Polyoxoanion-Supported Organometallic Complexes: Carbonyls of Rhodium(I), Iridium(I), and Rhodium(I) That Are Soluble Analogs of Solid-Oxide-Supported M(CO)\(_n^+\) and That Exhibit Novel M(CO)\(_n^+\) Mobility

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The Dawson-type P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\) polyoxoanion-supported Re(CO)\(_3^+\) complex, [Re(CO)\(_3\)]\(^+\)P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\) (1), has been synthesized and characterized in two different counter-cation compositions. The [(n-C\(_3\)H\(_8\))\(_3\)N] \(^+\) complex provides a highly soluble compound which exists as a single isomer in solution. The carbonyl stretching infrared frequencies suggest that the P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\) ligand serves as a strong electron donor to the Re(CO)\(_3^+\) fragment. The P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\) polyoxoanion-supported Ir(CO)\(_2^+\) complex [Ir(CO)\(_2\)]\(^+\)P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\) (2) has also been synthesized and characterized as its octakis(tetrabutylammonium), [(n-C\(_3\)H\(_8\))\(_3\)N] \(^+\) salt. This compound was characterized by NMR and IR, results which demonstrate that 2 also exists as a single isomer in solution. The [Ir(CO)\(_2\)]\(^+\)P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\) complex is stable in the absence of water, but decomposes quickly in the presence of even 1 equiv of water. Attempted preparation of the analogous P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\)-supported Rh(CO)\(_2^+\) complex (3), while monitoring by \(^{31}\)P NMR, revealed that this compound is unstable in solution at room temperature. In addition, we have discovered that added Na\(^+\) can induce the formation of non-C\(_{3v}\) symmetry isomers of supported Re(CO)\(_3^+\) and Ir(CO)\(_2^+\) and, by inference, supported Ir(1,5-COD)+. When Na\(^+\) is removed from these systems by addition of Kryptofix\([2.2.2]\), the non-C\(_{3v}\) isomers convert back to the single, C\(_{3v}\) isomer with heating, thereby providing a model system for the little studied mobility of M(CO)\(_n^+\) cations across a soluble-oxide surface. When [Rh(CO)\(_2\)]\(^+\)P\(_2\)W\(_{15}\)Nb\(_3\)O\(_{62}\)\(^-\) is irradiated in the presence of hydrogen and cyclohexene a novel polyoxoanion-stabilized Rh\(_n^0\) nanocluster is formed, results that bear a strong analogy to Yates’ work studying atomically-dispersed Rh(CO)\(_3^+\) on solid Al\(_2\)O\(_3\).\(^{10e}\) Yates and co-workers observe that Rh(CO)\(_3^+\)+Al\(_2\)O\(_3\) loses a CO upon photolysis, and that the resultant Rh(CO)\(_3^+\)+Al\(_2\)O\(_3\) is reduced under H\(_2\) to form Rh(0), which in turn yields Rh\(_n^0\) clusters on Al\(_2\)O\(_3\)—a process that, intriguingly, is largely reversible if CO is readded. Also briefly discussed is other relevant literature of solid-oxide-supported Re(CO)\(_3^+\) and M(CO)\(_n^+\) (M = Ir, Rh), literature that makes apparent the potential significance of these complexes as EXAFS and other spectroscopic models of solid-oxide-supported M(CO)\(_n^+\).

Introduction

Metal carbonyl complexes supported on the metal–oxide surface have been the focus of numerous studies.\(^2\) Interest in these systems stems from the fact that metal carbonyls supported on solid oxides are among the best studied probes of the difficult to study, and thus poorly understood, oxide-to-metal catalyst-support interaction. Particularly well-studied systems are Rh(CO)\(_2^+\) on Al\(_2\)O\(_3\)\(^-6\) and on other metal oxides\(^7,\(^8\)\) and Re(CO)\(_3^+\) on MgO\(^9\) for which the structures shown in Figure 1 have been proposed. Arguably, these structures are better characterized than any other oxide-supported complexes in heterogenous catalysts, although their structures are still not unequivocally established at the atomic level. More recently, photochemical activation of hydrocarbons by Al\(_2\)O\(_3\)-supported rhodium car-

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**Figure 1.** (A) Proposed structure of Rh\(^+\) geminal dicarbonyl sites on \(\gamma\)-Al\(_2\)O\(_3\). [Rh(CO)\(_2\)]\(^+\)-Al\(_2\)O\(_3\), suggested by van’t Blik et al.\(^4\) Note that the five-coordinate Rh(CO)\(_2^+\) species in Figure 1A is not what a considerable amount of organometalllic precedent suggests (see the references, and a more general discussion of the factors for or against five coordination in nominally four-coordinate, d\(_5\) complexes, provided elsewhere,\(^1\) especially footnotes 15, 26, and 30 therein). (B) Proposed structure of the rhenium tricarbonyl sites on magnesia, [Re(CO)\(_3\)]\(^+\)-MgO\(\cdot\), catalysis, although their structures are still not unequivocally established at the atomic level. More recently, photochemical activation of hydrocarbons by Al\(_2\)O\(_3\)-supported rhodium car-
bonyls that agglomerate, under \( H_2 \), to Rh\(^6\) particles has been reported,\(^{10}\) work which further illustrates the interest in well-characterized, oxide-supported M(CO)\(_3\)\(^+\) species.

The available solid-oxide-supported metal carbonyls have been studied by multiple physical techniques, the most powerful being EXAFS (extended X-ray absorption fine structure).\(^{11}\) EXAFS can provide bond lengths, numbers and types of neighboring atoms, and deviations of atoms from equilibrium position, as well as short-range order and local structure around particular atoms. However, in order to unequivocally interpret EXAFS spectra without error, discrete model or reference compounds are well-known to be invaluable. For the M(CO)\(_3\)\(^+\)–solid-oxide systems, the ideal model complexes—which are not presently available—should have the following properties: (i) a stoichiometrically well-defined, preferably 1:1, ratio of metal to support, (ii) a nonaggregated, monomeric form, (iii) existence as a single isomer, (iv) solubility in a variety of solvents, thereby facilitating solution structure determinations, and, ideally as well, (v) sufficient crystallinity to permit single-crystal X-ray diffraction structural determinations.

