Structural and Spectroscopic Study of Cyclopentadienylcobalt *N*-Phenyl-*o*-benzoquinone Diimines. A Case for Delocalized π Bonding

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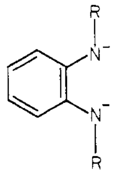
Received September 15, 1981

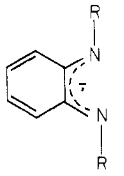
The compounds $(\eta^5\text{-}C_5H_5)Co(HNC_6X_4NC_6X_5)$, X = H and F, are produced by photolysis of $(\eta^5\text{-}C_5H_5)Co(C_6X_5N_4C_6X_5)$. The crystal structure of the complex $(\eta^5\text{-}C_5H_5)Co(HNC_6F_4NC_6F_5)$ has been determined at −60 °C by single-crystal X-ray diffraction techniques and shown to contain a bidentate α-diimine moiety, bonded through the nitrogen atoms to $(\eta^5$-cyclopentadienyl)cobalt. The metallacycle and perfluorophenylene ring are essentially coplanar. Short Co–N and N–C bond lengths in the former are indicative of delocalized π bonding. An intense $\pi \rightarrow \pi^*$ transition of the metallacycle dominates the electronic absorption spectrum. The C_5 portion of the C_5H_5 ring is planar; however, the H atoms are bent out of the plane toward the Co atom by an average of 0.07 Å. The C–C distances in the C_5H_5 ring show a significant distortion from idealized D_{5h} geometry. Crystals of $C_{17}H_6CoF_9N_2$ are triclinic, space group C_i^1—$P\bar{1}$, with two formula units in a unit cell of dimensions at −60 °C of $a = 9.832\ (3)$ Å, $b = 9.932\ (3)$ Å, $c = 8.922\ (3)$ Å, $\alpha = 103.88\ (1)°$, $\beta = 101.19\ (1)°$, and $\gamma = 74.02\ (1)°$. Least-squares refinement of 286 variables has led to a final value of the R index on F^2 of 0.054 for 5673 observations; the conventional R index on F is 0.043 for 4054 observations having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

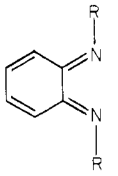
Much attention has been given to the chemistry and spectroscopic properties of α-diimine complexes of transition metals.[1-10] However, within this group the *o*-phenylenediimine, or *o*-benzoquinone diimine, species has received little attention.[11-17] The *o*-phenylenediimine ligand is particularly interesting in its versatility. There exist three potential redox forms for the isolated ligand: the reduced *o*-phenylenediimine dianion, Ia, the *o*-benzosemiquinone diimine radical anion, Ib, and the oxidized, neutral *o*-benzoquinone diimine, Ic. To facilitate discussion, we shall use the term "quinone diimine" to refer generally to ligands where the redox form has not been established. The term "α-diimine" refers to both aromatic and aliphatic diimines.



Ia

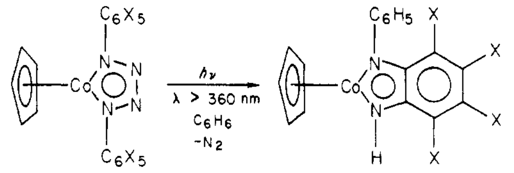


Ib



Ic

α-Diimine complexes are prepared most commonly by coordination of the appropriate diamine at the metal center followed by oxidative dehydrogenation.[11-13,18,19] Certain complexes of Mo, Fe, Co, and Rh will also react with azobenzene to produce coordinated *N*-phenyl-*o*-phenylenediimine.[16,20-22] Although free *o*-benzoquinone diimine has never been isolated,[23] other members of the α-diimine family are known and may be coordinated directly to transition metals.[1-6] We recently described a novel photochemical synthesis of the intensely colored compounds $(\eta^5\text{-}C_5H_5)Co(HNC_6X_4NC_6X_5)$, X = H and F, by irradiation of the tetraazadiene complex $(\eta^5\text{-}C_5H_5)Co(C_6X_5N_4C_6X_5)$, as shown in eq 1.[19] The unprecedented



(1)

IIa, X = H
b, X = F

IIIa, X = H
b, X = F

abstraction of a fluorine atom in the putative bis(nitrene) intermediate prompted us to elucidate the molecular structures of IIb and IIIb. Complex IIb exhibits unusually strong Co–N π interactions and partial π delocalization, in contrast to the localized bonding found in metallacyclopentadiene analogues.[24] We wondered whether the metalladiimine species IIIb would exhibit π-bonding in-

