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Polyoxoanions as Soluble Metal Oxide Analogs.[1] Synthesis and Characterization of the Polyoxoanion-Supported Iridium(I) Complex $(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}{}^{6-}$

Yin Lin, Kenji Nomiya, and Richard G. Finke[*,†]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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The synthesis and characterization of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$, a Keggin polyoxoanion-supported $Ir(1,5\text{-COD})^+$ complex, is reported (1,5-COD = 1,5-cyclooctadiene). The complex was characterized by means of an elemental analysis (all elements), ultracentrifugation solution molecular-weight measurements, and ^1H, ^{13}C, and ^{183}W NMR and IR spectroscopies in both weakly coordinating and strongly coordinating solvents. The solvent-dependent NMR results demonstrate that, in weakly coordinating solvents, a C_s symmetry complex obtains. On the basis of literature precedent, two most plausible, slightly different C_s symmetry structures are proposed, one involving $Ir(1,5\text{-COD})^+$ bonding to two ONbW bridging oxygens and one OW_2 bridging oxygen and another involving the same two ONbW bridging oxygens but then one ONb terminal oxygen. The significance of this work is 3-fold: it describes the first Keggin-type polyoxoanion-supported $Ir(1,5\text{-COD})^+$ complex; it describes the first Keggin anion-supported complex that also serves as an effective catalyst precursor; and it sets the stage for the first detailed comparison of the catalytic properties of two different polyoxoanion-supported catalysts of any type, namely the present Keggin anion-based complex $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ and the Wells–Dawson anion-based complex $(Bu_4N)_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ we reported previously.

Polyoxoanions[2] are soluble metal oxide clusters that resemble[3a] discrete fragments of the solid metal oxides widely used as supports for transition metal heterogeneous catalysts. Polyoxoanions offer, therefore, an unsurpassed opportunity to prepare oxide-supported "designer catalysts" where atomic-level structural, kinetic, and mechanistic information can be acquired, something virtually impossible for traditional solid-oxide-supported transition metal heterogeneous catalysts (even given the powerful surface-science tools now available[3b]). For these reasons, the preparation and unequivocal characterization of polyoxoanion-support systems and their transition metal supported (pre)catalysts are of interest.

The preparation of polyoxoanion-supported (pre)catalysts requires custom-made polyoxoanions[4] possessing sufficient surface basicity to covalently attach organotransition metal cations. Toward this end, we have prepared a series of new Keggin and Wells–Dawson polyoxoanions in which three adjacent tungstens have been regiospecifically replaced by three lower-valent elements, including Nb and V.[5-7] The resulting trisubstituted Keggin type and Wells–Dawson type polyoxoanions, $SiW_9M_3O_{40}{}^{7-}$ and $P_2W_{15}M_3O_{62}{}^{9-}$ (M = Nb, V; Figures 1 and 2), possess three additional negative charges; this provides them with a surface-oxygen basicity approaching that of OH^- (OH^- is required to deprotonate their conjugate acids[5,6]). The resultant polyoxoanions have been shown to bind covalently to organometallic cations such as $Rh(C_5Me_5)^{2+}$, $CpTi^{3+}$, and $Ru(C_6H_6)^{2+}$.[5-8] These custom-designed polyoxoanions also have the advantages of high symmetry plus a high solubility in organic solvents (as their Bu_4N^+ salts), features which greatly aid both their regiospecific support

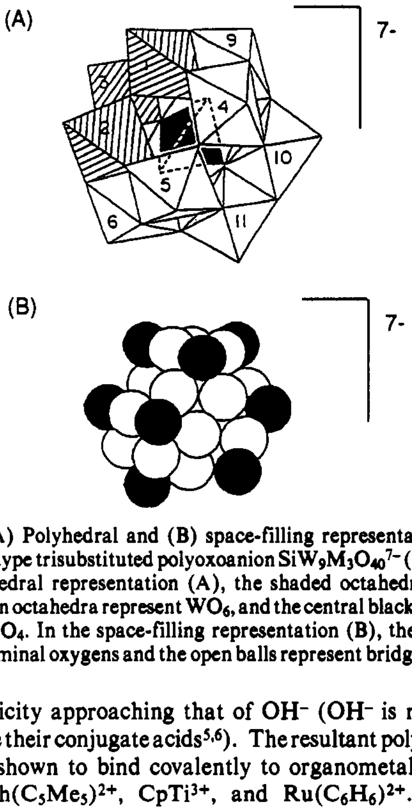

Figure 1. (A) Polyhedral and (B) space-filling representations of the A-β-Keggin type trisubstituted polyoxoanion $SiW_9M_3O_{40}{}^{7-}$ (M = Nb,V). In the polyhedral representation (A), the shaded octahedra represent MO_6, the open octahedra represent WO_6, and the central black tetrahedron represents SiO_4. In the space-filling representation (B), the black balls represent terminal oxygens and the open balls represent bridging oxygens.

[†] Present address: Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

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(1) For a review of earlier work in this series, see: Finke, R. G. In *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, 1993.

(2) (a) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (b) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.

(3) (a) Baker, L. C. W. In *Advances in the Chemistry of Coordination Compounds*; Kirschnerr, S., Ed.; MacMillian: New York, 1961; p 604. (b) For an excellent example of state-of-the-art structural characterization of oxide-supported heterogeneous catalysts, and for what structural and mechanistic information is and is not possible from EXAFS distance information, for example, see: Gates, B. *Chem. Tech.* **1989**, 173. Lamb, H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

(4) Traditional, commercially available polyoxoanions, such as the Keggin $SiW_{12}O_{40}{}^{4-}$ or $PW_{12}O_{40}{}^{3-}$ or the Wells–Dawson $P_2W_{18}O_{62}{}^{6-}$, do not covalently bind transition metal cations due to their very *nonbasic* nature. Pope's classic paper demonstrates this lack of surface-oxygen negative charge or basicity in polyoxoanions such as $XMo_{12}O_{40}{}^{n-}$ (X = P, Si), a lack of basicity which parallels that in ClO_4^-: Barcza, L.; Pope, M. T. *J. Phys. Chem.* **1973**, *77*, 1795.

(5) (a) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274–7. (b) Finke, R. G.; Nomiya, K.; Green, C. A.; Droege, M. W. In *Inorganic Syntheses*; Grimes, R. N., Ed.; John Wiley & Sons: New York, 1992; Vol. 29, p 239.

(6) (a) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692–704. (b) For a discussion of this "cation problem", see footnote 8 elsewhere.[6a]

(7) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947–60.

(8) Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175–8.

