Inorg. Chem. **2009**, *48*, 4411−4420

Inorganic Chemistry

Article

Reinvestigation of a Ru_2-Incorporated Polyoxometalate Dioxygenase Precatalyst, “$[WZnRu_2^{III}(H_2O)(OH)(ZnW_9O_{34})_2]^{11-}$”: Evidence For Marginal, $\leq$0.2 Equivalents of Ru Incorporation Plus Faster Catalysis by Physical Mixtures of $[Ru^{II}(DMSO)_4Cl_2]$ and the Parent Polyoxometalate $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$

Aimee M. Morris, Oren P. Anderson, and Richard G. Finke*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received January 8, 2009

A 1997 *Nature* paper (*Nature* **1997**, *388*, 353−355) and subsequent 1998 *J. Am. Chem. Soc.* paper (*J. Am. Chem. Soc.* **1998**, *120*, 11969−11976) reported that a putative Ru_2-substituted polyoxoanion, “$[WZnRu_2^{III}(H_2O)(OH)(ZnW_9O_{34})_2]^{11-}$”, (**1**), is an all inorganic dioxygenase able to incorporate one O_2 into two adamantane C—H bonds to yield 2 equiv of 1-adamantanol as the primary product. In a subsequent 2005 *Inorg. Chem.* publication (*Inorg. Chem.* **2005**, *44*, 4175−4188), strong evidence was provided that the putative dioxygenase chemistry is, instead, the result of classic autoxidation catalysis. That research raised the question of whether the reported Ru_2 precatalyst, **1**, was pure or even if it contained two Ru atoms, since Ru is known to be difficult to substitute into polyoxoanion structures (Nomiya, K.; Torii, H.; Nomura, K.; Sato, Y. *J. Chem. Soc. Dalton Trans.* **2001**, 1506−1521). After our research group had contact with three other groups who also had difficulties reproducing the reported synthesis and composition of **1**, we decided to re-examine **1** in some detail. Herein we provide evidence that the claimed **1** actually appears to be the parent polyoxoanion $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ with small amounts of Ru ($\leq$0.2 atoms) either substituted into the parent complex or present as a small amount of a Ru^{n+} impurity, at least in our and two other group’s hands. The evidence obtained, on three independent samples prepared from two research groups including ours, includes elemental analysis on the bulk samples, single crystal X-ray diffraction, elemental analysis on single crystals from the same batch used for X-ray diffraction, ^{183}W NMR, and adamantane oxidation oxygen uptake and product determination studies. Also re-examined herein are the two previously reported crystal structures of **1** that appear to be very similar to the structure of the parent polyoxoanion, $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$. Furthermore, we report that trace Ru alone, in the form of $[Ru(DMSO)_4Cl_2]$, or that the parent polyoxoanion $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ alone, are capable of producing the same products. More significantly, a simple physical mixture of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ plus the average 0.13 equiv of Ru found by analysis added as the $[Ru(DMSO)_4Cl_2]$ starting material is a ca. 2-fold kinetically more competent catalyst than is “$[WZnRu_2^{III}(H_2O)(OH)(ZnW_9O_{34})_2]^{11-}$”, (**1**). In short, the evidence is strong that the putative “$[WZnRu_2^{III}(H_2O)(OH)(ZnW_9O_{34})_2]^{11-}$”, (**1**), which underlies the previously reported all-inorganic dioxygenase catalysis claim, is probably not correct. That does not mean that **1** cannot or even does not exist, but just that (a) no reliable synthesis of it exists if it has actually been made before, and (b) that a simple mixture of the $[Ru(DMSO)_4Cl_2]$ plus $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ precursors gives about 2-fold faster catalysis of adamantane hydroxylation that occurs by, the evidence suggests, a radical-chain autoxidation mechanism rather than via the previously claimed, novel all-inorganic-based dioxygenase catalysis.

Introduction

A 1997 *Nature* paper[1] and subsequent 1998 *J. Am. Chem. Soc.* paper[2] by others claimed to have synthesized the first “all inorganic dioxygenase”, $Q_{11}[ZnWRu_2^{III}(OH)(H_2O)(ZnW_9O_{34})_2]$ (referred to hereafter as, Q_{11}-**1**), where Q = tricaprylmethylammonium ion; $\{CH_3N[(CH_2)_7CH_3]_3\}^+$. This claim involving Q_{11}-**1** is significant and of interest on several accounts: (i) first, only a few catalytically active second row metal di-M_2-substituted polyoxoanions derived from the parent compound $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ are known in the literature;[3] and second and more importantly, no other all-inorganic dioxygenase that will do unactivated C—H bond activation has been reported in the literature, to our knowledge. Such a dioxygenase is a current “Holy Grail” of oxidation catalysis because of its ability, by definition, to insert both atoms of O_2 into two C—H bonds to yield two

---

* To whom correspondence should be addressed. E-mail: rfinke@lamar.colostate.edu.

(1) Neumann, R.; Dahan, M. *Nature (London)* **1997**, *388*, 353–355.

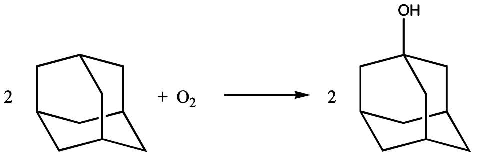
(2) Neumann, R.; Dahan, M. *J. Am. Chem. Soc.* **1998**, *120*, 11969–11976.

(3) Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143–155.

10.1021/ic9000363 CCC: $40.75

C—OH bonds, for example, all without the use of protons or electrons and, hence, without the formation of even trace H_2O.[4−6] Therefore, knowledge of the true composition and purity of **1**, as well as the critical question of the true nature of the underlying catalyst, is an important question.

The main evidence reported by others[2] for Q_{11}-**1** being a dioxygenase was hydroxylated alkane product studies, leading to the claimed stoichiometry shown in eq 1, plus the finding that the addition of the alkyl radical scavenger, 4-*tert*-butylcatechol, caused "only a very slight decrease in catalytic activity."[7]



(1)

However, in 2005 Yin et al. reinvestigated the claimed dioxygenase, Q_{11}-**1**.[8] Their results provided compelling evidence that the claimed Q_{11}-**1** is not a dioxygenase but, rather, is a classic autoxidation catalyst for which a detailed autoxidation mechanism could be written consistent with the re-evaluated kinetics.[8] The reported evidence for an autoxidation catalyst was extensive and included: (i) detection of trace amounts of peroxide, ROOH, the initial product of any autoxidation (peroxide would of course not be present if Q_{11}-**1** were in fact a dioxygenase as in eq 1 above); (ii) kinetic studies demonstrating a fractional rate law quantitatively consistent with, and highly characteristic of, a radical-chain mechanism but inconsistent with the previously suggested dioxygenase pathway;[1] (iii) a 1:1 products:O_2 stoichiometry (in distinct contrast to the previously claimed 2:1 dioxygenase stoichiometry, eq 1), evidence that by itself rules out a pure dioxygenase reaction; (iv) detection of $H_2{}^{18}O$ as a product, a product expected for autoxidation (but that could not be present if Q_{11}-**1** was a true dioxygenase); (v) initiation of the reaction by known radical initiators, AIBN and *t*-BuOOH, again indicative of a radical (and not a dioxygenase) mechanism; and (vi) complete inhibition of the progress of the reaction by four radical scavengers including 4-*tert*-butylcatechol that was previously[7] claimed to not be a strong inhibitor, evidence again consistent with and highly supportive of a radical-chain mechanism.[8] The results were so different than those reported in the 1997 Nature paper[1] that Yin, et al. stated in their paper "at times during our studies it seemed as if we were studying a different system [than the prior workers had studied]."[8] Hence, a closer look at the precatalyst Q_{11}-**1** also became important from that perspective and since others began using "Q_{11}-**1**" for additional chemistry.[9]