Polyoxoanion-supported M(CO)\(_3\)\(^+\) are promising candidates for modeling solid-oxide-supported metal carbonyls, in light of the close-packed oxide nature of both solid metal oxides and polyoxoanions.\(^{12,13}\) In addition, a few polyoxoanion-supported metal carbonyls have already been described in the literature,\(^{14,15}\) although the only—but still major—contributions to date were made by Klemperer, Day, and co-workers. Specifically, these authors have reported the first and still only examples of polyoxoanion-supported manganese and rhenium complexes\(^{14a,b}\) (\([\text{Mn(CO)}_3(\text{cis-Nb}_2\text{W}_6\text{O}_{19})^2\]\(^-\)) and \([\text{Re(CO)}_3(\text{cis-Nb}_2\text{W}_6\text{O}_{19})^2\]\(^-\)), as well as the first examples of iridium and rhodium carbonyl complexes,\(^{14d}\) \([\{\text{Rh(CO)}_2\}_2(\text{Nb}_2\text{W}_6\text{O}_{19})^2\]\(^-\)), \([\{\text{Rh(CO)}_3\}_2(\text{Nb}_2\text{W}_6\text{O}_{19})^2\]\(^-\)), and \([\{\text{Ir(CO)}_2\}_2\text{H(Nb}_2\text{W}_6\text{O}_{19})^2\]\(^-\)). Unfortunately, however, the complexes of Mn(CO)\(_3\)\(^+\) and Re(CO)\(_3\)\(^+\), are a mixture of three diastereomers, and both the iridium and the rhodium dicarbonyls exhibit metal to polyoxoanion stoichiometries other than the desired 1:1 ratio. These two facts preclude the use of the cis-Nb\(_2\)W\(_6\)O\(_{19}\)\(^-\)–supported complexes as soluble EXAFS models; the multiple support sites, and lower, non-C\(_{3v}\) symmetry of the most basic support site in cis-Nb\(_2\)W\(_6\)O\(_{19}\)\(^-\) are other nonoptimum features of this early system.

The trimetaphosphate-supported metal carbonyls, \([\text{Mn(CO)}_3(\text{P}_3\text{O}_9)]^2\]\(^-\), \([\text{Re(CO)}_3(\text{P}_3\text{O}_9)]^2\]\(^-\), and \([\text{Ir(CO)}_2\]\(^+\)(\text{P}_3\text{O}_9)]^3\(^+\) have also been reported by Klemperer, Day, and co-workers,\(^{14c,d}\) and these complexes do exist as single isomers in solution. In addition, they are also generally characterized by X-ray diffraction structural analyses, key results underpinning the development of polyoxoanion-supported metal carbonyls. They are, therefore, of (unexploited) interest as EXAFS models, their main limitation being that the trimetaphosphate support does not, of course, contain metal atoms and thus is not, strictly speaking, rigorously analogous to a transition-metal oxide.

For some time now we have had studies in progress aimed at well characterized, single isomer, 1:1 metal–polyoxoanion complexes of metal carbonyl complexes. Our choice of P\(_2\)W\(_15\)Nb\(_3\)O\(_{62}\)\(^9\)–. Figure 2, as the support system was prompted by its now well-documented tendency to form nonaggregated, 1:1 polynerncaboxylic to metal, single isomer adducts,\(^{16}\) as has been demonstrated for \([\text{Ir(1,5-COD)}]_2\text{P}_2\text{W}_15\text{Nb}_3\text{O}_{62}\]\(^9\)– by \(^{17}\)O and \(^{183}\)W NMR studies\(^{16}\) and for \([\text{Rh(C}_{6}\text{Me}_{13})]_2\text{P}_2\text{W}_15\text{Nb}_3\text{O}_{62}\]\(^7\)– by single-crystal X-ray crystallography and \(^{183}\)W NMR.\(^{16}\) The P\(_2\)W\(_15\)Nb\(_3\)O\(_{62}\)\(^9\)– based system is, therefore, as good a soluble-oxide systems as is presently available for preparing EXAFS

**Figure 2.** (A) Ball-and-stick representation of \(\alpha\)-1,2,3-P\(_2\)W\(_15\)Nb\(_3\)O\(_{62}\)\(^9\)– as determined by a single crystal X-ray diffraction structural analysis.\(^{16}\) (B) Polyhedral representation of \(\alpha\)-1,2,3-P\(_2\)W\(_15\)Nb\(_3\)O\(_{62}\)\(^9\)–. The three NbO\(_6\) octahedra are represented by the hatched octahedra in the top 1, 2, and 3 positions. The WO\(_6\) octahedra occupy positions 4–18 (the white octahedra), and the PO\(_4\) groups are shown as the two internal black tetrahedra.
and related spectroscopic models. Also of significance is that \( \text{P}_{2}\text{W}_{15}\text{Nb}_{3}\text{O}_{62}\text{Br} \) was prepared from \( \text{Re}_{2}\text{O}_{7}\text{Br} \) according to the literature procedures.\(^{18} \) \( \text{Re}(\text{CO})_{3}(\text{CH}_{3}\text{CN})_{3}\text{BF}_{4} \) was prepared from \( \text{Re}(\text{CO})_{5}\text{Br} \) according to the procedures described for the preparation of the analogous \( \text{ClO}_{4} \)-salt,\(^{19} \) but using \( \text{AgBF}_{4} \) instead of \( \text{AgClO}_{4} \).

**Instrumentation/Analytical Procedures.** Oxygen- and moisture-sensitive samples were routinely manipulated under an inert nitrogen atmosphere in a Vacuum Atmospheres drybox (±1 ppm oxygen as monitored by use of a Vacuum Atmospheres oxygen monitor, VAC Model AO 316-C). All glassware used in the drybox was dried overnight at 120 °C before use. Elemental analyses were obtained from Mikroanalytisches Labor Pascher, Remagen, Germany. Infrared spectra were obtained on a Nicolet 5DX spectrometer as either KBr discs or as solutions (CH\(_3\)CN) using an NaCl cell (pathlength 0.1 mm). KBr (Aldrich, spectrophotometric grade) was used as received.

Gas uptake experiments were conducted using standard techniques with a vacuum manometer and a vacuum line. The total volume of the system was 111 ± 1 cm\(^3\) as measured by the pressure change induced by opening the stopcock of a standard calibrated flask (28.6 cm\(^3\)). The uptake of gas was quantitatively determined by monitoring the pressure decrease with a manometer (±1 Torr; 1 Torr = 133.32 Pa; detailed procedures are available as Supporting Information). Control experiments showed a negligible uptake (<1 Torr) in the absence of \([\text{M}(1.5-\text{COD})_{6}\text{P}_{2}\text{W}_{15}\text{Nb}_{3}\text{O}_{62}]^{1+} (\text{M} = \text{Ir}, \text{Rh}) \) compound, thereby confirming the absence of leaks or other artifacts in the gas uptake experiments.

Gas-liquid chromatographic (GC) monitoring of the amount of 1,5-cyclooctadiene released from such CO uptake experiments was done using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP 3395 integrator. A DB-1 capillary column was used under the following conditions: initial temperature 50 °C, initial time 3 min, temperature ramp 10 °C/min, final temperature 160 °C, detector (FID) temperature 200 °C. He carrier gas flow 1.5−2 cm\(^3\)/min, and sample volume 2 µL. Toluene was used as an internal standard.

