(H_2O)]^{14-}$	–10.50	
$[PdP_2W_{20}O_{70}(H_2O)_2]^{8-}$ (**1**)	–12.85	–27.1 (2 W), –38.5 (2 W), –77.2 (2 W), –127.4 (2 W), –140.7 (6 W), –142 (2 W), –148.5 (1 W), –152.9 (2 W), –217 (1 W)
$[Pd_2P_2W_{19}O_{69}(H_2O)]^{10-}$ (**2**)	–14.20	
2′	–11.57	
$[Pd_3P_2W_{18}O_{68}]^{12-}$ (**3**)	–12.23	–59.4 (12 W), –151.3 (6 W)
$[\{Pd^{IV}{=}O(OH)\}\{WO(H_2O)\}P_2W_{18}O_{68}]^{13-}$	–11.70[41]	

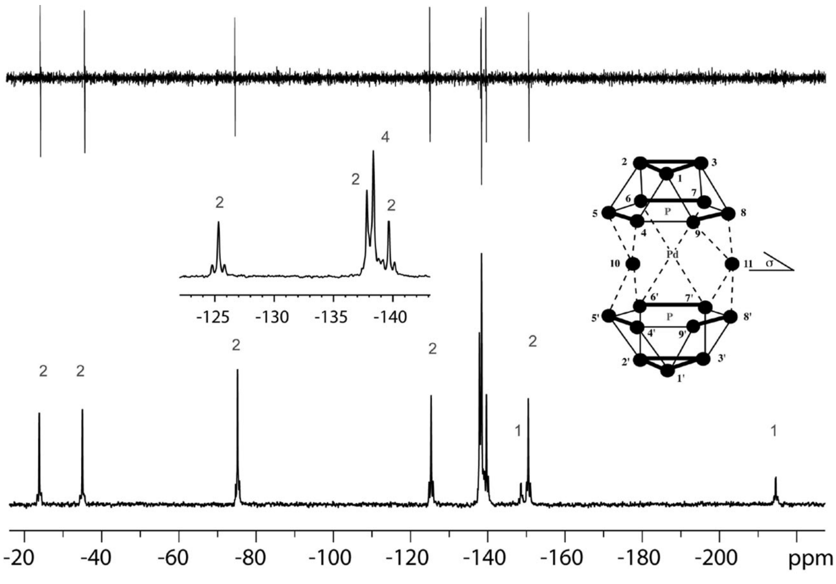
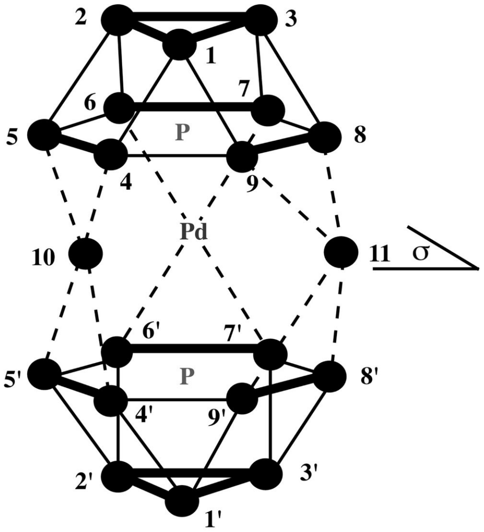


Figure 3. ^{183}W NMR spectra of $[PdP_2W_{20}O_{70}(H_2O)_2]^{8-}$; bottom: one-pulse spectrum (323K); top ^{31}P–^{83}W INEPT spectrum showing the resonances of the PW_9 moiety only.



Scheme 1. Schematic representation of **1** showing the labelling of the W atoms of the anion.

–214.5 ppm) compare well with those reported by Tourné for $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ (–152.3 ppm W_i and – 225.9 W_e, where i and e holds for internal and external water molecules).[59] Assignment of these lines to the equatorial W atoms is reinforced by the absence of any coupling with phosphorus: in particular these signals are missing in the ^{31}P–^{183}W INEPT spectrum (Figure 3). Moreover the signal around –150 ppm is sometimes hardly observable and appears as a single narrow resonance only in isotopically pure H_2O solutions: this agrees with an internal water molecule that exchanges slowly during the NMR spectroscopic recordings in mixed H_2O/D_2O solutions giving rise to isotopically shifted signals from the three isotopic water molecules H_2O, HDO and D_2O. For further assignment it is necessary to determine the W–W connectivity either by measuring homonuclear ^2J(W–W) coupling constants or by performing correlation (1D- or 2D-COSY) spectroscopy experiments.[60]

