

## PHOTOCHEMICAL LOSS OF DINITROGEN FROM CYCLOPENTADIENYLCOBALT 1,4-DIARYLTETRAAZADIENES

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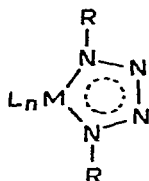
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### Summary

Irradiation of the thermally stable metallotetraazadiene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{RN}_4\text{R})]$  ( $\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{F}_5$ ) with visible or low-energy UV light, produces an unusual transformation to the diimine complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{HNC}_6\text{X}_4\text{NC}_6\text{X}_5)]$   $\text{X} = \text{H}$  (IVa),  $\text{F}$  (IVb). Disappearance quantum yields for both reactions are wavelength-dependent (IIIa  $\rightarrow$  IVa:  $\Phi_{366} = 2.4 \times 10^{-4}$ ;  $\Phi_{313} = 26 \times 10^{-4}$ ; IIIb  $\rightarrow$  IVb:  $\Phi_{366} = 9.8 \times 10^{-4}$ ;  $\Phi_{313} = 45 \times 10^{-4}$ ). Crossover experiments are consistent with an intramolecular rearrangement.

### Introduction

Although the thermal chemistry of metallocycles has been the subject of much research [1], there is a paucity of information about the photochemistry of these complexes [2]. Metallotetraazadiene complexes, I, particularly inter-

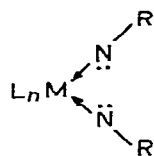


(I)

ested us because of the possibility of dinitrogen extrusion. By analogy to organic tetrazoline and tetrazene photochemistry [3], formation of the dinitrene, or diimido, II, might be anticipated.

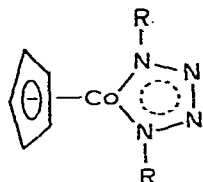
To date, only mononitrene or monoimido transition metal complexes have been prepared photochemically [4].

Cyclopentadienylcobalt 1,4-diaryltetraazadienes (aryl =  $\text{C}_6\text{H}_5$  (IIIa) or  $\text{C}_6\text{F}_5$



(II)

(IIIb)) were prepared by the reaction of  $C_6H_5N_3$  or  $C_6F_5N_3$  with  $(\eta^5-C_5H_5)-Co(CO)_2$  in benzene, and purified by chromatography on alumina.

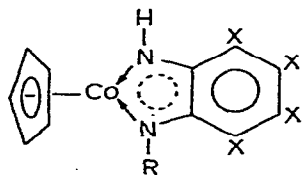


(III a, R =  $C_6H_5$ ;  
III b, R =  $C_6F_5$ )

Compound IIIa has been previously reported [5], and the analytical (C, H, N) analyses, mass spectrum, infrared,  $^1H$  and  $^{13}C$  NMR) data are entirely consistent with the metallotetraazadiene formulation. The structure of IIIb has been definitively established by a single crystal X-ray diffraction study [6].

Irradiation ( $1200\text{ nm} > \lambda > 350\text{ nm}$ ) of a benzene solution of IIIa, in vacuo, is accompanied by evolution of  $1.06 \pm 0.1$  mol of  $N_2$  gas (as determined by Toepler pumping) per mol of IIIa. As the photolysis proceeds, the color of the solution changes from green to violet and clean isobestic points are maintained at 692, 623, 476, 333 and 300 nm (Fig. 1). Spectroscopic data and thin layer chromatography indicate quantitative conversion to a single product, IVa. Isolated yields exceed 85%. Disappearance quantum yields of  $2.4 \times 10^{-4}$  and  $26 \times 10^{-4}$  are measured with 366 and 313 nm excitation, respectively. Complex IIIa does not react under similar conditions in the dark, nor upon refluxing in toluene for several hours. Pyrolysis in decalin results in slow decomposition and IVa is not obtained in significant quantities.

