like that of the dimethylglyoxime complexes.[22] However, the displacement of H_2O in aquocobalamin[23] by various nucleophiles is more rapid by a factor of approximately 10^2 than it is in $Co(DH)_2(SO_3)OH_2^-$. The rapidity of reaction of aquocobalamin is not well understood, but it seems doubtful that it arises largely from the *trans* effect of an imidazole ligand.

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[22] G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, *Chem. Ber.*, **98**, 3324 (1965).

[23] W. C. Randall and R. A. Alberty, *Biochemistry*, **5**, 3189 (1966); **6**, 1520 (1967).

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π-Cyclopentadienyl(1,4-tetraazendiyl)cobalt

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The reaction of organic azides with $\pi\text{-}C_5H_5Co(CO)_2$ gave air-stable complexes of a molecular formula $\pi\text{-}C_5H_5CoN_4R_2$ ($R = CH_3$, C_6H_5). Physical measurements as well as chemical reactions of these complexes suggest a structure involving a 1,4-tetraazendiyl ($R\underset{|}{N}N{=}N\underset{|}{N}R$) ligand.

In a systematic study[1] on the interaction of a variety of heterocumulenes or -dienes with transition metal compounds, we have investigated the interaction of organic azides. During the course of our study, the reaction of methyl azide with iron carbonyl has been reported.[2] We found that the reaction of methyl azide with π-cyclopentadienylcobalt dicarbonyl occurred at the reflux temperature of *n*-hexane. A deep green crystalline complex (1) of a molecular formula $C_5H_5CoN_4(CH_3)_2$ was isolated in 69% yield by cooling the reaction mixture. It is soluble in common organic solvents and slightly soluble in water to give air-stable green solutions. It sublimes at 70–80° (5 mm). Phenyl azide reacted very readily with $\pi\text{-}C_5H_5Co(CO)_2$ even at room temperature with vigorous evolution of gas and heat. An air-stable deep brown complex, $C_5H_5CoN_4(C_6H_5)_2$ (2), was obtained in 36% yield through repeated recrystallizations. The complex **2** was soluble in benzene, tetrahydrofuran, and methylene chloride but insoluble in water. The solution was stable in air. Compound **2** was sublimable at 180° (1 mm). The ir spectra (*cf.* Experimental Section) of these complexes showed the presence of the π-cyclopentadienyl group. No prominent bands are observed in the region of 2500–1600 cm^{-1}, implying the absence of triple-bond systems (such as $C{\equiv}O$, $-N{\equiv}N$, $C{\equiv}N$), cumulene systems ($-N{=}N{=}N$, $-N{=}C{=}O$), and double-bond systems ($C{=}O$, $C{=}N$). The phenyl derivative (2) exhibited characteristic bands due to a monosubstituted phenyl group. The far-infrared bands at 393 and 430 cm^{-1} for **1** and at 360, 400, and 403 (sh) cm^{-1} for **2** may be due to the π-cyclopentadienyl group. Bands at 489, 582, and 599 cm^{-1} for **1** and at 563 cm^{-1} for **2** probably have some connection to ν_{Co-N}. The electronic spectrum of **1** in C_2H_5OH showed maxima at 227 (ε 18,000), 258 (ε 9850), 337 (ε 1260), 430 (ε 6800), and 660 mμ (ε 470). The two bands in the visible region are similar to those of chlorophyll a (λ_{max} at 432 and 663 mμ in methanol). The absorption maxima of **1** may be compared with those of the phenyl derivative occurring at 270 (ε 19,000), 470 (ε 7700), and 660 mμ (ε 750).

The nmr spectrum of **1** (in $CDCl_3$) showed two singlets at τ 5.11 and 5.87 in a ratio of 5:6, which are assigned, respectively, to $\pi\text{-}C_5H_5$ and two equivalent CH_3 protons. The chemical shift of the methyl protons is near the value for the recently reported iron carbonyl complex $(CH_3)_2N_4Fe(CO)_3$[2] (τ 5.6), for which resonance structures involving 1,4-dimethyltetrazadiene and 1,4-dimethyltetraazendiyl groups are proposed. In comparison with the chemical shift of the $N{-}CH_3$ group in aliphatic or aromatic amines (τ 7.1–7.8), the observed value (τ 5.87) is low. Somewhat related complexes, $[(CH_3N{=}CHCH{=}NCH_3)_3Fe^{II}]^{2+}$ and $(CH_3\underset{|}{N}N{=}NCH_3)_3Al$, have their methyl resonances[3] at τ 6.8 in D_2O[4a] and at τ 6.8 in benzene,[4b] respectively. Although the chemical shift value of the free ligand 1,4-dimethyltetraazadiene is not available, the τ value of **1** is considered to be quite low and the downfield shift may be caused by the complex formation. In many cases the downfield shift of N-alkyl or S-alkyl protons upon lone-pair coordination has been observed.[5,6] In a few particular examples,[7] it was observed that the "metal atom field effect" caused a considerable downfield shift.[8] Therefore, until the effect is

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[1] S. Otsuka, A. Nakamura, and T. Yoshida, *J. Organometal. Chem.* (Amsterdam), **7**, 339 (1966); *Inorg. Chem.*, **7**, 261 (1968).