In the absence of such information we can nevertheless assign some lines with the help of empirical considerations. It is well established that ^{183}W NMR chemical shifts are very sensitive to subtle structural modifications, for example metal substitution in POMs induces both high- and low-frequency shifts of the different tungsten resonances; it is therefore difficult to assign the ^{183}W NMR lines of **1** by comparison with the spectra of the parent compounds $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ and $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$, which have been unambiguously assigned by Tourné and Domaille.[51,59] The stick spectra of Figure 4 show in particular that starting from $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ replacement of the three W atoms from the crown by Pd^{II} induces a dramatic deshielding (by ca. +70 ppm) of the two-bond remote belt nuclei and a significant shielding (ca. –40 ppm) of the four-bond remote cap nuclei. Removing one crown W atom from $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ also leads to shielding of the four-bond remote cap nuclei (ca. –30 ppm) while the farthest cap nucleus is deshielded (ca. +30 ppm); the belt nuclei that are close to the lacuna are also deshielded (ca. +30 ppm) while those still connected to the crown W atoms are shielded (–30 and –35 ppm). For Dawson and Dawson-like P-centred POMs, the ^2J(W–P) coupling constant is generally smaller for cap (ca. 1 Hz) than for belt W atoms (>1.5 Hz). From the INEPT experiment as well as from some well-resolved 1D spectra, the doublet at –77 ppm exhibits a small coupling of ca. 1.2 Hz. It is tempting to assign it to W1, the farthest atom from the lacuna at a very close chemical shift as for $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ (Scheme 1). Assuming that for belt nuclei the vicinity of palladium atoms is responsible for high frequency resonances, the two doublets at –27.2 and –38.6, both with ^2J(W–P) coupling values of ca. 1.6 Hz could be assigned to W6 and W7, deshielded by more than 60 ppm with respect to the corresponding nuclei (near the lacuna) in $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$.

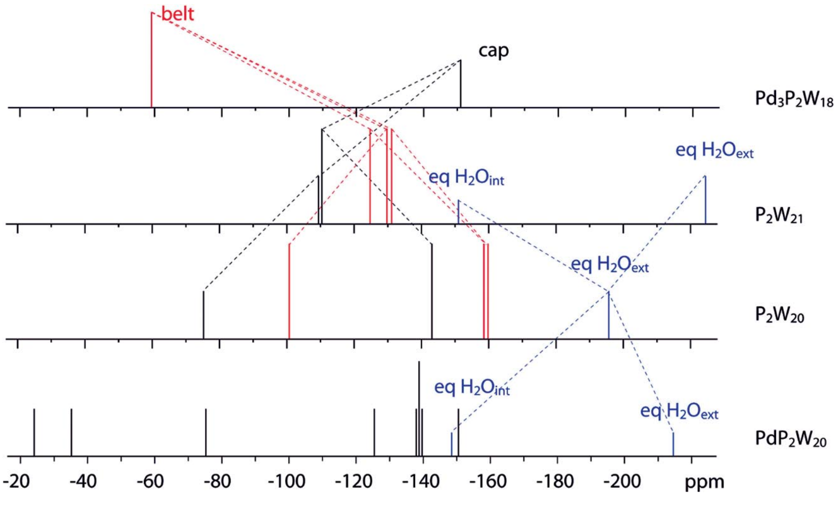


Figure 4. ^{183}W stick spectra of some POMs showing the differential shifts induced by W–Pd substitution or by W elimination.

