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Polyoxometalate Catalyst Precursors. Improved Synthesis, H^+-Titration Procedure, and Evidence for ^{31}P NMR as a Highly Sensitive Support-Site Indicator for the Prototype Polyoxoanion−Organometallic-Support System $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$

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An improved synthesis of the prototype polyoxoanion−organometallic-support system, $P_2W_{15}Nb_3O_{62}^{9-}$, as its organic solvent-soluble all-$[(n\text{-}C_4H_9)_4N]^+$ salt is described. The improvements result in a 30% faster procedure which also provides a 60% increase in yield of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**. One key improvement in this synthesis is a pH titration of protonated $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, **1**, using $[(n\text{-}C_4H_9)_4N]OH$ and phenolpthalein indicator, which leads to fully deprotonated **2**—the key synthon required for clean support of organometallic cations onto the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion's "$Nb_3O_9^{3-}$" cap. The material obtained from this procedure is of the highest purity (≥95%) seen to date as judged by ^{31}P NMR spectroscopy. $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ has been further characterized by ^1H, ^{13}C, ^{17}O, and ^{183}W NMR spectroscopy as well as IR spectroscopy and complete elemental analysis. Also reported are control experiments that (i) confirm the identical reactivity of **2**, obtained by either the procedure reported herein or by our previously published accounts, with organometallic cations such as $[Ir^I(1,5\text{-COD})]^+$, $[Rh^I(1,5\text{-COD})]^+$ and $[Rh^{III}(C_5Me_5)]^{2+}$, (ii) show that the pH titration employed herein may be used to cleanly deprotonate polyoxoanions containing varying degrees of protonation, (iii) show that trace amounts of excess OH^- present in $P_2W_{15}Nb_3O_{62}^{9-}$ prevent clean organometallic cation-support reactions, and (iv) show that ^{31}P NMR titration of $P_2W_{15}Nb_3O_{62}^{9-}$ using $[(1,5\text{-COD})Ir]^+$ is an effective and simple method of determining the purity of $P_2W_{15}Nb_3O_{62}^{9-}$.

Introduction

In recent years, the synthesis and characterization of polyoxoanion-supported organometallic complexes[2] has received much attention. Several polyoxoanions[3] [namely, $Nb_2W_4O_{19}^{4-}$,[4] $P_3O_9^{3-}$,[5] $SiW_9M_3O_{40}^{7-}$ ($M = Nb^{5+}$, V^{5+}),[6] and $P_2W_{15}M_3O_{62}^{9-}$ ($M = Nb^{5+}$, V^{5+})[7]] were developed with the specific goal of providing materials which can support cationic organometallic moieties. Subsequently, numerous organometallic complexes employing these basic polyoxoanions have been reported.[4−7] Of the above six polyoxoanions, the custom-designed polyoxometalate $P_2W_{15}Nb_3O_{62}^{9-}$, Figure 1, is unique in several important ways: (i) its high basicity at the "$Nb_3O_9^{3-}$" cap provides surface oxygens that have sufficient charge density to effectively bind cationic organometallic moieties, (ii) its strong tendency toward formation of single C_{3v} or pseudo-C_{3v} symmetry isomers of supported organometallic cations, such as $[C_5(CH_3)_5Rh]^{2+}$,[7a,g] $[(C_6H_6)Ru]^{2+}$,[7a,g] and $[(1,5\text{-COD})M]^+$ ($M = Rh$, Ir),[7h,i] leads to nonaggregated, 1:1 polyoxoanion-to-organometallic anion complexes, and (iii) its spectroscopic handles (i.e., ^{31}P, ^{17}O, and

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(2) (a) The first examples of polyoxometalate κ^3-O-supported metals and coordination compounds were reported in 1969, specifically $Cr(C_2H_8N_2)^{3+}$ [2d] and $Co(C_2H_8N_2)^{3+}$ [2d] (as 1:1) and Mn(IV)[2e] and Ni(IV)[2e] (as 1:2) complexes with the isopolyanion $Nb_6O_{19}^{8-}$. The first report[2b] of a polyoxometalate-supported κ^3-O-*organometallic* occurred 10 years later, in 1980. (b) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (c) The first single X-ray crystal structure of a κ^3-O-supported metal was for the 1:2 Mn(IV):$Nb_6O_{19}^{8-}$ complex, $Na_{12}[Mn^{IV}Nb_6O_{19}]_2\cdot 50H_2O$.[2f] (d) Stucky, G. D.; Flynn, C. M. *Inorg. Chem.* **1969**, *8*, 178. (e) Stucky, G. D.; Flynn, C. M. *Inorg. Chem.* **1969**, *8*, 332. (f) Flynn, C. M., Jr.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 335.

(3) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983. (b) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (c) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (d) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity,* Proceedings of the July 15−17, 1992 Meeting at the Center for Interdisciplinary Research in Bielefeld, Germany; Müller, A., Pope, M. T., Eds.; Kluwer Publishers: Dordrecht, The Netherlands, 1992.

(4) Studies by Klemperer, Day, and co-workers on the synthesis and characterization of $Nb_2W_4O_{19}^{4-}$-based polyoxoanion−organometallic complexes: (a) Besecker, C. J.; Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 6158. (b) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (c) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44. (d) Main, D. J. Ph.D. Dissertation, University of Illinois, Urbana-Champaign, 1987. (e) Klemperer, D. J.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2990. (f) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030.

(5) The tridentate $P_3O_9^{3-}$ ligand represents the least complex polyanion that has been shown to covalently bind cationic metals. Note, however, that this phosphorous-based ligand is, by definition,[3a] not a polyoxo-*metalate*. (a) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564. (b) Main, D. J. Ph.D. Dissertation, University of Illinois, Urbana-Champaign, 1987.

(6) Earlier work focused toward $SiW_9M_3O_{40}^{7-}$-based ($M = Nb^{5+}$, V^{5+}) polyoxoanion-supported complexes: (a) Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. (b) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947. (c) Finke, R. G.; Green, C. A.; Rapko, B. *Inorg. Synth.* **1990**, *27*, 128. (d) Finke, R. G.; Nomiya, K.; Green, C. A.; Droege, M. W. *Inorg. Synth.* **1992**, *29*, 239. (e) Lin, Y.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6040. (f) Rapko B. M.; Pohl, M.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 3625.

(7) Earlier work focused toward $P_2W_{15}M_3O_{62}^{9-}$-based ($M = Nb^{5+}$, V^{5+}) polyoxoanion-supported complexes: (a) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692. (b) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Weakley, T. J. R. *Acta Crystallogr.* **1990**, *C46*, 1592. (c) Trovarelli, A.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6034. (d) Pohl, M.; Finke R. G. *Organometallics* **1993**, *12*, 1453. (e) Rapko B. M.; Pohl, M.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 3625. (f) Nomiya, K.; Kaneko, M.; Kasuga, N.; Finke, R. G., Pohl, M. *Inorg. Chem.* **1994**, *33*, 1469. (g) Pohl, M.; Lin, Y.; Weakley, T. J. R.; Nomiya, K.; Kaneko, M.; Weiner, H.; Finke R. G. *Inorg. Chem.* **1995**, *34*, 767. (h) Pohl, M.; Lyon, D. K.; Mizuno, K.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1995**, *34*, 1413. (i) Nomiya, K.; Mizuno, N.; Lyon, D. K.; Pohl, M.; Finke, R. G. *Inorg. Synth.*, in press. (j) Nomiya, K.; Nozaki, C.; Kaneko, M.; Finke, R. G.; Pohl, M. *J. Organomet. Chem.* **1995**, *23*, 505.

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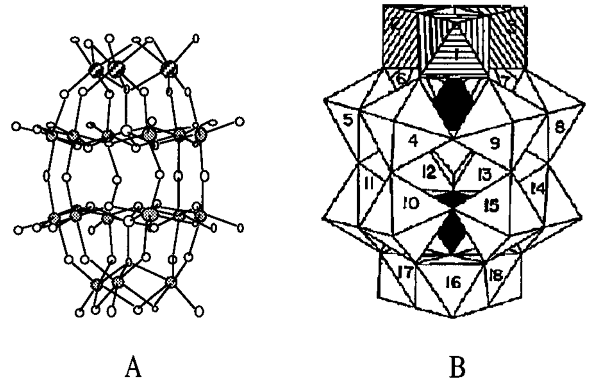


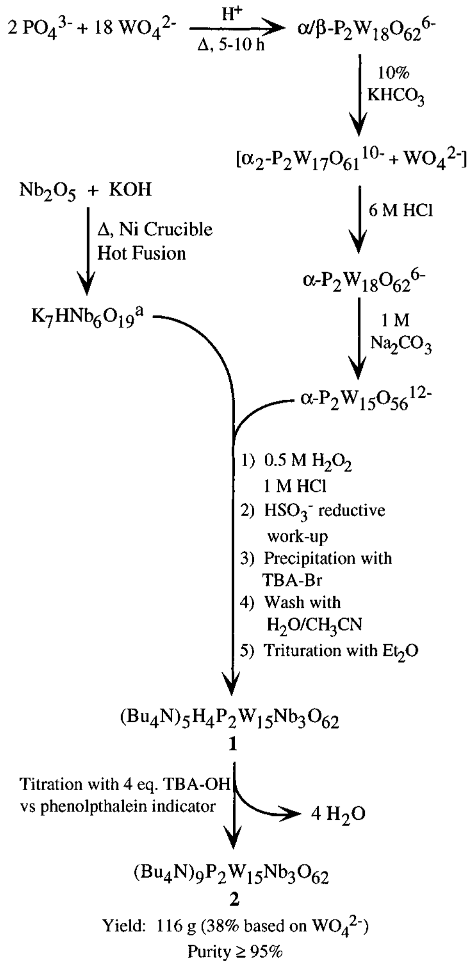
Figure 1. (A) Ball and stick representation of α-1,2,3-$P_2W_{15}Nb_3O_{62}^{9-}$ as determined by a previous single crystal X-ray diffraction structural analysis.[7b] The hatched circles show the position of the three Nb atoms. (B) Polyhedral representation of α-1,2,3-$P_2W_{15}Nb_3O_{62}^{9-}$. The 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.

