Full paper/Mémoire

Connecting ruthenium substituted Keggin-type tungstophosphates by oxotungstic bridges: Evidence for the steric effect of {RuL₃}²⁺ (L₃ = η⁶-arene, (DM$\underline{S}$O)₃) fragments

Connection de dérivés ruthenium-tungstophosphates à structure de Keggin par des ponts oxo-tungstiques: mise en évidence de l'effet stérique des fragments {RuL₃}²⁺ (L₃ = η⁶-arene, (DM$\underline{S}$O)₃)

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A B S T R A C T

The intrinsic reactivity of the organoruthenium-grafted tungstophosphates [α-PW₁₁O₃₉{Ru(η⁶-arene)(H₂O)}]⁵⁻ and [α-PW₁₁O₃₉{Ru(DM$\underline{S}$O)₃(H₂O)}]⁵⁻ has been studied as a prerequisite for later catalytic studies. Upon reflux in aqueous solution, they partially transform into [{PW₁₁O₃₉Ru(η⁶-arene)}₂{WO₂}]⁸⁻ (when arene = benzene, toluene...) and [α-PW₁₁O₃₉{Ru(DM$\underline{S}$O)}]⁵⁻, respectively. In the former case, the conversion is markedly increased by deliberate addition of tungstate: through a solution NMR study, we show that [{PW₁₁O₃₉Ru(η⁶-p-cymene)}₂{WO₂}]⁸⁻ is quantitatively obtained by refluxing a 2:1:2 mixture of [α-PW₁₁O₃₉]⁷⁻, [Ru(η⁶-p-cymene)Cl₂]₂ and [WO₄]²⁻ at pH 3. In contrast, a different type of complex, [{PW₁₁O₃₉Ru(DM$\underline{S}$O)₃}₂{(WO₂(H₂O))₂O}]⁸⁻, is formed by reaction of [α-PW₁₁O₃₉{Ru(DM$\underline{S}$O)₃(H₂O)}]⁵⁻ with tungstate; it has been characterized by single crystal X-ray diffraction analysis of an acidic potassium salt, and by ¹⁸³W solution NMR. The more sterically demanding {Ru(DM$\underline{S}$O)₃}²⁺ fragment probably does not allow the formation of [{PW₁₁O₃₉Ru(DM$\underline{S}$O)₃}₂{WO₂}]⁸⁻, while connection of {PW₁₁O₃₉Ru(DM$\underline{S}$O)₃}⁵⁻ subunits is possible through the larger {(WO₂(H₂O))₂O}²⁺ bridge.

R É S U M É

L'étude de la réactivité intrinsèque des complexes [α-PW₁₁O₃₉{Ru(η⁶-arène)(H₂O)}]⁵⁻ et [α-PW₁₁O₃₉{Ru(DM$\underline{S}$O)₃(H₂O)}]⁵⁻ a été complétée pour servir de base à l'étude ultérieure de leur activité catalytique. Par chauffage à reflux en solution aqueuse, les premiers se transforment partiellement en [{PW₁₁O₃₉Ru(η⁶-arène)}₂{WO₂}]⁸⁻ (arène = benzène, toluène...), alors que le complexe [α-PW₁₁O₃₉{Ru(DM$\underline{S}$O)₃(H₂O)}]⁵⁻ est partiellement converti en [α-PW₁₁O₃₉{Ru(DM$\underline{S}$O)}]⁵⁻. La formation du complexe [{PW₁₁O₃₉Ru(η⁶-arène)}₂{WO₂}]⁸⁻ à partir de [α-PW₁₁O₃₉{Ru(η⁶-arène)(H₂O)}]⁵⁻ est favorisée par l'addition délibérée d'ions tungstate. Ainsi, un suivi de la réaction par RMN a montré

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que [{PW$_{11}$O$_{39}$Ru(η^6-*p*-cymène)}$_2${WO$_2$}]$^{8-}$ est obtenu quantitativement par chauffage à reflux d'une solution de [α-PW$_{11}$O$_{39}$]$^{7-}$, [Ru(η^6-*p*-cymène)Cl$_2$]$_2$ et [WO$_4$]$^{2-}$ dans les proportions 2:1:2, à pH 3. Dans le cas du complexe [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)$_3$(H$_2$O)}]$^{5-}$, l'addition de tungstate conduit à la formation d'un complexe d'un type différent, [{PW$_{11}$O$_{39}$Ru(DM<u>S</u>O)$_3$}$_2${(WO$_2$(H$_2$O))$_2$O}]$^{8-}$, qui a été caractérisé par diffraction des rayons X sur monocristal et RMN ^{183}W en solution. Le fragment {Ru(DM<u>S</u>O)$_3$}$^{2+}$ est plus volumineux que le fragment {Ru(η^6-*p*-cymène)}$^{2+}$, de sorte que la connexion de deux unités {PW$_{11}$O$_{39}$Ru(DM<u>S</u>O)$_3$}$^{5-}$ nécessite un pont oxotungstique plus étendu.

1. Introduction

Over the past 20 years, much emphasis has been laid on the unique properties of polyoxoanionic ligands [1], and many catalysts resulting from the grafting of transition metal cations on polyoxometalates (POMs) have been synthesized [2]. In particular, because of the unique catalytic potential of ruthenium [3], its association with polyoxoanions has drawn considerable interest [4,5].

We, and others, have been particularly interested in the incorporation of ruthenium in a polyoxometalate by grafting of {Ru(η^6-arene)}$^{2+}$ or {Ru(DM<u>S</u>O)$_n$}$^{2+}$ (n = 1, 2, or 3) moieties on the polyoxoanionic framework [6–11]. A small number of these compounds have been tested in oxidation and racemisation catalysis [1e,12]. Unfortunately, only in one case has the effort been made to relate the catalytic activity to the intrinsic reactivity of the precatalyst [12c]. The result of the latter study was promising, thus showing that the investigation of the intrinsic reactivity of ruthenium derivatives of polyoxometalates is important in order to understand their catalytic activity. Moreover, a systematic investigation of the behaviour of these species could help finding the best experimental conditions which might lead to the formation of a catalytically active species.

Among the different compounds described, the [α-PW$_{11}$O$_{39}${RuL$_3$(H$_2$O)}]$^{5-}$ compounds (L$_3$ = η^6-arene, (DM<u>S</u>O)$_3$) have drawn the attention of our group (Fig. 1) [8a,b]. In these anions, the {RuL$_3$}$^{2+}$ fragment is linked to two non-equivalent oxygen atoms of the lacuna of [α-PW$_{11}$O$_{39}$]$^{7-}$, and the ruthenium achieves an 18 electron configuration by coordination to an aqua ligand.

On the one hand, we performed a computational study in order to account for the regiospecificity of the grafting of

the ruthenium on the monolacunary Keggin anion [8b]. On the other hand, we started to investigate the intrinsic reactivity of these species, in order to see what options are available to release coordination sites around the ruthenium center. Indeed, in these compounds, the ruthenium is linked to a water molecule, which is generally considered as a labile ligand, and which could thus be substituted by a substrate molecule during a catalytic cycle. We have thus shown that under thermal activation, the [α-PW$_{11}$O$_{39}${Ru(η^6-arene)(H$_2$O)}]$^{5-}$ anions transform into [{PW$_{11}$O$_{39}$Ru(η^6-arene)}$_2${WO$_2$}]$^{8-}$ complexes [8a], whereas the [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)$_3$(H$_2$O)}]$^{5-}$ anion leads to the formation of [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)}]$^{5-}$ (Fig. 2) [8b]. However, under conventional heating, both of these transformations are incomplete. Whereas alternative more efficient ways of synthesis of [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)}]$^{5-}$ have been described [7,8a], the [{PW$_{11}$O$_{39}$Ru(η^6-arene)}$_2${WO$_2$}]$^{8-}$ anion remained a species difficult to synthesize. Moreover, evidence for structurally analogous [{PW$_{11}$O$_{39}$Ru(DM<u>S</u>O)}$_2${WO$_2$}]$^{8-}$ has not been obtained.

