Homolytic Aromatic Substitution of Coordinated Ligands. Alkylation of Phenanthroline with Free Radicals from Organometals

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Methylation of both 1,10-phenanthroline (Phen) and α,α'-bipyridine (bpy) coordinated to iron(III), ruthenium(III), and osmium(III) occurs specifically at the 4-positions when effected with methyl radicals generated either from the thermolysis of acetyl peroxide or by the oxidative cleavage of alkylmetals such as $(CH_3)_4Sn$, $(CH_3)_4Pb$, or $(CH_3)_2Hg$. Primary alkyl radicals such as R = *n*-propyl, isobutyl, or neopentyl undergo a similar ligand substitution of $(Phen)_3Fe^{3+}$ without skeletal rearrangement. The second-order rate constants k_L for ligand substitution of $(Phen)_3Fe^{3+}$ are determined by the competition method relative to the rate constants k_{Br} for bromine atom transfer from bromotrichloromethane. Absolute and comparative kinetic measurements establish the 4-positions in phenanthroline which is coordinated to iron(III) and phenanthroline in its protonated form (i.e., $PhenH^+$) to be of comparable reactivity toward the methyl radical. A chemical mechanism is discussed for inner-sphere electron transfer leading to ligand substitution in $(Phen)_3Fe^{3+}$. Evidence for reversibility in the homolytic addition of *n*-propyl and neopentyl radicals to $PhenH^+$ is presented. The oxidative cleavage of organometals is described as a ready source of a variety of alkyl radicals.

Homolytic substitutions of a variety of aromatic systems have been examined with structurally different types of organic radicals.[1-5] Protonation of nitrogen heterocycles is known to facilitate the homolytic aromatic substitution.[6-9] The effect of metal coordination on homolytic aromatic substitution has been examined in the phenylation of some pyridine–metal complexes by Gritter and Godfrey,[10] who found that more 2- and 4-phenylpyridines were formed relative to the 3-isomer in the metal complexes than in the free ligand. The role of the metal center was not clearly delineated.

Our earlier studies showed that alkyl radicals are readily derived from a variety of organometals upon oxidation.[11] The availability of the tris(1,10-phenanthroline)(Phen) and α,α'-bipyridine (bpy) complexes of metal oxidants such as iron(III), ruthenium(III), and osmium(III) offers an excellent opportunity to examine homolytic aromatic substitution on coordinated ligands. This system is especially intriguing since the relatively high reduction potentials of $Fe(Phen)_3^{3+}$, $Ru(Phen)_3^{3+}$, and $Os(Phen)_3^{3+}$ could provide a significant driving force for the aromatic substitution.[12] Furthermore, these metal complexes are coordinatively saturated and are sufficiently inert to substitution to allow meaningful conclusions to be drawn from kinetic studies.

Results

Homolytic aromatic substitution by methyl radicals derived from the oxidative cleavage of a variety of permethylmetals with $(Phen)_3Fe^{3+}$ is initially compared in this study with methyl radicals derived by the thermolysis of acetyl peroxide, especially with respect to the products as well as the rates of methyl substitution. The higher homologues are also generated by similar procedures to effect homolytic alkylation of the iron triad analogues, viz., $(Phen)_3Fe^{3+}$, $(Phen)_3Ru^{3+}$, and $(Phen)_3Os^{3+}$.

(I) Methylation of Phenanthroline during the Oxidation of $(CH_3)_nM$ with Tris(phenanthroline)iron(III). The permethylated derivatives of Sn(IV), Pb(IV), and Hg(II) are readily oxidized by tris(phenanthroline)iron(III), $Fe(Phen)_3^{3+}$, in acetonitrile solution simply upon mixing at room temperature.[13] Methylation of the coordinated 1,10-phenanthroline ligand proceeds according to the stoichiometry in eq 1 for tetramethyltin. The methylphenanthroline complex was identified directly from the ^1H NMR spectrum of the reduced iron(II) complex or by isolation of the free ligand following alkaline hydrolysis. The cleaved Me_3Sn^+ group was analyzed gravimetrically after precipitation as the diammine adduct with ammonia.[14] Spectral titration of the $Fe(Phen)_3^{3+}$ consumed in the oxidation confirmed the stoichiometric requirements of 2 equiv for each mol of the alkylmetal $(CH_3)_4Sn$, as listed in Table I. The same stoichiometry was obtained for $(CH_3)_4Pb$ and $(CH_3)_2Hg$, with the exception that $(CH_3)_3Pb^+$ and CH_3Hg^+ were separately isolated as the diammine adduct and the bromide derivative, respectively.

$$Me_4Sn + 2Fe(Phen)_3^{3+} \xrightarrow[CH_3CN]{-H^+} MePhenFe(Phen)_2^{2+} + Fe(Phen)_3^{2+} + Me_3Sn^+ \quad (1)$$

(II) Methylation of Phenanthroline during the Thermolysis of Acetyl Peroxide in the Presence of Tris(phenanthroline)iron(III). Acetyl peroxide was decomposed at 75 °C in the presence of $Fe(Phen)_3^{3+}$. The evolved carbon dioxide was determined quantitatively by gas–liquid chromatography, and used to evaluate the extent of peroxide decomposition.[15] Indeed, the rate of

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(13) (a) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593. (b) The methyl and ethyl products were misassigned; see the Experimental Section.
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Table I. Oxidation of $(CH_3)_nM$ and Decomposition of Acetyl Peroxide in the Presence of $Fe(Phen)_3^{3+}$ [a]

Me_nM (amt × 10^4, mol)	amt of $Fe(Phen)_3^{3+}$ × 10^4, mol	% products [b] MePhen [d]	MeH	EtH	$Me_{n-1}M^+$	stoich [c]
Me_4Sn (2.9) [e]	5.0	91	2	<0.1	107 [f]	0.46
Me_4Sn (19)	10.0	98		<0.1		0.49
Me_4Pb (5.6)	11.2	96	3	<0.1	104 [f]	0.48
Me_2Hg (2.9)	5.0	84		<0.1	69 [g]	0.42
$(MeCO_2)_2$ (16) [h]	5.0	64	4	2		2.1 [i]

[a] In 20 mL of CH_3CN at 20 °C unless indicated otherwise. [b] Based on iron(III) charged. [c] Material balance as: ΣR/Fe(III) consumed (theoretical 0.50, according to eq 1). [d] Isolated as 4-methylphenanthroline after hydrolysis. [e] At 70 °C. [f] Isolated as $Me_3M(NH_3)_2ClO_4$. [g] Isolated as MeHgBr. [h] At 75 °C. [i] Based on CO_2 evolved.

Table II. Effect of Various Atom-Transfer Agents on the Oxidation of Tetramethyltin by $Fe(Phen)_3^{3+}$ [a]

transfer agent (concn, M)	methyl product, μmol (% yield) [b] CH_3X	CH_4
$BrCCl_3$ (0.05)	29 (73) [c]	1 (3)
$BrCCl_3$ (0.10)	32 (81) [c]	
$BrCCl_3$ (0.25)	37 (93) [c]	
$BrCCl_3$ (0.50)	39 (97) [c]	
$BrCCl_3$ (0.50) [d]	<0.2 [d]	
CCl_4 (4.0)	9 (23) [e]	3 (6)
$PhC(CH_3)_2H$ (4.0)		4 (10)

[a] In 2 mL of CH_3CN containing 8×10^{-5} mol of $Fe(Phen)_3^{3+}$ and Me_4Sn at 65 °C. [b] Based on 2 equiv of iron(III) for each equivalent of Me_4Sn. [c] Methyl bromide. [d] No iron(III) added. [e] Methyl chloride.

evolution of CO_2 could be employed directly as a measure of methyl radical production, since it was unaffected by the presence of $(Phen)_3Fe^{3+}$, i.e., eq 2.[16] Methylation

$$(CH_3COO)_2 \xrightarrow{\Delta} 2CH_3\cdot + 2CO_2 \qquad (2)$$

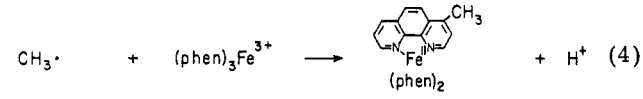
under these conditions afforded the same reduced iron product, $MePhenFe(Phen)_2^{2+}$, described in eq 1. It is noteworthy that only small amounts of methane and ethane were formed in the presence of $Fe(Phen)_3^{3+}$, as shown in Table I.[17]

(III) Methylation as a Homolytic Process. The formation of the same methylation product of $(Phen)_3Fe^{3+}$ from both acetyl peroxide and the organometals $(CH_3)_nM$ suggests that the methyl radical is the common precursor. This conclusion is supported by the observation that methyl radicals generated from each of the alkylmetals in Table I can be quantitatively scavenged by atom-transfer agents such as carbon tetrachloride and bromotrichloromethane.[18] (eq 3). Indeed, the results in Table II show

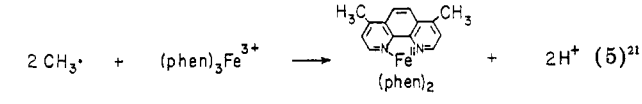
$$CH_3\cdot + BrCCl_3 \rightarrow CH_3Br + Cl_3C\cdot \qquad (3)$$

that only low concentrations of $BrCCl_3$ are sufficient to intercept most of the methyl radicals. The stoichiometric consumption of $Fe(Phen)_3^{3+}$ under these conditions remained at 2 (see Experimental Section). The latter suggests that the trichloromethyl radical formed in eq 3 is itself further oxidized by $Fe(Phen)_3^{3+}$. Although the primary product(s) of this oxidation has not yet been completely established, the presence of phosgene was apparent from its IR absorption at 1820 cm^{-1} and from its conversion to CO_2 following the addition of water to the reaction mixture.[19] The yield of phosgene determined by quantitative IR analysis and the yield of CO_2 obtained by gas chromatography were >75 and 100%, respectively, based on the methyl bromide formed. [The oxidation of trichloromethyl radical by $(Phen)_3Fe^{3+}$ is included in the kinetics which are described in Scheme II in the Experimental Section.]

