

Ge/Sb heteropolyatomic anions, since Ge homoatomic anions like  $\text{Ge}_9^{4-}$  and  $\text{Ge}_9^{2-21}$  and perhaps any mixed anions as well are much less soluble than the polyantimony anions. The situation with  $\text{KAuSb}$  is probably similar.

In closing, it is interesting to speculate whether the unknown  $\text{Bi}_7^{3-}$  ion can be produced. Zintl et al.<sup>22</sup> reported a  $\text{Bi}_7^{3-}$  species from exhaustive extraction of bismuth-rich sodium alloys, but their analytical data are much more appropriate to the composition  $\text{Bi}_4^{2-}$ .<sup>2</sup> It should be noted that they also saw no evidence for  $\text{Sb}_4^{2-}$ , only  $\text{Sb}_3^{3-}$  and  $\text{Sb}_7^{3-}$ .<sup>22,23</sup> Reactions of various

K/Bi alloys with crypt in en have produced only the  $\text{Bi}_4^{2-}$  salt, though various colored solutions have been noted in the course of the reaction.<sup>2</sup> Perhaps the use of Na/Bi alloys or an appropriate ternary composition would facilitate the isolation of a  $\text{Bi}_7^{3-}$  anion analogous to  $\text{Sb}_7^{3-}$ .

Registry No. I, 88524-92-9; II, 88510-57-0;  $\text{KGeSb}$ , 88510-55-8.

**Supplementary Material Available:** Listings of the positional and thermal parameters for all atoms, distances and angles in the crypt cations, and the observed and calculated structure factors for the  $\text{Sb}_4^{2-}$  and  $\text{Sb}_7^{3-}$  salts (37 pages). Ordering information is given on any current masthead page.

(21) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163.

(22) Zintl, E.; Dullenkopf, W. *Z. Phys. Chem., Abt. B* **1932**, *16*, 183.

(23) Zintl, E.; Goubeau, J.; Dullenkopf, W. *Z. Phys. Chem., Abt. A* **1931**, *154*, 1.

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## Rate-Determining $t_{2g}$ - $t_{2g}$ Electron Transfer: Reaction of (3-Formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III) with Titanium(III) and Formation of (Pentane-2,4-dionato)titanium(III)

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The rate constants for the reaction of enol and keto forms of pentane-2,4-dione with  $\text{Ti}^{3+}$  (at 25 °C in 1 M LiCl) are  $2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $0.7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. (3-Formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III) oxidizes  $\text{Ti(III)}$  in a reaction that involves two relaxations with rate constants  $k'_f \approx k[\text{Ti(III)}]h[\text{H}^+]^{-1} + k'$  and  $k'_s \approx 20 \text{ M}^{-1} \text{ s}^{-1}$ , where  $h = [\text{H}^+]/([\text{H}^+] + 0.004 \text{ M})$ ,  $k = 2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k' = 750 \text{ M}^{-1} \text{ s}^{-1}$ . These results are interpreted as indicating rate-determining electron transfer within a deprotonated binuclear intermediate.

Previous work in this laboratory has demonstrated several mechanisms for reactions that involve titanium(III) species as reductants and ruthenium(III) complexes as oxidants. If the  $\text{Ru(III)}$  oxidant contains only ligands (such as  $\text{NH}_3$  and en) that are not good bridging groups, then outer-sphere electron transfer (ET) occurs,<sup>1</sup> with  $\text{TiOH}^{2+}$  acting as reductant. If pentane-2,4-dione, or another electron-delocalizing ligand, is present in the coordination sphere of the oxidant, then outer-sphere ET also involves  $\text{Ti}^{3+}$  as reductant.<sup>2</sup> If the oxidant contains carboxylate, or another effective lead-in group, then an inner-sphere mechanism dominates.<sup>3</sup> In all  $\text{Ru(III)}$ - $\text{Ti(III)}$  inner-sphere reactions studied, formation of the binuclear intermediate is rate determining, through-bridge ET is rapid, and  $\text{Ti}^{3+}$  (rather than  $\text{TiOH}^{2+}$ ) is the reductant. We now report a kinetic study of the formation of (pentane-2,4-dionato)titanium(III) and also of the reaction of  $\text{Ti(III)}$  with (3-formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III). We conclude that ET through the bridging ligand is rate determining for this redox reaction.<sup>4</sup>

### Experimental Section

Methods and reagents were generally as described in previous papers.<sup>1-4</sup> During the course of this study, our stopped-flow spectrophotometers were interfaced to a microcomputer. Earlier data were

stored temporarily in a Biomation transient recorder and permanently as charts of absorbance or transmission vs. time. These data were interpreted by using standard graphical techniques. Later data were recorded on diskettes and interpreted by using BASIC codes. For both sets, rate parameters were accepted if differences between simulation and experiment were comparable to experimental uncertainty.

