more tedious than the first, gives the following result, to fourth order, for $T_{2,\mathrm{obsd}}^{-1} = (\sqrt{3}/2) \times$ derivative width

$$T_2^{-1} = T_{2,0}^{-1} + \tau^{-1}p_Ap_B[(\Delta^2 - \delta^2) + (p_A - p_B) \times \delta(3\Delta^2 - \delta^2) + (5p_Ap_B - 1)(\Delta^4 - 6\delta^2\Delta^2 + \delta^4)] \quad \text{(A5)}$$

Each of the terms within the brackets of (A5) multiplies a power series in τ; however, in the second- and third-order terms, the lowest power (other than zero) of τ occurring with a nonzero coefficient is fourth order, and in the fourth order term, the lowest nonzero term in τ is third order.

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Cuprous Complex of Methyldiazene

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The reaction of methyldiazene with aqueous cuprous chloride yields an air-sensitive, moderately stable, diamagnetic, red-brown solid with the formula $(CH_3N{=}NH)CuCl$ (I). The electronic spectrum shows transitions at 360 and 470 nm. Solubility characteristics suggest a polymeric structure, and two possibilities are discussed. The integrity of the nitrogen–nitrogen bond in the diazene is maintained both in the reaction of the compound with oxygen and in the thermal decomposition at 70–72°. Methyldiazene can be recovered from the compound by dissolving it in a medium which coordinates cuprous ion. The reaction of methyldiazene with cupric ion is examined in relationship to the failure of an alternate synthetic route to I.

Introduction

A number of monosubstituted diazenes (RN=NH), including alkyl-,[1] aryl-,[2] and alkenyldiazenes,[3] are now known. These molecules are highly reactive and inherently unstable, reacting with themselves *via* a bimolecular mechanism.[1–3] Stabilization of several monosubstituted aryldiazenes in complexes with platinum is possible.[4,5] An even greater variety of complexes of deprotonated monosubstituted aryldiazenes with platinum,[4,5] molybdenum,[5–8] and tungsten[7–9] have been prepared. One report of a platinum complex of deprotonated diazene itself has appeared,[10] as has one report of molybdenum and tungsten complexes of a deprotonated monosubstituted alkyldiazene.[11]

Most recently Balch, *et al.*, synthesized a cuprous chloride complex of phenyldiazene, $(C_6H_5N{=}NH)Cu_4Cl_4$, from the reaction of phenylhydrazine with aqueous cupric chloride.[12] This reaction parallels the established synthesis of the azomethane–cuprous chloride complex $(CH_3N{=}NCH_3)Cu_2Cl_2$.[13] They did not obtain a methyldiazene complex when methylhydrazine was substituted for phenylhydrazine. This paper is a report of the successful synthesis of a methyldiazene–cuprous chloride complex through the direct reaction of methyldiazene with aqueous cuprous chloride. This is the first synthesis of a monosubstituted alkyldiazene complex.

Experimental Section

Preparation of Compounds.—Hydroxylamine-*O*-sulfonic acid was prepared as described by Smith[14] and analyzed to be 98+% pure by iodometry.

N-Methylhydroxylamine was obtained as the oxalate salt by hydrogenation of nitromethane on 5% palladium on barium sulfate catalyst (Matheson Coleman and Bell) at atmospheric pressure.[15] Data for $(CH_3NH_2OH)_2C_2O_4$ follow: mp 158–160° (uncor), lit.[15] mp 158°; neutralization equivalent: calcd, 92.1; found, 93.3.

