complex in an appropriately noncoordinating, nonoxidizing aqueous medium. Experiments aimed at preparing and characterizing the hexaaquotechnetium(III) ion are currently being undertaken.

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Electron Transfer. 89. Reductions of Carboxylato-Bound Chromium(V) with Mercapto Acids[1]

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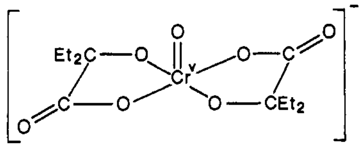
The chromium(V) chelate bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) rapidly oxidizes the mercapto acids thiolactic acid (II) and cysteine (III) in solutions buffered with the ligand acid, 2-ethyl-2-hydroxybutyric acid, and its sodium salt. With the thiol acids (RSH) in excess, nearly 2 equiv of reductant is consumed/mol of Cr(V), corresponding to the formation of the disulfide, R_2S_2, and Cr(III). The chromium(III) products consist mainly of a mixture of uncharged bis chelates derived from the ligand anion, each having, in addition, a unidentate coordinating group arising from either the buffering acid or the mercapto reagent. Both reactions are catalyzed by Cr(IV) and pass through thiyl radicals, $RS^\bullet$, for which Cr(IV) and Cr(V) compete. The suggested reaction sequence (eq 2-6), in combination with rate constants for the individual steps resulting from a least-squares refinement of the kinetic data, reproduces the experimental rate profiles. Dependencies of the component-specific rates on $[H^+]$ and on the concentration of ligand anion, $[Lig^-]$, indicate that oxidations of the two thiol-substituted acids, by both Cr(V) and Cr(IV), require deprotonation and that oxidations of both by Cr(IV) proceed by parallel paths, with a distribution governed by the ratio of $[Lig^-]$ to [RSH] in the generating solution. In addition, the 1e oxidation of thiolactic acid by Cr(V) (but not that of cysteine) is subject to kinetic saturation, implying the formation of a $Cr(V)-RS^-$ complex having an association constant near 7×10^2 M^{-1} and a limiting specific rate 3.5×10^2 M^{-1} s^{-1}. Persistence of the chelate rings originally present in the Cr(V) oxidant demonstrates the maintenance of chelation in all steps involving Cr(V) and Cr(IV). Comparisons of calculated electron-transfer rates with those observed for known outer-sphere reactions indicate that at least three of the four steps in the proposed mechanism involve bridged transition states. This is the sixth system in which autocatalysis in the reduction of Cr(V) by anionic donors has been observed. Mechanistic features thought to be common to all such systems are briefly considered.

Of the reported carboxylato complexes of chromium(V),[3] the most robust is the bis chelate of 2-ethyl-2-hydroxybutyric acid (I). Kinetic patterns associated with the reductions of this derivative to Cr(III) vary greatly in character. Action of 2e reagents, N_2H_4, H_2O_2, and Sn(II),[4] yield straightforward exponential traces, and the same is true for reductions by $IrCl_6^{3-}$ and $TiOH^{2+}$.[4b,5] Although the latter reactions pass through the atypical oxidation state Cr(IV), this state is, in these instances, reduced very rapidly and its intervention therefore overlooked. With the 1e donors Fe(II) and VO^{2+},[6] however, the formation and decay of a strongly absorbing Cr(IV) intermediate are mirrored in classical biphasic profiles.



I

Treatment with reductants that undergo both 1e and 2e transactions may lead to more intricate patterns, since four different 1e changes are possible. Depending upon the relative specific rates for the individual steps, slight[7] or severe[8] autocatalysis may occur, and slow growth of Cr(IV), followed by its quick decay, may result in a "clocklike" reaction profile.[8]

Table I. Stoichiometry of the Reactions of Chromium(V) Chelate I with Mercapto Acids[a]

reductant	amt, mmol			Δ[red]/ $\Delta[Cr^V]$
	Cr^V	red	Δ[red][b]	
thiolactic acid (II)	0.121	0.517	0.260	2.15
	0.098	0.517	0.225	2.30
	0.166	0.621	0.364	2.19
	0.202	0.621	0.420	2.08
cysteine (III)	0.055	0.393	0.097	1.76
	0.119	0.579	0.210	1.76
	0.221	0.610	0.390	1.77

[a] Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I); reactions were carried out in solutions buffered by the parent hydroxy acid and its sodium salt (see Experimental Section). [b] Determined by difference iodometrically (see Experimental Section).

Among organic reductants, only ascorbic acid, which may donate either one or two electrons,[9] has been shown to generate a Cr(IV) intermediate from a Cr(V) oxidant.[10] In this case, reaction is very rapid and autocatalysis striking. The present extension deals with the oxidations of the mercapto-substituted carboxylic acids thiolactic acid (II) and L-cysteine (III). These

$$\underset{\text{II}}{CH_3CH(SH)COOH} \qquad \underset{\text{III}}{HSCH_2CH(NH_3^+)COO^-}$$

reagents resemble iodide in the polarizability of their donor (–SH) center[11] and in the ease with which they are oxidized.[12,13] They

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(3) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

(4) (a) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176. (b) Ghosh, S. K.; Gould, E. S. *Ibid.* **1986**, *25*, 3357.

(5) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2465.

(6) (a) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832. (b) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Ibid.* **1985**, *24*, 4679.

(7) (a) Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737. (b) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Ibid.* **1987**, *26*, 2688.

(8) (a) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349. (b) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Ibid.* **1987**, *26*, 899.

(9) See, for example: (a) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1976**, *15*, 2898; **1978**, *17*, 1181. (b) Lannon, A. M.; Lappin, A. G.; Segal, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 619.

(10) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.

(11) Jørgensen, C. K. In *Hard and Soft Acids and Bases*; Pearson, R. G.; Ed.; Dowden, Hutchinson, and Ross: Stroudsburg, PA, 1973; p 137.

