

Bifunctional Rhodium-Oxometalate Catalysts

Sir:

It has recently been proposed that metal alkoxides¹ and heteropolyanions²⁻⁸ can provide useful models for chemical and magnetic⁶ interactions on oxide surfaces. Here described is the use of Keggin ions, which are molecular metal oxide clusters having the general formula $X^{n+}M_{12}O_{40}^{(8-n)-}$ ($M = Mo, W; X = P, Si; n$ is the formal oxidation number of the central heteroatom X)⁹ to represent molybdenum or tungsten oxide surfaces. Features that make Keggin ions attractive models as well as starting materials for new organometallic-metal oxide composites are (1) a closely packed arrangement of interior MO_6 octahedra and of exterior oxygen atoms, (2) relatively short exopolyhedral $M=O$ bond lengths with which is associated low oxide nucleophilicity, and (3) the electronic analogy between Keggin ions, which are reversibly reduced in successive one-electron steps,⁹ and tungsten or molybdenum bronzes, Na_xMO_3 . A significant defect of these models is the high charge to mass ratio, which can be remedied in part by the preparative reactions described below. In pursuit of this analogy, we have developed new solid-state synthetic routes to novel Keggin ion derivatives that contain coordinatively unsaturated $(Ph_3P)_2Rh(CO)^+$ units. These materials are bifunctional catalysts useful for the synthesis of C_{n+1} carboxylic acids from C_n olefins by sequential "one-pot" hydroformylation and oxidation steps. Further, the compounds reported here are structurally unique in that $(Ph_3P)_2Rh(CO)^+$ moieties are located in interstitial lattice sites and are not covalently bonded to the oxygen atoms of the surrounding metal oxide clusters. In this regard, the compounds are quite distinct from those in which an added transition metal is incorporated into oxometalate cages^{3,4,7,9} and from oxide-supported organometallic reagents in which surface oxide groups are sufficiently nucleophilic as to form covalent bonds to the metal.¹⁰⁻¹⁴

Addition of 1 mol of hydrated $(H_3O)_4SiW_{12}O_{40}^{4-}$ to 4 mol of $[(Ph_3P)_2Rh(CO)]^+[HC(SO_2CF_3)_2]^{-16,17}$ in 3:1 (v/v) $C_2H_5OH-CH_3CN$ produces insoluble $[(Ph_3P)_2Rh(CO)(CH_3CN)]_4SiW_{12}O_{40}$ (**1**), $\nu_{CO} = 2009\text{ cm}^{-1}$. Thermogravimetric analysis reveals that, when the compound is heated under a nitrogen stream, loss of coordinated acetonitrile is essentially quantitative.¹⁸ Desolvation

Table I. Thermal Programmed Desorption and Infrared Spectral Data

variables	compd ^a	ν_{CO}/cm^{-1}	$T_{max}/\text{°C}^b$	compd ^c	ν_{CO}/cm^{-1}
X = Si, M = W, n = 4	1	2009	140	5	1990
X = P, M = W, n = 3	2	2009	186	6	1993
X = P, M = Mo, n = 3	3	2019	210	7	2003
X = Si, M = Mo, n = 4	4	2018	175	8	1994

^a $[(Ph_3P)_2Rh(CO)(CH_3CN)]_nXM_{12}O_{40}$. ^b CH_3CN loss. ^c $[(Ph_3P)_2Rh(CO)]_nXM_{12}O_{40}$.

reactions of **1** and analogous compounds formed from $SiMo_{12}O_{40}^{4-}$, $PMo_{12}O_{40}^{3-}$, and $PW_{12}O_{40}^{3-}$ were followed by thermal programmed desorption mass spectrometry.¹⁹ The temperatures at which the maximum rate of CH_3CN release occur are shown in Table I. At higher temperatures, CO and biphenyl, presumably arising from decomposition of the Ph_3P ligands, are also evolved. Thus, vacuum pyrolysis of **1** at 150 °C quantitatively yields $[(Ph_3P)_2Rh(CO)]_4SiW_{12}O_{40}$ (**5**), $\nu_{CO} = 1990\text{ cm}^{-1}$, as a yellow, air-stable solid whose vibrational spectrum in the Si-O and W-O stretching regions is similar to that of **1** but with slightly broader peaks. The reaction is reversible, and addition of CH_3CN to **5** regenerates **1**. In an alternate synthesis, addition of silicotungstic acid to $[(Ph_3P)_2Rh(CO)]^+[HC(SO_2CF_3)_2]^-$ in pure ethanol provides **5** directly.