(3-Formylpentane-2,4-dionato)bis(pentane-2,4-dionato)ruthenium(III) (hereafter  $\text{Ru(fpd)}$ ) was prepared by using procedures similar to those developed by Collman<sup>5</sup> and used by Balahura and Lewis<sup>6</sup> in analogous preparations. Phosphorus oxytrichloride (4.6 mL) was slowly added to 10 mL of freshly distilled dry dimethylformamide (DMF) in a 250-mL round-bottomed flask immersed in an ice bath.  $\text{Tris(pentane-2,4-dionato)ruthenium(III)}$ ,<sup>2</sup> hereafter  $\text{Ru(pd)}_3$  (10 g), in dry freshly distilled DMF was added dropwise with stirring. The reaction mixture was warmed to room temperature and stirred for 4 h. An ice/water slurry of  $\text{NaHCO}_3$  (10.6 g) was slowly added, and the reaction mixture was stirred until effervescence ceased (14 h). Aliquots were evaporated to dryness. Residues were dissolved in anhydrous methanol and passed through silica gel (60-200 mesh) columns, using methanol as eluant. The product moved as a single band; a black powder was obtained by evaporating the solvent from it. The IR spectrum (KBr disks) of the product was similar to that<sup>2</sup> of  $\text{Ru(pd)}_3$ , except for the presence of an additional absorption peak at  $1670 \text{ cm}^{-1}$ , which peak is assigned to the  $\text{C}=\text{O}$  stretch of a carbonyl group in conjugation with the pseudoaromatic ring. A peak at  $1200 \text{ cm}^{-1}$ , assignable to the C-H stretch involving the central carbon of the pd ligand, is present both in the spectrum of the product and also in that of the starting material. The intensity of this peak is less in

(1) (a) Davies, K. M.; Earley, J. E. *Inorg. Chem.* **1978**, *17*, 3350. (b) Iadavia, R.; Earley, J. E. *Inorg. Chim. Acta* **1981**, *53*, L143. (c) Orhanovic, M.; Earley, J. E. *Inorg. Chem.* **1975**, *14*, 1478. (d) Chalilpoyil, P.; Davies, K. M.; Earley, J. E. *Ibid.* **1976**, *16*, 3344. (2) Earley, J. E.; Bose, R. N.; Berrie, B. H. *Inorg. Chem.* **1983**, *22*, 1836. (3) (a) Lee, R. A.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 1739. (b) Adequite, A.; Earley, J. E.; Ojo, J. F. *Ibid.* **1979**, *18*, 1535. (c) Bose, R. N.; Earley, J. E. *Ibid.* **1981**, *20*, 2739. (d) Ali, S. Z.; Chalilpoyil, P.; Earley, J. E. *Inorg. Chim. Acta* **1981**, *48*, 57. (e) Olubuyide, O.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 3569. (4) Berrie, B. H.; Earley, J. E. *J. Chem. Soc., Chem. Commun.* **1982**, 471.

(5) (a) Collman, J. P.; Kittleman, E. T. *J. Am. Chem. Soc.* **1961**, *83*, 3529. (b) Silverstein, R. M.; Ryskiewicz, E. E.; Willard, C. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 831. (c) Collman, J. P.; Marshall, R. L.; Young, W. L., III; Goldby, S. D. *Inorg. Chem.* **1962**, *1*, 704. (d) Collman, J. P. *Adv. Chem. Ser.* **1963**, No. 37, 78. (6) (a) Balahura, R. J.; Lewis, N. A. *J. Chem. Soc., Chem. Commun.* **1976**, 268. (b) Balahura, R. J.; Lewis, N. A. *J. Am. Chem. Soc.* **1977**, *99*, 4716. (c) Balahura, R. J.; Lewis, N. A. *Can. J. Chem.* **1979**, *57*, 1765.

Table I. Rate Constants for the Faster Relaxation during Reaction of  $Ti^{3+}$  with Hpd<sup>a</sup>

[Ti <sup>3+</sup> ], mM	[H <sup>+</sup> ], mM	$k_f$ , s <sup>-1</sup>	$k_f^{calcd}$ , s <sup>-1</sup>
2.0	20	3.5	5
2.0	20	4.7	5
2.0	35	3.1	5.1
2.0	46	3.9	5.2
2.0	58	5.4	5.3
2.0	74	5.5	5.5
2.0	138	4.2	6.0
2.0	150	4.6	6.2
2.0	50	5.0	5.3
4.0	50	10.1	10.1
5.7	50	13.8	14.1
8.0	50	19.1	19.7
10.0	50	24.0	24.5
2.0	250 <sup>b</sup>	4.7	
2.0	320 <sup>b</sup>	5.1	

<sup>a</sup>  $T = 25.0^\circ C$ ,  $I = 1.0 M$  (LiCl),  $[Hpd] = 0.4 mM$ . <sup>b</sup> Not included in evaluation of parameters, since too much of the medium had been replaced by acid for the medium to be considered constant.

the product spectrum than in the reactant spectrum. As in the corresponding rhodium complexes,<sup>5</sup> only one ligand is carboxylated.

Anal.<sup>7</sup> Calcd for  $RuC_{16}H_{21}O_7$ : Ru, 23.71; C, 45.08; H, 4.93. Found: Ru, 23.74; C, 45.11; H, 5.02.

The UV-visible spectrum of Ru(fpd) in 1.0 M LiCl at pH 2.0 shows maxima (nm) as follows (extinction coefficients,  $M^{-1} cm^{-1} \times 0.001$ ): 512 (1.05), 338 (6.16), 220 (14.2). The spectrum varies only slightly between pH 1 and 11. Cyclic voltammograms, obtained by using carbon-paste electrodes described by Adams,<sup>8</sup> gave the reduction potential of Ru(fpd) in 1.0 M LiCl as  $-0.16 V$  vs. NHE, at  $25^\circ C$ , between pH 1 and 3.

