electron rather than atom transfer) can be retarded by reducing the accessibility of the π orbitals which accommodate the unpaired electron and that this might be accomplished by attachment of bulky substituents on the ring or by incorporating this ring into a larger structure of limited flexibility. Whether such structural modifications might selectively minimize destructive radical–radical interactions without proportionately retarding the desired reactions of the catalyst with the primary reaction centers remains to be seen.

The present study also points to significant differences in the ease with which the several catalyst radicals undergo further reduction. Those isonicotinate catalysts which, in our hands, exhibit essentially no deterioration have potentials very close to that of isonicotinamide[14a] and thus yield about the same concentrations of their radicals under comparable catalytic conditions. Their longevity in use must therefore be attributed to lower k_{rd} values, the specific rate for reductive deterioration (eq 5). Since the latter reaction requires two protons, it may be that this difference reflects, at least in part, the difficulty with which the esters and nitrile undergo diprotonation in comparison to the more basic amide. Further pursuit of this point is desirable.

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Registry No. I, 55-22-1; II, 72121-34-7; III, 499-80-9; IV, 536-20-9; V, 72121-35-8; isonicotinamide, 1453-82-3; ethyl isonicotinate, 1570-45-2; glyceryl triisonicotinate, 72121-36-9; 4-cyanopyridine, 100-48-1; 2-carboxy-4-(carbomethoxy)pyridine, 24195-03-7; *N*-methylisonicotinic acid, 824-77-1; *N*-methyl-2,4-pyridinedicarboxylic acid, 62778-02-3; dimethyl 2,4-pyridinedicarboxylate, 881-86-7; $(NH_3)_5Co(py)^{3+}$, 31011-67-3; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3.

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Electron-Transfer Reactions of Copper(I) and Copper(III) Complexes

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The reactions of bis(2,9-dimethyl-1,10-phenanthroline)copper(I), $Cu^{I}(dmp)_2^{+}$, and of bis(2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonate)cuprate(I), $Cu^{I}(dpmp)_2^{3-}$, with copper(III)–oligopeptide complexes are quite rapid with rate constants varying from 2×10^4 M^{-1} s^{-1} to 2.5×10^8 M^{-1} s^{-1}, indicating that outer-sphere electron transfer occurs. The cross exchange rate constants, k_{12}, for the reactions Cu^{III}(peptide) + $Cu^{I}L_2 \xrightarrow{k_{12}} Cu^{II}$(peptide) + $Cu^{II}L_2$, where L is dmp or $dpmp^{2-}$, are determined for a series of copper(III) peptides, where the E°_{12} values vary from −0.11 to +0.32 V. The values of k_{12} for the reduction of copper(III) by $Cu^{I}(dmp)_2^{+}$ exhibit a correlation with E°_{12} consistent with the Marcus theory. This is not the case for the reductions with $Cu^{I}(dpmp)_2^{3-}$, which have unusual behavior in two regards. First, the observed first-order rate constants reach limiting values as the concentration of excess reductant increases, but limiting values are not observed if Cu(III) is used in excess. Second, the k_{12} rate constants (obtained under conditions where the rate depends on both the Cu(III) and the Cu(I) concentrations) approach a limiting value of 10^6 M^{-1} s^{-1} and are independent of E°_{12}. Neither anomalous behavior is observed for the $Cu^{I}(dmp)_2^{+}$ reactions with Cu(III) complexes.

Introduction

The study of the aqueous chemistry of the copper(I) ion is severely limited by the disproportionation equilibrium[1] eq 1.

$$2Cu^{I} \rightleftarrows Cu^{II} + Cu^{0} \quad (1)$$

Metastable solutions of aquocopper(I) can be prepared only in highly acidic media.[2] The redox kinetics of this ion with iron(III),[3] vanadium(IV),[4] cobalt(III)[5], and mercury(II)[6] appear to follow inner-sphere mechanisms.

A number of ligands form strong complexes with the copper(I) ion[7] and may be used to prevent disproportionation. Among the better characterized of these copper(I) complexes are derivatives of 1,10-phenanthroline (phen). Several spectroscopic[8,9] and thermodynamic[10,11] studies have been reported. More recently,[12,13] the kinetics of redox reactions involving these complexes have been studied and there appears to be serious disagreement in the calculated self-exchange rate constants for $Cu^{II,I}(phen)_2^{2+,+}$ evaluated from different cross reactions. Holwerda and co-workers[12] report a value of 5×10^7 M^{-1} s^{-1} while Yandell[13] reports a value of 68 M^{-1} s^{-1}. Yandell also reports values of 1.7×10^4 and 4.4×10^4 M^{-1} s^{-1} for the $Cu^{II,I}(dmp)_2^{2+,+}$ self-exchange rate constant evaluated from studies of the reduction of $Cu^{II}(dmp)_2^{2+}$ by cytochrome *c* and $Co^{II}(phen)_3^{2+}$, respectively.[13]

Oligopeptide complexes of copper(III) have been prepared and UV–visible[14,15] and circular dichroism[16] spectroscopic properties and potentiometric behavior[15] have been investigated. Spectroscopic and kinetic properties of copper(III)–peptide complexes strongly suggest that they are square planar with structures typified by that of the triglycinamide complex (structure I). The reduction potentials of the copper(III)–oligopeptide complexes are sensitive to the nature of the lig-

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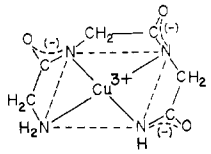

I

and[15] and span a range from 1.02 to 0.45 V. This permits investigation of the rate of reduction of copper(III) complexes over a wide range of free energy changes. Previous studies involving $IrCl_6^{3-}$[17] and $Co(phen)_3^{2+}$[18] as reductants for copper(III)–peptide complexes have been reported.

In the present work, the rates of reactions of the type shown in eq 2 are examined for L = $dpmp^{2-}$ and dmp. The rates of

$$Cu^{III}(peptide) + Cu^{I}L_2 \xrightarrow{k_{12}} Cu^{II}(peptide) + Cu^{II}L_2 \quad (2)$$

reactions of copper(III)–peptide complexes with $Cu^{I}(dmp)_2^{+}$ increase as redox potential, E°_{12}, is increased. On the other hand the reactions of copper(III)–peptide complexes with $Cu^{I}(dpmp)_2^{3-}$ exhibit unusual kinetic behavior.

Experimental Section

Chromatographically pure oligopeptides were obtained from Biosynthetika and Fox Chemical Co. Abbreviations for the peptides and their copper(III) complexes and the reduction potentials of the complexes are listed in Table I. Stock solutions of metal perchlorates were made by neutralizing the corresponding metal carbonates with $HClO_4$. Solutions of copper(II) oligopeptides were prepared by the reaction of $Cu(ClO_4)_2$ with the peptides in 5% excess. The pH was adjusted to form the fully deprotonated complex by using NaOH, and the ionic strength was raised to 0.1 M by using an appropriate supporting electrolyte.

