The principal subsequent product of $Os(CO)_4(H)CH_3$ decomposition, a moderately stable white solid, was quite unexpected. Mass spectrometry established its composition as $Os_3(CO)_{12}(CH_3)_2$ (**4**). Its ir spectrum,[23] very similar to that of the trinuclear hydride $H_2Os_3(CO)_{12}$,[24] and single nmr signal (τ 9.71 in C_6D_6) make **4** and its conformers the apparent structure. Compound **4** is thus the formal product of the oxidative addition of ethane to $Os_3(CO)_{12}$ and the first example of a dialkylated trinuclear complex.

4
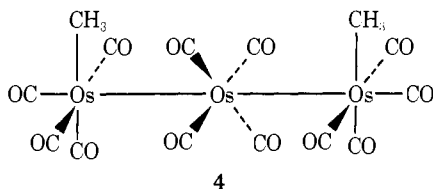
Compounds **2**, **3**, and **4** are all discrete molecules which represent various chemisorbed surface species stabilized by carbonyl ligands: **2** represents the chemisorption of methane onto a ligand-stabilized diosmium "mini-surface", and **3** represents the chemisorption of methyl chloride.[25] **4** corresponds to a triosmium "surface" with methyl groups on the end atoms. As a group, compounds **2–4** provide new evidence for the validity of the analogy between clusters and metal surfaces.[25,26]

References and Notes

(1) The only examples (other than the one discussed here) of which we are aware are $Ni[P(cyclohexyl)_3]_2(H)CH_3{}^2$ and $Ru(H)(CH_3)$ $(diphos)_2,{}^3$ in which the methyl and hydride ligands are kept trans to each other by bulky phosphine ligands, and $(\pi\text{-}C_5H_5)_2Zr(H)CH_3$.[4]
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(14) The osmium anions are also a great deal more basic toward protons than their iron counterparts: Et_3N in CH_2Cl_2 broadens but does not noticeably shift the hydride NMR resonance of $H_2Os(CO)_4$, implying that the pK_a of the first proton of $H_2Os(CO)_4$ is at least 13, compared to only 4.5 for $Fe(CO)_4H_2$.[15] As the pK_a of the second $Fe(CO)_4H_2$ proton is 14,[15] that of the second proton of $Os(CO)_4H_2$ must be above 20.
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(16) τ 17.75 and 9.88 in C_6D_6, $J = 2.8$ Hz, are near the values attributed to $Os(CO)_4(H)CH_3$ in the literature,[7] as are the ir data. Mass spectrometry confirms the identity of the compound.
(17) Characterized by mass spectrometry, NMR (τ, C_6D_6: 9.67 (3), 20.10 (1)), and ir (cm^{-1}, pentane 2130 (w), 2089 (s), 2056 (s), 2044 (s), 2039 (s), 2033 (s), 2025 (m), 2018 (m), 2007 (m), 2004 (w)).
(18) Parent ion in mass spectrum agrees with that calculated. Nmr (τ, C_6D_6): 9.77; ir, (cm^{-1}, pentane): 2103 (s), 2065 (s), 2060 (s), 2047 (m), 2034 (s), 2020 (m), 2013 (m), 2002 (w).
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# Free Energy Profile for an Electron Transfer Reaction

Sir:

Oxidation–reduction reactions between inorganic ions are generally complex, involving formation of discrete associated-ion intermediates.[1] Recent approaches to their study have emphasized direct measurement of the elementary reaction steps.[2,3] As described in the present report, we have taken advantage of the high binding affinity of copper(I) for olefin bonds[4] to obtain information on binuclear ion stabilities and intrinsic electron transfer rates for Cu(I) reduction of the 4-vinylpyridinepentaammineruthenium(III) ion. Comparison of reaction rates with similar systems for which π-bonding is precluded affords evidence that electron transfer occurs principally through the π-complex; i.e., the binuclear ion is a reaction intermediate.[5]

