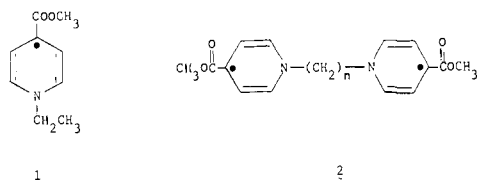# Stable Free Radicals. 9. Magnesium and Other Metal Halide Complexes of Pyridinyl Diradicals

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Abstract: Pyridinyl diradical complexes with metal halides (py·(CH$_2$)$_n$py·MX$_2$, in which py· = 4-CH$_3$OOCC$_5$H$_4$N–, M = Mg, Ca, Sr, Ba, Zn, Mn, $^2/_3$Gd, $^2/_3$Er, $^2/_3$Yb, X = I, Br, Cl, and n = 3-10) are produced by reaction of the corresponding bispyridinium halides with the metal, M, in CH$_3$CN under oxygen-free conditions. Most of the complexes are characterized by strong intramolecular charge-transfer bands and intensified pyridinyl radical absorptions. Ligand exchange at the metal ion leads to changes in the absorption spectra of the complexes in a manner dependent upon the donor strength of the ligand. The **3**:MgI$_2$ complexes are diamagnetic like the **3**:diradical (n = 3). Spin concentration increases in **4**:MgI$_2$ like **4**:diradical, but **5**:MgI$_2$ has a lower spin concentration than **5**:diradical. The complexes are further reduced by metals, in some cases by 1e. Oxidation of the complexes always leads to bispyridinium ion, and not to 1e oxidation products (cation radicals). The complexes disappear in the presence of alcohol, probably by intramolecular electron transfer. The complexes react with halocarbons by at least two pathways, atom transfer for reactive halocarbons and via formation of an "active" diradical metal halide complex in the case of unreactive halocarbons. Reactivity is defined by behavior toward pyridinyl monoradical. A strong complexing agent, tetraethylammonium ethylenediaminetetraacetate (TEA$_4$EDTA), converted **3**:MgI$_2$/CH$_3$CN into **3**:, but only on heating.

During the investigations which led to the isolation by distillation of 1-ethyl-4-carbomethoxypyridinyl radical (**1**), we noted that magnesium metal dissolved rapidly in acetonitrile solutions of 1-ethyl-4-carbomethoxypyridinium iodide at 0 °C.[2] However, pyridinyl radical could not be isolated from its complex with magnesium iodide except in low yield by distillation of the radical from a mixture of pyridinium iodide and metal at 135-140 °C. Subsequent attempts to characterize the complex itself were unsuccessful. After the discovery by Itoh and Nagakura[3] of the formation of intermolecular (π-mer) complexes from pairs of pyridinyl radicals, Itoh and Kosower[4] prepared pyridinyl diradicals, ·py(CH$_2$)$_n$py· (**2**), which ex-

hibited intramolecular complex formation (π-mer) for appropriate values of n. With a view to a possible simplification in metal ion complex structure, we tried the reaction of magnesium with a bispyridinium iodide, and discovered that beautifully colored and partially characterizable complexes could be thus generated. We here extend our preliminary report[5] to cover the preparation, analysis, and physical and chemical properties of magnesium and other metal halide complexes of a series of bispyridinyl radicals.

Results

Treatment of a polymethylene bis(4-carbomethoxypyridinium) dihalide with a metal of suitable reduction potential in acetonitrile at 0 °C leads to an intensely colored solution of the respective diradical metal halide complex (eq 1). The diradical
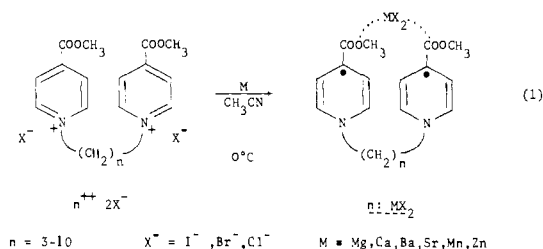
with n methylene groups in a chain between the pyridinyl moieties is written as n:, and the corresponding metal complex as n:MX$_2$. The stoichiometry of the parallel reaction with rare earth metals leads to (n:)$_3$(MX$_3$)$_2$ as the complex, M = Er, Yb, Gd.

A number of factors affect the rate of the reduction. Clean and plentiful surface (small particles) permits a high reduction potential to be expressed in a reduction time between 15 and 45 min, using the series Mg, Ca, Sr, and Ba (E_0 = +2.37, +2.87, +2.89, and +2.90 V, respectively).[6] The salt must be reasonably soluble in the solvent (ca. 10^{-4} M), the temperature kept near 0 °C, and the time restricted for many cases to prevent further reduction. No method for cleaning the surface of beryllium was found sufficient to allow reduction, although the reduction potential of beryllium (+1.85 V)[6] should certainly lead to reaction.

The rare earth metals reacted more slowly than the group 2 metals, manganese (E_0 = +1.18 V)[6] or zinc (E_0 = +0.76 V),[6] 2-2.5 h being needed for optimum formation of gadolinium (E_0 = +2.40 V)[6] complex and 10-11 h required for the complexes of erbium (E_0 = +2.30 V) and ytterbium (E_0 = +2.27 V).[6] Aluminum amalgam yielded mostly polymeric material and a solution containing complexed pyridinyl radicals; titanium, vanadium, chromium, and iron failed to react.

The number of electrons introduced into the pyridinium rings by reductions was determined by titration with 1,1'-dimethyl-4,4'-bipyridylium dication, the absorption coefficients for the product cation radical ("Paraquat" cation radical) being known from previous work[7] (eq 2). The metal ion
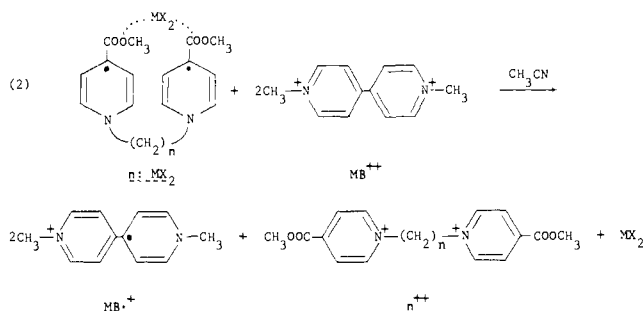

content was determined by ethylenediaminetetraacetic acid (EDTA) titration for many of the complexes. One metal ion

Table I. Absorption Maxima of the Polymethylene Diradical II-mer-Metal Halide Complexes in Acetonitrile

