Trisubstituted Heteropolytungstates as Soluble Metal Oxide Analogs. Isolation and Characterization of $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ and $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, Including the First Crystal Structure of a Dawson-Type Polyoxoanion-Supported Organometallic Complex

Matthias Pohl,[1a,b] Yin Lin,[1a] Timothy J. R. Weakley,[1a] Kenji Nomiya,[1c] Masahiko Kaneko,[1c] Heiko Weiner,[1b,d] and Richard G. Finke*,[1b]

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

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The heteropolyoxoanion-supported complexes $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, **1**, and $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, **2**, have been prepared by addition of $[(C_5Me_5)Rh(CH_3CN)_3]^{2+}$ or $[(C_6H_6)Ru(CH_3CN)_3]^{2+}$ to a solution of $P_2W_{15}Nb_3O_{62}{}^{9-}$ in acetonitrile. Isolation of these complexes as homogeneous, yellow solids as their all-$[(n\text{-}C_4H_9)_4N]^+$ salts (for **1**) or as complexes with mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ cation composition (for **1** and **2**) was accomplished by repeated reprecipitation from acetonitrile with ethyl acetate. Molecular formulas for these complexes were established by complete elemental analyses, in conjunction with a sedimentation-equilibrium molecular-weight measurement. Further characterization in solution relied heavily on multinuclear NMR spectroscopy. The solution data are in accord with $[(C_5Me_5)Rh]^{2+}$ and $[(C_6H_6)Ru]^{2+}$ being supported on three niobium-bridging oxygens on the "$Nb_3O_9{}^{3-}$" surface of the heteropolyoxoanion. The structural characterization of **1** in the solid state was accomplished by a single-crystal X-ray structural analysis: $P6_3/m$; $a = 20.544(5)$, $b = 20.544(5)$, $c = 34.648(6)$ Å; $Z = 2$; $R = 0.096$ for 3023 observed independent reflections. The Rh atom in **1** lies on the polyoxoanion's 3-fold axis within experimental error and is bonded to the three Nb−O−Nb bridging oxygen atoms (Rh−ONb$_2$ 2.06 Å) that cap the $P_2W_{15}Nb_3O_{62}{}^{9-}$ Dawson-type polyoxoanion. This crystallographic analysis, although limited by considerable disorder, represents the first solid-state structure of a Dawson-type heteropolyoxoanion-supported organometallic complex.

Introduction

One interest in heteropolyoxoanion[2] chemistry results from the fact that these compounds resemble discrete fragments of solid metal oxides (Figure 1),[3] an important component of heterogeneous-insoluble, metal oxide-supported catalysts. Given the difficulties[4] in determining the structures and therefore the mechanisms of oxide-supported catalysts, and thus the subsequent problems in rationally improving such catalysts, the attraction of using polyoxoanion-supported, atomically dispersed transition metals as analogs[5] becomes apparent. In addition,

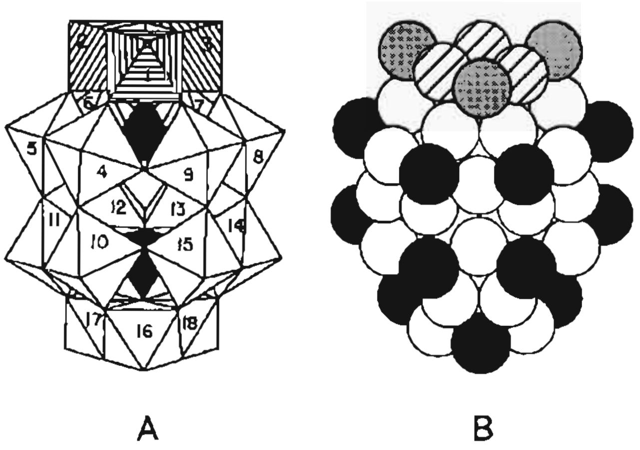

Figure 1. (A) Polyhedral and (B) space-filling representations of the Dawson-type heteropolyanion α-1,2,3-$P_2W_{15}Nb_3O_{62}{}^{9-}$. In (A) the three niobiums are represented by hatched octahedra in the 1−3 positions. The WO_6 octahedra occupy the 4−18 positions, and the PO_4 are shown as the two internal, black tetrahedra. In (B) the open circles represent bridging tungsten oxygens (W_2O), while the black circles represent terminal tungsten oxygens (WO). Niobium bridging oxygens (Nb_2O) are depicted by hatched circles, whereas niobium terminal oxygens (NbO) are shown as gray circles. From the space-filling representation it becomes clear that heteropolyoxoanions are composed of a close-packed array of oxygens, and this representation in turn reveals their potential as soluble metal oxide analogs.

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[1] (a) University of Oregon. (b) Present address: Colorado State University, Ft. Collins, CO 80523. (c) Present address: Department of Materials Science, Kanagawa University, Hiratsuka, Kanagawa 259-12, Japan. (d) Department of Chemistry, TU Bergakademie Freiberg, D-09596 Freiberg, Germany.

[2] (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.

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

[4] (a) The case in 1992 is only somewhat advanced from the 1976 conclusion of a workshop of experts that "no definitive proof of any structure of an oxide-supported catalyst has been reported".[4b] With modern methods such as EXAFS, some progress has been made in proposing poisoned catalyst structures (e.g. $Rh(CO)_2\cdot Al_2O_3$)[4c] or crude catalyst "structures" constructed from EXAFS distance information only (plus chemical intuition), but even that work has not been able to provide complete structures at the atomic level.[4d] (b) *Proceedings of the 1st International Workshop on Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ugo, R., Eds.; Plenum Press: New York, 1977; p 218. (c) For lead references see: van't Bilk, H. F. J.; van Zon, J. B. A. D.; Huizinag, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 3139. Frederick, B. G.; Apai, G.; Rhodin, T. N. *J. Am. Chem. Soc.* **1987**, *109*, 4797. Basu, P.; Panayotov, D.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2074. (d) For lead references see: Gates, B. C. *CHEMTECH* **1989**, 173. Lamb, H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

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polyoxoanions having tetraalkylammonium or other organic countercations allow these polyanionic species to be solubilized in nonaqueous solvents, conditions often ideal for organic and organometallic reaction chemistry[6] as well as other kinds of reactivity such as oxygen atom- or group-transfer processes.[7] Because of these possibilities, polyoxometalate-supported organometallic complexes have attracted considerable interest over the past 10 years,[8,9] including our own efforts.[10,11]

Several years ago[10d] we reported the synthesis and characterization of $P_2W_{15}Nb_3O_{62}^{9-}$ as well as the preliminary synthesis and solution characterization of the covalently attached, polyoxoanion-supported complexes $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$, **1**, and $[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$, **2**.[12] However, due to the inherent presence of contaminating $[(n\text{-}C_4H_9)_4N]^+BF_4^-$, pure samples of **1** and **2** were not isolated nor could their solid-state composition and purity (e.g., by elemental analysis) or solid-state structure be established.

Herein we report the isolation and characterization of $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$, **1**, and $[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$, **2**, as homogeneous, yellow solids as their all-$[(n\text{-}C_4H_9)_4N]^+$ salt (for **1**) or as complexes with mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ cation composition (for **1** and **2**). The composition of these complexes was established by complete elemental analyses and solution molecular-weight measurements. Structural characterization in solution was accomplished by IR, ^{1}H NMR, ^{31}P NMR, and ^{183}W NMR spectroscopy. In addition, $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$ was characterized by a single-crystal X-ray crystallographic structural analysis, providing the long-sought first solid-state structure of a Dawson-type heteropolyoxoanion-supported organometallic complex.

Results and Discussion

Synthesis, Isolation, and Characterization of $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$. The synthesis of $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$, **1**, parallels those reported earlier for the $[(1,5\text{-}COD)M]^+$ analogs $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)M{\cdot}P_2W_{15}Nb_3O_{62}]$ (M = Ir, Rh).[13] It follows the conceptually straightforward route outlined in eqs 1a,b. The desired product is obtained as an analytically pure, homogeneous, yellow complex as its all $[(n\text{-}C_4H_9)_4N]^+$ salt, $[(n\text{-}C_4H_9)_4N]_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$, on a 2.3 g scale (50% yield). (The synthesis of the mixed $[(n\text{-}C^4H_9)_4N]^+/Na^+$ salt gives a higher yield (70%); however, this material is slightly impure by elemental analysis and hence is reported in the supplementary material).

$$[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62} + [(C_5Me_5)Rh(CH_3CN)_3][BF_4]_2 \xrightarrow{CH_3CN} [(n\text{-}C_4H_9)_4N]_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}] + 2[(n\text{-}C_4H_9)_4N]BF_4 \quad (1a)$$

$$[(n\text{-}C_4H_9)_4N]_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}] + 2[(n\text{-}C_4H_9)_4N]BF_4 \xrightarrow[3.\ -2[(n\text{-}C_4H_9)_4N]BF_4]{1.\ CH_3CN \quad 2.\ EtOAc\ precipitation} [(n\text{-}C_4H_9)_4N]_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]\downarrow \quad (1b)$$

The molecular formula of **1** is established by an elemental analysis (all elements, including oxygen; see the Experimental Section). Ultracentrifugation sedimentation-equilibrium molecular-weight experiments using isolated **1** confirm our previous finding[10d] that the compound is an unaggregated monomer under the conditions of the experiment $\bar{M}_w$(calc for the anion) 4328, $\bar{M}_w$(found) 4873 ± 600 in CH_3CN containing 0.1 $\underline{M}$ $[(n\text{-}C_4H_9)_4N]^+PF_6^-$ (supplementary material, Figure A; $\bar{M}_w$ = weight-average molecular weight).[14]

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(5) Obvious *disadvantages* of polyoxoanion-supported catalysts, relative to their commercially important and well-studied solid-oxide counterparts, include the limited flat surface-oxide area (6 oxygens) of the present polyoxoanions, the inability (at least presently) to support multimetal clusters or particles, and the lack of high-temperature thermal stability of the type commonly found in solid-oxide-supported heterogeneous catalysts. Hence, these polyoxoanion-supported *analogs* are not intended to replace or even to closely "model" polymetallic metal cluster particles supported on solid oxides; this work has *not* been undertaken in order to "model" oxide-supported catalysts. (Model studies in science generally provide information about the model system only, rigorously speaking.) Rather, these polyoxoanion-supported complexes are novel compositions of matter which are in principle completely characterizable structurally and mechanistically at the *atomic level*. In addition, as new and novel materials, they should have their *own* unique chemistry and reactivity. In selected cases they *may* provide the best available examples of badly needed spectroscopic models of atomically dispersed metal complexes, for example $Rh(CO)_2$·solid-oxides,[4c] but we emphasize that this has never been our primary goal.

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(11) (a) Recently we were able to show that $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}]$ is a precatalyst for both hydrogenation[11d] and oxygenation[11c] reactions. This complex was characterized by a complete elemental analysis plus ^{31}P, ^{183}W, ^{1}H, and ^{13}C NMR, IR, and sedimentation-equilibrium molecular-weight measurements.[11f] ^{17}O NMR studies demonstrate that $[(1,5\text{-}COD)Ir]^+$ binds in overall C_{3v} symmetry to three Nb_2O bridging oxygens of the $Nb_3O_9^{3-}$ oxygen surface in the soluble, metal-oxide support system, $P_2W_{15}Nb_3O_{62}^{9-}$.[11e] (b) The complex $[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$, **2**, has also been shown to catalyze the oxygenation of cyclohexene with molecular oxygen.[11c,17b] (c) Mizuno, N.; Lyon, D. K.; Finke, R. G. *J. Catal.* **1991**, *128*, 84. (d) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335. (e) Pohl, M.; Finke, R. G. *Organometallics* **1993**, *12*, 1453. (f) Pohl, M. Dissertation, University of Oregon, 1994; Chapter IV.