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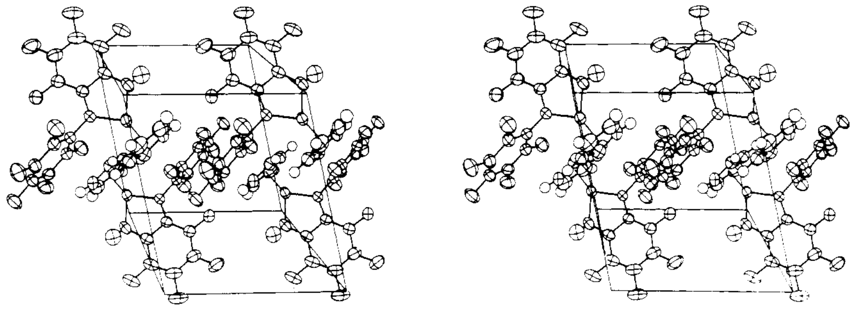

Figure 1. Stereoview of the unit cell of (η^5-C_5H_5)Co($HNC_6F_4NC_6F_5$) (IIIb). The *a* axis is almost vertical and the *c* axis is horizontal to the right. Vibrational ellipsoids are drawn at the 50% probability level; cyclopentadienyl hydrogen atoms are drawn at the 20% probability level for clarity.

termediate between the two extremes.

In previous work we showed that the covalent interaction between a metal dπ orbital (in a d^8 complex) and the empty π^* orbital of the tetraazadiene fragment leads to a low-lying unoccupied metallacycle π^* orbital.[24,25] Electronic transitions to this orbital result in characteristic electronic absorption bands. It seemed likely that the magenta colors of complexes IIIa and IIIb result from transitions analogous to those observed in the isoelectronic metallatetraazadiene complexes. Although electronic spectra of transition metal–bidentate α-diimine complexes have been extensively studied,[10,12,15-17] there have been little structural data to aid in the analysis. In this paper we report structural and spectroscopic parameters for IIIb and comparisons with structural results for IIb and spectroscopic data for IIa, IIb, and IIIa.

Experimental Section

The compounds (η^5-C_5H_5)Co($HNC_6X_4NC_6X_5$), X = H and F, were prepared by a previously described procedure.[19] Absorption spectra were recorded on a Perkin-Elmer 320 spectrophotometer at room temperature in various solvents and at 77 K in 2-methylpentane glasses.

Slow evaporation of heptane solutions of (η^5-C_5H_5)Co($HNC_6F_4NC_6F_5$) afforded dark violet crystals of rectangular prismatic habit suitable for X-ray diffraction study. Several attempts at recrystallization from benzene, hexane, and petroleum ether and by sublimation produced crystals of the aforementioned habit as well as hexagonal prisms. Preliminary X-ray photographic data showed the latter to be unsuitable for study, and all further investigations were carried out on the rectangular prisms.

X-ray Data Collection for (η^5-C_5H_5)Co($HNC_6F_4NC_6F_5$). An examination of a crystal by Weissenberg and precession methods revealed no symmetry, other than the trivial center of symmetry. For data collection, a crystal was mounted on a four-circle, computer-controlled Picker FACS-1 diffractometer. The first crystal, which was mounted in a stream of cold nitrogen at −150 °C,[26] shattered over a period of hours, presumably as a result of a phase change. A second crystal was mounted at −12 °C, and the intensities of two strong reflections were monitored as the temperature was lowered. Significant decreases in intensity were observed below −80 °C, at which time the crystal was visibly disintegrating. A third crystal was mounted at −60 ± 3 °C and remained intact throughout the data collection. The crystal, of rectangular prismatic habit, had faces of forms $\{10\bar{1}\}$, $\{1\bar{1}0\}$, and $\{110\}$, with distances between members of the forms of 0.294, 0.304, and 0.218 mm and a volume of 0.0255 mm^3.

Unit-cell dimensions were determined by a least-squares analysis of the angular positions of 15 hand-centered reflections[27] at −60 °C in diverse regions of reciprocal space ($25° \leq 2\theta(\text{Mo K}\alpha_1) \leq 29°$). A Delaunay reduction of these unit cell constants did not reveal any hidden symmetry. The assumption of space group C_i^1—$P\bar{1}$ was confirmed ultimately by the successful refinement of the structure. The complex $C_{17}H_6CoF_9N_2$, molecular weight 468.17 amu, crystallizes with two formula units in a cell of dimensions a = 9.832 (3) Å, b = 9.932 (3) Å, c = 8.922 (3) Å, α = 103.88 (1)°, β = 101.19 (1)°, γ = 74.02 (1)°, V = 805 Å^3, ρ_{obsd} = 1.87 (2) g/cm^3 (25 °C), and ρ_{calcd} = 1.932 g/cm^3 (−60 °C).

Data collection was carried out with techniques standard in this laboratory,[28] employing monochromatized Mo Kα radiation ($\lambda(\text{Mo K}\alpha_1)$ = 0.70930 Å). Intensities for reflections $\pm h,\pm k,+l$ were measured in the range $4.0° \leq 2\theta \leq 64.3°$. A scan speed of 2°/min in 2θ ranging from 1.0° below Kα_1 to 1.0° above Kα_2 was employed. The takeoff angle was 3.1°. Of the 5673 unique reflections collected, 4054 and $F_o^2 > 3\sigma(F_o^2)$. An absorption correction was applied to the data by using an absorption coefficient (Mo Kα) of 11.6 cm^{-1}; resultant transmission factors fell in the range 0.744–0.806.

