

Figure 5. ^1H NMR spectra of $[\text{Co}(\text{H}_2\text{O})\text{L}](\text{ClO}_4)_2$ in D_2O at the uncorrected pH values of 9.6 (A) and 7.8 (B) (for the determination of pH see the Experimental Section) and in the presence of 10^{-1} mol dm^{-3} N_3^- (C).

presence of 10^{-1} mol dm^{-3} NaN_3 are reported in Figure 5. The latter spectrum consists of four signals of intensities 2:1:3:3, which are assigned to the CH_2 group, to the C4 proton, and to the 5- CH_3 and the 3- CH_3 groups, respectively.²¹ In the

former spectra three signals of relative intensities 1:2:3 are observed; the 3- CH_3 signal is apparently underlying the intense peak of HDO protons. The large isotropic shift differences observed in the signals of the aqua complex at the two pH values, particularly evident in the CH_2 protons, point out that a considerable conformational change accompanies the deprotonation of the metal-bound water molecule. The NMR spectrum at high pH is somewhat similar to that of the azide derivative. The occurrence of some stereochemical rearrangement upon water deprotonation is also consistent with the variation of the electronic spectra, since switching from H_2O to OH^- is not expected to cause any major change in the energy levels, the two groups being close in both the spectrochemical and nephelauxetic series.²²

Longitudinal relaxation rates of the ^1H signal of water in cobalt enzyme solutions have been found to be pH independent.¹⁵ Actually, a decrease would be expected on passing from H_2O to OH^- owing to the decrease in the number of exchangeable protons interacting with the paramagnetic center, unless the metal-proton distance sensibly decreases in the latter case. In the present aqua complex, the T_1 values of water protons decrease from 3.5 to 2.0 s when the paramagnetic complex is dissolved in water at 1.0×10^{-3} mol dm^{-3} concentration. The measured effect is indeed substantially pH independent, although too small to be safely compared with the enzyme results.

Registry No. $[\text{Co}(\text{H}_2\text{O})\text{L}](\text{ClO}_4)_2$, 76773-04-1; $[\text{Co}(\text{N}_3)\text{L}](\text{ClO}_4)$, 76773-06-3; isoenzyme B, 9001-03-0; Co, 7440-48-4.

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Electrochemical Study of a Trinuclear Copper(II) System: The $\text{Cu}^{\text{II}}_2\text{Cu}^{\text{III}}-\text{Cu}^{\text{II}}$ Couple and Its Inhibition by Proton

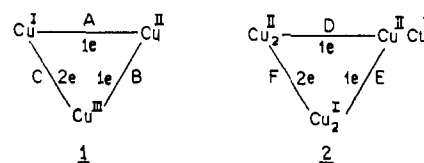
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An electrochemical study of a group of spin-doublet ($S = 1/2$) trinuclear copper(II) complexes, $[\text{Cu}_3\text{O}_p(\text{OH})_{1-p}(\text{ligand})_3](\text{ClO}_4)_{2-p}$ [$0 \leq p \leq 1$; ligand = $\text{RNC}(\text{R}')\text{C}(\text{R}')\text{NO}^-$; $\text{R} = \text{Et}, n\text{-Pr}, n\text{-Bu}, \text{Ph}$; $\text{R}' = \text{Me}, \text{Ph}$], is reported. In general, the complexes as isolated contain both Cu_3O and Cu_3OH cores held by three peripheral oximate bridges of the ligand. Cyclic voltammetry (both dc and ac) and constant potential coulometry establish that only the Cu_3O core displays the novel one-electron-transfer process $\text{Cu}^{\text{III}}\text{Cu}^{\text{II}}_2 + e^- \rightleftharpoons \text{Cu}^{\text{II}}_3$ with E°_{298} in the range 0.3–0.4 V vs. SCE in several solvents at a platinum working electrode. The rare $\text{Cu}(\text{III})-\text{Cu}(\text{II})$ mixed-valence species thus discovered have an intense electronic absorption band at ~ 830 nm. The heterogeneous rate constants of electron transfer are reported. Base (NEt_3) converts Cu_3OH to a Cu_3O species in an equilibrium deprotonation reaction. On the other hand an acid (HClO_4) brings about the reverse conversion, $\text{Cu}_3\text{O} \rightarrow \text{Cu}_3\text{OH}$. The influence of these reactions on the electrochemical response is analyzed. The identification of a second couple $\text{Cu}^{\text{II}}_3 + e^- \rightleftharpoons \text{Cu}^{\text{II}}_2\text{Cu}^{\text{I}}$ ($E^{\circ}_{298} \sim -0.4$ V vs. SCE) at a mercury working electrode in which only the Cu_3OH core can participate is briefly reported. The symbiotic relationship between electron transfer and proton transfer is noted.

The function of copper oxidases and oxygenases is dependent on the variable valency of the metal ion.¹⁻³ This has stimulated much current interest in electron-transfer studies of model mononuclear and dinuclear copper species having O, N, and S donor ligands. Electrochemical techniques have been effectively used in such studies. The electron-transfer steps thus far identified are A,⁴⁻⁸ B,⁹⁻¹² C,¹³ D,^{4,14-16} E,^{15,16} and F¹⁷

as schematically summarized in 1 and 2. Though unknown



at present, given proper ligand environment, a similar triangle

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Table I. Ligands and Characterization Data of $[\text{Cu}^{\text{II}}_3\text{O}_p(\text{OH})_{1-p}(\text{RL or RL}')_3](\text{ClO}_4)_{2-p}$