^{183}W NMR) allow one to obtain detailed purity and structural information in solution. Even more importantly, the polyoxoanion-supported $[(1,5\text{-COD})Ir]^+$ complex $(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}^{8-}$ has provided the first example of a *bona fide* polyoxoanion-supported oxidation catalyst[8] and has also led to the discovery of a new class of isolable transition-metal nanoclusters that are stabilized by polyoxoanions and $[(n\text{-}C_4H_9)_4N]^+$, notably,[8] $[Ir_{\sim 300}(P_4W_{30}Nb_6O_{123}^{16-})_{\sim 33}][(n\text{-}C_4H_9)_4N]_{\sim 300}Na_{\sim 233}$.

Given its interesting chemistry, considerable effort has been expended at arriving at a refined and reproducible synthesis of $P_2W_{15}Nb_3O_{62}^{9-}$; these efforts culminated in our recent report of an *Inorganic Syntheses* preparation.[7i] However, the procedure reported therein[7i] still suffers from some limitations. In particular, even the checked *Inorganic Syntheses* procedure has still proved difficult in the hands of less experienced researchers. The preparation of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ is (i) lengthy (seven steps) and somewhat time consuming (ca. 2 weeks) and (ii) proceeds in a modest overall yield of 24% (relative to $Na_2WO_4\cdot 2H_2O$). Furthermore, even we encountered trouble in preparing $(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}^{7-}$, which tended to give a low ruthenium analysis, problems which were eventually traced to the presence of residual protons on the polyoxoanion, that is, to $H_xP_2W_{15}Nb_3O_{62}^{9-x}$ ($x \neq 0$).[7g] In short, we found ourselves in need of a shorter, higher yield, and more easily reproduced synthesis of *fully deprotonated* $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ to meet our increased demands for this important precatalyst support and nanocluster-stabilizing material.

Herein, we report significant improvements in the preparation of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. Specifically, we report a two-step-shorter procedure that completely avoids the tedious isolation of the $[(CH_3)_4N]^+$ and $[(n\text{-}C_4H_9)_4N]^+$ salts[9] of $H_4P_4W_{30}Nb_6O_{123}^{12-}$. This results in an overall 4-day-shorter procedure (i.e., approximately 30% faster), while at the same time providing for a 60% increase in yield of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (116 g vs the 73 g previous[7i]). In addition, this material is of the highest purity[10] (≥95%) seen-to-date as judged by ^{31}P and ^{17}O NMR spectroscopy. We also introduce a ^{31}P NMR titration of $P_2W_{15}Nb_3O_{62}^{9-}$ using $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ as a simple and effective method of determining the purity of $P_2W_{15}Nb_3O_{62}^{9-}$.

Scheme 1. Improved Synthesis of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**



(a) Instead of $K_7HNb_6O_{19}\cdot 13H_2O$, $NbCl_5$ can also be employed as the niobium source; cf. ref 20.

Results and Discussion

Synthesis of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, 1, and $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, 2. An improved procedure for the synthesis of $P_2W_{15}Nb_3O_{62}^{9-}$ has been developed. The preparative route is summarized in Scheme 1 and has been independently repeated and fully reproducible in the hands of more than five different researchers in two different laboratories.

Starting from the trilacunary heteropolytungstate $P_2W_{15}O_{56}^{12-}$ which was prepared according to our published procedure,[7h,i] the incorporation of three niobiums into the polyoxoanion framework is accomplished by using $K_7HNb_6O_{19}\cdot 13H_2O$ (or, alternatively, commercially available $NbCl_5$) as the niobium source.

Addition of $[(n\text{-}C_4H_9)_4N]Br$ directly to the reaction mixture, *thereby avoiding the previous $(CH_3)_4N^+$ form of the polyoxoan-*

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(8) (a) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335. (b) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891. (c) Edlund, D. J.; Finke, R. G.; Saxton, R. J. U.S. Patent 5,116,796, May 29, 1992.

(9) The underlying reasoning behind our earlier preparative procedure[7a,h,i] isolating $H_4P_4W_{30}Nb_6O_{123}^{12-}$ as its $[(CH_3)_4N]^+$ salt was based on two experimental observations: (i) organic-solvent soluble $[(n\text{-}C_4H_9)_4N]^+$ salts of highly charged polyoxoanions are noncrystalline and hence nonoptimum for purification of such compounds by re*crystallization,* but (ii) recrystallization of water-soluble polyoxoanions (e.g. as their Na^+, K^+, or, for example, $[(CH_3)_4N]^+$ salts) from aqueous solutions is a well-known and accepted means of purification. Unfortunately, the $[(CH_3)_4N]^+$ salt of $H_4P_4W_{30}Nb_6O_{123}^{12-}$ in our original procedure[7a,h,i] also proved to be noncrystalline.

(10) Our experience in polyoxometalate chemistry leads us to suspect that purities of 95–98% often represent the best attainable for these ionic, labile complexes prepared in aqueous solution.

ion, precipitates the protonated tetrabutylammonium salt,[11] $H_4P_2W_{15}Nb_3O_{62}{}^{5-}$. The resultant $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ salt is then collected by filtration and washed with a 1:1 mixture of acetonitrile:water to remove any remaining $[(n\text{-}C_4H_9)_4N]Br$; collection of the light-yellow solid **1** is achieved by trituration with diethyl ether. Deprotonation of **1** is then accomplished by base ($[(n\text{-}C_4H_9)_4N]OH$) titration against phenolphthalein indicator,[12] reproducibly affording *fully deprotonated* $P_2W_{15}Nb_3O_{62}{}^{9-}$,[13] **2**, an important point since the presence of residual H^+ (i.e., $H_xP_2W_{15}Nb_3O_{62}{}^{9-x}$) inhibits clean support of organometallic cations.[7d,i]

Compositional and Spectroscopic Characterization. The molecular formulas of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, **1**, and $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, were established by elemental analyses (all elements; see the Experimental Section). For **1**, the C, H, and N analysis requires the formulation as a pentakis(tetrabutylammonium) salt with four H^+ present. The calculated C, H, and N values for $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ match the values found by elemental analysis within experimental error, whereas alternative formulations with one more or less $[(n\text{-}C_4H_9)_4N]^+$ show a larger discrepancy between calculated and found values (Supporting Information, Table A). Likewise, a millivolt titration of **1** in dimethylformamide (DMF) using aqueous $[(n\text{-}C_4H_9)_4N]OH$ as the titrant shows four inflection points (the final one at 3.9 ± 0.2 equiv of added OH^-), results consistant with aqueous $[(n\text{-}C_4H_9)_4N]OH$ titrations to a phenolpthalein endpoint (4.0 ± 0.2 equiv of added OH^-), and hence a $[(n\text{-}C_4H_9)_4N]_5\mathbf{H_4}P_2W_{15}Nb_3O_{62}$ formulation. Curiously, the W and Nb analyses are reproducibly a bit high and low, respectively, for the intermediate **1**, while they are within experimental error for the key, desired product $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**. We long ago learned, however, to put greater trust in especially the ^{31}P NMR spectroscopic results,[14] and they show that the end $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ is of the highest purity available to date.

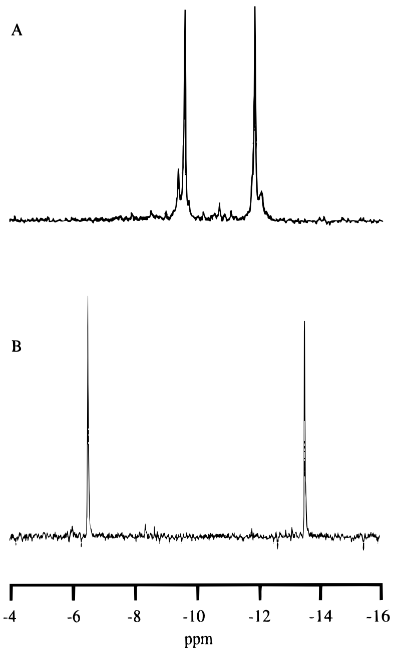

Figure 2. ^{31}P NMR spectra of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ (A) and of the fully deprotonated $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (B) in CD_3CN (14.3 mM, 22 °C), showing primarily two peaks. The relatively clean spectrum of the latter compound attests to this material's high homogeneity and purity of ≥95%. (A) δ ($\nu_{1/2}$) −12.1 (27.1 ± 0.5 Hz), −11.9 (12.1 ± 0.4 Hz), −9.7 (12.1 ± 0.4 Hz), −9.5 (15.7 ± 0.4 Hz)]; (B) δ (no. of P, $\Delta\nu_{1/2}$) −6.6 (1, 4.5 ± 0.3 Hz), −13.6 (1, 3.2 ± 0.3 Hz). The increased line width observed in the ^{31}P NMR spectrum of the protonated species (A) can be attributed to the presence of multiply protonated, probably interconverting, species.[18] Note that the integrated intensity of the two sets of peaks is approximately 1:1.