Pentane-2,4-dione (Aldrich), hereafter Hpd, was treated with water to remove acetic acid, extracted into toluene, and recovered by fractional distillation under vacuum. When Hpd is added to an acidic LiCl solution that contains Ti(III) in concentrations 30 times larger than that of Hpd, the color of the solution rapidly changes from lilac to red, and new peaks at 395 and 495 nm appear in the absorption spectrum. Final absorbance depends on  $[H^+]$  and on  $[Ti(III)]$  (total analytical concentration). Kinetic measurements were made by following the increase in absorbance at either 395 or 495 nm. Two processes, well-separated in rate, were observed. Pseudo-first-order rate plots for the slower relaxation, which accounted for about 90% of the absorbance increase, were linear for more than four half-times, yielding a rate constant  $k_s$ . If Hpd was freshly distilled, pseudo-first-order rate plots for the faster relaxation were linear for at least two half-times, yielding a rate constant  $k_f$ . In a few experiments that involved Hpd that had not been freshly distilled, curved rate plots indicated a third process of intermediate rate.

When Ti(III) was added to an acidic solution of Ru(fpd) in 1.0 M LiCl, the color changed from pink to yellow, corresponding to the decrease of an absorption peak at 338 nm and increase of a peak at 460 nm. Polarographic titration (dropping mercury electrode at  $-0.7 V$  vs. SCE) showed that 1 mol of Ru(fpd) was consumed for each mole of Ti(III) added. Spectrophotometric titration supported that conclusion. A well-defined isosbestic point at 370 nm was maintained for 15 min but not longer. Loss of the isosbestic is assigned to relatively slow hydrolysis of the initial Ru(II) product.<sup>9</sup> Kinetic data for the more rapid changes were acquired by measuring the increase in absorbance at 440 nm and also at 510 nm. Data were not fitted by a single exponential but were adequately described by a double exponential increase, yielding two rate constants,  $k_f'$  (for the faster relaxation, corresponding to the larger absorbance change) and  $k_s'$  (for the slower relaxation and the smaller absorbance change).

## Results

Under our conditions, the acidity constant of  $Ti^{3+}$  is  $K_a = 4 \times 10^{-3} M^{1c}$  so that  $Ti^{3+}$  is in large excess over  $TiOH^{2+}$ .

Table II. Rate Constants for the Slower Relaxation during Reaction of  $Ti^{3+}$  with Hpd<sup>a</sup>

[Ti <sup>3+</sup> ], mM	[H <sup>+</sup> ], mM	$k_s$ , $10^2 s^{-1}$	$k_s^{calcd}$ , $10^2 s^{-1}$
10	30	38	35
10	50	42	34
10	10	56	35
10	15	35	35
10	10	33	35
8.5	60	35	30
8.5	80	40	29
12	20	42	41
20.1	33	45	65
40	66 <sup>b</sup>	89	
2	10	36	9
2.8	10	33	11
5	10	30	19
7	10	36	25
10	10	34	35
10	184 <sup>b</sup>	57	
10	295 <sup>b</sup>	68	
10	300 <sup>b,c</sup>	57	
10	300 <sup>b,d</sup>	59	
10	300 <sup>b,e</sup>	61	
10	400 <sup>b</sup>	68	

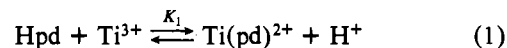
<sup>a</sup>  $T = 25.0^\circ C$ ,  $I = 1.0 M$  (LiCl),  $[Hpd] = 0.4 mM$ . <sup>b</sup> Not included in evaluation of parameters. <sup>c</sup>  $[Hpd] = 0.16 mM$ . <sup>d</sup>  $[Hpd] = 0.16 mM$ . <sup>e</sup>  $[Hpd] = 0.48 mM$ .

Table III. Rate Constants for Reaction of Ru(fpd) with  $Ti(III)^g$ 

[Ti(III)], mM	[H <sup>+</sup> ], mM	$k_f'$ , s <sup>-1</sup>	$k_f'$ (calcd), s <sup>-1</sup>	$k_s'$ , s <sup>-1</sup>
18	31	126	117	21
18	24	151	143	20
18 <sup>a</sup>	69	68	80	23
18	59	81	83	18
18	19	173	175	...
18	38	104	102	...
18 <sup>a</sup>	38	105	102	...
18	18	...	...	22
18	18	...	...	22
18 <sup>a</sup>	18	150 <sup>f</sup>	...	20
38	22	...	...	22
3	22	...	...	23
5	18	64	58	19
5 <sup>a</sup>	18	79	58	18
5	18	129	131	...
12.5	18	124	131	21
12	18	124	126	20
12 <sup>b</sup>	18	77		6
12 <sup>c</sup>	18	114		7
12 <sup>d</sup>	18	140		24
12 <sup>e</sup>	18	...		33

<sup>a</sup> 510 nm. <sup>b</sup> 13°C. <sup>c</sup> 16°C. <sup>d</sup> 27°C. <sup>e</sup> 33°C. <sup>f</sup> Not included in parameter determination. <sup>g</sup>  $10^4 [Ru^{III}fpd]_0 = 2-4 M$ ,  $I = 1.0 M$  (LiCl),  $T = 25^\circ C$ . Wavelength = 440 nm.

Infinite-time absorbance data for the reaction of Ti(III) and Hpd are consistent with equilibrium 1. Plots of the left-hand



side of eq 2 vs.  $([Ti(III)]h + [Hpd]_0)/[H^+]$ , where  $h$  is  $\frac{[Hpd]_0[Ti(III)]h}{\epsilon_{395}[H^+]} = \frac{[Ti(III)]h + [Hpd]_0}{\epsilon_{395}[H^+]} + \frac{1}{\epsilon_{395}K_1}$  (2)

$[H^+]/([H^+] + K_a)$ , gave the extinction coefficient at 395 nm ( $\epsilon_{395}$ ) as  $3.8 \times 10^2 M^{-1} cm^{-1}$  and  $K_1$  as 29 ( $K_1 = [Ti(pd)^{2+}][H^+]/[Ti^{3+}][Hpd]$ ). Values of rate constants for the Hpd-Ti(III) reaction are listed in Tables I and II. The rate of the faster relaxation depends on  $[Ti(III)]$  but is independent of  $[H^+]$ . The slower relaxation does not show clear dependence on  $[Ti(III)]$  or on  $[Hpd]_0$  but becomes somewhat faster at higher acidities.

