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Photochemistry of Cyclopentadienylcobalt 1,4-Diaryltetraazadienes. Examples of C–H, C–F, and C–C Bond Breaking

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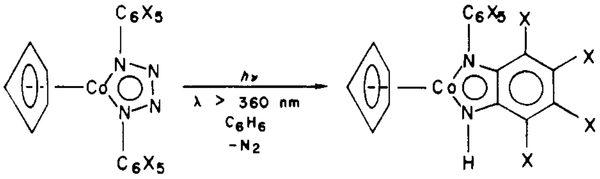
Irradiation of $(\eta^5\text{-}C_5H_5)Co[(2,4\text{-}F_2C_6H_3)N_4(2,4\text{-}F_2C_6H_3)]$ yields $(\eta^5\text{-}C_5H_5)Co[HN(FC_6H_3)N(2,4\text{-}F_2C_6H_3)]$ and $(\eta^5\text{-}C_5H_5)Co[HN(F_2C_6H_2)N(2,4\text{-}F_2C_6H_3)]$. Photolysis of $(\eta^5\text{-}C_5H_5)Co\{[2,6\text{-}(CH_3)_2C_6H_3]N_4[2,6\text{-}(CH_3)_2C_6H_3]\}$ produces $(\eta^5\text{-}C_5H_5)Co\{HN[(CH_3)C_6H_3]N[2,6\text{-}(CH_3)_2C_6H_3]\}$. These photochemical reactions appear to proceed by expulsion of N_2 from the unsaturated CoN_4 ring to produce a metal dinitrene, which undergoes a rapid intramolecular rearrangement to yield products that contain a coordinated *o*-benzoquinone diimine ligand. When $(\eta^5\text{-}C_5H_5)Co\{[2,6\text{-}(CH_3)_2C_6H_3]N_4[2,6\text{-}(CH_3)_2C_6H_3]\}$ is irradiated in cumene solvent, the evolved gas consists of an 0.94:1.0 CH_4:N_2 mixture. These data are consistent with an aromatic radical substitution process for methyl loss. It is suggested that the transition state necessary for this rearrangement is resonance stabilized, owing to the presence of the cobalt atom and the availability of a low-lying empty nitrogen p(π) orbital; Xα calculations of the hypothetical $(\eta^5\text{-}C_5H_5)Co(NH)_2$ species demonstrate the presence of low-lying empty nitrogen p(π) orbitals in the metal dinitrene. When the ortho substituents are hydrogen, as in $(\eta^5\text{-}C_5H_5)Co[(C_6H_5)N_4(C_6H_5)]$, photolysis to $(\eta^5\text{-}C_5H_5)Co[HN(C_6H_4)N(C_6H_5)]$ proceeds without production of H radicals in cumene solvent. Similarities exist between the photochemical reactions of metal–tetraazadiene complexes and their fragmentation pathways in a mass spectrometer.

Introduction

Photochemical fragmentation of metallotetraazadiene complexes has been observed[1] according to reaction 1.

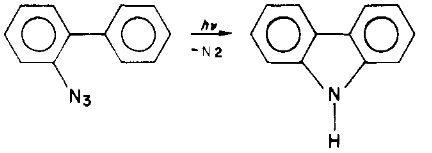


(1)

Ia, X = H
b, X = F

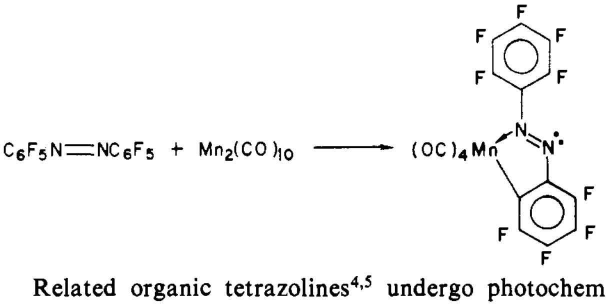
IIa, X = H
b, X = F

High-yield resultant bond breaking, as in the reaction of Ib, has no precedent in the organic chemistry of nitrenes, although ortho hydrogen insertion can occur[2] as in reaction 2.



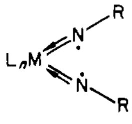
(2)

Precedent for ortho fluorine elimination in organometallic chemistry has been established[3] in the reaction (3).

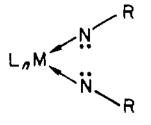


(3)

Related organic tetrazolines[4,5] undergo photochemical elimination of N_2 upon excitation of the $\pi \rightarrow \pi^*$ transition.[6] The resultant biradical may subsequently react via several routes, depending upon the ring substituent, X, and the solvent.[4,7] By analogy to organic tetrazoline and tetrazene[8] photochemistry, formation of the diradical, A, or diimido, B (hereafter denoted dinitrene), intermediate might be anticipated in reaction 1. This could occur as a primary photoproduct or secondary to thermal decomposition of an intermediate such as $L_nM(NR)(N_3R)$.

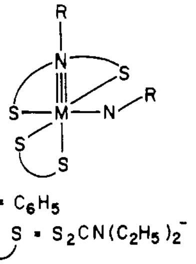


A



B

To date, only mononitrene or monoimido transition-metal complexes have been prepared photochemically;[9] however, Maatta and Wentworth have synthesized a stable "dinitrene" complex[10]



R = C_6H_5
S S = $S_2CN(C_2H_5)_2^-$

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by a nonphotochemical procedure.

In order to obtain further insight into the nature of the intermediates generated in reaction 1, we synthesized (η^5-C_5H_5)Co(RN_4R) species where R = an aryl group with ortho H, F, or CH_3 substituents. We now describe the photochemical reactions of these molecules, which include an unprecedented example of aryl–CH_3 bond homolysis.