π-mer n:$MgI_2{}^a$	Absorption maxima λ_{max} (ϵ_{max})				
	λ_1	λ_2	λ_3	$\lambda_4{}^b$	λ_5
3:MgI_2	605 (8900)	380 (16 300)	288 (25 600)	246 (38 800)	206 (56 000)
4:MgI_2	625 (6600)	383 (17 000)	288 (26 800)	246 (37 800)	206 (54 000)
			304 (sh. 22 600)		
5:MgI_2	668 (2000)	395 (16 500)	304 (31 200)	246 (39 400)	
6:MgI_2	634 (540)	399 (15 300)	307 (27 200)	246 (39 800)	
7:MgI_2	~630^c (~300)	396 (15 000)	306 (27 700)	246 (36 800)	
8:MgI_2	~630^c (~300)	396 (15 000)	306 (27 000)	246 (37 000)	
9:MgI_2	~630^c (~300)	396 (15 000)	306 (27 000)	246 (37 000)	
10:MgI_2	~630^c (~300)	396 (15 000)	306 (27 000)	246 (37 000)	
3:^{d}	703 (3800)	390 (4600)	304 (sh. 5500)		225 (30 400)
4:^{d}	708 (2060)	395 (5200)	302 (9700)		
5:^{d}	632 (<100)	395 (9660)	302 (36 600)		

^{a} n = number of methylene groups in $-(CH_2)_n-$ bridge connecting the nitrogens of 4-carbomethoxypyridinyl moieties. ^{b} Due to I^- in CH_3CN. ^{c} Very broad absorption. ^{d} From M. Itoh and E. M. Kosower. *J. Am. Chem. Soc.*, **90**, 1843 (1968).
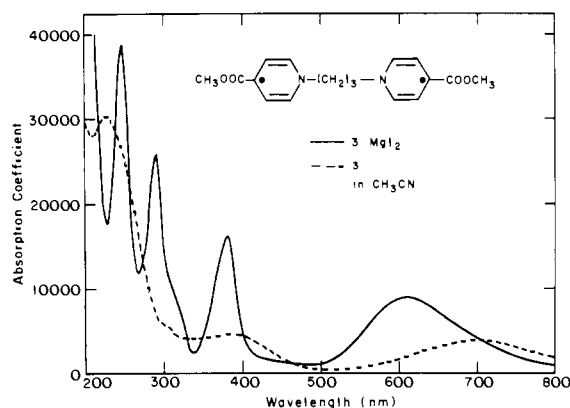
Figure 1. A comparison of the absorption spectra of 1,1'-trimethylene-bis(4-carbomethoxypyridinyl)magnesium iodide complex (3:MgI_2) and the diradical **3:** in CH_3CN.
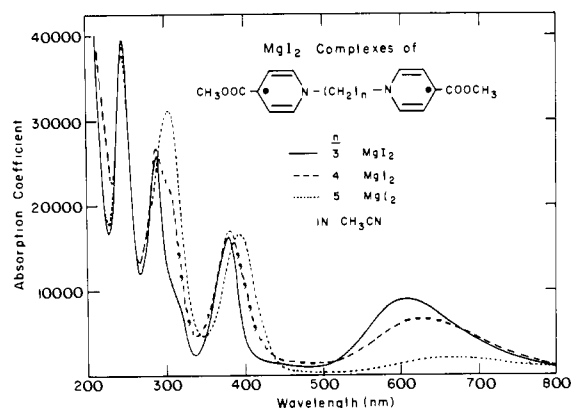
Figure 2. A comparison of the absorption spectra of 1,1'-polymethylene-bis(4-carbomethoxypyridinyl)magnesium iodide complexes. py·$(CH_2)_n$py·:MgI_2 (n:MgI_2) in which n = 3, 4, or 5 (in CH_3CN).

for each pair of pyridinyl radicals was found for the magnesium, calcium, strontium, zinc, and manganese complexes, whereas the erbium and gadolinium complexes had two metal ions for every three pairs of pyridinyl radicals, corresponding to the composition $(n:)_3(MX_3)_2$.

Spectroscopic Properties. The UV–visible absorption spectrum of **3:** (the trimethylene bridged bispyridinyl, **2**, n = 3) in acetonitrile has a visible maximum at 703 nm (ϵ 3800). a near-ultraviolet maximum at 390 nm (ϵ 4600), a shoulder at 304 nm (ϵ 5500), and a short-wavelength maximum at 225 nm (ϵ 30 400). Complexation with magnesium iodide changes the spectrum dramatically. the absorption bands shifting in wavelength, increasing greatly in intensity, and narrowing in width. The absorption bands for **3:MgI_2** are (illustrated in Figure 1) 605 nm (ϵ 8900), 380 (16 300), 288 (25 600), 246 (38 800), and 206 (56 000).

As the length of the chain connecting the pyridinyl moieties increases, the visible maximum shifts to longer wavelengths and the absorption intensity falls. At shorter wavelengths, the

most marked change is the replacement of the 288-nm maximum with a 304-nm absorption band as n is increased from 3 to 5. At n = 4, both transitions appear. The effect of chain length is shown in Figure 2 and the data for the whole series are summarized in Table I.

The change from magnesium to calcium in n:MI_2 causes only the most minor changes in the spectra of the complexes, a 10% decrease in the absorption intensity of the visible maximum being the most notable. The absorption spectra for **3:SrI_2** and **3:BaI_2** resemble those for the magnesium and calcium complexes with, however, lower absorption coefficients (Table II). More substantial differences are seen in the spectrum of the **3:ZnI_2** complex, which is compared to that of the erbium and magnesium complexes in Figure 3. Data for the Zn. Mn, Er, Yb, and Gd complexes are listed in Table III. The changes noted for replacement of I^- by Br^- or Cl^- in **3:MgX_2** are noteworthy (Table IV).

Table II. Absorption Maxima of the Group 2 Metal Iodide Complexes of 1,1'-Trimethylenebis(4-carbomethoxypyridinyl) (**3:**) in Acetonitrile

Metal	λ_{max} (ϵ_{max})			
	λ_1	λ_2	λ_3	$\lambda_4{}^a$
Mg	605 (8900)	380 (16 300)	288 (25 600)	246 (38 800)
Ca	605 (8000)	380 (16 000)	288 (24 000)	246 (38 000)
Sr	605(6000)	379 (12 400)	288 (19 500)	246 (41 000)
Ba	605 (4000)	379 (8500)	288 (15 200)	246 (41 400)

^{a} Due to I^- in CH_3CN.

