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## Electron-Transfer Reactions of Tris(picolinato)vanadate(II), a LOMI Reagent

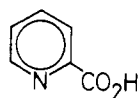
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Reductions of  $\text{Co}(\text{edta})^-$ ,  $\text{Co}(\text{NH}_3)_6^{3+}$ ,  $\text{Co}(\text{en})_3^{3+}$ , and  $\text{Co}(\text{sep})^{3+}$  by tris(picolinato)vanadate(II),  $\text{V}(\text{pic})_3^-$ , take place with second-order rate constants  $7.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $8.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $8.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , and  $8.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, at 25.0 °C and at 0.5 M ionic strength. Application of the Marcus theory to the latter three results leads to a self-exchange rate for  $\text{V}(\text{pic})_3^{0/-}$  of  $3.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . For  $\text{Co}(\text{edta})^-$  the observed rate is an order of magnitude slower than predicted by the Marcus theory and reasons for this discrepancy are proposed.

### Introduction

The dissolution of metal oxides is considerable importance in the descaling of high-temperature water-cooled plants. Many procedures currently available use strong acids or chelating agents in the dissolution of the oxide.<sup>2</sup> Blesa and co-workers have investigated the dissolution of  $\text{Fe}_3\text{O}_4$  using thioglycolate<sup>3</sup> and oxalate<sup>4</sup> and in the latter reaction have indicated the presence of a heterogeneous electron-transfer pathway. Zabin and Taube<sup>5</sup> noted the importance of electron transfer in the dissolution of metal oxides by  $\text{Cr}_{\text{aq}}^{2+}$ , and more recently tris(picolinato)vanadate(II),  $\text{V}(\text{pic})_3^-$ , has been in-



picolinic acid

roduced<sup>6</sup> as a powerful descaling agent capable of dissolving  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{NiFe}_2\text{O}_4$ .<sup>7</sup> This low-oxidation-state metal ion (LOMI) reagent is thought to be particularly effective because it reduces iron(III) to the more labile iron(II) in a heterogeneous outer-sphere electron-transfer reaction.

Tris(picolinato)vanadate(II) has a reduction potential of  $-0.41 \text{ V}$  (vs. NHE) on the basis of stability constants<sup>8</sup> measured at 25 °C and 0.5 M ionic strength, making it comparable in reducing power with the  $\text{Cr}_{\text{aq}}^{2+}$  ion. It is strongly colored with an absorption maximum at 660 nm ( $\epsilon = 3800 \text{ M}^{-1} \text{ cm}^{-1}$ ) and is readily monitored spectrophotometrically.

Although the redox chemistry of  $\text{V}(\text{H}_2\text{O})_6^{2+}$  in aqueous solution has been examined extensively, much less is known of vanadium(II) complexes. Bennett and Taube<sup>9</sup> have reported reactions of  $\text{V}(\text{bpy})_3^{2+}$  and other polypyridyl reagents with a number of oxidants, and the results suggest outer-sphere mechanisms. Gould and co-workers<sup>10</sup> have examined the effects of radical formation in the reduction of cobalt(III) complexes by vanadium(II) complexes with pyridinedicarboxylic acids, and there is a report<sup>11</sup> of an inner-sphere reaction of  $\text{V}(\text{pic})_3^-$  in the reduction of  $\text{Eu}_{\text{aq}}^{3+}$  but detailed studies have not been published. In this paper we present the

kinetics and mechanisms of reduction of a number of cobalt(III) complexes by  $\text{V}(\text{pic})_3^-$ . The choice of oxidant is governed largely by the high reactivity of  $\text{V}(\text{pic})_3^-$  and the limitations of the stopped-flow technique. However, the results are sufficient to establish that  $\text{V}(\text{pic})_3^-$  is a powerful outer-sphere reductant.