Infrared measurements for **1** and **2** (Supporting Information, Figure A) confirm the presence of a Dawson-type, "$P_2M_{18}O_{62}{}^{n-}$" heteropolytungstate framework. ^{31}P NMR spectroscopy of **1** and **2** in CD_3CN show primarily two lines of approximately equal intensity, Figure 2, as expected for the presence of two types of magnetically inequivalent phosphorus nuclei. Notably, the resonances in the ^{31}P NMR spectra of **1** are markedly shifted and show a substantial increase in line width compared to fully deprotonated **2**. These differences can readily be attributed to the precedented presence of multiple, probably interconverting, protonated forms of $H_4P_2W_{15}Nb_3O_{62}{}^{5-}$.[6f]

The ^{183}W NMR spectra of **1** and **2** exhibit three peaks; 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. The ^{17}O NMR of fully deprotonated **2** shows two peaks, one each for the terminal (δ 755, Nb−O) and bridging (δ 518, Nb_2O) niobium-oxygens; no resonances attributable to $Nb_2O{-}H^+$ were detected.

Control Syntheses of $P_2W_{15}Nb_3O_{62}{}^{9-}$-Supported Organometallic Cations. Previously we reported the synthesis and characterization of $P_2W_{15}Nb_3O_{62}{}^{9-}$-supported organometallic cations such as $(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}{}^{7-}$, $(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}{}^{8-}$, and $(C_6H_6)Rh{\cdot}P_2W_{15}Nb_3O_{62}{}^{7-}$. As a crucial test of the efficacy of the $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ produced by the

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(11) Organic solvent extractions of *acidic* aqueous solutions of (nonbasic) polyoxometalates is well-established; for example, see elsewhere.[11a−h] However, the presumably finite rate of decomposition under basic pH conditions of even stabilized polyoxoanions such as $P_2W_{15}Nb_3O_{62}{}^{9-}$ is conceivably a limitation in this method. To test this, a control experiment was done involving 8.2 mM $P_2W_{15}Nb_3O_{62}{}^{9-}$ in D_2O and ^{31}P NMR. Even after several days at room temperature, no detectable (≤5%) decomposition was seen in the ^{31}P NMR spectrum. (a) Drechsel, E. *Chem. Ber.* **1887**, *27*, 157. (b) Copaux, H. C. *R. Acad. Sci.* **1921**, *173*, 656. (c) Souchay, P. *J. Chim. Phys.* **1945**, *42*, 61. (d) Lange, G.; Hahn, H.; Dehnicke, K. *Z. Naturforsch.* **1969**, *24B*, 1498. (e) Flynn, C. M., Jr.; Pop, M. T. *Inorg. Chem.* **1971**, *10*, 2745. (f) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, 109, 6030. (g) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, 113, 7209. (h) Jeannin, Y.; Herve, G.; Proust, A. *Inorg. Chim. Acta* **1992**, *198*, 319. (i) Hou, Y.; Hill, C. L. *J. Am. Chem. Soc.* **1993**, *115*, 11823.

(12) (a) In the past we have noted a somewhat variable ratio of $[(n\text{-}C_4H_9)_4N]^+/H^+$ for the related $[(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}V_3O_{62}$ system (typically, $x = 3, 4$).[12b] (Compositional variability is always a potential cause for concern when one is forced to work with noncrystalline, "kinetically precipitated" powders.) Hence, we surmised previously[12b] that an improved procedure must employ a pH-monitored titration for each batch. (b) Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947. Finke, R. G.; Green, C. A.; Rapko, B. *Inorg. Synth.* **1990**, *27*, 128. Rapko, B.; Pohl, M.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 3625.

(13) Fully deprotonated $P_2W_{15}Nb_3O_{62}{}^{9-}$ is a *sine qua non* for the preparation of analytically pure organometallic polyoxoanion-supported complexes such as $(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}{}^{8-}$. On several occasions in the past we have encountered problems with low metal analyses (e.g., Ir), presumably due to the use of starting material that had not been fully titrated and, therefore, contained residual protons, $H_xP_2W_{15}Nb_3O_{62}{}^{9-x}$, cf. eq 1. An important insight into this problem came during the ^{17}O NMR studies of ^{17}O-enriched $P_2W_{15}Nb_3{}^{17}O_6O_{56}{}^{9-}$ which revealed the presence of a protonated form, $H_xP_2W_{15}Nb_3O_{62}{}^{9-x}$ via the direct detection of a $Nb_2O{-}H^+$ resonance at δ 180 ppm.[7g] Supporting evidence is provided by control experiments demonstrating that neither $[(1,5\text{-COD})Ir]^+$ [7b,i] nor $[C_5(CH_3)_5]Rh^{2+}$ [7h] afford their known $P_2W_{15}Nb_3O_{62}{}^{9-}$-supported organometallic complexes when added to $H_xP_2W_{15}Nb_3O_{62}{}^{9-x}$.

(14) See footnote 7 elsewhere.[14a] (a) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947. (b) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *6*, 1006, and especially footnote 12 therein. (c) For an example where total elemental analysis indicates that the *found* value of O was 1.1% off, see footnote 52 on p 1427 elsewhere.[7h]

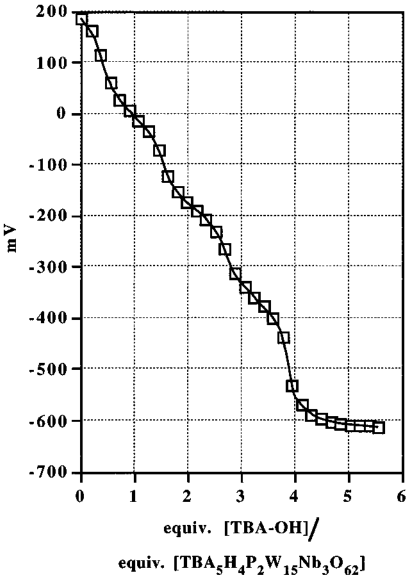

Figure 3. Millivolt titration of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ (804.3 mg/0.1516 mmol; solvent, 45 mL of DMF/5 mL of H_2O) with aqueous $[(n\text{-}C_4H_9)_4N]OH$ (0.692 M; Aldrich). Inflection points are observed at approximately 0.4, 1.5, 2.8, and 3.9 equiv of $[(n\text{-}C_4H_9)_4N]OH$ added, the latter data point being fully consistent with the formulation of a tetraequivalent acid, $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$.

procedure herein, we remade these complexes [on both larger (≥5 g) and smaller (≤3 g) scales]. In the case of the $[Ir(1,5\text{-}COD)]^+$, $[Rh(1,5\text{-}COD)]^+$, and $[Rh(C_5Me_5)]^{2+}$ complexes, the isolated yields were the same as those reported (Supporting Information, Tables B and C), and the ^{31}P and ^{183}W NMR spectroscopic data were identical with those in the literature (see below).

In the case of the $[Ru(C_6H_6)]^{2+}$ complex, we previously were able to prepare analytically pure $(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}{}^{7-}$ *only* using $P_2W_{15}Nb_3O_{62}{}^{9-}$ made by the new and improved procedure cited herein.[7g] However, it occurred to us that the proton *titration* employed herein might allow this complex to be made using $P_2W_{15}Nb_3O_{62}{}^{9-}$ derived from our *Inorganic Syntheses* procedure. The results (provided in the Experimental Section) show that, indeed, $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ can be titrated using the $[(n\text{-}C_4H_9)_4N]OH$/phenolpthalein method (6.0 ± 0.2 equiv of OH^-, Supporting Information, Figure B) to yield fully deprotoned $P_2W_{15}Nb_3O_{62}{}^{9-}$, which in turn cleanly supports $[Ru(C_6H_6)]^{2+}$. By having demonstrated the effectiveness of the $[(n\text{-}C_4H_9)_4N]OH$/phenolpthalein titration on *both* complex **1** (4.0 ± 0.2 equiv of OH^-) *and* the protonated intermediate reported in our previous procedure (6.0 ± 0.2 equiv of OH^-), deprotonation by the $[(n\text{-}C_4H_9)_4N]OH$/phenolpthalein titration described herein is shown to be an effective means of removing protons from polyoxoanions with differing degrees of protonation.

Control Titration Demonstrating the Effect of Excess OH^- on Polyoxoanion−Organometallic Support Reactions. Previously we obtained ^{17}O NMR evidence implicating the presence of excess *protons* in preventing clean support of organometallic cations onto the polyoxoanion's "$Nb_3O_9{}^{3-}$" cap.[7d] As the present studies progressed, we obtained evidence for the effects of trace amounts of excess *base* on such support reactions. Two independent and quantitative experiments show that, if present, trace amounts of excess base also prevent clean reactions between organometallic cations and $P_2W_{15}Nb_3O_{62}{}^{9-}$.

First, a sample of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, **1**, previously known to require exactly 4.0 equiv of OH^-, was prepared to which *4.25 equiv* (i.e., a 0.25 equiv excess) of $[(n\text{-}C_4H_9)_4N]OH$ was added. The resulting $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (containing 0.25 equiv excess OH^-) was then used to support $[(1,5\text{-}COD)Ir]^+$ as previously described[7h] and shown in eq 1.

