relative orbital energies and hence their occupancy. Consequently, the relative importance of ligand–metal vs. metal–ligand electron donation remains obscure and will likely be resolved only with the help of ab initio calculations.[11] The fact that phosphorus compounds, with empty 3d orbitals (π acceptors), fit the correlation reasonably well, suggests that metal–ligand donation is unimportant. This may, however, be the fortuitous result of a stronger π bond canceling the effects of a weaker σ bond to CpNi$^+$.[8,9] Additional studies of complexes which bind and readily exchange more than one ligand may help to further resolve such questions.

There are myriad possibilities for further studies of the ion chemistry, photochemistry,[12-15] and ligand binding energetics of transition metal complexes.[16,17] Of particular interest are ICR photodissociation spectra[12-14] of CpNiB$^+$, which currently are being explored to provide information relating electronic excitation energies to $D(\text{B–CpNi}^+)$ in these complexes.

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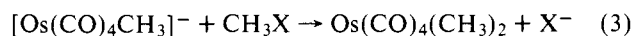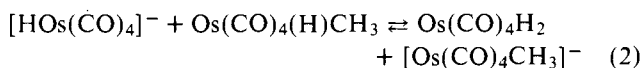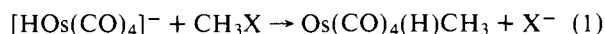## Synthesis of Di- and Trinuclear Methyl Osmium Complexes via cis-Hydridomethyltetracarbonylosmium

Sir:

Although they are frequently postulated as intermediates in homogeneous catalysis, transition metal complexes with both alkyl and hydrogen ligands are almost never stable.[1-4] Current interest in hydrocarbon activation[5] and our interest in elimination processes involving cis organic ligands[6] suggested the development of a synthesis of cis-Os(CO)$_4$(H)CH$_3$ (**1**) and the investigation of its chemistry. Reported as a minor by-

product of several reactions,[7,8] **1** proved stable enough to be observed spectroscopically. In this regard it contrasts with the analogous iron complexes Fe(CO)$_4$(H)R which are too unstable to be detected.[9]

We first attempted to synthesize **1** via the preparation and protonation of [Os(CO)$_4$CH$_3$]$^-$. However, attempts to make [Os(CO)$_4$CH$_3$]$^-$ by methods similar to those used for the analogous iron alkyl anions[9a] are thwarted by its high nucleophilicity. Even a weak methylating agent such as methyl chloride converts Na$_2$Os(CO)$_4$[8,10-12] speedily to Os(CO)$_4$(CH$_3$)$_2$. These results agree with the generalization[13] that anions of third-row transition elements are much more nucleophilic than their first-row counterparts.[14,15]

Methylation of the previously known[7] hydride anion HOs(CO)$_4$$^-$ proves somewhat more satisfactory. However, its reaction with such reagents as methyl tosylate gives a mixture of Os(CO)$_4$H$_2$, Os(CO)$_4$(H)CH$_3$, and Os(CO)$_4$(CH$_3$)$_2$ in the approximate ratio 1:2:1. This mixture presumably arises from competition between the desired alkylation of [HOs(CO)$_4$]$^-$ (reaction 1) and deprotonation by [HOs(CO)$_4$]$^-$ of Os(CO)$_4$(H)CH$_3$ (reaction 2).

$$[\text{HOs(CO)}_4]^- + \text{CH}_3\text{X} \rightarrow \text{Os(CO)}_4(\text{H})\text{CH}_3 + \text{X}^- \quad (1)$$

$$[\text{HOs(CO)}_4]^- + \text{Os(CO)}_4(\text{H})\text{CH}_3 \rightleftharpoons \text{Os(CO)}_4\text{H}_2 + [\text{Os(CO)}_4\text{CH}_3]^- \quad (2)$$

$$[\text{Os(CO)}_4\text{CH}_3]^- + \text{CH}_3\text{X} \rightarrow \text{Os(CO)}_4(\text{CH}_3)_2 + \text{X}^- \quad (3)$$

Although Os(CO)$_4$(H)CH$_3$ is probably less acidic than Os(CO)$_4$H$_2$, the high nucleophilicity of [Os(CO)$_4$CH$_3$]$^-$ and the consequent speed of reaction 3 make dimethylation an important side reaction.

