on the ^{1}H NMR line widths. Because d^8, 5-coordinate Ir(I) is well-known to be highly fluxional,[16] we presently assign the majority of the ^{1}H NMR line broadening (and the residual ^{183}W NMR line broadening) to such fluxionality, and variable-temperature ^{1}H NMR studies are in progress. Any detailed description of the fluxionality in **1** must take note of the fact that a (1,5-COD)Ir$^+$ fragment of inherent C_2 symmetry has been supported atop a $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion of inherent C_3 symmetry.

These NMR results demonstrate that the C_{3v} symmetry designed into $P_2W_{15}Nb_3O_{62}^{9-}$ (via triniobium substitution)[1d] leads to the unprecedented ability[1e,6] to form predominantly one type of support-site regioisomer, (1,5-COD)Ir$^+$ attached to the Nb_3O_9 "cap" in **1** with effective C_{3v} symmetry (Figure 3). The ability of $P_2W_{15}Nb_3O_{62}^{9-}$ to form 1:1 metal/polyoxoanion complexes that do not aggregate is a further, highly desirable, and distinguishing feature of **1**.

The ability of **1** to serve as an effective catalyst precursor, and initial kinetic and mechanistic studies of the resultant high-activity catalyst, are described in the following communication.[4]

Acknowledgment. We thank the reviewers for their helpful comments. Support from NSF Grant CHE-831345 and from a cooperative academic–industrial grant from Catalytica Associates is gratefully acknowledged.

Supplementary Material Available: Figures A and B (ln A vs r^2 MW plots for **1** and the catalyst, respectively), Figures C and D (^{31}P NMR spectra of **1** with and without Kryptofix 2.2.2. in DMSO), Figures E and F (^{31}P NMR spectra of **1** with and without Kryptofix 2.2.2. in CH$_3$CN, showing the more pronounced ion-pairing effects in that solvent in comparison to DMSO), text containing details of the control experiments ruling out O$_2$ contamination during the NMR studies of **1** in J. Young NMR tubes, and text containing the ^{1}H NMR data for **1** (6 pages). Ordering information is given on any current masthead page.

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(16) (a) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305 and references therein. (b) Churchill, M. R.; Lin, K.-K. G. *J. Am. Chem. Soc.* **1974**, *96*, 76 and earlier papers cited therein in this series. (c) Rossi, A. R.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 365. (d) Adams, H.; Bailey, N. A.; Mann, B. E.; Taylor, B. F.; White, C.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1987**, 1947. (e) Mestroni, G.; Camus, A.; Zassinovich, G. *J. Organomet. Chem.* **1974**, *73*, 119 and references 1–3 therein.

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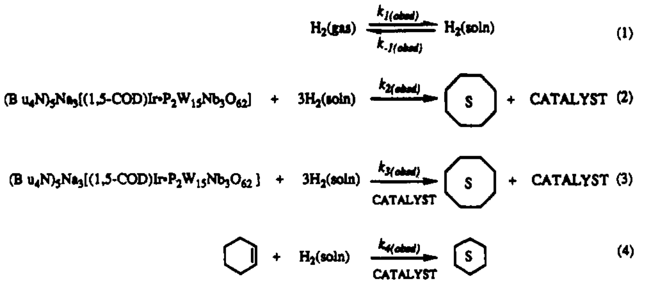
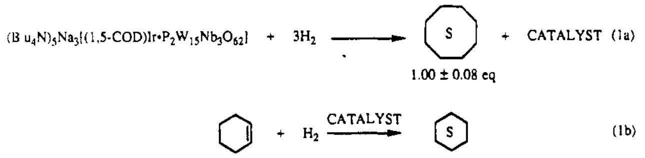
Polyoxoanions as Soluble Metal Oxide Analogues. 6.[1] Catalytic Activity and Initial Kinetic and Mechanistic Studies of Polyoxoanion-Supported, Atomically Dispersed Iridium(I), (1,5-COD)Ir·$P_2W_{15}Nb_3O_{62}^{8-}$

In the preceding communication[1] we described the synthesis and characterization of the polyoxoanion-supported Ir(I) precatalyst $(Bu_4N)_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ (**1**). Herein we (a) demonstrate that **1** leads to an active and long-lived catalyst in a prototypical catalytic reaction, olefin hydrogenation and (b) report initial kinetic and mechanistic data which provide evidence that the actual catalyst derived from **1** is indeed polyoxoanion-supported.