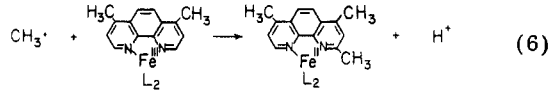
(IV) Identification of the Methylphenanthroline Isomers. The methyl group in $MePhenFe(Phen)_2^{2+}$ is visible in the ^1H NMR spectrum as a single sharp resonance at δ 2.9 in CD_3CN compared to δ 2.59 in the isolated free ligand. The substitution at the 4-position was established by comparing both the ^1H and ^{13}C NMR spectra with those of an authentic sample of 4-methyl-1,10-phenanthroline.[20] Homolytic alkylation as described in eq 4 is designated hereafter as a ligand-substitution process.



In order to establish the substitution pattern for multiple methylation, the reduced (phenanthroline)iron(II) complex was recycled by electrochemical oxidation back to the iron(III) precursor and resubjected to alkylmetal. This cycle was repeated five times, after which the iron complex was recovered and hydrolyzed and the free ligand isolated. At this point, the ^{13}C NMR spectrum was consistent with a mixture of only unsubstituted, 4-methyl-, and 4,7-dimethyl-1,10-phenanthroline. Separation by ion-exchange chromatography yielded the individual phenanthrolines as pure compounds which were characterized by their UV and ^1H NMR spectra, as well as their melting points (see the Experimental Section).



It was also of interest to ascertain the position of substitution when the 4- and 7-positions were already methylated. Accordingly, the experiment in eq 5 was repeated with $Fe(4,7\text{-}Me_2Phen)_3^{3+}$. The analysis of the ^1H NMR spectrum of the recovered phenanthroline suggested that substitution occurred cleanly at the 2-position, eq 6 where L = 4,7-dimethyl-1,10-phenanthroline.



The metal-free conjugate acid of phenanthroline, i.e., $PhenH^+$ as the trifluoromethane sulfonate salt, was also methylated with acetyl peroxide at 80 °C. Subsequent to

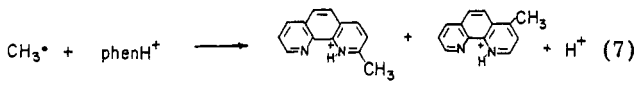
(16) The minor cage combination to methyl acetate notwithstanding.
(17) Most of the small amounts of methane are derived from protonolysis of the alkylmetals by acid formed during reaction.[19] [See: Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5405]. This can lead to yields of R_3Sn^+ in excess of 100% (compare Tables I and III).
(18) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 247 ff.
(19) Traces of water are also difficult to remove from acetonitrile.
(20) Richter, F.; Smith, G. F. *J. Am. Chem. Soc.* **1944**, *66*, 396.
(21) Equation 5 is not completely balanced.

Table III. Ligand Substitution on Coordinated (Phenanthroline)iron(III) by the Higher Alkyl Radicals [a]

alkyl radical (R·)	I_D, eV [b]	amt of $RSnMe_3$ × 10^4, mmol	amt of $Fe(Phen)_3^{3+}$ × 10^4, mmol	% products [c] Rphen	$[R^+]$ [d]	R_3Sn^+ [c]
ethyl	8.51	5.6	11.2	98	2	73
n-propyl	8.4	5.8	10.0	92	10	96
isopropyl	7.69	5.6	11.2	9	87	106
isobutyl	8.35	5.5	10.0	84	18	90
tert-butyl	6.92	5.6	11.2	<0.4	95	78
neopentyl	8.33	5.5	10.0	47	35	95
benzyl	7.20	6.9	10.0	<1	97	115
cyclohexyl	7.66	5.0	10.0	*f*	74	*f*

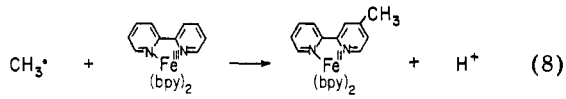
[a] In 20–25 mL of acetonitrile at 22 °C, except for cyclohexyl (50 mL). [b] From ref 22 and 41. [c] Based on iron(III) added; average of two or more runs. [d] Includes all alkenes and *N*-alkylacetamides; see ref 22. [e] Isolated as $Me_3Sn(NH_3)_2PF_6$ or Me_3SnCl(Et or *t*-Bu). [f] Not analyzed.

aeration and recovery of the free base, an NMR analysis showed that methyl substitution occurred at only the 2- and 4-positions (eq 7), in roughly a 60:40 ratio. The same results were obtained from the methylation of $PhenH^+$ with Me_4Pb and $Fe(Phen)_3^{3+}$.



Homolytic methylations of the iron(III) complexes as described in eq 4–6 are thus highly selective. The sterically hindered 2-position is methylated only after all the 4-positions have reacted. By contrast, the homolytic methylation of the conjugate acid $PhenH^+$ occurs indiscriminately at both the 2- and 4-positions. It may seem that the selective methylation of the phenanthroline in the iron complex by this pathway offers a synthetically attractive method. However, the multiple cycling of the iron complex required to achieve this end (see the Experimental Section) limits its practicability.

(V) Methylation of α,α′-Bipyridine. The tris(α,α′-bipyridine) complex of iron(III), $Fe(bpy)_3^{3+}$, reacted readily with tetramethyllead in acetonitrile at 25 °C to afford the methylbipyridine ((Me)bpy) complex in eq 8. The methyl



group in the iron(II) complex was characterized by a singlet resonance at δ 2.55 in the ^1H NMR spectrum, which was shifted to δ 2.35 in the free ligand. The methyl substitution was established to be at the 4-position by comparison of the ^1H and ^{13}C NMR spectra of the free ligand with those of analogous derivatives, as described in the Experimental Section.

(VI) Ligand Substitution with Higher Alkyl Radicals. Oxidative cleavage of tetraethyltin with 2 equiv of $Fe(Phen)_3^{3+}$ in acetonitrile at 25 °C led to ethylation of the phenanthroline ligand in high yield (>95%). Only small amounts (<5%) of ethane, ethylene, and *N*-ethylacetamide were formed. The same results were obtained in Table III with the unsymmetrical ethyltrimethyltin. It yielded $EtPhenFe(Phen)_2^{2+}$ according to the stoichiometry in eq 9, which is equivalent to that in eq 1 for tetramethyltin. The selective cleavage of the ethyl–tin bond in $EtSnMe_3$ was indicated by the high yields of the ethylation product $EtPhenFe(Phen)_2^{2+}$, the quantitative characterization of the cleaved tin moiety as the diammine adduct of Me_3Sn^+, and the small amounts (~2%) of the

$$EtSnMe_3 + 2Fe(Phen)_3^{3+} \xrightarrow[CH_3CN]{-H^+} EtPhenFe(Phen)_2^{2+} + Fe(Phen)_3^{2+} + Me_3Sn^+ \quad (9)$$

methylation product $MePhenFe(Phen)_2^{2+}$ observed. The ethylation product in eq 9 was readily detected from the characteristic resonances of the ethyl group [δ 1.38 (t, *J* = 7.6 Hz, 3 H), 3.11 (q, *J* = 7.6 Hz, 2 H)] in the ^1H NMR spectrum of the iron(II) complex and in the free ligand [δ 1.04 (t, *J* = 7.4 Hz, 3 H), 2.93 (q, *J* = 7.4 Hz, 2 H)] obtained by alkaline hydrolysis of the complex.

Although the nuclear position of substitution was not identified in each case, the ^1H NMR spectra unambiguously established that *n*-propyl and isobutyl radicals derived from the oxidative cleavage of *n*-$PrSnMe_3$ and *i*-$BuSnMe_3$, respectively, afforded substitution on the phenanthroline ligand without rearrangement of the alkyl group. For example, the ^1H NMR spectra of the free ligands after hydrolytic detachment from the complex showed splittings that were diagnostic of the *n*-propyl [δ 2.93 (t, *J* = 8.0 Hz, 2 H), 1.68 (sx, *J* = 7.4 Hz, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H)] and the isobutyl [δ 2.85 (d, *J* = 7.2 Hz, 2 H), 1.98 (m, *J* = 6.7 Hz, 1 H), 0.91 (d, *J* = 6.5 Hz, 6 H)] groups, respectively. Only a minor amount (<4%) of methylphenanthroline [δ 2.59 (s)] was present.

Neopentyl radicals (Np·) derived in high yields from the oxidative cleavage of neopentyltrimethyltin also effected substitution of the coordinated phenanthroline. The absence of skeletal rearrangement during ligand substitution, i.e., eq 10, was clearly indicated by the ^1H NMR spectrum

$$CH_3CCHSnMe_3 + 2Fe(Phen)_3^{3+} \xrightarrow{-H^+} (CH_3)_3CCH_2PhenFe(Phen)_2^{3+} + Fe(Phen)_3^{2+} + Me_3Sn^+ \quad (10)$$

of the isolated ligand [δ 2.93 (s, 2 H), 0.91 (s, 9 H)]. Although the yield of alkylphenanthroline was not as high (47%) as that derived from the other primary radicals, the selective cleavage of the neopentyl–tin bond in $NpSnMe_3$ was indicated by the formation of the cleaved Me_3Sn^+ in >95% yield, as determined by the gravimetric and ^1H NMR analyses of the diammine adduct. Furthermore, the amount of MePhen corresponded to only a 5% yield. The remainder of the neopentyl radicals was accounted for as a mixture of dimeric 2,2,5,5-tetramethylhexane (14%), *N*-*tert*-amylacetamides (14% after the addition of water), and amylenes (21%).[22] The same neopentylphenanthroline complex was obtained from the thermolysis of di-*tert*-butylacetyl peroxide in the presence of $(Phen)_3Fe^{3+}$.

