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Synthesis, Isolation, and Characterization of $[K(cryptand\ 2.2.2)]_2[Hf(CO)_6]$, the First Substance To Contain Hafnium in a Negative Oxidation State. Structural Characterization of $[K(cryptand\ 2.2.2)]_2[M(CO)_6]\cdot$Pyridine (M = Ti, Zr, and Hf)[†,1]

John E. Ellis* and Kai-Ming Chi

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received November 13, 1989*

Abstract: Reductive carbonylation of $M(CO)_4\{CH_3C(CH_2PMe_2)_3\}$, M = Ti, Zr, and Hf, by [K(cryptand 2.2.2)][naphthalene] at −70 [illegible] followed by warming provides practically quantitative yields of the thermally robust salts $[K(cryptand\ 2.2.2)]_2[M(CO)_6]$, includ[illegible] the previously inaccessible $[Hf(CO)_6]^{2-}$. X-ray crystal structure analyses show the presence of essentially unperturbed octah[illegible] hexacarbonyl metal units in all three salts. This study represents the first structural characterization of "pure" carbonylmetallates of the group 4 elements and establishes the existence of a compound containing hafnium in a negative (−2) oxidation state for the first time.

Introduction

Anionic derivatives of transition-metal carbonyls have been known since the pioneering research of Walter Hieber and associates[2] and provided the first examples of compounds to contain metals in formally negative oxidation states. While studies on the molecular structures, spectroscopic characteristics, and other physical properties of these materials have played a central role in our understanding of low-valent transition-metal compounds,[3] complementary investigations on the chemical properties of these reactive transition-metal nucleophiles/bases/reductants have shown many of them to be quite useful and important as stoichiometric and/or catalytic reagents in several areas of chemical synthesis.[3,4] Since the first report on the synthesis of a binary carbonylmetallate, $[Fe(CO)_4]^{2-}$, over 60 years ago,[5] there has been and continues to be substantial interest in the synthesis of new mononuclear carbonylmetallates and related materials.[6] Most d-block metals are now known to form such compounds, i.e., $[M(CO)_x]^z$, where $z = -1$ to -4,[7] but until recently no synthesis of binary carbonylmetallates of titanium, zirconium, or hafnium had been reported. Although the possible existence of such materials does not appear to have been considered previously in the scientific literature, the substantial thermal stabilities of certain salts of various dianionic carbonyls, e.g., $[Fe(CO)_4]^{2-}$ and $[Cr(CO)_5]^{2-}$,[8] as well as those of the heavier metal analogues, and the high kinetic stability often associated with low spin d^6 octahedral complexes,[9a] suggested many years ago that $[Ti(CO)_6]^{2-}$ might be an accessible species.[9b] The latter ion was recently obtained by two electron reductions of $Ti(CO)_5(dmpe)$, dmpe = $Me_2PCH_2CH_2PMe_2$, under a CO atmosphere and then subsequently via a more direct reductive carbonylation of $TiCl_4(THF)_2$, THF = tetrahydrofuran, in the absence of organophosphines.[10] Shortly afterwards, a similar reduction of $ZrCl_4(THF)_2$ provided $[Zr(CO)_6]^{2-}$,[11] but $[Hf(CO)_6]^{2-}$ was far more elusive and could not be obtained directly from Hf(IV) precursors. Recently, the availability of $Hf(CO)_4(trmpe)$, where trmpe = $CH_3C(CH_2PMe_2)_3$,[12] permitted us to determine whether a Hf(0) precursor could be converted to $[Hf(CO)_6]^{2-}$ and thereby provide the first example of a binary carbonylhafnate as well as a compound containing hafnium in a previously unknown oxidation state.

In this paper the results of this inquiry are described. Of particular interest are structural characterizations of all three hexacarbonylmetallates(2−), which provide proof for the existence of these materials in the solid state for the first time.

