aryl), 7.0-6.7 (m, 4, aryl), 6.17 (t, $J_{apparent}$ = 7 Hz, 1, $H_{1'}$), 5.58 (d, $J_{5,6}$ = 8 Hz, 1, H_5), 4.40 (m, 1, $H_{3'}$), 4.23 (m, 1, $H_{4'}$), 3.80 (s, 6, OCH_3), 3.37 (m, 2, $H_{5',5''}$), 2.8-1.9 (m, 2, $H_{2',2''}$). Anal. ($C_{30}H_{31}N_3O_6 \cdot {}^1/_2H_2O$) C, H, N, O.

5'-O-(Dimethoxytrityl)-4-N-benzoyl-2'-deoxycytidine (8b). To the solution obtained at the end of the first paragraph above was added 6.4 mL (50 mmol) of trimethylchlorosilane.[32] After 15 min 5.8 mL (50 mmol) of benzoyl chloride was added and the reaction stirred at room temperature for 10 h. The reaction was then cooled in an ice bath and 10 mL of water was added. After 5 min 20 mL of 29% aqueous ammonia was added and the solution stirred at room temperature for 30 min. The mixture was then evaporated to a gum and the gum partitioned between 200 mL of CH_2Cl_2 and 200 mL of 5% aqueous $NaHCO_3$. The aqueous layer was extracted with two 100-mL portions of CH_2Cl_2, the combined organic layers evaporated to dryness, and the residue purified by flash chromatography on silica gel.[34] Appropriate fractions were combined and evaporated and a methylene chloride solution of the residue was added dropwise to petroleum ether to precipitate 5.1 g (81%) of **8b**: UV and NMR were identical with those of material prepared according to the literature.[25] Anal. ($C_{37}H_{35}N_3O_7$) C, H, N.

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Registry No. 1a, 958-09-8; **1b**, 951-77-9; **1c**, 961-07-9; **4a**, 4546-72-9; **4b**, 4836-13-9; **4c**, 68892-42-2; **5a**, 17331-22-5; **5b**, 76512-82-8; **5c**, 80594-29-2; **8a**, 80594-30-5; **8b**, 80594-31-6; 6-*N*,*N*-dibenzoyl-2'-deoxyadenosine, 6711-37-1.

Oxidation-Reduction Mechanisms. Inner-Sphere and Outer-Sphere Electron Transfer in the Reduction of Iron(III), Ruthenium(III), and Osmium(III) Complexes by Alkyl Radicals

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Abstract: Alkyl radicals are readily oxidized by the tris(phenanthroline) and tris(bipyridine) complexes ML_3^{3+} of iron(III), ruthenium(III), and osmium(III) in acetonitrile solution, the second-order rate constants easily exceeding 10^6 M^{-1} s^{-1} at 25 °C. Two oxidative processes are identified as (a) *ligand substitution* on the coordinated 1,10-phenanthroline to yield various alkylphenanthrolines and (b) *cation formation* to afford alkenes and *N*-alkylacetamides (after hydrolysis). Cation formation is characterized by extensive skeletal rearrangement of neopentyl, isobutyl, and *n*-propyl groups, whereas ligand substitution by the same alkyl radicals occurs without any rearrangement. Steric effects hinder ligand substitution since the rate constant k_L increases in the order neopentyl < isobutyl < *n*-propyl and $Fe(4,7\text{-}Ph_2phen)_3^{3+} < Fe(4,7\text{-}Me_2phen)_3^{3+} < Fe(phen)_3^{3+}$. By contrast, cation formation is not subject to steric effects and the rate constant k_R is invariant for neopentyl, isobutyl, and *n*-propyl radicals, which all have essentially the same ionization potentials. An outer-sphere mechanism for electron transfer is described for the oxidative process leading to cation formation, in accord with the fit of k_R to the linear free energy relationship established by Marcus theory. An inner-sphere mechanism for the oxidative process leading to phenanthroline substitution is discussed in the context of steric effects on the rate constant k_L for ligand substitution.

Oxidation-reduction processes mediated by transition-metal complexes are playing an increasing role in organic chemistry.[1] However, the mechanistic distinction in such processes between outer-sphere and inner-sphere electron transfer has not been established, largely owing to inadequately developed criteria.[2] By contrast, electron transfer mechanisms in wholly inorganic systems have been considered for some time,[3] and reasonably reliable experimental and theoretical guidelines have been developed.[4]

The oxidation-reduction of organic free radicals by transition-metal complexes provides an excellent opportunity to examine the mechanism of electron transfer in organic systems, by relying on some of the mechanistic criteria developed in inorganic chemistry. Thus the various alkyl radicals (R·) by their paramagnetic nature are necessarily constrained to undergo one-electron changes, i.e.[5,6]

$$R:^- \xleftarrow{-e^-} R\cdot \xrightarrow{-e^-} R^+$$

Likewise, in the family of coordinatively saturated tris(polypyridine) complexes of the iron triad ML_3^{3+}

we have a structurally and chemically homologous series of one-electron oxidants with graded redox potentials. Furthermore, the availability of ligands, especially with L = substituted 1,10-phenanthrolines, allows further fine tuning of the redox potentials and the steric properties of these oxidants.[7,8] Coupled with the

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Table I. Cyclic Voltammetry of Fe(III), Ru(III), and Os(III) Complexes ML_3^{3+} in Acetonitrile Solution[a]

$ML_3(X)_3$	E^0,[b] V	i_c/i_a[c]	Δ,[d] mV
$Fe(phen)_3(ClO_4)_3$	0.99[e,g]	1.00	68
$Fe(4,7\text{-}Me_2phen)_3(ClO_4)_3$	0.86[e]	0.99	63
$Fe(bpy)_3(ClO_4)_3$	0.98[g]	1.02	70
$Fe(4,7\text{-}Ph_2phen)_3(PF_6)_3$	0.92[g]	1.01	65
$Fe(5\text{-}Clphen)_3(ClO_4)_3$	1.08[g]	1.01	67
$Fe(5\text{-}NO_2phen)_3(ClO_4)_3$	1.18[g]	1.02	72
$Ru(phen)_3(ClO_4)_3$	1.19[e]	0.98	70
$Os(phen)_3(PF_6)_3$	0.74[f]	1.01	70
$Co(phen)_3(PF_6)_3$	0.32[f]	1.04	97
$Cr(phen)_3(ClO_4)_3$	−0.36[e]	1.02	68

[a] At 25 °C, in the presence of either 0.1 M Et_4NClO_4 or Et_4NPF_6. [b] Relative to saturated NaCl SCE at 25 °C. [c] Ratio of cathodic and anodic peak currents. [d] Separation to the anodic and cathodic peak potentials at a scan rate of 50 mV s^{-1}. [e] Same E^0 obtained with the hexafluorophosphate salt. [f] Same result with the perchlorate salt. [g] From ref 11.

inextensible structural variations available in a variety of alkyl radicals with well-defined electronic and steric properties,[9] we were encouraged to employ this organic–inorganic pair for the examination of the mechanism of organic oxidation. Acetonitrile was chosen as the solvent in this study owing to its oxidative stability and its ability to support ions.[10]

Results

The driving force for the oxidation of alkyl radicals by the metal complexes of Fe(III), Ru(III), and Os(III) in acetonitrile was first examined electrochemically. The stoichiometry of alkyl oxidation was then established by careful analysis of all the products for complete material balance. Finally, the kinetics were measured by the competition method to delineate the structural dependence of the activation process for alkyl oxidation.

I. Standard Reduction Potentials of Fe(III), Ru(III), and Os(III) Complexes ML_3^{3+} in Acetonitrile. The reduction potentials of the low-spin tris(2,2′-bipyridine) (bpy) and various substituted 1,10-phenanthroline (phen) complexes of iron, ruthenium, and osmium, ML_3^{3+} as listed in Table I, were measured in anhydrous acetonitrile solutions by cyclic voltammetry (CV). All of these metal(III, II) redox couples were completely reversible in this medium, as indicated in Table I by the magnitude of the potential separation Δ of the anodic and cathodic peaks and the same magnitudes of their peak currents, i_c/i_a.[11] The values of E° for the various ML_3^{3+} are all independent of the counteranion, whether it is perchlorate or hexafluorophosphate, and were calibrated relative to ferrocene.[12]

II. Products and Stoichiometry of the Reduction of $Fe(phen)_3^{3+}$ by Alkyl Radicals. The various types of alkyl radicals (R·) employed in this study were generated in acetonitrile, either from the thermolysis of the corresponding diacyl peroxide[9]

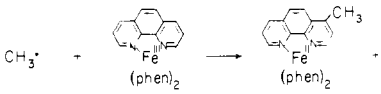
$$(RCO_2)_2 \rightarrow 2\ R\cdot + 2CO_2 \qquad (1)$$

or more conveniently from the oxidative homolysis of an alkylmetal with $Fe(phen)_3^{3+}$, e.g.

$$RSnMe_3 + Fe(phen)_3^{3+} \rightarrow Fe(phen)_3^{2+} + Me_3Sn^+ + R\cdot \qquad (2)$$

as elaborated in the Experimental Section.[11] Alkyl radicals produced by either method afforded the same distribution of products described individually below. The alkyl radical yield was based on the carbon dioxide evolved in eq 1 or on the iron(III) consumed in eq 2 (i.e., half the total). The Me_3Sn^+ cation formed in eq 2 was also measured directly from its characteristic ^1H NMR spectrum [δ 0.67 (s, J_{Sn} = 68 Hz) or gravimetrically after precipitation as the perchlorate or hexafluorophosphate salt of the diammine adduct with anhydrous ammonia.[13]

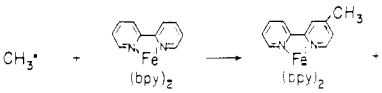
Methyl Radical. The thermal decomposition of acetyl peroxide in the presence of $Fe(phen)_3^{3+}$ is accompanied by a color change of the solution from blue to red, diagnostic of the concomitant reduction of the iron(III) to the iron(II) oxidation state. Only small amounts of methane and ethane are evolved in the oxidation. As listed in Table II, the fate of most of the methyl radicals was traced to nuclear substitution of the phenanthroline ligand, i.e.



(3)

The product of methyl oxidation in eq 3 was identified by (a) the characteristic methyl resonances in the ^1H and ^{13}C NMR spectra of the iron complex and (b) after isolation of the free ligand 4-methyl-1,10-phenanthroline and direct comparison with an authentic sample, as described in detail in the Experimental Section. Methyl radicals generated from the oxidative homolysis of Me_4Pb, Me_4Sn, and Me_2Hg according to eq 2, afforded the same results (Table II). In every case, major amounts (>85%) of 4-methylphenanthroline were formed and the conversion to methane and ethane was minor.[14] Furthermore, no *N*-methylacetamide (<2%) was detected after hydrolysis of the reaction mixture. The reduced iron(II) complexes were identified by their characteristic electronic absorption spectra (see Experimental Section).

The corresponding α,α'-bipyridine complex of iron(III), $Fe(bpy)_3^{3+}$, also reacts readily with methyl radicals by oxidative nuclear substitution exclusively at the 4-position of bipyridine, i.e.

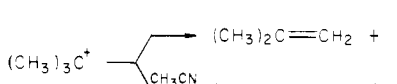


(4)

Only 4-methyl-2,2′-bipyridine was detected after hydrolytic detachment of the ligands from the iron complex (see Experimental Section). None of the isomeric methylbipyridine (<1%) was found.

***tert*-Butyl Radical.** The oxidative homolysis of *tert*-butyltrimethyltin (R = *tert*-butyl in eq 2) resulted in the cleavage of only the *tert*-butyl bond to tin, as shown in Table III. Unlike methyl radicals, however, the oxidation of *tert*-butyl radicals by $Fe(phen)_3^{3+}$ did not result in nuclear substitution since the recovered ligand (96%) contained no *tert*-butylphenanthroline. Instead, the *tert*-butyl radicals were converted in excellent yields to a mixture of isobutylene (11%) and *N*-*tert*-butylacetamide (84% after hydrolysis), the latter via well-known solvation of the *tert*-butyl cation.[15] The reduced $Fe(phen)_3^{2+}$ was identified by its visible absorption spectrum.[11]

$$(CH_3)_3C\cdot + Fe(phen)_3^{3+} \rightarrow Fe(phen)_3^{2+} + (CH_3)_3C^+ \qquad (5)$$



(6a) (6b)

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(14) Most of the methane is derived from alkylmetals by adventitious protonolysis. (See ref. 38 and 58 for details.) This leads to yields of R_3Sn^+ in excess of 100% (compare Tables III and IV).
(15) Commonly known as the Ritter reaction. (Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045. See: Beckwith,, A. J. In "The Chemistry of Amides"; Zabicky. J. Z., Ed.; Interscience: New York, 1970; p 119–125.) For pertinent examples see: Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843. Miller, L. L.; Hoffmann, A. K. *Ibid.* **1967**, *89*, 593. Pocker, Y.; Kevill, D. N. *Ibid.* **1965**, *87*, 4771. Eberson, L.; Nyberg, K. *Acta Chem. Scand.* **1964**, *18*, 1567. Kevill, D. N.; Lin, G. M. L. *Tetrahedron Lett.* **1978**, 949.

