

As compounds containing C-H-M interactions constitute attractive models for the activation of CH bonds,¹⁸ the factors promoting the formation of agostic hydrogens have been extensively discussed.² In mononuclear systems, a minimal requirement appears to be an unsaturated metal site.² Even at the phenomenological level, these new results show that for metal clusters a model focusing on protons on a main group-metal cluster surface chasing available charge is more appropriate than CH bonds satisfying unsaturated metal centers. Although the full implications of these observations will only be revealed by appropriate theoretical treatments presently in progress, the formation of V clearly shows that multinuclear coordination of carbon induces significantly different behavior than mononuclear coordination.

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Tungsten(IV) Aqua Ion

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Aqueous chemistry of molybdenum in oxidation states II-V is now well understood.¹ Aqua ions of molybdenum in these oxidation states show characteristic dimeric or trimeric structures containing metal-to-metal bonds,¹ and studies on their interconversion,² ligand substitution,^{3,4} and redox properties^{1,4,5} have provided basically important information on the reactivities of the metal-to-metal bonded cluster compounds. Other early transition metals in the second and the third transition series are also known to have extensive chemistry of metal-to-metal bond,⁶ but their aqueous chemistry has been virtually unchallenged.⁷ In this paper, we focus on tungsten(IV) as a comparison with the characteristic trimeric molybdenum(IV) ion $[\text{Mo}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$.^{8,9} A number of tungsten(IV) trimers with different ligands are known.¹⁰ Only one complex containing the $\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3$ unit ($[\text{W}_3\text{O}_4\text{F}_9]^{5-}$) has been reported,¹¹ however, and it was not known if a stable aqua ion of tungsten(IV) exists and is trimeric. We wish to report here the preparation and properties of the new orange tungsten(IV) aqua ion $[\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$.

Reaction of trivalent metal compounds with stoichiometric amounts of quinque- (or sexi-) valent ones, which is a standard

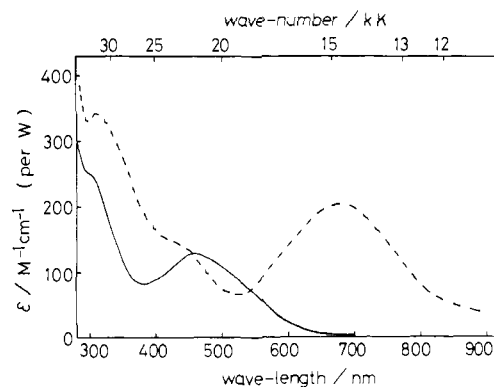


Figure 1. Absorption spectra of $[\text{W}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ (—) and its reduced form, $\text{W}^{\text{III,IV}}(\text{aq})$ (---) in 2 M *p*-toluenesulfonic acid.

method to prepare $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ ¹² did not give satisfactory results in the case of tungsten. Instead, following procedures that were carried out under a nitrogen atmosphere gave the desired tungsten(IV) aqua ion. Potassium hexachlorotungstate(IV), $\text{K}_2[\text{WCl}_6]$ (8.5 g, 0.017 mmol),¹³ in 100 cm³ of 2 M HCl, was kept at 95 °C for 2.5 h and then treated with a cation exchange column (Dowex 50W-X8 in H⁺ form) at room temperature. The orange aqua ion was eluted with 2 M *p*-toluenesulfonic acid (HPTS), indicating that the aqua ion carries similar charge (4+) to the molybdenum(IV) trimeric aqua ion.^{14,15} The yield was ca. 25% based on tungsten. The orange ion was prepared also from $(\text{NH}_4)_2[\text{W}^{\text{V}}\text{OCl}_5]$.¹⁶ A solution of the tungsten(V) complex in 2 M HCl was filtered to remove blue precipitate after heating at 95 °C for 2.5 h and the filtrate submitted to chromatography. The yield of the orange ion was ca. 13% based on tungsten. The ion was less stable than the molybdenum(IV) aqua ion and slowly oxidized within several hours under a nitrogen atmosphere at room temperature.

Tungsten content of the orange ion was determined by the atomic absorption analysis.¹⁷ The oxidation state was determined by titration with cerium(IV). Results were consistent with the quadrivalent state of tungsten in the aqua ion (the oxidation equivalent is 1.9–2.0 times of the tungsten content).

The reaction of the tungsten(IV) aqua ion with thiocyanate, oxalate, and nitritotriacetate gave tungsten(IV) complexes of these ligands. The X-ray crystal analysis of the purple thiocyanate complex revealed the trinuclear structure, $[\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{NCS})_9]^{5-}$.¹⁸ Reduction of the orange aqua ion in 2 M HPTS by zinc amalgam gave a green species, of which the oxidation state of tungsten was 3.3–3.4 as determined by the cerium(IV) titration. From these various observations, we conclude that the orange aqua ion is the trinuclear tungsten(IV) ion $[\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$.