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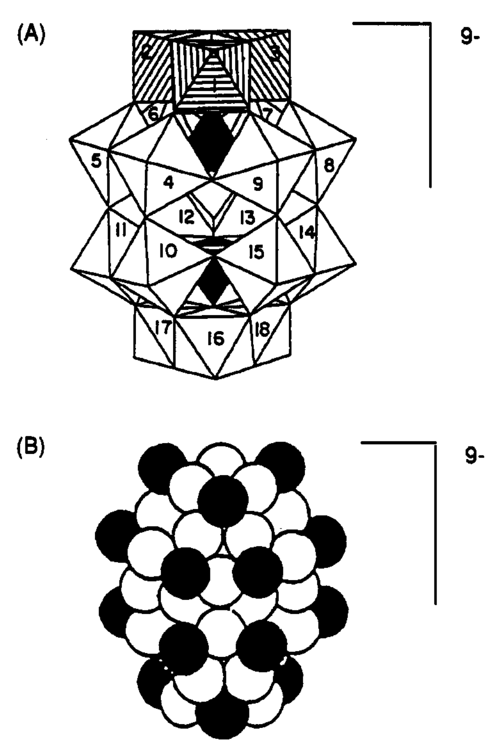

Figure 2. (A) Polyhedral and (B) space-filling representations of the B-α-Dawson type trisubstituted polyoxoanion $P_2W_{15}Nb_3O_{40}^{9-}$ (M = Nb, V). In the polyhedral representation (A), the shaded octahedra represent MO_6, the open octahedra represent WO_6, and the central black tetrahedron represents PO_4. In the space-filling representation (B), the black balls represent terminal oxygens and the open balls represent bridging oxygens.

properties and their spectroscopic identification in solution. The only limitation to date of these high-charge $SiW_9M_3O_{40}^{7-}$ and $P_2W_{15}M_3O_{62}^{9-}$ polyoxoanion support materials is that at least their Bu_4N^+ salts, not surprisingly, only rarely crystallize in a form suitable for single-crystal X-ray diffraction structural analyses. While this limitation can in principle be overcome simply by changing the countercations, doing so is tedious and dependent on choosing the proper cation or cation combinations; hence, a general solution to this "cation problem"[6b] remains to be accomplished.

It is worth noting that the first example of a polyoxoanion-supported catalyst has now been reported,[9] the catalyst derived during the oxidation of cyclohexene with O_2 while using the $P_2W_{15}Nb_3O_{62}^{9-}$-supported $Ir(1,5\text{-}COD)^+$ complex $[(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ (1,5-COD = 1,5 cyclooctadiene), Figure 3, as a precatalyst.[10] That work is unique in that extensive mechanistic studies demonstrate that it provides the only *bona fide* polyoxoanion-supported catalyst reported to date[10] from among more than a dozen polyoxoanion-supported complexes that have appeared in the literature over the last 10 years.[11,12]

An important goal in oxide-supported catalysis is to learn how different supports influence the catalytic activity of an otherwise identical metal center. Polyoxoanion-supported catalysts offer the opportunity to vary the oxide support while retaining a knowledge of the atomic-level bonding in at least the catalyst precursor; such information should eventually allow the molecular level fine-tuning now common in homogeneous catalysis to be applied to oxide-supported catalysts as well.

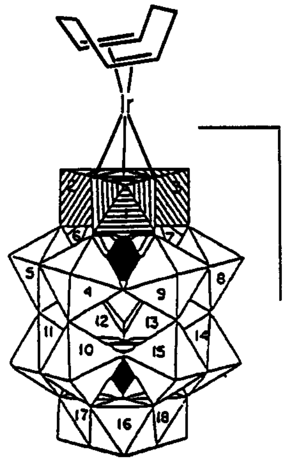

Figure 3. Polyhedral representation of the proposed average C_{3v} (pseudo) symmetry structure suggested for $(1,5\text{-}COD)Ir\cdot P_2W_{15}Nb_3O_{62}^{8-}$, as established[9] by ^{17}O and ^{183}W NMR spectroscopy. Note that $Ir(1,5\text{-}COD)^+$ is attached to three ONb_2 bridging oxygens.

Herein we detail the synthesis and characterization of a Keggin-type $SiW_9Nb_3O_{40}^{7-}$ polyoxoanion-supported $Ir(1,5\text{-}COD)^+$ complex, $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$. This work is the required first step underlying a comparison of the catalytic activity of the present Keggin-type $SiW_9Nb_3O_{40}^{7-}$ vs the Wells–Dawson-type $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion-supported $Ir(1,5\text{-}COD)^+$ complexes. Such a comparison of two polyoxoanion catalysts differing only in the metal-support interactions, arguably the only comparison of two oxide-supported catalysts where an atomic-level degree of knowledge of the metal-to-support interaction is known, has been completed and will be reported elsewhere.[10b]

Experimental Section

Materials. All commercially obtained compounds were Baker reagent grade and were used as received unless indicated otherwise: $1,2\text{-}C_2H_4Cl_2$, MeOH, 2-propanol, and 95% ethanol; $NaBF_4$ (Aldrich), $AgBF_4$ (Aldrich), Bu_4NBr (Fluka), $(NH_4)_3IrCl_6$ (Johnson Matthey), acetone (Burdick & Jackson), $1,2\text{-}C_2D_4Cl_2$, CD_3NO_2, CD_3CN, acetone-d_6, and DMSO-d_6 (all from Cambridge Isotopes). 1,5-Cyclooctadiene was stirred over Brockman activity I basic alumina (Fisher) and then distilled from Na under N_2. Acetonitrile was distilled from CaH_2 under N_2 and ethyl acetate from K_2CO_3, also under N_2. Anhydrous Et_2O was stored over active 3-Å molecular sieves (Linde, preactivated at 300 °C for 24 h) for at least 1 week and then filtered through Whatman No. 2 paper and purged with N_2 for 0.5 h prior to use.

Instrumentation and Analytical Procedures. Air-sensitive compounds were routinely manipulated under a N_2 atmosphere in a Vacuum Atmospheres drybox. Elemental analyses were obtained from Mikroanalytisches Labor Pascher, Remagen, Germany. Solution molecular weights were determined on a Beckman Instruments Spinco Model E ultracentrifuge using the sedimentation–equilibrium method.[7,13] IR spectra were recorded as KBr pellets and as acetone solutions in 0.1-mm path-length NaCl cells using a Nicolet 5DX spectrometer. For air-sensitive compounds, the KBr pellets were prepared in the following way. In the drybox, ca. 2 mg of the compound was ground together with ca. 200 mg of KBr to give a fine powder; the powder was then loaded carefully into a die. After removal from the drybox, the die was immediately evacuated and pressurized to 3500 psi for 5 min to give a KBr pellet, and an IR spectrum was taken immediately thereafter. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a General Electric QE-300 spectrometer, and ^{183}W NMR (15 MHz) spectra on a Nicolet

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(9) (a) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.* **1990**, *29*, 1784–7. (b) Pohl, M.; Finke, R. G. *Organometallics* **1993**, *12*, 1453.