### Experimental Details

All procedures involving  $\text{V}(\text{pic})_3^-$  were carried out in solutions rigorously outgassed with chromium(II)-scrubbed nitrogen gas. Reagent transfers were accomplished by using gas-tight syringes and Teflon needles. Tris(picolinato)vanadate(II) was produced by the electrolytic reduction of  $\text{VO}_2^+$  (Fluka purrum) to  $\text{V}(\text{H}_2\text{O})_6^{2+}$  in 0.1 M HCl on a mercury pool cathode. Aliquots of  $\text{V}(\text{H}_2\text{O})_6^{2+}$  were transferred onto a mixture of dry solids,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (Baker Analyzed or BDH AnalaR) and picolinic acid, picH (Sigma), previously weighed to give the desired ionic strength and picolinate concentrations. Stepwise constants for the formation of picolinate complexes of vanadium(II)<sup>8</sup> are  $K_1 = 10^{4.43} \text{ M}^{-1}$ ,  $K_2 = 10^{4.11} \text{ M}^{-1}$ , and  $K_3 = 10^{4.15} \text{ M}^{-1}$ , which require that  $[\text{pic}^-]$ , the free picolinate ion concentration, be in excess of  $10^{-2} \text{ M}$  to ensure >99% formation of the tris complex. The final pH of stock solutions was generally greater than 6, and effective buffer action was achieved with excess picolinate ( $\text{p}K_a = 5.4$ )<sup>12</sup> mixed with borate.

Production of the dark blue  $\text{V}(\text{pic})_3^-$  was instantaneous. The reagent has a broad absorption in the visible region of the spectrum with a maximum at 660 nm ( $\epsilon = 3800 \text{ M}^{-1} \text{ cm}^{-1}$ ) and a shoulder at 460 nm ( $\epsilon = 2200 \text{ M}^{-1} \text{ cm}^{-1}$ ). The stock solution of  $\text{V}(\text{pic})_3^-$  was stored under nitrogen to minimize aerial oxidation and was used within a few hours of production and then discarded.

Total vanadium content was measured by the absorbance of the peroxovanadium(V) complex<sup>13</sup> ( $\epsilon_{450} = 281 \text{ M}^{-1} \text{ cm}^{-1}$ ). Reduction to  $\text{V}(\text{H}_2\text{O})_6^{2+}$  achieved yields of 95% or better conversion. Conversion to  $\text{V}(\text{H}_2\text{O})_6^{2+}$  was estimated by measuring the absorbance of  $\text{V}(\text{H}_2\text{O})_6^{3+}$  at 400 nm<sup>7</sup> or by measuring the absorbance of  $\text{V}(\text{pic})_3^-$  at 680 nm.

The compounds  $\text{NaCo}(\text{edta})$ ,<sup>14</sup>  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ ,<sup>15</sup>  $\text{Co}(\text{en})_3\text{Cl}_3$ ,<sup>16</sup> and  $\text{Co}(\text{sep})\text{Cl}_3$ <sup>17</sup> were prepared by literature methods or minor modifications thereon. Analytical and spectrophotometric data were in good agreement with published values.<sup>17-20</sup> Solutions, rigorously outgassed with nitrogen and containing appropriate amounts of borate, NaCl, and pic<sup>-</sup>, were prepared gravimetrically, and concentrations were checked spectrophotometrically. Solutions of  $\text{Cr}(\text{bpy})_3^{2+}$  were prepared as outlined elsewhere.<sup>21</sup> Reactions of  $\text{Cr}(\text{bpy})_3^{2+}$  were run in

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phosphate buffer in the absence of picolinic acid.