Table II. Methyl Radical Products and Stoichiometry of the Oxidation of $Fe(phen)_3^{3+}$ in Acetonitrile

source, 10^2 M	$Fe(phen)_3^{3+}$, 10^2 M	temp, °C	products,[a] % Me_3M^+	phen[b]	MeH	EtH	Mephen[c]	Me-NHAc	Mephen/ $Fe(phen)_3^{3+}$
$(MeCO_2)_2$ 30	5.00	75	*d*	94	4	2	64		2.06
Me_4Pb 2.24	4.48	22	104[e]	95[f]	3	<0.1	96	<2	0.48
Me_4Sn 5.78	10.0	70	109[e]	95	2	<0.1	91	<4	0.46
18.8	10.0	19		98			98		0.49
Me_2Hg 1.43	2.50	20	78[g]	95	24	<0.1	84	<4	0.42
Me_4Pb 1.92	3.49[h]	25		98[i]			89[j]		0.49

[a] Based on a 2:1 stoichiometry with $(phen)_3Fe(III)$; see text. [b] Amount recovered. [c] 4-Methyl-1,10-phenanthroline. [d] 1.6 mmol of CO_2 evolved; yields of other products based on CO_2. [e] Isolated as $Me_3M(2NH_3)^+ClO_4^-$. [f] Isolated as free ligand. [g] Isolated as MeHgBr after addition of NaBr. [h] $Fe(bpy)_3^{3+}$. [i] Recovered α,α′-bipyridine. [j] 4-Methyl-2,2′-bipyridine. See also ref 14.

Table III. Products and Stoichiometry of the Oxidation of Alkyl Radicals by $Fe(phen)_3^{3+}$ [a]

alkyl radical (R·)	$RSnMe_3$, 10^4 mol	$Fe(phen)_3^{3+}$, 10^4 mol	products,[b] % RH	R(-H)	RNHAc	Rphen	phen[c]	Me_3Sn^+[d]	stoich[e]
ethyl	5.6	11.2	0.3	0.4	2	98	96	73	0.50
n-propyl	5.8	10.0	0.1	1	10[f]	92	96	96	0.53
isopropyl	5.6	11.2	<0.4	6	81	9	97	106	0.48
isobutyl	5.5	10.0	0.1	4[g]	14[h]	84	91	90	0.53
tert-butyl	5.6	11.2	0	11	84	<0.4	96	78	0.48
neopentyl	5.5	10.0	0.3[k]	21[j]	14[m]	47	92	95	0.50
benzyl	6.9	10.0	<2		97	<1	92	115	0.49
cyclohexyl	5.0	10.0	*n*	7	67	*n*	*n*	*n*	

[a] In 20-25 mL of acetonitrile at 22 °C, except cyclohexyl (50 mL). [b] Based on 2:1 with $(phen)_3Fe^{III}$; average of 2 or more runs. [c] Recovered. [d] Isolated as $Me_3Sn(NH_3)_2PF_6$ or Me_3SnCl (Et, *t*-Bu). [e] Material balance based on ΣR/Fe(III) consumed; theoretical 0.50. [f] Mixture of *i*-PrNHAc (41 μmol) and *n*-PrNHAc (11 μmol). [g] Mixture of isobutylene (10 μmol), *trans*-2-butene (7.5 μmol), *cis*-2-butene (2.5 μmol). [h] Mixture of *t*-BuNHAc (36 μmol), *s*-BuNHAc (26 μmol), *i*-BuNHAc (8.5 μmol). [j] Mixture of 2-methyl-2-butene (95 μmol), 2-methyl-1-butene (10 μmol). [k] In addition to dineopentyl (35 μmol). [m] *tert*-Amylacetamide only. [n] Not analyzed. See also footnote 14.

The unique products derived from methyl and *tert*-butyl radicals in eq 3 and 6, respectively, characterize the two principal types of oxidative processes which are possible with alkyl radicals, viz., that leading to ligand substitution (methylphenanthroline) and that leading to carbonium ions (*N*-*tert*-butylacetamide plus isobutylene), as represented by eq 7 and 8, respectively. The distinction between the oxidative processes in eq 7 and 8 is clearly delineated in the oxidation of a variety of primary and secondary alkyl radicals described below.

$$R\cdot + Fe(phen)_3^{3+} \longrightarrow R(phen)Fe(phen)_2^{2+} + H^+ \quad (7)$$

$$R\cdot + Fe(phen)_3^{3+} \longrightarrow [R^+] + Fe(phen)_3^{2+} \quad (8)$$

***p*-Alkyl Radicals.** The oxidation of *ethyl*, *n-propyl*, and *isobutyl* radicals with $Fe(phen)_3^{3+}$ in Table III afforded high yields (85–95%) of the corresponding alkylphenanthrolines. Although the nuclear position of substitution was not identified in each case, the ^1H NMR spectra unambiguously established that *n*-propyl and isobutyl substitution on the phenanthroline ligand occurred without rearrangement of the alkyl group. Nuclear substitution was also the principal course of oxidation of *neopentyl* radicals by $Fe(phen)_3^{3+}$—leading only to neopentylphenanthroline (~50%) without any skeletal rearrangement (see Experimental Section).

$$(CH_3)_3CCH_2\cdot + (phen)_3Fe^{3+} \longrightarrow \text{(neopentylphenanthroline)}(phen)_2 + H^+ \quad (9)$$

Although ligand addition was the principal course of oxidation of primary alkyl radicals by $Fe(phen)_3^{3+}$, the small but discrete amounts of the other products of alkyl oxidation were revealing. For example, *n*-propyl radical produced a mixture of *N*-propylacetamides (10%), consisting of a mixture of *n*-propyl and isopropyl isomers in a ratio of 1:4.

$$CH_2CH_2CH_2\cdot \xrightarrow[CH_3CN,\ H_2O]{Fe^{3+}} CH_3CH_2CH_2\text{-}NHAc \quad (2\%)\ (10a)$$

$$CH_2CH_2CH_2\cdot \xrightarrow[CH_3CN,\ H_2O]{Fe^{3+}} (CH_3)_2CH\text{-}NHAc \quad (8\%)\ (10b)$$

Similarly, isobutyl radical afforded *N*-butylacetamides in 14% yields, consisting of the isobutyl, *sec*-butyl, and *tert*-butyl isomers in a ratio of 1:4:5. In addition, isobutyl radical produced a small amount of butenes (4%), consisting of isobutylene and *trans*- and *cis*-2-butene in a molar ratio of 4:3:1.

$$(CH_3)_2CHCH_2\cdot \xrightarrow[CH_3CN]{FeL_3^{3+}} (CH_3)_2C{=}CH_2 + H^+ \quad (11a)$$

$$(CH_3)_2CHCH_2\cdot \xrightarrow[CH_3CN]{FeL_3^{3+}} CH_3CH{=}CHCH_3 + H^+ \quad (11b)$$

The skeletal rearrangement of the alkyl moiety was most dramatic in the oxidation of neopentyl radical, in which the acetamide fraction (14%) consisted solely of *N*-*tert*-amylacetamide, the amounts of the unrearranged *N*-neopentylacetamide being below the limits of detection (<0.1%). Furthermore, the rearranged pentenes, 2-methyl-2-butene (19%) and 2-methyl-1-butene (2%), were also formed in the oxidation of neopentyl radicals by $Fe(phen)_3^{3+}$.

$$(CH_3)_3CCH_2\cdot \xrightarrow[CH_3CN,\ H_2O]{Fe^{3+}} (CH_3)_3CCH_2NHCOCH_3 \quad (14\%)\ (12)$$

$$(CH_3)_3CCH_2\cdot \xrightarrow[CH_3CN,\ H_2O]{Fe^{3+}} (CH_3)_2C{=}CHCH_3 \quad (19\%)\ (13)$$

***sec*-Alkyl Radicals.** In contrast to primary alkyl radicals, the reaction of secondary alkyl radicals such as *isopropyl* and *cyclohexyl* radicals with $Fe(phen)_3^{3+}$ led to *N*-alkylacetamides as the primary oxidation product. The alkylphenanthrolines were formed only as minor byproducts. For example, *N*-isopropyl-

Table IV. Oxidation of *n*-Propyl and Isobutyl Radicals by Fe(III), Ru(III), and Os(III) Oxidants[a]

alkyl radical (R·)	$RSnMe_3$, 10^4 mol	metal oxidant (10^4 mol)	products,[b] % RH	R(-H)	RNHAc	Rphen	phen[c]	R_3Sn^+[d]	stoich[e]
n-propyl	2.48	$Os(phen)_3^{3+}$ (4.1)	0.3[f]	0.3	<2	71	97	101	0.44
n-propyl	2.64	$Fe(5\text{-}NO_2phen)_3^{3+}$ (4.5)	0.9	2.6	14	66	89	118	0.42
n-propyl	2.35	$Ru(phen)_3^{3+}$ (4.1)	<0.1	1.3	20	69	87	112	0.45
isobutyl	11.00	$Os(phen)_3^{3+}$ (4.1)	2.9[g]	1.1[h]	2.1[i]	91	97	117	0.49
isobutyl	1.50	$Fe(5\text{-}NO_2phen)_3^{3+}$ (2.9)	0.1	18[h]	27[i]	46	103	112	0.46
isobutyl	2.34	$Ru(phen)_3^{3+}$ (4.1)	<0.1	16[h]	26[i]	53	92	101	0.47

[a] In 20-25 mL of acetonitrile at 25 °C. [b] Based on 2:1 with L_3M^{III}, average of 2 or more runs. [c] Recovered. [d] Determined gravimetrically. For yields in excess of 100%, see ref 14. [e] Material balance as ΣR/M(III) consumed, theoretical 0.50. [f] In addition to n-hexane (17 μmol). [g] In addition to 2,5-dimethylhexane (3.8 μmol). [h] Mixture of isobutylene and *trans*- and *cis*-2-butene in a molar ratio of 4:3:1. [i] Mixture of *tert*-, *sec*-, and isobutylacetamides in a molar ratio of 5:4:1.

acetamide, propylene, and isopropylphenanthroline were formed in 81, 6, and 9% yields, respectively, from isopropyl radical. Similarly, the oxidation of cyclohexyl radicals by $Fe(phen)_3^{3+}$ produced high yields (67%) of *N*-cyclohexylacetamide, together with cyclohexene (7%).

Benzyl Radical. The oxidation of benzyl radical, derived in >95% yield from the oxidative homolysis of $PhCH_2SnMe_3$, afforded only *N*-benzylacetamide (97%). No nuclear-substituted benzylphenanthroline was detected.

It is important to emphasize that the stoichiometry for the oxidation of each alkyl radical by $Fe(phen)_3^{3+}$, as determined by the products described above, accords with the excellent material balances (based on the alkyl radical) obtained in Tables II and III. The oxidation of alkyl radicals by $Fe(phen)_3^{3+}$ must be facile, since it competed effectively with hydrogen atom transfer from solvent to produce alkane. Furthermore, the bimolecular coupling to alkyl dimers was not important, except with neopentyl radicals (vide infra). The kinetic measurements of the rates of alkyl oxidation to be described in a following section will bear out the rapidity of these oxidations.

