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Polyoxoanion-Supported Catalyst Precursors. Synthesis and Characterization of the Iridium(I) and Rhodium(I) Precatalysts $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})M{\cdot}P_2W_{15}Nb_3O_{62}]$ (M = Ir, Rh)

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The reaction of the triniobium-substituted polyoxometalate $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ with an equimolar amount of $[Ir(1,5\text{-COD})(CH_3CN)_2]BF_4$ or $[Rh(1,5\text{-COD})(CH_3CN)_2]BF_4$ (1,5-COD = 1,5-cyclooctadiene) leads to the formation of the air-sensitive polyoxometalate-supported organometallic complexes $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$, **1**, and $[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$, **2**. These complexes were isolated as their mixed $5[(n\text{-}C_4H_9)_4N]^+/3Na^+$ salts and have been characterized by ^1H, ^{13}C, ^{31}P, and ^{183}W NMR spectroscopy as well as IR spectroscopy, sedimentation-equilibrium molecular-weight measurements, and complete elemental analyses. Additional studies of **1** by ^{17}O NMR demonstrate that the iridium binds in overall average C_{3v} (pseudo) symmetry to the "$Nb_3O_9^{3-}$" minisurface (pseudo due to the 2-fold axis in 1,5-COD and thus the local C_s symmetry at iridium). For **2**, the results of the ^{17}O NMR studies are definitive in showing that **2** can also be successfully ^{17}O-enriched in the niobium−oxygen sites. However, the ^{17}O NMR data subsequently acquired for **2** require the formulation of two or more (possibly rapidly interconverting) support-site isomers in solution. These ^{17}O NMR results provide direct evidence for the $M{-}ONb_2$ bonding between $[(1,5\text{-COD})M]^+$ (M = Ir, Rh) and $P_2W_{15}Nb_3O_{62}^{9-}$ in solution, where catalysis beginning with **1** and **2** as a precatalyst has been demonstrated.

Introduction

Polyoxometalates[2] are soluble-oxide compounds that resemble discrete fragments[3] of the solid metal−oxide component of heterogeneous insoluble[4] catalysts. Because of this resemblance, polyoxometalates are of considerable interest as catalyst-support materials. One goal is to provide a correlation between atomic-level structure and function for catalysis by oxide-supported metals, *a level of understanding that is virtually unavailable for heterogeneous insoluble catalysts.* Polyoxometalate-supported organometallics also have potential as spectroscopic models and as systems where rational catalyst design and molecular fine-tuning would be possible. Perhaps most importantly, polyoxometalate-supported organometallics should also provide completely new types of catalyst materials with their own potentially unique reactivity[5] and chemistry. Because of these possibilities, the area of polyoxometalate-supported organometallic complexes has been active over the past 12

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(3) This resemblance was first noted by: Baker, L. C. W. In *Advances in the Chemistry of Coordination Compounds*; Kirschner, S., Ed.; Macmillan: New York, 1961; p 604.

(4) Schwartz (*Acc. Chem. Res.* **1985**, *18*, 302) has proposed definitions that limit a homogeneous catalyst to one with a single, chemically unique active (i.e., homogeneous) site and a heterogeneous catalyst as one with multiple, chemically different (i.e., heterogeneous), catalytically active sites. Schwartz further suggests the addition of the suffix -soluble or -insoluble for single-phase or multiphase systems, respectively. Within this context it is, therefore, homogeneous-soluble and homogeneous-insoluble catalysts that are of greatest current interest due to the expectation that they will exhibit the more selective catalytic chemistries.

(5) (a) Various systems have been researched as soluble (non-polyoxometalate) "oxo-type" homogeneous analogs for heterogeneous-insoluble, solid oxide-supported catalysts: metal carbonyl clusters,[5b] metal alkoxide compounds,[5c] Kläui's ligand $\{(C_5H_5)CoP[(O)(OR)_2]_3$,[5d] and Feher and co-workers' siloxide-bound organometallic fragments.[5e] More recently, Tanke and Crabtree have used Grim's triso[5f] ligand, $C(Ph_2PO)_3^-$, to prepare iridium, rhodium, and ruthenium complexes with the metals in an oxygen-donor ligand environment.[5g] (b) Muetterties, E. L. *Catal. Rev.−Sci. Eng.* **1981**, *23*, 69 and references therein. Evans, J. *Chem. Soc. Rev.* **1981**, 159 and references therein. Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977**, *2*, 229. (c) Chisholm, M. H.; Eichorn, B. W.; Folting, K.; Huffman, J. C. *Organometallics* **1989**, *8*, 49. Chisholm, M. H.; Eichorn, B. W.; Huffman, J. C. *Organometallics* **1989**, *8*, 67. Chisholm, M. H.; Eichorn, B. W.; Huffman, J. C. *Organometallics* **1989**, *8*, 80. Toth, R. T.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 172. (d) Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627. Lenders, B.; Kläui, W. *Chem. Ber.* **1990**, *123*, 2233. Kläui, W.; Huhn, M.; Herbst-Irmer, R. *J. Organomet. Chem.* **1991**, *415*, 133. Wedler, M.; Gilje, J. W.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *411*, 271. Thomas, J. A.; Davison, A. *Inorg. Chem.* **1992**, *31*, 1976. (e) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850. Feher, F. J.; Gonzales, S. A.; Ziller, J. W. *Inorg. Chem.* **1988**, *27*, 3440. Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *373*, 153. Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741 and references therein. Feher, F. J.; Liu, J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1990**, *29*, 5138. Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638. Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30*, 1689. Budzichowski, T. A.; Chacon, S. T.; Chisholm, M. H.; Feher, F. J.; Streib, W. *J. Am. Chem. Soc.* **1991**, *113*, 689. Feher, F. J.; Budzichowski, T. A. *Organometallics* **1991**, *10*, 812. Winkhofer, N.; Roesky, H. W.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 599. Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614. Feher, F. J.; Walzer, J. F.; Blanski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 3618. Feher, F. J.; Taijima, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 2145. (f) Grim, S. O.; Sangokoya, S. A.; Colquhoun, I. J.; McFarlane, W.; Khanna, R. K. *Inorg. Chem.* **1986**, *25*, 2699. (g) Tanke, R. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1056. Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984. Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 1714.

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years.[6-8] However, and despite such potential, polyoxometalate-supported catalysis has not been previously described until our recent reports.[9-12]

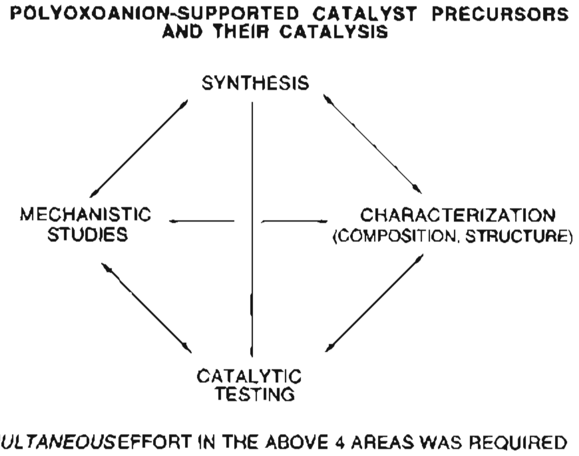

Figure 1. Central components of the effort aimed at developing a paradigm for polyoxoanion-supported catalysts.

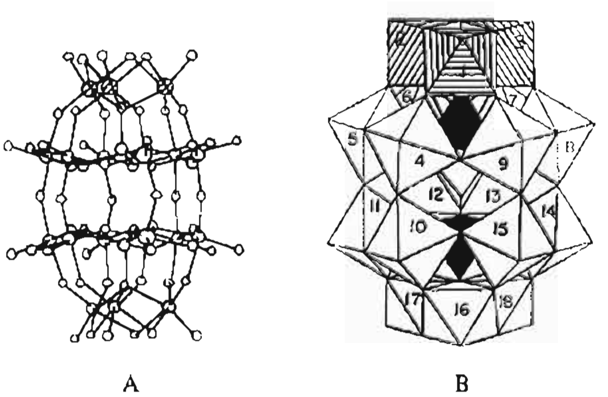

Figure 2. (A) Ball and stick representation of α-1,2,3-$P_2W_{15}Nb_3O_{62}^{9-}$ as determined by a single crystal X-ray diffraction structural analysis.[8g] The hatched circles show the position of the three Nb atoms. (B) Polyhedral representation of α-1,2,3-$P_2W_{15}Nb_3O_{62}^{9-}$. The three niobiums are represented by the hatched octahedra in the 1, 2, and 3 positions. The WO_6 octahedra occupy positions 4–18, and the PO_4 groups are shown as the two internal black tetrahedra.

Our approach to developing a polyoxometalate-supported organometallic catalyst began from the key conceptual point that catalysis is a wholly kinetic phenomenon,[13] accomplished by intermediates and other transients, but not generally by isolable complexes. Hence, the development of isolable—but reactive—polyoxometalate-supported organometallic *catalyst precursors* that are characterizable at the atomic level has been a key focus of our work. The development of a useful polyoxometalate-supported catalyst precursor has required simultaneous efforts in four areas, Figure 1: synthesis of the ML_x·polyoxometalate^{9-} catalyst precursor, its unequivocal characterization (often the slowest and most difficult step),[8,9] stoichiometric studies that demonstrate reactivity at the metal–ligand bonds without rupture of the metal–polyoxometalate bonds,[9c-e] and detailed mechanistic studies probing whether or not the polyoxometalate–metal bonding is retained during catalysis.[10c]

The choice of $[(1,5\text{-COD})M]^+$ as the organometallic component of $[(1,5\text{-COD})M{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ was based on the literature;[14] the decision of which polyoxometalate to employ, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (Figure 2), was based on our recent synthesis[9] and preliminary experiments demonstrating that this combination yields a superior system, in terms of both characterization and its subsequent reactivity.

There are two key variables to be probed in polyoxoanion-supported catalysts. The first is the effect of changing the poly-

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(10) (a) An initial study by our group concerning the catalytic oxygenation of cyclohexene by O_2 using either $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]$, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ or $[(n\text{-}C_4H_9)_4N]_4Na_3[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]$ has been published.[10b] (b) Mizuno, N.; Lyon, D. K.; Finke, R. G. *J. Catal.* **1991**, *128*, 84. (c) Weiner, H.; Trovarelli, A.; Finke, R. G. Manuscript in preparation. (d) Mizuno, N.; Lyon, D. K.; Finke, R. G. U.S. Patent 5,250,739, issued Oct 5, 1993. (e) An elegant crystallographic study of the stoichiometric reaction of $[(1,5\text{-COD})IrP_3O_9]^{2-}$ with O_2 has been reported: Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2031.

(11) (a) Initial catalytic hydrogenation studies using a partially oxidized form of "$[(n\text{-}C_4H_9)_4N]_7[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]$" have been reported.[11b] A novel iridium–catalyst complex was demonstrated starting from this material, the nature of which is almost surely the polyoxoanion-stabilized Ir^0_n nanoclusters that we recently reported elsewhere.[9h] (b) Edlund, D. J.; Finke, R. G.; Saxton, R. J. U.S. Patent 5,116,796, issued May 29, 1992 (*Chem. Abstr.* **1989**, *110*, 97553h). (c) Edlund, D. J. Dissertation, University of Oregon, 1987. (d) Edlund, D. J.; Finke, R. G.; Saxton, R. J. U.S. Patent 5,116,796, issued May 29, 1992.

(12) (a) Other reports have appeared[12b-e] of catalysis by mixtures containing certain types of polyoxoanions and organotransition metal complexes. However, in each case the active catalyst, although quite interesting, is clearly not a tightly supported transition metal–polyoxoanion complex either by design or due to the use of polyoxoanions with negligible or insufficient surface-oxygen charge density. (b) Urabe, K.; Tanaka, Y.; Izumi, Y. *Chem. Lett.* **1985**, 1595. (c) Che, T. M. U.S. Patent 4,590,298, assigned to Celanese Corp., May 20, 1986. (d) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219. (e) Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Skarjune, R. P.; Hodgson, K. O.; Roe, A. L.; Day, V. W. *Solid State Ionics* **1988**, *26*, 109.

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oxoanion (e.g., $P_2W_{15}Nb_3O_{62}^{9-}$ vs $SiW_9Nb_3O_{40}^{7-}$); such polyoxoanion variation studies are reported elsewhere.[8h] The second key variable is the supported transition metal[15] (e.g., Ir^I vs Rh^I), and for this reason we have simultaneously pursued the synthesis and characterization of both the Ir and the Rh analogs, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]$[16] (M = Ir, **1**; M = Rh, **2**). The reaction of the $[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ (M = Ir, Rh) complexes with CO to form the corresponding $[(OC)_2M^I\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ have also been investigated.[9d,f] These bis(carbonyls), and here especially the rhodium complex $[(OC)_2Rh\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, have potential as much needed EXAFS spectroscopic models for $(OC)_2Rh\cdot$solid oxides.[17]

An important piece of background structural information is the report of the atomic-level structural characterization of[8g] $P_2W_{15}Nb_3O_{62}^{9-}$ and its supported $[(C_5Me_5)Rh^{III}]^{2+}$ organometallic derivative $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, Figure 3,[8i] by X-ray crystallography, the first (and to date only) crystallographically determined structure of a Dawson-type polyoxoanion-supported organometallic complex. Significant for the present work, the crystal structure of $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ demonstrates that $[(C_5Me_5)Rh^{III}]^{2+}$ is supported rigidly on the C_{3v} support site (i.e., directly over the C_3 axis) via three bridging Nb−O−Nb oxygens.[8i]

The Ir congener, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$, is of special interest since most of our catalytic studies to date emphasize it. Separate reports describe the oxidative and reductive catalysis derived from the Ir complex **1**.[9,10] That work has provided both the first *bona-fide* polyoxoanion-supported (oxidation) catalyst[10b−d] and, under H_2, a novel $Ir_{\sim 300}\cdot$polyoxoanion nanocluster catalyst for reductions with H_2.[9e,h] Those catalytic results emphasize the importance of reporting herein the full details of the synthesis and characterization of $[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ (M = Ir, Rh). An overview of our work emphasizing $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ in homogenous catalysis is also available to the interested reader.[2d]

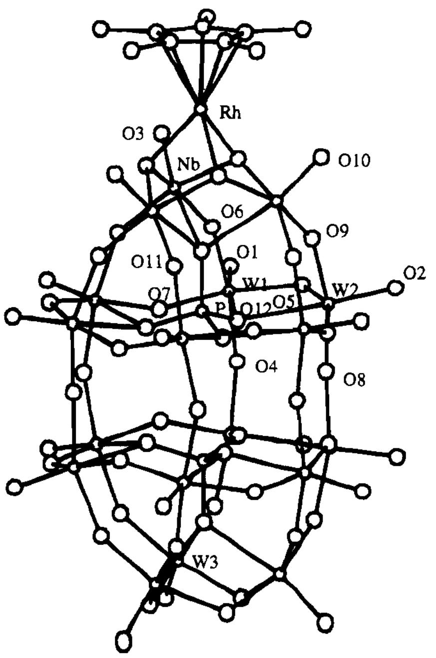

Figure 3. Crystallographically determined structure of $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$.[8i] The Nb and W3 atoms each are composite, $Nb_{0.5}W_{0.5}$, because the anion adopts two equally-weighted orientations related by the mirror plane of a 3/*m* (D_{3h}) crystallographic site. The C_5Me_5 group lies in a plane normal to the anion C_3 axis and is disordered because of the incompatibility of its 5-fold symmetry with that axis.[8i]

Herein we report the full details of the synthesis and especially the characterization of $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, **1**, and of its previously unreported Rh analog, $[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, **2**, including an improved synthesis of the underlying polyoxometalate support system, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, that is the result of more than 40 preparations by four of us. Characterization of the title compounds was accomplished in solution (where catalysis has been reported; *vide infra*) by a multitude of techniques. A somewhat larger scale, *Inorganic Synthesis* version of these preparations has been submitted for publication,[8j] and the synthesis and characterization of the water-soluble, all-Na^+ salt, $Na_9P_2W_{15}Nb_3O_{62}$, are also available elsewhere.[8k]

Results and Discussion

Synthesis of $[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$. The synthesis of $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, **1**, and of $[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, **2**, in greater than 95% purity follows the conceptually straightforward route outlined in eq 1a, provided that the

$$\begin{aligned}&[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62} + \\ &\qquad [M(1,5\text{-COD})(CH_3CN)_2]BF_4 \xrightarrow[\le 1\ \text{ppm}\ O_2]{\text{dry}\ CH_3CN} \\ &\qquad [(n\text{-}C_4H_9)_4N]_8[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}] + \\ &\qquad\qquad [(n\text{-}C_4H_9)_4N]BF_4 \end{aligned} \quad (1a)$$

synthesis is carried out under strict O_2-free conditions (less than 1 ppm[18]) in an inert-atmosphere drybox. It has not proven possible to isolate either **1** or **2** as its pure octakis(tetrabutylammonium) salt (i.e., in its all-$[(n\text{-}C_4H_9)_4N]^+$ form) in any

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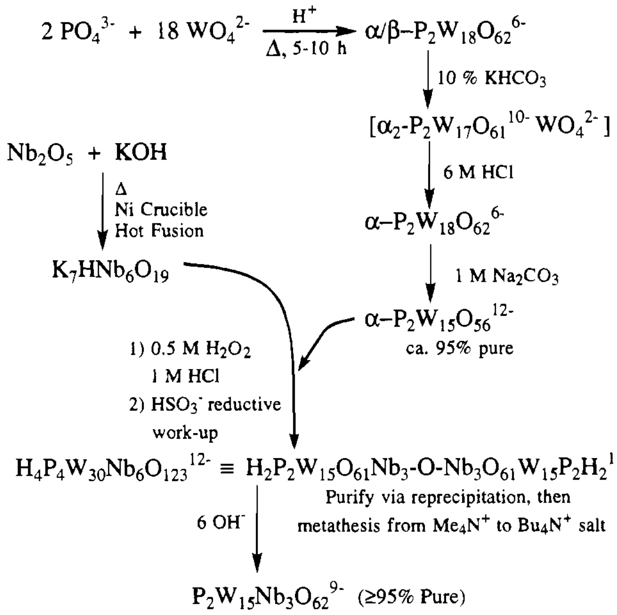
(15) Anticipated differences between second- and third-row transition metals include the following: second-row transition metals generally form weaker bonds than third-row transition metals;[15a] second-row transition metals also show an increased stability in lower oxidation states in comparison to third-row metals;[15b] and second-row metals show a lower tendency to be pentacoordinated in comparison to third-row transition metals.[15c] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; p 239. (b) Marks, T. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series; American Chemical Society: Washington, DC, 1990; p 428. Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper: San Francisco, CA, 1983. (c) Louw, W. J.; Hepner, C. E. *Inorg. Chem.* **1980**, *19*, 7. Mestroni, G.; Camus, A. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 261. Mestroni, G.; Camus, A.; Zassinovich, G. *J. Organomet. Chem.* **1974**, *65*, 119.