In order to better understand the reactivity of [α-PW$_{11}$O$_{39}${RuL$_3$(H$_2$O)}]$^{5-}$ complexes, we performed a detailed investigation of the formation of [{PW$_{11}$O$_{39}$Ru(η^6-arene)}$_2${WO$_2$}]$^{8-}$. In this article, we thus describe a high yield synthesis of [{PW$_{11}$O$_{39}$Ru(η^6-*p*-cymene)}$_2${WO$_2$}]$^{8-}$, and also report on the formation under analogous synthetic conditions of a new {Ru(DM<u>S</u>O)$_3$}$^{2+}$ derivative of a polyoxotungstate, [{PW$_{11}$O$_{39}$Ru(DM<u>S</u>O)$_3$}$_2${(WO$_2$(H$_2$O))$_2$O}]$^{8-}$, in which a {(H$_2$O)O$_2$W–O–WO$_2$(H$_2$O)}$^{2+}$ bridge ensures the connection between two {PW$_{11}$O$_{39}$Ru(DM<u>S</u>O)$_3$}$^{5-}$ subunits. Throughout the article, compounds [α-PW$_{11}$O$_{39}${Ru(η^6-arene)(H$_2$O)}]$^{5-}$, [{PW$_{11}$O$_{39}$Ru(η^6-arene)}$_2${WO$_2$}]$^{8-}$, [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)$_3$(H$_2$O)}]$^{5-}$, [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)}]$^{5-}$, , and [{PW$_{11}$O$_{39}$Ru(DM<u>S</u>O)$_3$}$_2${(WO$_2$(H$_2$O))$_2$O}]$^{8-}$ will be referred to as **PW$_{11}$Ru(arene)**, **{PW$_{11}$Ru(arene)}$_2$(WO$_2$)**, **PW$_{11}$Ru(dmso)$_3$**, **PW$_{11}$Ru(dmso)**, and **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)**, respectively.
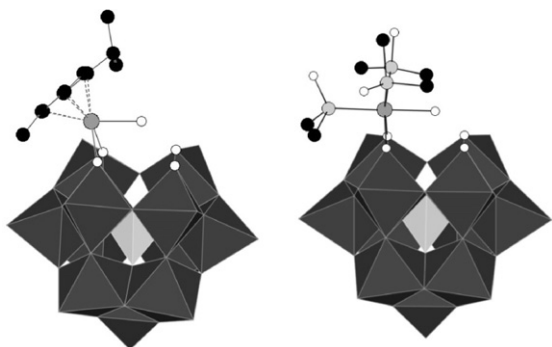
Fig. 1. Polyhedral representation of the structures of [α-PW$_{11}$O$_{39}${Ru(η^6-cymene)(H$_2$O)}]$^{5-}$ **PW$_{11}$Ru(pcym)** (left) and [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)$_3$(H$_2$O)}]$^{5-}$ **PW$_{11}$Ru(dmso)$_3$** (right) (for reasons of clarity, hydrogen atoms are not depicted.).

Fig. 2. Polyhedral representation of the structures of [{PW$_{11}$O$_{39}$Ru(η^6-C$_6$H$_6$)}$_2${WO$_2$}]$^{8-}$ **{PW$_{11}$Ru(benz)}$_2$(WO$_2$)** (left) and [α-PW$_{11}$O$_{39}${Ru(DM<u>S</u>O)}]$^{5-}$ **PW$_{11}$Ru(dmso)** (right) (for reasons of clarity, hydrogen atoms are not depicted.).
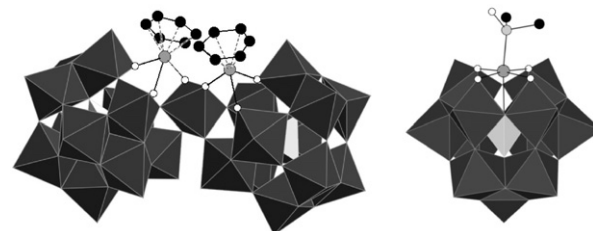
2. Experimental

2.1. Reagents

K$_7$[α-PW$_{11}$O$_{39}$]·14H$_2$O [13], K$_{10}$[P$_2$W$_{20}$O$_{70}$(H$_2$O)$_2$]·22H$_2$O [13], [Ru(*p*-cymene)Cl$_2$]$_2$ [14], *fac*-[RuCl$_2$(DM\underline{S}O)$_3$(DMS\underline{O})] [15] complexes were prepared as described in the literature. All other reagents were obtained from commercial sources and used as received.

2.2. Syntheses

2.2.1. Synthesis of Cs$_{8-x}$K$_x$[{PW$_{11}$O$_{39}$Ru(p-cymene)}$_2${WO$_2$}] (Cs$_{8-x}$K$_x$-{PW$_{11}$Ru(arene)}$_2$(WO$_2$))

To a solution of K$_7$[α-PW$_{11}$O$_{39}$]·14H$_2$O (0.819 g, 0.26 mmol, 1 eq) in 9 mL of distilled water, were subsequently added 248 µL of a 1 mol L^{-1} solution of Na$_2$WO$_4$ (0.25 mmol, 1 eq), 0.078 g of [Ru(*p*-cymene)Cl$_2$]$_2$ (0.13 mmol, 0.5 eq), and 13 mL of distilled water. The pH of the mixture was adjusted to pH = 3.0, by adding a few drops of 37% HCl. The suspension was refluxed for 16 h, during which time the ruthenium precursor progressively dissolved. After having been left to cool at room temperature, CsCl (0.344 g, 2.04 mmol, 8 eq) was added to the solution, leading to the precipitation of an orange solid, which was separated by filtration (0.5 g), and identified as a fairly pure mixed potassium/cesium salt of [{PW$_{11}$O$_{39}$Ru(*p*-cymene)}}$_2${WO$_2$}]$^{8-}$ based on comparison with the NMR and IR spectroscopic data previously reported for the potassium salt [8a].