Contact with three other research groups indicated that they, too, had concerns regarding the reported Q_{11}-**1**, either from trying to repeat its preparation or from trying to confirm its reported Ru_2 composition. Specifically, Nomiya and coworkers reported[10,11] that they were not able to reproduce the reported preparation of the Q_{11}-**1** precursor, K_{11}-**1**.[8] C. L. Hill's group shared that they, too, had issues with the original crystal structure of K_{11}-**1** and concerns over the reported composition of Q_{11}-**1**.[12] And, in 2004, Shannon and coworkers[9] reported the structure of Na_{11}-**1** to be $Na_{14}[Ru^{III}{}_2Zn_2(H_2O)_2(ZnW_9O_{34})_2]$, although their crystallographic data indicated only partial incorporation of Ru into the parent $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ polyoxoanion. Their work reported that Ru replaces one zinc atom and a partial W atom (as opposed to replacing two Zn atoms as originally suggested[7]), resulting in a composition of $Na_{14}[W_{0.76}Ru_{1.24}Zn_2(H_2O)_2(ZnW_9O_{34})_2]$ (*vide supra*). In short, the issues surrounding K_{11}-**1** and Q_{11}-**1** raised independently by three research groups,[9,11,12] along with the importance of claims of a dioxygenase catalyst and the key question of what is the true catalyst or at least precatalyst, led us to rescrutinize **1** in some detail.

Reported herein is our reinvestigation of **1**, $[ZnWRu_2{}^{III}(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$, and its claimed Ru_2 composition.[1,2] We find by elemental analysis of the bulk samples, single crystal X-ray structure determination, elemental analysis on single crystals from the same batch used for the X-ray diffraction structure, ^{183}W NMR, oxygen uptake, and product identification studies that there is little to no evidence of disubstitution of Ru(III) into the parent compound $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ by the reported synthesis[7,21] using $[Ru(DMSO)_4Cl_2]$ regardless if the source is Yin's,[8] Nomiya's,[11] Hill's,[12] Shannon's,[9] or our present preparation of **1**. Instead, we provide evidence for the composition of "**1**" being primarily $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ in at least three independent samples examined herein with only a small amount (≤ 0.2 atoms) of Ru being observed in any of the three independent samples—that low Ru level due presumably to either partial incorporation of Ru into the parent polyoxoanion *or* a small level of a Ru^{n+} impurity. Significantly, we also provide O_2 uptake and product identification studies herein that show the same

---

(4) Hayaishi, O.; Katagiri, M.; Rothberg, S. J. *J. Am. Chem. Soc.* **1955**, *77*, 5450–5451.

(5) Nozaki, M. *Top. Curr. Chem.* **1979**, *78*, 145–186.

(6) Oxygenases and model systems. In *Catalysis of Metal Complexes*; Funabiki, T., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; Vol. 19.

(7) Neumann, R.; Khenkin, A. M.; Dahan, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1587–1589.

(8) Yin, C.-X.; Finke, R. G. *Inorg. Chem.* **2005**, *44*, 4175–4188.

(9) Howells, A. R.; Sankarraj, A.; Shannon, C. *J. Am. Chem. Soc.* **2004**, *126*, 12258–12259.

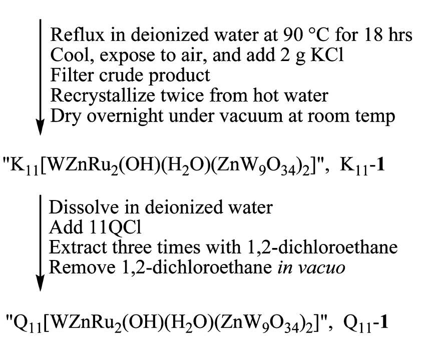
(10) Nomiya, K.; Torii, H.; Nomura, K.; Sato, Y. *J. Chem. Soc., Dalton Trans.* **2001**, 1506–1521.

(11) Nomiya, K.; Torii, H.; Nomura, K.; Sato, Y. These worker's results, cited with permission in the Supporting Information herein for the first time, detail six attempted preparations of **1** by the reported procedure[7,21] followed by characterization of "yellow-brown materials obtained sometimes as a mixture with crystals, which were characterized by IR, ^1H NMR, TG/DTA, and UV-visible absorption spectra, and magnetic susceptibility plus CV measurements." In no case could a pure sample of the putative **1** be obtained, however, and "the IR spectra were almost unchanged after the reaction, that is, they only showed a pattern due to the original Keggin fragments". For the full details, see the Supporting Information (see also the *Note Added in Proof* in our earlier publication[8]).

(12) Hill, C. L.; Anderson, T. M.; Hardcastle, K.; Fang, X., cited with permission.

products are obtained in similar yields and ratios for (i) the original[1,2] "Q_{11}-**1**" (i.e., based on the published yields[1,2]); (ii) three independent samples of "Q_{11}-**1**" containing ≤ 0.2 atoms (which is ≤ 0.2 equiv) of Ru, (iii) the parent compound $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ containing no Ru, (iv) 0.13 equiv of Ru added as the precursor $[Ru(DMSO)_4Cl_2]$, and (v) a mixture of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ plus 0.13 equiv of Ru added as $[Ru(DMSO)_4Cl_2]$. The significance of these studies is at least fourfold: (i) in providing evidence on whether Ru_2-substituted "K_{11}-**1**" and "Q_{11}-**1**" actually exist; (ii) in providing further evidence bearing on the prior claim of an all-inorganic dioxygenase;[8] (iii) in clarifying what the true catalyst probably is in the prior report of adamantane hydroxylation by Ru and polyoxoanion-containing precatalysts—the true catalyst being a central, but often perplexing part of modern catalysis,[13−17] and (iv) in bearing on the generally difficult problem of synthesizing Ru[7,10,18] (and other later transition-metal[19]) containing polyoxoanions cleanly. The present results also (v) tie, in a general way, into other areas of synthetic inorganic chemistry concerning the difficulties historically of putting Ru into other ligands (e.g., porphyrins).[20]

Scheme 1. Literature[7,21] Synthesis of "**1**"



Results and Discussion

Synthesis and Characterization of Independent Samples of "Q_{11}-1." Three independent samples of both "K_{11}-**1**" and "Q_{11}-**1**" were prepared according to the literature procedure,[7,21] shown in Scheme 1,[22] in two different laboratories by three individual researchers (A. M. Morris at Colorado State University (CSU) (vide infra), C.-X. Yin also at CSU,[8] and T. Anderson in C. L. Hill's laboratories at Emory University[12]), and then used in this study. Each of the three independent "**1**" samples was analyzed by elemental analysis, IR, comparison of O_2 uptake curves to the literature,[2] and adamantane oxidation product studies. The "**1**" sample prepared herein was also analyzed by single crystal X-ray diffraction and ^{183}W NMR.

Elemental Analysis Results. Elemental analysis on each of the three samples reported herein of "K_{11}-**1**," the "Q_{11}-**1**" precursor, and in comparison to the "K_{11}-**1**" originally reported,[2] are shown in Table 1. Three independent samples of "K_{11}-**1**," each prepared by the same procedure[7,21] insofar as possible, *show different compositions*. While no two analyses are the same (indicating that an impure sample is obtained as previously suggested[8]), each of the three independent samples *are low in Ru and two of the three are high in Zn content*, Table 1.

Crystal Structure of "Na_{11}-1" The X-ray structure of "Na_{11}-**1**," shown in Figure 1, confirms the previous findings[7,9,21] that "**1**" has a sandwich type polyoxoanion structure. In the previous study, it was reported that a ring containing WRuZnRu is sandwiched between the two (ZnW_9O_{34}) polyoxoanion units.[21] However, an issue with that

---

[13] (a) Yin, C.-X.; Sasaki, Y.; Finke, R. G. *Inorg. Chem.* **2005**, *44*, 8521–8530. (b) Yin, C.-X.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 9003–9013. (c) Yin, C.-X.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 13988–13996.