(7) Elemental analyses by Galbraith Laboratories, Knoxville, TN.

(8) Adams, R. N. "Electrochemistry and Solid Electrodes"; Marcel Dekker: New York, 1969.

(9) Meisel, D.; Schmidt, K. H.; Meyerstein, D. *Inorg. Chem.* 1979, 18, 971.

Table IV. Rates and Formation Constants for Reaction of Hpd with Cations<sup>a</sup>

cation	$k_{\text{ex}}^{\text{a}}$ $\text{M}^{-1} \text{s}^{-1}$	$k_{\text{HK}}^{\text{a}}$ $\text{M}^{-1} \text{s}^{-1}$	$k_{\text{HE}}^{\text{b}}$ $\text{M}^{-1} \text{s}^{-1}$	$K$	ref
Cu <sup>2+</sup>	10 <sup>8</sup>	15	2 × 10 <sup>4</sup>		12
Fe <sup>3+</sup>	10 <sup>3.5</sup>	0.29	5.2	32	10
FeOH <sup>2+</sup>		5.4	4.4 × 10 <sup>3</sup>	0.55	10
VO <sup>2+</sup>	10 <sup>3</sup>	4.4			13
UO <sub>2</sub> <sup>2+</sup>	10 <sup>4</sup>	3.6	5.3 × 10 <sup>3</sup>		13
Ni <sup>2+</sup>	10 <sup>3.5</sup>		19.3	8 × 10 <sup>-4</sup>	12
Ti <sup>3+</sup>	10 <sup>3</sup>	0.7	2.4 × 10 <sup>3</sup>	29	this work

<sup>a</sup>  $T = 25^\circ\text{C}$ ;  $I = 1.0 \text{ M}$ .

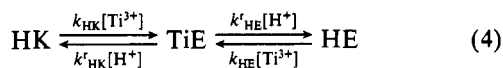
Table III contains data for faster and slower relaxations in the reaction between Ru(fpd) and Ti(III). The faster relaxation is dependent on [Ti(III)] and on  $[\text{H}^+]^{-1}$ . The slower relaxation has a rate constant  $k_s' = 20 \pm 2 \text{ s}^{-1}$ , independent of  $[\text{H}^+]$  and [Ti(III)]. Effective overall activation parameters ( $[\text{H}^+] = 18 \text{ mM}$ , [Ti(III)] = 12 mM) are, for the faster relaxation,  $\Delta H^* = 13 \pm 4 \text{ kJ mol}^{-1}$  and  $\Delta S^* = -160 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$ , and for the slower relaxation,  $\Delta H^* = 61 \pm 2 \text{ kJ mol}^{-1}$  and  $\Delta S^* = -20 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$ .

### Discussion

Hpd exists as both the enol (hereafter HE) and keto (hereafter HK) tautomers in aqueous solutions (eq 3).



Fay, Nichols, and Sutin<sup>10a</sup> report that  $[\text{HE}]/[\text{HK}]$  is 0.13 (in 1.0 M LiClO<sub>4</sub>, independent of acidity). The overall equilibrium constant ( $K_1 = 29$ ) can be partitioned into  $K_1 = 32$  (HK reactant) and  $K_e = 250$  (HE reactant). Formation of the Ti(III) complex from Hpd is faster than enolization of HK but slower than deprotonation of HE.<sup>11</sup> The faster relaxation corresponds to formation of  $\text{Ti}(\text{III})\text{pd}^{2+}$  from HE, and the slower relaxation to reaction of HK to form the same complex.



Neglecting (3), it follows<sup>12</sup> that

$$k_s = \frac{(k_{\text{HK}}k'_{\text{HE}} + k'_{\text{HK}}k_{\text{HE}})[\text{H}^+][\text{Ti(III)}] + k_{\text{HK}}k_{\text{HE}}[\text{Ti(III)}]}{(k'_{\text{HK}} + k'_{\text{HE}})[\text{H}^+] + (k_{\text{HK}} + k_{\text{HE}})[\text{Ti(III)}]} \quad (5)$$

$$k_f = (k'_{\text{HK}} + k'_{\text{HE}})[\text{H}^+] + (k_{\text{HK}} + k_{\text{HE}})[\text{Ti(III)}] - k_s \quad (6)$$

or, more approximately

$$k_s = k_{\text{HK}}[\text{Ti(III)}] + k'_{\text{HK}}[\text{H}^+] \quad (7)$$

$$k_f = k_{\text{HE}}[\text{Ti(III)}] + k'_{\text{HE}}[\text{H}^+] \quad (8)$$

A plot of  $k_f$  against [Ti(III)] gave  $k_{\text{HE}} = 2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $k'_{\text{HE}} \leq 30 \text{ M}^{-1} \text{ s}^{-1}$ . Values of  $k_f^{\text{calcd}}$  listed in Table I are calculated by using 5 and 6 and  $k_{\text{HE}} = 2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k'_{\text{HE}} = 7 \text{ M}^{-1} \text{ s}^{-1}$ . Values of  $k_s^{\text{calcd}}$  shown in Table II were calculated from eq 11 of ref 10a, which takes account of reaction 3, with  $k_e = 0.015 \text{ s}^{-1}$ ,  $k_f = 0.114 \text{ s}^{-1}$ ,  $k'_{\text{HK}} = 2.4 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_{\text{HK}} = 0.7 \text{ M}^{-1} \text{ s}^{-1}$ .