Cuprous chloride was prepared by the literature method.[16]

trans-**Methyldiazene**.—This substance was obtained from the reaction of hydroxylamine-*O*-sulfonic acid with *N*-methylhydroxylamine in aqueous sodium hydroxide.[1a] In a typical synthesis 0.37 g (3.3 mmol) of hydroxylamine-*O*-sulfonic acid and a magnetic stirring bar were placed in a flask on a vacuum line. This flask was connected to a side-arm flask *via* a standard taper arrangement. Into the side-arm flask was placed 40 ml of 1 *M* sodium hydroxide solution containing 0.51 g (5.5 mmol of *N*-methylhydroxylamine) of *N*-methylhydroxylammonium oxalate. After pumping for several minutes to remove air from the two flasks, the side-arm flask was rotated to add the sodium hydroxide solution to the solid hydroxylamine-*O*-sulfonic acid which dissolved within a few seconds after stirring commenced. Over

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[1] (a) M. N. Ackermann, J. L. Ellenson, and D. H. Robison, *J. Amer. Chem. Soc.*, **90**, 7173 (1968); (b) P.-k. C. Huang and E. M. Kosower, *ibid.*, **89**, 3911 (1967); (c) T. Tsuji and E. M. Kosower, *ibid.*, **92**, 1429 (1970).

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[14] P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, *J. Amer. Chem. Soc.*, **86**, 1139 (1964).

[15] E. Schmidt, A. Ascherl, and L. Mayer, *Ber.*, **58**, 2430 (1925).

[16] R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 1 (1946).

a period of 5 min the methyldiazene being generated was collected in a U tube at −196° with the aid of a Toepler pump. The condensed material included some water as well as the yellow methyldiazene. Finally, the U tube was warmed quickly with a beaker of room-temperature water, and the vaporized methyldiazene was collected in a 50-ml round-bottom flask at −196°. Little water is transferred in this final step. Methyldiazene may be stored at −196° for several hours without appreciable decomposition.

Methyldiazene-*N*-d_1 was prepared in an analogous manner using a sodium deuterioxide solution prepared by adding sodium to deuterium oxide (Diaprep, Inc., 99.8%).

Cuprous Chloride–Methyldiazene Complex.—This compound was prepared by the direct reaction of these two substances. In a nitrogen atmosphere 0.20 g (2.0 mmol) of cuprous chloride was dissolved in 7 ml of a 2 *M* potassium chloride solution buffered by addition of 2 drops of 2 *M* hydrochloric acid and 2 drops of a saturated sodium acetate solution. Nitrogen was admitted to a flask of methyldiazene at −196°, and the stopper was removed. Ten milliliters of 2 *M* potassium chloride was poured into the flask, and the flask was warmed by swirling it in a beaker of room-temperature water. When the methyldiazene had all dissolved and the ice had melted, the cuprous chloride solution was added to the pale yellow methyldiazene solution. A red-brown precipitate formed immediately. After transfer to a nitrogen atmosphere in a drybag the frothy mixture was filtered on a sintered-glass funnel and washed several times with small amounts of water. The moist red-brown solid (0.284 g) was stored in a stoppered flask under nitrogen.

In an alternate synthetic procedure the cuprous chloride solution was added directly to the frozen methyldiazene. A red-brown precipitate formed immediately. The mixture was warmed to room temperature, and the solid was isolated as described above.

The cuprous chloride–methyldiazene-*N*-d_1 complex was obtained using methyldiazene-*N*-d_1 and deuterium oxide for the preparation of solutions and for washing the filtered product.

Cuprous Chloride–Azomethane Complex.—$(CH_3N{=}NCH_3)$-Cu_2Cl_2 was prepared from 1,2-dimethylhydrazine and cupric chloride as described by Diels and Koll.[13]

All other chemicals were obtained commercially and used without further purification.