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(11) Pioneering efforts of the Klemperer and Day team have provided much of the necessary background information on, and important crystallographic characterization of, non-Keggin and non-Wells-Dawson polyoxoanion-organometallic complexes: (a) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533–41 and references therein. (b) Chae, H. K.; Klemperer, W. G.; Day, V. W. *Inorg. Chem.* **1989**, *28*, 1423. (c) Klemperer, W. G.; Yagasaki, A. *Chem. Lett.* **1989**, 2041. (d) Day, V. W.; Klemperer, W. G.; Yagasaki, A. *Chem. Lett.* **1990**, 1267. (e) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345. (f) Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2355.

(12) Hayashi, Y.; Ozawa, Y.; Isobe, K. *Inorg. Chem.* **1991**, *30*, 1025.

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Technology NT-360 spectrometer at 20 °C. Air-sensitive samples were placed in J-Young NMR tubes (Wilmad) equipped with airtight screw-type valves (5-mm-o.d. tubes for ^{1}H, ^{13}C; 10-mm-o.d. tubes for ^{183}W). Chemical shifts are reported using the δ scale with negative values upfield of the standard. ^{1}H and ^{13}C chemical shifts are referenced to the ^{1}H impurity in the deuterated solvent employed, while ^{183}W chemical shifts are referenced to a saturated Na_2WO_4/D_2O solution using the substitution method. Spectral parameters for ^{183}W NMR include the following: pulse width = 70 μs; acquisition time = 819.4 ms; delay time = 1 s; sweep width = ±2500 Hz. A 3-Hz exponential apodization of the FID was used in the ^{183}W NMR (this added line-broadening has been removed from all reported line widths).

Preparation of $(Bu_4N)_6H_2Si_2W_{18}Nb_6O_{77}$ and $(Bu_4N)_7SiW_9Nb_3O_{40}$. These two compounds were prepared according to our published procedure.[5] ^{183}W NMR of $(Bu_4N)_6H_2Si_2W_{18}Nb_6O_{77}$ (0.1 M in CH_3CN): δ −115.1 (3W) and −143.2 (6W); lit.[5] −114.3, and −142.6 ppm (0.14 M in 1:1 CH_3CN/DMF). IR of $(Bu_4N)_6H_2Si_2W_{18}Nb_6O_{77}$ (KBr pellet, polyoxoanion region, cm^{-1}): 1000, 971, 934, 914, 874, 805, 684. ^{183}W NMR of $(Bu_4N)_7SiW_9Nb_3O_{40}$ (0.1 M in CH_3CN): δ −97.8 (6W) and −114.9 (3W); lit[5] −97.5 and −114.5 ppm (0.14 M in CH_3CN). IR of $(Bu_4N)_7SiW_9Nb_3O_{40}$ (KBr pellet, polyoxoanion region, cm^{-1}): 989, 950, 880, 780. IR of $(Bu_4N)_7SiW_9Nb_3O_{40}$ (acetone solution, polyoxoanion region, cm^{-1}): 991, 950, 902, 785.

Preparation of $[Ir(1,5\text{-}COD)Cl]_2$. The (1,5-cyclooctadienyl)iridium dimer was prepared following the literature method[14] with slight modifications. Deionized water (20 mL), 2-propanol (7 mL), and 1,5-cyclooctadiene (3.6 mL, 29.3 mmol) were placed in a 100-mL round-bottom flask equipped with a side-arm stopcock, and the flask was purged with N_2 for 1 h. $(NH_4)_3IrCl_6$ (4.00 g, 8.72 mmol) was added, and the reaction mixture was refluxed under N_2 for 19 h. After cooling of the mixture to room temperature, the brick-red microcrystalline product was collected on a medium frit and washed with 25 mL of ice-cold water and 50 mL of ice-cold EtOH under steady N_2 flow, both solvents having been purged with N_2 for 0.5 h before use. The product was dried under N_2 flow on the frit for 1 h and under vacuum (at room temperature) for 12 h. Yield: 1.7 g, 70%. IR (KBr): 1001, 977, 971, and 905 cm^{-1}; lit.[14a] (Nujol) 1002, 980, 970, and 907. ^{1}H NMR ($CDCl_3$): δ 1.50–1.56 (q), 2.24–2.28 (m), 4.23 (d); lit.[14a] ($CDCl_3$) δ 4.3 ppm (vinyl proton).

Preparation of $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$. In the drybox, $AgBF_4$ (0.2944 g, 1.51 mmol) was added to a stirring suspension of $[Ir(1,5\text{-}COD)Cl]_2$ (0.5079 g, 0.756 mmol) in 10 mL of CH_3CN to give a white precipitate (AgCl) and an orange solution. The mixture was stirred for 15 min. The precipitate was removed by gravity filtration through Whatman No. 2 paper, and the filter paper was washed twice with ca. 5 mL of CH_3CN. The filtrate and the washing were directly added to a well-stirred CH_3CN solution (40 mL) of $(Bu_4N)_7SiW_9Nb_3O_{40}$ (6.50 g, 1.51 mmol) to give an orange-yellow solution. This solution was further stirred for 15 min, all while still in the drybox.

