Scheme II
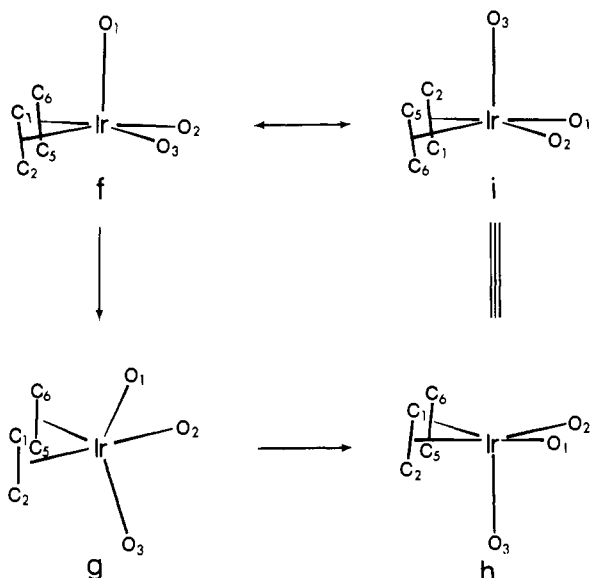

nonequivalent types of cyclooctadiene methine groups. NMR spectra of compound **4** in CH_2Cl_2 measured at ambient temperature, however, display only one phosphorus resonance, one methine carbon resonance, and one methine hydrogen resonance. When the solution temperature is lowered to −75 °C, the single ^{31}P NMR resonance shows no line broadening. Since mixtures of the cyclooctadieneiridium complex $(C_8H_{12})Ir(P_3O_9)^{2-}$ and the norbornadienerhodium complex $(C_7H_8)Rh(P_3O_9)^{2-}$ [2b] show two separate, single ^{31}P NMR resonances arising from the individual complexes, indicating no rapid trimetaphosphate exchange, the exchange process responsible for averaging phosphorus and methine environments in $(C_8H_{12})Ir(P_3O_9)^{2-}$ is presumed to be intramolecular. The equivalence of methine and of phosphorus

environments in $(C_8H_{12})Ir(P_3O_9)^{2-}$ on the NMR time scale can be accounted for by rapid intramolecular rearrangement along the Berry pseudorotation[40] pathway indicated in Scheme II. The intermediate configuration, g, is trigonal bipyramidal with the cyclooctadiene ligand spanning axial and equatorial sites.

Stability Studies. Acetonitrile was selected as a good σ-donor ligand to determine the relative ease with which ligands can be displaced from iridium(I) in complexes **1**, **3**, and **4**. Treatment of compound **1** in CD_3NO_2 with 50 equiv of CD_3CN/mol of iridium resulted in complete degradation of the complex according to ^1H NMR spectroscopy (see Experimental Section). Under the same conditions, compound **3** showed no evidence of degradation, but addition of 250 equiv of CD_3CN/mol of iridium caused about 20% decomposition. Compound **4**, however, showed no evidence of degradation upon addition of 250 equiv of CD_3CN. These results give the order of increasing stability $[(C_8H_{12})Ir]_5$-$(Nb_2W_4O_{19})_2^{3-} < [(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2^{5-} < (C_8H_{12})Ir$-$(P_3O_9)^{2-}$. This sequence cannot be interpreted solely in terms of the instability of coordinatively unsaturated square-planar Ir(I) relative to saturated square-pyramidal Ir(I), since $(C_8H_{12})Ir$-$(C_5H_7O_2)$, $C_5H_7O_2$ = acetylacetonate, is stable toward 250 equiv of CD_3CN in CD_3NO_2 solution. Ligand basicity thus appears to be an important factor.

Supplementary Material Available: Crystal structure reports for compounds **3**, {[(C₈H₁₂)Ir]₂H(Nb₂W₄O₁₉)₂}[(n-C₄H₉)₄N]₅, and **4**, [(C₈H₁₂)Ir(P₃O₉)][(n-C₄H₉)₄N]₂, Tables S1–S4, containing anisotropic thermal parameters for the metal atoms of **3**, bond lengths and angles in the cations of **3** and **4**, and anisotropic thermal parameters for non-hydrogen atoms in the anion of **4**, and Figures S1 and S2, showing perspective drawings of the cations of **3** and **4** (24 pages); structure factor tables for the crystal structure analyses of **3** and **4** (31 pages). Ordering information is given on any current masthead page.

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Polyoxoanion-Supported Metal Carbonyls: Synthesis and Characterization of {[(OC)₂Rh]₅(Nb₂W₄O₁₉)₂}³⁻, {[(OC)₂Rh]₃(Nb₂W₄O₁₉)₂}⁵⁻, {[(OC)₂Ir]₂H(Nb₂W₄O₁₉)₂}⁵⁻, and [(OC)₂Ir(P₃O₉)]²⁻

W. G. Klemperer* and D. J. Main

The first polyoxyanion-supported rhodium and iridium carbonyl complexes have been prepared as $(n-C_4H_9)_4N^+$ or $[(C_6H_5)_3P]_2N^+$ salts and assigned structures similar to those of known rhodium and iridium diene complexes by using multinuclear (^{17}O, ^{13}C, ^{183}W, and/or ^{31}P) NMR and IR spectroscopy. Reaction of either {[(C₇H₈)Rh]₅(Nb₂W₄O₁₉)₂}[(n-C₄H₉)₄N]₃ with CO in nitromethane solution or $Nb_2W_4O_{19}[(n-C_4H_9)_4N]_4$ with $[(OC)_2RhCl]_2$ in 1,2-dichloroethane solution yields crystalline {[(OC)₂Rh]₅(Nb₂W₄O₁₉)₂}[(n-C₄H₉)₄N]₃ (**1**) in 75% yield. The anion of **1** has a structure derived from its (norbornadiene)rhodium precursor by replacement of each C_7H_8 ligand by two CO ligands: two octahedral $Nb_2W_4O_{19}^{4-}$ anions are linked together face-to-face by five $(OC)_2Rh^+$ units. Reaction of $Nb_2W_4O_{19}[(n-C_4H_9)_4N]_4$ with $[(OC)_2RhCl]_2$ in chloroform yields {[(OC)₂Rh]₃(Nb₂W₄O₁₉)₂}[(n-C₄H₉)₄N]₅ (**2**) in 41% yield. The structure proposed for the anion of **2** is obtained by removing two $(OC)_2Rh^+$ units from the structure of the anion of **1**, specifically, those bonded to ONbW oxygens. Bubbling CO through a CH_3CN solution of {[(C₈H₁₂)Ir]₂H(Nb₂W₄O₁₉)₂}[(n-C₄H₉)₄N]₅ yields {[(OC)₂Ir]₂H(Nb₂W₄O₁₉)₂}[(n-C₄H₉)₄N]₅ (**3**) in >80% yield. The anion of **3** is proposed to have a structure derived from the structure of its (cyclooctadiene)iridium precursor by replacement of each C_8H_{12} ligand with two CO ligands. In this structure, two octahedral $Nb_2W_4O_{19}^{4-}$ anions are linked together edge-to-edge by a proton and two $(OC)_2Ir^+$ cations. The trimetaphosphate complex $[(OC)_2Ir(P_3O_9)]\{[(C_6H_5)_3P]_2N\}_2$ (**4**) is prepared by substitution of cyclooctadiene ligands in $[(C_8H_{12})Ir(P_3O_9)]\{[(C_6H_5)_3P]_2N\}_2$ with CO ligands. As was the case with compounds **1** and **3**, the anion of **4** is proposed to have a structure derived from the diene precursor structure by replacement of each diene ligand with two CO ligands, yielding a square-pyramidal Ir(I) complex having two basal CO ligands and a κ^3O-$P_3O_9^{3-}$ ligand spanning two adjacent basal and the apical sites.

