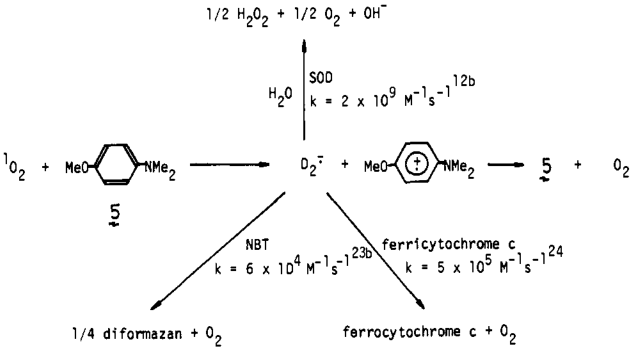
Scheme II



n-propylamine, did not produce $O_2^-\cdot$ by the reaction of **2** under similar conditions.[40] Note that *N*,*N*-dimethylbenzylamine[42] and *n*-propylamine[43] are known to be readily oxidized by $^1O_2$, leading to α-oxidation products probably via hydroperoxidic intermediates. Grossweiner[44] has proposed that the reaction of tryptophan with $^1O_2$ may proceed via an electron-transfer process. However, the reaction of tryptophan (3 mM), **2** (2.5 mM), and NBT (1 mM) in phosphate buffer (pH 7.5) under the specified conditions never produced diformazan. Likewise, Jefford and Boschung[45] have suggested the formation of $O_2^-\cdot$ by the reaction of $^1O_2$ with rose bengal. Under our conditions the reaction of **2** (2 mM) and rose bengal (0.045 mM) did not produce any trace of diformazan. These observations might imply that an electron-transfer reaction giving rise to $O_2^-\cdot$ is only possible for substrates with oxidation potentials *less than ~0.5 V vs. SCE in highly polar aqueous solvent*.

There is much current interest in uncovering chemical processes which could give rise to $O_2^-\cdot$ in vivo.[21,46] The results described here clearly demonstrate that the generation of $O_2^-\cdot$ from $^1O_2$ in the presence of electron donors is a viable process, although a definite conclusion on the electron-transfer process must await further studies. Furthermore, the newly developed water-soluble endoperoxide **2** may be used as a convenient, mechanistically less complicated, singlet oxygen source for the singlet oxygen reactions of biological systems in aqueous system under mild conditions. We are currently studing the electron-transfer reaction between $^1O_2$ and other electron-rich substrates of biological interests.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan. K.I. is indebted to the Japan Society for the Promotion of Science for financial support.

---

[40] The diformazan formation from the reaction of **2**, NBT, and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (0.22 V vs. SCE)[41] could not be measured accurately because of the rapid formation of colored Würster salt from the reaction of the amine with ground-state oxygen.

[41] Frank, N. C.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 7427.

[42] Inoue, K.; Saito, I.; Matsuura, T. *Chem. Lett.* **1977**, 607.

[43] Bartholomew, R. F.; Davidson, R. S. *J. Chem. Soc. C* **1971**, 2347.

[44] Grossweiner, L. I. *Curr. Top. Radiat. Res. Q.* **1976**, *11*, 141.

[45] Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1977**, *60*, 2673.

[46] (a) Michelson, A. M.; McCord, J. M.; Fridovich, I. In "Superoxide and Superoxide Dismutases"; Academic Press: New York, 1977. (b) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471.

Metal-Hydrogen Bond Energies in Protonated Transition-Metal Complexes

Amy E. Stevens and J. L. Beauchamp*

Contribution No. 6264 from the Arthur Amos Noyes
Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

Received July 14, 1980

Existing data for transition-metal-hydrogen bond dissociation energies of neutral complexes are few and controversial.[1-8] For the ion BH^+, the homolytic bond energy $D(B^+\text{–}H)$ can be determined readily and accurately from the proton affinity (PA) and adiabatic ionization potential (IP) of the base B, as shown in the thermodynamic cycle of Scheme I, which yields the relationship given in eq 1.