[14] (a) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A* **2003**, *198*, 317–341. (b) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609–679.

[15] (a) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891–4910. (b) Widegren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10301–10310. (c) Hagen, C. M.; Widegren, J. A.; Maitlis, P. M.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 4423–4432. (d) Finney, E. E.; Finke, R. G. *Inorg. Chim. Acta* **2006**, *359*, 2879–2887.

[16] (a) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65–68. (b) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055–8057.

[17] For this reason, so-called operando (from the Latin for "working" or "operating") methods, along with (by definition already operando) kinetic studies, are leading the way to the identification of true active catalysts: (a) Weckhuysen, B. M. *Chem. Commun.* **2002**, 97–110. (b) Guerrero-Perez, M. O.; Banares, M. A. *Chem. Commun.* **2002**, 1292–1293. (c) Meunier, F.; Daturi, M. *Catal. Today* **2006**, *113*, 1–2.

[18] (a) Rong, C. Y.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932–2938. (b) Randall, W. J.; Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 1068–1071. (c) Filipek, K. *Inorg. Chim. Acta* **1995**, *231*, 237–239. (d) Chen, S.-W.; Villaneau, R.; Li, Y.; Chamoreau, L.-M.; Boubekeur, K.; Thouvenot, R.; Gouzerh, P.; Proust, A. *Eur. J. Inorg. Chem.* **2008**, 2137–2142.

[19] For example, Rh, Pd, and Pt containing polyoxoanions: (a) Kuznetsova, N. I.; Detusheva, L. G.; Kuznetsoca, L. I.; Fefotov, M. A.; Likholobov, V. A. *J. Mol. Catal. A* **1996**, *114*, 131–139. (b) Wei, X.; Bachman, R. E.; Pope, M. T. *J. Am. Chem. Soc.* **1998**, *120*, 10248–10253. (c) Bi, L.-H.; Reicke, M.; Kortz, U.; Keita, B.; Nadjo, L.; Clark, R. J. *Inorg. Chem.* **2004**, *43*, 3915–3920. (d) Kortz, U.; Bi, L. *U.S. Patent Appl. Publ.* 2007,US 2006-445073 20060531. (e) See also the following two citations which independently reveal the non-trivial nature of making, and then adequately characterizing, late-transition-metal-substituted polyoxometalates: (i) Cao, R.; Anderson, T. M.; Hillesheim, D. A.; Kögerler, P.; Hardcastle, K. I.; Hill, C. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 9380–9382. (ii) Kortz, U.; Lee, U.; Joo, H.-C.; Park, K.-M.; Mal, S. S.; Dickman, M. H.; Jameson, G. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 9383–9384.

[20] (a) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137–1139. (b) Ke, M.; Rettig, S. J.; James, B. R.; Dophin, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1110–1112. (c) Collman, J. P.; Rose, E.; Venburg, G. D. *J. Chem. Soc., Chem. Commun.* **1994**, 11–12. (d) Cheng, S. Y. S.; Rajapakse, N.; Rettig, S. J.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2669–2670. (e) Reboucas, J. S.; Cheu, E. L. S.; Ware, C. J.; James, B. R.; Skov, K. A. *Inorg. Chem.* **2008**, *47*, 7894–7907.

[21] Neumann, R.; Khenkin, A. M. *Inorg. Chem.* **1995**, *34*, 5753–5760.

[22] Interestingly, the transition metal substituted derivatives of $[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ with M = Mn(II), Co(II), Ni(II), and Cu(II), have previously been synthesized using "temperatures near the boiling point, a large [8−12 fold molar] excess of M^{II}, and, typically, a long heating period.[3]" Other derivatives such as M = Mn(III), Fe(II), or Fe(III), Pd(II), Pt(II), and V(IV) di-substituted derivatives have also been formed using molar to slightly excess molar M precursors. In the cases of M(III) substitution, the previous syntheses either begin with a M(III) precursor or the M(II) substituted polyoxoanion is first prepared and then oxidized the M(II) to M(III).[3] However, in the synthesis of "**1**",[7,21] a molar ratio of $[Ru(DMSO)_4]Cl_2$ is used even though Ru has historically been difficult to substitute into polyoxoanions[10] or other ligands,[20] and a Ru(II) precursor is used rather than a Ru(III) or Ru(IV) precursor. Overall, the proposed synthesis of "**1**" appears to be inconsistent with the synthetic precedent[3] that might allow **1** to be formed with two Ru(III) atoms incorporated into the structure in high yield.

Table 1. Elemental Analyses for Three Independent Samples of “K_{11}-**1**” versus the Literature’s Reported Analysis[7,21]

	Calculated for K_{11}-**1**·15H_2O	Neumann’s[7,21] “K_{11}-**1**·15H_2O”	“K_{11}-**1**” prepared herein	Yin’s[8] “K_{11}-**1**”	Anderson’s[12] “K_{11}-**1**”
K	7.57	7.06	4.69	4.29	NM[a]
Na	0.00	NM[a]	0.59	1.39	NM[a]
Ru	*3.56*	*3.56*	*0.75*	*0.24*	*0.29*
Zn	*3.45*	*3.24*	*7.13*	*6.65*	*3.08*[b]
W	61.5	61.3	NM[a]	61.2	NM[a]
H_2O	4.76	4.69	NA[c]	NA[c]	NA[c]

[a] NM = not measured. [b] This Zn analysis appears to be low/in error in light of the low amount of Ru that is observed in this same sample. [c] NA = not applicable, since the number of hydrated waters in each sample found by TGA studies can vary depending upon the preparation and especially drying conditions.

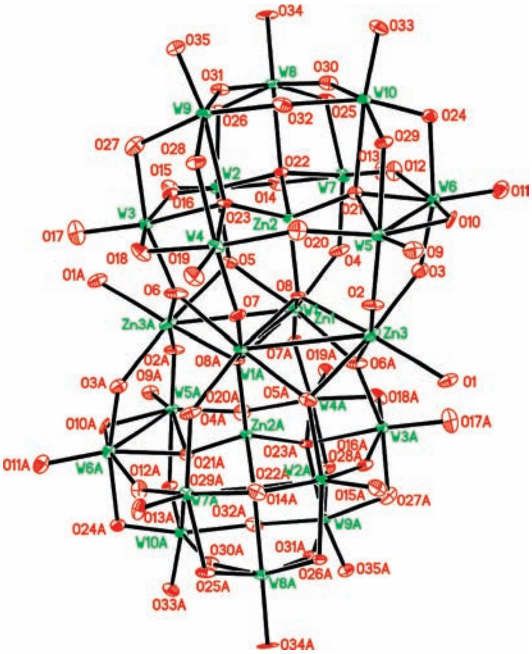


Figure 1. Thermal ellipsoid plot of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ (50% ellipsoids). Solvent (H_2O) and counter cations (Na^+) have been removed for clarity.

prior structure is the unusually large thermal coefficients reported for the two Ru atoms. The authors rationalized this by assuming that the two positions at which the Ru atoms are located are relatively labile.[21] However, upon examination of the two sites which Ru is thought to occupy, these sites contain 5 internal oxygen bonds, as well as one bond to a H_2O or OH^- ligand. Given that the estimated bond dissociation energy of a Ru—O is about 110 kcal/mol,[23] the probability of the atom in this site being labile is low. A simpler explanation for the unusually large thermal coefficient observed is that *the atom assignment is incorrect*, a hypothesis not just consistent with, but required by, three of the four elemental analysis results in Table 1 revealing relatively little incorporation of Ru into the polyoxoanion.