The chemistry of solid oxide supported rhodium and iridium carbonyl complexes has been studied in some detail.[1] In order to develop a similar chemistry of soluble organometallic oxide complexes, we have begun to investigate analogous polyoxo-

Table I. 33.9-MHz ^{17}O NMR Data for $Nb_2W_4O_{19}{}^{4-}$ Complexes[a]

complex	chemical shifts[b] (line widths[c])					
	OW	ONbM[d]	ONbW		OW$_2$	ONb$_2$X[e]	ONbWRh
$\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$[f]	781 (564), 724 (438)	573 (142)	458 (144)		397, 390 (614)[k]	344 (375)	289 (622)
$\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$[f]	801 (577), 751 (419)	528 (216)	473 (137)		412, 401 (633)[k]	280 (497)	229 (733)
$\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2\}^{5-}$[g]	740, 724 (1007)[k]	497 (295)	472 (115), 457, 454 (246)[k]		388 (482)	272 (1245)	
$\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$[h]	727 (571)	520 (207)	457 (148)		388 (343)	293 (1230)	
$\{[(OC)_2Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$[i]	732 (1511)	462 (598)	462 (299)		390 (708)		
$\{[(CH_3)_5C_5]Rh(Nb_2W_4O_{19})\}^{2-}$[j]	731 (115), 738, 741 (175)[k]		453 (256), 460,[l] 467 (141)		389–409[l]	199 (497)	151 (313)

[a] All complexes were studied as $(n\text{-}C_4H_9)_4N^+$ salts. [b] Positive chemical shifts in ppm downfield from pure tap water at 20–25 °C. Errors associated with chemical shift values are ±5 ppm for $\nu_{1/2} < 400$ Hz and ±7 ppm for $\nu_{1/2} > 400$ Hz. Unless specified otherwise, ONb_2W_4 oxygen resonances were not observed due to low ^{17}O content at this site. [c] Line widths fwhm, given in Hz, are enclosed in parentheses after the chemical shift of the resonance in question. Errors associated with line widths are ±20 Hz for $\nu_{1/2} < 100$ Hz, ±40 Hz for 100 Hz $< \nu_{1/2} < 350$ Hz, and ±15% for $\nu_{1/2} > 350$ Hz. [d] M = Rh or Ir. [e] X = Rh or H. [f] See Figure 3 for spectrum and Experimental Section for experimental parameters. [g] See Figure 5 for spectrum and Experimental Section for experimental parameters. The spectrum of this sample displayed a weak, <5-Hz line width ONb_2W_4 resonance at δ −52. [h] See Figure 7 for spectrum and ref 4 for experimental parameters. [i] See Figure 7 for spectrum and Experimental Section for experimental parameters. [j] See ref 3 for spectrum and experimental parameters. [k] Combined line width of two resonances at half-height of the more intense resonance. [l] Too many resonances in this region to allow meaningful line width measurements.

anion-supported rhodium and iridium carbonyl complexes. Reported here are the synthesis and spectroscopic characterization of the first complexes of this type, all of which have been prepared in pure, crystalline form as $(n\text{-}C_4H_9)_4N^+$ or $[(C_6H_5)_3P]_2N^+$ salts: $\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$, $\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2\}^{5-}$, $\{[(OC)_2Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$, and $[(OC)_2Ir(P_3O_9)]^{2-}$.

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: CO (Linde), ^{13}CO (Isotec), ^{17}O-enriched water (Monsanto), and $\{[(C_6H_5)_3P]_2N\}Cl$ (Aldrich). $[Rh(CO)_2Cl]_2$ (Aesar) was purified by vacuum sublimation before use. $Na_3P_3O_9\cdot6H_2O$,[2] $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$,[3] $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$,[4] and $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$[4] were prepared by using published procedures.

Acetonitrile (Aldrich), chloroform, nitromethane (both Fisher), and 1,2-dichloroethane (Baker) were distilled from P_4O_{10} under N_2. $C_6D_5NO_2$ and CD_3NO_2 (Aldrich) were vacuum-distilled from BaO (Fisher). Acetone (Fisher) was distilled from dehyrated boron oxide (Aldrich) under N_2. Diethyl ether (Mallinckrodt), tetrahydrofuran, and toluene (Fisher) were distilled from sodium benzophenone ketyl under N_2. All solvents (except acetone and benzene) were stored over 3-Å molecular sieves (Linde). Molecular sieves were activated by heating at 350 °C for 24 h and cooling under vacuum. Benzene (Fisher) was used as received.

Unless specified otherwise, $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ was enriched in ^{17}O by using the procedure described in ref 3. Selectively enriched $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$, in which only the ONb and ONb_2 oxygens were enriched appreciably, was prepared by adding 3 equiv of 51 atom % ^{17}O water to a 0.6 M acetonitrile solution of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$, stirring the solution for 2 min at ambient temperature, and adding excess diethyl ether to precipitate the product. This material was then recrystallized by using the procedure described in ref 3.

Carbon-13-enriched $[(OC)_2RhCl]_2$ dimer was prepared by stirring a solution of 150 mg of $[(OC)_2RhCl]_2$ in 6 mL of benzene under 35 psi 99 atom % ^{13}C CO in a 500-mL Fisher-Porter bottle.

Reactions involving iridium and rhodium reagents were routinely performed in a N_2 atmosphere. All manipulations of ^{17}O-enriched materials were performed in closed systems with rigorous exclusion of moisture to avoid isotopic dilution.

Analytical Procedures. Elemental analyses were performed by the School of Chemical Sciences analytical laboratory and by Galbraith

Laboratories, Knoxville, TN. Infrared spectra of solid materials were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer Model 1330 infrared spectrophotometer and were referenced to the 1028-cm^{-1} band of 0.05-mm polystyrene film. Solution infrared spectra were measured from 0.1 mm path length cells equipped with NaCl windows and referenced to the 2138.5-cm^{-1} band of (neat) cyclohexane.

$^{13}C\{^1H\}$ NMR spectra were recorded either at 90.5 MHz on a Nicolet NTC-360 spectrometer or at 75.5 MHz on a General Electric QE-300 spectrometer. Compounds **1**, **3**, and **4** were enriched in ^{13}CO with 99 atom % ^{13}C-enriched carbon monoxide in the appropriate preparation described below. Compound **2** was prepared from ^{13}C-enriched $[(O\text{-}C)_2RhCl]_2$ (see above). Chemical shifts were referenced internally to tetramethylsilane. Cation resonances, not reported below, appeared at about δ 59, 25, 21, and 14 in spectra of $(n\text{-}C_4H_9)_4N^+$ salts and in the δ 127–135 region of $[(C_6H_5)_3P]_2N^+$ salts.