(12) Formal potentials for thiol–disulfide systems that are devoid of strongly electron-attracting or electron-repelling groups lie between +0.02 and +0.30 V (vs NHE at pH 0).[13a] That for I^-–I_2 is +0.54 V at 25 °C.[13b]

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Table II. Major Chromium(III) Fractions from Reactions of Chromium(V) Chelate I with Cysteine and Thiolactic Acid[a]

$[Cr^V]$, M	[RSH], M	$[An^-]$,[b] M	ϵ_1[c]	λ_1[c]	ϵ_2	λ_2	% Cr[d]
			Cysteine Reactions				
0.0221	0.0663	0.050	51 (48)[c]	562 (567)[c]	60 (61)	443 (412)	53
0.0325	0.1438	0.20	51 (53)	571 (580)	61 (63)	438 (417)	83
0.0221	0.0663	0.40	58 (66)	582 (590)	68 (69)	420 (418)	90
			Thiolactic Acid Reactions				
0.0255	0.1277	0.050	59 (51)	575 (562)	67 (67)	443 (418)	49
0.0267	0.1335	0.40	52 (48)	582 (578)	66 (61)	435 (415)	75

[a] Reactions were carried out in solutions buffered by 1:2 mixtures of 2-ethyl-2-hydroxybutyric acid and its sodium salt. Fractions were eluted from Dowex 50-X7 cation-exchange resin with water (see Experimental Section). [b] 2-Ethyl-2-hydroxybutyrate. [c] Absorption maxima (λ values) are in nm; ε values are in M^{-1} cm^{-1}. Parenthetical values refer to spectra recorded immediately after acidification with 0.1 M $HClO_4$. [d] Percent Cr(V) taken recovered in major fraction.

are, however, more effective complexing agents and undergo partition between protonation levels in the buffered aqueous media, features that should be reflected in their kinetic behavior.

Experimental Section

Materials. Lithium perchlorate (used, after two recrystallizations, in kinetic experiments)[14] and sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I)[3,6b] were prepared as described. The "ligand acid", 2-ethyl-2-hydroxybutyric acid, and the mercapto acids, thiolactic acid (II) and cysteine (III) (Aldrich products), were used as received; concentrations of solutions of the latter two reagents were checked by titration with KI_3. Cation-exchange resin (Dowex 50-X8, 400 mesh, H^+ form) was pretreated as described[15] and was converted to its Na^+ form by washing with saturated $NaHCO_3$. All reactions were carried out in distilled water that had been vigorously boiled and then sparged with O_2-free nitrogen for at least 4 h before use.

Stoichiometric Studies. The stoichiometries of the reductions of Cr(V) complex I with excess thio acids were determined by carrying out the reactions in solutions buffered at pH 3.3 by the ligand carboxylic acid and its anion (each 0.10 M). Total volumes were 3.0 mL for thiolactic acid and 5.0 mL for cysteine. After 30 min, the mixtures were treated with 5 mL of 0.5 M H_2SO_4 and excess KI_3 solution. That portion of the I_3^- not consumed by the thio acid was titrated with standard $Na_2S_2O_3$. Results are summarized in Table I.

Examination of the Cr(III) Reaction Products. Reaction mixtures were 0.033 M in Cr(V) and 0.144 M in thio acid and were buffered by 1:2 mixtures of the ligand acid and its sodium salt. These were allowed to react for 20–30 min at room temperature and then subjected to ion-exchange chromatography[16] at 2 °C. The Cr(III) products passed unchanged through anion-exchange resin but were absorbed onto cation-exchange resin. In all cases the major Cr(III) fraction was eluted slowly with water, but the spectral characteristics of this fraction depended on the ratio of ligand anion to thio acid in the reaction mixture. For the reaction with cysteine (see Table II), maxima associated with this fraction migrated progressively from 560 to 582 nm and from 443 to 420 nm (with virtually no change in extinction coefficients) when this ratio was increased from 0.75 to 6.0. Analogous, but less marked, shifts were observed for the reaction with thiolactic acid. Treatment of these fractions with 0.1 M $HClO_4$ brought about further rapid changes, with the peaks at 435–445 nm moving consistently to 412–418 nm. The water-eluted fraction constituted 53–90% of the Cr(V) taken, with recovery best at the highest concentrations of ligand anion. Spectral maxima associated with a lesser fraction, which was eluted slowly with 1 M $NaClO_4$, were somewhat less scattered (λ_{max} 565–572 and 411–416 nm); molar absorbances were about two-thirds those of the major fraction, and peaks shifted only minimally on acidification. Between 10 and 25% of the chromium could not be recovered, even upon prolonged elution with 3 M $NaClO_4$. Attempts to effect more complete separations or to improve overall recovery were unsuccessful despite several alterations of technique.

The chief conclusions from these studies (amplified under Results and Discussion) are (1) that the principal fraction is a mixture of uncharged bis chelates of Cr(III) related to the original hydroxy acid but containing an additional thiyl- or carboxyl-bound ligand, with the distribution between products dependent on the ratio of carboxyl species in solution, (2) that the S-bound ligand, but not the carboxyl-bound ligand, is lost by aquation on treatment with strong acid, and (3) that all products undergo some aquation, with partial opening of at least one chelate ring, in contact with cation-exchange resin.

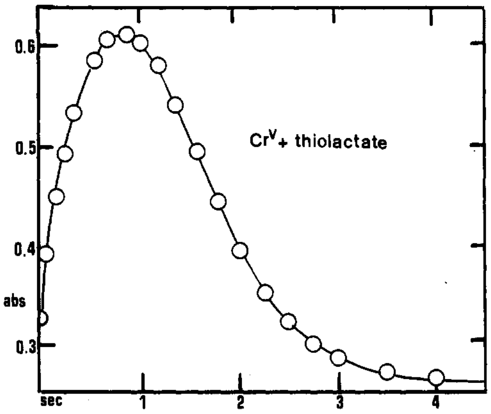

Figure 1. Kinetic profile at 600 nm for the reduction of Cr(V) chelate I (2.5 × 10^{-3} M) with thiolactic acid (II) (0.025 M) at 22 °C. The supporting medium was 0.20 M in 2-ethyl-2-hydroxybutyric acid, 0.20 M in its sodium salt, and 0.38 M in $LiClO_4$; the pH was 3.32. The solid line is the experimental curve, whereas the circles indicate absorbances calculated from sequence (2)–(6), by taking k_1 and k_3 as 16.5 and 50.1 M^{-1} s^{-1} and the ratio k_2/k_4 as 4.34. Extinction coefficients used (M^{-1} cm^{-1}): Cr(III), 52; Cr(IV), 412; Cr(V), 65. Mixing time = 0.005 s; optical path length = 2.00 cm.