The ^{183}W NMR spectrum of compound **3** (Figure 2) has been recorded at 343 K from a saturated solution of the potassium salt (less than 0.5 g in 2.5 mL H_2O/D_2O), and at room temperature from a more concentrated aqueous solution (0.7 g in 2.5 mL H_2O/D_2O) of its Li^+ salt obtained by metathesis with a saturated $LiClO_4$ solution. As expected for an anion with overall D_{3h} symmetry, the spectrum of **3** displays only two narrow resonances with a 2:1 relative intensity at –59.4 and –151.3 ppm (–42.5 and –140.6 ppm) for the Li^+ (K+) solution, respectively. The low frequency signal at –151.3 (–140.6) ppm is attributed to the six tungsten atoms from the two caps, and that at –59.4 (–42.5) ppm to the twelve tungsten atoms that are connected to the palladium centres. When compared with the Dawson anion [α-$P_2W_{18}O_{62}]^{6-}$ the relative positions of the two resonances are inverted and the "cap" signals are moderately shifted to low frequency (from –126 ppm) while the "belt" resonances are shifted to a higher frequency by more than 100 ppm (from –172 ppm). Moreover, while in the Dawson anion the homonuclear tungsten–tungsten cap-belt coupling $^2J_{W–W}$ amounts to 22 Hz, it is reduced to only 14 Hz in **3**. This demonstrates that the Pd–O–W interaction is not as strong as the W–O–W one, resulting in a relatively short W_{belt}–O(Pd) bond and, due to a *trans* influence, to a relatively large W_{belt}–O(W_{cap}) bond. The ^{183}W spectrum of **3** is reminiscent of those of the other derivatives of the [*A*,α-$PW_9O_{34}]^{9-}$ anion with C_{3v} symmetry. For instance, the spectra of the series of [*A*,α-$PW_9O_{34}(RSiOH)_3]^{3-}$ complexes (R = Et, Me, vinyl, Ph ...) also showed two resonances at about –80 (3 W) and –162 ppm (6 W), with a Δ(*δ*) in the range 81–86 ppm, which is typical of the *A* isomer.[61] More generally, both values are in the "classical" range for chemical shifts of tungsten atoms in diamagnetic heteropolytungstates, without any strongly shifted resonances. As usual for P-centred polyoxotungstates, both ^{183}W resonances of **3** appear – under resolution enhancement conditions – as doublets due to coupling with ^{31}P, with a small coupling ($^2J_{W–P}$ = 1.2 Hz) for the "cap" W atoms and a relatively larger coupling ($^2J_{W–P}$ = 1.8 Hz) for the "belt" ones.

Structural Characterization of Complexes 2 and 3

The structure of the compound $K_{10}[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ (**2**) has been determined by an X-ray diffraction study, and the corresponding anion is shown in Figure 5. The asymmetric unit contains half an anion, five cations and 15 water molecules of crystallization, the whole anion is localized on the mirror plane at *y* = 3/4. The structure of this anion can be described as the assembly of two {*A*,α-$PW_9O_{34}\}^{9-}$ subunits connected by one $\{WO(H_2O)\}^{4+}$ and two Pd^{2+} cations. The anion has the global C_{2v} symmetry. The coordination sphere of the three connecting cations is completed by two terminal oxo ligands from the lacuna of each {*A*,α-$PW_9O_{34}\}^{9-}$ subunit, where the O^{2-} ligands belong to the same dyad. The environment of both Pd^{II} ions is square planar, since the Pd–O distances are remarkably homogeneous [from 1.98(2) to 2.00(2) Å], and the O–Pd–O angles are all very close to 90° [from 87.9(6) to 91.9(6)°]. The $\{WO(H_2O)\}^{4+}$ fragment is quasi-linear with an $O_t(1)$–W(1)–$O_w(2)$ angle equal to 177.9(9)°, and presents a local approximate C_{4v} symmetry. The four O^{2-} ligands of the $\{PW_9\}$ do not display a square-planar environment around the tungsten atom. The deviation of the W atom from the calculated least-squares plane is 0.31 Å. With regard to this particular fragment, it is noteworthy that the water molecule $O_w(2)$ is pointing outside the lacuna. This represents a significant difference from the Si derivative $[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}SiW_9O_{34}\}_2]^{12-}$ described by the group of Kortz,[40] in which the terminal water molecule of the $\{WO(H_2O)\}^{4+}$ fragment is in an internal position. Also of interest is that the central belt of the anion of **2** is completed by three counterions as in the silicotungstate derivative. In our case, these cations are three potassium ions instead of one potassium and two caesium ions as in Kortz's compound (see Figure 6).