Isolation and purification of the reaction product was accomplished by the following procedures. $NaBF_4$ (0.3321 g, 3.024 mmol) was added, and the solution was stirred until all the $NaBF_4$ had dissolved (about 20 min). The solution was filtered through Whatman No. 2 paper, and the filtrate was rotary evaporated to dryness. The resulting orange-yellow solid was redissolved in 5–6 mL CH_3CN, and the solution was transferred into a 600-mL beaker; the amount of CH_3CN used in washing was no more than 5 mL. To this stirring solution, 500 mL of EtOAc was added in 100-mL portions over ca. 15 min; yellow-orange solid began to deposit after the addition of the first portion. After all the EtOAc was added, the suspension was further stirred for 30 min. The yellow-orange solid was collected on a medium glass frit by gravity filtration, redissolved in 7 mL of CH_3CN, and reprecipitated again by the addition of 500 mL of EtOAc as described above. The resulting bright-yellow powder was collected, washed with diethyl ether (3 × 40 mL), and dried at room temperature under vacuum [to completely remove the last traces of EtOAc, drying/desolvating at 60 °C under vacuum for up to 1 week is required (see elsewhere as well[15]); samples dried/desolvated only overnight will contain 0.1–0.3 equiv of EtOAc)]. Yield: 4.4 g, 74%. Anal. Calcd for $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$: C, 22.07; H, 4.01; N, 1.43; Na, 1.17; Si, 0.72; W, 42.2; Nb, 7.11; Ir, 4.91; O, 16.3; total 100.0%. Found: C, 22.26; H, 4.12; N, 1.55; Na, 1.53; Si, 0.74; W, 41.9; Nb, 7.06; Ir, 4.75; O, 17.3; total 101.0%. IR (KBr pellet, polyoxoanion region, cm^{-1}): 993 (m), 956 (s), 900 (sh), 881 (s, br), 796 (s) and 750 (s). IR (acetone solution, polyoxoanion region, cm^{-1}): 991 (m), 955 (s), 903, 802 (s), 756 (s). ^{1}H NMR (acetone-d_6): δ 4.2 (s, CH), 2.1 (s, CH_2), 1.3 (d, CH_2). ^{1}H NMR (CD_2Cl_2): δ 4.2 (s, CH), 2.2 (s, CH_2), 1.3 (d, CH_2). ^{1}H NMR (CD_3NO_2): δ 4.1 (s, CH), 2.2 (s, CH_2), 1.3 (d, CH_2). ^{13}C {^{1}H} NMR (CD_3NO_2): 58.5 (CH), 33.0 (CH_2). Weight-average molecular weight, M_r (sedimentation equilibrium method): calcd, 3917 for $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$; found, 4600 ± 700 for 8×10^{-6} M complex in 0.1 M $(Bu_4N)^{+}PF_6^{-}/CH_2Cl_2$.

In Situ Preparation of $(Bu_4N)_6[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$ and Its ^{183}W NMR Spectrum in Weakly Coordinating Solvents. The all Bu_4N^{+} salt was prepared in situ; it is required for the ^{183}W NMR studies due to its much greater solubility in weakly coordinating solvents in comparison to the mixed Bu_4N^{+}/Na^{+} salt.

To a suspension of 0.1016 g (0.155 mmol) of $[Ir(1,5\text{-}COD)Cl]_2$ in 4 mL of $1,2\text{-}Cl_2C_2H_4$ was added 0.0589 g (0.302 mmol) of $AgBF_4$. The mixture was stirred for 15 min. The resulting white AgCl precipitate was removed by filtration through Whatman no. 5 paper. The clear filtrate was added to a stirring solution of 1.300 g (0.302 mmol) of $(Bu_4N)_7SiW_9Nb_3O_{40}$ in 5 mL of $1,2\text{-}Cl_2C_2H_4$ to give an orange solution. The solution was stirred for an additional 15 min, and the solvent was removed by rotary evaporation. The resulting residue was then redissolved in 1:1 $1,2\text{-}C_2H_4Cl_2/1,2\text{-}C_2D_4Cl_2$ to give an orange solution. ^{183}W NMR, δ (relative intensity): −90.4 (1.0), −99.8 (0.9), −103.6 (1.0), −117.0 (0.6) and −118.9 (1.0). The $\Delta\nu_{1/2}$ values of the peaks are ca. 7 Hz.

The above ^{183}W sample was recovered by the addition of ether to give oily yellow material which solidified after washing with ether (3 × 10 mL). After being dried under vacuum for 5 h at room temperature, $(Bu_4N)_6[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$ plus 1 equiv of $(Bu_4N)BF_4$ was obtained as a fine yellow powder. ^{1}H NMR (1,5-COD resonances, acetone-d_6): δ 3.9 (s, CH), 2.1 (s, CH_2), 1.3 (d, CH_2). ^{1}H NMR (1,5-COD resonances, Cl_2CD_2): δ 3.8 (s, CH), 2.2 (s, CH_2), 1.3 (d, CH_2). Compared with $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$, the –CH– resonance of 1,5-COD in the all Bu_4N^{+} salt was shifted upfield 0.3 ppm, but the resonances of the two $-CH_2-$ groups did not change. (The slight change in the –CH– chemical shift is presumably due to the Na^{+} ion-paring effect[9] expected for $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$.)

Efforts Aimed at Growing Suitable Single Crystals for an X-ray Crystallographic Structural Analysis. Extensive efforts were expended at growing suitable single crystals for an X-ray structural determination, including crystallization trials of $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$ from acetone, 2-butanone, CH_2Cl_2, $1,2\text{-}C_2H_4Cl_2$, CH_3NO_2, DMF, and CH_3CN (the maximum solubility is often low, for instance ca. 5 mg of complex in 1 mL of acetone). Only acteone yielded any crystals, microcrystals or thin needles, depending on the conditions (see the supplementary matherial for details). These efforts, which include mounting crystals at low temperature to avoid lattice solvent loss, provided excellent appearing and tantilizing crystals that, however, diffract only weakly. (The details of these efforts are recorded in the supplementary material for the interested reader.)

A reviewer wondered why we did not use crystallization from acetone as a preparative purification method. First, the low solubility (e.g., 5 mg/mL of acetone) and even lower yield of recrystallized material preclude the use of crystallization as a preparative technique (i.e., on a scale of more than a few milligrams; recall that a few *grams* of material are needed for, say, a good signal-to-noise ^{183}W NMR). Second and fortunately, it proved unnecessary to work with only crystalline material, as analytically pure material is obtained from the reprecipitation techniques described above (and is obtained much more readily and on a 10^3 larger, 4–5-g scale, as long as the EtOAc is fully removed by sufficient drying/desolvating times). And third, the bulk precipitated material was shown to have IR and NMR spectroscopic properties *identical* to those of the crystalline sample $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$, thereby confirming the purity and interchangeability of the two samples.

Results and Discussion

Synthesis, Purity, and Molecular Formula. The conceptually straightforward synthesis of $(Bu_4N)_4Na_2[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$ is outlined in eqs 1 and 2. Reaction of $(Bu_4N)_7SiW_9Nb_3O_{40}$ with $(1,5\text{-}COD)Ir(CH_3CN)_2BF_4$, prepared in situ from $[Ir(1,5\text{-}COD)Cl]_2$ and $AgBF_4$, gives rise to $(Bu_4N)_6[(1,5\text{-}COD)Ir\cdot SiW_9Nb_3O_{40}]$ and 1 equiv of Bu_4NBF_4 (eq 1). As expected, on the basis of our earlier experience[9] with [(1,5-

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[15] Pohl, M.; Nomiya, K.; Finke, R. G. manuscript in preparation [the synthesis and characterization of $(1,5\text{-}COD)Rh\cdot P_2W_{15}Nb_3O_{62}^{8-}$].