Scheme I

$$\begin{tikzcd}
BH^+ \arrow[r, "D(B^+\text{-}H)"] \arrow[d, "PA(B)"'] & B^+ + H \\
B + H^+ \arrow[r, "IP(B)"'] & B^+ + H^+ + e^- \arrow[u, "-IP(H)"']
\end{tikzcd}$$

$$D(B^+\text{-}H) = PA(B) + IP(B) - IP(H) \qquad (1)$$

We report the proton affinities of 20 organotransition-metal complexes in the gas phase. For 16 of these complexes protonation occurs on the metal center, and the corresponding metal-hydrogen homolytic bond dissocation energies are determined. These data are summarized in Table I.

All proton affinities were determined by the techniques of ion cyclotron resonance spectroscopy,[9] by examining proton-transfer reactions in mixtures with compounds of known base strength. Ionization potentials are taken from a variety of sources and experimental procedures, as noted in Table I. The site of protonation in several of these compounds has been determined by either gas-phase or solution-phase studies; these results are also presented in Table I. For the cases indicated, ligand protonation corresponds to carbon-hydrogen, rather than metal-hydrogen, bond formation.

The following points emerge from the data presented in Table I:

(1) An average metal-hydrogen bond energy of 68 kcal/mol is computed from the 16 compounds for which protonation on the metal center is indicated. The enormous range of energies, from 53 kcal/mol for $D[CpFe(CO)_2CH_3{}^+\text{–}H]$ to 87 kcal/mol for $D[(CO_5)MnH^+\text{–}H]$, would suggest this average should be used only with extreme caution to predict the thermochemistry or reactivity of metal hydrides.

(2) Despite the wide range of bond strengths, periodic trends are apparent. In the first-row transition-metal carbonyls, the metal-hydrogen bond energy is a maximum for $D[(CO)_5Fe^+\text{–}H]$. On proceeding from a first-row compound to its second-row homologue, the metal-hydrogen bond energy increases. A difference of 7 kcal/mol is seen between $D[(CO)_6Cr^+\text{–}H]$ and $D[(CO)_6Mo^+\text{–}H]$ and between $D[CpCo(CO)_2{}^+\text{–}H]$ and $D[CpRh(CO)_2{}^+\text{–}H]$. A more substantial increase is evident with $D[Cp_2Ru^+\text{–}H]$, for which the bond energy is 25 kcal/mol stronger than $D[Cp_2Fe^+\text{–}H]$. There does not seem to be an increase in bond energy on proceeding from second- to third-row metals; however, the only example is $D[(CO)_6Mo^+\text{–}H]$ compared to $D[(CO)_6W^+\text{–}H]$. The 6 kcal/mol difference between $D[(CO)_5MnCH_3{}^+\text{–}H]$ and $D[(CO)_5ReCH_3{}^+\text{–}H]$ is consistent with these observations.

(3) Typically within a "homologous" series of compounds, the homolytic bond energy $D(B^+\text{–}H)$ remains constant.[11] It is clear on examining the three iron complexes listed in Table I that they do not constitute "homologous" molecules. We suggest that compounds with higher oxidation states of the same metal atom have substantially weaker metal-hydrogen bonds. Formation of several σ bonds causes changes in the electron density and orbital

---

[1] Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71 and references therein.

[2] Yoneda, G.; Blake, D. M. *J. Organomet. Chem.* **1980**, *190*, C71.

[3] Calado, J. C. G.; Dias, A. R.; Martinho Simões, J. A. *J. Organomet. Chem.* **1979**, *174*, 77.

[4] Private communication from J. Halpern, based upon data given in: Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335.

[5] Connor, J. A., private communication.

[6] Bronshtein, Yu. E.; Grankin, V. Yu.; Krinkin, D. P.; Rudkovskii, D. M. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1966**, *40*, 802.

[7] Ungvary, F. *J. Organomet. Chem.* **1972**, *36*, 363.

[8] Alemdaroğlu, N. H.; Penninger, J. M. L.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1043.

[9] Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.

