the ion pair between $Ru(NH_3)_6^{3+}$ and $N_2O_3^{2-}$. The negative salt effect produced by added LiCl could then result from displacement of trioxodinitrate from the ion pair by chloride ion. The smaller effect produced by the use of $NaClO_4$ could result from the lowered ability of ClO_4^- compared to that of Cl^- to compete with $N_2O_3^{2-}$. Such competition for ion-pair formation has been observed. Sulfate or phosphate prevents the formation of the yellow color due to the amidopentaammineruthenium(III) cation in solutions around pH 13 by ion pairing with the hexaammineruthenium(III) cation and so preventing ion pair formation with hydroxide ion.[13,16] The fall in reactivity at high pH in the present study is thus due initially to the displacement of trioxodinitrate from the ion pair by OH^-, which is the first stage in the formation of the deprotonated complex.[16]

Ruthenium(III) is a substitution-inert center[17,18] but undergoes facile electron transfer to the more labile Ru(II). An example of a fast reaction involving Ru(III) is that with NO to give $Ru(NH_3)_5N_2^{2+}$ with rate constant 21.9 $M^{-1}\ s^{-1}$ at 5.2 °C and pH 11.35. This reaction involves the amido species, and so the second-order rate constant continues to increase with pH. The reaction between $Ru(NH_3)_6^{3+}$ and $N_2O_3^{2-}$ represents unusually high reactivity of the hexaammineruthenium(III) cation, having a second-order rate constant at pH 11.2 and 2 °C of 44.8 $M^{-1}\ s^{-1}$.

Formation of a trioxodinitrate complex of Ru(III) as the first stage of the reaction seems unlikely, although bidentate complexes of $N_2O_3^{2-}$ are known.[19] An outer-sphere reaction involving oxidative cleavage of $N_2O_3^{2-}$ could occur by two pathways, giving $NO + NO_2^-$ or $NO^- + NO_2$. The former pathway seems more likely. The stoichiometric data suggest that at least 1 mol of nitrite is liberated per mole of $N_2O_3^{2-}$. Cleavage of the $N_2O_3^{2-}$ may occur synchronously with electron transfer from the (NO^-) fragment to Ru(III), generating Ru(II) and NO. The resulting NO may react with excess $Ru(NH_3)_6^{3+}$ to give N_2 at pH values greater than about 9, and the nitrosylpentaammineruthenium(II) cation at lower pH. The alternative cleavage to give NO^- and NO_2 may account for the formation of N_2O. In the case of N-1-labeled trioxodinitrate ($O^{15}NNO_2^{2-}$), this will give $^{46}N_2O$. If the two cleavage reactions occur together, NO and NO_2 will be products. These combine in aqueous solution to give N_2O_3 and hence nitrite and could accommodate NO_2^- production at a stoichiometry greater than 1:1. Combination of NO and NO_2 in aqueous solution is postulated to give the symmetrical isomer ONONO rather than the more stable form $ONNO_2$.[20] This allows the exchange of nitrogen atoms between NO and NO_2 and hence the formation of ^{14}NO and $^{45}N_2O$ in reactions with $O^{15}NNO_2^{2-}$. The $^{45}N_2O$ is suggested to result from reaction between $^{15}NO^-$ and $^{14}NO^-$ produced by reduction of ^{14}NO by $Ru(NH_3)_6^{2+}$. These reactions are summarized in Scheme I.

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Registry No. $Ru(NH_3)_6^{3+}$, 18943-33-4; $N_2O_3^{2-}$, 15435-67-3.

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Kinetics and Mechanism of the Reaction between *trans*-Dioxotetracyanotungstate(IV) and Azide in Aqueous Solution

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The reaction of *trans*-$[WO_2(CN)_4]^{4-}$ with N_3^- has been studied in the pH range 6–10. The kinetic data indicate that the protonated form *trans*-$[WO(H_2O)(CN)_4]^{2-}$ is the only reactive species and that the aquo ligand is substituted by the N_3^- ion according to the reaction

$$[WO(H_2O)(CN)_4] + N_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [WO(N_3)(CN)_4]^{3-} + H_2O$$

The values of k_1 and k_{-1} are 4.2 (1) $M^{-1}\ s^{-1}$ and 0.20 (6) s^{-1}, respectively, at 25 °C. The value of $\Delta V^{*}(k_1)$ (+10.6 (5) $cm^3\ mol^{-1}$) is indicative of a dissociatively activated substitution process.

