

## Electron Transfer. 53. Response of Inner-Sphere Reactions to Variation in Charge on the Oxidant<sup>1</sup>

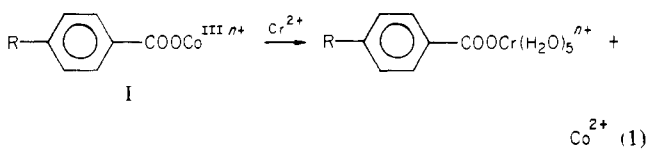
VANGALUR S. SRINIVASAN,<sup>2</sup> A. N. SINGH, C. A. RADLOWSKI, and EDWIN S. GOULD\*

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The specific rates of reduction, using chromium(II), vanadium(II), europium(II), and dihydriboflavin, of a series of di- and tripotitive  $(\text{NH}_3)_5\text{Co}^{\text{III}}$  complexes of saturated branched-chain carboxylic acids are compared. Variations in rates for the dihydro compound, which is an uncharged outer-sphere reagent, are almost random. With the metal-center reductants, effects of charge are separated from steric influences by comparing pairs of oxidants having similarly branched structures but differing in net charge. Data for five such isosteric pairs confirm the usual view that the additional unit of positive charge generally retards reaction. Reductions by  $\text{Cr}^{2+}$ , however, are found to be substantially more sensitive to charge than those by  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$ . This difference in response is attributed to partial misalignment, due to interaction with  $\text{N}^+$ , of water molecules in the second coordination sphere of the precursor complex, thus diminishing their effectiveness in distorting  $\text{Cr}-\text{OH}_2$  bonds in this precursor. Unsymmetric distortion of the latter type allows nonzero overlap between the  $e_g$  orbitals of  $\text{Cr}(\text{II})$  (the source of the electron being transferred) and the  $\pi$  orbitals of the carboxylato bridge; such distortion is not required for reductions by  $\text{Eu}^{2+}$  and  $\text{V}^{2+}$ .

It is generally taken to be axiomatic that the rate of electron transfer between ions is determined, in part, by the charges on these ions. The classical treatment of outer-sphere reactions by Marcus<sup>3</sup> includes, as contributions to the free energy of activation, work terms pertaining to bringing the ions together to their collision diameter and adjusting their charges to a critical value. Recent, more detailed, formulations have been based upon closely related approaches.<sup>4</sup> Although the importance of charge is recognized, this parameter cannot generally be varied independently, for any structural modification that alters the charge on the reagent will affect other contributory features such as formal potential, electron distribution, bond strengths, and the rate of self-exchange.

The picture with respect to inner-sphere reactions is still less clear, although there are indications that these may be less sensitive to charge variation than are the outer-sphere reactions. Thus, it has been found that  $\text{Cr}(\text{II})$  reductions of 4-substituted benzoato derivatives of  $(\text{NH}_3)_5\text{Co}^{\text{III}}$  (I) bearing



R	n	$k_{\text{Cr}^{2+}}$ , $\text{M}^{-1} \text{s}^{-1}$
$\text{NMe}_2\text{H}^+$	3	0.19
OH	2	0.20
$\text{SO}_3^-$	1	0.20

the 4-substituents  $\text{N}(\text{CH}_3)_2\text{H}^+$ , OH, and  $\text{SO}_3^-$  proceed at very nearly the same specific rate.<sup>5</sup> Such a comparison is perhaps subject to the criticism that charge alteration has been introduced well away from the reaction site (the carbonyl oxygen of the oxidant). Yet, if the charge variation were moved closer to the point of attack, ambiguities of interpretation similar to those encountered in outer-sphere reactions would be expected to intrude; i.e., the strength of the  $\text{Co}-\text{O}$  bond of the oxidant might be changed, nonbonded interaction between reactants

might assume a more prominent role, and possibilities for chelation in the precursor complex may arise.

In the present study of the effect of charge variation in reactions mediated by a carboxylato bridge between metal ion centers, we have chosen systems to which such objections appear to apply only minimally. We find that charge effects in reductions by  $\text{Eu}(\text{II})$  and  $\text{V}(\text{II})$  are indeed small (although generally detectable), even when alterations are made close to the bridging group. Reductions by  $\text{Cr}(\text{II})$ , however, are perceptibly more sensitive.