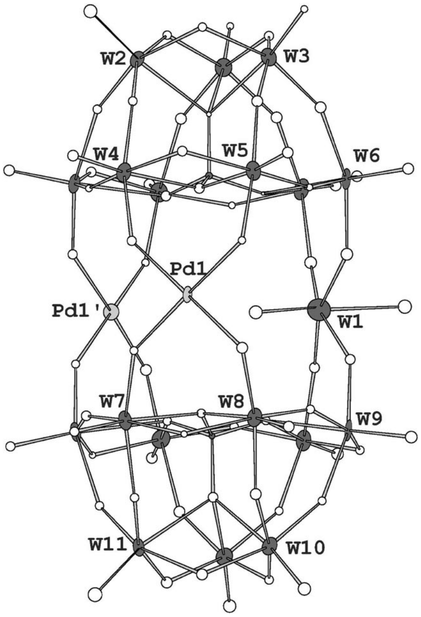


Figure 5. Structure of the anion of **2**. Thermal ellipsoids for tungsten, palladium and phosphorus atoms are given at the 80% probabilty level.

The preliminary single crystal analysis of **3** revealed that the asymmetric unit is composed of three independent thirds of an anion. Only 11 potassium cations have been found with the successive Fourier transforms because of the fairly poor quality of the crystals and consequently of the collected data. For these reasons it was not possible to determine the position of most of the water molecules of crystallization. The anion of **3** is composed of two {*A*,α-$PW_9O_{34}\}^{9-}$ subunits that are linked by three Pd^{II} cations, which form the central belt of the compound. The distances between each palladium ion and the four oxygen atoms, which delimit a square-planar environment, are in the range 1.72(4)–2.23(5) Å This large distribution of distances is due to the difficulty in refining the structure. Two other crystalline forms of this sandwich tripalladium structure have been recently reported by Hill and coworkers.[62] The all-potas-

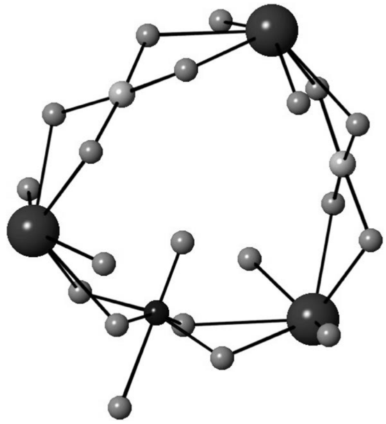


Figure 6. Drawing of the central belt of the anion of **2**. W atom: dark grey, O atoms: medium grey, Pd atom: pale grey, K atoms: large dark grey balls. The coordination sphere of the K^+ ions has not been completed for the sake of clarity.

sium salt $K_{12}[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 20H_2O$ crystallizes in the triclinic $P\bar{1}$ space group [a = 12.4963(10) Å, b = 15.7787(13) Å, c = 23.6600(19) Å, α = 81.443(2)°, β = 86.926(1)°, γ = 70.900(2)°], while the mixed Cs and K salt, $Cs_7K_5[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 18H_2O$, crystallizes in the triclinic $P\bar{1}$ space group [a = 13.1124(13) Å, b = 17.9240(18) Å, c = 19.687(2) Å, α = 96.873(2)°, β = 91.089(2)°, γ = 105.602(2)°].

Conclusion and Perspectives

In this paper we describe the high-yield synthesis of a series of stable water-soluble Pd^{II}-containing derivatives of the $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ anion with the general formula $[Pd_x\{WO(H_2O)\}_{3-x}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{(12-2x)-}$ for x = 1–3. These complexes, which differ in their palladium content, have been prepared by the direct reaction between Pd^{II} cations and the corresponding lacunary species, namely $[A,\alpha\text{-}PW_9O_{34}]^{9-}$, $[P_2W_{19}O_{69}(H_2O)]^{14-}$ and $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$. We have shown by ^{31}P NMR spectroscopy in solution that the reaction between $[P_2W_{19}O_{69}(H_2O)]^{14-}$ and palladium nitrate leads to the formation of two species that may be isomers. The structure of one of these compounds, $K_{10}[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ (**2**), has been determined by an XRD study. In this species the noble-metal cations display a square-planar environment since they are bound to four oxygen atoms of the two $\{PW_9\}$ subunits. A ^{183}W NMR spectroscopic study allowed us to fully characterize the compounds $K_8[Pd\{WO(H_2O)\}_2\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 20H_2O$ (**1**) and $K_{12}[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ (**3**). We have thus proved that the symmetry of the anion of **1** in solution is lower than the expected C_{2v} symmetry because of the opposite relative orientation of the two $\{W{=}O(H_2O)\}^{4+}$ fragments of the central belt. This study has also shown that the position of the water molecule (i.e. inside or outside the cavity of the POM) has a strong influence on the chemical shift of the corresponding W nucleus. More generally, despite the apparent ease of the preparation of these compounds, they have shown a certain versatility in solution: (i) an equilibrium has been highlighted between **2** and its isomer **2′** in water, (ii) at high temperature, and when the pH is controlled by acetate ligands, some of them quickly decomposed, leading in particular to rearrangements in the polyoxometalate framework and (iii) we probably observed the oxidation of Pd^{II} into Pd^{IV}, even if the evidence for the Pd^{IV} species is actually scarce. Efforts in this direction should nevertheless be followed since the characterization of noble-metal M=O oxo-containing POMs is of considerable interest for oxidation catalysis processes.