(12) (a) The first reports of polyoxoanion-supported $[(C_5Me_5)Rh]^{2+}$ are from Klemperer's laboratories: Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (b) Reports of fully characterized polyoxoanion-supported $[(C_6H_6)Ru]^{2+}$ from Klemperer's laboratories (see also ref 12c): Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Planalp, R. P.; Schiller, P. W.; Yagasaki, A.; Zhong, B. *Inorg. Chem.* **1993**, *32*, 1629. Klemperer, W. G.; Zhong, B. *Inorg. Chem.* **1993**, *32*, 5821. (c) Attanasio, D.; Bachechi, F.; Suber, L. *J. Chem. Soc., Dalton Trans.* **1993**, 2373.

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(14) 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 $[(C_5Me_5)Rh]^{2+}$ absorb.

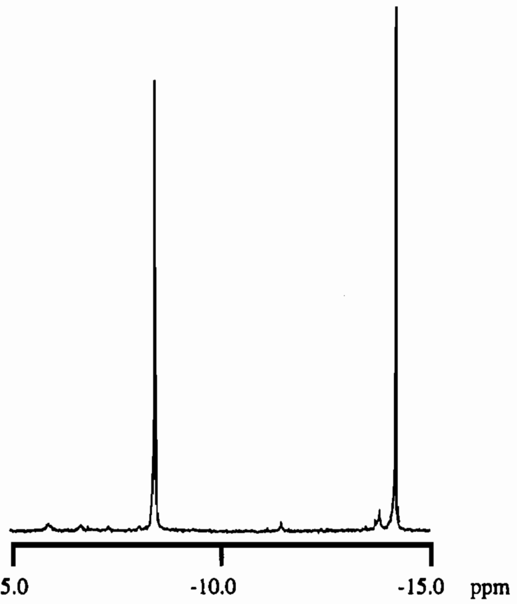

Figure 2. ^{31}P NMR spectrum in DMSO-d_6 of the all-[$(n-C_4H_9)_4N$]$_7$ complex of **1** showing its high homogeneity and purity (≥95%).

Infrared measurements (supplementary material, Figure B) 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 **1** as containing intact $P_2W_{15}Nb_3O_{62}^{9-}$ with $[(C_5Me_5)Rh]^{2+}$ firmly supported upon its surface. Moreover, a careful examination of the IR spectrum of **1** as a KBr disk reveals a lack of bands corresponding to coordinated CH_3CN. The only plausible inner-sphere ligands for the otherwise 12e$^-$ rhodium fragment $[(C_5Me_5)Rh]^{2+}$, then, are the surface oxygens of $P_2W_{15}Nb_3O_{62}^{9-}$.

Further solution characterization relied heavily on multinuclear NMR spectroscopy (^{31}P, ^{183}W, and ^{1}H NMR). The ^{31}P and ^{183}W NMR spectra are useful in characterizing the heteropolyoxoanion support's purity and framework, respectively (and provide initial evidence for the binding of the fragment). A ^{31}P NMR spectrum of **1** in DMSO-d_6 (Figure 2) shows primarily two resonances at δ −8.4 and −14.2 with integrated intensities of 1:1 as expected for the two types of phosphorus present. These ^{31}P NMR results demonstrate that **1** is obtained *as at least 95% of a single isomer.*

Also quite informative are changes in the ^{31}P NMR peak positions for **1** in DMSO-d_6 (−8.4 and −14.2 (±0.2) ppm) in comparison to the starting material $P_2W_{15}Nb_3O_{62}^{9-}$ (−7.2 and −14.2 (±0.2) ppm), as they show a pronounced upfield shift of the phosphorus resonance closest to the "$Nb_3O_9^{3-}$" cap in $P_2W_{15}Nb_3O_{62}^{9-}$ (recall Figure 1). This observation is in accord with, and actually *prima facie* evidence for, preferential binding of $[(C_5Me_5)Rh]^{2+}$ to the more basic "$Nb_3O_9^{3-}$" cap *in solution.* The observed line widths, $\Delta\nu_{1/2}$ = 3−4 Hz for the two resonances of **1** in the ^{31}P NMR spectrum are comparable to those observed for the unsupported polyoxoanion, $P_2W_{15}Nb_3O_{62}^{9-}$, which exhibits values for $\Delta\nu_{1/2}$ of 3−5 Hz.

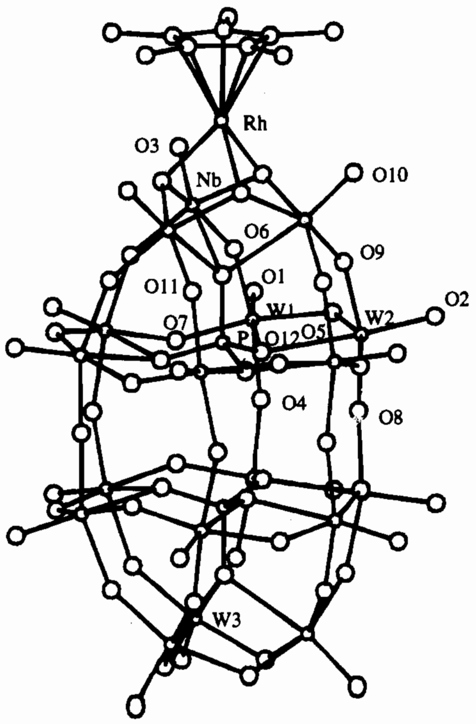

Figure 3. Structure of $[(C_5Me_5)Rh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$. The Nb and W(3) atoms each are composites, $Nb_{0.5}W_{0.5}$, because the anion adopts two equally-weighted orientations related by the mirror plane of a $3/m$ (D_{3h}) crystallographic site. The C_5Me_5 group lies in a plane normal to the anion C_3 axis and is disordered because of the incompatibility of its 5-fold symmetry with that axis. The C_5Me_5 could not be located by X-ray single-crystal structure analysis but is present by ^{1}H NMR spectroscopy and elemental analysis.

The ^{1}H NMR spectrum shows a single resonance for the C_5Me_5 group at δ 1.82 in CD_3CN (δ 1.84 in DMSO-d_6), providing further evidence (in addition to the ^{31}P NMR) for existence of a single species in solution. No resonances are observed at δ 1.87, indicating the absence of free $[Rh(C_5Me_5)(CD_3CN)_3]^{2+}$ (in a control experiment 10% of $[Rh(C_5Me_5)(CD_3CN)_3]^{2+}$ was added to the solution proving that it could have been easily detected had it been present).

Evidence for the covalent, inner-sphere bonding of $[(C_5Me_5)Rh]^{2+}$ to $P_2W_{15}Nb_3O_{62}^{9-}$ (rather than an $[(C_5Me_5)Rh(CH_3CN)_3]^{2+}$ ion-paired complex) is provided by ion-exchange experiments (as well as IR, ^{1}H, and ^{31}P NMR spectra; *vide supra),* specifically ion (non)-exchange experiments which demonstrate the nonexchangeability in acetonitrile of the cationic $[(C_5Me_5)Rh]^{2+}$ component of $[(C_5Me_5)Rh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$.

The ^{183}W NMR spectrum of **1** in DMSO-d_6 shows three peaks, indicating that $[(C_5Me_5)Rh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$ has C_{3v} pseudosymmetry on the ^{183}W NMR time scale[15] (pseudo, as the $Rh \cdot P_2W_{15}Nb_3O_{62}$ part of the molecule has C_{3v} symmetry, but the C_5Me_5 moiety does not, having a C_5 axis instead). The integrated intensities are in accord with the presence of two tungsten belts consisting of six WO_6 octahedra each and a tungsten cap of three WO_6 octahedra.

The ^{1}H, ^{31}P, and ^{183}W NMR spectroscopic data for the mixed $Na^+/[(n-C_4H_9)_4N]^+$ salt of **1** are identical to those for the all-$[(n-C_4H_9)_4N]^+$ salt. (When ^{31}P and ^{183}W NMR data for sodium-containing complexes are collected, addition of Kryptofix 2.2.2. to the sample solutions is necessary. Otherwise, ion-pairing interactions between Na^+ and primarily the more basic "$Nb_3O_9^{3-}$" end of $P_2W_{15}Nb_3O_{62}^{9-}$ lead to line-broadening and the observation of additional peaks.[11d]) However, note that the isolated complex of **1** with mixed $Na^+/[(n-C_4H_9)_4N]^+$ countercation composition is somewhat less pure than the analytically pure

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(15) (a) This argument assumes that any non-C_{3v} isomers would be detected by ^{183}W NMR spectroscopy. This assumption is supported by the fact that C_s symmetry isomers are detected by ^{183}W NMR for $[CpTi^{3+} \cdot P_2W_{15}V_3O_{62}^{9-}]^{6-}$, although a more strongly supported $CpTi^{3+}$ trication is involved,[15b] plus the fact that even Na^+ ion-pairing is detectable (in the absence of added Kryptofix 2.2.2.) as excess line width in the ^{183}W NMR spectrum of heteropolyoxoanion-supported complexes.[11d,12b] (However, our other work suggests that ^{183}W NMR *of $P_2W_{15}Nb_3O_{62}^{9-}$-supported organometallics* becomes relatively insensitive once *mono*-cations such as $[Ir(1,5\text{-}COD)]^+$ are supported.[11f]) (b) Rapko, B. M.; Pohl, M.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 3625.

Table 1. Crystallographic Data for $Na[(n\text{-}C_4H_9)_4N]_6[(C_5Me_5)Rh\cdot P_2Nb_3W_{15}O_{62}]\cdot 10MeCN\cdot 10Me_2CO$

approx compn	$C_{156}H_{321}N_{16}Na$-$Nb_3O_{72}P_2RhW_{15}$	d_{calc}	1.78 g cm^{-3}
		T	21 °C
fw	6798	λ	0.710 69 Å
space group	$P6_3/m$	μ	71.9 cm^{-1}
a	20.544(5) Å	rel transm coeff	0.78−1.00 (ψ)
b	20.544(5) Å	no. of obs rflns	3023 [$I \geq 3\sigma(I)$]
c	34.648(6) Å	$R(F_o)$[a]	0.096
V	12664(8) Å^3	$R_w(F_o)$[b]	0.147
Z	2		

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates and Isotropic and Thermal Parameters (Å^2) for Atoms in the Anion

atom	x	y	z	B_{eq},[c] Å^2
W(1)	0.48885(12)	0.17047(12)	0.19562(6)	3.9(1)
W(2)	0.64120(12)	0.15105(12)	0.19557(6)	3.9(1)
W(3)[a]	0.55610(17)	0.28886(17)	0.10743(8)	4.4(1)
Rh[a]	$^2/_3$	$^1/_3$	0.0398(4)	6.1(6)
Nb[a,b]	0.5561	0.2889	0.10744.4	
P	$^2/_3$	$^1/_3$	0.1934(7)	4.1(5)
O(1)	0.3947(17)	0.1009(17)	0.1854(8)	4.4(7)
O(2)	0.6429(16)	0.0651(17)	0.1857(8)	4.5(7)
O(3)	0.4890(18)	0.2565(18)	0.0731(9)	5.7(9)
O(4)	0.4979(27)	0.1673(27)	$^1/_4$	6(1)
O(5)	0.5376(16)	0.1104(16)	0.1890(8)	4.2(7)
O(6)	0.5129(16)	0.2090(16)	0.1436(8)	3.8(7)
O(7)	0.7438(15)	0.2262(15)	0.2078(8)	3.5(7)
O(8)	0.6183(27)	0.1384(28)	$^1/_4$	6(1)
O(9)	0.6605(15)	0.1856(16)	0.1430(8)	3.4(7)
O(10)	0.6211(17)	0.2527(17)	0.0826(9)	5.1(8)
O(11)	$^2/_3$	$^1/_3$	0.1469(16)	5(1)
O(12)	0.6168(14)	0.2518(15)	0.2064(7)	2.9(6)

[a] Site occupancy factor 0.5. [b] W(3) and Nb have the same x, y, z, and U_{ij} parameters. [c] For the metal atoms, $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i \cdot a_j$.

all-$[(n\text{-}C_4H_9)_4N]^+$ salt of **1** as judged by elemental analysis and ^{31}P NMR spectroscopy (see the supplementary material for more details).