Solutions of copper(III) oligopeptides were prepared by electrochemical oxidation using a flow system[19] with a graphite-powder working electrode packed in a porous-glass column and wrapped externally with a platinum wire auxiliary electrode. In general, the fully deprotonated copper(II) complex was oxidized at a potential 0.2 V above its E° value. The oxidized complex was collected in the dark in acetate or 2-(*N*-morpholino)ethanesulfonate buffer (pH 3.5–6) and used immediately.

Solutions of $Cu^{II}(dpmp)_2^{2-}$ were prepared by the addition of 2.2:1 $dpmp^{2-}$ (disodium salt, G. F. Smith Co.) to a solution of $Cu(ClO_4)_2$. Solutions of the copper(II) complex were partially reduced (25–90%) with sodium bisulfite (Baker Analyzed Reagent) at pH 5 to give $Cu^{I}(dpmp)_2^{3-}$. The solutions were standardized spectrophotometrically with a Cary 14 spectrophotometer (ϵ_{483} 12 250 M^{-1} cm^{-1}).[20] Solutions of $Cu^{I}(dmp)_2^{+}$ were prepared by addition of a 2.2:1 ratio of dmp to a solution of copper(II) acetate followed by stoichiometric reduction by ascorbic acid.

The kinetics of reduction of the copper(III)–peptide complexes were generally monitored at the absorption maxima of copper(III) complex at 365 nm. A Durrum stopped-flow spectrophotometer interfaced to a Hewlett-Packard 2115A general purpose computer was used for reactions with rate constants less than 10^7 M^{-1} s^{-1}.[21] Stopped-flow reactions were run under pseudo-first-order conditions with at least a tenfold excess of the reactants at 25.0 ± 0.1 °C in 0.005 M acetate or 2-(*N*-morpholino)ethanesulfonate buffer pH 3–6. For reactions with rate constants greater than 10^7 M^{-1} s^{-1} a pulsed-flow instrument[22,23] was used to measure the rates under second-order conditions.

Table I. Oligopeptides,[a] Copper(III) Complexes, and Their Reduction Potentials[16] Used in This Study (25.0 °C, μ = 0.10 M)

peptide	complex	E°, V vs. NHE
V_4	$Cu^{III}(H_{-3}V_4)^-$	0.51
A_4	$Cu^{III}(H_{-3}A_4)^-$	0.60
PG_2a	$Cu^{III}(H_{-3}PG_2a)$	0.60
AG_3	$Cu^{III}(H_{-3}AG_3)^-$	0.61
G_4	$Cu^{III}(H_{-3}G_4)^-$	0.63
G_3a	$Cu^{III}(H_{-3}G_3a)$	0.64
G_3AOCH_3	$Cu^{III}(H_{-3}G_3AOCH_3)$	0.70[b]
L_3	$Cu^{III}(H_{-2}L_3)$	0.77
A_3	$Cu^{III}(H_{-2}A_3)$	0.81
G_3	$Cu^{III}(H_{-2}G_3)$	0.92
$G_2\beta A$	$Cu^{III}(H_{-2}G_2\beta A)$	0.94

[a] Tripeptide and tetrapeptide ligands are used with the following abbreviations: G, glycyl; A, alanyl; βA, β-alanyl; L, leucyl; V, valyl; P, prolyl; a, amide. [b] Reduction potentials determined in ref 17.

Under conditions of excess copper(I), the observed kinetics followed the first-order rate law given in eq 3. Reductions of several copper(III)

$$-d[Cu^{III}]/dt = k_{obsd}[Cu^{III}] \quad (3)$$

peptides by $Cu^{I}L_2$ also were studied under conditions of excess oxidant, monitored at the absorption maximum of the copper(I) complexes (483 nm for dpmp and 454 nm for dmp). Under conditions of excess $Cu^{III}(H_{-3}G_4)^-$, the observed kinetics followed the first-order rate law given in eq 4. Excellent first-order plots were obtained and a nonlinear

$$-d[Cu^{I}L_2]/dt = k_{obsd}[Cu^{I}L_2] \quad (4)$$

analysis of 250 data points (taken over at least 3 half-lives) gave the pseudo-first-order rate constant k_{obsd}. Rate constants are the average of at least three determinations, each of which is the ensemble average of up to ten individual runs. The pH of the mixed solutions was determined immediately after reaction by using a Radiometer PHM 26 pH meter.

The reduction potentials of $Cu^{II}(dpmp)_2^{2-}$ and $Cu^{II}(dmp)_2^{2+}$ were determined at 25 °C in 0.01 M acetate or 2-(*N*-morpholino)-ethanesulfonic acid buffer and ionic strength 0.1 M. A three-electrode system consisting of a carbon-paste working electrode, a platinum wire auxiliary electrode, and a saturated KCl calomel reference electrode was used. Voltammograms were generated by using a Bioanalytical Systems Inc. CV-1 instrument and were recorded on a Hewlett-Packard HP703513 X-Y recorder.

Results

In the experiments to determine the reduction potentials of the copper(II) complexes, the initial solutions contain $Cu^{II}L_2$ (L = dpmp or dmp) which generates the reduction wave. The $Cu^{I}L_2$ which is formed generates the oxidation wave when the potential is reversed. When chemically prepared $Cu^{I}L_2$ solutions were used, a similar current–voltage response was obtained. The couples are quasi-reversible with large peak-to-peak separations (~110 mV). Reliable E° values were obtained for copper(III,II) couples with the same degree of reversibility.[15] The midpoints between the peaks yield potentials of 0.620 (±0.005) V and 0.615 (±0.005) V (vs. NHE) for $Cu^{II,I}(dpmp)_2^{2-,3-}$ and $Cu^{II,I}(dmp)_2^{2+,+}$, respectively, at 0.10 M ionic strength and 25 °C. These E° values are independent of pH from pH 4 to 7.

The $Cu^{II}(dpmp)_2^{2-}$ and $Cu^{II}(dmp)_2^{2+}$ complexes have reduction potentials which are intermediate in the range of reduction potentials of the copper(III)–oligopeptide complexes, Table I. Although the majority of the redox reactions of the type in eq 2 are thermodynamically favorable, some are not. It has been shown[17] that the reduction of copper(III) peptides is facilitated by the rapid dissociation of the copper(II)–peptide complexes which are products of the electron-transfer reaction. Hence, even the reactions with negative E°_{12} values occur