Experimental Section

General Procedures and Starting Materials. Operations were performed under an atmosphere of nitrogen, argon, or carbon monoxide further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials which are impermeable to air.[13] In addition, the carbon monoxide was passed through a column of Ascarite to remove carbon dioxide. Solutions were transferred via stainless steel cannulae whenever possible. Otherwise syringes or standard Schlenk techniques[14] were used in conjunction with a double manifold vacuum line.[13] Previously published comments concerning our reductive carbonylation procedures should be consulted prior to attempting these syntheses.[15] Solvents were dried and distilled under argon before use. All reactants and solvents were obtained from commercial sources except for $\{CH_3C(CH_2PMe_2)_3\}M(CO)_4$, M = Ti, Zr, and Hf, which were prepared according to literature procedures.[12] Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer in 0.1 mm sealed NaCl or CaF_2 cells fitted with three way Nylon stopcocks (Ace Glass 5851) to permit filling outside of the drybox. Nujol mulls of air-sensitive compounds were prepared in a Vacuum Atmospheres Corp. drybox filled with argon or nitrogen. NMR samples were sealed into 5-mm tubes (Wilmad 505-PS9) and were run on Nicolet NT-300 WB, IBM NR-200 AF, and NR-300 AF spectrometers. Carbon spectra

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[†] Dedicated to Professor Fred Basolo on the occasion of his 70th birthday.

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were acquired with a 45° pulse and a 4-s delay between pulses to aid in the detection of carbonyl ^{13}C resonances. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas-Hoover Unimelt apparatus. Microanalyses were carried out by H. Malissa and G. Reuter Analytische Laborotorien, Engelskirchen, West Germany.

$[K(cryptand\ 2.2.2)]_2[Hf(CO)_6]$. A cold solution (−70 °C) of $Hf(CO)_4(trmpe)$[12] (0.50 g, 0.93 mmol) in 50 mL of THF was transferred by cannula to a cold solution (−70 °C) containing $[K(cryptand\ 2.2.2)][C_{10}H_8]$ (1.87 mmol) in 50 mL of THF under an argon atmosphere. The latter was prepared by stirring a mixture of K metal (0.073 g), naphthalene (0.35 g), and cryptand 2.2.2 (0.70 g) in THF for 4 h at room temperature. Argon was then removed by evacuation and replaced by carbon monoxide within seconds. After stirring for 5 h at −60 °C the reaction mixture was warmed to room temperature over a period of 12 h, while stirring was continued. The resulting finely divided purple solid was separated by filtration, washed with THF, and dried in vacuo. Recrystallization from CH_3CN–THF at 0 °C provided finely divided deep red, nearly black crystals (mp ca. 185 °C with dec) in 80% yield (0.87 g). These crystals gave satisfactory elemental analyses for the proposed composition. Anal. Calcd for $C_{42}H_{72}N_4O_{18}HfK_2$: C, 42.83; H, 6.16; Hf, 15.16. Found: C, 42.73; H, 6.47; Hf, 15.30. Prior to recrystallization, essentially quantitative yields of the product were obtained. The salt dissolves in acetonitrile to provide deep red solutions which are quite moisture, oxygen, light, and heat sensitive. At room temperature these solutions begin to decay within minutes but not so quickly that their spectra cannot easily be obtained. In contrast, pyridine solutions of $[Hf(CO)_6]^{2-}$ and corresponding dianions of titanium and zirconium persist for several hours at room temperature in the dark under anaerobic conditions.

$[K(cryptand\ 2.2.2)]_2[Zr(CO)_6]$. Essentially identical procedures provided the previously unreported zirconium salt in analytically pure form as deep purple crystals (mp ca. 192 °C with dec) in 83% yield. Anal. Calcd for $C_{42}H_{72}N_4O_{18}K_2Zr$: C, 46.26; H, 6.66; K, 7.17. Found: C, 46.05; H, 6.78; K, 7.08.

