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The Polyoxoanion-Supported, Atomically Dispersed Transition-Metal Precatalyst $[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$: Direct ^{17}O NMR Evidence for Ir–ONb_2 Bonding and for a C_{3v} Average Symmetry, Iridium-to-Polyoxoanion Support Interaction

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Summary: Selective enrichment with $^{17}OH_2$ followed by ^{17}O NMR allows observation of just the Nb_3O_6 support site in the custom-designed polyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$ and in the polyoxoanion-supported organometallic precatalyst $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ (1) without interference from other ^{17}O NMR resonances. The ^{17}O NMR results provide direct evidence for Ir–ONb_2 bonding between $[(1,5\text{-COD})Ir^I]^+$ (1,5-COD = 1,5-cyclooctadiene) and $P_2W_{15}Nb_3O_{62}^{9-}$ in solution, where catalysis beginning with 1 has been demonstrated. The ^{17}O NMR results are also definitive in demonstrating that $[(1,5\text{-COD})Ir^I]^+$ is bound in overall average C_{3v} (pseudo) symmetry to the Nb_3O_6 minisurface in 1 (pseudo due to the 2-fold axis in 1,5-COD and thus the local C_s symmetry at Ir).

Polyoxoanions[1] are soluble metal oxides which resemble discrete fragments of the solid metal oxides that Schwartz has termed heterogeneous-insoluble[2] catalysts. This resemblance makes polyoxoanions of considerable interest as soluble transition-metal catalyst-support materials.[3,4] Our central goal is to develop a paradigm for this new class of oxide-supported catalysts, one in which an *atomic-level* understanding and correlation is established between structure, function, and mechanism *for the first time for any oxide-supported catalyst*—crucial knowledge if we are to learn how to *design* the next generation of active and selective oxide-supported catalysts.

Our efforts in this area, in progress for some time now,[3] have entered the advanced stages of characterization, catalysis, and mechanistic work.[3] Previously we reported the second-generation, custom-designed, massive polyoxoanion-support system $P_2W_{15}Nb_3O_{62}^{9-}$.[3a] The atomic-level, X-ray crystallographic structural characterizations of [3g] $P_2W_{15}Nb_3O_{62}^{9-}$ and its supported $[(C_5Me_5)Rh^{III}]^{2+}$ organometallic derivative[3h] have been reported, the latter constituting the first crystallographic results for this class of polyoxoanion–supported organometallics.[3h] Significant for the present work, the structure determination on $[(C_5Me_5)Rh^{III}\cdot P_2W_{15}Nb_3O_{62}^{7-}]$ demonstrated that $[(C_5Me_5)Rh^{III}]^{2+}$ is supported rigidly on the C_{3v} support site (i.e. directly over the C_3 axis) via three bridging Nb–O–Nb oxygens *only*.[3h]

Recently we reported the synthesis[5] of the polyoxoanion-supported catalyst precursor $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ (1; Figure 1) as well as its initial characterization by a complete elemental analysis plus ^{31}P, ^{183}W, ^1H, and ^{13}C NMR, IR, and a solution sedimentation-equilibrium molecular-weight measurement. Three key findings among others from that work are[5] (i) a single (≥95%), possibly time-averaged form of 1 is present in solution (by ^{31}P NMR), (ii) ^{183}W NMR suggests that 1 had effective C_{3v} symmetry on the ^{183}W NMR time scale in solvents such as CH_3CN or DMSO, and (iii) monovalent cations such as Na^+ were found to ion-pair to several sites in $P_2W_{15}Nb_3O_{62}^{9-}$, both in the solid state (by X-ray crystallography) and in solution (by ^{31}P and ^{183}W NMR). The polyoxoanion complex 1 was also shown to be a potent precatalyst[6] for both reductive[6a] and oxidative[6b] chemistries; intensive mechanistic studies since then indicate that the Ir·polyoxoanion bonding in 1 is retained under oxidative[6c] (but not under reductive[6d]) conditions. The novel precatalyst 1 provides, then, the first example of a polyoxoanion-supported catalyst.[6b,c] It is, therefore, highly desirable to obtain atomic-level structural detail on the Ir–O bonding, *in solution and ideally by a direct ^{17}O NMR*

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(1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983. (b) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (c) A systematic method for polyoxoanion nomenclature has recently been published.[1d] (d) Jeannin, Y.; Fournier, M. *Pure Appl. Chem.* **1987**, *59*, 1529.

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

(3) (a) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692. (b) Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. (c) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274. (d) Droege, M. W. Ph.D. Dissertation, University of Oregon, 1984. (e) Rapko, B. Ph.D. Dissertation, University of Oregon, 1986. (f) Nomiya, K.; Mizuno, N.; Lyon, D. K.; Finke, R. G. *Inorg. Synth.*, submitted for publication. (g) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Weakley, T. J. R. *Acta Crystallogr.* **1990**, *C46*, 1592. (h) Lin, Y.; Weakley, T. J. R.; Finke, R. G. Unpublished results (a crystallographic structural analysis on $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ showing that $[(C_5Me_5)Rh^{III}]^{2+}$ is supported rigidly on the C_{3v} axis via three bridging Nb_2O oxygens).