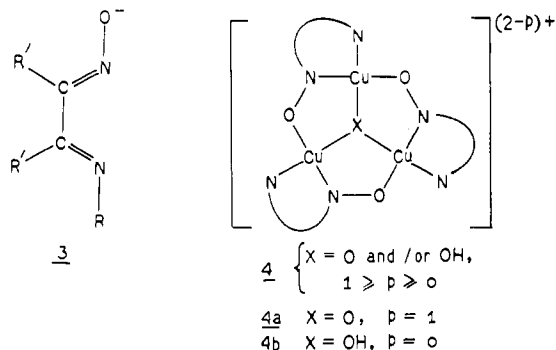
ligand (3)			complex (4) ^a						
R'	R	abbr	p	% C	% H	% N	% Cu	% ClO ₄	
Me	Et	EtL	0.81	30.21 (30.64)	4.82 (4.71)	11.70 (11.92)	26.98 (27.05)	16.21 (16.59)	
Me	n-Pr	PrL	0.44	32.36 (32.19)	5.10 (5.07)	10.62 (10.73)	24.25 (24.36)	19.40 (19.52)	
Me	n-Bu	BuL	0.38	34.86 (34.57)	5.54 (5.47)	10.14 (10.08)	22.97 (22.89)	18.90 (19.10)	
Me	Ph	PhL	0.00	38.47 (38.65)	3.67 (3.68)	9.15 (9.02)	19.98 (20.45)	20.97 (21.34)	
Ph	Et	EtL'	0.77	53.34 (53.21)	4.21 (4.18)	7.84 (7.76)	17.70 (17.62)	10.98 (11.22)	
Ph	n-Pr	PrL'	0.79	54.75 (54.42)	4.61 (4.56)	7.41 (7.49)	16.91 (16.99)	10.42 (10.66)	
Ph	n-Bu	BuL'	0.78	55.40 (55.59)	4.97 (4.91)	7.27 (7.21)	16.29 (16.37)	10.20 (10.34)	

^a Calculated percentages of elements are given in parentheses.

based on Cu^{II}_2 , $\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}$, and Cu^{III}_2 might be achievable. In contrast to mononuclear and binuclear systems, there is no report on the electron-transfer behavior of the trinuclear copper complexes possibly because these are relatively rare.¹⁸ Steps similar to but more diverse than those in **1** and **2** can occur with such complexes. Herein we report for the first time a study of this problem in a group of trinuclear copper complexes.

Results and Discussion

A. Complexes. The ligands (**3**) are Schiff bases (iso-



nitrosoketimines) of biacetyl monoxime and α -benzil monoxime with amines, RNH_2 . The two groups are respectively abbreviated as RL and RL' (Table I). The trinuclear complexes of RL were described earlier;^{19,20} the RL' species are new. The complexes are isolated as perchlorates by reacting the monoxime, amine, and copper(II) perchlorate in ethanol. As elaborated elsewhere,¹⁹ these complexes have a central $[\text{Cu}_3\text{X}]$ ($X = \text{O}$ or OH) core. Each copper is chelated to one

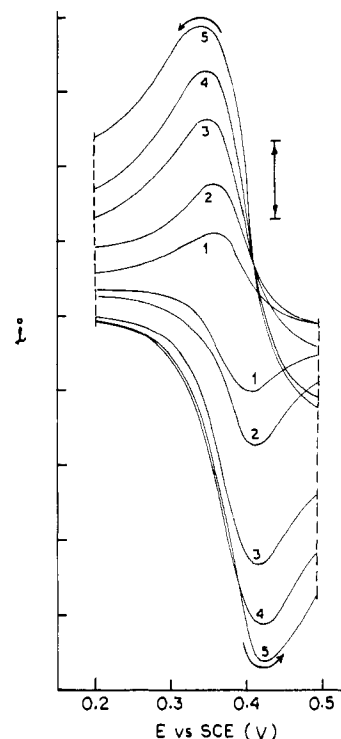


Figure 1. Cyclic voltammograms of the PrL' system in acetonitrile at various scan rates (V s^{-1}): (1) 0.010, (2) 0.100, (3) 0.300, (4) 0.500, (5) 0.700. Current scale is $100 \mu\text{A}$ for (1) and $200 \mu\text{A}$ for the rest; solute concentration, 1.11 mg mL^{-1} .

ligand molecule which also bridges two adjacent copper(II) atoms via the oximato function. In effect each ligand is tridentate and there are three peripheral oximato bridges. This is illustrated in **4**. Most of the RL and RL' complexes as synthesized consist partly of $[\text{Cu}_3\text{O}]$ and partly of $[\text{Cu}_3\text{OH}]$ cores. The general composition can thus be represented as $[\text{Cu}_3\text{O}_p(\text{OH})_{1-p}(\text{RL or RL}')_3](\text{ClO}_4)_{2-p}$. The limits $p = 1$ and $p = 0$ correspond to pure $[\text{Cu}_3\text{O}]$ (**4a**) and $[\text{Cu}_3\text{OH}]$ (**4b**) cores, respectively. The earlier report¹⁹ that the RL complexes for $R = \text{alkyl}$ uniformly have $p = 1$ is an oversimplification. The values of p are of central importance for the present work. These along with analytical data from which these are derived are collected in Table I. Proven structures of type **4** exist for the ligands pyridine-2-carboxaldoxime²¹ ($p = 0$) and 2-(propylamino)-2-methyl-3-butanone oxime²² ($p = 0.5$), which bind copper(II) the same way as **3** does. The general requirement

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Table II.^a Formal Electrode Potentials vs. SCE of Couple (1)

ligands ^b	solvent ^c	E_{pa}	E_{pc}	ΔE_p	$E^{\circ}_{298'}$
EtL	CH ₃ CN	0.365	0.307	58	0.336
	MeOH	0.326	0.268	58	0.297
	DMF	0.338	0.280	58	0.309
PrL	CH ₃ CN ^d	0.395	0.335	60	0.365
	CH ₃ CN	0.397	0.330	67	0.364
	MeOH	0.332	0.273	59	0.302
BuL	CH ₃ CN ^e	0.370	0.310	60	0.340
	CH ₃ CN	0.382	0.300	82	0.341
	MeOH	0.335	0.275	60	0.305
EtL'	CH ₃ CN	0.416	0.358	58	0.387
PrL'	CH ₃ CN	0.415	0.357	58	0.386
	DMF	0.395	0.335	60	0.365
BuL'	CH ₃ CN	0.429	0.370	59	0.399