Experimental Section

^{1}H (79.54 MHz) and ^{13}C (20 MHz) NMR spectra were recorded on a Varian CFT-20 spectrometer or JEOL FX-270 instrument and ^{1}H (89.56 MHz), ^{13}C (22.50 MHz), and ^{19}F (84.26 MHz) NMR spectra were measured on a JEOL FX-90Q spectrometer. Chemical shifts are reported in ppm downfield from external references [$(CH_3)_4Si$ for ^{1}H and ^{13}C; $CFCl_3$ for ^{19}F] or, in some cases, from solvent reference peaks (C_6D_5H, δ_H 7.15; C_6D_6, δ_C 128.0; $CD_3C(O)CD_3$, δ_C 206.0). Tris(acetylacetonato)chromium(III), an intermolecular relaxation agent, was added to samples whose ^{13}C NMR spectra were recorded on the CFT20 or FX-90Q spectrometers. Electronic absorption spectra were measured with a Perkin-Elmer 320 spectrophotometer. Gas-phase IR spectra were obtained in a 10-cm cell (CaF_2 windows), employing a Nicolet 7199 Fourier transform instrument. Mass spectra of the positive ions were obtained by Dr. Doris Hung (Northwestern University, Analytical Services Laboratory) on a Hewlett-Packard 5985 GCMS system using 15-eV ionization energy. In all cases, the identification of the parent ion was confirmed by chemical ionization mass spectrometry (with CH_5^+). Complete tables of mass spectra are available as supplementary material. Elemental analyses were performed by Micro Tech, Skokie, IL. All samples submitted for elemental analysis were dried under high vacuum for several hours.

Reactions and manipulations involving air-sensitive materials were carried out under an atmosphere of prepurified nitrogen, employing standard Schlenkware and drybox techniques.[11] Solvents (benzene, toluene, and 2-methyltetrahydrofuran (MeTHF)) were distilled from sodium benzophenone ketyl under prepurified nitrogen. Toluene-d_8 was vacuum distilled from $LiAlH_4$. Cyclopentadienyldicarbonylcobalt (Strem Chemicals Inc.) was vacuum distilled, and cumene (Aldrich) was passed through a column of activated alumina prior to use. The complexes $Fe[P(OCH_3)]_3[(CH_3)N_4(CH_3)]$, $Fe(CO)_3[(CH_3)N_4(CH_3)]$, and $Fe(CO)_3[(CD_3)N_4(CD_3)]$ were available from a previous study. The complex $Fe(^{13}CO)_{1.35}(^{12}CO)_{1.65}[N_4(CH_3)_2]$ was prepared by visible irradiation (200-W Hg–Xe arc lamp and Corning 3-73 glass filters $\lambda > 400$ nm) of a methanol solution of $Fe(CO)_3[(CH_3)N_4(CH_3)]$ for several hours under 600 torr of ^{13}CO (90% isotopic purity). After the solvent was removed, sublimation (0.01 torr, 30 °C) yielded the above-mentioned complex. Methyl azide was prepared according to the literature method,[12] and 2,4-difluorophenyl azide[13a] and 2,6-dimethylphenyl azide[13b] were synthesized from the corresponding aniline compounds. *Caution*! Organic azides are explosives, and therefore we stored them as solutions (2 M) in benzene. Complexes Ia,b were synthesized as described previously.[1,14]

Unless otherwise specified, irradiations for the photochemical reactions described below employed the output of an Osram 450-W high-pressure Xe arc lamp, fitted with a Corning 0-52 filter to eliminate high-energy ($\lambda < 340$ nm) UV light. A cooled 10-cm water filter removed most infrared radiation. Solutions were degassed and irradiated in Pyrex Schlenkware.

Low-temperature irradiations (77 K) in MeTHF were carried out in a glass Dewar with quartz windows. Solutions of the tetraazadiene complexes in Pyrex cuvettes were immersed in liquid nitrogen that was slowly purged with He to suppress bubble formation.

The purification of reaction products by column chromatography employed neutral alumina with toluene–hexane mixtures in varying ratios, depending upon the system (increasing the proportion of toluene after more readily eluted compounds were removed). Alternatively, dichloromethane eluant also proved successful. All products purified in this manner were air-stable, and no attempt was made to exclude oxygen at this stage. Thin-layer chromatography (on silica plates) provided a convenient check of product purity and is a simple method for following the progress of the photochemical reactions.

Cyclopentadienylcobalt 1,4-Dimethyltetraazadiene, (η^5-C_5H_5)Co[$(CH_3)N_4(CH_3)$] (Ic). The literature procedure[15] was used in the preparation of this compound. Column chromatography or sublimation at 90 °C (10^{-3} torr) afforded a dark green solid with ^{1}H NMR parameters identical with those reported.[15] Mass spectrum, *m/e* (relative intensity): 210 (57, $M^+ \equiv Co(C_5H_5)(CH_3N_4CH_3)$).

Synthesis of Cyclopentadienylcobalt 1,4-Bis(2,4-difluorophenyl)tetraazadiene, (η^5-C_5H_5)Co($C_6H_3F_2N_4C_6H_3F_2$) (Id). A 2 M benzene solution of 2,4-difluorophenyl azide (4 mL, 8 mmol) was added slowly under nitrogen to a vigorously stirred solution of (η^5-C_5H_5)Co$(CO)_2$ (0.22 g, 1.2 mmol) in 10 mL of benzene. An immediate exothermic reaction subsided after several minutes, and stirring was continued for 1 h. The solution was then concentrated under vacuum, and subsequent steps were carried out under room atmosphere. Purification by column chromatography and evaporation of the solvent from the eluent afforded crystals, having green reflections, in 40% yield. ^{19}F{^{1}H} NMR (acetone-d_6): −111.92 (d, 2 F, ortho), −118.23 (d, 2 F, para) ppm. Anal. Calcd for $C_{17}H_{11}CoF_4N_4$: C, 50.28; H, 2.73; N, 13.80. Found: C, 50.8; H, 2.83; N, 13.4. Mass spectrum, *m/e* (relative intensity): 406 (15, $M^+ \equiv Co(C_5H_5)(F_2C_6H_3N_4C_6H_3F_2)$).