$^{31}P\{^1H\}$ NMR spectra were recorded at 101.3 MHz in 12-mm-o.d. vertical sample tubes on an unlocked FT NMR system equipped with a 5.87-T Oxford Instruments magnet and a Nicolet NIC-1280 data processor. The magnet was shimmed by tuning the probe to deuterium and observing the deuterated solvent signal. All spectra were externally referenced to 85% H_3PO_4 by the sample replacement method.

^{17}O NMR spectra were measured at 33.9 MHz in 12-mm-o.d. vertical sample tubes without sample spinning on an unlocked FTNMR system equipped with a 5.87-T Oxford Instruments magnet and a Nicolet NIC-1280 data processor. The magnet was shimmed by tuning the probe to ^{133}Cs and observing an aqueous CsI sample. All spectra were externally referenced to 22 °C fresh tap water by the sample replacement method. Chemical shifts are reported as positive numbers for resonances that were observed at high frequency (low field) relative to the reference frequency. The pulse repetition rate was 5.88 Hz. When ^{17}O NMR parameters are specified below, the following abbreviations are used: sol for solvent, T for temperature in °C, [X] for molar concentration of X, enr for ^{17}O content in atom percent ^{17}O, np for number of pulses, sw for spectral bandwidth in Hertz, exp for exponential line broadening in Hertz, de for preaquisition delay in microseconds, and dp for number of data points. All reported line widths (fwhm) were corrected for exponential line broadening.

^{183}W NMR spectra were recorded at 12.5 MHz on a General Electric GN-300 spectrometer equipped with a deuterium lock. Chemical shifts were externally referenced to 0.67 M aqueous $H_4SiW_{12}O_{40}$ by the sample replacement method and were reported as positive numbers for resonances that were observed at high frequency (low field) relative to the reference frequency. On this chemical shift scale, 2 M aqueous Na_2WO_4 appears at +103.6 ppm. A 0.5-Hz pulse repetition rate was employed. When spectral parameters are specified below, the abbreviations defined above for ^{17}O NMR parameters are used.

Preparation of $\{[(CO)_2Rh]_5(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$ (1). Method 1. Carbon monoxide was bubbled through a suspension of 1.26 g (0.30 mmol) of $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$ in 2 mL of CH_3NO_2 for 10 min to give a clear, red-orange solution. Addition of 1 mL of diethyl ether caused the product to precipitate as a red-orange crystalline solid or powder, which was collected by suction filtration, washed with 4 × 5 mL of diethyl ether, and dried under vacuum for 24 h (1.0 g, 0.25 mmol, 83%). Recrystallization was accomplished by dissolving the crude product in 10.5 mL of CH_3NO_2, filtering the mixture through cotton, and adding 22 mL of toluene to the filtrate. The vial containing the solution was then placed in the freezer, and after 2–3 h, red-orange needles had formed. These were collected by suction filtration, washed with 2 × 5

(1) Representative studies: (a) Rode, E. J.; Davis, Mark, E.; Hanson, B. E. *J. Catal.* **1985**, *96*, 574. (b) van't Blik, H. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* **1985**, *107*, 3139. (c) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 587. (d) Basset, J. M.; Chopin, A. *J. Mol. Catal.* **1983**, *21*, 95. (e) Gelin, P.; Ben Taarit, Y.; Naccache, C. *Proceedings of the 7th International Congress on Catalysis*; Tokyo, Japan, 1980; Seiyama, T., Tanabe, K., Eds.; Elsevier: Amsterdam, 1981; Part B, p 898.
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(3) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.
(4) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.*, preceding paper in this issue.

mL of THF, and dried under vacuum for 12 h (0.90 g, 0.23 mmol, 77% overall yield). Anal. Calcd for $C_{58}H_{108}N_3Rh_5Nb_4W_8O_{48}$: C, 17.54; H, 2.74; N, 1.06; Rh, 12.95; Nb, 9.36. Found: C, 17.49; H, 2.70; N, 1.03; Rh, 12.76; Nb, 9.20. IR (Nujol, 650–1000 cm^{-1}): 736 (s, br), 790 (s), 828 (s), 890 (m), 963 (s) cm^{-1}. IR (CH$_3$NO$_2$, 1900–2200 cm^{-1}): 2029 (s), 2092 (s) cm^{-1}. ^{13}C{^{1}H} NMR (75.5 MHz, CD$_3$NO$_2$, 22 °C): δ 184.2 (d, 4, $^1J_{RH-C}$ = 75 Hz), 182.9 (d, 2, $^1J_{Rh-C}$ = 76 Hz), 182.1 (d, 4, $^1J_{Rh-C}$ = 77 Hz). ^{17}O NMR (sol = CH$_3$NO$_2$, T = 20, [Nb] = 64 mM, enr $\leq$ 10, np = 194400, sw = 50000, exp = 15, de = 20, dp = 16384): see Table 1 and Figure 3a.

Method 2. A solution containing 0.32 g (0.15 mmol) of (Nb$_2$W$_4$O$_{19}$)[(n-C$_4$H$_9$)$_4$N]$_4$ in 1.5 mL of 1,2-dichloroethane was added dropwise to a suspension of 0.20 g (0.51 mmol) of [Rh(CO)$_2$Cl]$_2$ in 0.5 mL of 1,2-dichloroethane over a period of 2 min. The resulting dark red solution was stirred for 5 min, during which time a red-orange crystalline solid precipitated. The crystals were collected by suction filtration, washed with 2 × 2 mL of 1,2-dichloroethane and 2 × 5 mL of diethyl ether, and dried under vacuum for 24 h (0.23 g, 0.06 mmol, 77% based on Nb$_2$W$_4$O$_{19}^{4-}$).