Kinetic Measurements and Estimation of Specific Rates. Reductions with thiolactic acid were monitored by recording absorbance changes at 600 nm with a Durrum-Gibson stop-flow spectrophotometer. The much slower reductions with cysteine were followed on a Cary 14 recording spectrophotometer at 510 nm. Total ionic strength was kept near 0.4 M by addition of twice-recrystallized $LiClO_4$, and pH values were regulated by adding known quantities of 2-ethyl-2-hydroxybutyric acid (pK_A = 3.32)[4a] and its sodium salt. Stop-flow runs were carried out at 23.0 ± 0.3 °C; Cary runs were at 25.0 ± 0.2 °C.

In most instances, the reductant was taken in excess, under which conditions kinetic curves featured the growth of a strongly absorbing intermediate and then its consumption. These traces were more nearly symmetric (see Figures 1 and 2) than the more familar[17] profiles resulting from a pair of consecutive first-order processes (in which the "rise" is more rapid than the "fall"), thus indicating significant autocatalysis. Fits of our traces to a sequence involving catalysis by a Cr(IV) intermediate (see Results and Discussion) were accomplished initially with the program INTEGRAL to produce curves that were compared to those observed.[8a,18,19] Individual rate constants giving acceptable agreement

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(13) (a) See, for example: Clark, W. M. *Oxidation–Reduction Potentials of Organic Systems*; Williams and Wilkins: Baltimore, MD, 1960; p 486. (b) Latimer, W. H. *Oxidation Potentials*, 2nd ed.; Prentice-Hall; Englewood Cliffs, NJ, 1952; p 63.

(14) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

(15) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

(16) Separations were carried out with a 5-cm column, capacity 2 mequiv. For estimation of molar absorbances of Cr(III) species, aliquots were oxidized with basic H_2O_2, and the total chromium content was determined as chromate. (See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.)

(17) See, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapter 4.

(18) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,[19] were accomplished by a FORTRAN-77 program on an IBM 3081D computer system. The FORTRAN-IV version of the program, for which we thank Professor Gilbert Gordon (Miami University, Oxford, OH), was modified to incorporate the appropriate differential equations and stoichiometric relationships. Copies of the modified program may be obtained from R.N.B.

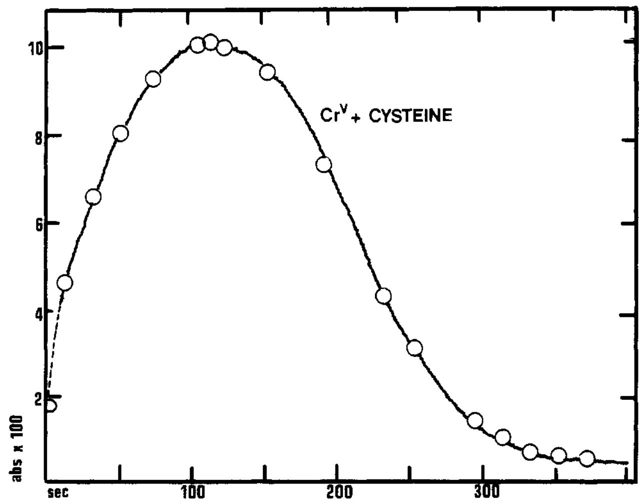

Figure 2. Kinetic profile at 510 nm for reduction of Cr(V) chelate I (1.2 × 10^{-4} M) with cysteine (III) (2.50 × 10^{-3} M) at 25 °C. The supporting medium was 0.060 M in 2-ethyl-2-hydroxybutyric acid, 0.03 M in its sodium salt, and 0.37 M in $LiClO_4$; the pH was 3.02. The solid line is the experimental curve, whereas the circles designate absorbances calculated from sequence (2)–(6), taking k_1 and k_3 as 1.36 and 3.84 M^{-1} s^{-1} and the ratio k_2/k_4 as 7.05. Extinction coefficients used (M^{-1} cm^{-1}): Cr(III), 48; Cr(IV), 2.1 × 10^3; Cr(V), 150. Optical path length = 1.00 cm.

between observed and calculated absorbances were then refined further by using an iterative nonlinear least-squares procedure.[20,21]

Refinements of data for reductions by thiolactic acid were generally more satisfactory than those for the much slower cysteine reductions. Parameters resulting from treatments pertaining to individual runs generated the observed curves closely in all cases, but cysteine parameters obtained from replicate runs were poorly reproducible. This difficulty, which persisted despite several modifications in experimental procedure, may mirror, at least in part, competing internal oxidation of the coordinated ligand(s).

Results and Discussion

Stoichiometric data (Table I) indicate that the predominant reaction involves 2 mol of thio acid/mol of Cr(V):

$$\mathrm{Cr^V + 2RSH \rightarrow RSSR + Cr^{III} + 2H^+} \qquad (1)$$

The slight positive departures from 2:1 stoichiometry observed with thiolactic acid may reflect air oxidation (possibly catalyzed by Cr^V), whereas the negative departures with cysteine, which is consumed much more slowly, may be attributed reasonably to competing slow internal oxidation of the carboxyl ligand, which has been shown to intrude also during electrochemical studies of the oxidant.[22]

The ion-exchange behavior and the variable spectral properties (Table II) of the major Cr(III)-containing fractions from both reactions tell us that we are dealing with mixtures of uncharged species, and the relatively high extinction coefficients correspond to those of bischelated complexes.[23] The positions of the (very broad) maxima at 560–590 nm are less informative than those between 420 and 440 nm, for absorption of 435–440 nm may be considered characteristic of Cr(III) having a single S-bound ligand, in addition to five O-bound ligands.[24] The percent S-bound product, as adduced from the position of the peak near 420 nm, is seen to decrease as the ratio of ligand anion to thio acid in the reaction mixture increases, indicating a competition between hydroxy acid and thio acid for a fifth coordination position on chromium. The rapid shift of this peak to 412–418 nm upon acidification must be attributed to aquation of the Cr–S bond and suggests that this bond is considerably more labile in our carboxyl-substituted systems than in $(H_2O)_5Cr^{III}$[24a] or $(en)_2Cr^{III}$[24b] systems.[25] The spectrum of the principal product from the cysteine reaction in the solution with the largest excess of ligand anion corresponds to that of the compound formed by reduction of the same Cr(V) chelate I with ascorbic acid,[10] which has been assigned a bischelated structure having still another (axially bound) carboxyl group. This product is altered only minimally by treatment with acid.