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Table II. Observed Rate Constants for the Reduction of Copper(III)–Peptide Complexes by $Cu^{I}(dpmp)_2^{3-}$ and $Cu^{I}(dmp)_2^{+}$ (25.0 °C, μ = 0.10 M)

pH	$10^6 \times$ [Cu^{III}], M	$10^6 \times$ [Cu^{I}], M	k_{obsd},[a] s^{-1}
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-3}G_4)^-$		
6.96	30.0	1.5	16.7 ± 0.80[b]
6.96	50.0	1.5	33.8 ± 3.2[b]
6.82	100.0	1.5	64.8 ± 2.1[b]
5.51	0.5	13.7	6.3 ± 0.4
5.48	3.0	20.6	7.8 ± 0.4
5.48	3.0	34.3	10.4 ± 0.4
5.50	3.0	85.8	15.1 ± 0.8
5.50	3.0	129	16.3 ± 0.8
5.04	3.0	32.5	9.6 ± 0.4
5.01	3.0	45.9	9.9 ± 0.4
5.06	3.0	55.1	14.0 ± 0.7
5.03	3.0	64.9	12.8 ± 0.5
5.02	3.0	71.4	15.3 ± 0.8
5.01	3.0	86.6	14.1 ± 0.7
5.35	0.5	7.9	3.74 ± 0.16
4.79	0.5	7.9	4.99 ± 0.05
4.43	0.5	7.9	4.41 ± 0.05
4.06	0.5	7.9	10.26 ± 0.32
3.82	0.5	7.9	11.63 ± 0.39
6.52	2.0	87.7	15.4 ± 0.8
6.33	0.5	7.9	5.93 ± 0.09
6.24	2.0	87.7	12.8 ± 0.5
5.22	2.0	6.9	4.0 ± 0.2
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-3}A_4)^-$		
4.45	1.0	21.6	1.56 ± 0.04
4.23	1.0	21.6	1.54 ± 0.06
4.20	1.0	21.6	1.81 ± 0.04
4.05	1.0	21.6	2.73 ± 0.07
3.99	1.0	21.6	3.21 ± 0.03
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-3}V_4)^-$		
5.32	1.0	17.1	0.339 ± 0.014
5.18	1.0	17.1	0.290 ± 0.011
5.07	1.0	17.1	0.330 ± 0.009
4.87	1.0	17.1	0.500 ± 0.019
4.69	1.0	17.1	0.399 ± 0.023
4.51	1.0	17.1	0.540 ± 0.027
4.35	1.0	17.1	0.496 ± 0.009
4.14	1.0	17.1	0.582 ± 0.006
4.08	1.0	17.1	0.742 ± 0.007
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-3}AG_3)^-$		
6.22	1.0	17.1	2.77 ± 0.11
5.21	1.0	17.1	3.08 ± 0.10
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-2}G_3)$		
6.32	1.0	17.1	7.3 ± 1.2
6.25	1.0	17.1	7.41 ± 0.49
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-2}A_3)$		
6.37	1.0	17.1	6.03 ± 0.28
4.80	640	11.6	242 ± 20
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-2}Leu_3)$		
6.16	1.0	17.1	6.26 ± 0.56
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-3}G_3a)$		
5.10	1.0	13.0	5.1 ± 1.0
5.16	1.0	17.1	7.90 ± 0.02
5.10	1.0	26.0	8.8 ± 0.6
5.10	1.0	71.0	19.1 ± 0.4
5.10	1.0	88.0	22.0 ± 1.0
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-3}PG_2a)$		
6.35	1.0	17.1	6.00 ± 0.22
5.16	1.0	17.1	5.85 ± 0.25
4.80	128	11.6	62.0 ± 1.0
4.80	256	11.6	98.0 ± 5.0
	$Cu^{I}(dpmp)_2^{3-} + Cu^{III}(H_{-3}G_3AOCH_3)$		
6.32	1.0	17.1	13.1 ± 1.1
5.16	1.0	17.1	16.2 ± 1.6
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-3}G_4)^-$		
6.02	1.1	11.5	36.0 ± 3.0
6.00	1.1	11.5	108 ± 14
6.01	5.8	34.5	194 ± 15
6.01	5.8	80.5	249 ± 15
6.04	90.0	5.0	285 ± 15
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-3}PG_2a)$		
6.02	5.0	50	92.0 ± 2.0
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-3}G_3a)$		
6.01	5.0	50	80.4 ± 3.2
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-3}G_2AOMe)$		
6.01	5.0	50	300
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-3}V_4)^-$		
4.53	1.0	50	22.0 ± 0.5
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-2}Leu_3)$		
6.00	10	10	1.1 (±0.1) × 10^7 M^{-1} s^{-1} [c]
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-2}GA_2)$		
6.00	10	10	5.2 (±0.6) × 10^7 M^{-1} s^{-1} [c]
	$Cu^{I}(dmp)_2^{+} + Cu^{III}(H_{-2}G_2\beta A)$		
6.00	10	10	2.5 (±0.3) × 10^8 M^{-1} s^{-1} [c]

[a] Rate = $-d[Cu^{III}]/dt = k_{obsd}[Cu^{III}]$, λ = 365 nm unless otherwise indicated (see footnotes *b* and *c*). [b] Rate = $-d[Cu^{I}]/dt = k_{obsd}[Cu^{I}]$, λ = 483 nm. [c] Rate = $-d[Cu^{I}]/dt = k_{obsd}[Cu^{I}][Cu^{III}]$, λ = 454 nm, determined by pulsed flow.

readily in slightly acidic solutions.

Table II lists observed pseudo-first-order rate constants under various conditions for the reactions of copper(III)–peptide complexes with $Cu^{I}(dpmp)_2^{3-}$ and $Cu^{I}(dmp)_2^{+}$. The reduction of $Cu^{III}(H_{-3}G_4)^-$ by $Cu^{I}(dpmp)_2^{3-}$ was studied under conditions in which each of the reactants was varied in excess over the other. Under conditions of excess oxidant, the reaction is first order in both $Cu^{III}(H_{-3}G_4)^-$ and $Cu^{I}(dpmp)_2^{3-}$. Under conditions of excess reductant the reaction is first order in $Cu^{III}(H_{-3}G_4)^-$ but changes from first order to zero order in $Cu^{I}(dpmp)_2^{3-}$ as the concentration of the copper(I) complex is increased to greater than 2×10^{-5} M. The observed first-order rate constant approaches a limiting value of 18 s^{-1}. The reduction of $Cu^{III}(H_{-3}G_4)^-$ by $Cu^{I}(dmp)_2^{+}$ was studied under conditions of excess reductant as well as excess oxidant and the reaction was found to be first order in both reactants. The kinetic dependence on $Cu^{I}(dmp)_2^{+}$ remained first order up to a concentration of 8.0×10^{-5} M. The kinetic results of the reduction of $Cu^{III}(H_{-3}G_4)^-$ by $Cu^{I}(dpmp)_2^{3-}$ and $Cu^{I}(dmp)_2^{+}$ are given in Figure 1.