^a All symbols have the same meaning as in the text. Units: E_{pa} , V; E_{pc} , V; $E^{\circ}_{298'}$, V; ΔE_p , mV; unless otherwise stated ν is 0.020 V s^{-1} . ^b Concentration of complexes was $\sim 1 \times 10^{-3} \text{ M}$ except for the very sparingly soluble EtL' system for which a saturated solution of unknown concentration was used. ^c Electrolyte is 0.1 M TEAP. ^d $\nu = 0.010 \text{ V s}^{-1}$. ^e $\nu = 0.005 \text{ V s}^{-1}$.

for structure **4** appears to be the presence of an oximate function two carbon atoms away from a donor nitrogen atom. The most characteristic property of all^{19,21,22} type **4** complexes known to date is that they have only one unpaired electron ($S = 1/2$). A semiquantitative study of this strong exchange interaction has appeared.¹⁹

B. Formal Potential and Electron-Transfer Rate. All complexes except the PhL species have $p > 0$, and all complexes except this one are electroactive at a platinum working electrode in acetonitrile, dimethylformamide (DMF), and methanol in the voltage range 0.0–1.0 V vs. SCE. The cyclic voltammetric response in the active part of this range for the PrL species is displayed in Figure 1. At relatively slow scan rates (ν) the separation (ΔE_p) between cathodic (E_{pc}) and anodic (E_{pa}) peak potentials is exactly or nearly equal to 58 mV for all systems (Table II). The cathodic (i_{pc}) and anodic (i_{pa}) peak currents are also nearly equal in magnitude. The presence of a Nernstian one-electron process is indicated. When the potential of the working electrode is held at E , good electrolytic response occurs at $E > E_{pa}$ but not at $E < E_{pc}$. The electroactivity of **4** is thus due to its oxidation and not reduction. Since the PhL species with $p = 0$ is not electroactive, the response in the domain 0.0–1.0 V can arise only from the [Cu₃O] core (**4a**) and not [Cu₃OH] core (**4b**). The correctness of this proposal is proved beyond doubt in the next sections. The electrode process is then



Here **5a** is believed to have the gross structure of **4a** except that it contains one less electron. The uniform Nernstian character of (1) is good evidence that no substantial stereochemical rearrangements or chemical reactions attend the electron-transfer process. Formal potential ($E^{\circ}_{298'}$) data calculated from relation 2 are set out in Table II. All mea-

$$E^{\circ}_{298'} \simeq 0.5(E_{pa} + E_{pc}) \quad (2)$$

Table III.^a Heterogeneous Electron-Transfer Rate Constants in Acetonitrile^b

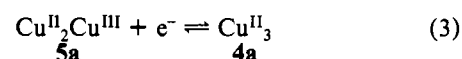
ligand ^c	$10^6 D_{Ox}$	$10^6 D_{Red}$	ν^d	ΔE_p^e	$\psi \nu^{1/2}$	$10^3 k_{s,h}$
EtL	7.3	6.1	0.350–0.500	0.087–0.094	0.51 ± 0.01	13.9
PrL	12.4	9.5	0.200–0.400	0.103–0.120	0.23 ± 0.02	7.7
BuL	17.1	15.2	0.100–0.200	0.127–0.140	0.12 ± 0.01	5.0
PrL'	10.3	9.9	0.650–0.700	0.090–0.095	0.71 ± 0.06	24.8
BuL'	16.8	14.2	0.500–0.700	0.097–0.105	0.43 ± 0.01	18.0

^a All symbols have the same meaning as in the text. Units: D_{Ox} and D_{Red} , $\text{cm}^2 \text{ s}^{-1}$; ν , V s^{-1} ; ΔE_p , V; $k_{s,h}$, cm s^{-1} . ^b Electrolyte is 0.1 M TEAP. ^c Concentration of complex $\sim 1 \times 10^{-3} \text{ M}$. ^d Measurements were done at several points within the range shown in each case. ^e The range of values in each case corresponds to range of scan rates.

surements reported in this were made at 298 K and all potentials were referenced to a saturated calomel electrode (SCE). The $E^{\circ}_{298'}$ values of the RL complexes are more or less independent of R, and the same comment applies for the RL' species. However, in going from RL to RL' chelates, the redox potentials become more positive in consonance with the presence of electron-withdrawing phenyl groups in RL'.

Progressive deviation from Nernstian ΔE_p occurs as ν is increased and a condition of quasi-reversibility is established (Figure 1, Table III). The heterogeneous electron-transfer rate constant $k_{s,h}$ for the backward step in eq 1 was determined by using the ψ - ΔE_p curve of Nicholson²³ and experimentally measured diffusion coefficients. Representative results are set out in Table III. Even though the absolute values of $k_{s,h}$ may not be very accurate due to iR compensation problems in nonaqueous media, the following observed trends remain valid: (i) $k_{s,h}$ decreases on increasing the size of R, and (ii) $k_{s,h}$ increases in going from RL to more aromatic RL' species.

C. Comments on 5a. The electrode reaction (1) corresponds to the oxidation-state description (3). No precedents exist



with which the present results can be compared. Mononuclear copper(III)–copper(II) couples in peptide complexes are known^{11,12} to have $E^{\circ}_{298'}$ values in the range 0.30–0.75 V vs. SCE. We wish to stress that mixed-valence copper(III,II) species are virtually unknown in the literature. Since in **4a** the copper(II) centers interact¹⁹ strongly via O and NO bridges, strong intervalence bands are expected in **5a**. Indeed an intense ($\epsilon \sim 10^4$) absorption band is observed at $\sim 830 \text{ nm}$ in **5a**. This band is absent in **4a**, which displays only a ligand field band¹⁹ at $\sim 600 \text{ nm}$. Attempts have been made to isolate **5a** in the crystalline state, with encouraging results. The first indications are that it is diamagnetic. A full account on this unusual species will be published in due course.