Elemental analysis (C, H, N) and mass spectrometry of IVa establish its molecular formula as  $(\eta^5-C_5H_5)Co(N_2(C_6H_5)_2)$ . The presence of an N-H stretch in the infrared spectrum, however, indicates that it is not a simple azobenzene complex. An identical compound may be prepared in low yields by the reaction between azobenzene and  $(\eta^5-C_5H_5)Co(CO)_2$  at  $160^\circ C$  [7]. The following structure was proposed on the basis of chemical degradation studies and precedent for similar rearrangements of azobenzene [8].



(IV a, R =  $C_6H_5$ , X = H  
IV b, R =  $C_6F_5$ , X = F)

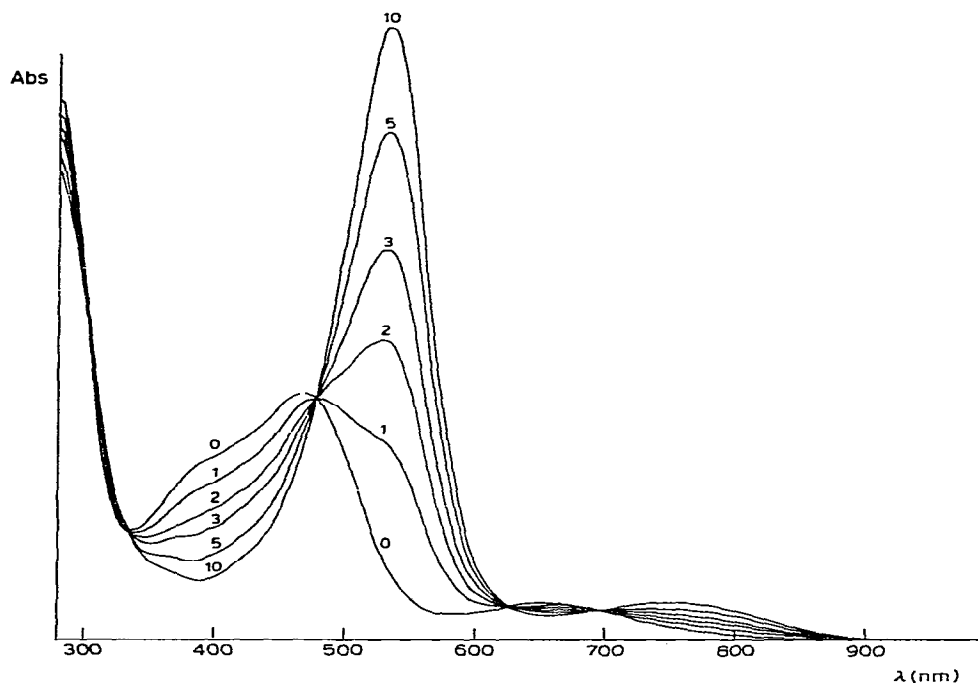


Fig. 1. Spectral changes for  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{N}(\text{C}_6\text{H}_5)\text{NNN}(\text{C}_6\text{H}_5))$  (Ia) upon irradiation ( $\sim 1200 \text{ nm} > \lambda > 350 \text{ nm}$ ) in benzene solvent. Numbers in figure indicate hours of irradiation.