2.2.2. Synthesis of {PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)

2.2.2.1. From [α-PW$_{11}$O$_{39}$]$^{7-}$. To a solution of K$_7$[α-PW$_{11}$O$_{39}$]·14H$_2$O (0.819 g, 0.26 mmol, 1 eq) in 9 mL of distilled water, were subsequently added 248 µL of a 1 mol.L^{-1} solution of Na$_2$WO$_4$ (0.25 mmol, 1 eq), 0.122 g of *fac*-[RuCl$_2$(DM\underline{S}O)$_3$(DMS\underline{O})] (0.25 mmol, 1 eq), and 1.5 mL of distilled water. The pH of the mixture was adjusted to pH = 3.0, by adding a few drops of 37% HCl. The solution was refluxed for 16 h, during which time the colour of the medium switched from yellow to dark brown. After having been left to cool at room temperature, KCl (0.650 g, 8.72 mmol, 35 eq) was added to the solution, leading to the progressive formation of a brown solid. After 24 h of stirring at room temperature, the precipitate was separated by filtration, dried with Et$_2$O, and identified as a fairly pure sample of K$_8$[{PW$_{11}$O$_{39}$Ru(DM\underline{S}O)$_3$}$_2${(WO$_2$(H$_2$O))$_2$O}]·12H$_2$O (K$_8$-{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)·12H$_2$O) (0.289 g, η ≈ 32%). IR (KBr, cm^{-1}): 3016 (w), 2924 (w), 1420 (w), 1320 (w), 1299 (w), 1125 (sh), 1098 (m), 1052 (m), 1040 (m), 1020 (w), 957 (s), 900 (m), 856 (sh), 834 (s), 809 (s), 775 (sh), 745 (sh), 706 (m), 620 (m), 516 (w), 429 (w), 365 (m), 263 (w). ^{1}H NMR (D$_2$O): δ = 3.25, 3.59, 3.60, 3.75, 3.81, 3.87 ppm (all singlets with equal intensities)[1]. ^{31}P NMR (D$_2$O): δ = −12.05 ppm. ^{183}W NMR (H$_2$O/D$_2$O): δ = −231.5, −179.4, −170.2, −149.0, −134.3, −131.6,

−131.1, −127.5, −109.5, −101.8, −98.8, −95.8 ppm (all singlets with equal intensities). Anal. Calcd for C$_{12}$H$_{64}$K$_8$P$_2$W$_{24}$O$_{103}$Ru$_2$S$_6$: C, 2.05; H, 0.92; S, 2.73; P, 0.88; Ru, 2.87; W, 62.69; K, 4.44. Found: C, 2.24; H, 1.25; S, 2.73; P, 0.86; Ru, 2.53; W, 65;77; K, 4.79[2].

2.2.2.2. From [P$_2$W$_{20}$O$_{70}$(H$_2$O)$_2$]$^{10-}$. To a solution of K$_{10}$[P$_2$W$_{20}$O$_{70}$(H$_2$O)$_2$]·22H$_2$O (0.940 g, 0.165 mmol, 0.5 eq) in 10 mL of distilled water, were added 0.162 g of *fac*-[RuCl$_2$(DM\underline{S}O)$_3$(DMS\underline{O})] (0.330 mmol, 1 eq), and 2 mL of distilled water. The pH of the mixture was adjusted to pH = 3.0, by adding a few drops of 37% HCl. The solution was refluxed for 20 h, during which time the colour of the medium switched from yellow to dark brown. After having been left to cool at room temperature, 0.492 g of KCl (6.60 mmol, 20 eq) were added (without precipitation) to the solution, which was then left to evaporate at 25 °C. After a few days, a small number crystals of K$_7$H[{PW$_{11}$O$_{39}${Ru(DM\underline{S}O)$_3$}}$_2${(WO$_2$(H$_2$O))$_2$O}]·10H$_2$O (K$_7$H–{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)·10H$_2$O). X-Ray-data: monoclinic, P 2$_1$/n, a = 23.345(2), b = 35.664(6), c = 25.817(3) Å, $β$ = 93.113(9)°, V = 21463(5) Å^3. The quality of these crystals was suitable for structure resolution.

Alternatively, when a greater quantity of KCl was added (0.738 g, 9.90 mmol, 30 eq) to the mixture of K$_{10}$[P$_2$W$_{20}$O$_{70}$(H$_2$O)$_2$]·22H$_2$O and *fac*-[RuCl$_2$(DM\underline{S}O)$_3$(DMS\underline{O})] after the 20 h reflux, a precipitate formed after several hours of stirring at room temperature. After filtration of the precipitate, which mainly contains the potassium salt of {PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$), small crystals formed in the filtrate upon slow evaporation at room temperature over a few days. X-Ray-data: monoclinic, C 2/c, a = 23.689(4), b = 35.384(7), c = 27.085(5) Å, $α$ = $γ$ = 90°, $β$ = 90.756(8)°, V = 21463(5) Å^3. A partial structure determination has confirmed the presence of {PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$), but a complete determination could not be achieved for these crystals due to the severe crystalline disorder.

2.3. Physical methods

2.3.1. Spectroscopic characterization

The ^{1}H (300.13 MHz, TMS) and ^{31}P (121.5 MHz, external 85% H$_3$PO$_4$) NMR spectra were obtained in solution on a Bruker Avance II 300 spectrometer equipped with a QNP probehead. The ^{183}W NMR spectrum was recorded in a 10 mm OD tube on a Bruker DRX 500 apparatus, operating at 20.8 MHz. The concentrated solution required for ^{183}W NMR was prepared by dissolving 800 mg of the potassium precipitate of {PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$) in a minimum volume of an aqueous saturated solution of LiClO$_4$, filtering off the precipitate of KClO$_4$, and adding 10% D$_2$O for field frequency lock. Chemical shifts were measured with reference to an external solution of Na$_2$WO$_4$ in alkaline D$_2$O.

2.3.2. X-ray crystallography

Crystal structure data for K$_7$H-{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)·10H$_2$O were collected, using a combination of φ and

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[1] In some cases, the signals located at δ(H) = 3.59 and 3.60 ppm overlap, to give only one signal of double intensity at 3.59 ppm.

[2] The EDXS analysis of the precipitate leads to a n(Ru)/n(W) ratio of 12.5.

ω scans, on a Nonius Kappa-CCD diffractometer (Table 1) with graphite monochromated Mo-Kα (0.71073 Å) radiation. Measurements were performed at 250 K. Unit cell parameters determination, data collection strategy and integration were carried out with the Nonius Eval-14 suite of programs [16a]. The data were corrected for absorption by a multiscan method [16b]. The structure was solved by direct methods with SHELXS-86 [16c], refined by full least-squares on F^2 and completed with SHELXL-97 [16d]. Graphics were carried out with DIAMOND [16e]. W, Ru and S atoms were refined with anisotropic displacement parameters. The H atoms identified on difference Fourier maps were included by using a riding model.

3. Results and discussion

3.1. Formation of $[\{PW_{11}O_{39}Ru(\eta^6\text{-}arene)\}_2\{WO_2\}]^{8-}$ ($\{PW_{11}Ru(arene)\}_2(WO_2)$)

In a previous study [8a], we had shown that by reacting $[Ru(\eta^6\text{-}arene)Cl_2]_2$ (arene = benzene, toluene, p-cymene) and $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ in water at 100 °C, $[\alpha\text{-}PW_{11}O_{39}\{Ru(\eta^6\text{-}arene)(H_2O)\}]^{5-}$ (**PW₁₁Ru(arene)**) first formed, and then evolved partially into $[\{PW_{11}O_{39}Ru(\eta^6\text{-}arene)\}_2\{WO_2\}]^{8-}$ (**{PW₁₁Ru(arene)}₂(WO₂)**). The formation of **{PW₁₁Ru(arene)}₂(WO₂)**, which consists of two $\{PW_{11}O_{39}Ru(\eta^6\text{-}arene)\}^{5-}$ subunits connected by a $\{WO_2\}^{2+}$ bridge, had not been anticipated. It can be formally expressed by Eq. (1), where the additional tungstate ions possibly result from the decomposition of some $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anions in situ[3]:

$$2[\alpha\text{-}PW_{11}O_{39}\{Ru(\eta^6\text{-}arene)(H_2O)\}]^{5-} + [WO_4]^{2-}$$
$$+ 4H_3O^+ = [\{PW_{11}O_{39}Ru(\eta^6\text{-}arene)\}_2\{WO_2\}]^{8-} + 6H_2O$$
$$\tag{1}$$
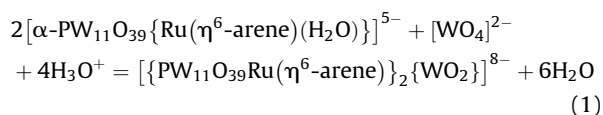
More recently, an alternative way of preparing these **{PW₁₁Ru(arene)}₂(WO₂)** compounds with a higher yield was reported by Nomiya et al. [10c]. In this case, $[PW_{11}O_{39}]^{7-}$ was first formed in situ by degradation of $[PW_{12}O_{40}]^{3-}$, before adding $[Ru(benzene)Cl_2]_2$, lowering the pH, and precipitating the resulting product. By this method, the tungstate fragments released in the first step are still available for the last step.