Alkenes and *N*-alkylacetamides (that were formed as byproducts in the oxidation of primary alkyl radicals) became the principal products in the oxidation of secondary alkyl radicals. Thus isopropyl and cyclohexyl

(22) For a further description of the oxidation products derived from the alkyl cation, see: Rollick, K.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.

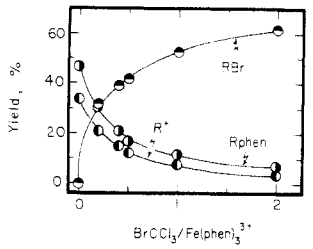


Figure 1. Typical effect of bromotrichloromethane on the alkyl products (R = neopentyl) derived from the oxidative cleavage of neopentyltrimethyltin by $(Phen)_3Fe^{3+}$ in acetonitrile.[23]

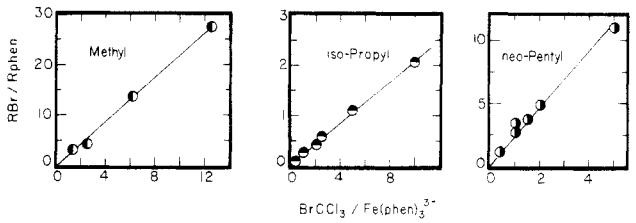


Figure 2. Relative rates of formation of akyl bromide (RBr) and ligand substitution product (as RPhen) during the oxidative cleavage of alkylmetals ($RSnMe_3$) by $Fe(Phen)_3^{3+}$ in the presence of various amounts of bromotrichloromethane. Left: R = methyl (RPhen = MePhen). Center: R = isopropyl (RPhen = *i*-PrPhen + *i*-Pr^+). Right: R = neopentyl (RPhen = neoPentPhen + neoPent$^+$).

radicals afforded less than 20% yield of the corresponding alkylphenanthroline. With tertiary alkyl radicals such as *tert*-butyl and the readily oxidized benzyl radical, no ligand substitution product was detected. The high yields (>95%) of alkenes and *N*-alkylacetamides listed in Table III were derived from a competing process in which alkyl cations resulted from electron transfer oxidation of the alkyl radical[22] (eq 11). The addition of even small

$$R\cdot + Fe(Phen)_3^{3+} \rightarrow Fe(Phen)_3^{2+} + R^+, \text{ etc.} \quad (11)$$

amounts (<0.05 M) of bromotrichloromethane as a radical trap was sufficient to divert the alkyl groups to alkyl bromides, i.e., eq 12. Thus, the competition from eq 12

$$R\cdot + BrCCl_3 \rightarrow RBr + Cl_3C\cdot \quad (12)$$

resulted in a corresponding reduction in the yields of alkylphenanthroline, alkene and alkylacetamide, as illustrated in Figure 1 for a typical example. Among various alkyl radicals, it was noteworthy that the cleaved neopentyl group affords only neopentyl bromide, and the *tert*-butyl group produced *tert*-butyl bromide. Likewise, chlorine atom donors such as carbon tetrachloride and trichloroacetonitrile produced the corresponding alkyl chlorides in excellent yields.

(VII) Kinetics of Ligand Substitution by Methyl and Other Alkyl Radicals. The efficient trapping of alkyl radicals by bromotrichloromethane in eq 12 allowed the kinetics of ligand substitution to be examined by the competition method.

(A) Ligand Substitution by Methyl Radical. When $Fe(Phen)_3^{3+}$ was treated with tetramethyltin at 25 °C in the presence of varying amounts of $BrCCl_3$, the cleaved methyl group was accounted for as a mixture of MeBr and MePhen (after hydrolytic removal of the ligand from the iron complex). The ratio of MeBr to MePhen in Figure 2 shows a linear dependence on the ratio of $BrCCl_3$ to $Fe(Phen)_3^{3+}$ over a 10-fold change in the concentration of bromotrichloromethane. The integrated rate expression for the competition is given by eq 13, as described in the Experimental Section. From the slope in Figure 2, the ratio of the rate constants for ligand substitution (eq 4) and bromine transfer (R = CH_3 in eq 12) is evaluated as $k_L/k_{Br} \approx 1$ at 65 °C. Since the second-order rate constant k_{Br} for bromine atom transfer to the methyl radical in eq 12 is 7×10^5 M^{-1} s^{-1} at this temperature,[24] we obtain a value of $\sim 7 \times 10^5$ M^{-1} s^{-1} for the rate constant k_L for ligand methylation. This magnitude of k_L is in reasonable agreement with that obtained from the relative rate data for either chlorine atom abstraction from carbon tetrachloride (2×10^5 M^{-1} s^{-1}) or for hydrogen atom abstraction from cumene (1×10^7 M^{-1} s^{-1}), especially if one considers the larger uncertainties in the rate constants of the monitoring reactions, i.e., k_{Br}, k_{Cl}, and k_H, which involve structurally different traps.[25,26] The competition experiment was also carried out with methyl radicals generated from the thermolysis of acetyl peroxide at 80 °C. The value of k_L/k_{Br} obtained with this precursor was essentially the same as that obtained from tetramethyltin, as listed in Table IV.

$$\frac{[\Delta MePhen]}{[\Delta MeBr]} = \frac{k_L}{k_{Br}} \frac{[Fe(Phen)_3^{3+}]}{[BrCCl_3]} \quad (13)$$

Table IV. Rates of Ligand Substitution of $Fe(Phen)_3^{3+}$ by Various Alkyl Radicals[a]

alkyl radical	source	k_L/k_{Br}
methyl	Me_4Pb	2.2 ± 0.6
	Ac_2O[b]	1.4 ± 0.1[b]
n-propyl	*n*-$PrSnMe_3$	2.1 ± 0.2
	$(n\text{-}PrCO_2)_2$	2.4 ± 0.1[c]
isopropyl	*i*-$PrSnMe_3$	~1
isobutyl	*i*-$BuSnMe_3$	1.00 ± 0.04
tert-butyl	*t*-$BuSnMe_3$	<0.1
neopentyl	*neo*-$PentSnMe_3$	0.26 ± 0.04

[a] In acetonitrile solution containing (1–3) × 10^{-2} M $Fe(Phen)_3^{3+}$ at 25 °C, except as noted otherwise. [b] At 80 °C. [c] At 70 °C.

(B) Ligand Substitution by Other Alkyl Radicals. The same kinetic technique was applied to the other alkyl radicals in Table IV. Once the optimum conditions were found for the simultaneous observation of alkylphenanthroline and alkyl bromide, the concentration of bromotrichloromethane was varied as in Figure 2. In every case, the ratio of alkyl bromide to alkylphenanthroline was established to be a linear function of the bromotrichloromethane concentration. The material balance based on alkyl radicals was in excess of 95% in these competition experiments. The ratio of rate constants k_L/k_{Br} for the *n*-propyl radical obtained from *n*-propyltrimethyltin and $Fe(Phen)_3^{3+}$ was the same as that obtained from *n*-butyryl peroxide as shown in Table V. The other alkyl radicals in Table IV were generated from the corresponding alkyltrimethyltin compounds.

(C) Alkylation of Various Phenanthroline Complexes. The rates of ligand substitution by methyl and *n*-propyl radicals were also evaluated for phenanthroline complexed to ruthenium(III) and osmium(III), viz.,

(23) RBr = neopentyl bromide, R^+ = 2-methyl-2-butene, 2-methyl-1-butene, or *N*-*tert*-amylacetamide, and RPhen = neopentyl-1,10-phenanthroline as described in ref 22.

(24) Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511. The authors give the second-order rate constant for eq 5 in the gas phase as: $k_{Br} = 10 \exp(8.1 \pm 0.3)e \exp{-(3.5 \pm 0.5/RT)} = 7 \times 10^5$ M^{-1} s^{-1} at 65 °C and 2×10^5 at 0 °C. We employ the same values in solution.

(25) From ref 24, $k_{Cl} = 10 \exp(8.8 \pm 0.3)e \exp{-(10.1 \pm 0.5/RT)} = 2 \times 10^2$ M^{-1} s^{-1} at 65 °C.

(26) Obtained from the rate constants by: Cher, M.; Hollingsworth, C. S.; Sicilio, F. *J. Phys. Chem.* **1966**, *70*, 877. Meyer, J. A.; Stannett, V.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 25. $k_H = 3.5 \times 10^3$ M^{-1} s^{-1} at 65 °C for cumene.

Table V. Comparative Rates of Ligand Substitution of Various Phenanthroline Complexes[a]

Phen complex	E^0, V[b]	methyl radical, 80 °C[c]	methyl radical, 25 °C[d]	*n*-propyl radical, 70 °C[e]	*n*-propyl radical, 25 °C[f]
$(Phen)_3Fe^{3+}$	0.99	1.4 ± 0.1	2.2 ± 0.6	2.4 ± 0.1	2.1 ± 0.2
$(Phen)_3Ru^{3+}$	1.19		4.9 ± 0.2	7.0 ± 0.6	8.9 ± 0.4
$(Phen)_3Os^{3+}$	0.74	0.15 ± 0.02	0.18 ± 0.01	0.67 ± 0.08	1.0 ± 0.1
$PhenH^+O_3SCF_3^-$		1.3 ± 0.2	1.7 ± 0.7[g]		

[a] In acetonitrile solution. Relative rates expressed as k_L/k_{Br}. [b] Relative to saturated NaCl-SCE at 25 °C in acetonitrile solution. [c] From acetyl peroxide thermolysis. [d] From tetramethyllead for M = Os and Fe and from tetramethyltin for M = Ru. [e] From di-*n*-butyryl peroxide thermolysis. [f] From *n*-propyltrimethyltin. [g] From Me_4Pb and $(Phen)_3Fe^{3+}$.