(4) For work on polyoxoanion–organometallic complexes see: (a) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564. (b) Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597. (c) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (d) Besecker, C. J.; Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 6158. (e) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44. (f) Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2355. (g) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345. (h) Day, V. W.; Klemperer, W. G.; Yagasaki, A. *Chem. Lett.* **1990**, 1267. (i) Main, D. J. Ph.D. Dissertation, University of Illinois, Urbana-Champaign, IL, 1987.

(5) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.* **1990**, *29*, 1784.

(6) (a) Lyon, D. K.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1787. (b) Mizuno, N.; Lyon, D. K.; Finke, R. G. *J. Catal.* **1991**, *128*, 84 (the "Note Added in Proof" in Figure 1 therein was based on preliminary ^{17}O NMR work and can now be updated and replaced by the work reported herein). (c) Trovarelli, A.; Finke, R. G. Unpublished results and experiments in progress. (d) Lin, Y.; Finke, R. G. Unpublished results and experiments in progress.

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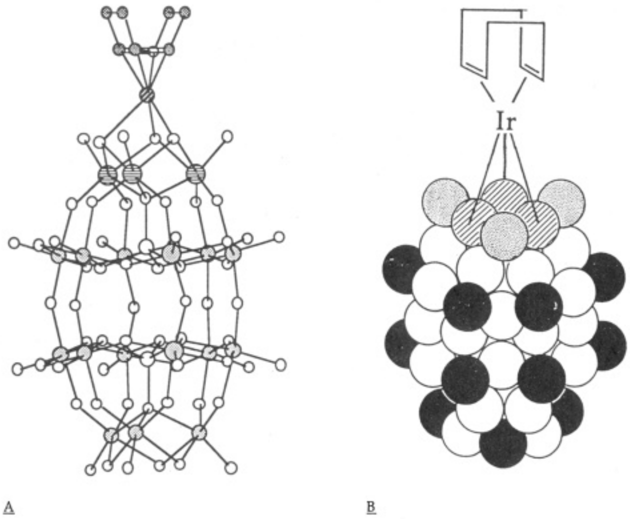

Figure 1. (A) Ball and stick representation of the proposed average C_{3v} (pseudo) symmetric structure for the $[(1,5\text{-COD})\text{Ir}^{\text{I}}]^+$ fragment supported on the "Nb_3O_6" face of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ serving as a stereochemically rigid tripodal ligand. This figure, generated from the crystal structure parameters[3g] of $Na_9P_2W_{15}Nb_3O_{62}$ and modified using Chem 3-D, does not emphasize the expected[4i] two-short plus one-elongated iridium-to-ONb_2 bonds, which would make the rigorous, static symmetry C_s for the structure shown. (B) Space-filling representation, where the black circles represent terminal oxygens, the white circles bridging oxygens, the gray circles terminal Nb–O oxygens, and the hatched circles the three Nb–O–Nb oxygens.

probe of the Nb_3O_6 *support site*, first for the polyoxoanion-supported catalyst precursor $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})\text{Ir}\cdot P_2W_{15}Nb_3O_{62}$ (**1**) and later separately for any isolable catalyst(s) derived from **1**.

Herein we report a solution ^{17}O NMR study of the support interaction between $[(1,5\text{-COD})\text{Ir}^{\text{I}}]^+$ and $P_2W_{15}Nb_3O_{62}{}^{9-}$. The data are definitive in two respects: in providing direct evidence for Ir–O–Nb_2 bonds in solution and in demonstrating the overall average C_{3v} (pseudo) symmetry in **1** (and thus the regiospecific binding, at least on the average, of the $[(1,5\text{-COD})\text{Ir}^{\text{I}}]^+$ fragment to the Nb_3O_6 minisurface in **1**). Possible fluxionality of the $[(1,5\text{-COD})\text{Ir}^{\text{I}}]^+$ moiety in **1** is also presented and discussed in light of all the experimental evidence and relevant literature.

Experimental Section

Acetonitrile (Baker) was dried and deoxygenated by refluxing over CaH_2 under N_2 for at least 24 h. Acetonitrile-d_3 (Cambridge Isotope Laboratories) and $H_2{}^{17}O$ (10% enrichment, Cambridge Isotope Laboratories) were degassed by three freeze–pump–thaw cycles. Kryptofix 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) was obtained from Aldrich. $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ and $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})\text{Ir}\cdot P_2W_{15}Nb_3O_{62}]$ were prepared according to our published procedure;[5] the purity of the final product was checked both by ^{31}P NMR and via its quantitative catalytic activity.[6a] $[\text{Ir}(1,5\text{-COD})\text{Cl}]_2$ was prepared according to the literature.[7] All manipulations were carried out in a drybox ($\leq$1 ppm O_2) to avoid isotopic dilution with H_2O and to protect the highly air-sensitive $[(1,5\text{-COD})\text{Ir}\cdot P_2W_{15}Nb_3O_{62}]^{8-}$.