Degradation conditions were, however, drastic and several products were observed [7]. Therefore, we performed some additional experiments to establish the proposed structure. Complex IVa may be prepared at room temperature from  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  and *N*-phenyl-*o*-phenylenediamine (30% yield) in the presence of oxygen. Previous yields of only 0.6% were reported [7] for this reaction in the absence of oxygen. Apparently oxidation of the diamine molecule to a diimine species must take place during the reaction. Although this reaction sequence is well-known in coordination chemistry, we are aware of no organometallic examples [9]. Perhaps most conclusive from a structural viewpoint, the proton-decoupled  $^{13}\text{C}$  NMR spectrum of IVa ( $\text{C}_6\text{D}_6$  solution) exhibits resonances at  $\delta$  128.59 (2C), 125.26 (2C), 125.07 (1C), 120.66 (1C), 119.32 (1C), 116.79 (1C), and 113.75 ppm (1C), relative to TMS, which are assigned to the phenyl carbons not bound to nitrogen atoms. Signals for the carbon atoms bound to nitrogen are weak because of long relaxation times. The proton-decoupled  $^{13}\text{C}$  spectrum of the chelated diimine correlates well with that of *N*-phenyl-*o*-phenylenediamine ( $\delta$  129.33 (2C), 125.74 (1C), 124.91 (1C), 119.32 (1C), 119.15 (1C), 116.15 (1C), and 115.22 ppm (2C)). An additional resonance at  $\delta$  76.41 ppm in the spectrum of IVa is assigned to the cyclopentadienyl carbon atoms. A summary of the synthetic pathways are shown in Fig. 2.

Irradiation of a benzene solution of IIIb ( $1200 \text{ nm} > \lambda > 350 \text{ nm}$ ) causes a change in color from green to violet, again accompanied by evolution of gas. Isobestic points at 696, 647, 555, 511, and 310 nm are initially maintained;

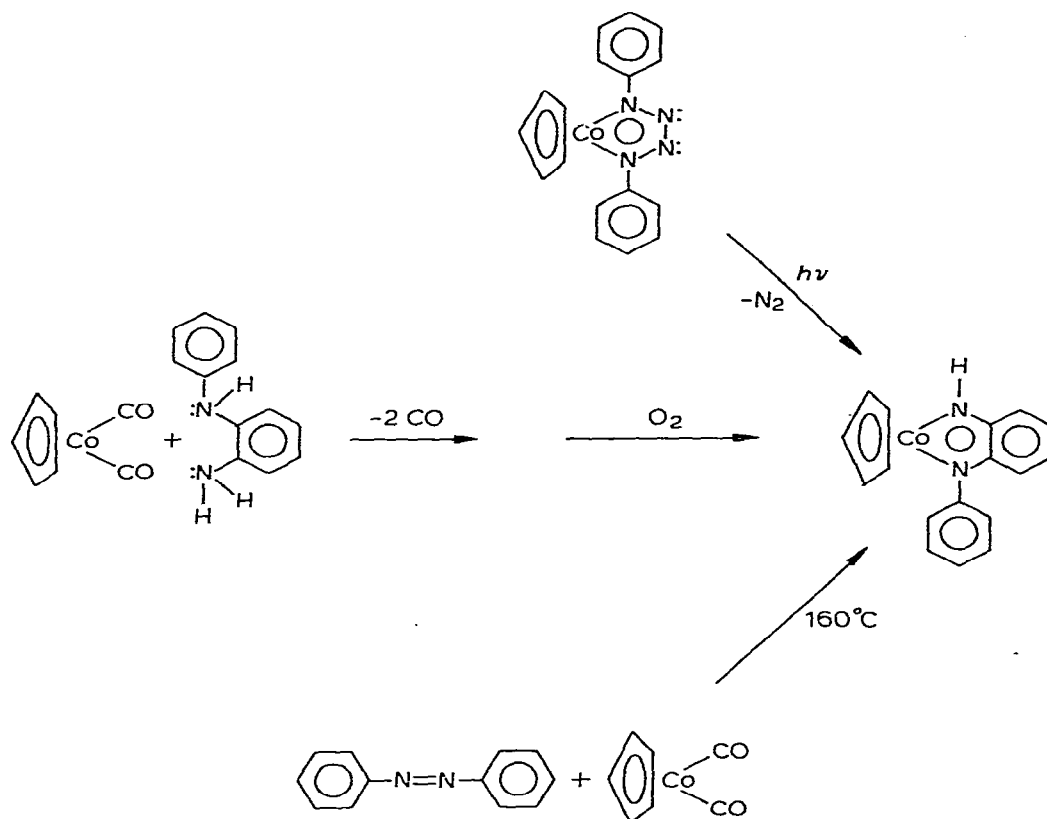


Fig. 2. Summary of the available synthetic routes to  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{HN}(\text{C}_6\text{H}_4)\text{NC}_6\text{H}_5)$ .