Addition of $Cu(I)$[6] to argon-swept A_5Ru^{III}-4-vinyl(py)[7,8] solutions caused rapid appearance of an absorption band in the visible spectral region, characteristic of the A_5Ru^{II}-4-vinyl(py) ion (λ 453 nm; log ϵ 3.99);[9] quantitative evaluation of Ru(II) ion formation established the overall reacion stoichiometry to be:

$$Cu(I) + A_5Ru^{III}\text{-4-vinyl(py)} \rightleftharpoons Cu(II)$$
$$+ A_5Ru^{II}\text{-4-vinyl(py)}$$
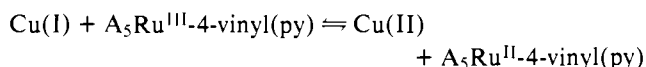
Redox rates were measured spectrophotometrically using the stopped-flow method; results are given in Figure 1. The observed decrease in apparent reaction order with increasing reactant concentrations is indicative of extensive ion-association preceding electron transfer, i.e., the following minimal reaction scheme (Scheme I) where, under pseudo-first-order conditions with $(Ru(III))_0 \gg (Cu(I))_0$, $k_0 = k'/[1 + 1/K_a(Ru(III))]$, $k' = k_a + k_b/K_a$. Kinetic parameters obtained are: $k' = 0.18 (\pm 0.02)$ s^{-1}, $K_a = 8.0 (\pm 1) \times 10^3$ M^{-1}.

Scheme I
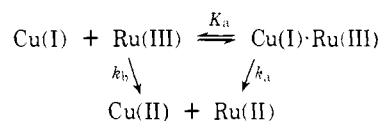
The ion-association step can be identified with Cu(I) π-complexation of the pendant vinyl group of the organic ligand, its assignment being substantiated by two pieces of evidence: (1) The magnitude of the kinetically determined constant, K_a, is nearly identical with those directly measured at equilibrium for Cu(I) π-bonding[10] to 4-vinyl(py)H$^+$, $K = 8.4 (\pm 1.2) \times 10^3$ M^{-1}, and to Co^{III}-4-vinyl(py), $K = 3.4 (\pm 1.2) \times 10^3$ M^{-1}, medium conditions in all instances being 0.1 M TFA at 23°. (2) Reduction of A_5Ru^{III}-4-Et(py) ion,[8] whose reactivity should be comparable excepting preclusion of Cu(I) π-bonding, proceeds by simple second-order kinetics, $d(Ru(II))/dt = k_{Et}(Ru(III))(Cu(I))$, with $k = 9.7 (\pm 0.3)$ M^{-1} s^{-1} in 0.1 M TFA at 23°. No evidence of saturation phenomena could be found with reactant concentrations as high as 4×10^{-3} M,
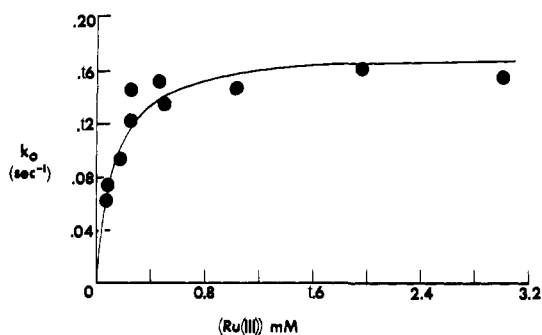
Figure 1. Specific rate constants for the $Cu(I)-A_5Ru^{III}-4$-vinyl(py) reaction. Conditions: $Ru(III) \gg Cu(I)$, 0.1 M TFA at 23°. Data points are average values for four runs; the curve was generated from kinetic parameters given in the text.

Table I. Distribution of Ruthenium Oxidation States at Equilibrium[a]

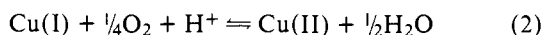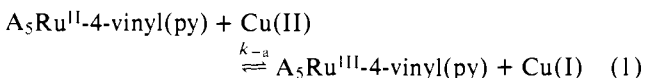| $Cu(II)_0$ (mM)	$Ru(II)_0$ (mM)	$f_{Ru(II)}$ (calcd)[b,c]	$f_{Ru(II)}$ (exptl)[b]
10	0.050	0.46	0.46
10	0.043	0.43	0.34
2.5	0.039	0.64	0.52
0.5	0.051	0.83	0.79

[a] Reaction initiated by mixing $Cu(II)$ and $Ru(II)$ in 0.1 M TFA at 23°. [b] Fraction ruthenium ions present as $Ru(II)$ species. [c] Calculated according to the reaction scheme given in Figure 2 and additional binding given by: $Cu(I) + A_5Ru^{II}-4$-vinyl(py) $\rightleftharpoons$ π-complex, with the association constant assumed equal to K_a.

i.e., $(Ru(III)) = 0.3-4.1$ mM, $Cu(I) = 0.1-0.2$ mM, with $Ru(III)/Cu(I) = 3-20$.