Scheme I



In the presence of 40 psig H$_2$ and 1.65 M purified[2] cyclohexene in acetone at 22.0 ± 0.1 °C, seven independent preparations of **1** (0.0012 M) evolve *reproducibly* into a highly active, yellow, clear and thus *apparently* homogeneous hydrogenation catalyst (eq 1 and Figure 1).[3] The catalyst evolves from **1** during a reproducible 1.2 ± 0.5 h induction period and with the production of 1.00 ± 0.08 equiv of cyclooctane but without producing any visible or insoluble Ir(0).[4] Separate H$_2$-uptake experiments (13 mM **1**, acetone, 22 °C, 500 Torr H$_2$, *no olefin*) show that **1** consumes 3.0 equiv of H$_2$ over 15 h (eq 1a) to yield 1.0 equiv of cyclooctane and a species showing a ^{1}H NMR hydride resonance at −14.5 ppm. The H$_2$-pressure-loss kinetic data (Figure 1, squares with center dots) can be curve-fit (Figure 1, solid line) by the four-step *minimum kinetic model*[5] shown in Scheme I, eqs 1–4.



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(1) Part 5: Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.*, preceding communication in this issue. Non-SI units employed herein: 1 psig = 0.068 atm = 51.68 Torr = 6.89 × 10^3 Pa.

(2) Cyclohexene (Baker) was distilled from Na under dry N$_2$ and stored in the drybox. Acetone (Burdick and Jackson) was distilled from K$_2$CO$_3$ under dry N$_2$ and stored in the drybox. Both liquids were dispensed and stored in glassware that had been dried at 250 °C and cooled under a dry nitrogen flow. H$_2$ (Air Products) was purified by passage through an indicating moisture trap and disposable cartridge O$_2$ trap (Scott).

(3) Details of the catalytic hydrogenations are available as supplementary material.

(4) No Ir(0) metal precipitates visible to the naked eye appear in the hydrogenation experiments described in the text. If the experiment is run at higher catalyst (≥1 mM) or olefin (≥1 M) concentrations, a precipitate is formed at the end of the experiment that is 3–4 times less soluble than **1** and that we are attempting to characterize (the precipitate, which is both acetone and acetonitrile soluble, is not $[Ir(0)]_n$).

(5) (a) The numerical integration curve-fitting[5b] presented in Figure 1 was performed with the GEAR[5c] and the GEAR Iterator[5d] (GIT) programs. (b) McKinney, R. J.; Weigert, F. J. Quantum Chemistry Program Exchange, Program No. QCMP022. (c) Stabler, R. N.; Chesick, J. *Int. J. Kinet.* **1978**, *10*, 461. (d) Weigert, F. J. *Comput. Chem.* **1987**, *11*, 273. (e) As incorporated herein, the correct approach[5d] (Occam's razor) toward such numerical integration curve-fitting is to use the minimum number of steps but also to be sure that only *elementary steps* are used in any final kinetic model. Step 4 ($k_{4,obsd}$) cannot be an elementary step since it goes from a first-order to a zero-order dependence (i.e. exhibits saturation kinetics)[7d] in both H$_2$ and cyclohexene at ca. ≥30 psig and ca. ≥1.5 M, respectively. Steps 2 and 3 are unlikely to be elementary steps since they are greater than termolecular. [In fact, the stoichiometry-based steps 2 and 3 had to be approximated in the actual modeling by incorporating only 2 and 1 equiv of H$_2$, respectively, since the program[5a–d] is (correctly) limited to termolecular (elementary) steps.] Hence, we have not reported the physically meaningless $k_{2,obsd}$, $k_{3,obsd}$, and $k_{4,obsd}$ values corresponding to eqs 2–4 (Scheme I). However, some type of autocatalytic step (e.g. step 3) is essential even in a seven-step mechanism,[7d] our best fit to date. Moreover, the formation of cyclooctane (and not the anticipated cyclooctene)[5h] can be explained by such a step. (f) Under the conditions of the kinetic studies (1.65 M cyclohexene, 0.0012 M **1**), measurable H$_2$ consumption (≥0.02 psi) occurs only via eq 4. (g) The solubility data for H$_2$ in acetone is from: *The Matheson Unabridged Gas Book*; *Hydrogen*; Matheson: East Rutherford, NJ, 1974. (h) Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc., Chem. Commun.* **1970**, 1553. Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