(16) The systematic names for **1** and **2** are (i) trisodium pentakis(tetrabutylammonium) [[(1,2,5,6-η)-1,5-cyclooctadiene]iridate][heptacosa-μ-oxopentadecaoxo[μ_9-[phosphato(3−)-*O*:*O*:*O*:*O*′:*O*′:*O*″:*O*″:*O*‴:*O*‴]]pentatungstate]hexa-μ-oxotri-μ_3-oxotrioxo[μ_9-[phosphato(3−)-*O*:*O*:*O*:*O*′:*O*′:*O*″:*O*″:*O*‴:*O*‴]]triniobate(8−), **1**, and (ii) trisodium pentakis(tetrabutylammonium) [[(1,2,5,6-η)-1,5-cyclooctadiene]rhodate][heptacosa-μ-oxopentadecaoxo[μ_9-[phosphato(3−)-*O*:*O*:*O*:*O*′:*O*′:*O*″:*O*″:*O*‴:*O*‴]]pentatungstate]hexa-μ-oxotri-μ_3-oxotrioxo[μ_9-[phosphato-(3−)-*O*:*O*:*O*:*O*′:*O*′:*O*″:*O*″:*O*‴:*O*‴]]triniobate(8−), **2**. We thank Dr. Tom Sloan of Chemical Abstracts Service for his help in deriving these systematic names.

(17) Lead references (see also the references therein): (a) van't Blik, H. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* **1985**, *107*, 3139. (b) Frederick, B. G.; Apai, G.; Rhodin, T. N. *J. Am. Chem. Soc.* **1987**, *109*, 4797. (c) Binsted, N.; Evans, J.; Greaves, G. N.; Price, R. J. *Organometallics* **1989**, *8*, 613. (d) Herrero, J.; Blanco, C.; Gonzalez-Elipe, A. R.; Espinós, F. P.; Oro, L. A. *J. Mol. Catal.* **1990**, *62*, 171. (e) Basu, P.; Panayotov, D.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2074. (f) Buchanan, D. A.; Hernandez, E., Solymosi, F., White, J. M. *J. Catal.* **1990**, *125*, 456.

(18) ^{31}P NMR spectra of **1** that has been prepared in a glovebag in the presence of an estimated 20−50 ppm of O_2 show approximately 30−50% of unidentified impurities: Nomiya, K.; Finke, R. G. Unpublished results.

Scheme 1. Seven-Step Synthesis of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$



reasonable yield.[19] It did prove possible, however, to obtain **1** and **2** as analytically pure, homogeneous, bright yellow solids by employing our mixed-cation method[8j,9b] ($[(n\text{-}C_4H_9)_4N]^+/Na^+$) followed by at least two ethyl acetate reprecipitations of paper-filtered solutions, eq 1b. (The multiple countercations associated

$$[(n\text{-}C_4H_9)_4N]_8[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}] + 3NaBF_4 \xrightarrow[\text{2. EtOAc reppt}]{\substack{\text{1. } \leq 1 \text{ ppm } O_2\\ \text{dry } CH_3CN}} [(n\text{-}C_4H_9)_4N]_5Na_3[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]\downarrow + 3[(n\text{-}C_4H_9)_4N]BF_4 \quad (1b)$$

with polyoxometalate polyanions provide great flexibility in controlling their solubility properties by altering which cations are present. However, discovering which cation combinations give the desired properties is often experimentally tedious.[20])

It is worth mentioning that, to the best of our knowledge, the synthesis of $[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, M = Ir and Rh, constitutes a record in terms of complexity and number of synthetic steps (eight steps) involved in a polyoxoanion synthesis. Seven of the eight steps are involved in the underlying synthesis of the $P_2W_{15}Nb_3O_{62}^{9-}$ support system, Scheme 1. Note that the ca. 95% purity of the lacunary, polyoxoanion synthon, $P_2W_{15}O_{56}^{12-}$, as a noncrystalline powder is a key to the purity of the final product (≥95%); see the supplementary material for a ^{31}P NMR spectrum of $P_2W_{15}O_{56}^{12-}$ demonstrating its ≥95% purity.

Compositional Characterization of 1 and 2. The molecular formulas of **1** and **2** are established by elemental analyses (all elements, including oxygen; see the Experimental Section and the supplementary material, Tables A and B, where alternative formulations are ruled out). The C, H, and N analyses require the formulation of pentakis(tetrabutylammonium) trisodium salts and are inconsistent with formulations with even one more (or less) $[(n\text{-}C_4H_9)_4N]^+$ or Na^+. Ultracentrifugation sedimentation-equilibrium molecular-weight experiments demonstrate that these compounds are unaggregated monomers under the conditions of the experiment. [**1**: $\bar{M}_w$(calc) = 5670, $\bar{M}_w$(found) = 5600 ± 600 (supplementary material, Figure A). **2**: ($\bar{M}_w$(calc) 5584, $\bar{M}_w$(found) 5910 ± 600 (supplementary material, Figure B). ($\bar{M}_w$ = weight-average molecular weight)].[21] Consistent with these solution MW measurements, the fast-atom-bombardment mass spectra (FAB-MS) also support unaggregated, monomeric formulations for **1** and **2** and reveal no peaks at higher mass. However, neither the positive nor the negative ion FAB-MS of **1** or **2** show any signal due to the parent ion. (A detailed analysis of the FAB-MS spectrum of **1** has appeared elsewhere;[22] the positive and negative ion FAB-MS spectra of **2** are available in the supplementary material, Figures C and D, respectively.)

Infrared measurements for **1** and **2** (supplementary material, Figure E) confirm that the Dawson-type "$P_2M_{18}O_{62}^{n-}$" heteropolytungstate framework remains intact under the conditions of the synthesis, consistent with formulation of both complexes as containing intact $P_2W_{15}Nb_3O_{62}^{9-}$ with $[(1{,}5\text{-COD})M]^+$ supported upon its surface. Moreover, a careful examination of the IR spectra reveals a *lack of bands corresponding to coordinated CH_3CN.* The only plausible inner-sphere ligands for $[(1{,}5\text{-COD})M]^+$, then, are the surface oxygens of $P_2W_{15}Nb_3O_{62}^{9-}$, a result confirmed by the ion-exchange experiments and NMR spectroscopic characterization which follow.

Chemical Evidence for Inner-Sphere M^I-to-Polyoxoanion Binding. Evidence for the covalent, inner-sphere bonding of $[(1{,}5\text{-COD})M]^+$ to $P_2W_{15}Nb_3O_{62}^{9-}$ (rather than an $[(1{,}5\text{-COD})M(CH_3CN)_2]^+$ ion-paired complex) is provided by ion-exchange experiments (as well as IR and ^1H and ^{31}P NMR spectra; *vide infra*), specifically experiments with ion-exchange resins which demonstrate the nonexchangeability in acetonitrile of the cationic $[(1{,}5\text{-COD})M]^+$ complexes bonded to the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion.

As detailed in the Experimental Section, in two separate experiments acetonitrile solutions of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]$ (M = Ir, Rh) were loaded (in an inert atmosphere drybox) onto a cation-exchange column in the $[(n\text{-}C_4H_9)_4N]^+$ form, $P\text{-}SO_3^-[(n\text{-}C_4H_9)_4N^+]$ (P = macroreticular polymer), and then slowly eluted down the column. No retention of the colored, anionic $[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ was observed. A ^{31}P NMR spectrum of each of the individual eluants showed the familiar two-line spectrum confirming the integrity of the eluted parent complexes, **1** and **2**. In a second series of experiments $[(n\text{-}C_4H_9)_4N]_5Na_3[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]$ was loaded onto an anion-exchange column in its Cl^- form, $P\text{-}NR_3^+Cl^-$ (P = macroreticular polymer). Here the colored, anionic $[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ was retained on the column. As a control in separate experiments, a solution of $[(1{,}5\text{-COD})M(CH_3CN)_2]BF_4$ in acetonitrile was loaded onto the same cation- and anion-exchange columns. As expected, in the control experiment the cationic, colored $[(1{,}5\text{-COD})M(CH_3CN)_2]^+$ is retained on a cation-exchange column but passes

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(19) Attempts to perform EtOAc reprecipitations on nearly saturated CH_3CN solutions of the mixture of $[(n\text{-}C_4H_9)_4N]_8[(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]$ plus 1 equiv of $[(n\text{-}C_4H_9)_4N]BF_4$ lead to intolerably low yields of less than 10%.

(20) See footnote 8 in ref 8a.

(21) In the determination of the molecular weight, the absorbance of the solution is measured in the UV region (335 nm), where both the heteropolyoxoanion and the $[(1{,}5\text{-COD})M]^+$ absorb. In the strictest sense ultracentrifugation shows only that the polyoxoanion portion of **1** and **2** is unaggregated. Ideally one would also check the molecular weight by following the absorbance in a region characteristic *only* of $[(1{,}5\text{-COD})M]^+$. However, attempts to follow the absorbance at wavelengths above 400 nm, a region where the polyoxoanion portion does not absorb, were unsuccessful, due to low absorbance of the sample solution in this wavelength range. The next logical experiment, increasing the sample concentration, is not feasible experimentally, as sedimentation equilibrium cannot be attained for concentrated solutions.

(22) Trovarelli, A.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6034.

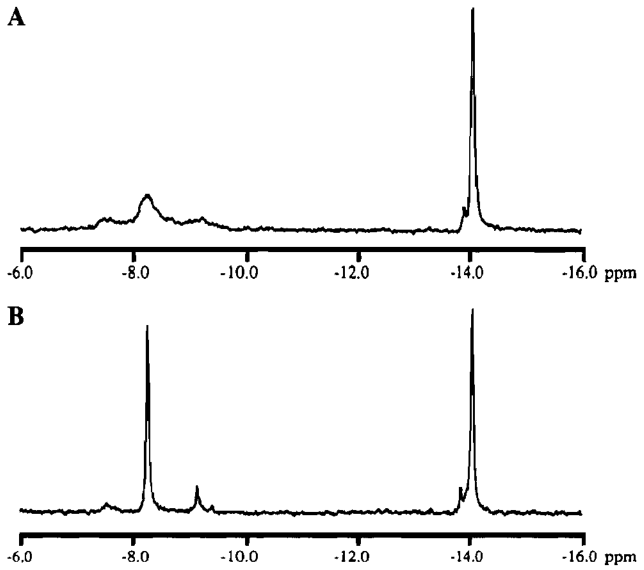

Figure 4. ^{31}P NMR spectrum of **1** in DMSO-d_6 (top; A) without Kryptofix 2.2.2. added and (bottom; B) with 3 equiv of Kryptofix 2.2.2. added showing that the initially observed, excessive line widths are caused by $Na^{+}\cdots P_2W_{15}Nb_3O_{62}^{9-}$ ion pairing.

through (presumably as $[(1,5\text{-COD})MCl]_2$) when applied to the anion-exchange column. In summary, even by themselves, these simple ion-exchange experiments provide good evidence for inner-sphere bonding of the $[(1,5\text{-COD})M]^+$ fragments to $P_2W_{15}Nb_3O_{62}^{9-}$.

Multinuclear (^{31}P, ^{183}W) NMR Characterization. Further characterization of **1** and **2** in solution, the medium of greatest interest for catalytic reactivity, relied heavily on multinuclear NMR, especially ^{31}P and ^{183}W NMR spectroscopy. ^{31}P and ^{183}W NMR are useful in characterizing the heteropolyoxoanion support's purity and framework, respectively (recall Figure 2) and provide additional evidence for the binding of $[(1,5\text{-COD})M]^+$ to $P_2W_{15}Nb_3O_{62}^{9-}$.

^{31}P NMR spectroscopy of **1** in DMSO-d_6 showed primarily two lines of approximately equal intensity, Figure 4, consistent with the presence of a single isomer. However, in DMSO the phosphorus resonance (δ −8.2) assigned to the "north" PO_4^{3-} group that is closer to the "$Nb_3O_9^{3-}$" cap in the $P_2W_{15}Nb_3O_{62}^{9-}$ moiety becomes flanked by two smaller peaks at δ −7.5 and −9.2, Figure 4A. Since $Na^{+}\cdots P_2W_{15}Nb_3O_{62}^{9-}$ ion pairing (*vide supra*) was suspected as the source of the extra peaks in the ^{31}P NMR spectrum obtained in DMSO, 3 equiv of the cryptand Kryptofix 2.2.2. (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) were added to the DMSO-d_6 NMR solution in the drybox, and the ^{31}P NMR spectrum was remeasured. The smaller peaks collapsed into the center, −8.2 ppm, resonance and the half-width of this resonance was reduced 10-fold to their normal $\Delta\nu_{1/2}$ = 4−6 Hz values. A ^{31}P NMR spectrum of **2** in DMSO-d_6 (Figure 5) also showed, following addition of 3 equiv of Kryptofix 2.2.2., a primarily two-line spectrum (δ −8.2, −14.1) as observed above for $[(1,5\text{-COD})IrP_2W_{15}Nb_3O_{62}]^{8-}$, **1**. ^{31}P NMR spectra of **1** and **2** collected in CD_3CN (and in the presence of 3 equiv of Kryptofix 2.2.2.) also exhibit two lines of approximately equal intensity and are available in the supplementary material, Figures F and G.

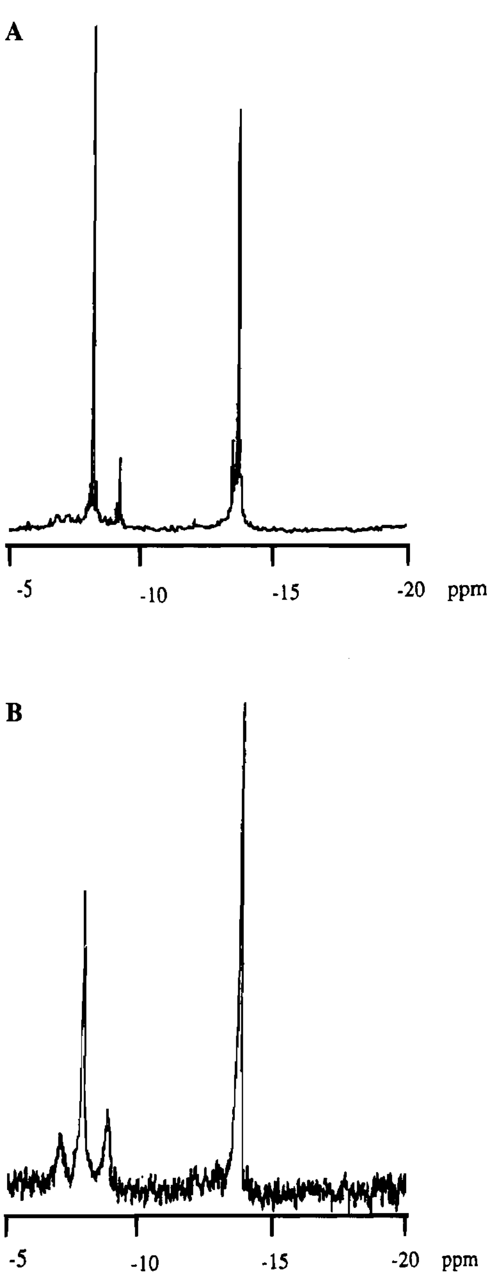

Figure 5. ^{31}P NMR spectra of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **2**, in DMSO-$d_6$ with 3 equiv of Kryptofix 2.2.2. added (top) and without Kryptofix 2.2.2. added (bottom). These spectra show the effect of added Na^+-binding Kryptofix 2.2.2. (top vs bottom) and the relatively high homogeneity and purity (≥95%) for the polyoxoanion-supported $[(1,5\text{-COD})Rh]^+$.

For comparison, the $P_2W_{15}Nb_3O_{62}^{9-}$ heteropolyoxoanion support shows two lines of equal intensity in the ^{31}P NMR spectrum in either DMSO-d_6 [δ −7.2 ($\Delta\nu_{1/2}$ = 3.5 ± 0.3 Hz), −14.2 ($\Delta\nu_{1/2}$ = 4.6 ± 0.3 Hz)] or CD_3CN [δ −7.2 ($\Delta\nu_{1/2}$ = 3.1 ± 0.3 Hz), −14.3 ($\Delta\nu_{1/2}$ = 4.6 ± 0.3 Hz)]. Hence, upon binding of the organometallic fragment to form **1** or **2**, the resonance for the phosphorus closer to the triniobium cap is shifted markedly to higher field (from δ −7.2 to −8.2). This upfield shift is much more pronounced than that seen for the "south" phosphorus, that is, the phosphorus closer to the tritungsten cap, which does not shift within experimental error (from δ −14.3 ± 0.2 to −14.1 ± 0.2). This observation is in accord with, and actually *prima facie* evidence for, preferential binding of $[1,5\text{-COD})M]^+$ to the more basic "$Nb_3O_9^{3-}$" cap *in solution.* The observed line widths, $\Delta\nu_{1/2}$ = 5−6 Hz, for the two resonances of **1** and **2** in the ^{31}P NMR spectrum are comparable to those observed for the unsupported polyoxoanion, $P_2W_{15}Nb_3O_{62}^{9-}$, which showed values for $\Delta\nu_{1/2}$ of 3−5 Hz.