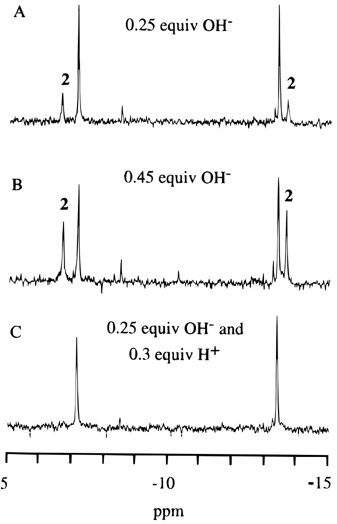

Figure 4. ^{31}P NMR spectra of the reaction of $[(1,5\text{-}COD)Ir(CH_3CN)_2]^+$ with $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, in the presence of (i) 0.25 equiv of OH^- (A), (ii) 0.45 equiv of OH^- (B), and (iii) 0.25 equiv of OH^- *and* 0.3 equiv of H^+ (C). The resonances at δ −6.7 and −13.6 (labeled as **2**) are assigned to unreacted $P_2W_{15}Nb_3O_{62}{}^{9-}$ remaining in the product (ca. 21% in A and ca. 45% in B).

$$\begin{aligned}&[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62} + \\ &\qquad [(1,5\text{-}COD)Ir(CH_3CN)_2]BF_4 \rightarrow \\ &\qquad\quad [(n\text{-}C_4H_9)_4N]_8[(1,5\text{-}COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}] + \\ &\qquad\qquad [(n\text{-}C_4H_9)_4N]BF_4 + 2CH_3CN \quad (1)\end{aligned}$$

The ^{31}P NMR of the product (Figure 4A) shows the presence of a small amount of unreacted $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (ca. 21% by integration). Likewise, when the $[(1,5\text{-}COD)Ir]^+$ support reaction was carried out using a sample of $P_2W_{15}Nb_3O_{62}{}^{9-}$ that contained *0.45 equiv of excess* OH^-, the ^{31}P NMR of the product (Figure 4B) shows *even more* unreacted $P_2W_{15}Nb_3O_{62}{}^{9-}$ present (ca. 45% by integration).

Second, when the reaction between $[(1,5\text{-}COD)Ir(CH_3CN)_2]^+$ and $P_2W_{15}Nb_3O_{62}{}^{9-}$ is carried out in the presence of roughly equal amounts of added base *and* acid (i.e., 0.25 equiv of OH^- and 0.3 equiv of H^+), the ^{31}P NMR (Figure 4C) shows only the expected product, $(1,5\text{-}COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}{}^{8-}$, and *no* unreacted $P_2W_{15}Nb_3O_{62}{}^{9-}$, indicating that, as expected, the 0.3 equiv of added H^+ neutralized the 0.25 equiv of OH^- present, in turn allowing a clean stoichiometric reaction between the iridium cation and the polyoxoanion.

Determination of Polyoxoanion Purity via a Control Titration with $[(1,5\text{-}COD)Ir(CH_3CN)_2]^+$ and by ^{31}P NMR. Because of the sensitivity of the organometallic support reaction to the presence of excess base, and knowing that the ^{31}P NMR is an exceptionally sensitive spectroscopic handle of the polyoxoanion's $Nb_3O_9{}^{3-}$ support site, we designed a ^{31}P NMR titration method of $P_2W_{15}Nb_3O_{62}{}^{9-}$ (prepared by the method described herein) and using $[(1,5\text{-}COD)Ir(CH_3CN)_2]^+$. The titration, an important piece of evidence demonstrating both the purity of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, and the ^{31}P NMR sensitivity to the chemical-bonding environment at the basic cap of the polyoxoanion, shows the continuous disappearance of $P_2W_{15}Nb_3O_{62}{}^{9-}$ (at δ −6.6 and −13.7) and appearance of $(1,5\text{-}COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}{}^{8-}$ (at δ −7.2 and −13.4) in the ^{31}P NMR spectrum (Figure 5) upon addition of [(1,5-COD)Ir(CH3-

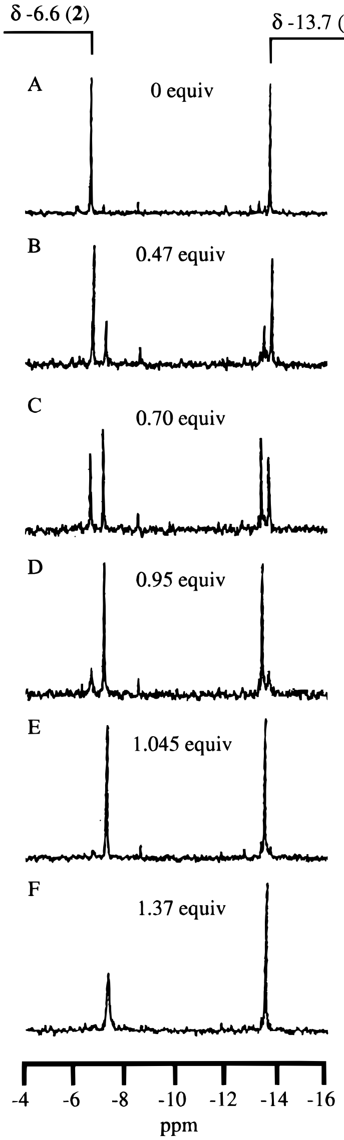

Figure 5. ^{31}P NMR titration of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, in CD_3CN with 0.0 (A), 0.47 (B), 0.70 (C), 0.95 (D), 1.045 (E), and 1.37 (F) equiv of $[(1,5\text{-COD})Ir]^+$. The resonances at δ −6.6 and −13.7 show the disappearance of **2** while the resonances as δ −7.2 and −13.4 show the appearance of the expected product. The clean break at 1.045 equiv of added $[(1,5\text{-COD})Ir]^+$ demonstrates that the $P_2W_{15}Nb_3O_{62}^{9-}$ used is of ≥95% purity.

$CN)_2]^+$ to $P_2W_{15}Nb_3O_{62}^{9-}$. The consumption of **2** and subsequent production of $(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}^{8-}$ (eq 1) proceeds smoothly, showing the expected clean, two-line spectum of $(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}^{8-}$ upon addition of 1.045 added equiv of $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$.

However, upon the addition of even a small *excess* of $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ (1.37 equiv, 0.33 equiv excess) the resonance (at δ −7.2) of the P atom directly beneath the $Nb_3O_9^{3-}$ cap of the polyoxoanion (the site upon which $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ binds) diminishes and becomes broadened, a broadening presumably due to an addition/elimination $[(1,5\text{-COD})Ir]^+$ exchange mechanism of the type first reported by Klemperer.[15]

Taken together, the two control ^{31}P NMR titrations described above demonstrate the following: (i) the presence of even traces of excess base (or protons[7d]) prevents clean support of organometallic cations onto the basic $Nb_3O_9^{3-}$ cap of the polyoxoanion; (ii) the ^{31}P NMR titration of $P_2W_{15}Nb_3O_{62}^{9-}$ using $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ is an exceptionally sensitive and simple experiment that can be used to determine the purity (i.e., presence of excess OH^- or protons) of $P_2W_{15}Nb_3O_{62}^{9-}$; (iii) the $[(n\text{-}C_4H_9)_4N]OH$/phenolpthalein titration is a simple and effective means of completely removing protons from $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, **1** (and other polyoxoanions, see below); and finally (iv) the $P_2W_{15}Nb_3O_{62}^{9-}$, **2**, produced by the procedure described herein is shown to be ≥95% pure (i.e., to within ≤±0.05 equiv of $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ as titrant).

Solubility of 2 in Water. To our surprise, we discovered that the tetrabutylammonium salt, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, readily dissolves in water [approximately 221 g/L (0.035 mol/L)], giving a clear and colorless solution. We hypothesize that this must be due to the protonation reaction, eq 2, and the high

$$P_2W_{15}Nb_3O_{62}^{\ 9-} + xH_2O \rightleftharpoons H_xP_2W_{15}Nb_3O_{62}^{\ x-9} + xOH^- \tag{2}$$

solubility in water of the resultant $H_xP_2W_{15}Nb_3O_{62}^{x-9}$. Consistent with this intepretation, the pH was found to be basic and dependent on the concentration of dissolved $P_2W_{15}Nb_3O_{62}^{9-}$ (pH ≈ 8.9 at 1.17×10^{-3} M $H_xP_2W_{15}Nb_3O_{62}^{x-9}$; Supporting Information, Figure C). Additional studies of the composition and structure of aqueous solutions of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ are planned.

Aqueous solutions of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ in D_2O gave clean two-line ^{31}P and three-line ^{183}W NMR spectra (Supporting Information, Figure D), as expected on the basis of our earlier report of the all-inorganic, water-soluble $Na_9P_2W_{15}Nb_3O_{62}$.[7f]

Summary

The present work reports an improved procedure for the synthesis of the $P_2W_{15}Nb_3O_{62}^{9-}$-based polyoxoanion−organometallic-support system. The key concepts behind the improved preparation include avoiding the tedious isolation of both the $[(CH_3)_4N]^+$ and $[(n\text{-}C_4H_9)_4N]^+$ salts of $H_4P_4W_{30}Nb_6O_{123}^{12-}$, as well as a pH-indicator titration of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$; the net result is 60% more (116 g) of high-purity $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ in 2 days (30%) faster time. Furthermore, we demonstrate that ^{31}P NMR is a simple and reliable way of determining the purity of $P_2W_{15}Nb_3O_{62}^{9-}$, and the effects of even trace amounts of H^+ or OH^- on the support of organometallics cations have been demonstrated and quantitated.

We believe that the present synthesis is one of the most optimized syntheses of a polyoxoanion reported to date. We also anticipate that this is our final, synthesis-based publication on the $P_2W_{15}Nb_3O_{62}^{9-}$ system.