**Nuclear Magnetic Resonance (NMR).** All NMR spectra were obtained in Wilmad NMR tubes (5 mm or 10 mm o.d.) equipped with a J. Young valve, at room temperature unless otherwise stated. The chemical shifts are reported on the δ scale with downfield resonances as positive.

\(^{31} \)P NMR (121.5 MHz) spectra were recorded in 5 mm o.d. tubes on a Bruker AC-300P NMR spectrometer. A 33 mM CD\(_3\)CN solution (0.200 mmol of polyyoxoanion in 0.6 mL) was used unless otherwise stated. An external reference of 85% H\(_3\)PO\(_4\) was used by the substitution method.\(^{11} \) Acquisition parameters are as follows: pulse width 5 s, acquisition time 0.819 s, relaxation delay 1.500 s, and sweep width ±10000 Hz. An exponential line broadening apodization (1.5 Hz) was applied to all spectra, but removed for any line widths reported herein.

\(^{31} \)P NMR (282.4 MHz) spectra were also recorded in 5 mm o.d. tubes on a Bruker AC-300P NMR spectrometer. In all measurements, we used a CD\(_3\)CN solution containing 33 mM of polyyoxoanion and 28 mM (0.85 equiv) of \( \text{(CH}_{3}\text{CN})_{3}\text{PF}_{6} \). The \( \text{PF}_{6}^{-} \)resonance (δ = −72.3 ppm) is seen for the CyT\(^{1+}\) supported upon the vanadium analog, \( \text{P}_{2}\text{W}_{15}\text{Nb}_{3}\text{O}_{62}\text{Br} \), in the spectra recorded in CD\(_3\)CN.

(21) The reported chemical shifts are not corrected for the volume diamagnetic susceptibility of the sample’s solution, but proved reproducible in house within ±0.2 ppm when using the same NMR instrument, similar NMR sample tubes, and similar volumes and concentrations (as was done for all samples in the present study). Elsewhere (see especially footnotes 34 and 51),\(^{16} \) we have discussed the problem that literature chemical shifts variations as large as ±0.5 ppm are not uncommon due to the solution’s volume susceptibility.

ppm, referenced to neat CFC13 by the external substitution method.21
doublet, \( \delta (^{19}F) = 706 \) Hz was used as internal standard both for
chemical shifts and quantitative analysis by integration of the signals;
the “number of fluorines, \( F \)” in the text that follows was calculated from
the ratio of integrated intensities, assuming this −72.3 ppm signal to be
5.1 F (= 0.85 equiv of PF6−; this internal standard signal is not
listed among the data for each individual compound). Acquisition
parameters are as follows: pulse width 3.0 \( \mu \)s, acquisition time 0.623
s, relaxation delay 1.500 s, and sweep width ±13158 Hz (i.e., from
−63 ppm to −155 ppm). An exponential line-broadening apodization
(1.5 Hz) was applied to all spectra, but was removed from any reported
line widths. To ensure that the delay was long enough for the complete
relaxation of all signals, a longer delay (4.500 s.) was also applied in
control experiments; the resultant integrated intensities of the signals
were the same within experimental error (±5%).

\(^{18}F\) NMR (20.8 MHz) spectra were recorded on a Bruker AM500
NMR spectrometer. Spectra were recorded at room temperature in 10
mm o.d. NMR tubes and referenced to saturated Na2O2D2O by the
external substitution method.21 Acquisition parameters were as follows:
pulse width 30.0 \( \mu \)s, acquisition time 1.114 s, relaxation delay 1.000 s, and sweep width ±14705 Hz. An exponential line-broadening
apodization (5 Hz) was applied to all spectra, but was removed for
any line widths reported herein.

Preparations. \([(n-C_{4}H_{9})_{n}][Re(CO)_{3}P_{2}W_{15}Nb_{3}O_{62}](n-C_{4}H_{9})_{2}B F_{4}] 1a. In the drybox, \( [(n-C_{4}H_{9})_{n}][P_{2}W_{15}Nb_{3}O_{62}(3.0 \text{ g}, 0.48 \text{ mmol) was dissolved in 18 mL of CH}_{3}CN. To this clear, colorless
solution a solution of \( 1a, \mu \) (ppm, referenced to neat CFCl3 by the external substitution method, 21
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\( 1b \). In the drybox, \( 1b \), \( 0.25 \text{ mmol, 22%)} \). \(^{19}F\) NMR of this material showed the presence of 0.83
equiv of \((n-C_{4}H_{9})_{2}B F_{4}\), that is, only 0.17 equiv of this contaminant
was removed by this procedure.

\( [(n-C_{4}H_{9})_{n}][Na][Re(CO)_{3}P_{2}W_{15}Nb_{3}O_{62}] 1b. In the drybox, the 2.32
g. 23 (a) The compound \([Ir(1,5-COD)(CH_{3}CN)_{2}]B F_{4}\) was prepared according
the literature method, 23 except that AgBF4 was used instead of
AgBF3. The product was obtained in 83% yield and characterized by

(23)
\(^{31}\)P NMR (32 scans), \(\delta\) (no of F, \(\Delta\nu_{1/2}\)): \(-151.1 (3.6 \text{ F} [=0.90 \text{ equiv of BF}_3], 2.0 \pm 0.7 \text{ Hz}). \) Note that no attempt was made to remove the 1.0 equiv of \((n-\text{C}_4\text{H}_9)\text{BF}_4\) in this product (nor in 2a below), since this was accomplished by preparing the mixed \((n-\text{C}_4\text{H}_9)\text{Na}^{\delta^+}\) salt, 2b (vide infra). This \((n-\text{C}_4\text{H}_9)\text{Na}^{\delta^+}\) salt is, however, a key complex for the NMR and Ir(1.5-COD)\(^n^+\) and Ir(CO)\(^n^+\) mobility discovery which follows.

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\{[n-(\text{C}_4\text{H}_9)\text{N}]_2[Ir(CO)_2P_2W_12NbO_{24}]\} [n-(\text{C}_4\text{H}_9)\text{N}]_2[\text{BF}_4]^-, 2a. \]

