the Research Corp. which made possible the purchase of the luminescence apparatus.

Registry No. PIC, 98-98-6; NIC, 59-67-6; DPA, 499-83-2; Eu, 7440-53-1; Tb, 7440-27-9.

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Electron Transfer. 36. Reductions of Pentaamminecobalt(III) Derivatives of Dinitrophenols[1]

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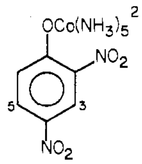
The 2,4- and 2,5-dinitrophenylato complexes of $(NH_3)_5Co^{III}$, the first phenoxide derivatives of this type to be reported, are reduced by $Ru(NH_3)_6^{2+}$ and by V^{2+} at the Co(III) center and by Cr^{2+} and Eu^{2+} both at the nitro substituents and at Co(III). The $Ru(NH_3)_6^{2+}$ reductions are 10^2–10^4 times as rapid as those of the carboxylato complexes of $(NH_3)_5Co^{III}$, a difference attributed to the relative ground-state instability of the nitro complexes, which is reflected also in the ease with which they undergo aquation. Specific rates for reduction by V^{2+} exceed the substitution-controlled limit for inner-sphere reactions with dipositive oxidants, indicating that a major path for these reductions is outer sphere. Reactions with Eu^{2+} and Cr^{2+} proceed at specific rates in excess of 10^3 M^{-1} s^{-1}, with a ratio of ligand/cobalt(III) reduction about 3 and independent of the reductant used and isomer taken. The very rapid release of Co^{2+}, which continues after the nitro groups have been reduced to the nitroso and azo levels, points to a chemical mechanism in which one-electron reduction of a ring substituent to a radical–cation intermediate precedes internal electron transfer to cobalt(III). It is further suggested that the predominant path in each of these instances is initiated by inner-sphere attack at the 2 substituent. The ratio k_V/k_{Ru} for the 2,4 complex is approximately 3, in contrast to a ratio <0.4 for "normal" outer-sphere oxidants.[8a,9] This reversal in reactivity is consistent with preliminary outer-sphere electron transfer from V^{2+} to a nitro group.

The array of varied organic ligands which have been reported to mediate electron transfer to bound cobalt(III) does not yet include substituted phenoxides,[2] an omission which can be attributed, in large part, to preparative difficulties. The ease with which phenols and their anions generally undergo oxidation complicates attempts to attach them to strongly oxidizing metal ions. Moreover, the high basicities of most phenoxides would be expected to lead to serious side reactions in ligation procedures involving those metals forming slightly soluble hydroxides.

These undesirable features can presumably be minimized by using phenols bearing strongly electron-withdrawing substituents. In 1974, Fan[3] described the preparation of the $(NH_3)_5Co^{III}$ complex of 2,4-dinitrophenol, I, the first phenol-coordinated derivative of this type reported. The present communication deals with the reactions of this complex, and those of its 2,5 isomer, with several dipositive reducing agents. As might be anticipated from earlier studies of the reductions of nitrobenzoato complexes,[3,4] reactions with Cr^{2+} and Eu^{2+} are complicated by reduction of the nitro group, but reactions with the more weakly reducing species V^{2+} and $Ru(NH_3)_6^{2+}$ have been found to be more straightforward.



I

Experimental Section

Materials. Lithium perchlorate,[5] carbonatopentaamminecobalt(III) perchlorate,[3] and solutions of chromium(II),[6] europium(II),[7] vanadium(II),[8] and hexaammineruthenium(II)[9] were prepared as described. Organic ligands (Aldrich products) were used as received.