Synthesis of Cyclopentadienylcobalt 1,4-Bis(2,6-dimethylphenyl)tetraazadiene, (η^5-C_5H_5)Co[$(CH_3)_2C_6H_3N_4C_6H_3(CH_3)_2$] (Ie). The procedure used is similar to that employed in the preparation of complex Id, with the following modifications. Following addition of the azide solution to a stirred solution of (η^5-C_5H_5)Co$(CO)_2$, the mixture was refluxed at 80 °C for 1 h. Purification of the reaction mixture by column chromatography and crystallization by slow evaporation from hexane solution afforded large crystals, having green reflections, in 83% yield. A small amount (<1% yield) of complex IIe (vide infra) was also isolated during chromatography. Purification of Ie can alternatively be achieved by sublimation at 75 °C (10^{-3} torr). ^{1}H NMR: (acetone-d_6) 7.27 (m, 6 H, C_6H_3), 4.67 (s, 5 H, C_5H_5) ppm; ($CDCl_3$) 7.23 (m, 6 H, C_6H_3), 4.56 (s, 5 H, C_5H_5), 2.19 (s, 12 H, CH_3) ppm; (C_6D_6) 4.11 (s, 5 H, C_5H_5), 2.18 (s, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR (acetone-d_6): 155.88 (2 C, CN), 132.36 (4 C, *C*CH_3), 128.62 (4 C, meta C_6H_3), 127.67 (2 C, para C_6H_3), 80.36 (5 C, C_5H_5), 18.12 (12 C, CH_3) ppm. Anal. Calcd for $C_{21}H_{23}CoN_4$: C, 64.61; H, 5.94; N, 14.35. Found: C, 64.4; H, 6.03; N, 13.8. Mass spectrum, *m/e* (relative intensity): 390 (18, $M^+ \equiv Co(C_5H_5)((CH_3)_2C_6H_3N_4C_6H_3(CH_3)_2)$).

Photochemical Syntheses of Cyclopentadienylcobalt *N*-(2,4-Difluorophenyl)-4-fluoro-*N*,*N'*-phenylenediimine, (η^5-C_5H_5)Co($HNC_6H_3FNC_6H_3F_2$) (IId), and Cyclopentadienylcobalt *N*-(2,4-Difluorophenyl)-3,5-difluoro-*N*,*N'*-phenylenediimine, (η^5-C_5H_5)Co($HNC_6H_2F_2NC_6H_3F_2$) (IId'). Complex Id (0.20 g) was dissolved in 200 mL of degassed benzene and placed in the well of a 450-W medium-pressure Hg immersion lamp with Pyrex and water filters. The solution was irradiated for 6 h, and its color was transformed from yellow ochre → violet → maroon. The solution was then reduced in volume to approximately 30 mL on a rotary evaporator and purified by column chromatography, resulting in yields of <7% and 86% for IId,d', respectively. The IR spectra of IId and IId' (in CH_2Cl_2) exhibit bands at 3390 and 3380 cm^{-1}, respectively, attributable to ν_{N-H}. Anal. Calcd for $C_{17}H_{11}CoF_4N_2$ (IId'): C, 54.01; H, 2.93; N, 7.41. Found: C, 54.1; H, 3.30; N, 7.46. The trace of complex IId was not isolated in sufficient quantity to obtain elemental analyses. Mass spectrum *m/e* (relative intensity): IId, 360 (38, $M^+ \equiv Co(C_5H_5)(HNC_6H_3FNC_6H_3F_2)$); IId', 378 (100, $M^+ \equiv Co(C_5H_5)(HNC_6H_2F_2NC_6H_3F_2)$). The parent ions M^+ were confirmed by chemical ionization mass spectrometry, employing CH_5^+. ^{19}F{^{1}H} NMR (IId', acetone-d_6): −114.04 (1, ortho $C_6H_3F_2$), −117.68 (1, para $C_6H_3F_2$), −122.64 (1, $C_6H_2F_2$), −131.94 (1, $C_6H_2F_2$) ppm.

Photochemical Synthesis of Cyclopentadienylcobalt *N*-(2,6-Dimethylphenyl)-3-methyl-*N*,*N'*-phenylenediimine, (η^5-C_5H_5)Co[$HNC_6H_3(CH_3)NC_6H_3(CH_3)_2$] (IIe). This compound was prepared by irradiation of a benzene solution of Ie using the procedure described above for the preparation of IId. Purification by column chromatography and sublimation at 60 °C (10^{-3} torr) resulted in yields