There can be little doubt, therefore (and given the analytical, MW, IR, ion-exchange, and ^{31}P NMR evidence), that even in solution $[(C_5Me_5)Rh]^{2+}$ is firmly attached to a single $P_2W_{15}Nb_3O_{62}{}^{9-}$. Moreover, the average symmetry of **1** in solution is also (pseudo) C_{3v} (based on the ^{183}W NMR). Hence, the $[(C_5Me_5)Rh]^{2+}$ must be attached to the "$Nb_3O_9{}^{3-}$" cap equally to each of the three Nb_2O oxygens (i.e., in order to achieve effective C_{3v} symmetry), a conclusion that is independently and unequivocally confirmed by a single-crystal X-ray structure analysis (*vide infra*) of **1** in the solid state.

X-ray Single-Crystal Structure Analysis of 1. An X-ray diffraction structure analysis shows that **1** is composed of discrete, disordered $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ anions (Figure 3, Table 1) and $[(n\text{-}C_4H_9)_4N]^+$ and Na^+ cations. (Due to its lower solubility, the mixed $Na^+/[(n\text{-}C_4H_9)_4N]^+$ salt of **1** crystallizes more easily than the all-$[(n\text{-}C_4H_9)_4N]^+$ salt.) The Dawson-type anion has approximate symmetry $3m$ (C_{3v}), with the Rh atom on or very close to the polyoxoanion's 3-fold axis and bonded ($Rh-ONb_2$ 2.06 Å) to three oxygen atoms, each of which bridges a pair of heavy atoms M in a cap of the Dawson unit. The M atoms each are composites, $Nb_{0.5}W_{0.5}$, 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, which could not be located but is present (by ^1H NMR spectroscopy and elemental analysis), must lie in a plane normal to the anion C_3 axis; its extreme disorder is due to the incompatibility of its 5-fold symmetry with the 3-fold axis of the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion axis. Atomic coordinates and

Table 3. Bond Lengths in the Anion (Å)[a]

W(1)−O(1)	1.77(3)	W(2)−O(12)	2.39(3)
W(1)−O(4)	1.90(1)	W(3)−O(3)	1.68(3)
W(1)−O(5)	1.95(3)	W(3)−O(6)	1.90(3)
W(1)−O(6)	1.93(3)	W(3)−O(9^i)	1.92(3)
W(1)−O(7^i)	1.88(3)	W(3)−O(10)	2.02(3)
W(1)−O(12)	2.33(3)	W(3)−O(10^i)	1.92(3)
W(2)−O(2)	1.82(3)	W(3)−O(11)	2.41(3)
W(2)−O(5)	1.87(3)	Rh−O(10)	2.06(3)
W(2)−O(7)	1.94(3)	P−O(11)	1.61(6)
W(2)−O(8)	1.93(1)	P−O(12)	1.53(3)
W(2)−O(9)	1.92(3)		

[a] Unrefined bond lengths: Rh−C(15), 2.20; Rh−C(16), 2.14.

anisotropic thermal parameters for non-hydrogen atoms of **1** are given with estimated standard deviations in Table 2. Bond angles and lengths for $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ are given in Tables 3 and 4; Table 5 lists the distances between heavy atoms.

An interesting and important point is that only two $[(n\text{-}C_4H_9)_4N]_6Na[(C_5Me_5)Rh\cdot P_2Nb_3W_{15}O_{62}]$ units are present *in a cell large enough to accommodate five or six in the absence of solvent* (supplementary material, Figure G). This is presumably one key reason that it has been very difficult to prepare diffracting crystals of the $[(n\text{-}C_4H_9)_4N]^+$ salts of such large polyoxoanions in non-hydrogen-bonding solvents.

Synthesis, Isolation, and Characterization of $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$. The preparation (eqs 2a,b) of $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, **2**, proceeds analogously to the one described above for the $[(C_5Me_5)Rh]^{2+}$ heteropolyoxoanion-supported complex. [Note that we had to use a refined procedure for the

$$[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62} + [(C_6H_6)Ru(CH_3CN)_3][BF_4]_2 \xrightarrow[]{\substack{\text{1. <1 ppm of } O_2 \\ \text{2. } CH_3CN}} [(n\text{-}C_4H_9)_4N]_7[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}] + 2[(n\text{-}C_4H_9)_4N]BF_4 \quad (2a)$$

$$[(n\text{-}C_4H_9)_4N]_7[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}] \xrightarrow[]{\substack{\text{1. } CH_3CN \\ \text{2. EtOAc precipitation} \\ \text{3. } +3\ NaBF_4 \\ \text{4. } -2\ [(n\text{-}C_4H_9)_4N]BF_4}} [(n\text{-}C_4H_9)_N]_{4.5}Na_{2.5}[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]\downarrow \quad (2b)$$

preparation of $P_2W_{15}Nb_3O_{62}{}^{9-}$ in its fully deprotonated form, as otherwise persistently low ruthenium analyses were obtained (see the Experimental Section for further details).] The desired product is obtained as a homogeneous, yellow solid in form of the mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ cation salt on a 8.4 g scale (76% yield). The synthesis of the mixed salt, eq 2b, allows for the isolation of $[(n\text{-}C_4H_9)_4N]^+BF_4{}^-$ free material in high yield.

The molecular formula of **2** is consistent with the elemental analysis (all elements, including oxygen; see the Experimental Section and the supplementary material, Table B, where alternative formulations are ruled out). The C, H, N, and Na analysis reveals an average countercation composition of 4.5 $[(n\text{-}C_4H_9)_4N]^+/2.5\ Na^+$ per anion.[16] In two separate control experiments (see the Experimental Section for a detailed account) it was shown that **2** is neither light- nor air-sensitive,[17] as judged by ^{31}P NMR spectroscopy. The lack of O_2 sensitivity

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(16) Note that the given composition of $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}$ (calc: C, 17.25; H, 3.12; N, 1.30; Na, 1.07) matches the experimental values (found: C, 17.28; H, 3.27; N, 1.44; Na, 1.24) better than the alternative formulations $[(n\text{-}C_4H_9)_4N]_5Na_2$ (calc: C, 18.69; H, 3.39; N, 1.25; Na, 0.83) and $[(n\text{-}C_4H_9)_4N]_4Na_3$ (calc: C, 15.80; H, 2.84; N, 1.32; Na, 1.30).

Table 4. Bond Angles (deg)

O(1)−W(1)−O(4)	105(2)	O(3)−W(3)−O(9)	104(1)
O(1)−W(1)−O(5)	99(1)	O(3)−W(3)−O(10)	97(1)
O(1)−W(1)−O(6)	96(1)	O(3)−W(3)−O(10)	100(1)
O(1)−W(1)−O(7)	104(1)	O(3)−W(3)−O(11)	169(1)
O(1)−W(1)−O(12)	173(1)	O(6)−W(3)−O(9)	85(1)
O(4)−W(1)−O(5)	90(2)	O(6)−W(3)−O(10)	94(1)
O(4)−W(1)−O(6)	159(2)	O(6)−W(3)−O(10)	159(1)
O(4)−W(1)−O(7)	82(2)	O(6)−W(3)−O(11)	84(1)
O(4)−W(1)−O(12)	77(2)	O(9)−W(3)−O(10)	159(1)
O(5)−W(1)−O(6)	92(1)	O(9)−W(3)−O(10)	95(1)
O(5)−W(1)−O(7)	157(1)	O(9)−W(3)−O(11)	86(1)
O(5)−W(1)−O(12)	74(1)	O(10)−W(3)−O(10)	78(2)
O(6)−W(1)−O(7)	87(1)	O(10)−W(3)−O(11)	73(1)
O(6)−W(1)−O(12)	84(1)	O(10)−W(3)−O(11)	75(1)
O(7)−W(1)−O(12)	83(1)	O(10)−Rh−O(10)	74(1)
O(2)−W(2)−O(5)	97(1)	O(11)−P−O(12)	107(1)
O(2)−W(2)−O(7)	106(1)	O(12)−P−O(12)	112(1)
O(2)−W(2)−O(8)	100(2)	W(1)−O(4)−W(1)	166(3)
O(2)−W(2)−O(9)	95(1)	W(1)−O(5)−W(2)	122(1)
O(2)−W(2)−O(12)	170(1)	W(1)−O(6)−W(3)	152(2)
O(5)−W(2)−O(7)	158(1)	W(1)−O(7)−W(2)	148(2)
O(2)−W(2)−O(8)	85(2)	W(2)−O(8)−W(2)	156(3)
O(5)−W(2)−O(9)	92(1)	W(2)−O(9)−W(3)	149(2)
O(5)−W(2)−O(12)	74(1)	W(3)−O(10)−W(3)	121(2)
O(7)−W(2)−O(8)	89(2)	W(3)−O(10)−Rh	97(1)
O(7)−W(2)−O(9)	88(1)	W(3)−O(10)−Rh	100(1)
O(7)−W(2)−O(12)	84(1)	W(3)−O(11)−W(3)	91(2)
O(8)−W(2)−O(9)	165(2)	W(3)−O(11)−P	125(1)
O(8)−W(2)−O(12)	80(2)	W(1)−O(12)−W(2)	90(1)
O(9)−W(2)−O(12)	86(1)	W(1)−O(12)−P	129(1)
O(3)−W(3)−O(6)	101(1)	W(2)−O(12)−P	126(1)

Table 5. Distances between Heavy Atoms (Å)

W(1)···W(2)	3.347(3)	W(2)···W(3)[c]	3.696(4)
W(1)···W(2)[a]	3.672(3)	W(2)···W(2)[b]	3.772(4)
W(1)···W(3)	3.715(4)	W(3)···W(3)[a]	3.429(5)
W(1)···W(1)[b]	3.769(4)	W(3)···Rh	3.07(1)

[a] Symmetry code: $1 - x + y$, $1 - x$, z. [b] Symmetry code: x, y, $\frac{1}{2} - z$. [c] Symmetry code: $1 - y$, $x - y$, z.

is noteworthy, given that **2** is an effective cyclohexene oxidation catalyst[17b] using O_2, and requires that **2** and O_2 do not react directly during catalysis.