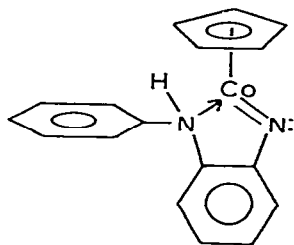
however, these disappear at long irradiation times (greater than 80% conversion). Spectral data indicate formation of a predominant photoproduct, IVb, and again, no reaction occurs in the dark nor upon refluxing in toluene for several hours. Quantum yields [12] for this process are markedly wavelength-dependent ( $\Phi_{366} = 9.8 \times 10^{-4}$ ;  $\Phi_{313} = 45 \times 10^{-4}$ ). Mass spectrometry, infrared and  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy support the formulation  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{HNC}_6\text{F}_4\text{NC}_6\text{F}_5)$  (for IVb) with a structure analogous to that of IVa. A preliminary refinement of the data from a single crystal X-ray diffraction study of IVb confirms this formulation. Absence of an N—F bond in IVb may result from hydrolysis during workup (chromatographic purification on alumina) as an N—F bond, if formed, would be susceptible to cleavage.

There are several interesting observations regarding the mechanism of nitrogen extrusion from these tetraazadiene complexes. Clean conversion of IIIa, IIIb to the diimine complexes IVa, IVb obtains photochemically but not thermally. Evidence for the intramolecular nature of the reaction derives support from the following crossover experiments. Irradiation of a benzene solution  $10^{-3} M$  in both IIIa and IIIb yields only IVa, IVb and unreacted materials, as monitored by thin layer chromatography. When IIIb ( $10^{-3} M$ ) is irradiated in the presence of azobenzene ( $10^{-2} M$ ), IVb is the only product. As evidence

against the intermediary of an azobenzene complex, we cite the lack of formation of IVa or IVb when  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{P}(\text{C}_6\text{H}_5)_3)_2$  is treated with either azobenzene or perfluoroazobenzene in benzene solvent at room temperature. Cyclopentadienylcobalt (bis)triphenylphosphine is kinetically labile at room temperature, unlike  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ .

Reactions performed in labeled solvents ( $\text{C}_6\text{D}_6$  or  $\text{CD}_3\text{OD}$ ) show no incorporation of deuterium into the cyclopentadienyl ring (determined by mass spectrometry of isolated product IVb). Participation of the cyclopentadienyl hydrogens is thereby eliminated as a possibility. Attempts to intercept a reactive intermediate with  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{CS}_2$  and other reagents have been unsuccessful, consistent with a facile intramolecular rearrangement.

A particularly attractive mechanism for the rearrangement of II would proceed via insertion of one coordinated nitrene into the *ortho* C—H bond of its partner. There is precedent for the aromatic C—H insertion process from the photochemistry of *o*-azidobiphenyls [11]. A subsequent [1,3] (NCoN) suprafacial hydrogen shift of the species depicted below would produce the desired product. Matrix isolation experiments are currently being conducted to further elucidate the mechanism.



## Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian CFT-20 spectrometer at 80 MHz.  $^{19}\text{F}$  NMR spectra were measured on a JEOL FX-90Q spectrometer operating at 84.26 MHz. Absorption spectra were recorded with a Perkin Elmer 320 spectrophotometer. Mass spectra were recorded by Dr. Hung on a Hewlett-Packard 5985 GC-MS system using 15 eV ionization energy. Elemental analyses were performed by H. Beck, Analytical Services Laboratory, Chemistry Department, Northwestern University, Evanston, Illinois.

Reactions and manipulations involving air-sensitive materials were carried out under an atmosphere of prepurified nitrogen, employing standard Schlenk ware and dry box techniques. Benzene and toluene solvents were distilled from sodium benzophenone ketyl under prepurified nitrogen. Cyclopentadienylcobalt dicarbonyl (Strem Chemicals Inc.) was vacuum distilled prior to use.