Solution and Refinement of the Structure. The cobalt atom was located from an origin-removed Patterson synthesis, and all remaining nonhydrogen and hydrogen atoms were found by Fourier methods. The usual procedure for refinement was employed.[28] The function $\sum w(F_o^2 - F_c^2)^2$ was minimized in the final cycle of refinement, in which all nonhydrogen atoms were refined anisotropically and all hydrogen atoms isotropically. This refinement involved 286 variables and 5673 observations (including those for which $F_o^2 < 0$) and converged to values of R and R_w (on F_o^2) of 0.054 and 0.105, respectively, and to an error in an observation of unit weight of 1.33 electrons^2. Values of the conventional R and R_w indices on $|F_o|$ for those reflections having $F_o^2 > 3\sigma(F_o^2)$ are 0.043 and 0.053, respectively. A final difference electron density map revealed no peaks above 0.51 e/Å^3. The atomic positional and thermal parameters are listed in Table I. The root-mean-square amplitudes of vibration and a listing of the observed and calculated structure amplitudes are available.[29]

Results and Discussion

Description of the Structure of (η^5-C_5H_5)Co($HNC_6F_4NC_6F_5$). The overall structure of the (η^5-C_5H_5)Co($HNC_6F_4NC_6F_5$) complex, illustrated in Figure 1, contains two well-separated molecules in the unit cell. Interatomic bond distances and angles are compiled in Table II according to the labeling scheme defined in Figure 2. The coordination sphere of the cobalt atom can be viewed as trigonal with the center of a η^5-C_5H_5 ligand occupying one coordination site and a perfluorinated *N*-phenyl-*o*-phenylenediimine ligand coordinated through atoms N(1) and N(2) occupying the other two sites. The CoN_2C_2 metallacycle is planar (average displacement of an atom from the least-squares plane of the ring being 0.003 Å) and is essentially perpendicular to the cyclopentadienyl group, the dihedral angle between the two planes being 89.16°. Table III[29] presents information on selected, weighted least-squares planes through the mol-

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[29] Supplementary material.

Table I. Positional and Thermal Parameters for the Atoms of $(\eta^5\text{-}C_5H_5)Co(HNC_6F_4NC_6F_5)$