In the drybox, \([n-(\text{C}_4\text{H}_9)\text{N}]_2[Ir(CO)_2P_2W_12NbO_{24}](n-(\text{C}_4\text{H}_9)\text{N})_2[\text{BF}_4]\) (999 mg, 0.15 mmol) and toluene (0.015 mL, as GC internal standard, see Instrumentation/Analytical Procedures for details of the GC setup and 1.1 mmol) was used as a starting material; \(2\text{CH}_2\text{CN} (3\text{ mL})\) was used as solvent instead of \(\text{CH}_2\text{Cl}_2\) (due to low solubility of the starting material in the latter solvent); and (3) reaction was carried out at \(0^\circ \text{C} \). The amounts of CO consumed (determined manometrically) and 1,5-cyclooctadiene released by GC were 0.18 mmol (1.9 equiv) and 0.099 mmol (1.1 equiv), respectively. The reaction solution was deep red, from which a pink solid was obtained by transferring the solution over 3 min to 30 mL of ether. Yield: 473 mg (0.078 mmol, 83%). IR (KBr pellet, cm\(^{-1}\)) \(\nu_{\text{CO}}\) 2047 (s), 1965 (s); polyoxometalate region 1084 (vs), 1062 (m), 938 (s), 913 (sh), 907 (s), 894 (s), 814 (sh), 520 (m). 31 P NMR, 33 mM with 99 mM (3 \(\text{CH}_2\text{CN}\)) of Kryptofix in \(\text{CH}_2\text{CN}\), after heating to \(60^\circ \text{C} \) for 40 min: \(\delta = 7.35 (1 \text{P}, 3.8 \text{ Hz}), -13.38 (1 \text{P}, 3.0 \pm 0.1 \text{ Hz}). \)

\[
\{[n-(\text{C}_4\text{H}_9)\text{N}]_2[\text{Rh}(1.5\text{-COD})P_2W_12NbO_{24}](n-(\text{C}_4\text{H}_9)\text{N})_2[\text{BF}_4]\} , 2b. \]

The same procedure as in the preparation of the all tetrabutylammonium salt, 2a, was followed to prepare this mixed, \([n-(\text{C}_4\text{H}_9)\text{N}]_2[Ir(CO)_2P_2W_12NbO_{24}][n-(\text{C}_4\text{H}_9)\text{N}]_2[\text{BF}_4]\) (from 536 mg, 0.094 mmol) was used as a starting material; \(2\text{CH}_2\text{CN} (3\text{ mL})\) was used as solvant instead of \(\text{CH}_2\text{Cl}_2\) (due to low solubility of the starting material in the latter solvent); and (3) reaction was carried out at \(0^\circ \text{C} \). The amounts of CO consumed (determined manometrically) and 1,5-cyclooctadiene released by GC were 0.18 mmol (1.9 equiv) and 0.099 mmol (1.1 equiv), respectively. The reaction solution was transferred to a glass vial and dried overnight at room temperature in vacuo. Yield: 314 mg (0.048 mmol, 64%). IR (KBr pellet, cm\(^{-1}\)) \(\nu_{\text{CO}}\) 2046 (s), 1966 (s); polyoxometalate region 1084 (vs), 1062 (m), 938 (s), 913 (sh), 907 (s), 894 (s), 814 (sh), 779 (vs). 31 P NMR (33 mM in \(\text{CD}_2\text{Cl}_2\)), \(\delta\) (no of F, \(\Delta\nu_{1/2}\)): -7.53 (1 \text{P}, 3.8 ± 0.1 Hz), -13.38 (1 \text{P}, 3.0 ± 0.1 Hz).
Hydrogenation of Cyclohexene by Photolyzed [(n-C₄H₉)₃N][Rh(CO)₃]P₂W₁₅Nb₃O₆²⁻·(n-C₄H₉)₄NBF₄. 3. The gas-uptake apparatus shown in Figure B of the Supporting Information was used, except that a larger calibration flask (113 cm³) was used and the stopcock between the calibration flask and the uptake line was left open, so that a larger amount of hydrogen gas can be used (total volume = 224 ± 1 cm³). In the drybox, 3 (50 mg, 7.7 µmol) was dissolved in anhydrous ethanol (2.5 mL), dried over 3 Å molecular sieves, to give a clear, orange-yellow solution. This solution was placed in a side-armed Schlenk tube (Figure A-a, Supporting Information), and cyclohexene (0.5 mL) was added. The Schlenk tube was attached to the gas-uptake line, and the uptake line was filled with 640 Torr of hydrogen (640 Torr is atmospheric pressure in our mile-high altitude laboratory). Note that the Schlenk tube was still under nitrogen atmosphere at this stage, that is, the reaction solution was not yet degassed. Next, a mineral-oil bubbler was connected to the Schlenk tube via its side arm, and a slow flow (ca. 1 cm³/s) of hydrogen was introduced from the uptake line to the Schlenk tube and exited through the bubbler.

The solution was vigorously stirred and irradiated with a sunlamp (300 W) for 15 min, while maintaining a slow flow of hydrogen. The solution turned dark brown and somewhat cloudy. Irradiation was then turned off, and the hydrogen flow was stopped. The stopcocks to the hydrogen tank and the oil bubbler were closed (i.e., the reaction system was closed with 640 Torr of hydrogen in it).

Stirring of the solution was continued for 12 h, after which time the pressure of hydrogen dropped to 430 Torr. This pressure change corresponds to consumption of ca. 2.5 mmol of hydrogen, although this is only approximate because no attempt was made to keep the temperature constant throughout this initial survey reaction. In the reaction mixture, a fine, black precipitate formed. A sample was collected by allowing the reaction mixture to stand overnight, followed by removal of the slightly cloudy, pale brown supernatant solution by pipet. The remaining black powder in a small amount of solution (ca. 0.5 mL) was centrifuged and the yellow supernatant was removed by pipet. The black powder was then dried under vacuum overnight. The sample (which was soluble in acetone) was shipped to the University of Oregon for TEM analysis, all as detailed previously.16 The results are shown in Figure 12. A GC analysis of the supernatant solution revealed that cyclohexene was completely hydrogenated to cyclohexane (the hydrogen uptake did not match exactly the amount of hydrogen consumed in this initial survey experiment, since part of the starting solution evaporated under a flow of hydrogen gas during the photolysis).

Note also that the absolute necessity of photolysis vs mild thermolysis (i.e., despite the presence of 1 equiv of (n-C₄H₉)₄NBF₄ in the isolated product), complex 1a is useful and has been included herein for the following reasons: (i) it establishes that a single isomer of supported [Re(CO)₃]P₂W₅Nb₃O₆²⁻ has been formed (vide infra), (2) it indicates that further isolation work, with different cation mixtures to obtain (n-C₄H₉)₄NBF₄-Free product, was warranted and likely to be successful, and (3) it is quite possible that in some applications (i.e., as EXAFS or other spectroscopic models) this high-solubility, [(n-C₄H₉)₄N]⁺ salt, 1a, will be preferred.

A ¹³P NMR spectrum of 1a in CD₃CN (Figure 3) shows two lines at δ = −7.7 and −13.3 with integrated intensities of 1:1; integration of this spectrum also shows that 1a is at least 95% of a single isomer. The changes in the ¹³P chemical shifts in 1a from the starting material [(n-C₄H₉)₃N][Re(CO)₃]P₂W₁₅Nb₃O₆²⁻ (−6.7 and −13.7 ppm) show the expected downfield shift of the ¹³P (−6.7 ppm) resonance closest to the “NbO₃⁻” cap in P₂W₁₅Nb₃O₆²⁻, and provide direct spectroscopic evidence for preferential binding, as expected, of Re(CO)₃⁺ to the more basic “NbO₃⁻” cap. The observed line widths, ∆ν₁/₂ = 1.8–2.0 (±0.1 Hz) are comparable to those observed for the unsupported polyoxoanion, P₂W₁₅Nb₃O₆²⁻, which exhibits values for ∆ν₁/₂ of 1–2 Hz.