These ^{31}P NMR results demonstrate that **1** and **2** are obtained as at least 95% of a *single (possibly time-averaged) isomer*, a nontrivial result in comparison to all prior, non-$P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion-supported organometallic complexes.[6,7]

The ^{183}W NMR spectrum of $[(1,5\text{-COD})IrP_2W_{15}Nb_3O_{62}]^{8-}$, **1**, in DMSO-$d_6$, Figure 6, exhibited the expected three peaks,

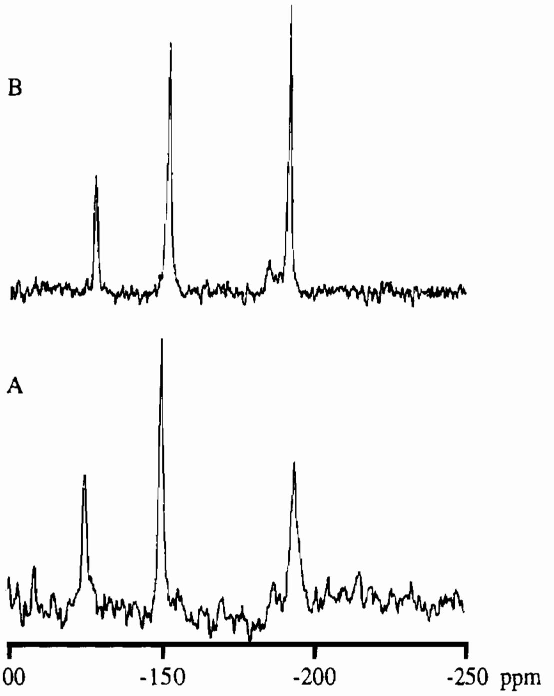

Figure 6. The 1:2:2 relative intensity three-line ^{183}W NMR spectra (DMSO-d_6) (A): 0.09 M **1** after 10 000 scans collected over 5 h, S/N = 12/1, δ (no. of W, $\Delta\nu_{1/2}$) -125.0 (3 W, 14.9 ± 1.0 Hz), -150.3 (6 W, 13.7 ± 0.7 Hz), -194.0 (6 W, 25.5 ± 1.5 Hz]); (B) 0.09 M **1**, with 3 equiv of Kryptofix 2.2.2., added after 10 000 scans collected over 5 h, S/N = 25/1, δ (no. of W, $\Delta\nu_{1/2}$) -128.1 (3 W, 12.0 ± 0.3 Hz), -152.2 (6 W, -13.9 ± 0.2 Hz), -191.4 (6 W, 11.1 ± 0.2 Hz). The ^{183}W NMR spectrum (referenced to 2 M Na_2WO_4 in 1:1 D_2O/H_2O by the external substitution method) shows a 2-fold increase in S/N upon addition of Kryptofix 2.2.2., which removes the ion-pairing effects.[9b]

suggesting *either* that $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ is of C_{3v} (average) symmetry on the ^{183}W NMR time scale (^{17}O NMR studies demonstrate this to be the case for **1**) *or* that any perturbations away from the inherent C_{3v} symmetry of $P_2W_{15}Nb_3O_{62}{}^{9-}$ are not detectable by ^{183}W NMR. The integrated intensities for the three peaks are 1:2:2, as expected for the presence of two tungsten belts consisting of six WO_6 octahedra each and a tungsten cap consisting of three WO_6 octahedra. Addition of 3 equiv of Kryptofix 2.2.2. increases the signal-to-noise (S/N) 2-fold (Figure 6A vs Figure 6B). (The increased S/N is, again, readily explained by the removal of the $Na^+\cdot\cdot P_2W_{15}Nb_3O_{62}{}^{9-}$ ion-pairing and thus the increased concentration of a single form of **1**.) A similar ^{183}W NMR spectrum (Figure 7) was observed in DMSO-d_6 for **2**, once again exhibiting three peaks with intensities of 1:2:2. However, as we will see in the ^{17}O NMR studies of $[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, **2**, the ^{183}W NMR is unable to detect deviations from the polyoxoanion's inherent C_{3v} symmetry which occur via the presence of two or more support-site isomers for **2**.

^{1}H and ^{13}C NMR Studies. The ^{1}H NMR of the coordinated 1,5-COD in **1** in DMSO-d_6 consists of three broad resonances at δ 1.82, 2.28, and 3.99 (intensities 4:4:4) over the temperature range 25–95 °C. In the case of **2**, the ^{1}H NMR spectrum in DMSO-d_6 (supplementary material, Figure H) showed the presence of three peaks (δ 1.89, 2.42, 4.29) which also integrated to 4 H each. In no case were peaks attributable to free 1,5-COD detected; hence, neither dissociation of 1,5-COD from Ir or Rh nor decomposition of **1** or **2** in room temperature DMSO is seen. The $^{13}C\{^1H\}$ NMR spectra of **1** and **2** in DMSO-d_6 (supplementary material, Figure I) show two resonances each. Interestingly, the ^{1}H NMR spectra of **1** and **2** are solvent-dependent (e.g., in CD_3CN and acetone-d_6, supplementary material, Figures J and K), a fact that we were unable to clarify further (e.g., even by variable temperature NMR studies; see the Experimental Section for further details).

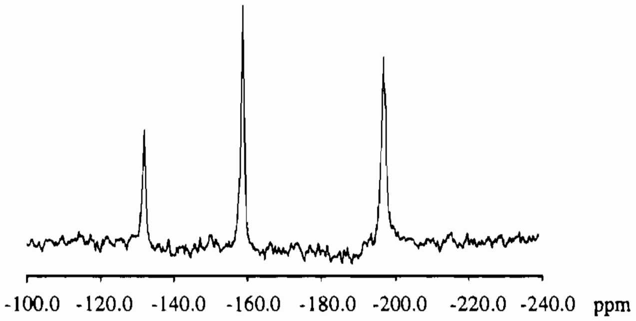

Figure 7. ^{183}W NMR spectrum of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$ in DMSO-d_6 with 3 equiv of Kryptofix 2.2.2. added, showing three peaks suggesting that $[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ has C_{3v} (average) symmetry on the ^{183}W time scale (or that any perturbations away from the inherent C_{3v} symmetry of $P_2W_{15}Nb_3O_{62}{}^{9-}$ are not detectable by ^{183}W NMR spectroscopy; see the text for further discussions of this point).

Overall, the observed two-line $^{13}C\{^1H\}$ and three-line ^{1}H NMR spectra for **1** and **2** in DMSO-d_6 are consistent with a five-coordinate metal-to-polyoxoanion complex (coordination by two olefinic C=C bonds of the cyclooctadiene ligand plus three oxygens of the heteropolyoxoanion). Klemperer and co-workers have reported similar spectra in CH_2Cl_2 for the five-coordinate iridium-polyanion complexes[7i,f] $(1,5\text{-COD})IrP_3O_9{}^{2-}$ and $(1,5\text{-COD})Ir(C_5Me_5TiW_5O_{18})$. (A detailed comparison of tabulated ^{1}H and ^{13}C NMR shifts for polyoxoanion-supported complexes of $[(1,5\text{-COD})Ir]^+$ is available elsewhere.[8h]) Furthermore, Kläui has also reported[23] a three-line ^{1}H NMR spectrum for $(1,5\text{-COD})Rh\cdot[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]$ in which rhodium is also five-coordinate (coordinated by two olefinic C=C bonds of the cyclooctadiene ligand plus three oxygens of the support).

^{17}O NMR Spectroscopy of $P_2W_{15}Nb_3O_{62}{}^{9-}$ and of $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, 1.[9g] Direct Detection of an Ir–O–Nb_2 Bond. First, the needed control and reference point for the ^{17}O NMR studies[24] was achieved by selectively enriching[24k] the parent polyoxoanion, $P_2W_{15}Nb_3O_{62}{}^{9-}$, in only its terminal Nb–O and bridging Nb_2–O oxygens (i.e., selective enrichment in six oxygens of the "$Nb_3O_9{}^{3-}$" minisurface).[25] This was accomplished by stirring $P_2W_{15}Nb_3O_{62}{}^{9-}$ for 1 week at 22

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[23] Scotti, M.; Valderrama, M.; Rojas, S.; Kläui, W. *J. Organomet. Chem.* **1986**, *301*, 369.

[24] References for seminal ^{17}O NMR methodologies and chemical shift data, which provide the needed background for the present work, are as follows (see also the table of ^{17}O NMR data presented elsewhere[9g]): (a) Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246. (b) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93. (c) Besecker, C. J.; Klemperer, W. G.; Maltbie, D. J.; Wright, D. A. *Inorg. Chem.* **1985**, *24*, 1027. (d) Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2355. (e) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44. (f) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345. (g) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 4891. (h) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (i) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (j) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030. (k) Stirring CH_3CN solutions of polyoxoanions in the presence of ^{17}O-enriched H_2O is reported by Klemperer and co-workers to enrich only the terminal (Nb–O) and bridging (Nb_2–O) niobium oxygens of $Nb_2W_4O_{19}{}^{4-}$ within <10 min. After 24 h, they find that enrichment of the NbWO positions is possible but that enrichment of the W_2O and WO positions (not observed under the above mild conditions) is possible for $Nb_2W_4O_{19}{}^{4-}$ only after stirring a slurry of the polyoxoanion in ^{17}O-enriched H_2O with base catalysis ($[(n\text{-}C_4H_9)_4N]OH$) and at elevated temperature (95 °C).[24b]

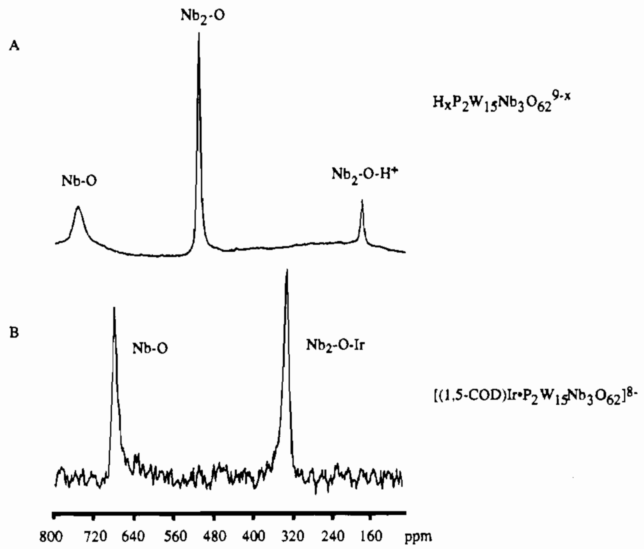

Figure 8. (A) Spectrum of $[(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}Nb_3O_{62}$ following enrichment with 10% $H_2{}^{17}O$ for 1 week. ^{17}O NMR (48.967 MHz, CD_3CN, 22 °C), δ (no. of O, assignment, $\Delta\nu_{1/2}$): 180 (s, 1 O, Nb_2-OH^+, 230 ± 30 Hz), 512 (s, 3 ± 1 O, Nb_2O, 260 ± 10 Hz), 752 (s, 3 ± 1 O, NbO, 990 ± 170 Hz). (B) Spectrum of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)IrP_2W_{15}Nb_3{}^{17}O_6O_{56}]$, which was prepared from preformed **1** by enrichment with 10% $H_2{}^{17}O$ over a (shorter) period of 36 h. ^{17}O NMR (48.967 MHz, CD_3CN, 22 °C, 3 equiv of Kryptofix 2.2.2. added), δ (no. of O, assignment, $\Delta\nu_{1/2}$): 680 (s, 3 ± 1 O, NbO, 440 ± 140 Hz), 333 (s, 3 ± 1 O, Nb_2-OIr, 510 ± 110 Hz). Plausible reasons for the lower S/N observed in the bottom spectrum (all other instrument and acquisition parameters were the same for the top and bottom spectra): the shorter enrichment time (36 h vs 1 week) for the sample in the bottom spectrum, plus coordination of the $[(1,5\text{-COD})Ir]^+$ fragment which should slow $^{17}OH_2$ exchange into **1**.

°C in a basic mixture (basic due to the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion's strong basicity) of 2 mL of acetonitrile/1 mL of 10% enriched $^{17}OH_2$, eq 2. Two resonances of approximately

$$[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62} \xrightarrow{\substack{\text{2. 1 week/22 °C} \\ \text{1. } CH_3CN/H_2{}^{17}O}} [(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56} \quad (2)$$

equally integrated intensities at δ 750 (Nb$-$O, 3 oxygens) and δ 510 (Nb_2-O, 3 oxygens) appear in the ^{17}O NMR, Figure 8. These chemical shift assignments as Nb$-$O and Nb_2-O oxygens are made with confidence by comparison to similar environments in related, structurally characterized polyoxoanions, in particular to those of the seminal ^{17}O NMR work of Klemperer and co-workers.[24] The assignments made are also consistent with the established relative rates of oxygen enrichment: Nb$-$O > Nb_2O >> NbWO >>> W$-$O$-$W ≈ WO ≈ PO ≈ 0.[24k] The ^{17}O NMR assignments are further secured by a careful inspection of the relative line widths of the observed peaks. For example, the resonance assigned to Nb$-$O terminal oxygens in $P_2W_{15}Nb_3O_{62}{}^{9-}$ has a line width more than triple of that assigned to the Nb_2-O bridging oxygens, as expected on the basis of the literature.[9g] A high-field resonance observed at δ 180 is assigned to Nb_2-O-H^+ by comparison to the literature. This assignment is further supported by titration experiments in which 0.6 equiv of $[(n\text{-}C_4H_9)_4N]^+OH^-$ resulted in the almost complete loss of this resonance. Hence the enrichment procedure in eq 2 in fact yields the protonated $H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}{}^{x-9}$ (a result which suggests that $P_2W_{15}Nb_3O_{62}{}^{9-}$ may be able to deprotonate H_2O and, therefore, has a basicity approaching that of OH^-; an alternative explanation is that a small amount of Nb^{5+}/W^{6+} polyoxoanion impurity hydrolyzes to give 5$-$6 H^+). The above ^{17}O enrichment procedure for $P_2W_{15}Nb_3O_{62}{}^{9-}$ has been repeated more than 10 times throughout these studies with *identical results each time.*

Unfortunately, the use of pre-enriched $H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}{}^{x-9}$ (obtained as in eq 2 above) failed to give clean samples of enriched **1**, but not unexpectedly due to the presence of protons in Nb_2O-H^+ which apparently block the iridium-support site. The successful, empirically discovered ^{17}O enrichment method[9g] involved, instead, stirring *preformed* **1** in a mixture of 2 mL of acetonitrile/1 mL of 10% enriched $^{17}OH_2$ for 36 h at 22 ± 2 °C (eq 3). (The use of shorter, selective enrichment times is crucial,

$$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})IrP_2W_{15}Nb_3O_{62}] \xrightarrow{\substack{\text{1. } CH_3CN/H_2{}^{17}O \\ \text{2. 36 h/22 °C}}} [(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})IrP_2W_{15}Nb_3{}^{17}O_6O_{56}] \quad (3)$$

since longer enrichment times lead to almost complete decomposition of **1**.[9g]) A ^{31}P NMR spectrum of the enriched product taken *after* the ^{17}O NMR cited next was acquired (supplementary material, Figure N) indicates two important points: (i) that the enrichment has proceeded cleanly to yield primarily **1** and (ii) that **1** is still intact *after* the ^{17}O NMR spectrum has been acquired. The ^{17}O NMR spectrum (Figure 8) of the resultant, enriched "$Nb_3O_9{}^{3-}$" minisurface in $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)IrP_2W_{15}Nb_3{}^{17}O_6O_{56}]$ shows only the expected terminal Nb$-$O (δ 680) and Nb_2-O-Ir oxygen resonances (δ 330), assigned again by analogy to the literature.[24] (Three equivalents of Kryptofix 2.2.2. was added to the sample to eliminate the peak broadening due to the $Na^+\cdot\cdot P_2W_{15}Nb_3O_{62}{}^{9-}$ ion-pairing interactions established previously.) The ratio of integrated peak intensities is unity, within experimental error, reflecting once again the presence of equal numbers of the two types of magnetically inequivalent oxygens, and *demonstrating that three Nb_2O-Ir bonds are present within experimental error.* This experiment has been repeated three times with identical results so long as the ^{31}P NMR of the enriched **1** shows it to be largely undecomposed (Figure O, supplementary material, shows the results of the two identical repeat experiments).

The observed two-line ^{17}O NMR spectrum for $[(1,5\text{-}COD)IrP_2W_{15}Nb_3O_{62}]^{8-}$, **1**, is definitive in requiring average C_{3v} (pseudo) symmetry in **1** (pseudo, as the local 2-fold axis at Ir limits the maximum symmetry in **1** to C_s, rigorously speaking). *Assuming* a static structure, it would also require that the polyoxoanion serves as a tripodal support (i.e., that iridium is five-coordinate, with $[(1,5\text{-COD})Ir]^+$ bound to *three* Nb_2-O bridging oxygens). [However, one should note the possibility that the two-line spectrum of $[(1,5\text{-COD})IrP_2W_{15}Nb_3O_{62}]^{8-}$ might also be accounted for by some group of fluxional structures that average to effective C_{3v} symmetry around

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(25) (a) Although ^{17}O NMR is a powerful structural tool, little discussed potential problems with this method that one needs to be aware of include (i) the possibility of selective, nonstatistical exchange of $^{17}OH_2$ (i.e., ideally, the exchange kinetics and mechanism should be known), (ii) the possibility of intermolecular exchange, and (iii) the possibility of intramolecular exchange or fluxional processes. (b) Although unproven, in the present case we suspect a low-level, prior-equilibrium dissociation of $(1,5\text{-COD})Ir(solv)_2{}^+$ as a key to the enrichment process:

$$[(1,5\text{-COD})IrP_2W_{15}Nb_3O_{62}]^{8-} \rightleftharpoons (1,5\text{-COD})Ir(solv)_2{}^+ + P_2W_{15}Nb_3O_{62}{}^{9-} \quad \text{(i)}$$

$$P_2W_{15}Nb_3O_{62}{}^{9-} + 6\,{}^{17}OH_2 \rightleftharpoons 6\,H_2O + P_2W_{15}Nb_3{}^{17}O_6O_{61}{}^{9-} \quad \text{(ii)}$$

$$P_2W_{15}Nb_3{}^{17}O_6O_{61}{}^{9-} + (1,5\text{-COD})Ir(solv)_2{}^+ \rightleftharpoons [(1,5\text{-COD})IrP_2W_{15}Nb_3{}^{17}O_6O_{56}]^{8-} \quad \text{(iii)}$$

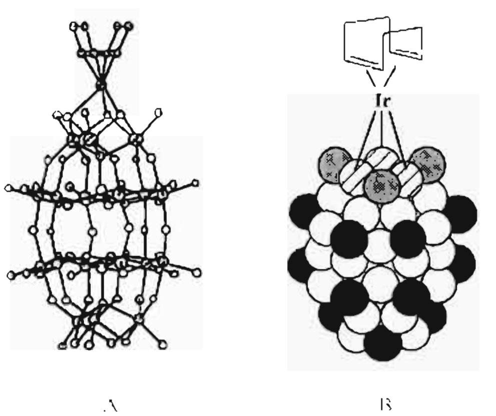

Figure 9. (A) Ball and stick representation of the proposed average C_{3v} (pseudo) symmetry structure for the $[(1,5\text{-COD})Ir]^+$ fragment supported on the "$Nb_3O_9^{3-}$" face of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ serving as a stereochemically rigid tripodal ligand. This figure, generated from the crystal structure parameters[8g] of $Na_9P_2W_{15}Nb_3O_{62}$ and modified using Chem 3-D, does not emphasize the expected[7g] two short plus one elongated iridium-to-ONb_2 bonds which make the rigorous, static symmetry C_s for the structure shown (see the discussion of this point in the text). (B) Space-filling representation, where the black circles represent terminal oxygens, the white circles are bridging oxygens, the gray circles are terminal Nb−O oxygens, and the hatched circles are the 3 Nb−O−Nb oxygens.

the C_3 axis of **1**; a detailed discussion of such a possible fluxionality in **1** is presented elsewhere.[9g]] In short, the ^{17}O NMR results require the C_{3v} *average-symmetry structure* shown in Figure 9.