Preparation of the Complexes. In a modification of the method of Fan,[3] 0.010 mol of the dinitrophenol was dissolved in 90 mL of absolute methanol, and to this mixture was added 400 mg of finely ground carbonatopentaamminecobalt(III) perchlorate. The mixture was refluxed for 2.5 h with stirring and then cooled to 0 °C. To the red solution was carefully added 1.2 mL of 12 M $HClO_4$, and the preparation was kept at 0 °C an additional 30 min. The mixture was then shaken with two 300-mL portions of ether, the precipitated complex filtered off, and the ether extracts discarded. The precipitate

Table I. Specific Rates for the Reductions of the $(NH_3)_5Co^{III}$ Complexes of 2,4- and 2,5-Dinitrophenoxide, Using Vanadium(II) and Hexaammineruthenium(II)[a]

complex	μ	k_{Ru}[b]	k_V[c]
2,4-$(NO_2)_2$	0.12	7.4	21
	1.0	21	
	1.2		47
2,5-$(NO_2)_2$	0.12	5.1×10^2	50
	1.0	1.3×10^3	
	1.2		92

[a] Specific rates are in $M^{-1}\ s^{-1}$. Reactions were carried out at 25 °C; $(H^+) = 0.12$ M. (Reductant) = 0.003–0.02 M; $(Co^{III})_0 = 2 \times 10^{-4}$ M. Values given are averages of three to five replicate runs; agreement between runs was better than 6%. [b] Supporting electrolyte LiCl + HCl. [c] Supporting electrolyte $LiClO_4 + HClO_4$.

was dried in air, dissolved in a minimum volume of distilled water at 60 °C, filtered, and cooled. The resulting deep red crystals of the 2,4-dinitro complex exhibited an absorption maximum at 528 nm ($\epsilon = 380$), the 2,5 isomer a maximum at 530 nm ($\epsilon = 330$). Solutions of both dinitro complexes in water appeared to be stable for 2 h at room temperature. In 0.1 M $HClO_4$, approximately 20% decomposition by aquation occurred within 1 h, whereas in 1.2 M $HClO_4$, aquation was much more rapid.

Anal. Calcd for $C_6H_{18}CoCl_2N_7O_{13}$: C, 13.7; H, 3.45; Co, 11.2. Found (2,4 isomer): C, 13.7; H, 3.52; Co,[6] 11.2. Found (2,5 isomer): C, 13.9; H, 3.51; Co,[6] 11.3.

Attempts were made to use the above method, and several variations of it, to prepare complexes of *o*- and *p*-nitrophenol, picric acid, pentachloro and pentafluorophenol, and 2,3,4,5-tetrachlorophenol. With the mono- and trinitro preparations, the principal product was aquopentaamminecobalt(III) perchlorate, whereas with the halogenated phenols, rapid decomposition of the reaction mixture and formation of a dark brown precipitate generally occurred. The latter dissolved readily in 12 N HCl to give Cl_2 and $CoCl_4^{2-}$ and is thus presumed to be Co_2O_3.

Kinetic Experiments. Specific rates for reductions by V^{2+} and $Ru(NH_3)_6^{2+}$ were estimated from absorbance changes using the Durrum-Gibson stopped-flow spectrophotometer as described.[10] Measurements were made at 529 nm. Reactions were first order each in oxidant and reductant, but rate measurements employed pseudo-first-order conditions with the reductant in greater than tenfold excess. Virtually all reactions were carried out at 0.12 M H^+, but in some cases the ionic strength was increased to unity by addition of $LiClO_4$ (in the case of the V^{2+} reductions) or LiCl (for the Ru(II) reductions).[11] Temperatures were kept at 25.0 ± 0.2 °C during the entire series of measurements. Replicate reactions, with the same pair of master solutions, were carried out until absorbance curves for three consecutive runs superimposed. Rate constants, obtained from logarithmic plots of absorbance differences against reaction time, agreed to better than 6% for runs with different master solutions.