Oxidation of  $V(pic)_3^-$  by the cobalt(III) complexes results in formation of  $V(pic)_3$ , which has a characteristic absorption at 365 nm ( $\epsilon$  1600  $M^{-1} cm^{-1}$ ). Precipitates are formed with the positively charged oxidants at high concentration. In the  $Co(edta)^-$  reaction where there is a possibility of further oxidation,  $V(pic)_3$  was recovered quantitatively by extraction into  $CHCl_3$  ( $\epsilon_{385} = 1400 M^{-1} cm^{-1}$ ).<sup>22</sup>

Kinetic experiments were run under pseudo-first order conditions with an excess of oxidant and were monitored at or near the absorption maxima of the reductants (680 nm for  $V(pic)_3^-$ ; 467 nm for  $Cr(bpy)_3^{2+}$ ) with an Applied Photophysics<sup>23</sup> or a Durrum D-110 stopped-flow spectrophotometer thermostated at  $25.0 \pm 0.1$  °C unless otherwise noted. Data were collected by using a Nicolet 3091 digital oscilloscope. Plots of  $\log(A - A_\infty)$  against time were linear for more than 3 half-lives, and pseudo-first-order rate constants were calculated by linear regression on an Apple II+ microcomputer. The pH was monitored immediately after reaction with either an EIL 7066 pH meter or a Beckman Selection 2000 meter. In all experiments the ionic strength was maintained at 0.5 M by using NaCl as supporting electrolyte.

Absorption spectra were run on a Beckman 5270 or Perkin-Elmer 552 instrument.

### Results

Reduction of the cobalt(III) complexes by  $V(pic)_3^-$  produces  $V(pic)_3$  in accord with eq 1. Subsequent reactions in the presence of excess oxidant are sufficiently slow not to interfere with this process.



For all the  $V(pic)_3^-$  reductions, pseudo-first-order rate constants,  $k_{obsd}$ , are presented in Table I. Plots of  $k_{obsd}$  against  $[Co(III)]$  are linear with  $Co(en)_3^{3+}$ ,  $Co(NH_3)_6^{3+}$  and  $Co(sep)^{3+}$  as oxidants, consistent with the second-order rate law, eq 2. In the case of  $Co(edta)^-$ , this rate law holds at low

$$\frac{-d[V(pic)_3^-]}{dt} = k_{12}[Co(III)][V(pic)_3^-] \quad (2)$$

concentrations of oxidant but, at high concentrations, the rate becomes less dependent on oxidant concentration, tending to a limiting first-order rate around 500  $s^{-1}$ .

There are a number of possible explanations for this behavior. The electron-transfer process could be limited by some oxidant-independent process of  $V(pic)_3^-$ , but this is unlikely since a number of other oxidants were examined, including  $Co(ox)_3^{3-}$ , and reactions under pseudo-first-order conditions were completed within the time of mixing, indicating a second-order rate constant  $\geq 10^7 M^{-1} s^{-1}$ . Precursor complex formation is also a possibility, but the magnitude of the formation constant required, around 200  $M^{-1}$ , is not consistent with association of two negatively charged complexes.

It should be noted that significant deviations from eq 2 are found with pseudo-first-order rate constants in excess of 200  $s^{-1}$ , close to the limit of the instruments used. It is unwise to place much credence in these rate values, and deviations are most likely due to limitations of the stopped-flow instrument in mixing solutions with high picolinate concentrations. Second-order rate constants,  $k_{12}$  (Table I), were calculated from data at lower  $[Co(edta)^-]$  concentrations and were found to be independent of pH in the range 5.3–7.7 and of  $[pic]_T$  in the range  $3 \times 10^{-2}$  to  $1.6 \times 10^{-1} M$ , consistent with reactions of  $V(pic)_3^-$ .