D. Coulometry, Peak Current, and Composition. Quantitative assay of the electroactive species was made with use of both constant-potential coulometric counts (Q) and peak current data normalized with respect to scan rate ($i_{pa}/\nu^{1/2}$). Coulometric data were collected at 0.6–0.7 V vs. SCE, i.e., at a potential $\sim 0.3 \text{ V}$ more positive than $E^{\circ}_{298'}$. Values of Q and $i_{pa}/\nu^{1/2}$ vary from complex to complex (Table IV) evidently due to variation of p from complex to complex (Table I). The PhL species ($p = 0$) gives $Q = 0$. The electrochemical data allow an independent determination of p . The weight w of a complex is

$$w = m_{4a}M_{4a} + m_{4b}M_{4b} \quad (4)$$

where m and M are respectively the number of moles and molecular weight while the subscripts 4a and 4b correspond to species **4a** and **4b**. If the proposal that **4a** alone is electroactive is correct, the value of Q directly measures m_{4a} and hence m_{4b} (since w , M_{4a} , and M_{4b} are known). With use of eq 5, p is readily calculated (Table IV). The good agreement

$$m_{4a}/m_{4b} = p/(1-p) \quad (5)$$

Table IV.^a Coulometric Assay of Composition

ligand	solvent ^b	coulometry		<i>p</i>	$\frac{m_{4a}}{m_{4b}}$	$\frac{i_{pa}}{v^{1/2}}$ ^e
		<i>Q</i> (found) ^c	<i>Q</i> (calcd) ^d			
EtL	CH ₃ CN	1.11	1.40	0.81	4.35	1535
	MeOH					1064
	DMF					1126
PrL	CH ₃ CN	0.54	1.32	0.43	0.78	969
	MeOH	0.55	1.32	0.45	0.81	578
BuL	CH ₃ CN	0.45	1.25	0.38	0.62	962
	MeOH					648
EtL'	CH ₂ Cl ₂ ^f	0.68	0.91	0.77	0.33	
PrL'	CH ₃ CN	0.66	0.88	0.77	0.32	1114
	MeOH	0.68	0.88	0.79	0.37	
	DMF					870
BuL'	CH ₃ CN	0.65	0.85	0.78	0.36	1362
PhL	CH ₃ CN	0.00	1.03	0.00	0.00	0

^a Symbols used have the same meaning as in the text. Units: *Q*, C; *i*_{pa}, μA; *v*, V s⁻¹. ^b Supporting electrolyte is 0.1 M TEAP. ^c Ten milligrams of complex was used in each case; value shown is an average of three independent determinations; coulometry was performed at a potential ~0.3 V more positive than the *E*₂₉₈^o values given in Table II. ^d Calculated on the assumption that the entire complex (10 mg) is oxidizable and that composition is 4b in the PhL system and 4 for the rest. ^e Ten milligrams of sample in 10 mL of solution under Nernstian conditions. ^f This solvent was chosen since the EtL' system is only very sparingly soluble in CH₃CN and MeOH.

among the *p* values of Tables I and IV indeed confirms that the electrochemical response in the 0.0–1.0 V range arises from 4a alone. The protonated 4b component is electrochemically silent. As expected the cyclic voltammogram of the coulometrically oxidized solution is identical with that of the original solution.

Whereas in the solution phase the complexes behave as mixtures of 4a and 4b, from the present experiments it is not clear whether in the crystalline state each complex is a particular mechanical mixture of 4a and 4b or whether it represents a single stable [Cu₃O]_{*p*}[Cu₃OH]_{1-*p*} phase as in the crystals of the trinuclear copper(II) complex²² of 2-(propylamino)-2-methyl-3-butanone oxime (*p* = 0.5). It is noted that the composition of a given complex does not vary from preparation to preparation as long as the synthetic procedure given in the Experimental Section is adhered to.

E. Proton Addition and Abstraction. In order to test further the hypothesis regarding the vastly different electron-transfer characters of Cu₃O and Cu₃OH cores, we attempted to chemically interconvert 4a and 4b with concomitant assay of the changes in electrochemical response.

The addition of a strong protonic acid (HClO₄) to systems containing both 4a and 4b diminishes the electrochemical response. The current heights (Figures 2 and 3) and Coulombic counts (Figure 3) decrease in exact proportion to the amount of acid added. Evidently the reaction (6) occurs



quantitatively. By extrapolation of cyclic voltammetric peak current to zero or Coulombic count *Q* to zero, the amount of acid needed to convert the whole of 4a in a sample to 4b could be determined (Figure 3). This amount is a direct measure of *p*. The values of *p* thus determined (Table V) are in complete agreement with values of Table IV.

Addition of a base such as triethylamine has an effect which is opposite to that of proton addition; i.e., the electrochemical response is augmented. Continued addition eventually yields limiting *i*_{pa} (in methanol solution). However, an excess of base is required to reach this limit. The presence of the equilibrium reaction

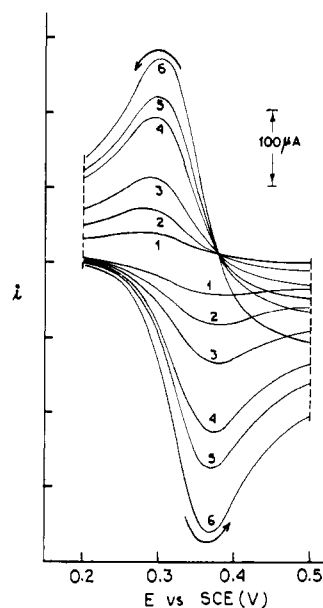


Figure 2. Effect of the addition of 10⁻² M perchloric acid on the EtL system (7.13 mg in 10 mL) in acetonitrile. Volume (mL) of acid added: (1) 1.00, (2) 0.82, (3) 0.62, (4) 0.30, (5) 0.20, (6) 0.00.

Table V.^a Stoichiometry of Proton Addition

ligand	solvent ^b	<i>w</i>	<i>C</i>	<i>p</i>
EtL	CH ₃ CN	7.13	8.47	0.83
	MeOH	7.95	9.18	0.81
PrL	CH ₃ CN	18.20	10.39	0.45
	CH ₃ CN	15.86	7.15	0.38
PrL'	MeOH	20.99	9.43	0.37
	CH ₃ CN	11.13	7.96	0.80
BuL'	CH ₃ CN	13.29	8.91	0.79

^a Symbols: *w*, weight of complex in mg taken in 10 mL of solvent; *C*, extrapolated (*i*_{pa} = 0) amount of perchloric acid in μM; *p*, mole % of 4a. ^b Supporting electrolyte is 0.1 M TEAP.