Stoichiometry Experiments. The reduction of Co(III) and the formation and destruction of colored intermediates in the reactions with Cr^{2+} and Eu^{2+} were followed using known concentrations of the dinitro complexes in a 10-cm cell. The solution was purged with nitrogen for at least 15 min, and known increments of reductant were added through the cap, using a microsyringe. After such addition, the visible spectrum was scanned, and an aliquot of the resulting solution was removed, using a 1-mL syringe, and added to 9.0 mL of concentrated HCl. Concentrations of Co(II) in the resulting aliquots were then determined by measuring the absorbances of the HCl solutions at 692 nm (ϵ for Co(II) in this medium was taken as 560), using the 0–0.1 range slide wire. The time interval between each addition of reductant and dilution of the aliquot with HCl was about 5 min.

A number of strongly absorbing materials were formed during these additions. During the Eu^{2+} reduction of the 2,4 complex, a brick red pigment (λ_{max} 520 nm) appeared within the 0.25–2.0 equiv range, but a second species (λ_{max} 500 nm) predominated in the 3–7 equiv range). No such absorption was observed during reaction of the 2,5 complex. During Cr^{2+} reductions of the 2,4 and 2,5 complexes, materials absorbing near 503 nm appeared in the 0.25–3 equiv range and gave way to species with maxima near 475 nm in the 4–10 equiv range. In all cases, these pigments disappeared when 10 or more equivalents of reductant were added.

Table II. Yields of Co(II) from Reductions of Dinitrophenylato Derivatives of $(NH_3)_5Co^{III}$[a]

	yield of Co(II), %
2,4 complex + Cr^{2+}[b]	23
2,4 complex + Eu^{2+}[b]	27
2,5 complex + Cr^{2+}[c]	26
2,5 complex + Eu^{2+}[c]	21

[a] $(H^+) = 0.1$ M. Equivalent quantities of Co(III) and reductant taken. [b] $(Co^{III}) = 1 \times 10^{-3}$ M. [c] $(Co^{III}) = 2 \times 10^{-4}$ M.

Results and Discussion

Kinetic data for reductions by V^{2+} and $Ru(NH_3)_6^{2+}$ are summarized in Table I. The observed changes in specific rate with ionic strength are consistent, in both direction and approximate magnitude, with kinetic salt effects reported for other electron-transfer reactions of this charge type.[12]

The substitution-inert character of $Ru(NH_3)_6^{2+}$ ensures that rapid reactions with this species occur without ligand bridging. The Ru(II) reductions of the dinitrophenylato complexes in the present study are found to be 10^2–10^4 times as fast as those of the carboxylato derivatives of $(NH_3)_5Co^{III}$.[9,13-16] We attribute these unusually high outer-sphere rates, at least in part, to the relative ground-state instability of the oxidants, an instability which is perceived also from the ease with which the phenylato complexes undergo aquation in dilute acid. We cannot as yet say why the 2,5 complex, which features two nitro groups in conjugation with each other, is more reactive than the 2,4 isomer, in which both nitro groups lie in conjugation with the coordinated phenolic oxygen.

The specific rates for reaction with V^{2+} (k_V values in Table I) may be compared with the substitution-controlled upper limit for inner-sphere reductions by this dipositive center. A value near 20 $M^{-1}\ s^{-1}$ (25 °C, $\mu = 1$) appears to be applicable to reactions of dipositive oxidants proceeding through nonchelated transition states.[17-20] Hence, k_V for the 2,5 complex at the higher ionic strength may be considered strong evidence that the major portion of that reaction is outer sphere. The ratio k_{Ru}/k_V near 10 for this isomer lies somewhat above the corresponding outer-sphere ratio (3–4) for a number of more slowly reacting cobalt(III) oxidants[9] but is in accord with the earlier observation[8a] that this ratio increases markedly for very rapid oxidants.

For the 2,4 derivative, k_{Ru} falls close to the range where Fan's linear free energy relationships for outer-sphere rates[9] have been shown to apply. Hence, these equations may be used to estimate outer-sphere specific rates for the reaction of this isomer with the other dipositive reductants in the absence of complicating factors. Values so calculated (which may be regarded as upper limits) are 7 $M^{-1}\ s^{-1}$ for k_V, 2 $M^{-1}\ s^{-1}$ for k_{Eu}, and 0.2 $M^{-1}\ s^{-1}$ for k_{Cr} (each at $\mu = 1$).