Table III. Absorption Maxima of the Complexes of 1,1'-Trimethylenebis(4-carbomethoxypyridinyl) (**3:**) with Transition and Rare Earth Metal Iodides

| Metal	λ_{max} (ϵ_{max})			
	λ_1	$\lambda_{2'}$	λ_2	λ_3
Zn	619 (1060)	428 (sh 1570)	384 (4200)	305 (sh 5000)
				282 (sh 8700)
Mn	619 (3870)	446 (sh 2640)	381 (9700)	306 (sh 9900)
				284 (16 300)
Er	618 (7500)		387 (17 000)	292 (26 600)
Yb	618 (7300)		385 (16 600)	290 (27 500)
Gd	618 (7200)		388 (16 700)	1290 (26 300)

Table IV. Effect of the Halide Ion on the Absorption Maxima of 1,1'-Trimethylenebis(4-carbomethoxypyridinyl)magnesium Halide (3: MgX_2) Complexes

Halide ion in 3:MgX_2	λ_{max} (ϵ_{max})				
	λ_1	λ_2	λ_3	$\lambda_{4'}$	λ_4
I^-	605 (8900)	380 (16 300)	288 (25 600)	246 (38 800)	
Br^-	597 (8840)	380 (16 700)	288 (26 600)	238 (sh 1200)	215 (24 100)
Cl^-	591 (8800)	380 (16 800)	288 (26 700)	246 (13 000)	

Table V. Solvent Effects on the Absorption Maxima of 1,1'-Trimethylenebis(4-carbomethoxypyridinyl)magnesium Iodide (3:MgI_2)

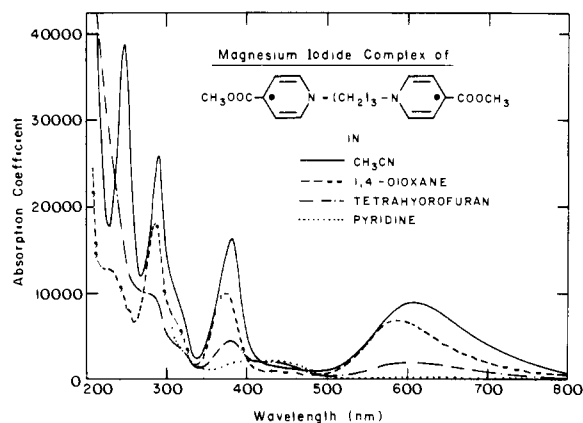| Solvent	λ_{max} (ϵ_{max})				
	λ_1		λ_2	λ_3	$\lambda_{4'}$[a]
CH_3CN	605 (8900)		380 (16 300)	288 (25 600)	246 (38 800)
$CH_3CH_2CH_2CN$	615 (8900)		381 (16 100)	289.5 (25 600)	246 (32 200)
1,4-Dioxane	586 (6860)		372 (9980)	286 (18 100)	
$CH_3OCH_2CH_2OCH_3$	615 (900)	425 (sh 1500)	383 (2800)	288 (sh 6100) 310 (sh 2700)	
THF^b	603 (1900)	425 (sh 2000)	380 (4500)	280 (sh 9900) 310 (sh 4050)	
2-MeTHF^c	595 (6800)		377 (11 000)	287 (18 100) 315 (sh 7000)	
C_5H_5N	617 (210)	430 (2130)	405 (2140)		
$(C_2H_5)_3N$	620 (240)	425 (1850)	400 (1900)		

[a] Due to I^- in CH_3CN. [b] Tetrahydrofuran. [c] 2-Methyltetrahydrofuran.
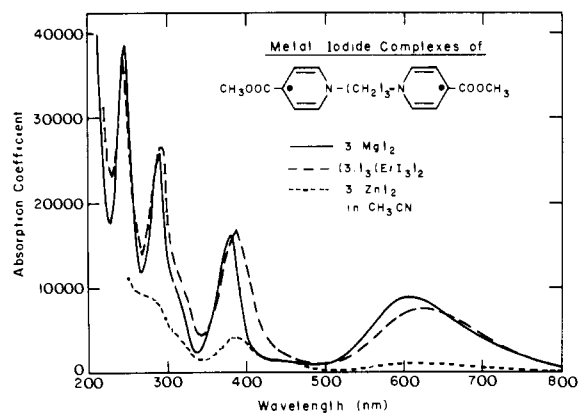
Figure 3. A comparison of the absorption spectra of 1,1'-trimethylenebis(4-carbomethoxypyridinyl) (3:) complexes with various metal halides, MgI_2, ErI_3, and ZnI_2.

Figure 4. A comparison of the absorption spectra obtained for the 1,1'-trimethylenebis(4-carbomethoxypyridinyl)magnesium iodide complex (3:MgI_2) in various solvents: CH_3CN, 1,4-dioxane, tetrahydrofuran, and pyridine.

Although 3:MgI_2 changes absorption intensities strictly in accord with concentration (5×10^{-5} to 1×10^{-3} M), both 4:MgI_2 and 5:MgI_2 increase in intensity with concentration by 25-40%, a behavior similar to that of the corresponding diradicals.[4] Solubility limitations precluded extensive studies on spectra at lower temperature but 3:MgI_2 had spectroscopic maxima in 2-methyltetrahydrofuran glass at 77 K similar to those observed in acetonitrile at 25 °C. The intensity of the visible absorption in butyronitrile (which can be introduced after removal of acetonitrile) increased markedly (45%) on lowering the temperature to −70 °C, whereas the 381-nm absorption band increased only 20%. In contrast, the visible absorption band of 3: shifts from 660 to 740 nm on lowering the temperature to 77 K for an isopentane-3-methylpentane solution.

The 3:MgI_2 solution in acetonitrile is usually stable for at least 48 h at 25 °C. The solvent can be evaporated and the residual solid redissolved in the same solvent without change in the spectroscopic properties. The stability of the solid under these conditions made it possible to effect solvent exchanges, like the exchange for butyronitrile alluded to above. A number of exchanges with solvents ranging in donor ability from 2-methyltetrahydrofuran to pyridine were carried out. Data are

summarized in Table V and illustrated for a few solvents in Figure 4. On replacing either "ether-type" or "amine-type" solvents with acetonitrile, the original spectrum of 3:MgI_2 in CH_3CN was recovered to the extent of 60-90%. Titration with MB^{2+} indicated that no radicals had "disappeared". In general, solvent changes diminish the strength of the visible and other absorption bands, and lead to the appearance of absorption between 400 and 500 nm.

EPR spectra of the complexes reveal a pattern somewhat like that found for the diradicals, e.g., 3:MgI_2 exhibits no detectable EPR spectrum in CH_3CN, 4:MgI_2 shows about 25-30% of the expected spin, and 5:MgI_2 shows about 65% of the expected spin. (5:diradical shows 100% of the spin expected.)[4]

Pyridine solvent increases the spin observed to 20-25% for 3:MgI_2 and 70-75% for 4:MgI_2, with the spectra showing some hyperfine structure superimposed over a broad, featureless band.

Chemical Properties. All of the complexes are susceptible to further reduction by the metal used for the original reaction. 3:MX_2 complexes are reduced slowly (over hours) with the

Table VI. Rate Constants for the Reaction of Halocarbons with the MgI_2 Complex of 1,1'-Trimethylenebis(4-carbomethoxypyridinyl) **3**: MgI_2 at 25 °C in Acetonitrile

Halocarbon	Concn. M	3:MgI₂ concn. M × 10⁴	Rate constant k, $M^{-1} s^{-1}$	No. of runs[a]
CH_3I	0.0034–0.01	0.11–9.4	$2.04 \pm 0.12 \times 10^{-3}$	7
CH_3CH_2I	0.68–1.8	9.1–10.7	$1.23 \pm 0.31 \times 10^{-4}$	3
CH_3CH_2Br	0.73–2.76	10.9–14.2	$1.47 \pm 0.27 \times 10^{-4}$	2
$(CH_3)_2CHI$	0.73–1.29	8.4–14.	$1.24 \pm 0.19 \times 10^{-4}$	3
$(CH_3)_2CHBr$	0.98–1.27	5.8–6.0	$1.20 \pm 0.10 \times 10^{-4}$	2
$(CH_3)_2CHCl$	0.53–1.37	16.–18.	$7.76 \pm 0.92 \times 10^{-5}$	2
CCl_4	0.000 16–0.001	10.6–12.6	0.6 ± 0.2	2
$ClCH_2I$	0.0035	13.	1.16×10^{-2}	1
$(CH_3)_2CHBr^b$	0.067	3.1–3.4	4.5×10^{-5}	2

[a] In most experiments, second-order behavior was observed at least for 40–60% of reaction. A much slower loss of optical absorption characterized the last part of the reaction. [b] In tetrahydrofuran solvent.