Instrumental Parameters. ^{17}O NMR (48.967 MHz) spectra were recorded at 22 ± 2 °C in 10 mm o.d. NMR tubes and referenced to fresh tap water by the external substitution method. Following the literature,[8] samples were not locked and were not spun during data collection. Instrument settings were as follows: frequency 48.967 MHz, pulse width 27 μs, acquisition time 200 ms, repetition rate 0.282 s, sweep width ±50 000 Hz. A line broadening of 100 Hz was applied to all spectra for exponential multiplication but was removed for any line widths reported herein.

^{17}O Enrichment of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (2). All manipulations were carried out in a Vacuum Atmospheres nitrogen drybox to prevent isotopic dilution of the ^{17}O-enriched material. In an 18 × 150 mm disposable test tube, $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (1.0 g, 0.16 mmol) was dissolved in 2.0 mL of CH_3CN. Enriched H_2O (10% $^{17}OH_2$, 1.0 g) was syringed into the test tube, leaving a clear, homogeneous solution, and the solution was stirred for 1 week at 22 ± 2 °C. After evacuation to dryness over 24 h the resulting solid was redissolved in 3.0 mL of CD_3CN. The solution was transferred to an NMR tube equipped with a J. Young airtight valve (Wilmad) and placed in the NMR probe within 5 min. ^{17}O NMR (48.967 MHz, CD_3CN, 22 °C): δ 180 (s, 1 O; $Nb_2O\text{–}H^+$; $\Delta\nu_{1/2} = 233 \pm 29$ Hz), 512 (s, 3 ± 1 O; Nb_2O; $\Delta\nu_{1/2} = 257 \pm 10$ Hz), 752 (s, 3 ± 1 O; NbO; $\Delta\nu_{1/2} = 988 \pm 169$ Hz). ^{31}P NMR of $[(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}$ of the same sample taken as a control after acquiring the ^{17}O NMR shows the familiar two-line spectrum[3a,5] (^{31}P (22 °C, 80 mM, CD_3CN): δ −7.6 (s, 1 P), −14.5 (s, 1 P) establishing therefore the integrity of the compound. Impurities are less than 6% (by integration and comparison with the two resonances for $P_2W_{15}Nb_3O_{62}{}^{9-}$). This enrichment experiment was carried out more than 10 times throughout the course of this work with identical results each time.

^{17}O Enrichment of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})\text{Ir}\cdot P_2W_{15}Nb_3O_{62}]$ (1). In an 18 × 150 mm disposable test tube, 1 g (0.18 mmol) of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})\text{Ir}\cdot P_2W_{15}Nb_3O_{62}]$ was dissolved in 2 mL of CH_3CN. To this solution was added H_2O (10% ^{17}O-atom enriched, 1.0 g), resulting in a clear yellow-orange solution. After it was stirred for 36 h at 22 ± 2 °C, the solution was evacuated to dryness and the solid was redissolved in 2 mL of CD_3CN. Following the addition of 3 equiv of Krytpofix 222 to minimize Na^+ ion-pairing effects,[5] the solution was transferred into a 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, 3 equiv of Kryptofix 222 added): δ 680 (s, 3 ± 1 O; Nb–O; $\Delta\nu_{1/2} = 437 \pm 137$ Hz), 333 (s, 3 ± 1 O; Nb_2–O–Ir; $\Delta\nu_{1/2} = 514 \pm 106$ Hz).

^{31}P NMR (22 °C, 90 mM, CD_3CN) shows the characteristic[5] two-line spectrum expected for this compound (δ −8.92 (1 P; $\Delta\nu_{1/2} = 4.79 \pm 2$ Hz), −14.41 (1 P; $\Delta\nu_{1/2} = 1.54 \pm 0.7$ Hz)) and confirms the homogeneity and identity of **1**. In a second control experiment the NMR sample solution was evacuated to dryness and the solid then redissolved in acetone and tested for catalytic activity under our typical hydrogenation conditions (40 psig of H_2, 0.5 mL of cyclohexene, 2.5 mL of acetone, 20 mg of precatalyst; note that the precatalyst has Krytpofix 222 added).[6a] The recovered solid was shown to be catalytically active with a turnover frequency of 140 h^{-1} (in comparison to typically 300 ± 50 h^{-1} for

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[7] Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebun-Khan, T. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.