Removal of Water from the Cuprous Chloride–Methyldiazene Complex.—The freshly prepared, moist complex (0.284 g) was placed in a flask on a vacuum line. The flask was maintained at room temperature with a water bath. Water was removed from the complex by repeatedly allowing the vapors in the flask containing the complex to expand into an evacuated volume. At no time, however, was the complex exposed directly to the vacuum pump. The gases in the expansion volume were monitored for evidence of loss of methyldiazene from the complex by condensing them at −196° periodically and noting any residual pressure with a manometer. The expansion cycle was halted when the residual pressure remained zero for ~5 min after the last cycle; yield, 0.163 g of dry red-brown solid. No paramagnetism was detectable in an electron spin resonance spectrum recorded with a Varian E 3 esr spectrometer. Reflectance spectra obtained with a Beckman DK-2 in the visible spectral range showed broad peaks centered at 360 and 470 nm.

Thermal Decomposition of the Cuprous Chloride–Methyldiazene Complex.—The dry complex (0.163 g) was heated gradually in a vacuum line and the pressure change was noted as a function of temperature. At ~50° the pressure began to increase slowly as the solid evolved gas. The pressure rose abruptly at about 70° while the red-brown solid frothed vigorously and turned dark brown. About 80% of the total gas evolution occurred at 70–72°. Heating to 100° produced no additional changes. After cooling, the amount of gas evolved was measured (1.72 mmol) and analyzed by gas chromatography and infrared spectrometry. The brownish solid residue (0.122 g) dissolved readily in aqueous ammonia with some bubble formation. After lengthy aeration of this solution, during which the color changed from pale yellow to deep blue, the solution was analyzed spectrophotometrically for copper (1.20 mmol) as the ammine complex[17] and potentiometrically for chloride (1.19 mmol) by titration with silver nitrate solution.[18]

Decomposition of the Cuprous Chloride–Methyldiazene Complex with Acetonitrile.—Freshly distilled acetonitrile (8 ml) was distilled onto 0.148 g of dry complex at −196°. Warming the acetonitrile to room temperature caused the complex to dissolve slowly to give a yellow solution. Gas evolved at the surface of the complex as it dissolved. When all the complex had dissolved and the pressure of the evolved gases had stabilized (~1 hr), the amount of gas was measured (1.70 mmol, corrected for acetonitrile vapor pressure). The infrared spectrum of the gas was recorded. Acetonitrile was removed by room-temperature distillation to a −196° trap. The pale yellow solid which remained was dissolved in aqueous ammonia, aerated, and analyzed for copper (1.07 mmol) and chloride (1.06 mmol) as previously described.

Reaction with Oxygen.—Oxygen was admitted to a flask containing dry complex. The solid flamed almost immediately. A brownish solid remained. Gases were examined by gas chromatography and infrared spectrometry.

Regeneration of Methyldiazene.—The method used was analogous to that employed in generating and collecting methyldiazene originally for reaction with cuprous chloride. A 4 *M* potassium cyanide solution (25 ml) made alkaline with some sodium hydroxide was placed in the side-arm flask. The complex and a magnetic stir bar were placed in the lower flask. After removal of the nitrogen atmosphere, the potassium cyanide solution was added to the complex which dissolved in a few seconds. The gases evolved were collected in a U tube at −196° and then transferred to an infrared cell for spectral analysis.

Reaction of Methyldiazene with Cupric Ion.—A solution of methyldiazene was prepared by isolating the diazene at −196°, adding 20 ml of distilled water, and warming rapidly to room temperature. The concentration of methyldiazene in this solution was monitored by following the optical density of an aliquot at 350 nm.[1a] Periodically a 5-ml portion of the diazene solution was added to 5 ml of a 0.01–0.05 *M* cupric sulfate or cupric chloride solution. In each case a dark orange-brown color developed immediately, followed by formation of a finely divided red-brown precipitate seconds later. Methyldiazene was no longer spectrophotometrically detectable in the copper-containing solution, although it was still easily detectable in the stock diazene solution. The precipitate in the cupric chloride solutions redissolved slowly (~30 min); the precipitate in the cupric sulfate solutions did not redissolve and was identified as cuprous oxide by it X-ray diffraction powder pattern. The amount of unprecipitated copper was determined as the ammonia complex.[17] The spent methyldiazene solution gave no reaction with cupric ion.