In each case, minor fractions, having elution behavior of +2 ions, exhibited spectra indicative of mono chelates of Cr(III).[23] In view of the ease with which (carboxylato)chromium(III) complexes are known to decompose on polysulfonate resin,[26] we suspect that these fractions are formed by partial aquation, with attendant breakage of one ring, of the principal bischelated products. As expected, this decomposition is most severe for reactions in which the yield of Cr(III)–S product is greatest.

Kinetic curves, recorded both at 510 and 600 nm, point to the generation and subsequent decay of an intermediate that absorbs strongly in the regions characteristic of Cr(IV) derivatives.[7,8] Traces (Figures 1 and 2) are nearly symmetric, in contrast to curves generated by consecutive first-order reactions, in which the decay of the intermediate is much more gradual than its formation. We are thus seeing autocatalytic systems. The importance of the autocatalytic component, as judged by the steepness of descent from maximal absorbance, is greater than that found in the reaction of Cr(V) with hypophosphite[7a] but less than that for reductions with sulfite,[8a] ascorbic acid,[10] or iodide.[8b]

As with analogous inorganic reductants,[7,8,10] the observed autocatalysis, in conjunction with the intermediacy of Cr(IV), requires that the two redox reagents partake in both 1e and 2e changes. Analysis of our kinetic profiles is in terms of sequence (2)–(6), which features four single-electron steps. During its early

$$\mathrm{Cr^V + RSH \xrightarrow{k_1} Cr^{IV} + RS^{\bullet} + H^+} \qquad (2)$$

$$\mathrm{Cr^V + RS^{\bullet} \xrightarrow{k_2} Cr^{IV} + RS^+} \qquad (3)$$

$$\mathrm{Cr^{IV} + RSH \xrightarrow{k_3} Cr^{III} + RS^{\bullet} + H^+} \qquad (4)$$

$$\mathrm{Cr^{IV} + RS^{\bullet} \xrightarrow{k_4} Cr^{III} + RS^+} \qquad (5)$$

$$\mathrm{RS^+ + RSH \rightarrow R_2S_2 + H^+} \quad \text{(rapid)} \qquad (6)$$

stages, the reaction proceeds only by (2) and (3). As the level of Cr(IV) increases, (4) becomes more prominent, and the concentration of radical $RS^{\bullet}$ rises. This radical reacts more rapidly with Cr(V) (k_2) than with Cr(IV) (k_4), and the Cr^V–$RS^{\bullet}$ reaction regenerates Cr(IV), resulting in the autocatalysis that is observed.

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(19) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. In *Investigations of Rates and Mechanisms of Reactions*; Lewis, E. S., Ed.; Techniques of Chemistry, 3rd ed., Vol. VI, Part I; Wiley: New York, 1974; p 764.

(20) This program, which was developed by R. Moore and T. W. Newton of Los Alamos National Laboratory, was obtained from Professor Gilbert Gordon. The FORTRAN-IV version was changed, with the help of Dr. J. W. Reed, to FORTRAN-77 in order to adapt to the IBM 3100 system. The program, which minimizes the function $(\mathrm{Abs_{calcd} - Abs_{obsd}})^2$, uses the Gaussian method described by McWilliams and co-workers.[21] Trial values of the rate constants were those obtained from the "INTEGRAL" procedure. Individual experimental points were unweighted.

(21) McWilliams, P.; Hall, W. S.; Wegner, H. E. *Rev. Sci. Instrum.* **1965**, *33*, 76.

(22) Bose, R. N.; Neff, V. D.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 165. A reviewer raises the possibility that the observed departure from 2:1 stoichiometry for the cysteine oxidation results in part from hydrogen abstraction at its α-position, yielding a keto acid. We regard this as an unlikely possibility in view of the recognized resistance of α-amino acids to oxidation in dilute aqueous solution.

(23) Visible spectra of a number of chelated and nonchelated carboxylato complexes of Cr(III) have been compiled by Fanchiang.[6b]

(24) (a) Ardon, M.; Taube, H. *J. Am. Chem. Soc.* **1967**, *89*, 3661. (b) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682. Data from the latter report indicate that substitution of an S-donor for an O-donor in the primary coordination sphere of Cr(III) bathochromically shifts the λ_{max} lying near 400 nm by 15–20 nm and that this effect is cumulative on multisubstitution.

(25) See, for example: Ogino, H.; Masuko, A.; Ito, S.; Miura, N.; Shimura, M. *Inorg. Chem.* **1986**, *25*, 708.

(26) See, for example: Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740 (footnote 10).