Unless otherwise specified, irradiations for the photochemical reactions described below were obtained from the output of an Osram 450-watt high pressure Xe arc lamp, employing a Corning O-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 Schlenk ware. Quantum yield measurements were carried out on samples exposed to air or rigor-

ously degassed. The presence of oxygen did not alter the results.

The quantum yield apparatus employed a 500 watt super pressure mercury arc lamp, driven by an Oriel 8530 DC power supply to maintain a constant ( $\pm 1\%$ ) light intensity. The output from the lamp was collimated, filtered through 10 cm of cooled distilled water and focussed onto the entrance slit of a monochromator from a Beckman DU-2 spectrometer. All of the optics were UV-grade fused silica or quartz. Samples were exposed to the monochromatic (10 nm band pass at 366 and 5 nm at 313 nm) radiation in 1 cm quartz cells thermostatted to  $25.0 \pm 0.5^\circ\text{C}$ . Compositions of the photolyzed solutions were monitored spectrophotometrically. Spectra of isolated reactant and product were measured independently to determine molar extinction coefficients. Light intensities were calibrated by ferrioxalate actinometries [12].

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). All products purified in this manner were air-stable, and no attempt was made to exclude oxygen at this stage of purification.

*Preparation of cyclopentadienylcobalt 1,4-diphenyltetraazadiene, ( $\eta^5\text{-C}_5\text{H}_5$ )- $\text{Co}(\text{C}_6\text{H}_5\text{N}_4\text{C}_6\text{H}_5)$  (IIIa)*

The literature procedure was used in the preparation of this compound [5]. Column chromatography and recrystallization from hexane or sublimation at  $120^\circ\text{C}$  ( $10^{-3}$  Torr) afforded microcrystals with green reflections.

*Preparation of cyclopentadienylcobalt 1,4-bis(pentafluorophenyl) tetraazadiene, ( $\eta^5\text{-C}_5\text{H}_5$ ) $\text{Co}(\text{C}_6\text{F}_5\text{N}_4\text{C}_6\text{F}_5)$  (IIIb)*

A 2 M benzene solution of pentafluorophenyl azide (4 ml, 9 mmol) was added slowly under nitrogen to a vigorously stirred solution of ( $\eta^5\text{-C}_5\text{H}_5$ ) $\text{Co}(\text{CO})_2$  (0.22 g, 1.2 mmol) in 10 ml of benzene. An exothermic reaction began immediately, subsiding after several minutes, and stirring was continued for an additional hour. The brown solution was concentrated under high vacuum, and subsequent purification of air-stable IIIb was carried out under room atmosphere. The concentrated solution was chromatographed; evaporation of the solvent from the eluent afforded microcrystals, having green reflections, in 30% yield. The sample for elemental analysis was dried under high vacuum for several hours. IIIb did not decompose in refluxing toluene (under nitrogen) over 24 h, as determined by thin layer chromatography. Anal. Found: C, 39.82; H, 1.02; N, 10.63. Calcd for  $\text{C}_{17}\text{H}_5\text{CoF}_{10}\text{N}_4$ : C, 39.71; H, 0.98; N, 10.90%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 4.17 ppm (s,  $\text{C}_5\text{H}_5$ ), relative to TMS.  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ):  $-148.51$  (4F, *ortho*),  $-156.17$  (2F, *para*),  $-162.53$  (4F, *meta*) ppm, relative to  $\text{CFCl}_3$ . Mass spectrum:  $m/e$  (rel intensity): 514 (3,  $M^+ \equiv \text{Co}(\text{C}_5\text{H}_5)(\text{C}_6\text{F}_5\text{N}_4\text{C}_6\text{F}_5)^+$ ), 466 (13,  $M^+ - \text{N}_2\text{FH}$ ), 305 (100,  $M^+ - \text{N}_3\text{C}_6\text{F}_5$ ), 291 (11,  $M^+ - \text{N}_4\text{C}_6\text{F}_5$ )).