### Experimental Section

**Materials.** Lithium perchlorate<sup>6</sup> and solutions of  $\text{Eu}(\text{ClO}_4)_2$ ,<sup>7</sup>  $\text{V}(\text{ClO}_4)_2$ ,<sup>8</sup>  $\text{Cr}(\text{ClO}_4)_2$ ,<sup>9</sup> and  $\text{Ru}(\text{NH}_3)_6\text{Cl}_2$ <sup>10</sup> were prepared as described. Riboflavin, an Aldrich product, was used as received; master solutions, 0.001 M in this compound, were prepared in deaerated 1.0 M  $\text{HClO}_4$  just before use. Cobalt(III) complexes not available from previous studies<sup>9,11</sup> were prepared<sup>9</sup> and purified<sup>11</sup> as described. Elemental analyses of new complexes appear in Table I.

**Rate Measurements.** Rates were estimated from measurements of absorbance changes on a Cary 14 or a Beckman Model 5260 recording spectrophotometer as described.<sup>7,9,12</sup> Reactions were first order each in  $\text{Co}(\text{III})$  and reductant but were generally carried out under pseudo-first-order conditions. Reactions with metal-center reductants were run with a 10-fold excess of reductant and were monitored at 502 nm (the low-energy maximum of the cobalt(III) oxidants), whereas reactions with dihydriboflavin (which was prepared in situ by reduction of riboflavin itself with  $\text{Eu}^{2+}$ )<sup>12</sup> employed a 10-fold excess of the  $\text{Co}(\text{III})$  oxidant and were monitored at 495 nm, the maximum for the riboflavin radical, Rb, the one-electron oxidation product of the dihydro derivative. The majority of reactions were carried out in 1.0 or 1.2 M  $\text{HClO}_4$ , but a few were run at lower acidities with ionic strength adjusted to near unity with thrice-recrystallized  $\text{LiClO}_4$ . Rates of reaction with the metal-center reductants, but not with the dihydro compound, were in most cases independent of acidity. Reactions were followed for at least 4 half-lives. Rate constants evaluated from successive half-life values in a single

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.  
(2) On leave from Vivekananda College, Mylapore, Madras, India.  
(3) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966, 979.  
(4) See, for example: (a) Beattie, J. K.; Binstead, R. A.; Broccardo, M. *Inorg. Chem.* **1978**, *17*, 1822. (b) Phillips, J.; Haim, A. *Ibid.* **1980**, *19*, 76.  
(5) Gould, E. S. *J. Am. Chem. Soc.* **1970**, *92*, 6797. Specific rates cited here refer to reactions carried out at 25 °C at ionic strength near 1.2.

(6) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.  
(7) (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2369.  
(8) (a) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769. (b) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.  
(9) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318. Complexes of amino acids were prepared by heating solutions of  $(\text{NH}_3)_5\text{Co}(\text{H}_2\text{O})(\text{ClO}_4)_3$  and the parent amino acid in the absence of added base.  
(10) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.  
(11) Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289. Oxidants III and VII were prepared from  $\text{Co}(\text{NH}_3)_5\text{CO}_3^+\text{ClO}_4^-$  in methanol, by using the procedure of Fan.<sup>7b</sup> For most complexes, purification required two passages through Bio-Gel; elution was with water.  
(12) Singh, A. N.; Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.*, preceding paper in this issue.