Compounds **1**, **5**, and $[(Ph_3P)_3Rh(CO)]^+[HC(SO_2CF_3)_2]^-$ are heterogeneous catalysts for hydroformylation of olefins. The oxometalate derivatives **1** and **5** are soluble only in highly polar, coordinating solvents such as dimethyl sulfoxide or propylene carbonate in which they ionize, and so activity was assessed by using suspensions of the catalysts in toluene. 1-Hexene produces heptanal, 2-methylhexanal, and 2-ethylpentanal in a ratio of ca. 8.5:1.²⁰ Part of the low selectivity is due to olefin isomerization, since heating 1-hexene and **5** in toluene at 100° produces 2- and 3-hexene.²¹ The rhodium oxometalates also heterogeneously catalyze oxidation of aldehydes to carboxylic acids. In one experiment, the hydroformylation products obtained from 1-hexene were exposed to air at atmospheric pressure for 30 days, then analyzed by GC-MS. The carboxylic acid:aldehyde ratios from **1**, **5**, and $[(Ph_3P)_3Rh(CO)]^+[HC(SO_2CF_3)_2]^-$ were 156, 104, and 1 respectively, indicating that the oxidation process is associated with the silicotungstate moieties in **1** and **5** and not Rh(I). In addition, the hexane:(carboxylic acid + aldehyde) ratios for these same three compounds were 0.12, 0.04, and 0.005 respectively. Because oxidation proceeds slowly at ambient temperature and pressure, preparative reactions are routinely carried out in a glass-lined autoclave at 100 °C under 650 psig of air pressure for 4 h. Under these conditions, conversion of aldehydes to carboxylic acids using **1** or **5** as catalysts is essentially quantitative but only 16% in the presence of $[(Ph_3P)_3Rh(CO)]^+[HC(SO_2CF_3)_2]^-$.

Incisive characterization of these rhodium oxometalate catalysts is difficult because they are insoluble in nonionizing solvents. However, rhodium K-edge EXAFS data have been obtained for **1** and **5** at 23 °C. Remarkably, the Fourier transforms of the EXAFS curves of both disclose only one strong peak at 2.3 Å due to backscattering from phosphorus; cf. Figure 1 (supplementary material). Further, the absorption edges of these two compounds are virtually congruent (Figure 2, supplementary material). Because both the EXAFS and edge structure are sensitive to significant changes in the coordination environment of the absorbing metal, it appears that rhodium does not move closer to the tungsten oxide cluster, with concomitant W-O-Rh bond formation, on ejection of acetonitrile from $[(Ph_3P)_2Rh(CO)(CH_3CN)]_4SiW_{12}O_{40}$. Coordination to the oxometalate oxygens

- Chisholm, M. H.; Foltling, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389.
- Sethuraman, P.; Leparulo, M. A.; Pope, M. T.; Zonnevrije, F.; Brevard, C.; Lemerle, J. *J. Am. Chem. Soc.* **1981**, *103*, 7665.
- Besecker, C.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.
- Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759.
- McCarron, E. M., III; Harlow, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 6179.
- Siedle, A. R.; Padula, F.; Baranowski, J.; Goldstein, C.; DeAngelo, M.; Kokoszka, G. F.; Azevedo, L.; Venturini, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 7447.
- Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. In their discussion of $CpTiSiW_5V_3O_{40}^{4-}$, these authors make the important distinction between organometallic groups incorporated into vs. those incorporated onto metal oxide clusters.
- Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148.
- Molecular metal oxide cluster chemistry has been incisively reviewed by Pope in: Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.
- Burwell, R. L., Jr. *J. Catal.* **1984**, *86*, 301.
- Basset, J. M.; Besson, B.; Choplin, A.; Theolier, A. *Phil. Trans. R. Soc. London, A* **1982**, *308*, 115.
- Li, X. J.; Gates, B. C. *J. Catal.* **1983**, *84*, 55.
- Psaro, P.; Dossi, C.; Ugo, R. *J. Mol. Catal.* **1983**, *21*, 331.
- Watson, P. L.; Schraeder, G. L. *J. Mol. Catal.* **1980**, *9*, 129.
- Potentiometric titration of this tetrabasic acid in water indicates that the equivalent weight is 837 so that the commercially available solid acid contains 22 water molecules of hydration.
- Siedle, A. R.; Newmark, R. A.; Pignolet, L. H.; Howells, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1510.
- Siedle, A. R.; Howells, R. D. U.S. Pat. 4 556 720.
- At 190 °C, a 2.6% weight loss is observed; the calculated value is 2.9%.