We note, however, that the static C_{3v} average symmetry structure shown in Figure 9 is almost surely somewhat fluxional, given the following precedent. Klemperer and Day[7h] have shown that the three iridium−oxygen bonds in $[(1,5\text{-COD})Ir\cdot P_3O_9]^{2-}$ are of different lengths (in the solid-state, and by X-ray crystallography), giving rise to a square-pyramidal Ir atom (with one long Ir−O bond, 2.70 Å, in the apical position and two shorter Ir−O bonds, 2.15 and 2.20 Å). However, in solution their complex is fluxional by a process that makes the Ir−O bonds all equivalent on the NMR time scale even down to −75 °C.[24d] Hence, there is every reason to expect that five-coordinate Ir in **1** will also have these same two short and one long $Ir{-}ONb_2$ bonds in an instantaneous static and C_s symmetry picture. But, these three $Ir{-}ONb_2$ bonds should similarly[24d] be fluxional in solution, becoming equivalent on the ^{17}O NMR time scale via a dynamic elongation and shortening such that the average effective ^{17}O, ^{31}P, and ^{183}W NMR-determined symmetry of **1** is (pseudo) C_{3v}. This type of precedented fluxionality,[24d,26] plus the line width effect of supporting the inherently C_s symmetry $[(1,5\text{-COD})Ir]^+$ on the inherently C_{3v} symmetry $P_2W_{15}Nb_3O_{62}^{9-}$, readily explains the small residual line widths of ca. 1−2 Hz observed in the ^{31}P NMR spectra of $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ (i.e., in comparison to the ^{31}P NMR spectra of the parent $P_2W_{15}Nb_3O_{62}^{9-}$).

Finally, before leaving this section on the ^{17}O NMR studies of **1**, it will prove relevant to the ^{17}O NMR studies of **2** which follow to describe a control experiment which was also done for **1**, but which was originally designed for the Rh complex **2** (*vide infra*). The purpose of this control experiment was to provide a further and independent check on whether or not the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion in **1** had been cleanly enriched with ^{17}O in only the Nb−O and Nb_2−O oxygens and with little decomposition of **1**. In this control experiment, a large excess of $[(n\text{-}C_4H_9)_4N]Cl$ was added to a solution of ^{17}O-enriched Ir complex **1** to effect the deliberate cleavage of the $[(1,5\text{-COD})Ir]^+$ moiety from the heteropolyoxoanion support (i.e., cleavage ideally as the well-known $[(1,5\text{-COD})IrCl]_2$). Note that this control experiment is not trivial, as it tests the results of the unknown kinetics and mechanism of the ^{17}O enrichment process involving preformed, supported $[(1,5\text{-COD})Ir]^+$, **1**. ^{17}O NMR spectroscopy (supplementary material, Figure W) of the resultant Cl^- cleavage product showed primarily two resonances of approximately equal intensities at δ 720 and 500, that is, within experimental error of the resonances for $H_xP_2W_{15}Nb_3O_{62}^{x-8}$ (δ 750 and 510), given the width of these peaks and the unavoidably somewhat different experimental conditions (e.g., the large amount of $[(n\text{-}C_4H_9)_4N]Cl$ and lack of H_2O/H^+ in the Cl^- cleavage sample). In addition, the sharp resonance assigned to Nb_2O−Ir at δ 330 is, as anticipated, nearly completely absent following the addition of Cl^-. Hence, this Cl^- cleavage control (i) confirms that the ^{17}O NMR enrichment of preformed **1** has worked as desired (i.e., enriching just the 3 Nb−O and 3 Nb_2O oxygens in **1**), (ii) provides confirming evidence that the assignment of the δ 330 resonance as a Nb_2O−Ir oxygen is correct, and (iii) demonstrates that the Cl^- cleavage control reaction works largely as anticipated. Lastly, a ^{183}W NMR spectrum of the Cl^- cleavage experiment shows a low S/N but primarily three-line, C_{3v} symmetry type spectrum (supplementary material, Figure X), as expected if the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion is largely intact following the sequence of ^{17}O enrichment and then Cl^- cleavage of its supported-organometallic fragment.

^{17}O NMR Spectroscopy of $[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, 2. Direct Detection of $Rh{-}ONb_x$ Bonds. In three repeats of the same experiment, the Rh complex **2** was enriched in ^{17}O in the same manner as its Ir congener **1**. The clean two-line ^{31}P NMR spectrum (supplementary material, Figure Y) of the ^{17}O-enriched product demonstrates that the enrichment reliably produces clean and undecomposed **2**. Unexpectedly, however, the ^{17}O NMR spectrum (Figure 10, top) contains a new, strong resonance at δ ≈ 500 in addition to the two peaks at δ 680 and 330 seen for the Ir congener. Hence, in a control experiment, the organometallic moiety, $[(1,5\text{-COD})Rh]^+$, of **2** was removed from the heteropolyoxoanion support, $P_2W_{15}Nb_3O_{62}^{9-}$, by addition of a large excess of $[(n\text{-}C_4H_9)_4N]Cl$ (see the Experimental Section for a detailed account). A ^{17}O NMR spectrum collected afterward (Figure 10, bottom) showed two lines at δ 740 and 500 (relative intensities of 1:1), confirming that **2** had, as desired, successfully been enriched in only the three terminal (NbO) and three bridging (Nb_2O) niobium−oxygen sites, *exactly analogous* to the Ir complex $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$.

Returning to the ^{17}O NMR spectrum of **2**, the δ 330 resonance provides direct evidence for a $Rh{-}ONb_2$ bond by comparison to chemical shift data reported for similar heteropolyoxoanion-supported transition metal complexes (cf. Table C, supplementary material) and by analogy to the δ 330 resonance seen for the iridium congener, **1**. However, the presence of a resonance at approximateley δ 500 can be attributed only to a Nb_2−O or a Nb−O−Rh oxygen (based on the ^{17}O NMR assignments for

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(26) Lead references to the fluxionality of d^8, five-coordinate Ir(I) and related species: (a) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305. (b) Rodman, G. S.; Mann, K. R. *J. Organomet. Chem.* **1989**, *378*, 255. Adams, H.; Bailey, N. A.; Mann, B. E.; Taylor, B. F.; White, C.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1987**, 1947. (c) For a study of the fluxionality of *four-coordinate* $Ir(1,5\text{-COD})(Tripod)^-BF_4^+$, where Tripod = $HC(Ph_2)_3$, see: El-Amouri, H.; Bahsoun, A. A.; Osborn, J. A. *Polyhedron* **1988**, *7*, 2035. (d) Computational studies: Koga, N.; Jin, S. Q.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3417. (e) Stereochemically rigid five-coordinate Ir(I) species are also known: Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855. Rhodes, L. F.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259. Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165.

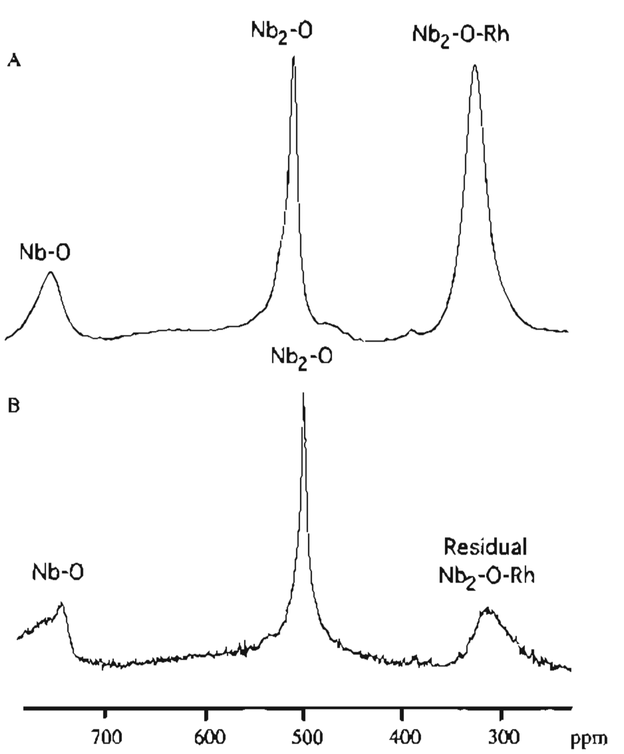

Figure 10. (A) Top: ^{17}O NMR spectrum of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Rh\cdot P_2W_{15}Nb_3{}^{17}O_6O_{56}]$, which was prepared from preformed **2** by enrichment with 10% $H_2{}^{17}O$ over a period of 36 h (repeat experiment). ^{17}O NMR (20 °C, 90 mM, CD_3CN, 3 equiv of Kryptofix 2.2.2. added), δ (no. of O, $\Delta\nu_{1/2}$): 750 (1 ± 0.5, 2300 ± 850 Hz), 500 (2.5 ± 1, 700 Hz ± 100 Hz), 330 (4.3 ± 1, 1600 ± 300 Hz). (B) Bottom: ^{17}O NMR spectrum (90 mM, CD_3CN, 25 °C, with 3 equiv of Kryptofix 2.2.2.) collected after cleavage (by addition of 20 equiv of $[(n\text{-}C_4H_9)_4N]Cl$) of the $[(1,5\text{-}COD)Rh]^+$ moiety from the support-heteropolyoxoanion of ^{17}O-enriched **2**. Two lines at δ 740 and 500 of approximately equal intensities are assigned to niobium-terminal and -bridging oxygens, respectively. The peak at δ 330 can be attributed to a residual Nb_2-O-Rh (i.e., a residual $[(1,5\text{-}COD)Rh(Cl)-O-Nb(P_2W_{15}Nb_2O_{61})]^8$ species in possible equilibrium with $P_2W_{15}Nb_3O_{62}{}^{9-}$ and $[(1,5\text{-}COD)RhCl]_2$). These spectra were collected on a Bruker AM500 NMR instrument at Colorado State University. Instrumental parameters differ from those reported in the main text and are as follows: ^{17}O NMR (67.80 MHz); pulse width 13 μs; acquisition time 16 ms; sweep width ±125 000 Hz.

related niobium-containing polyoxometalates; cf. supplementary material, Table C). This in turn *demands some form of an off-C_3 axis isomer*, such as the C_s symmetry isomer shown in Figure 12. Restated, either a $Nb-O-Rh$ or a (Rh free) Nb_2O oxygen resonance (ca. δ 500), a Nb_2-O-Rh (δ 330) resonance, and a $Nb-O$ (δ 750) resonance are just the types of ^{17}O NMR resonances expected for the C_s symmetry isomer of **2**, Figure 11.[27]

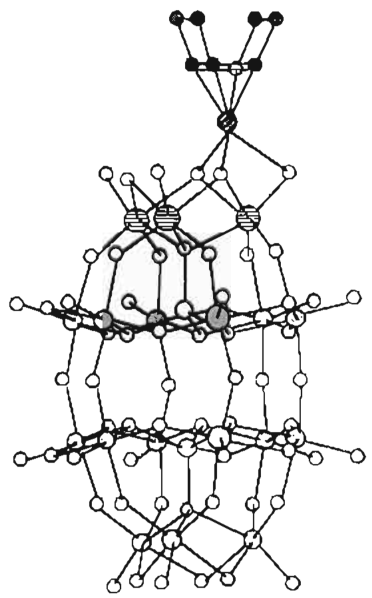

Figure 11. Ball and stick representation of an instantaneous C_s symmetry isomer for $[(1,5\text{-}COD)Rh]^+$ supported on the "$Nb_3O_9{}^{3-}$" face of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, this time via two bridging Nb_2O oxygens plus *one terminal Nb−O oxygen*. This figure, generated from the crystal structure parameters of $Na_9P_2W_{15}Nb_3O_{62}$ and modified using Chem 3-D, does illustrate the expected[7h] two short rhodium-to-ONb_2 bonds plus the one significantly longer rhodium-to-ONb (terminal oxygen) bond in this static C_s symmetry structure.

Attempted Crystallographic Characterization of $[(1,5\text{-}COD)M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$. All of our many attempts to date at the nontrivial growth of crystals of $[(1,5\text{-}COD)M\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, M = Ir and Rh, suitable for X-ray diffraction have been unsuccessful (see the Experimental Section and the supplementary material),[28] although we are still engaged in a final, extensive, and broad search to find other cation combinations that will yield diffracting crystals of **1** and **2**.

However, recall that we were able to obtain the structure[8g] shown as part of Figure 2 for the nonasodium salt of the parent heteropolytungstate, $P_2W_{15}Nb_3O_{62}{}^{9-}$, which corroborates the solution structure we previously deduced from solution NMR studies.[8a] The previously unpublished packing diagram for $Na_9P_2W_{15}Nb_3O_{62}$ shows $Na^+\cdots P_2W_{15}Nb_3O_{62}{}^{9-}$ solid-state "ion-pairing" interactions, with $Na^+\cdots O-M$ (M = Nb, W) distances of 2.3−2.5 Å, which form a Na^+ cloud around the polyoxometalate as shown in Figure 12. Such ion-pairing[29] persists in solution, causing the initially puzzling extra peaks and line

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[27] That is not to say that the ^{17}O NMR for **2** is fully understood. A *static* C_s symmetry isomer of **2** should show *four* ^{17}O NMR resonances (integrals, assignments, and anticipated chemical shifts): 2 Nb−O, ca. 750 ppm; 1 Nb_2O, ca. 500 ppm; 1 Nb−O−Rh, ca. 500 ppm; 2 Nb_2-O-Rh, ca. 330 ppm. Instead, only *three* ^{17}O NMR resonances [δ = 750 (ca. 1), 500 (ca. 2.5), 330 (ca. 4)] are observed (note that their approximate, quantitatively unreliable integrations given above in parentheses are of little use). Because a C_{3v} structure (cf. Figure 9) has two ^{17}O NMR resonances (Nb−O, $\delta \approx 750$; Nb_2-O-Rh, $\delta \approx 330$) and the C_s symmetry structure should have four, the observation of three ^{17}O NMR peaks for **2** suggests some fluxional process (albeit none we can write gives three peaks, unless the peaks near δ 500 are superimposed and unresolved, a hypothesis not supported by the fact that a single lorentzian fits the δ 500 peak in Figure 10A reasonably well, save the shoulders on both left and right sides of the peak). Low-temperature ^{17}O NMR studies (to attempt to freeze out any fluxional processes) proved nonfeasible (only broad, nondiscernible peaks are seen) due to the expected severe quadrapolar line broadening of the ^{17}O NMR resonances at lower temperatures.

[28] Small (ca. 0.3 mm × 0.1 mm × 0.1 mm) yellow needles (in ≈5% yield) of, presumably, the $[(n\text{-}C_4H_9)_4N]^-{}_8$ salt of $[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ were fortuitously obtained from an approximately 4:1 $CD_3CN:H_2O$ solution that had been prepared for the ^{17}O NMR study of **1**. These small, fragile, air-sensitive crystals rapidly desolvated, making their placement in a capillary extremely difficult. The few crystals that were ultimately placed in capillaries diffracted only weakly, precluding even the determination of a unit cell. (In response to a referee's query, low-temperature mounting of the crystals using a liquid N_2 stream was not tried, as low-temperature crystallography was not available at the time at Oregon.)

[29] (a) Ion-pairing effects in *aqueous* polyoxometalate chemistry have been reported;[29b−e] hence, it follows that they should also exist in organic solvents with a lower dielectric constant. (b) Clare, B. W.; Kepert, D. L.; Watts, D. W. *J. Chem. Soc., Dalton Trans.* **1973**, 2481. (c) Druskovich, D. M.; Kepert, D. L. *J. Chem. Soc., Dalton Trans.* **1975**, 947. (d) Druskovich, D. M.; Kepert, D. L. *Aust. J. Chem.* **1975**, *28*, 2365. (e) Kepert, D. L.; Kyle, J. H. *J. Chem. Soc., Dalton Trans.* **1978**, 137. (f) Chorglade, G. S.; Pope, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 5134. (g) In organic solvents, Na^+ to $P_2W_{15}Nb_3O_{62}{}^{9-}$ ion-pairing effects are reminiscent of the multiple sites of H^+ attachment and slow proton mobility (tautomerism) first observed in polyoxoanion chemistry in the $SiW_9V_3O_{40}{}^{7-}$ system: Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

broadening observed in the solution ^{31}P and ^{183}W NMR spectra of **1** (*vide supra*).

Structural Conclusions for [(1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}$]$^{8-}$, 1. From the above data it is apparent that (i) the iridium–bis(olefin) complex, **1**, is supported on the "$Nb_3O_9^{3-}$" minisurface of the heteropolyoxoanion support $P_2W_{15}Nb_3O_{62}^{9-}$ in such a way that overall average C_{3v} (pseudo) symmetry results, (ii) at least 95% of a single isomer of **1** has been obtained (and in a 1:1 Ir:polyoxoanion, unaggregated complex), (iii) ^{17}O NMR is the preferred, direct structural method for characterizing the binding of the iridium–bis(olefin) complex to the heteropolyoxoanion support in solution, and (iv) the ^{17}O NMR studies are definitive in revealing that [(1,5-COD)Ir]$^+$ binds via Ir–ONb$_2$ bonds 100% of the time within experimental error.