Infrared measurements (supplementary material, Figure D) confirm that the Dawson-type, $P_2W_{15}Nb_3O_{62}^{9-}$ heteropolytungstate framework remains intact under the conditions of the synthesis, consistent with the formulation of **2** as containing intact $P_2W_{15}Nb_3O_{62}^{9-}$ with $[(C_6H_6)Ru]^{2+}$ supported upon its surface. Confirming evidence for the covalent, inner-sphere bonding of $[(C_6H_6)Ru]^{2+}$ to $P_2W_{15}Nb_3O_{62}^{9-}$ includes experiments with ion-exchange resins which demonstrate the nonexchangeability in acetonitrile of the cationic $[(C_6H_6)Ru]^{2+}$ in **2**.

An ultracentrifugation sedimentation-equilibrium molecular-weight experiment shows that the compound is an unaggregated monomer under the conditions of the experiment (supplementary material, Figure C).

Further solution characterization was accomplished by multinuclear NMR spectroscopy (^{31}P, ^{183}W, ^{1}H NMR). A ^{31}P NMR spectrum of **2** in CD_3CN (Figure 4) acquired after addition (again to remove the ion-pairing[11e,f]) of 3 equiv of Kryptofix 2.2.2. shows primarily two resonances at δ −7.7 and −13.3 with integrated intensities of 1:1, as expected for the two types of phosphorus present, and requires that **2** is obtained as at least 94% of a single species and isomer.

The ^{1}H NMR spectrum shows primarily a single resonance for the C_6H_6 group at δ 5.99 in CD_3CN, providing further evidence (in addition to the ^{31}P NMR) for existence of a single supported-$(C_6H_6)Ru^{2+}$ species in solution. [A smaller, unidentified resonance at δ 6.06 (less than 5% by integration and by comparison to the main δ 5.99 resonance) is also observed. However, an elemental analysis for Cl^- shows the absence of chloride within the detection limits (<0.05%); hence, on the basis of these data, we exclude the presence of any (C_6H_6)-RuCl species.] Significantly, no resonances are observed at δ 6.20, indicating the absence of $[Ru(C_6H_6)(CD_3CN)_3]^{2+}$ (in a control experiment 10% of $[Ru(C_6H_6)(CD_3CN)_3]^{2+}$ was added to the solution proving that it could have been easily detected had it been present).

The ^{183}W NMR spectrum of **2** in CD_3CN (Figure 5) shows three peaks, indicating that $[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$ has C_{3v}

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(17) (a) (Arene)ruthenium(II) complexes are known to undergo arene-exchange reactions in aromatic solvents when heated or irridiated with UV light.[21b] Furthermore, photolysis of the (benzene)ruthenium complex $[(C_6H_6)Ru(P_3O_9)][(n\text{-}C_4H_9)_4N]$ by UV light for 25 h in acetonitrile has been shown to result in benzene loss and formation of $[(CH_3CN)_3Ru(P_3O_9)][(n\text{-}C_4H_9)_4N]{\cdot}CH_3CN$.[12b] (b) Previously we surmised that, because **2** is an effective catalyst for a reaction involving O_2, "the spectroscopic data reported (previously, for **2** in solution; see ref 10d) *may be* for an oxidized form (of **2**)".[11c] Now we can state that, in point of fact, **2** *is not* O_2 sensitive over 12 h in air at room temperature (nor are *any* of the seven Ru−polyoxoanion complexes recently reported by Klemperer and co-workers[12b] air sensitive). The important mechanistic implication for the cyclohexene oxidation by **2** using O_2 over 20 h, then, and one consistent with our other mechanistic data to date (Trovarelli, A.; Weiner, H.; Finke, R. G., unpublished results), is that **2** is part of an autooxidation reaction involving **2** reacting with trace cyclohexene-OOH, present initially, and in a radical-chain reaction. (c) The additional mechanistic implication is that *both* O_2 and olefin, not O_2 alone,[12b] should be employed when polyoxoanion-supported Ru complexes are tested for stoichiometric or catalytic oxidation activity.

(18) (a) Modified to allow for acquisition of spectra by M. Strain, Institute of Molecular Biology, University of Oregon. (b) It is well-known in the ^{31}P NMR literature that chemical shift data reliable to, e.g., ±0.2 ppm or better require referencing to an *internal*, not external, standard[18c] 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 a 85% H_3PO_4 *external* standard, yields chemical shifts that are offset by 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.[18c] 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.[18d] (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) Under acidic conditions, possible internal (so-called secondary) reference standards[18b] 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 mean 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 in ref 18c and Domaille's treatment of this in the specific case of a polyoxoanion sample: Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239 (see footnote 12 therein). See also: Batley, M.; Redmond, J. W. *J. Magn. Reson.* **1982**, *49*, 172. (f) ^{51}V NMR chemical shifts and corrections for the volume diamagnetic susceptibility of the solvent: Harrison, A. D.; Horwath, O. W.; *J. Chem. Soc., Dalton Trans.* **1985**, 1173.

(19) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

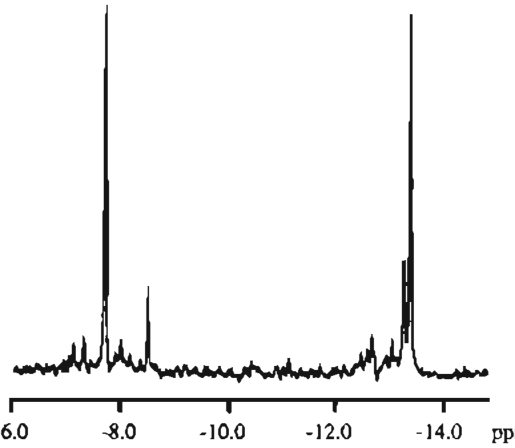

Figure 4. ^{31}P NMR spectrum of $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]$, **2**, in CD_3CN showing its purity of ca. 94%. The ^{31}P NMR spectrum shows the presence of ca. 6% unreacted $P_2W_{15}Nb_3O_{62}{}^{9-}$, compared to typically 15–20% in all other previously attempted preparations. This spectrum was collected on a Bruker 300 NMR instrument at CSU.

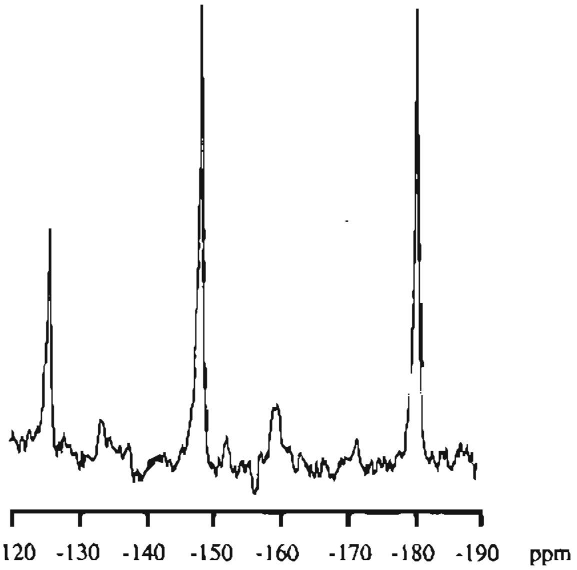

Figure 5. ^{183}W NMR spectrum of $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]$ in CD_3CN with 3 equiv of Kryptofix 2.2.2. added, showing primarily three peaks indicating that the predominant form of $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ has C_{3v} (pseudo) symmetry on the ^{183}W time scale[15] (spectrum collected on a Bruker AM500, CSU).

symmetry on the ^{183}W NMR time scale. The integrated intensities are in accord with the presence of two tungsten belts consisting of six WO_6 octahedra each and a tungsten cap of three WO_6 octahedra.

On the basis of our previous characterization[10,11] of heteropolyoxoanion-supported complexes employing $P_2W_{15}Nb_3O_{62}{}^{9-}$, and given the ^{183}W NMR data indicating a C_{3v} (pseudo) symmetry structure for **2**, the solution structure depicted in Figure 6 is proposed, one that enjoys considerable precedent[10-12] and is the simplest interpretation consistent with all the data.

Summary

The complexes $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, **1**, and $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, **2**, have been isolated in good yield and as their all-$[(n\text{-}C_4H_9)_4N]^+$ salt (for **1**) or as complexes with mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ cation composition (for **1** and **2**). These inner-sphere, covalently bonded organometallic derivatives were characterized by IR, multinuclear NMR, and ultracentrifugation molecular-weight measurements. The results of ^{183}W NMR

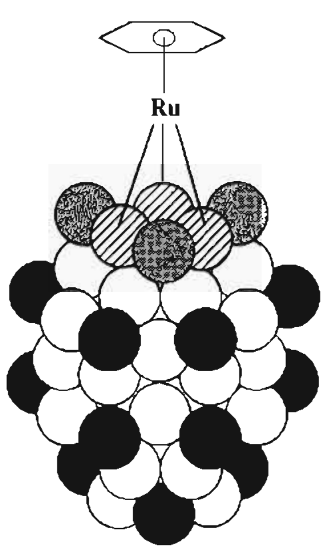

Figure 6. Space-filling, static C_{3v} symmetry structure proposed for $Ru(C_6H_6)^{2+}$ fragment supported on the "$Nb_3O_9{}^{3-}$" face of $P_2W_{15}Nb_3O_{62}{}^{9-}$ serving as a stereochemically rigid tripodal ligand. The open circles represent bridging tungsten oxygens (W_2O), while the black circles represent terminal tungsten oxygens (WO). Niobium bridging oxygens (Nb_2O) are depicted by hatched circles, whereas niobium terminal oxygens (NbO) are shown as gray circles.

spectroscopy are in accord with an overall C_{3v} (pseudo) symmetry for these compounds in solution. A single-crystal X-ray structure analysis was successful for $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, thereby providing the first X-ray diffraction study of a Dawson-type heteropolyoxoanion-supported complex.

Experimental Section

Materials. All commercially obtained compounds were reagent grade unless otherwise specified, and the following were used as received: ethanol (Baker), 1,3-cyclohexadiene (Aldrich), "$RuCl_3\cdot xH_2O$" ($x = 0-1$)[20] (Aldrich), $NaBF_4$ (Aldrich), $AgBF_4$ (Aldrich), 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane [Kryptofix 2.2.2.] (Aldrich), CaH_2 (Aldrich), C_5Me_5H (Aldrich), $RhCl_3\cdot xH_2O$ ($x = 2-3$) (Aldrich), Dowex ion exchange resins (Aldrich), and K_2CO_3 (Baker). Acetonitrile (Baker), ethyl acetate (Baker), diethyl ether (Baker), acetonitrile-d_3 (Cambridge Isotope Laboratories), and DMSO-d_6 (Cambridge Isotope Laboratories) all were used as received for the preparation of non-air-sensitive $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$. For the preparation of $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$, acetonitrile (from CaH_2), acetone (from K_2CO_3), and ethyl acetate (from K_2CO_3) were refluxed under N_2 for at least 24 h and then distilled into glassware that had been thoroughly cleansed, dried at 250 °C, and allowed to cool under a dry N_2 flow. NMR solvents used with $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ were degassed by three freeze–pump–thaw cycles. $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ used in the synthesis of $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ was prepared as previously described;[10d,13a] the purity was checked by ^{31}P NMR for each preparation and was 95% or higher.