Considering Eq. (1), we looked at the possibility of improving the formation of **{PW₁₁Ru(arene)}₂(WO₂)** by deliberately adding tungstate to the reaction mixture. A mixture of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$, $[Ru(\eta^6\text{-}p\text{-}cymene)Cl_2]_2$, and $[WO_4]^{2-}$ in a 2:1:2 ratio was refluxed at pH = 3.0; after 16 h, **{PW₁₁Ru(pcym)}₂(WO₂)** is the only species detected in the mother liquor according to ^{31}P NMR. It is noteworthy that a slight excess of $[WO_4]^{2-}$ is necessary for the quantitative formation of **{PW₁₁Ru(pcym)}₂(WO₂)** in solution. This compound was then isolated by precipitation, by adding CsCl.

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[3] The minority signals observed on the ^{31}P NMR spectrum of the mother liquor during the transformation of **PW₁₁Ru(arene)** into **{PW₁₁Ru(arene)}₂(WO₂)** could result from the degradation of part of the $[PW_{11}O_{39}]^{7-}$ anions, which leads to the release of oxotungstic fragments.

Table 1
Crystal data and structure refinement parameters.

	$K_7H\text{-}\{PW_{11}Ru(dmso)_3\}_2(W_2O_5)\cdot 10H_2O$
Empirical Formula	$C_{12}K_7O_{101}P_2Ru_2S_6W_{24}$
$M_r/\text{g.mol}^{-1}$	6902.48
Color	Orange
Temperature/K	250
Crystal System	Monoclinic
Space Group	$P\,2_1/n$
a/Å	23.345(2)
b/Å	35.664(6)
c/Å	25.817(3)
α/°	90
β/°	93.113(9)
γ/°	90
V/Å³	21463
Z	8
$\rho_{calcd}/\text{g.cm}^{-3}$	4.272
μ/mm^{-1}	26.407
θ_{min}–$\theta_{max}/°$	2.04–25.06
h,k,l max	27,42,30
Reflcns collected	189215
Reflcns reported	37659
obsd reflcns (I > 2σ(I))	20845
refined param	1643
$R_{(int)}$	0.1037
R	0.0823
R_w (all data)	0.1938
goodness of fit S	1.085
$\Delta\rho(max/min)/\text{e.Å}^{-3}$	−3.53/3.23

All in all, these different studies demonstrate that **{PW₁₁Ru(arene)}₂(WO₂)**-type structures can be formed from **PW₁₁Ru(arene)**, by working under acidic conditions and in the presence of tungstate ions, in agreement with Eq. (1).

3.2. Formation of $[\{PW_{11}O_{39}Ru(DM\underline{S}O)_3\}_2\{(WO_2(H_2O))_2O\}]^{8-}$ ($\{PW_{11}Ru(dmso)_3\}_2(W_2O_5)$)
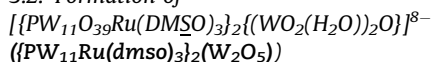
Previously, the progressive formation of $[\alpha\text{-}PW_{11}O_{39}\{Ru(DM\underline{S}O)\}]^{5-}$ (**PW₁₁Ru(dmso)**) was observed upon refluxing an aqueous solution of $[\alpha\text{-}PW_{11}O_{39}\{Ru(DM\underline{S}O)_3(H_2O)\}]^{5-}$ (**PW₁₁Ru(dmso)₃**) [8b]: the water molecule and two DMSO ligands are substituted by oxygen atoms of the lacuna. Given the investigation performed on the synthesis of **{PW₁₁Ru(arene)}₂(WO₂)**, we tried to see whether isostructural **{PW₁₁Ru(dmso)₃}₂(WO₂)** derivatives could be obtained. These efforts led to the characterization of a new species, **{PW₁₁Ru(dmso)₃}₂(W₂O₅)**, which has been obtained by two alternative methods.

On the one hand **{PW₁₁Ru(dmso)₃}₂(W₂O₅)** was obtained from a mixture of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$, fac-$[RuCl_2(DM\underline{S}O)_3(DMS\underline{O})]$, and $[WO_4]^{2-}$. Initially, a 2:2:1 mixture was refluxed at pH = 3.0 for 24 hours. At this stage, according to the ^{31}P NMR spectrum of the mother liquor, several compounds were present in solution: two major species ($\delta(P) = -12.05$ and -12.25 ppm), **PW₁₁Ru(dmso)₃** ($\delta(P) = -11.03$ ppm), and two minor species ($\delta(P) = 0.54$ ppm – phosphate ions – and $\delta(P) = -6.69$ ppm)[4]. The chemical

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[4] The corresponding ^1H NMR spectrum is particularly complicated in the region in which the signals of the DM\underline{S}O ligands appear.

shifts of the major species are shifted towards lower frequency with respect to **PW$_{11}$Ru(dmso)$_3$**. Since the chemical shifts of **{PW$_{11}$Ru(arene)}$_2$(WO$_2$)** anions are also shifted towards lower frequencies in comparison with those of **PW$_{11}$Ru(arene)** [8a] (at variance with that of **PW$_{11}$Ru(dmso)** found at −10.89 ppm), we supposed that the signals at −12.05 and −12.25 ppm might correspond to species in which {PW$_{11}$O$_{39}$\{Ru(DM$\underline{S}$O)$_3$\}}$^{5-}$ subunits are associated through oxotungstic bridges.

Then, in order to achieve higher conversion of **PW$_{11}$Ru(dmso)$_3$**, the reaction was repeated in the presence of an extra equivalent of tungstate. After 15 minutes of reflux, four major species were present in the mother liquor: **PW$_{11}$Ru(dmso)$_3$**, and three other complexes (δ(P) = −11.20, −11.90 and −12.05 ppm). After 16 hours of reflux, three major species were present (δ(P) = −12.05, −12.20 and −12.25 ppm), while **PW$_{11}$Ru(dmso)$_3$** was no longer detected[5]. These observations tend to show that after 16 hours, the major signals correspond to species resulting from the reaction of **PW$_{11}$Ru(dmso)$_3$** with tungstate anions. At this stage, addition of KCl (25 eq) led to the progressive formation of a brown solid, which was separated by filtration and characterized by solution NMR: the ^{31}P NMR spectrum shows only one major signal at −12.05 ppm[6], while the corresponding ^{1}H NMR spectrum displays six signals of equal intensity in the region which corresponds to DM$\underline{S}$O ligands. All attempts to get single crystals suitable for X-ray crystallography from this precipitate were unfortunately unsuccessful.