The structural characterization of **1** achieves our goal of atomic-level structural characterization of an oxide-supported catalyst; it also demonstrates the need for, and both the power of and the limitations to, the spectroscopic handles available in **1**. It furthermore highlights the importance of the seminal efforts of Day, Klemperer, and co-workers on smaller, less charged polyoxoanions where X-ray diffraction studies of supported organometallics (including supported [(1,5-COD)Ir]$^+$) have successfully been carried out[7,24] and where the solid-state data have been correlated with ^{17}O NMR data for the solution species.

Structural Conclusions for [(1,5-COD)Rh·$P_2W_{15}Nb_3O_{62}$]$^{8-}$, 2. The analytical, MW, IR, ion-exchange, and ^{31}P and ^{183}W NMR spectroscopic evidence cited earlier demonstrate that **2** is obtained as an analytically pure, homogeneous solid with the $P_2W_{15}Nb_3O_{62}^{9-}$ framework being intact and with [(1,5-COD)-Rh]$^+$ attached to the "$Nb_3O_9^{3-}$" cap of a $P_2W_{15}Nb_3O_{62}^{9-}$. However, the results of the ^{17}O NMR studies for **2** (*vide supra*), and the distinctively different ^{17}O NMR spectra obtained for **2** when compared to **1**, require **2** to differ structurally from its Ir congener, **1**. Two or more C_{3v} and C_s support-site isomers[9g,30] are implied. The ^{183}W NMR spectrum nominally suggests a structure with C_{3v} (average) symmetry, but ^{183}W NMR spectroscopy is apparently insensitive to the exact symmetry of **2** and/or the fluxional processes of [(1,5-COD)Rh]$^+$ on the "$Nb_3O_9^{3-}$" oxygen surface in **2**.

The proposed structure or structures for **2** are generally in accord with the structures established for the related complexes (NBD)Rh·$P_3O_9^{2-}$ [7a] (NBD ≡ norbornadiene) and (1,5-COD)-Rh·[(C_5H_5)Co{P(O)(OC_2H_5)$_2$}$_3$],[23] where it has been unequivocally shown that the organometallic fragment binds to three oxygens. For both of these systems, the support provides a similar surface-oxygen arrangement (three basic oxygen sites) as provided by the "$Nb_3O_9^{3-}$" oxygen surface of $P_2W_{15}Nb_3O_{62}^{9-}$. In contrast, four-coordination of rhodium[30] (the rhodium binds to two oxygens of the support plus two bonds to the norbornadiene ligand) is observed in [(NBD)Rh]$_5$[$Nb_2W_4O_{19}$]$_2^{3-}$.[7e] Here, however, only two niobium-bridging oxygens with sufficient basicity (i.e., to bind the cationic organometallic fragment) are present. *Taken together, these examples suggest that four vs five-coordination of heteropolyoxoanion-supported rhodium is not just an inherent property of the metal (i.e. of Ir vs Rh)[15] but also depends strongly upon the support.*

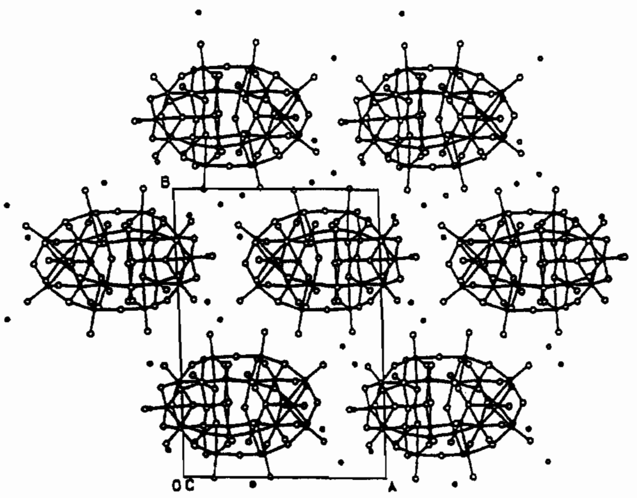

Figure 12. Packing diagram for the single-crystal X-ray structure[8g] of α-1,2,3-$P_2W_{15}Nb_3O_{62}^{9-}$. This diagram clearly shows the Na$^+$ "cloud" that surrounds each heteropolytungstate, with the Na$^+$ 2.3–2.5 Å from the terminal O···M (M = Nb, W) positions.

Summary

The synthesis and characterization of [(n-C_4H_9)$_4$N]$_5$Na$_3$[(1,5-COD)M·$P_2W_{15}Nb_3O_{62}$] (M = Ir, Rh) provides an entry into 1:1 metal to polyoxometalate-supported organometallic precatalysts. The results demonstrate, in a general sense, the level of compositional and structural characterization that can be achieved for this size and type of inorganic–organometallic material—as well as the problems therein—through the use of complete elemental analyses, solution molecular-weight measurements, and extensive solution spectroscopy, especially the ^{1}H, ^{13}C, ^{17}O, ^{31}P, and ^{183}W NMR handles available for **1** and **2**. Overall, the full details of the synthesis and characterization of the [(1,5-COD)M·$P_2W_{15}Nb_3O_{62}$]$^{8-}$ (M: Ir, **1**; Rh, **2**) complexes provided herein are important in comparison to all the existent polyoxoanion literature in that the precatalyst **1** leads to a polyoxometalate-*supported* oxidation catalyst using dioxygen[10b–d] and to a novel Ir$_{\sim 300}$·polyoxoanion nanocluster hydrogenation catalyst.[9h] The Rh congener **2** is similarly an effective precatalyst for oxidative[10b–d] and reductive[9h,11] catalysis, and the evidence presently available from our continuing mechanistic studies indicates analogous polyoxoanion-supported oxidation and Rh$_x$·polyoxoanion nanocluster reductive catalysts.

Experimental Section

Materials. All commercially obtained compounds were Baker reagent grade unless otherwise specified. Nitrogen gas was obtained from the boil-off of the house liquid nitrogen container and purified by passing over 4 Å molecular sieves (Linde) and a R3 11 catalyst (BASF) in the reduced (black) form. Acetonitrile (from CaH$_2$) and ethyl acetate (from anhydrous K$_2$CO$_3$) were distilled under N$_2$ and dispensed into glassware that had been thoroughly cleansed, dried at

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[30] Note also that the presence of aggregates of the type {[(1,5-COD)-Rh]$_n$·[$P_2W_{15}Nb_3O_{62}$]$_n$}$^{8n-}$, where the rhodium is four-coordinated, was also considered, but these are apparently not present. [The solution molecular-weight data for **2** demonstrate a monomeric formulation *under the conditions of the sedimentation-equilibrium experiment*, but these molecular-weight determinations are typically carried out at concentrations of 10^{-5} M (and in the presence of 0.1 M [(n-C_4H_9)$_4$N]-PF$_6$), whereas ^{17}O and ^{183}W NMR data are typically collected at concentrations of 0.09 M. At this higher concentration, a precedented equilibrium as described by eq iv cannot be unequivocally ruled out

$$n[(1,5\text{-COD})\text{Rh}\cdot P_2W_{15}Nb_3O_{62}]^{8-} \rightleftharpoons \{[(1,5\text{-COD})\text{Rh}]_n\cdot [P_2W_{15}Nb_3O_{62}]_n\}^{8n-} \quad \text{(iv)}$$

(especially given the inherent differences between second- and third-row transition metals[15]).] But, as shown for five-coordinated, d^8 iridium(I) in [(1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}$]$^{8-}$ and for five-coordinated, d^6 rhodium(III) (as determined by single-crystal X-ray crystallography)[8i] in [(C_5Me_5)Rh·$P_2W_{15}Nb_3O_{62}$]$^{7-}$, the polyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$ prefers to act as a tridentate ligand. Therefore, proposed structures in which the rhodium binds to three surface oxygens of "$Nb_3O_9^{3-}$" are implied, consistent both with the literature precedent and with our own findings.

250 °C, and allowed to cool under a N_2 flow. Anhydrous diethyl ether (Aldrich, HPLC grade, glass distilled under N_2 and filtered through 0.5 μm filters by the manufacturer) was used without further purification. 1,5-Cyclooctadiene (1,5-COD) was stirred over Brockman activity I basic alumina (Fisher) and purged for 1 h with N_2 prior to use. Obtained from Aldrich and used as received were $NaBF_4$, $AgBF_4$, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane [Kryptofix 2.2.2.], 2-propanol, 95% ethanol, tetrahydrofuran (THF), benzene, $NaHSO_3$, $(CH_3)_4NCl$, 30% H_2O_2, 37% HCl, $RhCl_3{\cdot}xH_2O$ ($x = 2-3$), and Amberlyst ion-exchange resins. Similarly, $[(n\text{-}C_4H_9)_4N]Br$, $(n\text{-}C_4H_9)_4N]Cl$ (Fluka), and $(NH_4)_3IrCl_6$ (Johnson-Mathey) were used as received. Deuterated NMR solvents (acetone-d_6, DMSO-d_6, CD_3CN; Cambridge Isotope Laboratories) were used as received. If the NMR sample was to be prepared in the drybox, the deuterated solvent was degassed by purging either with the drybox atmosphere or with argon (outside the box) for 0.5 h. Aqueous $[(n\text{-}C_4H_9)_4N]OH$ solutions were prepared according to the literature[31] and titrated with 0.1 M HCl to the methyl red and phenolphthalein end points (i.e., for both amine and total base content) immediately prior to use. Isomerically pure α-$K_6P_2W_{18}O_{62}$[32] and the hexaniobate $K_7HNb_6O_{19}$[33] were prepared as previously described.

Instrumentation/Analytical Procedures. Elemental analyses were obtained from Mikroanalytisches Labor Pascher (Remagen, Germany). Oxygen- and moisture-sensitive samples were routinely manipulated under an inert atmosphere in a Vacuum Atmospheres Inert "Dry" Box. O_2 levels were maintained at less than 1.0 ppm and monitored by use of a Vacuum Atmospheres O_2 level monitor. Infrared spectra were obtained on a Nicolet 5DX as KBr disks.

All nuclear magnetic resonance (NMR) spectra of routine samples were obtained as $CDCl_3$, CD_3CN, acetone-d_6, or DMSO-d_6 solutions in Spectra Tech or Wilmad NMR tubes. Air-sensitive samples were prepared in the drybox, and the solution was placed in an NMR tube equipped with a J. Young airtight valve (Wilmad). ^1H NMR (300.15 MHz) and ^{13}C NMR (75.0 MHz) spectra were recorded in 5 mm o.d. tubes on a General Electric QE-300 spectrometer, at 21 °C unless otherwise noted, and were referenced to the residual impurity in the deuterated solvent (^1H NMR) or to the deuterated solvent itself (^{13}C NMR). Chemical shifts are reported on the δ scale and resonances downfield of $(CH_3)_4Si$ (δ 0) are reported as positive. Spectral parameters for ^1H include pulse width 3.0 μs, acquisition time 1.36 s, repetition rate 2.35 s, and sweep width ±6024 Hz, while spectral parameters for ^{13}C NMR include pulse width 15.0 μs, acquisition time 819.2 ms, repetition rate 1.31 s, and sweep width ±20 000 Hz. All ^1H and ^{13}C NMR spectra of $[(n\text{-}C_4H_9)_4N]^+$ salts of the polyoxometalates have the characteristic resonances [^1H NMR δ 1.04, 1.56, 1.72, 3.35; ^{13}C NMR δ 14.0, 19.8, 23.7, 58.1] associated with the cation; hence these resonances are not reported for individual compounds. ^{31}P NMR (146.16 MHz) and ^{183}W NMR (15.04 MHz) obtained at the University of Oregon were recorded on a Nicolet NT-360 NMR spectrometer, at 30 °C unless otherwise noted, in 12 mm o.d. or 10 mm o.d. NMR tubes. ^{31}P NMR spectra were referenced *externally* by the substitution method to 85% H_3PO_4 (i.e., the chemical shifts reported are uncorrected for the volumic diamagnetic susceptibility[34]), and ^{183}W NMR spectra were referenced externally by the substitution method to 2 M Na_2WO_4/D_2O (pD 8.0). Spectral parameters for ^{31}P NMR include pulse width 28 μs, acquisition time 409.65 ms, repetition rate 2.41 s, and sweep width ±10 000 Hz. Spectral parameters for ^{183}W NMR include pulse width 70 ms, acquisition time 754.03 ms, repetition rate 1.25 s, and sweep width ±5000 Hz. A 5 Hz (^{31}P NMR), 5 Hz (^{183}W NMR), or 0.5 Hz (^1H and ^{13}C NMR) exponential apodization of the FID was used on all spectra but was removed for any line widths reported herein. More recently, ^{31}P and ^{183}W NMR spectra were collected at Colorado State University (CSU) on Bruker 300 (^{31}P) and Bruker AM500 (^{183}W) NMR instruments employing 5 mm (^{31}P) or 10 mm (^{183}W) o.d. NMR tubes. ^{31}P NMR spectra were referenced *externally*[34] to 85% H_3PO_4 using a sealed capillary. ^{183}W NMR spectra were referenced externally by the substitution method to 2 M Na_2WO_4/D_2O. Spectral parameters differ from those listed above and are as follows. ^{17}O NMR (67.80 MHz): pulse width 30 μs; acquisition time 16 ms; sweep width ±62 500 Hz. ^{31}P NMR (121.50 MHz): pulse width 5 μs; acquisition time 819 ms; sweep width ±20 000 Hz. ^{183}W NMR (20.838 MHz): pulse width 30 μs; acquisition time 1114 ms; sweep width ±14 705 Hz. A 2 Hz (^{31}P NMR), 10 Hz (^{183}W NMR), or 100 Hz (^{17}O) exponential apodization of the FID was used on all spectra but was removed for any line widths reported herein. Spectra collected at CSU are marked as such.

The extreme air sensitivity of **1** and **2** necessitated the following control experiments. In the first control experiment, a ca. 1 mM solution (i.e., 30 times more dilute than any of the NMR samples) of the very air-sensitive, deep blue Co(I) compound $Co(CO)\{C_2(DO)(DOH)_{pn}\}$[35] was prepared in the drybox and placed in a 5 mm J. Young valve NMR tube. The tube was then brought out of the drybox and left to sit on the laboratory bench for 1 week, during which time no perceptible change in color was observed. Deliberate exposure of the NMR solution to air resulted in a rapid (less than 5 s) loss of the blue color. In a second control experiment, a fresh 30 mM solution of **1** in CD_3CN was prepared with an added 3 equiv of Kryptofix 2.2.2. (added to minimize any line broadening due to Na^+ ion-pairing effects) and placed in a 5 mm NMR tube equipped with a J. Young airtight valve. An initial ^1H NMR spectrum was recorded within 15 min. This same, sealed NMR tube was then purposely stored outside the drybox for 1 week. A second ^1H NMR spectrum was then obtained. No new line broadening was observed, demonstrating that O_2-induced line

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(31) (a) Cundiff, R. H.; Markunas, P. C. *Anal. Chem.* **1958**, *30*, 1447. (b) Cundiff, R. H.; Markunas, P. C. *Anal. Chem.* **1958**, *30*, 1450. (c) Cundiff, R. H.; Markunas, P. C. *Anal. Chem.* **1956**, *28*, 792.

(32) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886.

(33) (a) Flynn, C. M.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 178. (b) Flynn, C. M.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 335. (c) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93.

(34) (a) It is well-known in the ^{31}P NMR literature that chemical shift data reliable to, say, ±0.2 ppm or better require referencing to an *internal*, not external, standard[34b] so that the solvent's diamagnetic susceptibility is removed from the reported chemical shift. When using an external standard, either in a sealed capillary or by the substitution method, we often find larger variations, ±0.5 ppm or more, in chemical shift. For example, just using a 5 mm (rather than a 10 mm) NMR tube, along with an 85% H_3PO_4 *external* standard, yields chemical shifts that are offset ca. +0.5 ppm (i.e., vs those in the 10 mm tube) due presumably to the differing magnitudes of the volume diamagnetic susceptibility of the solvent.[34b] (b) Thus, and despite the fact that corrections for the volume diamagnetic susceptibility of the solvent are virtually never reported in the polyoxoanion literature, *we conclude that they should be*, and we are engaged in a search for suitable nonreactive *internal* standards.[34c] (c) See for example: Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981; pp 39−46. Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987; p 370 and references therein. (d) Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239−1242 (see footnote 12 therein). (e) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1173 (volume diamagnetic susceptibility effects on polyoxovanadates in ^{51}V NMR; bottom lines, first column, p 1173). (d) Under acidic conditions, possible internal (so-called secondary) reference standards[34b] might include $PW_{12}O_{40}{}^{3-}$ or $P_2W_{18}O_{62}{}^{6}-$. Under neutral to basic conditions, $P_2W_{15}Nb_3O_{62}{}^{9-}$ might be a useful internal, secondary-reference standard. This compound seems particularly well-suited as an internal, secondary standard for the measurement of ^{31}P NMR chemical shift data of polyoxoanions under higher pH conditions for several reasons: (i) its ^{31}P NMR resonances are observed in a chemical shift range typical of most polyoxoanions, (ii) it is available both in an organic solvent-soluble formulation (as its $[(n\text{-}C_4H_9)_4N]_9$ salt) and in a water-soluble formulation (as its Na_9 salt), and (iii) it is relatively stable in organic and in higher-pH-controlled aqueous solutions. (The basicity and nucleophilic reactivity of the "$Nb_3O_9{}^{3-}$" end of this polyoxoanion means that it will not be suitable for more acidic or electrophilic reagent conditions.) (e) A related problem exists when chemical shifts uncorrected for the volume diamagnetic susceptibility of the solvent that are measured on older Fe core magnets (i.e., with horizontal fields perpendicular to the sample axis) are compared to uncorrected chemical shifts measured on superconducting magnets (i.e., with vertical fields parallel to the sample axis); see p 41 of ref 34c (first citation) and Domaille's treatment of this in the specific case of a polyoxoanion sample: Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239−1242 (see footnote 12 therein).