Infrared measurements (Figure 4) confirm that the Dawson-type heteropolytungstate framework remains intact under the conditions of the synthesis. The presence of two carbonyl bands (2006 and 1876 cm⁻¹) is consistent with the expected Cs₃₆ symmetry for the polyoxoanion–Re(CO)₃⁺ complex. These bands have lower frequencies than other Re(CO)₃⁺ complexes with tridentate oxygen ligands, namely [Re(CO)₃][Nb₅W₁₀O₃₀]⁺, [Re(CO)₃][P₃O₁₀]⁻, and [CrP₃O₉][OP(OEt)₃]·Re(CO)₃).²⁻ The fact implies that the quite basic P₂W₁₅Nb₃O₆²⁻ ligand is a stronger donor than other oxo ligands listed above.

Results and Discussion

Synthesis, Isolation, and Characterization of [(n-C₄H₉)₃N]₃[Re(CO)₃][P₂W₁₅Nb₃O₆²⁻][n-C₄H₉]₄NBF₄ 1a. The target complex [Re(CO)₃][P₂W₁₅Nb₃O₆²⁻] was obtained initially as its octakis(tetraethylammonium) salt by the reaction of (n-C₄H₉)₃N][P₂W₁₅Nb₃O₆₂ with [Re(CO)₃(CH₃CN)]BF₄ (eq 1).

\[
[(n-C₄H₉)₃N][P₂W₁₅Nb₃O₆₂] \rightleftharpoons \text{CH₃CN} + [\text{Re(CO)}₃(CH₃CN)]BF₄ \quad \text{(1)}
\]

The product, 1a, was obtained as a yellow-brown powder. Elemental analysis and ¹⁹F NMR showed that 1a had not been

Figure 3. ¹³P NMR spectrum of [(n-C₄H₉)₃N][Re(CO)₃][P₂W₁₅Nb₃O₆²⁻][n-C₄H₉]₄NBF₄, 1a, in CD₃CN showing that it is ca. 95% of a single isomer.
isomer, efforts to remove the 1 equiv of (n-C4H9)4N+CN). Study of solid-oxide-supported Re(CO)3 is significant: it is discrete, single isomer analog of the well-studied, tetrabutylammonium counterion composition means that ion-pairing effects, which are well-established to alter spectroscopic properties,16d,22 (this works since NaBF4 is very soluble in EtOAc, and the addition of 3 equiv of NaBF4 to a solution of (n-C4H9)4NBF4 contaminant 16d,22 is broad and multiline (Figure 6a), as expected and as previously observed in [(n-C4H9)3N][Na][1,5-COD]M-P2W15-Nb3O62( M = Ir and Rh) due to Na+···P2W15Nb3O622− ion-pairing effects).16 After addition of 3 equiv of Kryptofix[2.2.2] at room temperature, the spectrum became sharper, but, interest-
The 183W NMR, C for 40 min; the spectral changes are complete within 30 min at room temperature. Prolonged heating (at 60°C, this solution to 60°C after being heated at 70°C for 40 min, the spectrum looked exactly the same as that of 1a (Figure 7c), the expected IR spectrum also makes sense intuitively: the monocations Re(CO)3H+, (Na+)P2W15NB3O62−, all tetrabutyl ammonium salt, [Re(CO)3]−, and [Re(CO)3]+, the heating of solution b to 60°C in CH3CN (NaCl cell): (a) in the absence of Kryptofix[2.2.2]; (b) after addition of 3 equiv of Kryptofix[2.2.2] at room temperature, (c) after the heating of solution b to 60°C for 40 min. The IR spectra of [(Re(CO)3)−, (Na+)P2W15NB3O62−]− complex has non-C3v symmetry. The exact structures of the non-C3b isomer(s) are not known and thus are only given as a guide to the needed additional studies.

Scheme 1. C3b, Symmetry Structure of [Re(CO)3]+P2W15NB3O628−, I, and Its Na+ Cation-Induced Symmetry Change to Non-C3v Symmetrya


(24) It is possible that 1H NMR or, ideally, a single-crystal X-ray diffraction structural analysis of [Re(CO)3H]+(Na+)P2W15NB3O62− will provide direct structural insight for or against this proposal. Hence, such additional studies are an important goal of future work.

(25) The exact structures of the non-C3b isomer(s) are not known and thus are only given as a guide to the needed additional studies.

temperature). One conceivable, but unlikely, explanation for these unusual observations is a slow reaction between Na+ and Kryptofix[2.2.2] (i.e., a slow removal of precedent16d ion-pairing effects between Na+ and [Re(CO)3]+P2W15NB3O62−). However, this explanation was ruled out by an examination of the 1H NMR after the addition of Kryptofix. This NMR experiment clearly shows, as expected, that the Kryptofix reacts immediately with Na+ after its addition (i.e., no peaks due to free Kryptofix, easily distinguishable in a control experiment, are observed; see Figure D, Supporting Information). Hence, given the slower timescale of the spectral changes, the only other explanation consistent with all the data, at least that we can see, is that, in the presence of Na+, the [Re(CO)3H+]−(Na+)P2W15NB3O62−[−]− complex has non-C3v symmetry. The addition of Kryptofix then binds Na+ immediately (as proved above), but the change to the C3v symmetry structure established for the Na+−free, all tetrabutyl ammonium salt, [Re(CO)3]+P2W15NB3O62− (i.e., established for 1a) is slow. This explanation also makes sense intuitively: the monocations Re(CO)3H+ and Na+ are in competition for the most basic, “Nb3O93−”, binding and support site in P2W15NB3O62−. This necessarily results in a non-C3b symmetry complex, since both monocations cannot simultaneously bind at the single C3v site atop P2W15NB3O62−.

The C3b to non-C3b symmetry changes induced by the Na+ cation are summarized in Scheme 1, along with two plausible and partially precededmented but unproved structures for the non-
The infrared spectrum (KBr pellet, Figure 9) shows two sharp carbonyl bands at 2046 and 1966 cm⁻¹ characteristic of gem-dicarbonyl species of $C_3$ symmetry.

The [Ir(CO)$_2$P$_2$W$_{15}$Nb$_3$O$_6$]⁺⁺ product, 2a, is moderately stable in CD$_3$CN. After a solution was allowed to stand for 48 h in room temperature CD$_3$CN (with or without protection from diffuse room light), we observed a set of new, although small, 31P peaks around −7 ppm (Supporting Information, Figure G). The color of the solution also changed from yellow to brown. Heating this solution to 60 °C for 50 min did not cause further substantial change.

