The principal objective in deriving the data presented in Table I is the determination of metal-hydrogen homolytic bond energies for a large number of organometallic complexes. The base strengths as well as other reactions observed with many of these species are also of interest. These will be discussed separately.

Acknowledgment. This work was supported in part by the United States Department of Energy. A.E.S. thanks the National Science Foundation for a Graduate Fellowship (1976–1979) during which time many of these data were determined.

Delocalized π Bonding in Tetraazadiene Metallocycles

Michal E. Gross, William C. Trogler,* and James A. Ibers

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received July 3, 1980

Whether there is delocalization of π bonding in complexes which contain a metallocyclic moiety remains an intriguing question. Metallocyclopentadienes have been extensively studied,[1] and the available evidence[2] seems to indicate little π delocalization in these sytems. Because of the importance of metallocycles in organometallic reactions and mechanisms,[3] it is crucial that we understand the bonding factors which influence their formation and structures. The nitrogen-based metallotetraazadiene complexes have received surprisingly little attention[4-8] but offer several points of interest: (1) the viability of several valence-bond configurations;[4-8] (2) the elucidation of photochemical reaction pathways from low-lying excited states;[9] (3) the anomalous stability of the unsaturated RN_4R ligand fragment when coordinated.[10]

(Cyclopentadienyl)cobalt 1,4-diaryltetraazadienes [aryl = C_6H_5 (Ia) or C_6F_5 (Ib)] were prepared by a literature method.[11] A single-crystal X-ray structural determination (−150 °C) of Ib[12] exhibits the features shown in Figure 1. The coordination sphere of the cobalt ion can be described as a distorted trigonal bipyramid with the η^5-cyclopentadienyl ligand occupying three coordination sites and the bidentate tetraazadiene ligand coordinated through the 1,4-nitrogen atoms. The metallocycle is essentially planar with the average displacement of an atom from the least-squares plane of the ring being 0.009 Å; this plane is almost perpendicular to that of the cyclopentadienyl ring (dihedral angle = 85.6°).

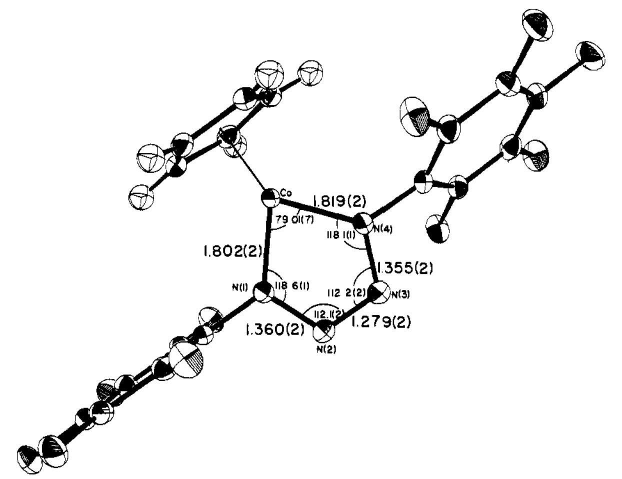
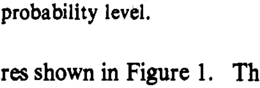


Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)Co((C_6F_5)N_4(C_6F_5))$. Selected distances (Å) and angles (deg) are shown. Thermal ellipsoids are drawn at the 50% probability level.

Of particular interest is the bonding within the metallocycle. The N(2)–N(3) bond [1.279 (2) Å] is considerably shorter than the N(1)–N(2) [1.360 (2) Å] and N(3)–N(4) [1.355 (2) Å] bonds, the latter two being equivalent within experimental error. These correspond, respectively, to one double and two single nitrogen–nitrogen bonds.[13] Extremely short Co–N(1) [1.802 (2) Å] and Co–N(4) [1.819 (2) Å] bond lengths and the planarity of the ring provide compelling evidence for Co–N multiple bonds, as a Co–N single bond would be expected[14] to lie within the 1.95–2.15-Å range. Steric congestion or differential conjugation with the two aryl substituents may be responsible for the small difference between the Co–N(1) and Co–N(4) bond lengths.[15] Structural data therefore indicate the diene resonance form to be inappropriate.