Instrumentation/Analytical Procedures. The synthesis of $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ was carried out, outside the drybox under N_2, as described in the experimental procedure (vide supra). The synthesis of $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ was carried out under an inert nitrogen atmosphere in a Vacuum Atmospheres drybox (≤1.0 ppm of oxygen as monitored by use of a Vacuum Atmospheres oxygen monitor, VAC Model AO 316-C). Elemental analyses were obtained from Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were obtained on a Nicolet 5DX as KBr disks. All nuclear magnetic resonance (NMR) spectra were obtained as CD_3CN or DMSO-d_6 solutions in SpectraTech or Wilmad NMR tubes. ^{1}H NMR (300.15

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(20) Commercially available "$RuCl_3\cdot xH_2O$" is known to be a complicated and 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.

MHz) were recorded in 5 mm o.d. tubes on a General Electric QE-300 spectrometer, at 21 °C and were referenced to the residual impurity in the deuterated solvent (^{1}H 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 ^{1}H NMR: pulse width, 3.0 μs; acquisition time, 1.36 s; repetition rate, 2.35 s; sweep width, ±6024 Hz. All ^{1}H NMR spectra of $[(n\text{-}C_4H_9)_4N]^+$ salts of polyoxometalates have the characteristic resonances (^{1}H NMR: δ 0.98, 1.42, 1.65, 3.18) associated with the tetrabutylammonium 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 equipped with an IBM-PC and a 16-bit digitizer board and the NMR software package Felix V1.1.[18a] Spectra were recorded at 21 °C in 10 mm o.d. NMR tubes. ^{31}P NMR spectra were referenced *externally*[18b] to 85% H_3PO_4, and ^{183}W NMR spectra were referenced externally by the substitution method to 2 M Na_2WO_4/D_2O. Spectral parameters for ^{31}P NMR: pulse width, 20 μs; acquisition time, 1.638 s; repetition rate, 2.838 s; sweep width, ±5000 Hz. Spectral parameters for ^{183}W NMR: pulse width, 60 μs; acquisition time, 0.8 s; repetition rate, 4.319 s; sweep width, ±10 000 Hz. A 5 Hz (^{31}P NMR), 5 Hz (^{183}W NMR), or 0.5 Hz (^{1}H NMR) exponential apodization of the FID was applied to all spectra but was removed from 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. Spectral parameters differ from those listed above and are as follows. ^{31}P NMR (121.50 MHz; in 5 mm o.d. NMR tubes[18b]): pulse width, 5 μs; acquisition time, 819 ms; sweep width, ±20 000 Hz. ^{183}W NMR (20.838 MHz; in 10 mm o.d. NMR tubes): pulse width, 30 μs; acquisition time, 1114 ms; sweep width, ±14 705 Hz. A 2 Hz (^{31}P NMR) or 10 Hz (^{183}W NMR) 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. ^{17}O NMR spectra were collected as detailed elsewhere.[11e]

GLC measurements were carried out using a Apiezon grease column of 2 m length and a Shimadzu GC-8APT GC instrument.

Molecular-weight data were collected as previously described by the sedimentation equilibrium method.[10d,i] All molecular weights are weight-average molecular weights, $\bar{M}_w$. Molecular weight measurements were obtained in CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ and were monitored at 335 nm, a wavelength characteristic of both the polyoxoanion and the organometallic groups.

Preparations. $\mathbf{[(C_5Me_5)RhCl_2]_2}$ was prepared from C_5Me_5H and $RhCl_3{\cdot}xH_2O$ in refluxing solvent according to the literature.[10d,19] ^{1}H NMR (25 °C, 4.05 M, DMSO-d_6) δ (multiplicity): 1.61 (s). Lit. δ (in $CDCl_3$):[19] 1.60 (s). In latter preparations of **1**, $[(C_5Me_5)RhCl_2]_2$ obtained commercially (Strem) was used; this material was found to be satisfactory as judged by ^{1}H NMR and partial elemental analysis. Anal. Calc (found): C, 38.87 (38.8); H, 5.16 (4.89).

$\mathbf{[Ru(C_6H_6)Cl_2]_2}$ was prepared from "$RuCl_3{\cdot}xH_2O$"[20] and 1,3-cyclohexadiene according to the literature.[21] ^{1}H (25 °C, 4.05 M, DMSO-d_6) δ (multiplicity): 5.94 (s). Lit. δ (in DMSO-d_6):[21] 5.93 (s). ^{1}H (25 °C, 4.05 M, CD_3CN) δ (multiplicity): 5.69 (s). Lit. δ (in CD_3CN):[21] 5.70. Anal. Calc (found): C, 28.82 (28.84); H, 2.42 (2.45); Ru, 40.41 (38.5).

$\mathbf{[(\mathit{n}\text{-}C_4H_9)_4N]_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]}$, **1**.[22] $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (4.74 g, 0.756 mmol) was placed in a 100 mL three-neck round-bottom flask and dissolved in 50 mL of dry CH_3CN (dried over 3 Å molecular sieves). Using a long needle, N_2 was passed through the resulting solution for 30 min. Separately, in a 20 mL beaker $[(C_5Me_5)RhCl_2]_2$ (0.234 g, 0.379 mmol) was slurried in 10 mL of CH_3CN. Solid $AgBF_4$[23] (0.294 g, 1.51 mmol) was added to the slurry, causing the immediate formation of an AgCl precipitate. The mixture was stirred for 10 min (magnetic stir bar) and filtered through a medium glass frit directly into the clear, stirred solution of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. The precipitate on the glass frit was washed with 1−2 mL of CH_3CN using a pipet, and the washings were quantitatively transferred to the heteropolyoxoanion solution. Upon introduction of the *in situ* generated $[(C_5Me_5)Rh(CH_3CN)_3]BF_4$ solution, the color of the heteropolytungstate solution changed from clear to red. The resulting solution was refluxed for 1 h under a N_2 stream (with the N_2 inlet needle being above the solution). After cooling to room temperature, the solution was rotavapped to dryness and the remaining solid was dried in vacuum overnight. The solid, still in the round-bottom flask, was dissolved in ca. 2.5−4 mL of CH_3CN, and the solution was then transferred to a 500 mL beaker; the solution at this point of the preparation was deep red. After slow addition of 400 mL of EtOAc ($[(n\text{-}C_4H_9)_4N]BF_4$ is soluble in EtOAc whereas the heteropolyoxoanion complex is not),[24] a red powder composed of large particles precipitated initially, but later an orange powder of smaller particles precipitated. This suspension was stirred in an ice bath for 30 min, after which the precipitate was collected on a medium glass frit. The solid was washed three times with 40 mL of ether, dried on the glass frit by suction, and further dried overnight under reduced pressure. The reprecipitation was repeated twice more, and the product was then dried under vacuum for several hours. Yield: 2.30 g (0.38 mmol, 50%), orange powder.

Anal. Calc for $C_{128}H_{276}N_{10}RhP_2W_{15}Nb_3O_{62}$ (found): C, 25.00 (25.50); H, 4.52 (4.67); N, 2.28 (1.78); Rh, 1.67 (1.72); P, 1.01 (0.94); W, 44.85 (44.73); Nb, 4.53 (4.40); O, 16.1 (17.2); total, 100 (100.9). The elemental analysis and TGA (and GLC and NMR) data require an adduct with three acetonitriles, $[(n\text{-}C_4H_9)_4N]_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]{\cdot}3CH_3CN$.

Solvate analysis: GLC measurements were carried out using a Apiezon L column of 2 m length, at 130 °C, and using a Shimadzu GC-8APT GLC; the results indicated between 3 and 4 CH_3CN of solvation. TG/DTA: weight loss of 2.4% (calc for 3 CH_3CN, 2.0%) below 250 °C. Sample decomposition occurred at 227.8 °C. ^{1}H NMR showed a CH_3CN resonance at δ 2.1 ppm in DMSO-d_6, within error of the δ 2.07 ppm found for authentic CH_3CN in DMSO-d_6.

IR (KBr disk, cm^{-1}) (polyoxometalate region): 1085 (vs), 938 (s), 904 (m), 883 (m), 773 (br, vs), 531 (m).

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(21) (a) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063. (b) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

(22) The instruments and parameters used in acquiring physical data for **1** differ from those listed in the Experimental Section, since this work was performed at Kanagawa University. The crucial parameters and details are as follows: Elemental analyses were obtained from Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were obtained on a Nicolet 510 spectrometer as KBr disks at room temperature. ^{1}H NMR (399.65 MHz), ^{13}C NMR (100.40 MHz), and ^{31}P NMR (161.70 MHz) was recorded in 5 mm o.d tubes, while ^{183}W NMR (16.5 MHz) was recorded in 10 mm o.d. tubes, all on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL EX-400 NMR data processing system. ^{1}H and ^{13}C NMR spectra were referenced to an internal standard of $Si(CH_3)_4$ (TMS). Chemical shifts are reported on the δ scale, and resonances downfield of TMS (δ 0) were recorded as positive. Spectral parameters for ^{1}H NMR: pulse width 6.0 μs; acquisition time 2.05 s; repetition rate 7.00 s; sweep width ±4000 Hz. Spectral parameters for ^{13}C NMR: pulse width 4.7 μs; acquisition time 0.54 s; repetition rate 3.00 s; sweep width ±15 060 Hz. ^{31}P NMR spectra were referenced externally[18b] to 25% H_3PO_4 sealed in a capillary. Chemical shifts on the δ scale are reported as negative for resonances upfield of H_3PO_4 (δ 0). Spectral parameters for ^{31}P NMR: pulse width 6.0 μs; acquisition time 0.41 s; repetition rate 1.61 s; sweep width ±20 000 Hz. ^{183}W NMR (16.50 MHz) were recorded in 10 mm o.d. tubes and referenced to an external standard of saturated Na_2WO_4/D_2O solution by the substitution method. Chemical shifts on the δ scale are reported as negative for resonances upfield of Na_2WO_4 (δ 0). Spectral parameters for ^{183}W NMR: pulse width 24.0 μs; acquisition time 1.64 s; repetition rate 2.84 s; sweep width ±2500 Hz. A 0.25 Hz (^{31}P NMR), 0.50 Hz (^{183}W NMR), 0.25 Hz (^{1}H NMR), or 1.84 Hz (^{13}C NMR) exponential apodization of the FID was applied to all spectra but was removed from any line widths reported herein. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Seiko SSC 5000 TG/DTA 300. TG/DTA were run with a temperature ramp of 10.0 °C/min between 20 and 500 °C.

(23) The $AgBF_4$ (Wako Pure Chemicals) used in this synthesis was stored in *n-hexane; before use, the solvent was evaporated and the* $AgBF_4$ was thoroughly dried in vacuo.

(24) (a) In the case[24b] of $[(C_5Me_5)Rh{\cdot}SiW_9Nb_3O_{40}]^{5-}$, the removal of $[(n\text{-}C_4H_9)_4N]BF_4$ could be monitored in the IR (KBr) by following the disappearance of the ~1084 cm^{-1} band (due to BF_4^-). However, this approach was not feasible for $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$ as the BF_4^- band is obscured by intense P−O stretching bands of the Dawson-type heteropolyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$. (b) Finke, R. G.; Nomiya, K.; Green, C. A.; Droege, M. W. In *Inorganic Syntheses*; Grimes, R. N., Ed.; Wiley & Sons: New York, 1992; Vol. 29, p 239.