Experimental Section

Materials. All commercially obtained compounds were Baker reagent grade unless otherwise noted. The following reagents were obtained from Aldrich and used as received: $NaBF_4$, $AgBF_4$, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8.]hexacosane [Kryptofix 2.2.2.], $NaHSO_3$, 30% H_2O_2, 37% HCl, $[(n\text{-}C_4H_9)_4N]Br$, anhydrous Et_2O (HPLC grade, stored in a drybox), CH_3CN (HPLC grade, stored in a drybox), EtOAc (HPLC grade, stored in a drybox), DMF, NaOH, and phenolphthalein (0.5 wt % in EtOH/H_2O). The following reagents were obtained from Strem and used as received: $[(C_5Me_5RhCl_2]$, [(1,5-

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[15] (a) Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (b) The diminuation of the ^{31}P NMR resonance at δ −7.2 is also seen upon addition of excess $H_3O^+BF_4^-$ (Supporting Information, Figure G), $[(1,5\text{-COD})IrCl]_2$, or $[(1,5\text{-COD})RhCl]_2$ to solutions of $(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}^{8-}$ (Aiken, J. D., III; Finke, R. G. Unpublished results and experiments in progress).

COD)IrCl]$_2$, [(1,5-COD)RhCl]$_2$, "$RuCl_3 \cdot xH_2O$" (x = 0−1),[16] and $NbCl_5$. Argon (99.998%) was used as received from General Air. Deuterated NMR solvents (DMSO-d_6, CD_3CN, D_2O; Cambridge Isotope Laboratories) were used as received. When the NMR sample was to be prepared in the drybox, the deuterated solvent was degassed by either purging with the drybox atmosphere or with argon (outside the box) for 0.5 h. Immediately prior to use, aqueous $[(n\text{-}C_4H_9)_4N]OH$ solutions (40 wt %; Aldrich) were titrated separately with 0.1 M HCl to methyl red and phenolphthalein endpoints (i.e., for both amine and total base content) and were then diluted 1:1 with deionized H_2O to obtain a 0.692 M solution. $K_7HNb_6O_{19} \cdot 13H_2O$,[17] $[Ru(C_6H_6)Cl_2]_2$,[18] and $[(1,5\text{-}COD)Ir(CH_3CN)_2]BF_4$ [19] were prepared and characterized as described elsewhere. $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}] \cdot 18H_2O$ was prepared and characterized as previously reported.[7h,i]

Instrumentation/Analytical Procedures. 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 as monitored by use of a Vacuum Atmospheres O_2 level monitor. Infrared spectra were obtained on a Nicolet 5DX as KBr disks. Elemental analyses were obtained from Mikroanalytisches Labor Pascher (Remagen, Germany). Nuclear magnetic resonance (NMR) spectra were obtained as D_2O, CD_3CN, 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, ^{13}C, ^{17}O, ^{31}P, and ^{183}W NMR spectra were collected on Bruker 300 (^1H, ^{13}C, ^{31}P) and Bruker AM500 (^{17}O, ^{183}W) NMR instruments. ^1H NMR (300.15 MHz) and ^{13}C NMR (75.0 MHz) spectra were recorded in 5 mm o.d. tubes 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. ^{31}P NMR (121.50 MHz), ^{183}W NMR (15.04 MHz), and ^{17}O NMR (67.80 MHz) were recorded in 5 (^{31}P) or 10 (^{183}W, ^{17}O) mm o.d. NMR tubes. ^{31}P NMR spectra were referenced externally by the substitution method to 85% H_3PO_4; ^{183}W NMR spectra were referenced externally by the substitution method to 2 M Na_2WO_4/D_2O (pD 8.0, as measured using pH paper); ^{17}O NMR spectra were referenced externally by the substitution method to tap water. Spectral parameters for ^1H include the following: pulse width, 6.5 μs; acquisition time, 2.72 s; repetition rate, 2.72 s (no relaxation delay); sweep width, ±6024 Hz. Spectral parameters for ^{13}C NMR include the following: pulse width, 3.0 μs; acquisition time, 819.0 ms; repetition rate, 1.819 s; 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 associated with the cation [^1H NMR: δ 1.04, 1.56, 1.72, 3.35. ^{13}C NMR: δ 14.0, 19.8, 23.7, 58.1]; hence, these resonances are not reported for individual compounds. Spectral parameters for other nuclei were 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 NMR) exponential apodization of the FID was used on all spectra but was removed for any line widths reported herein. The pH values reported herein were determined with a pH meter (Corning, Model 125) equipped with an Orion Perphect electrode. The pH meter was calibrated against commercially available, standardized buffers (Corning) of pH 4.00, 7.00, and 10.01.

Preparation of $\mathbf{[(\mathit{n}\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}}$, 1. $K_7HNb_6O_{19} \cdot 13H_2O$ [20] (5.90 g; 4.30 mmol) was placed in a 1500 mL beaker equipped with a magnetic stir bar. Addition of H_2O_2 (650 mL of 0.5 M) resulted in a pale yellow solution of pH 4.12. Next, 1 M HCl (58 mL; 58 mmol) was added whereupon the solution color changed to bright yellow (solution pH 1.46). *Immediately* after the addition of HCl, and while the mixture was rapidly stirred, finely powdered $Na_{12}P_2W_{15}O_{56} \cdot 18H_2O$ (36.5 g; 8.42 mmol)[7h,i] was added in a single step, resulting in a clear, yellow solution of pH 3.93. *CAUTION*: *The following step yields a vigorous reaction in which SO_2 is evolved. Proceed with caution in a well-ventilated fume hood*. $NaHSO_3$ (50 g; 480.4 mmol, excess) was gradually added over 10−15 min, destroying excess hydrogen peroxide, to yield a clear and colorless solution. Stirring was continued for 0.5 h. Next, $[(n\text{-}C_4H_9)_4N]Br$ (25 g, 9.2 equiv, 84% excess) was added in a single step (analogous to our previously published procedure[7h,i]), immediately producing a white precipitate. Stirring of the suspension was continued until it had air-cooled to room temperature (approximately 1 h). The white precipitate was allowed to settle and was then collected on a 350 mL medium glass frit, transferred to a 1 L beaker, and throughly washed with 500 mL of 40−50 °C in-house distilled water. This material was, once again, collected on a 350 mL medium glass frit and, without further drying, dissolved in 250−300 mL of acetonitrile. (If the solution was cloudy at this stage, it was filtered through a Whatman No. 2 filter paper.) Addition of 30−40 mL of deionized water gave a cloudy solution which was reduced in volume by rotary evaporation to about 200 mL. A green-yellow oily, lower CH_3CN layer[11] containing the tetrabutylammonium salt of the polyoxometalate formed. The upper, cloudy aqueous layer was removed with a pipet, and the remaining yellow-green oily layer was transferred into a 250 mL separatory funnel and washed four times with 80 mL (320 mL total) acetonitrile:water (1:1). After 3 h (allowing the layers to fully separate) a clear, oily layer separated which was transferred to a 250 mL beaker. Next, this oil was triturated 5 times with 40 mL (200 mL total) diethyl ether to yield a yellow powder. The powder was collected on a 100 mL medium glass frit by suction filtration and dried overnight under ≤10 mmHg vacuum at 40 °C. Yield: 28−30 g (5.27−5.65 mmol; 62−67% based on the $Na_{12}P_2W_{15}O_{56} \cdot 18H_2O$ starting material).[20] Elem anal. Calcd for $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ (found; an average of three to four analyses for each element on separate samples; individual analyses are provided in the Supporting Information as a part of Table A): C, 18.11 (18.65); H, 3.49 (3.70); N, 1.32 (1.46); P, 1.17 (1.09); W, 51.97 (50.2); Nb, 5.25 (6.28); O, 18.69 (18.58, by difference). Note that this analysis, which implies a molecular formula of "$[(n\text{-}C_4H_9)_4N]_{5.5}P_{1.9}W_{15.0}Nb_{3.7}O_{63.7}$", is within experimental error of the $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ formulation above,[21] *except* that W is low and Nb is high, data that is, however, inconsistent with the ±0.2 W analysis and publishable Nb analysis in $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, given below (i.e., given that **2** is made from **1** by only $[(n\text{-}C_4H_9)_4N]OH$ addition and removal of the solvent, a process that *cannot change* the relative W *vs* Nb analysis). Note also that we specifically considered $[(n\text{-}C_4H_9)_4N]Br$ as a contaminant but can rule it out as elemental analysis of **1** shows ≤0.05% Br present, thereby demonstrating the effectiveness of the CH_3CN/H_2O washing steps at removing any excess $[(n\text{-}C_4H_9)_4N]Br$ present. Moreover, the spectroscopic data, especially the ^{31}P NMR, indicates that these compounds are of high purity, as discussed further in the text. See Table A, Supporting Information, for calculations as a function of various $[(n\text{-}C_4H_9)_4N]_{5+x}H_{4-x}{}^{9+}$ counterion compositions, showing that the $[(n\text{-}C_4H_9)_4N]_5H_4{}^{9+}$ composition best fits the analytical data. ^{31}P NMR (CD_3CN, 18.8 mM, 22 °C): δ ($\Delta\nu_{1/2}$) −10.1 ($\Delta\nu_{1/2}$ =

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(16) Commercially available "$RuCl_3 \cdot xH_2O$" is known to be a variable mixture of mono- to polymetallic $Ru^{III/IV}$ complexes. For a summary of references to that literature see: Randall, W. J.; Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 1068, and refs 19a−d and 20 therein.