Experimental Section

Materials and Method: Palladium acetate and nitrate were purchased from Strem Chemicals and used as received. The heteropolytungstates $K_{10}[P_2W_{20}O_{70}(H_2O)_2]\cdot 24H_2O$,[56] $K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot xH_2O$[52] and $K_9[PW_9O_{34}]\cdot xH_2O$[56] have been prepared according to the literature. It is noteworthy that in solution $K_{10}[P_2W_{20}O_{70}(H_2O)_2]\cdot 24H_2O$ always shows two ^{31}P NMR lines at –12.35 (90%) and –10.05 (10%) ppm.[63] The latter signal cannot be attributed to the $[P_2W_{19}O_{69}(H_2O)]^{14-}$ anion since addition of solid $K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot xH_2O$ in the same NMR tube gives rise to a distinguishable signal at –10.5 ppm. The presence of both signals at δ = –12.35 and –10.05 ppm may then be due to an equilibrium between $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ and an unidentified species. The synthesis of $K_{12}[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot xH_2O$ was adapted from the literature[11] using the potassium salt $K_9[A,\alpha\text{-}PW_9O_{34}]\cdot xH_2O$ instead of $Na_8H[A,\alpha\text{-}PW_9O_{34}]\cdot 10H_2O$ as reported above. All solvents were obtained from commercial sources and used as received. IR spectra were recorded from KBr pellets with a Biorad FT 165 spectrometer. The ^{31}P MAS NMR experiments were performed on powdered samples at room temperature with a Bruker Avance 400 spectrometer (9.4 T) operating at 162 MHz. The samples were spun at 15 kHz in 2.5 mm-diameter rotors. The spectral width was 20 kHz (i.e. 125 ppm). The spectra were acquired using a simple one-pulse sequence with phase cycling (CYCLOPS sequence). The pulse duration was 0.5 µs, (ca. 15° flip angle) and the preacquisition and interpulse delays were 36 µs and 5 s, respectively. The ^{31}P NMR solution spectra were recorded at 121.5 MHz, in 5-mm o. d. tubes with a Bruker Avance 300 spectrometer equipped with a QNP probehead. The ^{183}W NMR spectra were recorded in 10-mm o. d. tubes at 20.8 MHz with a Bruker DRX500 spectrometer equipped with a broadband VSP probehead. Chemical shifts are referenced with respect to an external 85% H_3PO_4 solution (^{31}P NMR), and to an external alkaline 2 M Na_2WO_4 aqueous solution (^{183}W NMR), and were measured by the substitution method. For ^{183}W NMR spectroscopy a saturated aqueous solution of the dodecatungstosilicic acid ($H_4SiW_{12}O_{40}$) was used as a secondary standard (δ = –103.8 ppm). The ^{183}W NMR spectrum of $[Pd\{WO(H_2O)\}_2\{A,\alpha\text{-}PW_9O_{34}\}_2]^{8-}$ (**1**) in Figure 2 was recorded at room temperature from the mother solution in which 0.2 mL of D_2O was added and from an aqueous solution of its isolated potassium salt. The ^{31}P–^{183}W INEPT spectrum of **1** (Figure 3) has been recorded from a solution of its lithium salt obtained by Li^+/K^+ metathesis with a saturated aqueous $LiClO_4$ solution. The spectrum was recorded at 12.5 MHz with the Bruker Avance 300 spectrometer equipped with a triple-resonance low-frequency probehead with a ^{31}P external decoupling coil. A standard INEPT sequence from the Bruker library was used with the following parameters: ^{183}W 90° pulse: 38 µs, ^{31}P 90° pulse: 46.5 µs, acquisition time: 2.18 s, 1/4 J delay: 178 ms, with optimal transfer for ^{2}J(W–P) = 1.4 Hz; interpulse delay (for ^{31}P relaxation): 5 s. Total experimental time: 63 h for 33600 transients. The ^{183}W NMR spectra of $[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]^{12-}$ (**3**) have been recorded at room temperature from a solution of its lithium salt obtained by Li^+/K^+ metathesis with a saturated aqueous $LiClO_4$ solution and at 343 K from a less-concentrated aqueous solution of its potassium salt. Elemental analyses were performed by the Service Central d'Analyse of the CNRS (Vernaison, France). Atomic absorption measurements for tungsten analysis were performed with a Perkin–Elmer Analyst 100 spectrophotometer. Gravimetric titrations for tungsten were performed according to the classical method using cinchonium hydrochloride.[64]