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The key finding is that the autocatalytic step (Scheme 1, step 3) is essential; extremely poor fits are obtained if this step is omitted (Figure 1, dotted line), regardless of what other mechanistic steps are added. Confidence in the curve-fitting procedure is provided by the identical value of the curve-fit K_{eq} value, $K_{eq} = k_{1,obsd}/k_{-1,obsd} = (2.2 \pm 0.2) \times 10^{-4}$ M psi^{-1}, in comparison to that calculated from literature H_2 solubility data, K_{eq} (lit., in acetone)[5f] = 2.28 × 10^{-4} M psi^{-1}. However, we emphasize that steps 1–4 are *not* elementary steps but instead describe net reactions (stoichiometries).[5e] Kinetic and other evidence for a seven-step mechanism involving the reversible formation of catalyst·$(H)_2$, catalyst·$(H)_2$(olefin), and catalyst·(H)(cyclohexyl) intermediates is accumulating and will be reported in due course.[7d]

The catalytic activity from **1** is noteworthy. The initial turnover frequency (TOF)[6] is $\mathrm{TOF_{init}}$ = 760 ± 120 mmol of H_2·(mmol of catalyst)$^{-1}$·h^{-1} (7 separate batches of precatalyst, 15 hydrogenation experiments). This value is 2.3-fold below the activity of the most highly dispersed sample of oxide-supported Ir available,[7a] *ultra* (ca. 80%) dispersed 1% Ir/η-Al_2O_3, which exhibits $\mathrm{TOF_{init}}$ = 1740 ± 250 mmol of H_2·(mmol of catalyst)$^{-1}$·h^{-1} under identical conditions (including where *identical rate laws* for the two catalysts are operative).[7b]

Starting from **1** a total of 18 000 turnovers for cyclohexene hydrogenation have been demonstrated, during which no visible Ir(0) is produced. Several control experiments further document the ability of the triniobium-substituted polyoxoanion in **1** to greatly inhibit Ir(0) formation.[8] For example, an Ir(0) precipitate is rapidly produced (<1 min) when a 0.1 M $[Ir(1,5\text{-}COD)(NCCH_3)_2]^+BF_4^-$ acetone solution under N_2 in a Fischer–Porter bottle is flushed with H_2 and then exposed to 40 psig of H_2 at 22 °C, either with or without polyoxoanions that formally have zero surface-oxygen charge density,[9] specifically $(Bu_4N)_6[P_2W_{18}O_{62}]$ or $(Bu_4N)_4[SiW_{12}O_{40}]$. On the other hand, no Ir(0) is seen when **1**, *in acetone*,[8] is treated with 40 psig of H_2 at 22 °C for 15 h even in the absence of cyclohexene. An explanation for these observations is apparent from rewriting and then comparing $P_2W_{18}O_{62}^{6-}$ $(=\{(PO_4)_2^{6-}(W_{18}O_{54})^0\})$ or $SiW_{12}O_{40}^{4-}$ $(=\{(SiO_4)^{4-}(W_{12}O_{36})^0\})$ to $P_2W_{15}Nb_3O_{62}^{9-}$ $(=\{(PO_4)_2^{6-}(W_{15}Nb_3O_{54})^{3-}\})$: the lack of Ir(0) formation is the result of the 3 extra units of anionic surface-oxygen charge density and thus the strong component of Ir^+–polyoxoanion^{3-} ionic bonding in **1**. In other words, the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion stabilizes the positive oxidation states of Ir relative to Ir(0). These control experiments plus the catalytic studies emphasize the novelty of **1** in comparison to all previous work.[10]