Table VI. Relative Reactivities of $(Phen)_3Fe^{3+}$ and $PhenH^+$ toward Various Alkyl Radicals[a]

alkyl radical	source	$k_{FeL_3^{3+}}/k_{Br}$[b]	k_{LH^+}/k_{Br}[c]	$k_{FeL_3^{3+}}/k_{LH^+}$, indirect[d]	$k_{FeL_3^{3+}}/k_{LH^+}$, direct[e]
methyl	Me_4Pb[f]	2.2 ± 0.6			1.3 ± 0.1
	$(MeCO_2)_2$[g]	1.4 ± 0.1	1.3 ± 0.1	1.1	1.9-2.5[j]
n-propyl	*n*-$PrSnMe_3$[f]	2.1 ± 0.2			
	$(n\text{-}PrCO_2)_2$[h]	2.4 ± 0.1	0.018 ± 0.002	130	3-10[j]
neopentyl	$C_5H_{11}SnMe_3$[f]	0.26 ± 0.04			1-8[j]
	$(C_5H_{11}CO_2)_2$[h]	0.25 ± 0.02	<0.003	>80	

[a] In acetonitrile solution containing 0.02-0.1 M $(Phen)_3Fe^{3+}$ and 0.02-0.5 M $PhenH^+$. [b] $k_{FeL_3^{3+}}$ is k_L for $(Phen)_3Fe^{3+}$. [c] k_{LH^+} is the rate constant for eq 7. [d] Ratio of column 3 to column 4. [e] Obtained from direct competition of $(Phen)_3Fe^{3+}$ and $PhenH^+$. [f] At 24 °C. [g] At 80 °C. [h] At 70 °C. [j] Variable with $[FeL_3^{3+}]/[LH^+]$; see the Experimental Section.

$(Phen)_3Ru^{3+}$ and $(Phen)_3Os^{3+}$ in Table V. Although the rates of ligand substitution in these complexes increase in the order ($Os^{III} < Fe^{III} < Ru^{III}$), the magnitude of the variation is not large, especially if the large differences in the reduction potentials E^0 of the metal oxidant is taken into account. To assess the role of the metal in ligand substitution, we examined the rate of homolytic alkylation of the metal-free ligand in the form of the conjugate acid $PhenH^+$ as the trifluoromethanesulfonate salt.[27] It is noteworthy that the value of k_L/k_{Br} for $PhenH^+$ with methyl radical lies in the region of that for $(Phen)_3Fe^{3+}$. The relative reactivity of $(Phen)_3Fe^{3+}$ and $PhenH^+$ with methyl radicals is 1.1, which is obtained by dividing the respective values of k_L/k_{Br}. In order to test the validity of this ratio, we redetermined the relative reactivity of $(Phen)_3Fe^{3+}$ and $PhenH^+$ under actual competition conditions, in which various amounts of $PhenH^+$ and $(Phen)_3Fe^{3+}$ were simultaneously methylated, i.e., eq 14.

$$(Phen)_3Fe^{3+} + PhenH^+ \xrightarrow{[CH_3\cdot]} MePhenFe(Phen)_2^{2+} + MePhenH^+, \text{ etc.} \quad (14)$$

The results in Table VI show that both the indirect method (column 5) and direct method (column 6) of analysis afford essentially the same values for the relative reactivity of $(Phen)_3Fe^{3+}$ and $PhenH^+$ toward methyl radicals. However, this consistency does not pertain to either the *n*-propyl radical or the neopentyl radical, both of which show striking variations in the apparent relative reactivities determined by the indirect and direct methods. Furthermore, the apparent relative reactivities in the direct method for these alkyl radicals vary with the relative concentrations of $(Phen)_3Fe^{3+}$ and $PhenH^+$, the extrapolated value of which more or less approaches that obtained by the indirect method. Reversibility in the homolytic addition of *n*-propyl and neopentyl radicals can account for this effect, e.g., eq 15 and 16. According to this formulation, the competition between ligand substitution in $(Phen)_3Fe^{3+}$ and homolytic substitution in $PhenH^+$ in the direct method will be dependent on the reversibility in eq 15.[28] Since the reversion of the methyl adduct is expected to be the smallest among these radicals,[29] the discrepancy between the indirect and direct methods will also be the smallest with this alkyl radical.

$$R\cdot + PhenH^+ \rightleftharpoons RPhenH^+\cdot \quad (15)$$

$$RPhenH^+\cdot + Fe(Phen)_3^{3+} \rightarrow RPhenH^+ + Fe(Phen)_3^{2+} + H^+ \quad (16)$$

(27) The rate constant represents all the products of homolytic substitution of $PhenH^+$ determined as the integrated ^1H NMR signal.

Discussion

The oxidative cleavage of alkylmetals leading to ligand substitution of coordinated phenanthroline in eq 1 may be considered in two parts: first, with regard to the formation of alkyl radicals as in eq 17 and second, relative

$$R_4Sn + Fe(Phen)_3^{3+} \rightarrow Fe(Phen)_3^{2+} + R_3Sn^+ + R\cdot \quad (17)$$

to the homolytic substitution step itself (eq 18). Eqs 15 and 16 together constitute the overall stoichiometry for ligand substitution as given in eq 1.

$$R\cdot + Fe(Phen)_3^{3+} \rightarrow RPhenFe(Phen)_2^{2+} + H^+ \quad (18)$$

(I) Formation of Alkyl Radicals during Oxidative Cleavage of Alkylmetals. The comparisons with alkyl radicals generated independently from the thermolysis of diacyl peroxides provide compelling support for free alkyl radicals as prime intermediates in the oxidative cleavage of alkylmetals, as presented in eq 17. (Note their similarity with respect to the common products in Table I, the trapping with bromotrichloromethane in Table II, the scavenging by dioxygen,[13a] and the uniformity of the rate constants in Table IV.) Although homolysis of acetyl peroxide in eq 2 is a well-established process,[30] the production of methyl radicals in the course of eq 17 requires some elaboration. It is known that alkylmetals such as $(CH_3)_4Sn$, $(CH_3)_4Pb$, and $(CH_3)_2Hg$ are excellent reducing agents by virtue of their low ionization potentials.[31] In-

(28) For a discussion of reversibility in homolytic aromatic substitution, see ref 5.

(29) (a) For example, Szwarc and co-workers[47] indicate no reversibility in the addition of methyl radicals to arenes. (b) Quantitative solution of the effects in Table VI require a knowledge of the rate constants in eq 15 and 16, as well as in eq 4.

(30) Nonhebel, D. C; Walton, J. C. "Free-Radical Chemistry"; Cambridge University Press: London, 1974.

deed, the standard reduction potential of $(Phen)_3Fe^{3+}$ is sufficient (E^0 = 0.99 V vs. SCE) to effect ready oxidation in acetonitrile, i.e.,[32] eq 19. The spontaneous fragmen-

$$(CH_3)_4Sn + (Phen)_3Fe^{3+} \rightarrow (CH_3)_4Sn^{+}\cdot + (Phen)_3Fe^{2+} \quad (19)$$

tation of the resultant metastable cation–radical affords high yields of methyl radicals, i.e., eq 20, even at tem-

$$(CH_3)_4Sn^{+}\cdot \rightarrow (CH_3)_3Sn^{+} + CH_3\cdot \quad (20)$$

peratures below 0 °C.[33] For unsymmetrical alkylmetals such as $RSnMe_3$, the selectivity in the formation of alkyl radicals, i.e., the relative amounts of R· and Me·, is determined during the fragmentation of the cation-radical. The preferential cleavage of the alkyl–metal bond in eq 21a, compared to the methyl–metal bond in eq 21b (as

$$RSnMe_3^{+}\cdot \rightarrow R\cdot + SnMe_3^{+} \quad (21a)$$

$$RSnMe_3^{+}\cdot \rightarrow Me\cdot + RSnMe_2^{+} \quad (21b)$$

determined by the products in Table III), is in accord with their expected relative strengths evaluated from the mean bond energies for R_4Sn and Me_4Sn, respectively.[34] Furthermore, the cracking patterns of various tetraalkyltin compounds upon electron impact afford similar selectivities in the fragmentation of alkyltin cation–radicals in the gas phase.[35]

It is important to emphasize that the production of alkyl radicals by the oxidative cleavage of alkylmetals as in eq 17 occurs under mild reaction conditions. It is limited solely by the rate of oxidation by the metal oxidant in eq 19, which can typically have a second-order rate constant in excess of 10^3 M^{-1} s^{-1}.[13a] Such a facile oxidative process for alkyl radicals is substantially less severe than the pyrolytic methods employed in the classic Paneth technique.[36]