Figure 5. A comparison of the absorption spectra of 1,1'-heptamethylenebis(4-carbomethoxypyridinyl)magnesium iodide complex (**7**:MgI₂) and the corresponding radical anion, **7⁻**:MgI₂, in CH₃CN.

formation of shorter wavelength absorbing material unreactive toward the MB²⁺. **4**:MX₂ complexes are more reactive toward magnesium, with the final solutions resembling those from **3**:MgI₂. For n:MgI₂, complexes with $n \geq 5$, further reduction with Mg results in a new long-wavelength absorption band and some additional absorption near 400 nm (Figure 5). Titration with MB²⁺ revealed that three electrons per mole were present in the case of $n = 7$, i.e., that **7⁻**:MgI₂ had been produced.

The glycol ester derivative **11** yields a species with visible absorption (λ_{max} 640 nm (ϵ 150), 680 sh (140)) on reduction with sodium amalgam in acetonitrile, presumably to a diradical (**11**:) (eq 3). Reduction of **11²⁺** with magnesium leads to a

solution with a visible absorption at 580 nm (ϵ 6500) and a near-ultraviolet band at 400 nm (ϵ 12 000), which changes on further reduction to **11⁻**:MgI₂, λ_{max} 680 nm (ϵ 8500) and 400 (12 000).

The n:MgI₂ complexes are very sensitive to oxygen, yielding 1 mol of hydrogen peroxide per mol of n:MgI₂. In fact, as we have mentioned elsewhere,[8] the **3**:MgI₂ complex is a very effective agent for final purification of acetonitrile on a vacuum line, removing the last traces of oxygen and radical-reactive

substances without adding any light-absorbing impurities. Attempts to oxidize the **3**:MgI₂ complex to **3⁺**·MgI₂ complex using silver nitrate or tetraethylammonium tribromide (1 equiv) led immediately to 0.5 equiv of dication, **3²⁺**.

The reactivity of pyridinyl radicals toward halocarbons has been studied intensively[9,10] and it was of interest to examine the behavior of diradical complexes such as **3**:MgI₂. The rate constant for the reaction of **3**:MgI₂ with methyl iodide was about 100 times greater than that for the reaction of the 1-ethyl-4-carbomethoxypyridinyl (**1**). However, only a small range of rate constants was found when a variety of homologous alkyl halides (ethyl iodide and bromide, isopropyl iodide, bromide, and chloride) was reacted with **3**:MgI₂. Considerably higher rate constants were found for the reaction of **3**:MgI₂ with tetrachloromethane and iodochloromethane, but the rate constants are lower than those for the reaction of **1** with the same halocarbons. In most cases. second-order behavior was found only for 40–60% of the reaction, the reaction rate decreasing very much after that. The rate constants are summarized in Table VI. Some attempts to study reaction rates in other solvents were also made. The rate constant for the reaction of **3**:MgI₂ with isopropyl bromide in tetrahydrofuran was about 0.4 of that found in acetonitrile, with the possible appearance of the less reactive diradical toward the end of the reaction.

The complex of **3**: with MgI₂ disappears in the presence of primary, secondary, or tertiary alcohols. The rate constant for the disappearance in the presence of ethanol is 30 times greater than that in the presence of isopropyl alcohol, but appears to be first order in **3**:MgI₂ and in either alcohol. In the presence of added *tert*-butyl alcohol, the reaction is more sensitive to the concentration of the alcohol than in the other cases, and fits third-order behavior, second order in the *tert*-butyl alcohol. Rate data are summarized in Table VII. Replacement of ethanol by ethanol-d leads to a lower bimolecular rate constant, corresponding to an isotope effect, k_H/k_D, of 1.52. The diradical **3**: is unreactive toward alcohols.

The final spectrum of the solutions after **3**:MgI₂ had disappeared in the presence of alcohol suggests that only one pyridinium ion was formed for each complex. (Spectroscopic changes during a typical reaction in the presence of ethanol are shown in Figure 6.) After an approximate correction at 273 nm for the strong absorption of iodide ion in acetonitrile (2I⁻), λ_{max} 246.1 nm (ϵ_{max} 12 500) (ϵ_{21}– 25 000).[11] the ϵ at 273 nm is 6900. The 1-ethyl-4-carbomethoxypyridinium ion has ϵ_{273} of 4600, and the presence of maxima at 308 nm (ϵ 1200) and 378 (800) favor the view that another absorbing material is present with a maximum in the region of 273 nm with ϵ of 2300. A compound (or compounds) in which a trimethylene group links a 1,4-dihydropyridine (or a 1,2-dihydropyridine) to a pyridinium ion could give rise to an absorption spectrum of the type shown, since 1,4,4-trimethyl-1,4-dihydropyridine

Figure 6. Absorption spectra of a solution of 1,1'-trimethylenebis(4-carbomethoxypyridinyl) (**3**:MgI$_2$) in acetonitrile containing 0.03 M ethanol at 25 °C as a function of time.

Table VII. Rate Constants for the Disappearance of 1,1'-Trimethylenebis(4-carbomethoxypyridinyl)magnesium Iodide Complex (**3**:MgI$_2$) in Acetonitrile at 25 °C in the Presence of Alcohols

Concn of 3:MgI$_2$, $\times 10^4$ M	Alcohol	Concn, M	Rate constants[a] k_2, M^{-1} s^{-1} $\times 10^4$	k_3, M^{-2} s^{-1} $\times 10^5$
3.5	C$_2$H$_5$OH	0.03	13.	
2.7		0.045	13.8	
4.5	(CH$_3$)$_2$CHOH	0.173	0.48	
4.5		0.68	0.40	
4.5		1.17	0.40	
4.5	(CH$_3$)$_3$COH	1.28	0.7	5.4
1.4		0.7	0.41	5.8
9.0		0.32	0.15	4.7
2.5	CH$_3$CH$_2$OD	0.069	8.3[b]	
		0.030	9.2[b]	

[a] The diradical 1,1'-trimethylenebis(4-carbomethoxypyridinyl) (**3**:) was unreactive toward alcohol solutions similar to those used to follow the disappearance of **3**:MgI$_2$. For example, the absorption spectrum of **3**: in ethanol-acetonitrile remained unchanged for 10 days. [b] $k_H/k_D = 1.52$.

has an absorption at 273.2 nm (ϵ 3200) in acetonitrile[12] and intramolecular complex formation is known for pyridinium ion derivatives. No acetaldehyde was detected in the final solution.