[8] Important ^{17}O NMR methodologies and chemical shift data, which provide the needed background for the present work, are: (a) Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246. (b) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93. (c) Besecker, C. J.; Klemperer, W. G.; Maltbie, D. J.; Wright, D. A. *Inorg. Chem.* **1985**, *24*, 1027. (d) Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2355. (e) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44. (f) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345. (g) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 4891. (h) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (i) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. (j) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030. (k) Stirring CH_3CN solutions of polyoxoanions in the presence of ^{17}O-enriched H_2O is reported by Klemperer and coworkers to enrich only the terminal (Nb–O) and bridging (Nb_2–O) niobium oxygens of $Nb_2W_4O_{19}{}^{4-}$ within <10 min. After 24 h, they find that enrichment of the NbWO positions is possible but that enrichment of the W_2O and WO positions (not observed under the above mild conditions) was possible for $Nb_2W_4O_{19}{}^{4-}$ only after stirring a slurry of the polyoxoanion in ^{17}O-enriched H_2O with base catalysis ($[(n\text{-}C_4H_9)_4N]OH$) and at elevated temperature (95 °C).[8b]

Table I. ^{17}O NMR Data for Niobium-Containing Polyoxotungstates[a]

entry no.	compd	Nb–O	Nb_2–O	Nb–W–O	Nb–O–M	Nb_2O–M
1	$NbW_5O_{19}^{5-}$	799 (–)[b]		456 (710)		
2	$Nb_2W_4O_{19}^{4-}$	753 (270)[c]	493 (110)[c]	435 (95)[c]		
3	$(C_5Me_5)Rh{\cdot}Nb_2W_4O_{19}^{2-}$ [d]	801 (479)	514 (370)	453 (256)		199 (497)
4	$[(COD)Ir]_2H[Nb_2W_4O_{19}]_2^{5-}$			457 (148)	520 (207)	293 (1230) (M = H)
5	$[(C_7H_8)Rh]_5[Nb_2W_4O_{19}]_2^{3-}$			458 (144)	573 (142)	344 (375)
6	$[(OC)_2Rh]_5[Nb_2W_4O_{19}]_2^{3-}$			473 (138)	528 (216)	280 (497)
7	$[(OC)_2Rh]_3[Nb_2W_4O_{19}]_2^{5-}$			472 (115)	497 (295)	272 (1245)
8	$[(OC)_2Ir]_2H[Nb_2W_4O_{19}]_2^{5-}$			463 (543)	462 (598)	
9	$Nb_2W_4O_{19}H^{3-}$	765 (274)		442 (137)		187 (423) (M = H)
10	$H_xP_2W_{15}Nb_3O_{62}^{9-x}$	752 (988)[e]	512 (257)			180 (233) (M = H)
11	$[(COD)Ir{\cdot}P_2W_{15}Nb_3{}^{17}O_6O_{56}]^{8-}$	680 (437)				333 (514)

[a] All resonances were obtained at 22 ● 2 °C and are reported in ppm relative to 25 °C tap water. Line widths at half-height (Hz) are reported in parentheses. Data for entries 1–8 are taken from ref 8. [b] Peak not observed unless ^{93}Nb decoupling was employed.[8c] [c] Line widths interpolated to 28 °C from data reported at –16 and 52 °C.[8c] [d] This compound is a mixture of two or three isomers, depending upon the conditions of the preparation.[8i] The values listed represent the chemical shifts of only one of the isomers. [e] The unusually broad resonance here is perhaps indicative of some (fast) exchange with residual $H_2{}^{17}O$; note that this excessive line width is absent in the supported $[(1,5\text{-COD})Ir^I]^+$ complex in entry 11 which, presumably, might sterically block and thus slow such a putative exchange.

fresh material which was not subjected to ^{17}O enrichment and did not have added Krytopofix 222); that is, the enriched material is still catalytically active.

Results and Discussion

Enrichment Procedures, Controls, and ^{17}O NMR. First, the needed control and reference point for the ^{17}O NMR studies was done by selectively enriching[8] the parent polyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$ (anion of 2) in only its terminal Nb–O and bridging Nb_2–O oxygens (six oxygens total; i.e. selective enrichment in the Nb_3O_6 minisurface in 1 only). This was accomplished by stirring $P_2W_{15}Nb_3O_{62}^{9-}$ for 1 week at 22 °C in a basic mixture (due to the polyoxoanion acting as a strong base) of 2 mL of acetonitrile/1 mL of 10% enriched $^{17}OH_2$ (eq 1). Two

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

equal integrated intensity resonances at δ 752 (Nb–O, three oxygens) and δ 512 (Nb_2–O, three oxygens) appear in the ^{17}O NMR (Figure 2). These chemical shifts and assignments as Nb–O and Nb_2–O oxygens are made with confidence by comparison to similar environments in related, structurally characterized polyoxoanions, in particular to the seminal ^{17}O NMR work of Klemperer and co-workers (Table I, entries 1, 2, 3, and 9). The assignments made are also consistent with established relative rates of oxygen enrichment: Nb–O > Nb_2O ≫ NbWO ≫ W–O–W ≈ WO ≈ PO ≈ 0.[8k]

The ^{17}O NMR assignments are further secured by a careful inspection of the relative line widths of the observed peaks. For example, the resonance assigned to Nb–O terminal oxygens in $P_2W_{15}Nb_3O_{62}^{9-}$ has a line width more than triple of that assigned to the Nb_2–O bridging oxygens (Table I, entry 10), as expected on the basis of the literature (Table I, entries 2 and 3). A high-field resonance observed at δ 180 is assigned to Nb_2–O–H^+ in comparison to the literature (Table I, entries 4 and 9). This assignment is further supported by titration experiments, in which addition of 0.33 equiv of $[(n\text{-}C_4H_9)_4N]^+OH^-$ resulted in the complete loss of this resonance. Hence, the enrichment procedure in eq 1 in fact yields the protonated $H_xP_2W_{15}Nb_3O_{62}^{x-9}$.