Several lines of evidence effectively rule out an $[Ir(0)_n]$ colloid as the catalyst formed from **1** plus H_2. The catalyst derived from **1** can undergo at least three cycles of being evaporated to dryness (24 h, 10^{-4} Torr) without exposure to air and then recharged with acetone and cyclohexene in the drybox. Each cycle again yields a homogeneous, yellow solution (no *visible* Ir(0)) with hydrogenation activity identical (±10%) with that of the original catalyst solution. *There is no example of an authentic, "pure" metal colloid (i.e. one not stabilized by an organic polymer or by some other means) where this is possible.*[11-13] Moreover, ultracentrifugation molecular weight measurements *on the catalyst* (1 × 10^{-5} M; in CH_3CN/0.1 M Bu_4NPF_6), isolated as above under vacuum and without exposure to air, reveal a $\bar{M}_r$ of 5600 ± 600, as expected for a monomer (M_r(calcd) = 5643 ± 79 for $(TBA)_5Na_3[L_2Ir{\cdot}P_2W_{15}Nb_3O_{62}]$, where L = H, cyclohexene, or acetone, for example). This result is inconsistent with a colloid, at least under the stated conditions, especially since colloids have been detected intact by ultracentrifucation molecular weight measurements.[11m-o] The reproducibility (±15%) of the hydrogenation curve and turnover frequency provides further strong

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(6) $\mathrm{TOF_{init}}$ is calculated after the active catalyst is produced from **1** (i.e. after the induction period). Identical numbers within experimental error are obtained either from the linear $P(H_2)$ vs time (zero-order)[5e] plot that results when isolated catalyst is redissolved in acetone with 1.65 M cyclohexene and 40 psig H_2 (TOF ≃ 620 h^{-1}) or from the middle, approximately linear (zero-order kinetics)[5e] part of 15 runs analogous to Figure 1, average TOF ≃ 760 ± 120 h^{-1} (TOF ≃ 820 h^{-1} for Figure 1 itself).

(7) (a) We gratefully acknowledge Dr. R. L. Garten (Catalytica Inc.) and Dr. G. B. McVicker (Exxon Research) for supplying this well-characterized sample of ultradispersed 1% Ir/η-Al_2O_3. For a description of this material (including a BET surface area analysis, hydrogen and CO chemisorption, and TEM studies), see: McVicker, G. B.; Baker, R. T. K.; Garten, R. L.; Kugler, E. L. *J. Catal.* **1980**, *65*, 207. (b) Conditions: 0.5 mM catalyst, 1.65 M cyclohexene, acetone solvent, 22 °C, 40 psig H_2, and vortex stirring (a sigmoidal plot of hydrogenation rate vs stirring rate demonstrates that the hydrogenation rate has become stirring-rate independent). Under these conditions, the 1% Ir/Al_2O_3 catalyst is first-order in [catalyst] but zero-order in [olefin] and $[H_2]$[7c] (the same limiting rate law seen for **1**).[5e,7d] (c) Edlund, D. J. Ph.D. Dissertation, University of Oregon, 1987. (d) Finke, R. G.; Lyon, D. K. Unpublished results and experiments in progress.