However, in the reactions of the dinitro complexes with the more powerful reductants, Cr^{2+} and Eu^{2+}, reduction of the nitro group(s) clearly competes with electron transfer to Co(III). As seen in Table II, partition between paths is nearly independent of the reductant used and the isomer taken. Under second-order conditions, with oxidant and reductant each at concentrations below 10^{-3}, reactions are complete within a few seconds after mixing, indicating specific rates well in excess of $10^3\ M^{-1}\ s^{-1}$ for ligand reduction and near $10^3\ M^{-1}\ s^{-1}$ for Co(III) reduction in each case. The release of Co^{2+}, as known quantities of Cr^{2+} are added to a solution of the 2,4 complex, is indicated in Figure 1. Very similar release profiles were obtained from the reaction of the 2,5 isomer with Cr^{2+} and from both isomers with Eu^{2+}.

Reductions of Co(III) in the 2,4 complex by Cr^{2+} or Eu^{2+} are more rapid, by several orders of magnitude, than the corresponding reductions of N- and O-coordinated $(NH_3)_5Co^{III}$ derivatives which react, without complication, via outer-sphere

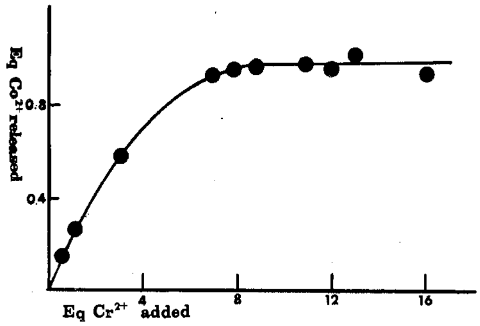


Figure 1. Release of Co^{2+} from the 2,4-dinitrophenoxide derivative of $(NH_3)_5Co^{III}$ on treatment with Cr^{2+}. $[H^+] = 0.12$ M; $[Co(III)]_{initial} = 1.0 \times 10^{-3}$ M; 5-min waiting period after each addition of Cr^{2+}. Very similar curves were obtained for the reaction of the 2,5-dinitro complex with Cr^{2+} and for reactions of both complexes with Eu^{2+}.

paths.[7] Moreover specific rates are far in excess of the outer-sphere values that are estimated from consideration of k_{Ru} for the 2,4 isomer. There is thus marked rate enhancement, not only by the nitro group(s) but also by one or more of the ligand reduction products,[21] for the rapid release of Co^{2+} continues as the total number of equivalents of added Cr^{2+} is increased from 0 to beyond 6. The release profiles are steeper in the 0–2 equiv Cr^{2+} region than in the 3–6 equiv region, suggesting that the dinitro ligand is a slightly more effective electron-transfer mediator than its reduction product(s), which may be presumed to feature nitroso substituents (in the 2–4 equiv range) or azo groups (in the 4–8 equiv range).

The Cr^{2+} reductions of *o*- and *p*-nitrobenzoato derivatives of $(NH_3)_5Co^{III}$ may be regarded as early and striking examples of what has since become known as the "chemical mechanism" for electron transfer, i.e., a sequence in which reduction of a ligand to a radical intermediate precedes the act of internal electron transfer to the oxidizing metal center.

$$Co^{III}OC(=O)ArNO_2 \xrightarrow{Red^{2+}} Co^{III}OC(=O)ArNO_2\cdot \rightarrow Co^{II}OC(=O)ArNO_2$$