The clean ^{17}O enrichment of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}]$ (1) without its decomposition was accomplished only after a trial and error examination[9] of the possible routes.[10] The use of preenriched $H_xP_2W_{15}Nb_3{}^{17}O_6O_{56}^{x-9}$ (obtained as in eq 1 above) failed to give clean samples of enriched 1, presumably due to the

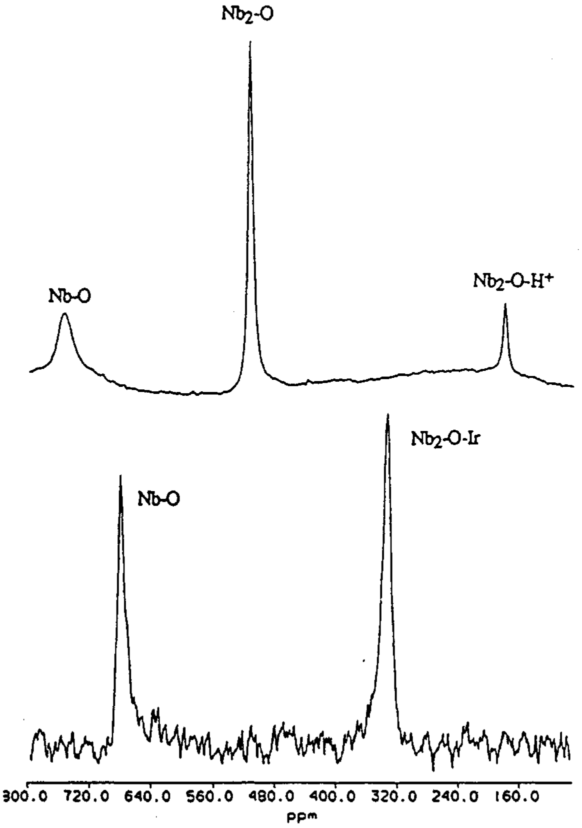

Figure 2. (Top) Spectrum of $[(n\text{-}C_4H_9)_4N]_{9-x}H_xP_2W_{15}Nb_3O_{62}$ following enrichment with 10% $H_2{}^{17}O$ for *1 week*. ^{17}O NMR (48.967 MHz, CD_3CN, 22 °C): δ 180 (s, 1 O; Nb_2O–H^+; $\Delta\nu_{1/2}$ = 233 ± 29 Hz), 512 (s, 3 ± 1 O; Nb_2O; $\Delta\nu_{1/2}$ = 257 ± 10 Hz), 752 (s, 3 ± 1 O; NbO; $\Delta\nu_{1/2}$ = 988 ± 169 Hz). (Bottom) Spectrum of $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Ir{\cdot}P_2W_{15}Nb_3{}^{17}O_6O_{56}]$, which was prepared from preformed 1 by enrichment with 10% $H_2{}^{17}O$ over a (shorter) period of *36 h*. ^{17}O NMR (48.967 MHz, CD_3CN, 22 °C, 3 equiv of Kryptofix 222 added) δ 680 (s, 3 ± 1 O; NbO; $\Delta\nu_{1/2}$ = 437 ± 137 Hz), 333 (s, 3 ± 1 O; Nb_2O–Ir; $\Delta\nu_{1/2}$ = 514 ± 106 Hz). The shorter enrichment time (36 h vs 1 week) for the sample in the bottom spectrum plus the presence of a $[(1,5\text{-}COD)Ir^I]^+$ fragment in 1 that should slow $^{17}OH_2$ exchange into 1 are plausible reasons for the lower S/N observed in the bottom spectrum (all other instrument and acquisition parameters were the same for the top and bottom spectra).

presence of protons in $Nb_2O\text{–}H^+$ which blocked the iridium support site.[10] The successful method involved, instead, stirring preformed 1, synthesized according to our published procedure,[5] in a mixture of 2 mL of acetonitrile/1 mL of 10% enriched $^{17}OH_2$ for 36 h at 22 ± 2 °C (eq 2).

$$[(n\text{-}C_4H_9)_4N]_5Na_3\,[(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}] \xrightarrow[2.\ 36\ h/22\ ^\circ C]{1.\ CH_3CN/H_2{}^{17}O} [(n\text{-}C_4H_9)_4N]_5Na_3[(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3{}^{17}O_6O_{56}] \quad (2)$$

Mild temperatures and short times, which maximized the ^{17}O enrichment while minimizing the decomposition of 1, proved crucial for successful enrichment. For example, longer enrichment times (1 week at 22 °C) lead to partial decomposition of the compound, as evidenced by the appearance of new resonances in the ^{31}P NMR over and above those characteristic of 1.[5] The successful enrichment route (eq 2) proved to be the rate-determining step in the present work.