In a second, literature study of the crystal structure of “Na_{11}-**1**”, the crystallographic data indicated a $Ru^{III}_{1.24}W_{0.76}Zn_2$ ring.[9] However, the reported composition in the main text of the previous publication[9] suggests a $Ru^{III}_2Zn_2$ ring is present in “Na_{11}-**1**” giving the composition $Na_{14}[Ru^{III}_2Zn_2(H_2O)_2(ZnW_9O_{34})_2]$. Moreover, the structure suggests that the Ru atoms substitute into the Zn and W positions of the ring[9] and not the two Zn atom positions containing terminal H_2O ligands as previously suggested.[7,21] In addition, in that study,[9] the composition of “Na_{11}-**1**” is reported *to vary* from six independent crystals studied by both X-ray diffraction and energy dispersive X-ray (EDX) spectroscopy. The average EDX composition was consistent with Ru_2Zn_2 but not with the $Ru_{1.24}W_{0.76}Zn$ ring of the crystal structure. This second study[9] again illustrates the variation and inconsistency of “**1**.”

To further test the hypothesis that there is little to no Ru incorporation into the parent polyoxoanion, we grew crystals of “Na_{11}-**1**” according to the literature procedure[21] and performed an independent single crystal X-ray structure determination. Our structural results agree with our bulk elemental analysis results above (Table 1), *as well as our elemental analysis results on the single crystals from the same batch used for X-ray diffraction* (Table 3, vide infra), in that there appears to be *no Ru* present in at least this sample of “Na_{11}-**1**”, Figure 1. Attempts to introduce even partially occupied Ru sites into the refinement were unsuccessful. Instead our reported structure suggests that “Na_{11}-**1**” is primarily, if not completely, the parent precursor polyoxoanion, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$, Table 2, last column. To rule out the possibility of having some crystals which contain Ru, three separate crystals from two different crystal batches were analyzed and each of the three data sets refined to the same structure, Ru-free $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$.

While reinvestigating the crystal structure of “Na_{11}-**1**”, similarities between the two previous structure determinations[9,21] of “Na-**1**” and Tourné’s[10] determination of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ became apparent (Table 2). The structure determination reported herein appears at first glance to be different from the reported structures of “Na_{11}-**1**”[21] and $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$[10] as the space group is different (we chose to solve the structure in the International Union of Crystallographers’ preferred space group of $P2_1/n$). However, Table S1 of the Supporting Information shows that the alternative $P2_1/c$ space group for the structure reported herein gives a unit cell that exhibits similar cell constants to those shown for the structures of “Na_{11}-**1**” and $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ in Table 2. This provides further support consistent with the hypothesis that **1** made in at least our hands is the parent polyoxoanion, $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$; our crystallography result also raises the possibility that the atom assignments in the previous structure may have been misinterpreted.

---

(23) Meier, U. C.; Scopelliti, R.; Solari, E.; Merbach, A. E. *Inorg. Chem.* **2000**, *39*, 3816–3822.

Table 2. Crystallographic Data for the Structure Solved in This Publication Compared to Structures Previously Solved by Tourné,[10] Neumann,[21] and Shannon[9]

	Tourné's[10] $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 46H_2O$	Neumann's[21] $Na_{11}[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]\cdot 42H_2O$	Shannon's[9] $Na_{14}[W_{0.76}Ru_{1.24}Zn_2(H_2O)_2(ZnW_9O_{34})_2]\cdot 46H_2O$	$Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 39H_2O$ solved herein
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
M	6047.9	6023.9	6110.4	5995.0
a/Å	13.027(4)	13.069(3)	13.0374(6)	13.0017(6)
b/Å	17.788(5)	17.827(4)	17.7859(8)	17.8485(7)
c/Å	24.124(4)	24.182(5)	21.1030(10)	21.0260(9)
β/deg	118.94(2)	118.97(2)	93.3800(10)	93.223(3)
U/Å^3	4892(2)	4929(1)	4884.9(4)	4871.6(4)
crystal size /mm	0.21 × 0.16 × 0.34	NR[a]	0.088 × 0.102 × 0.326	0.067 × 0.166 × 0.263
R	0.039	0.051	0.0380	0.0509
GOF	NR[a]	NR[a]	1.061	1.120

[a] NR = not reported.

Table 3. Elemental Analysis Data for the Single Crystals of "Na_{11}-**1**" from the Batch Used for the X-ray Diffraction Structural Analysis

	calculated for Na_{11}-**1**$\cdot 13H_2O$	calculated for $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})]\cdot 13H_2O$	observed for "Na_{11}-**1**" sample prepared herein
Na	4.60%	5.06%	4.62%
Zn	3.57%	5.99%	5.99%
Ru	3.67%	0%	<0.1%
W	63.5%	64.1%	62.8%[a]
O	24.1%	24.4%	24.2%

[a] Low W analyses are unfortunately prevalent in the polyoxometalate area (for example see the repeat W analyses required in the experimental section of ref 25); W analyses can vary by about ± 2% even when performed (as was done here) by inductively coupled plasma (ICP) emission spectroscopy.[26]

As noted above, elemental analysis of the crystals from the batch used for X-ray diffraction gave the composition $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 13H_2O$. This composition is identical to the polyoxoanion precursor used (Table 3), and supports the results from the crystal structure determination. Like the bulk sample, the crystal batch sample also indicates no detectable Ru substitution into the parent polyoxoanion. That there is little to no Ru substitution is not surprising as Ru has been shown to be difficult to substitute into polyoxoanions.[10] Furthermore, the synthesis published[7,21] uses a neutral pH, whereas acidic (or sometimes basic) pH is often required for polyoxoanion substitutions.[24] An alternative hypothesis here is that it is simply our failure (i.e., in our hands) to be able to incorporate Ru into the desired structure. However, the same low to no Ru results for two independent researchers in our laboratories, in C. L. Hill's laboratories, and Nomiya's inability to repeat the reported synthesis of Ru_2-**1**,[11] all argue strongly *that there is a problem with the reported synthesis*, Scheme 1, and the claimed composition of **1**. The catalytic results provide additional, highly suggestive evidence that "Ru_2-**1**" may have never been made, vide infra.

^{183}W NMR Studies. Tourné previously reported the ^{183}W NMR spectrum for the Li^+ salt of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ taken at 22 °C. To collect further evidence on the composition of the bulk sample, ^{183}W NMR on the Li^+ exchanged "K_{11}-**1**" prepared herein (i.e., by A. M. Morris) was taken at 52 °C to increase the solubility of "**1**", Figure 2. The spectrum shown in Figure 2, while a relatively poor signal/noise, is the same within experimental error as the spectrum of Li^+ exchanged $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ once the difference in temperature of the two spectra are taken into account.[3] Both spectra contain the expected 10 W signals, 9 of which correspond to the W atoms in the 2 (ZnW_9O_{34}) units. The one (tenth) signal at about +20 ppm has half the intensity of the other signals and can be assigned to the single W atom contained in the WZn_3 ring of the polyoxoanion and labeled W1/W1A (each having 50% occupancy) in Figure 1. The ^{183}W NMR spectrum of Li^+-"**1**" is consistent with the elemental analysis studies as well as the crystal structure in showing that "**1**" is at least mostly composed of the parent polyoxoanion, $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$. The caveat here is, however, that ^{183}W NMR is notoriously insensitive to smaller, trace components, especially in non-ideal signal/noise spectra such as we were able to obtain (Figure 2).

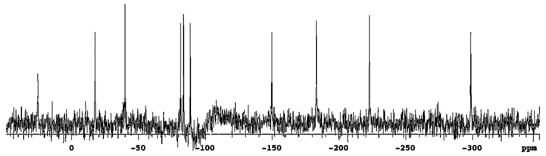


Figure 2. ^{183}W NMR spectrum of Li^+ exchanged "K_{11}-**1**" in D_2O at 52 °C.