An experiment designed to reveal how difficult it was to remove the magnesium halide from the complex, with the formation of the diradical, was carried out. To avoid the introduction of proton donors, in view of the disappearance of **3**:MgI$_2$ in the presence of alcohols, the tetraethylammonium salt of EDTA (ethylenediaminetetraacetic acid) was prepared and reacted with **3**:MgI$_2$ in acetonitrile. The original spectrum rapidly changed into one which resembled that of **3**:MgI$_2$ in pyridine. Only heating the reaction solution to 58 °C (see Experimental Section) caused the spectrum to change into that of the diradical **3**: with an estimated diradical yield near 80%.

Discussion

Our work has demonstrated that pyridinyl radicals form complexes with divalent and trivalent metal ions associated with halides. Ikegami and co-workers[13] have noted the formation of a crystalline blue sodium iodide complex with 1-methyl-4-carbomethoxypyridinyl radicals at −76 °C from MTHF, having the composition (py·)$_2$NaI.

Pyridinyl diradicals give rise to complexes with metal halides which are obviously different from either the monoradicals or the diradicals. The most spectacular change is in the visible and ultraviolet spectrum, but the chemical properties are also altered by complexation. In some cases, it is rather difficult to remove the metal ion from the complex, a fact which should suggest caution in the use of metals or metal ions as reductants for pyridinium ions bearing ligand groups.

The visible absorption of the diradicals is a charge-transfer band.[3] Complexation with metals must increase the degree of overlap between the rings, thus causing a considerable rise in intensity. Magnesium ion leads to a particularly favorable arrangement for the trimethylene complex, **3**:MgX$_2$. As n increases, intensity decreases and the absorption maximum moves to longer wavelengths. Complexes of two or more π systems (π complexes) are conveniently referred to as π-mers. Polymethylene bis(4-carbomethoxypyridinyl) diradicals exhibit intramolecular π-merization for $n = 3$ and 4, i.e., trimethylene and tetramethylene bridges. The magnesium iodide complexes show intramolecular π-merization, as judged by the intensity of the visible absorption band, for $n = 3–6$. The shift in the maximum for the **3**:diradical to shorter wavelengths in the **3**:MgX$_2$ complexes by 6.6 kcal (from 703 nm to 605 nm in CH$_3$CN) is explicable in terms of a lowering of the ground state through complexation. The orbital carrying the unpaired

electron has on density on the carbonyl of the ester and metal ions should lower the energy of the orbital.

The ultraviolet bands appear to be complex with evidence that both the 390- and 305-nm bands of the monoradical are doubled, both in the diradicals and the diradical metal complexes. The situation must thus be more complex than indicated by Itoh,[15,16] who suggested that only the 390-nm band would be split. The shortest wavelength band of the diradical is shifted to shorter wavelengths in the magnesium complexes. The 246-nm band is mainly due to a charge transfer to solvent absorption of I$^-$ in acetonitrile[11] but also contains a contribution from diradical complex absorption (see Table IV).
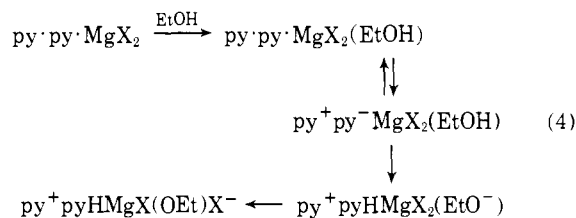
Except for the charge-transfer bands, the absorptions are probably due to transitions localized mainly on one ring, an idea supported by the fact that the EPR properties of the magnesium complexes are not very different from those of the corresponding diradicals. It is, however, likely that more than one type of complex is present. (1) EDTA changes the spectrum without releasing diradical before heating. (2) Magnesium halides do not react with diradical **3** or with monoradical[17a] to produce complexes and equilibrium between various complexes may not be fast. Thus, further work involving somewhat more stable metal ion complexes would be desirable before definite spectroscopic assignments can be made.

A tentative formulation of the structure of **3**:MgI$_2$ is given in Figure 7. The halide ion effect on the visible absorption band requires that at least one halide be bound to the metal ion. The fact that there are several kinds of solvated complexes[17b] could mean several solvent molecules coordinated with the metal ion, assuming that there are not structural rearrangements. With a minimum of two ligand sites being occupied by diradical oxygen atoms, the sixth site is shown as occupied by an iodide ligand.

We have discovered in related work[18,19] that pyridinyl radicals react with themselves by electron transfer according to the following scheme (cf. also parallel results by Neta and Paterson[20]).

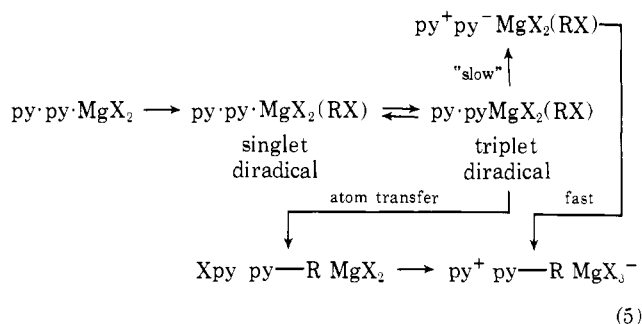(1) py· + H$^+$ $\rightleftharpoons$ pyH$^+$·   (2) py· + pyH$^+$· $\rightarrow$ py$^+$ + pyH
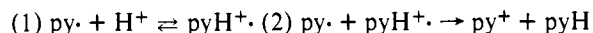
The magnesium ion in the diradical complex could replace the proton and a coordinated alcohol molecule could supply the proton for completing the oxidation–reduction. The lower acidity of *tert*-butyl alcohol apparently requires that two *tert*-butyl alcohol molecules participate in the proton-transfer step. The proposed mechanism is illustrated in eq 4. Reversible

$$py \cdot py \cdot MgX_2 \xrightarrow{EtOH} py \cdot py \cdot MgX_2(EtOH)$$

$$\updownarrow$$

$$py^+py^- MgX_2(EtOH) \quad (4)$$

$$\downarrow$$

$$py^+pyHMgX(OEt)X^- \longleftarrow py^+pyHMgX_2(EtO^-)$$

formation of the reactive intermediate is suggested by the isotope effect on the reaction in the presence of ethanol-*d* with $k_H/k_D = 1.52$.

