# Microwave-Assisted Rapid Incorporation of Ruthenium into Lacunary Keggin-Type Polyoxotungstates: One-Step Synthesis, $^{99}$Ru, $^{183}$W NMR Characterization and Catalytic Activity of $[PW_{11}O_{39}Ru^{II}(DMSO)]^{5-}$

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Microwave irradiation for 15 minutes allowed the highly selective hydrothermal synthesis of the diamagnetic, air-stable oxidation catalyst $[PW_{11}O_{39}Ru^{II}(DMSO)]^{5-}$, as confirmed by $^{1}$H, $^{31}$P, $^{99}$Ru and $^{183}$W NMR techniques.

## Introduction

The design of transition metal based catalysts is finding new resources within the field of polyoxometalate chemistry.[1] In this respect, Keggin-type polyoxotungstates with mono-lacunary structures of formula $[XW_{11}O_{39}]^{n-}$ (X = B, Si, Ge, P, As), represent a unique class of ligands.[1][2] Properly referred to as inorganic porphyrin analogs,[2] they provide a rigid, hydrolytically stable, thermally robust, nonoxidizable framework that behaves as a pentadentate environment to include a catalytically active transition metal center.[1][2] Derivatization of such species with ruthenium retains a major interest in the field of homogeneous catalysis, especially within the domain of metal-mediated oxidations.[3−7] In fact, ruthenium porphyrin-based systems have been proved to carry out dioxygen activation,[8] to react with $N_2O$[9] and, in general, to promote highly chemo- and stereoselective oxidative transformations in the presence of various oxygen donors.[3][10] Despite their appealing potential, the synthesis of ruthenium-substituted polyoxotungstates is not straightforward and presents a series of problems, as indicated by the few literature reports published to date.[4−7] In particular: (i) use of the commercially available ruthenium source "$RuCl_3{\cdot}nH_2O$" produces either a mixture of undefined species or a low yield of the target compound; (ii) high temperatures and prolonged reaction times are generally needed; (iii) the formation of paramagnetic $Ru^{III}$ complexes hampers both the NMR monitoring of the reaction and the structural elucidation of the final product.

Herein we report that $[RuCl_2(DMSO)_4]$ (**1**)[11] reacts with the lacunary tungstate ligand $[PW_{11}O_{39}]^{7-}$ (**2**)[12] in water at 200 °C under microwave irradiation,[13] leading, after 15 minutes, to the complete incorporation of a ruthenium atom into the polyoxometalate framework, and to the selective production of the diamagnetic, air-stable, complex $[PW_{11}O_{39}Ru^{II}(DMSO)]^{5-}$ (**3**). Scheme 1 illustrates the synthetic approach described above and presents the optimized geometries of both **2** and **3** obtained with PM3(tm) semiempirical calculations.

$^{183}$W NMR spectroscopy provides an elegant tool to monitor the progress of the reaction. In Figure 1, spectra (a) and (b) allow us to examine the outcome of the metalation performed in water under conventional heating (100 °C, 1 atm, 48 hours), or under microwave irradiation (200 °C, 15 atm, 15 min), respectively.

As expected,[5] the formation of a $Ru^{II}$ complex leads to a marked deshielding of the signals relative to the two W atoms adjacent to the substituted center ($W_1$ and $W_4$ in Scheme 1). The new set of six resonances is consistent with the formation of a unique species **3**.[5] This can be easily seen in Figure 1a, where the resonances of both **3** and of the unreacted **2** are present in a ca. 50:50 ratio. Therefore, the spectroscopic analysis of both reaction mixtures highlights the remarkable acceleration of the process achieved by the microwave irradiation, as it results in the complete disappearance of the ligand signals after only 15 minutes (Figure 1b).

The assignment of the six resonances pertaining to the ruthenium complex **3** (W atom labels are shown in Scheme 1) is based on the analysis of W−W connectivities and $^{2}J_{WOW}$ scalar couplings determined from $^{183}$W NMR COSY experiments with selective excitation (see Experimental Section). A sample spectrum is shown in Figure 2, while the complete set of results is collected in Table 1.