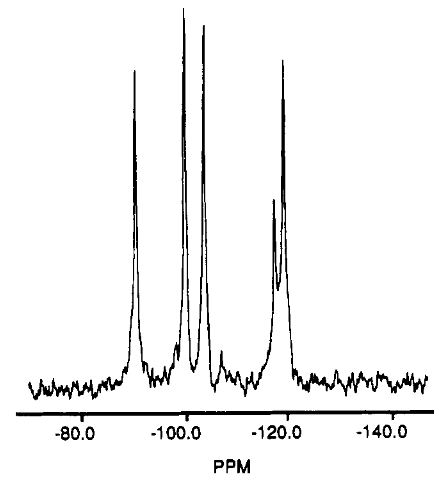

Figure 4. ^{183}W NMR spectrum of $[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]^{6-}$ in 1:1 $C_2H_4Cl_2/C_2D_4Cl_2$ (0.1 M), exhibiting a five-line spectrum characteristic[5,7] of overall C_s symmetry.

$COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, it was not possible to isolate the all Bu_4N^+ salt $(Bu_4N)_6[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ in both a pure form (i.e. free of Bu_4NBF_4) and also in reasonable yield. However, application of our recently developed mixed-cation method,[5b] in eq 2, involving the addition of 2 equiv of $NaBF_4$ to reduce the solubility of the compound, worked nicely to afford pure product as its mixed $(Bu_4N)_4Na_2{}^{6+}$ salt in 74% yield following two precipitations using EtOAc. [$(Bu_4N)BF_4$ is very soluble in EtOAc and thus is completely removed after two EtOAc reprecipitations as demonstrated by IR spectroscopy (no detectable $\nu(BF_4^-) = 1085\ cm^{-1}$).]

$$(Bu_4N)_7SiW_9Nb_3O_{40} + [(1,5\text{-COD})Ir(CH_3CN)_2]BF_4 \xrightarrow[CH_3CN]{\le 1\ ppm\ O_2} (Bu_4N)_6[(1,5\text{-COD})Ir\cdot SiS_9Nb_3O_{40}] + (Bu_4N)BF_4 \tag{1}$$

$$(Bu_4N)_6[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}] + 2NaBF_4 \xrightarrow[\substack{CH_3CN \\ EtOAc\ reppt}]{\le 1\ ppm\ O_2} (Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}] + 2(Bu_4N)BF_4 \tag{2}$$

The homogeneity and composition of the product were established by elemental analysis, an ultracentrifugation solution molecular-weight measurement, and NMR spectroscopies (*vide infra*). The elemental analysis and solution molecular weight measurement confirm the expected molecular formula [calcd M_r for $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ of 3917; obsd M_r, 4600 ± 700 in weakly coordinating CH_2Cl_2 solvent (supplementary material, Figure A)]. The solution molecular-weight also confirms that a 1:1 $[Ir(1,5\text{-COD})^+]:(SiW_9Nb_3O_{40}{}^{7-})$ complex is obtained, not a 5:2 or 2:2 adduct analogous to the $\{[(1,5\text{-COD})Ir]_5(Nb_2W_4O_{19})_2\}^{3-}$ and $\{[(1,5\text{-COD})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ reported by Klemperer, Day, and co-workers for the smaller $Nb_2W_4O_{19}{}^{4-}$ polyoxoanion.[11e] This is as expected, as our work indicates that it is the specific type of polyoxoanion that largely determines the stoichiometry of the resultant complex, with both $SiW_9Nb_3O_{40}{}^{7-}$ and $P_2W_{15}Nb_3O_{62}{}^{9-}$ exhibiting only 1:1 metal: polyoxoanion complexes in all of our studies to date.[5-8,15] The fact that crystallized material (see the Experimental Section) shows the exact same spectroscopic properties as the bulk, isolated product is an independent, compelling piece of evidence which confirms the purity and the interchangeability of both the crystalline and the bulk products.

Table I. ^1H NMR Resonances of $Ir(1,5\text{-COD})^+$ Complexes

compd	solvent	δ (ppm), COD	ref
$[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]Na_2(Bu_4N)_4$	CD_3COCD_3	4.2, 2.1, 1.3	this work
$[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]Na_2(Bu_4N)_4$	$C_2D_2Cl_2$	4.2, 2.2, 1.3	this work
$[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]Na_2(Bu_4N)_4$	CD_3NO_2	4.1, 2.2, 1.3	this work
$[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}](Bu_4N)_6$	CD_3COCD_3	3.9, 2.1, 1.3	this work
$[(1,5\text{-COD})Ir\cdot (CH_3CN)_2]BF_4{}^a$	$CDCl_3$	4.20, 2.25, 1.73	16
$[(1,5\text{-COD})Ir\cdot (CH_3CN)_2]PF_6{}^b$	CD_2Cl_2	4.27, 2.29, 1.78	11e
$[(1,5\text{-COD})Ir\cdot (CH_3COCH_3)_2]BF_4$	CD_3COCD_3	4.13, 2.34, 1.54	16
$[(1,5\text{-COD})Ir\cdot P_3O_9](Bu_4N)_2$	CD_2Cl_2	3.6, 2.1, 1.2	11e
$[(1,5\text{-COD})Ir\cdot P_3O_9](Bu_4N)_2$	CD_3NO_2	3.7, 2.2, 1.3	11e
$[(1,5\text{-COD})Ir)_2H(Nb_2W_4O_{19})_2](Bu_4N)_5$	CD_3NO_2	3.9, 2.2, 1.4	11e
$[(1,5\text{-COD})Ir\cdot (C_5Me_5)TiW_5O_{18}](Bu_4N)_2$	$CDCl_3$	4.35, 2.19, 1.29	11c

[a] Note that a peak assignable to coordinated CH_3CN appears at 2.59 ppm, thereby showing that the CH_3CN remains coordinated in $CDCl_3$. [b] A peak assignable to coordinated CH_3CN appears at 2.53 ppm indicating that CH_3CN remains coordinated in CD_2Cl_2.

Table II. ^{13}C NMR Resonances of $Ir(1,5\text{-COD})^+$ Complexes

compd	solvent	δ (ppm), COD	ref
$[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]Na_2(Bu_4N)_4$	CD_3NO_2	58.5, 33.0	this work
$[(1,5\text{-COD})Ir\cdot (CH_3CN)_2]PF_6$	CD_3NO_2	72.9, 32.2	11e
$[(1,5\text{-COD})Ir\cdot P_3O_9](Bu_4N)_2$	CD_2Cl_2	55.5, 31.1	11e
$[(1,5\text{-COD})Ir\cdot P_3O_9](Bu_4N)_2$	$C_6D_5NO_2$	55.8, 32.2	11e
$[(1,5\text{-COD})Ir)_2H(Nb_2W_4O_{19})_2](Bu_4N)_5$	CD_3NO_2	58.5, 32.8	11e

Solution Structure by ^1H, ^{13}C, and ^{183}W NMR Spectroscopies in Weakly Coordinating Solvents. The NMR spectra of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ proved to be quite dependent on whether weakly or strongly coordinating solvents were used. Only the results in weakly coordinating solvents provide unambiguous evidence for the symmetry of the complex (and only in those solvents); hence, only the NMR results in weakly coordinating solvents are presented below. [The spectroscopic results in coordinating solvents are, however, collected in the supplementary material, for the interested reader (Tables A and B and Figures D–H).]