ATOM	X[A]	Y	Z	B11[B] OR B, $Å^2$	B22	B33	B12	B13	B23
CO	-0.192771(27)	0.210735(29)	0.011780(28)	93.13(32)	113.06(36)	88.26(35)	-20.78(24)	3.19(23)	24.44(25)
N(1)	-0.02642(19)	0.27003(19)	0.06866(20)	102.8(20)	122.5(22)	99.2(22)	-22.9(17)	-17.4(17)	11.4(18)
N(2)	-0.17669(16)	0.23406(18)	-0.18426(18)	82.0(16)	117.8(20)	90.3(19)	-32.1(15)	-2.3(14)	21.4(16)
C(11)	0.15247(22)	0.34311(22)	-0.03380(28)	88.0(21)	94.7(22)	179.4(36)	-21.7(18)	-19.2(22)	12.5(22)
C(12)	0.19140(23)	0.36847(24)	-0.15945(33)	85.3(22)	107.0(25)	244.3(47)	-31.2(19)	8.9(26)	40.9(27)
C(13)	0.10475(24)	0.35310(26)	-0.30372(31)	104.4(25)	147.1(31)	205.6(42)	-36.6(22)	29.1(26)	64.2(29)
C(14)	-0.01838(21)	0.31072(25)	-0.31881(26)	92.6(21)	148.6(30)	140.7(32)	-34.5(20)	2.9(20)	46.3(25)
C(15)	-0.06109(19)	0.28071(20)	-0.19229(23)	77.3(19)	97.0(21)	118.4(26)	-16.8(16)	3.7(17)	22.7(19)
C(16)	0.02566(19)	0.29993(19)	-0.04551(23)	83.1(19)	86.7(20)	126.6(27)	-15.9(16)	-5.9(18)	14.4(19)
F(11)	0.23479(15)	0.35755(17)	0.10635(18)	121.8(17)	174.0(21)	209.0(26)	-62.2(16)	-54.5(17)	19.4(19)
F(12)	0.31531(15)	0.40599(17)	-0.15027(22)	100.3(16)	174.8(21)	335.5(38)	-64.8(15)	0.4(19)	71.6(23)
F(13)	0.14490(17)	0.37938(22)	-0.42703(22)	152.1(21)	299.3(34)	274.3(35)	-93.0(22)	33.8(22)	140.6(29)
F(14)	-0.09712(15)	0.29564(20)	-0.46066(16)	136.6(19)	291.0(29)	133.8(20)	-93.8(19)	-7.9(15)	91.6(20)
C(21)	-0.39693(19)	0.31916(20)	-0.35142(21)	89.0(20)	100.6(22)	100.2(23)	-27.9(17)	9.7(17)	21.7(18)
C(22)	-0.49786(19)	0.29807(22)	-0.47902(22)	81.2(20)	123.6(25)	114.5(25)	-30.3(18)	3.1(17)	45.9(20)
C(23)	-0.48294(21)	0.16679(24)	-0.57766(21)	105.8(23)	151.8(28)	89.2(23)	-61.7(21)	-10.9(18)	35.2(20)
C(24)	-0.36698(22)	0.05797(22)	-0.54858(23)	123.1(25)	114.1(24)	99.7(25)	-46.3(20)	14.7(19)	8.0(19)
C(25)	-0.26601(21)	0.08039(21)	-0.42073(22)	93.4(21)	110.8(23)	108.5(24)	-20.1(17)	10.9(18)	19.8(19)
C(26)	-0.27763(19)	0.21140(20)	-0.31892(20)	79.9(19)	109.2(22)	86.0(21)	-30.3(16)	5.4(16)	22.0(17)
F(21)	-0.41384(14)	0.44651(13)	-0.25659(15)	134.1(17)	105.9(15)	139.1(19)	-19.5(12)	3.7(14)	4.7(13)
F(22)	-0.60957(13)	0.40571(14)	-0.50812(16)	95.9(14)	154.7(18)	178.8(21)	-14.8(13)	-14.1(14)	70.5(16)
F(23)	-0.58143(15)	0.14460(16)	-0.70133(15)	151.4(19)	195.3(22)	127.4(19)	-81.5(17)	-46.4(15)	39.7(16)
F(24)	-0.35261(17)	-0.06997(15)	-0.64522(16)	193.1(23)	134.3(18)	138.9(20)	-53.1(16)	10.4(17)	-21.0(15)
F(25)	-0.15253(15)	-0.02759(14)	-0.39669(17)	130.1(17)	125.6(17)	178.9(22)	9.2(13)	0.6(15)	5.4(15)
C(1)	-0.38924(25)	0.27286(27)	0.08533(27)	116.9(27)	147.0(31)	131.5(32)	-30.3(24)	31.1(23)	18.8(25)
C(2)	-0.28211(29)	0.25454(35)	0.20981(27)	149.7(34)	246.4(49)	97.3(28)	-72.8(34)	17.9(24)	23.8(30)
C(3)	-0.20305(32)	0.11030(43)	0.17897(38)	127.9(34)	307.4(65)	230.1(50)	-35.5(38)	-9.6(33)	194.1(50)
C(4)	-0.26488(32)	0.04251(32)	0.03223(39)	169.8(38)	129.7(35)	240.5(54)	-19.3(29)	64.6(37)	66.0(35)
C(5)	-0.37944(25)	0.14539(24)	-0.02225(26)	128.3(28)	134.1(27)	127.1(29)	-49.9(22)	20.7(23)	21.1(22)
H(1)	-0.4482(29)	0.3683(29)	0.0700(31)	5.86(61)					
H(2)	-0.2594(29)	0.3306(29)	0.3018(34)	7.38(64)					
H(3)	-0.1337(40)	0.0666(38)	0.2185(42)	8.34(94)					
H(4)	-0.2330(31)	-0.0468(31)	-0.0199(33)	6.28(68)					
H(5)	-0.4410(32)	0.1301(32)	-0.1187(37)	6.36(73)					
H	0.0218(33)	0.2780(32)	0.1570(37)	6.28(71)					

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

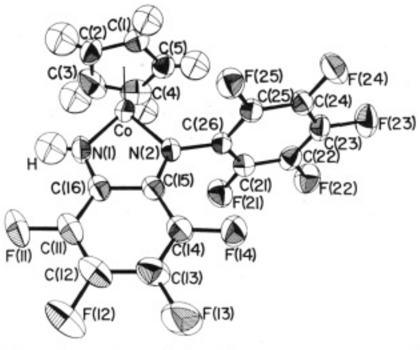

Figure 2. Drawing of an individual molecule of $(\eta^5\text{-}C_5H_5)Co(HNC_6F_4NC_6F_5)$ (IIIb) showing the labeling scheme. Vibrational ellipsoids are drawn at the 50% probability level.