Table VI.^a Proton Abstraction Equilibria in Methanol^b

ligand	<i>C</i> (0)	<i>b</i> (l)	<i>i</i> _{pa} (0)	<i>i</i> _{pa} (l)	$\frac{m_{4a}}{m_{4b}}$	<i>K</i>
EtL	0.655	0.74	225	280	4.17	5
PrL	0.575	0.91	100	220	0.83	3
BuL	1.100	0.84	210	500	0.72	1

^a Symbols: *C*(0), initial concentration of complex in mg mL⁻¹; *b*(l), concentration of NEt₃ in μmol mL⁻¹ corresponding to the limiting current *i*_{pa}(l); *i*_{pa}(0) and *i*_{pa}(l) (in μA) and other symbols have the same meaning as in the text. ^b Supporting electrolyte is 0.1 M TEAP.

Table VII.^a Equilibrium Constant *K* for the BuL System in Methanol

mL of NEt ₃ ^b added	[4a]	Δ[4a]	[4b]	[NEt ₃]	<i>K</i>
0.0	0.505		0.811		
0.4	0.671	0.166	0.645	0.168	1.0
0.6	0.739	0.234	0.577	0.266	1.1
0.8	0.823	0.318	0.493	0.249	1.5
1.0	0.872	0.367	0.444	0.466	1.5
					av 1.3

^a All symbols have the same meaning as in the text; concentrations are given in mM. Supporting electrolyte is 0.1 M TEAP. ^b 10.00 × 10⁻³ M methanolic solution of NEt₃ was used.

is indicated. Results are shown in Figures 4 and 5 and Table VI. The normally electroinactive Cu₃OH(PhL)₃(ClO₄)₂ gives well-defined voltammograms (Figure 4) on addition of NEt₃. Unfortunately, the solutions containing excess amine did not

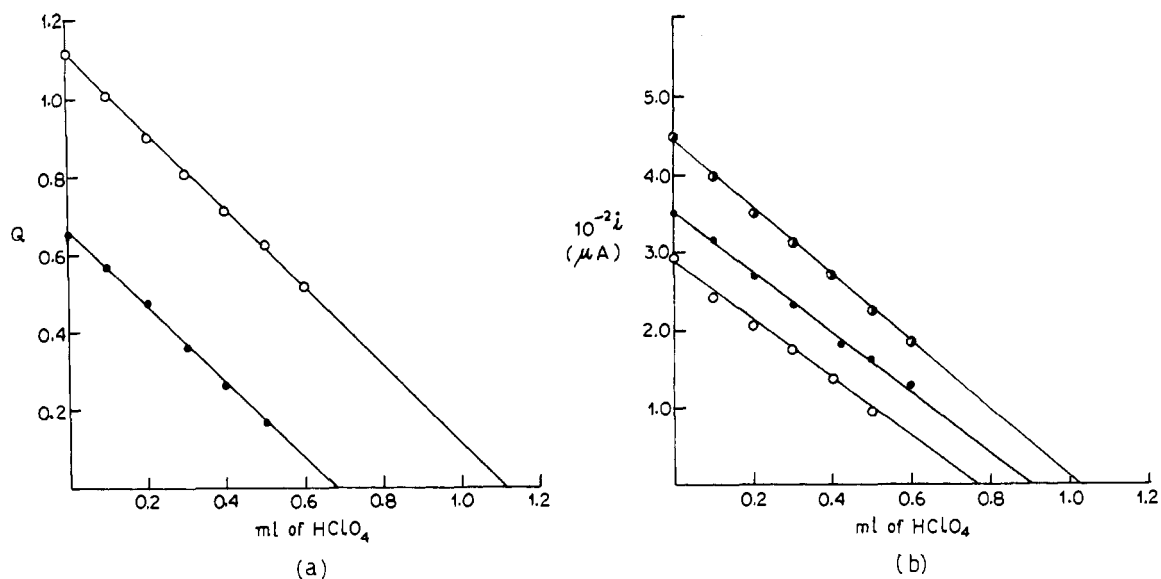


Figure 3. Coulomb count and anodic peak current ($v = 0.100 \text{ V s}^{-1}$) as a function of the volume of 10^{-2} M perchloric acid added (solid lines are least-squares fitted): (a) ●, PrL' system, 10 mg in 25 mL of acetonitrile; ○, EtL system, 10 mg in 25 mL of acetonitrile. (b) ○, PrL system, 18.20 mg in 10 mL of acetonitrile; ●, BuL system, 20.99 mg in 10 mL of methanol; ○, BuL system, 15.86 mg in 10 mL of acetonitrile.

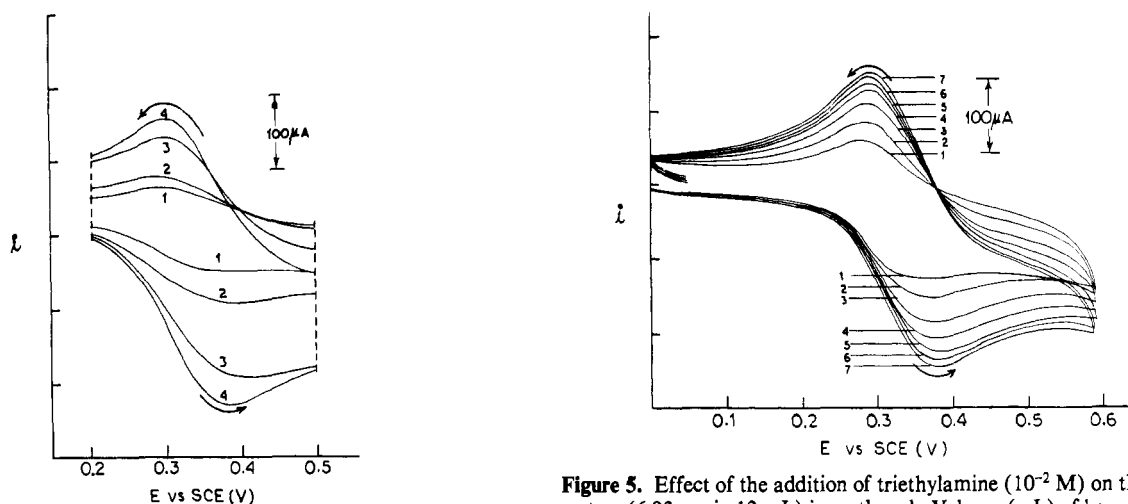


Figure 4. Effect of the addition of triethylamine (10^{-2} M) on the PhL complex (9.60 mg in 12 mL) in methanol. Volume (mL) of base added: (1) 0.5, (2) 0.7, (3) 1.1, (4) ≥ 1.5 . Scan rate was 0.100 V s^{-1} .