In the weakly coordinating solvents acetone, nitromethane, and dichoromethane, the ^1H and $^{13}C\{^1H\}$ NMR data reveal that the chemical shifts of the $Ir(1,5\text{-COD})^+$ moiety in $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ differ substantially from those indicative of the uncoordinated $(1,5\text{-COD})Ir(CH_3CN)_2{}^+$ [11e,16] starting material (Tables I and II). Note that the upfield δ 1.3–1.78 ppm ^1H NMR peak is most sensitive to changes in the $Ir(1,5\text{-COD})^+$ moiety's environment (see Table I), while, in the ^{13}C NMR, the downfield δ 55.5–72.9 ppm peak is most sensitive (Table II). On the other hand, the ^1H and $^{13}C\{^1H\}$ NMR data for $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ match closely those reported by Klemperer, Day, and co-workers for the crystallographically characterized, polyoxoanion-supported complexes

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(16) Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 489.

(17) In strongly coordinating solvents such as CH_3CN or DMSO, a very broad, primarily two-line ^{183}W NMR spectrum is seen (which, however, contains additional smaller peaks; see Figures D–H and Tables A and B in the supplementary material for details); such a primarily two-line spectrum indicates approximate C_{3v} (average) symmetry. The simplest interpretation of these solvent-dependent ^{183}W NMR results is that $Ir(1,5\text{-COD})^+$ is dissociating from $SiW_9Nb_3O_{40}{}^{7-}$ and then re-adding to the other two equivalent C_s symmetry sites (i.e. around the C_3 axis in the structures in Figure 6A,B), all fast on the ^{183}W NMR time scale at 20 °C. The result is a C_{3v} average symmetry sturcture on the NMR time scale and thus the observed two-line ^{183}W NMR.

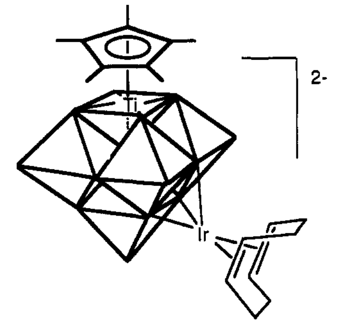

Figure 5. Polyhedral representation of (1,5-COD)Ir·$[(C_5Me_5)TiW_5O_{18}]^{2-}$, redrawn for the purpose of easy comparison based on the crystal structure of the compound.[11c] The octahedra represent WO_6, with oxygen at each vertice. At the top, a W=O group has been replaced by a $Ti(C_5Me_5)^{3+}$ group. The $Ir(1,5\text{-COD})^+$ moiety is attached to three W_2O bridging oxygens forming two short equatorial Ir–O bonds and one long apical Ir–O bond with a distorted square-pyramidal coordination geometry around Ir(I).[11c]

(1,5-COD)Ir·$P_3O_9^{2-}$ [11e] and (1,5-COD)Ir·$[(C_5Me_5)TiW_5O_{18}]^{3-}$,[11c] Tables I and II.

The oxygen sites for binding $Ir(1,5\text{-COD})^+$ atop $SiW_9Nb_3O_{40}^{7-}$, and again in weakly coordinating solvents, were inferred from ^{183}W NMR and IR studies in comparison to our earlier literature.[5,8] Because of the less clean spectra seen in coordinating solvents,[17] and then because of the high concentrations required for reasonable S/N spectra, a switch to the more soluble all Bu_4N^+ salt $(Bu_4N)_6[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]$ was required in order to obtain satisfactory ^{183}W NMR in less polar solvents such as 1,2-$C_2H_4Cl_2$.[18] However, the ^{183}W NMR results in 1,2-$C_2H_4Cl_2$, Figure 4, proved clean and informative, exhibiting the five-line ^{183}W NMR spectrum characteristic of C_s symmetry $SiW_9Nb_3O_{40}^{7-}$ supported organometallics.[5,8] The five somewhat broadened[19] lines appear at −90.4, −99.8, −103.6, −117.0, and −118.9 ppm and exhibit the expected relative intensities of 2:2:2:1:2.

Recalling the trihapto polyoxoanion and thus 5-coordinate Ir(I) geometry found previously both by Klemperer and Day for (1,5-COD)Ir·$[(C_5Me_5)TiW_5O_{18}]^{2-}$,[11c] Figure 5, and through our own work on (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$ (recall Figure 3), two most plausible (and only slighty different) structures can be proposed,[20,21] Figure 6A,B. In Figure 6A, $Ir(1,5\text{-COD})^+$ is attached to one OW_2 bridging oxygen[22] and then to two ONbW bridging oxygens of *edge-sharing octahedra*;[20a] this may be the favored of the two structures since 5-coordinate $Ir^I(1,5\text{-COD})^+$ wants a *long and weak* fifth ligand if in a square-pyramidal structure (e.g. as found in (1,5-COD)Ir·$[(C_5Me_5)TiW_5O_{18}]^{2-}$ [11c] and in (1,5-COD)Ir·$P_3O_9^{2-}$ [11e]). The second possible structure, Figure 6B, involves $Ir(1,5\text{-COD})^+$ attached to these same two ONbW bridging oxygens but then to a more basic ONb terminal oxygen as the fifth ligand.

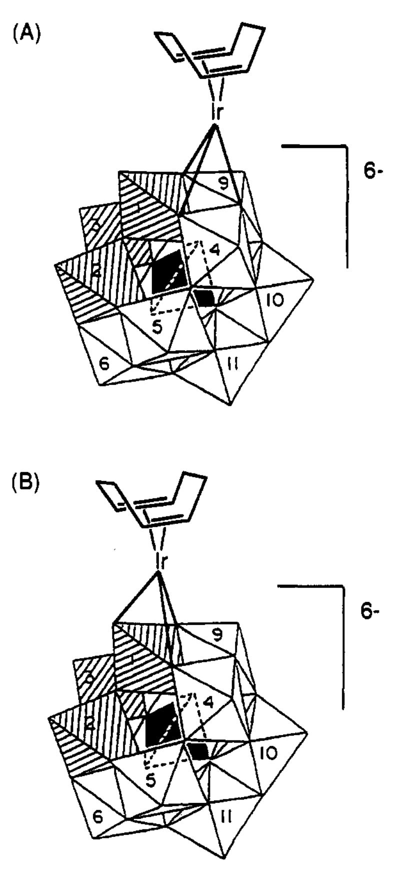

Figure 6. The two most plausible slightly different structures proposed for (1,5-COD)Ir·$SiW_9Nb_3O_{40}^{6-}$ on the basis of the ^{183}W NMR data and on literature precedent. In (A), $Ir(1,5\text{-COD})^+$ is attached to two ONbW bridging oxygens and to one OW_2 bridging oxygen; in (B), $Ir(1,5\text{-COD})^+$ is attached to these same two ONbW bridging oxygens but then to one ONb terminal oxygen for the third oxygen.