A more rapid and definitive change was observed when H$_2$O or O$_2$ was deliberately added. Addition of 1 equiv of H$_2$O to a fresh CD$_3$CN solution of 2a caused appearance of a few new 31P peaks within 15 min (Supporting Information, Figure H). Exposure to air of another fresh CD$_3$CN solution of 2a also caused appearance of new peaks within 30 min (Supporting Information, Figure I).

Preparation and Isomer Characterization of the Mixed Salt, [(n-C$_5$H$_{11}$)$_3$N]$_3$[Ir(CO)$_2$P$_2$W$_{15}$Nb$_3$O$_6$], 2b. In an attempt to remove the contaminating 1 equiv of (n-C$_5$H$_{11}$)NBf$_4$ in 2a, we tried to prepare the mixed [(n-C$_5$H$_{11}$)$_3$N]$_3$Na$^{8+}$ salt of [Ir(CO)$_2$P$_2$W$_{15}$Nb$_3$O$_6$]$^{8-}$. The well-established, fully characterized compound [(n-C$_5$H$_{11}$)$_3$N]$_3$Na[15-COD]·P$_2$W$_{15}$Nb$_3$O$_6$]$^{16}$ was allowed to react with carbon monoxide (486 Torr) in CH$_3$CN at 0 °C. The brown-yellow solution turned deep red within 30 min, and a pink solid was obtained after precipitation by diethyl ether (83% yield). The infrared spectrum (KBr pellet) showed two sharp carbonyl bands at 2047 and 1965 cm⁻¹ characteristic of gem-dicarbonyl species of $C_3$ symmetry.

The 31P NMR (Figure 8) in CD$_3$CN, Figure 10, also showed the same, “slow spectroscopic changes” detailed above after the addition of Kryptofix, but the final spectrum was slightly more complicated than that of the Re(CO)$_3$⁺⁺ compound, 1b (not unexpectedly; note that Ir(CO)$_2$⁺⁺ is a 2-fold rotor whereas the 3-fold rotor Re(CO)$_3$⁺⁺ matches the polyoxoanion’s 3-fold symmetry, “Nb$_3$O$_9$³⁻” site). Specifically, the 31P NMR in CD$_3$CN without added Kryptofix showed two sets of multiple lines around −8 ppm and −13 ppm, Figure 10a. Upon addition of

\[
\begin{align*}
\text{Synthesis, Isolation, and Characterization of (n-C$_5$H$_{11}$)$_3$N Ir(CO)$_2$P$_2$W$_{15}$Nb$_3$O$_6$}: 2a. &
\text{The conceptually simplest route to the polyoxoanion-supported iridium carbonyl [Ir(CO)$_2$P$_2$W$_{15}$Nb$_3$O$_6$]$^{8-}$ is the reaction of carbon monoxide with the well-known 1,5-cyclooctadiene complex [Ir(1,5-COD)]$^{2-}$ (eq 2).}^{1,6,17}
\end{align*}
\]

\[
\begin{align*}
[(n-C$_5$H$_{11}$)$_3$N]_3[\text{Ir(CO)$_2$P$_2$W$_{15}$Nb$_3$O$_6$}]^{2-} + 2\text{CO} &
\rightarrow (1) \text{CHCl}_3, -78 ^\circ \text{C} \quad \text{pH with Et}_2\text{O} \\
[(n-C$_5$H$_{11}$)$_3$N]_3[\text{Ir(CO)$_2$P$_2$W$_{15}$Nb$_3$O$_6$}]^{2-} + 1,5-\text{COD} &
\text{ (2)}
\end{align*}
\]

The previously unknown all tetrabutylammonium salt, [(n-C$_5$H$_{11}$)$_3$N]$_3$[Ir(1,5-COD)]$^{2-}$ was prepared and characterized following our well-established methods to give the mixed [(n-C$_5$H$_{11}$)$_3$N]$_3$Na$^{8+}$ salt. It was then allowed to react with carbon monoxide (486 Torr) in CH$_3$Cl$_2$ at −78 °C for 1.5 h (the reaction was complete within 20 min). The pale yellow powder of 2a was obtained in 75% yield by precipitation with diethyl ether. The uptake of 2.0 ± 0.2 equiv of carbon monoxide and the release of 1.0 ± 0.1 equiv of 1,5-cyclooctadiene were confirmed by manometry and GC measurements, respectively.

The 31P NMR (Figure 8) in CD$_3$CN solution showed a clean, two-line spectrum (−7.6 and −13.2 ppm) at room temperature. The infrared spectrum (KBr pellet, Figure 9) shows two sharp
Another control experiment (control B) using a predominantly clean two-line $^{31}$P spectrum, which was observed to have chemical shifts identical to those for $^{2b}$ iridium, in comparison to the all-$^{31}$P lines per polyoxoanion) are present in an estimated 70:30 ratio (based on the $^{31}$P NMR integral intensities). The chemical shifts of the major species (−7.6 and −13.2 ppm) were identical within experimental error with those of the all-tetrafluorobutylammonium salt, $^{2a}$.

The presence of Na$^+$ in $^{2b}$ is the obvious explanation for the additional $^{31}$P NMR lines in comparison to the clean, two-line spectrum seen for the all-(n-C$_4$H$_9$)$_3$ salt, $^{2a}$ (recall Figure 8). Hence, a control experiment (hereafter, control A) was performed in which 3 equiv of NaBF$_4$ was added to $^{2a}$. Specifically, the addition of 3 equiv of NaBF$_4$ to a yellow solution of the all-(n-C$_4$H$_9$)$_3$ salt $^{2a}$ in CD$_3$CN gave a deep-red solution. After this solution was stirred for 12 h at room temperature and heated at 60 °C for 40 min, the resultant solution exhibited a $^{31}$P NMR spectrum similar to that observed for a CD$_3$CN solution of $^{2b}$, Figure 11a. The addition of 3 equiv of Kryptofix changed this spectrum some, but failed to convert it into a cleaner spectrum in the absence of heating, Figure 11b. Heating this solution to 60 °C for 50 min yielded a predominantly four-line spectrum, Figure 10c, in which the two major sets of species (i.e., with two $^{31}$P lines per polyoxoanion) are present in an estimated 70:30 ratio (based on the $^{31}$P NMR integral intensities). The chemical shifts of the major species (−7.6 and −13.2 ppm) were identical within experimental error with those of the all-tetrafluorobutylammonium salt, $^{2a}$.