(8) In the more coordinating solvent CH_3CN, $[Ir(0)]_n$ is formed in ≤30 min at 22 °C, 40 psig, due perhaps to the dissociation of free $[Ir(1,5\text{-}COD)(NCCH_3)_2]^+$ and then its H_2 reduction.

(9) Barcza, L.; Pope, M. T. *J. Phys. Chem.* **1973**, *77*, 1795.

(10) See ref 5 in the preceding communication.[1]

(11) (a) Interpreting evidence for or against catalysis by Ir or other metal colloids requires being aware that solutions containing *aqueous* colloidal Ir(0) particles as large 1000 Å appear yellow and transparent to the naked eye.[11b] Furthermore, colloids in *organic* solvents, while little precedented until recently, are rapidly becoming more common[11c,d] and include reports in ketones,[11d,e] including acetone,[11e] and the solvent used in the present work. Logically, one must also consider that Ir(0) colloids, but not polyoxoanion-supported metals, are precedented as catalysts (e.g., in hydrogenations).[11f] Hence, careful consideration of these points teaches that completely convincing evidence will require either the isolation and characterization of key catalytic intermediates (*and* kinetic studies connecting them to the catalytic cycle) or the preparation—*if possible*—of the first *authentic* example of an organic-solvent-soluble (e.g. acetone soluble), anion-stabilized Ir(0) colloid *plus* investigation of the unstudied but intriguing possibility of polyoxoanion-stabilized colloids—*assuming* they exist. (b) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (c) Lin, S.-T.; Franklin, M. T.; Klabunde, K. J. *Langmuir* **1986**, *2*, 259. Duff, D. G.; Curtis, A. C.; Edwards, P. P.; Jefferson, D. A.; Johnson, B. F. G.; Logan, D. E. *J. Chem. Soc., Chem. Commun.* **1987**, 1264. Duff, D. G.; Curtis, A. C.; Edwards, P. P.; Jefferson, D. A.; Johnson, B. F. G.; Kirkland, A. I.; Logan, D. E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 676. (d) Esumi, K.; Tano, T.; Meguro, K. *Langmuir* **1989**, *5*, 268. (e) Cardenas-Trivino, G.; Klabunde, K. J.; Dale, E. B. *Langmuir* **1987**, *3*, 986. (f) Belloni, J.; Delcourt, M. O.; Leclère, C. *Nouv. J. Chim.* **1982**, *6*, 507. This work actually describes "Ir(0)/IrO_2" colloids, whose molecular formula is poorly understood. (g) Very recently Klabunde and co-workers have described soluble 10–20-Å, nonuniform metal/perfluorocarbon clusters of *average* formula $Au_{17}[C_{20}H_{30}F_{26}NO_7]$ prepared from condensing Au atoms with $(CF_3CF_2CF_2CF_2)_3N$. The surface of these clusters was reacted with, and apparently is protected by, the "$C_{20}H_{30}F_{26}NO_7$" fragment of unknown structure(s). Hence, the finding that they can be taken to dryness and then redissolved in solvents that include acetone is probably not relevant to the present work (where Ir is exposed and reactive). Zuckerman, E. B.; Klabunde, K. J.; Oliver, B. J.; Sorensen, C. M. *Chem. Mater.* **1989**, *1*, 12–14. (h) Klabunde, K. J.; Habdas, J.; Cardenas-Trivino, G. *Chem. Mater.* **1989**, *1*, 481–483. (i) Thomas, J. M. *Pure Appl. Chem.* **1988**, *60*, 1517–1528. (j) Lin, M. Y.; Lindsay, H. M.; Weitz, D. A.; Ball, R. C.; Klein, R.; Meakin, P. *Nature* **1989**, *339*, 360. (k) Andrews, M. P.; Ozin, G. A. *Chem. Mater.* **1989**, *1*, 174. (l) Vargaftik, M. N.; Zagorodnikov, V. P.; Stolyarov, I. P.; Moiseev, I. I.; Likholobov, V. A.; Kochubey, D. I.; Chuvilin, A. L.; Zaikovsky, V. I.; Zamaraev, K. I.; Timofeeva, G. I. *J. Chem. Soc., Chem. Commun.* **1985**, 937. (m) Vargaftik, M. N.; Zagorodnikov, V. P.; Stolarov, I. P.; Moiseev, I. I.; Kochubey, D. I.; Likholobov, V. A.; Chuvilin, A. L.; Zamarev, K. I. *J. Mol. Catal.* **1989**, *53*, 315. The distribution of clusters therein, approximated by "$Pd_{561}phen_{60}O_{60}(PF_6)_{60}$", shows a molecular weight of (1.0 ± 0.5) × 10^5 g/mol by ultracentrifugation sedementation equilibrium and a 10–30% *decrease* in catalytic activity for olefin oxidation following precipitation from solution. (n) A $Pt_{309}phen_{36}O_{30\pm10}$ cluster showing M_r = (7.9 ± 0.8) × 10^4 g/mol by ultracentrifugation: Schmid, G.; Morun, B.; Malm, J.-O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 778. (o) Recent work on $Ph_2PC_6H_4SO_3^-$-stabilized gold colloids that can be dried and then redissolved *in H_2O*, and that show M_r = (38 ± 8) × 10^6 g/mol by ultracentrifugation: Schmid, G.; Lehnert, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 780.