^{31}P NMR (22 °C, 60 mM, CD_3CN) δ (no. of P, $\Delta\nu_{1/2}$): -8.2 (1.0, 3.2 ± 1.2 Hz), -13.9 (1.1, 3.2 ± 1.2 Hz).[18b] ^{31}P NMR (22 °C, 60 mM, DMSO-d_6) δ (no. of P, $\Delta\nu_{1/2}$) (Figure 2): -8.4 (1.0, 4.8 ± 1.2 Hz), -14.2 (1.1, 4.4 ± 1.2 Hz).[18b]

^{183}W NMR (22 °C, 100 mM, DMSO-d_6) δ (no. of W, $\Delta\nu_{1/2}$): -130.6 (3.0, 15.4 ± 0.3 Hz), -153.0 (5.7, 12.1 ± 0.3 Hz), -185.5 (6.0, 10.8 ± 0.3Hz). No $^2J_{W-O-W}$ couplings are observed after 100 000 scans.

^{1}H NMR (23 °C, 60 mM, DMSO-d_6) δ: 1.84 (s).

$^{13}C\{^1H\}$ NMR (24 °C, 60 mM, CD_3CN) δ: 95.08, 9.33. $^{13}C\{^1H\}$ NMR (24 °C, 60 mM, DMSO-d_6) δ: 93.31, 8.54.

$[(n\text{-}C_4H_9)_4N]_{5.5}Na_{1.5}[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]$. The synthesis and characterization of this material yield, in even our best efforts to date, a product that is somewhat less pure by ^{31}P NMR and elemental analysis than the analytically pure all-$[(n\text{-}C_4H_9)_4N]$ salt of **1** (*vide supra*). Hence, this particular synthesis is reported only in the supplementary material for the interested reader.

Control Experiment Probing the Detectability of $[(C_5Me_5)Rh(CD_3CN)_3]^{2+}$ in a Solution of 1. In a control experiment, 50 mg (0.0088 mmol) of the mixed $Na^+/[(n\text{-}C_4H_9)_4N]^+$ salt of **1** was dissolved in 1 mL of CD_3CN. In a separate disposable test tube, $[(C_5Me_5)RhCl_2]_2$ (0.010 g, 0.0162 mmol) was slurried in 2 mL of CD_3CN. Solid $AgBF_4$ (0.013 g, 0.067 mmol) was added to the slurry, causing the immediate formation of an AgCl precipitate. The mixture was stirred for 30 min (magnetic stir bar) and filtered through Whatman No. 2 filter paper. The filter paper was washed with 1 mL of CD_3CN, and the washings were combined with the filtrate. The volume of the filtrate was then adjusted to 3.7 mL by addition of CD_3CN. Of this solution, containing $[(C_5Me_5)Rh(CD_3CN)_3]^{2+}$, 0.1 mL of $[(C_5Me_5)Rh(CD_3CN)_3]^{2+}$ (0.000 88 mmol; 10% relative to **1**) was added to the heteropolyoxoanion solution. A ^{1}H NMR spectrum showed a new, separate resonance at δ 1.87, attributable to free $[(C_5Me_5)Rh(CD_3CN)_3]^{2+}$, in addition to the normal ^{1}H NMR resonance (δ 1.82) identified with the C_5Me_5 ligand in $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$. This experiment demonstrates (i) that no free $[(C_5Me_5)Rh(CD_3CN)_3]^{2+}$ has dissociated from **1** in CD_3CN (as, otherwise, it would have been detected) and (ii) that free $[(C_5Me_5)Rh(CD_3CN)_3]^{2+}$ and the $(C_5Me_5)Rh^{2+}$ in **1** are not in rapid exchange on the ^{1}H NMR time scale.

Experiments Demonstrating Non-Ion-Exchangeability of the Supported $[(C_5Me_5)Rh]^{2+}$ in 1. Results of ion (non)-exchange experiments have been reported earlier[10d] but were independently repeated for the present account (i.e., using isolated **1**). Twenty-five grams of macroreticular, strongly acidic resin Dowex 50 × 8−400 (H^+ form; $PSO_3^-H^+$) was placed in a beaker together with ca. 100 mL of 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 50 cm × 2.5 cm (length × diameter) column. A large excess, ca. 30 mL, of 40% $[(n\text{-}C_4H_9)_4N]^+OH^-/H_2O$ was diluted by ca. 1 part in 10 with distilled water, and the solution was 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 resulting $PSO_3^-[(n\text{-}C_4H_9)_4N]^+$ column was then washed with five 100-mL portions of acetonitrile. A solution of ca. 0.5 g of the mixed $Na^+/[(n\text{-}C_4H_9)_4N]^+$ salt of **1** in 10 mL of CH_3CN was passed dropwise through the column. This colored solution passed through the column with no apparent retention, indicating that the $[(C_5Me_5)Rh]^{2+}$ group remains firmly attached to **1**. A previous control experiment demonstrates that authentic, free $[(C_5Me_5)Rh(CH_3CN)_3]^{2+}$ $(BF_4^-)_2$ sticks tightly to, and does not readily elute from, a $PSO_3^-[(n\text{-}C_4H_9)_4N]^+$ anion-exchange column (see p 1702 in ref 10d).

An anion exchange column of identical size was packed with strongly basic resin, Dowex 1 × 2−400 (Cl^- form; $PNR_3^+Cl^-$), and was washed with acetonitrile. A sample of **1** was passed through this column of anion exchange resin 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, indicating that the cationic $[(C_5Me_5)Rh]^{2+}$ group had been rendered anionic by its tight binding to $P_2W_{15}Nb_3O_{62}^{9-}$ in **1**.

Single-Crystal X-ray Structure of 1. Yellow prismatic crystals were grown by vapor diffusion of acetone into an acetonitrile solution of **1** over a period of 6 months. A partial elemental analysis of crystalline material of composition $[(n\text{-}C_4H_9)_4N]_6Na[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]\cdot 10CH_3CN\cdot 10Me_2CO$ (as determined by single-crystal X-ray crystallographic structural analysis; *vide infra*) gave the following results. Anal. Calc (found for the single crystals): C, 27.56 (26.12); H, 4.76 (5.03); N, 3.30 (1.82); Na, 0.34 (0.22); Rh, 1.51 (1.41); P, 0.91 (0.95). Several crystals were transferred from solution to Apiezon grease and then into Lindemann glass capillaries which were flame-sealed. They diffracted weakly with considerable background, although the peak profiles were acceptable. The orientation matrix and cell dimensions for the crystal selected were obtained initially from 25 reflections in the range 10.9° ≤ 2 Θ ≤ 13.5°, and improved values were then obtained from 25 relatively strong reflections in the range 21° ≤ 2Θ ≤ 30°. Measurement of the intensities of equivalent reflections showed the Laue symmetry to be $6/m$. A summary of crystal data is given in Table 1, together with the residuals. A complete table containing particulars of data collection and structure refinement is included in the supplementary material. The Laue symmetry, the only systematic absence ($00l$ for l odd), and the centric distribution of intensities indicated that the space group was $P6_3/m$. The intensities of three standard reflections fell by *ca.* 14% during data collection (48 h). A decay correction was therefore applied.

The three independent W atoms were located by use of direct methods (*SHELXS*[25]) at positions consistent with the stronger vector peaks of the Patterson function. The Rh, P, and O atoms of the anion were located in successive difference syntheses. The crystallographic site symmetry of the anion was $3/m$. The Rh atom lies on the 3-fold axis of the $P_2W_{15}Nb_3O_{62}$ unit. The only possible element of symmetry of the anion was therefore a 3-fold axis (if the C_5Me_5 group was disregarded), so the anion was taken to have two equally-weighted orientations related by the crystallographic mirror plane. A model refined satisfactorily in which the Rh site on the 3-fold axis was half-occupied and the cap heavy atom site [W(3)] was occupied by a composite atom $Nb_{0.5}W_{0.5}$. When the starting point was an ordered set of atoms, $RhNb_3W_{15}$, in space group $P6_3$ the less unsatisfactory model had the Rh on the Nb_3 rather than on the W_3 cap, but not all the oxygen atoms could be located; least-squares refinement showed many strong correlations between corresponding parameters of atoms that would be equivalent in $P6_3/m$, and the thermal parameters for some pairs of atoms (*e.g.*, the P atoms) became improbably different. These observations were taken to mean that the centrosymmetric but disordered model was the correct one. *Ab initio* structure solution in space group $P\bar{3}$ (*i.e.*, with the crystallographic mirror plane omitted but the inversion center retained) showed the anion at the same position with noncrystallographic mirror symmetry about the plane $z = 0.25$ and with the same disorder of the Rh and Nb atoms. An empirical absorption correction (*DIFABS*[26]) was applied after convergence of isotropic refinement. The refinement was continued with anisotropic parameters for the heavy atoms. A difference synthesis showed numerous weak peaks in the interanion spaces. These comprised most of each of two independent $[(n\text{-}C_4H_9)_4N]^+$ ions, in one of which the N atom and two $n\text{-}C_4H_9$ groups lay on a crystallographic mirror plane. Also, two peaks at 2.14 and 2.20 Å from Rh appeared to be fractional carbon atoms of the disordered C_5 ring. Attempts to refine the C and N atoms with various combinations of site occupancy factors led to some large B_{iso} values and poor bond lengths and to only slight reductions in the residuals. Consequently, these atoms were all fixed at their original positions in the last cycles of refinement with B_{iso} set at 8 Å[26] and with an S.O.F. of $^1/_3$ for the C atoms on Rh. The *TEXSAN* program suite,[27] incorporating scattering factors from ref 28, was used in all calculations.

The anion lies at a site of crystallographic point symmetry $3/m$ (C_{3h}) in two equally-related orientations related by the mirror plane. The Rh atom is constrained to lie on the crystallographic 3-fold axis, although a small apparent anisotropy of motion (rms amplitude 0.21 Å parallel to the axis and 0.31 Å normal to it) may imply that it is actually disordered over three sites close to the axis. It is bonded to three oxygen atoms [Rh−O 2.06(3) Å] which are each also shared between two composite M ($W_{0.5}Nb_{0.5}$) atoms of the capping set of three edge-sharing MO_6 octahedra (note that the disorder makes it uncertain, *on the basis of the crystallography alone*, whether the Rh is actually

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(25) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175-189.

(26) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. C* **1983**, *39*, 158.

attached to a Nb_3 or to a W_3 cap). The forcing of the 3-fold crystal axis on the 5-fold symmetry of the C_5Me_5 group leads to the prediction that the ring atoms will appear as one-third atoms 24° apart, and so will the Me carbons; because of the additional end-for-end disorder of the anion, it is not surprising that even the ring atoms are not clearly defined, although two peaks lying very nearly in the same plane normal to the C_3 axis could be distinguished (see above). This situation is in contrast with that found for $[(n\text{-}C_4H_9)_4N]_2[(C_5Me_5)Rh{\cdot}Nb_2W_4O_{19}]$, space group $P1$, where the C_5Me_5 ligand had a single, well-defined location and orientation.[29] As regards the rest of the anion, the heavy atom frameworks of the two orientations coincide closely and so do the sets of oxygen and of P atoms. This seems clear from the small apparent anisotropy of the W atoms, and from the close similarity of $W{\cdots}W$ distances to those in the $P_2W_{18}O_{62}{}^{6-}$ and $P_2Nb_3W_{15}O_{62}{}^{9-}$ anions.[30,31] On the assumption of $3m$ (C_{3v}) symmetry for the anion, corresponding bond lengths differ from the mean values by around 1σ. The coincidence of like atoms in the two orientations is surprising in view of the presence of the $[(C_5Me_5)Rh]^{2+}$ group on one cap only and seems to be associated with the presence of a large amount of highly disordered (non-hydrogen bonding) solvent[32] and the preponderance of noncoordinating $[(n\text{-}C_4H_9)_4N]^+$ rather than Na^+ cations (supplementary material, Figure G).