Preparation of {[(CO)$_2$Rh]$_3$(Nb$_2$W$_4$O$_{19}$)$_2$}[(n-C$_4$H$_9$)$_4$N]$_5$ (2). A solution containing 1.13 g (0.51 mmol) of (Nb$_2$W$_4$O$_{19}$)[(n-C$_4$H$_9$)$_4$N]$_4$ in 2 mL of CHCl$_3$ was added dropwise to a stirred solution of 0.20 g (0.51 mmol) of [Rh(CO)$_2$Cl]$_2$ in 1 mL of CHCl$_3$ over a period of 2 min. Within 5 min an orange crystalline solid precipitated from the red-orange reaction mixture. The crystals were collected by suction filtration, washed with 2 × 3 mL of CHCl$_3$ and 2 × 5 mL of diethyl ether, and dried under vacuum for 24 h (0.43 g, 0.10 mmol, 39% based on Nb$_2$W$_4$O$_{19}^{4-}$). Although pure as prepared, this material could be recrystallized by dissolving the solid in a minimum amount of 1,2-dichloroethane and slowly adding toluene to the point of saturation. Anal. Calcd for C$_{86}$H$_{180}$N$_5$Rh$_3$Nb$_4$W$_8$O$_{44}$: C, 24.95; H, 4.38; N, 1.69; Rh, 7.46; Nb, 8.98; W, 35.53. Found: C, 24.77; H, 4.32; N, 1.69; Rh, 7.33; Nb, 8.79; W, 35.33. IR (Nujol, 650–1000 cm^{-1}): 765 (s), 805 (s), 885 (m), 957 (s), 977 (w, sh) cm^{-1}. IR (1,2-dichloroethane, 1900–2200 cm^{-1}): 1991 (m, sh), 2017 (s), 2076 (m), 2090 (s) cm^{-1}. ^{13}C{^{1}H} NMR (90.5 MHz, C$_6$D$_5$NO$_2$, 22 °C): δ 185.5 (d, 4, $^1J_{Rh-C}$ = 73 Hz), 184.1 (d, 2, $^1J_{Rh-C}$ = 75 Hz). ^{17}O NMR (sol = 1,2-dichloroethane, T = 20, [Nb] = 32.2 mM, enr = 10 except for ONb and ONb$_2$ where enr = 30, np = 280000, sw = 50000, exp = 10, de = 20, dp = 16384): see Table 1 and Figure 5. ^{183}W NMR (sol = 1,2-dichloroethane, T = 20, [W] = 0.2 M, np = 23800, sw = 5128, exp = 1, de = 195, dp = 16384): δ 165.3 (2), 146.2 (4), 145.5 (2).

Preparation of {[(CO)$_2$Ir]$_2$H(Nb$_2$W$_4$O$_{19}$)$_2$}[(n-C$_4$H$_9$)$_4$N]$_5$ (3). Carbon monoxide was bubbled through a solution of 0.43 g (0.10 mmol) of {[(C$_8$H$_{12}$)Ir]$_2$H(Nb$_2$W$_4$O$_{19}$)$_2$}[(n-C$_4$H$_9$)$_4$N]$_5$ in 2 mL of CH$_3$CN for 10 min. During this time the color changed from yellow to orange to brown. Addition of 10 mL of diethyl ether over a 5-min period caused the product to precipitate as a light green, crystalline solid. The crystals were isolated by suction filtration, washed with 4 × 10 mL of diethyl ether, and dried under vacuum for 12 h (0.34 g, 0.08 mmol, 82%). Anal. Calcd for C$_{84}$H$_{181}$N$_5$Ir$_2$Nb$_4$W$_8$O$_{42}$: C, 24.25; H, 4.39; N, 1.68; Ir, 9.24; Nb, 8.93. Found: C, 24.33; H, 4.54; N, 1.69; Ir, 9.31; Nb, 8.99. IR (Nujol, 650–1000 cm^{-1}): 763 (s, br), 808 (s, sh), 903 (m), 933 (s, sh), 953 (s) cm^{-1}. IR (CH$_3$NO$_2$, 1900–2200 cm^{-1}): 1956 (s), 2059 (s) cm^{-1}. ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_5$NO$_2$, 22 °C): δ 170.4 (s). ^{17}O NMR (sol = 1,2-dichloroethane, T = 20, [Nb] = 32 mM, enr = 10, np = 57000, sw = 40000, exp = 15, de = 25, dp = 16384): see Table 1 and Figure 7b. ^{17}O NMR (sol = 1,2-dichloroethane, T = 20, [Nb] = 40 mM, enr = 25 at ONbIr and ONb$_2$H only, np = 61600, sw = 40000, exp = 15, de = 25, dp = 8192): see Table I.

Preparation of P$_3$O$_9${[(C$_6$H$_5$)$_3$P]$_2$N}$_3$·H$_2$O. To a solution containing 25.7 g (44.8 mmol) of {[(C$_6$H$_5$)$_3$P]$_2$N}Cl in 800 mL of deionized water (60 °C) was added, with rapid stirring, a second solution containing 6.30 g (15.2 mmol) of Na$_3$P$_3$O$_9$·6H$_2$O in 100 mL of deionized water (60 °C). A white solid precipitated from solution immediately. The reaction mixture was stirred for 30 min at 60 °C, during which time the solid turned to an oil. Stirring was then discontinued, and the solution was allowed to cool to room temperature, causing the oil to resolidify. After settling for 12 h, the crystalline material was collected on a medium glass frit filter funnel, washed with 8 × 100 mL of deionized H$_2$O, and dried under vacuum for 24 h (26.5g, 14.2 mmol, 95%). Recrystallization was accomplished by dissolving 1 g of the crude material in 9 mL of acetone, filtering the mixture through cotton, and adding 4.5 mL of toluene to the filtrate. The clear solution was allowed to sit at room temperature for 12 h, during which time block-shaped crystals formed. These were collected by suction filtration, washed with 2 × 10 mL of diethyl ether, and dried at 60 °C in vacuo for 24 h (0.71 g, 0.38 mmol, 67% overall yield). Anal. Calcd for C$_{108}$H$_{92}$N$_3$O$_{10}$P$_9$: C, 69.34; H, 4.96; N, 2.25; P, 14.90. Found: C, 69.12; H, 5.09; N, 2.12; P, 14.73. IR (Nujol, 650–1000 cm^{-1}): 695 (m), 724 (s), 750 (m), 757 (m), 770 (m, sh), 795
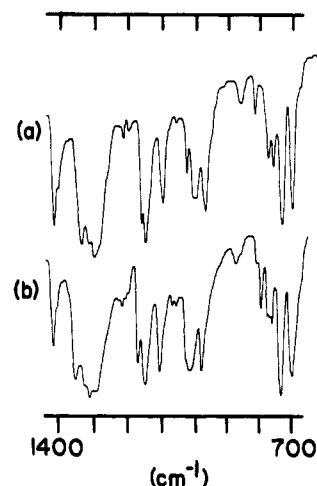
Figure 1. IR spectra of (a) [(C$_8$H$_{12}$)Ir(P$_3$O$_9$)]{[(C$_6$H$_5$)$_3$P]$_2$N}$_2$ and (b) [(OC)$_2$Ir(P$_3$O$_9$)]{[(C$_6$H$_5$)$_3$P]$_2$N}$_2$ measured from Nujol mulls between KBr plates. See Experimental Section for numerical data.

(w, sh), 972 (s, br), 1000 (m, sh), 1030 (w), 1082 (m), 1118 (m), 1160 (w, br), 1185 (w, br), 1265 (s, br), 1288 (s) cm^{-1}. ^{31}P NMR (CH$_3$CN, 22 °C): δ −19.9 (anion), +22.2 (cation).