In spite of the considerable effort devoted to the kinetics of reaction of alkyl halides with 3:MgI₂, the details of the mechanism remain obscure. Highly reactive halides (iodochloromethane and tetrachloromethane) have the same relative reactivity toward 3:MgI₂ as found in the reaction with the pyridinyl monoradical. Less reactive halides differ rather little in reactivity, and the rate of reaction of 3:MgI₂ with these halocarbons in acetonitrile is independent of the concentration of the halocarbon. (The concentration of the halocarbon is, however, much greater than that of 3:MgI₂.) Thus, it appears as if some active species is formed and this species reacts rapidly with halocarbon complexed to the magnesium. The rates of reaction of 3:MgI₂ with the "unreactive" halides are considerably greater than might have been expected for a reaction with pyridinyl monoradical. A scheme which incorporates these possibilities in a mechanistic form is given in eq 5.

$$py^+py^- MgX_2(RX) \longrightarrow$$

$$\text{"slow"} \uparrow$$

$$py \cdot py \cdot MgX_2 \longrightarrow py \cdot py \cdot MgX_2(RX) \rightleftarrows py \cdot pyMgX_2(RX)$$

singlet diradical triplet diradical

atom transfer fast

$$Xpy \; py{-}R \; MgX_2 \longrightarrow py^+ \; py{-}R \; MgX_3^-$$

$$(5)$$

Conclusions

1. Metal ion halides (M⁺, M²⁺, M³⁺) form complexes with 1-alkyl-4-carbomethoxypyridinyl radicals and 1,1′-polymethylenebis(4-carbomethoxypyridinyl) diradicals.

2. In acetonitrile, striking differences between the absorption spectra of the complexes and the corresponding diradicals exist, with complexes like 3:MgI₂ possessing well-defined and intense visible and ultraviolet absorption bands.

3. It is relatively difficult to remove the metal ion from complexes like 3:MgI₂. No metal halide (MgX₂, ZnI₂, NaI) has been reinserted into a bispyridinyl diradical complex but it is worth noting that magnesium reduction of 3:ZnI₂ does lead to a solution which contains 3:MgI₂ (ca. 70% from absorption coefficients).

4. The chemical reactivity of the complexes is different from that of the pyridinyl monoradical.

5. Metal reduction of pyridinium ions and, by extension, other heterocyclic quaternary ions, may lead to radical metal ion complexes with properties different from those of the radicals themselves.

Experimental Section

Ultraviolet and visible absorption spectra were measured with a Cary Model 14 spectrophotometer, and EPR spectra with a Varian 4502 spectrometer. Small quantities were weighed with a Cahn electrobalance, Model G2.

Solvents. Acetonitrile (Matheson Coleman and Bell "Spectroquality") was degassed and distilled onto previously dried and degassed Linde molecular sieve 4A (400–450 °C at 10^{-6} mmHg until pressure
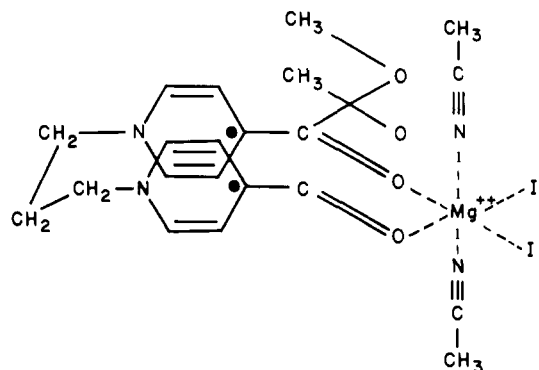

Figure 7. Proposed formulation for the 1,1′-trimethylenebis(4-carbomethoxypyridinyl)magnesium iodide complex (3:MgI₂) in acetonitrile. Magnesium ion is bonded to the carbonyl oxygens on the basis of its considerable effect upon the absorption of spectrum of the diradical. Halide ion effects (see Table IV) indicate that at least one halide ion is present in the magnesium iodide coordination shell. Solvent effects show that at least one solvent molecule is also present.

is constant—ca. 24 h). The solvent was distilled onto a mixture of 1,1′-trimethylenebis(4-carbomethoxypyridinium) diiodide and magnesium turnings, generating the complex 3:MgI₂, and from this solution the solvent was distilled into the desired reaction vessel. **Butyronitrile** (Aldrich, bp 115–117 °C) was washed with hydrochloric acid, H₂O, NaHCO₃ solution, and H₂O and stored over CaCl₂ for 10–16 h, then purified as for CH₃CN. **Isopentane** (2-methylbutane, Matheson Coleman and Bell "Spectroquality") was degassed and dried on molecular sieves 4A (see above), then distilled and stored over potassium mirror. **Benzene** (Fisher, thiophene-free) was purified in the same way and stored over sodium mirror. **Tetrahydrofuran** (Baker, "Anal") was purified in the same way but stored in the presence of sodium anthracenide. It was distilled onto dry 3:MgI₂ before being distilled into a reaction vessel. **2-Methyltetrahydrofuran** (Eastman), **1,4-dioxane** (Fisher), and **1,2-dimethoxyethane** (Eastman) were purified in the same way. **Pyridine** (Baker, "Anal") and triethylamine (Eastman) were degassed, dried on Linde molecular sieves 4A (see above), distilled onto diradical 3:, and stored for at least 10 h before use.

Metals and Other Reagents. Halocarbons were dried over P₂O₅, distilled, and degassed before use. Alcohols (ethanol, ethanol-*d*, isopropyl alcohol, and *tert*-butyl alcohol) were degassed and distilled onto diradical 3: and then into a reaction vessel. **Magnesium** (Fisher turnings "for Grignard") used without further treatment after experiment had shown no difference between metal washed with solvent before use and untreated metal. **Calcium** (6 mesh, >99%), **erbium** (chips, 99%), **ytterbium** (chips, 99.9%), **gadolinium** (chips, 99.7%), **vanadium** (random pieces, 99.7%), and **titanium**, (sponge crystal, 99.7%) (Research Organic and Inorganic Corp., Sun Valley, Calif.) were used without further treatment except to remove adhering oil with hexane when necessary. **Strontium** (rods, >99%) and **barium** (pieces, >99%) (Research Organic and Inorganic Corp.) were cut up under oil, washed well with hexane, and sealed into the reaction flask under (frozen) hexane and argon, followed by degassing. **Manganese** (Baker >99%, electrolytic chips) was broken up into small pieces (6 mesh). **Zinc** (Fisher, granular 20 mesh), **chromium** (Baker, "Anal" powder), and iron (Baker, "Anal" powder) were used as such. **Aluminum amalgam** was prepared using 5% aqueous HgCl₂ and granular aluminum. **Beryllium** (turnings, 99%, Research Organic and Inorganic, Corp.) was broken into pieces with a hammer, care being taken to ensure that no fragments escaped from the cloth in which the metal was enclosed, because of possible dangers from beryllium.