### Discussion.

The second-order rate constants,  $k_{12}$ , obtained in this study are presented in Table II. It is of some interest to probe the nature of the homogeneous electron-transfer reactions of  $V(pic)_3^-$  since heterogeneous studies<sup>6,7</sup> predict efficient out-

Table I. Pseudo-First-Order Rate Constants for the Reduction of Cobalt(III) Complexes by  $V(pic)_3^-$  at 25 °C and 0.5 M (NaCl) Ionic Strength<sup>a</sup>

oxidant	pH	$10^2 \times [pic]_T,^b$ M	$10^3 \times [Co(III)],$ M	$10^{-3} \times k_{obsd}/[Co(III)],$ $M^{-1} s^{-1}$
Co(edta) <sup>-</sup> Oxidant				
7.64	3.30	0.81	72 ± 13	89
5.34	16.0	1.01	87 ± 9	86
5.62	13.3	1.01	84 ± 12	83
6.34	10.0	1.01	82 ± 5	81
7.14	6.6	1.01	78 ± 3	77
7.68	3.3	1.01	95 ± 10	94
7.64	3.3	1.06	94 ± 3	89
6.13	10.0	1.18	90 ± 5	76
6.13	10.0	1.30	104 ± 1	80
6.12	10.0	1.59	129 ± 4	81
6.13	10.0	1.98	170 ± 4	86
6.15	10.0	2.17	152 ± 2	70
7.64	3.3	2.57	163 ± 20	63
6.24	10.0	2.72	180 ± 15	66
6.12	10.0	3.17	235 ± 5	74
6.38	10.0	3.26	227 ± 9	70
7.64	3.3	5.38	248 ± 10	c
6.22	10.0	6.28	330 ± 30	c
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup> Oxidant				
6.18	10.0	1.96	12 ± 5	6.0
5.31	16.6	2.17	17 ± 1	7.7
5.32	16.6	2.86	31 ± 6	10.8
5.34	16.6	4.65	32 ± 5	6.9
6.18	10.0	8.17	64 ± 6	7.8
5.35	16.6	11.2	102 ± 7	9.1
6.12	10.0	12.8	86 ± 4	6.7
6.19	10.0	13.4	92 ± 8	6.9
6.12	10.0	16.0	124 ± 9	7.7
5.31	16.6	21.7	198 ± 6	9.1
6.18	10.0	27.3	218 ± 9	8.0
Co(en) <sub>3</sub> <sup>3+</sup> Oxidant				
6.21	10.0	1.00	0.80 ± 0.03	0.80
6.19	10.0	2.00	1.74 ± 0.03	0.87
6.22	10.0	5.00	4.32 ± 0.08	0.86
6.17	10.0	8.00	6.86 ± 0.15	0.86
6.14	10.0	20.0	15.6 ± 0.6	0.78
6.17	10.0	25.0	18.5 ± 0.3	0.74
Co(sep) <sup>3+</sup> Oxidant				
6.33	10.0	0.49	42 ± 3	86
6.32	10.0	0.61	48 ± 2	79
6.31	10.0	1.52	131 ± 9	86

<sup>a</sup> pH controlled by addition of 0.1 M borate;  $[V(pic)_3^-] = (5-40) \times 10^{-6} M$ . <sup>b</sup> Total picolinic acid added. <sup>c</sup> Reaction not first order in  $[Co(III)]$ .

er-sphere reactivity. Vanadium(II) complexes are  $d^3$  systems, not noted for great lability. However, pH-jump experiments indicate that dissociation of picH from the complex takes place with a first-order specific rate around 40  $s^{-1}$ , setting an upper limit for an inner-sphere pathway. Such a pathway is unlikely since the oxidants  $Co(edta)^-$ ,  $Co(NH_3)_6^{3+}$ ,  $Co(en)_3^{3+}$ , and  $Co(sep)^{3+}$  are all inert to substitution with no "lead-in" substituents, and in most instances, first-order rates are in excess of the limiting value.