Preparation of [(C$_8$H$_{12}$)Ir(P$_3$O$_9$)]{[(C$_6$H$_5$)$_3$P]$_2$N}$_2$·nH$_2$O. A solution containing 0.40 g (0.76 mmol) of [(C$_8$H$_{12}$)Ir(NCCH$_3$)$_2$]PF$_6$ in 1 mL of acetone was added dropwise to a solution of 1.43 g (0.76 mmol) of P$_3$O$_9${[(C$_6$H$_5$)$_3$P]$_2$N}$_3$·H$_2$O in 3 mL of acetone with stirring over a period of 2 min. The yellow crystalline solid that precipitated was washed with 2 × 5 mL of diethyl ether and dried under vacuum for 24 h (0.98 g, 0.59 mmol, 78% for n = 3). At this stage the product was quite pure and suitable for use in subsequent reactions. Recrystallization could be accomplished as follows. The crude product (0.66 g) was dissolved in 5 mL of 1,2-dichloroethane/acetone (1/4 v/v), and ca. 5 mL of diethyl ether was added slowly just until the solution became cloudy. The solution was left at ambient temperature for 1 h until yellow crystals formed. The crystals were collected by suction filtration, washed with 2 × 5 mL of diethyl ether, and dried at 60 °C in vacuo for 12 h (0.37 g). Anal. Calcd for n = 3, C$_{80}$H$_{78}$N$_2$IrP$_7$O$_{12}$: C, 57.59; H, 4.71; N, 1.68; P, 12.99. Found: C, 57.39; H, 4.59; N, 1.71; P, 12.70. IR (Nujol, 650–1325 cm^{-1}; see Figure 1a): 693 (s), 721 (s), 748 (m), 763 (w), 802 (w), 843 (w, br), 945 (s), 976 (s, br), 1001 (m), 1031 (w), 1069 (m), 1119 (s), 1131 (s), 1171 (w), 1185 (w), 1266 (s, br), 1283 (s), 1303 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD$_3$CN, 22 °C): δ 3.56 (m, CH), 2.15 (m, CH$_2$), and 1.26 (q, CH$_2$) ppm. ^{31}P NMR (CH$_3$CN, 22 °C): δ −11.4 (anion), +22.2 (cation).

Preparation of [(OC)$_2$Ir(P$_3$O$_9$)]{[(C$_6$H$_5$)$_3$P]$_2$N}$_2$ (4). Carbon monoxide was bubbled through a solution of 0.50 g (0.30 mmol) of [(C$_8$H$_{12}$)Ir(P$_3$O$_9$)]{[(C$_6$H$_5$)$_3$P]$_2$N}$_2$·3H$_2$O in 1 mL of 1,2-dichloroethane plus 4 mL of acetone for 10 min. The product was precipitated as a pale yellow microcrystalline solid by slowly adding 8 mL of diethyl ether dropwise, with stirring. The crystals were collected by suction filtration, washed with 4 × 5 mL of diethyl ether, and dried under vacuum for 24 h (0.43 g, 0.28 mmol, 93%). Anal. Calcd for C$_{74}$H$_{60}$N$_2$IrP$_7$O$_{11}$: C, 56.89; H, 3.87; N, 1.79; Ir, 12.30; P, 13.88. Found: C, 56.84; H, 4.01; N, 1.75; Ir, 12.22; P, 13.69. IR (Nujol, 650–1325 cm^{-1}; see Figure 1b): 687 (s), 720 (s), 746 (m), 757 (m), 780 (w), 792 (w, sh), 854 (w, br), 951 (s), 984 (s, br), 1026 (w), 1038 (w), 1072 (s), 1112 (s), 1135 (s), 1182 (w), 1260 (s, br), 1274 (s), 1287 (sh), 1316 (s) cm^{-1}. IR (1,2-dichloroethane, 1900–2200 cm^{-1}): 1997 (s), 2071 (s) cm^{-1}. ^{13}C{^{1}H} NMR (CD$_3$NO$_2$, 75.5 MHz, 22 °C): δ 168.3 (s). ^{31}P{^{1}H} NMR (CH$_3$CN, 22 °C): δ −15.6 (anion), +22.5 (cation).

Oxygen-17 NMR Spectrum of {[(C$_7$H$_8$)Rh]$_5$(Nb$_2$W$_4$O$_{19}$)$_2$}[(n-C$_4$H$_9$)$_4$N]$_3$. ^{17}O NMR (sol = CH$_3$NO$_2$, T = 20, [Nb] = 55 mM, enr $\leq$ 10, np = 100000, sw = 40000, exp = 15, de = 25, dp = 8192): see Table I and Figure 3a.

X-ray Crystallographic Examination of {[(OC)$_2$Rh]$_3$(Nb$_2$W$_4$O$_{19}$)$_2$}[(n-C$_4$H$_9$)$_4$N]$_5$ (2). After repeated attempts to grow large single crystals of compound **2** suitable for single-crystal X-ray diffraction studies, well-formed orange-red plates with maximum dimensions of 0.70 × 0.38 × 0.18 mm were finally obtained from CH$_3$NO$_2$/toluene. These proved, however, to have sufficiently weak diffractive properties as to preclude space group determination or intensity data collection. Preliminary investigation of the largest of these crystals with Mo K$\bar{\alpha}$ radiation as well as Cu K$\bar{\alpha}$ radiation indicated a primitive orthorhombic unit cell with lattice constants of 30.6 × 30.9 × 32.0 Å ($V \cong$ 30400 Å^3). The weak
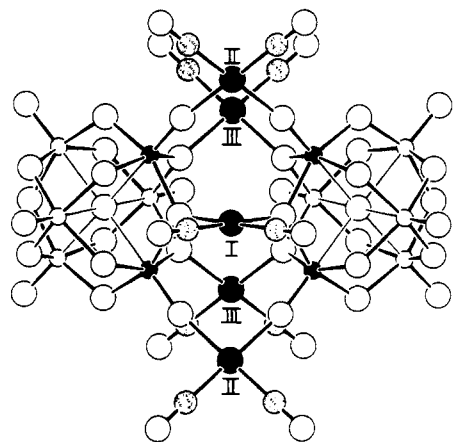
Figure 2. SCHAKAL drawing of the C_{2v} structure proposed for the $\{[(CO)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion. Carbon atoms are represented by shaded circles, oxygen atoms by large open circles, tungsten atoms by small open circles, niobium atoms by small filled circles, and rhodium atoms by large filled circles. The three types of symmetry-equivalent $(CO)_2Rh^+$ units are labeled I, II, and III.

diffraction was therefore obviously due at least in part to the extremely large unit cell.

Results

$\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$ (**1**). Bubbling carbon monoxide through a nitromethane solution of $\{[(C_7H_8)Rh]_5$-$(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$[5] results in displacement of each norbornadiene ligand by two CO ligands to form $\{[(OC)_2Rh]_5$-$(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$ (**1**) according to eq 1. The product

$$\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-} + 10CO \rightarrow$$
$$\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-} + 5C_7H_8 \quad (1)$$

forms beautiful red-orange crystals in 75% overall yield upon crystallization from nitromethane/toluene and is formulated on the basis of elemental analysis. Compound **1** can also be prepared from $[(OC)_2RhCl]_2$ and $(Nb_2W_4O_{19})[(n\text{-}C_4H_9)_4N]_4$ according to eq 2. When $[(OC)_2RhCl]_2$ is used in slight excess in 1,2-dichloroethane solution, the product crystallizes directly from the reaction solution in 79% yield.