give reproducible coulometric end points (at 0.6 V). Continuous accumulation of coulombs took place due to unidentified side reactions. We therefore had to depend only on i_{pa} measurements. The problem of progressive deviation from reversibility (increase in ΔE_p) with increasing amine concentration still remained (Figure 5). Due to these complications the results with base addition are only of semiquantitative significance.

If $i_{pa}(0)$ is the initial (no base added) current and $i_{pa}(1)$ is the current when the limiting situation is just reached, it is readily seen that

$$i_{pa}(0) / [i_{pa}(1) - i_{pa}(0)] = m_{4a} / m_{4b} \quad (8)$$

The m_{4a}/m_{4b} ratios thus determined (Table VI) agree well with values in Table IV. Since $i_{pa}(0)$ and concentrations of **4a** in a sample are known (Table IV), the increment in current height due to addition of a known amount of base gives a measure of the increment of **4a** due to the equilibrium reaction (7). This allows determination of the equilibrium constant K for this reaction. The results are in Table VI. The acidity of **4b** in methanol increases slightly in the order BuL < PrL

Figure 5. Effect of the addition of triethylamine (10^{-2} M) on the PrL system (6.93 mg in 12 mL) in methanol. Volume (mL) of base added: (1) 0.0, (2) 0.2, (3) 0.4, (4) 0.6, (5) 0.8, (6) 1.0, (7) ≥ 1.2 . Scan rate was 0.100 v s^{-1} .

< EtL. The RL' systems could not be studied due to their lack of solubility in methanol. Replacement of triethylamine by pyridine yielded qualitatively similar results. Starting with a given sample, the effect of addition of acid can be reversed by subsequent addition of base and vice versa, and the process can be repeated over several cycles, showing that the trinuclear species remain intact during protonation and deprotonation.

F. Proton Valve. There is a symbiotic relationship between electron transfer and proton transfer. Simply stated the effect is of electrostatic origin: the removal of a proton decreases the potential barrier to the removal of an electron. In aqueous solutions cases are well documented²⁴ where electron loss from the metal ion under an applied dc potential is associated with "concerted" proton transfer from the ligand to the solvent. In the present systems such a situation could not be achieved under the accessible range of potential even when a protic solvent such as methanol was used. Voltammetric studies were also performed in methanol-water and acetonitrile-water mixtures. The results were essentially the same as those in the neat solvents. Here, the electron-transfer pathway remains

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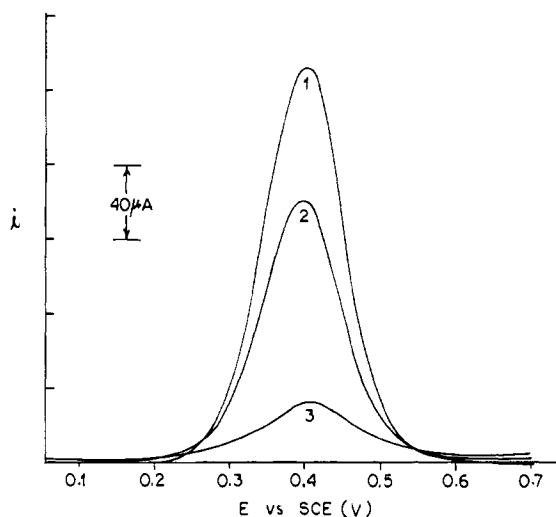
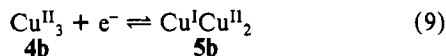


Figure 6. Phase-sensitive ac polarogram of the PrL' system (12.62 mg in 11 mL) and the effect of addition of 10^{-2} M HClO_4 . Volume (mL) of acid added: (1) 0.0, (2) 0.3, (3) 0.7. Ac modulation and frequency were 10 mV and 200 Hz; scan rate was 0.002 V s^{-1} .

shut off as long as the proton is present on the oxygen bridge. Opening of the pathway occurs only when the inhibiting proton is removed by prior addition of a strong base.

Conversely, the addition of proton should decrease the potential barrier to the addition of an electron. Preliminary work has indeed shown that **4** displays a quasi-reversible ($\Delta E_p \sim 70\text{--}100 \text{ mV}$) one-electron reduction at a hanging mercury drop electrode near -0.4 V vs. SCE in acetonitrile. Here *only* the **4b** component is electroactive and **4a** is not. The electrode process can be written as



where **5b** is believed to have the same gross structure as **4b** except that it has an *extra* electron. Further details will be reported elsewhere.

Thus the proton in **4b** acts in a valvelike fashion allowing an extra electron to come in (couple (9)) but disallowing removal of any of the original electrons (inapplicability of couple (3) to **4b**).

G. Phase-Sensitive Alternating-Current Cyclic Voltammetry.

In a few cases, reaction 1 was also investigated with the use of this technique. At low dc scan rates the peak potentials for forward and backward scans coincide as expected for Nernstian dc processes. The width of the peak at half-height is $\sim 100 \text{ mV}$, showing that the electrode process is more or less ac reversible.²⁵ In each case the observed peak potential is found to be the same as E°_{298} tabulated earlier (Table II). On the addition of acid the height of the peak diminishes (reaction 6). One case is illustrated in Figure 6.