$[K(cryptand\ 2.2.2)]_2[Ti(CO)_6]$. This previously reported titanium complex[10] was prepared from $Ti(CO)_4(trmpe)$ by the same procedure in 78% yield as a pure recrystallized substance.

X-ray Structural Analyses of $[K(cryptand\ 2.2.2)]_2[M(CO)_6]$·pyridine, M = Ti, Zr, Hf. Collection and Reduction of X-ray Data. Tetrahydrofuran was slowly layered on and allowed to diffuse through nearly saturated deep red (Ti) to red-violet (Zr, Hf) solutions of $[K(cryptand\ 2.2.2)]_2[M(CO)_6]$ in pyridine at 0 °C. After 1–3 days, air-sensitive prisms of the compounds had formed. Deep red-to-purple crystals were washed with THF, coated with heavy mineral oil, and placed in capillaries which were mounted on a goniometer head. The crystals were found to belong to the monoclinic class by the Enraf-Nonius CAD 4-SDP peak search, centering and indexing programs and by a Delauney reduction calculation. All calculations were carried out on PDP 8A and 11/34 computers by using the crystallographic computing package of Enraf-Nonius CAD 4-SDP programs. This package is described in the following: (a) Frenz, B. A. In *Computing in Crystallography*; Schenk, B. H., Olthof-Hazekamp, R.; van Koningsvele, J., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. (b) *CAD 4 and SDP Users Manual*; Enraf-Nonius; Delft, Holland, 1978.

As a result of systematic absences ($h0l$, $h+l = 2n+1$; $0k0$, $k = 2n+1$), the centrosymmetric space group $P2_1/n$ (nonstandard setting of no. 14) was chosen, and this assignment was verified by successful refinement of the structure. Data were collected on a CAD 4 Nonius diffractometer. Background counts were measured at both ends of the scan range with the use of a ω–2θ scan which was equal, at each side, to one-fourth of the scan range of the peak. Thus, the total duration of measuring background was equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure; no delay in intensity was found over the entire period of data collection. The intensities of 8202 (Ti), 8370 (Zr), or 8359 (Hf) ($+h,+k,\pm l$) unique reflections were measured at −94 °C (Ti), −98 °C (Z), or −97 °C (Hf) out to $2\theta = 60°$ by using monochromatized Mo Kα radiation. The data were corrected for Lorentz polarization, absorption, and background effects, by using a value of 0.05 for p. The intensity data were processed with the aforementioned computers by using Enraf-Nonius programs. The net intensity is equal to (K/NPl)(C-2B), where $K = 20.1166 \times$ (attenuator) factor, NPl = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/\mathrm{NPl})^2[C + 4B + (pI)^2]$, where p is a factor used to down-weight intense reflections. The observed structure factor amplitude, F_o, is equal to $(I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors, $\sigma(F_o)$, by the equation of $\sigma(F_o) = {}^1/_2(\sigma(I)/I)F_o$. Of the 8202 (Ti), 8370 (Zr), or 8359 (Hf) total reflections, 5749 (Ti), 5502 (Zr), or 6368 (Hf) had $F_o^2 \geq 1.0\sigma(F_o^2)$ and were used for the final solution and refinement of the structures. A summary of the crystal and intensity collection data is shown in Table I. Bond distances and angles of the anions are shown in Table II.

Table I. Summary of Crystal and Intensity Collection Data for $[K(cryptand\ 2.2.2)]_2[M(CO)_6]$·pyridine, M = Ti, Zr, Hf