For reaction between $Cu^{III}(H_{-3}G_4)^-$ and $Cu^{I}(dpmp)_2^{3-}$, there is no kinetic dependence on $Cu^{II}(dpmp)_2^{2-}$ concentration or with excess ligand ($dpmp^{2-}$) concentration. A limited study of the reduction of $Cu^{III}(H_{-3}G_3a)$ by $Cu^{I}(dpmp)_2^{3-}$ showed a copper(I) dependence similar to that observed with $Cu^{III}(H_{-3}G_4)^-$, approaching a limiting rate constant of approximately 20 s^{-1} at high [$Cu^{I}(dpmp)_2^{3-}$]. Thus the shifting of the $Cu^{I}(dpmp)_2^{3-}$ order from one to zero is not peculiar to the $Cu^{III}(H_{-3}G_4)^-$ reduction.

A kinetic study of the reduction of copper(III)–peptide complexes by $IrCl_6^{3-}$[17] shows that tetrapeptide complexes of copper(III) form outside protonated complexes in which a proton adds to the carboxylate group and to the carbonyl oxygen of the third deprotonated peptide group. These outside protonated complexes are more reactive toward $IrCl_6^{3-}$ than the corresponding unprotonated complexes because the electrostatic repulsion between reactants is decreased and the effective copper(III)-reduction potential is increased.[17] The

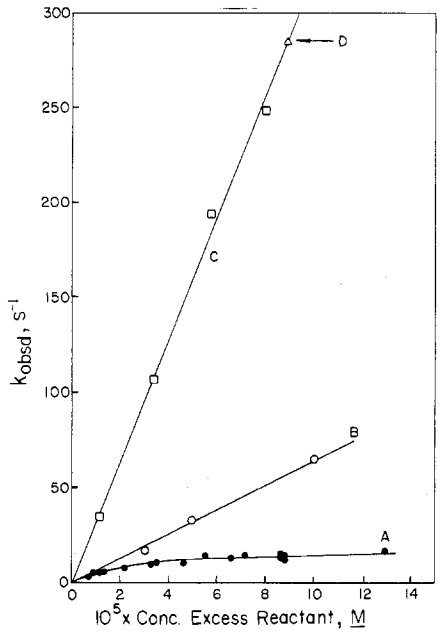

Figure 1. Pseudo-first-order rate constants for the reduction of $Cu^{III}(H_{-3}G_4)^-$ by $Cu^I(dpmp)_2^{3-}$ and $Cu^I(dmp)_2^+$: (A, ●) $Cu^{III}(H_{-3}G_4)^-$ with variable excess $Cu^I(dpmp)_2^{3-}$; (B, ○) $Cu^I(dpmp)_2^{3-}$ with variable excess $Cu^{III}(H_{-3}G_4)^-$; (C, □) $Cu^{III}(H_{-3}G_4)^-$ with variable excess $Cu^I(dmp)_2^+$; (D, △) $Cu^I(dmp)_2^+$ with excess $Cu^{III}(H_{-3}G_4)^-$.

value of the outside protonation constant for $Cu^{III}(H_{-3}G_4)^-$ is approximately 10^4 M^{-1}.[17,24] The rate of reaction of $Cu^I(dpmp)_2^{3-}$ with $Cu^{III}(H_{-3}G_4)^-$, $Cu^{III}(H_{-3}A_4)^-$, and $Cu^{III}(H_{-3}V_4)^-$ increases below pH 4.2 (Table II), reflecting the formation of outside protonated complexes with equilibrium constants of approximately 10^4 M^{-1}. Hence, the pH behavior of the reactions of $Cu^I(dpmp)_2^{3-}$ with copper(III)–peptide complexes closely parallels the pH behavior seen for the reactions of $IrCl_6^{3-}$. For the present study, a full resolution of the kinetic dependence on hydrogen ion concentration was not performed. It is sufficient to realize that above pH 4.2, the rates of reactions of copper(III)–peptide complexes with copper(I) complexes are independent of hydrogen ion concentration, indicating that the kinetically important form of copper(III) is the unprotonated complex rather than the outside protonated complex.

The second-order rate constants, k_{12} (Table III), for reactions of copper(I) with copper(III) were evaluated from pseudo-first-order rate constants under conditions of excess copper(I) at pH >4.2. For the reduction of copper(III) complexes by $Cu^I(dpmp)_2^{3-}$, a low concentration ($<2.2 \times 10^{-5}$ M) of the Cu(I) complex was used in order to avoid complications due to rate limitations at higher concentrations. The values of k_{12} for the reactions of $Cu^I(dpmp)_2^{3-}$ show no increase with increasing values of K_{12} (Table III). It was first thought that, even at the low concentrations used, the dependence in $Cu^I(dpmp)_2^{3-}$ might be approaching a limiting first-order rate constant, making the calculated values of k_{12} invalid and thus apparently insensitive to free energy change. However, the values of k_{12} for three copper(III) complexes covering a wide range of $E°$, $Cu^{III}(H_{-3}PG_2a)$, $Cu^{III}(H_{-3}G_4)^-$, and $Cu^{III}(H_{-2}A_3)$, were determined under conditions of excess oxidant and were found to be in fair agreement with those determined under conditions of excess $Cu^I(dpmp)_2^{3-}$ (Table III). Thus the lack of free energy correlation is not due to the problem of a rate limitation in $Cu^I(dpmp)_2^{3-}$.

The calculation of k_{12} values for the reactions of $Cu^I(dmp)_2^+$ was straightforward since the copper(I) kinetic dependence is always first order. The values of k_{12} for the reaction of copper(III) complexes with $Cu^I(dmp)_2^+$ (Table III) increase with increasing free energy change.

(24) Rybka, J. S.; Margerum, D. W., unpublished results.

Table III. Second-Order Rate Constants for the Reduction of Copper(III) Peptide Complexes by $Cu^I(dpmp)_2^{3-}$ and $Cu^I(dmp)_2^+$