Introduction

trans-Dioxotetracyanotungstate(IV) and -molybdate(IV) ions may be protonated to form the oxo–hydroxo and oxo–aquo complexes,[1,2] reactions 1 and 2.

$$[MO_2(CN)_4]^{4-} + H^+ \rightleftharpoons [MO(OH)(CN)_4]^{3-} \qquad (1)$$

$$[MO(OH)(CN)_4]^{3-} + H^+ \rightleftharpoons [MO(H_2O)(CN)_4]^{2-} \qquad (2)$$

The existence of the protonated forms was duly established by means of the structure determination of $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$,[3] $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$,[3] and $(PPh_4)_2[MoO(H_2O)(CN)_4]\cdot 4H_2O$.[4]

These structure determinations, as well as the structural data of $[MoO_2(CN)_4]^{4-}$,[5] showed that the Mo═O and Mo—OH bonds are much stronger than the Mo—OH_2 bond. It was recently discovered that the bidentate ligand, 1,10-phenanthroline (Phen), reacts with *trans*-$[MoO_2(CN)_4]^{4-}$ with the formation of the

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Table I. Molar Absorptivities of the Compounds Studied

complex ion	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
$[WO_2(CN)_4]^{4-}$	520	24
$[WO(OH)(CN)_4]^{3-}$	539	33
$[WO(H_2O)(CN)_4]^{2-}$	563	37
$[WO(N_3)(CN)_4]^{3-}$	591	39

$[MoO(Phen)(CN)_3]^-$ ion.[6,7] This ground-state destabilization of the metal–oxygen bond on protonation indicates that it is actually the protonated forms that are reactive toward substitution. This supposition was confirmed by the observation that no reaction occurred at a high pH where $[MoO_2(CN)_4]^{4-}$ is the main species. The fact that a cyano ligand was also displaced from the parent ion raised the question of which ligand (aquo, hydroxo or cyano) will first be substituted during a presumably two-step substitution process with a bidentate ligand. The crystal structure determination of $Cs_2Na[MoO(N_3)(CN)_4]$[8] clearly indicated that the aquo ligand is preferentially substituted by the azide ligand.

Along these lines, $[WO(Pic)(CN)_3]^{2-}$ (Pic = 2-picolinate) was recently synthesized by means of the reaction between $[WO_2(CN)_4]^{4-}$ and 2-picolinic acid at a pH of 6.0. The crystal structure determination of $(AsPh_4)_2[WO(Pic)(CN)_4]\cdot 2H_2O$[9] revealed that the aquo ligand was displaced by the oxygen atom of the carboxylic group, whereas the cyano ligand was substituted by the pyridine nitrogen atom. This result was interpreted as evidence that the aquo ligand was first substituted, followed by ring closure and displacement of the cyano ligand.

We have now studied the kinetics and mechanism of the reaction between $[WO_2(CN)_4]^{4-}$ and N_3^- in order to establish the intimate nature of the substitution behavior of this tungsten complex.

Experimental Section

$K_3Na[WO_2(CN)_4]\cdot 6H_2O$ was prepared as described previously.[9] $[WO_2(N_3)(CN)_4]^{3-}$ was synthesized in the following way: A 1.3-g sample of NaN_3 (0.02 mol) and 0.2 g of $K_3Na[WO_2(CN)_4]\cdot 6H_2O$ (0.0005 mol) were dissolved in 5 cm^3 of a buffer solution (0.1 M citrate and 0.3 M Tris). The pH was adjusted to about 6.5 with 0.5 M acetic acid. A 0.2-g sample of CsCl (0.0012 mol) was dissolved in 1 cm^3 of the same buffer solution. Both solutions were heated to about 40 °C, mixed, and covered. Royal blue crystals of $Cs_2Na[WO(N_3)(CN)_4]$ were obtained after about 10 h. The cell dimensions and space group of this compound were determined from Weissenberg photographs, which proved it to be isomorphous with the corresponding molybdenum compound:[8] space group *Pnma*, $a = 16.03$ (2) Å, $b = 7.94$ (1) Å, $c = 10.26$ (2) Å, and $Z = 4$.