	M =		
	Ti	Zr	Hf
(A) Crystal Parameters: Space Group $P2_1/n$			
temperature	−94 °C	−98 °C	−97 °C
a, Å	14.473 (9)	14.597 (4)	14.599 (10)
b, Å	13.674 (12)	13.681 (3)	13.696 (10)
c, Å	14.412 (15)	14.497 (3)	14.492 (9)
β, deg	97.05 (7)	96.82 (2)	97.00 (5)
V, Å^3	2830 (7)	2874 (2)	2876 (6)
Z	2	2	2
mol wt, g/mol	1126.26	1169.58	1256.85
ρ(calcd), g/cm^3	1.321	1.351	1.451
crystal dimens, mm	0.15 × 0.20 × 0.30	0.15 × 0.25 × 0.25	0.15 × 0.20 × 0.30
(B) Measurement of Intensity Data			
radiation (Mo Kα), Å	0.71073	0.71073	0.71073
monochromator	graphite	graphite	graphite
abs. coeff, cm^{-1}	3.634	3.989	20.086
2θ limits, deg	0–60	0–60	0–60
final no. of variables	331	331	332
unique data used ($F_o^2 \geq 1.0\ \sigma(F_o^2)$)	5749	5502	6368
R^a	0.055	0.062	0.034
$R_w{}^a$	0.060	0.059	0.038
goodness of fit	1.306	1.103	0.970

[a] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $R = (\sum||F_o| - |F_c||)/(\sum|F_o|)$, and $R_w = [\sum w(|F_o| - |F_c|)]^2/(\sum w|F_o|^2)^{1/2}$.

Solution and Refinement of the Structures. Conventional heavy atom techniques were used in solving the structure of $[K(cryptand\ 2.2.2)]_2[Ti(CO)_6]$·$C_5H_5N$. The positions of titanium and potassium atoms were determined from a Patterson map. Since the zirconium and hafnium compounds were found to be isomorphous with the titanium species, the final structure of $[K(cryptand\ 2.2.2)]_2[Ti(CO)_6]$·$C_5H_5N$ was used as the trial structure for the zirconium and hafnium analogues. The least-squares refinement of the structures ran smoothly on this basis. Subsequent difference Fourier maps and cycles of least-squares refinements revealed the positions of the remaining non-hydrogen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - \}F_c||)/(\sum|F_o|$ and $R_w = |(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|)^2]^{1/2}$. The goodness of fit or error in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ where NO and NV are the number of observations and variables, respectively. The atomic scattering factors were obtained from the following source: Cromers, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Volume IV, Tables 2.2.4, 2.3.1.

All non-hydrogen atoms in the molecule were refined anisotropically. Hydrogen atoms were included at idealized positions with assigned B's of 3.0 and not refined. The disordered pyridines of crystallization were treated as benzene rings and the hydrogens were omitted. Tables of final positional and thermal parameters, interatomic distances and angles of the cations, and observed and calculated structure factor amplitudes are available as Supplementary Material.

Results and Discussion

Our recent discovery that $[Ti(CO)_6]^{2-}$ and $[Zr(CO)_6]^{2-}$ could be prepared and isolated under appropriate conditions[10,11] convinced us that $[Hf(CO)_6]^{2-}$ should also be an accessible species. A previous route, which provided essentially quantitative yields of hexacarbonyltitanate(2−), involved the atmospheric pressure reductive carbonylation of $Ti(CO)_5(dmpe)$ in tetrahydrofuran by $[K(cryptand\ 2.2.2)][C_{10}H_8]$,[10] where $C_{10}H_8^-$ is the radical anion of naphthalene and cryptand 2.2.2 is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (eq 1). Since attempts to

$$Ti(CO)_5(dmpe) + 2[K(cryptand\ 2.2.2)][C_{10}H_8] \xrightarrow[\text{CO (1 atm P)}]{-78\ °C} [K(cryptand\ 2.2.2)]_2[Ti(CO)_6] + 2C_{10}H_8 + dmpe \quad (1)$$

obtain $[Hf(CO)_6]^{2-}$ by direct reductive carbonylations of $HfCl_4$

Table II. Selected Bond Distances (Å) and Angles (deg) for $[M(CO)_6]^{2-}$, M = Ti, Zr, Hf[a]