Synthesis of $K_8[Pd\{WO(H_2O)\}_2\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 20H_2O$ (1): A sample of $Pd(NO_3)_2\cdot H_2O$ (0.219 g, 0.88 mmol) was added to a solution of $K_{10}[P_2W_{20}O_{70}(H_2O)_2]\cdot 24H_2O$ (4.000 g, 0.70 mmol) in distilled water (10 mL). The colour of the solution turned brown, and a brown precipitate of **1** immediately appeared. The suspension was stirred for 30 min at room temperature. Potassium chloride (6 g) was added to the filtrate, which was then stirred at room temperature for a further two hours. The brown precipitate of **1**, which had progressively grown, was filtered, washed with ethanol (10 mL) and then air dried. Yield 4.49 g, 90%. $H_{44}K_8O_{92}P_2PdW_{20}$ (6065.41): calcd. K 5.51, P 1.09, Pd 1.88, W 64.80; found K 6.01, P 0.99, Pd 1.94, W 65.92. ^{31}P MAS NMR (15 kHz): δ = –12.9 (s) ppm. ^{31}P NMR (50% D_2O, 50% H_2O): δ = –12.9 (s) ppm. ^{183}W NMR (50% D_2O, 50% H_2O): δ = –27.1 (2 W), –38.5 (2 W), –77.2 (2 W), –127.4 (2 W), –140.7 (6 W), –142 (2 W), –148.5 (1 W), –152.9 (2 W), –217 (1 W) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1089 (s), 1030 (m), 1020 (sh), 958 (s), 927 (s), 855 (sh), 774 (vs), 720 (sh), 661 (m), 526 (m), 447 (m), 358 (s) cm^{-1}.

Syntheses of Complexes $K_{10}[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ (2) and 2′: A sample of $Pd(NO_3)_2\cdot H_2O$ (0.135 g, 0.54 mmol) was added to a solution of $K_{12}[P_2W_{19}O_{69}(H_2O)]\cdot 24H_2O$ (1.410 g, 0.25 mmol) in distilled water (10 mL). The colour of the solution immediately turned brown. After the addition of potassium chloride (1.5 g), the solution was stirred for a further 2 h during which a light brown precipitate progressively appeared. This precipitate was then filtered and washed with ethanol (10 mL); yield 1.1 g, 75%. $H_{62}K_{10}O_{100}P_2Pd_2W_{19}$ (5821.35):[65] calcd. K 6.72, P 1.06, Pd 3.66, W 60.01; found K 6.81, P 1.01, Pd 3.34, W 54.99, 60.42 (atomic absorption), 60.04 (gravimetric). ^{31}P NMR (50% D_2O, 50% H_2O): δ = –11.6 (**2′**) and –14.2 (**2**) ppm in a 1:1.1 ratio. ^{31}P MAS NMR (15 kHz): δ = –11.85 (**2′**) and –14.6 (**2**) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1090 (s), 1018 (m), 951 (s), 920 (s), 788 (vs), 715 (sh), 593 (m), 522 (m), 446 (w), 414 (w), 365 (s), 323 (sh) cm^{-1}.

Red plate crystals of **2** suitable for X-ray diffraction analysis were grown by room-temperature slow evaporation of the aqueous solution of $[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]^{10-}$.