On the other hand, **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** was obtained by reacting [P$_2$W$_{20}$O$_{70}$(H$_2$O)$_2$]$^{10-}$ with *fac*-[RuCl$_2$(DM$\underline{S}$O)$_3$(DM$\underline{S}$O)]. After 20 hours of reflux of an aqueous solution containing a 1:2 mixture of K$_{10}$[P$_2$W$_{20}$O$_{70}$] and *fac*-[RuCl$_2$(DM$\underline{S}$O)$_3$(DM$\underline{S}$O)] at pH = 3.0, the ^{31}P NMR spectrum of the mother liquor indicates the presence of three major species (δ(P) = 0.50, −12.05 and −12.25 ppm) and of one minor species (δ(P) = −10.05 ppm). The signal located at 0.50 ppm can be assigned to phosphate anions, which attests to the decomposition of some [P$_2$W$_{20}$O$_{70}$(H$_2$O)$_2$]$^{10-}$ anions with release of oxotungstate fragments. The two other major signals display the same chemical shifts as those observed in the course of the synthesis from [PW$_{11}$O$_{39}$]$^{7-}$ (*vide supra*), thus suggesting that by working at the same pH and with similar n(Ru)/n(P) and fairly similar n(Ru)/n(W) ratios (Ru/W = 2/20 *vs* 2/24), the same species tend to form in the mother liquor.

By adding a small quantity of KCl to this solution, a few red crystals appeared after several weeks of slow evaporation at room temperature, whose IR spectrum was identical to that of the compound obtained from [PW$_{11}$O$_{39}$]$^{7-}$, and which allowed a single crystal X-ray analysis. Crystals obtained upon addition of a larger quantity of KCl proved unsuitable for complete X-ray structure analysis (Section 2.2.2.2).

Table 2
Interatomic distances and bond angles around the ruthenium and the ditungstate bridges in the two independent anions in K$_7$H-{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)·10H$_2$O. The labeling of the atoms corresponds to the one given in Fig. 4.

	Anion 1		Anion 2	
Distance (Å)				
W$=\!=$O	1.70 (4)	1.72 (3)	1.70 (4)	1.73 (4)
W–OH$_2$	2.23 (4)	2.19 (3)	2.28 (4)	2.28 (4)
W–O$_{L1}$	1.86 (4)	1.85 (4)	1.87 (4)	1.87 (3)
W–O$_{L2}$	2.28 (4)	2.05 (4)	2.16 (5)	2.16 (4)
W–O$_{Ru}$	1.81 (3)	1.75 (4)	1.77 (3)	1.67 (3)
W–O$_B$	1.88 (4)	1.94 (4)	1.89 (4)	1.90 (4)
Ru–O$_{L3}$	2.18 (4)	2.01 (4)	2.07 (4)	2.06 (4)
Ru–O$_{L4}$	2.43 (4)	2.17 (3)	2.09 (3)	2.10 (3)
Ru–O$_{Ru}$	1.95 (4)	2.07 (4)	2.02 (3)	2.13 (3)
Ru–S	2.224 (17)	2.224 (17)	2.24 (2)	2.206 (17)
	2.274 (15)	2.262 (17)	2.25 (2)	2.237 (18)
	2.251 (16)	2.287 (17)	2.27 (2)	2.245 (17)
Ru···Ru	8.84		8.65	
Angles (°)				
W–O$_B$–W	145.1 (19)		146 (2)	
W–O$_B$–Ru	163 (2)		161.1 (19)	
	164 (2)		165.3 (18)	

3.3. X-ray crystal structure analysis of K$_7$H[{PW$_{11}$O$_{39}$Ru(DM$\underline{S}$O)$_3$}}$_2$\{(WO$_2$(H$_2$O))$_2$O}]·10H$_2$O

The asymmetric unit contains two crystallographically independent [{PW$_{11}$O$_{39}$Ru(DM$\underline{S}$O)$_3$}$_2$\{(WO$_2$(H$_2$O))$_2$O}]$^{8-}$ anions, which only slightly differ in their interatomic distances and bond angles (Table 2). A polyhedral representation of one of these is depicted on Fig. 3, while ball and stick representations of both anions showing the full atom labelling scheme can be found in the supplementary material.

{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$) can be described as the assembly of two {α-PW$_{11}$O$_{39}$Ru(DM$\underline{S}$O)$_3$}$^{5-}$ subunits through a {(WO$_2$(H$_2$O))$_2$O}$^{2+}$ bridge. The metal-oxygen distances within the two subunits are similar, and the anion has an overall *pseudo-C$_2$* symmetry, with the binary axis bisecting the {(WO$_2$(H$_2$O))$_2$O}$^{2+}$ group. In each {α-PW$_{11}$O$_{39}$\{Ru(DM$\underline{S}$O)$_3$\}}$^{5-}$ entity, the ruthenium is linked to two non equivalent oxygen atoms of the lacuna of [α-PW$_{11}$O$_{39}$]$^{7-}$,[7] three DM$\underline{S}$O ligands, and one oxo ligand of the {(WO$_2$(H$_2$O))$_2$O}$^{2+}$ bridge.

As depicted on Fig. 4, the environment around the tungsten atoms of the bridge, which will be referred to as W$_p$, is strongly distorted. Each tungsten is linked to the two remaining oxygen atoms of the lacuna of [α-PW$_{11}$O$_{39}$]$^{7-}$, two other bridging oxygen atoms (O$_{Ru}$ and O$_B$), one

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[5] At this stage, two very minor species are also detected (δ(P) = 2.27 and −13.05 ppm).

[6] Signals of very weak intensity are also detected at δ(P) = 2.27, −11.21 and −12.95 ppm.

[7] It is noteworthy that so far, no crystal structure of **PW$_{11}$Ru(dmso)$_3$** has been obtained. For this anion, the regiospecific grafting of the ruthenium onto the lacuna has been deduced from the comparison of its IR spectrum with that of **PW$_{11}$Ru(pcym)**, and from a complete computational study of the coordination of {RuL$_3$(H$_2$O)}$^{2+}$ (L$_3$ = (DM$\underline{S}$O)$_3$, η^6-arene) fragments on [PW$_{11}$O$_{39}$]$^{7-}$ [8b]. The crystal structure of **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** completely confirms these results. Indeed, given that **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** can form by reaction between two **PW$_{11}$Ru(dmso)$_3$** entities, and considering the fact that the mode of grafting of the ruthenium is similar for **PW$_{11}$Ru(arene)** and **{PW$_{11}$Ru(arene)}$_2$(WO$_2$)**, it appears that in **PW$_{11}$Ru(dmso)$_3$**, the metal is also linked to two non equivalent oxygen atoms of the lacuna.
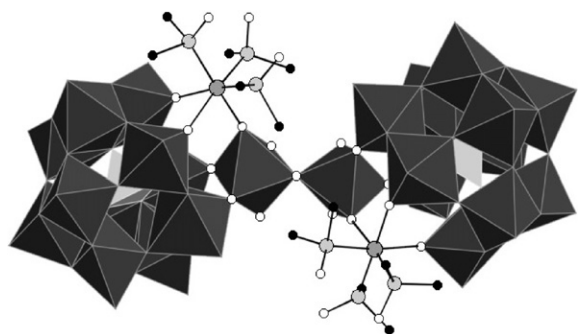
Fig. 3. Polyhedral representation of $[\{PW_{11}O_{39}Ru(DM\underline{S}O)_3\}_2\{(WO_2(H_2O))_2O\}]^{8-}$.
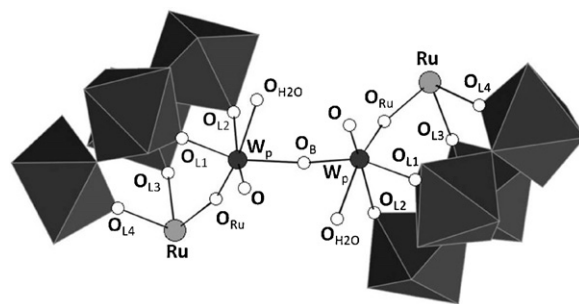