- (10) (a) Fay, D. P.; Nichols, A. R., Jr.; Sutin, N. *Inorg. Chem.* **1971**, *10*, 2096. (b) Jaffe, M. R.; Fay, D. P.; Cefola, M.; Sutin, N. *J. Am. Chem. Soc.* **1971**, *93*, 2878.  
 (11) Eigen, M.; Kruse, W.; Maass, G.; DeMaeyer, L. In "Progress in Reaction Kinetics"; Porter, G., Ed.; Pergamon Press: Oxford, 1964.  
 (12) (a) Pearson, R. G.; Anderson, O. P. *Inorg. Chem.* **1970**, *9*, 39. (b) Pearson, R. G.; Moore, J. W. *Inorg. Chem.* **1966**, *5*, 1523.  
 (13) (a) Hynes, M. J.; O'Regan, B. D. *J. Chem. Soc., Dalton Trans.* **1980**, *7*. (b) Hynes, M. J.; O'Regan, B. D. *Proc. R. Ir. Acad., Sect. B* **1977**, *77B*, 285. (c) Hynes, M. J.; O'Regan, B. D. *J. Chem. Soc., Dalton Trans.* **1979**, 162. (d) Hynes, M. J.; O'Shea, M. T. *Ibid.* **1983**, 331.

Table IV shows that rate constants for substitution of HK are consistently lower than rates of water exchange on the same metal ion and remarkably similar from one metal to another. This has been taken to imply rapid formation of a bidentate ketone complex and rate-determining removal of a proton from the coordinated diketone by solvent or another base.<sup>11</sup> (Lack of the HK path for nickel is attributed to low stability of the precursor complex.) Values of  $k_{\text{HE}}$  for Cu<sup>2+</sup>, FeOH<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, and Ti<sup>3+</sup> are all close to 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> (less than water-exchange rate constants). Substitution of the first ligand oxygen onto the metal ion is rapid, but closure of the six-member chelate ring<sup>19</sup> is rate determining. (Slower values of  $k_{\text{HE}}$  for Fe<sup>3+</sup> and for Ni<sup>2+</sup> indicate a metal-dependent rate-determining process.) Our results are consistent with a ring-closure-limited mechanism. The rate constant for substitution of HE onto Ti<sup>3+</sup> is  $\geq 2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

Both<sup>10,11</sup> for Fe<sup>3+</sup> and for VO<sup>2+</sup>,  $k_{\text{HE}}$  decreases at higher acidity. Jaffe, Fay, Cefola, and Sutin<sup>10b</sup> interpret this to indicate that substitution of HE on FeOH<sup>2+</sup> is 10<sup>3</sup> times faster than the same reaction involving Fe<sup>3+</sup>. Chaudhuri and Diebler<sup>14a</sup> found no significant contribution to the overall rate from an inverse-acid term for the reaction of oxalic acid with Ti(III). They concluded that substitution on TiOH<sup>2+</sup> is not more than 5 times faster than substitution on Ti<sup>3+</sup>. Sasaki and Sykes<sup>15</sup> reached a similar conclusion. Our work on substitution-limited inner-sphere Ru(III)-Ti(III) reactions<sup>3</sup> also indicates that Ti(III) substitution reactions go through Ti<sup>3+</sup> rather than through TiOH<sup>2+</sup>. Our present data do not require that  $k_{\text{HE}}$  be acid dependent.

Rates of outer-sphere Ru(III)-Ti(III) reactions depend on the reduction potential of the oxidant.<sup>1a</sup> The reduction potential we report for Ru(fpd) is quite similar to that previously measured<sup>2</sup> for Ru(pd)<sub>3</sub>. Rates of outer-sphere ET for these two oxidants with a single reductant should be similar. Rate constants for the redox reaction between Ru(fpd) and Ti(III) are  $>10^3$  faster than rate constants measured for the corresponding Ti(III) reduction of Ru(pd)<sub>3</sub>.<sup>2</sup> We infer that the reaction of Ti(III) with Ru(fpd) is not outer-sphere ET but rather that it follows an inner-sphere mechanism with carbonyl as the lead-in group. The geometry of the binuclear intermediate makes "through-space" ET improbable. The low reducing power of Ti(III) renders a "radical-ion" mechanism (reduction of the bridging ligand) unlikely.

The "intrinsic" barrier to Ru<sup>II</sup>-Ru<sup>III</sup> self-exchange<sup>20</sup> is low; that for Ti(III)-Ti(IV) is also small.<sup>1d,21b</sup> Oxidation of Ti(III) at electrodes is rapid, but reduction of Ti(IV) is irreversible.<sup>21</sup> Once ET to form Ti(IV) occurs, the reverse reaction is blocked by the rapid subsequent rearrangement (deprotonation and polymerization) of Ti(IV). The net rate of the Ru(III)-Ti(III) redox reaction is rapid, even though the overall driving force is low.