Before proceeding with homolytic substitution, it is worthwhile discussing the alternative mode of fragmentation of the cation–radical, viz.,[37] eq 22. Methylation of

$$(CH_3)_4Sn^{+}\cdot \rightarrow (CH_3)_3Sn\cdot + CH_3^{+} \quad (22)$$

phenanthroline under these circumstances would correspond to electrophilic aromatic substitution. To test this possibility, we treated both $(Phen)_3Fe^{2+}$ and $(Phen)_3Fe^{3+}$ with the electrophilic methyl trifluoromethanesulfonate under the reaction conditions. No methyl incorporation into either iron complex was observed after 8 h at 35 °C. Indeed, eq 20 is expected to be more favorable than eq 22, owing to the high heat of formation of the methyl cation.[38]

(II) Mechanism of Ligand Substitution by Alkyl Radicals. The attack by an alkyl radical on $(Phen)_3Fe^{3+}$ leading to ligand substitution on the coordinated phenanthroline corresponds to an oxidation, since the iron(III) center is concomitantly reduced to iron(II) (eq 23). As

$$R\cdot + (Phen)_3Fe^{III} \xrightarrow{k_L} RPhenFe^{II}(Phen)_2 + H^{+} \quad (23)$$

such, ligand substitution in eq 23 is formally related to a variety of other oxidation–reduction processes, particularly

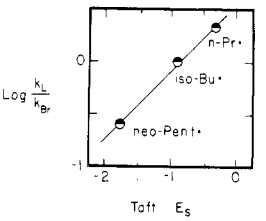


Figure 3. Steric effects (E_s) on the rates of ligand substitution ($\log k_L$) of $(Phen)_3Fe^{3+}$ by *n*-propyl (◓), isobutyl(◑), and neopentyl (◒) radicals relative to trapping by bromotrichloromethane (k_{Br}).

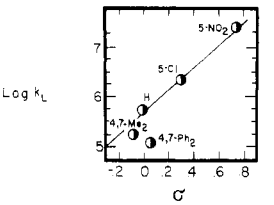


Figure 4. Hammett correlation of the rate of ligand substitution ($\log k_L$) by methyl radical of substituted phenanthroline complexes of iron(III) FeL_3^{3+} [Note the line is arbitrarily drawn only through the points for H-, 5-Cl-, and 5-NO_2Phen.]

those proceeding via inner-sphere electron transfer.[39]

In a recent study, we demonstrated how the sensitivity to steric effects can be used as a criterion for inner-sphere electron transfer.[32] Steric effects in ligand substitution are most effectively probed with the series of β-branched alkyl radicals, viz., *n*-propyl, isobutyl, and neopentyl, since the Taft steric parameter E_s shows significant increases of 0.36, 0.93, and 1.74, respectively,[40] while the ionization potentials of these alkyl radicals remain relatively constant at I_D = 8.35 ± 0.05 eV.[41] Figure 3 shows that the rates of ligand substitution ($\log k_L$) are severely retarded by steric effects under conditions of constant driving force, i.e., I_D. The enhanced sensitivity of this oxidative process to steric effects is thus in accord with a constained transition state characteristic of an inner-sphere electron transfer.

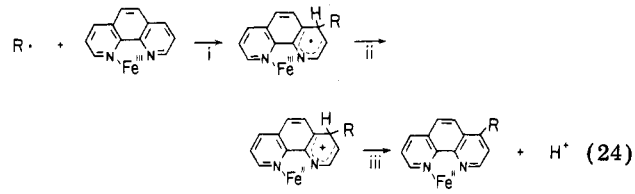
The mechanisms of inner-sphere electron transfer have been subclassified into several specific categories.[42] As applied to ligand substitution, two extreme roles can be envisaged for phenanthroline as the bridging ligand between the alkyl radical and the iron center.[39] In the *resonance mechanism*, the phenanthroline merely act as a mediator (there being no specifically bound states of phenanthroline along the reaction coordinate), and the rates will be dependent mainly on the identity of the metal oxidant. On the other hand in the *chemical mechanism*, the alkyl radical initially adds to the phenanthroline ligand, and the electron is transferred to the metal in a fast, subsequent step.

The rather pronounced sensitivity of ligand substitution to the electron availability in the phenanthroline ligand is shown by the Hammett correlation of the rate constant k_L in Figure 4.[43] Such a trend accords with the chemical

(31) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; p 501.
(32) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.
(33) For example, the lifetime of the cation–radical has an upper limit of 1 ms by double-step chronoamperometry (see: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790).
(34) See ref 31, p 237 ff.
(35) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961.
(36) Paneth, F.; Hofeditz, W. *Chem. Ber.* **1929**, *62*, 1335. See ref 18 and 30.
(37) Cf.: Eaton, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 3278.
(38) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.
(39) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264.
(40) Taft, R. W., Jr., "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 556 ff.
(41) (a) Lossing, F. P.; DeSousa, J. B. *J. Am. Chem. Soc.* **1959**, *81*, 281. (b) Taubert, R.; Lossing, F. P. *Ibid.* **1962**, *84*, 1523. (c) Elder, F. A.; Giese, C.; Steiner, B.; Inghram, M. *J. Chem. Phys.* **1962**, *36*, 3292. These authors report 8.1 eV, and Lossing et al. in ref 41a report 8.69 eV for *n*-propyl radical. We used a value of 8.4 eV which is more in line with the values for isobutyl and neopentyl (see: ref 31, pp 307, 453, and Nugent, W. A.; Wu, M. M.-H.; Fehlner, T. P.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1976**, 456).
(42) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: London, 1980; p 230 ff.
(43) Note that the deviation of the points for the iron(III) complexes of 4,7-dimethyl- and 4,7-diphenylphenanthrolines reflects the increased steric effects with these oxidants.

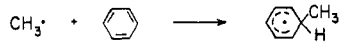
mechanism for ligand substitution. By contrast, the sensitivity of k_L to the metal oxidant (as an indicator of the resonance mechanism) is minor, despite the rather large driving forces for reduction as indicated by the values of E^0 in Table V. The value of k_L will be sensitive to the metal only in so far as the ligand orbitals (LUMO) are affected by coordination. Indeed, the similarity of the electronic spectra of $(Phen)_3Fe^{3+}$, $(Phen)_3Ru^{3+}$, and $(Phen)_3Os^{3+}$ to that of $PhenH^+$ indicates that the phenanthroline π oribitals are relatively unaffected by the metal.[22]

The chemical mechanism for ligand substitution may be considered in the sequence of three steps: (i) addition of the alkyl radical to the coordinated phenanthroline and (ii) intramolecular electron transfer from the ligand-centered radical to iron(III), followed by (iii) proton loss, as depicted in eq 24. The intramolecular electron transfer



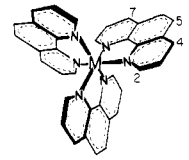
(24)

in step ii is akin to the relaxation process associated with the chemiluminescence observed during the facile reduction of $Ru(Phen)_3^{3+}$ with hydrazine.[44] Such processes are also related to the emission following the metal to ligand [M → π*] charge-transfer transition.[45] In this regard it is noteworthy that the decays of these excited states of $*Fe(Phen)_3^{3+}$, $*Ru(Phen)_3^{3+}$, and $*Os(Phen)_3^{3+}$ proceed at the measured rates of $\tau_{1/2}$ = 0.80, 920, and 84 ns, respectively. Accordingly, we consider the radical addition to the coordinated phenanthroline in step i to represent the rate-limiting process in ligand substitution.[46] It is reminiscent of the well-known addition of alkyl radicals to aromatic π-systems, e.g.[47]



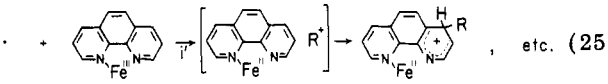
Such a homolytic process is usually described in organic chemistry as a nucleophilic addition of an alkyl radical to an aromatic LUMO, since it is favored by electron-withdrawing substituents in a variety of aromatic systems.[1-5] In the nitrogen heteroaromatic compounds, protonation significantly increases the selectivity for homolytic aromatic substitution, with a strong preference for the 2- and 4-positions of both pyridine and quinoline.[6,7] We observe the same selectivity in the homolytic addition of methyl radical to the 2- and 4-positions in the triflic acid salt of 1,10-phenanthroline in eq 7. The increased reactivity of the 2- and 4-positions of protonated pyridine derivatives towards homolytic substitution accords with theoretical studies based on free valence numbers and atom-localization energies.[48]

The direct relationship between the activation process for ligand substitution and that for homolytic aromatic substitution is underscored by the similarity in the rate constants for $(Phen)_3M^{3+}$ and $PhenH^+$ which are listed in Table V. Coordination of phenanthroline to a reducible metal center in $(Phen)_3M^{3+}$ clearly provides only limited assistance in radical addition, the effect of the metal not being significantly greater than that by protonation.[49] It suggests that metal coordination, like protonation, consists of localized σ bonding to the nitrogen heteroatom, the metal functioning largely as a simple Lewis acid. In order to account for the selective methylation of $(Phen)_3Fe^{3+}$ at the 4- and 7-positions in eq 5, we invoke the steric effects at the 2-position, which are evident from an examination of the structure below. Nonetheless, the importance of



electronic factors is emphasized by the observation of 2-substitution in eq 6 when the 4- and 7-positions are occupied as in $(4,7\text{-MePhen})_3Fe^{3+}$, despite the steric accessibility of the 5- and 6-positions in this iron complex.

Homolytic addition of an alkyl radical as the rate-limiting step i in eq 24 is to be contrasted with a two-step mechanism in which prior electron transfer is followed by collapse of the ion pair which corresponds to an electrophilic aromatic substitution by an alkyl cation, i.e., eq 25.