III. Comparison of Ru(III) and Os(III) with Fe(III) Complexes in the Products of Alkyl Oxidation. The ruthenium(III) and osmium(III) complexes were compared with the analogous iron(III) oxidants using *n*-propyl and isobutyl radicals to probe the differences in the partitioning between the two principal types of products, namely, alkylphenanthrolines and alkylacetamides. The results in Table IV show that the relative amounts of these oxidation products parallel the trend in the reduction potentials of the metal complexes listed in Table I. Thus the reaction of $Os(phen)_3^{3+}$ with either *n*-propyl or isobutyl radicals produces mainly alkylphenanthrolines, with the alkylacetamides present only in minor amounts (<2%). By contrast, $Ru(phen)_3^{3+}$, which is the strongest oxidant, produces more than 20% of alkylacetamides and correspondingly smaller amounts of alkylphenanthrolines. Furthermore, among the iron(III) oxidants, $Fe(5\text{-}NO_2phen)_3^{3+}$ afforded oxidation products consisting of significantly higher proportions of alkylacetamides compared to those produced from $Fe(phen)_3^{3+}$, which is a weaker oxidant.

IV. Kinetics of Alkyl Radical Oxidation. The rates of alkyl radical oxidation were evaluated by the competition method, using the well-known abstraction of bromine atom from bromotrichloromethane as the monitoring reaction,[16] i.e.

$$R\cdot + BrCCl_3 \xrightarrow{k_{Br}} RBr + Cl_3C\cdot \qquad (14)$$

Since bromine atom transfer in eq 14 is facile, it is possible to intercept all of the alkyl radicals (including Me·, Et·, *n*-Pr·, *i*-Pr·, *t*-Bu·, and neo-Pent·) generated in eq 1 or 2, as the alkyl bromide (MeBr, EtBr, *n*-PrBr, *i*-PrBr, *t*-BuBr, and neo-PentBr, respectively), even at relatively low concentrations (0.5 M) of $BrCCl_3$. (Indeed, such a quantitative trapping of alkyl radicals by bromotrichloromethane constitutes a convenient and independent verification of the radical-generating procedure employed in eq 2.) It was thus necessary to establish the optimum conditions (see Experimental Section) under which accurately measurable

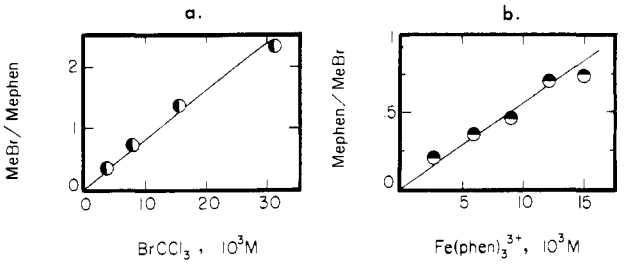


Figure 1. Relative rates of formation of $MephenFe(phen)_2^{2+}$ (indicated as Mephen) and MeBr during the oxidation of Me_4Pb by $Fe(phen)_3^{3+}$ in the presence of bromotrichloromethane: (a) various amounts of $BrCCl_3$ (◐) with $[Fe(phen)_3^{3+}] = 1.7 \times 10^{-3}$ M; (b) various amounts of $Fe(phen)_3^{3+}$ (◓) with $[BrCCl_3] = 1.7 \times 10^{-2}$ M.

amounts of both the oxidation products as well as the alkyl bromide could be produced from each alkyl radical for the competition experiments.

Methyl radical was used initially to establish the validity of the kinetics in the competition experiments by generating it in the presence of varying amounts of $Fe(phen)_3^{3+}$ and $BrCCl_3$. Figure 1a shows that the ratio of the products MeBr and Mephen (as the iron(II) complex) is linearly dependent on the concentration of $BrCCl_3$ at a given level of $Fe(phen)_3^{3+}$. Similarly, Figure 1b shows the ratio of MeBr to Mephen to be linearly dependent on the concentration of $Fe(phen)_3^{3+}$ when the same amount of $BrCCl_3$ is employed, i.e.

$$\frac{d[Mephen]}{d[MeBr]} = \frac{k_{Ox}}{k_{Br}} \frac{[FeL_3^{3+}]}{[BrCCl_3]} \qquad (15)$$

From the slopes in Figure 1, the ratio of the rate constants for oxidation and bromine transfer to the methyl radical is evaluated as $k_{Ox}/k_{Br} = 0.86$ at 0 °C. Using the previously determined value of $k_{Br} = 2 \times 10^5$ M^{-1} s^{-1} in the gas phase at this temperature,[17] we evaluate the rate constant k_{Ox} for methyl oxidation by $Fe(phen)_3^{3+}$ to be $\sim 2 \times 10^5$ M^{-1} s^{-1}.[18] The magnitude of this rate constant is supported by analogous competition experiments using different types of monitoring reagents such as carbon tetrachloride for chlorine atom transfer

$$CH_3\cdot + CCl_4 \xrightarrow{k_{Cl}} CH_3Cl + Cl_3C\cdot \qquad (16)$$

and cumene for hydrogen atom transfer

$$CH_3\cdot + \text{C}_6\text{H}_5\text{CH(CH}_3\text{)}_2 \xrightarrow{k_H} CH_4 + \text{C}_6\text{H}_5\dot{\text{C}}\text{(CH}_3\text{)}_2 \qquad (17)$$

for which the second-order rate constants k_{Cl} and k_H are also available.[19,20] The values of k_{Ox} evaluated with these trapping

(16) Ingold, K. U. *Free Radicals* **1973**, *1*, 37.

(17) Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511 give for $k_{Br}(Me\cdot + BrCCl_3) = 10 \exp(8.1 \pm 0.3)e \exp((-3.5 \pm 0.5)/RT)$ M^{-1} s^{-1} or 6.9×10^5 M^{-1} s^{-1} at 65 °C, 2×10^5 M^{-1} s^{-1} at 0 °C, and 3.4×10^5 M^{-1} s^{-1} at 25 °C.

(18) Assuming no change in k_{Br} from the gas phase to acetonitrile solution.

(19) From ref 17, $k_{Cl}(Me\cdot + CCl_4) = 10 \exp(8.8 \pm 0.3)e \exp((-10.1 \pm 0.5)/RT)$ M^{-1} s^{-1} or 1.9×10^2 M^{-1} s^{-1} at 65 °C.

Table V. Rates of Alkyl Radical Oxidation by Fe(III), Ru(III), and Os(III) Complexes Relative to Trapping by $BrCCl_3$[a]

	$Ru(phen)_3^{3+}$		$Fe(phen)_3^{3+}$		$Os(phen)_3^{3+}$	
alkyl radical	k_R/k_{Br}	k_L/k_{Br}	k_R/k_{Br}	k_L/k_{Br}	k_R/k_{Br}	k_L/k_{Br}
methyl[b]	<0.2	4.9 ± 0.2	<0.1	2.2 ± 0.6	<0.02	0.18 ± 0.01
ethyl[c]			0.10 ± 0.06	5.3 ± 0.6		
n-propyl[d]	3.6 ± 0.2	8.9 ± 0.3	0.26 ± 0.03	2.1 ± 0.2		1.0 ± 0.1
isopropyl[d]			12 ± 2	~1		
isobutyl[b]	2.8 ± 0.5[e]	4.0 ± 0.9	0.22 ± 0.02	1.00 ± 0.04	0.041 ± 0.007	0.55 ± 0.06
tert-butyl[d]			35 ± 18	<0.1		
neopentyl[b]			0.20 ± 0.06	0.26 ± 0.04		
cyclohexyl[d]			4.3 ± 0.1			

[a] In acetonitrile solution at 25 °C. [b] Using 4 equiv of $(phen)_3M^{III}$ per tetraalkyltin. [c] At 0 °C. [d] Using 10 equiv of $(phen)_3M^{III}$ per tetraalkyltin. [e] Obtained from $R^+/RL = 0.80$ in the product study in Table IV and by the direct measurement.

Table VI. Temperature Dependence of the Rates of Oxidative Substitution of Various Tris(phenanthroline)metal Complexes[a]

M-$(phen)_3^{3+}$	methyl radical		*n*-propyl radical	
	80 °C[b]	25 °C[c]	70 °C[d]	25 °C[e]
Ru		4.9 ± 0.2	7.0 ± 0.6	8.9 ± 0.3
Fe	1.4 ± 0.1	2.2 ± 0.6	2.4 ± 0.1	2.1 ± 0.2
Os	0.15 ± 0.02	0.18 ± 0.01	0.67 ± 0.08	1.0 ± 0.1
Co	0.05 ± 0.01		0.12 ± 0.03	
Cr	0.04 ± 0.01		0.064 ± 0.006	

[a] In acetonitrile solution. Relative rates expressed as k_L/k_{Br}. [b] From acetyl peroxide thermolysis. [c] From tetramethyltin. [d] From di-*n*-butyryl peroxide thermolysis. [e] From *n*-propyltrimethyltin.

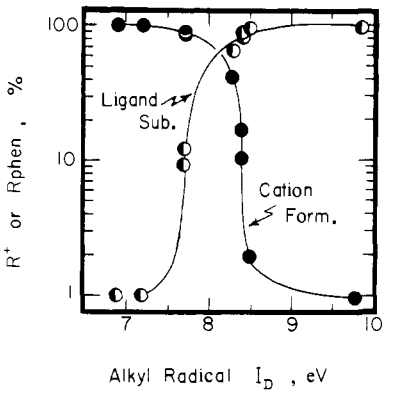


Figure 2. The relative amounts of ligand substitution (◐) and cation formation (●) during the $Fe(phen)_3^{3+}$ oxidation of various alkyl radicals as a function of their ionization potentials I_D.

agents are 1×10^7 M^{-1} s^{-1} (cumene) and 2×10^5 M^{-1} s^{-1} (carbon tetrachloride) at 65 °C. These are in acceptable agreement with the value of 7×10^5 M^{-1} s^{-1} obtained with bromotrichloromethane at the same temperature, especially when the large uncertainties[21] in the values of k_{Br}, k_{Cl}, and k_H are taken into account. The rates are insensitive to ionic strength maintained with sodium perchlorate up to 0.5 M.

The same kinetic technique was also employed with the other alkyl radicals. Once the optimum conditions were found for the simultaneous observation of oxidation products and alkyl bromide, the concentration of bromotrichloromethane was varied. In every case, the ratio of alkyl bromide to oxidation products was established to be a linear function of the bromotrichloromethane concentration (compare Figure 1). The material balance based on alkyl radicals was always in excess of 95% in these competition experiments.

In order to describe the oxidation of various alkyl radicals by $Fe(phen)_3^{3+}$, the overall rate process must be delineated into several components—that leading to alkylphenanthrolines and that leading to alkylacetamides (plus alkenes), which we designate by the second-order rate constants k_L and k_R, respectively. When we consider these to be the two principal oxidative processes, the rate constant for alkyl oxidation k_{Ox} can be represented as the sum of k_L and k_R. These rate constants were measured relative to k_{Br} for $Fe(phen)_3^{3+}$, $Ru(phen)_3^{3+}$, and $Os(phen)_3^{3+}$ with the various alkyl radicals listed in Table V. (See the Experimental Section for details of the individual kinetic procedures.)

The temperature dependence of the rates of oxidative substitution of methyl and *n*-propyl radicals was also examined with the tris(phenanthroline) complexes of iron(III), ruthenium(III), and osmium(III), in addition to those of the isostructural analogues, cobalt(III) and chromium(III). The ratios of the second-order rate constants k_L/k_{Br} presented in Table VI are rather invariant over a 50° span in temperature. The results in Table VI also show that consistent values of the rate constants obtain for methyl and propyl radicals, as derived from diacyl peroxides and alkyltin compounds.

Discussion

The facile oxidation of various alkyl radicals by the tris(phenanthroline) complexes $M(phen)_3^{3+}$ derived from iron(III), ruthenium(III), and osmium(III) is characterized by two processes, which are readily distinguished by the products formed in acetonitrile solution. Thus alkyl substitution on the 1,10-phenanthroline ligand occurs without skeletal rearrangement—isobutyl and neopentyl radicals affording only isobutylphenanthroline and neopentylphenanthroline (eq 9), respectively. On the other hand, the remaining fraction which consists of a mixture of alkenes and *N*-alkylacetamides (after hydrolysis) is extensively, if not completely isomerized—isobutyl radicals yielding 2-butenes and *N-sec*-butylacetamide while neopentyl radicals afford 2-methylbutenes and *N-tert*-amylacetamide (eq 11-13).