^{17}O NMR of Enriched $[(n\text{-}C_4H_9)_4N]_5Na_3[(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3{}^{17}O_6O_{56}]$. The ^{17}O NMR spectrum of the resultant, cleanly enriched Nb_3O_6 minisurface in $[(n\text{-}C_4H_9)_4N]_5Na_3[(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3{}^{17}O_6O_{56}]$ shows only the expected terminal Nb–O (δ 680) and $Nb_2\text{–}O\text{–}Ir$ oxygen resonances (δ 333), assigned again by analogy to the literature (Table I). (Three equivalents of Kryptofix 222 was added to the sample to eliminate the peak broadening due to the $Na^+\cdots P_2W_{15}Nb_3O_{62}{}^{9-}$ ion-pairing interactions established previously.[5]) Comparison of the spectra obtained for the supported complex 1 and its parent $P_2W_{15}Nb_3O_{62}{}^{9-}$ complex 2 shows a dramatic downfield shift for the $Nb_2\text{–}O$ resonance upon binding $[(1{,}5\text{-COD})Ir^I]^+$ and provides the first direct observation of the $Nb_2\text{–}O\text{–}Ir$, polyoxoanion-to-iridium support interaction in $(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}{}^{8-}$. The ratio of integrated peak intensities is unity, within experimental error, reflecting once again the presence of equal numbers of two types of magnetically inequivalent oxygens. Although even semiquantitative peak integration in ^{17}O NMR is difficult, it is especially important here as it rules out differential enrichments of the Nb–O and Nb_2O sites, results which (if they had been present) could have led to misinterpreted ^{17}O NMR spectra.[9]

The observed two-line spectrum for $[(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ is definitive in requiring average C_{3v} (pseudo) symmetry in 1 (pseudo, as the local 2-fold axis at Ir limits the maximum symmetry in 1 to C_s, rigorously speaking). *Assuming* a static structure (see below, however), it would also require that the polyoxoanion be a tripodal support (i.e. that Ir is 5-coordinate, with $[(1{,}5\text{-COD})Ir^I]^+$ bound to three $Nb_2\text{–}O$ bridging oxygens).

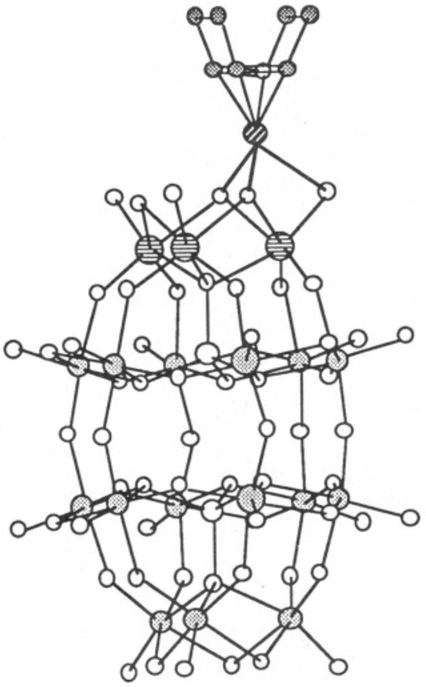

Figure 3. Ball and stick representation of a hypothetical, instantaneous C_s-symmetric isomer for $[(1{,}5\text{-COD})Ir^I]^+$ supported on the Nb_3O_6 face of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$, this time via two bridging Nb_2O oxygens plus *one terminal Nb–O oxygen*. The three equivalent such C_s-symmetric structures would have to be interconverting rapidly on the ^{17}O NMR time scale, becoming averaged about the C_3 axis of $P_2W_{15}Nb_3O_{62}{}^{9-}$, in order to be consistent with the observed ^{17}O NMR results (discussed in the text). This figure, generated from the crystal structure parameters[3g] of $Na_9\text{-}P_2W_{15}Nb_3O_{62}$ and modified using Chem 3-D, does illustrate the expected[4i] two short iridium-to-ONb_2 bonds plus the one, significantly longer iridium-to-ONb (terminal oxygen) bond in this static C_s-symmetric structure.

Hence, *nonfluxional* structures in which $[(1{,}5\text{-COD})Ir^I]^+$ might bind in a square-planar fashion to two oxygens can be ruled out, as can (extremely unlikely) one-oxygen-bound, static, 14-electron iridium structures.