reduction by $Cu^I(dpmp)_2^{3-}$	k_{12}, M^{-1} s^{-1}	K_{12}
$Cu^{III}(H_{-3}V_4)^-$	$2 (\pm 1) \times 10^4$	1.4×10^{-2}
$Cu^{III}(H_{-3}A_4)^-$	$7 (\pm 1) \times 10^4$	4.6×10^{-1}
$Cu^{III}(H_{-3}PG_2a)$	$3.5 (\pm 0.1) \times 10^5$	4.6×10^{-1}
	$4.8 (\pm 0.2) \times 10^5$ [a]	
$Cu^{III}(H_{-3}AG_3)^-$	$1.7 (\pm 0.1) \times 10^5$	6.8×10^{-1}
$Cu^{III}(H_{-3}G_4)^-$	$6.1 (\pm 1.4) \times 10^5$	1.5
	$6.7 (\pm 0.5) \times 10^5$ [a]	
$Cu^{III}(H_{-3}G_3a)$	$4.7 (\pm 0.1) \times 10^5$	2.2
$Cu^{III}(H_{-3}G_3AOMe)$	$8.5 (\pm 1.7) \times 10^5$	1.5×10
$Cu^{III}(H_{-2}Leu_3)$	$3.7 (\pm 0.4) \times 10^5$	3.5×10^2
$Cu^{III}(H_{-2}A_3)$	$3.5 (\pm 0.4) \times 10^5$	1.6×10^3
	$3.8 (\pm 0.5) \times 10^5$ [a]	
$Cu^{III}(H_{-2}G_3)$	$4.1 (\pm 0.1) \times 10^5$	1.2×10^5
reduction by $Cu^I(dmp)_2^+$	k_{12}, M^{-1} s^{-1}	K_{12}
$Cu^{III}(H_{-3}V_4)^-$	$4.2 (\pm 0.3) \times 10^6$	1.4×10^{-2}
$Cu^{III}(H_{-3}PG_2a)$	$1.8 (\pm 0.1) \times 10^6$	4.6×10^{-1}
$Cu^{III}(H_{-3}G_4)^-$	$3.1 (\pm 0.2) \times 10^6$	1.5
$Cu^{III}(H_{-3}G_3a)$	$1.6 (\pm 0.1) \times 10^6$	2.2
$Cu^{III}(H_{-3}G_3AOMe)$	$6.0 (\pm 0.2) \times 10^6$	1.5×10
$Cu^{III}(H_{-2}L_3)$	$1.1 (\pm 0.1) \times 10^7$	3.5×10^2
$Cu^{III}(H_{-2}GA_2)$	$5.2 (\pm 0.5) \times 10^7$	7.7×10^3
$Cu^{III}(H_{-2}G_2\beta A)$	$2.5 (\pm 0.3) \times 10^8$	2.6×10^5

[a] The two rate constants given are determined under pseudo-first-order conditions with excess copper(I) and excess copper(III), respectively.

Table IV. Reduction Potentials and Copper Complexation Constants for Derivatives of 1,10-Phenanthroline

	Cu^{II}		Cu^I	
	$\log K_1$	$\log K_2$	$\log \beta_2$	$E°$, V
phen[a]	8.82	6.57	15.82	+0.17
mp[a,b]	7.4	6.4	16.95	+0.34
dmp[a]	6.1	5.6	19.1	+0.615
dpmp				+0.620

[a] Reference 10 (0.3 M K_2SO_4, 25 °C). [b] 2-Methyl-1,10-phenanthroline.

Discussion

The Reduction Potential of $Cu^{II}L_2^{2-}$. The reduction potential of $Cu^{II}L_2$, eq 5, is 0.620 and 0.615 V for the dpmp and dmp

$$Cu^{II}L_2 + e^- \rightleftarrows Cu^IL_2 \quad (5)$$

complexes, respectively. While the addition of methyl substituents at positions 2 and 9 has a marked effect on the potential as shown in Table IV, bulky substituents in the 4 and 7 positions appear to have little effect. Steric interaction of methyl groups in the 2 and 9 positions favors the tetrahedral geometry of the copper(I) complex and forces the copper(II) complex into the same geometry.

Self-Exchange Rates of Copper(II,I) Couples. The similarity in the $E°$ values for the $Cu^{II}(dpmp)_2^{2-}$ and $Cu^{II}(dmp)_2^{2+}$ systems suggests that the complexes might have similar complexation constants. The overall stability constant K_1K_2 for $Cu^I(dmp)_2^+$ is around 10^{20} M^{-2}. For $Cu(dmp)_2^+$ both ligands add to Cu^+ simultaneously, indicating that $K_2 > K_1$. With a value of 10^{10} M^{-1} for K_2 and on the assumption that the rate constant for complex formation is diffusion controlled, 10^9 M^{-1} s^{-1}, an upper limit for the dissociation rate constants for the copper(I) complexes is 10^{-1} s^{-1}. Copper(III) complexes are very sluggish toward equatorial substitution.[14] The rates of reaction of $Cu^I(dpmp)_2^{3-}$ and $Cu^I(dmp)_2^+$ with copper-

(III)–peptide complexes exceed the dissociation rate constants of the participating reactants. Hence, it is reasonable to assume that these reactions occur by an outer-sphere mechanism.

According to Marcus,[25] the rate constant, k_{12}, for an outer-sphere electron-transfer reaction is a function of the overall equilibrium constant for the reaction, K_{12}, and the self-exchange rate constants k_{11} and k_{22}. This function may be written as shown in eq 6 and 7, where Z, the collision frequency

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (6)$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (7)$$

between two uncharged particles, is taken to be 10^{11} M^{-1} s^{-1}. Thus, for an outer-sphere electron-transfer reaction, provided the reduction potentials of both reactants and the self-exchange rate constant for one reactant are known, the self-exchange rate constant for the other reactant may be evaluated from the rate constant of the cross reaction.

Values of 1.7×10^4 and 4.4×10^4 M^{-1} s^{-1} have been reported for the $Cu^{II,I}(dmp)_2^{2+,+}$ self-exchange rate constant evaluated from studies of the reduction of $Cu^{II}(dmp)_2^{2+}$ by cytochrome c and $Co^{II}(phen)_3^{2+}$, respectively.[13] There is serious disagreement in reported values for the self-exchange rate constant of $Cu^{II,I}(phen)_2^{2+,+}$ calculated by using data from different cross reactions. From a study of the reduction of $Co^{III}(EDTA)^-$ by $Cu^{I}(phen)_2^+$ the value obtained for the copper(II,I) self-exchange rate constant is 5×10^7 M^{-1} s^{-1}.[12] The reported self-exchange rate constant for $Cu^{II,I}(phen)_2^{2+,+}$ determined by the reaction of $Cu^{II}(phen)_2^+$ with cytochrome c is 68 M^{-1} s^{-1}.[13] Yandell has argued that the difference in the self-exchange rate constants for $Cu^{II,I}(dmp)_2^{2+,+}$ and $Cu^{II,I}(phen)_2^{2+,+}$ is due to the changes in coordination number and geometry which are required for electron exchange with $Cu^{II,I}(phen)_2^{2+,+}$ but not with $Cu^{II,I}(dmp)_2^{2+,+}$.[13] The coordination of the phen ligands in $Cu^{II,I}(phen)_2^{2+,+}$ changes from square planar to tetrahedral upon reduction, while for $Cu^{II,I}(dmp)_2^{2+,+}$, both oxidation states are approximately tetrahedral. In evaluating the copper(II,I) self-exchange rate constants cited above, it was assumed that the cross-exchange rate constants obey the Marcus theory. In view of the serious disagreement in the self-exchange rate constants, this assumption cannot be valid in each case. For neither of the above cross reactions was it possible to show that the measured cross-exchange rate constants indeed obey the Marcus theory. Electron-transfer reactions of $Co(phen)_3^{2+}$, including those with copper(III)–peptide complexes which were studied in our laboratory,[18] often exhibit free energy correlations which do not strictly obey the Marcus theory.[26-29] However, all of the self-exchange rate constants quoted above, with the exception of that for $Cu^{II,I}(phen)_2^{2+,+}$ determined by reduction of $Cu^{II}(phen)_2^{2+}$ with cytochrome c (68 M^{-1} s^{-1}), indicate that electron exchange in the copper(II,I) system is a facile process. Hence, it appears that self-exchange rates are rapid for copper(II,I) couples such as $Cu^{II,I}(dmp)_2^{2+,+}$ and $Cu^{II,I}(dpmp)_2^{2-,3-}$ in which the exchange requires no substantial stereochemical change.