The tungsten(IV) aqua ion shows an absorption peak at 455 nm (ϵ 125 M⁻¹ cm⁻¹ per W) in 2 M HPTS and in 2 M HClO₄ (Figure 1).¹⁹ The green aqua ion, $\text{W}_3^{\text{III,IV}}(\text{aq})$, shows two peaks

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(3) For recent example: Finholt, J. E.; Leupin, P.; Sykes, A. G. *Inorg. Chem.* **1983**, *22*, 3315–3818 and references cited therein.

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(5) Richens, D. T.; Harmer, M. A.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1984**, 2099–2015 and references cited therein.

(6) See, for example: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 822–901.

(7) The dimeric tungsten(V) aqua ion is obtained as a reaction product on reacting $[\text{W}_2\text{O}_4(\text{edta})]^{2-}$ (edta^{4-} = ethylenediaminetetraacetate(4-) ion) with 2 or 3 M HCl (Soares, A. B.; Taylor, R. C.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1101–1104).

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(13) Kennedy, D.; Peacock, R. D. *J. Chem. Soc.* **1963**, 3392–3397.

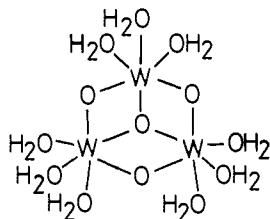
(14) Another orange species, eluted with 1 M HPTS, degraded quickly after the elution. This species appears to contain coordinated chloride ion(s) as observed for the corresponding molybdenum(IV) species (Ojo, J. F.; Sasaki, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 1006–1009).

(15) We found that $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ can be prepared from K_2MoCl_6 similarly as the preparation of the tungsten(IV) aqua ion.

(16) Collenberg, O. *Z. Anorg. Allg. Chem.* **1918**, *102*, 247–276.

(17) Atomic absorption analysis of tungsten was seriously disturbed by various foreign ions involved in the solution. Thus the calibration curve was carefully determined in the presence of the same amount of foreign ions as the sample solution.

(18) Segawa, M.; Kabuto, C.; Sasaki, Y., unpublished results. The anion crystallizes as $(\text{NH}_4)_2(\text{C}_2\text{H}_5)_4\text{N}_3[\text{W}_3\text{O}_4(\text{NCS})_9] \cdot n\text{H}_2\text{O}$. Crystals belong to the monoclinic space group $P2_1/C$ with 4 formula units in a cell with dimensions $a = 22.065$ (3) Å, $b = 14.819$ (2) Å, $c = 19.896$ (2) Å, $\beta = 96.73$ (3)°, and $V = 6460.6$ (3) Å³. Refinement of the structure using 4331 reflections gave $R = 0.084$. Average bond distances and angles: W–W, 2.534; W–O(cap), 2.039; W–O(bridge), 1.911; W–N, 2.110 Å; W–O(cap)–W, 76.91°; W–O(bridge)–W, 83.10°.



at 678 (ϵ 202) and 313 nm (ϵ 342) and a shoulder at ca. 418 nm (ϵ ca. 154) in 2 M HPTS (Figure 1). General features of these absorption spectra are similar to those of the corresponding molybdenum species: $[\text{Mo}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$ (peaks at 508 (ϵ 64) and 304 nm (ϵ 270))^{12b} and $\text{Mo}_3^{\text{III,III,IV}}(\text{aq})$ (peaks at 1050 (ϵ 100) and 398 nm (ϵ 230), and a shoulder at 495 nm (ϵ ca. 115)).²⁰ All the absorption bands of the tungsten species are shifted to shorter wavelength.

Cyclic voltammogram of the orange aqua ion in 2 M HPTS showed an irreversible reduction wave at ca. -0.5 V vs. SCE at 25 °C, which is more negative than $E_{1/2}$ (-0.341 V vs. SCE) of the molybdenum(IV) aqua ion. There is no other inflection in the CV curve between $+1$ and -1 V. Oxidation of the trimer to W(V) is difficult since the tungsten(V) aqua ion appears to be dimeric.⁷

The tungsten(IV) aqua ion is slowly converted to $[\text{W}_3\text{O}_4(\text{NCS})_9]^{5-}$ (λ_{max} at 532 nm with ϵ ca. $280 \text{ M}^{-1} \text{ cm}^{-1}$ per W) in 1.3 M NH_4NCS and 1.0 M HPTS. The change in absorption spectrum occurred in roughly two steps: first step finished within a few minutes at 25 °C with more than 70% of the absorbance change (300–700 nm) and second step took ca. 2 h. Neither of the two steps showed good exponential absorbance change. The two-step change was observed also for the reaction of $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ with NCS^- .^{9b}

Acknowledgment. We thank Professor Kazuo Saito, Institute for Molecular Science, for his valuable discussions. Thanks are also due to Drs. T. M. Suzuki and M. Nishizawa, Government Industrial Research Institute, Tohoku, for the atomic absorption analysis.