Table III. Kinetic Parameters for the Reduction of Carboxylato-Bound Chromium(V) with Thiolactic Acid[a]

[RSH], M	pH	[LigH],[b] M	[Lig$^-$],[c] M	k_1[d,e]	$10^{-2}k_3$[d,e]	k_2/k_4[d,e]	$\epsilon_{Cr(IV)}$[d,f]
0.0063	3.33	0.050	0.050	59	1.8	1.9	4.7
0.0125	3.31	0.050	0.050	32	1.9	2.2	4.8
0.0250	3.35	0.050	0.050	18	1.5	1.5	4.0
0.0250[g]	3.34	0.050	0.050	17	1.6	1.7	4.0
0.0375	3.30	0.050	0.050	12	1.4	1.7	3.8
0.0250	3.29	0.10	0.10	16	0.90	3.1	3.7
0.0250	3.32	0.15	0.15	16	0.68	3.5	3.8
0.0250	3.32	0.20	0.20	17	0.50	4.3	4.1
0.0250	2.56	0.30	0.050	9	0.81	2.1	4.5
0.0250	2.75	0.20	0.050	10	1.2	1.8	3.9
0.0250	3.04	0.10	0.050	13	1.5	2.0	4.7
0.0250	4.09	0.050	0.30	19	0.64	4.1	3.1
0.0250	3.73	0.10	0.30	20	0.42	8.5	2.5

[a] Reactions were carried out at 22 °C; μ = 0.4 M ($LiClO_4$); chromium(V), added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I), was 0.0025 M unless otherwise indicated. [b] 2-Ethyl-2-hydroxybutyric acid. [c] 2-Ethyl-2-hydroxybutyrate. [d] Parameters obtained from nonlinear least-squares refinement in which observed absorbances were compared with those obtained by integration of differential equations based on sequence (2)–(5). (See text and ref 8a and 18). [e] Values of k_1 and k_3 are in M^{-1} s^{-1}; k_2/k_4 is dimensionless. [f] M^{-1} cm^{-1} × 10^{-2} (600 nm). [g] [Cr^V] = 0.0050 M.

Table IV. Kinetic Parameters for Reduction of Carboxylato-Bound Chromium(V) with L-Cysteine[a]

[RSH], M	pH	[LigH],[b] M	[Lig$^-$],[c] M	k_1[d,e]	k_3[d,e]	k_2/k_4[d,e]	$\epsilon_{Cr(IV)}$[d,f]
0.0025	2.68	0.120	0.030	0.77	3.1	6.2	2.2
0.0025	3.02	0.060	0.030	1.4	3.8	7.1	2.2
0.0050	3.01	0.060	0.030	1.2	4.0	7.7	2.1
0.0025	3.32	0.030	0.030	2.1	4.0	15	2.1
0.0025[g]	3.32	0.030	0.030	1.9	4.1	15	2.1
0.0025	3.32	0.060	0.060	1.2	2.0	14	2.2
0.0025	3.34	0.090	0.090	0.83	1.8	13	2.2
0.0025	3.32	0.120	0.120	0.54	1.9	11	2.2
0.0025	3.34	0.180	0.180	0.35	1.5	15	2.3
0.0025	3.65	0.090	0.180	0.59	4.6	12	2.2

[a] Reactions were carried out at 25 °C; μ = 0.40 M ($LiClO_4$). Chromium(V), added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I), was 1.2 × 10^{-4} M unless otherwise indicated. [b] 2-Ethyl-2-hydroxybutyric acid. [c] 2-Ethyl-2-hydroxybutyrate. [d] Parameters obtained from nonlinear least-squares refinement in which observed absorbances were compared to those obtained by integration of differential equations based on sequence (2)–(5). (See text and ref 8a and 18.) [e] Values of k_1 and k_3 are in M^{-1} s^{-1}; k_2/k_4 is dimensionless. [f] M^{-1} cm^{-1} × 10^{-3} (510 nm). [g] [Cr^V] = 0.00025 M.

Combination of the sulfenyl cation, RS^+, with excess thiol (reaction 6) is taken to be rapid in analogy to the corresponding reaction in the Cr(V)–I^- system,[8b] but this step does not enter into the electron-transfer sequence.

Generation of the differential equations implied by reactions 2–5, application of the steady-state approximation to $RS^•$, and subsequent numerical integration were accomplished in a manner analogous to that described for the Cr(V)–HSO_3^- reaction.[8a] Specific rates k_1 and k_3 and the ratio k_2/k_4 were varied independently. Runge–Kutta integration[18,19] then gave concentrations of Cr(V), Cr(IV), and Cr(III) at intervals of 10 s (for cysteine) and 0.2 s (for thiolactic acid). Incorporation of extinction coefficients for the three oxidation states of chromium yielded calculated absorbances at each point.[27] The set of parameters fitting the observed traces most closely was used as a set of trial values for an iterative least-squares refinement.[20]

Values of k_1, k_3, k_2/k_4, and $\epsilon_{Cr(IV)}$ resulting from these refinements are listed in Tables III (for the thiolactic acid reaction) and IV (for the cysteine reaction). Absorbances calculated from a representative set of parameters (circles) are compared to the corresponding experimental profiles in Figures 1 and 2.

We stress here, as previously,[8] that parameters obtained from such multivariant refinements are much less precise than those associated with exponential or straightforward biphasic profiles. Despite this uncertainty, the resulting specific rates exhibit obvious variation with the reaction medium. Most important, for thiolactic acid the apparent value of k_1 (pertaining to the Cr^V–RSH reaction) decreases markedly at higher concentrations of reductant; i.e., this step exhibits kinetic saturation, indicating the reversible formation of a Cr(V)–thiolactate complex. Kinetic measurements in themselves cannot be informative as to whether electron transfer takes place within the complex or between the uncomplexed species in equilibrium with it, although consideration of individual specific rates (see below) points toward involvement of the complex. The limiting rate constant ($(k_1)_{lim}$) for this step and the association constant for the complex (K) are related to the k_1 values as

$$k_1 = \frac{(k_1)_{lim}}{1 + K[RSH]} \tag{7}$$

Least-squares refinement of k_1 values at pH 3.33 leads to $(k_1)_{lim}$ = (2.8 ± 0.4) × 10^2 M^{-1} s^{-1} and an association constant (5.9 ± 0.8) × 10^2 M^{-1}.