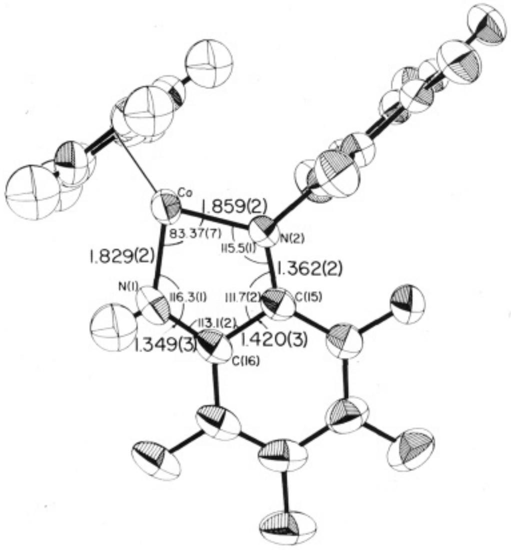

Figure 3. Selected bond distances (Å) and bond angles (deg) for the metallacycle moiety of $(\eta^5\text{-}C_5H_5)Co(HNC_6F_4NC_6F_5)$ (IIIb). Vibrational ellipsoids are drawn at the 50% probability level.

ecule. There is no crystallographically imposed symmetry but the molecule conforms to a local point group symmetry close to $C_s(m)$; a pseudo mirror plane bisects the C_5H_5 and C_6F_5 rings and lies in the plane of the metallacycle. The C–F distances of the pentafluorophenyl substituent range from 1.330 (2) to 1.342 (2) Å and average 1.338 (5) Å. The standard deviation of a single observation of 0.005 Å is obtained on the assumption that the distances averaged are from the same population. The fact that the standard deviation estimated in this way is more than twice that estimated from the inverse matrix indicates that either the standard deviations from the inverse matrix are underestimated or that there are possibly some significant variations. We favor the former explanation because similarly large standard deviations for the average distances are seen in the C–C (of C_6F_5) and C–F (of C_6F_4) distances.

The Metallacycle Fragment. Of particular interest is the bonding within the metallacycle and tetrafluorophenylene ring (Figure 3). Several modes of coordination

Table II. Intramolecular Bond Distances (Å) and Angles (Deg) in $(\eta^5\text{-}C_5H_5)Co(HNC_6F_4NC_6F_5)$

Bond Distances

Co-N(1)	1.829 (2)	N(1)-C(16)	1.349 (3)	C(26)-C(21)	1.390 (3)
Co-N(2)	1.859 (2)	N(2)-C(15)	1.362 (2)	C(21)-C(22)	1.373 (3)
Co-C(1)	2.046 (2)	N-C(av)	1.356 (9)	C(22)-C(23)	1.375 (3)
Co-C(2)	2.026 (2)	N(1)-H	0.835 (32)	C(23)-C(24)	1.370 (3)
Co-C(3)	2.014 (3)	N(2)-C(26)	1.416 (2)	C(24)-C(25)	1.377 (3)
Co-C(4)	2.044 (3)	C(16)-C(15)	1.420 (3)	C(25)-C(26)	1.387 (3)
Co-C(5)	2.056 (2)	C(16)-C(11)	1.404 (3)	C-C(av)	1.379 (8)
Co-C(av)	2.038 (17)[a]	C(11)-C(12)	1.350 (4)	C(21)-F(21)	1.330 (2)
C(1)-C(2)	1.383 (3)	C(12)-C(13)	1.399 (4)	C(22)-F(22)	1.339 (2)
C(2)-C(3)	1.419 (5)	C(13)-C(14)	1.360 (3)	C(23)-F(23)	1.338 (2)
C(3)-C(4)	1.425 (5)	C(14)-C(15)	1.398 (3)	C(24)-F(24)	1.342 (2)
C(4)-C(5)	1.393 (4)	C-C(av)	1.392 (27)	C(25)-F(25)	1.341 (2)
C(5)-C(1)	1.385 (3)	C(11)-F(11)	1.351 (3)	C-F(av)	1.338 (5)
C-C(av)	1.396 (20)	C(12)-F(12)	1.351 (2)		
C(1)-H(1)	0.99 (3)	C(13)-F(13)	1.341 (3)		
C(2)-H(2)	1.01 (3)	C(14)-F(14)	1.348 (3)		
C(3)-H(3)	0.77 (4)	C-F(av)	1.348 (5)		
C(4)-H(4)	0.90 (3)				
C(5)-H(5)	0.96 (3)				
C-H(av)	0.94 (10)				