Experimental Section

Materials. Biacetyl monoxime was prepared by a reported method.²⁶ Benzil was converted to α -benzil monoxime by using a standard method.²⁷ The commercially available amines were freshly distilled over KOH pellets before use. Anhydrous ethylamine was generated by dropping 50% aqueous solution on KOH pellets. For deprotonation experiments, solutions of triethylamine of known concentration were prepared by directly adding a known weight of the amine to the appropriate solvent. Standard ($\sim 0.01 \text{ M}$) perchloric acid solutions in various solvents were prepared by adding known amounts of standardized concentrated (70% in aqueous solution) acid. Tetra-

ethylammonium bromide was converted to tetraethylammonium perchlorate²⁸ (abbreviated as TEAP). Acetonitrile for electrochemical work was prepared from the commercial solvent by CaH_2 and P_4O_{10} treatment. Electrochemically pure methanol was prepared²⁹ by treating the commercial analytical grade solvent with magnesium and iodine. Fresh analytical grade dimethylformamide was used directly without further purification. A standard method³⁰ was used to purify dichloromethane. In every case electrochemical inertness of the solvent up to at least $+1.0 \text{ V}$ vs. SCE at a platinum electrode was carefully established before undertaking experiments with complexes.

Preparation of Complexes. The syntheses of the RL complexes were reported¹⁹ to yield pure **4b** species for the case of PhL and pure **4a** species for EtL, PrL, and BuL. While the former case could be reproduced, it has now been found that pure samples of **4a** are not readily obtained. With use of excess amines, species which approach the composition of **4a** sometimes result, but the compounds crystallize with difficulty and the reproducibility of preparation is rather poor. When the prescription given below is followed, crystalline products are invariably obtained.

$[\text{Cu}_3\text{O}_p(\text{OH})_{1-p}(\text{RL})_3](\text{ClO}_4)_{2-p}$. A 1-g (10-mmol) sample of biacetyl monoxime was dissolved in 20 mL of dry ethanol. To this a solution of 3.7 g (10 mmol) of copper perchlorate hexahydrate was added with stirring. The resulting mixture was deep green. Freshly distilled amine was slowly added dropwise with constant stirring to this solution. Initially a green muddy precipitate was formed. This progressively dissolved with further addition of amine. Addition of amine was discontinued when a small fraction of the precipitate still remained undissolved. About 20 mmol of amine was needed. The mixture was then heated to reflux on a water bath for 1 h and was filtered hot. The clear filtrate was evaporated to 20 mL and was kept in the refrigerator for 5 h. The shining crystals that separated were filtered off, recrystallized from ethanol, and finally dried over P_4O_{10} . The yield was $\sim 50\%$.

$[\text{Cu}_3\text{O}_p(\text{OH})_{1-p}(\text{RL}')_3](\text{ClO}_4)_{2-p}$. A 2.25-g (10-mmol) sample of α -benzil monoxime was dissolved in a minimum volume of absolute ethanol, and 3.7 g (10 mmol) of copper perchlorate hexahydrate was then dissolved in it. To the resulting deep green solution, amine was added dropwise with constant stirring. The muddy precipitate thus formed did *not* dissolve much with addition of amine. The total amount of amine added was $\sim 25 \text{ mmol}$. The mixture was heated to reflux on a water bath for 3–4 h, during which the whole of precipitate dissolved and shining crystals started appearing in the flask. The mixture was cooled to room temperature and filtered. The crystals were washed thoroughly with ethanol and dried over P_4O_{10} . The yield was $\sim 80\%$.

The room-temperature magnetic moments (μ_{eff} in μ_B /copper) of the complexes used in the present study are as follows: EtL, 1.06; PrL, 1.08; BuL, 1.08; PhL, 1.01; EtL', 1.09; PrL', 1.10; BuL', 1.10. Moments were determined by the Gouy method using $\text{HgCo}(\text{SCN})_4$ as standard. Molar electrical conductivity (Λ_M in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) data in acetonitrile solution ($\sim 10^{-3} \text{ M}$), measured with the help of a Philips conductivity bridge, are as follows: EtL, 160; PrL, 249; BuL, 249; PhL, 267; PrL', 136; BuL', 133.

Electrochemical and Related Experiments. (a) **General Instrumentation.** A PAR Model 370-4 Electrochemistry System was used. Cyclic voltammetry was performed with the help of a PAR 174A polarographic analyzer, a PAR 175 universal programmer, and a RE 0074 X-Y recorder. A Beckman Model 39273 platinum-inlay electrode was used as the working electrode. A platinum wire constituted the auxiliary electrode while a saturated calomel electrode (SCE) provided the reference. All results reported in this work are uncorrected for junction potentials. Constant-potential coulometry was performed with the use of a PAR 173 potentiostat, a PAR 179 digital coulometer, and a PAR 377A cell system. A platinum wire gauge was used as the working electrode. Determination of current-time curves at constant potential required the use of PAR 173 potentiostat and the three-electrode configuration described earlier taken in conjunction with the X-Y recorder. Phase-sensitive alternating current voltammetry was performed with use of a PAR 124A lock-in amplifier, a PAR 174A polarographic analyzer, and a PAR 372 ac polarography interface. A modulation amplitude of 10 mV (peak to peak) and a

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sinusoidal frequency of 200 Hz were used. All measurements were performed in solvents which were 0.1 M in TEAP at 298 K.

(b) Determination of Electrode Area, Diffusion Coefficients, and Heterogeneous Rate Constants. In our work three different electrodes of the same model were used. The area in each case was determined by the chronoamperometric technique by following Lingane's procedure³¹ for unshielded planar diffusion. Aqueous $K_4Fe(CN)_6 \cdot 3H_2O$ ($D_{Red} = 6.58 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) in 0.1 M KCl was used as the standard. The area of the three electrodes was found to lie in the narrow range $0.18 \pm 0.01 \text{ cm}^2$. With the electrode area known, the diffusion coefficients of the complexes, D_{Ox} and D_{Red} were calculated from cyclic voltammetric peak current data under Nernstian conditions with the help of the Randles-Sevcick equation.³²⁻³⁴ The heterogeneous oxidative rate constant, $k_{s,h}$, was then derived from the equation

$$\psi = \gamma \alpha^{-1} k_{s,h} / (\pi n F v D_{Red} / RT)^{1/2} \quad (10)$$

where $\gamma = (D_{Ox}/D_{Red})^{1/2}$, taken in conjunction with the working curve.²³ The transmission coefficient α was set at 0.5.

