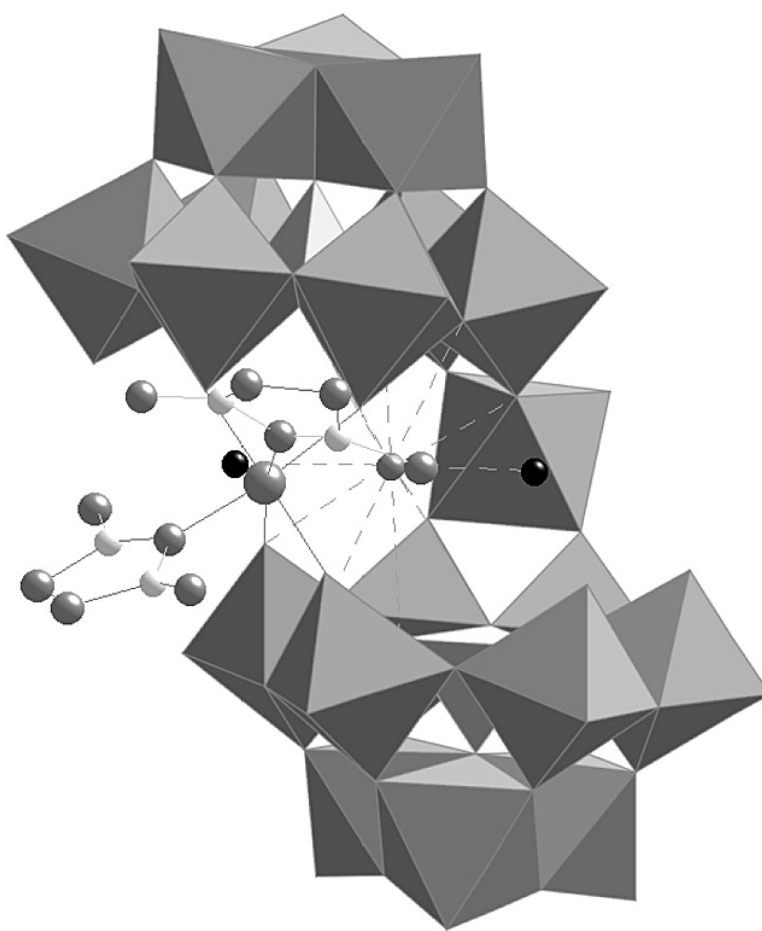


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## Synthesis and Characterization of the First Carbene Derivative of a Polyoxometalate

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Organometallic oxides,<sup>1</sup> which contain both hard (oxo) ligands and soft (largely organic) ligands and/or combine low- with high-valent metal centers, are attractive species, from which new reactivity patterns should be expected, as masterly demonstrated by the methyltrioxorhenium catalyst.<sup>2</sup> A special class of organometallic oxides comprises organometallic derivatives of polyoxometalates.<sup>3,4</sup> Since they can be well characterized at the molecular level, they can provide structural and spectroscopic models for heterogeneous metal oxide-supported catalysts. In addition, they also display their own reactivity, and cooperative effects<sup>5</sup> as well as bifunctional catalytic activity<sup>6</sup> have been reported. In some cases, the mobility of the organometallic moiety on the polyoxometallic core has even been evidenced<sup>7</sup> and some core rearrangements also mimic the dissolution–reaggregation processes sometimes occurring at oxide surfaces during their impregnation by the catalyst phase.<sup>8</sup> We have recently characterized a variety of organometallic oxides on the basis of {Ru(arene)}<sup>2+</sup> and molybdate or tungstate fragments.<sup>9</sup> To broaden the scope of these reactions and since *N*-heterocyclic carbenes<sup>10</sup> are an emergent class of ligands in organometallic chemistry,<sup>11,12</sup> we then explored the reactivity of the tetrakis-carbene ruthenium precursor [RuL<sup>Me</sup><sub>4</sub>Cl<sub>2</sub>] (L<sup>Me</sup> = 1,3-dimethylimidazolidine-2-ylidene)<sup>13</sup> toward polyoxometalates. We could only characterize isopolymolybdates during the course of the reaction of [RuL<sup>Me</sup><sub>4</sub>Cl<sub>2</sub>] with either (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Mo<sub>2</sub>O<sub>7</sub>] or (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Mo<sub>4</sub>O<sub>10</sub>(OMe)<sub>4</sub>Cl<sub>2</sub>] in acetonitrile or dichloromethane, at room temperature. On the contrary, the reaction with the monovacant Keggin-type polyanion [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> leads to the first carbene derivative of a polyoxometalate, [(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>(*cis*-WO<sub>2</sub>)(*cis*-RuL<sup>Me</sup><sub>2</sub>)]<sup>13-</sup> (**1**).