I. Ligand Substitution vs. Cation Formation. We describe the oxidative process which leads to alkylphenanthrolines as *ligand substitution* with the rate constant k_L. The accompanying oxidative process, with the rate constant k_R, which affords *N*-alkylacetamides and alkenes is designated as *cation formation* since the production of these characteristic products in acetonitrile is truly diagnostic of alkyl cation precursors.[15] Furthermore, skeletal rearrangement is a natural consequence of cation formation,[22] in contrast to alkyl radicals which are much less prone to rearrange.[23]

$$R\cdot + M(phen)_3^{3+} \xrightarrow{k_L} RphenM(phen)_2^{2+} + H^+ \quad (18)$$

$$\xrightarrow{k_R} R^+ + M(phen)_3^{2+} \quad (19)$$

The relative importance of ligand substitution and cation formation is dependent on both the structure of the alkyl radical and the reduction potential of $M(phen)_3^{3+}$. Figure 2 represents the summary of the product studies with $Fe(phen)_3^{3+}$ in Table

(20) Cher, M.; Hollingsworth, C. S.; Sicilio, F. *J. Phys. Chem.* **1966**, *70*, 877 give $k_H(Me\cdot + PhCH_3) = 10 \exp(8.6e) \exp(-9.5/RT)$ M^{-1} s^{-1} or 2.7×10^2 M^{-1} s^{-1}. Coupled with $k_H(PhC(CH_3)_2H)/k_H(PhCH_3) = 12.9$ given by: Meyer, J. A.; Stannett, V.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 25. $k_H(Me\cdot + PhC(CH_3)_2H) = 3.5 \times 10^3$ M^{-1} s^{-1}.

(21) Large discrepancies in the reported absolute rate constants are not unusual. For example, using the error limits given in ref 17, $k_{Br}(Me\cdot + BrCCl_3)$ ranges from 0.2 to 3×10^6 M^{-1} s^{-1} at 65 °C and k_{Cl} in ref 19 ranges from 0.4 to 8×10^2 M^{-1} s^{-1}.

(22) Keating, J. T.; Skell, P. S. *Carbonium Ions* **1970**, *2*, 573.

(23) Wilt, J. W. *Free Radicals* **1973**, *1*, 333.

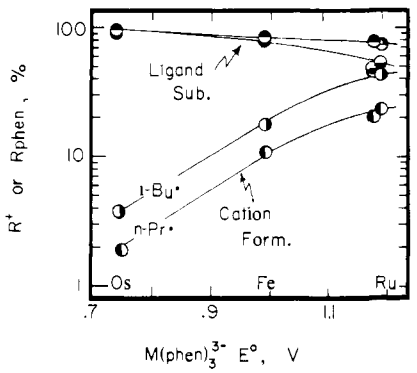


Figure 3. The change in ligand substitution (◐ or ◑) and cation formation (◓ or ◒) resulting from the oxidation of either *n*-propyl or isobutyl radical. Plotted as a function of the standard reduction potential $E°$ of the metal oxidant.

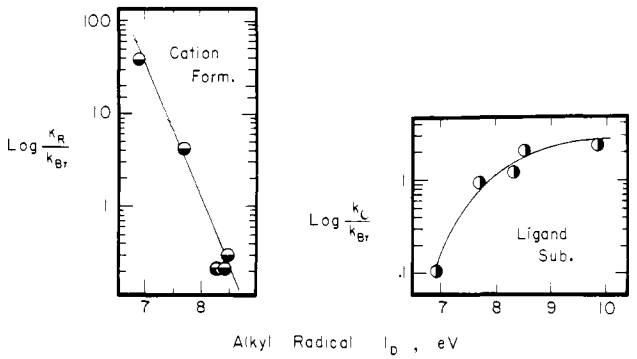


Figure 4. Structural effects of the alkyl radical on the rates of (a) cation formation (◒ in the left figure) and (b) ligand substitution (◑ in the right figure), as measured by k_R/k_{Br} and k_L/k_{Br}, respectively. Plotted as a funciton of the ionization potential of the alkyl radical.

II, in which we have evaluated on the ordinate the ligand substitution as the normalized yield of alkylphenanthroline (Rphen) and the cation formation as the combined yields of *N*-alkylacetamide and alkene (R^+). The abscissa identifies the various alkyl radicals and their ionization potentials I_D in the gas phase.[24] Figure 2 illustrates how ligand substitution and cation formation depend strongly on the ionization potential of the alkyl radical, particularly in the neighborhood of 8 eV. Cation formation is severely diminished and ligand substitution markedly enhanced at about 8 eV, and the converse is true sharply below this value.

A similar plot showing the dependence of ligand substitution and cation formation on the metal oxidant ML_3^{3+} is presented in Figure 3. The importance of cation formation increases monotonically with the reduction potential $E°$ of ML_3^{3+} for both *n*-propyl and isobutyl radicals, the slope being approximately the same for them. Figures 2 and 3 thus present complementary evidence for the importance of the driving force (i.e., $-I_D$ of the alkyl radical and $E°$ of the metal oxidant) in determining the relative importance of ligand substitution and cation formation. Furthermore, it is noteworthy that $Fe(5\text{-}NO_2phen)_3^{3+}$ and $Ru(phen)_3^{3+}$, having essentially the same $E°$, afford equivalent results, which are distinct from that effected by the milder oxidant $Fe(phen)_3^{3+}$. In other words, the identity of the metal center is not a crucial factor in the dichotomy.

II. Rates of Ligand Substitution and Cation Formation. Although the plots in Figures 2 and 3 graphically underscore the dichotomy of the oxidative process between ligand substitution and cation formation, they do not really reveal how *each*, individually, is affected by the driving force. However, an independent measure of ligand substitution and of cation formation is provided by the separate second-order rate constants k_L and k_R, respectively, in Table V. Since the competition experiments provide values of k_L and k_R relative to k_{Br} (the rate constant for bromine atom transfer from bromotrichloromethane in eq 14), these ratios from Table V are plotted against the ionization potentials I_D of the alkyl radicals in Figure 4. Several features in this figure are noteworthy. First, the rates (log k_R) of cation formation increase sharply with the ease of oxidation of the alkyl radical, as indicated by $-I_D$ in Figure 4a. Second, the rate (log k_L) of ligand substitution follow the opposite trend and generally increase with I_D. Indeed, the intersection of the two plots at roughly 8 eV coincides with the region in which there is a dramatic change in product distribution, which was illustrated in Figure 2.

The absolute rates of ligand substitution and cation formation could be evaluated from the kinetic data in Table V, if the rate of the monitoring reaction in eq 14 were known for each alkyl radical. Unfortunately, the list of alkyl radicals is very short. The only available direct measure for k_{Br} at 25 °C is 3×10^5 M^{-1} s^{-1} for methyl radical.[17] However, the value of k_{Br} can be evaluated for *tert*-butyl radical (2×10^8 M^{-1} s^{-1}) by an indirect method.[25] Similarly, k_{Br} for isopropyl radical can be equated to that for cyclohexyl radical (6×10^7 M^{-1} s^{-1}), obtained by an indirect method.[26] Based on these indications, we conclude that the value of k_{Br} increases regularly and by a factor of about 10^3 on proceeding from methyl to *tert*-butyl radical.[27] Accordingly, the slope of the plot for cation formation in Figure 4a is minimal, and the actual variation of k_R with I_D is significantly more pronounced. Since the same correction would be applied to ligand substitution, the relationship between cation formation in Figure 4a and ligand

Table VII. Steric and Polar Parameters for Alkyl Radicals[a]

α branching			β branching		
alkyl	E_S	I_D	alkyl	E_S	I_D
methyl	0	9.84	ethyl	-0.07	8.51
ethyl	-0.07	8.51	*n*-propyl	-0.36	8.4
isopropyl	-0.47	7.69	isobutyl	-0.93	8.35
tert-butyl	-1.54	6.92	neopentyl	-1.74	8.33

[a] Values of E_S from ref 28 and I_D from ref 24.

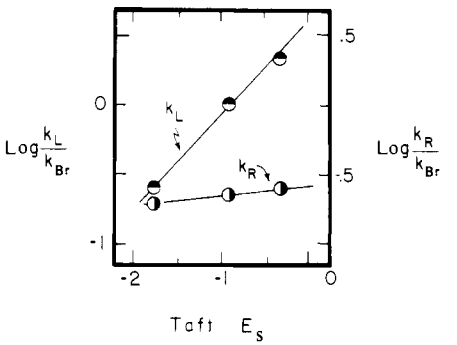


Figure 5. Steric effects (E_s) on the relative rates of ligand substitution k_L/k_{Br} (◓) and cation formation k_R/k_{Br} (◑) for the β-branched alkyl radicals, identified from left to right as neopentyl, isobutyl, and *n*-propyl.

(24) (a) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067. (b) *Ibid.* **1978**, *100*, 3290. (c) Lossing, F. P.; DeSousa, J. B. *Ibid.* **1959**, *81*, 281. (d) Taubert, R.; Lossing, F. P. *Ibid.* **1962**, *84*, 1523. (e) Pottie, R. F.; Harrison, A. G.; Lossing, F. P. *Ibid.* **1961**, *83*, 3204. (f) A value of 8.4 eV is taken for *n*-propyl radical rather than either 8.1 or 8.69 eV by Elder, F. A.; Giese, C.; Steiner, ,B.; Inghram, M. *J. Chem. Phys.* **1962**, *36*, 3292 and by Lossing and DeSousa in ref c above, respectively.

(25) Frith, P. G.; McLauchlan, K. A. *J. Chem. Soc. Faraday Trans. 2* **1976**,, *72*, 87 give $k_{Cl}(t\text{-Bu}\cdot + CCl_4) = 10 \exp(7.0)e \exp(-3.3 \pm 1.0/RT) = 3.8 \times 10^4$ M^{-1} s^{-1} at 25 °C. $\Delta H_{Cl}^{\ddagger} - \Delta H_{Br}^{\ddagger}$ can be estimated as 5.3 kcal mol^{-1} and $\Delta S_{Cl}^{\ddagger} - \Delta S_{Br}^{\ddagger}$ can be estimated as 0.52 eu based on the linear relationship given by Giese, . *Angew Chem. Int. Ed. Engl.* **1976**, *15*, 173 or $k_{Cl}/k_{Br} = 1.7 \times 10^{-4}$, from which $k_{Br}(t\text{-Bu}\cdot + BrCCl_3) = 2 \times 10^8$ M^{-1} s^{-1} at 25 °C. Compare also: Dütsch, H. R.; Fischer, H. *Int. J. Chem. Kinet.* **1981**, *13*, 527.

(26) Katz, M. G.; Horowitz, A.; Rajbenbach, L. A. *Int. J. Chem. Kinet.* **1975**, *7*, 183 give $k_{Cl}(c\text{-}C_6H_{11}\cdot + CCl_4) = 10 \exp(9.40 \pm 0.08)e \exp(-5.88 \pm 0.15/RT)$ M^{-1} s^{-1} but Alfassi, Z. B. *Ibid.* **1980**, *12*, 217 reports $k_{Cl} = 10 \exp(9.4 \pm 0.08)e \exp(-6.88/RT) = 2.3 \times 10^4$ M^{-1} s^{-1}. The relative rate $k_{Cl}/k_{Br} = 3.5 \times 10^{-4}$ from Giese, B. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 173 leads to $k_{Br}(c\text{-}C_6H_{11}\cdot + BrCCl_3) = 6.5 \times 10^7$ M^{-1} s^{-1} at 25 °C.

(27) We infer a factor of about 10^2 and 10 for secondary and primary radicals, respectively.

substitution in Figure 4b will remain unchanged, irrespective of the value of k_{Br} which is ultimately determined for each alkyl radical. This point is important to establish because the opposite trends in parts a and b of Figure 4 do provide insight into the mechanisms of these oxidative processes, especially as they are affected by steric effects.

III. Steric Effects in Ligand Substitution and Cation Formation. Steric effects in alkyl radicals may be considered in terms of α branching and β branching, which are evaluated by the Taft steric parameter by E_s in Table VII.[28] In α-branched alkyl radicals, the steric effect cannot be considered independently of the ionization potential, since they are both strongly affected by increasing methyl substitution. Therefore, let us initially consider only the alkyl radicals in the β series for which the ionization potentials are relatively constant. Figure 5 shows that cation formation and ligand substitution respond in quite different ways to steric effects—cation formation being quite insensitive to steric effects whereas ligand substitution is severely retarded. Such opposite effects are therefore responsible for the divergent product trends of the β-branched alkyl radicals described in Figure 3. Moreover, the relatively large combined yield of *tert*-amylacetamide and 2-methylbutenes derived from the oxidation of the sterically hindered neopentyl radical in Figure 2 is not due to a higher rate of cation formation, but it arises from a diminished rate of ligand substitution. This accords well with the otherwise inexplicable observation in Table III that the dimeric dineopentyl is formed in unusually high yields (vide supra).