Bond Angles

N(1)-Co-N(2)	83.37 (7)	F(11)-C(11)-C(16)	118.2 (2)	C(2)-C(1)-C(5)	109.4 (2)
Co-N(1)-C(16)	116.3 (1)	F(11)-C(11)-C(12)	121.0 (2)	C(1)-C(5)-C(4)	109.0 (2)
Co-N(2)-C(15)	115.5 (1)	F(12)-C(12)-C(11)	121.3 (2)	C(1)-C(2)-C(3)	107.1 (2)
Co-N(1)-H	127 (2)	F(12)-C(12)-C(13)	118.5 (2)	C(3)-C(4)-C(5)	106.7 (3)
Co-N(2)-C(26)	124.6 (1)	F(13)-C(13)-C(14)	120.4 (2)	C(2)-C(3)-C(4)	107.8 (2)
N(1)-C(16)-C(15)	113.1 (2)	F(13)-C(13)-C(12)	119.3 (2)	F(21)-C(21)-C(26)	119.1 (2)
N(2)-C(15)-C(16)	111.7 (2)	F(14)-C(14)-C(15)	120.7 (2)	F(21)-C(21)-C(22)	119.0 (2)
H-N(1)-C(16)	117 (2)	F(14)-C(14)-C(13)	118.0 (2)	F(22)-C(22)-C(21)	120.0 (2)
C(26)-N(2)-C(15)	119.9 (1)	N(2)-C(26)-C(25)	122.2 (2)	F(22)-C(22)-C(23)	120.2 (2)
C(15)-C(16)-C(11)	119.3 (2)	N(2)-C(26)-C(21)	121.0 (2)	F(23)-C(23)-C(22)	120.4 (2)
C(16)-C(15)-C(14)	118.0 (2)	C(21)-C(26)-C(25)	116.7 (2)	F(23)-C(23)-C(24)	119.9 (2)
C(16)-C(11)-C(12)	120.9 (2)	C(26)-C(21)-C(22)	121.9 (2)	F(24)-C(24)-C(25)	120.4 (2)
C(11)-C(12)-C(13)	120.2 (2)	C(21)-C(22)-C(23)	119.9 (2)	F(24)-C(24)-C(23)	119.6 (2)
C(12)-C(13)-C(14)	120.2 (2)	C(22)-C(23)-C(24)	119.8 (2)	F(25)-C(25)-C(26)	119.6 (2)
C(13)-C(14)-C(15)	121.3 (2)	C(23)-C(24)-C(25)	119.9 (2)	F(25)-C(25)-C(24)	118.5 (2)
		C(24)-C(25)-C(26)	121.8 (2)		

[a] The standard deviation in parentheses following an average value is the larger of that estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population.

Table IV. Comparison of Metallacycle Bond Distances (Å) in Quinone Diimine Complexes

	compd	M-N(av)	N-C-(phenylene)(av)	C(5)-C(6)[a]	N-C
IIIb	$(\eta^5\text{-}C_5H_5)Co(HNC_6F_4NC_6F_5)$[b]	1.844 (21)[c]	1.356 (9)	1.420 (3)	1.416 (2)
IV	$[Co(C_6H_4(NH)_2)_3][BPh_4]$[d]	1.877 (25), 2.079 (10)[e]	1.337 (19)	1.454 (18), 1.465 (17)	
V	$[Fe(CO)_3]_2\text{-}\mu\text{-}N,N'\text{-}(HNC_6H_4NC_6H_5)$[f]	2.001 (32)	1.447 (14)	1.363 (15)	1.441 (14)
VI	$Ni(C_6H_4(NH)_2)_2$[g]	1.832 (12)	1.38 (2)	1.40 (2) 1.43 (2)	
VII	$[Fe(CN)_4(C_6H_4(NH)_2)][Me_2Dabco]$[h]	1.909 (5)	1.321 (6)	1.443 (4)	

[a] Numbering scheme is that used in the text. [b] This work. $t = -60$ °C. All other structural data tabulated here were obtained at room temperature. [c] The standard deviation in parentheses following the average value for bond lengths of the same type in a given complex is the larger of that estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population. [d] Reference 13. [e] Co-N bond of the singly coordinated *o*-benzosemiquinone diimine ligand. [f] Reference 18. [g] Reference 22. [h] Reference 10.

of the diimine to the cobalt atom may be envisioned, differing in the formal oxidation state of the ligand and reflecting varying degrees of metal–nitrogen multiple bonding. That partial π delocalization occurs within the cobalt–bicyclic moiety is indicated by the Co–N(1) and Co–N(2) bond lengths (1.829 (2) and 1.859 (2) Å, respectively), which are much shorter than the expected range for M–N single bonds of 1.95–2.15 Å.[30] They may be contrasted with the Ni–N single bond length of 2.118 (9) Å in the complex $NiCl_2(H_2O)_2(C_6H_4[N(CH_3)_2]_2)$[31] and compared with the Co–N bond lengths of 1.802 (2) and 1.819 (2) Å in the symmetric tetraazadiene complex IIb.[24] Longer Co–N distances in the present system relative to those in complex IIb probably reflect the presence of competing π delocalization between the phenylene and metallacycle moieties.