$$5[(OC)_2RhCl] + 4Nb_2W_4O_{19}^{4-} \rightarrow$$
$$2\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-} + 10Cl^- \quad (2)$$
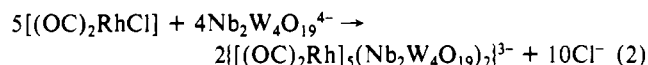
^{13}C and ^{17}O NMR spectroscopy support a structure for the anion of **1** derived from the crystallographically established $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ structure[5] by replacement of each norbornadiene ligand with two CO ligands (see Figure 2). In this C_{2v} structure, two octahedral $Nb_2W_4O_{19}^{4-}$ anions are linked together in a face-to-face fashion by five four-coordinate $(OC)_2Rh^+$ cations. One type of rhodium, Rh_I in Figure 2, is bonded to two ONb_2 oxygen atoms. The two Rh_{II} centers are each bonded to two ONb oxygen atoms, and the two Rh_{III} centers are each bonded to two $ONbW$ oxygen atoms. In agreement with this proposed structure, ^{13}C NMR spectroscopy in CH_3NO_2 solutions shows three resonances in the carbonyl region with relative intensities 2:1:2 (see Experimental Section). Comparison of the ^{17}O NMR spectra of $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ and $\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ as $(n\text{-}C_4H_9)_4N^+$ salts in CH_3NO_2 shown in Figure 3a,b, respectively, provides further support for the proposed structure. As shown at the top of Figure 3, both anions contain twelve types of symmetry-equivalent oxoanion oxygens: one type of ONb_2W_4 oxygen (two O_A oxygens), one type of ONbWRh oxygen (four O_B oxygens), one type of ONb_2Rh oxygen (two O_C oxygens), three types of OW_2 oxygens (two O_D,
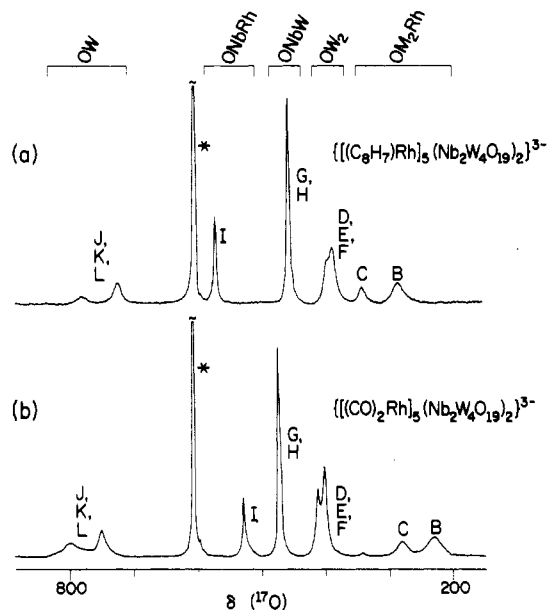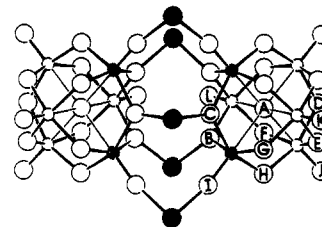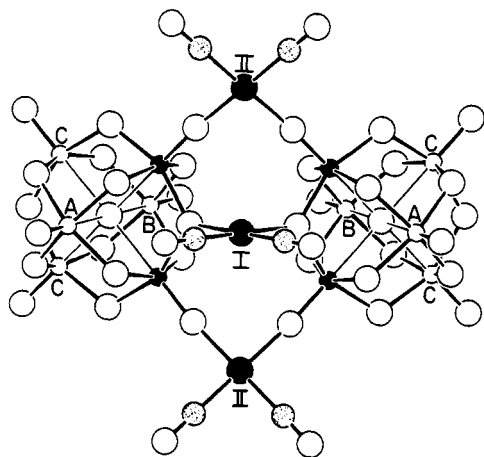

Figure 3. Top: SCHAKAL drawing of the proposed C_{2v}-$Rh_5(Nb_2W_4O_{19})_2$ core of $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ and $\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$. Atoms are represented as described in the Figure 2 caption. Bottom: ^{17}O NMR spectra of (a) $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ and (b) $\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ as $(n\text{-}C_4H_9)_4N^+$ salts in nitromethane. Polyoxoanion ligand resonances are assigned by using the labeling scheme shown in the SCHAKAL drawing at the top of the figure (see text). Solvent resonances are marked with an asterisk (*). The small resonance in (b) at ca. 340 ppm is assigned to unenriched carbonyl oxygens.[6] See Table I and Experimental Section for numerical data and experimental parameters, respectively.

four O_E, and four O_F oxygens), two types of ONbW oxygens (four O_G and four O_H oxygens), one type of ONbRh oxygen (four O_I oxygens), and three types of OW oxygens (four O_J, two O_K, and two O_L oxygens). Resonances in the spectra of both anions labeled J–L, G–H, and D–F are assigned to OW, ONbW, and OW_2 oxygens, respectively, by comparison of their chemical shift values with the values for resonances assigned to these types of oxygens in spectra of $\{[(CH_3)_5C_5]Rh(Nb_2W_4O_{19})\}^{2-3}$ (see Table I) and $[(OC)_3M(Nb_2W_4O_{19})]^{3-}$, M = Mn and Re.[7] Since no resonances are observed for O_A oxygens due to insufficient [17]O enrichment (see ref 3), three resonances remain to be assigned to the three remaining types of oxygens: O_B (ONbWRh), O_C (ONb$_2$Rh), and O_I (ONbRh). Since cation binding to an $Nb_2W_4O_{19}^{4-}$ oxygen causes the resonance for that type of oxygen to be displaced upfield,[3,7,8] the resonance labeled I must be assigned to the ONbRh oxygens, O_I, since it appears downfield relative to the ONb_2 (δ 493) and ONbW (δ 435) resonances but upfield relative to the ONb (δ 753) resonance of $Nb_2W_4O_{19}^{4-9}$ (see Table I). The remaining two resonances, labeled B and C in Figure 3, are assigned to the O_B and O_C oxygens, respectively, on the basis of their relative intensities.

(5) Besecker, C. J.; Klemperer, W. G.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 6158.

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Figure 4. SCHAKAL drawing of the C_{2v} structure proposed for the $\{[(CO)_2Rh]_3(Nb_2W_4O_{19})_2\}^{5-}$ anion. Atoms are represented as described in the Figure 2 caption. The two types of symmetry-equivalent $(CO)_2Rh^+$ units are labeled I and II and the three types of symmetry-equivalent tungsten atoms are labeled A, B, and C.

$\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$ (2). Reaction of $Nb_2W_4O_{19}[(n\text{-}C_4H_9)_4N]_4$ with $[(OC)_2RhCl]_2$ in chloroform solution results in formation of $\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$ (2) according to eq 3. Higher yields are obtained

$$4Nb_2W_4O_{19}{}^{4-} + 3[(OC)_2RhCl]_2 \rightarrow$$
$$2\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2\}^{5-} + 6Cl^- \quad (3)$$
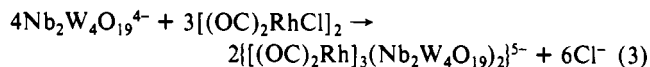
if a slight excess of $[(OC)_2RhCl]_2$ is employed $(Rh:Nb_2W_4 \cong 2:1)$. The product crystallizes in analytically pure form from the reaction solution as orange microcrystals in 41% yield.