(35) Finke, R. G.; Smith, B. L.; McKenna, W. A.; Christian, P. A. *Inorg. Chem.* **1981**, *20*, 687.

broadening does not occur during the NMR experiments reported herein (i.e., no paramagnetic impurities due to Ir(I) oxidation are present).

Molecular-weight data were collected as previously described by the sedimentation equilibrium method.[36] All molecular weights are weight-average molecular weights ($\bar{M}_w$). As a control against air leakage into the molecular-weight cell during data collection on air-sensitive samples, an approximately 1×10^{-6} M solution of the very air-sensitive $Co(CO)\{C_2(DO)(DOH)_{pn}\}$[35] (*vide supra*) in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ was syringed into the molecular-weight cell in the drybox. This cell was then placed under the experimental conditions (hard vacuum at 20 000 rpm for 24 h) and then placed (unopened) on the laboratory bench for 48 h. During this 72 h period (more than 3 times the length of the molecular-weight experiment) no visual loss of the deep blue color was noted, demonstrating that no significant leakage of O_2 into the cell occurred over the course of a typical molecular-weight experiment. Molecular-weight measurements obtained in CH_3CN were monitored in the ultraviolet region between 280 and 335 nm (the absorbance associated with the polyoxometalate framework).

Fast-atom-bombardment mass spectra were obtained on a Kratos MS-50 mass spectrometer at Oregon State University. Samples were dissolved in the FAB matrices on the stainless steel probe. The matrix was either dithiothreitol/dithioerythritol (5:1) or 3-nitrobenzyl alcohol and was *not* deoxygenated even for air-sensitive **1** and **2**. (In the case of **1** and **2**, earlier FAB-MS spectra recorded at Princeton University, with the assistance of Professor Jeffrey Schwartz, employed a sample-admitting apparatus which allowed the rigorous exclusion of O_2. However, the resultant FAB-MS still did not exhibit parent peaks containing the $[Ir(1,5\text{-}COD)]^+$ moiety. Hence, the better S/N spectra obtained at Oregon State and which were obtained without the exclusion of O_2 are presented herein.) Analyses were carried out at a mass resolution of 1000, using raw data (integrated multichannel averaging) or centroided data collection. Scan rates were 30 or 100 s/decade. Xenon gas was used to generate the primary ionizing beam from an Ion-Tech FAB gun operated at 7−8 keV. Molecular weights and isotope abundance patterns were calculated using Kratos DS-90 software.

[(1,5-COD)IrCl]₂. The 1,5-cyclooctadienyliridium chloride dimer is prepared by following literature methods,[8j,37] but with slight modifications. Despite an early report[38] that the iridium dimer is air stable, the complex has been shown to react with O_2 and, therefore, is treated as mildly air-sensitive.[39] Our treatment includes collecting and drying the material under a N_2 flow and storing the compound in an inert atmosphere box. The spectroscopic properties of the bright-orange powder were consistent with those reported in the literature, and the product was used without further purification. A detailed experimental procedure follows.

H_2O (20 mL), 2-propanol (7 mL), and 1,5-cyclooctadiene (3.6 mL, 29.3 mmol, excess) were placed in a 50 mL round-bottomed flask. This biphasic mixture was then bubbled with N_2 for 1 h. $(NH_4)_3IrCl_6$ (4.0 g, 8.72 mmol) was added, and the mixture was refluxed for 8−19 h under a N_2 flow (somewhat higher yields have been seen at longer reflux times). After 1−2 h, the reaction mixture turned brick-red. The flask was allowed to cool to room temperature, and the reddish precipitate was collected on a medium frit. The precipitate was washed with 25 mL of 5 °C H_2O and 50 mL of 5 °C 95% EtOH, both of which had been bubbled with N_2 for at least 1 h prior to use. The reddish-orange powder was then dried under a N_2 flow on the frit for 1 h and then at room temperature under vacuum for 12 h. Yield: 1.74−2.00 g, 2.59−2.98 mmol, 60−68%. The slightly air-sensitive compound was stored in an inert atmosphere box. IR (KBr disks, cm^{-1}): 905, 971, 977, 1001. Literature[37] (Nujol, cm^{-1}): 907, 970, 980, 1002. ^1H NMR ($CDCl_3$): δ 1.51−1.54, 2.24−2.27, 4.23. ^1H NMR (CD_3CN): δ 1.54−1.57, 2.16−2.21, 3.95. Literature[37] ($CDCl_3$): δ 4.3 (vinyl protons). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.8, 62.2. Literature[40] (solvent unreported): δ 62.1 (vinyl carbons).

[(1,5-COD)RhCl]₂. This compound was prepared by the following slight modification of the literature.[41] In particular, the solvent used for the reaction (ethanol/water vs ethanol), the reaction conditions (refluxing under N_2), and the isolation procedure are different.

Into a 500 mL round-bottomed flask with a sidearm were placed water (40 mL), ethanol (120 mL), and 1,5-COD (6 mL, 0.083 mol, excess; treated for 1−2 h over Al_2O_3 prior to usage). This mixture was purged with N_2 for 1 h. Then, 3 g of $RhCl_3 \cdot xH_2O$ was added. After refluxing under N_2 for 5 h, the solution was allowed to cool to room temperature. The bright-orange product was collected on a medium glass frit under a N_2 stream, washed with 30 mL of cold water (if this step is omitted, the precipitate contains a small amount of black powder, presumably unreacted $RhCl_3 \cdot xH_2O$), and then washed with 45 mL of cold ethanol, both of which had been purged well with N_2. The solid was allowed to dry under a N_2 stream on the glass frit for 1 h and then further dried overnight under vacuum. The bright-orange powder was stored in the drybox. Yield: 2.3 g (4.67 mmol, 77%). IR (KBr disks, cm^{-1}): 1323, 1299, 1228, 1212, 1171, 1152, 1079, 994, 960, 877, 865, 830, 814, 795, 773. Literature[41] (cm^{-1}): 1325, 1301, 1227, 1210, 1171, 1153, 1076, 993, 961, 878, 866, 831, 817, 795, 771. ^1H ($CDCl_3$) NMR: δ 1.73, 2.47, 4.21. $^{13}C\{^1H\}$ NMR: δ 30.86 (CH_2), 78.68 (CH).

$Na_{12}P_2W_{15}O_{56}\cdot 18H_2O$.[8j] The trilacunary heteropolytungstate was prepared identically to our modification[42] of the original French literature.[43] A ^{31}P NMR spectrum of a saturated solution of the lacunary heteropolytungstate in an acetate buffer containing LiCl (supplementary material, Figure M) shows that a freshly prepared solution of $Na_{12}P_2W_{15}O_{56}$ *contains more than 95% of a single compound*, a result which confirms Contant's findings.[44] [Previously, we had been unable to spectroscopically characterize this compound due to its decomposition in solution. However, it is obviously not true that this material is impure (it was previously thought to contain both "P_2W_{15}" and "P_2W_{16}" or "P_2W_{17}" species,[43] since subsequent substitution chemistry has been reported to lead to both "$P_2W_{16}M_2$" ($M = V^{5+}$)[45] and "$P_2W_{15}M_3$" ($M = V^{5+}$,[46] Mo^{6+} [47]) type compounds.] Further monitoring of this solution shows that the trilacunary $P_2W_{15}O_{56}^{12-}$ polyoxometalate is unstable in solution; within 2 h it decomposes to compounds which include the monolacunary species $\alpha_2\text{-}P_2W_{17}O_{61}^{10-}$ (by ^{31}P NMR). Hence, the lacunary $P_2W_{15}O_{56}^{12-}$ is sufficiently pure and stable in solution to allow the synthesis of >95% pure $P_2W_{15}Nb_3O_{62}^{9-}$ if the solid polyoxometalate is added to a solution of the Nb^{5+} heterometal (i.e., not the reverse order of addition).

$[(CH_3)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}\cdot 16H_2O$.[8j] The tetramethylammonium salt of $P_4W_{30}Nb_6O_{123}^{16-}$ is prepared according to our literature[8a] with some improvements. Key changes in the preparation include the following: (i) The finely-powdered $Na_{12}P_2W_{15}O_{56}$ must be added in a single step. If the trilacunary species is added when it has not been finely powdered, (i.e., it will not rapidly go into solution) or if the trilacunary heteropolytungstate is added in successive portions over more than 2 h, at least two unidentified species are observed in the ^{31}P NMR spectrum of the final product in addition to the desired triniobium

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compound, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. (ii) Excess solvent is added to dissolve the $[(CH_3)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ initially, since it is kinetically insoluble in unbuffered pH 4.6 H_2O, but then this excess solvent must be removed. Typically, this requires reducing the solution from 400−500 mL (the amount of unbuffered pH 4.6 H_2O that the compound initially dissolves in) to 150 mL for the first reprecipitation and to 75 mL for the second reprecipitation. A detailed experimental procedure follows.

A pale yellow solution was prepared by dissolving 2.95 g (2.15 mmol) of $K_7HNb_6O_{19}\cdot 13H_2O$ in 325 mL of 0.5 M H_2O_2. HCl (29 mL of 1 M, 29 mmol, excess) was added. The solution turned bright yellow. Immediately, 18.25 g (4.21 mmol) of finely powdered $Na_{12}P_2W_{15}O_{56}\cdot 19H_2O$ was added in a single step, resulting in a clear colorless solution. [Note: If the $Na_{12}P_2W_{15}O_{56}\cdot 19H_2O$ is added slowly (over 2 h), at least six lines are observed in the ^{31}P NMR]. *Caution: The following step is a vigorous reaction in which SO_2 is evolved. Proceed with caution in a well-ventilated fume hood.* $NaHSO_3$ (25 g, 240.2 mmol, excess) was gradually added to the solution over 10−15 min, destroying the excess peroxides. The solution was stirred for 1−2 h until it had cooled to room temperature. $(CH_3)_4NCl$ (10 g, 91.2 mmol, excess) was added to the solution in a single step, causing the immediate formation of a white precipitate. The white precipitate was collected and reprecipitated twice from a homogeneous solution of 90 °C unbuffered pH 4.6 H_2O. After the compound was dissolved in the hot pH 4.6 water, the volume of the solution was reduced to 150 and 75 mL for the first and second precipitations, respectively, and cooled in an ice bath. The product was collected and dried under vacuum overnight. Yield: 12−14 g (1.28−1.50 mmol, 61−71%). This reaction was productively scaled up as much as 5-fold, which resulted in a yield of 78 g (16.6 mmol, 79%) of product. Characterization of this compound prepared by this improved procedure demonstrates that it is identical to that described in our first report.[8a]

$[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ and $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$.[8j] These preparations are again based on our literature,[8a] but with an improvement in the collection and washing of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$, which results in a reproducible procedure yielding at least 95% pure material when cleaved/deprotonated with $[(n\text{-}C_4H_9)_4N]OH$ to form the desired $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. (This modified preparation is the result of more than 40 preparations by four people and represents our best effort to date *with this synthesis*,[9i] in terms of both the purity of the final compound and the speed of collection. However, we are presently investigating an even further improvement of this procedure, in an attempt to avoid the $[(CH_3)_4N]^+$ salt of $P_4W_{30}Nb_6O_{123}{}^{16-}$ completely.[48]) The key changes in what follows are in the collection and washing of the precipitated $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$. Briefly, the procedure involves placing the precipitate and the supernatant on a coarse glass frit for 1 h with no aspiration, during which time three layers form. The uppermost layer and half of the middle layer are removed by pipet and discarded. Water is then added to the frit, taking care not to disturb the material that has been collected. Three layers again form; the above process is then repeated three or four additional times. Approximately 1 L of water is then used to wash the material on the frit with aspiration, again taking care not to disturb the material on the frit. The purified white solid is then dried at 60 °C on a large weighing dish. The material obtained in this manner is analytically pure, with spectroscopic properties consistent with our previous formulation as $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$, and reproducibly gives $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ [as determined by ^{31}P NMR and ^{183}W NMR (*vide infra*)] when cleaved/deprotonated with 6 equiv of $[(n\text{-}C_4H_9)_4N]OH$. A detailed experimental procedure follows.

$[(CH_3)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}\cdot 16H_2O$ (15 g, 1.60 mmol) was dissolved in 500 mL of 90 °C unbuffered pH 4.6 H_2O. The homogeneous solution was allowed to cool to room temperature. $[(n\text{-}C_4H_9)_4N]Br$ (7 g, 21.7 mmol, excess) was added in a single step to give a white precipitate. The precipitate was collected on a coarse frit as follows: (1) The solution was placed on a coarse glass frit for 1 h with no aspiration, during which time three layers appeared. (2) The uppermost layer was removed completely by pipet, and half of the middle layer was also removed. (3) A 100−200 mL portion of H_2O was then added to the frit, taking care not to disturb the material on the frit. (4) Steps 1−3 were repeated three or four times. (5) One liter (3 × 350 mL) H_2O was then used to wash the material on the frit with aspiration (again without disturbing the sample). This step usually takes 1−2 h to complete. The sample was spread on a large weighing dish and dried at 60 °C overnight. Yield: 8.4−10.0 g (0.76−0.90 mmol, 47−56%). Anal.[49] Calcd (found): C, 20.82 (20.41); H, 3.97 (3.98); N, 1.52 (1.48); P, 0.99 (0.99). This procedure has been productively scaled up 5-fold to yield 45 g (4.06 mmol, 51%).[9i] Characterization of this compound by ^{31}P NMR (DMSO-d_6 [δ −7.2 ($\Delta\nu_{1/2} = 3.5 \pm 0.3$ Hz), −14.2 ($\Delta\nu_{1/2} = 4.6 \pm 0.3$ Hz); CD_3CN [δ −7.2 ($\Delta\nu_{1/2} = 3.1 \pm 0.3$ Hz), −14.3 ($\Delta\nu_{1/2} = 4.6 \pm 0.3$ Hz)] and IR demonstrate that this material is identical to that described in our previous report.[8a]

$[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ (10.0 g, 0.903 mmol) was dissolved in 33 mL of CH_3CN in a 100 mL round-bottomed flask that contained a 1-in. magnetic stir bar. An aqueous solution of $[(n\text{-}C_4H_9)_4N]OH$ (13.1 mL of 0.415 M, 5.44 mmol, 6 equiv) was added to the polyoxometalate solution, and the resulting clear solution was stirred for 0.5 h at room temperature. A quantitative yield of solid $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ was obtained by removal of the solvent under vacuum overnight. ^{31}P NMR (DMSO-d_6): δ −7.1, −14.2.[51d] The residual colorless material, in a 100 mL round-bottomed flask under vacuum, was taken into the drybox for use in the next preparation. (The IR band reported[8a] at 660−665 cm^{-1} in the spectrum of the product has proved somewhat variable in intensity and appears to depend on the amount of H_2O present.)

$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$, 1.[8j] All solids used in this preparation were dried at room temperature under vacuum for 24 h and then transferred into the drybox. All manipulations were performed in the drybox. Freshly prepared $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (6.78 g, 1.08 mmol) was placed in a 100 mL round-bottomed flask and dissolved in 20 mL CH_3CN. (If this solution is cloudy or contains a white precipitate, the yield is lower.) This solution was filtered through Whatman No. 2 paper into a 200 mL round-bottomed flask. The filter paper was washed with 5 mL of CH_3CN, and the washings were combined with the original filtrate. In a separate disposable 18 × 150 mm culture tube, $[(1,5\text{-}COD)IrCl]_2$ (0.364 g, 0.542 mmol) was slurried in 4 mL of CH_3CN. Solid $AgBF_4$ (0.212 g, 1.09 mmol, 2.01 equiv relative to $[(1,5\text{-}COD)IrCl]_2$) was added to the slurry, causing an immediate AgCl precipitate. The mixture was stirred for 30 min. The AgCl precipitate was removed by gravity filtration through Whatman No. 2 paper and the filtrate introduced directly into the clear, vigorously stirred CH_3CN solution of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. The filter paper was then washed with an additional 5 mL of CH_3CN. The clear, colorless heteropolytungstate solution changed from clear to orange-red upon addition of the *in situ* generated $[Ir(1,5\text{-}COD)(CH_3CN)_2]BF_4$ solution. The homogeneous iridium−heteropolytungstate solution was stirred for 30 min. Solid $NaBF_4$ (0.3578 g, 3.259 mmol, 3.01 equiv relative to $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$) was added to the orange-red solution. The 18 × 150 mm disposable culture tube that had contained the $NaBF_4$ was rinsed with 3 mL of CH_3CN, and this mixture was added to the iridium−heteropolytungstate solution. This mixture was stirred for approximately 45 min, during which time the $NaBF_4$ dissolved. (Note: $NaBF_4$ is only minimally soluble in CH_3CN but has increased solubility in the presence of the heteropolytungstate.) The dark red-orange solution was then evacuated to dryness, and the residue was dried under vacuum for 4 h.

Purification of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$ (i.e., removal of the 4 equiv of $[(n\text{-}C_4H_9)_4N]BF_4$) was accomplished by dissolving the deep orange-red solid in 5 mL of CH_3CN and then transferring the solution to a 600 mL beaker. EtOAc (400 mL) was added in 40 mL portions over 15 min, precipitating a light-yellow powder. This powder was collected on a medium frit, washed with 40 mL of diethyl ether, and dried on the frit for 30 min. The filtrate was light-yellow and cloudy. The reprecipitation was performed a

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(48) Weiner, H.; Aiken, J. D., III; Finke, R. G. Unpublished results and experiments in progress.