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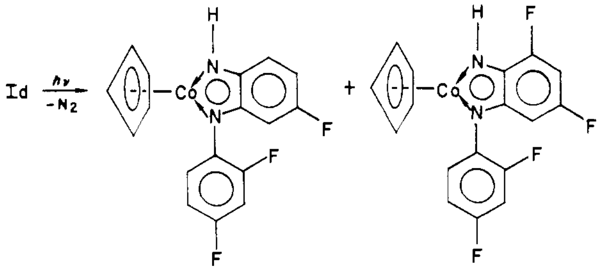
of 65%. The only other characterizable reaction product, the azo compound $(CH_3)_2C_6H_4N{=}NC_6H_4(CH_3)_2$, was isolated in less than 1% yield. The IR spectrum of IIe (in CH_2Cl_2) shows a band at 3373 cm^{-1} attributable to ν_{N-H}. ^1H NMR: ($CDCl_3$) 9.68 (1 H, NH), 7.25 (m, 6 H, C_6H_3), 4.67 (s, 5 H, C_5H_5), 2.36 (s, 3 H, CH_3), 2.16 (s, 6 H, CCH_3) ppm; (acetone-d_6, -60 °C) 11.03 (1 H, NH), 7.25 (m, 6 H, C_6H_3), 4.67 (s, 5 H, C_5H_5) ppm; (C_6D_6) 4.40 (s, 5 H, C_5H_5), 2.39 (s, 3 H, CCH_3), 2.21 (s, 6 H, CCH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6, -60 °C): 156.57 (1 C, phenyl CN), 152.15 (1 C, phenylene CN), 148.15 (1 C, phenylene CN), 131.84 (2 C,) 128.71 (2 C), 125.85 (1 C), 124.46 (1 C), 120.38 (1 C), 119.86 (1 C), 110.74 (1 C), 76.89 (5 C, C_5H_5), 18.29 (2 C, phenyl CH_3), 17.42 (1 C, phenylene CH_3). Anal. Calcd for $C_{20}H_{21}CoN_2$: C, 68.96; H, 6.08; N, 8.04. Found: C, 69.65; H, 6.17; N, 7.90. Mass spectrum *m/e* (relative intensity): 348 (100, $M^+{\equiv}Co(C_5H_5)(HNC_6H_3(CH_3)NC_6H_3(CH_3)_2)$). Occasionally an impurity with ^1H NMR ($CDCl_3$) peaks at 7.16 and 2.43 ppm contaminated the product.

Xα Calculations. The calculation of the electronic structure of the hypothetical (η^5-C_5H_5)$Co(NH)_2$ employed the SCF–DV–Xα procedure. The Hartree–Fock–Slater equations were solved iteratively by the discrete variational (DV) procedure,[16] and the Coulomb potential was approximated by a least-squares fit of the charge density at the $l = 0$ level.[17] A molecular exchange parameter, α, of 0.70 was assumed. Numerical atomic orbitals from exact atomic HFS calculations were used as basis functions. The 1s, 2s, and 2p electrons on cobalt and the 1s electrons on C and N were tested as a frozen core in the molecular calculations. Orbitals through 4s and 4p on Co were included, and a minimal basis set was used for the light atoms. The geometry of (η^5-C_5H_5)$Co(NH)_2$ was identical with that used[18] for (η^5-C_5H_5)$Co(HN_4H)$ except that the two remote nitrogens of the metallotetraazdiene were removed.

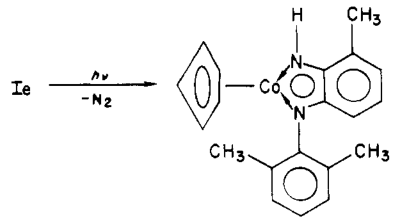
Results and Discussion

The reaction of (η^5-C_5H_5)$Co(CO)_2$ with $N_3(2,4\text{-}F_2C_6H_3)$ and $N_3[2,6\text{-}(CH_3)_2C_6H_3]$ yielded the new tetraazadiene complexes Id and Ie, respectively, in good yield. Attempts to prepare other tetraazadiene derivatives from $N_3[1,4\text{-}(NO_2)\text{-}C_6H_4]$ or from (η^5-Me_5C_5)$Co(CO)_2$ and several organic azides were not successful. Loss of dinitrogen and ortho attack occurs when solutions of Id and Ie are irradiated with Pyrex-filtered light from a mercury or xenon arc lamp. Products form according to reactions 4 and 5. Illumination of complex Ic, the alkyl derivatives, only led to slow decomposition and the evolution of N_2 gas.



(4)

IId IId'



(5)

IIe

The structures of Id, Ie, IId, IId′, and IIe have been established by a combination of spectroscopic techniques (IR, ^1H NMR, ^{19}F NMR, ^{13}C NMR, mass spectrometry). Because we have previously characterized the related molecules Ib and IIb by *both* spectroscopic and X-ray diffraction methods,[1,14,18] the spectroscopic structural assignments proposed herein should be sound. For example, the unprecedented loss of a methyl group in reaction 5 is supported by (1) the intensity ratio of the two methyl resonances in the ^1H NMR spectrum, (2) the intensity ratio of the two methyl resonances in the ^{13}C NMR spectrum, (3) the observation of an approximately 1:1 CH_4:N_2 gas mixture evolved during the photolysis of Ie in isopropylbenzene (cumene) solvent, and (4) chemical ionization mass spectrometry that establishes the parent ion at *m/e* 348. Although the NMR data do not unambiguously fix the location of the phenylene methyl substituent in IIe, given the mechanistic arguments below it seems likely that it remains ortho to the original nitrogen.

Mechanistic Aspects. When complexes Ia and Ib are irradiated at 77 K in a MeTHF glass, the visible absorptions due to the parent complexes fade (by visual and spectrophotometric observation) to yield a species with no apprecibale visible absorption. If these irradiated glasses are removed from the liquid-nitrogen bath, the electronic absorption features of the photoproducts IIa and IIb grow in as the glass melts. The EPR spectrum of Ia photolyzed in a toluene glass at 4.2 K or of Ie in 3-methylpentane at 77 K did not reveal radical intermediates.