O_2 Uptake and Product Identification and Quantitation Studies: General Procedure. Following the previously published literature procedure for O_2-uptake studies,[8] 6.0 mmol of adamantane, 6.0 μmol of the precatalyst, and 12.0 mL of 1,2-dichloroethane were combined and equilibrated at 80 °C under ~1.0 atm of O_2. The oxygen uptake curves for each of the experiments discussed below can be seen in Figure 3 and the Supporting Information, Figures S3−S8. Control experiments of the appropriate added Zn and $[Ru(DMSO)_4Cl_2]$ plus QCl, along with discussion, are also provided in the Supporting Information for the interested reader. Following the O_2-uptake experiments, the products of each reaction were identified and quantified by comparison to authentic samples with Gas Chromatography (GC).

---

(24) Pope, M. T. Preparation, structural principles, properties and applications. In *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983, pp 15−32.

(25) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7209–7221.

(26) Brenner, I. B.; Erlich, S. *Appl. Spectrosc.* **1984**, *38*, 887–890.

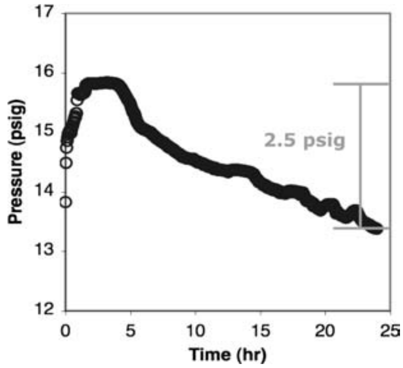


Figure 3. Pressure vs time curves recorded by an O_2 pressure transducer. The initial pressure rise is due to the 1,2-$C_2H_4Cl_2$ solvent pressure equilibration following flushing the Fischer−Porter bottle with O_2 and then pressurizing it with about 14 psig of O_2. (The noise in the pressure curve arises from temperature variations since the reaction temperature is at 80 °C yet the rest of the apparatus is at ambient temperature with ± 3 °C variation.) However, the net pressure loss shown matters, so that this experiment more than suffices for its intended purpose of monitoring the net O_2 uptake over the time (24 h) that the adamantane oxidation products were also monitored. Reaction conditions: 6.0 mmol of adamantane, 6.0 μmol of “Q_{11}-**1**,” 12 mL of 1,2-$C_2H_4Cl_2$, 80 °C, and about 14 psig of O_2 pressure.

O_2 Uptake and Product Identification and Quantitation Studies with “Q_{11}-1” For each of the three independently prepared samples of “Q_{11}-**1**”, there was approximately 2.5−3 psig of O_2 taken up during the course of 24 h over which the reaction was monitored (following the previous literature procedure[2]). A sample O_2 uptake is shown in Figure 3. The resulting products from the O_2-uptake curves for each of the three independent samples of “Q_{11}-**1**” are the same within experimental error, Table 4, entries 1, 2, and 6, despite the varying amounts of Ru present in each of the samples. In addition, the products obtained from each of the three independent samples (entries 1, 2, and 6 of Table 4) of “Q_{11}-**1**” gave the same yields and selectivities as the previously reported “Q_{11}-**1**” reported to contain >1.8 more Ru atoms, entry 7, Table 4. This implies that “Q_{11}-**1**” reported previously[1,2,7,21] (i.e., and with its claimed two incorporated Ru atoms) either (i) coincidentally gives the same oxidation products in the same yields as we see with “**1**” that has ≤0.2 equiv of Ru, *or* more likely we believe (ii) that the previously reported[1,2,7,21] “Q_{11}-**1**” is similar to our “Q_{11}-**1**” samples—samples prepared by the same method[7,21] and reported herein to contain ≤0.2 Ru. The latter is certainly the simplest, “Ockham’s razor” interpretation of the extant data.

O_2 Uptake and Product Identification and Quantitation Studies with Just [Ru(DMSO)$_4$Cl$_2$] as the Precatalyst. By using just 0.13 equiv of Ru (by adding the 0.77 μmol of Ru which is the same amount of Ru if one could add 1.0 equiv of $Q_{12}[WRu_{0.13}Zn_{2.87}(H_2O)_2(ZnW_9O_{34})_2]$) in the form of [Ru(DMSO)$_4$Cl$_2$] (an amount that is the same as the average Ru seen in the elemental analysis of “Q_{11}-**1**” from our laboratories, entries 1 and 6 of Table 4), an O_2 uptake curve the same within experimental error of Figure 3 was produced, see Supporting Information, Figure S3. Furthermore, 1-adamantanol and 2-adamantanone products are again obtained as reported for[2] “Q_{11}-**1**” in a similar selectivity (ca. the same within experimental error), albeit in a bit less than half as much yield (entry 3, Table 4, in comparison to entries 1 and 2)—half the yield that may simply reflect that there is about half the Ru in this control experiment as in entries 1 and 2. Overall, this control experiment shows that starting with [Ru(DMSO)$_4$Cl$_2$] gives similar adamantane hydroxylation products, but more slowly in ca. half the yield.

O_2 Uptake and Product Identification and Quantitation Studies with $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot n$QCl. The next obvious control experiment was to use the Ru-free Q^+ salt of the polyoxoanion precursor, $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$, instead of “$Q_{11}$-**1**”. Again, the identical two main 1-adamantanol and 2-adamantanone products were observed for $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ (entry 4, Table 4 in comparison to entries 1 and 2). However, no products were observed after 24 h for $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot n$QCl since the reaction time is variable (as expected for a radical-chain autoxidation reaction[8]) and requires 95 to 140 h for completion (Supporting Information, Panels a and b of Figure S4). In combination with the prior control of just [Ru(DMSO)$_4$Cl$_2$] alone, these results would seem to indicate that (i) both [Ru(DMSO)$_4$Cl$_2$] and Ru-free $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot n$QCl are able to exhibit the observed (radical-chain[8]) catalysis, but (ii) that their combination is more effective. This is in fact the case as the third control reaction described next demonstrates.

O_2 Uptake and Product Identification and Quantitation Studies with Premixed $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot n$QCl plus [Ru(DMSO)$_4Cl_2$]. The third control of premixing 0.13 equiv [Ru(DMSO)$_4$Cl$_2$] with $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ produced the anticipated accelerated hydroxylation reaction. The induction period was shortened as expected, the same two main products were produced as with “Q_{11}-**1**”, but the yields were higher beyond experimental error (entry 5, Table 4). *This is an important result, one of the most telling results in this report.* It indicates higher kinetic competence of low levels of Ru not necessarily *in* the polyoxoanion structure as would be the case for authentic **1**; it argues for enhanced catalysis by a perhaps polyoxoanion-supported[27] (and not polyoxoanion-framework incorporated,[28] such as **1**) form of Ru^{n+} (e.g., $Ru^{n+}/[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ is one possibility). It also makes an important connection between our results and the work in question:[2] we get *the same catalysis in terms of yields (rates) and selectivities with just low levels of Ru and the parent polyoxoanion*. This strongly implies that *if* the prior complex **1** really contains the 2.0 equiv of Ru as listed in Table 4, then that Ru is not essential to catalysis! The alternative hypothesis is that the previously reported[1,2,7] “**1**”

---

(27) (a) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274–7277. (b) Rapko, B. M.; Pohl, M.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 3625–3634. (c) Pohl, M.; Lin, Y.; Weakley, T. J. R.; Nomiya, K.; Kaneko, M.; Weiner, H.; Finke, R. G. *Inorg. Chem.* **1995**, *34*, 767–777. (d) Nagata, T.; Pohl, M.; Weiner, H.; Finke, R. G. *Inorg. Chem.* **1997**, *36*, 1366–1377. (e) Finke, R. G. Polyoxoanions in Catalysis: From Record Catalytic Lifetime Nanocluster Catalysis to Record Catalytic Lifetime Catechol Dioxygenase Catalysis. In *Polyoxometalate Chemistry*; Pope, M. T., Müller, A., Eds.; Kluwer: Netherlands, 2001; pp 363−390.

(28) For the definitions of, and differences between, POM-supported vs POM-incorporated transition metal catalysts, see: (a) Weiner, H.; Hayashi, Y.; Finke, R. G. *Inorg. Chem.* **1999**, *38*, 2579–2591.