The N(1)–C(16) and N(2)–C(15) bond lengths of 1.349 (3) and 1.362 (3) Å, respectively, are substantially shorter

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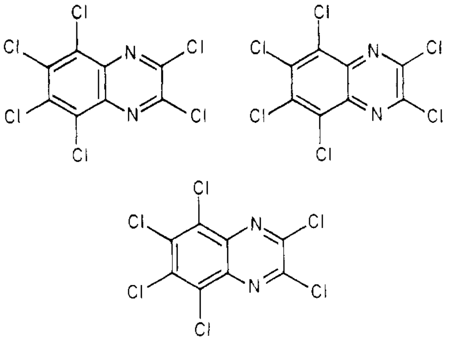
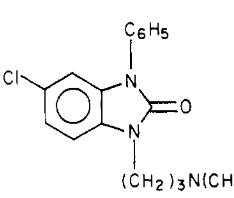
than the exocyclic N(2)–C(26) bond length of 1.416 (2) Å. The angles about atoms N(1) and N(2) and the planarity of the metallacycle are consistent with sp^2 hybridization of the nitrogen atoms. Hexachloroquinoxaline, a planar 10 π-electron aromatic molecule, exhibits an average N–C(phenylene) bond length of 1.368 (5) Å,[32] reflecting approximately 35% double-bond character, as calculated by assuming equivalent contributions of the three valence-bond resonance structures.[33]

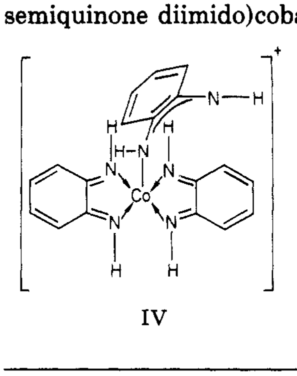


A longer average N–C bond length of 1.400 (4) Å is found between the sp^3-hybridized nitrogen and phenylene carbon atoms of the substituted benzimidazole molecule, Clodazone.[34]



The six-carbon ring of the tetrafluorophenylene moiety is planar,[29] essentially coplanar with the CoN_2C_2 plane (dihedral angle = 1.4°), enabling substantial π-orbital overlap between the rings. Variations of the C–C bond distances within the phenylene moiety, with short C(11)–C(12) and C(13)–C(14) bond lengths of 1.350 (4) and 1.360 (3) Å and a long C(15)–C(16) bond length of 1.420 (3) Å, implicate a contribution from the quinone diimine valence-bond form.

The structures of some related organometallic complexes containing the phenylenediimine moiety, compared in Table IV, exemplify the three different valence-bond configurations, Ia, Ib, and Ic, although the large errors associated with the bond lengths and angles in two of these structures must be considered. Bond lengths throughout the heterocycle in the present structure compare well with those found in bis(1,2-benzoquinone diimide)(1,2-benzosemiquinone diimido)cobalt(II), IV.[15] In contrast, the Fe–N and N–C distances in μ-(*N,N'*-dehydrosemidinato)-bis(tricarbonyliron), V, are consistent with Fe–N single bonds and sp^3-hybridized nitrogen atoms, revealing scant π delocalization in that molecule.[16] The bis(*o*-benzosemiquinone diimine)nickel(II) complex, VI, was so formulated on the basis of its redox chemistry and the planarity of the molecule, indicating that nickel is in a divalent rather than zerovalent oxidation state; however, the ligands still exhibit alternating double bonds rather than complete delocalization.[17] The bidentate ligand in (*o*-benzoquinone diimine)tetracyanoiron(II), VII, was formulated as having the completely oxidized structure, Ic.[12] All of the above structures, irrespective of their assignments, exhibit alternating double bonds to some degree. A molecular orbital description would ascribe the variations to differing amounts of π-back-bonding into the low-lying empty π* orbital of Ic. This closely resembles the bonding model advanced for the tetraazadiene complexes.[24,25]



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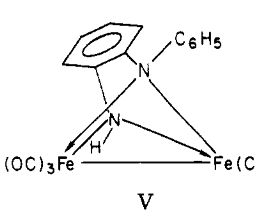
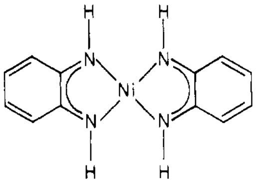
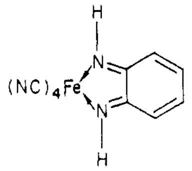


V



VI



VII

The Cyclopentadienyl Group. Differences in the Co–C distances to coordinated cyclopentadiene indicate a symmetric tilting of the C_5 ring such that atoms C(2) and C(3) are closest to, and atom C(5) furthest from, the cobalt atom. Two noteworthy features involve the variations in the carbon–carbon bond distances and bending of the hydrogen atoms out of the C_5-ring plane.