Base catalysis of the redox reaction is extraordinary. Prior

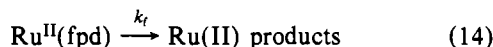
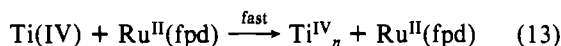
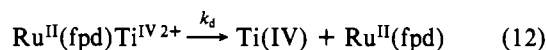
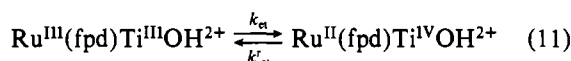
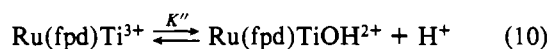
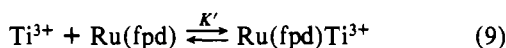
- (14) (a) Chaudhuri, P.; Diebler, H. *J. Chem. Soc., Dalton Trans.* **1977**, 596. (b) Diebler, H. *Z. Phys. Chem. (Wiesbaden)* **1969**, *68*, 64. (c) Diebler, H. Paper S-13, XVI International Conference on Coordination Chemistry, Dublin, 1974, and personal communication.  
 (15) Sasaki, Y.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1048.  
 (16) (a) Chmelnick, A. N.; Fiat, D. *J. Chem. Phys.* **1969**, *51*, 4238. (b) Charles, H. L., Jr., Thesis, University of California, Berkeley, 1971.  
 (17) (a) Fiat, D.; Connick, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 608. (b) Hunt, J. P.; Plane, R. A. *J. Am. Chem. Soc.* **1954**, *74*, 5960.  
 (18) Wroblewski, J. T.; Brown, D. B. *Inorg. Chim. Acta* **1980**, *38*, 227.  
 (19) Kustin, K.; Pasternak, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 2805.  
 (20) (a) Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 1522. (b) Bernhard, P.; Buerger, H. B.; Hauser, J.; Lehmann, H.; Ludi, A. *Ibid.* **1982**, *21*, 4341.  
 (21) (a) Pecsok, R. L.; Fletcher, A. N. *Inorg. Chem.* **1962**, *1*, 155. (b) Brunschwig, B. S.; Sutin, N. *Ibid.* **1979**, *18*, 1731. (c) See ref 3a.  
 (22) C. F. Hammer has found that the chemical shift for the carbonyl deuterium in pyridoxal in D<sub>2</sub>O is significantly less than that of the same compound in CDCl<sub>3</sub> (8.1 ppm/9.8 ppm), a clear indication of extensive hydration in the former solvent (personal communication, 1983).

Table V. Rate Constants for Substitution on  $Ti^{3+}$  <sup>a</sup>

ligand	$k$ , $M^{-1} s^{-1}$	ref
$C_2O_4^{2-}$	$2.8 \times 10^6$	14a
$HC_2O_4^-$	$4 \times 10^5$	14b
$SCN^-$	$8 \times 10^3$	14c
$CH_3COO^-$	$2 \times 10^6$	14c
$CCl_2HCOO^-$	$2 \times 10^5$	14c
$CCl_2HCOO^-$	$6 \times 10^4$	14c
$CH_3COOH$	$1.1 \times 10^3$	14c
Hpd (HE)	$\geq 2.4 \times 10^3$	this work
$H_2O$	$10^5$	17, 16
$Ru(NH_3)_5ox^+$	$2.5 \times 10^4$ <sup>b</sup>	3a
$Ru(NH_3)_4ox^+$	$3.6 \times 10^4$ <sup>b</sup>	3a
$Ru(NH_3)_5OAc^{2+}$	$7 \times 10^2$ <sup>b</sup>	3a
$Ru(NH_3)_5NCS^{2+}$	$8 \times 10^2$ <sup>b</sup>	3b
$Ru(NH_3)_5sal^{2+}$	$6.3 \times 10^2$ <sup>b</sup>	3c

<sup>a</sup>  $T = 25^\circ C$ .  $I = 1.0 M$ . <sup>b</sup> Rate of redox reaction taken to be substitution limited.

examples of inner-sphere Ru(III)-Ti(III) ET have been acid independent. A possible mechanism for the faster relaxation involves the formation of a binuclear intermediate from  $Ti^{3+}$  and Ru(fpd) and subsequent rate-determining ET within the conjugate base of that intermediate. (This mechanism operates in a number of Co(III)-Ti(III) reactions.<sup>3d,e</sup>)



If the first two steps of this mechanism reach equilibrium relatively rapidly, then<sup>23</sup>

$$k_f' \cong k_{et}K'K'' [Ti(III)]h[H^+]^{-1} + k_{et}^r \quad (15)$$

$$k_s' \cong k_d \quad (16)$$

where  $h = ([H^+]/[H^+] + 0.004 M)$ . These equations and  $k_{et}K'K'' \cong 2 \times 10^2 M^{-1} s^{-1}$  and  $k_{et}^r = 750 M^{-1} s^{-1}$  were used to compute  $k_{et}^{calc}$  in Table IV. On the basis of the acidity of  $Ti^{3+}$  we take  $0.01 M > K'' > 0.001 M$ . From the data shown in Table IV we infer that  $K' \leq 1 M^{-1}$ . Thus  $k_{et} \geq 10^4 s^{-1}$ . The slower relaxation corresponds to a Ti(IV) substitution reaction. The value  $20 s^{-1}$  is quite slow for such a process. The eventual loss of the isosbestic would then correspond to decomposition of the Ru(II) product, as is observed in the related simpler reactions.

An alternative, and more direct, interpretation<sup>4</sup> is that the faster relaxation represents formation of the binuclear complex from  $TiOH^{2+}$  and Ru(fpd). On this basis, formation of the binuclear complex by substitution on  $TiOH^{2+}$  has a rate constant  $>10^5 M^{-1} s^{-1}$  and this substitution reaction of  $TiOH^{2+}$  is  $>10^2$  times faster than the corresponding reaction of  $Ti^{3+}$ . On this basis the slower relaxation corresponds to intramolecular ET with a rate constant of  $20 s^{-1}$ .