Table 4. Products Quantitation and Other Relevant Data for Adamantane Hydroxylation Under 1 atm of O_2, at 80 °C, and after 24 h

entry	sample	equiv Ru	1-adamantanol yield	2-adamantanone yield	mass balance^a	selectivity^b	induction period?
1	"Q_{11}-**1**" sample prepared herein	0.21	13 ± 1%	2.2 ± 0.4%	98 ± 4%	5.9	yes
2	C. Hill's "Q_{11}-**1**" sample	<0.1	13 ± 1%	2.3 ± 0.4%	96 ± 4%	5.7	yes
3	$[Ru(DMSO)_4Cl_2]$	0.13	5.4%	1.3%	98%	4.2	yes
4	$Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^c$	0	0%	0%	98 ± 2%	0	yes
	At 120 ± 20 h^d	0	30 ± 5%	6 ± 1%	96 ± 4%	5.0	yes
5	$Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2 + [Ru(DMSO)_4Cl_2]$	0.13	23%	5.6%	95%	4.1	yes
6	Yin et al.'s Literature[8]	0.05	12 ± 1%	2.2 ± 0.4%	95 ± 5%	5.5	yes
7	Neumann et al.'s Literature[2]	2.0	12.3%	NR^e	NR^e	NR^e	yes

^{a} The mass balance is calculated from the product mass observed by GC in comparison to the initial amount of adamantane substrate used. ^{b} The selectivity calculated refers to the preference of 1-adamantanol over 2-adamantanone. ^{c} $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ alone exhibits variable and long induction periods and hence, yields no products at 24 h. However, after longer reaction times of ~120 h, the products are observed. ^{d} The yields reported are a reflection of two averaged data sets where the product analysis was performed at ~ 120 h. ^{e} NR = not reported.

does not contain two Ru but, instead, is really the same as our low-Ru material.

O_2 Uptake and Product Identification and Quantitation Studies with Premixed $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$ plus $[Ru(DMSO)_4Cl_2]$ plus 4-*tert*-butylcatechol. The above experiments, along with our prior demonstration[8] of a radical-chain mechanism for the formation of 1-adamantanol and 2- adamantanone beginning with "Q_{11}-**1**" as the precatalyst, strongly imply that the results in Table 4 are all due to radical-chain chemistry. However, to provide evidence for this in the now important case of premixed $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ plus $[Ru(DMSO)_4Cl_2]$, these two precursors were combined under the standard reaction conditions employed herein. After about 8 h when O_2 uptake was observed to be underway, 4-*tert*-butylcatechol (a radical inhibitor used in both our and the literature previous studies[2,8]) was added. As shown in Supporting Information, Figure S8, the addition of 4-*tert*-butylcatechol *completely halted* the otherwise ongoing O_2 uptake; no further hydroxylated adamantane products were observed by GC. While only a single experiment, in light of the now extensive evidence for a radical-chain mechanism when using "Q_{11}-**1**" as the precatalyst[8] and given that 4-*tert*-butylcatechol is an established inhibitor of that chain,[8] even this single result provides prima facie evidence of a similar mechanism, and a close connection, between "Q_{11}-**1**" and a physical mixture of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ plus $[Ru(DMSO)_4Cl_2]$.

Conclusions

The main findings from the present study can be summarized as follows:

- "Q_{11}-**1**" prepared in at least our laboratories by two independent researchers (reported herein and ref 8) and in Hill's[12] laboratories (as well as in Nomiya's laboratories[11]) is *not* consistent with the previously claimed[1,2] $Q_{11}[Ru^{III}_2ZnW(H_2O)(OH)(ZnW_9O_{34})_2]$ on the basis of elemental analysis, single crystal X-ray diffraction, ^{183}W NMR, and oxygen uptake and product quantification studies plus appropriate control experiments. In particular, to date no one has reported being able to independently prepare a sample of **1** that contains the claimed two Ru atoms.
- Instead, "Q_{11}-**1**" at least as we or others can synthesize, appears to be primarily the parent polyoxoanion precursor, $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ with small amounts of Ru ($\leq$0.2 atoms) either substituted into the complex, or perhaps more likely variable amounts of Ru^{n+} present as an impurity.
- The two previous crystal structure determinations of "Na_{11}-**1**" as $Na_{11}[Ru^{III}_2ZnW(H_2O)(OH)(ZnW_9O_{34})_2]$ or $Na_{14}[W_{0.76}Ru_{1.24}Zn_2(H_2O)_2(ZnW_9O_{34})_2]$ show strong similarities to the parent polyoxoanion, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$. While this is to be expected based on the similarities of their structures, this does reillustrate[19e] the need for other physical methods able to show the amount and location of low-valent metals in polyoxoanion structures—a difficult topic.[19e]
- Control O_2 uptake and product identification studies using $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ alone, $[Ru(DMSO)_4Cl_2]$ alone, or a combination of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ and $[Ru(DMSO)_4Cl_2]$ provide evidence that premixed $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ and 0.13 equiv of $[Ru(DMSO)_4Cl_2]$ is a about *2-fold faster, kinetically more competent catalyst to the same products* that were reported for the original "Q_{11}-**1**" with its claimed two Ru atoms. This is an important new piece of evidence, one as important as any reported herein, evidence that either (i) raises the hypothesis that the claimed 2-Ru containing "Q_{11}-**1**" may actually be a mixture of low levels of Ru plus the parent polyoxoanion (and since their catalysis is basically the same), or (ii) alternatively suggests that if **1** exists, then the two framework incorporated Ru atoms are not relevant to catalysis.
- Another conclusion is that the *catalysis* is an important additional handle, one that allows an independent, albeit indirect, probe of the amount of Ru^{n+} and its location. Such an independent handle would be valuable in other areas where metal content and location in late-transition-metal-substituted polyoxometalates remains controversial.[19e]
- The radical-chain mechanism previously elucidated for "Q_{11}-**1**" in our prior work[8] still appears to be operative. That mechanism can now be updated slightly by replacing the "Ru_2^{III}" and "$Ru_2^{III/IV}$" species in Scheme 3 elsewhere[8] with a more general Ru^{n+} and Ru^{n+1} species in the chain mechanism (see Supporting Information, Figure S1 for the slightly revised radical-chain mechanistic scheme).

Overall, we find no independent evidence for Ru_2 containing "**1**." We emphasize that the evidence herein does not mean that **1** cannot or even does not exist, but just that (a) *no reliable synthesis of it exists*. Another important implication of our results is that if authentic Ru_2-containing **1** were made with its framework-incorporated[28] Ru_2, it might still be an inferior oxidation catalyst versus simply beginning with a physical mixture of low levels of $[Ru(DMSO)_4Cl_2]$ plus 1.0 equiv of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$.

An overall message of the present and our prior[8] work is that claims of Ru and other late-metal substituted polyoxometalates will need to consider carefully the problems and issues present in getting pure samples of fully substituted, non-disordered, non-late-metal contaminated products. Then, catalysis with those precatalyst complexes[13−17] will need to rely on the appropriate kinetic and other, ideally operando,[17] studies needed to rule out the conceivable catalyst possibilities en route to providing evidence for the true catalyst and true reaction type. In oxidation chemistry, ruling out "omnipresent autoxidation"[29] continues to be job #2, while obeying Platt's scientific method of the disproof of all alternative hypotheses[30] continues to be job #1 here and in science in general.

Experimental Section

Materials. All reaction solutions were prepared under oxygen and moisture-free conditions in a Vacuum Atmosphere drybox (O_2 level ≤ 5 ppm, as continuously monitored by an oxygen sensor). 1,2-Dichloroethane (Aldrich, HPLC grade) was dried with preactivated 4 Å molecular sieves and stored in the drybox. Adamantane (Aldrich, 99+%) was used as received and stored in the drybox. $Na_2WO_4 \cdot 2H_2O$ (Aldrich, 99%), $Zn(NO_3)_2 \cdot 6H_2O$ (Fisher Chemicals), $RuCl_3 \cdot xH_2O$ (Aldrich, 99.98%), NaCl (Fisher Chemicals, ACS grade), and Aliquat 336 (Aldrich) were used as received. 4-*tert*-Butylcatechol (Aldrich, 97%) was stored in the freezer. Deionized water was used for solution preparations.