Fig. 4. Representation of the $\{(WO_2(H_2O))_2O\}^{2+}$ bridge in **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** showing the labelling scheme used in Table 2.
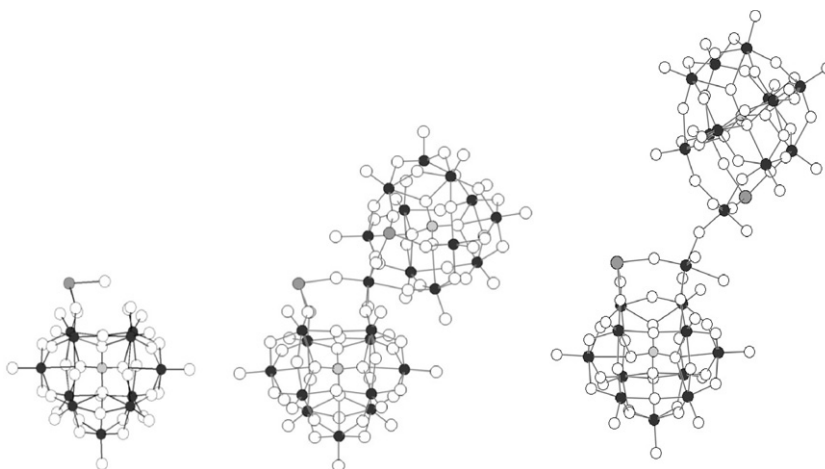

Fig. 5. Oxometallic frameworks of PW$_{11}$Ru(arene) and PW$_{11}$Ru(dmso)$_3$ (left), {PW$_{11}$Ru(arene)}$_2$(WO$_2$) (middle) and {PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$) (right).

terminal oxygen atom, and one aqua ligand. The latter is unambiguously identified by the corresponding W–O bond length (Table 2), by comparison with other W^{VI}–OH$_2$ distances reported in the literature [17].

The oxometallic frameworks of **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** and **{PW$_{11}$Ru(arene)}$_2$(WO$_2$)** are clearly different, as shown in Fig. 5. Indeed, although they are both based on the association of two $\{\alpha\text{-}PW_{11}O_{39}(RuL_3)\}^{5-}$ subunits (L$_3$ = η^6-arene, (DM$\underline{S}$O)$_3$; Fig. 5 left), they contain different types of oxotungstic bridges: a small $\{WO_2\}^{2+}$ bridge is present in **{PW$_{11}$Ru(arene)}$_2$(WO$_2$)**, whereas a bigger $\{(WO_2(H_2O))_2O\}^{2+}$ bridge is found in **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)**. This leads to Ru···Ru distances between the two connected $\{\alpha\text{-}PW_{11}O_{39}(RuL_3)\}^{5-}$ fragments of ~6.2 Å in **{PW$_{11}$Ru(benz)}$_2$(WO$_2$)** [8a], and ~8.7 Å in **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** (Table 2). The more sterically demanding $\{Ru(DM\underline{S}O)_3\}^{2+}$ fragment probably does not allow the formation of $[\{\alpha\text{-}PW_{11}O_{39}Ru(DM\underline{S}O)_3\}_2\{WO_2\}]^{8-}$.

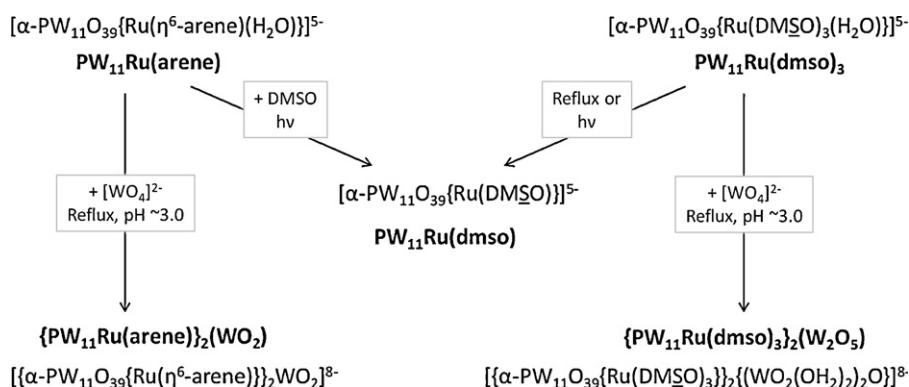### 3.4. Solution NMR characterization of {PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)

In solution, the ^{31}P NMR spectrum of **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** only displays one signal (δ = –12.05 ppm), suggesting that the whole anion has C_2 symmetry, with the

C_2 axis passing through the central oxygen atom of the $\{(WO_2(H_2O))_2O\}^{2+}$ bridge, in agreement with the solid state structure. On the ^{1}H NMR spectrum, the observation of six singlets of equal intensity shows that the methyl groups are inequivalent, which means that there is no rotation around the Ru–S bond, as in the case of **PW$_{11}$Ru(dmso)$_3$** [8b].

The ^{183}W NMR spectrum of **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** was recorded on a solution prepared by addition of the potassium salt to a saturated aqueous solution of LiClO$_4$, followed by filtration of precipitated KClO$_4$. As depicted on Fig. 6, the spectrum mainly displays a twelve-line pattern, in agreement with the C_2 symmetry of the whole anion[8].

^{183}W NMR chemical shifts of diamagnetic Keggin oxotungstate anions and of their lacunary derivatives are generally higher than –200 ppm [18]. This is also the case for **PW$_{11}$Ru(arene)** and **{PW$_{11}$Ru(arene)}$_2$(WO$_2$)** [8a]. Thus, in the case of **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)**, the 11 peaks with chemical shifts between –90 and –180 ppm are assigned to the tungsten atoms of the $\{\alpha\text{-}PW_{11}O_{39}Ru(DM\underline{S}O)_3\}^{5-}$ subunits, whereas the peak at

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[8] A few signals of weak intensity, due to unidentified impurities, also appear on the spectrum.

$[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{Ru}(\eta^6\text{-arene})(\text{H}_2\text{O})\}]^{5-}$

PW$_{11}$Ru(arene)

$[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{Ru}(\text{DM}\underline{\text{S}}\text{O})_3(\text{H}_2\text{O})\}]^{5-}$

PW$_{11}$Ru(dmso)$_3$

| | + DMSO hv | Reflux or hv | |

$[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{Ru}(\text{DM}\underline{\text{S}}\text{O})\}]^{5-}$

PW$_{11}$Ru(dmso)

| + [WO$_4$]$^{2-}$ Reflux, pH ~3.0 | | + [WO$_4$]$^{2-}$ Reflux, pH ~3.0 |

{PW$_{11}$Ru(arene)}$_2$(WO$_2$)

$[\{\alpha\text{-PW}_{11}\text{O}_{39}\{\text{Ru}(\eta^6\text{-arene})\}\}_2\text{WO}_2]^{8-}$

{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)

$[\{\alpha\text{-PW}_{11}\text{O}_{39}\{\text{Ru}(\text{DM}\underline{\text{S}}\text{O})_3\}\}_2\{(\text{WO}_2(\text{OH}_2))_2\text{O}\}]^{8-}$

Scheme 1. Summary of the reactivity of $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{RuL}_3(\text{H}_2\text{O})\}]^{5-}$ species (L$_3$ = η^6-arene, (DM$\underline{\text{S}}$O)$_3$).
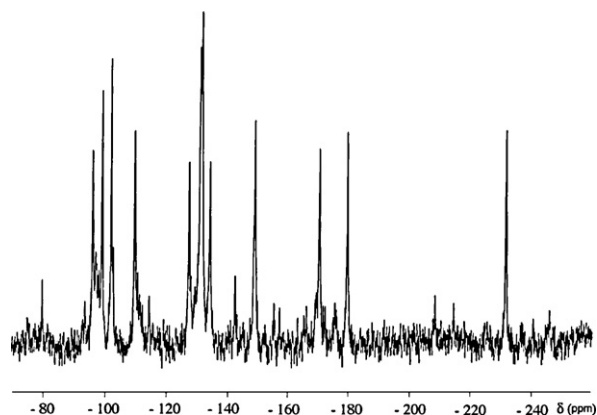
Fig. 6. ^{183}W NMR spectrum of an aqueous solution of the lithium salt of **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)** (spectrometer time: 39 h).