The complex $[Ir(RN_4R)(CO)(P(C_6H_5)_3)_2][BF_4]$, R = p-FC_6H_4, was found[5] to have one short N–N bond; however, the Ir–N bond lengths were not indicative of multiple bonding. Three N–N bond lengths in a $Ni(RN_4R)_2$, R = 3,5-$Me_2C_6H_3$, complex are equivalent;[8] however, clear evidence for metal–nitrogen π bonding was not present because of strong conjugation with the coplanar aryl substitutents. The first X-ray structural determination[4] of a tetraazadiene complex, $Fe(CO)_3(CH_3N_4CH_3)$, exhibited short metal–nitrogen bond lengths, but the large standard deviations did not permit an assessment of nitrogen–nitrogen bond orders.

In order to obtain a better understanding of the apparently strong π-acceptor properties of the RN_4R ligand, we performed SCC DV Xα calculations[16] on $(\eta^5\text{-}C_5H_5)Co(HN_4H)$ and the

---

[1] A few examples may be found in: (a) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157–167. (b) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298–1303. (c) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454–2459.

[2] Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39–45.

[3] Some examples are found in: (a) Mango, F. D. *Coord. Chem. Rev.* **1975**, *15*, 109–205. (b) Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677–690. (c) Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808–5815. (d) Grubbs, R. H.; Miyashita, A. *Ibid.* **1978**, *100*, 7416–7418.

[4] Relevant bond distances (Å): average Fe–N, 1.83 (3); average N–N, 1.32 (7). Doedens, R. J. *Chem. Commun.* **1968**, 1271–1272.

[5] Relevant bond distances (Å): Ir–N(1), 1.941 (13); Ir–N(4), 1.971 (10); N(1)–N(2), 1.400 (16); N(3)–N(4), 1.350 (16); N(2)–N(3), 1.270 (16). Einstein, F. W. B.; Sutton, D. *Inorg. Chem.* **1972**, *11*, 2827–2831.

[6] Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1971**, 1805–1809.

[7] Cenini, S.; Fantucci, P.; La Monica, G. *Inorg. Chim. Acta* **1975**, *13*, 243–245 and references therein.

[8] Relevant bond distances (Å): Ni–N(1), Ni–N(4), 1.853 (3); N(1)–N(2), N(3)–N(4), 1.325 (3); N(2)–N(3), 1.319 (4). Overbosch, P.; van Koten, G.; Overbeek, O. *J. Am. Chem. Soc.* **1980**, *102*, 2091–2093.

[9] Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.*, in press.

[10] The free tetraazadiene ligand is unknown. The cobalt complexes reported here do not decompose upon refluxing in toluene for several hours.

[11] Otsuka, S.; Nakamura, A. *Inorg. Chem.* **1968**, *7*, 2542–2544.

[12] Dark green crystals of $(\eta^5\text{-}C_5H_5)Co((C_6F_5)N_4(C_6F_5))\cdot{}^1/_2C_6H_6$ were obtained by evaporation of a benzene solution of Ib; space group $P2_1/c$, $Z = 4$, unit cell dimensions: $a = 8.612$ (4) Å, $b = 22.687$ (12) Å, $c = 9.820$ (6) Å, $\beta = 91.58$ (2)° (−150 °C). Density obtained by flotation in $ZnCl_2$ solution (25 °C): 1.71; d(calcd) (−150 °C): 1.796 g cm^{-3}. The data set was collected on a computer-controlled Picker diffractometer with the crystal at −150 °C. A total of 5367 unique reflections in the range $3.5 \leq 2\theta \leq 59°$ was measured. The structure was solved and refined by standard procedures. The final cycle of anisotropic refinement (on F^2), in which the hydrogen atoms were refined isotropically, resulted in convergence to R (on F^2) of 0.047 and R_w (on F^2) of 0.086 for the 315 variables and 5367 observations. Conventional agreement indices on F for those reflections with $F_o^2 > 3\sigma(F_o^2)$ are $R = 0.033$ and $R_w = 0.043$.

[13] Compare, for example, with tetrakis(trimethylsilyl)tetrazene: N–N single bond, 1.394 (5) Å; N–N double bond, 1.268 (7) Å. Veith, M. *Acta Crystallogr., Sect. B* **1975**, *31*, 678–684.

[14] Davis, B. R.; Payne, N. C.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2719–2728.