The equimolar reaction of [RuL<sup>Me</sup><sub>4</sub>Cl<sub>2</sub>] with K<sub>7-x</sub>Na<sub>x</sub>[PW<sub>11</sub>O<sub>39</sub>]<sup>14</sup> in water, followed by air oxidation and recrystallization in molar NaCl, gives brown, X-ray diffraction quality crystals of Na<sub>4</sub>K<sub>9</sub>[(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>(*cis*-WO<sub>2</sub>)(*cis*-RuL<sup>Me</sup><sub>2</sub>)]·23H<sub>2</sub>O (Na<sub>4</sub>K<sub>9</sub>·1·23H<sub>2</sub>O, yield 42%). The number of water molecules in the compound has been determined by TGA measurements and is in agreement with elemental analysis. However, only 15 of these 23 water molecules have been located in the course of the structure determination. Written as above, the formula implies that the oxidation state of the ruthenium in **1** is Ru(III), which is further supported by electrochemical measurements<sup>15</sup> and X-ray absorption studies (see below).

Air oxidation of Ru(II) precursors to Ru(III) in the course of their reaction with vacant polyoxometalates is preceded.<sup>16a-c,17</sup> [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> itself is readily oxidized by air to give [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>.<sup>18</sup> Ru(III) derivatives of polyoxometalates are often more air-stable than their Ru(II) analogues<sup>16d</sup> and can be isolated more easily.<sup>16a</sup> A Ru(IV) derivative has also been characterized.<sup>16e</sup> The formation of the α-A[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> subunits in **1** from [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> implies a partial degradation in solution. The formation of the related anion

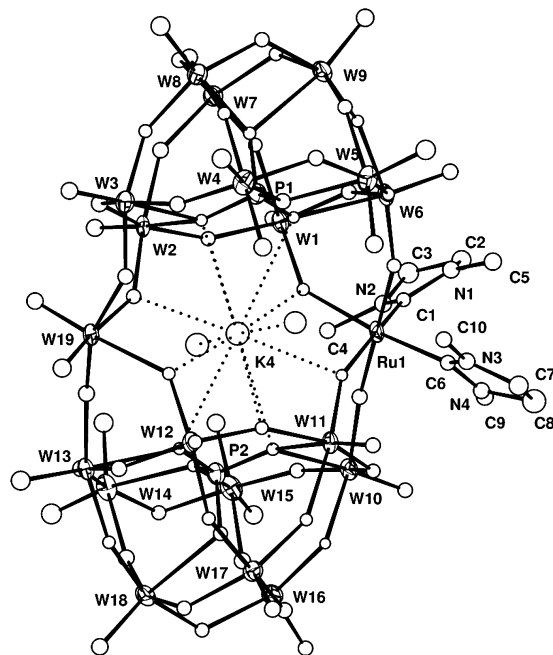
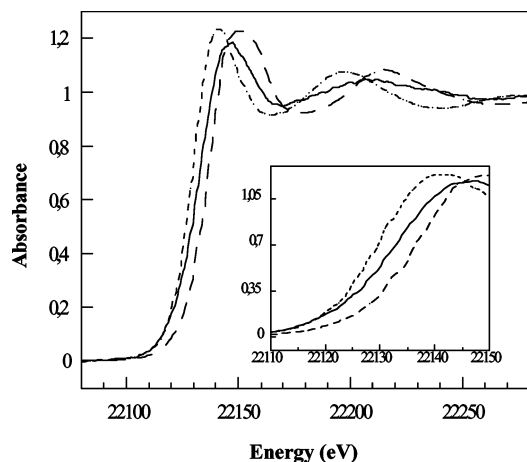


Figure 1. Molecular structure of (H<sub>2</sub>O)<sub>2</sub>K**1** in Na<sub>4</sub>K<sub>9</sub>·1·~15H<sub>2</sub>O.

[KCP<sub>2</sub>W<sub>20</sub>O<sub>72</sub>]<sup>13-</sup> (**2**)<sup>19</sup> also results from the basic degradation of [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> by aqueous carbonate. The relationships between routes of formation of polyoxometalates and their structures have been recently discussed.<sup>20</sup> In the present case, we postulate that strongly basic *N*-heterocyclic carbenes,<sup>11</sup> released from [RuL<sup>Me</sup><sub>4</sub>Cl<sub>2</sub>], would induce the degradation of [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup>. In a control <sup>31</sup>P NMR experiment, we could verify that several species are present in the solution, until it is exposed to air, which causes an evolution to a main product, that precipitates as K<sub>13</sub>·**1**. The formation of **1** is thus probably triggered by Ru(III) carbene fragments, acting as Lewis acids.