The kinetic and equilibrium measurements were carried out in a citrate–TRIS buffer medium. In the case of the high-pressure study, 2-morpholinoethanesulfonic acid (MES) was used as a buffer. The ionic strength of the test solutions was adjusted to 1.0 M (KNO_3) for all measurements. The pH measurements were performed on an Orion, Model 701, pH meter with a combined glass and calomel electrode.

All the absorbance measurements were done at 620 nm. The stability constant of $[WO(N_3)(CN)_4]^{3-}$ was determined spectrophotometrically at pH 6.0. The kinetics of the anation reaction were studied under pseudo-first-order conditions on a Durrum D-110 stopped-flow spectrophotometer. The kinetic runs at high pressures were performed in a thermostated (±0.1 °C) high-pressure stopped-flow system.[10] Linear first-order plots were obtained for at least 2–3 half-lives of the reaction under all conditions.

Results and Discussion

The substitution of only the aquo ligand in $[WO(H_2O)(CN)_4]^{2-}$ by azide ions (even at a very high $[N_3^-]$) was proven by the isomorphism of the reaction product $Cs_2Na[WO(N_3)(CN)_4]$ and the corresponding molybdenum complex.[8] No reaction was observed at a high pH where $[WO_2(CN)_4]^{4-}$ is the predominant species. (The pK_{a1} and pK_{a2} values of $[WO(H_2O)(CN)_4]^{2-}$ are 7.8 and 11.7, respectively.[2]) All the compounds showed only one absorption maximum in the 400–650-nm region. The wavelengths, λ_{max}, and molar absorptivities at the maxima are given in Table I.

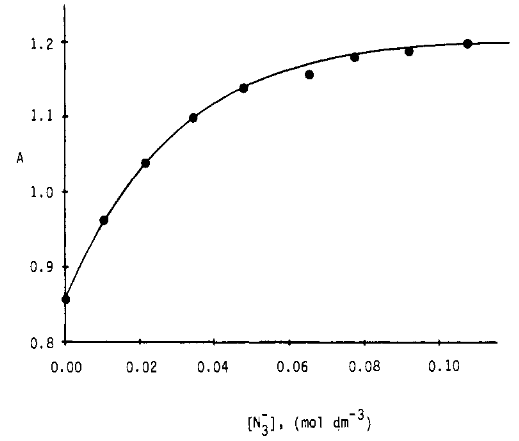


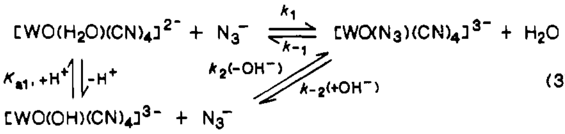
Figure 1. Plot of absorbance vs. $[N_3^-]$ at 25.0 °C, $\mu = 1.0$ M (KNO_3), pH 6, and $\lambda = 620$ nm.

Table II. Kinetic and Equilibrium Data at 25 °C and $\mu = 1.00$ M

k_1,[a] M^{-1} s^{-1}	4.2 (1)	pK_{a1}[d]	7.76
$10k_{-1}$,[a] s^{-1}	0.20 (6)	$\Delta S^*(k_1)$,[a] cal deg^{-1} mol^{-1}	−2.4 (2)
K_1,[b] M^{-1}	4.8 (11)	$\Delta H^*(k_1)$,[a] kcal mol^{-1}	16.0 (5)
k_1,[c] M^{-1} s^{-1}	4.0 (1)	$\Delta V^*(k_1)$,[e] cm^3 mol^{-1}	10.6 (5)
k_2,[c] M^{-1} s^{-1}	0.01 (4)	$\Delta S^*(k_{-1})$,[a] cal deg^{-1} mol^{-1}	−1 (5)
pK_{a1}[c]	7.60 (4)	$\Delta H^*(k_{-1})$,[a] kcal mol^{-1}	18.0 (16)

[a] From data in Figure 2. [b] From data in Figure 1. [c] From data in Figure 3. [d] Reference 2. [e] From data in Table III.