*Photochemical preparation of cyclopentadienylcobalt N,N'-N-phenyl-o-phenylenediamine, ( $\eta^5\text{-C}_5\text{H}_5$ ) $\text{Co}(\text{HNC}_6\text{H}_4\text{NC}_6\text{H}_5)$  (IVa)*

A benzene solution (0.2 g per 20 ml) of IIIa, in Pyrex Schlenk ware, was degassed by means of two freeze-pump-thaw cycles. Irradiation was carried out

in vacuo or under an atmosphere of prepurified nitrogen to give a deep pink solution. Yields of IVa were in excess of 90% as determined by UV-visible spectroscopy and thin-layer chromatography. The only other species present was unreacted starting material. Isolated yields after column chromatography were 85–90%. Spectroscopic data agreed with those previously reported for IVa [8]. Anal. Found: C, 66.68; H, 5.12; N, 9.25. Calcd for  $C_{17}H_{15}CoN_2$ : C, 66.67; H, 4.94; N, 9.15%. Mass spectrum:  $m/e$  (rel intensity): 306 (100,  $M^+ \equiv Co(C_5H_5)-(CHNC_6H_4NC_6H_5)^+$ ), 181 (35,  $C_6H_5NC_6H_4N^+$ ).

*Preparation of IVa by the reaction of N-phenyl-o-phenylenediamine with cyclopentadienylcobalt dicarbonyl*

To 10 ml of toluene (under nitrogen) was added N-phenyl-o-phenylenediamine (1.45 g, 7.87 mmol) and  $(\eta^5-C_5H_5)Co(CO)_2$  (0.55 g, 3.05 mmol). No IVa formed at room temperature, as determined by thin-layer chromatography in the absence of oxygen. The solution was then exposed to air and vigorously stirred for 10 h, developing a deep red color. Purification by column chromatography and recrystallization in hexane afforded IVa in 30% yield.

*Photochemical preparation of cyclopentadienylcobalt N,N'-N-pentafluorophenyl-o-tetrafluorophenylenediamine,  $(\eta^5-C_5H_5)Co(HNC_6F_4NC_6F_5)$  (IVb)*

IIIb (0.5 g, 0.97 mmol) was dissolved in 200 ml of degassed benzene and placed in the well of a 450 Watt medium pressure Hg immersion lamp with Pyrex and water filters. The solution was irradiated for 6 h and its color transformed from green to red. The solution was then reduced in volume to approximately 30 ml on a rotary evaporator, and purified by column chromatography. Recrystallization from benzene/heptane or sublimation at 60°C ( $10^{-3}$  Torr) resulted in yields of 80%. The IR spectrum (in  $CH_2Cl_2$ ) shows a band at 3375  $cm^{-1}$  attributable to  $\nu(N-H)$ .  $^1H$  NMR ( $C_6D_6$ ): 4.13 ppm (s,  $C_5H_5$ ), relative to TMS.  $^{19}F$  NMR ( $C_6D_6$ ): -149.46 (2F), -159.03 (1F), -162.38 (1F), -163.57 to -164.11 (3F), -169.56 (1F), -171.99 ppm (1F), relative to  $CFCl_3$ . Anal. Found: C, 45.68; H, 2.12; N, 5.24. Calcd for  $C_{17}H_6CoN_2F_9$ : C, 43.6; H, 1.29; N, 5.98%. Mass spectrum:  $m/e$  (rel intensity): 468 (100,  $M^+ \equiv Co(C_5H_5)-(HNC_6F_4NC_6F_5)^+$ ), 325 (27,  $M^+ - NC_6F_3$ ), 149 (63,  $HC_6F_4^+$ ), 124 (27,  $M^+ - HNC_6F_4NC_6F_5$ ).

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