Several studies of d^8 tetraazadiene complexes show that intense visible absorptions characterize the intact MN_4 ring.[8,14,18-20] The weakly absorbing intermediate in the experiments cited above must therefore be attributed to a complex whose MN_4 ring has been disrupted, probably by extrusion of N_2. These observations tend to rule out the alternative possibility of an (η^3-C_5H_5)$Co(RN_4R)$ intermediate similar to that observed in low-temperature photochemical studies of (η^5-C_5H_5)$Co(CO)_2$.[21a] It should be noted that a π,π-coordinated tetraazadiene would be a possible precursor for N_2 extrusion. Such an intermediate has been postulated in low-temperature photochemical reactions of a metal–diazabutadiene complex.[21b]

A complex such as (η^5-C_5H_5)$Co(NR)(N_3R)$ would also be a reasonable precursor to N_2 loss as illustrated in eq 6. Such a species is thought to be an important intermediate in the thermal synthesis of metallotetraazadienes.[21c,d] In all of our preparations of (η^5-C_5H_5)$Co(RN_4R)$ complexes (R = aryl), we observed the formation of small amounts of the "photoproducts" (IIa → IIe). Control experiments (in the dark) established that these products were not derived from photolysis during workup. Furthermore, we showed that thermal decomposition of Ia → Ie does not yield IIa → IIe. Thus, the small yields of IIa → IIe from the thermal preparations of (η^5-C_5H_5)$Co(RN_4R)$ could arise due to the loss of N_2 from a (η^5-C_5H_5)$Co(NR)(N_3R)$ precursor. Such an azido–nitrene complex could also regenerate the reactant (eq 6) by re-forming the metal–tetraazadiene ring. This could account for the low photochemical efficiencies of reactions 4 and 5.

Previously, we demonstrated the intramolecular nature of the photochemical reactions of Ia and Ib.[1] The facility of these rearrangements in fluid solution (even at low temperatures) is remarkable. Attempts to intercept a reactive intermediate

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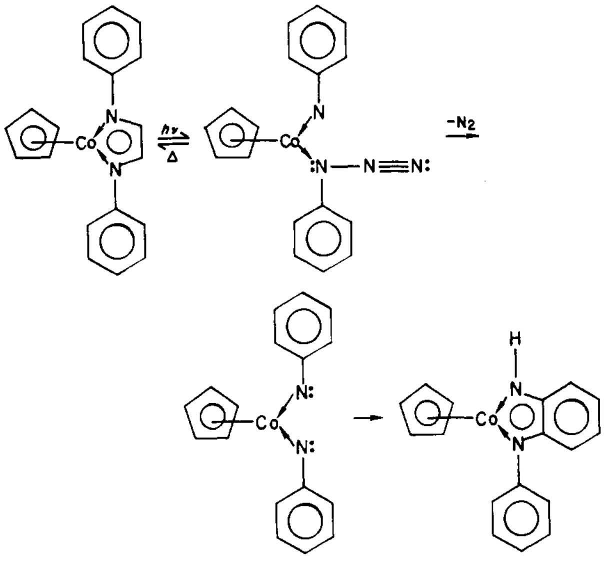


(6)

by irradiation of solutions of complex Ia in neat dimethylacetylenedicarboxylate, phenylacetylene, styrene, and carbon disulfide, or with an excess of triphenylphosphine in benzene have been unsuccessful. In all cases, only IIa forms or ill-defined decomposition takes place. In this context, it should be noted that (η^5-C_5H_5)Co[(CH_3)N_4(CH_3)], which cannot undergo an intramolecular "insertion", does not produce any well-defined products upon irradiation.

The product distribution in reaction 4 is consistent with ortho bond breaking being important in the transition state that leads to product formation from the intermediate dinitrene. Only a trace of the product resulting from C–F bond cleavage is found, and this agrees with the greater strength[22] of aryl C–F bonds in comparison to aryl C–H bonds. Ortho attack and bond cleavage should be even more difficult in the intermediate generated by irradiating Ie. In fact, this reaction does not occur in as high yield as those of Ia, Ib, and Id. Small amounts of the nitrene coupling product (2,6-$Me_2C_6H_3N$)$_2$ are found, along with other uncharacterized side products, when Ie is irradiated in benzene solution.

Activation of an ortho C–H bond has precedent in the photochemistry of organic azido biphenyls and in thermal reactions of organometallic complexes. Activation of an ortho C–F bond is comparatively rare, and we can find no examples of ortho C–C bond breaking. Ortho metalation of an intermediate azoarene complex seems an unlikely possibility in these photochemical reactions.[23] Direct insertion of a nitrene nitrogen into the ortho C–H bond to form IIa is plausible; however, the absence of N–F and N–CH_3 bonds in the products IIb, IId, and IIe suggests direct insertion does not occur in these cases. Attempts to determine the fate of the eliminated F atom (eq 1) by ^{19}F NMR, IR, and GC–mass spectrometry proved unsuccessful. Initial attempts to locate the CH_3 group lost in the formation of IIe were also fruitless. We considered the possibility that the ortho substituents departed via a radical substitution process at the aromatic ring.[24] For example, the liberated methyl radical could undergo several reactions (with solvent, with Ie, and with IIe), thereby making detection difficult. The fluoro complex could yield low concentrations of F· that would be converted to HF and scavenged by the glass vessel. Therefore, complex Ie was photolyzed in cumene, a solvent containing a readily abstractable hydrogen. The evolved gas was collected by Toepler pumping, quantitatively analyzed by FT IR spectroscopy, and found to be a 0.94:1 mixture (±10%) of CH_4:N_2. Analysis of the solvent by GC–mass spectrometry also revealed significant quantities of the dimerization product of the cumyl radical. These results implicate the intermediacy of a methyl radical, which abstracts hydrogen from the solvent.