Spectrometry and Gas Chromatography.—Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer. Infrared spectra of all complexes were recorded in Nujol and Fluorolube mulls held between KBr disks or polyethylene plates and prepared under a nitrogen atmosphere. Gas spectra were taken in a 10-cm cell with potassium bromide windows. Ultraviolet and visible spectra were recorded on a Bausch and Lomb Spectronic 505 and/or a Beckman DU modified by Gilford Instruments. Nitrogen and hydrocarbon analyses were performed by gas chromatography using a 2-m silica gel column with hydrogen carrier gas at 40°.[19] Hydrogen was determined using a 2-m Linde 5A molecular sieve column with nitrogen carrier gas at room temperature.

Results and Discussion

The direct reaction between methyldiazene and a cuprous chloride solution forms an air-sensitive, mod-

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erately stable solid. The diamagnetism, red-brown color, and electronic absorption band at 470 nm are all typical of cuprous–diazene complexes.[12,13,20] When dry the solid may be kept at room temperature for several days before decomposition becomes appreciable. However, the moist solid decomposes completely within a few hours leaving a residue of cuprous chloride. If the solid is left in contact with the solution from which it was precipitated, bubbles (presumably methane and nitrogen) form on the surface of the solid as decomposition occurs. Analysis of all preparations of the complex yielded a 1:1 ratio of copper to chlorine. However, the ratio of copper to methyldiazene varied with each preparation. This variation is attributed to differing amounts of coprecipitated cuprous chloride and/or degrees of decomposition which occurred between synthesis and isolation of the dry product.

Trends observed in the copper to methyldiazene ratio as more care was exercised in the preparation of the complex suggest the formula $(CH_3N{=}NH)CuCl$, I. Thus, synthesis of I by direct addition of a cuprous chloride solution to frozen methyldiazene at −196° (conditions conducive to coprecipitation of uncomplexed cuprous chloride) gave copper to methyldiazene ratios of 1.68, 1.84, and 2.33. Dissolving the methyldiazene in an aqueous potassium chloride solution prior to addition of the cuprous chloride solution reduced the ratio to 1.26, 1.48, 1.50, and 1.57. Attempts to obtain a better product through slow addition of the cuprous chloride solution with good stirring were thwarted by incipient decomposition of the solid which already had been formed.

It is possible that the formula of the complex is $(CH_3N{=}NH)Cu_2Cl_2$ and that the copper to methyldiazene ratios below 2:1 are caused by occluded methyldiazene. This seems unlikely on two grounds. First, one might expect that the occluded diazene molecules would be less tightly held in the crystal and, thus, easily lost, yet no evidence for diazene loss was found when the moist crystals were dried under vacuum. Second, the copper-to-diazene ratio decreased when the synthesis was carried out using a dilute diazene solution rather than the pure, frozen diazene. If occlusion were important, this ratio would be expected to increase, not decrease.

At 70–72° I undergoes thermal decomposition to yield a variety of gaseous products and solid cuprous chloride. Gaseous products were primarily methane and nitrogen, with 5–10% each of hydrogen and ethylene and less than 1% of acetylene. By comparison gaseous methyldiazene decomposes to only methane and nitrogen. No evidence was found for cleavage of the nitrogen–nitrogen bond. Free methyldiazene does not appear to be evolved in the thermal decomposition.

Exposure of I to oxygen also caused decomposition as it ignited spontaneously, burning with a bluish flame. Gaseous products included nitrogen, carbon dioxide, carbon monoxide, methane, and small amounts of ethylene, acetylene, and methanol (trace). Once again the integrity of the nitrogen–nitrogen bond was maintained. This reaction parallels the reaction of gaseous methyldiazene with oxygen both in its explosive character and in its product distribution.