A comparison of the IR spectrum of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]$, Figure 7B (KBr) and 7D (in acetone),

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[18] The mixed salt $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]$ is expected to have the same C_s symmetry as the all Bu_4N^+ salt, since there is no evidence that the presence of Na^+ ion-pairing effects[9] can change the overall symmetry of a covalently bonded, polyoxoanion-supported complex. In fact, there is considerable evidence to the contrary,[9] specifically the following: (i) Na^+ ion-pairing is outer sphere and thus weaker than the inner-sphere, covalent bonding of $Ir(1,5\text{-COD})^+$ to the polyoxoanion; (ii) the ^1H NMR chemical shifts of the 1,5-COD group in the all Bu_4N^+ salt, $(Bu_4N)_6[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]$, are very close to that of the mixed $(Bu_4N)_4Na_2^{6+}$ salt, indicating no major change has occurred in the $Ir(1,5\text{-COD})^+$ coordination sphere as a result of the presence of Na^+; (iii) the exact same five-line Cs symmetry ^{183}W NMR spectrum is seen for the $(Bu_4N)_6^{6+}$ salt vs the mixed $(Bu_4N)_4Na_2^{6+}$ salt of $(C_5Me_5)Rh{\cdot}SiW_9Nb_3O_{40}^{5-}$,[5] again indicating no change (at least when a *dication* like $(C_5Me_5)Rh^{2+}$ is bound to $SiW_9Nb_3O_{40}^{7-}$); (iv) the addition of cryptand to nullify the Na^+ ion-pairing in $(Bu_4N)_5Na_3[(COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}]$ in CH_3CN did not change the number of the ^{183}W peaks nor, therefore, the symmetry of the complex (instead, it only sharpens the three-line ^{183}W spectrum); (v) the same primarily two broad-line spectrum is seen for both $(Bu_4N)_4Na_2^{6+}$ and the all tetrabutylammonium, $(Bu_4N)_6^{6+}$, salt in strongly coordinating solvents such as CH_3CN or DMSO (see the supplemental material); and (vi) overall, the coordinating ability of the *solvent*, and not the counterion or the solvent's polarity (as expected if ion-pairing were dominant), is most important in the ^{183}W NMR spectra of $[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]^{6-}$.

[19] The observation of only three ^1H peaks and two ^{13}C peaks (rather than the six ^1H peaks and four ^{13}C peaks expected for C_s symmetry) *requires* fluxionality at Ir for $[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]^{6-}$ in solution. This well-known[9,11e] fluxionality of d^8 five-coordinate Ir(I) is undoubtedly a source of the peak broadening seen in the ^{183}W NMR (the peaks are about twice as broad as normal,[5a,6,8] $\Delta\nu_{1/2}$ = ca. 7 Hz in the ^{183}W NMR of 0.09 M $(Bu_4N)_6[(1,5\text{-COD})Ir{\cdot}SiW_9Nb_3O_{40}]$ in 1,2-$C_2H_4Cl_2$).

[20] (a) These proposed structures also take into account Klemperer's literature[20b] indicating that *edge-sharing octahedra* ONb_2 bridging oxygens are the most basic sites in $Nb_2W_4O_{19}^{4-}$ (and are also sterically accessible oxygens), followed by the nearly as basic terminal O–Nb oxygens (which are the most accessible, sterically). Quite relevant here too is that surface oxygen basicity is also present at the ONbW bridging oxygens in $Nb_2W_4O_{19}^{4-}$.[20c] Since there are no edge-sharing ONb_2 oxygens in $SiW_9Nb_3O_{34}^{7-}$, and since the *corner-sharing octahedra* ONb_2 oxygens in this polyoxoanion are sterically inaccessible, the two most plausible structures for (1,5-COD)Ir·$SiW_9Nb_3O_{40}^{6-}$ are those shown in Figure 6A,B. (b) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991–3002. (c) Only the very nonbasic, formally $^-W{\equiv}O^+$, terminal oxygens in polyoxoanions do not bind organometallic cations; in fact, they seem to associate with the partial *negative* charge at oxygen in species such as $[H_2N^+{=}C(NH_2)O^-]$, see: Williamson, M. M.; Bouchard, D. A.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 1436 (and see also ref 12 therein to their earlier communication).

[21] (a) The site preference for the C_s symmetry NbW_2 triad, B-type site of edge-sharing octahedra over the C_{3v} site composed of the more basic[20] triad of Nb–O–Nb containing, A-type,[5a] corner-sharing octahedra is due to the steric crowding of the B-type site,[21b] strictly analogous to that observed[5,8] in the related complexes $(C_5Me_5)Rh{\cdot}SiW_9Nb_3O_{40}^{5-}$ and $(C_5H_5)Ti{\cdot}SiW_9Nb_3O_{40}^{4-}$. (b) Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587–9.

[22] Precedent does exist for structures involving the less basic[20] OW_2 bridging oxygens, notably Klemperer and Day's crystallographically characterized $(C_5Me_5)Rh{\cdot}(Nb_2W_4O_{19})^{2-}$: Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125–36.