Dependence on K_{12}. Reduction potentials of the copper(III)–peptide complexes are very sensitive to the nature of the ligand, allowing the study of the kinetics of reduction by copper(I) over a wide range of free energy changes. If the reaction of copper(I) with copper(III) peptides is outer sphere and if all of the copper(III,II)–peptide couples have the same self-exchange rate constant, the Marcus theory predicts that a plot of log $(k_{12}/f^{1/2})$ against log K_{12} should be linear with a slope of 0.5 (eq 6 and 7). In a previous study of the rates of reduction of copper(III) peptides by $IrCl_6^{3-}$ a Marcus correlation was observed and an apparent copper(III,II) peptide self-exchange rate constant was evaluated as 7×10^7 M^{-1} s^{-1}.[17] However, NMR line-broadening studies and kinetics studies of the reduction of copper(III)–peptide complexes by copper(II)–peptide complexes are in progress and results indicate that the true copper(III,II) peptide self-exchange rate constant is approximately 10^5 M^{-1} s^{-1}.[30] Electron transfer to $IrCl_6^{3-}$ probably occurs via a chloride bridge, causing the rate of reaction to be faster than is the case for the outer-sphere electron transfer in the direct self-exchange reaction.

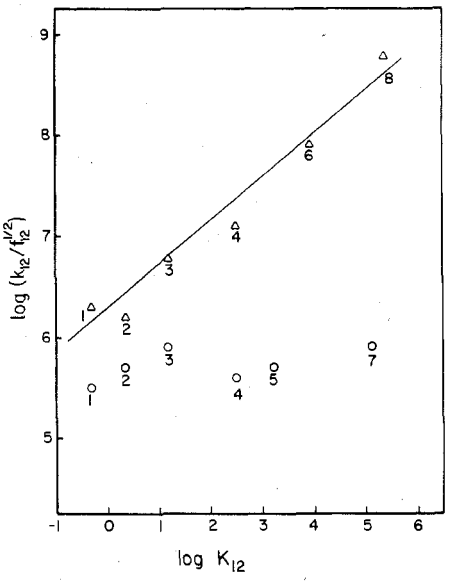

Figure 2. log $(k_{12}/f^{1/2})$ vs. log K_{12} for the reduction of neutral copper(III)–peptide complexes by $Cu^{I}(dpmp)_2^{3-}$ (○) and $Cu^{I}(dmp)_2^+$ (△) (25 °C, μ = 0.10 M): (1) $Cu^{III}(H_{-3}PG_2a)$; (2) $Cu^{III}(H_{-3}G_3a)$; (3) $Cu^{III}(H_{-3}G_3AOMe)$; (4) $Cu^{III}(H_{-3}L_3)$; (5) $Cu^{III}(H_{-2}A_3)$; (6) $Cu^{III}(H_{-2}GA_2)$; (7) $Cu^{III}(H_{-2}G_3)$; (8) $Cu^{III}(H_{-2}G_2\beta A)$.

A plot of log $(k_{12}/f^{1/2})$ against log K_{12} for the reduction of neutral copper(III) peptides by $Cu^{I}(dpmp)_2^{3-}$ in Figure 2 shows that there is not a significant trend of k_{12} with K_{12}. Since eq 6 and 7 do not describe the reactions of $Cu^{I}(dpmp)_2^{3-}$, f was not evaluated but assigned a value of unity for convenience in Figure 2. For the reactions of $Cu^{I}(dpmp)_2^{3-}$ with the negatively charged complexes $Cu^{III}(H_{-3}AG_3)^-$, $Cu^{III}(H_{-3}A_4)^-$, and $Cu^{III}(H_{-3}V_4)^-$ values of k_{12} are lower than those of the other copper(III) reductions (Table II). This is probably due to a combination of electrostatic and steric factors as the remaining complexes are either uncharged or contain no peptide side chains.

Figure 2 also shows the Marcus plot for the reduction of neutral copper(III) peptides by $Cu^{I}(dmp)_2^+$. Values of f for each point were obtained by an iterative method using eq 6 and 7. The slope of this plot is 0.45 ± 0.08, which agrees within experimental error with the theoretically expected slope. Rate constants for the reduction of the negatively charged complexes $Cu^{III}(H_{-3}G_4)^-$ and $Cu^{III}(H_{-3}V_4)^-$ fall very close to the observed line but were not included so that the slope and the intercept are not affected by electrostatic interaction. However, even with these points included, the slope is still 0.5 within experimental error.

The fact that different copper(III)–peptide complexes do actually fall along a Marcus plot for $IrCl_6^{3-}$ and $Cu^{I}(dmp)_2^+$ reactions indicates that they all have very similar self-exchange

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Table V. Rate Constants and Self-Exchange Constants Derived from Reactions of $Cu^{I}L_2$ with $Ir^{IV}Cl_6^{2-}$ (μ = 0.10 M, 25.0 °C)

$[Cu^{I}(dpmp)_2^{3-}]$, M	$[Ir^{IV}Cl_6^{2-}]$, M	pH	k_{12}, M^{-1} s^{-1}	K_{12}, M^{-1}	f	k_{22}, M^{-1} s^{-1}
1.5×10^{-5}	1.5×10^{-5}	4.5	2.9×10^{8}	4.0×10^{4}	0.266	3.7×10^{7}
4.5×10^{-6}	4.5×10^{-6}	4.5	3.1×10^{8}			
$[Cu^{I}(dmp)_2^{+}]$, M	$[Ir^{IV}Cl_6^{2-}]$, M	pH	k_{12}, M^{-1} s^{-1}	K_{12}, M^{-1}	f	k_{22}, M^{-1} s^{-1}
5.0×10^{-6}	5.0×10^{-6}	6.0	1.4×10^{9}	4.9×10^{4}	0.192	9.0 ± 10^{8}

rate constants. This seems to be true in spite of a variety of differences in the structures of the copper(III) species. Changing the groups coordinated to the metal, changing the alkyl substituents in the peptide, and changing the chelate ring size cause the reduction potentials of the copper(III) complexes to change considerably but do not appear to affect the rate of the copper(III,II) self-exchange. The wide variety in $E°$, combined with the lack of variety in self-exchange rate constants, makes the copper(III,II) peptide series an excellent model for the Marcus theory.