−231.5 ppm can be assigned to the tungsten atoms of the $\{(\text{WO}_2(\text{OH}_2))_2\text{O}\}^{2+}$ bridge. Such a shielding can be related to the significantly different local geometry of bridging W$_p$ [19]. It is noteworthy that, in polyoxotungstates, six-coordinated tungsten centres bearing an aqua ligand generally give rise to the lowest-frequency resonances [17].

4. Conclusion

In this article, the synthesis of polyoxoanions made of two $\{\alpha\text{-PW}_{11}\text{O}_{39}(\text{RuL}_3)\}^{5-}$ subunits (L$_3$ = η^6-arene, (DM$\underline{\text{S}}$O)$_3$) connected via oxotungstic bridges has been described. This study completes our investigation of the reactivity of $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{RuL}_3(\text{H}_2\text{O})\}]^{5-}$ [8a,b,e], as summarized in Scheme 1.

On the one hand, an improved synthesis of $[\{\alpha\text{-PW}_{11}\text{O}_{39}\text{Ru}(\eta^6\text{-arene})\}_2\{\text{WO}_2\}]^{8-}$ anions is proposed for arene = p-cymene. On the other hand, a new ruthenium-substituted polyoxotungstate, $[\{\alpha\text{-PW}_{11}\text{O}_{39}\text{Ru}(\text{DM}\underline{\text{S}}\text{O})_3\}_2\{(\text{WO}_2(\text{H}_2\text{O}))_2\text{O}\}]^{8-}$, has been prepared by two alternative routes. To the best of our knowledge, it is the first polyoxotungstate that contains a bridging $\{\text{W}_2\text{O}_5\}^{2+}$ unit. The difference between the two structural types is ascribed to the greater bulkiness of the $\{\text{Ru}(\text{DM}\underline{\text{S}}\text{O})_3\}^{2+}$ fragment. It

should be remembered that through a computational study of the relative stabilities of the monolacunary Keggin anions and of their ruthenium-grafted derivatives, we had already underscored the influence of the steric bulk of the $\{\text{RuL}_3(\text{H}_2\text{O})\}^{2+}$ fragment [8e]. In that context, we wish to emphasize that Marie-Madeleine Rohmer was, together with Marc Bénard, the first to study the isomerism of organometallic derivatives of POMs and related compounds by computational methods [8f,g].

Appendix A. Supplementary material

CCDC 827349 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data (IR spectra of **[PW$_{11}$Ru(dmso)$_3$**, **{PW$_{11}$Ru(pcym)}$_2$(WO$_2$)** and **{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)**) and ball and stick representation displaying the labelling for the two independent $[\{\text{PW}_{11}\text{O}_{39}\text{Ru}(\text{DM}\underline{\text{S}}\text{O})_3\}_2\{(\text{WO}_2(\text{OH}_2))_2\text{O}\}]^{8-}$ anions present in the asymmetric unit of K$_7$H-**{PW$_{11}$Ru(dmso)$_3$}$_2$(W$_2$O$_5$)**. 10H$_2$O) can be found, in the online version, at doi:10.1016/j.crci.2011.08.009.

References

[1] (a) M.T. Pope, in: J. Mc Cleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 4, Elsevier, Oxford, UK, 2004, 635 p.;
(b) D.E. Katsoulis, M.T. Pope, J. Chem. Soc. Chem. Commun. (1986) 1186;
(c) C.L. Hill, R.B. Brown, J. Am. Chem. Soc. 108 (1986) 536;
(d) D. Mansuy, J.F. Bartoli, D.K. Lyon, R.G. Finke, J. Am. Chem. Soc. 113 (1991) 7222;
(e) M. Bonchio, M. Carraro, A. Sartorel, G. Scorrano, U. Kortz, J. Mol. Catal. A 251 (2006) 93;
(f) S.P.D. Visser, D. Kumar, R. Neumann, S. Shaikh, Angew. Chem. Int. Ed. 43 (2004) 5661;
(g) C.L. Hill, Chem. Rev. 98 (1998) 1, special issue on polyoxometalates.
[2] (a) C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407;
(b) R. Neumann, Prog. Inorg. Chem. 47 (1998) 317;
(c) N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev. 249 (2005) 1944;

(d) T.M. Anderson, K.I. Hardcastle, N. Okun, C.L. Hill, Inorg. Chem. 40 (2001) 6418;
(e) C.L. Hill, J. Mol. Catal. A 262 (1) (2007), special issue polyoxometalates in catalysis.

[3] (a) T. Naota, H. Takaya, S. Murahashi, Chem. Rev. 98 (1998) 2599;
(b) S. Komiya, M. Hirano, Ruthenium in Organic Synthesis, Wiley-VCH-Verlag, Weinheim, 2004;
(c) A. Fürstner, Angew. Chem. Int. Ed. Engl. 39 (2000) 3013;
(d) R.A. Sheldon, I.W.C.E. Arends, A. Dijksman, Catal. Today 57 (2000) 157;
(e) J.T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, J. Am. Chem. Soc. 118 (1996) 8961;
(f) R. Noyori, Angew. Chem. Int. Ed. 41 (2002) 2008;
(g) B.M. Trost, M.U. Frederiksen, M.T. Rudd, Angew. Chem. Int. Ed. 44 (2005) 6630.

[4] (a) C.Y. Rong, M.T. Pope, J. Am. Chem. Soc. 114 (1992) 2932;
(b) M. Sadakane, M. Higashijima, Dalton Trans. (2003) 659;
(c) M. Sadakane, D. Tsukuma, M.H. Dickman, B.S. Bassil, U. Kortz, M. Capron, X. Ueda, Dalton Trans. (2007) 2833;
(d) S.W. Chen, R. Villanneau, Y. Li, L.M. Chamoreau, K. Boubekeur, R. Thouvenot, P. Gouzerh, A. Proust, Eur. J. Inorg. Chem. (2008) 2137.