The comparative kinetics of reduction for the two $Ru(III)$ complexes also provides a basis for distinguishing between electron transfer by intramolecular (k_a) and intermolecular (k_b) pathways. To account for the net measured reaction rate in the 4-vinylpyridine system, k_b ($= k'K_a$) must equal ca. 1.4×10^3 M^{-1} s^{-1}. However, reduction of the 4-ethylpyridine-containing ion, for which the pathways corresponding to k_b should be equally accessible, is sufficiently slow to suggest only ca. 10^2 $k_{Et}/k'K_a = 0.7\%$ intermolecular reaction.

Given that reaction proceeds by a pathway involving the intermediacy of the π-complexed binuclear ion, it is still possible that redox occurs through an activated complex in which $Cu(I)$ is not olefin-bound. Lifetimes for $Cu(I)$ π-complexes are only a few microseconds,[11] sufficiently rapid that dissociation of or substitution for the olefin ligand could precede electron transfer in approaching the transition state. However, to account for the magnitude of the measured intramolecular rate constant under these constraints, it becomes necessary to postulate the existence of a relatively stable $Cu^I \cdot Ru^{III}$ associated ion not involving olefin bonds which is accessible only by prior formation of the π-complex and possesses an anomalously low activation energy for electron transfer.[12] As this circumstance is difficult to envisage, it appears likely that the $Cu(I)$-olefin bond is maintained in the transition state.

Cupric ion was found to be an effective catalyst of oxidation of $A_5Ru^{II}-4$-vinyl(py) by dioxygen. Reaction presumably occurs by the following sequence:

$$A_5Ru^{II}\text{-}4\text{-vinyl(py)} + Cu(II)$$

$$\overset{k_{-a}}{\rightleftharpoons} A_5Ru^{III}\text{-}4\text{-vinyl(py)} + Cu(I) \quad (1)$$

$$Cu(I) + \tfrac{1}{4}O_2 + H^+ \rightleftharpoons Cu(II) + \tfrac{1}{2}H_2O \quad (2)$$

although the reduced oxygen species has not yet been identified. Inasmuch as reaction of $Cu(I)$ with dioxygen, step 2, is extremely rapid,[13] the overall reaction is likely controlled by

$$Ru^{III} + Cu^I \rightleftharpoons [\ddagger] \rightleftharpoons \pi\text{-complex} \rightleftharpoons [\ddagger] \rightleftharpoons Ru^{II} + Cu^{II}$$
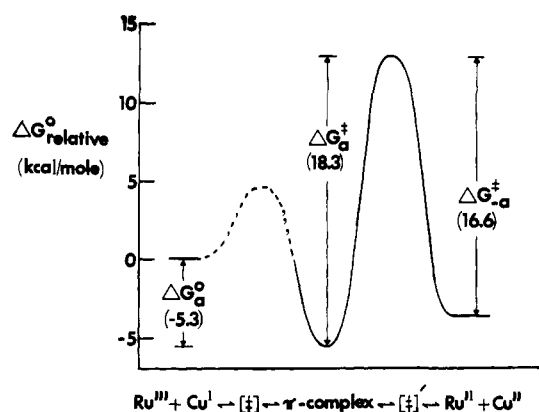
Figure 2. Reaction coordinate diagram for electron transfer.

step 1, permitting evaluation of the rate constant for cupric ion oxidation of $A_5Ru^{II}-4$-vinyl(py). This expectation has been confirmed experimentally, the rate law being $-d(Ru(II))/dt = k_{-a}(Ru(II))(Cu(II))$, with $k_{-a} = 3.4$ (± 0.6) M^{-1} s^{-1} in 0.1 M TFA at 23°. Reactant ion concentrations were varied over the ranges $(Cu(II)) = 0.5-2.0$ mM, $(Ru(III)) = 0.12-0.0017$ mM, with $Cu(II)/Ru(II) = 10-10^3$; rates were independent of solution concentrations of dioxygen, which was maintained in excess. Rate constants were corrected for the slow, direct reaction of dioxygen with the $Ru(II)$ ion,[14] the latter pathway accounting for less than 5% of the total reaction.