We reach the same conclusion with α-branched alkyl radicals when steric effects are examined by encumbering the phenanthroline ligand with substituents, as in 4,7-dimethyl- and 4,7-diphenylphenanthroline. Thus the corresponding iron(III) complexes, $Fe(4,7\text{-}Me_2phen)_3^{3+}$ and $Fe(4,7\text{-}Ph_2phen)_3^{3+}$, effect cation formation (k_R) from either *tert*-butyl or isopropyl radical at essentially the same rate as that obtained with the sterically less hindered $Fe(phen)_3^{3+}$.[29] By contrast, the rate of ligand substitution (k_L) of $Fe(4,7\text{-}dMe_2phen)_3^{3+}$ by methyl or ethyl radical is significantly slower than that of $Fe(phen)_3^{3+}$. (The ligand substitution rates for isopropyl and *tert*-butyl are too slow to measure.)

IV. Mechanism of Alkyl Oxidation by Ligand Substitution and Cation Formation. In a recent study,[30] we demonstrated how the sensitivity to steric effects can be employed as an effective probe for distinguishing inner-sphere and outer-sphere mechanisms of electron transfer. Since an outer-sphere mechanism perforce entails the minimal interpenetration of the coordination spheres of the reactants,[4] the electron-transfer rate constant will be insensitive to steric effects.

Cation Formation as an Outer-Sphere Electron Transfer. According to the diagnostic method outlined above,[30] the oxidation of alkyl radicals leading to cation formation proceeds by an outer-sphere mechanism, since we have shown that the rate constant k_R is insensitive to steric effects when the driving force is more or less constant. Furthermore, a second criterion can be applied to an outer-sphere electron transfer process; viz., Marcus theory[31] predicts a linear correlation of the rate constant (log k_R) with the oxidation potential of the alkyl radical. Accordingly, the values of k_R for the oxidation of *tert*-butyl, cyclohexyl, and isopropyl radicals[32] are plotted against the ionization potentials

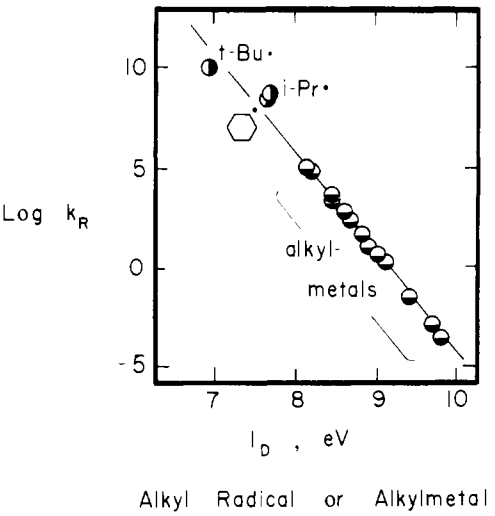


Figure 6. Unity in the linear free energy correlations of the rate of cation formation (log k_R) from alkyl radicals (◑) and the rate of outer-sphere oxidation of alkylmetals (◒) by $Fe(phen)_3^{3+}$. (See ref 32 for the identity of each data point.)

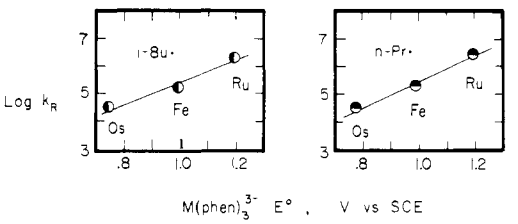


Figure 7. Linear free energy correlation of the rates of cation formation (log k_R) from (a) isobutyl radicals (◐) and (b) *n*-propyl radicals (◒). Plotted as a function of the standard reduction potentials of the metal oxidants from left to right as $(phen)_3Os^{3+}$, $(phen)_3Fe^{3+}$, and $(phen)_3Ru^{3+}$.

in Figure 6. These data are included remarkably well with the correlation of the rate constants obtained from the oxidation of various alkylmetals (RM) in the same medium, for which an outer-sphere mechanism was previously established.[30,33]

$$RM + FeL_3^{3+} \xrightarrow{k_{os}} RM^+ + FeL_3^{2+} \qquad (20)$$

It is noteworthy that the correlation also applies to the sterically hindered iron(III) oxidant with L = 4,7-diphenylphenanthroline as well as it does to the sterically more accessible $Fe(bpy)_3^{3+}$.

The correlation of the rate constant (log k_R) with the reduction potential of the metal oxidants, as shown in Figure 7 for *n*-propyl and isobutyl radicals, also accords with Marcus theory for outer-sphere electron transfer.[30]

In an outer-sphere mechanism for the oxidation of an alkyl radical, the rate-limiting transition state leads directly to an alkyl cation as a discrete intermediate, i.e.

$$R\cdot + M(phen)_3^{3+} \xrightarrow[CH_3CN]{k_R} R^+ + M(phen)_3^{2+} \qquad (21)$$

which is subsequently partitioned in a fast, follow up step.

$$R^+ \longrightarrow R(-H) + H^+ \qquad (22a)$$

$$R^+ \xrightarrow{CH_3CN} RNCCH_3^+, \text{ etc} \qquad (22b)$$

In accord with this formulation, the results in Table IV show that the isomeric distributions of rearranged alkenes and *N*-alkylacetamides from the oxidation of isobutyl radicals are singularly unaffected by the nature of the metal oxidant. Furthermore, the smooth trends in Figure 2 with minimal scatter of the data also

(28) (a) Taft, R. W., Jr., In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 556 ff. (b) See also: MacPhee, J. A.; Panaye, A.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 3553.

(29) Values of k_R/k_{Br} for *tert*-butyl radical are 70 ± 40 for these iron(III) complexes.

(30) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.

(31) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966; *Ibid.* **1957**, *26*, 867. Marcus, R. J.; Zwolinski, B. J.; Eyring, H. *J. Phys. Chem.* **1954**, *58* 432. For summaries, see ref 4.

(32) The data for the alkyl radicals, as designated in Figure 6, were obtained from the results in Table V and the rate constants k_{Br} discussed above. The data for the alkylmetals were obtained from ref 11 and 30 and are Et_4Pb, $t\text{-}Bu_2SnMe_2$, Et_2Hg, $s\text{-}Bu_4Sn$, Et_2PbMe_2, $t\text{-}BuSnMe_3$, $t\text{-}Bu_4Sn$, Et_4Sn, Et_2SnMe_2, $EtSnMe_3$, Et_4Ge, Me_4Sn, Et_4Si, in the order of their decreasing second-order rate constants for oxidation by $Fe(phen)_3^{3+}$.

(33) The constancy of the reorganization and the solvation energies for these related systems is not completely unexpected. See ref 30 and Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790.

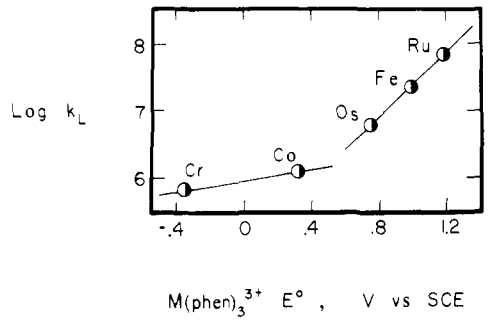
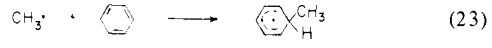


Figure 8. Dependence of the rate of ligand substitution (log k_L) of *n*-propyl radical (◑) on the reduction potentials $E°$ of a series of tris(phenanthroline) complexes $M(phen)_3^{3+}$ in acetonitrile solution.

support the alkyl cation as the common precursor. (If the alkenes and alkylacetamides were formed via different rate-limiting transition states, each would have to be treated separately. We hope to provide further experimental evidence for a common cationic intermediate at a later time.[34]) Taking the various kinetic and product criteria together, we thus conclude that cation formation proceeds via an outer-sphere electron transfer.

Ligand Substitution as an Inner-Sphere Electron Transfer. The oxidation of alkyl radicals by $Fe(phen)_3^{3+}$ leading to ligand substitution with the rate constant k_L may conceptually be considered sequentially as alkyl addition to and electron transfer and proton loss from the phenanthroline ligand. The enhanced sensitivity of this oxidative process to steric effects is in accord with a constrained transition state, reminiscent of the well-known addition of alkyl radicals to aromatic π-systems, e.g.[35]



(23)

Such a 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 homolytic systems.[36,37]

The rates of ligand substitution (log k_L) by methyl radical increase in an analogous manner for the series of substituted 1,10-phenanthrolineiron(III) complexes.[38] The deviation of the iron(III) complexes of 4,7-dimethyl- and 4,7-diphenylphenanthrolines, reflects the increased steric effects in these oxidants.[39] Coupled with the trend in k_L for the β-branched alkyl radicals shown in Figure 4b, we describe ligand substitution as an inner-sphere process.

The mechanisms of inner-sphere electron transfer in inorganic chemistry have been subclassified into several specific categories.[40,41] As applied to ligand substitution, two extreme roles can be envisaged for phenanthroline as the bridging ligand between the alkyl radical and the metal center. In the *chemical mechanism*, the alkyl radical initially adds to phenanthroline and the electron is transferred in a subsequent step from the alkylphenanthroline adduct radical to the metal. On the other hand, in the *resonance mechanism* the phenanthroline merely acts as an electron conduit, and there are no specifically bound states of phenanthroline along the reaction coordinate.

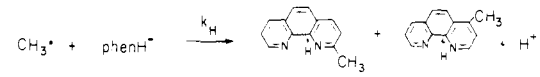
Table VIII. Ultraviolet Spectra of Tris(phenanthroline)metal Complexes[a]

$M(phen)_3^{n+}X_n$	A λ (log ε)	B λ (log ε)	C λ (log ε)
$FeL_3^{2+}(PF_6)_2$	268 (5.00)	228 (4.94)	199 (4.99)
$FeL_3^{3+}(PF_6)_3$	270 (4.92)	225 (4.99)	202 (5.03)
$RuL_3^{2+}(BF_4)_2$	262 (5.07)	224 (4.91)	200 (4.86)
$RuL_3^{3+}(BF_4)_3$	264 (5.00)	226 (4.95)	201 (4.90)
$OsL_3^{2+}(PF_6)_2$	263 (5.07)	221 (4.99)	202 (4.98)
$OsL_3^{3+}(PF_6)_3$	267 (4.91)	223 (4.92)	198 (4.93)
$CoL_3^{3+}(PF_6)_3$	280 (4.89) 274 (4.89)	219 (5.14)	202 (5.06)
$CrL_3^{3+}(PF_6)_3$	269 (4.86)	221 (4.97)	200 (5.02)
$Hphen^+OTf^-$	271 (4.49)	221 (4.52)	203 (4.47)
phen[b]	263 (4.42)	231 (4.73)	226 (4.63)

[a] In acetonitrile solution. [b] Free ligand from ref 47.

The rather pronounced sensitivity of ligand substitution to electron availability in the phenanthroline ligand is shown by the Hammett correlation of the rate constant k_L for methyl radical in its reaction with a series of substituted phenanthroline complexes of iron(III) FeL_3^{3+}. (These results are presented separately in ref 38.) Such a trend accords with a chemical mechanism for ligand substitution. The resonance mechanism may be evaluated by the dependence of k_L on the metal. As illustrated in Figure 8, however, we note that the magnitude of the change in k_L is small, especially if one considers a large span of more than 1.5 V in the driving force encompassed between the extremes of $Ru(phen)_3^{3+}$ and $Cr(phen)_3^{3+}$.[42] By comparison, the reductions of various $(NH_3)_5Ru^{III}$ complexes by the resonance mechanism yield rates which are more than 10^6 times faster than the reduction of analogous Co(III) and Cr(III) complexes, despite similar values of $E°$.[44] The value of k_L will be sensitive to the metal only in so far as the ligand orbitals are affected by coordination.[45] Indeed the UV spectra of a series of $M(phen)_3^{3+}$ in Table VIII indicate that the phenanthroline orbitals are relatively unaffected by the metal.