The infrared spectrum of compound 2 is extremely similar to the spectrum of $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$ in the 650–1000-cm^{-1} metal–oxygen stretching vibration region (see Experimental Section and ref 4). According to a single-crystal X-ray diffraction study of the cyclooctadiene iridium(I) compound, the $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ anion contains two octahedral $Nb_2W_4O_{19}{}^{4-}$ anions linked together in an edge-to-edge fashion by three cations.[4] Two of these cations are four-coordinate $(C_8H_{12})Ir^+$ cations, each bonded to two ONb oxygens, and the third cation is a proton bridging between two ONb$_2$ oxygens. We therefore propose a similar structure for the anion of 2, where two $Nb_2W_4O_{19}{}^{4-}$ anions are linked together by three $(OC)_2Rh^+$ cations, one bonded to two ONb$_2$ oxygens (Rh$_I$ in Figure 4) and two bonded to two ONb oxygens (Rh$_{II}$ in Figure 4). The proposed structure can be derived from the $\{[(OC)_2Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ structure, shown in Figure 2, by removal of two $Rh(CO)_2{}^+$ units.

The structure proposed for the $\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2\}^{5-}$ anion shown in Figure 4 is supported by ^{13}C, ^{183}W, and ^{17}O solution NMR spectroscopy. This C_{2v} structure contains two types of $Rh(CO)_2$ groups and three types of tungsten atoms labeled I and II and A–C in Figure 4, respectively. Compound 2 accordingly displays two groups of ^{13}C NMR resonances with relative intensities of 2:1 for two types of carbonyl groups plus three ^{183}W NMR resonances with relative intensities of 1:2:1. An ^{17}O NMR spectrum of compound 2 is shown in Figure 5. Resonances in this spectrum are assigned to oxygen environments in the proposed structure by using the labeling scheme given at the top of Figure 5. Resonances are assigned to OW, ONbW, OW$_2$, and ONb$_2$Rh oxygens by comparison of their chemical shift values with values observed for oxygens of the same types in other $Nb_2W_4O_{19}{}^{4-}$ rhodium complexes (see Table I). The weak -52 ppm resonance is assigned to the ONb$_2$W$_4$ oxygens (O$_A$), since it appears in the upfield region associated with OM$_6$ oxygens.[8–10] The remaining resonance at δ 497 is assigned to the ONbRh oxygens (O$_I$) by default. Within the ONbW region, the δ 457 and 454 resonances
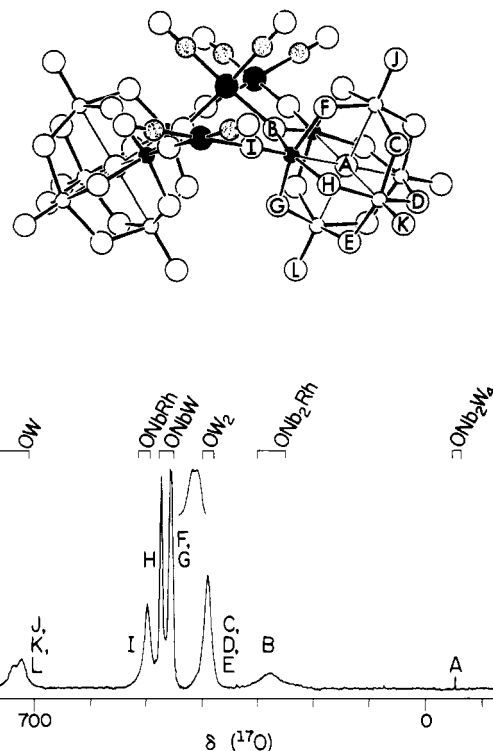

Figure 5. Top: SCHAKAL drawing of the proposed C_{2v}-$\{[(OC)_2Rh]_3$-$(Nb_2W_4O_{19})_2\}^{5-}$ structure. Atoms are represented as described in the Figure 2 caption. One atom from each set of symmetry-equivalent polyoxoanion oxygen atoms is labeled. Bottom: ^{17}O NMR spectrum of $\{[(OC)_2Rh]_3(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$ in 1,2-dichloroethane. Resonances are assigned by using the oxygen labeling scheme given in the SCHAKAL drawing shown at the top of the figure (see text). The insert is an expansion of the O$_F$/O$_G$ resonances. The small resonance at ca. 340 ppm is assigned to unenriched carbonyl oxygens.[6] See Table I and Experimental Section for numerical data and experimental parameters, respectively.

are assigned to the O$_F$ and O$_G$ oxygens (or vice versa), since their extremely similar environments should be reflected in very similar chemical shift values.

Infrared spectroscopy is able to distinguish between the two types of Rh(CO)$_2$ groups in 2. In 1,2-dichloroethane solution, a pair of strong absorptions are observed at 2017 and 2090 cm^{-1} in addition to a pair of weaker bands at 1991 and 2076 cm^{-1}, each pair arising from the $\nu_{asym}(C\text{–}O)$ and $\nu_{sym}(C\text{–}O)$ stretching vibrations[11] for one of the two nonequivalent Rh(CO)$_2$ groups. Note, however, that the bands for nonequivalent Rh(CO)$_2$ groups in compound 1 cannot be resolved. Compound 1 displays a single pair of bands in the C–O stretching vibration region.

$\{[(OC)_2Ir]_2H(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$ (3). Bubbling carbon monoxide through an acetonitrile solution of the (cyclooctadiene)iridium(I) complex $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$[4] results in the displacement of each cyclooctadiene ligand by two molecules of CO to form $\{[(CO)_2Ir]_2H\text{-}(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_5$ (3) according to eq 4. Slow addition of ether causes the product to precipitate as an analytically pure, light green crystalline solid in 82% yield.
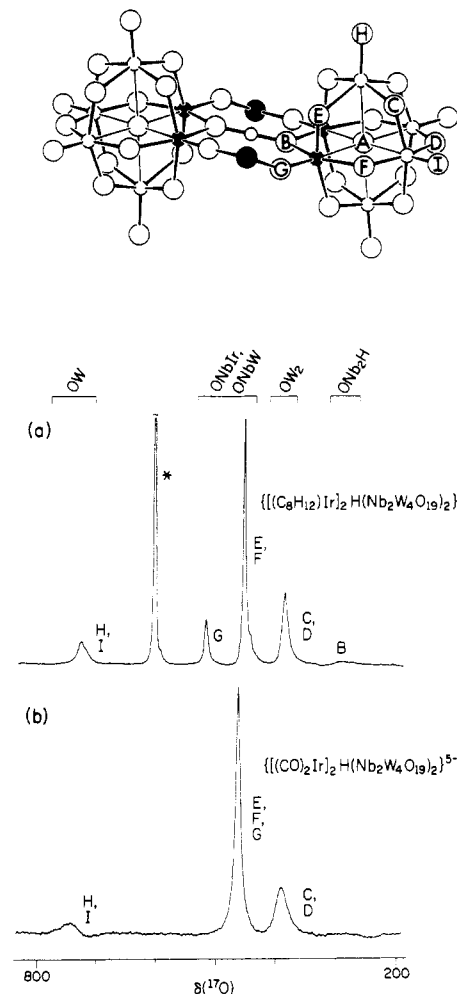
$$\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-} + 4CO \rightarrow$$
$$\{[(CO)_2Ir]_2H(Nb_2W_4O_{19})_2\}^{5-} + 2C_8H_{12} \quad (4)$$
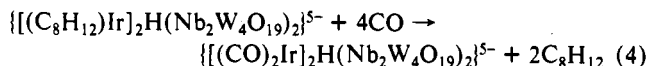
Solution ^{13}C and ^{17}O NMR spectra of 3 are consistent with a $\{[(OC)_2Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ anion structure derived from the structure established crystallographically for $\{[(C_8H_{12})Ir]_2H\text{-}(Nb_2W_4O_{19})_2\}^{5-}$[4] by replacement of each cyclooctadiene ligand with two carbonyl groups (see Figure 6). Assuming D_{2h} symmetry on the NMR time scale, all carbonyl groups in this structure are