The molecular structure of (H<sub>2</sub>O)<sub>2</sub>K**1** is shown in Figure 1. It is related to that of [KCP<sub>2</sub>W<sub>20</sub>O<sub>72</sub>]<sup>13-</sup> (**2**) reported by Fuchs and Palm:<sup>19</sup> two α-A[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> subunits are linked through a *cis*-{RuL<sup>Me</sup><sub>2</sub>}<sup>3+</sup> fragment and a *cis*-{WO<sub>2</sub>}<sup>2+</sup> group. The whole anion encapsulates a potassium cation interacting with 10 oxo ligands of the polyanion and two extra water molecules. The two {PW<sub>9</sub>} subunits are not eclipsed but moved forward from each other. Although the anion has no crystallographically imposed symmetry, it has approximate C<sub>2</sub> symmetry with the axis passing through the ruthenium, the potassium, and the linking tungsten. The polyhedral arrangement thus differs from that encountered in the family of [P<sub>2</sub>W<sub>21</sub>O<sub>71</sub>(H<sub>2</sub>O)<sub>3</sub>],<sup>6-21a</sup> its lacunary<sup>21b,22</sup> and metallic derivatives.<sup>23</sup> Both the linking tungsten and the ruthenium achieve six-coordination by linking to four oxo ligands, two from each {PW<sub>9</sub>} unit.



**Figure 2.** Ru-K edge XANES spectra of  $[\text{RuCl}_2\text{L}^{\text{Me}}_4]$  (---),  $\text{Na}_4\text{K}_9\text{[PW}_9\text{O}_{34}]_2\{\text{WO}_2\}\{\text{RuL}^{\text{Me}}_2\}$  (—), and  $\text{RuO}_2$  (- - -).

The *trans*-influence of the multiply bonded terminal ligands expresses in the lengthening of the Ru–O bonds *trans* to the carbene ligands (2.16(2) Å compared to 1.95(2) and 1.97(2) Å for the other two oxo ligands). The Ru–C bond lengths (2.00(3)–2.05(3) Å) are typical of double bonds.

As the sodium cations could hardly be distinguished from the lattice water molecules, the whole charge of the anion and thus the oxidation state of the ruthenium could not be unambiguously determined only from the single-crystal X-ray determination.  $\text{Na}_4\text{K}_9\text{[PW}_9\text{O}_{34}]_2\cdot 23\text{H}_2\text{O}$  appears to be EPR silent at 77. Preliminary results at 4 K show a signal, which needs to be confirmed and simulated. A definite conclusion upon the oxidation state of the ruthenium center in **1** was reached by electrochemical<sup>15</sup> and XANES experiments at the ruthenium K-edge (Figure 2 and also Supporting Information). As expected, the position of the rising edge is dependent on the oxidation state of the ruthenium, the higher the oxidation state the higher its energy. The rising edge of **1** thus falls in the range of those of  $[\text{Ru}^{\text{III}}(\text{acac})_3]$ <sup>24</sup> and  $[\text{Ru}^{\text{III}}\text{Cl}_4(\text{DMSO})_2]^-$ <sup>25</sup> but is surrounded, at low energy, by that of  $[\text{Ru}^{\text{IV}}\text{L}^{\text{Me}}_4\text{Cl}_2]$  and, at high energy, by that of  $\text{Ru}^{\text{IV}}\text{O}_2$ .

In this contribution, we have reported the synthesis and characterization of the first carbene derivative of a polyoxometalate,  $[(\text{PW}_9\text{O}_{34})_2(\text{cis}\text{-WO}_2)(\text{cis}\text{-RuL}^{\text{Me}}_2)]^{13-}$  which displays an original molecular structure. As far as their electronic properties are concerned, *N*-heterocyclic carbenes such as  $\text{L}^{\text{Me}}$  are more similar to phosphanes than to alkylidenes. Even if alkylidene moieties are not required for olefine metathesis,<sup>26</sup> the investigation of the catalytic activity of **1** will require some activation at the ruthenium center. Compound **1** can also be a new entry for the synthesis of Ru-containing polyoxometalates, some of which are good oxidation catalysts.<sup>27</sup> Our perspectives also include the introduction of functionalized *N*-heterocyclic carbenes for attachment to a surface or to a polymer, and the use of chiral or multidentate *N*-heterocyclic carbenes.