Since no reaction took place at a high pH and only the aquo ligand is substituted, even at a high azide ion concentration, the following reaction scheme can be suggested:



(3)

For the spectrophotometric determination of the stability constant of $[WO(N_3)(CN)_4]^{3-}$, the concentration of N_3^- was varied from 0.015 to 0.5 M at a pH of 6.0. Figure 1 is a plot of absorbance vs. $[N_3^-]$. From the definition of K_1, see reaction 3, the mass balance and Beer's law, eq 4, can be derived. *A* is the

$$A = \frac{A_r + A_pK_1[N_3^-]}{1 + K_1[N_3^-]} \tag{4}$$

absorbance at a given concentration of N_3^-; A_r and A_p are the absorbances of $[WO(H_2O)(CN)_4]^{2-}$ and $[WO(N_3)(CN)_4]^{3-}$, respectively. The concentration of the free N_3^- was calculated for each point. The absorbance vs. $[N_3^-]$ data were fitted to eq 4 by using a nonlinear least-squares program to obtain the value of K_1. This value of K_1 is in reasonable agreement with the value of k_1/k_{-1} determined kinetically (see Table II).

According to the reaction scheme (eq 3), the pseudo-first-order rate constant is given by eq 5. At a low pH ($[H^+] >> K_{a1}$), the

$$k_{obsd} = \frac{(k_1 + k_2K_{a1}/[H^+])[N_3^-]}{1 + K_{a1}/[H^+]} + k_{-1} + k_{-2}[OH^-] \tag{5}$$

pseudo-first-order rate constant for the anation of $[WO(H_2O)(CN)_4]^{2-}$ is thus given by eq 6. The values of k_1 and k_{-1}

$$k_{obsd} = k_1[N_3^-] + k_{-1} \tag{6}$$

were obtained from a least-squares fit of the k_{obsd} vs. $[N_3^-]$ data, determined at pH 6.0, to eq 6. The experimental data are rep-

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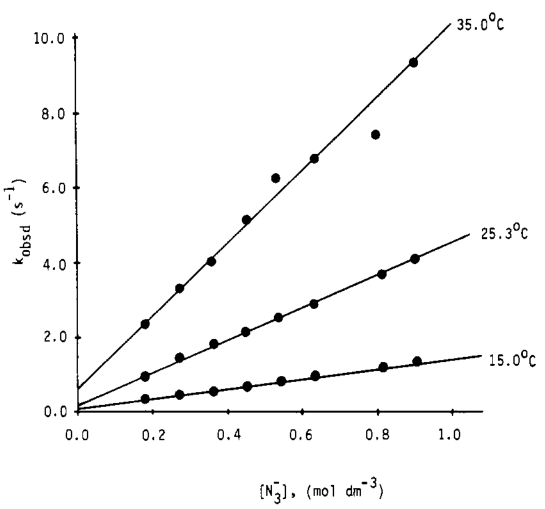

Figure 2. Plot of k_{obsd} vs. $[N_3^-]$ at different temperatures, pH 6.0, and $\mu = 1.0$ M (KNO_3).

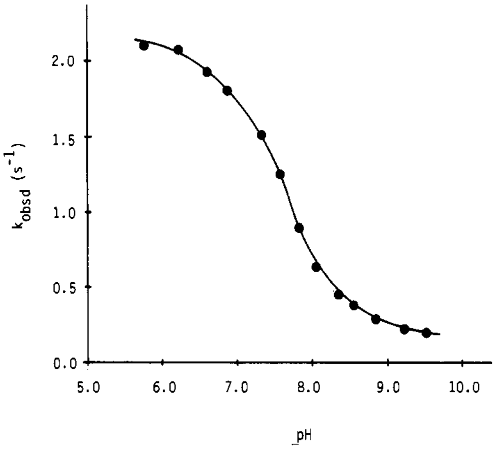

Figure 3. Plot of k_{obsd} vs. pH at 25.0 °C, $[N_3^-] = 0.5$ M, and $\mu = 1.0$ M (KNO_3).

resented in Figure 2. The values of k_1 and k_{-1}, together with the activation parameters, are given in Table II.