In addition, k_1 for the thiolactic acid reaction is seen to decrease with increasing [H^+]. Data at [RSH] = 0.0250 M conform to (8), which implies partition of one of the reactants into an unreactive protonated form (with acidity constant K_A) and a reactive deprotonated form (having a specific rate k'). Refinement yields k' = 21.1 ± 1.4 M^{-1} s^{-1} and K_A = (1.9 ± 0.5) × 10^{-3} M (pK_A = 2.7). Since the latter value falls well below the experimental pK_A for thiolactic acid (3.54),[28] we assign it the Cr^V–RSH complex that has been shown to form here.

$$(k_1)_{obsd} = \frac{k'K_A}{K_A + [H^+]} \tag{8}$$

Values of k_3 (which describes the Cr^{IV}–RSH component) for thiolactic acid depend both on [H^+] and on [Lig^-], the concentration of the ligating anion. The relationship appears to be of the form (9), where a = 26.8 ± 7.2 M^{-1} s^{-1}, b = 8.0 ± 0.9, and K_A = (2.6 ± 0.7) × 10^{-3} M. Here again, there is a distribution

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(27) Values of $\epsilon_{Cr(V)}$ and $\epsilon_{Cr(III)}$ were taken from the initial and final absorbances of the reaction mixtures and were kept fixed, whereas $\epsilon_{Cr(IV)}$ was allowed to float. Absorbances of the sulfur species were negligible at the frequencies chosen.

(28) This value, which pertains to 25 °C and μ = 0.4 M, was estimated by partial titration in aqueous $LiClO_4$.

$$(k_3)_{\text{obsd}} = \frac{K_A}{K_A + [\text{H}^+]}\left(a + \frac{b}{[\text{Lig}^-]}\right) \qquad (9)$$

of one reaction component (probably an RSH–Cr(IV) complex) between a reacting basic and a nonreacting acidic form. In addition, the binomial term indicates two contributing paths, one of which is inhibited by excess ligand anion. The latter may reflect a competition between that anion and an additional unit of thio acid, as seen also in the alteration of the composition of the principal Cr(III) product (Table II) as the ratio of competing species is varied.

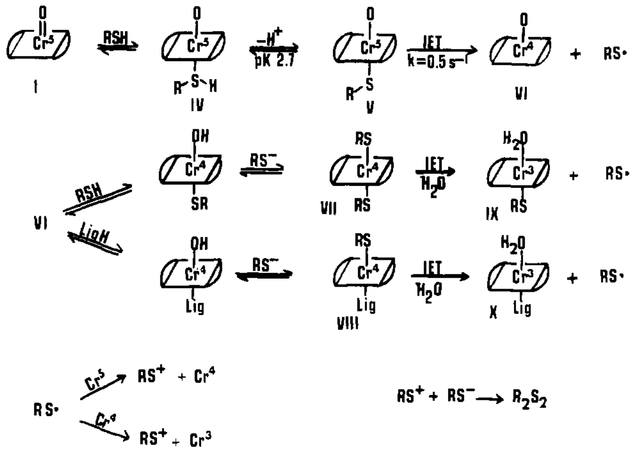
Although kinetic parameters pertaining to the cysteine reduction (Table IV) are insufficiently precise to justify quantitative refinement, we note that the Cr(IV)–RSH reaction (k_3) is again inhibited by both H^+ and the ligand anion, Lig^-, but that neither dependency is steep enough to correspond to a simple inverse proportionality. The partition between protonation levels and competing reaction paths suggested for the corresponding component in thiolactic acid reaction may apply here as well. In contrast to the thiolactic acid sequence, there is no evidence for kinetic saturation in the Cr(V)–RSH step (k_1). Cysteine is undoubtedly the more weakly complexing species, reflecting, in large part, the added positive charge ($-NH_3^+$) interposed between the two donor centers in the zwitterionic reductant.

Because the Cr(III) products from both reactions suffer eventual aquation in the media employed, none can be a thermodynamically favored species. Since the two chelate rings in the oxidant are maintained in each of the primary products, chelation may be taken to persist during all steps involving both Cr(V) and Cr(IV). The competition between buffering ligand and thio acid for an additional site on the chromium center (reflected in the observed mix of uncharged chelated products) must occur, in large part, at the Cr(IV) level, for this state is known to undergo substitution much more readily than the tri- or pentapositive states.[7a] The marked differences in the calculated values of $\epsilon_{\text{Cr(IV)}}$ for the two reductants (Tables III and IV), as well as the dependence of this parameter on the ratio $[\text{RSH}]/[\text{Lig}^-]$ in the generating solution, are in accord with this suggestion.

The specific rates for the initial Cr(V)–RSH step in the thiolactic acid sequence (k_1 = 10–100 M^{-1} s^{-1}) are about 10^3 times that for the reaction of the same Cr(V) chelate with $IrCl_6^{3-}$ (3.4 × 10^{-2}),[5] a reductant which may be assumed to operate via an outer-sphere path. Although direct comparison of the two systems, using the formalism of Marcus,[29] is complicated by the apparent absence of thermodynamic and self-exchange data on the couple $RS^-/RS^•$, approximate parameters listed by Nord and co-workers[30] for the structurally related couple $SCN^-/SCN^•$ ($E°$ = 1.62 V, $k_{\text{self-exchange}} = 10^7$ M^{-1} s^{-1}) may be taken as reasonable surrogates. From the self-exchange rate of the Ir(III,IV) couple (2.3 × 10^5 M^{-1} s^{-1})[31] and its formal potential (0.92 V),[32] the outer-sphere oxidation of thiolactate to its radical may be estimated[29,32] to proceed only 10^{-5} times as rapidly as the oxidation of the more strongly reducing $IrCl_6^{3-}$ anion, or at a specific rate <10^{-6} M^{-1} s^{-1}. The conclusion from this (admittedly rough) estimate is that the Cr(V)–thiolactic acid (k_1) reaction proceeds almost exclusively by an inner-sphere path. This inference is applicable, with only slightly less force, to the initial (k_1) step in the Cr(V)–cysteine sequence, which is found to be about 10^2 times as rapid as the Cr(V)–$IrCl_6^{3-}$ reaction.