[15] The two C_6F_5 groups describe dihedral angles of 90.2 and 61.4° with the CoN_4 plane. We thank Professor Roald Hoffmann for pointing out the possibility of residual conjugation with the nonperpendicular aryl group.

0002-7863/81/1503-192$01.00/0

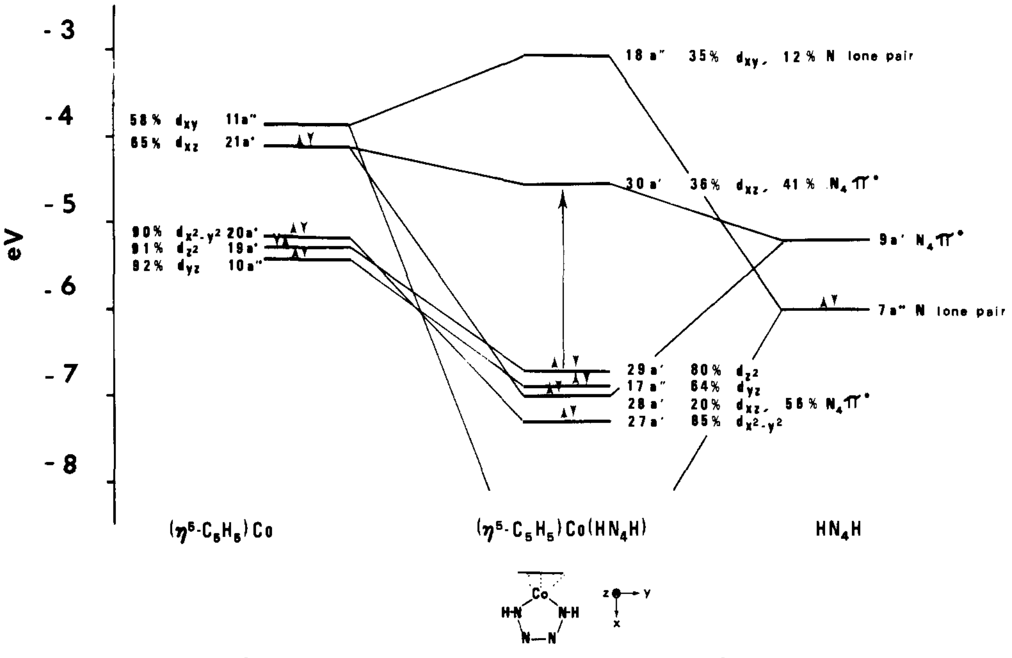
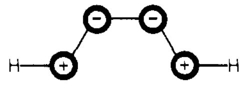


Figure 2. Orbital energy diagrams of the $(\eta^5\text{-}C_5H_5)Co$ and HN_4H fragments as well as of the $(\eta^5\text{-}C_5H_5)Co(HN_4H)$ molecule. Orbital symmetries (C_s) and their atomic compositions are given. The orientation of the metal x,y,z coordinates is shown at the bottom. All calculations employed the SCC DV Xα method.

$(\eta^5\text{-}C_5H_5)Co$ and HN_4H fragments. Frontier orbital energies and their atomic compositions are depicted in Figure 2. When the HN_4H and $(\eta^5\text{-}C_5H_5)Co$ fragments overlap, an important bonding interaction occurs between the 7a″ lone-pair orbitals of the 1,4-nitrogen atoms and the metal d_{xy} function. This constitutes the usual dative σ-type bonding interaction between an electron-pair donor and electron-pair acceptor. The extraordinary feature of the HN_4H fragment is the presence of a low-lying unoccupied 9a′ (π*) orbital with the nodal pattern



This lowest unoccupied molecular orbital (LUMO) is of proper symmetry and energy to accept electron density from the highest occupied molecular orbital, 21a′, (HOMO) of the $(\eta^5\text{-}C_5H_5)Co$ fragment. Because of the nodal pattern of the acceptor orbital, short N(2)–N(3) and long N(1)–N(2) and N(4)–N(3) bonds will be found when the 9a′ orbital is occupied. Structural data are consistent with this description. Another consequence of the HOMO–LUMO interaction is the introduction of $Co(d_{xz})\text{-}N_4(p_z)$ π bonding. The short Co–N bond lengths provide experimental confirmation of this view. Note that all of the occupied cobalt d orbitals are stabilized (shown in Figure 2), owing to the removal of electron density by the HN_4H ligand. Our bonding model readily accounts for the variable N–N and metal–nitrogen bond lengths found in other reported tetraazadiene structures if one permits differing degrees of the metal d → N_4 (π*) interaction.