[2] M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

[3] Converted to τ values (reported values: 3.21 ppm from sodium 2,2-dimethyl-2-silapentane-5-sulfonate and 4.03 ppm from benzene, respectively).

[4] (a) N. Tanaka and T. Ito, private communication; (b) F. E. Brinckman, H. S. Haiss, and R. A. Robb, *Inorg. Chem.*, **4**, 936 (1965).

[5] R. R. Holmes and R. P. Carter, *ibid.*, **2**, 1146 (1963).

[6] R. B. King and M. B. Bisnette, *ibid.*, **4**, 486 (1965); **5**, 293 (1966).

[7] (a) R. B. King, *J. Am. Chem. Soc.*, **85**, 1922 (1963); (b) S. Trofimenko, *ibid.*, **89**, 6288 (1967).

[8] The authors are grateful to a referee who pointed out these examples.

clarified more completely, it is difficult to find the unambiguous reason for the shift in our case. The phenyl derivative (2) is diamagnetic ($\chi_{\mathrm{sg}} = -0.257 \times 10^{-6}$) and showed nmr peaks at τ 5.7 (singlet) for π-cyclopentadienyl and at τ 2.5 (multiplet) for phenyl protons (in benzene and in CH_2Cl_2, respectively).

An intense parent peak was observed in the mass spectrum of **1** (*cf.* Table I). The fragmentation proceeded as the first step by the loss of 1 mol of nitrogen and one methyl group. Thus, fragment ions such as $CpCoN_2CH_3^+$, $CpCOH^+$, $CoC_3H_3^+$, and Co^+ are found. The easy loss of nitrogen is in line with the case of the phenyl derivative. The mass spectrum of **2** (*cf.* Table II) showed not only the parent peak but also weak peaks at higher *m/e* values. These and other salient peaks are assigned as shown in Table II. The pattern also shows nitrogen loss as the first fragmentation process. Elimination of phenyl group occurs rather sluggishly and peaks assigned as $C_5H_5CoNC_6H_5$, $C_5H_5CoC_6H_5$, and $CoNC_6H_4$ were observed. As seen from the mass spectral patterns, it is worth noting that nitrogens in the ligand are not protonated; hence species such as RNHN=NNHR or RNHNHN=NR are not involved as the ligand whose hydrogens might be difficult to locate by other means.

TABLE I

MASS SPECTRUM[a] OF π-$C_5H_5CoN_4(CH_3)_2$ (1)

m/e (relative abundance) probable assignment

211 (8) M + 1, 210 (72) M^+, 152 (77) $M^+ - N_2CH_3$, 125 (29) $CpCoH^+$, 124 (100) $CpCo^+$, 98 (68) $CoC_3H_3^+$, 97 (19) $CoC_3H_2^+$, 86 (17) $CoC_2H_3^+$, 66 (17) $C_5H_6^+$, 65 (13) $C_5H_5^+$, 59 (29) Co^+, 39 (22) $C_3H_3^+$

[a] Measured at an electron energy of 70 eV; ion source at 200°. Abundances of 10% or more of the base peak except M + 1 peak are listed.

TABLE II

MASS SPECTRUM[a] OF π-$C_5H_5CoN_4(C_6H_5)_2$ (2)

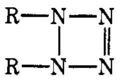
m/e (relative abundance) probable assignment

410 (0.3) $M^+ + C_6H_4$, 382 (0.5) $M^+ + C_6H_4 - N_2$, 334 (5) M^+, 306 (5) $M^+ - N_2$, 291 (3) $M^+ - N_3H$, 278 (4) $M^+ - 2N_2$, 227 (6) $M^+ - 2N_2 - H$, 218 (7) ?, 215 (10) $C_5H_5Co(NC_6H_5)^+$, 201 (10) $C_5H_5CoC_6H_5^+$, 170 (8) ?, 149 (9) $CoNC_6H_4^+$, 142 (100) $(C_5H_5C_6H_5)^+$, 124 (14) $C_5H_5Co^+$, 115 (22) $C_9H_7^+$, 97 (29) $CoC_3H_2^+$, 95 (28) CoC_3^+, 77 (34) $C_6H_5^+$

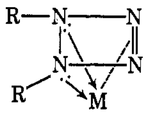
[a] Measured at an electron energy of 80 eV; ion source at 200°.