The solubility of I is limited to solvents or solutions capable of coordinating cuprous ions. Thus, I dissolved readily in acetonitrile, aqueous ammonia, and 4 *M* aqueous potassium cyanide with release of methyldiazene but was insoluble in water and 2 *M* aqueous potassium chloride. Immediate collection of the evolved gases by trapping at −196° gave a good yield of methyldiazene. Methane and nitrogen, the usual products of gaseous methyldiazene decomposition, were the only other gaseous products found.

Infrared spectra of azomethane (1,2-dimethyldiazene), methyldiazene, *N*-deuteriomethyldiazene-d_1, and their cuprous chloride complexes are summarized in Table I. The spectra of azomethane and its complex are included for comparison. The infrared spectrum of $(CH_3N{=}NCH_3)Cu_2Cl_2$ includes more bands than that recently published and shows no 895 (m) cm^{-1} band.[20] The spectrum of gaseous azomethane differs appreciably from the low resolution data found in the literature.[21] In every case there is a marked similarity between the gas-phase spectrum of the diazene and its corresponding complex. Cuprous chloride is transparent in the 4000–400-cm^{-1} region except for a rather broad weak band in the 1000–1200-cm^{-1} region. For purposes of this study the important features of the spectra of methyldiazene complexes are the N—H (N—D) and N=N stretching frequencies. The N—H stretching frequency in I occurs at 3150 cm^{-1}, a slight increase over the free diazene value of 3130 cm^{-1}. The N—D stretching frequency in the N-deuterated complex, II, is also slightly larger than that for the free diazene. The 2340-cm^{-1} N—D band is not present initially in the mull spectra of the complex. Rather it grows in gradually while the 2270-cm^{-1} band, which is present initially, disappears. This behavior suggests some reorganization of the diazene in the complex. No other bands in the spectra showed this behavior; no such behavior was observed with the N—H band in I. On long standing the mull of II also showed growth of a band at 3150 cm^{-1}. This N—H band probably arises from exchange of deuterium with hydrogen from absorbed water vapor. The N=N stretching frequency occurs at 1520 cm^{-1} in I and at 1510 cm^{-1} in II. These are a reduction of 55 and 40 cm^{-1}, respectively, from the free diazenes and parallel the 46-cm^{-1} reduction observed in the Raman spectra of azomethane and its complex.[22] The weakness of the Cu—Cl stretch probably accounts for the failure to find it in the spectra of either I or II. The Cu—Cl stretch appears at 311 cm^{-1} in $(CH_3N{=}NCH_3)Cu_2Cl_2$.

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[21] G. Herzberg, "The Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 359.

[22] A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2247 (1969).

TABLE I

INFRARED SPECTRA OF GASEOUS DIAZENES AND THEIR CUPROUS CHLORIDE COMPLEXES[a]

trans-$CH_3N{=}NCH_3$			*trans*-$CH_3N{=}NH$			*trans*-$CH_3N{=}ND$		
Gas	Band shape[c]	Complex	Gas[b]	Band shape[c]	Complex	Gas[b]	Band shape[c]	Complex
3340 vw	B	2970 m	3130 m	A	3150 m	2985 m	C	2970 w
3260 vw	B	2895 w	2900–3000 m		3090 w	2920 m	A	2920 w
~3100 w		1430 s			2970 w	~2870 m		2340 m
2980 s	C	1405 s	1575 w	A	2930 w	2320 m	A	2300 w
2925 s	B	1380 vs	1470 m	C	1520 m	2110 w	A?	2270 m
2855 m	B	1120 m	1410 m	B	1475 m–s	1550 w	A	1510 m
2750 w	B?	1095 m	1140 m	C	1460 m	1450 m	C	1460 m
2560 vw	B	1010 m	1125 m		1425 m	1405 m	B	1405 m
2380 vw	B?	660 vw	920 w	A	1405 m	1060 m	A	1365 m
2180 vw	C?	630 vw	844 m	C	1375 m–s	890 m	A	1110 w
1975 vw	B	455 w	550 m	B	1365 w	662 m	C	1070 w
1445 s	B	311 w			1130 vw	535 m	A	950 vw
1300 w					1105 m			905 m–s
1110 m	C				960 m			860 vw
1010 m	B				855 m–s			695 s
730 w	A				650 m			660 vw
								635 vw
								610 m–s

[a] Uncertainty in frequencies is ±5 cm^{-1}. [b] From ref 1a. [c] Approximate only.