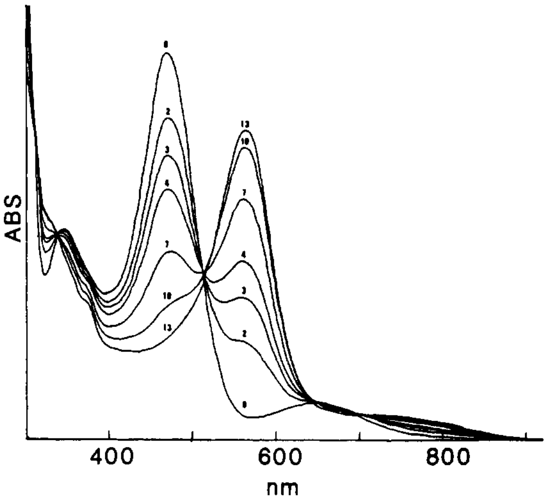
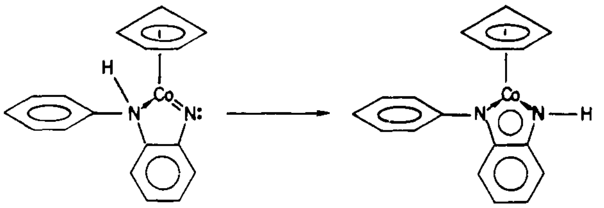


Figure 1. Spectral changes for (η^5-C_5H_5)Co($C_6F_5N_4C_6F_5$) (Id) upon irradiation (~1200 nm > λ > 350 nm) in benzene solvent. Numbers indicate hours of irradiation. Note the loss of isosbestic points at long irradiation times.

Next we considered the possibility that Ia also reacted via a radical substitution pathway (yielding H·). This complex was irradiated in cumene solvent and the evolved gas collected and separated by adsorption on activated silica gel at 77 K. In this instance the amount of H_2 gas formed was less than 5%. Therefore, complex Ia does not appear to photochemically rearrange by a radical pathway similar to that for Ie.

The insertion and subsequent [1,3] (NCoN) hydrogen shift mechanism (eq 7) originally suggested[1] for the reaction of Ia still seems reasonable. Rearrangement of the dinitrene complex generated by irradiating Ie results in the formation of methyl radicals, perhaps by donation of electrons from an ortho p(π) orbital on the xylyl ring into an empty p(π) orbital on nitrogen as depicted in C. Aromatic radical substitutions are relatively rare; however, in this instance the metal can stabilize a transition state resulting from ortho attack in C. The N–H group in the product benzoquinone diimines IIb →



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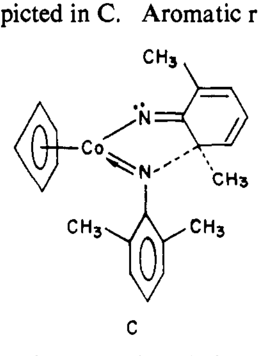

C

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[22] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 309.

[23] In view of the expected stability of the Co(III) complex derived by ortho metalation, this process seems unlikely. For an example of stable cyclometalated aryl nitrogen ligands, see: Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327–352.

[24] March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 622–629. These cases are not entirely analogous because a second radical abstracts the leaving radical fragment.

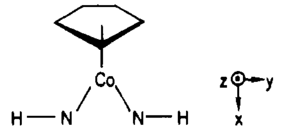
Table I. Frontier Orbitals, Eigenvalues, and Atomic Orbital Character for $(\eta^5\text{-}C_5H_5)Co(NH)_2$

orbital	energy, eV	dominant atomic compn
7a″	−10.74	40% Co d_{xy}, 35% N p_{xy}
13a′	−9.44	43% Co d_{xz}, 49% $\eta^5\text{-}C_5H_5$
14a′	−8.71	45% Co $d_{x^2-y^2}$, 19% Co d_{z^2}, 29% N $p_{x,y}$
8a″	−8.53	77% $\eta^5\text{-}C_5H_5$, 15 N $p_{x,y}$
9a″	−8.30	83% d_{yz}, 12% N p_z
15a′	−7.67	58% N p_z, 11% Co d_{xz}, 26% $\eta^5\text{-}C_5H_5$
16a′	−7.43	58% Co d_{z^2}, 20% Co $d_{x^2-y^2}$
10a″	−6.32	76% N $p_{x,y}$, 8% N s
17a′	−6.03[a]	62% N $p_{x,y}$, 22% Co $d_{x^2-y^2}$
11a″	−5.26	82% N p_z, 17% Co d_{yz}
18a′	−4.95	39% N p_z, 33% Co d_{xz}, 25% $\eta^5\text{-}C_5H_5$
12a″	−3.39	32% d_{xy}, 34% N $p_{x,y}$, 25% $\eta^5\text{-}C_5H_5$

[a] Denotes highest occupied molecular orbital. See text for the orientation of the molecular coordinate system.

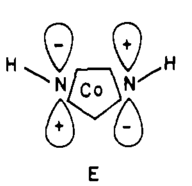
IIe must arise from hydrogen abstraction. Labeling studies in C_6D_6 did not reveal the incorporation of deuterium in products IIb → IIe. Unlike the photochemical formation of IIa, which was quantitative, the formation of IIb → IIe (e.g., Figure 1) was not quantitative as evidenced by the absence of clean isosbestic points during irradiation. If these cases we suspect that the metal complexes serve as a source of abstractable hydrogen.