Two other insights are apparent following reflection upon these results and some of our earlier work. Apparently, [(n-C$_4$H$_9$)$_3$N]$_3$Na$^+$[Ir(1,5-COD)+P$_2$W$_{15}$Nb$_3$O$_{62}$] in CD$_3$CN after ad-
diation of 3 equiv of Kryptofix. The spectrum collapses quickly (i.e., within 30 min at room temperature) to a two-line spectrum indicating a single isomer (i.e., on the $^{31}$P NMR time scale). These mild conditions contrast with the 35 °C higher (60 °C) temperature required to interconvert the isomers of 2b. The higher mobility of Ir(1,5-COD)$^{+}$ over that for Ir(CO)$_{2}^{+}$ about the “Nb$_{3}$O$_{9}^{3-}$” cap is, of course, reasonable given the stronger $\pi$-accepting nature of carbonyl ligands and their anticipated synergetic interaction with the electron-donating oxygens atop P$_{2}$W$_{15}$Nb$_{3}$O$_{62}^{-}$.

Preparation and Isolation of the Unstable Rhodium Dicarbonyl Congener [($n$-C$_{4}H$_{9})$_{4}N[$][Rh(CO)$_{2}$P$_{2}$W$_{15}$Nb$_{3}$O$_{62}$]$_{3}$.

We also synthesized and isolated at low temperature the analogous P$_{2}$W$_{15}$Nb$_{3}$O$_{62}^{-}$-supported Rh(CO)$_{2}^{+}$ complex, as it is one of the best studied, solid-oxide-supported M(CO)$_{2}^{+}$ from among the three better studied monometallic carbonyls, Re(CO)$_{2}^{+}$, Ir(CO)$_{2}^{+}$, and Rh(CO)$_{2}^{+}$. Indeed, our studies actually began here long ago,$^{13f}$ but our concern about the unstable nature of this complex, a concern validated by the results which follow, caused us to return to this Rh(CO)$_{2}^{+}$ complex only after the data on the more stable Re(CO)$_{2}^{+}$ and Ir(CO)$_{2}^{+}$ analogs were in hand.

The previously unreported all tetrabutylammonium salt, [($n$-C$_{4}H$_{9})$_{4}N][Rh(1,5-COD)P$_{2}$W$_{15}$Nb$_{3}$O$_{62}$], was prepared and characterized following our well-established methods for the [($n$-C$_{4}H$_{9})$_{4}N]$_{3}$Na$_{3}$ complex.$^{16}$ In a largely optimized experiment that followed several survey experiments (i.e., mostly at higher temperature and for longer times, following input from what was successful in the support of the Re(CO)$_{2}^{+}$ and closely analogous Ir(CO)$_{2}^{+}$ cation), the well-established precursor$^{16}$ [($n$-C$_{4}H$_{9})$_{4}N][Rh(1,5-COD)P$_{2}$W$_{15}$Nb$_{3}$O$_{62}$] was allowed to react with carbon monoxide in CH$_{2}$Cl$_{2}$ at −78 °C for 90 min (the majority of the reaction was complete within 30 min). A pale yellow powder was obtained in 64% yield by the procedure detailed in the Experimental Section. The infrared spectrum (KBr pellet, Figure K, Supporting Information) showed two sharp carbonyl bands at 2059 and 1984 cm$^{-1}$ characteristic of gem–dicarbonyl species of $C$_{6} symmetry. Product 3 is stable in CD$_{2}$Cl$_{2}$ at −60 °C for at least 2 h as monitored by $^{31}$P NMR, exhibiting two main peaks at −8.5 ppm and −14.2 ppm (Figure L, part a, Supporting Information). At −40 °C the $^{31}$P NMR of this material in CD$_{3}$CN showed two main peaks at −8.0 and −13.6 ppm (Figure M, part a, Supporting Information). Both spectra show impurity peaks; the relative $^{31}$P integrals indicated a purity of ca. 80%, even in these low temperature CD$_{2}$CN or CD$_{3}$CN spectra. Note, however, that the reaction with carbon monoxide is complete, since the expected stoichiometry of CO uptake and 1,5-cyclooctadiene release was observed within ±5% (2.0 and 1.0 equiv, respectively). In addition, although the $^{31}$P NMR spectrum in CD$_{3}$CN (Figure M, Supporting Information) remained unchanged for 2.5 h at −40 °C, warming to room temperature led to decomposition within 30 min (broadening of the lower-field $^{31}$P signal and change in solution color from yellow to dark brown). A similar change was observed in CD$_{2}$Cl$_{2}$ (Figure L, Supporting Information). It follows, therefore, that the product 3 is unavoidably partially decomposed during the workup. Given the unstable nature of 3 in solution, we can now rationalize our earlier, mostly unsuccessful results from higher temperature and longer time synthetic attempts.$^{13f}$

The above results too are of more than just passing interest. They definitively show, for the first time, the low stability of Rh(CO)$_{2}^{+}$ (on at least the very basic P$_{2}$W$_{15}$Nb$_{3}$O$_{62}^{-}$ oxide and in solution), and also clearly demonstrate the difference between Rh(CO)$_{2}^{+}$ and the more stable Ir(CO)$_{2}^{+}$ and Re(CO)$_{3}^{+}$. In addition, they provide a clean system for additional product, kinetic and mechanistic studies for a mode of decomposition in which a full, proved mass balance can in principle at least be obtained, a complete stoichiometry that is difficult to impossible to obtain quantitatively (and sometimes even qualitatively) for analogous solid-oxide-supported systems. (Preliminary, separate thermolysis studies of both of the M(CO)$_{2}^{+}$ (M = Ir, Rh) compounds 2a and 3 show that M(0) metal apparently seen previously$^{13f}$ for partially decomposed samples of 3 is not produced upon thermolysis of a 30 mM solution in CH$_{3}$CN for 48 h under nitrogen at 60 °C.)

Formation of Rh$_{0}$ Nanoclusters from [Rh(CO)$_{2}$P$_{2}$W$_{15}$Nb$_{3}$O$_{62}^{-}$] Under H$_{2}$ and Photolysis: Evidence for the Relationship of [M(CO)$_{2}$P$_{2}$W$_{15}$Nb$_{3}$O$_{62}^{-}$] (M = Rh, Ir) to Solid-oxide-supported M(CO)$_{2}$Al$_{2}$O$_{5}$. Worth noting here is our preliminary work in 1987 with less well characterized “[Rh(CO)$_{2}$P$_{2}$W$_{15}$Nb$_{3}$O$_{62}^{-}$]” made at room temperature. In solution, when irradiated in the presence of hydrogen and cyclohexene, an active hydrogenation catalyst is formed, one that even our 1987 ultracentrifugation molecular weight and other evidence indicated was a Rh$_{0}$ “colloid.”$^{13f}$ We now know that a novel polyoxoanion-stabilized$^{16l, 27}$ Rh$_{0}$ nanocluster is formed.$^{13l}$ We repeated this key experiment as part of the present work (see the details provided in the Experimental Section), and again observe the formation of black, isolable and acetone-soluble precipitate, after the hydrogenation of cyclohexene is complete. A TEM (transmission electron microscopy) study of this material verifies that ca. 10 to 40 Å nanoclusters have been formed, Figure 12.