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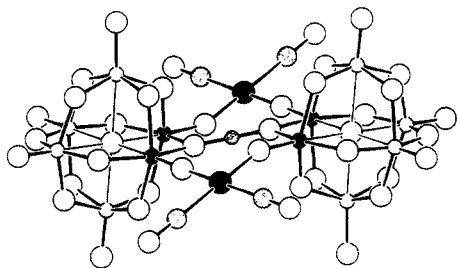
Figure 6. SCHAKAL drawing of the structure proposed for the $\{[(OC)_2Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ anion. The hydrogen atom is represented by a small shaded circle. The iridium atoms are represented by large filled circles. The remaining atoms are labeled as described in the Figure 2 caption.

Figure 7. Top: SCHAKAL drawing of the proposed $Ir_2H(Nb_2W_4O_{19})_2$ core structure of $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ and $\{[(OC)_2Ir]_2H-(Nb_2W_4O_{19})_2\}^{5-}$. Atoms are represented as described in the Figure 6 caption. One atom from each set of symmetry-equivalent oxygen atoms is labeled. Bottom: ^{17}O NMR spectra of (a) $\{[(C_8H_{12})Ir]_2H-(Nb_2W_4O_{19})_2\}^{5-}$ and (b) $\{[(OC)_2Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ as $(n\text{-}C_4H_9)_4N^+$ salts in nitromethane and 1,2-dichloroethane, respectively. Polyoxoanion ligand resonances are assigned by using the oxygen scheme shown in the SCHAKAL drawing at the top of the figure (see text). See Table I and Experimental Section for numerical data and experimental parameters, respectively.

symmetry-equivalent, and the ^{13}C solution NMR spectrum of **3** displays only a single resonance in the carbonyl region. This same D_{2h} structure contains nine nonequivalent types of polyoxoanion oxygen atoms, labeled A–I at the top of Figure 7, but the ^{17}O solution NMR spectrum of **3** displays only three resonances (see
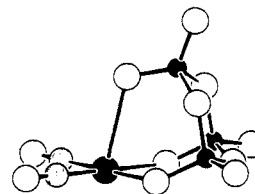
Figure 8. SCHAKAL drawing of the structure proposed for the $[(OC)_2Ir(P_3O_9)]^{2-}$ anion. Carbon atoms are represented by shaded circles, oxygen atoms by large open circles, and phosphorus atoms by small filled circles, and the iridium atom is represented by a large filled circle.

Figure 7b). A resonance for the ONb_2W_4 oxygens O_A is not observed due to insufficient enrichment at this site, a consequence of the ^{17}O enrichment procedure employed. The resonances for the OW (O_H, O_I), ONbW (O_E, O_F), and ONbW (O_C, O_D) oxygens can be assigned by comparison with the ^{17}O NMR spectrum of $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{3-}$, which has been assigned in ref 4 (see Figure 7a and Table I). There remain then only two types of oxygens to be accounted for, the ONb_2H (O_B) and ONbIr (O_G) oxygens. Since these are the only types of $Nb_2W_4O_{19}^{4-}$ oxygens bonded exclusively to niobium, they can be selectively enriched in ^{17}O by water exchange.[3] When the ^{17}O NMR spectrum of compound **3** prepared from selectively enriched $Nb_2W_4O_{19}^{4-}$ is recorded under the same conditions employed for measurement of the spectrum shown in Figure 7b, only a single resonance at δ 462 is observed. Although it is possible that resonances for the ONb_2H and ONbIr oxygens are not resolved, comparison with the spectrum of $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ suggests a more likely possibility, namely, that the ONbIr resonance is observed at δ 462 and the ONb_2H is too broad to observe. Replacement of norbornadiene ligands in $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ with carbonyl groups displaces with ONbRh resonance upfield by 45 ppm; an upfield displacement of the ONbIr resonace in $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ by 58 ppm upon replacement of its cyclooctadiene ligands by carbonyl groups is therefore reasonable. Given the >1000 Hz line width of the ONb_2H resonance in $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}^{5-}$ and the known line-broadening effect of ^{93}Nb coupling,[9] a very large ONb_2H line width is also expected.

$[(OC)_2Ir(P_3O_9)]\{[(C_6H_5)_3P]_2N\}_2$ (4). Bubbling carbon monoxide through a 1,2-dichloroethane/acetone solution of $[(C_8H_{12})Ir-(P_3O_9)]\{[(C_6H_5)_3P]_2N\}_2$ results in loss of cyclooctadiene and formation of $[(OC)_2Ir(P_3O_9)]\{[(C_6H_5)_3P]_2\}$ (4) according to eq 5. The product crystallizes directly from the reaction solution in >90% yield upon addition of diethyl ether.

$$[(C_8H_{12})Ir(P_3O_9)]^{2-} + 2CO \rightarrow [(OC)_2Ir(P_3O_9)]^{2-} + C_8H_{12}$$
(5)
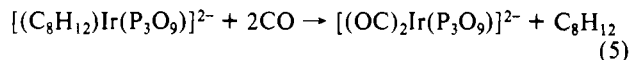
On the basis of spectroscopic data, the $[(OC)_2Ir(P_3O_9)]^{2-}$ anion is assigned a structure derived from the X-ray crystallographically determined structure of the $[(C_8H_{12})Ir(P_3O_9)]^{2-}$ anion[4] by replacement of the cyclooctadiene ligand with two carbonyl ligands (see Figure 8). The two anions display very similar infrared spectra in the P–O stretching region, suggesting similar ligand geometries (see Figure 1). Solution infrared spectra of **4** in nitromethane show the symmetric (2073 cm^{-1}) and asymmetric (1997 cm^{-1}) carbonyl stretching vibrations expected for a *cis*-Ir(CO)$_2$ moiety.[11] On the ^{31}P NMR time scale, all phosphorus nuclei in **4** are equivalent, suggesting rapid Berry pseudorotation of the type proposed for $[(C_8H_{12})Ir(P_3O_9)]^{2-}$ in ref 4.