The data in Table I give comparison of reaction equilibria measured under conditions favoring the back reaction with values calculated from K_a, k_a, and k_{-a}; the good agreement obtained provides independent verification of the kinetic analysis.

Rate data are summarized in Figure 2. The activation energy for π-complex formation is not known but cannot be more than a few kilocalories per mole, based upon the rapid rates measured for $Cu(I)$-alkenoic acid π-complexation.[11] Other intermediates, e.g., outer ion-pairs, may well exist; nonetheless, it seems evident that these reactions will afford a relatively detailed examination of the molecular events leading to net electron transfer.

Caution: Perchlorate salts of $Ru(III)$-ammines are potentially explosive; they should be prepared in only small quantities.

References and Notes

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(8) Abbreviations used are A = ammine, 4-vinyl(py) = 4-vinylpyridine TFA = trifluoroacetic acid, 4-Et(py) = 4-ethylpyridine.
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(10) Addition of Cu(I) to 4-vinyl(py)H$^+$ or its $A_5Co(III)$ complex caused appearance of strong absorption bands at 352 (log ϵ 3.58) and 340 nm (log ϵ 3.67), respectively, diagnostic of π-bond formation. Association constants were determined as described in ref 4a.
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The Stabilization of Trivalent Nickel in Deprotonated-Peptide Complexes

Sir:

Trivalent nickel has been considered to be a relatively rare oxidation state until recently. Nickel(III) complexes of the macrocyclic tetraaza ligands have been prepared and characterized in acetonitrile solution[1,2] and as solids.[2] Complexes of Ni(III) cyclam and its derivatives are stable as solids in a dry atmosphere, but decompose rapidly in aqueous solution.[2,3] Pulse radiolysis has been used to generate the Ni(III) complexes of ethylenediamine and of glycine in aqueous solution where the complexes rapidly decompose.[4] On the other hand a Ni(III)-EDTA complex, also prepared by the reaction of hydroxyl radicals, has recently been reported to be stable in deoxygenated aqueous solution for several days.[5]

In the present work Ni(III) deprotonated-peptide complexes are prepared and characterized in aqueous solution. This laboratory recently reported[6] that the Cu(III) oxidation state is substantially stabilized, both thermodynamically and kinetically, by metal–ligand bonding involving deprotonated-peptide nitrogen coordination. We find similar behavior for Ni(III)-peptide complexes, where the electrode potentials are lower than for other Ni(III) complexes due to the strong electron-donor properties of the deprotonated-peptide nitrogens. The suggested coordination is the same as that proposed for Ni(III)-bis(biuret),[7] except that there cannot be as much π-delocalization. The magnetic susceptibility and the reflectance spectrum were reported for the highly insoluble $KNi^{III}(bi)_2$ compound,[7] but this complex could not be characterized in solution.

The crystal structure of the Ni(II) complex of tetraglycine (G_4) shows that $Na_2[Ni(H_{-3}G_4)]\cdot 8H_2O$ is a square-planar complex with four nitrogens coordinated to the metal ion (one amine N and three deprotonated-peptide N).[8] This complex can be oxidized electrochemically or chemically to the corresponding Ni(III) species, but it decomposes easily, oxidizing the ligand to triglycinamide (G_3a), formaldehyde, and carbon dioxide.[9,10] Hence, most of the present studies were carried out with the more stable G_3a complex. The $[Ni^{II}(H_{-3}G_3a)]^-$ complex is oxidized quantitatively, either electrochemically or chemically (with $Ir^{IV}Cl_6{}^{2-}$), to the corresponding $Ni^{III}(H_{-3}G_3a)$ species, which is relatively stable in slightly acidic solution, but decomposes rapidly in base. Electrochemical oxidation was performed with a flow system in which the electrode arrangement included a graphite powder working electrode packed in a porous glass column, wrapped externally with a Pt wire electrode.[11] Oxidation causes a change in the electronic spectrum from an absorption band of the $[Ni^{II}(H_{-3}G_3a)]^-$ at 410 nm, ϵ 140 M^{-1} cm^{-1}, to an intense charge-transfer absorption for the Ni(III) species with a band at 320 nm, ϵ 5360 $\pm$ 150 M^{-1} cm^{-1}. The molar absorptivity was determined by quantitative reactions between the trivalent nickel complex and several different reducing agents including di(*tert*-butyl)nitroxide, hydroquinone, and $Fe(CN)_6{}^{4-}$. Immediate quenching of the electrochemically generated $Ni^{III}(H_{-3}G_3a)$ complex by a reducing agent affords nearly quantitative recovery of the original peptide ligand. This re-