(49) (a) An elemental analysis was carried out on this sample (C, H, N, and P only) to ensure that the slightly different method used to prepare and wash this sample did not result in a different TBA^+/H^+ ratio (an effect we have seen before for different preparations of "$(TBA)_5H_4P_2W_{15}V_3O_{62}$" where a "$(TBA)_6H_3$" salt has also been occasionally obtained[49b]). (b) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

second time and the light-yellow powder was collected on a medium glass frit, washed with 75 mL of diethyl ether, and dried under vacuum for 4 h. (Drying under vacuum at 60 °C for 1 week is required to remove the last traces of solvents *which, otherwise, interfere with the ^1H and ^{13}C NMR spectra, for example.*) Infrared spectroscopy is a convenient method to establish that the contaminating $[(n\text{-}C_4H_9)_4N]BF_4$ has been removed [$\nu(BF_4^-)$ = 1050−1090 cm^{-1}]. Yield: 4.2 g (0.74 mmol, 69%). This preparation has been successfully scaled up 2.7-fold, giving a 12 g, 2.1 mmol, 65% yield. This compound is stored in a screw-capped polyethylene bottle in the drybox, preferably double-bottled to protect it from trace amounts of oxygen. [In addition, the product may be stored over a small layer of the compound in the outer bottle topped by a layer of tissue (i.e., using some of the complex as its own, sacrificial, ideal-affinity oxygen scavenger).] Anal. Calcd (found) [and repeat analysis on an independent, earlier preparation]: C, 18.63 (18.99) [18.95]; H, 3.41 (3.52) [3.54]; N, 1.23 (1.40) [1.49]; Na, 1.22 (1.20) [1.43]; Ir, 3.39 (3.24) [2.74]; P, 1.09 (1.07) [1.09]; W, 48.6 (48.5) [48.4]; Nb, 4.91 (4.66) [4.80]; O, 17.5 (17.6) [17.0]; total, 99.98 (100.18) [99.4]. Molecular weight (sedimentation-equilibrium method, 1 × 10^{-5} M **1** in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$): $\bar{M}_w$(calc) 5670, $\bar{M}_w$(found) 5600 ± 600 (supplementary material, Figure A) ($\bar{M}_w$ = average molecular weight). An attempted molecular-weight measurement by FAB-MS did not reveal a parent peak for **1**, presumably due to loss of (1,5-COD)Ir as a neutral fragment, and has been analyzed in detail elsewhere.[22] Infrared spectrum (KBr disk, cm^{-1}): 766, 899, 913, 948, 1089. The IR resonances for $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ (in comparison to $P_2W_{18}O_{62}^{6-}$)[50] at 948 (960), 913 (912), and 766 (780) cm^{-1} suggest (but do not prove) the assignment of these bands as follows: the asymmetric stretching vibrations of the $W-O_{terminal}$ bonds (948 cm^{-1}); the W−O−W bridges between corner-sharing octahedra (913 cm^{-1}); and the W−O−W bridges between edge-sharing octahedra (766 cm^{-1}). ^{31}P NMR (DMSO-d_6), δ (no. of P, $\Delta\nu_{1/2}$): −8.2 (1 P, 54.6 ± 5.0 Hz), −14.1 (1 P, 3.9 ± 0.4 Hz) (Figure 4A). ^{31}P NMR (DMSO-d_6, with 3 equiv of Kryptofix 2.2.2. added), δ (no. of P, $\Delta\nu_{1/2}$): −8.2 (1 P, 4.7 ± 0.4 Hz), −14.1 (1 P, 4.4 ± 0.4 Hz) (Figure 4B). ^{31}P NMR (CD_3CN), δ (no. of P) (supplementary material, Figure F): −9.7 (1 P), −14.2 (1 P). ^{31}P NMR (CD_3CN, with 3 equiv of Kryptofix 2.2.2. added), δ (no. of P): −8.3 (1 P), −14.5 (1 P).[51a,d] ^{183}W NMR (DMSO-d_6, 0.09 M), S/N 12/1 after 10 000 scans, δ (no. of W, $\Delta\nu_{1/2}$) (Figure 6A): −125.0 (3 W, 14.9 ± 1.0 Hz), −150.3 (6 W, 13.7 ± 0.7 Hz), −194.0 (6 W, 25.5 ± 1.5 Hz). ^{183}W NMR (DMSO-d_6, 0.09 M, with 3 equiv of Kryptofix 2.2.2. added), S/N 25/1 after 10 000 scans, δ (no. of W, $\Delta\nu_{1/2}$) (Figure 6B): −128.1 (3 W, 12.0 ± 0.3 Hz), −152.2 (6 W, 13.9 ± 0.2 Hz), −191.4 (6 W, 11.1 ± 0.2 Hz). ^1H NMR (DMSO-d_6), δ (no. of H, $\Delta\nu_{1/2}$): 1.87 (4.0 ± 0.2 H, 10.5 ± 0.6 Hz), 2.28 (3.9 ± 0.3 H, 8.6 ± 1.5 Hz), 3.99 (4.0 ± 0.1 H, 8.2 ± 0.7 Hz). ^1H NMR (DMSO-d_6, with 3 equiv of Kryptofix 2.2.2. added), δ: 1.89 (br, 4 H), 2.28 (br, 4 H), 4.04 (br, 4H). The temperature-varied NMR spectrum of **1** in DMSO-d_6 shows no change between 25 and 95 °C. ^1H NMR (CD_3CN), δ (multiplicity): 2.40 (br), 4.20 (br). $^{13}C\{^1H\}$ NMR (DMSO-d_6), δ (assignment, $\Delta\nu_{1/2}$): 31.5 (CH_2, 7.2 ± 0.5 Hz), 55.8 (CH, 8 ± 1 Hz). $^{13}C\{^1H\}$ NMR (DMSO-d_6, with 3 equiv of Kryptofix 2.2.2. added), δ (assignment, $\Delta\nu_{1/2}$): 31.4 (CH_2, 6.5 ± 0.5 Hz), 55.8 (CH, 9.6 ± 1.5 Hz). ^{17}O NMR (CD_3CN, 22 °C, with 3 equiv of Kryptofix 2.2.2. added) (Figure 8B), δ: 680 (s, 3 ± 1 O; Nb−O) ($\Delta\nu_{1/2}$ = 440 ± 140 Hz); 330 (s, 3 ± 1 O; Nb_2-O-Ir) ($\Delta\nu_{1/2}$ = 510 ± 110 Hz).

$[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, 2.[8j] In the drybox, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (10.25 g, 1.63 mmol) is placed in a 100 mL round-bottomed flask and dissolved with stirring in 30 mL of CH_3CN to yield a clear solution. This solution is filtered through a folded filter paper (Whatman No. 2). The clear filtrate is collected in a 200 mL round-bottomed flask that includes a stir bar. The filter paper is washed with a small amount of CH_3CN, the washings are combined with the above filtrate, and the combined filtrate is stirred. (By this step, a total of ca. 38 mL of CH_3CN has been used.) Next, ca. 15 mL of CH_3CN is placed in a graduated cylinder (a portion of it is used below as a solvent for the reaction of $[Rh(1,5\text{-COD})Cl]_2$ with 2 equiv of $AgBF_4$; the remaining portion is used for washing of the test tubes). About 5−6 mL of CH_3CN is put with the $[Rh(1,5\text{-COD})Cl]_2$ (0.4007 g, 0.813 mmol) into a test tube, and the resulting yellowish suspension is stirred. Into this is added a homogeneous solution of $AgBF_4$ (0.3183 g, 1.635 mmol; dissolved in a few milliliters of CH_3CN) using a pipet. The $[Rh(1,5\text{-COD})Cl]_2$ dissolves completely, a white precipitate of AgCl deposits, and a yellow mother liquor remains. The test tube that contained the $AgBF_4$ is washed with a few milliliters of CH_3CN, and the washings are also added to the well-stirred suspension, which now contains $[Rh(1,5\text{-COD})(CH_3CN)_2]BF_4$ and 2 equiv of AgCl.

Still in the drybox, the white precipitate of AgCl is removed by filtration with a folded filter paper, and the filtrate is directly introduced into the clear, well-stirred solution of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. The precipitate on the filter paper is washed several times with a small amount of CH_3CN (a total of ca. 15 mL of CH_3CN is used for this washing), and the washings are combined to the above stirred solution. This combined, red solution is further stirred for 15 min. The total volume in the 200 mL round-bottomed flask is ca. 68 mL. To this solution is added solid $NaBF_4$ (0.5354 g, 4.876 mmol, 3 equiv). The $NaBF_4$ left on a wall of the test tube is also washed out with a few milliliters of CH_3CN, and the washings are added to the red solution. The stirring is continued at room temperature until all of $NaBF_4$ dissolves. (It takes about 20 min.) The resulting orange-red solution is filtered with a folded filter paper, and the filtrate is collected in a 200 mL round-bottomed flask, which is rotary-evaporated (using a small rotary-evaporator placed inside the drybox) to dryness and then further dried under vacuum for 5 h. The residual solid, which contains $(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$ and 4 equiv of $[(n\text{-}C_4H_9)_4N]BF_4$, is a darker yellow to darker orange.

To remove the contaminating three equivalents of $[(n\text{-}C_4H_9)_4N]BF_4$, the solid is placed into a 200 mL round-bottomed flask and dissolved in ca. 8 mL of CH_3CN (excess CH_3CN lowers the yield). The orange-red solution is then transferred to a 600 mL beaker using a polyethylene pipet. The round-bottomed flask is rinsed with a small amount of CH_3CN, and the washings are combined with the solution in the beaker. (By this step, a total of ca. 15 mL of CH_3CN has been used; this orange-red solution is clear and homogeneous.) To this solution, while stirring with a spatula, is slowly added in 100 mL portions a total of 400 mL of EtOAc. A yellow precipitate forms. After the addition of the final portion of EtOAc, the stirring (with a magnetic stirrer and a stir bar) is continued for 15 min. The orange-yellow precipitate is collected on a 30 mL medium glass frit, washed twice with 60 mL of Et_2O, and dried for 30 min under vacuum. The filtrate is pale orange and slightly cloudy. To completely remove the contaminating $[(n\text{-}C_4H_9)_4N]BF_4$, reprecipitation is repeated twice more from a CH_3CN solution (ca. 15 mL; an excess lowers the yield) using 400 mL of EtOAc, followed by washing twice with 60 mL of Et_2O. The final product is an orange-yellow powder, yield 7.0 g (1.25 mmol, 77%), which is stored in the drybox. [In addition, the product may be stored over a small layer of the compound in the outer bottle topped by a layer of tissue (i.e., using some of the complex as its own, sacrificial, ideal-affinity oxygen scavenger).] Drying under vacuum at 60 °C for 1 week is required to remove the last traces of solvents *which, otherwise, interfere with the ^1H NMR and ^{13}C NMR spectra.* Anal. Calcd (found): C, 18.94 (18.50); H, 3.47 (3.50); N, 1.26 (1.52); Na, 1.24 (1.25); Rh, 1.84 (1.70); P, 1.11 (1.11); W, 49.4 (49.6); Nb, 4.95 (5.09); O, 17.8 (16.6); total, 100 (98.87).[52] Molecular weight (sedimentation-equilibrium method, 1 × 10^{-5} M **2** in 0.1 M ($[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ (supplementary material,

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(50) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *Spectrosc. Lett.* **1979**, *12*, 127.

(51) (a) ^{31}P NMR spectra of **1** collected more recently at Colorado State University afforded the following chemical shift data: δ −7.1, −13.6. (b) ^{31}P NMR spectra of **2** collected more recently at Colorado State University afforded the following chemical shift data: δ −7.4, −13.4. (c) ^{31}P NMR spectra of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ collected more recently at Colorado State University afforded the following chemical shift data: δ −6.6, −13.6. (d) The difference in the observed chemical shifts is attributed to (i) different sample size (5 mm o.d. vs 10 mm o.d. NMR tube) and (ii) use of an external reference standard sealed in a capillary vs an external reference by substitution (see also footnote 34). However, when $P_2W_{15}Nb_3O_{62}^{9-}$ is used as an internal secondary standard,[51d] the observed ^{31}P chemical shifts are reproducible within ±0.2 ppm. (d) ^{31}P NMR chemical shifts for $P_2W_{15}Nb_3O_{62}^{9-}$, referenced externally to 85% H_3PO_4, have previously been reported.[8a] However, no correction for the volumic susceptibility of the sample solution was applied.

Figure B): $\bar{M}_w$(calc) 5584, $\bar{M}_w$(found) 5910 ± 600. An attempted molecular-weight measurement by FAB-MS did not contain a parent peak for **2**, presumably due to the expected loss of the (1,5-COD)Rh as a neutral fragment[22] (supplementary material, Figures C and D). IR (KBr disks, cm^{-1}) (supplementary material, Figure E): 1090, 1008, 981, 949, 914, 895, 771. ^{31}P NMR (DMSO-d_6), δ ($\Delta\nu_{1/2}$) (Figure 5): −8.2 (18.7 ± 0.3 Hz), −14.1 (17.0 ± 0.2 Hz). ^{31}P NMR (DMSO-d_6, with 3 equiv of Kryptofix 2.2.2.), δ (no. of P, $\Delta\nu_{1/2}$) (Figure 5): −8.6 (1 P, 4.1 ± 0.2 Hz), −14.1 (1 P, 5.3 ± 0.3 Hz). ^{31}P NMR (CD_3CN), δ (supplementary material, Figure G): −8.9, −13.9. ^{31}P NMR[34] (CD_3CN, with 3 equiv of Kryptofix 2.2.2.), δ (no. of P) (supplementary material, Figure G): −8.2 (1 P), −14.2 (1 P).[51b,d] ^{183}W NMR (DMSO-d_6, 0.09 M, with 3 equiv of Kryptofix 2.2.2.), δ (no. of W, $\Delta\nu_{1/2}$) (Figure 7): −136.5 (3 W, 9.3 ± 3.5 Hz), −160.4 (6 W, 7.9 ± 2.0 Hz), −199.8 (6 W, 9.1 ± 2.5 Hz). ^{183}W (CD_3CN, 0.09 M, with 3 equiv of Kryptofix 2.2.2.), δ (no. of W, $\Delta\nu_{1/2}$): −131.9 (3 W, 8.9 ± 2.9 Hz), −158.94 (6 W, 8.9 ± 1.6 Hz), −196.31 (6 W, 15.0 ± 3.1 Hz). ^{1}H NMR (DMSO-d_6, 25 °C, 3.58 mM), δ (multiplicity, no. of H, $\Delta\nu_{1/2}$) (supplementary material, Figure H): 1.89 (br, 4 H, 18.56 ± 0.49 Hz, CH_2), 2.42 (br, 4 H, 18.59 ± 0.82 Hz, CH_2), 4.29 (br, 4 H, 11.09 ± 0.26 Hz, CH). ^{1}H NMR (CD_3CN, 25 °C, 3.58 mM), δ (multiplicity, no. of H) (supplementary material, Figure J): 2.44 (br, 6 H), 4.20 (br, 2 H). No resonances attributable to $[(1,5\text{-COD})Rh(\text{acetone-}d_6)_2]^+$ are seen in the ^{1}H NMR spectrum of **2** using acetone-d_6 as solvent (supplementary material, Figure K). Variable-temperature ^{1}H NMR spectroscopy of **2** in acetone-d_6 (−20 to +40 °C), CD_3CN (−20 to +60 °C) and DMSO-d_6 (20−60 °C) showed the maintenance of the peaks for the polyoxoanion-bound $[(1,5\text{-COD})Rh]^+$ moiety with no new signals observed. ^{13}C{^{1}H} NMR (DMSO-d_6, 25 °C, 15.7 mM), δ (multiplicity, $\Delta\nu_{1/2}$) (supplementary material, Figure I): 29.95 (s, 3.34 ± 0.14 Hz, CH_2), 86.04 (br, 40.16 ± 2.90 Hz, CH). ^{13}C NMR (25 °C, 15.7 mM, DMSO-d_6), δ (multiplicity, $^{1}J_{CH}$) (supplementary material, Figure L): 30.4 (t, 154 Hz), 85.8 (d, 100 Hz). This ^{13}C{^{1}H} NMR experiment confirms the assignment for the methylene and methine carbons of **2**. ^{17}O NMR (20 °C, 90 mM, CD_3CN, 3 equiv of Kryptofix 2.2.2. added) (supplementary material, Figure P), δ (no. of O, $\Delta\nu_{1/2}$): 790 (2 ± 1, 2300 ± 850 Hz), 740−530 (5 ± 1, estimated 7800 Hz), 350 (1 ± 0.2, 760 ± 220 Hz). ^{17}O NMR (55 °C, 90 mM, CD_3CN, 3 equiv of Kryptofix 2.2.2.), δ (no. of O, $\Delta\nu_{1/2}$) (supplementary material, Figure N): 800 (2 ± 1, 1600 ± 480 Hz), 710 (6 ± 1, 1650 ± 320 Hz), 350 (1 ± 0.2, 360 ± 60 Hz).

^{1}H and ^{13}C NMR Studies of $[(1,5\text{-COD})M{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$. The collection of ^{1}H NMR spectra requires the use of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})M{\cdot}P_2W_{15}Nb_3O_{62}]$ (M = Ir, Rh) which has been *thoroughly desolvated and dried*, as otherwise additional peaks relating to diethyl ether, acetonitrile, and ethyl acetate (solvents used in the preparation) show up and can be misinterpreted as $[(1,5\text{-COD})M]^+$ resonances. Therefore, samples of **1** and **2** used in the acquisition of ^{1}H and ^{13}C NMR spectra *were rigorously dried and desolvated for 1 week in a drying pistol under vacuum at 60 °C*. In CD_3CN as solvent, two of the three expected resonances for the 1,5-COD ligand were observed for samples of **1** and **2**; a third 1,5-COD resonance, observed at δ 1.89 in DMSO-d_6, is obscured by the residual protic impurities of the deuterated solvent used (δ = 1.93 for CH_3CN). In contrast to the three peaks observed in DMSO-d_6, in acetone-d_6 no peaks assignable to COD resonances are observed. Only broad, featureless resonances are observed that cannot readily be attributed to the cyclooctadiene ligand. (An experimental limitation here is the decreased solubility of complexes **1** and **2** in acetone, when compared to CH_3CN and DMSO as solvent.) Due to the even lower solubility of the mixed $5[(n\text{-}C_4H_9)_4N]^+/3Na^+$ salt of $[(1,5\text{-COD})M{\cdot}P_2W_{15}Nb_3O_{62}]$ (M = Ir, Rh) in nonpolar and noncoordinating solvents, no resonances for $[(1,5\text{-COD})M]^+$ were observable in $CDCl_3$, even though signals for the much more abundant protons of $[(n\text{-}C_4H_9)_4N]^+$ could clearly be seen.