Instrumentation. Infrared spectra were obtained on a Nicolet 5DX spectrometer using neat samples in a press-fit KBr cell. The ^1H nuclear magnetic resonance (NMR) spectra in D_2O or $CDCl_3$ were obtained on a Varian Inova (JS-300) NMR spectrometer and referenced to the residual proton impurity in the deuterated solvent. The ^{183}W NMR spectrum was obtained on a Varian Inova 500 MHz NMR and was referenced to an external Na_2WO_4 sample. The 500 MHz NMR was kept at 52.0 ± 0.2 °C by heating the carrier gas. A high precision (±0.015 psig) oxygen pressure transducer (Omegadyne Inc., model PX02C1-100G10T-OX) connected to an analog-to-digital converter (Omega D1131) and integrated with LabView 6.1 software was used for O_2-uptake data collection, all as previously described.[31] GC analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a FID detector and a SPB-1 capillary column (30 m, 0.25 mm i.d.) with the following temperature program, as before[8] for adamantane hydroxylation products: initial temperature, 140 °C (initial time, 4 min.); heating rate, 5 °C/min; final temperature, 180 °C (final time, 3 min.); FID detector temperature, 250 °C; injector temperature, 250 °C. An injection volume of 1 μL was used. Product peaks were identified by comparison to authentic sample peaks. Elemental analyses were performed by Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany) or, where indicated, by Galbraith Laboratories, Inc. (Knoxville, TN). Diffraction data were collected on a Bruker APEX2 diffractometer employing Mo Kα radiation for three independent crystals. Standard Bruker APEX2 control and integration software was employed, and Bruker SHELXTL[32] software was used for structure solution, refinement, and graphics. A face-indexed absorption correction yielded results that were not better than obtained using SADABS[33] alone. The structure was solved by direct methods and refined by a full-matrix, weighted least-squares process. Residual electron density representing solvent molecules (H_2O) and the countercations (Na^+) were included in the model.

Preparation of Putative "$\{[WZnRu_2(OH)(H_2O)](ZnW_9O_{34})_2\}^{11-}$", 1, Precatalyst. The precursor $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2] \cdot xH_2O$ (precrystallization yield 37 g, 27%) was synthesized and recrystallized according to the literature.[3,8] ^{183}W NMR (D_2O) observed at 52 °C [reported[3], estimated from the spectrum provided at 32 °C]: δ +24 [+21], −14.2 [−20], −37 [−55], −77 [−95], −83 [−100], −89 [−105], −147 [−155], −178 [−190], −218 [−230], −313 [−310]. Elemental analysis on a sample dried at room temperature under vacuum yields: Calculated [found]: Na 5.02 [4.99]; W 63.6 [63.0]; O 24.8 [24.6]; Zn 5.95 [5.99].

Similarly, $[Ru(DMSO)_4Cl_2]$ was synthesized and recrystallized according to the literature[10,34] (recrystallized yield 70−75%). The ^1H NMR of recrystallized $[Ru(DMSO)_4Cl_2]$ was identical within experimental error to a recent published preparation.[10] ^1H NMR ($CDCl_3$): δ (major peaks) 2.67, 2.78, 3.37, 3.49, 3.55, and 3.58; literature[10] ($CDCl_3$): δ (major peaks) 2.60, 2.72, 3.32, 3.43, 3.48, and 3.50. Elemental analysis from Galbraith Laboratories, Inc. on a recrystallized sample dried overnight at room temperature under vacuum yields: Calculated [found]: Ru 20.9 [20.7]; C 19.8 [20.0]; H 4.99 [5.23]; S 26.5 [27.0]; Cl 14.6 [14.3].

Next, "$K_{11}[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2] \cdot 15H_2O$" was prepared and recrystallized twice from hot water according to the literature:[21] specifically and in brief, 22.5 g (3.7 mmol) of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2] \cdot 46{-}48\ H_2O$ was dissolved in ~10 mL of deionized water under Ar. Under a flow of Ar, 4.0 g (8.3 mmol) of $[Ru(DMSO)_4Cl_2]$ was added, and the solution was refluxed under Ar at 90 °C for 18 h. Following the reflux, the solution was exposed to air and 2 g (27 mmol) of KCl was added causing an immediate formation of a yellow precipitate. The product was filtered and recrystallized twice from hot water and finally dried under vacuum overnight at room temperature. Yield 4.1 g (18%); literature: 3.7 g (16%)[8] and 24%.[21] Neat IR: 720 (s), 770 (s), 881 (m), 924 (m). Elemental analysis, calculated [found]: K, 7.53 [4.69]; Na, 0 [0.59]; **Zn, 3.43 [7.13]**; **Ru, 3.54 [0.75]**.

Next, the organic counterpart of the polyoxometalate salt "$Q_{11}[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2] \cdot nQCl$" was synthesized via the published method,[7,21] specifically and briefly as follows: equimolar amounts of "$K_{11}[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2] \cdot 15H_2O$" (0.18 mmol) and QCl (2.0 mmol) were combined in deionized water and the product was extracted three times using ~5 mL of 1,2-dichloroethane. The 1,2-dichloroethane was then removed in vacuo to yield of the gum-like, red-orange compound. Yield 51%; literature[8] 50−65%. IR data (as a neat sample): 714 (s), 797 (s), 874 (m), 924 (m) cm^{-1}; literature:[8] 723 (s), 766 (s), 871 (m), 921 (m) cm^{-1}. The IR spectrum can be seen in Supporting Information, Figure S1. Elemental analysis of the above prepared sample which had been dried under vacuum overnight at room temperature gave the following analysis, calculated [found]: C,

---

(29) Limburg, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5932–5954.

(30) Platt, J. R. *Science* **1964**, *146*, 347; As Platt notes, "for exploring the unknown, there is no faster way".

(31) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891–4910.

(32) Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112–122.

(33) Sheldrick, G. M. *SADABS, program for Siemens Area Detection Absorption Correction*, 2000.

(34) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204–209.

39.91 [39.75]; H, 7.28 [7.10]; N, 1.86 [1.62]; **Ru, 0.21 [0.21]**; **Zn, 3.21 [3.50]**, which in turn yields the composition $Q_{12}[WRu_{\sim0.2}Zn_{\sim2.8}(H_2O)_2(ZnW_9O_{34})_2]\cdot QCl$. An independent sample of "Q_{11}-**1**" and "K_{11}-**1**" was also generously donated by C. Hill's laboratory; elemental analysis of the Hill K^+ salt yields: **Ru, <0.1**; **Zn, 2.92**; Elemental analysis results of a third independent sample prepared by C.-X. Yin from the Finke group yields the composition, $Q_{12}[WRu_{\sim0.05}Zn_{\sim3}(H_2O)_2(ZnW_9O_{34})_2]\cdot 2.5QCl$. Calculated [found]: C, 41.93 [41.44]; H, 7.64 [7.92]; N, 1.96 [1.83]; O, 10.8 [10.3]; W, 33.6 [32.7]; **Ru, 0.05 [0.05]**; **Zn, 3.15 [3.49]**. Unless otherwise indicated, the "K_{11}-**1**" and "Q_{11}-**1**" samples prepared at Colorado State University by A. M. Morris were used in subsequent experiments.