The significance of these results is in their very strong analogy to Yates’ work studying atomically-dispersed Rh(CO)$_{2}^{+}$ on solid Al$_{2}$O$_{3}$. In this analogous work, Yates and co-workers observe that Rh(CO)$_{2}^{+}$•Al$_{2}$O$_{3}$ loses a CO upon photolysis and that the resultant Rh(CO)$_{2}^{+}$•Al$_{2}$O$_{3}$ is reduced under H$_{2}$ to form Rh(0),
which in turn yields Rh\(^{0}\) clusters on Al\(_2\)O\(_3\)—a process that, intriguingly, is largely reversible if CO is readed.\(^{2b,4,8,10}\)

As is perhaps obvious, the formation of a black, active Rh\(^{0}\) nanocluster catalyst herein from the [Rh(CO)\(_2\)P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) precursor is, at least presently and phenomenologically, one of the best examples available of the very close resemblance between the reaction chemistry of a solid metal-oxide-supported monometallic carbynol and polyoxoanion-supported M(CO)\(_n\)^+.  

### Summary

1. The polyoxoanion-supported, C\(_3\)v symmetry Re(CO)\(_3\)^+ complex, [Re(CO)\(_2\)P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\), has been synthesized and characterized in two different counterion formations. The \([(n-C\(_4\)H\(_9\))\(_2\)N][Na]\(^{8+}\) salt is a highly soluble, air-stable compound which exists as a single isomer in solution. The \([(n-C\(_4\)H\(_9\))\(_3\)N]Na\(^{8+}\) salt provides a lower solubility, chemically pure product (i.e., without contaminating \((n-C\(_4\)H\(_9\))\(_2\)NBF\(_4\)), which also exists as a single isomer in solution (following treatment with Kryptofix[2.2.2] and brief heating to remove Na\(^{+}\) ion-pairing effects).

2. The polyoxoanion-supported Ir(CO)\(_2\)^+ complex [Ir(CO)\(_2\)P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) has been synthesized and characterized as its \([(n-C\(_4\)H\(_9\))\(_2\)N][Na]\(^{8+}\) salt. The \(^{31}\)P NMR and IR spectra show that this complex also exists as a single isomer in solution. This complex is found to be air- and water-sensitive.

3. Attempted preparation of the analogous P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)^8–-supported Rh(CO)\(_2\)^+ complex has revealed that this compound is unstable in solution at room temperature. Even low-temperature isolation yields a material that is 20% decomposed.

4. Work with the Na\(^{+}\)-containing salts of both the supported Re(CO)\(_2\)^+, \(1b\), and the Ir(CO)\(_2\)^+, \(2b\), complexes has revealed that two isomers (one C\(_3\)w and one non-C\(_3\)w symmetry) are present for each of these complexes. As such, they (or, possibly better, their mono-Na\(^{+}\) salts) are identified as key systems for further structural, \(^{25}\)kinetic, mechanistic and \(\Delta H^\circ\) and \(\Delta S^\circ\) activation parameter studies of metal cation, M(CO)\(_n\)^+ mobility on an oxide surface.

5. The three [M(CO)\(_n\)^n-P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) (M = Re, Ir, Rh) systems reported herein have been identified as useful ones for product, kinetic, and mechanistic studies of the mode(s) of decomposition of M(CO)\(_n\)^+ on oxides, a topic of interest since such metal carbonyls are used as precursors to heterogeneous catalysts.

6. The photochemical activation under H\(_2\) of the Rh(CO)\(_2\)^+ complex 3 has been demonstrated, results which (a) provide a new route to novel polyoxoanion-stabilized nanoclusters\(^{27}\) (i.e., from [M(CO)\(_n\)^n-P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) precursors) and (b) establish one of the best connections to date between the reaction chemistry of a polyoxoanion-supported and a solid-oxide-supported organometallic.

7. Finally, the present three [M(CO)\(_n\)^n-P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) complexes provide 1-to-1 metal-to-soluble oxide, unaggregated, and single isomer (M = Re, Ir), model complexes for needed EXAFS and other spectroscopic studies of solid-oxide-supported M(CO)\(_n\)^+ (M = Re, Ir, Rh). Their only—but main—disadvantage is that such 8– salts of Dawson-type polyoxoanions have not proven crystalline (i.e., for X-ray diffraction structures) despite considerable efforts toward this goal (see the Supplementary Material elsewhere\(^{19}\)).

In closing, we note that only conclusions 1, 2, 5, and 7 were among our initial goals when this work was initiated more than a decade ago.\(^{13}\) The present studies illustrate a few of the hidden, additional findings (i.e., points 3, 4, and 6 above) available in polyoxoanion soluble metal oxides, but also the time and effort required to uncover them.

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### Supporting Information Available:

Table of CO stretching wavenumbers for various M(CO)\(_n\)^+ compounds (Table A), text giving the calibration procedure for the gas-uptake line, and figure showing the apparatus for reaction with carbon monoxide (Figure A), gas-uptake apparatus (Figure B), positive FAB-MS spectrum of \([(n-C\(_4\)H\(_9\))\(_3\)N][Re(CO)\(_2\)P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) (Figure C), \(^1\)H NMR of \([(n-C\(_4\)H\(_9\))\(_3\)N][Na][Re(CO)\(_2\)P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) (Figure D), \(^{31}\)P NMR of \(1b\) (Figure E), \(^{183}\)W NMR of \(1b\) (Figure F), \(^{31}\)P NMR of \(1b\) after multiple reprecipitations (Figure G), time-dependent change of \(^{31}\)P NMR of \([(n-C\(_4\)H\(_9\))\(_3\)N][Ir(CO)\(_2\)P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) (Figure H), change of \(^{31}\)P NMR of \(2a\) in the presence of H\(_2\)O (Figure I); change of \(^{31}\)P NMR of \(2a\) after exposure to air (Figure J), \(^{31}\)P NMR of \(2a\) with subsequent addition of 3 equiv of NaBF\(_4\), and 3 equiv of Kryptofix in CD\(_3\)CN (Figure K), IR spectrum of \(3\) (Figure L), and the time-dependent change in the \(^{31}\)P NMR of \([(n-C\(_4\)H\(_9\))\(_3\)N][Rh(CO)\(_2\)P\(_2\)W\(_{12}\)Nb\(_2\)O\(_{62}\)]\(^{8-}\) in (n-C\(_4\)H\(_9\))\(_3\)NBF\(_4\), 3, in CD\(_3\)Cl (Figure L) and in CD\(_3\)CN (Figure M) (16 pages). Ordering information is given on any masthead page.

\(^{27}\) A Perspective on Nanocluster Catalysis: Polyoxoanion and (n-C\(_4\)H\(_9\))N\(^{+}\) Stabilized Ir(0)-10 Nanocluster “Soluble Heterogeneous Catalysts.” Aiken, J. D., III; Lin, Y.; Finke, R. G. J. Mol. Catal. 1996, 114, 29.