(25)

Such a formulation for ligand substitution is disfavored for two reasons. Electrophilic attack on the coordinated phenanthroline is expected to occur at the 5-position, judging by the previous results for electrophilic nitration of $(Phen)_3Fe^{3+}$ and $(Phen)_3Co^{3+}$ by Tobe and co-workers.[50] Next, alkyl cations are known to undergo rapid skeletal rearrangement.[51] The absence of the isomerized isopropylphenanthroline from *n*-propyl radicals, *sec*-butylphenanthroline from isobutyl radicals, and *tert*-amylphenanthroline from neopentyl radicals suggests that alkyl cations are not intermediates in ligand substitution.[52] Electron transfer as depicted in step i′ in eq 25 is, however, a viable process (particularly with secondary and tertiary alkyl radicals with lower ionization potentials), but they are either solvated by acetonitrile to afford *N*-alkylacetamide (after hydrolysis) or undergo β-proton loss to pro-

(44) Hercules, D. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1966**, *88*, 4745; *Photochem. Photobiol.* **1971**, *13*, 123. See also Tokel, N. E.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 2862.

(45) Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 310. Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *Ibid.* **1980**, *102*, 1309. Nagle, J. K.; Bernstein, J. S.; Young, R. C.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1760. Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301. Elfring, W. H., Jr.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 2683.

(46) (a) The rapidity of the intramolecular electron-transfer in step ii effectively renders the addition irreversible. (b) Although we have no direct evidence, step iii in eq 24 is presumed to be fast. A measurement of the deuterium kinetic isotope effect would be enlightening in this regard.

(47) Levy, M.; Szwarc, M. *J. Am. Chem. Soc.* **1955**, *77*, 1949. Smid, J.; Szwarc, M. *Ibid.* **1956**, *78*, 3322; **1957**, *79*, 1534. Heilman, W. J.; Rembaum, A.; Szwarc, M. *J. Chem. Soc.* **1957**, 1127.

(48) (a) Coulson, C. A. *Trans. Faraday. Soc.* **1946**, *42*, 265. Longuet-Higgins, H. C.; Coulson, C. A. *J. Chem. Soc.* **1949**, 971. Brown, R. D.; Harcourt, R. D. *Ibid.* **1959**, 3451. Brown, R. D.; Heffernan, M. L. *Aust. J. Chem.* **1956**, *9*, 83. (b) Similarities in homolytic and nucleophilic aromatic substitutions have led to discussions of the nucleophilicity of radicals (see ref 5–7 and 46). For nucleophilic substitution in nitrogen heterocycles see: Kiel, W.; Kröhnke, F.; Schneider, G. *Justus Liebigs Ann. Chem.* **1972**, *766*, 45. Hirota, M.; Masuda, H.; Hamada, Y.; Takeuchi, I. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1498.

(49) The statistical (partial rate) factors notwithstanding. The quantitative difference is difficult to ascertain, owing to the reversibility in the homolytic substitution of $PhenH^+$ as described in Table VI.

(50) Richards, A. F.; Ridd, J. H.; Tobe, M. L. *Chem. Ind. (London)* **1963**, 1727.

(51) For example, see: Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082 and related papers.

(52) Furthermore the activation process in eq 25 is more akin to that in a resonance mechanism and would require a strong influence of the metal on the rate of oxidation.

duce alkenes.[22] Such a competing process accounts for the product distribution for various alkyl radicals listed in Table III.

Finally, it is important to emphasize the similarity as well as the essential difference between ligand substitution (as given in eq 24) and the more conventional homolytic aromatic substitution processes. Thus both can involve addition as the rate-limiting step. However, such an addition in ligand substitution is irreversible, owing to the rapidity of the subsequent relaxation involving the intramolecular electron-transfer step ii in eq 24. The addition is therefore tantamount to an *oxidative* substitution, as written in eq 4 by a single step. By contrast, the addition in the more conventional homolytic substitution affords a discrete adduct radical (e.g., cyclohexadienyl) with a substantial longer lifetime. As a result, the addition step in the more conventional homolytic processes can be reversible.[5] Indeed, the longer lifetime of the adduct radical in the latter allows hydrogen transfer from the solvent to generate significant amounts of dihydro aromatic products.

Experimental Section

Materials. 1,10-Phenanthroline (Alpha Chemical Co.) was recrystallized from a mixture of hexane and toluene, and the complexes with iron(II) and iron(III) were prepared as previously described.[13] **Warning**: the perchlorates exploded on several occasions while drying, and the hexafluorophosphates prepared from ammonium hexafluorophosphate (Ozark-Mahoning) were thus the salts of choice. The behavior of the hexafluorophosphates was the same as the perchlorates insofar as the electrochemical reduction potentials and the absorption spectra were concerned. The 5-methyl- and the 4,7-dimethyl-substituted phenanthrolines were obtained from G. F. Smith Chemical Co., and the 2,9-dimethyl derivative was obtained from J. T. Baker Chemical Co. The 4-methyl derivative was synthesized as follows. Lepidine (City Chemical Corp.) was nitrated in concentrated H_2SO_4 to a mixture containing mostly 8-nitrolepidine, which was reduced with iron powder in ethanol according to general methods.[53] The crude 8-aminolepidine was converted (by the modified procedure of Richter and Smith[20] and Manske et al.[54]) as follows. The aminolepidine (16 g) was added portionwise to 50 mL of concentrated H_2SO_4 with occasionally cooling. Anhydrous glycerol (40 mL) was added, and the mixture heated on a steam bath for 1 h. This premix was added in small portions with vigorous stirring to 17 g of As_2O_5 and 1.5 g of $FeSO_4$ in 20 mL of concentrated H_2SO_4 at approximately 130 °C. The mixture was heated for 3 h and then poured over ice. The reaction mixture was partially neutralized with NaOH and filtered, and 27 g of $FeSO_4 \cdot 7H_2O$ was added. After the mixture was stirred for 1 h, the iron(II) complex was precipitated with $HClO_4$ and collected on a glass frit (care!). After being washed with alcohol and ether, it was decomposed with a solution of aqueous NaOH. The 4-methyl-1,10-phenanthroline was extracted with benzene several times, and the combined extracts were decolorized with charcoal and concentrated in vacuo: yield 11.6 g (61%); mp 143–145 °C.

The various organometals were obtained from previous studies.[11] Acetyl peroxide was prepared by following the procedures of Slagle and Shine.[55] *n*-Butyryl and *tert*-butylacetyl peroxide were prepared as previously described.[56] The *N*-alkylacetamides were prepared from the corresponding amines and either acetyl chloride or acetic anhydride in ether. The amines were commercial samples, but neopentylamine was synthesized by the reduction of pivalamide with lithium aluminum hydride. The various alkyl bromides were commercial samples, but neopentyl bromide was prepared from neopentyl alcohol (Aldrich Chem. Co.) with bromine and triphenylphosphine.[57] 2,2,5,5-Tetramethylhexane was prepared by the reductive coupling of neopentyl Grignard reagent and neopentyl bromide with silver nitrate:[58] bp 135–137 °C. ^1H NMR ($CDCl_3$) δ 1.13 (s, 4 H), 0.85 (s, 18 H).

Reagent grade acetonitrile (Mallinckrodt Chem. Co.) was purified by fractional distillation from calcium hydride. It was stirred with a mixture of $KMnO_4$ and Na_2CO_3 (10 g of each/L) for 24 h and then filtered. After bulb-to-bulb distillation, it was redistilled from P_2O_5, followed by CaH_2. Acetonitrile obtained in this manner did not reduce $(Phen)_3Fe(PF_6)_3$.

Oxidative Cleavage of Me_4Pb by $Fe(Phen)_3^{3+}$. Typical Procedures for Product Analysis and Isolation. $Fe(Phen)_3(ClO_4)_3$ (1.00 g, 1.12 mmol) was weighed into a 200-mL round bottomed flask equipped with a side arm and stopcock. After the flask was evacuated and filled with argon three times, 20 mL of oxygen-free acetonitrile was added, followed by a solution of Me_4Pb (0.16 g, 0.6 mmol, in 5 mL of CH_3CN). The mixture was magnetically stired for 1 h at 22 °C. Analysis of the gas phase by gas chromatography (1 ft × $^1/_8$ in. column, Porapak Q) using the internal standard method indicated the presence of 16 μmol (3%) of methane. The iron(II) complex was precipitated by the addition of ether. The ^1H NMR spectrum of the dried complex showed a methyl singlet resonance (δ 2.9 in CD_3CN) that was slightly variable with concentration. The complex was decomposed with aqueous NaOH, and the phenanthroline fraction was extracted with CH_2Cl_2 repeatedly. The combined extracts were dried with $MgSO_4$ and evaporated to dryness in vacuo. The yield was 0.58 g (95%) of recovered phenanthroline, for which the ^1H NMR spectrum showed the presence of a methyl singlet (δ 2.59 in $CDCl_3$) slightly shifted upfield from that in the iron(III) complex. The integration indicated that 16% of the phenanthroline was methylated, corresponding to a 95% yield of methylphenanthroline.

Since the precipitated iron(II) complex consisted of a mixture of partially alkylated material, no attempt was made to purify the material into its components. Instead, the ligand was hydrolytically detached from the iron(II) center and analyzed as the free ligands.