distances	Ti	Zr	Hf
M-C1A	2.041 (2)	2.205 (4)	2.180 (3)
M-C2A	2.037 (2)	2.214 (4)	2.179 (3)
M-C3A	2.035 (2)	2.212 (4)	2.174 (3)
M-C (mean)	2.038 (3)	2.210 (4)	2.178 (3)
C1A-O1A	1.168 (3)	1.168 (4)	1.162 (4)
C2A-O1A	1.171 (3)	1.161 (4)	1.165 (4)
C3A-O1A	1.166 (3)	1.157 (4)	1.162 (4)
C-O (mean)	1.168 (3)	1.162 (5)	1.163 (4)
angles	**Ti**	**Zr**	**Hf**
M-C1A-O1A	178.8 (2)	179.1 (3)	179.8 (3)
M-C2A-O1A	178.1 (2)	177.8 (3)	177.6 (3)
M-C3A-O3A	178.3 (2)	177.7 (3)	178.2 (3)
M-C-O (mean)	178.4 (4)	178.2 (5)	178.5 (9)
C1A-M-C2A	88.87 (8)	88.7 (1)	88.6 (1)
C1A-M-C3A	88.29 (9)	88.3 (1)	88.2 (1)
C2A-M-C3A	87.53 (9)	86.5 (1)	86.9 (1)

[a] Interatomic distances and angles for [K(cryptand 2.2.2)]$^+$ units are available as supplementary material.

Table III. Selected Spectroscopic Data for $[K(2.2.2)]_2[M(CO)_6]$

M	IR ν(CO),[a] cm^{-1}	$^{13}C\{^1H\}$ NMR[b] δ(CO), ppm
Ti	1748 vs	245.8
Zr	1757 vs	245.3
Hf	1757 vs	244.4

[a] Solvent: CH_3CN. [b] Solvent: CD_3CN. All show nitrile ^{13}C resonance of CD_3CN at δ 118.25 (±0.05) ppm at 20 °C. Cation resonances are not shown.

were unsuccessful, there was hope that an analogous reduction of a zerovalent hafnium carbonylphosphine would provide the desired substance. Although dmpe stabilized Zr(0) and Hf(0) carbonyls are still unknown,[16] recently we succeeded in preparing the first family of phosphine stabilized group 4 M(0) carbonyls by using the tripodal ligand trmpe or $CH_3C(CH_2PMe_2)_3$.[12] The availability of these materials permitted us to develop the initial general route to the hexacarbonylmetallates(2−) of all three group 4 elements.

Reductions of $M(CO)_4$(trmpe) by potassium naphthalenide in the presence of cryptand 2.2.2 under an atmosphere of purified CO consistently provided high (≥80%) yields of the corresponding $[M(CO)_6]^{2-}$, as shown in eq 2. For M = Ti, Zr, 2 equiv of

$$M(CO)_4(\text{trmpe}) + 2KC_{10}H_8 + 2\text{cryptand } 2.2.2 + 2CO \xrightarrow{\text{THF}} [K(\text{cryptand } 2.2.2)]_2[M(CO)_6]\downarrow + 2C_{10}H_8 + \text{trmpe} \quad (2)$$

15-crown-5, i.e., 1,4,7,10,13-pentaoxacyclopentadecane, were also effective in providing the previously described $[K(15\text{-}C\text{-}5)_2]_2[M(CO)_6]$.[10,11] Attempts to obtain $Hf(CO)_6^{2-}$ as alkali metal–crown ether salts were unsuccessful, however. So far, $Hf(CO)_4$(trmpe) is the only known precursor to $[Hf(CO)_6]^{2-}$.