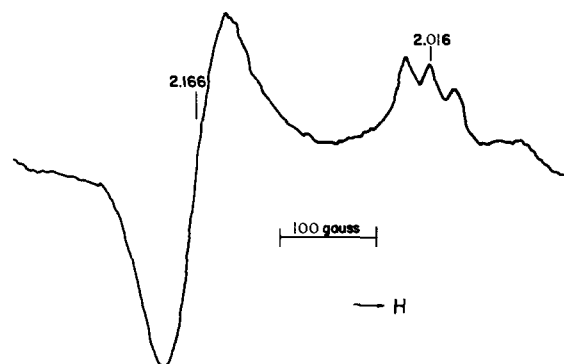**Figure 1.** EPR spectrum of $Ni^{III}(H_{-3}G_3a)$. The Ni(II) complex (2.0 $\times$ 10^{-2} M, pH 9.5) was oxidized on a graphite column at 0.83 V vs. Ag|AgCl. The spectrum was obtained at 77 K and 9.074 GHz.
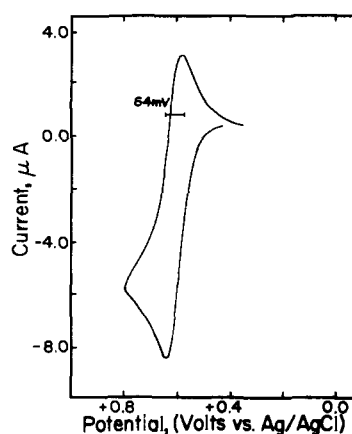

Figure 2. Cyclic voltammogram of $[Ni(H_{-3}G_3a)]^-$ in aqueous solution at a carbon paste electrode. $[NiG_3a]_T = 2.0 \times 10^{-3}$ M, $\mu = 0.1$ M NaClO$_4$, scan rate = 20 mV s^{-1}. $E^0 = 0.83$ V vs. NHE.

versible redox property provides one piece of evidence that it is the metal ion and not the ligand which has been oxidized.

The $Ni^{III}(H_{-3}G_3a)$ complex is much slower to decompose in acid than is the $[Ni^{II}(H_{-3}G_3a)]^-$ complex. The Ni(II) complex has a half-life of only 0.026 s at pH 3,[12] while the half-life of the Ni(III) complex is 900 s at this pH. Reduced lability of the metal–N(peptide) toward acid attack was also found in the case of Cu^{III}.[6]

More definitive evidence that the oxidized complex contains Ni^{III} is provided by its EPR spectrum. The $[Ni^{II}(H_{-3}G_3a)]^-$ complex is a low spin, d^8 species which is EPR inactive. After electrochemical oxidation an EPR spectrum was obtained at liquid nitrogen temperatures as shown in Figure 1. The spectrum with $g_\perp$ (2.166) greater than $g_\parallel$ (2.016) is similar to that found for Ni(III) complexes of the tetraaza macrocycles.[2,3,13] The existence and value of $g_\perp$ indicates that the initial oxidation gives a d^7, tetragonal nickel complex[13] rather than a nickel(II) ligand radical.[14] The value for $g_\parallel$ is a tentative assignment, and the factors contributing to its splitting are under investigation.

Cyclic voltammetry is used to characterize the triglycinamide and other peptide complexes of nickel. Figure 2 shows the current–voltage response for the nickel–triglycinamide complex. The voltammogram shows quasi-reversible behavior at slow scan rates, and therefore the potential of 0.83 V (vs. NHE), the midpoint between the oxidation peak and the reduction peak, is a reasonable estimate of E^0 for the $[Ni^{III,II}(H_{-3}G_3a)]^{0,-1}$ couple.

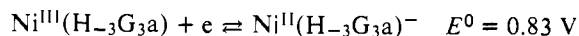$$Ni^{III}(H_{-3}G_3a) + e \rightleftarrows Ni^{II}(H_{-3}G_3a)^- \qquad E^0 = 0.83 \text{ V}$$

Table I lists the electrode potentials for a series of Ni(III) peptide complexes. Thermodynamic stability within this series