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(20) In place of $K_7HNb_6O_{19} \cdot 13H_2O$, $NbCl_5$ may be employed as the niobium source. The following procedure was used successfully in four independent preparations: $NbCl_5$ (6.97 g; 25.8 mmol) was dissolved in H_2O_2 (5%; 650 mL). (The resulting yellow solution is apparently stable for at least 6 days without any visible changes.) The pH of the solution was adjusted to 1.45 by adding NaOH (108 mL of 1 M; 108 mmol). Subsequent steps in the preparation of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ were carried out exactly as described in the main text. In two independent experiments the material prepared using $NbCl_5$ as the niobium source was identical by ^{31}P NMR spectroscopy to material prepared by employing $K_7HNb_6O_{19} \cdot 13H_2O$ $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, ^{31}P NMR (CD_3CN): δ −9.5, −9.7, −12.0, −12.2. [$K_7HNb_6O_{19} \cdot 13H_2O$ prepared material, see experimental section: δ −9.5, −9.7, −11.9, −12.1]. $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ ^{31}P NMR (CD_3CN): δ −6.5, −13.6 [Lit.:[7h] δ −6.6, −13.6]. However, no elemental analysis was obtained.

25.1 ± 0.5 Hz), −11.9 ($\Delta\nu_{1/2}$ = 10.1 ± 0.4 Hz), −9.7 ($\Delta\nu_{1/2}$ = 10.1 ± 0.4 Hz), −9.5 ($\Delta\nu_{1/2}$ = 13.7 ± 0.4 Hz); Figure 2A. ^{183}W NMR (DMSO-d_6, 80 mM, 22 °C): δ −124.0 (3, $\Delta\nu_{1/2}$ = 25.9 ± 2.5 Hz), −150.6 (6, $\Delta\nu_{1/2}$ = 19.6 ± 2.2 Hz), −172.9 (6, $\Delta\nu_{1/2}$ = 32.2 ± 3.0 Hz); Supporting Information, Figure E, top. ^{17}O NMR (CD_3CN, 26.5 mM, 22 °C): δ (assignment, no. of O, $\Delta\nu_{1/2}$) 649 (Nb−O, 3 ± 1 O, $\Delta\nu_{1/2}$ = 833 ± 140 Hz); 510 (Nb−O−Nb, 3 ± 1 O, $\Delta\nu_{1/2}$ = 553 ± 110 Hz); Supporting Information, Figure F, top. IR (KBr disk, cm^{-1}; polyoxometalate region): 1097 (vs), 960 (s), 920 (s), 904 (s), 776 (br), 648 (s), 593 (m), 561 (m), 526 (m); Supporting Information, Figure A, top.

Preparation of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, 2. In a 50 mL round-bottom flask, $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ (1 g, 0.19 mmol) was dissolved in acetonitrile (20 mL). Argon was bubbled through the solution for at least 15 min (to remove any dissolved CO_2) after which time the solution was kept under a constant argon stream with the gas outlet above the solution surface to prevent recontamination with atmospheric carbon dioxide. Two drops of phenolphthalein indicator were added and the solution was titrated with aqueous tetrabutylammonium hydroxide (0.692 M) to the endpoint of the indicator as detailed below; in all cases, the number of equivalents of OH^- required was 4.0 ± 0.2 (determined from at least eight independently prepared samples of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ prepared by four different researchers, Supporting Information, Table D). [The titration was judged completed when the color change of the indicator to red *persisted for at least 15 min* under a continuous argon flow; this is crucial for a successful, reproducible titration. One should note, however, that on this scale (i.e., 1 g of $P_2W_{15}Nb_3O_{62}{}^{9-}$) and when a buret (KIMAX) calibrated in 0.02 mL increments is used, each drop of $[(n\text{-}C_4H_9)_4N]$OH solution (0.02 mL) added beyond the *true* endpoint results in an approximately 8% excess of OH^-. As shown below, this is a sufficient excess to affect significantly the support of organometallic cations; hence, we urge that care be taken when approaching the endpoint in the titration.] Next, the solution was evaporated to dryness under vacuum and 200 mg of the recovered light-purple-colored (i.e., phenolpthalein-stained) solid was dissolved in CD_3CN for ^{31}P NMR spectroscopy. If the ^{31}P NMR of the product showed the expected two line spectrum, as it did in at least seven out of eight titrations examined throughout these studies, then a bulk $[(n\text{-}C_4H_9)_4N]$OH addition in the *absence* of phenolphthalein indicator was performed on a larger scale (typically 10 g of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ in 50 mL of acetonitrile). (If the titrated material *did not* show the expected two line ^{31}P NMR spectrum, then the titration was repeated on a second gram of material. If the second titration produced material that also *did not* show the expected two line ^{31}P NMR spectrum, then the material was discarded. This happened only in 1 of 12 preparations, however.) The bulk $[(n\text{-}C_4H_9)_4N]$OH addition was carried out in the *absence* of phenolphthalein indicator with the amount of aqueous tetrabutylammonium hydroxide to be added *calculated* from the above small-scale experiment. (Again, the aqueous tetrabutylammonium hydroxide was added dropwise to the stirred solution.) The colorless solid formed after evaporation of the solvent was dried overnight at 40 °C *in vacuo* and then immediately transferred into the drybox for storage at room temperature. Elem anal. Calcd for $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (found) [and repeat analysis on an independent preparation]: C, 27.57 (27.12) [27.55]; H, 5.21 (5.34) [5.50]; N, 2.01 (2.13) [2.23]; P, 0.99 (1.06) [1.08]; W, 43.96 (43.7) [43.1]; Nb, 4.45 (5.29) [5.47]; O, 15.81 (15.0) [14.9]; total, (99.64) [99.83]. Note that only the Nb analysis is slightly off (±0.8) but is still within the ±0.6−0.8 error limits for Nb that our experience has indicated (and despite Pascher's stated ±0.2 error limits for Nb, ±0.7 for W, and ±0.5 for O). ^{31}P NMR (CD_3CN, 14.3 mM, 22 °C): δ (no. of P, $\Delta\nu_{1/2}$) −6.6 (1, $\Delta\nu_{1/2}$ = 2.5 ± 0.3 Hz), −13.6 (1, $\Delta\nu_{1/2}$ = 1.2 ± 0.3 Hz); Figure 2B. ^{183}W NMR (DMSO-d_6, 80 mM, 22 °C): δ (no. of W, $\Delta\nu_{1/2}$) −135.8 (3 W, $\Delta\nu_{1/2}$ = 5.0 ± 1.0 Hz), −161.1 (6 W, $\Delta\nu_{1/2}$ = 3.8 ± 0.8 Hz), −204.4 (6 W, $\Delta\nu_{1/2}$ = 12.4 ± 1.1 Hz); Supporting Information, Figure E, bottom. ^{17}O NMR (CD_3CN, 26.5 mM, 22 °C): δ (assignment, no. of O, $\Delta\nu_{1/2}$) 755 (Nb−O, 3 ± 1 O, $\Delta\nu_{1/2}$ = 789 ± 166 Hz), 518 (Nb−O−Nb, 3 ± 1 O, $\Delta\nu_{1/2}$ = 155 ± 12 Hz); Supporting Information, Figure F, bottom. IR (KBr disk, cm^{-1}) (polyoxometalate region): 1085 (s), 1057 (w), 1011 (w), 943 (s), 914 (m), 892 (m), 776 (vs), 523 (m); Supporting Information, Figure A, bottom.

^{17}O NMR Spectroscopy of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3{}^{17}O_6O_{56}$. Selective ^{17}O enrichment of **1** in only its terminal Nb−O and bridging Nb_2−O oxygens (i.e., selective enrichment in the six oxygens of the $Nb_3O_9{}^{3-}$ minisurface) was accomplished analogous to our previously reported procedure[7d] as detailed next. All manipulations were carried out under nitrogen in order to avoid isotopic dilution with atmospheric H_2O. Pale yellow $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ (2.5 g, 0.47 mmol; as prepared above) was dissolved in a solvent mixture comprised of acetonitrile/$H_2{}^{17}O$ [4 mL of CH_3CN; 1.5 mL of $H_2{}^{17}O$ (12.5% enriched in ^{17}O, supplied by Isotec)]. The resultant clear, yellow-green solution was placed in a double sealed glass vial and stirred for 1 week at room temperature. After evacuating to dryness for at least 24 h, the resulting solid was redissolved in 3 mL of CD_3CN, transferred to a NMR tube, and placed in the NMR probe for data acquisition. ^{17}O NMR (CD_3CN, 26.5 mM, 22 °C): δ (assignment, no. of O, $\Delta\nu_{1/2}$) 649 (Nb−O, 3 ± 1 O, $\Delta\nu_{1/2}$ = 833 ± 140 Hz), 510 (Nb−O−Nb, 3 ± 1 O, $\Delta\nu_{1/2}$ = 553 ± 110 Hz); Supporting Information, Figure F, top.