The lack of dependence of the rate of reduction of copper(III) by $Cu^{I}(dpmp)_2^{3-}$ upon free energy change is rather unusual. The obvious differences between $Cu^{I}(dpmp)_2^{3-}$, which has no dependence on log K_{12}, and $Cu^{I}(dmp)_2^{+}$, which exhibits Marcus behavior, are electrostatic and steric. It is unlikely that the charge on $Cu^{I}(dpmp)_2^{3-}$ is responsible for the lack of dependence upon log K_{12} because the majority of copper(III)–peptide complexes employed in this study are neutral. Also a reductant of identical charge, $IrCl_6^{3-}$, exhibits a Marcus type of behavior in its reactions with copper(III)–peptide complexes. It is more likely that steric factors are responsible for the different behavior of $Cu^{I}(dpmp)_2^{3-}$.

The outer surface of $Cu^{I}(dpmp)_2^{3-}$ is dominated by the four sulfonated phenyl groups at the 4 and 7 positions of each phenanthroline ring. The phenyl rings increase the radius of the complex. The phenyl rings are perpendicular (or at least nonplanar) with respect to the phenanthroline ring system and this breakup of the continuous aromaticity in the complex may preclude a facile pathway for electron transfer by not allowing contact between the phenanthroline ring and the edge of the copper(III) complex. McArdle, Yocom, and Gray have argued that the presence of methyl groups in the 4 and 7 positions of phenanthroline effectively block the overlap of the phenanthroline edge with the heme edge in the reduction of $Co^{III}(4,7\text{-}Me_2phen)_3$ by ferrocytochrome *c*.[27] A more serious steric interference would certainly be expected from the phenyl groups in $Cu^{I}(dpmp)_2^{3-}$. Such steric interference by the phenyl groups may force the electron transfer to occur through a pathway in which the overall activation barrier is not dependent on the reaction driving force.

Extrapolation of the Marcus plot for the $Cu^{I}(dmp)_2^{+}$ data in Figure 2 to log K_{12} = 0 allows the evaluation of the $Cu^{II,I}(dmp)_2^{2+,+}$ self-exchange rate constant provided the copper(III,II) peptide self-exchange rate constant is known. A lower limit of 3×10^{4} M^{-1} s^{-1} for the $Cu^{II,I}(dmp)_2^{2+,+}$ self-exchange rate constant is obtained by using the upper limit of 7×10^{7} M^{-1} s^{-1} for the copper(III,II) peptide self-exchange evaluated from the cross reaction of copper(III) with $IrCl_6^{3-}$, which appears to occur via chloride bridging. However, using the value of 10^{5} M^{-1} s^{-1} for the copper(III,II) peptide self-exchange rate constant yields a $Cu^{II,I}(dmp)_2^{2+,+}$ self-exchange rate constant of approximately 10^{7} M^{-1} s^{-1}. The latter value is several orders of magnitude greater than the values obtained from the cross reactions of $Cu^{II}(dmp)_2^{2+}$ with the cytochrome *c* or with $Co(phen)_3^{2+}$. At present, it appears that the calculated self-exchange rate constant for $Cu^{II,I}(dmp)_2^{2+,+}$ depends on the choice of redox couple used for the cross reaction. The self-exchange rate constants for $Cu^{II,I}(dmp)_2^{2+,+}$ and $Cu^{II,I}(dpmp)_2^{2-,3-}$ also were evaluated from the cross reactions of the copper(I) complexes with $IrCl_6^{2-}$. The $Ir^{IV,III}Cl_6^{2-,3-}$ couple has a self-exchange rate constant of 2.3×10^{5} M^{-1} s^{-1} [31] and an $E°$ value of 0.892 V[14] at μ = 0.1 and 25 °C. The data in Table V were obtained by using the pulsed-flow technique[22,23] and yielded self-exchange rate constants of 9.0×10^{8} M^{-1} s^{-1} and 3.7×10^{7} M^{-1} s^{-1} for $Cu^{II,I}(dmp)_2^{2+,+}$ and $Cu^{II,I}(dpmp)_2^{2-,3-}$, respectively. Hence, the cross reaction of $Cu^{I}(dmp)_2^{+}$ with $IrCl_6^{2-}$ gives yet another value for the $Cu^{II,I}(dmp)_2^{2+,+}$ self-exchange rate constant.

Reaction Order in $Cu^{I}(dpmp)_2^{3-}$. There are a number of possible mechanisms which might explain a change in the reaction order in $[Cu^{I}(dpmp)_2^{3-}]$ from one to zero as the $Cu^{I}(dpmp)_2^{3-}$ concentration is increased, but most are not consistent with the data. A rapid preequilibrium to form $[Cu^{III}(H_{-3}G_4)Cu^{I}(dpmp)_2^{4-}]$ can be ruled out because the reaction order with respect to excess $[Cu^{I}(dpmp)_2^{3-}]$ is zero at concentrations greater than 4×10^{-5} M, while the reaction order with respect to $[Cu^{III}(H_{-3}G_4)^{-}]$ is still one at 1×10^{-4} M. A mechanism in which self-association of $Cu^{I}(dpmp)_2^{3-}$ to form an unreactive oligomer was considered but does not fit the zero-order dependence found. A shift in the rate-determining step at high copper(I) concentration to a preceding step involving activation of $Cu^{III}(H_{-3}G_4)^{-}$ (eq 8 and 9) can be fit to the data. If this explanation is correct, it means that

$$Cu^{III}(H_{-3}G_4)^{-} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [Cu^{III}(H_{-3}G_4)]^{*} \quad (8)$$

$$[Cu^{III}(H_{-3}G_4)^{-}]^{*} + Cu^{I}(dpmp)_2^{3-} \xrightarrow{k_{12a}} Cu^{II}(H_{-3}G_4)^{2-} + Cu^{II}(dpmp)_2^{2-} \quad (9)$$

$Cu^{I}(dpmp)_2^{3-}$ requires a more reactive form of copper(III) than does $Cu^{I}(dmp)_2^{+}$. Otherwise the change in copper(I) reaction order would occur for $Cu^{I}(dmp)_2^{+}$ just as it does for $Cu^{I}(dpmp)_2^{3-}$. Apparently $Cu^{I}(dmp)_2^{+}$ reacts directly with $Cu^{III}(H_{-3}G_4)^{-}$ without the need for the activation step shown in eq 8. The mechanism in eq 8 and 9 leads to the expression for k_{obsd} in eq 10 which fits the data well and yields k_a = 18

$$k_{obsd} = \frac{k_a k_{12a}[Cu^{I}(dpmp)_2^{3-}]}{k_{-a} + k_{12a}[Cu^{I}(dpmp)_2^{3-}]} \quad (10)$$

s^{-1} and $k_{-a}/k_{12a} = 2.3 \times 10^{-5}$ M^{-1}. Although this mechanism fits the data, the nature of the activation step (eq 8) is not known. A plausible explanation is that axial solvation of the d^8 square-planar copper(III) complex occurs to form a five- or six-coordinate species. Determinations of the copper(III,II) half-reaction entropies indicate that the copper(II) product has tetragonal geometry with two axial water molecules while the copper(III) reactant has no axial solvation.[32] Hence, axial solvation of the copper center must occur at some point in the reduction of copper(III). Perhaps for $Cu^{I}(dpmp)_2^{3-}$ reduction, a more reactive axially solvated copper(III) complex is required for electron transfer in order to overcome the larger distance of separation of the copper centers, while the smaller $Cu^{I}(dmp)_2^{+}$ complex can react directly with the square-planar

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copper(III) complex. The marked difference in behavior suggests that there are important aspects about the pathway of electron-transfer reactions which need exploration.