Indirect evidence was presented in 1966 that both nitro and nitroso substituents, if properly positioned, favor such a mechanism,[4a] and the intervention of nitro radical-ion intermediates in closely related reactions has since been demonstrated.[4b,22] In the present study, the rapidity of reduction of cobalt(III) in the dinitrophenoxide complexes, using Cr^{2+} and Eu^{2+}, points to such a mechanism in these instances as well, as does the appearance of deeply colored reduction products which are similar in spectra and behavior to the nitro and nitroso radicals observed in the nitrobenzoato studies.[4,22] It has been emphasized that formation of such a radical intermediate does not guarantee reduction of the metal center, for the radical may undergo further reduction or disproportionation instead of internal electron transfer with formation of Co(II). The systems at hand are further complicated by the presence of two nonequivalent nitro substituents on each aromatic ligand. The mediating effectiveness of nitro has been shown to depend markedly upon how it is situated with respect to the acceptor center, and in view of the demonstrated superiority of the 2-NO_2 group in this respect,[4a,22] we suggest that the predominant path for reduction of Co(III) involves this position in each instance.

We cannot at this point be certain as to whether the transfer of an electron from Cr^{2+} or Eu^{2+} to $-NO_2$ is an inner- or outer-sphere process. It has been shown,[23] however, that Cr^{2+} and Eu^{2+} react with aromatic oxidants which are devoid of lead-in donor groups at specific rates well below 1 $M^{-1}\ s^{-1}$, whereas for oxidants of comparable potential featuring such groups, rates may be several order of magnitude greater.[24] The very high rates at which nitro groups are found to accept electrons from these aquated reducing centers then leads us to favor preliminary nitro–metal coordination, i.e., an inner-sphere route for the initial step.

A different conclusion probably applies to reduction of the 2,4 isomer with V^{2+}. The observed specific rate is more than twice that for $Ru(NH_3)_6^{2+}$ (Table I), whereas for "normal" outer-sphere oxidants, reductions by that ruthenium species are substantially more rapid.[8a9] This reversal of reactivities is again consistent with preliminary electron transfer to a nitro group by V^{2+} ($E° = -0.242$ V)[23] but not by the more weakly reducing $Ru(NH_3)_6^{2+}$ ($E° = +0.214$ V).[25] However, since the observed specific rate for the overall reaction with V^{2+} exceeds the substitution-controlled upper limit for inner-sphere reactions with dipositive oxidants, we may infer that at least a portion of this accelerated reduction proceeds without preliminary substitution in the vanadium(II) coordination shell.[26-28]

Registry No. $[2,4\text{-}(NO_2)_2C_6H_3OCo(NH_3)_5](ClO_4)_2$, 67271-78-7; $[2,5\text{-}(NO_2)_2C_6H_3OCo(NH_3)_5](ClO_4)_2$, 67271-80-1; V^{2+}, 15121-26-3; $Ru(NH_3)_6^{2+}$, 19052-44-9; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6; $[(CO_3)Co(NH_3)_5]ClO_4$, 65774-48-3.

References and Notes

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) Redox studies of a catecholato complex of cobalt(III) have been described by P. A. Wicklund, L. S. Beckmann, and D. G. Brown, *Inorg. Chem.*, **15**, 1996 (1976). The changes described by these workers involve oxidation of the ligand rather than reduction of Co(III).

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(9) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974).

(10) E. S. Gould, *J. Am. Chem. Soc.*, **96**, 2373 (1974).

(11) To minimize decomposition of the dinitro complexes, these were dissolved in water or in aqueous solution of LiCl or $LiClO_4$ without added acid. The acidity of the final reaction mixture was then just half that of the reductant solution taken.

(12) See, for example (a) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965); (b) A. Liang and E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6791 (1970).

(13) This comparison is striking in view of the similar acidities of dinitrophenols and ordinary carboxylic acids.[14] Although an inverse relationship between the basicities of ligands and the rates of outer-sphere reductions of their complexes has been noted,[15] it is recognized[9,15,16] that such a treatment is expected to apply only to groups of ligands having related structures. Moreover, in the present instance the correlation breaks down entirely, for the 2,5 complex, which is derived from the less acidic phenol, is reduced more than 50 times as rapidly as its 2,4 isomer.