From the reaction scheme in eq 3 it is apparent that the concentration of $[WO(OH)(CN)_4]^{3-}$ increases with increasing pH of the solution. Since the W–OH bond is much stronger than the W–OH_2 bond,[3,4] it is expected that the aquo ligand would be significantly more labile than the hydroxo ligand. It is thus anticipated that the pseudo-first-order rate constant should decrease with increasing pH. Figure 3 represents the effect of pH on k_{obsd} at a constant $[N_3^-]$. A plot of k_{obsd} vs. $[N_3^-]$ at pH 9.46 is also linear with a slope of 0.06 (2) $M^{-1}\ s^{-1}$ and an intercept of 0.18 (1) s^{-1}. The value of the intercept is within the experimental error the same as at pH 6.0 (see Table II) indicating, according to eq 5, that the k_{-2} path is negligible compared to the k_{-1} path. Equation 5 may thus be rearranged to

$$\frac{k_{obsd} - k_{-1}}{[N_3^-]} = \frac{k_1[H^+] + k_2K_{a1}}{K_{a1} + [H^+]} \qquad (7)$$

The k_{obsd} vs. pH data, Figure 3, were fitted to eq 7 by using a nonlinear least-squares program. The value of k_2 was found to be zero within the experimental error limits, indicating that $k_2 << k_1$. This is also required by the principle of microscopic reversibility since, as pointed out above, $k_{-2}[OH^-] << k_{-1}$. Furthermore, this result is not unexpected, since one would anticipate $[WO(OH)(CN)_4]^{3-}$ to be much less reactive toward substitution than $[WO(H_2O)(CN)_4]^{2-}$.

The pressure dependence of the pseudo-first-order rate constant was studied at pH 5.8 and 0.5 M $[N_3^-]$. The results in Table III indicate a significant decrease in k_{obsd} with increasing pressure, and the corresponding volume of activation is +10.6 (5) $cm^3\ mol^{-1}$ at 25 °C. Under the selected conditions, $k_{-1} << k_1[N_3^-]$ (see Figure 2), such that the observed volume of activation is for k_1 and can be interpreted in terms of a dissociative substitution of the aquo ligand.

Table III. k_{obsd} as a Function of Pressure[a]

P, bar	50	250	500	750	1000
k_{obsd},[b] s^{-1}	2.00 (5)	1.81 (3)	1.68 (2)	1.49 (5)	1.31 (4)

[a] pH 5.8, $\mu = 1.00$ M, $T = 25$ °C, $[N_3^-] = 0.5$ M. [b] Mean value of six kinetic runs.

The suggested mechanism is given in reactions 8 and 9 and the corresponding expression for k_{obsd} is given in eq 10. Since it was

$$[WO(H_2O)(CN)_4]^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [WO(CN)_4]^{2-} + H_2O \qquad (8)$$

$$[WO(CN)_4]^{2-} + N_3^- \xrightarrow{k_4} [WO(N_3)(CN)_4]^{3-} \qquad (9)$$

$$k_{obsd} = k_3k_4[N_3^-]/(k_{-3} + k_4[N_3^-]) \qquad (10)$$

observed that plots of k_{obsd} vs. $[N_3^-]$ are linear, $k_{-3} >> k_4[N_3^-]$, eq 10 simplifies to

$$k_{obsd} = k_3k_4[N_3^-]/k_{-3} \qquad (11)$$

such that $k_1 = k_3k_4/k_{-3} = K_3k_4$.

It follows that $\Delta V^{\ddagger}(k_1) = \Delta \bar{V}(K_3) + \Delta V^{\ddagger}(k_4)$, with the result that $\Delta \bar{V}(K_3) > \Delta V^{\ddagger}(k_1)$ since $\Delta V^{\ddagger}(k_4)$ must be significantly negative for a bond formation reaction accompanied by charge concentration, i.e. increasing electrostriction. The large positive value for $\Delta \bar{V}(K_3)$ $(= \Delta V^{\ddagger}(k_3) - \Delta V^{\ddagger}(k_{-3}))$ indicates that $\Delta V^{\ddagger}(k_3)$ must even be more positive, and thus in line with a limiting dissociative (D) mechanism. The composite nature of k_1 can account for the slightly negative $\Delta S^{\ddagger}$ value (see Table II). The apparent discrepancy between the signs of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ once again underlines the difficulty to assign mechanisms on the basis of $\Delta S^{\ddagger}$ values. Numerous examples are now available that emphasize the mechanistic discrimination ability of $\Delta V^{\ddagger}$,[11] which is more definitive than $\Delta S^{\ddagger}$.