To get further information on the structure and bonding of these complexes, we have examined some of the chemical reactivity. Thus, concentrated hydrochloric acid dissolved complex **1** but the solution decomposed in a few minutes to give a purple solution. On dissolution in concentrated sulfuric acid, evolution of gas occurred and a deep violet solution resulted. Dilute aqueous sulfuric acid also dissolved the complex and the solution was stable for several hours. Thermal decomposition was observed at *ca.* 220° in air with evolution of a gas. The complex also showed no sign of change on prolonged irradiation with direct sunlight in moist air and also on treatment with metallic sodium in tetrahydrofuran. The phenyl derivative **2** underwent protolysis more easily than the methyl derivative in concentrated hydrochloric acid to give aniline. It is also decomposed by chloroform. An attempt to decompose **2** thermally in boiling *o*-dichlorobenzene resulted in an almost complete recovery. Irradiation with visible or ultraviolet light gave an unidentified deep red complex in a small amount. Vigorous evolution of nitrogen occurred on treatment of **2** with lithium aluminum hydride in ether or tetrahydrofuran. Aniline was the only identifiable, major organic product of this reaction.

Although several structures are conceivable for the complexes, all of the experimental evidence as described above appears to be best explained by the structure involving 1,4-dimethyl- or diphenyltetraazadiene coordinated to the π-C_5H_5Co group. The alternative structures involving, *e.g.*, 1,3-dimethyltriazeno ($CH_3NN{=}NCH_3$) plus the nitride ligand, *i.e.*, π-$C_5H_5Co{-}N(CH_3N_3CH_3)$, or methyl azide plus the methylimido group, π-$C_5H_5Co(NCH_3)(N_3CH_3)$, are excluded by the diamagnetism, nmr, and mass spectrum. Possibility for a structure involving ligation of an N_2 molecule in an "end-on" or a "side-on" manner is excluded primarily by the absence of any ir peaks in the 1600–2500-cm^{-1} region. A considerable thermal stability of the complexes also points to the improbability of N_2 ligation. As a further structural possibility, one can assume 1,2-dialkylcyclotetraazene

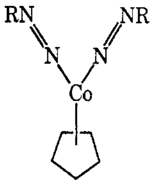


as a tridentate chelate ligand



This possibility cannot be excluded, but the chemical behaviors, *e.g.*, the protolysis and hydride reduction of **2** giving aniline, indicated it to be less probable. Neither hydrazobenzene nor phenylhydrazine is detected among the reaction products.

The bis-azo structure



should also be examined as a possibility.[9] The infrared and the mass spectra are reconcilable with this. However, the thermal stability and the inertness to the attack of strongly coordinating ligands suggest this structure to be less probable. The result of the protolysis of **2** giving gaseous nitrogen and aniline is difficult to explain with the bis-azo structure.

Now, we examine the mode of ligation of the tetra-

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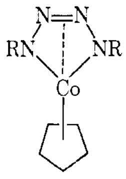
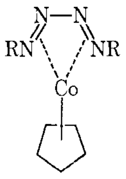
(9) The authors are indebted to a referee for this point.

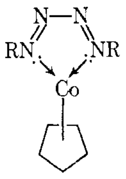
azadiene to a metal. Three different modes are shown below. Although no definite conclusion could be drawn, A is favored by the following reasons among these structures. (a) Nmr chemical shift of methyl protons in **1** suggests deshielding upon coordination and the π-complexed structure B to be unlikely.[1] However, the shift can also result from the magnetic anisotropy or "metal atom field effect."[7] (b) The protolysis and the hydride reduction prefer the metal amide structure A. (c) Inertness to strongly coordinating ligands such as CO (at 150 atm and 150°), 2,2′-dipyridyl, and $((C_6H_5)_2PCH_2)_2$ (150°) can be taken to favor structure A over structures B and C.



A



B



C

In the structure A, complex **1** may be regarded as an octahedral Co(III) complex with ligancy six rather than a Co(I) complex with ligancy five. If the proposed structure is correct, π coordination of the central N=N bond to metal is a remarkable feature of this type of complex.

To confirm the structure, single-crystal X-ray analyses of **1** and **2** have been attempted.[10] However, formation of twinned crystals has prevented the analysis in the case of **2**. The proposed structure of the complex finds a close relationship with the iron carbonyl complex of 1,4-dimethyltetraazadiene, $(CH_3)_2N_4Fe(CO)_3$,[2] prepared from iron carbonyls and methyl azide. Also in the iron carbonyl complex the tetraazadiene seems to act as the tetraazendiyl ligand.

The formation of the complex of the general formula π-$C_5H_5CoN_4R_2$ by the reaction of organic azides with π-$C_5H_5Co(CO)_2$ seems to be of a general applicability to produce hitherto unknown 1,4-dialkyl- or diaryltetraazadiene (tetraazabutadiene) stabilized as a metal complex. Attempts to prepare the similar tetraazendiyl complexes with rhodium, palladium, and nickel using their low-valent phosphine or carbonyl derivatives have been fruitless.