Homonuclear $^{183}$W 2D COSY or INADEQUATE techniques have been employed for the structural elucidation of polyoxotungstates.[12] However, since the number of scalar couplings present in such systems is relatively small, the 1D COSY technique with selective excitation[14] provides an attractive alternative, since it allows for the collection of all connectivity information in separate experiments (whose number will not exceed the number of tungsten resonances) retaining the high resolution typical of 1D spectra.

As further evidence confirming the complete substitution and the selectivity of the process, analysis of the reaction mixture by $^{99}$Ru NMR spectroscopy revealed a single signal, relative to **3**, at $\delta = 7737$ (Figure 3), whereas the signal for the precursor **1** is found at $\delta = 3976$. To the best of our

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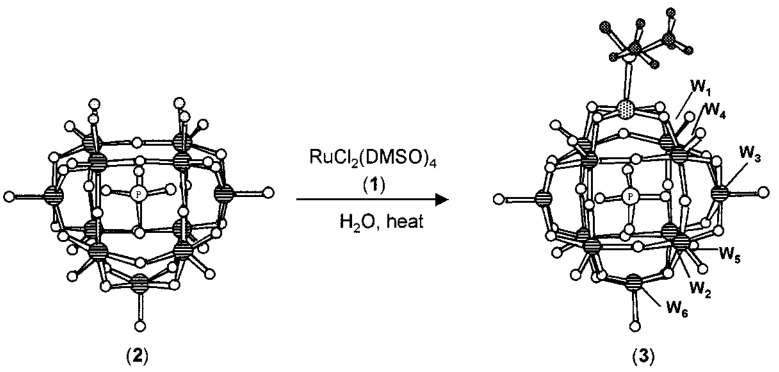

Scheme 1. W hatched, O white, Ru dotted; dark pattern spheres represent the atoms of the DMSO residue; W atoms are labelled according to the $^{183}$W NMR assignments (see text)

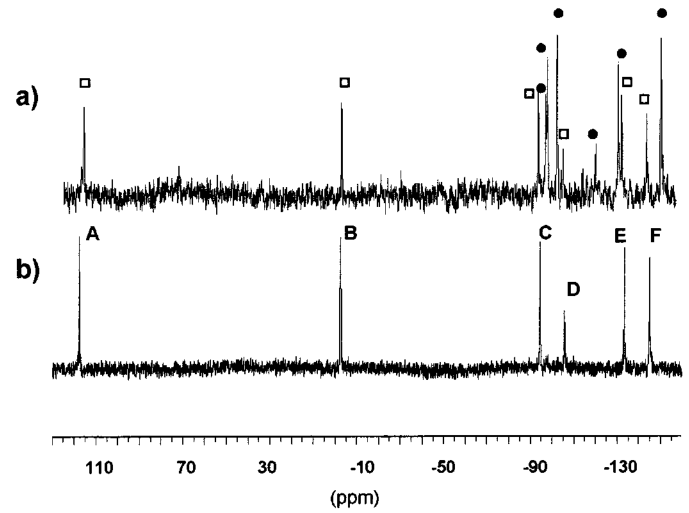

Figure 1. $^{183}$W NMR spectra of the reaction mixtures (a) conventional heating, filled circles: signals of the unchanged **2**; open squares: signals of (**3**); (b) MW irradiation; letters indicate the resonances of **3** as reported in Table 1

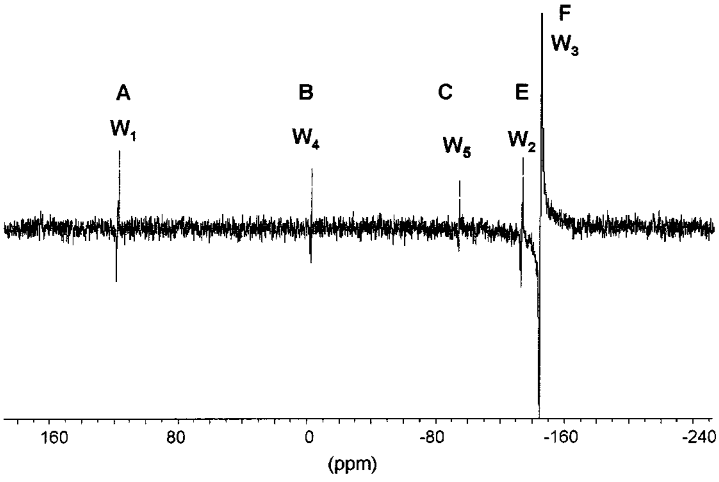

Figure 2. $^{183}$W selective COSY spectrum carried out upon excitation of the resonance at δ = −145