In order to isolate the methylphenanthroline, the precipitated iron(II) complex (0.44 g, 0.56 mmol) from a separate run was reoxidized electrochemically at 1.5 V vs. NaCl SCE until the current dropped to nil (corresponding to a passage of ~1 electron per iron) in an acetonitrile solution containing 1 M $NaClO_4$. Me_4Pb (38 μL, 0.28 mmol) was added directly to the electrochemical cell as the solution was stirred. After several minutes, the reduced iron(II) complex was oxidized again, and the cycle was repeated for a total of seven times. The iron(II) complex was precipitated with ether, and the phenanthroline was recovered as described above. The ^{13}C NMR spectrum consisted of the following resonances [peak number, chemical shift (assignment)]: 1, δ 155.7 (4-Me); 2, 151.9 (4,7-Me_2); 3, 149.1 (4-Me); 4, 146.3 (1,10-Phen); 5, 145.4 (4,7-Me_2); 6, 142.4 (4-Me); 7, 141.0 (1,10-Phen); 8, 138.0 (4-Me); 9, 135.3 (4-Me); 10, 134.8 (1,10-Phen); 11, 134.1 (4,7-Me_2); 12, 128.1 (1,10-Phen); 13, 127.5 (4-Me); 14, 127.3 (4-Me); 15, 126.9 (4-Me); 16, 126.6 (4,7-Me_2); 17, 126.4 (1,10-Phen); 18, 125.6 (4-Me, 4,7-Me_2); 19, 125.1 (4-Me, 1,10-Phen); 20, 122.2 (4,7-Me_2); 21, 121.3 (4-Me); 22, 19.0 (4-Me); 23, 18.4 (4,7-Me_2). The assignments in parentheses completely correspond to a mixture of 4-methyl- and 4,7-dimethyl-1,10-phenanthrolines and unsubstituted 1,10-phenanthroline. The ^{13}C NMR spectral data of the authentic samples are given in Table VII. Finally, 0.25 g of the phenanthroline mixture was dissolved in chloroform and anhydrous HCl bubbled in. The collected salt was loaded onto an ion-exchange column consisting of 30 g of Bio-Rad AG 50W-X2 100–200-mesh resin in the H^+ form and successively eluted with 1 L of 0.5 M HCl, 2 L of 1 M HCl, and 4 L of 2 M HCl. The separated phenanthrolines were identified by their UV spectra[59] and further characterized by the ^1H NMR spectral data in Table VIII and their melting points: 1,10-phenanthroline, 114–115 °C; 4-methylphenanthroline, 143–144 °C; 4,7-dimethylphenanthroline, 192–194 °C.

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Table VII. ^{13}C Chemical Shifts of Some Methyl-Substituted 1,10-Phenanthroline Hydrochlorides[a]

substituents	carbon assignment												
	2	3	4	5	6	7	8	9	11	12	13	14	Me
H	146.5	125.2	141.2	126.6	126.6	141.2	125.2	146.5	135.1	135.1	128.3	128.3	
4-Me	149.1	121.2	155.7	125.5	127.2	137.9	125.1	142.3	135.1	133.1	126.7	127.4	19.0
5-Me	144.7	124.3	136.6	133.6	125.1	140.8	125.1	146.7	135.0	134.3	127.7	127.7	17.6
4,7-Me_2	145.5	122.1	151.9	125.5	125.5	151.9	122.1	145.5	134.2	134.2	126.6	126.6	18.4
2,9-Me_2	158.2	125.4	140.5	126.0	126.0	140.5	125.4	158.2	133.8	133.8	127.5	127.5	22.0

[a] Sample (0.25 g) dissolved in 3 mL of 2 M HCl in D_2O; δ relative to external ethylene glycol at δ 63.00. ^1H-decoupled spectra obtained with a Varian XL-100-15 spectrometer with an external ^{19}F lock; probe temperature 35 °C. Data collected on a Nicolet Model 290 computer equipped with a 36K 1080 memory and a 1010 pulse generator operating in quadrature FT mode.

Table VIII. ^1H NMR Data for Some Methyl-Substituted 1,10-Phenanthrolines[a]

substituent	hydrogen assignment[b]								
	2	3	4	5	6	7	8	9	Me
H	9.10 (dd, 4.5, 1.5)	7.51 (dd, 8.1, 4.5)	8.10 (dd, 8.1, 1.5)	7.64 (s)	7.64 (s)	8.10 (dd, 8.1, 1.5)	7.51 (dd, 8.1, 4.5)	9.10 (dd, 4.5, 1.5)	
4-Me	8.91 (d, 4.5)	7.28 (d, 4.5)		7.56 (d, 9.0)	7.75 (d, 9.0)	8.02 (dd, 8.1, 1.8)	7.44 (dd, 8.1, 4.5)	9.06 (dd, 4.5, 1.8)	2.59 (s)
5-Me	9.05 (dd, 4.2, 1.8)	7.50 (dd, 8.0, 4.4)	8.03 (dd, 8.0, 1.8)		7.46 (s)	8.25 (dd, 8.2, 1.8)	7.57 (dd, 8.2, 4.2)	9.12 (dd, 4.4, 1.8)	2.62 (s)
4,7-Me_2	8.92 (d, 4.6)	7.30 (d, 4.6)		7.80 (s)	7.80 (s)		7.30 (d, 4.6)	8.92 (d, 4.6)	2.64 (s)
2,9-Me_2		7.37 (d, 8.2)	7.98 (d, 8.2)	7.56 (s)	7.56 (s)	7.98 (d, 8.2)	7.37 (d, 8.2)		2.88 (s)

[a] In $CDCl_3$ with internal Me_4Si on a Varian HR-220 spectrometer; probe temperature ~16 °C. [b] Each position given in the following format: δ (splitting pattern, J, Hz), with d = doublet, dd = doublet of doublets, and s = singlet.

The combined filtrates from the iron(II) precipitation were concentrated in vacuo, and a 1:1 mixture of ether and hexane was added. After the extract was dried, anhydrous ammonia was bubbled in and the precipitate collected on a tared frit: yield 0.22 g (104%); ^1H NMR (D_2O) δ 2.03 (s, J_{Pb} = 78 Hz; signal for $Me_3Pb(NH_3)_2ClO_4$ with sodium trimethylsilylpropanesulfonate as an internal standard). No *N*-methylacetamide (<10 μmol) could be detected in the filtrate by gas chromatography (6 ft × 1/8 in. column, FFAP).

The methylation of (4,7-Me_2Phen)$_3$Fe(PF_6)$_3$ (0.50 g) was carried out with Me_4Pb in a manner similar to that above. The ^1H NMR of the recovered phenanthroline showed two new methyl resonances at δ 2.83 and 2.60 of roughly equal intensity, in addition to the original resonance at δ 2.64. The region of the spectrum assigned to the aromatic protons showed a decrease in the intensity of the resonance assigned to the 2,9-positions (compare Table VIII). A new signal appeared 0.04 ppm upfield from the original 5,6-resonance as well as a new singlet 0.08 ppm upfield from the original doublet assigned to the 3,8-positions.

Fe(bpy)$_3$(PF_6)$_3$ (0.88 mmol) was treated with Me_4Pb (0.48 mmol) in a manner similar to that described above. Analysis of the reaction mixture indicated the presence of 89% [Me(bpy)]-Fe(bpy)$_2^{2+}$ showing a methyl singlet at δ 2.55. Alkaline hydrolysis of the iron(II) complex yielded the free ligand (δ 2.35 in $CDCl_3$). The position of methyl substitution was confirmed by carrying out the methylation repeatedly (vide supra) for seven cycles. The isolated 4-methylbipyridine showed a ^1H NMR spectrum [δ 8.11 (1 H), 6.96 (1 H), 8.41 (1 H), 2.35 (3 H)] which was similar to that of 4,4′-dimethyl-α,α′-bipyridine [δ 8.08 (1 H), 6.95 (1 H), 8.37 (1 H), 2.38 (3 H)] obtained from G. F. Smith Chem. Co. Furthermore, the ^{13}C NMR spectrum of the isolated 4-methyl-α,α′-bipyridine (δ 143.2, 128.8, 126.6, 144.5, 22.1) was also similar to that of 4,4′-dimethyl-2,2′-bipyridine (δ 143.4, 128.8, 126.4, 144.0, 21.9, relative to external ethylene glycol at δ 63.00).

Tetramethyltin (290 μmol) in 1 mL of CH_3CN was added to Fe(Phen)$_3$(PF_6)$_3$ (500 μmol) in 14 mL of CH_3CN at 70 °C under argon. After the mixture was stirred for 2 h, GC analysis indicated methane (4.6 μmol, 2%) and ethane (<0.1 μmol). Addition of 1 drop of water followed by ether yielded Fe(Phen)$_3$(PF_6)$_2$ as a red precipitate. Hydrolysis with NaOH afforded 0.26 g (95%) of phenanthroline containing 228 μmol (91%) of 4-methylphenanthroline by ^1H NMR analysis [δ 2.59 (s) in $CDCl_3$]. The filtrate was dried with $MgSO_4$ and treated with anhydrous NH_3. Filtration yielded 0.094 g (109%) of $(CH_3)_3Sn(NH_3)_2PF_6$, ^1H NMR δ 0.41 (J_{Sn} = 68 Hz). Concentration of the filtrate to ~1 mL followed by GC analysis showed no *N*-methylacetamide [<10 μmol (4%)]. It was reported previously that the ^1H NMR spectrum of the original reaction mixture showed a resonance at δ 3.6, which was shifted to δ 2.9 upon the addition of water.[13] We repeated these experiments under carefully controlled conditions and confirmed these spectral shifts. The previous assignment of the latter to *N*-methylacetamide, however, is in error since GC analysis (vide supra) showed none to be present. Fortunately, we later found the chemical shifts of *N*-methylacetamide and 4-methylphenanthroline to be fortuitously the same. Thus the previous assignment of the resonance at δ 3.6 to $CH_3CNCH_3^+$ is probably incorrect. We tentatively suggest that it arises from the conjugate acid CH_3(PhenH)Fe(Phen)$_2^{3+}$, which is the precursor of the product, prior to proton loss (see eq 24). Such an assignment is consistent with the observed splitting of the resonance at δ 2.9 of (4-MePhen)$_3Fe^{2+}$, upon the addition of a mixture of anhydrous HF–BF_3, into four peaks which progressively shift downfield with time, finally reached δ 4.7–5.5 in ~0.5 h.[60] The ^1H NMR

Table IX. Decomposition of Acetyl Peroxide in the Presence and Absence of (Phen)$_3$Fe(PF_6)$_3$[a]

time, min	[L_3Fe^{III}], mM	product, μmol				
		CO_2	MeH	EtH	L_3Fe^{II}[b]	MeL[c]
15	0	4.2	6.0	0.2		
15	20	3.6			6.1	5.5
30	0	15	13	0.8		
30	20	18			9.8	11
60	0	45	28	2.0		
60	20	52			16	25
120	0	68	43	2.8		
120	20	74			20	46

[a] Reactions carried out at 80 °C in 10 mL of CH_3CN containing ~60 μmol of acetyl peroxide. [b] Analysis by spectrophotometry at 510 nm [ϵ 5.82 × 10^2 for Fe(III) and ϵ 1.13 × 10^4 for Fe(II)]. [c] Analysis of recovered phenanthroline by quantitative ^1H NMR spectroscopy of the resonance at δ 2.6.