Table I. Analyses of (Carboxylato)pentaamminecobalt(III) Perchlorates

complex	% C		% H		% Co	
	calcd	found <sup>a</sup>	calcd	found <sup>a</sup>	calcd	found <sup>b</sup>
CH <sub>3</sub> CH(NH <sub>3</sub> <sup>+</sup> )COOC <sub>o</sub> (NH <sub>3</sub> ) <sub>5</sub> (ClO <sub>4</sub> ) <sub>3</sub>	6.77	6.66	3.95	4.09	11.1	10.6
(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>3</sub> <sup>+</sup> )COOC <sub>o</sub> (NH <sub>3</sub> ) <sub>5</sub> (ClO <sub>4</sub> ) <sub>3</sub>	8.77	8.61	4.39	4.40	10.9	10.8
<sup>+</sup> NH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOC <sub>o</sub> (NH <sub>3</sub> ) <sub>5</sub> (ClO <sub>4</sub> ) <sub>3</sub>	6.77	6.72	3.95	4.12	11.1	10.8
<sup>+</sup> NH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOC <sub>o</sub> (NH <sub>3</sub> ) <sub>5</sub> (ClO <sub>4</sub> ) <sub>3</sub>	8.77	8.56	4.39	4.37	10.8	10.0
CH <sub>3</sub> C(O)NHCH <sub>2</sub> COOC <sub>o</sub> (NH <sub>3</sub> ) <sub>5</sub> (ClO <sub>4</sub> ) <sub>2</sub>	10.43	10.40	4.57	4.67	12.8	12.0
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> COOC <sub>o</sub> (NH <sub>3</sub> ) <sub>5</sub> (ClO <sub>4</sub> ) <sub>2</sub>	15.69	15.98	5.67	5.65	12.9	12.3

<sup>a</sup> Microanalyses by Galbraith Laboratories. <sup>b</sup> See ref 9.

Table II. Specific Rates for Reductions of (Carboxylato)pentaamminecobalt(III) Complexes<sup>a</sup>

oxidant	<i>k</i> <sub>Cr</sub>	<i>k</i> <sub>V</sub>	<i>k</i> <sub>Eu</sub>	<i>k</i> <sub>Ru</sub> <sup>b</sup>	<i>k</i> <sub>RbH<sub>2</sub></sub> <sup>c</sup>
Dipositive Complexes					
CH <sub>3</sub> COOC <sub>o</sub> <sup>III</sup>	0.35 <sup>d</sup>	1.15 <sup>f</sup>	2.43 <sup>e</sup>	0.022	18.0
	0.46 <sup>e</sup>				
CH <sub>3</sub> CH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (II)	0.173 <sup>k</sup>	1.09 <sup>l</sup>			
(CH <sub>3</sub> ) <sub>2</sub> CHCOOC <sub>o</sub> <sup>III</sup> (III)	0.055	0.36	0.45	0.069	41
(CH <sub>3</sub> ) <sub>3</sub> CCOOC <sub>o</sub> <sup>III</sup> (IV)	0.0070 <sup>f</sup>	0.22	0.18	0.0087	5.0
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (V)	0.16	0.92	1.10	0.056	
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COOC <sub>o</sub> <sup>III</sup> (VI)	0.087 <sup>g</sup>	0.62	0.70		
CH <sub>3</sub> C(O)NHCH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (VII)	0.26	1.45	2.0	0.048	2.0
Tripositive Complexes					
<sup>+</sup> NH <sub>3</sub> CH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (VIII)	0.064 <sup>h</sup>	0.85	1.83	0.082	2.3
CH <sub>3</sub> NH <sub>2</sub> CH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (IX)	0.044 <sup>h</sup>				
(CH <sub>3</sub> ) <sub>2</sub> NHCH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (X)	0.038 <sup>h</sup>				
(CH <sub>3</sub> ) <sub>3</sub> NCH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (XI)	0.016 <sup>h</sup>	0.24	0.74	0.27	4.0
(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>3</sub> <sup>+</sup> )COOC <sub>o</sub> <sup>III</sup> (XII)	0.0033	0.14	0.19		22
CH <sub>3</sub> CH(NH <sub>3</sub> <sup>+</sup> )COOC <sub>o</sub> <sup>III</sup> (XIII)	0.026	0.38	0.68		7.0
<sup>+</sup> NH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (XIV)	0.098	0.99	1.28		6.4
<sup>+</sup> NH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOC <sub>o</sub> <sup>III</sup> (XV)	0.136	0.55	1.0		10
py <sup>+</sup> CH <sub>2</sub> COOC <sub>o</sub> <sup>III</sup> (XVI)	0.039 <sup>i</sup>	1.14	0.82 <sup>i</sup>	0.29	
<i>o</i> -NH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COOC <sub>o</sub> <sup>III</sup> (XVII)	0.0086 <sup>j</sup>	0.38	0.41		