knowledge this is the first observation of a $^{99}$Ru signal in a polyoxometalate inorganic matrix.

Complex **3** displays a remarkable catalytic activity in the presence of sodium periodate ($NaIO_4$) or potassium monopersulfate ($KHSO_5$) which were used as primary oxidants in the oxidation of cyclooctene and adamantane, respectively.[15] Particularly interesting is the ruthenium-promoted cleavage of the olefinic double bond which proceeds in water, with no need of organic solvent or phase transfer agent, leading to 90% conversion of the substrate in 4 hours

Table 1. $^{183}$W NMR data for (**3**) as lithium salt in $D_2O$

| | | | $^2J_{WOW}$ (Hz)[c] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| W[a] | δ[b] | assign. | A | B | C | D | E | F | $^2J_{WOP}$[d] |
| A(2) | 117.39 | W1 | – | – | – | – | 16.1 | 26.2 | 1.23 |
| B(2) | −2.66 | W4 | – | – | 10.0 | – | – | 10.4 | 1.46 |
| C(2) | −94.43 | W5 | – | – | – | 18.5 | – | 10.0 | 1.01 |
| D(1) | −105.76 | W6 | – | – | – | – | 8.7 | – | 1.35 |
| E(2) | −133.30 | W2 | – | – | – | – | – | 20.3 | 1.23 |
| F(2) | −145.14 | W3 | – | – | – | – | – | – | 1.12 |

[a] Letters indicate resonances as shown in Figure 1b (integration ratio). − [b] ± 0.02 ppm. − [c] ± 0.2 Hz. − [d] ± 0.3 Hz. $\delta(^{31}P) = -10.8$ ($D_2O$), $\delta(^1H) = 3.40$ ($D_2O$) (s).

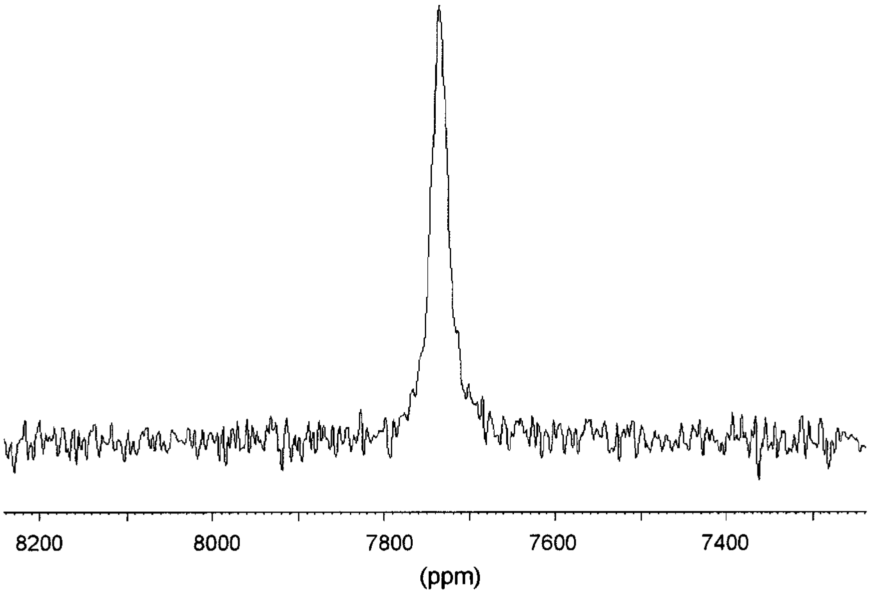

Figure 3. $^{99}$Ru NMR spectrum of (**3**)

