Tables S-1 to S-3. Detailed kinetic data for redox reactions.

S-1

Table S-1. Reduction of $[(NH_3)_5Co(C_2O_4)]^+$ by titanium(II): kinetic data[a]

$[Co^{III}]$, mM	[Ti(II)], mM	$[H^+]$, M	10^2k_2, s^{-1} [b]
0.60	40	0.50	7.8 (7.2)
0.80	30	0.50	5.1 (5.4)
0.90	25	0.50	4.9 (4.5)
1.00	20	0.50	3.4 (3.6)
0.60	15.0	0.50	2.5 (2.7)
1.40	8.0	0.50	1.32 (1.44)
1.00	8.0	0.20	9.2 (9.0)
1.00	8.0	0.30	3.2 (4.0)
1.40	8.0	0.40	1.91 (2.25)
1.50	8.0	0.60	0.85 (1.00)
1.50	8.0	0.70	0.78 (0.73)

[a]Reactions at 22 °C, μ = 1.0 M (CF_3SO_3H/CF_3SO_3Na), λ = 504 nm. [b]First order rate constants; parenthetical values were obtained calculated from eq. (4) in text, taking $\underline{k}$ as 0.45 Ms^{-1}.

Table S-2. Reductions of $[(NH_3)_5BrCo]^{2+}$ by Ti(II) as catalyzed by Ti(IV). Initial rates.[a]

[Ti(II)], mM	[Ti(IV)], mM	$[H^+]$, M	10^6(rate), Ms^{-1} [b]
40	40	0.70	11.0 (13.4)
25	25	0.70	5.3 (5.3)
20	20	0.70	3.8 (3.4)
16.0	16	0.70	2.6 (2.2)
12.0	12.0	0.70	1.5 (1.2)
12.0	24	0.70	2.4 (2.4)
12.0	36	0.70	3.6 (3.6)
12.0	48	0.70	4.5 (4.8)
12.0	60	0.70	5.7 (6.1)
12.0	72	0.70	7.6 (7.3)
25	25	0.40	5.5 (5.3)
25	25	0.60	4.9 (5.3)
25	25	0.90	4.7 (5.3)

[a]Reactions at 22 °C, μ = 1.0 M ($NaClO_4/HClO_4/CF_3SO_3H$); λ = 551 nm. [Co(III)] = 1-2 mM. [b]Initial rates; parenthetical values obtained from rate law (5), taking *k* as 8.4×10^{-3} $M^{-1}s^{-1}$.

Table S-3. Reductions of $[(NH_3)_5CoI]^{2+}$ by Ti(II) as catalyzed by Ti(IV). Initial rates[a]

[Co(III)], mM	Ti(II)], mM	[Ti(IV)], mM	$[H^+]$, M	10^6(rate), Ms^{-1} [b]
3.2	25	25	0.70	5.6 (5.6)
4.0	20	20	0.70	4.3 (3.6)
2.6	16.0	16.0	0.70	2.1 (2.3)
0.70	12.0	12.0	0.70	1.5 (1.3)
2.8	12.0	24	0.70	3.2 (2.6)
2.2	12.0	36	0.70	4.6 (3.9)
1.70	12.0	48	0.70	5.2 (5.2)
1.70	12.0	60	0.70	6.7 (6.5)
1.70	12.0	72	0.70	7.7 (7.8)
0.50	32	32	0.20	7.0 (9.2)

[a]Reactions at 22 °C, μ = 1.0 M ($NaClO_4/HClO_4/CF_3SO_3H$); λ = 580 nm. [b]Initial rates; parenthetical values were obtained from rate law (5), taking $\underline{k}$ as 9.0 x 10^{-3} $M^{-1}s^{-1}$.