Removal of $[(1,5\text{-COD})M]^+$ from 1 and 2 by Addition of Cl^-. In two separate control experiments, to a solution of 0.5 g (0.09 mmol) of **1** or **2** in 2 mL of CD_3CN was added 0.49 g (1.78 mmol, 20 equiv) of $[(n\text{-}C_4H_9)_4N]Cl$. No change in solution color was observed for **1**, whereas for **2** the solution color changed from orange to bright yellow immediately following the addition of $[(n\text{-}C_4H_9)_4N]Cl$. A ^{31}P NMR spectrum of this solution acquired in the presence of 3 equiv of Kryptofix 2.2.2. showed two lines. ^{31}P NMR[34] (25 °C, 44.5 mM, CD_3CN, with 3 equiv of Kryptofix 2.2.2.): δ −7.1, −14.1 (±0.2). The chemical shifts in the resulting ^{31}P NMR spectrum are identical to those observed for $P_2W_{15}Nb_3O_{62}^{9-}$. Most characteristic here is the downfield shift of the phosphorus resonance closer to the "$Nb_3O_9^{3-}$" cap indicative of cleavage of $[(1,5\text{-COD})M]^+$ (presumably as $[(1,5\text{-COD})MCl]_2$) from the heteropolyoxoanion support, hence re-forming the starting material, $P_2W_{15}Nb_3O_{62}^{9-}$, used in the synthesis of **1** and **2**.

Addition of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ to a Solution of $[(1,5\text{-COD})M{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$. In a control experiment designed to prove that unreacted, "free" $P_2W_{15}Nb_3O_{62}^{9-}$ (supplementary material, Figure T) could be detected if it were present as an impurity in **1** or **2**, 0.10 g (0.45 equiv, 0.016 mmol) of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ was deliberately added to a solution of 0.20 g of **1** (0.035 mmol) in DMSO-d_6. ^{31}P NMR (DMSO-d_6; with 3 equiv of Kryptofix 2.2.2.), δ (no. of P): −7.1 (1 P), −8.1 (2 P), −14.1 (3 P) (supplementary material, Figure R). [An analogous experiment where $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ was added to a solution of **2** in DMSO-d_6 yielded similar results, supplementary material, Figure R.] Separate, clearly identified resonances at δ −7.1 and −8.1 are seen as expected for the phosphorus atoms closest to the "$Nb_3O_9^{3-}$" cap in $P_2W_{15}Nb_3O_{62}$ and in $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$, respectively, that are closest to the "$Nb_3O_9^{3-}$" cap. The resonances for those phosphorus closest to the "W_3O_6" cap coincide at δ −14.1. The observation of two distinct signals (and their integrated intensities) at δ −7.1 and −8.1 rules out, at least on the ^{31}P NMR time scale and under the conditions of the experiment, a dissociation/readdition mechanism ("intermolecular fluxionality") for $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ (e.g., yielding $P_2W_{15}Nb_3O_{62}^{9-}$ and $[(1,5\text{-COD})Ir(\text{DMSO-}d_6)_2]^+$), followed by diffusion of the iridium moiety through solution and readdition to a different polyoxoanion. It also shows that, even in such strongly coordinating solvents as DMSO, $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ is stable and the iridium moiety is not cleaved from the polyoxoanion support.

Experiments Demonstrating Non-Ion-Exchangeability for 1 and 2. In the inert atmosphere box, 10 g of macroreticular, strongly acidic resin, Amberlyst 15 (H^+ form; P-SO_3H) was placed in a beaker together with ca. 50 mL of degassed water. The resin was swirled for ca. 1 min, followed by decanting the water. This process was repeated until the aqueous phase was clear and colorless. The resin was then packed onto a 27 cm × 1 cm (length × diameter) column. A large excess, ca. 30 mL, of degassed 40% $[(n\text{-}C_4H_9)_4N]^+OH^-/H_2O$ was diluted by ca. 1 part in 10 with distilled water and then passed dropwise through the column. When the eluant tested basic with litmus paper, distilled water was passed through the column until the eluant tested neutral with litmus paper. The resultant P-$SO_3^-[(n\text{-}C_4H_9)_4N]^+$ column was then washed with five 50 mL portions of dry acetonitrile. Still in the drybox, a solution of ca. 0.5 g of **1** or **2** in 10 mL of CH_3CN was loaded onto the column. This colored solution was passed through the column dropwise with no apparent retention. The colored eluant was collected and the solvent removed by rotary evaporation under reduced pressure, again all in the drybox. The $[(1,5\text{-COD})M{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ (M = Ir, Rh) appeared unchanged (by ^{31}P NMR spectroscopy). An anion exchange column of identical size was packed with strongly basic resin, Amberlyst A-27 (Cl^- form; P-$NR_3^+Cl^-$) and was then washed with dry acetonitrile. A sample of **1** or **2** was loaded onto the column as described above for the cation exchange resin. All of the colored sample was retained on the resin in the upper half of the column.

^{17}O NMR Studies of $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$, 1. A detailed account of these studies, including experimental procedure and instrumental parameters, has been presented elsewhere and is available to the interested reader.[9g] The ^{17}O-enrichment of **1** reported therein has been repeated a total of three times. In three of those experiments, collection of ^{17}O NMR spectra yielded a two-line spectrum for ^{17}O-enriched **1**, with the data in Figure 8B proving representative. The ^{17}O NMR spectra of two more, independent repeat experiments are also available (supplementary material, Figure O). ^{31}P NMR spectra taken as a control *after* acquiring the ^{17}O NMR spectra of ^{17}O-enriched **1** and confirming that **1** is intact are listed in the supplementary material, Figure N.

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(52) We note that the difference between % O_{calc} and % O_{found} is of the same magnitude as the difference between % Σ_{found} and % Σ_{calc}. Restated, if the % O_{found} is adjusted (1.1% higher) to the calculated value of 17.8%, the % Σ_{found} adds up to 100%.

Removal of [(1,5-COD)Ir]$^+$ from ^{17}O-Enriched 1 by Addition of Cl$^-$. This control experiment was done in order to verify the assignments of ^{17}O NMR resonances in ^{17}O-enriched **1**.[9g] In the drybox, to 1.0 g (0.18 mmol) of ^{17}O-enriched[9g] **1** in 2 mL of CD_3CN was added 0.98 g (3.56 mmol, 20 equiv) of $[(n\text{-}C_4H_9)_4N]Cl$. One milliliter of the resulting solution was transferred into an airtight J. Young NMR tube, and ^{31}P, ^{183}W, and ^{17}O NMR spectral data were collected. The ^{31}P NMR[34] spectrum (supplementary material, Figure V) showed the two ^{31}P resonances (at δ −7.1 and −14.1) of the support-polyoxoanion, confirming that the [(1,5-COD)Ir]$^+$ has been cleaved. A ^{183}W NMR spectrum (supplementary material, Figure X) shows *primarily* three lines at δ −132, −159, −203 and reflects the C_{3v} symmetry of the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion in solution, although, the spectrum is of relatively low signal/noise. The ^{17}O NMR spectrum (supplementary material, Figure W) acquired after cleavage of the iridium moiety from the polyoxoanion-support shows two broad lines of approximately equal intensity at δ 720 and 500, plus a very small and broad resonance at ca. δ 330. The chemical shifts of these resonances compare favorably, especially given the broad nature of the signals and the different conditions (i.e. the presence of ≈1 equiv of $[(n\text{-}C_4H_9)_4N]Cl$), with those reported for niobium−terminal and −bridging oxygens in $H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}{}^{9-x}$ (δ 750 and 510, respectively). Moreover, the absence of a sharper and more intense resonance at δ 330, previously[9g] assigned by analogy to the literature to Nb_2−O−Ir, lends further support to the correctness of the assignment of the δ 330 resonance.

^{17}O NMR Studies of $[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$, 2. These experiments were modeled after our successful approach[9g] employed in deriving ^{17}O NMR data for $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]$. All manipulations were carried out in a Vacuum Atmospheres nitrogen drybox to prevent isotopic dilution of the ^{17}O-enriched material and to protect the air-sensitive $[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$. In an 18 × 150 mm disposable test tube, 1 g (0.18 mmol) of $[(n\text{-}C_4H_9)_4N]_5Na_3(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ was dissolved in 2 mL of CH_3CN. To this solution was added H_2O (20% ^{17}O-enriched, 1.0 g), resulting in a clear orange solution. After being stirred for 36 h at 22 ± 2 °C, the solution was evacuated to dryness and the solid was redissolved in 2 mL of CD_3CN. Following addition of 3 equiv of Kryptofix 2.2.2., the solution was transferred into an NMR tube equipped with a J. Young airtight valve, transferred out of the drybox, and placed in the NMR probe. ^{17}O NMR (20 °C, 90 mM, CD_3CN, 3 equiv of Kryptofix 2.2.2. added) (Figure 10, top), δ (no. of O, $\Delta\nu_{1/2}$): 750 (1 ± 0.5, 2300 ± 850 Hz), 500 (2.5 ± 1, 700 Hz ± 100 Hz), 330 (4.3 ± 1, 1600 ± 300 Hz). A ^{31}P NMR spectrum (supplementary material, Figure Y) taken as a control after acquiring the ^{17}O NMR spectra (20 °C, 90 mM, CD_3CN, 3 equiv of Kryptofix 2.2.2.) shows the clean, characteristic two-line ^{31}P NMR spectrum for **2**, δ (no. of P) −8.1 (1 P), −14.0 (1 P), confirming that the sample had not degraded.

Removal of [(1,5-COD)Rh]$^+$ from ^{17}O-Enriched 2 by Addition of Cl$^-$. Given the unexpected ^{17}O NMR spectra seen for enriched **2**, this control experiment was designed to remove the [(1,5-COD)Rh]$^+$ from ^{17}O-enriched **2** and thereby to test if the unusual ^{17}O NMR spectra are (i) a result of a problem in the enrichment procedure (i.e., in the case of rhodium-containing **2**), (ii) a result of multiple support-site isomers, or (iii) a result possibly of some other conditions. If the problems are *not* in the ^{17}O-enrichment procedure, then this control experiment should result in a clean two-line ^{17}O NMR spectrum[9g] of $P_2W_{15}Nb_3O_{62}^{9-}$ following cleavage of [(1,5-COD)Rh]$^+$ from **2** (as in fact is seen; *vide infra*).

In the drybox, to the solution of ^{17}O-enriched **2** in CD_3CN (the exact same sample as used in above experiment) was added 20 equiv of $[(n\text{-}C_4H_9)_4N]Cl$ (0.98 g, 3.56 mmol). The solution color immediately changed from orange to a yellow, characteristic of $[(1,5\text{-COD})RhCl]_2$. The sample solution was then transferred out of the drybox, and ^{17}O NMR and ^{31}P spectra were acquired. ^{17}O NMR (20 °C, 90 mM, CD_3CN, 3 equiv of Kryptofix 2.2.2.), δ (no. of O, $\Delta\nu_{1/2}$) (Figure 10, bottom): 740 (2 ± 1, 2400 ± 850 Hz), 500 (5 ± 0.5, 600 ± 180 Hz), 330 (1.6 ± 0.2, 1500 ± 350 Hz). Following addition of 20 equiv of $[(n\text{-}C_4H_9)_4N]Cl$, the intensity of the peak at δ 330, tentatively identified previously as due to a Rh−ONb bond, is dramatically decreased. However, a residual resonance at δ 330 is still present and is presumably the result of incomplete displacement and some type of intra- or intermolecular exchange process (eq v), in which a Rh−ONb bond is retained. A ^{31}P NMR spectrum (supplementary material, Figure AA) taken, as a control, *after* acquiring the ^{17}O NMR would seem to be inconsistent with the ^{17}O NMR spectra since it shows the clean two-line spectrum, δ (no. of P) −7.2 (1 P), −14.1 (1 P), characteristic for the free heteropolyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$, which instead suggests cleavage of the [(1,5-COD)Rh]$^+$ from **2** by the added Cl$^-$. However, we recently discovered that the peak width (and apparent peak height) of the δ −7.2 resonance in the ^{31}P NMR spectrum is a measure of the reaction shown in eq v, and this will be reported elsewhere.[48] The ^{183}W NMR spectrum after cleavage shows the familiar three-line spectrum, ^{183}W NMR (20 °C, 140 mM, CD_3CN, 3 equiv of Kryptofix 2.2.2.) (supplementary material, Figure X), δ (no. of W) (supplementary material, Figure V): −131.8 (3 W), −158.3 (6 W), −201.4 (6 W).

$$P_2W_{15}Nb_3O_{62}{}^{9-} + {}^1/_2[(1,5\text{-COD})RhCl]_2 \rightleftharpoons [(1,5\text{-COD})(Cl)_{1-n}Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{8-} + nCl^- \ (n = 0, 1) \qquad \text{(v)}$$

To summarize, the ^{17}O NMR spectra collected after enriching **2** in a mixture of $CH_3CN/H_2{}^{17}O$ showed only broad resonances that sharpened slightly upon raising the sample temperature to 55 °C during NMR data collection. A ^{17}O NMR spectrum collected (Figure 10, bottom) after addition of a large excess (20 equiv) of $[(n\text{-}C_4H_9)_4N]Cl$ showed two lines at δ 770 and 510 (relative intensities of 1:1), confirming that **2** had successfully enriched in the terminal (NbO) and bridging (Nb_2O) niobium−oxygen sites.

Attempts To Grow X-ray Diffraction Quality Crystals of 1 and 2. At least 150 experiments (summarized in the supplementary material) were carried out in attempts to obtain X-ray quality crystals. In none of the cases described in the supplementary material was a crystalline material obtained. We are, nevertheless, continuing our search to find other cation combinations that will yield diffracting crystals of **1** and **2**.

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Supplementary Material Available: Sedimentation-equilibrium molecular-weight plot (ln *A* vs r^2) for **1** (Figure A), sedimentation-equilibrium molecular-weight plot (ln *A* vs r^2) for **2** (Figure B), positive ion FAB-MS of **2** (Figure C), negative ion FAB-MS of **2** (Figure D), expanded IR of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ (KBr, cm^{-1}) (Figure E), ^{31}P NMR spectra of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]$, **1**, in CD_3CN (Figure F), ^{31}P NMR spectra of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]$, **2**, in CD_3CN (Figure G), ^{1}H NMR spectrum of rigorously desolvated and dried $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ in DMSO-d_6 (Figure H), $^{13}C\{^1H\}$ NMR spectrum of **2** in DMSO-d_6 (Figure I), ^{1}H NMR spectrum of $[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ in CD_3CN (Figure J), ^{1}H NMR spectrum of $[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ in acetone-d_6 (Figure K), ^{13}C NMR (^{1}H-coupled) of **2** in DMSO-d_6 (Figure L), ^{31}P NMR spectrum of freshly dissolved, metastable $Na_{12}P_2W_{15}O_{56}$ in 1.5 M HOAc/0.5 M NaOAc/1 M LiCl (Figure M), account of additional ^{17}O NMR experiments of **2**, ^{31}P NMR spectra taken as a control after acquiring the ^{17}O NMR spectra for ^{17}O-enriched **1** (Figure N), ^{17}O NMR spectra of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3{}^{17}O_6O_{56}]$, which was prepared from pre-formed **1** by enrichment with 10% $H_2{}^{17}O$ over a period of 36 h (repeat experiments) (Figure O), ^{17}O NMR spectra of **2** following enrichment for 36 h in a mixture of $CH_3CN/H_2{}^{17}O$ (20% oxygen 17-enriched) (Figure P), ^{17}O NMR spectra (top) at 20 °C and (bottom) at 55 °C of **2** following cleavage of [(1,5-COD)Rh]$^+$ from the heteropolyoxoanion-support (Figure Q), ^{17}O NMR spectra of **2** following enrichment for 36 h in a mixture of $CH_3CN/H_2{}^{17}O$ (10% oxygen 17-enriched) (Figure R), ^{17}O NMR spectrum of **2** after enriching in a mixture of 2 mL of CH_3CN/1 mL of $H_2{}^{17}O$ (10% ^{17}O enrichment) for 1 week (Figure S),

^{31}P NMR spectrum of **1** and **2** (0.035 mmol; DMSO-d_6; with three equiv of Kryptofix 2.2.2. added) after deliberate addition of 0.016 mmol of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (Figure T), account of attempts to grow X-ray diffraction quality crystals of **1** and **2**, preliminary single-crystal X-ray structure analysis for crystals obtained by addition of Ph_4PBF_4 to **2** which was dissolved in a mixture of H_2O/CH_3CN (Figure U), ^{31}P NMR spectrum of ^{17}O-enriched **1**, following cleavage of the $[(1,5\text{-}COD)Ir]^+$ moiety from the support-heteropolyoxoanion by addition of 20 equiv of $[(n\text{-}C_4H_9)_4N]Cl$ (Figure V), ^{17}O NMR spectrum collected after cleavage, by addition of 20 equiv of $[(n\text{-}C_4H_9)_4N]Cl$, of the $[(1,5\text{-}COD)Ir]^+$ moiety from the support-heteropolyoxoanion of ^{17}O-enriched **1** (Figure W), ^{183}W NMR spectrum of **1** and **2** following cleavage, by addition of 20 equiv of $[(n\text{-}C_4H_9)_4N]Cl$, of the organometallic fragment $[(1,5\text{-}COD)M]^+$ from the heteropolyoxoanion-support in ^{17}O-enriched **1** and **2** (Figure X), ^{31}P NMR spectra taken as a control after acquiring the ^{17}O NMR spectra for ^{17}O-enriched **2** (Figure Y), ^{17}O NMR spectrum of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Rh{\cdot}P_2W_{15}Nb_3{}^{17}O_6O_{56}]$, which was prepared from preformed **2** by enrichment with 10% $H_2{}^{17}O$ over a period of 36 h (Figure Z), ^{31}P NMR spectra taken as a control after cleavage (by addition of 20 equiv of $[(n\text{-}C_4H_9)_4N]Cl$) of the $[(1,5\text{-}COD)Rh]^+$ moiety from the support-heteropolyoxoanion of ^{17}O-enriched **2** (Figure AA), complete elemental analysis for $(TBA)_5Na_3[(1,5\text{-}COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}]$ showing the calculated percentages as a function of various countercation compositions (Table A), complete elemental analysis for $(TBA)_5Na_3[(1,5\text{-}COD)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ showing the calculated percentages as a function of various countercation compositions (Table B), ^{17}O NMR data for niobium-containing polyoxotungstates (Table C), crystallographic information for the crystals obtained by the addition of Ph_4PBF_4 to **2** in CH_3CN/H_2O (Table D) (37 pages total). Ordering information is given on any current masthead page.

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