- Siedle, A. R.; Filipovich, G.; Toren, P. E.; Palensky, F. J.; Cook, E.; Newmark, R. A.; Stebbings, W. L.; Melancon, K.; Mishmash H. E. *J. Organomet. Chem.* **1983**, *246*, 83.
- Typically, hydroformylation reactions were carried out by heating 1 mL of 1-hexene, 10 mL of toluene and 0.1 g of catalyst under 1000 psig of 1:1 H_2-CO at 110 °C for 3 h. Total aldehyde yields are ca. 76%.
- ¹³C NMR analysis reveals that the olefin mixture contains 60% *trans*-2-hexene, 25% *cis*-2-hexene, 9% *trans*-3-hexene, 2% *cis*-3-hexene and 5% 1-hexene. We are grateful to Dr. R. A. Newmark for this result.

necessarily requires a shorter separation between Rh and the strongly scattering W atoms and adds a higher frequency component to the EXAFS due to tungsten backscattering. Calculations and experiments with model compounds such as $(n\text{-Bu}_4\text{N})[(\text{Me}_5\text{C}_5\text{Rh})\text{W}_5\text{O}_{18}(\text{TiC}_5\text{H}_5)]$ indicate that a Rh-W contact of $\leq 4 \text{ \AA}$ can be detected by EXAFS, cf. $d(\text{Rh-O}) = 2.20 \text{ \AA}$ in $(n\text{-Bu}_4\text{N})_2[(\text{Me}_5\text{C}_5\text{Rh})\text{Nb}_2\text{W}_4\text{O}_{19}]$ in which $d(\text{Rh-W}) = 3.26 \text{ \AA}$.³ We propose that, instead, coordinatively unsaturated $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})$ units are located in *interstitial* sites, between the $\text{SiW}_{12}\text{O}_{40}$ cages. In this regard, compounds such as **5** may be regarded as inverse zeolites in that they can exhibit inter- rather than intracluster chemistry.

These results establish that members of the two new rhodium oxometalate classes $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{CH}_3\text{CN})]_{8-n}\text{XM}_{12}\text{O}_{40}$ and $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})]_{8-n}\text{XM}_{12}\text{O}_{40}$ are bifunctional catalysts capable of activating carbon monoxide and hydrogen at the rhodium centers as well as oxygen²² at tungsten or molybdenum. This latter property is shared with bulk tungsten oxide surfaces.²³ In addition, the catalytic activity of rhodium is modified when $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})^+$ units are associated with the $\text{SiW}_{12}\text{O}_{40}$ cluster in **1** and **5** in that selectivity for olefin hydroformylation vs. hydrogenation is significantly decreased relative to $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$.

Acknowledgment. X-ray absorption data were recorded at the Stanford Synchrotron Radiation Laboratory, which is supported by the U.S. Department of Energy and the Research Resources Division of the National Institutes of Health. Research at Stanford University is supported in part by a grant from the 3M Corporate Research Laboratories. We are grateful to Prof. Walter Klemperer for gifts of model compounds and to Manfred Riechert for performing the high-pressure reactions.

Supplementary Material Available: Figure 1, Fourier transforms of background-subtracted Rh EXAFS spectra of **1** and **5**, and Figure 2, normalized edge spectra of **1** and **5** (2 pages). Ordering information is given on any current masthead page.

- (22) Oxygen is activated in the sense that it appears in the reaction product. The actual mechanism of oxidation is not yet established and could involve electron transfer or C-H bond cleavage. See: Gates, B. C.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; pp 336-388.
- (23) Figueras, F.; Figlarz, M.; Portefaix, B.; Gerand, B.; Guenot, J. *J. Catal.* **1981**, *71*, 389.

Science Research Laboratory
3M Corporate Research Laboratories
St. Paul, Minnesota 55144

A. R. Siedle*
C. G. Markell
P. A. Lyon

Department of Chemistry
Stanford University
Stanford, California 94305

K. O. Hodgson
A. L. Roe

Received April 24, 1986

Lifetimes and Spectra of the Excited States of *cis*-Dicyanobis(2,2'-bipyridine)iron(II) and -ruthenium(II) in Solution

Sir:

The excited-state manifolds of the tris(polypyridine) complexes of iron(II), ruthenium(II), and osmium(II) are fairly well characterized.^{1,2} The metal centers in these complexes possess $(d\pi)^6$ electronic configurations while the polypyridine complexes possess

empty, low-lying π^* orbitals. The metal-to-ligand charge-transfer (MLCT) transitions are therefore intense and also of relatively low energy: this accounts for the very strong absorption of the polypyridine complexes in the visible region of the spectrum. The photophysics and photochemistry of these complexes are, however, complicated by the presence of ligand field (LF) excited states. These states arise from population of the empty metal $d\sigma^*$ orbitals. Although optical transitions to yield the LF excited states are not dipole-allowed and are therefore of low probability, the LF states can become populated by crossing from the MLCT states. This occurs readily in FeL_3^{2+} (L is 2,2'-bipyridine or 1,10-phenanthroline) where the LF state lies below the MLCT state and also in RuL_3^{2+} where the LF and MLCT states are of comparable energies but not in OsL_3^{2+} where the LF state lies well above the MLCT state.^{1,2} This ordering parallels the increasing ligand field splitting for this triad.