In order to gain a qualitative understanding of the electronic structure of a metal–bis(nitrene) complex, we performed SCF–Xα–DV calculations for $(\eta^5\text{-}C_5H_5)Co(NH)_2$. The geometry assumed was that used for the tetraazadiene complex[18] excluding the two remote ring nitrogens. In Table I are listed the atomic orbital contributions to the important frontier orbitals (coordinate system shown in D). The calculation



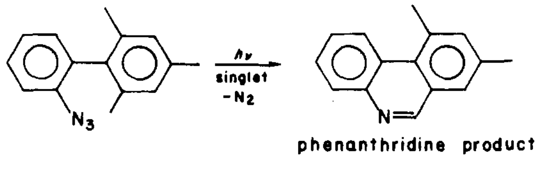
D

suggests that the metal dinitrene would be diamagnetic. It would also be expected to exhibit electrophilic tendencies by virture of the low-lying unoccupied 11a″ orbital. From the population analysis it can be seen that this orbital consists primarily of empty p orbitals on the $(NH)_2$ fragment as sketched in E. This supports the presence of a suitable nitrogen-localized acceptor orbital as required for the intermediate shown in C.



E

Extrusion of N_2 forms a general class of organic photochemical reactions. In this context, the photoextrusion of N_2 from metallotetraazadienes parallels the photoreactivity of tetrazolines and tetrazenes. The ring N–N distances[8] in Ib resemble the tetrazene geometry even though these molecules are formally denoted tetraazadienes. However, the reactivity of these metal-bound aryl nitrenes contrasts with that of free aryl nitrenes. Irradiation of the organic nitrene analogue to Ie produces the product[2]



Direct insertion into the ortho methyl C–C bond does not occur photolytically: abstraction of the methyl hydrogen leads to a phenanthridine derivative as the predominant photoproduct. When the photolysis is performed with triplet sensitization,[2] amine or azo derivatives form. These reactions further illustrate the unique reactivity of Ie. We could find no precedent for the photochemical reaction of Ib in the chemistry of aryl nitrenes;[2] however, the reaction of Ia appears to parallel that of *o*-azidobiphenyl as shown in eq 2. Thus, reactions of these Co–N aryl species may differ significantly from those of their organic brethren.

Correlation between Photochemical Behavior and Mass Spectral Fragmentation. It has not proved possible to correlate the photochemical reactions of $Fe(CO)_3(RN_4R)$ or $(\eta^5\text{-}C_5H_5)Co(RN_4R)$ complexes with the nature of the electronic states. In both systems intense electronic transitions in the visible and near-UV spectral regions can be attributed to excitation from one of several occupied orbitals into an empty metallacycle π* orbital.[18,20] Yet, the tricarbonyliron complexes lose CO with high quantum efficiencies (0.1–0.5),[25] and the cyclopentadienylcobalt derivatives extrude N_2 with low $(10^{-3}\text{–}10^{-4})^1$ quantum yields. Earlier we suggested[25] that this behavior might reflect the tendency for the excited state to decay by breaking the weakest bond in the complex. In a sense this is equivalent to a hot-ground-state model for excited-state reactivity.[26] We were curious to what extent the chemical decay pathways of the excited state resembled the fragmentation of the molecules upon electron impact in a mass spectrometer. Low electron energies (15 eV) were chosen in order to avoid excessive fragmentation.

Comparison of the mass spectra of $Fe(CO)_3[(CH_3)N_4(CH_3)]$, $Fe(CO)_3[(CD_3)N_4(CD_3)]$, and $Fe(^{13}CO)_{1.35}(^{12}CO)_{1.65}[(CH_3)N_4(CH_3)]$ unambiguously establishes the assignments of fragment ions arising from loss of N_2 or CO (supplementary material). Although extrusion of N_2 from the parent ion seems a likely possibility, the isotopic pattern for the ^{13}CO-enriched species proves that the *m/e* 198 ion corresponds to loss of CO from the parent ion, M. Dinitrogen extrusion contributes less that 10%, if any, to this peak. The mass spectrum of $Fe[P(OCH_3)_3]_3[(CH_3)N_4(CH_3)]$ also exhibits no detectable M − N_2 ion. In contrast to the iron complexes, the isoelectronic $(\eta^5\text{-}C_5H_5)Co[(CH_3N_4(CH_3)]$ (Ic) fragments with loss of N_2, $N_2(CH_3)_2$, and $(H_3C)N_4(CH_3)$. Expulsion of the $\eta^5\text{-}C_5H_5$ ligand does not readily occur.

Aryltetraazadiene analogues that contain the $(\eta^5\text{-}C_5H_5)Co$ moiety exhibit more complex behavior. The most intense ion in the mass spectra of compounds Ia, Ib, Id, and Ie (supplementary material) corresponds to loss of aryl azide, N_3R. Complexes Ia, Id, and Ie also show fragment ions resulting from loss of N_2; however, the perfluoro derivative, Ib, exhibits loss of N_2HF. Reexamination of the mass spectrum of complex Id, the R = $2,4\text{-}F_2C_6H_3$ species, also reveals a relatively large M − N_2HF fragment ion. These observations suggest that rapid elimination of HF [a $(\eta^5\text{-}C_5H_5)$ hydrogen and ortho fluorine] accompanies loss of N_2 in these complexes.

The mass spectral fragmentation pathways show considerable similarity to the photochemical behavior of these complexes. Ligand, L, loss dominates in the FeL_3-based metallatetraazadienes, and RN_4R fragmentation occurs in the $(\eta^5\text{-}C_5H_5)Co$ systems. In most cases the simplest molecular fragment (i.e., of highest *m/e*), derived by electron impact at 15 eV, resembles that produced by irradiation with 2–3-eV photons. This behavior can be rationalized in the context of the strong coupling model proposed.[25] For low-energy photochemical excitation, when there are few energetically ac-

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cessible decomposition routes, the weakest bond(s) breaks first. The abundance of fragment ions produced by electron impact is thought to reflect[27] a partitioning of excess energy of the parent ion into the energetically accessible decomposition pathways. Because of the greater excitation energy in mass spectrometry, numerous fragments form; however, the simplest (i.e., highest *m/e*) fragment usually results from the lowest energy decomposition pathway.