Alternatively, the value of $\Delta V^{\ddagger}(k_1)$ could be interpreted as evidence for a dissociative interchange mechanism (I_d). This possibility is outlined in

$$[WO(H_2O)(CN)_4]^{2-} + N_3^- \overset{K_5}{\rightleftharpoons} [WO(H_2O)(CN)_4{}^{2-},N_3^-] \qquad (12)$$

$$[WO(H_2O)(CN)_4{}^{2-},N_3^-] \xrightarrow{k_6} [WO(N_3)(CN)_4]^{3-} + H_2O \qquad (13)$$

for which

$$k_{obsd} = k_6K_5[N_3^-]/(1 + K_5[N_3^-]) \qquad (14)$$

Equation 14 simplifies to eq 15, since the plots of k_{obsd} vs. $[N_3^-]$ are linear.

$$k_{obsd} = k_6K_5[N_3^-] \qquad (15)$$

From eq 15 it follows that $k_1 = k_6K_5$ and $\Delta V^{\ddagger}(k_1) = \Delta V^{\ddagger}(k_6) + \Delta \bar{V}(K_5)$. The value of $\Delta \bar{V}(K_5)$ can be assumed to be slightly negative, since the equilibrium (reaction 12) involves the concentration of charges. From this argument it follows that $\Delta V^{\ddagger}(k_6) > \Delta V^{\ddagger}(k_1)$, i.e. larger than 11 $cm^3\ mol^{-1}$, which is more in line with the value expected for a limiting dissociative mechanism than for an interchange process.[11]

Tungsten(IV) is known to form complexes with a coordination number greater than six, but the coordination of an incoming ligand in the vicinity of the aquo ligand (associative activation) is not likely due to the way of distortion in the $[WO(H_2O)(CN)_4]^{2-}$ ion. In the case of the corresponding molybdenum complex,[3] the metal ion is displaced by 0.34 Å out of the plane formed by the four carbon atoms of the cyanide ligands towards the oxo ligand

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with the result that the C–Mo–OH$_2$ angles are significantly smaller than 90°. On the other hand, this distortion in the $[WO(H_2O)(CN)_4]^{2-}$ ion together with the large trans effect of the oxo ligand, will promote dissociation of the aquo ligand and thus a dissociative reaction mode. This is in agreement with the positive value of $\Delta V^{\ddagger}(k_1)$. The large trans influence of the oxo ligand is clearly observed in the Mo–N bond distances in $[MoO(Phen)(CN)_3]^-$[6] (the corresponding tungsten complex is isomorphous with the molybdenum complex): The Mo–N bond distance trans to the oxo ligand is 2.363 (7) Å, whereas the Mo–N bond distance trans to the cyanide ligand is only 2.174 (7) Å.

Finally, the results of this investigation clearly demonstrate the close correlation between ground-state structure and transition-state energetics as facilitated by the trans effect of the oxo ligand.

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Registry No. *trans*-$[WO_2(CN)_4]^{4-}$, 42720-52-5; *trans*-$[WO(H_2O)(CN)_4]^{2-}$, 105121-19-5; N_3^-, 14343-69-2.

Contribution from the Solar Energy Research Institute,
Golden, Colorado 80401

Synthesis, Characterization, and Electrochemical Studies of Iron, Cobalt, and Nickel Complexes of Polyphosphine Ligands