The best way to overcome this side reaction is the use of methyl fluorosulfonate to increase the speed of reaction 1. In a typical preparation 94 mg of Na$_2$Os(CO)$_4$ is suspended in tetraglyme under nitrogen and protonated with 1 equiv of trifluoroacetic acid, and 2 equiv of methyl fluorosulfonate are then added. Under high vacuum at room temperature a mixture of product and methyl trifluoroacetate distills into a $-196°$ cold trap. Redistillation through a $-63°$ bath traps 60 mg (70% yield) of Os(CO)$_4$(H)CH$_3$. NMR[16] shows the material to be 97% pure, with 3% Os(CO)$_4$(CH$_3$)$_2$.

In the absence of air and light, Os(CO)$_4$(H)CH$_3$ decomposes slowly (several days) at room temperature. One-half equivalent of methane, but no carbon monoxide, is evolved. Preparative TLC allows the separation and identification of the initial organometallic product, a colorless liquid which yellows immediately upon exposure to light, as HOs(CO)$_4$Os(CO)$_4$CH$_3$ (**2**).[17] This characterization was confirmed by the conversion of **2** upon treatment with CCl$_4$ to the expected derivative ClOs(CO)$_4$Os(CO)$_4$CH$_3$ (**3**), a stable white solid.[18]

A product such as **2** was expected from the thermolysis of **1** by analogy to the H$_2$Os$_2$(CO)$_8$ previously observed[6] as the primary decomposition product of Os(CO)$_4$H$_2$. The absence of observable coupling between the methyl and hydride protons in the NMR of **2** and the resemblance of its infrared spectrum to those of H$_2$Os$_2$(CO)$_8$[19] and X$_2$Os$_2$(CO)$_8$[19,20] suggest the structure shown below and its conformers. Compound **2** thus resembles the recently reported clusters HOs$_3$(CO)$_{10}$R, where R contains a coordinating double bond or organic carbonyl.[21,22] However, **2** is stable without such additional binding of its organic ligand.

2
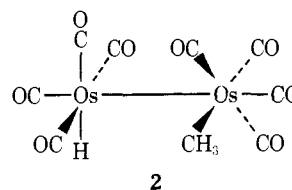
The principal subsequent product of $Os(CO)_4(H)CH_3$ decomposition, a moderately stable white solid, was quite unexpected. Mass spectrometry established its composition as $Os_3(CO)_{12}(CH_3)_2$ (**4**). Its ir spectrum,[23] very similar to that of the trinuclear hydride $H_2Os_3(CO)_{12}$,[24] and 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
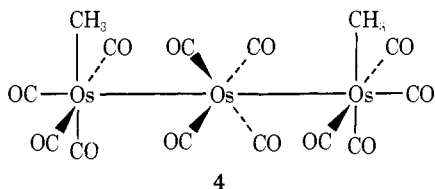
Compounds **2**, **3**, and **4** are all discrete molecules which represent various chemisorbed surface species stabilized by carbonyl ligands: **2** represents the chemisorption of methane onto a ligand-stabilized diosmium "mini-surface", and **3** represents the chemisorption of methyl chloride.[25] **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)CH₃² and Ru(H)(CH₃) (diphos)₂,³ in which the methyl and hydride ligands are kept trans to each other by bulky phosphine ligands, and (π-C₅H₅)₂Zr(H)CH₃.⁴
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(17) Characterized by mass spectrometry, NMR (τ, C₆D₆: 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, C₆D₆): 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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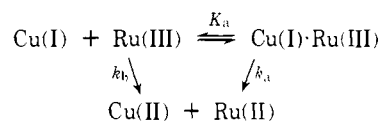## Free Energy Profile for an Electron Transfer Reaction

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:

$$Cu(I) + A_5Ru^{III}\text{-}4\text{-vinyl(py)} \rightleftharpoons Cu(II)$$
$$+ A_5Ru^{II}\text{-}4\text{-vinyl(py)}$$
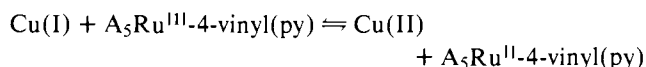
Redox rates were measured spectrophotometrically using the stopped-flow method; results are given in Figure 1. The observed decrease in apparent reaction order with increasing reactant concentrations is indicative of extensive ion-association preceding electron transfer, i.e., the following minimal reaction 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

$$Cu(I) + Ru(III) \underset{K_a}{\rightleftharpoons} Cu(I)\cdot Ru(III)$$

$$k_b \searrow \qquad \swarrow k_a$$

$$Cu(II) + Ru(II)$$

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,