^{17}O NMR Studies and Attempted Synthesis of ^{17}O-Enriched $[(n\text{-}C_4H_9)_4N]_7[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3{}^{17}O_6O_{56}]$ Starting from $[(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}$. ^{17}O-enriched $[(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}$ (1.0 g, 0.159 mmol), prepared as described elsewhere,[11e] was placed in a 50 mL round-bottom flask (equipped with a magnetic stir bar) and dissolved in 3 mL of CH_3CN, resulting in a clear solution. In a separate disposable test tube, $[(C_5Me_5)RhCl_2]_2$ (0.0491 g, 0.0795 mmol) was slurried in 4 mL of CH_3CN. Solid $AgBF_4$ (0.062 g, 0.318 mmol) was added to the slurry, causing the immediate formation of an AgCl precipitate. The mixture was stirred for 30 min (magnetic stir bar) and filtered through Whatman No. 2 filter paper, and the filtrate was then directly introduced into the clear, stirred solution of $[(n\text{-}C_4H_9)_4N]_{(9-x)}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}$. Upon introduction of the *in situ* generated $[(C_5Me_5)Rh(CH_3CN)_3]BF_4$ solution, the color of the heteropolytungstate solution changed from clear to orange-red. After being refluxed for 1 h, the solution was evacuated to dryness, and the remaining solid was dried under vacuum overnight. The solid was dissolved in 2 mL of CD_3CN, and the solution was transferred into an NMR tube equipped with a J. Young airtight valve and placed in the NMR probe. (^{17}O NMR, 48.967 MHz, CD_3CN, 22 °C) (supplementary material, Figure F) δ: 761, 520, 186. The observed ^{17}O NMR spectrum is characteristic[11e] of the starting material $[(n\text{-}C_4H_9)_4N]_{(9-x)}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}$, indicating that little to no reaction of the organometallic fragment $[(C_5Me_5)Rh(CH_3CN)_3]^{2+}$ with the support-heteropolyoxoanion $H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}{}^{9-x}$ has occurred. This failure to yield the supported ^{17}O-enriched heteropolyoxoanion $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3{}^{17}O_6O_{56}]^{7-}$ is not surprising, given the well-documented[11e] protonation of the bridging-oxygen binding sites ($Nb_2O\text{-}H^+$, δ 186) in the ^{17}O-enriched starting material $[(n\text{-}C_4H_9)_4N]_{(9-x)}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}$, effectively preventing binding of the organometallic moiety to the support. [However, a ^{31}P NMR spectrum (supplementary material, Figure F) of this reaction mixture showed, in addition to two major resonances at δ -7.2 and -14.2 that are characteristic of $P_2W_{15}Nb_3O_{62}{}^{9-}$, two smaller resonances at δ -8.2 and -13.9. These latter two signals indicate that indeed some $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3{}^{17}O_6O_{56}]^{7-}$ has formed during the course of the reaction. The extent of this incomplete reaction is, however, insufficient to allow for any meaningful accumulation of ^{17}O NMR data.] An experiment with just enough $[(n\text{-}C_4H_9)_4N]OH$ added to remove the residual H^+ attached to $H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}{}^{x-9}$ is an important experiment, especially in light of the results presented herein and our early problems in this work with low Rh and Ru analyses. However, this experiment is being pursued as part of other studies.[33]

In summary, this important control experiment shows that the synthesis of **1** (and, by inference, presumably other supported-organometallic complexes of $P_2W_{15}Nb_3O_{62}{}^{9-}$) is very sensitive to protonation at the Nb_2O bridging oxygens of the "$Nb_3O_9{}^{3-}$" minisurface support site.

$[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]$, 2. The preparation described herein yields a complex with mixed countercation composition from which the contaminating $[(n\text{-}C_4H_9)_4N]^+BF_4{}^-$ is removed by repeated reprecipitation with ethyl acetate. During the course of this study, we discovered that the use of fully deprotanated $P_2W_{15}Nb_3O_{62}{}^{9-}$, minimizing the presence of protonated $H_xP_2W_{15}Nb_3O_{62}{}^{x-9}$, is the key to obtaining analytically pure **2**. The fully deprotanated $P_2W_{15}Nb_3O_{62}{}^{9-}$ starting material was synthesized by an even further refined procedure,[33] when compared to our previously reported procedure,[10d,13a] and will be reported elsewhere.[33]

In the two elemental analyses reported at the end of this section, fully deprotonated $P_2W_{15}Nb_3O_{62}{}^{9-}$ was employed as the starting material for the first data set reported; the second data set was obtained using $P_2W_{15}Nb_3O_{62}{}^{9-}$ prepared by our previoulsy published procedure.[10d,13a] In the drybox, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (13.1 g, 2.09 mmol) was placed in a 100 mL round-bottom flask and dissolved in 40 mL of CH_3CN. If this solution was cloudy, it was filtered through a folded filter paper (Whatman No. 2). The clear filtrate was collected in a 200 mL round-bottom flask equipped with a stir bar. The filter paper was washed with a small amount of CH_3CN, and the washings were also combined with the above filtrate. The combined filtrate was stirred. By this step, a total of ca. 50 mL of CH_3CN was used. Approximately 40 mL of CH_3CN was placed in a separate graduated cylinder, a portion (ca. 15 mL), of which was used as a solvent for the reaction of $[Ru(C_6H_6)Cl_2]_2$ with 4 equiv of $AgBF_4$. About 15 mL of CH_3CN was put into a test tube containing $[Ru(C_6H_6)Cl_2]_2$ (0.5255 g, 1.05 mmol) and the resulting reddish-green suspension was stirred. To this suspension was added a solution of $AgBF_4$ (0.8180 g, 4.21 mmol) dissolved in a few milliliters of CH_3CN, resulting in the immediate formation of an AgCl precipitate. The white precipitate of AgCl was removed by filtration with a folded filter paper, and the filtrate was directly introduced into the clear, well-stirred solution of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$. [The AgCl precipitate on the filter was washed several times with small amounts of CH_3CN (a total of ca. 20 mL of CH_3CN was used for this washing), and the washings were also added to the above stirred, light red solution.] After this solution was stirred for 15 min, solid $NaBF_4$ (0.6892 g, 6.28 mmol) was added. Stirring was then continued until all of the $NaBF_4$ had dissolved. The resulting reddish solution was filtered through a folded filter paper and the filtrate was collected in a 200 mL round-bottom flask. After being refluxed for 1 h, this solution was rotavapped to dryness. The residual orange-yellow solid (which contains $[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$ and 4 equiv of $[(n\text{-}C_4H_9)_4N]BF_4$) was dissolved in ca. 10 mL of CH_3CN, and the solution was transferred to a 600 mL beaker using a polyethylene pipet. To this solution was added 400 mL of EtOAc with slow stirring using a magnetic stir bar ($[(n\text{-}C_4H_9)_4N]BF_4$ is soluble in EtOAc whereas the heteropolyoxoanion complex is not), after which the stirring was continued for 30 min. The orange-yellow powder which precipitated was collected on a medium glass frit and washed twice with 30 mL of

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(27) *TEXSAN: TEXRAY Program for Structure Analysis*, Version 5.0; Molecular Structure Corp.: 3200A Research Forest Drive, The Woodlands, TX 77381, 1989.

(28) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71, 148.

(29) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. $[(C_5Me_5)Rh{\cdot}Nb_2W_4O_{19}]^{2-}$ lacks any crystallographically-required symmetry and contains a disordered M_6O_{19} core. Here, the $[(C_5Me_5)Rh]^{2+}$ group has no preference as to the point of attachment to the polyoxoanion, and the orientation of the whole anion is determined by packing considerations.

(30) D'Amour, H. *Acta Crystallogr., Sect. B* **1976**, *32*, 729.

(31) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Weakley, T. J. R. *Acta Crystallogr., Sect. C* **1990**, *C46*, 1592.

(32) (a) Countercation and lattice solvate disorder are common in heteropolyoxoanion structure determinations; often, some or even all of the cations or lattice solvates cannot be located by X-ray structure analysis.[32b] (b) Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1235. See footnote 13 and references therein.

(33) Weiner, H.; Finke R. G. Manuscript in preparation. One key improvement (as it relates to the present work) is that great care is being taken to completely remove all protons present in the precursor (nominal formula $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$) and to completely deprotonate any $H_xP_2W_{15}Nb_3O_{62}{}^{9-x}$ present (using a phenolphtalein end-point titration) which otherwise interferes (as shown herein and elsewhere[11f,13b]) with the binding of the organometallic moiety, $[(C_6H_6)Ru]^{2+}$, to the heteropolyoxoanion-support, $P_2W_{15}Nb_3O_{62}{}^{9-}$.

ether. The filtrate was light yellow and cloudy. The reprecipitation was repeated twice more, and the product was then dried under vacuum at room temperature for several hours. Yield: 8.4 g (1.6 mmol, 76%), red-orange powder. Note that this preparation has been repeated independently more than 10 times by two of us, primarily as we sought to solve a 0.93% low Ru analysis problem in our earlier preparations. The elemental analysis and the ^{31}P NMR data below are for our most recent and best syntheses (as detailed above).

Anal. Calc (found) using fully deprotonated[33] $P_2W_{15}Nb_3O_{62}^{9-}$ [second analysis for an independent preparation, *but* using $P_2W_{15}Nb_3O_{62}^{9-}$ prepared by our previously published procedure,[10d,13a] results which show a reproducible problem with a low Ru analysis]: C, 17.25 (17.31) [17.28]; H, 3.12 (3.23) [3.27]; N, 1.30 (1.44) [1.42]; Na, 1.07 (1.09) [1.24]; Ru, 1.87 (1.84) [0.94]; P, 1.14 (1.09) [1.14]; W, 50.6 (49.1) [50.8]; Nb, 5.14 (5.82) [5.06]; O, 18.3 (18.8) [17.0]; total, 100.0 (99.61) [98.17].

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, Figure C), $\bar{M}_w$: calc for **2**, 5418; found, 6960 ± 600.

IR (KBr disk, cm^{-1}) (supplementary material, Figure D) (polyoxometalate region): 1088, 1049, 1010, 947, 915, 896, 768. The IR resonances for $[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ (in comparison to $P_2W_{18}O_{62}^{6-}$)[34] at 947 (960), 915 (912), and 768 (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 (945 cm^{-1}), the W−O−W bridges between corner-sharing octahedra (913 cm^{-1}), and the W−O−W bridges between edge-sharing octahedra (773 cm^{-1}). Resonances at 1088 (1090), 1049 (1022), and 1010 (975) cm^{-1} are attributed to PO_4 stretching vibrations.