For outer-sphere electron-transfer reactions, the cross-reaction rate constant,  $k_{12}$ , is related to the self-exchange rates  $k_{11}$  and  $k_{22}$  for the reactants and the thermodynamic driving force  $K_{12}$  for the reaction by the Marcus equations<sup>24</sup> (3) and (4), where  $Z$  is the collision number for neutral molecules in

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (3)$$

$$\log f_{12} = (\log K_{12})^2 / (4 \log(k_{11}k_{22}Z^{-2})) \quad (4)$$

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Table II. Second-Order Rate Constants for the Reduction of Cobalt(III) Complexes at 25 °C and 0.5 M (NaCl) Ionic Strength

		Co(sep) <sup>3+</sup>	Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	Co(en) <sub>3</sub> <sup>3+</sup>	Co(edta) <sup>-</sup>
$V(\text{pic})_3^-$	$k_{12}$ , M <sup>-1</sup> s <sup>-1</sup>	$8.4 \times 10^4$	$8.0 \times 10^3$ <sup>a</sup>	$8.2 \times 10^2$	$7.7 \times 10^4$ <sup>b</sup>
	$k_{12}$ <sup>calcd</sup> , M <sup>-1</sup> s <sup>-1</sup>	$8.3 \times 10^4$	$8.5 \times 10^3$	$7.8 \times 10^2$	$4.8 \times 10^5$
Cr(bpy) <sub>3</sub> <sup>2+</sup>	$k_{12}$ , M <sup>-1</sup> s <sup>-1</sup>		$0.65 \times 10^3$ <sup>c</sup>	$1.6 \times 10^2$ <sup>c</sup>	$2.2 \times 10^6$
	$k_{12}$ <sup>calcd</sup> , M <sup>-1</sup> s <sup>-1</sup>		$2.1 \times 10^3$	$2.6 \times 10^2$	$1.6 \times 10^6$

<sup>a</sup>  $\Delta H^\ddagger = 10 \pm 1$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger = -7 \pm 5$  cal K<sup>-1</sup> mol<sup>-1</sup> ( $T = 5-25$  °C). <sup>b</sup>  $\Delta H^\ddagger = 7 \pm 1$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger = -13 \pm 4$  cal K<sup>-1</sup> mol<sup>-1</sup> ( $T = 5-25$  °C). <sup>c</sup> Reference 28; extrapolated to ionic strength 1.0 M from 0.2 M.

Table III. Reduction Potentials and Self-Exchange Rate Constants Used in the Marcus Calculations

reagent		$E^\circ_1$ , V	$E^\circ_2$ , V	$k_{11}$ , M <sup>-1</sup> s <sup>-1</sup>	$k_{22}$ <sup>calcd</sup> , M <sup>-1</sup> s <sup>-1</sup>
Co(sep) <sup>3+</sup>	$V(\text{pic})_3^-$	-0.32 <sup>a</sup>	-0.41	11.5 <sup>a</sup>	$3.1 \times 10^6$
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	$V(\text{pic})_3^-$	0.06 <sup>b</sup>	-0.41	$1 \times 10^{-7}$ <sup>b</sup>	$2.7 \times 10^6$
Co(en) <sub>3</sub> <sup>3+</sup>	$V(\text{pic})_3^-$	-0.26 <sup>b</sup>	-0.41	$7.7 \times 10^{-5}$ <sup>c</sup>	$3.5 \times 10^6$
Co(edta) <sup>-</sup>	$V(\text{pic})_3^-$	0.37 <sup>d</sup>	-0.41	$4 \times 10^{-7}$ <sup>e</sup>	$5.6 \times 10^4$
Co(edta) <sup>-</sup>	Cr(bpy) <sub>3</sub> <sup>2+</sup>	0.37 <sup>d</sup>	-0.25 <sup>f</sup>	$4 \times 10^{-7}$ <sup>e</sup>	$8.8 \times 10^8$

<sup>a</sup> Reference 17. <sup>b</sup> Estimated from ref 28 and 29. <sup>c</sup> Reference 26 (1.0 M ionic strength). <sup>d</sup> Reference 31. <sup>e</sup> Reference 27 (extrapolated from data at higher temperatures). <sup>f</sup> Reference 32.