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Registry No. $Cu^{I}(dpmp)_2^{3-}$, 72251-87-7; $Cu^{I}(dmp)_2^{+}$, 21710-12-3; $Cu^{III}(H_{-3}G_4)^{-}$, 57692-61-2; $Cu^{III}(H_{-3}A_4)^{-}$, 68628-66-0; $Cu^{III}(H_{-3}V_4)^{-}$, 62959-93-7; $Cu^{III}(H_{-3}AG_3)^{-}$, 69088-03-5; $Cu^{III}(H_{-2}G_3)$, 69814-94-4; $Cu^{III}(H_{-2}A_3)$, 69042-71-3; $Cu^{III}(H_{-2}Leu_3)$, 69042-72-4; $Cu^{III}(H_{-3}G_3a)$, 62801-36-9; $Cu^{III}(H_{-3}PG_2a)$, 24212-63-3; $Cu^{III}(H_{-3}G_3AOCH_3)$, 69042-73-5; $Cu^{III}(H_{-2}G_2BA)$, 69814-95-5; $Cu^{II}(dpmp)_2^{2-}$, 72244-80-5; $Ir^{IV}Cl_6^{2-}$, 16918-91-5; $Cu^{III}(H_{-2}GA_2)$, 69814-92-2.

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Synthesis and Structural Isomerism of Some (Silylamino)phosphine Oxides[1]

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The reactions of various (silylamino)phosphines with molecular oxygen and with *tert*-butyl trimethylsilyl peroxide have been investigated. The silyl peroxide was found to be a milder and more generally effective oxidant than O_2. Depending upon the steric bulk of the nitrogen substituents in the starting (silylamino)phosphine, the oxidation products were either the structurally rearranged siloxyphosphinimines $Me_3SiN{=}P(R)MeOSiMe_3$ (**1**, R = Me; **2**, R = Ph) and *t*-BuN=PMe_2OSiMe_3 (**3**) or the (silylamino)phosphine oxides $Me_2SiCH_2CH_2SiMe_2N{-}P(O)Me_2$ (**4**) and $RMe_2SiN(Me)P(O)Me_2$ (**5**, R = Me; **6**, R = *t*-Bu). In one case where two different silyl groups were present, the disproportionation products $RMe_2SiN{=}PMe_2OSiMe_2R$ (**1**, R = Me; **7**, R = *t*-Bu) were obtained. Proton, ^{13}C, and ^{31}P NMR spectroscopic data are reported for the new oxidation products.

Introduction

The derivative chemistry of (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ is dominated by a combination of two factors: the ease of oxidation of the P^{III} center to various P^{V} forms and the ease of Si–N bond cleavage in the presence of nucleophiles. This second feature often gives rise to structurally rearranged products from reactions which would be straightforward or routine when considered solely within the realm of organophosphorus chemistry. For example, while treatment of $(Me_3Si)_2NPMe_2$ with MeI readily yields the expected phosphonium salt, subsequent dehydrohalogenation with *n*-BuLi (eq 1) results in the formation of the (silylmethyl)phosphin-

$$[(Me_3Si)_2NP^{+}Me_3]I^{-} \xrightarrow{n\text{-BuLi}} Me_3SiN{=}PMe_2CH_2SiMe_3 \quad (1)$$

imine derivative[2] rather than a phosphorus ylide. Similar [1,3] silyl shifts are sometimes observed in the reactions of (silylamino)phosphines with silyl azides (eq 2).[3] The factors which

$$R(Me_3Si)NPMe_2 \xrightarrow[-N_2]{Me_3SiN_3} RN{=}PMe_2N(SiMe_3)_2 \quad (2)$$

$$R = t\text{-Bu},\ t\text{-BuMe}_2\text{Si}$$

appear to influence the course of these reactions have been discussed in earlier papers.[2,3]

The direct oxidation of (silylamino)phosphines may also involve silyl migration since, in one previous report,[4] the siloxyphosphinimine **1** was obtained when dry O_2 was bubbled through a solution of $(Me_3Si)_2NPMe_2$ (eq 3). We report here

$$(Me_3Si)_2NPMe_2 \xrightarrow{O_2} \underset{\mathbf{1}}{Me_3SiN{=}PMe_2OSiMe_3} \quad (3)$$

the results of a more detailed study in which several (silylamino)phosphines were treated either with O_2 or with the nonradical oxidizing agent *tert*-butyl trimethylsilyl peroxide, *t*-BuO_2SiMe_3. The purpose of this study was twofold: (1) to determine if similar steric and electronic effects are operative in these oxidations as were found in the rearrangements involving the phosphorus ylides (eq 1) and imines (eq 2) and (2) to find a milder and safer oxidizing agent than O_2 for carrying out these reactions.

Results and Discussion

Reactions with O_2. When dry oxygen was bubbled through a dichloromethane solution of [bis(trimethylsilyl)amino]methylphenylphosphine for 2.5 h at room temperature, the product obtained (eq 4) in 59% yield was the rearranged

$$(Me_3Si)_2N{-}\underset{\displaystyle Me}{\overset{\displaystyle Ph}{P}} \xrightarrow{O_2} \left\{(Me_3Si)_2N{-}\overset{\displaystyle O}{\overset{\|}{P}}{-}Ph\right\} \longrightarrow \underset{\displaystyle Me}{\overset{\displaystyle Ph}{Me_3SiN{=}P{-}OSiMe_3}} \quad (4)$$

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siloxyphosphinimine **2**. Thus, one *P*-phenyl substituent does not prevent the oxidation from taking a course similar to that followed by the dimethyl analogue (eq 3).[4] Two phenyl groups on phosphorus are sufficient, however, to prevent oxidation since we observed no reaction, under the same conditions, between O_2 and $(Me_3Si)_2NPPh_2$. Alternatively, the diphenyl analogue of **1** and **2** has been prepared by another procedure and it also exists in the phosphinimine form.[5]

Including compound **2**, the new derivatives prepared in this study were either liquids of low volatility or low-melting solids which were purified by fractional distillation and characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis (Table I). The structure of **2** is confirmed by the observation of two distinct signals for the Me_3Si groups in both the ^1H and ^{13}C NMR spectra. The substantial P–C coupling constant of 3.5 Hz for one of the Me_3Si groups is also indicative of the $Me_3SiN{=}P$ linkage.[2-6]

(1) Taken in part from the Ph.D. dissertation of J. C. Wilburn, Duke University, Durham, N.C., 1978.
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