Infrared and ^{13}C NMR spectra of the hexacarbonylmetallates(2−) are collected in Table III and show close similarities. Although the small change ($\Delta\delta \sim 2$ ppm) in carbonyl ^{13}C NMR chemical shifts on proceeding from titanium to hafnium for these dianions is unusual in terms of trends previously reported for later metal carbonyls, e.g., the group 6 hexacarbonyls,[17] similar observations have been noted recently for zerovalent group 4 carbonyls.[18]

Slow recrystallization of $[K(\text{cryptand } 2.2.2)]_2[M(CO)_6]$ from THF–pyridine provided single crystals suitable for X-ray analysis. These crystals proved to be isomorphous with each other and of the composition $[K(\text{cryptand } 2.2.2)]_2[M(CO)_6]\cdot$pyridine, where the pyridine of crystallization (disordered with respect to the position of the nitrogen atom) and ordered potassium–cryptand complex cations are well separated from the anions in the crystalline lattice. Spectroscopic properties of the anions in $[K(\text{cryptand } 2.2.2)]_2[M(CO)_6]$ and corresponding pyridine solvates appear to be identical in solution and in the solid state. Metrical parameters for the [K(cryptand 2.2.2)]$^+$ units are essentially the same for all three salts and are in good agreement with those previously reported for the corresponding iodide salt.[19] Essentially unperturbed octahedral $[Ti(CO)_6]^{2-}$, $[Zr(CO)_6]^{2-}$, and $[Hf(CO)_6]^{2-}$ units are also present (Figure 1 for Hf compound). The metal atoms in these anions lie on an inversion center which results in three independent M–C and C–O bond lengths and M–C–O angles. The centroids of the pyridine rings are also situated on centers of inversion. A summary of interatomic data for the anions appears in Table II. Mean M–C lengths are similar to those found in $(C_5H_5)_2M(CO)_2$ for a given metal and decrease in the usual order Zr > Hf > Ti.[20] However, these mean bond lengths are about 0.1 Å longer than those of the group 5 $M(CO)_6^-$,[21] which in turn have mean M–C lengths only about 0.02 Å longer than corresponding values for the neutral group 6 hexacarbonyls.[22] Mean C–O distances are not significantly different for the three dianions, which is in accord with the very similar ν(CO) values (Table III) observed for these species. As expected, the latter distances are somewhat longer than those of the less electron-rich monoanionic hexacarbonyls of the group 5 metals.[21]

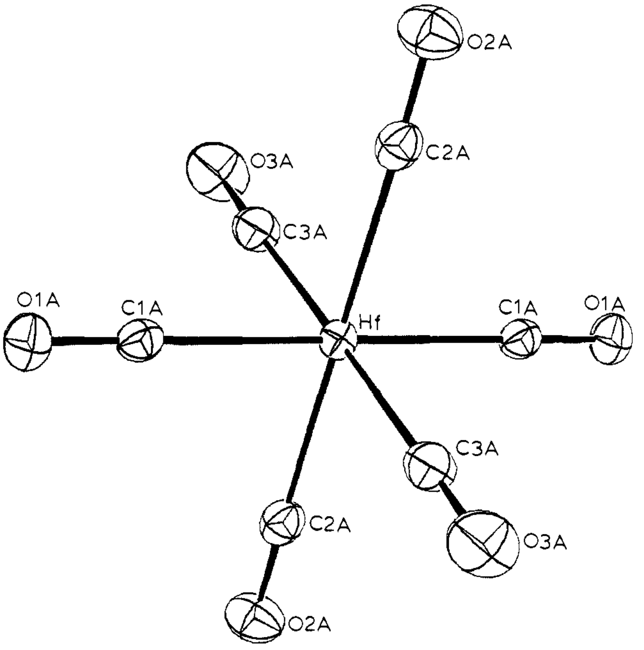

Figure 1. ORTEP drawing of $[Hf(CO)_6]^{2-}$ in $[K(\text{cryptand } 2.2.2)]_2[Hf(CO)_6]\cdot$pyridine. Thermal ellipsoids are drawn with 50% probability boundaries. See Table II for bond distances and angles.

Further studies on these novel materials are in progress and will be reported on soon.