^{17}O NMR Spectroscopy of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3{}^{17}O_6O_{56}$. All manipulations were carried out under nitrogen in order to avoid isotopic dilution with atmospheric H_2O. Pale yellow $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3{}^{17}O_6O_{56}$ (2.5 g, 0.47 mmol) was dissolved in 40 mL of acetonitrile. Two drops of phenolphthalein indicator (0.5 wt % in 1:1 ethanol:water) were added, and the solution was titrated with aqueous tetrabutylammonium hydroxide (0.692 M) to the endpoint. The solvent was removed under vacuum, affording the fully deprotonated, ^{17}O-enriched $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3{}^{17}O_6O_{56}$ in quantitative yield. ^{17}O NMR (CD_3CN, 26.5 mM, 22 °C): δ (assignment, no. of O, $\Delta\nu_{1/2}$) 755 (Nb−O, 3 ± 1 O, $\Delta\nu_{1/2}$ = 789 ± 166 Hz), 518 (Nb−O−Nb, 3 ± 1 O, $\Delta\nu_{1/2}$ = 155 ± 12 Hz); Supporting Information, Figure F, bottom. A ^{31}P NMR spectrum of the same sample, taken as a control, shows the familiar two line spectrum (δ −6.6, $\Delta\nu_{1/2}$ = 2.5 ± 0.3 Hz; −13.6, $\Delta\nu_{1/2}$ = 1.2 ± 0.3 Hz), thereby confirming the integrity of the compound. Impurities (δ −8.4 and −13.3) are less than 5% [by integration and comparison with the two resonances for authentic[7a,h,i] $P_2W_{15}Nb_3O_{62}{}^{9-}$ (δ −6.6 and −13.6)].

Millivolt Titration of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ with $[(n\text{-}C_4H_9)_4N]$OH. In a typical experiment, $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ (0.5−1 g; 0.09−0.19 mmol) was dissolved in 45 mL of reagent grade DMF. Deionized water (5 mL) was added, and argon was bubbled through the solution for 15 min to remove dissolved CO_2. The solution was then kept under an argon stream with the gas outlet above the solution surface to prevent recontamination with atmospheric carbon dioxide. $[(n\text{-}C_4H_9)_4N]$OH (0.692 M) was used as titrant and was added to the well-stirred solution of the polyoxoanion in 0.04 mL steps (0.0272 mmol) by means of a buret. The progress of the titration was monitored with a pH meter; data points were recorded in millivolts. The titration results are given in Figure 3.

Control Experiment Establishing Identical Chemical Reactivity for 2 Prepared Both by the Procedure Herein and by the Previous Synthesis.[7h,i] In order to establish identical reactivity for [(*n*-

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(21) (a) Note that both a monomer, $H_xP_2W_{15}Nb_3O_{62}{}^{x-9}$, and a Nb−O−Nb bridged anhydride form, $H_{2x-2}P_4W_{30}Nb_6O_{123}{}^{2x-18}$, are known to exist, as previously we[7a] and Klemperer[4f] have demonstrated. In addition, Beer and co-workers[21c] have crystallographically characterized $[O_{18}W_5\text{-}Nb\text{−}O\text{−}NbW_5O_{18}]^{4-}$. However, we formulate $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}\text{-}Nb_3O_{62}$, **1**, as a monomer rather than as the Nb−O−Nb bridged, condensed aggregate, "$[(n\text{-}C_4H_9)_4N]_{10}H_6P_4W_{30}Nb_6O_{123}$", for the following reasons: (i) the IR of **1** shows the *absence* of a strong band at 665 cm^{-1}, a band indicative of the Nb−O−Nb aggregate, and (ii) the $2P_2W_{15}Nb_3O_{62}{}^{9-} + 2H^+ \rightleftharpoons P_4W_{30}Nb_6O_{123}{}^{16-} + H_2O$ equilibrium lies to the left under all but the most anhydrous and acidic conditions (i.e., in H_2SO_4; see the supplemental materials elsewhere[7a])—note that the present preparation involves an aqueous step (acetonitrile/H_2O washing) at pH ∼ 7. (b) Most importantly, however, the exact position of this equilibrium and formulation of the precursor as $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$ or $[(n\text{-}C_4H_9)_4N]_{10}H_6P_4W_{30}Nb_6O_{123}$ *does not matter*. That is, we developed the present synthesis so that a prior knowledge of the exact formula unit (and the exact number of H^+) is *not* a prerequisite for arriving at the desired end product, fully deprotonated $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. The titration method with $[(n\text{-}C_4H_9)_4N]$OH and phenolphthalein indicator developed herein is, in this sense and *by design*, a "formula-insensitive" method. (c) Lu, Y.-J.; Lalancette, R.; Beer, R. H. Deoxygenation of Polynuclear Metal Oxo Anions: Synthesis, Structure, and Reactivity of the Condensed Polyoxoanion $[(C_4H_9)_4N]_4(NbW_5O_{18})_2O$. *Inorg. Chem.* **1996**, *35*, 2524.

$C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, prepared by either (a) the procedure described herein or (b) procedures given in our previously published accounts,[7h,i] we prepared several polyoxoanion-supported organometallic complexes on both larger (≥5 g; Supporting Information, Table B) and smaller (≤3 g; Supporting Information, Table C) scales. Specifically, complexes (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$,[7h,i] (1,5-COD)Rh·$P_2W_{15}Nb_3O_{62}^{8-}$,[7h,i] and (C_5Me_5)Rh·$P_2W_{15}Nb_3O_{62}^{7-}$ [7a,g] were prepared according to our cited, published procedures, except employing $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ that had been prepared as detailed herein. The physical data (by ^{31}P and ^{183}W NMR spectroscopy; *vide infra*) of the products confirm their identity and establishes identical chemical reactivity, at least for the reactions surveyed, of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ prepared by the present vs our earlier literature.[7a,g,h,i] Spectroscopic data. (i) $[(n\text{-}C_4H_9)_4N]_5Na_3$(1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}$. ^{31}P NMR (CD_3CN; with 3 equiv of Kryptofix 2.2.2. added): δ −7.1, −13.4 [Lit.:[7h] δ −7.1, −13.6 (see also footnotes 34 and 51a,d elsewhere)[7h]]. ^{183}W NMR (DMSO-d_6; with 3 equiv of Kryptofix 2.2.2. added): δ −133, −158, −198 [Lit.:[7h] δ −128; −152; −191]. (ii) $[(n\text{-}C_4H_9)_4N]_5Na_3$(1,5-COD)Rh·$P_2W_{15}Nb_3O_{62}$. ^{31}P NMR (CD_3CN; with 3 equiv of Kryptofix 2.2.2. added): δ −7.4, −13.4 [Lit.:[7h] δ −7.4; −13.4]. (iii) $[(n\text{-}C_4H_9)_4N]_7(C_5Me_5)$Rh·$P_2W_{15}Nb_3O_{62}$. ^{31}P NMR (CD_3CN): δ −8.1, −13.8 [Lit.:[7g] δ −8.2, −13.9].

Control Experiment Demonstrating by ^{31}P NMR that Excess OH^- Prevents Clean Polyoxoanion Organometallic-Support Reactions. In order to determine if excess OH^- prohibited a clean organometallic cation−polyoxoanion-support reaction[7h] of $[(1,5\text{-COD})Ir]^+$ and $P_2W_{15}Nb_3O_{62}^{9-}$, **2**, a sample of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, *containing an excess of 0.25 equiv of OH^-* was prepared in the following manner: $[(n\text{-}C_4H_9)_4N]OH$ (1.55 M, 16.34 mL, 4.25 equiv) was added dropwise as described above to a sample of $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, **1** (31.6 g, 5.96 mmol, in 100 mL of CH_3CN), previously shown by ^{31}P NMR (see the control titration below) to require exactly 4.0 equiv of OH^- to fully deprotonate the polyoxoanion. The product (now containing 0.25 equiv of *excess* OH^-) was then isolated and dried as described above, transferred into a drybox, and used for the organometallic-support reactions described immediately below.

(1) Reaction of $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ and $P_2W_{15}Nb_3O_{62}^{9-}$ in the Presence of 0.25 Equiv of OH^-. In a drybox, the $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ {plus 0.25 equiv of OH^- mixture, see above} (125 mg, 0.020 mmol) was dissolved in 0.3 mL of CD_3CN in an airtight J. Young NMR tube (the resulting solution was slightly cloudy). To this solution, a yellow solution of $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ (9.4 mg, 0.020 mmol, in 0.3 mL of CD_3CN) was added via disposable pipet. A yellow solid appeared which dissolved after being shaken to give a clear yellow-brown solution. The ^{31}P NMR spectrum of this solution (Figure 4A) shows the presence of ca. 21% (by peak integration) unreacted $P_2W_{15}Nb_3O_{62}^{9-}$ (δ −6.7, −13.6) relative to the expected product, (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$ (δ −7.2, −13.4; ca. 79% by integration). No other resonances were seen.

(2) Reaction of $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ and $P_2W_{15}Nb_3O_{62}^{9-}$ in the Presence of 0.45 Equiv of OH^-. In a drybox, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ {plus 0.25 equiv of OH^- mixture, see above} (125 mg, 0.020 mmol) was dissolved in 0.3 mL of CD_3CN in an airtight J. Young NMR tube (the resulting solution was slightly cloudy). The NMR tube was sealed and taken out of the drybox, and a $[(n\text{-}C_4H_9)_4N]OH$ solution (40% aqueous, 2.6 mg, 0.004 mmol, 0.2 equiv) was added to the NMR tube under argon gas. Next, the NMR tube was transferred into the drybox, where a yellow solution of $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ (9.4 mg, 0.020 mmol, in 0.3 mL of CD_3CN) was added via disposable pipet. A yellow solid appeared which dissolved after being shaken to give a clear yellow-brown solution. The ^{31}P NMR spectrum of this solution (Figure 4B) shows the presence of ca. 45% (by peak integration) unreacted $P_2W_{15}Nb_3O_{62}^{9-}$ (δ −6.7, −13.6) relative to the expected product, (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$ (δ −7.2, −13.4; ca. 55% by integration). No other resonances were seen.