The ratio of copper to diazene in known cuprous chloride–diazene complexes varies markedly. Thus, this ratio is 1:1 in $(CH_3N{=}NH)CuCl$, 2:1 in $(CH_3N{=}NCH_3)Cu_2Cl_2$[13] and $(C_2H_5N{=}NC_2H_5)Cu_2Cl_2$,[20] and 4:1 in $(C_6H_5N{=}NH)Cu_4Cl_4$.[12] The number of diazene molecules accommodated in the crystal apparently is correlated with the size of the diazene molecule. The stoichiometries of two complexes of azoisopropane with formulas $(C_3H_7N{=}NC_3H_7)CuCl \cdot 2H_2O$ and $(C_3H_7N{=}NC_3H_7)Cu_2Cl_2 \cdot 2H_2O$ are subject to question since only copper and chlorine analyses were used to characterize them.[13] The structure of $(CH_3N{=}NCH_3)Cu_2Cl_2$ has been determined by X-ray crystallography.[23] In this crystal cuprous chloride forms infinite chains of alternating copper and chlorine atoms. These chains are connected in pairs through the bonding of chlorine and copper atoms from different chains. Successive pairs of chains are joined by bridging azomethane molecules with each nitrogen lone pair coordinated to a copper atom on a different chain to form a large planelike structure. These planes are stacked in layers in the full crystal. The copper atom is coordinated approximately tetrahedrally by three chlorine atoms from one pair of chains and by a nitrogen lone pair from azomethane. The stoichiometry of the phenyldiazene complex can be rationalized in terms of a similar crystal structure in which half of the positions for diazene are vacant, due probably to the steric requirements of the phenyl group.

In the case of the methyldiazene complex, I, any proposed structure must accommodate twice as many diazene molecules as found in the azomethane case. The lack of solubility of I in noncomplexing media strongly suggests a polymeric structure. Hydrogen bonding does not appear to be important in the crystal since the N–H stretching frequency shows no reduction over that in the gaseous diazene. The electronic spectrum of I shows bands at 470 and 360 nm. The 470-nm band is comparable to that observed for azomethane and azoethane complexes of cuprous halides.[20] The 360-nm band is assigned to the n → π* band in methyldiazene; this band appears at 350 nm in the free ligand. The n → π* transition in the azomethane and azoethane complexes is also only moderately shifted from the free-ligand values. In view of these similarities it is suggested that the bonding in I is *via* the lone pairs on nitrogen and not the N=N double bond. It also seems reasonable to assume that all nitrogen lone pairs are coordinated to copper atoms. Each copper atom must then be coordinated to two nitrogen atoms from different diazene molecules. Consistent with this expectation, but by no means a proof, is the reduced N=N stretching frequency in I compared with the free diazene; again this parallels the azomethane data. The N=N stretching frequency has not been unambiguously assigned in the phenyldiazene spectra. In $(CH_3N{=}NCH_3)_2PdCl_2$ only one end of the azomethane molecule is coordinated to palladium and the azomethane N=N stretching frequency is higher than in the free molecule by 22 cm^{-1}.[22] The reason for this shift is unknown. However, because of the differences in the metal ions involved, it is not clear that an azomethane molecule with only one of its nitrogen atoms coordinated to copper(I) also should be expected to show an increase in the N=N stretching frequency. Use of models suggests that it is possible to adapt the azomethane complex structure to I. In this structure the additional diazene molecules are used to bridge copper atoms from different *layers*. This requires that the pairs of chains of cuprous chloride be somewhat flattened. The unattractive feature of such a model is that copper would be pentacoordinate, being bound to three chlorine and two nitrogen atoms. While pentacoordinate com-