There is no precedent for base catalysis in the literature for Ti(III) substitution reactions, including our data on the Ti(III)-Hpd reaction. Table V shows that there is substantial variation in Ti(III) substitution rates, depending both on the charge of the nucleophile and on its structure. As noted above,

Ti(III) substitution reactions show less tendency for base catalysis than do Fe(III) reactions.<sup>15</sup> Chmelnick and Fiat, and also Charles, report<sup>16</sup> that the enthalpy of activation for water exchange on  $Ti^{3+}$  is about one-quarter of that for water exchange<sup>17</sup> on  $Al^{3+}$  or  $Cr^{3+}$ . Entropies of activation for water exchange on  $Cr^{3+}$  and  $Al^{3+}$  are large and positive, but that for  $Ti^{3+}$  is negative. Seven-coordinate Ti(III) species are known in solids.<sup>18</sup> All of this indicates associative character for  $Ti^{3+}$  substitution reactions.

The tendency of ketones conjugated with electron-withdrawing groups to hydration,<sup>22</sup> together with associative character in Ti(III) substitution reactions, might rationalize the unusual acid dependence of this reaction. Attack of hydroxyl oxygen on carbon could assist the associative reaction of carbonyl oxygen with titanium, through a four-center structure involving four-coordinate carbon.

On the basis of either of the overall mechanisms considered above, the rate of ET through bridging fpd is slower than that of ET through bridging thiocyanate, acetate, oxalate, or salicylate ions.<sup>3</sup> This is the first report of a ligand that is moderately efficient at mediating electron translation between  $t_{2g}$  orbitals. There is a vast literature on Ru(II)-Ru(III) mixed-valence dimers, but only one successful ET rate measurement.<sup>24</sup> Ru(III)-V(III) redox reactions have measurable rates, but these are dominated by non-redox rate-determining steps<sup>25</sup>.

To the extent that they are sensitive to the magnitude of the interaction between product and reactant states, rates of through-bridge electron transfer should depend on the same factors that control magnetic interaction and energies and overlap of interacting orbitals. There is no evidence that the energies of the LUMO of Ru(fpd) and  $Ru(NH_3)_5OOCCH_3^{2+}$  differ greatly. Szecsy and Haim<sup>26</sup> report that the rates of intramolecular ET are inversely proportional to the distance between metal centers. This effect seems large enough to rationalize our result if electron transfer is involved in the faster relaxation but not if ET is involved with the second relaxation. Carboxylate ions provide an effective path for magnetic exchange between Ti(III) ions,<sup>18</sup> but not for Fe(III) ions.<sup>27</sup> The C-O stretching frequency that we observe indicates that the carbonyl group is in conjugation with the ring, so that at least moderate cross-bridge interaction would be expected in the binuclear Ru/Ti intermediate. A direct explanation of slow ET is that the  $J$  value for fpd is low relative to that of carboxylate, but still large enough to give the IR spectrum observed. If reaction 10 is replaced by a reaction between  $TiOH^{2+}$  and Ru(fpd) to form a binuclear complex containing a hydrated ketone, then dehydration of the intermediate would influence  $k_{et}$ .

Balahura and Lewis<sup>6</sup> found that replacing CHO by C(C-H<sub>3</sub>)O in the Co(III) analogue of Ru(fpd) causes a 200-fold decrease in the rate of inner-sphere reduction by Cr(II). They ascribe most of this decrease to the steric hindrance of the coplanarity of the lead-in group and the ring. Patterns of bridge efficiency in redox reactions indicate that  $\pi$ -orbital effects are relatively more important in Ru(III)-Ti(III) reactions than in Co(III)-Cr(II) reactions.<sup>3a,d</sup> The best explanation of the barrier to through-bridge ET is the steric hindrance of the coplanarity of the coordinated carbonyl and the six-membered ring in the binuclear intermediate (contact

(23) (a) Castellan, G. W. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 898. (b) Bernasconi, C. E. "Relaxation Kinetics"; Academic Press: New York, 1976.

(24) Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T. L.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 5442.

(25) (a) Kristine, F. J.; Gard, D. R.; Shepherd, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 994. (b) Kristine, F. J.; Shepherd, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 4398. (c) Kristine, F. J.; Shepherd, R. E. *Inorg. Chem.* **1981**, *20*, 215. (d) Glennon, C. S.; Edwards, J. D.; Sykes, A. G. *Ibid.* **1977**, *16*, 1654.

(26) Szecsy, A. P.; Haim, A. *J. Am. Chem. Soc.* **1981**, *103*, 1679.

(27) Anderson, F.; Buckingham, D. A. *J. Inorg. Biochem.* **1982**, *16*, 21.

between methyl groups of the ligand and the coordination sphere of Ti(III)). Activation parameters are consistent with this interpretation.

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**Registry No.** Ru(fpd), 76790-97-1; Ti, 7440-32-6; Hpd, 123-54-6.

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## Metal-Assisted, Facile Syntheses of Chelating Triphosphine Ligands on Platinum(II)<sup>1</sup>

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Chelated unsymmetrical triphosphine ligands of the type  $R_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PR'_2$  and  $R_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2PR'_2$  ( $R = R' = C_6H_5$ ;  $R = R' = C_6H_{11}$ ;  $R = C_6H_{11}$ ,  $R' = C_6H_5$ ) can be synthesized rapidly on platinum by  $Et_3N$ -catalyzed condensation of simpler phosphine units onto a coordinated secondary phosphine. The resulting  $[PtCl(triphos)]X$  ( $X = Cl, AsF_6$ ) complexes are characterized by elemental analyses and by  $^1H$ ,  $^{31}P$ , and  $^{195}Pt$  NMR spectroscopy. For those complexes that contain a five-membered chelate ring, the  $^{195}Pt$   $\delta$  values are shifted to higher fields, whereas the  $^{31}P$   $\delta$  values are shifted to lower fields, when compared with analogous phosphino groups in six-membered chelate rings.