(14) Reported pK_A values in water are 3.96 for 2,4-dinitrophenol (15 °C) and 5.22 for the 2,5 isomer (18 °C). See, for example, G. G. Barlin and D. D. Perrin, *Q. Rev., Chem. Soc.*, **20**, 75 (1966).

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(18) A higher value, 40 $M^{-1}\ s^{-1}$, which is sometimes cited,[8a,19] is probably appropriate for chelating oxidants.[20]

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(21) Although analogous rate enhancements may be inferred in the Cr^{2+} and Eu^{2+} reductions of the 2,5-dinitro complex, the k_{Ru} value (which is presumed to represent an outer-sphere rate uncomplicated by ligand–metal interactions) for this isomer is so great that accelerations associated specifically with the more powerful reductants are relatively less prominent.

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(26) Note, however, that there is no indication of preliminary ligand reduction in the reaction of V^{2+} with the *p*-nitrobenzoato derivative of $(NH_3)_5Co^{III}$, which undergoes electron transfer to Co(III) at a specific rate a little

below that of the unsubstituted benzoato derivative.[17b]

(27) The several strongly absorbing species appearing during the course of the Cr(II) and Eu(II) reductions, which are taken to be radicals analogous to the nitro[22] and nitroso[4a] reduction products observed in nitrobenzoato systems, persist in solution, whereas the reactions yielding Co^{2+} are complete in a few seconds. The colored materials must therefore be secondary products, almost certainly from reduction of the liberated ligand, rather than intermediates in the primary electron-transfer sequence. Pigments of this type are obtained from the Eu(II) reduction of the 2,4, but not the 2,5, complex, suggesting that these result from reduction of the 4-NO_2 group, with the species first formed (λ_{max} 520 nm) a nitro radical and that formed later in the addition sequence (λ_{max} 500 nm) a nitroso radical. Nitro (λ_{max} 503 nm) and nitroso (λ_{max} 475 nm) radicals appear to be formed also in the Cr(II) reduction sequences, but with this reductant, either the 2 substituent or the more distant substituent (or both) may be converted to a radical center. The pigments formed in the Cr(II) sequences appear to be much more intensely colored than those in the Eu(II) sequence, leading us to suspect that the former may be Cr(III)-bound radicals analogous to the Cu(III)-bound pyrazine radicals described by Wu and co-workers.

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Intramolecular Exchange in the Molybdenum(VI) Complex with Nitrilotriacetate and a Comparison of the Labilities of the Molybdenum and Tungsten Complexes with Various Aminopolycarboxylates

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NMR spectra of MoO_3NTA^{3-} in an organic solvent at a series of temperatures clearly indicate that the unbound glycinate arm of the ligand readily exchanges with the bound arms. Exchange is also induced by the introduction of water. A unique, plausible mechanism is suggested. The corresponding W(VI) complex is also fluxional but the activation energy is larger. A general comparison of the Mo(VI) and W(VI) complexes with various aminopolycarboxylates indicates a larger lability for the molybdenum complexes. It is also shown that the ^1H NMR spectra of several complexes of W(VI) were reported incorrectly.

Introduction

The ability of molybdenum to form stable chelates with the aminopolycarboxylates, ethylenediaminetetracetate (EDTA), methyliminodiacetate (MIDA), iminodiacetate (IDA), and nitrilotriacetate (NTA), has been established by ^1H NMR.[1-7] With the exception of the Mo^{VI}–NTA complex, all the molybdenum(VI)–aminopolycarboxylate chelates display AB splitting in the resonances due to the methylene protons. To account for the singlet observed in the spectrum of MoO_3NTA^{3-} it has been suggested that, in the absence of an exchange process, NTA could use all four donor sites to generate a seven-coordinate, capped octahedron with C_{3v} symmetry.[1,8] However, the similarities which exist between MoO_3NTA^{3-} and other aminopolycarboxylate complexes in terms of ligand donor atoms and stability constants[9] suggest that all of these complexes should assume similar geometries. This expectation was confirmed, at least in the solid state, by the recent crystal structure of $K_3MoO_3NTA\cdot H_2O$.[10] The structure has shown that the coordination number of molybdenum is six and that one of the glycinate arms is not bound to the metal atom.