Pyridinium Halides. Methyl isonicotinate (redistilled) and a polymethylene diiodide, I(CH₂)ₙI (*n* = 3 or more), were dissolved together in acetone and the solution was allowed to stand in the dark. The crystals which separated were recrystallized from boiling methanol using charcoal. For the diiodide with *n* = 1, diiodomethane and methyl isonicotinate were allowed to stand in the dark for 60 days. A dark black solid was filtered off and washed with acetone, then ether. Recrystallization of 2.4 g of crude red salt from hot CH₃OH–H₂O (4:1) yielded 0.58 g of pure diiodide as small, red, shimmery plates. For the diiodide with *n* = 2, the corresponding dibromide was prepared from 1,2-dibromoethane and methyl isonicotinate in refluxing methanol

APPARATUS FOR PREPARATION AND ISOLATION
OF DIRADICAL·METAL HALIDE COMPLEXES
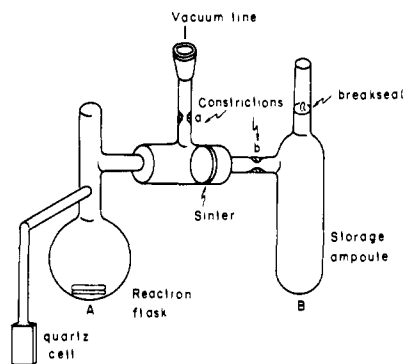
Figure 8. Typical apparatus for reaction of metals with pyridinium halides. Metals (including sodium amalgam), a glass-coated stirrer, and the pyridinium halide are added to the reaction flask (A) through a long funnel and the opening is sealed. After degassing, acetonitrile is distilled into the reaction flask from the line. After sealing off at a, the reaction mixture is usually stirred at 0 °C, and the course of the reaction followed by measurement of the absorption spectrum. After the reaction has progressed to the desired point, the solution is filtered through the sinter into ampule B and the ampule sealed off at b.

Table VIII. Properties of Polymethylenebis(4-carbomethoxypyridinium) Diiodides. $py^+(CH_2)_npy^+\cdot2I^{-a}$

$py^+(CH_2)_npy^+\cdot2I^-$				Anal.[c]		
n	Color	Mp, °C	Equiv wt[b]	C	H	N
1[d]	Red	169–170	271.2[g]	33.34	3.02	5.16
			271.1[h]	33.23	2.98	5.17
2[e]	Yellow	208.5–209	277.8	34.62	3.24	5.01
			278.1	34.55	3.26	5.04
3[f]	Orange	177–178	285.5	35.76	3.58	4.97
			285.1	35.81	3.54	4.91
4[f]	Red-orange	200–202	292.8	37.13	3.89	4.74
			292.1	37.00	3.80	4.79
5[f]	Orange	161–162	299.2	38.10	4.04	4.60
			299.1	38.14	4.04	4.68
6	Yellow	160–162	306.7	39.01	4.39	4.52
			306.1	39.03	4.28	4.58
7	Red-orange	152–155	313.8	40.28	4.40	4.55
			313.2	40.27	4.51	4.47
8	Yellow-orange	187–188	320.1	41.45	4.87	4.49
			320.2	41.26	4.72	4.38
9	Orange	179–180	328.8	42.21	4.83	4.21
			327.2	42.22	4.93	4.28
10	Orange	190–191	335.1	43.13	5.15	4.32
			334.2	43.13	5.13	4.19

[a] All compounds were prepared by Dr. P-k. C. Huang. In some cases, additional material was synthesized by the same method. [b] By Volhard titration (AgNO₃, KSCN). [c] Spang Laboratories, Ann Arbor, Mich. [d] Preliminary attempts to generate diradical or diradical complex were unsuccessful. [e] Diradical described by E. M. Kosower and Y. Ikegami, *J. Am. Chem. Soc.*, **89**, 461 (1967). Preliminary attempts to produce a magnesium complex were unsuccessful. [f] Utilized by M. Itoh and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 1843 (1968). [g] Found. [h] Calculated.

and converted to the diiodide in water by the addition of a concentrated aqueous solution of sodium iodide. The crude precipitate of salt was washed with water and acetone, then recrystallized from water. The properties of the bispyridinium diiodides are summarized in Table VIII. The structures were also confirmed by NMR spectra. The bisisonicotinate ester of 1,2-ethanediol, mp 173–175 °C, was prepared from the diol and isonicotinic acid chloride hydrochloride in pyridine. The bismethyl quaternary salt was prepared by refluxing with methyl iodide in acetone, equiv wt found 278.3 (calcd 278.1). When needed, dibromides were prepared from the polymethylene dibromide. Dichlorides were prepared by exchange of chloride for iodide from the diiodides with anion exchange resin (Dowex 1-X8) in the chloride form in dry CH_3OH.

Diradicals. 1,1'-Trimethylenebis(4-carbomethoxypyridinyl) (**3:**) and 1,1'-tetramethylenebis(4-carbomethoxypyridinyl) (**4:**) were prepared according to Itoh and Kosower[4] except that the acetonitrile of the original reaction mixture was replaced by benzene before filtration of the reaction mixture, thus increasing the diradical yield by a factor of 10 over that obtained previously.

Diradical Metal Halide Complexes. Metal (normally in excess), pyridinium salt (0.01–0.03 mmol), and a glass-coated stirring bar were sealed into a round-bottom flask (A, in Figure 8) and the apparatus was maintained under high vacuum for at least 3 h. (Heating most of the apparatus with a flame aided the degassing.) Acetonitrile (ca. 15–25 mL) was distilled in from the reservoir on the line. After thawing to check the approximate volume of solvent, the apparatus was sealed off (at a) from the line after refreezing the CH_3CN. After thawing, the mixture was stirred at 0 °C until visible absorption had reached a limit. For reasonably stable complexes, the solution was filtered through the sinter and the ampule B containing a solution of the product frozen and sealed off (at b). For analysis and further spectroscopic work, the storage tube was connected to a suitable apparatus. For barium and strontium, the metals were introduced as described under materials, and the pyridinium salt was introduced through a break-seal, using CH_3CN to wash in the salt. For beryllium, the activation procedure required that the pyridinium salt be introduced after the metal through a break-seal. Activation of beryllium was attempted by (a) amalgamation with $HgCl_2$ in dry C_2H_5OH, (b) forming a potassium mirror on the Be surface and removing volatile metal by subsequent heating under vacuum, (c) ultrasonic irradiation during reaction with the pyridinium diiodide, and (d) using **3:**ZnI_2 in place of $3^{2+}2I^-$. In no case was any reaction observed. Reaction was noted for magnesium, calcium, strontium, barium, zinc, manganese, erbium, gadolinium, and ytterbium. Aluminum amalgam produced a green solution, λ_{max} 620 nm (ϵ 1500), and a dark green precipitate. Vanadium, titanium, chromium, and iron did not react.

Analysis. A. Radical Content. As an example, **3:**MgI_2 in CH_3CN was introduced into an apparatus with an optical cell and its spectrum determined. 1,1'-Dimethyl-4,4'-bipyridylium (MB^{2+}) dichloride (BDH recrystallized, 2 mg, excess) was introduced through a break-seal. The solution rapidly deepened a bit in color. When reaction was complete, as judged by constancy of absorption at 605 nm (ϵ_{605} 10 600 for $MB^+\cdot$)[7] and shape of the absorption curve (different from that of the initial complex), the radical concentration was calculated. The stoichiometry is shown in eq 2 with $2MB^+\cdot$ forming for each **3:**MgI_2, the concentration of which was known from the amount of pyridinium salt originally introduced into the reaction flask. In the case cited above, the bispyridinium salt reacted with magnesium corresponded to 6.81×10^{-4} M, which should yield 1.36×10^{-3} M $MB^+\cdot$ with optical density 1.45 (0.1-cm cell). The optical density found was 1.43. Radical contents were measured for many of the complex solutions in the same way, including the complex solutions generated from calcium, strontium, barium, zinc, manganese, erbium, ytterbium, and gadolinium.