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(23) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **13**, 28 (1960).

plexing of copper(II) is well known, it is yet unknown for copper(I).[24]

A simpler polymeric structure for I can be envisaged in which copper is four-coordinate and in a tetrahedral environment. This structure consists of single chains of copper and chlorine atoms bridged by molecules of methyldiazene. Each copper atom is coordinated to two chlorine atoms and to two nitrogen atoms from different diazene molecules. Layers of this type are stacked together in the solid. Clearly, the larger number of diazene molecules in I poses no problem for proposing a reasonable crystal structure.

It is surprising that I cannot be obtained by the method of Diels and Koll[13] from the oxidation of aqueous methylhydrazine with cupric ion in the presence of chloride ion.[12] By anology with other systems,[12,13] methyldiazene should be produced in this reaction. The only evidence for this reaction found in the present study was the appearance of a small amount of a red-brown solid on the surface of the *unmixed* solution obtained by slowly adding a cupric sulfate solution to a nearly saturated sodium acetate solution containing some sodium chloride and methylhydrazine. This solid dissolved quickly and a yellow solution resulted which after ~15 min began to deposit metallic copper.[25] Methane was the only infrared-active gaseous product. Use of other buffer systems proved equally unsuccessful in yielding I.

Methyldiazene reacted rapidly with cupric ion in aqueous solution, but the final products depended upon the cupric salt used. With cupric chloride a reddish precipitate formed within seconds and redissolved slowly. This could be I, which was formed after reduction of some Cu(II) to Cu(I). The amount was too small to work with. With cupric sulfate a permanent reddish precipitate of cuprous oxide quickly formed.[25] Approximately one copper atom precipitated for every four molecules of methyldiazene present when the cupric sulfate was added. Thus, the failure to obtain I by the method of Diels and Koll could be explained by a rapid reaction of methyldiazene and cupric ion. However, the different products observed in the three reactions remain unexplained.

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[25] Identified by its X-ray diffraction powder pattern.

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Preparation and Oxygenation of Some Five-Coordinate Lewis Base Adducts of Iron Bis(1,2-dithiolenes)

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Triphenylphosphine oxide, triphenylarsine oxide, pyridine *N*-oxide, and halide ions cleave the dimers $Fe_2S_8C_8R_8^{2-}$ (R = CN, CF_3) to give adducts of the type (base)$FeS_4C_4R_4^-$. The isolation and physical properties of certain of these adducts, which have quartet ground states, are reported. Triphenylphosphine and triphenylarsine also cleave the dimers to give adducts which have been characterized in solution but not isolated. Exposure of these latter adducts to oxygen results in the oxidation of the bases to triphenylphosphine oxide and triphenylarsine oxide. No evidence for the formation of discrete oxygen complexes with any of these dithiolene complexes has been found. Cobalt dithiolene complexes are not effective in activating the oxidation of these bases.

Introduction

The ability of dithiolene complexes to undergo electron-transfer reactions has been extensively studied.[2] In addition dithiolene complexes have been shown to exert effects on the oxidation of other substrates. The neutral complexes $MS_4C_4(C_6H_5)_4$ (M = Ni, Pd, Pt) and $(C_4H_9)_3PCoS_4C_4(C_6H_5)_4$ have been shown to be effective as free-radical acceptors and hydroperoxide decomposition agents; consequently they act as autoxidation inhibitors.[3] In contrast iron dithiolenes have been observed to promote the oxidation of certain species. It has been reported that exposure of solutions of the ions $XFeS_4C_4R_4^{2-}$ (X^- = N_3^-, NCO^-; R = CN, CF_3) to air produces the corresponding $ONFeS_4C_4R_4^{2-}$ in

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