<sup>a</sup> Specific rates are in M<sup>-1</sup> s<sup>-1</sup>. Reactions were carried out in 1.0–1.2 M HClO<sub>4</sub> unless otherwise noted. <sup>b</sup> Reductions by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> carried out at [H<sup>+</sup>] = 0.030 M, μ = 0.50; supporting electrolyte LiCl (see ref 10). <sup>c</sup> Reactions by dihydriboflavin were carried out in 1.3 M HClO<sub>4</sub> (see ref 12). <sup>d</sup> Limiting specific rate at low acidity; μ = 1.0 (LiClO<sub>4</sub>) (see ref 13). <sup>e</sup> Limiting specific rate at low acidity; μ = 4.0 (LiClO<sub>4</sub>) (see ref 14). <sup>f</sup> Reference 14. <sup>g</sup> Reference 5. <sup>h</sup> Reference 15. <sup>i</sup> Reference 11. <sup>j</sup> Reference 16. <sup>k</sup> Reference 7b. <sup>l</sup> Value in 0.02 M H<sup>+</sup> (μ = 1.0) measured by N. Rajasekar (unpublished experiments, 1981).

run agreed to within 6%. Specific rates obtained from replicate runs checked to better than 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

## Results and Discussion

Specific rates are summarized in Table II, along with some values from previous studies<sup>10–16</sup> included here for comparison. Although rates of reductions by V<sup>2+</sup>, Eu<sup>2+</sup>, and Cr<sup>2+</sup> in the present study generally do not vary with acidity (within the range 0.1–1.0 M H<sup>+</sup>), those by the dihydro derivative of riboflavin have been shown<sup>12</sup> to conform to eq 2, where *k*<sub>lim</sub> is

$$k_{\text{obsd}} = k_{\text{lim}}K_A / (K_A + [\text{H}^+]) \quad (2)$$

the specific rate for the reactive basic form of the reductant and *K*<sub>A</sub> (=0.13 M at 25 °C and μ = 1.2) is the acidity constant for the unreactive acidic form. Specific rates entered for this reductant are those for reactions in 1.3 M HClO<sub>4</sub>, rather than the *k*<sub>lim</sub> values (which are 11 times as great in all cases). This choice does not affect the relative reactivities within the series. Alteration of the oxidant is seen to result in appreciable changes in *k*<sub>RbH<sub>2</sub></sub>, the rate constant for reduction by this uncharged outer-sphere<sup>12</sup> reagent, but such changes appear, at this point, to be almost random.

Of the three reductants that react predominantly<sup>10</sup> via inner-sphere paths, specific rates for Cr<sup>2+</sup> (*k*<sub>Cr</sub>) span a signifi-

Table III. Effect of Charge on the Specific Rates of Reduction of Isosteric (Carboxylato)pentaamminecobalt(III) Derivatives<sup>a</sup>

isosteric complexes		relative rates, 3+/2+		
2+	3+	Cr <sup>2+</sup>	V <sup>2+</sup>	Eu <sup>2+</sup>
II	VIII	0.37	0.77	
III	XI	0.29	0.67	1.6
IV	XII	0.47	0.63	1.1
V	XVI	0.24	1.17	0.75
VI	XVII	0.10	0.61	0.66

<sup>a</sup> Individual specific rates (25 °C), reaction conditions, and structural formulas of the oxidants are given in Table II.

cantly wider range (about 10<sup>2</sup>) than those for V<sup>2+</sup> and Eu<sup>2+</sup>, even when, as in the present comparison, chelating substituents and rate-enhancing unsaturated functions are excluded from consideration. This difference may be attributed, in part, to the greater sensitivity of the Cr<sup>2+</sup> reductions to steric factors. This latter facet, which has been noted previously,<sup>10</sup> stands out most prominently when the reactivities of complexes of branched-chain fatty acids (e.g., III and IV) are compared to those of the straight-chain analogues but, unaccountably, becomes subdued when the specific rate for the glycinate oxidant (VIII) and its N-alkylated derivatives (IX, X, and XI) are considered.