In order to assess the role of the metal in ligand substitution, we also examined the metal-free ligand in the form of the conjugate acid $Hphen^+$. Homolytic substitution with methyl radical affords both the 4- and 2-methylphenanthrolines.[48]



The second-order rate constant k_H determined by two independent competition experiments falls in the same range as k_L (vide infra). [$k_H(CH_3·) = 6 \times 10^5$ M^{-1} s^{-1} at 25 °C and $k_H(n\text{-}Pr·) \geq 2 \times 10^5$ M^{-1} s^{-1} at 70 °C.] We thus conclude that ligand substitution proceeds via a chemical mechanism in which radical addition to the π^* orbital of phenanthroline produces a reactive intermediate (e.g., Rphen·Ru^{III}) which then undergoes a rapid intramolecular electron transfer ($RphenRu^{II}$) in a subsequent step.[49] Indeed the

(34) Compare the earlier studies showing a common intermediate in copper(II) oxidations of alkyl radicals: Kochi, J. K.; Bemis, A.; Jenkins, C. L. *J. Am. Chem. Soc.* **1968**, *90*, 4616.

(35) (a) Heilman, W. J.; Rembaum, A.; Szwarc, M. *J. Chem. Soc.* **1957**, 1127. Herk, L.; Feld, M.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 2998 and earlier papers. (b) Cowley, B. R.; Norman, R. O. C.; Waters, W. A. *J. Chem. Soc.* **1959**, 1799.

(36) Shelton, J. R.; Uzelmeier, C. W. *J. Am. Chem. Soc.* **1966**, *88*, 5222.

(37) (a) Minisci, F. *Synthesis* **1973**, 1 and references therein. Minisci, F.; Porta, O. *Adv. Heterocycl. Chem.* **1974**, *16*, 123. (b) Bass, K. C.; Nababsing, P. *Adv. Free-Radical Chem.* **1972**, *4*, 1.

(38) Rollick, K. L.; Kochi, J. K. *J. Org. Chem.* **1982**, *47*, 435.

(39) Note that methyl radical substitution in $Fe(4,7\text{-}Me_2phen)_3^{3+}$ occurs in the 2-position.[38]

(40) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264.

(41) (a) Halpern, J.; Orgel, L. E. *Discuss. Faraday Soc.* **1960**, *29*, 32. (b) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321.

(42) The distinct break in the curve in Figure 9 for $Fe(phen)_3^{3+}$, $Ru(phen)_3^{3+}$, and $Os(phen)_3^{3+}$, when it is extended to $Co(phen)_3^{3+}$ and $Cr(phen)_3^{3+}$, can be attributed to orbital symmetry considerations.[43] Since the LUMO in M(III) for the iron triad is t_{2g}, the orbital overlap of the phenanthroline π orbitals is better than with Co(III) or Cr(III) in which the LUMO is e_g.

(43) Taube, H. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 964. Davies, R.; Jordan, R. B. *Inorg. Chem.* **1971**, *10*, 2432.

(44) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627.

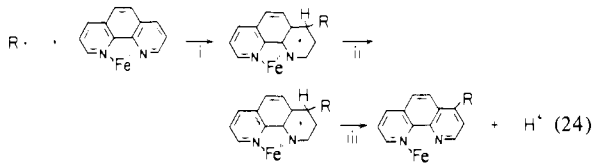
(45) Interaction between the orbitals on the metal with those on phenanthroline is included in previous NMR and visible spectral studies.[46]

(46) See, e.g.: DeSimone, R. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 2343. Rosenberger, H.; Pettig, M.; Madeja, K. *Z. Chem.* **1966**, *6*, 30. Pankuch, B. J.; Lacky, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2061. McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428.

(47) Perkampus, H.-H.; Kassebeer, G., "UV Atlas of Organic Compounds", Sandeman, I., Perkampus, H.-H., Eds.; Verlag Chemie: Weinheim, 1967; Vol. 3 H2O/2.

(48) The absence of substitution at the 2-position in ligand substitution of $M(phen)_3^{3+}$ is clearly due to steric hindrance. When the 4- and 7-positions are blocked as in 4,7-dimethyl- and 4,7-diphenylphenthrolines, ligand substitution of methyl radical does occur at the 2-position, but at diminished rates.[38]

latter is akin to the relaxation process associated with the chemiluminescence during the facile reduction of $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{3+}$ with hydrazine.[50] Such processes are also related to the emission following the metal-to-ligand [M → π*] charge-transfer transition which is spectroscopically observable for the series of $M(phen)_3^{2+}$ of the iron triad.[51] Thus the chemical mechanism for ligand substitution is best described by the multistep sequence in eq 24, in which the initial step i represents the rate-limiting activation process. The intramolecular electron transfer in step ii and proton loss in step iii are relatively fast.



Summary and Conclusion

The dichotomy between inner-sphere and outer-sphere mechanisms of electron transfer during the facile oxidation of alkyl radicals by metal oxidants such as $Fe(phen)_3^{3+}$ is strongly underscored by the competition between ligand substitution and cation formation in eq 7 and 8, respectively. Thus the activation process for cation formation ($\log k_R$) is dependent on the driving force, as determined by the ionization potential I_D of the alkyl radical (Figure 4a) and the standard reduction potential $E°$ of the metal oxidant in Table I. The linear free energy relationship established for cation formation in Figures 6 and 7 accords with Marcus theory for outer-sphere electron transfer. As such, it is independent of steric effects in either the alkyl radical or the metal oxidant in Figure 5. Contrastingly, the activation process for ligand substitution is markedly dependent on steric effects, as illustrated by the increasing values of k_L for neopentyl < isobutyl < *n*-propyl radicals in Figure 5 and for $Fe(4,7\text{-}Ph_2phen)_3^{3+}$ < $Fe(4,7\text{-}Me_2phen)_3^{3+}$ < $Fe(phen)_3^{3+}$.[38] The substituent effects on the phenanthroline ligand and the insensitivity to $E°$ of the metal oxidant support a chemical or multistep mechanism for the inner-sphere pathway in ligand substitution in eq 24.

Experimental Section

Materials. $Ru(phen)_3(BF_4)_2$ was prepared by following the procedure of Palmer and Piper[52] for the analogous tris(α,α′-bipyridine) complex. $Ru(phen)_3(BF_4)_3$ was prepared by the electrochemical oxidation of the ruthenium(II) complex at 1.7 V vs. SCE in acetonitrile saturated with $NaBF_4$. $Os(phen)_3(PF_6)_3$ was prepared from $OsBr_6(NH_4)_2$[53] by the method described by Dwyer et al.[54] $Cr(phen)_3(PF_6)_3$ was prepared by stirring $Cr_2(OAc)_4{\cdot}2H_2O$ (0.50 g, 1.3 mmol) with phenanthroline (2.0 g, 11 mmol) in 200 mL of a 1:1 mixture of ethanol and water.[55] $Co(phen)_3(PF_6)_3$ was synthesized following the procedure described by Schilt and Taylor,[56] except the complex was precipitated with NH_4PF_6. $Fe(phen)_3(ClO_4)_3$, $Fe(phen)_3(PF_6)_3$, and all the substituted 1,10-phenanthroline complexes of iron(III), as well as the various alkylmetals, were obtained as described earlier.[11] The salt $phenH^+\ O_3SCF_3^-$ was prepared by adding a stoichiometric amount of trifluoromethanesulfonic acid (3 M Co·) to a solution of 1,10-phenanthroline in absolute ethanol, followed by precipitation with anhydrous ether. After recrystallizaiton from toluene containing a small amount of ethanol, it was dried in vacuo. Acetonitrile and 1,10-phenanthroline were purified by the methods described earlier.[11] Bromotrichloromethane (Aldrich) was purified by a literature method. The preparations and NMR spectra data of authentic samples of all the *N*-alkylacetamides described in this study are presented elsewhere.[58]

Alkyl Oxidations with $Fe(phen)_3^{3+}$. Typical Procedures for Product Analysis. $Fe(phen)_3(PF_6)_3$ (1.03 g, 1.0 mmol) was weighed into a stoppered flask which was repeatedly evacuated and refilled with argon. Degassed acetonitrile (20 mL) was added with the aid of a hypodermic syringe, followed by a solution of *neo-PentSnMe*$_3$ (550 μmol) in 5 mL of acetonitrile. After the solution was stirred for 8 h, the hydrocarbons were analyzed by gas chromatography (GC) by the internal standard method using a 10 ft × $^1/_8$ in. column of either dibutyl tetrachlorophthalate or diethyleneglycol succinate. Analysis: methane (40 μmol), neopentane (1.5 μmol), 2-methyl-2-butene (95 μmol), 2-methyl-1-butene (10 μmol), 2,2,5,5-tetramethylhexane (17.5 μmol). The latter was confirmed by comparison of its mass spectral cracking pattern with that of an authentic sample: *m/e* (%) 142 (0.25), 127 (6.1), 71 (28), 58 (4.4), 57 (100), 56 (56), 55 (15), 53 (3.9). A small amount (50 μmol) of tetramethyltin was formed during the reaction. To the solution was added a drop of water, and the iron(II) complex precipitated with ether. The precipitate was collected on a glass frit and heated with dilute aqueous NaOH until the red color of the ferrous complex disappeared. Extraction with methylene chloride repeatedly, followed by concentration in vacuo, afforded a solution whose ^{1}H NMR spectra showed the presence of a neopentyl substituent on phen (235 μmol) [δ 2.93 (s, 2 H), δ 0.91 (s, 9 H)].[39,58] The remaining etheral solution was dried with $MgSO_4$ and anhydrous NH_3 bubbled in until precipitation of the diammine adduct R_3Sn^+ was complete (0.18 g, 95%).[13] The filtrate was concentrated in vacuo and analyzed by GC (10 ft × $^1/_8$ in. DEGS) to afford *N-tert*-amylacetamide (70 μmol): ^{1}H NMR δ 6.01 (b, 1 H), 1.93 (s, 3 H), 1.73 (q, *J* = 7.1 Hz, 2 H), 1.29 (s, 6 H), 0.85 (t, *J* = 7.1 Hz, 3 H).

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 solution was stirred for 2 h, GC analysis indicated methane (4.6 μmol, 2%) and ethane (<0.1 μmol). Addition of a 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%) phenanthroline, containing 228 μmol (91%) 4-methylphenanthroline by ^{1}H NMR analysis. Separation by column chromatography yielded pure 4-methylphenanthroline by comparison with an authentic sample.[59] The filtrate was dried with $MgSO_4$ and treated with anhydrous NH_3. Filtration yielded 0.094 g (109%) of $(CH_3)_3Sn(NH_3)_2PF_6$: ^{1}H 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 ^{1}H 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.[11] 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. The chemical shifts of *N*-methylacetamide and the 4-methylphenanthroline complex are 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 is due to the conjugate acid $CH_3(phenH)Fe(phen)_2^{3+}$, which is the precursor of the product, prior to proton loss. Such an assignment is consistent with the observed splitting of the resonance at δ 2.9 of $(4\text{-Mephen})_3Fe^{2+}$, upon the addition of a mixture of anhydrous HF–BF_3, into four peaks which progressively shift downfield with time, finally reaching δ 4.7–5.5 in ~0.5 h.[57] The ^{1}H NMR spectrum of $(CH_3)_3SnClO_4$ at δ 0.67 (J_{Sn} = 68 Hz in CD_3CN) is shifted to δ 0.61 (J_{Sn} = 66 Hz), not δ 1.2 as previously reported,[11] upon the addition of D_2O and LiCl.

EtSnMe$_3$ (560 μmol) reacts 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, *J* = 7.2 Hz) in the ^{1}H NMR spectrum, which was previously misassigned to *N*-ethylacetamide.[11] Workup of the solution, followed by GC analysis, showed the presence of only 10 μmol (2%) of *N*-ethylacetamide. Major amounts of ethylphenanthroline [^{1}H NMR δ 2.93 (q, *J* = 7.4 Hz) and 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 ^{1}H NMR spectral analysis. After precipitation of $Me_3Sn(NH_3)_2PF_6$, it was converted to the chloride

(49) Accordingly, the rate-limiting transition state is essentially the same as that in homolytic addition (as in eq 23). This ligand substitution is to be distinguished from an electrophilic process observed in the nitration of the tris(phenanthroline) complexes of iron(III) and cobalt(III), which occurs at the 5-position. See: Richards, A. F.; Ridd, J. H.; Tobe, M. L. *Chem. Ind. (London)* **1963**, 1727.