solution. These equations are generally used in the form of (5) and (6), where  $\Delta G^{**}$  is the electrostatically corrected free

$$\Delta G_{12}^{**} = \frac{1}{2}(\Delta G_{11}^{**} + \Delta G_{22}^{**} + \Delta G_R^\circ(1 + \alpha^{**})) \quad (5)$$

$$\alpha^{**} = \Delta G_R^\circ / 4(\Delta G_{11}^{**} + \Delta G_{22}^{**}) \quad (6)$$

energy of activation and  $\Delta G_R^\circ$  is the electrostatically corrected free energy change for the reaction.<sup>25</sup>

The electrostatics correction is an attempt to account for noncanceling work terms associated with the assembly of reactant precursors from charged complexes and is readily approximated by using eq 7 at 0.5 M ionic strength where  $z_i$

$$w_{ij} = \frac{4.24z_i z_j}{\bar{r}(1 + 0.233\bar{r})} \quad (7)$$

and  $z_j$  are the charges on the reactants and  $\bar{r}$  is the distance in angstroms between reactant centers, assumed to be the sum of the radii of the reactants.<sup>25</sup>

Although reduction potentials and self-exchange rates for the complexes Co(edta)<sup>-</sup>, Co(en)<sub>3</sub><sup>3+</sup>, and Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> have not been determined unambiguously and in some cases have been revised recently,<sup>26-29</sup> values for Co(sep)<sup>3+</sup> are well-defined.<sup>16,30</sup> With the parameters in Table III, the self-exchange rate for  $V(\text{pic})_3^{0/-}$  was calculated from the four cross-reactions by using eq 5 and 6. For the positively charged oxidants, the values of  $k_{11}$  varied between  $2.7 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> and  $3.5 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> with a geometric mean of  $3.1 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> leading to the calculated rate constants,  $k_{12}$ <sup>calcd</sup>, shown in Table II. For the reaction of Co(edta)<sup>-</sup>, agreement is poorer, with  $k_{12}$ <sup>calcd</sup> an order of magnitude faster than the observed rate constant. While not serious, this disagreement between the apparent self-exchange rates obtained with Co(edta)<sup>-</sup> and with the positively charged oxidants may be due to a number of factors such as the inadequacy of the work terms, eq 7. This expla-

Table IV. Comparisons of Low-Oxidation-State Metal Ion Complexes at 25 °C

	$E^\circ$ , V	$k_{11}$ , M <sup>-1</sup> s <sup>-1</sup>	$k_{\text{rel}}^a$
Cr(edta) <sup>-2-</sup>	-1.00 <sup>b</sup>	$6 \times 10^{-2}$ <sup>c</sup>	13
$V(\text{pic})_3^{0/-}$	-0.41	$3 \times 10^6$	1
Cr(bpy) <sub>3</sub> <sup>3+/2+</sup>	-0.25	$1 \times 10^9$	0.8
$V(\text{H}_2\text{O})_6^{3+/2+}$	-0.26 <sup>d</sup>	$1 \times 10^{-2}$ <sup>e</sup>	$3 \times 10^{-6}$
Cr(H <sub>2</sub> O) <sub>6</sub> <sup>3+/2+</sup>	-0.40 <sup>d</sup>	$2 \times 10^{-10}$ <sup>f</sup>	$8 \times 10^{-9}$

<sup>a</sup> Relative rate ( $V(\text{pic})_3^- = 1$ ) with hypothetical reagent  $E^\circ = 0.0$  V. <sup>b</sup> H. Ogino, personal communication cited in ref 38. <sup>c</sup> Estimated from the cross-reaction with Co(edta)<sup>-</sup> (ref 39) and Co(en)<sub>3</sub><sup>3+</sup> (ref 41). <sup>d</sup> Reference 11. <sup>e</sup> Reference 42. <sup>f</sup> Reference 30.

nation is unlikely since eq 7 has been used successfully in a large number of studies.<sup>25</sup>