The situation is much more complicated for mixed-ligand complexes. Because of their lower symmetry, there are more excited states in such systems. In addition the relative ordering of the LF and MLCT transitions can be tuned by a suitable choice of the ligands and solvent. This communication is concerned with the excited states of *cis*-dicyanobis(2,2'-bipyridine)iron(II). There is very good evidence³ that in $\text{Ru}(\text{bpy})_2(\text{CN})_2$ the MLCT excited state lies below the LF excited state, and it has recently been proposed⁴ that a similar situation may also obtain in $\text{Fe}(\text{bpy})_2(\text{CN})_2$. On the basis of sensitization studies, a lifetime of $\geq 56 \text{ ns}$ was calculated for the lowest energy excited state of $\text{Fe}(\text{bpy})_2(\text{CN})_2$. This lifetime is considerably longer than the 0.81-ns lifetime reported for the LF excited state of $\text{Fe}(\text{bpy})_3^{2+}$.^{1a} The relatively long $\text{Fe}(\text{bpy})_2(\text{CN})_2$ lifetime implicated by the sensitization studies was rationalized⁴ by proposing that the LF excited state in $\text{Fe}(\text{bpy})_3^{2+}$ is raised in energy upon replacement of a bpy by 2CN^- so that the lowest excited state in $\text{Fe}(\text{bpy})_2(\text{CN})_2$ is the MLCT state. In order to obtain further information on this question we undertook a study of $\text{Fe}(\text{bpy})_2(\text{CN})_2$ by picosecond flash-photolysis techniques.⁵ The longest lived excited state of $\text{Fe}(\text{bpy})_2(\text{CN})_2$ detected in this study has a lifetime of more than 2 orders of magnitude shorter than that estimated in the sensitization studies⁴ and the absorption spectrum of this excited state is not consistent with a MLCT assignment.

$\text{Fe}(\text{bpy})_2(\text{CN})_2 \cdot 3\text{H}_2\text{O}$ was synthesized according to a published procedure.⁶ As previously noted,^{6,7} the visible absorption spectrum of the complex is very solvent dependent, a result that can be rationalized in terms of specific solvent effects on the redox potential of the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ center and, to a lesser extent, the change in dipole moment associated with the $d\pi \rightarrow \pi^*(\text{bpy})$ MLCT transition. In ethanol the absorption maxima were determined to be 570 nm ($\epsilon = 6.83 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 373 nm ($\epsilon = 6.68 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), in good agreement with the values reported by Schilt.⁶ A single excited state can be detected by transient absorption spectroscopy following 532 nm (25-30 ps) excitation of $\text{Fe}(\text{bpy})_2(\text{CN})_2$ in methanol. This excited state decays with greater than 98% recovery of the initial absorbance and is well fit by a single exponential function with a lifetime of 0.33 ns at room temperature, very similar to the lifetime of the LF excited state of $\text{Fe}(\text{bpy})_3^{2+}$ ^{1a} but considerably shorter than the 0.39- μs lifetime (methanol, 293 K) of the MLCT excited state of $\text{Ru}(\text{bpy})_2(\text{CN})_2$.^{3a} Moreover the lifetime of the MLCT state of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ decreases from 0.39 to 0.22 μs when the solvent is changed from methanol to DMF^{3a} while the lifetime of the excited state of $\text{Fe}(\text{bpy})_2(\text{CN})_2$ increases from 0.33 to 0.78 ns upon

- (1) (a) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 309. (b) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. (c) Sutin, N.; Creutz, C. *J. Chem. Educ.* **1983**, *60*, 809. (d) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834. (e) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
- (2) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *23*, 5583. Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098. Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877.

- (3) (a) Belsler, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Gazz. Chim. Ital.* **1985**, *115*, 723. (b) Barigelletti, F.; Belsler, P.; von Zelewsky, A.; Juris, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3680. (c) Kitamura, N.; Kim, H.-B.; Kawanishi, Y.; Obata, R.; Tazuke, S. *J. Phys. Chem.* **1986**, *90*, 1488.
- (4) Brewer, K. J.; Murphy, W. R., Jr.; Moore, K. J.; Eberle, E. C.; Petersen, J. D. *Inorg. Chem.* **1986**, *25*, 2470.
- (5) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* submitted for publication.
- (6) Schilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000.
- (7) Burgess, J. *Spectrochim. Acta, Part A* **1970**, *26A*, 1369, 1957. Toma, H. E.; Takasugi, M. S. *J. Solution Chem.* **1983**, *12*, 547.