Acknowledgment. We thank the National Science Foundation (Grant 81-050698) and the Air Force Office of Scientific Research (Grant AFOSR-84-0021) for support of this work.

Supplementary Material Available: Tables of mass spectra fragmentation patterns for $Fe(CO)_3[(CH_3)N_4(CH_3)]$, $Fe[P(OCH_3)_3]_3[(CH_3)N_4(CH_3)]$, $(\eta^5\text{-}C_5H_5)Co[(CH_3)N_4(CH_3)]$, $(\eta^5\text{-}C_5H_5)Co[(C_6H_5)N_4(C_6H_5)]$, $(\eta^5\text{-}C_5H_5)Co[(C_6F_5)N_4(C_6F_5)]$, $(\eta^5\text{-}C_5H_5)Co[(2,4\text{-}F_2C_6H_3)N_4(2,4\text{-}F_2C_6H_3)]$, and $(\eta^5\text{-}C_5H_5)Co[(2,6\text{-}(CH_3)_2C_6H_3)N_4(2,6\text{-}(CH_3)_2C_6H_3)]$ (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Biology Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Structural Characterization of a Hexameric Cobalt–Carbonyl–Sulfur Complex, $[Co_3(CO)_9C](\mu_3\text{-}SCS)[Co_3(CO)_7S]$, Consisting of Two Tricobalt Carbonyl Clusters Dissymmetrically Linked by a Bridging SCS Group[1]

CHIN HSUAN WEI

Received December 8, 1983

The reaction of $Co_2(CO)_8$ with CS_2 at room temperature has resulted in the formation of the new hexameric cobalt–carbonyl–sulfur complex $[Co_3(CO)_9C](\mu_3\text{-}SCS)[Co_3(CO)_7S]$ containing a four-electron-donor SCS ligand dissymmetrically linked to two tricobalt clusters, as opposed to the structural isomer $[Co_3(CO)_9C](\mu_3\text{-}CS_2)[Co_3(CO)_7S]$, in which the linkage of the CS_2 group to the identical two tricobalt clusters is symmetric. The structure has been unambiguously characterized by X-ray analysis. The crystals contain four formula species in an orthorhombic cell of symmetry *Pnma* and of dimensions $a = 17.067$ (5) Å, $b = 13.074$ (5) Å, and $c = 13.493$ (5) Å. Full-matrix least-squares refinement of 32 independent atoms has yielded discrepancy indexes $R(F) = 0.056$ and $R(F^2) = 0.049$ based on 777 reflections with $F_o^2 \geq \sigma(F_o^2)$. The disordered-crystal model successfully utilized in the refinement assumes a random distribution of each molecule in one of two orientations related to each other by a crystallographic mirror plane. In the $Co_3(CO)_9C$ fragment, which is related to itself by the mirror plane, the Co_3C unit forms a tetrahedron with an idealized C_{3v}-$3m$ symmetry with its apical carbon being utilized to form a σ bond with one ligand sulfur atom, while in the $Co_3(CO)_7S$ fragment the triangle of basal cobalt atoms takes up an isosceles array due to distortion caused by the formation of cobalt–carbon and cobalt–sulfur bondings. As in other cases of statistically disordered structures, the resulting molecular configuration precludes the accurate determination of molecular parameters, thereby resulting in some anomalous geometries in the molecule.

Introduction

The reactions of dicobalt octacarbonyl with carbon disulfide under varying conditions have resulted in a number of organometallic complexes.[2-7] In addition to the sulfur-free bis(methinyltricobalt enneacarbonyl), $[CCo_3(CO)_9]_2$, the structure of which has been determined,[8] at least eight different sulfur-containing polynuclear complexes of the formula $Co_m(CO)_nC_pS_q$ have been separated by column chromatography[2,3] or by thin-layer chromatography[4-6] and their structures established by X-ray analyses: $SCo_3(CO)_9$,[9] $S_2Co_4(CO)_{10}$,[10] $[Co_3(CO)_8](\mu_5\text{-}CS_2)[Co_3(CO)_7S]$,[11] $[Co_3(CO)_9C](\mu_3\text{-}CS_2)[Co_3(CO)_7S]$,[11b] $Co_6C(CO)_{12}S_2$,[4] $SCo_6(C_2)(CO)_{14}$,[5] $Co_8(CO)_{21}C_3S_3$,[6] and $[Co_3(CO)_9C]_2SCO$.[12] The large assortment of these structures provides a dramatic illustration of the importance of metal–metal and metal–ligand interactions in determining the molecular configurations of the polynuclear cobalt carbonyl complexes.

In addition to the above-quoted complexes, another complex, initially formulated as $Co_4(CO)_{10}CS_2$ on the bases of its elementary analyses and IR absorption bands, was considered to be an isomer of $[Co_3(CO)_8](\mu_5\text{-}CS_2)[Co_3(CO)_7S]$[11,13] and was designated Ia.[2,3] Markó et al.[2] further reported that this complex contains no bridging carbonyl group and that the CS_2

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(1) (a) Research supported by the Office of Health and Environmental Research, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corp. (b) Wei, C. H. *Annu. Prog. Rep.—Oak Ridge Natl. Lab., Biol. Div.* **1967**, 325.

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(12) Gervasio, G.; Rossetti, R.; Stanghellini, P. L.; Bor, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1613.

(13) It should be pointed out that this compound was also initially proposed to have a molecular formula $Co_4(CO)_{10}CS_2$ and hence was assigned isomer Ib. The most pronounced difference between Ia and Ib was that in their IR absorption patterns in the bridging carbonyl stretching region the former showed no band while the latter showed a band at 1838 cm^{-1}. The molecular weight for either compound, however, was not reported.[2,3]

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