The lack of cylindrical symmetry in the $Co(HNC_6F_4NC_6F_5)$ moiety, which lifts the degeneracy of the cobalt $3d_{xz}$ and $3d_{yz}$ orbitals that interact with the cyclopentadienyl ligand, is the most plausible explanation for the observed asymmetry in the C–C distances. Detailed discussions of this phenomenon are available.[35–46]

Hydrogen atoms of the C_5H_5 group deviate from the five-carbon ring plane toward the Co atom by an average of 0.07 Å. The few structures containing accurate data for cyclopentadienyl hydrogen atom positions also show a trend of bending toward the metal.[24,46–48] Although less common for hydrogen substituents in C_5H_5,[49] bending away from the metal is frequently observed for the methyl substituents of coordinated pentamethylcyclopentadienyl

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Table V. Electronic Absorption Spectral Data (nm) for (η^5-C_5H_5)Co(N-N) Complexes

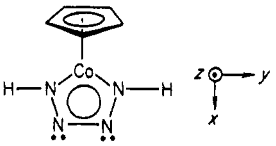
	N-N	solvent[a]	λ_{max}^1 (ϵ)	λ_{max}^2 (ϵ)
IIIa	($HNC_6H_4NC_6H_5$)	C_5H_{12}	758 (640)	528 (13 900)
		CH_3CN	757 (930)	534 (14 300)
IIIb	($HNC_6F_4NC_6F_5$)	C_5H_{12}	753 (670)	556 (13 500)
		CH_3CN	744 (930)	557 (17 600)
IIa	($C_6H_5N_4C_6H_5$)	$C_6H_5CH_3$	671 (690)	470 (6200)
IIb	($C_6F_5N_4C_6F_5$)	$C_6H_5CH_3$	657 (430)	470 (5190)
IIc	($CH_3N_4CH_3$)	C_6H_6	598 (260)	424 (9260)

[a] All spectra were measured at room temperature.

groups.[37,38,50] The (η^5-C_5H_5)Co(η^4-C_4H_4) complex exhibits a slight bending of the cyclopentadienyl hydrogen atoms toward the cobalt atom, while the cyclobutadiene hydrogen atoms are bent away.[35]

Electronic Spectra. In early studies of α-diimine complexes it was proposed that their intense colors were characteristic of π bonding between the unsaturated ligands and metal d electrons;[5,51] more recent work supports this proposal.[6-10] Norman, Chen, Perkins, and Rose[7] recently examined the electronic structure of the model bis(α-diimine) iron complex $Fe(N_2C_2H_4)X_2$. They concluded that significant Fe dπ → $N_2C_2H_4$ π* back-donation was present, owing to the essentially equivalent energies of C–N π* orbitals and Fe 3d orbitals.[7]

Electronic absorption spectra of the quinone diimine complexes IIIa,b and of the tetraazadiene complexes IIa,b exhibit several bands in the visible region (Table V). The molecular structure of complex IIIb displays the covalent nature of quinone diimine–metal bonding. Similarly strong cobalt–nitrogen interactions are found in the molecular structure of complex IIb. Calculations on the model complex (η^5-C_5H_5)Co(HN_4H) (coordinate system shown below) demonstrated the presence of a low-lying unoccupied metallacycle π* orbital (LUMO) of proper symmetry to accept electron density from the predominantly metal d_{z^2} and d_{xz} molecular orbitals.[24] A related SCC-DV-Xα study of $Fe(CO)_3(HN_4H)$ showed little overlap between metal d_{z^2} and N π* orbitals.[25] This is consistent with the weak intensity of λ_{max}^1 of IIa,b and a d_{z^2} → LUMO assignment. The intense visible absorption, λ_{max}^2, was assigned to a transition from a lower lying occupied molecular orbital, composed of metal d_{xz} and HN_4H π* contributions, to the LUMO, that is, the π → π* transition of the metallacycle. The significantly greater overlap between the d_{xz} and N π orbitals is reflected in the greater intensity of λ_{max}^2 relative to λ_{max}^1.



In comparison with the visible spectra of metallatetraazadiene complexes IIa,b, the two low-energy absorptions of complexes IIIa,b are systematically red-shifted, their separation ($\lambda_{max}^1 - \lambda_{max}^2$) remaining essentially constant. This bathochromic shift is consistent with extension of the conjugated chromophore. Note that a similar shift is observed on substitution of phenyl for methyl substituents in the tetraazadiene complexes. A simple charge transfer assignment of the visible absorption bands of IIIa,b is ruled out by the insensitivity of the band energies to solvent polarity and electronegative ring substituents. Absorption bands in the spectra of complexes IIIa,b at 77K in 2-methylpentane glasses are not significantly shifted in energy relative to their room-temperature values, although the expected narrowing is observed. The above data support assignments of the visible absorption bands of IIIa,b as a d_{z^2} → metallacycle π* transition for λ_{max}^1 and a metallacycle π → π* transition for λ_{max}^2, analogous to our assignments of the tetraazadiene spectra.

Acknowledgment. We thank the National Science Foundation for research support (Grants CHE78-01615 and 81-05069 to W.C.T. and CHE80-0967 to J.A.I.).

Supplementary Material Available: Table III, the table of least-squares planes, and Table VI, the root-mean-square amplitudes of vibration, and a listing of the observed and calculated structure amplitudes (23 pages). Ordering information is given on any current masthead page.

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