Synthesis of $K_{12}[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ (3): A sample of $[Pd(NO_3)_2]\cdot H_2O$ (0.250 g, 1.01 mmol) was added to a solution of $K_9[A,\alpha\text{-}PW_9O_{34}]\cdot 16H_2O$ (1.5 g, 0.55 mmol) in distilled water (12 mL). A light-brown solid precipitate appeared immediately, and the mixture was stirred at room temperature for five minutes. The solid, which remains unidentified, was discarded by filtration, and potassium chloride (1.7 g) was then added to the orange/red solution, leading to the precipitation of $K_{12}[Pd_3\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ (**3**) as a light-brown solid; yield 0.70 g, 45%. $H_{60}K_{12}O_{98}P_2Pd_3W_{18}$ (5788.05): calcd. K 8.11, P 1.07, Pd 5.51, W 57.17; found K 7.80, P 1.16, Pd 5.67, 6.08 (atomic absorption), W 55.64. ^{31}P NMR (50% D_2O, 50% H_2O): δ = –12.25, (–12.35 for the Li^+ salt) ppm. ^{183}W NMR (343 K, H_2O/D_2O 90/10 v/v): δ = –42.5 (12 W, d, $^{2}J_{W-P}$ = 1.7 Hz), –140.6 (6 W, d, $^{2}J_{W-P}$ = 1.2 Hz) ppm. ^{183}W NMR (in saturated $LiClO_4$ solution + 10% D_2O): δ = –59.4 (12 W, d, $^{2}J_{W-P}$ 1.7, $^{2}J_{W-W}$ 14 Hz), –151.3 (6 W, d, $^{2}J_{W-P}$ 1.1, $^{2}J_{W-W}$ 14 Hz) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1077 (s), 1016 (m), 942 (s), 917 (s), 790 (vs), 693 (m), 524 (m), 451 (m), 418 (m), 394 (w), 370 (s), 355 (sh), 335 (m) cm^{-1}.

A preliminary single crystal analysis of **3** has been done on a crystal obtained by recrystallization of the crude product in water, but, unfortunately, the poor quality of the data set prevented the structural analysis from being completed (see Structural Characterization section). Crystallographic data: hexagonal lattice, space group *P*3, a = 19.751(2) Å, c = 18.006(2) Å, V = 5972.7(11) Å^3.

Crystal Structure Analysis of 2: A red plate crystal of $K_{10}[Pd_2\{WO(H_2O)\}\{A,\alpha\text{-}PW_9O_{34}\}_2]\cdot 30H_2O$ (**2**) was analyzed with a Kappa-CCD Enraf–Nonius diffractometer with Mo-K_α radiation (0.71073 Å). ϕ- and ω-scans were used. The data collection was performed at 250(2) K. Compound **2** crystallizes in the orthorhombic space group *Pnma*. The unit cell parameters are a = 24.856(5) Å, b = 19.729(3) Å, c = 18.119(3) Å, V = 8886(3) Å^3, Z = 4, ρ_{calc} = 4.209 g·cm^{-3}. The data were collected in the *hkl* range –31 to 34, –20 to 27, –25 to 10; 12811 independent reflections (R_{int} = 0.093); 7113 reflections had $I > 2\sigma(I)$. The structure was solved by direct methods using the program SHELXS86[66] and refined with full-matrix least-squares methods on F^2 using the SHELXL97 program.[67] Non-hydrogen atoms were refined anisotropically. Final R = 0.0738, R_w = 0.1821 for observed reflections. Structures were drawn with the program CAMERON.[68]

Supporting Information (see also the footnote on the first page of this article): Crystallographic CIF file for compound **2**, deposited at Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD 418950. ^{31}P NMR spectrum of the mother liquor from the reaction between $K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot xH_2O$ and $[Pd(NO_3)_2]\cdot H_2O$, and ^{31}P MAS NMR spectrum of the mixture of **2** and **2′** as their potassium salts in the solid state (Figure S1).^{31}P NMR spectrum of the solution obtained after reaction between $[Pd(OAc)_2]$ and $K_{10}[P_2W_{20}O_{70}(H_2O)_2]$ (Figure S2). ^{31}P MAS NMR spectrum of the mixture of **2** and **1** as their potassium salts in the solid state, obtained by slow evaporation of the mother liquor from the reaction between $K_{10}[P_2W_{20}O_{69}(H_2O)_2]$ and $[Pd(OAc)_2]$ (Figure S3).

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