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Supplementary Material Available: Tables of final positional and thermal parameters, interatomic distances and angles, and general temperature factor expressions (24 pages); tables of observed and calculated structure factor amplitudes (72 pages). Ordering information is given on any current masthead page.

Alkene Oxidation Catalyzed by a Ruthenium-Substituted Heteropolyanion, $SiRu(L)W_{11}O_{39}$: The Mechanism of the Periodate Mediated Oxidative Cleavage

Ronny Neumann* and Chalil Abu-Gnim

Contribution from the Casali Institute of Applied Chemistry, Graduate School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, Israel 91904.

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Abstract: A ruthenium-substituted heteropolyanion $SiRu(H_2O)W_{11}O_{39}{}^{5-}$ was synthesized and characterized. The hydrophobic quaternary ammonium salt of the heteropolyanion $((C_6H_{13})_4N)_5SiRu^{III}(H_2O)W_{11}O_{39}$ was used as a catalyst for the oxidation of alkenes with *tert*-butyl hydroperoxide, potassium persulfate, iodosobenzene, and sodium periodate as primary oxidants. Reactivity and selectivity were found to be dependent on the oxidant used; several different types of oxidation processes could be identified including allylic oxidation, epoxidation, and oxidative cleavage. Use of sodium periodate as oxidant enabled selective bond cleavage with aldehydes as the exclusive product. Different product selectivity and UV–vis and IR spectra of the ruthenium heteropoly compound in the presence of the various oxidants shows that unique mechanisms are operating in each case. A series of further experiments into the oxidation of styrene derivatives to benzaldehydes by sodium periodate including investigation of the reaction kinetics, substituent effects, and isotope incorporation enabled the formulation of a reaction mechanism. The reaction proceeds by interaction of the styrene with the catalyst forming a metallocyclooxetane which rearranges in the rate-determining step to a cyclic diester through two different transition states depending on the ring substituent. In the final step the cyclic diester decomposes yielding the cleavage products.

Introduction

The vast field of heteropolyanion chemistry has historically been centered around the preparation, structure, properties, and analytical chemistry applications of these compounds.[1] Only recently has the potential use of heteropolyanions as catalysts slowly gained recognition, both as Brönsted acid[2] and oxidation catalysts.[3] Heteropolyanions are attractive as robust oxidation catalysts because the exclusively inorganic nature of the anions makes them inherently stable toward decomposition under extreme oxidation conditions. Perusal of the literature reveals that liquid phase oxidation reactions catalyzed by heteropolyanions may be divided into four categories based on the type of reaction performed. The first category includes reactions where the heteropolyanion catalyst, HPC, generally $PV_2Mo_{10}O_{40}{}^{5-}$ is used in electron-transfer-type oxidations, eq 1. Substrates in the context of the above reaction

$$\text{substrate} + HPC_{ox} \rightarrow \text{product} + HPC_{red} \qquad (1)$$

$$HPC_{red} + \tfrac{1}{2}O_2 \rightarrow HPC_{ox} + H_2O$$

may be organic molecules as in the oxidation of sulfides,[4] dehydrogenation of dienes,[5] and the oxidative cleavage of ketones.[6] Substrates may be of an inorganic nature as in the oxidation of hydrogen bromide to molecular bromine[7] or primary catalysts such as Pd(0) (product is Pd(II)) as in the Wacker-type oxidation of ethylene to acetaldehyde[8] or acetoxylation of aromatics.[9] Systems whereby heteropolyanions undergo photoactivation represent a second group of reactions and include the dehydrogenation of alcohols[10] and alkanes.[11] A third set of reactions are those where complete molybdenum or tungsten Keggin anions have been used as catalysts in tandem with hydrogen peroxide in oxidations of alcohols,[12] allyl alcohols,[13] alkenes,[14] and alkynes[15] which are typical of molybdenum and tungsten catalytic centers.

The fourth category of reactions where heteropolyanions are used as liquid phase oxidation catalysts is based on transition-

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