The Cr(V)–thiolactate complex, the formation of which is reflected in the observed kinetic saturation (eq 7) for k_1 in this sequence, may then be taken as the precursor complex in the initial act of electron transfer. At pH 3.33, 79% of this complex (pK_{HA} = 2.7) exists as the reactive deprotonated form. The limiting bimolecular rate constant (at very low acidities) is then 100/79 times k_{lim} at pH 3.33, or 3.5 × 10^2 M^{-1} s^{-1}. The unimolecular specific rate for electron transfer within this complex ($(k_3)_{\text{lim}}/K$) is 0.5 s^{-1}.

Scheme I



In systems where Cr(IV) and Cr(V) react competitively with a given species by outer-sphere routes, the ratio $k_{\text{Cr(IV)}}/k_{\text{Cr(V)}}$ has been found to lie between 10 and 60.[5,8b,34] On that basis, outer-sphere Cr(IV)–RSH reactions would be expected to exhibit specific rates in the range 10^{-5}–10^{-4} M^{-1} s^{-1}, in obvious contrast to k_3 values (10^0–10^2) determined in this study. The inference is, again, that the Cr(IV)–RSH reaction is, for both thio acids, predominantly inner sphere. Moreover, the inversions, in relative rates (k_2/k_4) for oxidation of the $RS^•$ radicals, which react with Cr(V) 2–15 times as rapidly as with Cr(IV), indicate the predominance of an inner-sphere path for Cr(V)/$RS^•$ but are not informative as to the Cr(IV)–$RS^•$ (k_4) step.[35] As is the case for the reduction with ascorbic acid,[10] rate comparisons with known systems thus point to bridged activated complexes for at least three of the four steps in the proposed redox sequences.

The reactions depicted in Scheme I appear to be consistent with our observations (the indicated parameters apply to the thiolactic acid reaction). In analogy to the oxidations of alcohols with Cr(VI) and Cr(V) centers, which are thought to proceed through "esters" featuring a Cr–O–C sequence,[36] we suggest similar species ("precursor complexes" V, VII, and VIII) as intermediates in inner-sphere steps involving RSH or its anion. Internal electron transfer (IET) within V yields radical $RS^•$ and Cr(IV) intermediate VI, both of which subsequently undergo partition between competing processes. Competition between RSH and the parent ligand for VI is ultimately mirrored in the mix of Cr(III) complexes IX and X in the products,[37] whereas competition between Cr(V) and Cr(IV) for $RS^•$ (as measured by the ratio k_2/k_4) determines the degree of autocatalysis.[38] An alternate possibility, in which $RS^•$ formed by internal electron transfer within precursor VI remains bound to the Cr(IV) center and undergoes a second transfer to yield Cr(III) and RS^+, cannot be a major route, for release of $RS^•$ is necessary to maintain the observed autocatalysis.

Since autocatalytic behavior has already been described for the reductions of chromium(V) by bisulfite,[8a] hypophosphite,[7a] iodide,[8b] ascorbic acid,[10] and nitrite,[7b] one may reasonably inquire as to

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[29] See, for example: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

[30] Nord, G.; Pederson, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2333.

[31] Hurwitz, P.; Kustin, K. *Trans. Faraday Soc.* **1966**, *62*, 427.

[32] George, P.; Hanania, G. I. H.; Irvine, G. H. *J. Chem. Soc.* **1957**, 3048. This value was measured at 20.3 °C and μ = 0.2 M.

[33] Loar, M. K.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 3689.

[34] Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 94.

[35] Gould, E. S. *Inorg. Chem.* **1979** *18*, 900.

[36] See, for example: (a) Beattie, J. K.; Haight, G. P., Jr. *Prog. Inorg. Chem.* **1972**, *17*, 97. (b) Mitewa, M.; Bontchev, P. R. *Coord. Chem. Rev.* **1985**, *61*, 241. (c) Wiberg, K. B. *Oxidation in Organic Chemistry, Part A* Academic: New York, 1965; p 69.

[37] Additional Cr(III) products, e.g., a complex in which the thio acid is coordinated through its carboxyl function, but not its SH group, cannot be excluded.

[38] A reviewer suggests that reactions of the thiyl radical, $RS^•$, with Cr(V) and Cr(IV) involve the thiol-bound complexes of these oxidation states, i.e., $Cr^V(SR) + RS^• \rightarrow Cr^{IV} + R_2S_2$. Such a route, which would bypass the species RS^+ is kinetically indistinguishable from that indicated in Scheme I.

the connecting thread shared by this array of donors and by the present thio acids as well. It now appears that the initial 1e act involving Cr(V) is, in all systems, an inner-sphere process, but in each case, the radical intermediate must depart from the site at which it is generated. Its release is not unexpected, for removal of an electron from a donor center generally makes it a much less effective ligating species. Nevertheless, the radical is, in each instance, consumed preferentially by Cr(V) (again by an inner-sphere transaction), rather than by the stronger oxidant, Cr(IV). Its preference for Cr(V) may reflect an accommodation, by this coordinatively unsaturated center, of the weakened ligand, which, however, competes less effectively with water or carboxylate for a site at hexacovalent chromium(IV).[39]

Acknowledgment. We thank Drs. James Espenson and David Stanbury for valuable discussions and Arla White for technical assistance.

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(39) There is uncertainty concerning the ligand configuration about Cr(IV) in aqueous solution. Although formal similarity to V(IV) suggests that it may be a 5-coordinate oxo ion, an octahedral configuration appears, at this time, to be more likely. See, for example: Espenson, J. H. *Acc. Chem. Res.* **1970**, *3*, 347.