Discussion of Possible Fluxionality in $[(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$. Once must also consider the possibility that the two-line spectrum of $[(1{,}5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ might also be accounted for by some group of fluxional structures that averages to effective C_{3v} symmetry around the C_3 axis of 1 (Figure 3). Three facts are worth recalling here, all of which argue for the C_{3v} symmetry structure presented back in Figure 1 and argue against other possibilities (e.g. Figure 3): the crystallographic investigation cited earlier on $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$ unequivocally demonstrating that $[(C_5Me_5)Rh^{III}]^{2+}$ is supported rigidly on the C_{3v} axis via three bridging Nb_2O oxygens only (this is a dication, however, and is also not a solution structure, the point of discussion), secondly, and more importantly, the ^{17}O NMR results provided herein which establish that a direct $Ir\text{–}ONb_2$ bond to the Nb_3O_6 minisurface exists in 1, *of integrated relative intensity 1 (that is, this bond exists 100% of the time)*, and thirdly, the crucial fact that even the normally highly mobile H^+'s *are not mobile at all on polyoxoanions on the NMR time scale via intramolecular mechanisms in nonaqueous solvents.*[11] The important implication here is that the kinetics of dissociative $[(1{,}5\text{-COD})Ir^I]^+$ mobility should be even slower since more than one metal–O bond is involved. In short, the *C_{3v} average-symmetry structure*

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[9] (a) Although ^{17}O NMR is a powerful structure tool, problems with $^{17}OH_2$ enrichment procedures are perhaps the Achilles' heel of this method. Specifically, the lack of detailed knowledge about the enrichment kinetics and mechanisms and thus the lack of crucial knowledge of the relative amounts of ^{17}O at each different oxygen site make misinterpretations a possibility. For this reason, it is important to use the (albeit imprecise) integration of broad, quadrupolar ^{17}O NMR resonances, with appropriate error estimates, to guide interpretations, as has been done in the present work. (b) We considered the possibility of *inter*molecular exchange of any type[12b] which, if occurring between the 10% enriched and the 90% (predominant) unenriched polyoxoanion sites, could conceivably also lead to interpretation errors (e.g. $(1{,}5\text{-COD})Ir^+$ exchange in the present case between ^{17}O-labeled and unlabeled polyoxoanion). However, in the present example such a hypothetical process should not influence the interpretation.

[10] Lyon, D. K.; Mizuno, N.; Nomiya, K.; Pohl, M.; Finke, R. G. Manuscript in preparation.

shown in Figure 1 is the simplest interpretation of all our evidence plus the literature data.[12]

There is, however, one set of three *fluxional structures* worth discussing in which the required Ir–ONb_2 bond is always retained, the three C_s (instantaneous) symmetry structures where Ir is bound to the Nb_3O_6 minisurface in 1 via two bridging Nb_2–O and one terminal Nb–O oxygen (Figure 3). These three equivalent C_s symmetry structures would then have to be rapidly interconverting on the ^{17}O NMR time scale about the C_3 axis of the Nb_3O_6 surface in 1 (and the observed two ^{17}O NMR lines would then be the weighted averages of two terminal Nb–O and one bridging Nb_2O–Ir for one of the lines and one terminal Nb–O and two bridging Nb_2–O–Ir for the other ^{17}O NMR line; see Figure 3). A strong, seemingly compelling argument against this set of three fluxional structures is the cited lack of precedent for such fluxionality and, in fact, evidence strongly arguing against it.[11] (Moreover, there is recent literature demonstrating that 5-coordinate Ir(I) can even be *stereochemically* rigid,[13] rather than extremely stereochemically mobile.) We cannot, however, *unequivocally* rule out the fluxional structures shown in Figure 3 involving bonding between Ir and terminal Nb–O oxygens. (We did attempt to use low-temperature ^{17}O NMR (258 K) in order to obtain direct evidence for or against such $[(1,5\text{-COD})Ir^I]^+$ mobility, but the results were uninformative as anticipated, giving only the expected,[8c,14] low S/N spectra composed of broad, nondiscernable peaks due to the increase in T_2 (and resultant broader peaks) at *lower* temperature for the quadrupolar ^{17}O nucleus.)

Finally, we note that even the preferred structure in Figure 1 with Ir bound to three Nb_2O oxygens is almost surely not completely static, given the following precedent. Klemperer and Day[4i] have shown that the three iridium–oxygen bonds in $[(1,5\text{-COD})Ir{\cdot}P_3O_9]^{2-}$ are of different lengths (in an instantaneous, X-ray crystallographic picture), giving rise to a square-pyramidal Ir atom (with one lone Ir–O bond in the apical position). Their complex is, however, fluxional in a process that makes the Ir–O bonds all equivalent on the NMR time scale even down to −75 °C.[8d] Hence, 5-coordinate Ir in 1 should have these same two short and one long Ir–ONb_2 bond in an instantaneous picture of static C_s symmetry, but these three Ir–ONb_2 bonds should also be fluxional, becoming equivalent on the ^{17}O NMR time scale via a dynamic elongation and shortening such that the average effective symmetry of 1 is (pseudo) C_{3v}. This type of precedented fluxionality,[8d,15] plus the line-width effect of supporting the inherently C_s-symmetric $[(1,5\text{-COD})Ir^I]^+$ on the inherently C_{3v}-symmetric $P_2W_{15}Nb_3O_{62}^{9-}$, can readily explain the residual (excess) line widths observed[5] in the ^{31}P and ^{183}W NMR of $[(1,5\text{-COD})\text{-}Ir{\cdot}P_2W_{15}Nb_3O_{62}]$.