### Introduction

During the past 20 years, tremendous interest and research activity has been expanded on transition-metal complexes of polydentate ligands. Particularly, the syntheses of the tetradentate "tripod-like" ligands of the type



by the research groups of Venanzi,<sup>2</sup> Meek,<sup>3</sup> and Sacconi<sup>4</sup> in the 60s and early 70s depended on Grignard or alkali-metal organophosphide reagents. However, complete variation of the donor groups A, B, C, and D, as well as the length of the connecting chain, was limited by the availability and stability of the appropriate organic halides. During the 70s the research groups of King<sup>5</sup> and Meek<sup>6</sup> developed two valuable alternatives for general syntheses of polydentate ligands containing ethylene chains, i.e., the base- and radical-catalyzed addition of P-H, As-H, and S-H across the double bond of a vinyl group. Thus, by choosing the appropriate route and reagents, one can now "tailor-make" polydentate ligands to incorporate just about any electronic and/or steric effect desired.<sup>7</sup> However, the

practical problem of purification of the ligand, often a high-boiling oil, still exists, particularly if the ligand has been constructed from 3-4 fragments.

Triphosphine ligands that contain trimethylene chains are valuable chelating ligands with the larger transition-metal ions (e.g., Rh, Pt, Ir, Ru),<sup>8</sup> and such ligands are becoming increasingly important in the areas of catalysis, asymmetric synthesis, and organometallic stereochemistry.<sup>7,9</sup> In an effort to develop easier routes to a wide variety of  $R_2P(CH_2)_n(R')P(CH_2)_mPR''_2$  ligands ( $n = 1-4$ ,  $m = 2,3$ ), we have examined metal-assisted coupling of vinyl-, allyl-, and (3-chloropropyl)phosphine units to coordinated secondary phosphines.<sup>10</sup> This report describes the successful, high-yield syntheses of five triphosphine ligands, including two new ones, on platinum.

### Results and Discussion

Symmetric triphosphine ligands such as  $PhP(CH_2CH_2CH_2PPh_2)_2$  (ttp) and  $PhP(CH_2CH_2PPh_2)_2$  (etp),<sup>11</sup> which have been used by our research group for several years, have previously been synthesized via coupling reactions between alkali-metal phosphides (e.g.,  $Li_2PPh$ ) and chloroalkylphosphines or by the radical addition of a P-H bond

- (1) Condensed in part from: Waid, R. D. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1982.
- (2) Venanzi, L. M. *Angew. Chem.* **1964**, *76*, 621-628; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 453-460.
- (3) (a) Benner, G. S.; Hatfield, W. E.; Meek, D. W. *Inorg. Chem.* **1964**, *3*, 1544-1549. (b) Dyer, G.; Meek, D. W. *Ibid.* **1965**, *4*, 1398-1402. (c) McAuliffe, C. A.; Meek, D. W. *Inorg. Chim. Acta* **1971**, *5*, 270-272; (d) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076-3083.
- (4) (a) Sacconi, L., *Coord. Chem. Revs.* **1972**, *8*, 351-367. (b) Sacconi, L. *J. Chem. Soc. A* **1970**, 248-256. (c) Morrassi, R.; Bertini, I., Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343-402.
- (5) (a) King, R. B. *Acc. Chem. Res.* **1972**, *5*, 177-185. (b) King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 53-60. (c) King, R. B.; Bakos, J.; Hoff, C. D.; Marko, L. *J. Org. Chem.* **1979**, *44*, 3095-3100.
- (6) (a) DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc. Dalton Trans.* **1975**, 1011-1015. (b) Uriarte, R.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79-85. (c) Uriarte, R. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1978.
- (7) Meek, D. W. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L., Ed.; Plenum Press: New York, 1983; Chapter 8.

- (8) Mason, R.; Meek, D. W. *Angew. Chem.* **1978**, *90*, 195; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183. (b) Mazanec, T. J.; Meek, D. W. *Acc. Chem. Res.* **1981**, *14*, 266.
- (9) (a) Unruh, J. D.; Wells, W. J., III U.S. Patent 4,138,420, 1979. (b) Unruh, J. D.; Wade, L. E. U.S. Patent 4,139,565, 1979. (c) Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19.
- (10) (a) Waid, R. D. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1982. (b) Waid, R. D.; Meek, D. W., *Organometallics*, **1983**, *2*, 932 (ligand syntheses assisted by rhodium complexes). (c) Noble, R. L., unpublished data on ligand syntheses assisted by palladium complexes.
- (11) The ligand abbreviations ttp and etp were derived from the lengths of the alkyl chains connecting the phosphorus atoms, i.e., trimethylene- and ethylenetriphosphine, respectively. The nonsymmetric triphosphine  $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$  is then abbreviated etpt. The secondary diphosphine  $(C_6H_5)_2PCH_2CH_2CH_2P(Ph)H$  is abbreviated ppH; analogously,  $(C_6H_{11})_2PCH_2CH_2CH_2P(Ph)H$  is labeled cypH. The other unsymmetrical triphosphine ligands are shown by the formulas that specify the length of the connecting chain in abbreviated form, i.e.,  $PC_3P$  and  $PC_2P = (CH_2)_3$  and  $(CH_2)_2$  connectors, respectively.