We have reexamined the nature of the MoO_3NTA^{3-} anion in solution in order to determine whether the magnetic equivalence of the methylene protons is the result of an exchange process, which is not accessible to the other aminopolycarboxylate complexes, or whether it reflects a geometry in solution which is different from that observed in the solid state. In addition, we have examined the congeneric W^{VI}–NTA complex as well as other aminopolycarboxylate complexes with W(VI) in order to augment our comparison of the complexes derived from Mo(VI) and W(VI).[4]

Experimental Section

Reagents. Reagent grade chemicals were used without further purification. Enriched $Na^{13}CN$ (90 atom %), CD_3OD (99.5 atom %), bis(triphenylphosphine)iminium chloride (PPNCl), and $Na_3NTA\cdot H_2O$ were purchased from Merck Sharpe and Dohme Canada Ltd., Aldrich Chemical Co., Ventron Corp., and Sigma Chemical Corp., respectively.

Analysis. Microanalyses (C, H, N, and P) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Tungsten was analyzed gravimetrically by digesting the complex in $HClO_4$, dissolving the resulting tungstic oxide in base, and precipitating the tungsten as the oxinate.[11]

Synthesis of ^{13}C-Enriched Nitrilotriacetic Acid, $N(CH_2CO_2H)(CH_2{}^*CO_2H)_2$. The acid form of the ligand, enriched in ^{13}C at two of the three carboxylate carbon atoms, was prepared by the carboxymethylation of glycine[12] using ^{13}C-enriched NaCN. Since we planned to achieve a total enrichment which was 3.4 times the ^{13}C content in natural abundance, a solution containing CN^- enriched in ^{13}C to 5.1 atom % was used. A moderate yield (55%) of the desired crystalline material was obtained. The synthesis was confirmed by comparisons of the melting point and infrared spectrum of the labeled compound with those of an authentic sample containing ^{13}C in natural abundance. The level of enrichment was confirmed by comparing ^{13}C NMR spectra of equimolar solutions of the labeled and unlabeled compounds. Careful integrations of the signals arising from the carboxylate carbon atoms indicated that the intensity of the signal from the enriched compound was greater than that from the compound containing ^{13}C in natural abundance by a factor of 3.48. The theoretical value is 3.42.

Synthesis of $(PPN)_3(MoO_3NTA)$. To prepare the bis(triphenylphosphine)iminium salt of MoO_3NTA^{3-}, the pH of a solution of $Na_2MoO_4\cdot 2H_2O$ (0.06 M) and $Na_3NTA\cdot H_2O$ (0.06 M) was adjusted to 7.5 with concentrated HCl. Twenty milliliters of the MoO_3NTA^{3-} solution was added to 300 mL of a solution of PPNCl (0.012 M). Complete precipitation was accomplished by cooling for 6 h at 10° C. The white solid was recrystallized from ethanol through the addition of water. The solid was dried for 24 h under vacuum over P_2O_5. An average yield of 55% was obtained. The analytical results indicate that the compound is probably hydrated, at least at the time of analysis. The extremely hydroscopic nature of this compound makes handling it difficult. Anal. Calcd for $(PPN)_3MoO_3(NTA)\cdot 4H_2O$: C, 67.7; H, 5.2; N, 2.8; P, 9.2. Found: C, 67.8; H, 5.6; N, 2.5; P, 9.4. The ^{13}C and ^1H NMR spectra

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