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Synthesis, Reactivity, and X-ray Structure of *fac*-$W(CO)_3(dppm)(CH_3CN)$. Stereoselective Preparation of *fac*-$W(CO)_3(^{13}CO)(dppm)$ and Subsequent Intramolecular Rearrangement Processes

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The reaction of *fac*-$W(CO)_3(CH_3CN)_3$ with an equimolar quantity of bis(diphenylphosphino)methane (dppm) results in the quantitative formation of *fac*-$W(CO)_3(dppm)(CH_3CN)$. The solid-state structure of *fac*-$W(CO)_3(dppm)(CH_3CN)$ was established by X-ray diffraction [$P2_1/c$ (monoclinic), a = 10.937 (2) Å, b = 18.399 (4) Å, c = 15.194 (3) Å, β = 108.33 (1)°, Z = 4]. This compound reacts with ^{13}CO to afford stereoselective *fac*-$W(CO)_3(^{13}CO)(dppm)$. The reaction proceeds by a dissociative pathway, with activation parameters for loss of CH_3CN being $\Delta H^{*} = 23.5$ kcal/mol and $\Delta S^{*} = -6.0$ eu. In a subsequent, intramolecular ligand rearrangement facial $\rightleftharpoons$ meridional isomerization occurs. Reaction of *fac*-$W(CO)_3(dppm)(CH_3CN)$ with an additional 1 mol of dppm leads initially to formation of *fac*-$W(CO)_3(dppm)_2$, which contains both bidentate and monodentate dppm ligands. Isomerization and oxidation of the unattached phosphine eventually provided *mer*-$W(CO)_3(dppm)(Ph_2PCH_2P(O)Ph_2)$. The structure of the latter species was determined by X-ray diffraction [$P4_1$ (tetragonal), a = 11.186 (4) Å, c = 40.498 (9) Å, Z = 4].

Introduction

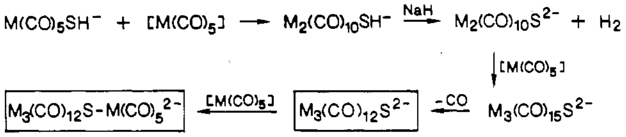
We have been interested in cluster synthesis of group 6 metal carbonyl species utilizing a thiolate ligand as the nucleating agent.[2,3] The reaction sequence provided below in Scheme I has afforded routes into tri- and tetranuclear derivatives. Attempts to prepare phosphine-substituted derivatives by means of CO displacement in the polynuclear species have been unsuccessful. An alternative synthetic approach is apparent in that the unsaturated $[M(CO)_5]$ moiety is prominent in Scheme I. Hence, it should be possible to introduce phosphine ligands into these anionic clusters by using substituted $[M(CO)_{5-n}L_n]$ species.

In this regard we have examined the chemistry of $W(CO)_3(dppm)(CH_3CN)$, where dppm = bis(diphenylphosphino)methane, with respect to ligand substitution processes involving the labile acetonitrile ligand. These investigations have allowed for an assessment of the kinetic parameters for CH_3CN dissociation from an unencumbered transition-metal center. In addition, stereoselective substitution with ^{13}CO was achieved to provide *fac*-$W(CO)_3(dppm)(^{13}CO)$, and its subsequent intramolecular ligand rearrangement process is reported upon herein.

Experimental Section

Methods and Materials. All manipulations were performed on a double-manifold Schlenk vacuum line under an atmosphere of dry nitrogen or in an argon-filled glovebox. Solvents were dried and deoxygenated by distillation from the appropriate reagent under a nitrogen atmosphere. Infrared spectra were recorded in 0.10-mm CaF_2 cells on an IBM IR/32 spectrometer. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Scheme I



$W(CO)_6$, PPh_3, PMe_3, and $H_2C(PPh_2)_2$ were purchased from Strem Chemicals, Inc., and were used without further purification. Carbon monoxide (99 atom % ^{13}C) was obtained from Isotec, Inc. $W(CO)_3(CH_3CN)_3$ was prepared by refluxing $W(CO)_6$ in acetonitrile according to the published procedure.[4]

Syntheses. *fac*-$W(CO)_3(CH_3CN)(dppm)$. $W(CO)_3(CH_3CN)_3$ (0.583 g, 1.49 mmol) and bis(diphenylphosphino)methane (0.586 g, 1.52 mmol) were placed in a 50-mL Schlenk flask containing a magnetic stirring bar. The flask was fitted with a rubber septum, evacuated, and backfilled with a nitrogen atmosphere. Fifteen milliliters of dry acetonitrile was added to the flask, and the mixture was allowed to stir for 5 h. During this time period, all of the $W(CO)_3(CH_3CN)_3$ was consumed and a yellow precipitate of *fac*-$W(CO)_3(dppm)(CH_3CN)$ was formed when the reaction mixture was allowed to stand overnight at subambient temperatures. The yellow product was isolated by removing the solution with a cannula. The product was washed with 10 mL of diethyl ether and dried under vacuum to afford 0.646 g of *fac*-$W(CO)_3(CH_3CN)(dppm)$. The mother solution was evaporated under vacuum to provide a yellow solid, which was washed with diethyl ether and recrystallized from CH_2Cl_2/hexane to give an additional 0.113 g of product (73.5% total yield). IR (cm^{-1} in THF): 1930.0 (vs), 1837.4 (s), 1823.0 (sh). ^1H NMR ($CDCl_3$): 7.4 (multiplet), 5.5 (dt; J_{P-H} = 8 Hz, J_{H-H} = 15.2 Hz), 4.2 ppm (dt; J_{P-H} = 10 Hz, J_{H-H} = 15.2 Hz). ^{31}P NMR (THF/acetone-d_6): −11.06 ppm(s). Anal. Calcd: C, 51.97; H, 3.63; P, 8.93. Found: C, 51.90; H, 3.82; P, 9.08.

***fac*-$W(CO)_3(PPh_3)(dppm)$.** *fac*-$W(CO)_3(CH_3CN)(dppm)$ (0.264 g, 0.38 mmol) and PPh_3 (0.132 g, 0.50 mmol) were added to a 50-mL Schlenk flask along with a magnetic stirring bar. The flask was fitted with a rubber septum, evacuated, and backfilled with a nitrogen atmo-

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(1) Nicolet Instrument Corp., Madison, WI 53711.

(2) (a) Darensbourg, D. J.; Zalewski, D. J. *Organometallics* **1984**, *3*, 1598. (b) Darensbourg, D. J.; Zalewski, D. J.; Delord, T., submitted for publication in *Inorg. Chem.*

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(4) (a) Tate, C. P.; Knipple, W. R.; Augi, J. M. *Inorg. Chem.* **1962**, *1*, 433. (b) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

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