at 50 °C, 1,8-octanedioic acid (suberic acid) being formed in 83% yield. In the hydroxylation of adamantane, complex **3** exhibits the high selectivity typical of ruthenium-based catalysts.[3][10] The reaction occurs smoothly at 50 °C in a two-phase medium (1,2-dichloroethane/$H_2O$) and performs the preferential attack at the tertiary C−H site of the substrate (54% conversion after 20 hours) affording 1-adamantanol and 1-chloroadamantane as major products.[16] Further studies concerning the synthesis of tungstoruthenate catalysts together with the scope and mechanism of their promoted oxidations are currently in progress, especially with the aim to devise environmentally sustainable oxidation processes.[17]

## Experimental Section

**Preparation of $[PW_{11}O_{39}Ru^{II}(DMSO)]^{5-}$ (3):** $K_7PW_{11}O_{39}$ (2.0 g) and $RuCl_2(DMSO)_4$ (0.3 g) in 50 mL of water were placed in a closed reactor (HPR-1000/10S, Milestone) equipped with temperature and pressure control units and irradiated inside the cavity of the MW Ethos-1600 labstation (Milestone) according to the following parameters: initial power, 350 W; initial time, 2 min; final power, 300 W; $T_{max}$ = 200 °C; reaction time, 15 min. Before $^{183}$W and $^{99}$Ru NMR spectroscopic analysis, the reaction mixture was passed through a $Li^+$-form resin (Amberlite IR 120). Further purification of **3** can be achieved by chromatography on a Sephadex G-15 column with water as eluent. − IR (KBr): ṽ = 1067, 1049, 1018, 964, 885, 793, 691, 589, 513 cm$^{-1}$. − MS (FAB); *m/z*: 2893−2891 [(M + H)$^+$, $HLi_5PW_{11}O_{39}Ru(DMSO)^+$], calcd. 2893.

The reported procedure for the synthesis of **3** involves a two-step reaction requiring the reduction of $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$ by electrolysis or prolonged heating in DMSO.[5]

**NMR Characterization:** $^{183}$W and $^{99}$Ru spectra were obtained at 9.4 T (16.67 and 18.43 MHz, respectively) on a Bruker Avance DRX 400 instrument, equipped with a standard ($^{31}$P-$^{109}$Ag) 10-mm broadband probe which could be tuned below its specifications. The π/2 pulse duration was ca. 50 μs for both nuclei. $^{183}$W and $^{99}$Ru chemical shifts are externally referenced to 2 M aq. $Na_2WO_4$ or 0.3 M aq. $K_4Ru(CN)_6$, respectively. Typically, ca. $10^3$ transients were collected in 32K or 1K data points, respectively. Selective COSY spectra were carried out with the standard sequence,[14] employing a 20-ms Gaussian-shaped selective pulse (π/2) at the desired offset and a 10-ms delay (the total evolution delay being ca. 20 ms). This value was found to be the optimum compromise between the need to emphasize the smallest couplings (4−5 Hz) and the relatively fast longitudinal relaxation ($T_1$ values being between 0.7−1.1 s). In order to gain insight into the molecular structure and the magnetic properties of the catalytically active ruthenium nucleus, ab initio calculations of the NMR properties of **3** are being performed.

**Catalytic Oxidations:** Cyclooctene (0.51 mmol) was suspended in 5 mL deionized water containing $NaIO_4$ (1.95 mmol) and **3** (5 μmol). After 4 hours, the unreacted olefin and the products were extracted with $Et_2O$ (5 × 5 mL) from the acidified reaction mixture and analyzed by GC and $^1$H and $^{13}$C NMR spectroscopy.

Adamantane (0.195 mmol) and $Bu_4NHSO_4$ (0.096 mmol) were dissolved in 1,2-dichloroethane (2 mL) and reacted at 50 °C with an aqueous solution (2 mL) containing **3** (0.01 mol) and Oxone (0.4 mmol, added in 3 portions over 3 hours). The reaction was monitored by GC and products were identified by GC-MS analysis and by comparison with authentic samples. The observed product distribution was as follows: 1-adamantanol (53%), 1-chloroadamantane (32%), adamantanone (10%), 2-chloroadamantane (5%); 2-adamantanol was detected only in traces.