Although one can describe bonding tendencies in terms of π-acceptor properties of the HN_4H fragment, the molecular orbitals 28a′ and 30a′ are extensively mixed (see Figure 2). They are the frontier orbitals of a 6π-electron five-membered ring. The calculation further predicts low-lying electronic excitations to 30a′, a metallocycle π* orbital. All of the complexes $(\eta^5\text{-}C_5H_5)Co(RN_4R)$ (R = CH_3, C_6H_5, C_6F_5) exhibit electronic absorption bands throughout the visible spectral region. For example, the lowest transition in the complex with R = CH_3 is found at 2.07 eV and transition-state calculations[17] place the 29a′ → 30a′ transition at 2.38 eV. It is interesting that the photochemical reactions we have observed for these complexes lead to extrusion of N_2 from the metallocycle.[9] Perhaps this reflects the 41% HN_4H π* character of the 30a′ orbital.

In summary, $(\eta^5\text{-}C_5H_5)Co((C_6F_5)N_4(C_6F_5))$ is the first complex to exhibit such pronounced metal–nitrogen π bonding that the tetraazadiene resonance form is completely inappropriate. In fact, no single valence bond structure satisfactorily describes the situation.[18] Nonempirical Xα calculations for the model system show appreciable occupation of the lowest π* orbital of the tetraazadiene fragment. Other metallotetraazadiene complexes have exhibited lesser degrees of metal–nitrogen π bonding. We suspect that a range of structures will be found for the nitrogen-based systems, depending on the amount of π delocalization present. The corresponding ligand π-acceptor orbital in metallocyclopentadiene systems does not lie nearly so low in energy,[2] and this may be a reason for the lack of delocalized bonding in such systems. If the above results can be used as a guide, then decreasing the metal(HOMO)–C_4R_4(LUMO) energy gap (e.g., one could use metals in very low formal oxidation states) might promote delocalized π bonding in metallocyclopentadiene complexes.

Acknowledgments. This research was supported by the National Science Foundation (Grant CHE78-01615 to W.C.T., Grant CHE76-10335 to J.A.I.). Acknowledgment is made to the donors of the Petroleum Research Fund, adminitered by the American Chemical Society, for partial support of this work. W.C.T. thanks the Rohm and Haas Company for a summer (1980) faculty fellowship.

Supplementary Material Available: Tables of positional and thermal parameters for $(\eta^5\text{-}C_5H_5)Co((C_6F_5)N_4(C_6F_5))$ and eigenvalues and eigenvectors for $(\eta^5\text{-}C_5H_5)Co(HN_4H)$ (12 pages). Ordering information is given on any current masthead page.

---

(16) Details pertaining to the calculational procedure and orbital analysis may be found in: Averill, F. W.; Ellis, D. E. *J. Chem. Phys.* **1973**, *59*, 6412. Trogler, W. C.; Ellis, D. E.; Berkowitz, J. *J. Am. Chem. Soc.* **1979**, *101*, 5896–5901. In our calculations the molecular geometry of the title complex was idealized to C_s symmetry and N–H bond lengths were taken as 1.01 Å. A complete listing of molecular wave functions and eigenvalues is available as supplementary material. Only one prior calculation of a tetraazadiene complex, in which a CNDO technique was used, has been reported: Armstrong, D. R.; Perkins, P. G.; Scott, J. M.; Stewart, J. J. P. *Theor. Chim. Acta* **1972**, *26*, 237–248. An interesting Hückel analysis of an MN_4 ring has been provided by: Shustorovich, E. M.; Kagan, G. I.; Kagan, G. M. *J. Struct. Chem. Engl. Transl.* **1970**, *11*, 95–105.

(17) A spin-restricted transition-state calculation was performed for the lowest allowed transition in $(\eta^5\text{-}C_5H_5)Co(HN_4H)$.

(18) Trogler, W. C.; Johnson, C. E.; Ellis, D. E. *Inorg. Chem.*, in press. This work discusses, at length, the six possible resonance structures.