(19) The absorption spectrum strictly obeyed Beer's law in the concentration range of 0.001–0.008 M (per W).

(20) Richens, D. T.; Sykes, A. G. *Inorg. Chem.* **1982**, *21*, 418–422.

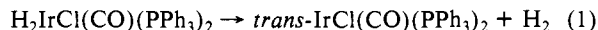
Common Intermediates in the Flash Photolysis of Vaska's Compound $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and Its Dihydride Adduct $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. Implications with Regard to Reductive Elimination Mechanisms

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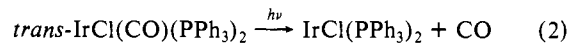
Phosphine complexes of low-valent metal complexes have a long history in the chemistry of homogeneous catalytic activation of small molecules.¹ In the investigation of such reactivities, Vaska's complex $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ has served as an important model for mechanistic investigation of catalytically relevant reactions such as oxidative addition of the small molecules O_2 and H_2 and the corresponding reductive eliminations to reform Vaska's complex, e.g.,



The dihydrogen elimination depicted in eq 1 has been shown to

occur slowly in thermally activated processes ($k_1 = 3.8 \times 10^{-5} \text{ s}^{-1}$ in 25 °C benzene solution²) but quite readily when the dihydride complex is photolyzed with 366-nm light.³ In the course of investigating reactive intermediates in the chemistry of rhodium(I) and iridium(I) phosphine complexes, we have observed that a common transient is produced in the flash photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ and of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. This result suggests that the mechanism of the photoinduced version of eq 1 occurs by a stepwise mechanism involving CO dissociation as the primary photoreaction of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. The resulting pentacoordinated Ir(III) intermediate appears to be dramatically activated toward H_2 elimination as predicted in theoretical treatments.⁴ Preliminary experiments with the orthometalated species $\text{HIrCl}(\text{CO})(\text{PPh}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$ lead to similar conclusions.

Flash photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ in stringently deaerated benzene solution under argon ($\lambda_{\text{irr}} > 254 \text{ nm}$)⁵ resulted in the formation of a transient with strong absorption in the spectral region 390–550 nm. This species decayed to the initial base line via cleanly second-order kinetics. The return to the initial spectrum is consistent with the earlier report that continuous photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ leads to no net photoreactions.^{3a} When similar flash experiments were carried out under various pressures of CO, the transient decay kinetics were first order with the observed rate constants k_{obsd} linearly dependent on P_{CO} . This observation leads to the conclusions that the intermediate formed is the product of CO photodissociation

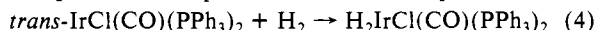


and that the decay process is



The second-order rate constant $k_{\text{CO}} = (2.7 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was determined from the linear plot⁶ of k_{obsd} vs. $[\text{CO}]$. These results are very similar to the chemistry induced by the flash photolysis of the rhodium(I) analogue $\text{trans-RhCl}(\text{CO})(\text{PPh}_3)_2$,⁷ although k_{CO} is about 4-fold faster for the Ir(I) transient.

Consistent with the earlier report,³ we found that $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ undergoes facile photoelimination of H_2 (eq 1). The quantum yield was 0.56 mol/einstein for continuous photolysis at 313 nm, a value close to that reported^{3b} for the similar complex $\text{H}_2\text{IrCl}(\text{PPh}_3)_3$ (0.55). Flash photolysis of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ in benzene under 1.0 atm of H_2 ($\lambda_{\text{irr}} > 254 \text{ nm}$) resulted in transient absorbance in the spectral region 400–550 nm qualitatively the same as that seen for the flash photolysis of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$. This transient decayed via second-order kinetics to give Vaska's compound. Over a period of 10 min, the latter underwent subsequent reaction with H_2 to reform the starting complex according to eq 4 ($k_{\text{obsd}} = 1.2 \text{ M}^{-1} \text{ s}^{-1}$).² The identical kinetics behavior was found for the flash photolysis under 0.25 atm of H_2 with the exception that the rate of eq 4 was a factor



of 4 slower. Flash photolysis of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ under H_2/CO mixtures gave decay rates linearly dependent on P_{CO} . Plots of k_{obsd} vs. $[\text{CO}]$, as above, gave the second-order rate constant

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