^{31}P NMR (25 °C, 44.5 mM, CD_3CN, with 3 equiv of Kryptofix 2.2.2) δ (no. of P, $\Delta\nu_{1/2}$) (Figure 4): −7.7 (1.0 ± 0.1, 3.0 ± 0.8 Hz), −13.3 (1.0 ± 0.1, 3.0 ± 0.8 Hz).[18b] ^{183}W NMR (25 °C, 89.0 mM, CD_3CN, with 3 equiv of Kryptofix 2.2.2.) δ (no. of W, $\Delta\nu_{1/2}$) (Figure 5): −125.4 (3.0 ± 0.2, 11.1 ± 0.5 Hz), −148.0 (6.0 ± 0.3, 10.4 ± 0.5 Hz), −180.2 (6.0 ± 0.3, 10.9 ± 0.5 Hz). ^1H NMR (25 °C, 15.7 mM, CD_3CN) δ: 5.99 (s).

Experimental Variations in the Synthesis of 2. In three control experiments which lead to the improved synthetic procedure reported above (specifically, experiments designed to improve the low percent-ruthenium obtained in early preparations), several parameters in the synthesis and isolation procedure (vide supra) were examined and varied. Specifically, these were as follows (note that (i) and (ii) were performed with $P_2W_{15}Nb_3O_{62}^{9-}$ prepared by our published procedure[10d,13a]): (i) addition of an excess of $[(C_6H_6Ru(CH_3CN)_3]^{2+}$ (1.3 equiv, 30% excess) to see if this improved the early low ruthenium analyses (supplementary material, Figure J); (ii) prolonged heating under reflux (20 h instead of 2 h) to test for substitution inertness of d^6 Ru^{II} as a possible cause (supplementary material, Figure J); and (iii) use of starting material, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, that has been prepared by a new and improved procedure (supplementary material, Figure J) to rule out residual protonation of the support polyoxoanion $H_xP_2W_{15}Nb_3O_{62}^{9-x}$.[33] These variation studies show that the addition of an excess of $[(C_6H_6Ru(CH_3CN)_3]^{2+}$ or longer reflux times do not markedly improve the appearance of the ^{31}P NMR product spectra in terms of impurities and unreacted $P_2W_{15}Nb_3O_{62}^{9-}$ present. *However, it was through these experiments that we discovered that the use of fully deprotonated* $P_2W_{15}Nb_3O_{62}^{9-}$, *minimizing the presence of protonated* $H_xP_2W_{15}Nb_3O_{62}^{x-9}$, *is the key to obtaining analytically pure 2.*[33] Using this fully deprotonated material, the ^{31}P NMR of **2** shows the presence of approximately 6% unreacted $P_2W_{15}Nb_3O_{62}^{9-}$ (Figure 4) compared to typically 15−20% in all other previously attempted preparations.

Control Experiment Testing the Solubility of $[(C_5Me_5)Rh(CH_3CN)_3]^{2+}$ and $[(C_6H_6)Ru(CH_3CN)_3]^{2+}$ in Ethyl Acetate/Acetonitrile. In order to test whether or not the low percent rhodium and percent ruthenium elemental analyses, obtained in early syntheses of the mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ complexes of **1** and **2**, were due to solubility of the organometallic fragments in the precipitating solvent mixture of ethyl acetate/acetonitrile (i.e., possibly due a putative dissociation of the organometallic fragments from **1** and **2**, followed by their selective precipitation), the following control experiments were performed. In two separate experiments 80 mL of ethyl acetate was added to a solution of $[(C_5Me_5)Rh(CH_3CN)_3]^{2+}$ (0.16 M) and $[(C_6H_6)Ru(CH_3CN)_3]^{2+}$ (0.2 M) in 2 mL of acetonitrile. ($[(C_5Me_5)Rh(CH_3CN)_3]^{2+}$and $[(C_6H_6)Ru(CH_3CN)_3]^{2+}$ were prepared by reaction of $[(C_5Me_5)RhCl_2]$ and $[(C_6H_6)RuCl_2]$ with $AgBF_4$ in acetonitrile, respectively.) *No precipitate was formed upon addition of the ethyl acetate*; hence, limited solubility of the organometallic fragments in a mixture of ethyl acetate/acetonitrile, which is used in the purification and isolation of **1** and **2**, can be ruled out as the cause for the low percentage of rhodium and ruthenium in the elemental analysis (in the early syntheses of the mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ complexes of **1** and **2**). Restated, this control demonstrates that the mixed $[(n\text{-}C^4H_9)_4N]^+/Na^+$ salt reprecipitation works as desired, without "knocking-off" the supported organometallic moiety.

Control for the Potential Light Sensitivity of 2.[17] In the drybox, a solution of 0.5 g (0.1 mmol) of **2** in 1 mL of acetonitrile-d_3 was placed in an airtight J. Young NMR tube. [The sample of **2** used in this experiment was synthesized and isolated under an inert nitrogen atmosphere in a Vacuum Atmospheres drybox while precautions were taken to minimize light exposure (i.e., covering the reaction flask with aluminum foil and performing the isolation under dim lighting only).] The NMR tube was removed from the drybox and was exposed to the laboratory neon lighting for 24 h. A ^{31}P NMR spectrum subsequently acquired remained unchanged when compared to the ^{31}P NMR spectrum collected on the same sample solution prior to light exposure. This control experiment shows that **2** is not light sensitive[17] under the conditions of the experiment and, therefore, can be handled without taking additional precautions to minimize exposure to laboratory lighting.

Control for the Potential Air-Sensitivity of 2. In a control experiment, a solution of 0.5 g (0.1 mmol) of **2** in 1 mL of acetonitrile-d_3 was placed in a 2 dram vial equipped with a magnetic stirbar and vigorously stirred for 12 h under air. During the experiment, acetonitrile-d_3 was added as needed to replenish the solvent lost due to evaporation and to maintain a solution volume of approximately 2 mL. A ^{31}P NMR spectrum subsequently acquired remained unchanged when compared to the ^{31}P NMR spectrum collected on the same sample solution of **2** prior to air exposure. The sample of **2** used in this experiment was synthesized and isolated under an inert nitrogen atmosphere in the drybox. In summary, this control experiment shows that **2** is not air sensitive under the conditions of the experiment and as such can be handled without taking additional precautions to minimize exposure to air, *despite* the fact that it is an oxidation catalyst for cyclohexene oxidation using O_2 (a fact that has important mechanistic implications).[17b]

Experiments Demonstrating Non-Ion-Exchangeability of 2. Results of ion (non)-exchange experiments have been reported earlier[10d] but were independently repeated with the isolated complexes. In the drybox, 25 g of the macroreticular, strongly acidic resin Dowex 50 × 8−400 (H^+ form; $PSO_3^-H^+$) was placed in a beaker together with ca. 50 mL of degassed water. The resin was swirled for ca. 1 min, followed by decantation of the water. This process was repeated until the aqueous phase was clear and colorless. The resin was then packed onto a 50 cm × 2.5 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 the solution was 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 resulting $PSO_3^-[(n\text{-}C_4H_9)_4N]^+$ column was then washed with five 50-mL portions of dry acetonitrile. A solution of ca. 0.5 g of **2** in 10 mL dry acetonitrile was passed dropwise through the column. This colored solution passed through the column with no apparent retention, indicating that the $[(C_6H_6)Ru]^{2+}$ group remained firmly attached to **2**. Previously, a control experiment demonstrated that authentic, free $[(C_6H_6)Ru(CH_3CN)_3]^{2+}(BF_4^-)_2$ does indeed stick tightly to, and does not readily elute from, a $PSO_3^-[(n\text{-}C_4H_9)_4N]^+$ ion-exchange column (see p 1703 elsewhere in ref 10d).

An anion-exchange column of identical size was packed with strongly basic resin, Dowex 1 × 2−400 (Cl^- form), and was washed with dry acetonitrile. A sample of **2** was passed through this column

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

of anion-exchange resin 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, indicating that the cationic $[(C_6H_6)Ru]^{2+}$ group has been rendered anionic by its tight binding to $P_2W_{15}Nb_3O_{62}{}^{9-}$ in **2**.

Control Experiment Probing the Detectability of $[(C_6H_6)Ru(CD_3CN)_3]^{2+}$ in a Solution of 2. In a control experiment, 50 mg (0.0092 mmol) of **2** was dissolved in 1 mL of CD_3CN. In a separate disposable test tube, $[(C_6H_6)RuCl_2]_2$ (0.008 g, 0.0162 mmol) was slurried in 2 mL of CD_3CN. Solid $AgBF_4$ (0.013 g, 0.067 mmol) was added to the slurry, causing the immediate formation of an AgCl precipitate. The mixture was stirred for 30 min (magnetic stir bar) and filtered through Whatman No. 2 filter paper. The filter paper was washed with 1 mL of CD_3CN, and the washings were combined with the filtrate. The volume of the filtrate was then adjusted to 3.7 mL by addition of CD_3CN. Of this solution, containing $[(C_6H_6)Ru(CD_3CN)_3]^{2+}$, 0.11 mL (0.000 92 mmol; 10% of $[(C_6H_6)Ru(CD_3CN)_3]^{2+}$ relative to **2**] was added to the heteropolyoxoanion solution. A ^1H NMR spectrum showed a new, separate resonance at δ 6.20, attributable to $[(C_6H_6)Ru(CD_3CN)_3]^{2+}$, in addition to the ^1H NMR resonance (δ 5.99) identified with the C_6H_6 ligand in $[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$. These results demonstrate that (i) no $[(C_6H_6)Ru(CD_3CN)_3]^{2+}$ has dissociated from **2** in CH_3CN (as, otherwise, it would have been detected) and (ii) the $[(C_6H_6)Ru]^{2+}$ moiety in **2** and free $[(C_6H_6)Ru(CD_3CN)_3]^{2+}$ are not in rapid exchange with one another on the ^1H NMR time scale.

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Supplementary Material Available: Textual presentation of the preparation of $[(n\text{-}C_4H_9)_4N]_{5.5}Na_{1.5}[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$, sedimentation-equilibrium molecular-weight plot for **1** (Figure A), IR spectrum (KBr; cm^{-1}) of $[(n\text{-}C_4H_9)_4N]_{5.5}Na_{1.5}[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ (Figure B), sedimentation-equilibrium molecular-weight plot for **2** (Figure C), expanded IR (KBr; cm^{-1}) of $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]$ (Figure D), text describing the ^{17}O NMR experiments for **1**, ^{17}O and ^{31}P NMR spectra obtained after attempted ^{17}O-enrichment of **1** (Figure E), ^{17}O and ^{31}P NMR spectra obtained following the attempted synthesis of ^{17}O-enriched **1** starting from $[(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}$ (Figure F), packing diagram for the single-crystal X-ray structure of **1** (Figure G), ^{31}P NMR spectrum of the mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ salt of **1** in CD_3CN (Figure H), ^{183}W NMR spectrum of the mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ salt of **1** (Figure I), ^{31}P NMR spectra (CD_3CN, with 3 equiv of Kryptofix 2.2.2. added) of $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]$ showing the presence of up to 20% unreacted $P_2W_{15}Nb_3O_{62}{}^{9-}$ in early preparations (Figure J), calculated percentages of various countercation compositions for the elemental analysis (all elements) of $[(n\text{-}C_4H_9)_4N]_{5.5}Na_{1.5}[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]$ (Table A), calculated percentages of various countercation compositions for the elemental analysis (all elements) of $[(n\text{-}C_4H_9)_4N]_{4.5}Na_{2.5}[(C_6H_6)Ru{\cdot}P_2W_{15}Nb_3O_{62}]$ (Table B), details of the X-ray single-crystal structure data collection and refinement, distances, unrefined coordinates of N and C atoms, anisotropic thermal parameters, and least-squares planes (Tables C−H) (21 pages). Ordering information is given on any current masthead page.

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