Negative deviations from Marcus' theory have been predicted for reactions at large thermodynamic driving forces.<sup>33</sup> It is noteworthy that the reaction between Co(edta)<sup>-</sup> and  $V(\text{pic})_3^-$  has the largest thermodynamic driving force of those studied,  $\log K_{12} = 13.20$ , the others have  $\log K_{12} < 8$ . In the present case, the deviation is not as large as has been detected in other systems and may well be the result of<sup>34</sup> solvent reordering to form  $[\text{Co}(\text{edta}), V(\text{pic})_3]^{2-}$  as a precursor to electron transfer.

By way of support for this explanation, the cross-reaction between Co(edta)<sup>-</sup> and Cr(bpy)<sub>3</sub><sup>2+</sup>, with  $\log K_{12} = 10.5$ , was examined and the observed rate constant,  $2 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>, is comparable with the calculated value of  $1.5 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> although uncertainties in the self-exchange rate for Cr(bpy)<sub>3</sub><sup>3+/2+</sup> preclude detailed comment.<sup>35-37</sup> In this reaction the precursor  $[\text{Co}(\text{edta}), \text{Cr}(\text{bpy})_3]^+$  is of lower charge than the reactants, and substantial solvent orientation is not required.

The reagent  $V(\text{pic})_3^-$  is a powerful outer-sphere reductant, which lends support to a heterogeneous outer-sphere mechanism for efficient reductive dissolution of metal oxide films. In Table IV are listed reduction potentials and self-exchange rates for a number of low-oxidation-state metal ion complexes

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together with a parameter  $k_{rel}$  indicating the relative outer-sphere reactivity. The order for  $k_{rel}$  parallels the rates of dissolution of metal oxide films by these reagents and suggests that of these common reductants, only  $\text{Cr}(\text{edta})^{2-}$  is more potent than  $\text{V}(\text{pic})_3^-$ .

The self-exchange rate for  $\text{V}(\text{pic})_3^{0/-}$  of  $3.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  is 8 orders of magnitude larger than the value for  $\text{V}(\text{H}_2\text{O})_6^{3+/2+}$ .<sup>42</sup> This may imply that the structural rearrangement associated with the electron-transfer process is

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smaller for  $\text{V}(\text{pic})_3^{0/-}$  than for  $\text{V}(\text{H}_2\text{O})_6^{3+/2+}$ . It is noteworthy that the estimate for the  $\text{V}(\text{bpy})_3^{3+/2+}$  exchange is  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>9</sup>

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**Registry No.**  $\text{V}(\text{pic})_3^-$ , 76298-57-2;  $\text{Co}(\text{edta})^-$ , 87698-06-4;  $\text{Co}(\text{NH}_3)_6^{3+}$ , 14695-95-5;  $\text{Co}(\text{en})_3^{3+}$ , 14878-41-2;  $\text{Co}(\text{sep})^{3+}$ , 72496-77-6.

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## Oligo(phosphine) Ligands. 7.<sup>1</sup> Free-Radical-Catalyzed Synthesis of Some Completely Alkylated Oligo(tertiary phosphines) Containing Trimethylene Linkages