(12) (a) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743. (b) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. (c) Lewis, L. N.; Lewis, N. *Chem. Mater.* **1989**, *1*, 106.

(13) Rigorously, the data cited means that either: (i) we have a nonaggregated *polyoxoanion-supported* catalyst or (ii) we have discovered a previously unknown *polyoxoanion-supported* and stabilized "colloid" of a highly uniform and thus novel type. Note, however, that this colloid would also have to be unstable under the conditions of our molecular weight measurement (i.e. converted to individual polyoxoanion–Ir units during the molecular weight measurements)—a remote possibility that we seriously doubt.

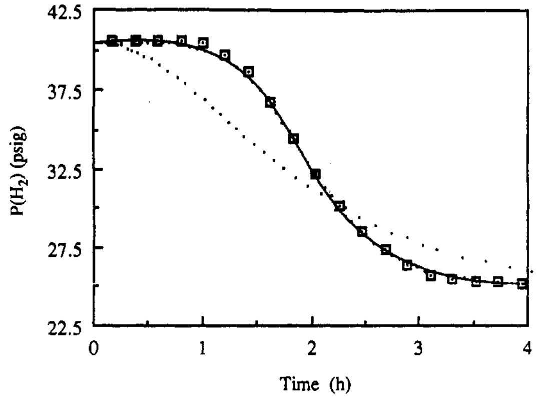

Figure 1. Plot of hydrogen loss vs time for 1.1×10^{-3} M **1** in cyclohexene (1.65 M)/acetone in comparison to curves generated by numerical integration curve-fitting[5] of the experimental data according to the stepwise sequence of reactions shown in Scheme I, eqs 1–4: experimental data (squares with center dots); curve computed by including eq 3 (solid line); curve computed by excluding eq 3 (dotted line), showing the necessity of the autocatalysis (step 3) for a close fit of the experimental data. Additional experimental details are available.[3]

evidence against *traditional types*[13] of colloids (and all other species) of *nonuniform reactivity*, for example those of *nonuniform size* or *surface area* (and thus variable number of exposed metal atoms).

We have also tried the well-known, but often problematic, Hg(0) test. Unfortunately, a control experiment reveals that under our normal conditions of catalysis (acetone, 1.65 M cyclohexene), **1** reacts with, and is precipitated by, Hg(0); this test is useless for the present example.