(50) 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.

(51) (a) Chum, H. L.; Koran, D.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 310. (b) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *Ibid.* **1980**, *102*, 1309. (c) The decay of the excited states of $*Fe(phen)_3^{3+}$, $*Ru(phen)_3^{2+}$, and $*Os(phen)_3^{2+}$ are reported (above) to proceed at the measurable rates of $\tau_{1/2}$ = 0.80, 920, and 84 ns. (d) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301.

(52) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864.

(53) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 204.

(54) Dwyer, F. P.; Gibson, N. A.; Gyarfas, E. C. *J. Proc. R. Soc. N. S. W.* **1950**, *84*, 68.

(55) Herzog, S. *Chem. Tech. (Leipzig)* **1956**, *8*, 544.

(56) Schilt, A. A.; Taylor, R. C. *J. Inorg. Nucl. Chem.* **1959**, *9*, 211.

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

(58) For additional details, see: Rollick, K. L. Ph.D. Dissertation, Indiana University.

(59) Richter, F.; Smith, G. F. *J. Am. Chem. Soc.* **1944**, *66*, 396. Manske, R. H. F.; Ledingham, A. E.; Ashford, W. R. *Can. J. Res.* **1949**, *27F*, 359.

and sublimed to yield 0.082 g (73%) of $(CH_3)_3SnCl$ δ 0.61, J_{Sn} = 58 Hz).

***i*-PrSnMe$_3$** was oxidized in a similar manner with $Fe(phen)_3(PF_6)_3$. The same analytical procedure was followed, with the exception that the filtrate following the separation of $Me_3Sn(NH_3)_2^+PF_6^-$ was concentrated and then placed on a silica gel column. Elution with ether afforded *N*-isopropylacetamide (0.046 g, 81%): ^{1}H NMR δ 7.8 (b, 1H), 4.0 (octet, J = 6.6 Hz, 1 H), 1.89 (s, 3 H), 1.14 (d, J = 6.6 Hz, 6 H); IR 3290 (s), 1659 (s), 1548 (s), 1385, 1371 (m) cm^{-1}.

***t*-BuSnMe$_3$** was also oxidized and analyzed as described above.[58] After precipitation of $Me_3Sn(NH_3)_2PF_6$, it was dissolved in dilute aqueous HCl and the solution saturated with NaCl. Me_3SnCl was extracted with ether and purified by sublimation (0.087 g, 78%); ^{1}H NMR ($CDCl_3$) δ 0.61 (J_{Sn} = 58 Hz). *N-tert*-Butylacetamide was analyzed by GC (6 ft × $^1/_8$ in. FFAP) to yield 480 μmol (84%). Evaporation of the solution to dryness followed by sublimation afforded 0.051 g (79%) of *N-tert*-butylacetamide: mp 100–101 °C; ^{1}H NMR δ 7.3 (b, 1 H), 1.89 (s, 3 H), 1.32 (s, 9 H); IR ($CDCl_3$) 3400 (s), 1668 (s), 1515 (s), 1393, 1370 (m) cm^{-1}.

Alkyl Oxidations with (5-NO$_2$phen)$_3$Fe^{3+}. Since $Fe(5\text{-}NO_2phen)_3^{3+}$ could not be isolated, it was generated electrochemically as needed. In a typical example, 0.46 g of $Fe(5\text{-}NO_2phen)_3(PF_6)_2$ was placed in the working compartment of the electrochemical cell, 10 mL of CH_3CN (saturated with $NaBF_4$) added to each arm,, and the solution oxidized at 1.8 V vs. SCE. The solution was transferred to a flask and degassed with a stream of argon and a solution of *n*-PrSnMe$_3$ (264 μmol) in 3 mL of CH_3CN added. After 2 h, GC analysis yielded: methane (3.8 μmol), propane (2.1 μmol), and propylene (5.9 μmol). The iron complex was precipitated with ether and digested with H_3PO_4 to liberate the ligand (0.27 g, 89% recovery). ^{1}H NMR analysis indicated a yield of 149 μmol of *n*-propyl groups attached to the nitrophenanthroline ligand. Two sets of resonances were observed in a ~60:40 ratio: δ 3.09 (t, J = 7.8 Hz), 2.76 (*t*, J = 7.8 Hz), 1.81 (m), 1.66 (m), 1.06 (t, J = 7.2 Hz), 0.92 (t, J = 7.1 Hz). $R_3Sn(NH_3)_2PF_6$ (270 μmol, 118%) was isolated, and GC analysis indicated the presence of *N*-isopropylacetamide (24.7 μmol) and *N*-*n*-propylacetamide (5.7 μmol).

Alkyl Oxidations with Os(phen)$_3$(PF$_6$)$_3$ were carried out in the same manner as those with $Fe(phen)_3(PF_6)_3$, except the phenanthroline ligands could not be stripped. NMR analyses were therefore carried out directly on the osmium(II) complex. If peak broadening was observed (owing to the presence of unreacted osmium(III)), a small amount of zinc dust was added and the tube shaken and then centrifuged prior to spectral analysis.

Alkyl Oxidations with Ru(phen)$_3^{3+}$. The ruthenium(III) complex $Ru(phen)_3^{3+}$ could not be isolated. It was prepared electrochemically at 1.8 V vs. SCE and used in situ, as described above for $Fe(5\text{-}NO_2phen)_3^{3+}$. Precipitation of the ruthenium(II) complex was followed by washing with a small amount of water to remove $NaBF_4$, weighing, and NMR analysis.

The yields of the organic products reported in Tables II, III, and IV are reliable to within ±10% (relative).

Relative Rate Measurements with M(phen)$_3^{3+}$. Typical Procedure. The kinetics were 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 15 mL. A solution of *n*-PrSnMe$_3$ (94.4 μmol) in 0.5 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 14 must be efficiently oxidized by $Fe(phen)_3^{3+}$. The products of oxidation were 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 I thus derives from the earlier study[11] and R_{Ox} and Cl_3C_{Ox}

Scheme I

$$RSnMe_3 + Fe(phen)_3^{3+} \xrightarrow{k_1} Fe(phen)_3^{2+} + Me_3Sn^+ + R\cdot \quad (25)$$

$$R\cdot + Fe(phen)_3^{3+} \xrightarrow{k_{Ox}} R_{Ox} + Fe(phen)_3^{2+} \quad (26)$$

$$R\cdot + BrCCl_3 \xrightarrow{k_{Br}} RBr + Cl_3C\cdot \quad (14)$$

$$Cl_3C\cdot + Fe(phen)_3^{3+} \xrightarrow{k_2} Fe(phen)_3^{2+} + Cl_3C_{Ox} \quad (27)$$

represent the oxidation products of the alkyl radical ($k_{Ox} = k_L + k_R$) and the trichloromethyl radical, respectively. Initially, the ratio of rate constants k_{Ox}/k_{Br} in eq 15 was obtained by setting d[Mephen]/d[MeBr] 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,[60] was followed by a rigorous solution of the kinetics in Scheme I by using the digital simulation technique of Feldberg[61] 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.[58]

Table IX. Rate Constants for the Oxidation of Alkyl Radicals by the Competition Method[a]

a. Isopropyl Radical

$(phen)_3Fe(PF_6)_3$, M	$BrCCl_3$, M	products, 10^6 mol: C_3H_6	*i*-PrNHAc	*i*-PrBr	k_R/k_L
0.017	0.16	4.1	24	19	16
0.020	0.04	5.0	44	7.1	16
0.020	0.10	4.3	32	15	14
0.020	0.20	3.5	27	26	13
0.020	0.40	2.5	17	37	12
0.016	0.10	0.7	28	15	13
0.012	0.10	0.8	20	20	11
0.008	0.10	<0.2	13	27	8
0.020[b]	0.10	2.7	32	16	12
0.020[c]	0.10	1.1	32	17	11

b. *tert*-Butyl Radical

$(phen)_3Fe(PF_6)_3$, M	$BrCCl_3$, M	products, 10^6 mol: C_4H_8	*t*-BuNHAc	*t*-BuBr	k_R/l_L
0.017	0.17	11	16	9.5	32
0.017	0.66	15	9.7	19	57
0.017	1.67	8.0	6.9	28	62
0.017	0.20	4.4	6.6[d]	20	21
0.017	0.29	3.3	2.0[e]	25	20
0.017	0.49	1.7	3.0[f]	32	21
0.017	0.98	0.8	4.3[g]	39	28

c. Cyclohexyl Radical

$(phen)_3Fe(PF_6)_3$, M	$BrCCl_3$, M	product, 10^6 mol: c-C_6H_{10}	c-C_6H_{11}NHAc	c-C_6H_{11}Br	k_R/k_L
0.017	0.018	15	29	13	4.1
0.017	0.053	9.5	21	25	4.3
0.017	0.088	7.9	16	33	4.4
0.017	0.18	4.8	11	44	4.3

[a] In acetonitrile at 25 °C. [b] Contains 0.05 M $NaClO_4$. [c] Contains 0.50 M $NaClO_4$. [d–g] d, 22, e, 19, f, 16, g, 2 μmol of *tert*-butyl alcohol to be included in R^+ products.

The relative rates of oxidation of the isopropyl radical by $(phen)_3Fe^{3+}$ were also carried out by varying both the concentration of iron(III) and $BrCCl_3$. Thus to weighed amounts of $(phen)_3Fe(PF_6)_3$, $BrCCl_3$, and $NaClO_4$ (to maintain ionic strength) in a 50-mL flask was added sufficient acetonitrile to bring the volume of the solution to 25 mL. After the flask was purged with a stream of argon, a solution of *i*-PrSnMe$_3$ (50 μmol) in 5 mL of CH_3CN was added. The solution was stirred for 1 h, and the propylene, isopropyl bromide, and *N*-isopropylacetamide were analyzed by gas chromatography on three separate 10 ft × $^1/_8$ in. columns consisting of 20% DBTCP, 5% FFAP, and 15% DEGS, respectively. The reference compounds employed as the internal standards were isobutane, *n*-butyl bromide, and *N*-propylacetamide, respectively. The results are listed in Table IXa. A similar procedure was used for the measurement of the relative rate of oxidation of *tert*-butyl radical by $(phen)_3Fe^{3+}$. The reactions were set up with 500 μmol of $(phen)_3Fe(PF_6)_3$, 50 μmol of *t*-BuSnMe$_3$, and various amounts of $BrCCl_3$ in 30 mL of CH_3CN, as listed in Table IXb. Isobutylene, *tert*-butyl bromide, *tert*-butyl alcohol, and *N-tert*-butylacetamide were analyzed by gas chromatography using isobutane, *n*-butyl bromide, *n*-butyl bromide, and

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Table X. Decomposition of Acetyl Peroxide in the Presence and Absence of $(phen)_3Fe(PF_6)_3$[a]

time, min	$[L_3Fe(III)]$, mM	products, 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 resonances at δ 2.6.

N-isopropylacetamide, respectively, as internal standards. The oxidation of cyclohexyl radicals was examined with a reaction system consisting of 500 μmol of $(phen)_3Fe(PF_6)_3$, 63 μmol of c-HxSnMe$_3$, and various amounts of $BrCCl_3$ in 30 mL of acetonitrile as listed in Table IXc. The analysis of cyclohexene, cyclohexyl bromide, and *N*-cyclohexylacetamide was carried out with 1-hexene, *n*-octyl bromide, and *N*-butylacetamide as internal standards, respectively, on a 10 ft × $^1/_8$ in. DEGS column. The ratio of rate constants k_R/k_{Br} for each radical, as calculated by the procedure described above, are also listed in Table IX. The rates of oxidation for the other alkyl radicals are presented separately.[58]

Salt Effects on the Oxidation of Methyl and Isopropyl Radicals by $(phen)_3Fe^{3+}$. The salt effect on the oxidation of methyl radical was examined by adding various amounts of sodium perchlorate to a standard reaction consisting of $(phen)_3Fe(PF_6)_3$ (400 μmol) in 18 mL of acetonitrile. After the mixture was flushed with a stream of argon, 382 μmol of $BrCCl_3$ in 1 mL of CH_3CN was added, followed by a solution of 103 μmol of Me_4Pb in 1 mL of CH_3CN. The mixture was stirred for 1 h at room temperature and the methyl bromide analyzed by gas chromotography [10 ft × $^1/_8$ in. column containing 20% DBTCP on Chromosorb), using methyl chloride as the internal standard. The iron complex was precipitated with ether and the mixture of phenanthroline ligands isolated following hydrolysis and analyzed by ^1H NMR spectroscopy. For runs containing 0.00, 0.01, 0.05, 0.10, and 0.50 M $NaClO_4$, the yields of MeBr and Mephen (in parentheses) were found to be 42 (29), 42 (29), 42 (28), 42 (29), and 36 (29) μmol, respectively.