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[1] Recent reviews on polyoxometalates: [1a] M. T. Pope, A. Muller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34−48. − [1b] C. L. Hill, C. M. Prosser-McCharta, *Coord. Chem. Rev.* **1995**, *143*, 407−455. − [1c] Polyoxometalates (Ed.: C. L. Hill), Chem. Rev. (Special Issue) **1998**, 98, 1−390.

[2] [2a] L. C. W. Baker, J. S. Figgis, *J. Am. Chem. Soc.* **1970**, *92*, 3794−3797. − [2b] C. L. Hill, R. B. Brown, *J. Am. Chem. Soc.* **1986**, *108*, 536−538.

[3] [3a] W. P. Griffith, *Chem. Soc. Rev.* **1992**, *21*, 179−185. − [3b] T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599−2660.

[4] [4a] R. Neumann, C. J. Abu-Gnim, *J. Chem. Soc., Chem. Commun.* **1989**, 1324−1325. − [4b] R. Neumann, C. J. Abu-Gnim, *J. Am. Chem. Soc.* **1990**, *112*, 6025−6031.

[5] [5a] C. Rong, M. T. Pope, *J. Am. Chem. Soc.* **1992**, *114*, 2932−2938. − [5b] M. Bressan, A. Morvillo, G. Romanello, *J. Mol. Catal.* **1992**, *77*, 283−288.

[6] W. J. Randall, T. J. R. Weakley, R. G. Finke, *Inorg. Chem.* **1993**, *32*, 1068−1071.

[7] [7a] R. Neumann, A. M. Khenkin, *Inorg. Chem.* **1995**, *34*, 5753−5760. − [7b] R. Neumann, M. Dahan, *J. Am. Chem. Soc.* **1998**, *120*, 11969−11976 and references therein.

[8] J. T. Groves, R. Quinn, *J. Am. Chem. Soc.* **1985**, *107*, 5790.

[9] J. T. Groves, J. S. Roman, *J. Am. Chem. Soc.* **1995**, *117*, 5594−5595.

[10] [10a] J. T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, *J. Am. Chem. Soc.* **1996**, *118*, 8961−8962. − [10b] J. T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, in *Studies in Surface Science and Catalysis* vol. 110 (Eds.: R. K. Grasselli, S. T. Oyama, A. M. Gaffney, J. E. Lions), Elsevier, Amsterdam, **1997**, 865−872. − [10c] J. T. Groves, T. Carofiglio, M. Bonchio, A. Sauve, *PCT Int. Appl.*, WO 9804538 A1 19980205, patent 48 pp.

[11] E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sava, S. Zorzet, *Inorg. Chem.* **1988**, *27*, 4099−4106 and references therein.

[12] C. Brevard, R. Schimpf, G. Tourné, C. M. Tourné, *J. Am. Chem. Soc.* **1983**, **105**, 7059−7063.

[13] [13a] D. M. P. Mingos, D. R. Baghurst, *Chem. Soc. Rev.* **1991**, *20*, 1−47. − [13b] S. Caddick, *Tetrahedron* **1995**, *51*, 10403−10432. − [13c] R. S. Varma, *Green Chemistry* **1999**, *1*, 43−55.

[14] H. Kessler, H. Oschkinat, C. Griesinger, W. Bermel, *J. Magn. Reson.* **1986**, *70*, 106−133.

[15] Related ruthenium catalysts have previously been employed in oxidation reactions.[4][5] However, because of the different experimental conditions (catalyst, oxygen donor and substrate) such results are not directly comparable to our own.

[16] During catalytic oxidation the DMSO ligand is oxidized to dimethyl sulfone, as shown by the $^1H$ NMR spectrum (singlet at $\delta = 3.17$) of the reaction mixtures.

[17] J. H. Clark, *Green Chemistry* **1999**, *1*, 1−8.

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