Preparations of crystals of "$Na_{11}[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]\cdot 42H_2O$" X-ray quality crystals of "$Na_{11}[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]\cdot 42H_2O$" were grown according to the literature procedure.[2] Briefly, "$K[WZnRu^{III}_2(OH)(H_2O)(ZnW_9O_{34})_2]\cdot 15H_2O$" was dissolved in a 0.5 M solution of NaCl and allowed to slowly evaporate in air at room temperature. After approximately 1 week, spear-shaped, clear-orange crystals were obtained. Elemental analysis of this crystalline sample gives: calculated [found]: Na, 5.06 [4.62]; Zn, 5.99 [5.99]; W, 64.0 [62.8]; O, 24.4 [24.2], consistent with. the composition, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 13H_2O$.

Preparation of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$. $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$ was prepared in the analogous manner to the literature preparation of "$Q_{11}[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]\cdot nQCl$."[7,21] Specifically, 410−520 mg (70−90 μmol) of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 46{-}48H_2O$ was dissolved in about 10 mL of deionized water with heating and stirring. This solution was cooled to room temperature and 320−420 mg (0.8−1.0 mmol) of Aliquat 336 (Aldrich) was added. The solution was then extracted three times with about 5 mL of 1,2-dichloroethane, each time collecting the lower, organic layer. The 1,2-dichloroethane solvent was then removed in vacuo resulting in a colorless to orange gel. Yield 260−380 mg (37−38%). IR data (as a neat sample): 722 (s), 765 (s), 873 (m), and 923 (m) cm^{-1}. The full IR spectrum can be seen in Supporting Information, Figure S2.

Preparation of the ^{183}W NMR Sample. 1.0 g (0.18 mmol) of "K_{11}-**1**" was dissolved with heating and stirring in about 3 mL of D_2O. To this solution, 0.17 g (1.6 mmol) of $Li(ClO_4)_2$ was added to exchange the potassium cation and improve solubility. The solution was filtered to remove the solid $KClO_4$ and transferred into a 10 mm NMR tube. The solution was kept at or above 50 °C at all times to prevent the product from recrystallizing. ^{183}W NMR (D_2O, 52 °C): δ +25.2, −17.6, −40.0, −81.5, −83.7, −88.8, −149.7, −183.1, −222.9, −298.5; literature (D_2O, 22 °C):[3] δ (estimated from spectrum) +20, −20, −55, −95, −100, −105, −155, −190, −230, −310.

General Procedures for Oxygen-Uptake Experiments. Adamantane hydroxylation was monitored by oxygen pressure loss on a computer-interfaced, high precision O_2-pressure transducer apparatus (vide supra). The reaction flask was a pressurized Fischer−Porter bottle attached via Swagelock quick-connects and flexible stainless steel tubing to both an oxygen tank and to the pressure transducer. (A schematic of this general apparatus, but where instead a H_2-compatible pressure transducer is instead used, is provided elsewhere.[31]) In the drybox, adamantane (ca. 815 ± 8 mg, 6.0 mmol) was weighed into a 5 dram vial and transferred using the 1,2-dichloroethane solvent into a new 22 mm × 175 mm Pyrex culture tube along with a new 5/8 in. × 5/16 in. Teflon stir bar. The precatalyst, "Q_{11}-**1**" (ca. 60 ± 5 mg, 6.0 μmol) was dissolved in about 5 mL of 1,2-dichloroethane, and then quantitatively transferred into the culture tube via a disposable pipet. The remaining solvent (total = 12 mL) was added to the culture tube, and the culture tube was then placed inside the Fischer−Porter bottle, sealed, and brought out of the drybox. The bottle was connected via the quick-connects, placed in a temperature controlled oil bath (80 °C), and stirring was initiated. The solution was equilibrated with stirring at 80 °C for 40 min under the inert N_2 atmosphere of the Fischer−Porter bottle. The Fischer−Porter bottle was then purged 15 times with ~14 psig of O_2; 15 s/purge, equilibrate 1 min 15 s; 5 min total time elapsed before the pressure recordings were initiated. The reaction vessel pressure was set at 14 ± 2 psig and $t = 0$ was set. The reactions shown here were stopped after 24 h following literature precedent unless otherwise noted.[1,2] At the end of the reaction, GC analysis was used for the determination of the final products following the hydroxylation. The Fischer−Porter bottle was vented, opened in air, and the contents were poured into a 5 dram vial. A 0.2 mL sample from the vial was dissolved in 8.2 mL of 1,2-dichloroethane (41 × dilution) and used for the GC analyses.

O_2-Uptake Experiments with $[Ru(DMSO)_4Cl_2]$. The same procedure as above ("General Procedures for Oxygen-Uptake Experiments") was used except, instead of dissolving 60 mg of the precatalyst, "Q_{11}-**1**," in about 5 mL of 1,2-dichloroethane, 0.1 mL of a solution containing 3.6 mg (7.7 μmol) of $[Ru(DMSO)_4Cl_2]$ in 1.0 mL of 1,2-dichloroethane was added. This $[Ru(DMSO)_4Cl_2]$ solution permitted 0.77 μmol of Ru to be added to the reaction which is the average amount (0.13 equiv) of Ru present in the "Q_{11}-**1**" sample by elemental analysis from the two samples prepared in our laboratories (entries 1 and 6, Table 4).

O_2-Uptake Experiments with $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$. The same procedure as above ("General Procedures for Oxygen-Uptake Experiments") was used except instead of 60 mg of "Q_{11}-**1**," 60 ± 4 mg (~6 μmol) of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$ was dissolved in about 5 mL of 1,2-dichloroethane, and the reaction time was lengthened to ~120 h since no O_2 uptake was observed after the normal 24 h.

O_2-Uptake Experiments with Premixed $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$ and $[Ru(DMSO)_4Cl_2]$. The same procedure as above ("General Procedures for Oxygen-Uptake Experiments") was used except instead of 60 mg of "Q_{11}-**1**," 60 ± 3 mg of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$ and 0.1 mL of the $[Ru(DMSO)_4Cl_2]$ solution described in "O_2-Uptake Experiments with $[Ru(DMSO)_4]Cl_2$" were combined and dissolved in about 5 mL of 1,2-dichloroethane. In a separate experiment, the premixed $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot nQCl$ and $[Ru(DMSO)_4Cl_2]$ solution was monitored by its O_2 uptake and at $t = 8.3$ h, 35 mg (0.21 mmol) of the previously employed[2,8] radical trap, 4-*tert*-butylcatechol, was added. The results are shown in Supporting Information, Figure S8.

Acknowledgment. The authors would like to thank Ms. Susie Miller for assistance with the crystal structure data collection and determination, as well as Dr. Travis M. Anderson and Prof. Craig L. Hill for supplying their samples of "K_{11}-**1**" and "Q_{11}-**1**". Prof. Kenji Nomiya and his co-workers[11] are also gratefully acknowledged for allowing us to cite in the Supporting Information the results and details of their six attempted preparations of **1**. This work was supported by NSF Grant CHE 9531110.

Supporting Information Available: IR spectrum of "Q_{11}-**1**" prepared herein; IR spectrum of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$;

Crystallographic data table for the structure solved herein in the alternative $P2_1/c$ space group and comparison to Neumann and Tourné's structures; Adamantane O_2-uptake curve using $[Ru(DMSO)_4Cl_2]$; Adamantane O_2-uptake curves using $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$; Adamantane O_2-uptake curve and discussion of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ plus $[Ru(DMSO)_4Cl_2]$; Experimental, O_2-uptake, and discussion of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ plus 1 equiv of Zn; Experimental, O_2 uptake, and discussion of QCl plus $[Ru(DMSO)_4Cl_2]$; Adamantane O_2-uptake and discussion of $Q_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ plus $[Ru(DMSO)_4Cl_2]$ with added 4-*tert*-butylcatechol; Slightly updated mechanism for the radical chain initiated adamantane hydroperoxylation plus concurrent Ru-catalyzed ROOH-based adamantane reaction; Details of six attempts to prepare **1** by Nomiya and co-workers; Crystallographic tables of atomic coordinates, isotropic displacement, bond lengths, and bond angles for $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ solved herein. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9000363