*The results provided herein demonstrate that Ir to polyoxoanion bonding must be retained in the catalyst derived from **1**.* This has encouraged us to attempt to characterize polyoxoanion-supported catalytic intermediates, such as the species formed from **1** plus 3.0 equiv of H_2 showing a ^1H NMR peak at −14.5 ppm, which we *tentatively* formulate as $\{[(H)_2(\text{solvent})Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-}\}_x$. Our goal from here is to fully define each stage of the catalytic cycle[14] and then to develop other polyoxoanion-supported catalytic reactions.

Acknowledgment. Support from NSF Grant CHE-831345 and from DOE Grant DE-FG06-089ER13998 is gratefully acknowledged.

Supplementary Material Available: Text presenting details of the catalytic hydrogenation studies (1 page). Ordering information is given on any current masthead page.

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[14] As has proven possible, for example, in classic studies of Wilkinson's catalyst: (a) Halpern, J.; Okamoto, T.; Zakharier, A. *J. Mol. Catal.* **1976**, *2*, 65. Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; Chapter 10.

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Chemistry of Zerovalent Tungsten Alkoxides. Synthesis, X-ray Structure, and Reactivity toward Carbon Dioxide

Zerovalent group 6 transition-metal alkoxide complexes have been established as intermediates in the catalytic hydrogenation of ketones and aldehydes to alcohols.[1] Because of the reversible nature of eq 1, it has not been possible to isolate and characterize

$$(CO)_5M{-}H^- + O{=}CRR' \rightleftharpoons (CO)_5M{-}OCHRR'^- \quad (1)$$

the metal alkoxides formed in the reaction due to their general instability toward β-hydride elimination.[2] However, the analogous group 6 pentacarbonyl aryloxide complexes have been synthesized and structurally defined and their reactivity investigated.[3]

In addition, monomeric group 6 metal carbonyl hydroxide, alkoxide, and aryloxide complexes are prone to condensation reactions subsequent to carbonyl loss to form clusters having bridging hydroxide, alkoxide, and aryloxide ligands.[3-8] The conversions illustrated in Scheme I have been established for hydroxides, aryloxides (R = C_6H_5, $C_6H_4CH_3$-*m*), and alkoxides (R = CH_3, CH_2CH_3). All the derivatives shown, except for the dimer in the box, have been previously observed, with several of these being isolated and fully characterized. The metal pentacarbonyl hydroxide, aryloxide, and alkoxide anions, in the absence of excess carbon monoxide, form the tetranuclear species $[W_4(CO)_{12}(\mu\text{-}OR)_4]^{4-}$, where the oxygen and tungsten atoms occupy the opposite tetrahedral sites of a distorted cubane skeleton, with no spectral evidence for the intermediacy of a dimer of the type $[W_2(CO)_8(\mu\text{-}OR)_2]^{2-}$. Only dimeric species of the sort $[W_2(CO)_6(\mu\text{-}OR)_3]^{3-}$ have been isolated, which are formed from either the monomer or the tetramer in the presence of excess hydroxide, aryloxide, or alkyloxide. There is precedence for carbonyl dimers of tungsten with two alkane- and arenethiolates, $[W_2(CO)_8(\mu\text{-}SR)_2]^{2-}$, which are produced following thermal CO loss from the monomeric anion $[W(CO)_5SR]^-$.[9]

In this communication, we report the synthesis, characterization, and the reactivity toward carbon dioxide of tungsten 2,2,2-trifluoroethoxide mononuclear and polynuclear carbonyl derivatives. Included in this report is the X-ray structure determination of a novel double-bridged μ_2-alkoxide dimer. As previously mentioned there is a problem with β-elimination inherent to transition-metal alkoxide chemistry which we avoided by the use of the alkoxide 2,2,2-trifluoroethoxide, which has electron-withdrawing substituents on the γ-carbon. In general, electron-withdrawing substituents on the alkoxide ligand stabilize the metal–alkoxide complex toward decomposition by β-hydrogen elimination.[10]

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