The inclusion in Table II of several pairs of oxidants having similarly branched structures but differing in net charge allows a reasonable separation of electrostatic influences from steric influences. To this end, the glycinate (VIII) and propionate (II) complexes may be compared, as may four other pairs of

(13) Barrett, M. B.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1983.

(14) Thomas, J. C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 1696.

(15) Holwerda, R.; Deutsch, E.; Taube, H. *Inorg. Chem.* **1972**, *11*, 1965.

(16) Martin, A. H.; Liang, A.; Gould, E. S. *Inorg. Chem.* **1976**, *15*, 1925.

isosteres listed in Table III. In 11 of the 14 instances for which data are at hand, the tripositive complexes, as expected, react more slowly, and for all five pairs the difference is most pronounced for reductions by  $\text{Cr}^{2+}$ . Thus, of the three inner-sphere metal-center reductants,  $\text{Cr}^{2+}$  is clearly the most sensitive to charge variation as well as to steric influences.<sup>17</sup>

We suspect that both effects arise from the same source. Alone among the three reducing centers, chromium(II) suffers a mismatch of symmetry between the metal orbital supplying the reducing electron (in the case of  $\text{Cr}^{2+}$ , a centrosymmetric  $e_g$  orbital) and the  $\pi$  orbitals of the bridging carboxyl group. This reductant requires, for inner-sphere transfer, a distortion of the reducing center that is unsymmetric with respect to the carboxyl plane in the precursor complex.<sup>10</sup> The burden of this distortion falls mainly on interaction with water molecules comprising the second coordination sphere. Hence,  $\text{Cr}^{2+}$  reductions are expected to be most sensitive to disturbances in this sphere. On one hand, large lipophilic groups on the periphery of the precursor will disfavor ordering in nearby solvent molecules. On the other, a positively charged substituent near the reaction center should increase ordering in the surrounding medium, but the ordering will be in the "wrong" direction; i.e., the oxygen ends of the water dipoles will point toward  $\text{N}^+$  rather than toward the hydrogens of those water molecules in the primary sphere. The result will be the same in the two cases—a less effective secondary sphere.

An earlier observation appears also to be related to the special sensitivity of inner-sphere Cr(II) reductions to variations in the secondary coordination sphere. Liang<sup>18</sup> has reported that the reductions, by  $\text{Cr}^{2+}$ , of unsaturated carboxylato  $(\text{NH}_3)_5\text{Co}^{\text{III}}$  complexes are substantially retarded by substitution of 1 M  $\text{HClO}_4$  for 1 M  $\text{LiClO}_4$  as a reaction medium. Since reactions of the same oxidants with  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$  proceed at rates independent of acidity at unit ionic strength,<sup>19</sup> it may be inferred that the variations found with  $\text{Cr}^{2+}$  reflect a medium effect rather than one of the more usual kinetic acidity patterns. Here again, it may be argued that the strongly solvated hydrogen ions tend to orient the solvent dipoles so that their hydrogens, rather than their oxygens, face outward, thus weakening their interaction with the Cr(II)-

bound water molecules constituting a portion of the primary coordination sphere of the precursor. (This reasoning, however, leaves unanswered the question as to why this medium-related retardation is observed for oxidants derived from olefinic acids but not for those from aromatic or saturated acids.)

Finally, it may be reasonably asked whether the marginal charge effects observed here for reductions by  $\text{Eu}^{2+}$  and  $\text{V}^{2+}$  suggest the need for revision of the widespread belief that rates of electron-transfer reactions are significantly charge sensitive. We feel such a view to be an overinterpretation of experiments which, in actuality, deal with only a small portion of the entire spectrum of such reactions. Note, moreover, that the reactions at hand are inner-sphere reactions, that their rates are generally determined jointly by the association constant of a precursor complex and the specific rate of internal electron transfer within the precursor, and that electron-attracting substituents (e.g., an additional positive charge) on the oxidant, while facilitating internal electron transfer,<sup>20</sup> also serve to destabilize the precursor. Hence, it is arguable that we are seeing a near cancellation of the two effects. At the same time, it must be remembered that the presumed sensitivity of outer-sphere reactions to charge type, although eminently reasonable, has not yet been experimentally demonstrated in a manner that bars the intervention of other important effects. Skepticism on this point is not unjustified.<sup>21-23</sup>