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Novel alkylated tri- and tetradentate phosphine ligands containing trimethylene connecting chains between the donor atoms have been prepared through free-radical addition of P-H functionalized alkylphosphines to allylphosphines. Thus, the permethylated tris(phosphine)  $\text{MeP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_2$  has been obtained in high yield by irradiating a mixture of  $\text{MeP}(\text{CH}_2\text{CH}=\text{CH}_2)_2$  and excess  $\text{Me}_2\text{PH}$  at  $\lambda > 300 \text{ nm}$  in the presence of catalytic amounts of azo-2,2'-bis(isobutyronitrile). The terminally ethylated homologue  $\text{MeP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PET}_2)_2$  has been synthesized similarly from  $\text{MeP}(\text{CH}_2\text{CH}=\text{CH}_2)_2$  and  $\text{Et}_2\text{PH}$ . Radical-initiated addition of  $\text{Me}_2\text{PH}$  to  $t\text{-BuP}(\text{CH}_2\text{CH}=\text{CH}_2)_2$  has been applied as an efficient method of synthesis for the tridentate  $t\text{-BuP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_2$ . Furthermore, the completely aliphatic tripod tetrakis(tertiary phosphines)  $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PR}_2)_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) have been made accessible by coupling  $\text{Me}_2\text{PH}$  and  $\text{Et}_2\text{PH}$ , respectively, onto triallylphosphine. The NMR ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ ) and mass spectra of these new oligo(phosphine) ligands are described.

### Introduction

Oligo(phosphines) containing flexible trimethylene linkages are valuable chelating ligands for the platinum metal ions. This has mainly been demonstrated by Meek and his co-workers in a series of papers dating back to the early 1970s.<sup>2</sup> One straightforward route to this class of compounds involves coupling reactions between (3-chloropropyl)phosphines  $\text{R}_2\text{P}(\text{CH}_2)_3\text{Cl}$  and phosphide nucleophiles, e.g.  $\text{R}_2\text{P}(\text{CH}_2)_3\text{P}(\text{R})\text{Li}$ , or between chlorophosphines  $\text{R}_3\text{-}_n\text{PCl}_n$  ( $n = 1-3$ ) and  $\text{R}_2\text{P}(\text{CH}_2)_3\text{MgCl}$  Grignard reagents.<sup>3-6</sup> However, the range of application of this method is limited by the stability of the 3-chloropropyl key compounds, which appear to be available only with bulky substituents such as phenyl or cyclohexyl on phosphorus.

Various efforts have therefore been made to develop more variable methods of synthesis from which three major strategies have begun to emerge: (1) base-assisted coupling of vinyl and allyl (and 3-chloropropyl) phosphine units onto trimethylene-linked secondary-tertiary bis(phosphines) within the coordination sphere of a  $d^8$  transition-metal ion;<sup>7</sup> (2) radical-catalyzed P-H addition to allyl derivatives of  $\text{P}(\text{V})$ , viz.  $\text{H}_2\text{C}=\text{CHCH}_2\text{P}(\text{O})(\text{O}-i\text{-Pr})_{2-n}\text{Me}_n$  ( $n = 0, 1$ ), followed

by  $\text{LiAlH}_4$  reduction;<sup>8</sup> (3) free-radical addition of P-H functionalized mono- and bis(phosphines) to an appropriate allylphosphine  $\text{H}_2\text{C}=\text{CHCH}_2\text{PR}_2$ .<sup>9,10</sup> With allyl alcohol, allyl ethers, and allylamines as reactants, the latter method has been used recently also by Meek's group for the synthesis of a variety of  $\text{C}_3$ -linked phosphine ligands containing mixed P,O and P,N donor sets.<sup>4</sup>

In this report we demonstrate how the radical-chain addition of P-H groups across the double bonds of allylphosphines containing two or three  $\text{H}_2\text{C}=\text{CHCH}_2-$  functions can conveniently be exploited for the high-yield synthesis of the hitherto unknown  $\text{P}^3\text{P}$  and



compounds  $\text{MeP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_2$ ,  $\text{MeP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PET}_2)_2$ ,  $t\text{-BuP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_2$ ,  $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ , and  $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PET}_2)_3$ . Due to their completely aliphatic character, these flexible tris(tertiary phosphine) and tripod tetrakis(tertiary phosphine) ligands should be particularly suitable for the preparation of low-valent transition-metal complexes, which then should exhibit increased basicity and, hence, reactivity at the central atom.

### Experimental Section

**General Procedures and Instrumentation.** All manipulations were carried out under nitrogen atmosphere with standard Schlenk tech-

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