The reaction of carboethoxy azide $(N_3CO_2C_2H_5)$ with a wide variety of organometallic π complexes, such as carbonyls of chromium, iron, cobalt, and nickel, has also been examined. So far we are unable to isolate any well-defined complex. The reaction product with cyclopentadienylcobalt dicarbonyl was a deep brown solid whose insolubility prevented purification.

Experimental Section

Reagents.—Phenyl azide,[11a] methyl azide,[11b] carboethoxy azide,[11c] and cyclopentadienylcobalt dicarbonyl[12] were prepared by established methods. The solvents and other reagents were of reagent grade. The ir, nmr, mass, and electronic spectra were measured on a Hitachi Perkin-Elmer 225, a Jeol JNM-4H-100, a Hitachi RMU-7HR, and a Hitachi EPS-2U, respectively. Molecular weight was obtained by a vapor pressure osmometer, Hitachi Model-115, in benzene.

Reaction of Cyclopentadienylcobalt Dicarbonyl with Methyl Azide.—An *n*-hexane solution (8 ml) of cyclopentadienylcobalt dicarbonyl (0.1 g, 0.6 mmol) and of methyl azide (0.4 g, 7 mmol) was mixed and heated at a gentle reflux in nitrogen for 7 hr. The original reddish brown color gradually changed to dark brown. On cooling, the mixture yielded deep green crystals which were separated from the solution and washed with a small amount of *n*-hexane on a clay plate; yield, 80 mg (69%); mp 130–132° (in air). The solvent was removed from the solution under vacuum and the deep greenish brown residue was sublimed at 90° (5 mm) to give deep green crystals (5 mg). A further crop was obtained from the residue through alumina chromatography.

Anal. Calcd for $C_7H_{11}CoN_4$: C, 40.01; H, 5.28; N, 26.65; mol wt, 210. Found: C, 40.26; H, 5.40; N, 26.30; mol wt (mass), 210.

Reaction of Cyclopentadienylcobalt Dicarbonyl with Phenyl Azide.—To a solution containing 0.95 g (5 mmol) of cyclopentadienylcobalt dicarbonyl in 10 ml of benzene was added with stirring 2.4 g (10 mmol) of phenyl azide in air at ambient temperature. In 2–3 sec an exothermic reaction occurred with vigorous gas evolution. The gas evolution amounted to *ca.* 300 ml (12 mmol) in 5 min and the mixture became deep brown while the temperature rose to *ca.* 80°. When the reaction subsided in 10 min, some black precipitates formed. Then, the reaction mixture was allowed to cool down to room temperature to complete the precipitation under nitrogen. The supernatant liquor was decanted and the precipitates were washed with benzene and dried under vacuum over calcium chloride to yield 1.0 g of almost black powder (**2**). The additional 0.7 g of the less pure complex was obtained by concentration of the benzene filtrate. These crude products were recrystallized from benzene or tetrahydrofuran. The first portions of the crystals were found impure containing paramagnetic impurities. The middle fractions, mp 200° (yield 36%), were analytically pure having green reflection.

Anal. Calcd for $C_{17}H_{15}CoN_4$: C, 61.08; H, 4.49; N, 16.77; mol wt, 334. Found: C, 61.01; H, 4.69; N, 16.57; mol wt (vapor pressure osmometer), 357 (mass 334).

Infrared Spectra.—Compound **1** in Nujol mull: 324 w, 344 w, 393 s, 430 s, 489 m, 570 w, 582 s, 599 s, 817 s, 838 s, 843 vs, 855 s, 872 m, 1000 vs, 1011 vs, 1021 m, 1056 s, 1110 s, 1166 m, 1210 vs, 1269 vs, 1350 m, 1400 m, 1415 s, 1700 m, 3085 m. Compound **2** in Nujol mull: 360 m, 400 m, 403 m, 563 s, 696 vs, 754 m, 768 vs, 774 m, 839 m, 853 s, 868 m, 1010 m, 1016 m, 1060 m, 1075 m, 1112 w, 1227 w, 1266 w, 1450 s, 1580 m, 1590 w, 3060 w, 3110 w.

Acknowledgment.—Partial financial support of this research from the Matsunaga Science Foundation is gratefully acknowledged.

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[10] X-Ray investigation was done by Professor N. Kasai of Osaka University.

[11] (a) "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., p 710; (b) O. Dimroth and W. Wislicenus, *Ber.*, **38**, 1573 (1905); (c) W. Lwowsky and Y. W. Matlingly, *J. Am. Chem. Soc.*, **87**, 1947 (1965).

[12] R. B. King, *Organometal. Syn.*, **1**, 118 (1965).