In summary, the ^{17}O NMR studies provided herein are definitive in revealing that $[(1,5\text{-COD})Ir^I]^+$ binds via Ir–ONb_2 bonds 100% of the time within experimental error and in demonstrating that the average solution structure of $[(1,5\text{-COD})Ir^I]^+$ about the N_3O_6 minisurface in 1 is C_{3v}. Even ^{17}O NMR cannot, however, unequivocally distinguish whether or not terminal Nb–O bonds are also involved in bonding $[(1,5\text{-COD})Ir^I]^+$ to the Nb_3O_6 minisurface in 1, although the available evidence disfavors this conceivable explanation. *Overall, a remarkable level of structural knowledge, in comparison to all previous heterogeneous metal-oxide-supported transition-metal catalysts, has been attained for the only known polyoxoanion-supported catalyst precursor, 1.* Hence, one key component of our efforts to develop a paradigm for this new class of oxide-supported catalysts has been pursued largely to completion. (We still hope to obtain a strongly diffracting single crystal of $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$ for a solid-state structure determination; efforts toward this goal are continuing.) The other required component of such a paradigm, detailed mechanistic studies aimed at identifying the true catalyst in reactions beginning from $[(1,5\text{-COD})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}$, are also nearing completion and will be reported in due course.

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(11) (a) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947. (b) Moreover, Norton has recent evidence suggesting that slow H^+ kinetics at bridging M–O–M oxygens may be quite general. Carroll, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 8744. ("The Protonation of a Bridging Oxygen Is Slow"). (c) It is worth noting that an examination of the polyoxoanion-supported organometallics literature[3,4] confirms that supported cations are not mobile over the polyoxoanion surface via intramolecular pathways (bimolecular mechanisms exist, however[11d]). (d) In the case of both H^+ and M^{n+} (M = metals) there is precedent for *inter*molecular (bimolecular) "fluxionality" where added[11a] H^+ or[4c] $Rh(C_5Me_5)^{2+}$, for example, induces an addition/elimination mechanism and thus effects mobility of H^+ and M^{n+} over polyoxoanion surfaces.

(12) (a) A reviewer inquired as to whether or not fluxionality between structures involving Nb–(W)O-to-Ir bonds might also be possible (i.e. where Ir is attached to the upper *side* of the polyoxoanion structure (Figure 1 or 3) far removed from the C_3 axis of $P_2W_{15}Nb_3O_{62}^{9-}$). We discount this possibility, at least presently,[12b] since it runs counter (i) to the crystallographically determined structure of $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$ (ii) to the requirement of an Ir–ONb_2 bond 100% of the time, (iii) to the expectation that the maximum anionic charge density should be in the Nb–O and Nb–O–Nb bonds, and not in the W–O–Nb bonds (a prediction fully consistent with the crystallographically determined location of the $Rh(C_5Me_5)^{2+}$ cited above), (iv) to the fact that even H^+'s are nonmobile on polyoxoanion surfaces in nonaqueous solvents on the NMR time scale, and (v) to the complete lack of precedent whatsoever for any type of *intra*molecular $(1,5\text{-COD})Ir^+$ mobility[11] (much less the required extremely facile, large-distance mobility around the whole polyoxoanion circumference, a total distance of[3g] ca. 23 Å(!), with making and breaking of *at least* nine Ir–O bonds (see Figure 1 or 3)). Note also that the most probable "intermediate" in such a pathway is, in any event, just the C_s-symmetry structure shown in Figure 3. (b) We note, however, that a precedented[5] Na^+ (or even Bu_4N^+) ion pairing in 1 could fullfill the role of an added, "external" cation in an addition/elimination mechanism,[11d] in turn allowing the precedented dissociation[8d] of $(1,5\text{-COD})Ir(solvent)_2^+$ in coordinating solvents as CH_3CN, followed by simple diffusion through solution and readdition to a new site in the polyoxoanion as a "fluxionality" mechanism. This possibility deserves further investigation, since ion-pairing effects are little studied but likely important in this type of polyoxoanion chemistry.

(13) Stereochemically *rigid* 5-coordinate Ir(I) complexes are known: Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855. Rhodes, L. F., Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259. Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165.

(14) Howarth, O. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 151.

(15) Lead references to the fluxionality of d^8, 5-coordinate Ir(I) and related species: (a) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305. (b) Rodman, G. S.; Mann, K. R. *J. Organomet. Chem.* **1989**, *378*, 255. Adams, H.; Bailey, N. A.; Mann, B. E.; Taylor, B. F.; White, C.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1987**, 1947. (c) For a study of the fluxionality of *four-coordinate* $Ir(1,5\text{-COD})(Tripod)^-BF_4^+$, where Tripod = $HC(Ph_2)_3$, see: El-Amouri, H.; Bahsoun, A. A.; Osborn, J. A. *Polyhedron* **1988**, *7*, 2035. (d) Computational studies: Koga, N.; Jin, S. Q.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3417.