Daniel L. DuBois* and Alex Miedaner

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The reaction of $[M(CH_3CN)_6](BF_4)_2$ (where M = Fe, Co, and Ni) with $P(CH_2CH_2PPh_2)_3$ (PP$_3$), $PhP(CH_2CH_2PPh_2)_2$ (PP$_2$), and $Ph_2PCH_2CH_2PPh_2$ (dppe) results in the formation of $[Fe(PP_3)(CH_3CN)_2](BF_4)_2$, $[Fe(PP_2)(CH_3CN)_3](BF_4)_2$, $[Fe(dppe)_2(CH_3CN)_2](BF_4)_2$, $[Co(PP_3)(CH_3CN)](BF_4)_2$, $[Co(dppe)_2(CH_3CN)](BF_4)_2$, $[Ni(PP_3)(CH_3CN)](BF_4)_2$, $[Ni(PP_2)(CH_3CN)](BF_4)_2$, and $[Ni(dppe)_2](BF_4)_2$, respectively. Electrochemical studies have been carried out on these complexes to examine the influence of the nature of the polyphosphine ligand on the redox properties of each metal. For $[Fe(PP_3)(CH_3CN)_2](BF_4)_2$ the reversibility of both the Fe(II/III) and Fe(I/0) couples are enhanced relative to those of $[Fe(dppe)_2(CH_3CN)_2](BF_4)_2$. For $[Co(PP_3)(CH_3CN)](BF_4)_2$ the lowest oxidation state accessible in CH$_3$CN is +1, while for $[Co(dppe)_2(CH_3CN)](BF_4)_2$ the −1 oxidation state can be observed. The Ni(I/0) couple is reversible for $[Ni(dppe)_2](BF_4)_2$ and irreversible for $[Ni(PP_2)(CH_3CN)](BF_4)_2$ and $[Ni(PP_3)(CH_3CN)](BF_4)_2$. The electrochemical studies of the latter complex have led to the synthesis of a Ni(0) dimer, $[Ni(PP_3)]_2$.

Introduction

This paper is the first of a series investigating the electrochemical properties of transition-metal complexes containing polyphosphine ligands and their use as redox catalysts. Previous electrochemical investigations of metal complexes containing monodentate phosphine ligands have revealed that, in general, the reductions or oxidations of such complexes are irreversible due to cleavage or formation of metal–phosphorus bonds.[1] The use of chelating diphosphine ligands increases the reversibility of the redox couples of a number of metal complexes when compared to that of their monodentate analogues.[2-5] This tendency of a diphosphine ligand to promote reversible electron-transfer processes can be attributed to their ability to prevent metal–phosphorus bond cleavage. This suggests that other polyphosphine metal complexes may also display enhanced electrochemical reversibility by preventing metal–phosphorus bond cleavage.

By systematically varying the nature of the polyphosphine ligand in various metal complexes, we hope to gain a better understanding of the factors controlling the stability of different oxidation states of (polyphosphine)metal complexes. Such understanding could be useful in the rational development of metal phosphine complexes as redox catalysts. Currently transition-metal complexes of phosphine ligands are known to catalyze the electrochemical reduction of CO$_2$ to formic acid[6] and CO[7] and that of aryl halides to biaryls.[8]

In this paper we report the synthesis, characterization, and electrochemical studies of Fe, Co, and Ni complexes containing tetradentate, tridentate, and bidentate phosphine ligands as well as weakly coordinating acetonitrile ligands. These complexes permit a comparison of the ability of the various polyphosphine ligands to stabilize different oxidation states for a given metal.

Experimental Section

Acetonitrile and dichloromethane were dried by distillation from calcium hydride under nitrogen. Toluene and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. Except where mentioned all reactions were carried out by using standard Schlenk techniques. All reagents and products were handled with exclusion of air with the exception of the air-stable nickel complexes. $P(CH_2CH_2PPh_2)_3$ (PP$_3$), $PhP(CH_2CH_2PPh_2)_2$ (PP$_2$), $Ph_2PCH_2CH_2PPh_2$ (dppe), and Ni(COD)$_2$ (COD is 1,5-cylooctadiene) were purchased from Strem Chemicals. The acetonitrile complexes of Fe, Co, and Ni were prepared as described in ref 9.

Infrared spectra were obtained on a Perkin-Elmer 599B spectrophotometer. All of the BF$_4$ salts showed a broad strong infrared absorption between 900–1150 cm^{-1}. A Varian E109 spectrometer was used for obtaining EPR spectra. All EPR spectra were recorded on 1×10^{-3} M dichloromethane solutions unless indicated otherwise. A JEOL FX90Q FT NMR spectrometer equipped with a tunable, variable-temperature probe was used to collect ^1H and ^{31}P NMR spectra. Me$_4$Si was used as an internal reference for all ^1H spectra. A capillary filled with phosphoric

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