(60) Compare: Brouwer, D. M.; Mackor, E. L.; MacLean, C. In "Carbonium Ions"; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, p 837 ff.

Table X. Total Rates of Oxidation of Methyl Radicals by Substituted-Phenanthroline Complexes of Iron(III) Relative to Bromine Atom Transfer from $BrCCl_3$ [a]

substituted phenanthroline L	$[FeL_3^{3+}]$, mM	$[BrCCl_3]$, mM	$[Me_4M]$, mM	k_L' [b]
4,7-Me_2Phen	2-10	1-5	1-6 [c]	1.4 ± 0.2
4,7-Ph_2Phen	2-10	1-10	1-8 [c]	1.0 ± 0.1
Phen	1-10	5-50	1-6 [c]	5.9 ± 1.8
5-ClPhen	2-20	10-200	4-30 [d]	18 ± 5
5-NO_2Phen	2-10	500-3000	1-7 [d]	(2 ± 1) × 10^2

[a] In acetonitrile solutions at 0 °C with the reagents in the concentration range indicated. [b] Relative rate of ligand substitution and bromine atom transfer, in arbitrary units. [c] Me_4Pb. [d] Me_4Sn.

spectrum of Me_3SnClO_4 at δ 0.67 (J_{Sn} = 68 Hz in CD_3CN) was shifted to δ 0.61 (J_{Sn} = 66 Hz), not δ 1.2 as previously reported, upon the addition of D_2O and LiCl.

$EtSnMe_3$ (560 μmol) reacted with $Fe(Phen)_3(ClO_4)_3$ (1120 μmol) in CD_3CN to afford a solution showing two peaks at δ 3.2 (q, J = 7.2 Hz) and 1.2 (t, 7.2 Hz) in the ^1H NMR spectrum, which were previously misassigned to *N*-ethylacetamide.[13] Workup of the solution followed by GC analysis showed the presence of only 10 μmol (2%) of *N*-ethylacetamide. Major amounts of ethylphenanthroline [^1H NMR: δ 2.93 (q, J = 7.4 Hz), 1.04 (t, J = 7.4 Hz); 550 μmol, 98%] as well as 4-methylphenanthroline (22 μmol, 4%) together with recovered phenanthroline (0.58 g, 96%) were detected by ^1H NMR spectral analysis. After the precipitation of $Me_3Sn(NH_3)_2PF_6$, it was converted to the chloride and sublimed to yield 0.082 g (73%) of $(CH_3)_3SnCl$, δ 0.61 (J = 58 Hz). Isopropyl-, isobutyl-, and *tert*-butyltrimethyltin were treated with $(Phen)_3Fe^{3+}$ in a similar manner.[22]

Methylation with Acetyl Peroxide. $Fe(Phen)_3(PF_6)_3$ (0.5 mmol) was weighed into a 200-mL flask equipped with a side arm and stopcock. After the addition of 10 mL of CH_3CN, the flask was cooled to 0 °C, and a solution of 2 mmol of acetyl peroxide in ether was introduced with the aid of a pipet. The flask with its contents was initially evacuated to allow ether to be separated, filled with argon, and heated at 75 °C for 10 h. After cooling the flask, ethylene (1 mL) was added as an internal standard for methane and ethane analysis on a 2 ft × $^1/_4$ in. Porapak Q column. Subsequently, additional ethylene (20 mL) was added for CO_2 analysis. The iron(II) complex was isolated as described above. The effect of $(Phen)_3Fe^{3+}$ on the thermolysis of acetyl peroxide is included in Table IX. The important features of the data in Table IX are as follows: (1) the rate of CO_2 evolution is largely unaffected by the presence of $(Phen)_3Fe^{3+}$; (2) the methyl products in the presence of $(Phen)_3Fe^{3+}$ could be accounted for almost wholly as methylphenanthroline; (3) the yield of the iron(II) product $(Phen)_3Fe^{2+}$ determined spectrophotometrically [at 510 nm with ε 5.82 × 10^2 for Fe(III) and ε 1.13 × 10^4 for Fe(II)] was equal to the yield of methylphenanthroline (according to the stoichiometry in eq 4), particularly in the initial phases of the decomposition. These results are accommodated by the mechanism in Scheme I. The presence of iron(III) does not affect the

Scheme I

$$(CH_3CO_2)_2 \xrightarrow{\text{slow}} 2CH_3\cdot + 2CO_2 \quad (26)$$

$$CH_3\cdot + CH_3CN \rightarrow CH_4 + \cdot CH_2CN, \text{ etc.} \quad (27)$$

$$CH_3\cdot + (Phen)_3Fe^{3+} \rightarrow CH_3PhenFe(Phen)_2^{2+} + H^+ \quad (28)$$

decomposition of acetyl peroxide in the well-established slow step (eq 26) leading to CO_2 and methyl radical. The methyl products are determined in the subsequent rapid steps described by eq 27 and 28. The efficient diversion of methyl radicals in eq 28, even at low concentrations of $(Phen)_3Fe^{3+}$, attests to the rapidity of ligand substitution in competition with hydrogen atom abstraction from acetonitrile in eq 27.

Relative Rate Measurements with $M(Phen)_3^{3+}$. Typical Procedure. The experiment was carried out by adding a known amount of $M(Phen)_3(PF_6)_3$ to a stoppered flask, which was deaerated by purging with argon. Bromotrichloromethane was weighed in and sufficient CH_3CN added to bring the volume to 12 mL. A solution of Me_4Pb (54.3 μmol) in 1.0 mL of CH_3CN was slowly added with the aid of a hypodermic syringe as the solution was rapidly stirred. After 2 h, the reaction mixture was analyzed by the usual procedure. It is noteworthy that the stoichiometric consumption of $Fe(Phen)_3^{3+}$ under these conditions was the same as that observed in the absence of added bromotrichloromethane, viz., 2 equiv of oxidant were required for each mole of alkyltin. Thus the trichloromethyl radical formed in eq 12 must be efficiently oxidized by $Fe(Phen)_3^{3+}$. The product of oxidation was identified as phosgene by its IR absorption at 1820 cm^{-1} and by its facile hydrolytic conversion to carbon dioxide. The high yields of phosgene (>75% by quantitative IR analysis) and carbon dioxide (100% by GC analysis) attest to the rapid oxidation of trichloromethyl radicals by $Fe(Phen)_3^{3+}$. Indeed, there was no evidence for the formation of the dimeric hexachloroethane (<5%). The kinetic scheme for the competition experiments in Scheme II thus derive from the earlier study[13] as

Scheme II

$$Me_4Pb + Fe(Phen)_3^{3+} \xrightarrow{k_1} Fe(Phen)_3^{2+} + Me_3Pb^+ + Me\cdot \quad (29)$$

$$Me\cdot + Fe(Phen)_3^{3+} \xrightarrow{k_L} MePhenFe(Phen)_2^{2+} + H^+ \quad (30)$$

$$Me\cdot + BrCCl_3 \xrightarrow{k_{Br}} MeBr + Cl_3C\cdot \quad (31)$$

$$Cl_3C\cdot + Fe(Phen)_3^{3+} \xrightarrow{k_2} Fe(Phen)_3^{2+} + Cl_3C_{ox} \quad (32)$$

shown, where Cl_3C_{ox} represents the oxidation product(s) of the trichloromethyl radical. Initially, the ratio of rate constants k_L/k_{Br} in eq 13 was obtained by setting [ΔMePhen]/[ΔMeBr] to the corresponding yield ratio and $[FeL_3^{3+}]$ to the average concentration. This approximation, which is more or less equivalent to that employed by Zavitsas and Ehrenson,[61] was followed by a rigorous solution of the kinetics in Scheme II by using the digital stimulation technique of Feldberg[62] to convert the system of partial differential equations into partial finite difference equations. The details of the kinetic analysis and the listing of the Fortran program (available upon request) is included elsewhere.[59]

Rates of Oxidation of Methyl Radicals by Substituted Phenanthroline Complexes of Iron(III). The rates of oxidation of methyl radicals by various substituted phenanthroline complexes of iron(III), FeL_3^{3+}, was also examined by the competition method. For these studies, no attempt was made to identify the methyl products of oxidation. The relative rates of oxidation relative to bromine transfer reported in Table X as k_L' were determined by the analysis of methyl bromide formed from various amounts of FeL_3^{3+} and bromotrichloromethane. Values of k_L' thus have significance only in relationship to one another and were used in the construction of Figure 4.

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