B. Metal Content. A sample of complex solution with known pyridinium and radical content was exposed to air and diluted fourfold with water. Ammonia–ammonium chloride buffer (pH 10) and solid Eriochrome Black T in NaCl were added and the solution was titrated with 0.01 M EDTA (ethylenediaminetetraacetic acid sodium salt).[21a] Additional pyridinium halide did not change the end point which corresponded to one metal ion for each bispyridinyl, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, and Zn^{2+}, except in the cases of erbium, gadolinium, and ytterbium, for which there were 2 g-atoms of metal ion per 3 mol of bispyridinyl. The titrations of rare earth ion content were carried out with excess EDTA and back-titration with magnesium sulfate solution.

C. Oxidation. Exposure of a **3:**MgI_2/CH_3CN solution to air, followed by addition of 2 drops of water, led to a spectrum with pyridinium ion absorption (λ_{max} 273.5 nm (ϵ_{max} 4550)[9]). A spot test for H_2O_2 using 0.4% $FeCl_3$ and 0.8% $K_3Fe(CN)_6$ (which produces Prussian blue in the presence of hydrogen peroxide[21b]) in comparison with H_2O_2 solutions of known concentration indicated that between 0.87 and 1.04 mol of H_2O_2 formed for each bispyridinyl.

D. Spin Concentration. Quartz sample tubes were loaded with n:MI_2 solutions of known concentration (determined by absorption spec-

trum) and the EPR spectrum was determined at high modulation. Similar curves were obtained for dilute solutions of 1-ethyl-4-carbomethoxypyridinyl (1) and the spin concentrations determined by comparing the weights of the area under the curves, assuming that the monopyridinyl radical had 100% of the spin expected for its concentration.

Solvent Transfers. An apparatus carrying at least two break-seals was used. In many cases, the acetonitrile was removed from $3:MgI_2$ and, after 20–40 min pumping, another solvent (e.g., tetrahydrofuran) distilled in from the line. The apparatus was sealed off, the spectrum of the solution determined under a variety of conditions (concentration, temperature), the apparatus reconnected to the line through the first break-seal, and the solvent removed and replaced with acetonitrile. The apparatus was again sealed off, the spectrum redetermined (usually a substantial recovery of the original $3:MgI_2/CH_3CN$ spectrum was observed) and, in some cases, a titration with MB^{2+} carried out through the second break-seal. In the case of a transfer from acetonitrile to dioxane and back to acetonitrile, a 97% recovery of the original diradical was ascertained through titration.

Kinetic Studies. A reactant (halocarbon, halocarbon in acetonitrile, alcohol in acetonitrile) was distilled into a calibrated pipet after degassing elsewhere on the line. The apparatus was sealed off from the line, and the reagent introduced through a break-seal into a solution of known concentration of 1,1′-trimethylenebis(4-carbomethoxypyridinyl)magnesium iodide complex ($3:MgI_2$) in acetonitrile. After mixing, the reaction solution was transferred to an optical cell and the spectrum of the solution followed as a function of time. The temperature of the spectrophotometer compartment was controlled at 25 °C. The concentration of the second reactant (i.e., halocarbon or alcohol) was usually checked by gas chromatography after the completion of the reaction. Chromatography on a 20% di-*n*-butyl phthalate/Chromosorb column at 50 °C revealed no acetaldehyde in reactions carried out with ethanol, although control samples containing 10^{-4} M CH_3CHO were analyzed without difficulty.

Tetraethylammonium Ethylenediaminetetraacetate (TEA₄EDTA). Aqueous tetraethylammonium hydroxide (K & K Laboratories) was diluted to 0.1 M and an equivalent amount of ethylenediaminetetraacetic acid (B & A Allied Chemicals) added, yielding a solution of pH 10.5. The solution was diluted with ethanol to yield a 5×10^{-3} M $(TEA^+)_4EDTA^{4-}$ stock solution, always freshly prepared for each experiment. A sample of this solution (1.5 mL, 7.5 μmol) was placed in a tube carrying a break-seal and attached to the vacuum line. Solvent was removed and degassed benzene distilled in yielding a solution. Benzene was removed and the sequence repeated twice more with fresh benzene. The anhydrous salt was dissolved in acetonitrile from the line, the tube sealed off after freezing, and the solution introduced

through the break-seal into a solution of $3:MgI_2$ (8.2 mL, 3.6×10^{-4} M, 2.95 μmol) in acetonitrile. The visible absorption of the complex decreased by 90% immediately. The solution was warmed at 58 °C until absorption appearing at 703 nm had reached a limit. The spectrum of the solution was like that of the diradical **3:**, and the yield 78% using λ_{max} 703 nm (ϵ 3800). Titration with MB^{2+} indicated 85% diradical yield from the original $3:MgI_2$. The product diradical was soluble in benzene, as is authentic diradical **3:** (see synthesis).

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AlCl₃ σ Complexes of Cyclobutadienes[1]

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Contribution from the Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands. Received May 23, 1977

Abstract: The permethyl substituted AlCl₃ σ complex of cyclobutadiene **1** (a cyclobutenyl cation) is involved in a dynamic process, which has been investigated by NMR spectroscopic techniques and found to consist predominantly, if not exclusively, of consecutive 1–2 shifts of the AlCl₃ group. The extension of complex **1** to those provided with one or two oligomethylene chains (**2–6**) is described; attention is paid to the different effect of a tetra- and a pentamethylene chain (**2** and **3**) on the rate of migration of the AlCl₃ group between the possible sites of the cyclobutenyl ring. Finally the chemical properties of the cyclobutadienes, generated from the complexes **2** and **3**, are described.

The interest in AlCl₃ σ complexes of cyclobutadienes can be viewed as resulting from two successful synthetic procedures, both employing 2-butyne and AlCl₃. A first procedure, developed by Schäfer, involved trimerization of 2-butyne, yielding hexamethyl(Dewar benzene), by catalytic action of AlCl₃ (5% by weight) for about 6 h at 35 °C.[2] In a second

procedure, reported by Rosenberg and Eimutis, 2 equiv of 2-butyne and 1 equiv of AlCl₃ were used; after 18 h at room temperature a tetramerization product of 2-butyne, octamethyl-*syn*-tricyclo[4.2.0.0²,⁵]octa-3,7-diene, was obtained.[3] In both cases an AlCl₃-bonded cyclobutadiene complex seemed to be the key intermediate. Later it was found by van Bekkum[4]