(3) Reaction of $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ and $P_2W_{15}Nb_3O_{62}^{9-}$ + 0.25 Equiv of the OH^- Mixture with 0.1, 0.2, 0.3, and 1.0 Equiv of H^+. A stock solution of $H^+BF_4^-$ in CD_3CN was prepared outside of the drybox by dissolving $H_3O^+BF_4^-$ (48% aqueous $H^+BF_4^-$ solution, 7.5 mg, 0.040 mmol) in 1 mL of CD_3CN (the latter having been stored in a drybox, but taken out immediately before use). Next, $H_3O^+BF_4^-$ (0.15 mL of stock solution, 0.3 equiv) was added via syringe to an airtight J. Young NMR tube. The solution was degassed (via brief exposure to vacuum at −20 °C) and then purged with argon gas. An NMR tube was transferred into a drybox where the $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ {plus 0.25 equiv of the OH^- mixture, see above} (125 mg, 0.020 mmol), dissolved in 0.2 mL of CD_3CN, was added to the $H_3O^+BF_4^-/CD_3CN$ solution (the $H_3O^+BF_4^-/CD_3CN$ solution was slightly cloudy, and no drastic visible change in cloudiness was observed upon mixing the two solutions). Next, a yellow solution of $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ (9.4 mg, 0.020 mmol) was added via pipet to the NMR tube. A yellow solid appeared which dissolved after being shaken to give a clear yellow-brown solution. The two lined ^{31}P NMR spectrum of the solution (Figure 4C) showed only the expected product, (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$ (δ −7.2, −13.4), and *no* unreacted $P_2W_{15}Nb_3O_{62}^{9-}$, indicating that the 0.3 equiv of added H^+ neutralized the 0.25 equiv of OH^- already present, thereby allowing a clean 1:1 reaction between the iridium cation and the polyoxoanion. This experiment was also repeated in an identical manner *except* using only 0.1 (0.5 mL of stock solution), 0.2 (0.10 mL of stock solution), and 1.0 (0.06 mL of 37 mg of $H_3O^+BF_4^-$ dissolved in 0.6 mL of CD_3CN) equiv of added H^+. The ^{31}P NMR spectra of these solutions (Supporting Information, Figure G) show the presence of ca. 26% (0.1 equiv of H^+ added) and 13% (0.2 equiv of H^+ added) unreacted $P_2W_{15}Nb_3O_{62}^{9-}$ (δ −6.7, −13.6) relative to the expected product, (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$ (δ −7.2, −13.4). In the case of 1.0 added equiv of H^+, the resonance at δ −7.2 in the ^{31}P NMR spectrum, attributable to the P atom directly beneath the $Nb_3O_6^{3-}$ cap of the polyoxoanion (the site upon which cations bind), is diminished and broadened relative to the resonance at δ −13.4 (although both resonances still integrate roughly 1:1), as discussed in the Results and Discussion.

^{31}P NMR Control Titration of $P_2W_{15}Nb_3O_{62}^{9-}$ by $[(1,5\text{-COD})Ir]^+$. To further demonstrate the purity of the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion, we performed a ^{31}P NMR titration of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ using $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ as the titrant. This simple experiment allowed us to monitor the continuous disappearence of $P_2W_{15}Nb_3O_{62}^{9-}$ and appearance of (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$ in the ^{31}P NMR spectrum. In a drybox, a 0.057 M clear solution of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, (212.9 mg, 33.9 μmol, 0.6 mL of CD_3CN) was prepared and placed via disposable pipet in a 5 mm o.d. Omni-Fit NMR tube (Wilmad) sealed by a PTFE/silicon septum valve. Also in a drybox, a 0.32 M clear yellow solution of $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ (30.4 mg, 64.8 μmol, 0.20 mL of CD_3CN) was prepared in a small screw cap vial which was then sealed using a Mini-Inert valve and septum as a cap. Next, both the sealed NMR tube and vial were brought outside of the drybox. The ^{31}P NMR titration of **2** was performed by adding the clear yellow $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ solution in 10−25 μL aliquots via a 100 μL gastight syringe to the NMR tube containing the $P_2W_{15}Nb_3O_{62}^{9-}$ solution. After each addition, the sealed NMR tube was shaken quickly by hand and the ^{31}P NMR spectrum was collected. The ^{31}P NMR spectra obtained after addition of 0, 0.47, 0.70, 0.95, 1.045, and 1.37 equiv of $[(1,5\text{-COD})Ir(CH_3CN)_2]^+$ added to $P_2W_{15}Nb_3O_{62}^{9-}$ are shown in Figure 5.

Control Titration of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ Prepared by the Previous *Inorganic Syntheses* Procedure[7i] with $[(n\text{-}C_4H_9)_4N]OH$. As a control experiment to verify the efficacy of the $[(n\text{-}C_4H_9)_4N]OH$/phenolpthalein titration and to show that this titration may be generalized to a polyoxoanion with a different degree of protonation, we prepared $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ as described in the earlier *Inorganic Syntheses* procedure[7i] and titrated it to the phenolpthalein endpoint using $[(n\text{-}C_4H_9)_4N]OH$ as the titrant. This complex is known to require 6 equiv of OH^-, eq 3.[7a]

$$H_4[P_4W_{30}Nb_6O_{123}]^{12-} + 6OH^- \rightleftharpoons P_2W_{15}Nb_3O_{62}^{9-} + 5H_2O \qquad (3)$$

The titration experiment was carried out as described above with the only difference being that $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ (2.0 g, 0.181 mmol, dissolved in 40 mL of CH_3CN) was used instead of the intermediate complex **1**. The phenolpthalein endpoint was reached after aqueous tetrabutylammonium hydroxide (0.765 M, 1.43 mL, 6.0 ± 0.2 equiv of OH^-) was added dropwise, corresponding to the expected 6 equiv of added OH^-. The resultant plot of millivolts vs added equivalents of $[(n\text{-}C_4H_9)_4N]OH$ is provided in the Supporting Information, Figure B.

Control Synthesis of $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}$ Using Titrated $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$. In order to determine if the $P_2W_{15}Nb_3O_{62}^{9-}$ made by the $[(n\text{-}C_4H_9)_4N]OH$ titration of $H_4[P_4W_{30}Nb_6O_{123}]^{12-}$ above would support $(C_6H_6)Ru^{2+}$, an organometallic cation whose clean support has proven problematic in the past,[7h] we synthesized $(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}^{7-}$ according to our published procedure *except* using $P_2W_{15}Nb_3O_{62}^{9-}$ made by the phenolpthalein titration procedure of $H_4P_4W_{30}Nb_6O_{123}^{12-}$. The ^{31}P NMR of the $(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}^{7-}$ product is spectroscopically *identical* to that we published previously[7g] (including the small impurity peaks, ca. 6% total, at δ −7.1, −7.9, −8.4, and −13.1), indicating that support of $(C_6H_6)Ru^{2+}$ upon the polyoxoanion was obtained. ^{31}P NMR (CD_3CN; with Kryptofix 2.2.2. added): δ −7.6, −13.3 [Lit.:[7g] δ −7.7, −13.3].

Solubility in, and Basicity of, Aqueous Solutions of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2**, was added to 40 mL of H_2O at 25 °C in steps of 10−30 mg. Following each addition, the solution pH was measured with a pH-meter (Supporting Information, Figure C). The experiment was continued until 294 mg of **2** had been added, equivalent to a final concentration of **2** of 1.17 mM. At a concentration of 8.2 mM (and hence at a resulting pH of ∼9.0), the ^{31}P NMR of $[(n\text{-}C_4H_9)_4N)_4]_9P_2W_{15}Nb_3O_{62}$ showed the expected two line spectrum (Figure D, top, Supporting Information), indicating that the complex is both soluble and stable in aqueous solution at pH ∼9 and at room temperature for ≥3−4 h. Likewise, the ^{183}W NMR of $[(n\text{-}C_4H_9)_4N)_4]_9P_2W_{15}Nb_3O_{62}$ (48.4 mM, D_2O; Figure D, bottom, Supporting Information) showed that the polyoxoanion remains intact under these conditions (pH ∼9.0, 25 °C, ≥15 h).

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Supporting Information Available: Table A, complete elemental analysis for $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, **1**, showing the calculated percentages as a function of various countercation compositions, Tables B and C, larger scale (≥5 g) and smaller scale (≤3 g) polyoxoanion-supported organometallic syntheses utilizing **1** and **2**, respectively, prepared by the procedure described in the text, Table D, equivalents of added OH^- required in the titration of **1** by $[(n\text{-}C_4H_9)_4N]OH$, and Figure A, IR spectra of **1** and of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, **2** (KBr disk, cm^{-1}), showing the characteristic bands for the Dawson-type heteropolytungstate framework, Figure B, titration of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ with $[(n\text{-}C_4H_9)_4N]OH$, Figure C, pH of an aqueous solution of **2** as a function of concentration, Figure D, ^{31}P NMR (A, top) and ^{183}W (B, bottom) spectra of **2** in D_2O, Figure E, the three line ^{183}W NMR spectra of **1** and of fully deprotonated **2** in DMSO-d_6, Figure F, ^{17}O NMR spectra of **1** (top) and of fully deprotonated **2** (bottom) in CD_3CN, Figure G, reaction of **2** and $[(1,5\text{-COD})Ir(CH_3CN)_2]BF_4$ in the presence of acid or base, and a listing of references (12 pages). Ordering information and Internet access instructions are given on any current masthead page.

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