**Registry No.** II, 19173-62-7; III, 80327-80-6; IV, 33887-25-1; V, 40544-43-2; VI, 30931-78-3; VII, 80327-72-6; VIII, 68582-30-9; XI, 45127-13-7; XII, 31133-42-3; XIII, 55132-09-7; XIV, 61202-26-4; XV, 31133-39-8; XVI, 69421-16-5; XVII, 31133-44-5;  $\text{CH}_3\text{COOC}^{\text{III}}$ , 16632-78-3; Cr, 7440-47-3; V, 7440-62-2; Eu, 7440-53-1;  $\text{Ru}(\text{NH}_3)_6^{2+}$ , 19052-44-9;  $\text{RbH}_2$ , 13345-95-4.

(20) See, for example: Bifano, C.; Linck, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3945.

(21) Two comments by reviewers deserve response. First, our view that the  $\text{V}^{2+}$  reductions at hand are predominantly inner sphere is based upon the report of Fan,<sup>10</sup> who has estimated the outer-sphere fraction for  $\text{V}^{2+}$  reactions of (carboxylato)cobalt(III) complexes of this type to fall between 0.003 and 0.09. A second reviewer has observed that plots of  $\log k_{\text{Cr}}$  vs.  $\log k_{\text{V}}$  are reasonably linear, as are plots of  $\log k_{\text{Cr}}$  vs.  $\log k_{\text{Eu}}$ . Relationships of this type were noted in earlier reports,<sup>7b,22</sup> which also pointed out that all three sets of  $\log k$  values were linear functions of Taft's steric substituent constants.<sup>23</sup> These linear free-energy relationships are thought to reflect the circumstance that rate ratios in all three series are governed by nonbonded interactions within the precursor complex, augmented, in the case of  $\text{Cr}^{2+}$ , by distortions in the second coordination sphere (as described in the present text), which are also related to the bulk of substituents on the carboxyl.

(22) Chen, J. C.; Gould, E. S. *J. Am. Soc.* **1973**, *95*, 5539.

(23) Taft, R. W., Jr. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 598.

(17) As anticipated, the retarding action of the positive nitrogen toward reduction by Cr(II) becomes attenuated as the positive center is progressively removed from the site of reaction (compare  $k_{\text{Cr}}$  values for oxidants VIII, XIV, and XV). Somewhat surprisingly, no such trend is noted in the V(II) and Eu(II) series.

(18) Liang, A.; Gould, E. S. *Inorg. Chem.* **1973**, *12*, 12.

(19) Thamburaj, P. K.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 15.

Contribution from the Department of Chemistry, University of California, Davis, California 95616

## Ambidentate Binding of Thiocyanate to Palladium. <sup>31</sup>P NMR Observation of the Distribution of Linkage Isomers in (diphosphine)Pd(CNS)<sub>2</sub> and (diphosphine)<sub>2</sub>Pd<sub>2</sub>(CNS)<sub>2</sub>

CATHERINE T. HUNT and ALAN L. BALCH\*

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The distribution of linkage isomers of  $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{Pd}(\text{CNS})_2$  ( $n = 1-3$ ),  $[\text{cis-Ph}_2\text{PCH}_2\text{PPh}_2]\text{Pd}(\text{CNS})_2$ , and  $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Pd}_2(\text{CNS})_2$  in a variety of solvents has been determined by <sup>31</sup>P NMR spectroscopy. Near 25 °C only a single broadened resonance due to time averaging over several environments is observed for each of these compounds, but at -40 to -60 °C, well-defined resonances assignable to the various possible linkage isomers can be observed. The resonances of the individual components have been identified by their spectral pattern and their line widths.

The ambidentate nature of the thiocyanate ligand, which may bind in a linear fashion A through the nitrogen atom or

in a bent fashion B through the sulfur atom, is well recognized. It is known that a variety of factors including the nature of