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**Supporting Information Available:** Experimental preparation of  $\text{Na}_4\text{K}_9\text{[PW}_9\text{O}_{34}]_2\cdot 23\text{H}_2\text{O}$ , its crystallographic data, and XANES spectra of the  $\text{Ru}^{\text{III}}$  compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1998**, *28*, 339.
- (a) Hermann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169. (b) Hermann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149.
- Pope, M. T. *Hetero and Isopoly Oxometalates*; Springer-Verlag: Berlin, New York, 1983.
- Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77 and references therein to contributions from Klemperer's, Finke's, and Isobe's groups.
- Takahashi, K.; Yamaguchi, M.; Shido, T.; Ohtani, H.; Isobe, K.; Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1301. Ichikawa, M.; Pan, W.; Imada, Y.; Yamaguchi, M.; Isobe, K.; Shido, T. *J. Mol. Catal. A* **1996**, *107*, 23.
- Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 220.
- (a) Nagata, T.; Pohl, M.; Weiner, H.; Finke, R. G. *Inorg. Chem.* **1997**, *36*, 1366. (b) Abe, M.; Isobe, K.; Kida, K.; Yagasaki, A. *Inorg. Chem.* **1996**, *35*, 5114. (c) Artero, V.; Proust, A.; Herson, P.; Thouvenot, R.; Gouzerh, P. *Chem. Commun.* **2000**, 883.
- Villanneau, R.; Proust, A.; Robert, F.; Gouzerh, P. *Chem. Eur. J.* **2003**, *9*, 1982.
- Artero, V.; Proust, A.; Herson, P.; Gouzerh, P. *Chem. Eur. J.* **2001**, *7*, 3901.
- (a) Wanzlick, H.-W.; Schikora, E. *Angew. Chem.* **1960**, *72*, 494. (b) Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141.
- Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.
- Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913.
- Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 826.
- Tourné, C.; Revel, A.; Tourné, G. *Rev. Chim. Min.* **1977**, *14*, 537.
- The polarogram of  $\text{Na}_4\text{K}_9\text{[PW}_9\text{O}_{34}]_2\cdot 23\text{H}_2\text{O}$  on a platinum electrode in aqueous molar lithium acetate buffer (pH = 4.6) shows a 1-electron reduction wave at  $-0.1$  V/SCE and a 1-electron oxidation wave at  $+0.68$  V, both quasireversible according to cyclic voltammetry in the same conditions, and which can be unambiguously assigned to the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  and  $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}$  couples, respectively. In addition, the cyclic voltammogram displays two reversible 2-electron reduction waves associated with the polyoxotungstic framework ( $-0.63$  and  $-0.85$  V/SCE).
- (a) Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932. (b) Neumann, R.; Khenkin, A. M.; Dahan, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1587. (c) Neumann, R.; Dahan, M. *Polyhedron* **1998**, *17*, 3557. (d) Nomiya, K.; Torii, H.; Nomura, K.; Sato, Y. *J. Chem. Soc., Dalton Trans.* **2001**, 1506. (e) Randall, W. J.; Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 1068.
- Note however the formation of  $[(\text{PW}_9\text{O}_{34})_2\text{Ru}^{\text{IV}}(\text{DMSO})]^{5-}$  under microwave conditions in Bagno, A.; Bonchio, M.; Sartorel, A.; Scorrano, G. *Eur. J. Inorg. Chem.* **2000**, *1*, 17.
- Seddon, E. A.; Seddon, K. R. *The chemistry of Ruthenium*, monograph 19, Topics in inorganic and general chemistry; Clark, R. J. H., Ed.; Elsevier: Amsterdam, 1984; p 351.
- Fuchs, J.; Palm, R. Z. *Naturforsch.* **1984**, *39B*, 757.
- Contant, R.; Hervé, G. *Rev. Inorg. Chem.* **2002**, *22*, 63.
- (a) Tourné, C. M.; Tourné, G. F.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2237. (b) Tourné, C. M.; Tourné, G. F. *J. Chem. Soc., Dalton Trans.* **1988**, 2411.
- Contant, R. *Can. J. Chem.* **1987**, *65*, 570.
- Knott, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577.
- Figgis, B. N.; Lewis, J.; Mabbs, F. E.; Webb, G. A. *J. Chem. Soc. A* **1966**, 422.
- Jaswal, J. S.; Retty, S. J.; James B. *Can. J. Chem.* **1990**, *68*, 1808. (b) Alessio, E.; Balducci, G.; Calligaris M.; Costa, G.; Attia, W. A.; Mestroni, G. *Inorg. Chem.* **1991**, *30*, 609.
- (a) Hafner, A.; Mühlebach, A.; van der Schaaf, P. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2121. (b) Fürstner, A.; Ackermann, L. *J. Chem. Soc., Chem. Commun.* **1999**, 95.
- Adam, W.; Alsters, P. L.; Neumann, R.; Saha-Möller, C. R.; Sloboda-Rozner, D.; Zhang, R. *J. Org. Chem.* **2003**, *68*, 1721.

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