The salt effects on the oxidation of isopropyl radicals were carried out in a similar manner by using 50 μmol of *i*-PrSnMe$_3$, 500 μmol of $(phen)_3Fe(PF_6)_3$, and 2500 μmol of $BrCCl_3$ in a total volume of 25 mL of acetonitrile. For reactions containing 0.00, 0.05, and 0.5 M $NaClO_4$, the yields of propylene, *N*-isopropylacetamide (parentheses), and isopropyl bromide (brackets) were 4.3 (32) [15], 2.7 (32) [16], and 1.1 (32) [17], respectively. Thus there is little or no influence of ionic strength on either ligand substitution by methyl radical or cation formation by isopropyl radical as a result of oxidation by $(phen)_3Fe^{3+}$.

Acetyl Peroxide as a Source of Methyl Radicals. Owing to its capriciously dangerous properties, the acetyl peroxide used for the generation of methyl radicals was treated with special precautions, as follows. Acetyl peroxide was initially prepared in ethereal solution from acetic anhydride and sodium peroxide, according to the procedure described by Slagle and Shine.[62] An aliquot of the purified ethereal solution containing the appropriate amount of peroxide was transferred to a Schlenk tube, which was cooled to −78 °C. All subsequent manipulations were carried out behind a safety shield. The supernatant ether was removed from the crystalline peroxide with the aid of a filter stick (care!) under a reverse flow of argon and an aliquot of hexane added immediately. The mixture was permitted to warm up to a temperature sufficient to allow the complete dissolution of the crystalline peroxide. The hexane solution was cooled again to −78 °C to effect the recrystallization of acetyl peroxide. The supernatant hexane was removed with a filter stick (care!), and the desired amount of acetonitrile was added. The resulting CH_3CN solution of acetyl peroxide (which contained minor amounts of hexane) was used directly in all subsequent studies.

The decomposition of acetyl peroxide was carried out in duplicate systems. One tube contained only the solution of acetyl peroxide in acetonitrile and the other contained the same amount of the acetyl peroxide solution, together with an appropriate amount of $(phen)_3Fe(PF_6)_3$, as listed in Table X. The evolution of carbon dioxide at 80 °C was followed by gas chromatographic analysis, using a 4 ft × $^1/_4$ in. column of Porapak Q and ethylene as the internal standard. (The system was previously calibrated under reaction conditions.) Methane and ethane were also analyzed by gas chromatography using a 4 ft × $^1/_8$ in. column of Porapak Q and ethylene as the internal standard. In decompositions carried out in this medium, the methane and ethane accounted for more than 70% of the liberated CO_2, if the stoichiometry is considered as $[CH_4 + 2C_2H_6] = CO_2$. Other products such as methyl acetate and those derived from the solvent were not examined.[9] The important features of the data in Table X 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 [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 3), particularly in the initial phases of the decomposition. These results are accommodated by the mechanism in Scheme II. The presence of iron(III)

Table XI. The Decomposition of Acetyl Peroxide in the Presence and Absence of $(phen)_3Fe(PF_6)_2$[a]

time, min	$[L_3Fe^{II}]$, mM	products, μmol			
		CO_2	MeH	EtH	MeL[b]
15	0	5.2	5.1	0.1	
15	20	17	7.9	0.1	2.0
30	0	13	9.9	0.3	
30	20	34	16	0.3	4.4
60	0	30	28	0.8	
60	20	49	25	0.3	5.9
120	0	55	42	1.4	
120	20	70	35	0.8	7.6

[a] Reactions carried out at 80 °C in 10 mL of CH_3CN containing ~60 μmol of acetyl peroxide. [b] Analysis of recovered phenanthroline by quantitative ^1H NMR spectroscopy of the singlet resonance at δ 2.6.

Scheme II

$$(CH_3CO_2)_2 \xrightarrow{\text{slow}} 2CH_3\cdot + 2CO_2 \quad (28)$$

$$CH_3\cdot + CH_3CN \rightarrow CH_4 + \cdot CH_2CN \text{ etc.} \quad (29)$$

$$CH_3\cdot + (phen)_3Fe^{3+} \rightarrow CH_3phenFe(phen)_2^{2+} + H^+ \quad (30)$$

does not affect the decomposition of acetyl peroxide in the well-established slow step (eq 28) leading to CO_2 and methyl radical.[9] The methyl products are determined in the subsequent rapid steps described by eq 29 and 30. The efficient diversion of methyl radicals in eq 30 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 29.

A closer inspection of the results in Table X reveals that the yield of the iron(II) product becomes progressively less than the yield of methylphenanthroline as the peroxide is converted. Control experiments established that $(phen)_3Fe(PF_6)_3$ and $(phen)_3Fe(PF_6)_2$ were both stable at 80 °C in acetonitrile for the duration of the thermolysis. Indeed, the low yields of the iron(II) product arise from losses owing to its subsequent reaction with acetyl peroxide. Table XI lists the results of a comparative study of the thermolysis of acetyl peroxide, in the presence and absence of the iron(II) complex, $(phen)_3Fe(PF_6)_2$. The results from this iron(II) series differ from those obtained from the analogous iron(III) series of experiments in two important ways. First, the presence of $(phen)_3Fe^{2+}$ clearly leads to an enhanced rate of decarboxylation. Second, if methylphenanthroline is included, the combined yields of products derived from methyl radical accord with the carbon dioxide yield in more or less the same way as those obtained in the absence of the iron(II) additive. The enhanced rate of acetyl peroxide decomposition in the presence of iron(II) $(phen)_3Fe^{2+}$ can be explained by essentially the same mechanism as that established for the well-known catalytic decomposition of peroxides with a variety of transition-metal complexes (Scheme III).[9] The catalytic process assumes increasing importance in the latter stages of the peroxide decomposition in the presence of $(phen)_3Fe^{3+}$, as listed in Table X.

Scheme III

$$(CH_3CO)_2 + (phen)_3Fe^{2+} \rightarrow (phen)_3Fe^{3+} + CH_3CO_2^- + CO_2 + CH_3\cdot \quad (31)$$

$$CH_3\cdot + (phen)_3Fe^{3+} \rightarrow CH_3phenFe(phen)_2^{2+} + H^+ \quad (32)$$

(62) Slagle, J. R.; Shine, H. J. *J. Org. Chem.* **1959**, *24*, 107.

Peroxide as a Source of Alkyl Radicals. In a typical procedure Co(phen)$_3$(PF$_6$)$_3$ (0.41 g, 400 μmol) was placed in a 50-mL tube and a calculated amount of $BrCCl_3$ in CH_3CN added, followed by 50 mmol of butyryl peroxide dissolved in CH_3CN. The volume was brought up to 10 mL, the solution degassed by a freeze–pump–thaw cycle, and the tube sealed in vacuo. After the tubes were left sitting in the bath for 8 h at 70 °C, they were opened and filled with argon. After GC analysis of CO_2 on a Porapak Q column, hexane and n-propyl bromide were analyzed on a Carbowax 20 M column. The cobalt complex was collected by concentrating the solution in vacuo and then adding ether. The recovered complex was analyzed directly for its *n*-Prphen content (12.7 μmol for 200 μmol of $BrCCl_3$). Analysis: *n*-propyl bromide (45.1 μmol), *n*-propylacetamide (1.0 μmol), *N*-isopropylacetamide (2.2 μmol). The latter resulted from the ionic decomposition of the peroxide.

The direct competition between (phen)$_3$Fe^{3+} (500 μmol) and phenH$^+$ for methyl radical was carried out with 0.25, 0.50, and 1.00 mmol of phenH$^+$ OTf$^-$, using Me_4Pb (98 μmol) in 20 mL of CH_3CN. After 1 h, the solution was analyzed and then concentrated in vacuo. The phenanthroline complexes were precipitated with ether, and the protonated derivative was separated by extraction with successive portions of ethanol.

Cyclic Voltammetry. The standard reduction potentials of the $ML_3^{3+,2+}$ couples were measured by cyclic voltammetry on a Princeton Applied Research model 173 potentiostat/galvanostat equipped with a Houston Instrument Series 2000 Omnigraphic X-Y recorder, as previously described.[11] The measurements were carried out at 25 °C in CH_3CN containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. A platinum microelectrode was employed with a saturated NaCl calomel reference electrode.

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Registry No. Methyl, 2229-07-4; ethyl, 2025-56-1; *n*-propyl, 2143-61-5; isopropyl, 2025-55-0; isobutyl, 4630-45-9; *tert*-butyl, 1605-73-8; neopentyl, 3744-21-6; benzyl, 2154-56-5; cyclohexyl, 3170-58-9; Fe(phen)$_3^{3+}$, 13479-49-7; Os(phen)$_3^{3+}$, 47837-53-6; Ru(phen)$_3^{3+}$, 23633-32-1; Co(phen)$_3^{3+}$, 18581-79-8; Cr(phen)$_3^{3+}$, 15276-16-1; Fe(5-NO$_2$phen)$_3^{3+}$, 22327-24-8; Fe(4,7-Me$_2$phen)$_3^{3+}$, 17378-76-6; Fe(bpy)$_3^{3+}$, 18661-69-3; Fe(4,7-Ph$_2$phen)$_3^{3+}$, 53204-05-0; Fe(5-Cl(phen))$_3^{3+}$, 22327-23-7; Me(phen), 31301-28-7; Et(phen), 80206-19-5; *n*-Pr(phen), 80186-77-2; *i*-Pr(phen), 80186-78-3; *i*-Bu(phen), 80186-79-4; neopentyl(phen), 80186-80-7.

Generation of 2-(Trimethylsiloxy)allyl Cations and Their Reactions with 1,3-Dienes. Change in Mechanism of 3 + 4 → 7 Cycloaddition with Solvent[1]

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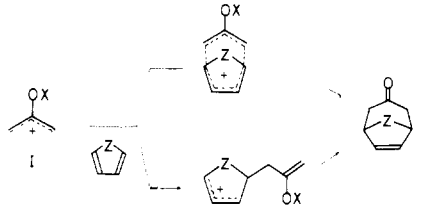
Abstract: A series of 12 different 2-(trimethylsiloxy)allyl cations **34a**–**l** is generated from various 2-(trimethylsiloxy)allyl chlorides (**3**–**5**) with silver perchlorate. In nitromethane solution, all the cations smoothly react with furan and cyclopentadiene in a 3 + 4 → 7 manner to give a comprehensive series of 8-oxabicyclo[3.2.1]oct-6-en-3-ones and bicyclo[3.2.1]oct-6-en-3-ones in good yields. The cycloaddition with furan proceeds in a stereospecific manner with the retention of allyl cation configurations, in accord with a concerted mechanism. The 3 + 4 → 7 reactions in THF/ether contrast with those in nitromethane in the following ways. (1) The yield of the adducts strongly depends on the structure of the allyl cations. (2) The reaction with furan is nonstereospecific. (3) An electrophilic substitution reaction strongly competes with the cycloaddition. (4) The cycloaddition between the cation **34a** and 2-methylfuran is highly regioselective (**11**/**12** = 19) as compared to that in nitromethane (the ratio being only 1.9). These findings in THF/ether are reasonably explained by a stepwise mechanism via an intermediate **40**. Reactions with acyclic dienes (isoprene and 2,3-dimethylbutadiene), naphthalene, anisole, and methanol are also described.

The chemistry of 2-oxyallyl species (I) has increasingly received wide attention from synthetic and mechanistic interests.[2-9] One of the characteristic reactions of the oxyallyls is a 3 + 4 → 7 cycloaddition with a conjugated diene, providing a unique and important route to seven-membered rings in organic synthesis.[2,3,10]



Mechanistically, this cycloaddition has been classified as either a concerted $2_\pi + 4_\pi$ pericyclic reaction[2,11-13] or a stepwise reaction initiated by an electrophilic addition followed by cyclization of an intermediate.[14,15] However, details are not yet fully understood.

In connection with our study on the reactions of 2-functionalized allyl halides, we have found that 1,1-dimethyl-2-(trimethylsil-

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