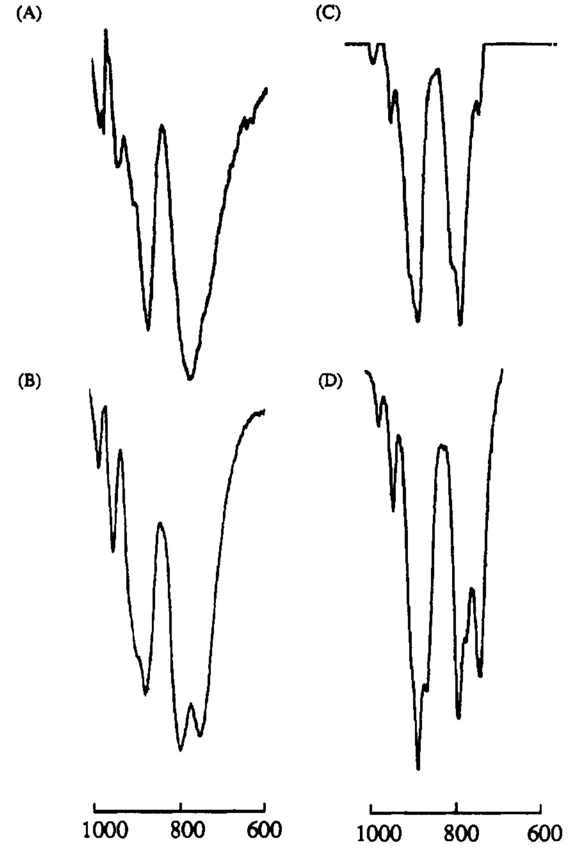

Figure 7. IR spectra of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ as a KBr pellet (B) and in acetone (D). The IR spectra of $(Bu_4N)_7SiW_9Nb_3O_{40}$ as a KBr pellet (A) and in acetone (C) are provided for comparative purposes. Note the splitting of the ca. 800-cm^{-1} band, assigned to a ν_{asym}-(M–O–M) vibration of edge-shared octahedra, that occurs as a result of attaching Ir(1,5-COD)$^+$ to $SiW_9Nb_3O_{40}{}^{7-}$.

vs that of the parent polyoxoanion $(Bu_4N)_7SiW_9Nb_3O_{40}$, Figure 7A (KBr) and 7B (in acetone), provides confirming evidence that the structures in Figure 6A,B involving a triad of *edge-sharing* octahedra are correct.[20,21] In particular, the IR spectra of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ show a 46-cm^{-1} splitting (Figure 7B,D) of the 800-cm^{-1} band assigned[23] to an asymmetric stretching vibration of a M–O–M bridging *edged-sharing* octahedra. The splitting of this band strongly suggests that the Ir(1,5-COD)$^+$ moiety is attached to the M–O–M bridging oxygens of edge-sharing octahedra (and not to the other conceivable C_s symmetry sites within $SiW_9Nb_3O_{40}{}^{7-}$ that involve corner-sharing octahedra; see Figure 6A,B). This evidence and the above reasoning is further fortified by the crystallographically characterized complexes $(C_5Me_5)Rh\cdot(P_2W_{15}Nb_3O_{62})^{7-}$,[24] $(C_5Me_5)Rh\cdot(Nb_2W_4O_{19})^{2-}$,[22] and $(OC)_3Mn(Nb_2W_4O_{19})^{3-}$,[25] all three of which display an organotransition metal cation attached to OM_2 (M = Nb, W) bridging oxygens of edge-sharing octahedra (as verified crystallographically) plus a *strong* splitting[26] of the IR band assigned to this M–O–M vibration.

Summary. In conclusion, a new Keggin-type polyoxoanion-supported Ir(1,5-COD)$^+$ complex, $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$, has been prepared and characterized. Significantly, it is clear that the Ir(1,5-COD)$^+$ moiety is attached to $SiW_9Nb_3O_{40}$ via quite different oxygens [two ONbW bridging oxygens and most likely one OW_2 bridging oxygen (or, possibly, one ONb terminal oxygen)] in comparison to $P_2W_{15}Nb_3O_{62}{}^{9-}$ (three ONb_2 bridging oxygens). Hence, the stage is set for the first comparison of two different polyoxoanion-supported catalysts of any type, specifically the Keggin anion-supported $[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]^{6-}$ and the Dawson anion-supported $[(COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$. Such a comparison, of two otherwise identical oxide-supported catalysts where the structure of the metal-support interaction is known at essentially the atomic level,[10b] is arguably unique among known oxide-supported catalysts.[3b]

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Supplementary Material Available: Figure A, a plot of ln absorbance (*A*) vs r^2 from the ultracentrifugation molecular weight measurement for $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ in CH_2Cl_2, Figure B, ^{1}H NMR spectrum of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ in acetone-d_6, Figure C, ^{13}C NMR spectrum of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ in CD_3NO_2, a section of text titled NMR Studies in Strongly Coordinating Solvents, Table A, titled The Effects of Solvents, Counterions and Temperature on the ^{183}W NMR Chemical Shift of $Ir(1,5\text{-COD})\cdot SiW_9Nb_3O_{40}{}^{6-}$, Table B, titled The Effects of Solvents and Counterions on the ^{1}H and $^{13}C\{^1H\}$NMR Chemical Shift of $Ir(1,5\text{-COD})\cdot SiW_9Nb_3O_{40}{}^{6-}$, Figure D, ^{183}W NMR spectra of $(Bu_4N)_6[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ (plus 1 equiv of Bu_4NBF_4) in CH_3CN at varying temperatures, Figure E, ^{183}W NMR spectra of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ in CH_3CN and DMSO, Figure F, ^{183}W NMR spectra of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ at varying temperatures in DMSO in the presence of 2 equiv of cryptand to remove the Na$^+$ ion-pairing and with the addition of 1 equiv of $(1,5\text{-COD})Ir\cdot(DMSO)_x{}^+$, Figure G, ^{1}H NMR spectrum of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ in DMSO-d_6, Figure H, ^{1}H NMR spectrum of $(Bu_4N)_4Na_2[(1,5\text{-COD})Ir\cdot SiW_9Nb_3O_{40}]$ in CD_3CN, and a section of text titled Efforts Aimed at Growing Suitable Single Crystals for an X-ray Crystallographic Structural Analysis (12 pages). Ordering information is given on any current masthead page.

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(23) (a) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598. (b) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

(24) Pohl, M.; Lin, Y.; Weakley, T. J. R.; Kaneko, M. C.; Nomiya, K.; Finke, R. G. Unpublished results [a single-crystal structural analysis of $(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}{}^{7-}$ showing that $Rh(C_5Me_5)^{2+}$ is attached to three ONb_2 bridging oxygens, i.e. directly over the C_{3v} axis in $P_2W_{15}Nb_3O_{62}{}^{9-}$].

(25) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44–50.

(26) In further support of this point, there is very little splitting of the broad, ca. 800-cm^{-1} band in related complexes that are bonded to $Nb_2W_4O_{19}{}^{4-}$ via only terminal Nb–O oxygens, specifically $[(Bu_4N)_5]\{[(1,5\text{-COD})Ir]_2\cdot H\cdot[Nb_2W_4O_{19}]_2\}$.[11e] However, there is a visible splitting in $[(Bu_4N)_3]\{[(1,5\text{-COD})Ir]_5[Nb_2W_4O_{19}]_2\}$, in which three of the five iridiums bind via ONb_2 bridging oxygens (compare Figure 1b,c elswhere).[11e]