[5] (a) Y.V. Geletii, B. Botar, P. Kögerler, D.A. Hillesheim, D.G. Musaev, C.L. Hill, Angew. Chem. Int. Ed. 47 (2008) 3896;
(b) A. Sartorel, M. Carraro, G. Scorrano, R.D. Zorzi, S. Geremia, N.D. McDaniel, S. Bernhard, M. Bonchio, J. Am. Chem. Soc. 130 (2008) 5006;
(c) Y.V. Geletii, C. Besson, Y. Hou, Q.S. Yin, D.G. Musaev, D. Quinonero, R. Cao, K.I. Hardcastle, A. Proust, P. Kogerler, C.L. Hill, J. Am. Chem. Soc. 131 (2009) 17360;
(d) Y.V. Geletii, Q. Yin, Y. Hou, Z. Huang, H. Ma, J. Song, C. Besson, Z. Luo, R. Cao, K.P. O'Halloran, G. Zhu, C. Zhao, J.W. Vickers, Y. Ding, S. Mohebbi, A.E. Kuznetsov, D.G. Musaev, T. Lian, C.L. Hill, Isr. J. Chem. 51 (2011) 238.

[6] (a) D.J. Edlung, R.J. Saxton, D.K. Lyon, R.G. Finke, Organometallics 7 (1988) 1692;
(b) V.W. Day, T.A. Eberspacher, W.G. Klemperer, R.P. Planalp, P.W. Schiller, A. Yagasaki, B. Zhong, Inorg. Chem. 32 (1993) 1629;
(c) M. Pohl, Y. Lin, T.J.R. Weakley, K. Nomiya, M. Kaneko, H. Werner, R. Finke, Inorg. Chem. 34 (1995) 767.

[7] A. Bagno, M. Bonchio, A. Sartorel, G. Scorrano, Eur. J. Inorg. Chem. (2000) 17.

[8] (a) V. Artero, D. Laurencin, R. Thouvenot, P. Herson, P. Gouzerh, A. Proust, Inorg. Chem. 44 (2005) 2826;
(b) D. Laurencin, R. Villanneau, H. Gérard, A. Proust, J. Phys. Chem. A. 110 (2006) 6345;
(c) D. Laurencin, R. Villanneau, P. Herson, R. Thouvenot, Y. Jeannin, A. Proust, Chem. Commun. (2005) 5524;
(d) D. Laurencin, R. Thouvenot, K. Boubekeur, A. Proust, Dalton Trans. (2007) 1334, and references therein;
(e) D. Laurencin, A. Proust, H. Gérard, Inorg. Chem. 47 (2008) 7888;
(f) D. Laurencin, E. Garcia Fidalgo, R. Villanneau, F. Villain, P. Herson, J. Pacifico, H. Stoeckli-Evans, M. Bénard, M.M. Rohmer, G. Suss-Fink, A. Proust, Chem. Eur. J. 10 (2004) 208;
(g) D. Laurencin, R. Thouvenot, K. Boubekeur, F. Villain, R. Villanneau, M.-M. Rohmer, M. Bénard, A. Proust, Organometallics 28 (2009) 3140.

[9] (a) L. Bi, F. Hussain, U. Kortz, M. Sadakane, M. Dickman, Chem. Commun. (2004) 1420 (L.H. Bi, U. Kortz, B. Keita and L. Nadjo, Dalton Trans. (2004) 3184;

(b) L.H. Bi, U. Kortz, M.H. Dickman, B. Keita, L. Nadjo, Inorg. Chem. 44 (2005) 7485;
(c) L.H. Bi, N.H. Nsouli, E. Chubarova, M.H. Dickman, U. Kortz, B. Keita, L. Nadjo, Inorg. Chem. 45 (2006) 8575;
(d) S.S. Mal, N.H. Nsouli, M.H. Dickman, U. Kortz, Dalton Trans. (2007) 2627;
(e) L.H. Bi, S.S. Mal, N.H. Nsouli, M.H. Dickman, U. Kortz, S. Nellutla, N.S. Dalal, M. Prinz, G. Hofmann, M. Neumann, J. Clust. Sci. 19 (2008) 259;
(f) L.H. Bi, G. Al-Kadamany, E.V. Chubarova, M.H. Dickman, L. Chen, D.S. Gopala, R.M. Richards, B. Keita, L. Nadjo, H. Jaeensch, G. Mathys, U. Kortz, Inorg. Chem. 48 (2009) 10068.

[10] (a) K. Nomiya, H. Torii, K. Nomura, Y. Sato, Dalton Trans. (2001) 1506;
(b) Y. Sakai, A. Shinohara, K. Hayashi, K. Nomiya, Eur. J. Inorg. Chem. (2006) 163;
(c) K. Nomiya, K. Hayashi, Y. Kasahara, T. Iida, Y. Nagaoka, H. Yamamoto, T. Ueno, Y. Sakai, Bull. Chem. Soc. Jpn 80 (2007) 724.

[11] (a) L.H. Bi, B. Li, S. Bi, L.X. Wu, J. Solid State Chem. 182 (2009) 1401;
(b) L.H. Bi, G.F. Hou, B. Li, L.X. Wu, U. Kortz, Dalton Trans. (2009) 6345;
(c) L.H. Bi, G.F. Hou, L.X. Wu, U. Kortz, Cryst. Eng. Commun. 11 (2009) 1532.

[12] (a) M. Bonchio, G. Scorrano, P. Toniolo, A. Proust, V. Artero, V. Conte, Adv. Synth. Catal 344 (2002) 841;
(b) C.N. Kato, A. Shinohara, N. Moriya, K. Nomiya, Catal. Commun. 7 (2006) 413;
(c) D. Laurencin, R. Villanneau, A. Proust, A. Brethon, I.W.C.E. Arends, R. Sheldon, Tet. Asym. 18 (2007) 367.

[13] R. Contant, Can. J. Chem. 65 (1987) 568.

[14] (a) M.A. Bennett, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233;
(b) M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.

[15] (a) I.P. Evans, A. Spencer, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1973) 204;
(b) E. Alessio, G. Mestroni, G. Nardin, W.M. Attia, M. Calligaris, G. Sava, S. Zorzet, Inorg. Chem. 27 (1988) 4099;
(c) A. Mercer, J. Trotter, J. Chem. Soc., Dalton Trans. (1975) 2480.

[16] (a) A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, J. Appl. Crystallogr 36 (2003) 220;
(b) R.H. Blessing, Acta Cryst. A51 (1995) 33;
(c) G.M. Sheldrick, SHELX86 Computer Program for Structure Solution, University of Göttingen, Germany, 1986;
(d) G.M. Sheldrick, SHELX97 Computer Program for Structure Refinement, University of Göttingen, Germany, 1997;
(e) K. Brandenburg, M. Berndt, Diamond; Crystal Impact GbR, Bonn, Germany, 1999.

[17] (a) Y. Jeannin, J. Martin-Frère, J. Am. Chem. Soc 103 (1981) 1664;
(b) C.M. Tourné, G.F. Tourné, T.J.R. Weakley, J. Chem. Soc., Dalton Trans (1986) 2237;
(c) C.M. Tourné, G.F. Tourné, Chem. Soc., Dalton Trans (1988) 2411;
(d) Y. Jeannin, C.R. Acad. Sci. Paris, Série IIc 2 (1999) 161;
(e) R. Contant, R. Thouvenot, Y. Dromzée, A. Proust, P. Gouzerh, J. Clust. Sci. 17 (2006) 317;
(f) R. Villanneau, S. Renaudineau, P. Herson, K. Boubekeur, R. Thouvenot, A. Proust, Eur. J. Inorg. Chem. (2009) 479.

[18] Y.G. Chen, J. Gong, L.Y. Qu, Coord. Chem. Rev. 248 (2004) 245.

[19] L. Vilà-Nadal, J. Pedro-Sarasa, A. Rodriguez-Fortea, J. Igual, L.P. Kazansky, J.M. Poblet, Chem. Asian J. 5 (2009) 97.