(c) Equilibrium Constant K for Reaction 7

$$K = [4a][HNEt_3^+]/[4b][NEt_3] \quad (11)$$

If a_0 and b_0 are the total concentrations of complex and base, respectively, one has $a_0 = [4b] + [4a]$ and $b_0 = [NEt_3] + [HNEt_3^+]$.

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From coulometric data (Table IV) the initial concentration, $[4a]_i$, of **4a** is known. From the increment in peak current due to addition of base the increment $\Delta[4a]$ in the concentration of **4a** can be monitored. Then the relations $[4a] = [4a]_i + \Delta[4a]$, $[4b] = a_0 - [4a]$, $[HNEt_3^+] = b_0 - \Delta[4a]$, and $[NEt_3] = b_0 - \Delta[4a]$ allow the determination of K . Data for the BuL complex is given in Table VII.

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Note Added in Proof. Due to an error in recorder amplification setting all reported currents are exactly 10 times the actual values. This, however, does not affect any of the conclusions drawn.

Registry No. $[Cu^{II}_3O(EtL)_3](ClO_4)$, 53598-80-4; $[Cu^{II}_3O(PrL)_3](ClO_4)$, 73668-62-9; $[Cu^{II}_3O(BuL)_3](ClO_4)$, 73689-14-2; $[Cu^{II}_3O(EtL)_3](ClO_4)$, 76986-51-1; $[Cu^{II}_3O(PrL)_3](ClO_4)$, 76986-49-7; $[Cu^{II}_3O(BuL)_3](ClO_4)$, 76986-47-5; $[Cu^{II}_3(OH)(EtL)_3](ClO_4)_2$, 76986-64-6; $[Cu^{II}_3(OH)(PrL)_3](ClO_4)_2$, 76986-62-4; $[Cu^{II}_3(OH)(BuL)_3](ClO_4)_2$, 76986-60-2; $[Cu^{II}_3(OH)(PhL)_3](ClO_4)_2$, 73689-16-4; $[Cu^{II}_3(OH)(EtL)_3](ClO_4)_2$, 76986-58-8; $[Cu^{II}_3(OH)(PrL)_3](ClO_4)_2$, 76986-56-6; $[Cu^{II}_3(OH)(BuL)_3](ClO_4)_2$, 76998-84-0.

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Synthesis and Reactivity of a New Methylene phosphine

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A new, stable methylene phosphine $(Me_3Si)_2N-P=CHSiMe_3$ (**4**) was prepared via dehydrohalogenation of the chlorophosphine $(Me_3Si)_2N-P(Cl)-CH_2SiMe_3$ (**1**), using $LiN(SiMe_3)_2$ as the base. Compound **1** and the related phosphine $(Me_3Si)_2NP(CH_2SiMe_3)_2$ (**2**) were obtained by treating $(Me_3Si)_2NPCL_2$ with either 1 or 2 equiv of Me_3SiCH_2MgCl . Reaction of **1** with *t*-BuLi proceeded via chloride displacement rather than dehydrohalogenation to afford the *tert*-butyl phosphine $(Me_3Si)_2NP(t-Bu)CH_2SiMe_3$ (**3**). Two different modes of reactivity of **4** were observed: methanol added to the $p\pi$ bond, yielding the methoxyphosphine $(Me_3Si)_2NP(OMe)CH_2SiMe_3$ (**5**), while treatment with Me_3SiN_3 gave the novel imino-methylene phosphorane $(Me_3Si)_2NP(=NSiMe_3)(=CHSiMe_3)$ (**6**). Compound **6** also added methanol to form a *P*-methoxyphosphinimine, $(Me_3Si)_2NP(OMe)(=NSiMe_3)CH_2SiMe_3$ (**7**). The reaction of **1** with Me_3SiN_3 gave the azidophosphine $(Me_3Si)_2NP(N_3)CH_2SiMe_3$ (**8**), which on being heated underwent elimination of N_2 with formation of the dimeric forms (**10a** and **10b**) of the diiminophosphorane $(Me_3SiN=)_2PCH_2SiMe_3$ (**9**). Decomposition of **8** in the presence of Me_3SiCl , however, gave a *P*-chlorophosphinimine, $(Me_3Si)_2NP(Cl)(=NSiMe_3)CH_2SiMe_3$ (**11**). Proton, ^{13}C , and ^{31}P NMR spectroscopic data for this new series of compounds are reported.

Introduction

In recent years there has been considerable interest in the synthesis and reactivity of "low-coordinate" phosphorus compounds which contain $P=C$ or $P=N$ ($p-p$) π bonds. Aside from the well-known phosphabenzene,¹ compounds of this type include a relatively few examples of methylene phosphines,² $R_2C=PR'$, iminophosphines,³ $RN=PR'$, and aminophosphonium cations,⁴ $(R_2N)_2P^+$. In addition to being significant from a theoretical viewpoint, these $p\pi$ -hybridized phosphines appear to have great potential as new ligands in transition-metal chemistry⁵ and as possible precursors to new phosphorus-based polymer systems. It is this latter aspect to which some of our attention is now being directed.

As a major part of our continuing study⁶ of the chemistry of compounds which contain the Si-N-P linkage, we have demonstrated that certain easily prepared *N*-silyl phosphinimines are extremely effective precursors to new polyphosphazenes including $(Me_2PN)_n$.⁷ The success of this method is based on the relatively high reactivity of the Si-N bond. We are now attempting to extend this approach to the synthesis of different types of phosphorus-containing polymers. Accordingly, we have begun a study of the synthesis, reactivity, and stereochemistry of new $p\pi$ -hybridized phosphorus compounds that contain silicon-nitrogen substituents. In this initial paper we report the synthesis, characterization, and some reactions of a new 2-coordinate P^{III} compound, $(Me_2Si)_2NP=CHSiMe_3$.

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