0002-7863/81/1503-190$01.00/0

Table I. Proton Affinities, Ionization Potentials, and Metal–Hydrogen Homolytic Bond Energies of Transition-Metal Compounds

compound (B)	PA(B) – PA(NH_3),[a] kcal/mol	PA(B),[b] kcal/mol	adiabatic IP(B),[a,c] eV	homolytic bond energy $D(B^+–H)$, kcal/mol	site of protonation[a,d]
Group 5B					
$(CO)_6V$	−9.7 ± 1.3	197 ± 3	7.45 ± 0.1 (PES)[k]	56 ± 3	
Group 6B					
$(CO)_6Cr$	−23.3 ± 1.1	184 ± 2	8.142 ± 0.017 (PIMS)[l]	58 ± 3	
$(CO)_6Mo$	−18 ± 1	189 ± 2	8.227 ± 0.011 (PIMS)[l]	65 ± 3	
$(CO)_6W$	−19 ± 1	188 ± 2	8.242 ± 0.006 (PIMS)[l]	64 ± 3	
$CpCr(CO)_2NO$	−7.2 ± 1.3	200 ± 2	7.2 ± 0.1 (PES)[m]	52 ± 3	L(g)
$CpCr(CO)_3CH_3$	1.8 ± 1.8	209 ± 3	7.2 ± 0.2 (ICR)	61 ± 4	L(g)
$BzCr(CO)_3$	1 ± 2	208 ± 3	7.0 ± 0.1 (PES)[n]	56 ± 4	M(s)[u]
Group 7B					
$(CO)_5MnCH_3$	−18.7 ± 1.4[e]	188 ± 3	8.3 ± 0.1 (PES)[o]	67 ± 3	
$(CO)_5ReCH_3$	−16.3 ± 1.0[e]	191 ± 2	8.5 ± 0.1 (PES)[p]	73 ± 3	
$(CO)_5MnH$	−3.5 ± 1.5	204 ± 3	8.55 ± 0.1 (PES)[p]	87 ± 3	
$(CH_3C_5H_4)Mn(CO)_3$	−3.9 ± 0.2[f]	203 ± 2	7.86 ± 0.1 (MS)[q]	71 ± 3	M(s)[v]
Group 8					
$(CO)_5Fe$	−3 ± 3[g]	204 ± 4	7.98 ± 0.01 (PIMS)[r]	74 ± 5	M(s)[w]
$CpFe(CO)_2CH_3$	−13.3 ± 1.1	194 ± 2	7.5 ± 0.1 (PES)[s]	53 ± 3	
Cp_2Fe	6 ± 4[h]	213 ± 5	6.72 ± 0.1 (PES)[t]	54 ± 5	M(s)[x]
Cp_2Ru	13 ± 2	220 ± 3	7.5 ± 0.2 (ICR)	79 ± 5	M(s)[x,y]
$CpCo(CO)_2$	0 ± 2	207 ± 3	7.8 ± 0.2 (ICR)	73 ± 5	M(g)
$CpRh(CO)_2$	7 ± 2	214 ± 3	7.8 ± 0.2 (ICR)	80 ± 5	M(g)
$(CO)_4Ni$	−23 ± 1	184 ± 2	8.32 ± 0.01 (PIMS)[r]	62 ± 3	
Cp_2Ni	17.9 ± 1[i]	225 ± 3	6.2 ± 0.1 (PES)[t]	54 ± 3	L(s)[z]
CpNiNO	−4.5 ± 2.5[j]	203 ± 3	8.21 ± 0.03 (PIMS)[j]	78 ± 3	L(g)[j]

[a] All references are from this work unless otherwise noted. [b] Relative to PA(NH_3) = 207 ± 2 kcal/mol. Although PA(NH_3) remains controversial, lower and upper limits of 204 and 208 kcal/mol seem well established [Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1979, *101*, 4067]. A lower value of PA(NH_3) would result in lowering all of the homolytic bond dissociation energies by the same amount. [c] The technique used for determination is indicated in parentheses: photoelectron spectroscopy (PES), photoionization spectroscopy (PIMS), or mass spectroscopy (MS). Those IP denoted ICR were determined by the extrapolated voltage-difference method [Warren, J. W. *Nature (London)* 1950, *165*, 810] on our instrument. [d] Metal protonation denoted by M, ligand by L; s and g refer to either solution-phase (s) or gas-phase (g) studies. Compounds for which no reference is given are assumed to protonate on the metal. [e] Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1979, *101*, 245. [f] Fernando, J.; Faigle, G.; Ferreira, A. M. da C.; Galembeck, S. E.; Riveros, J. M. *J. Chem. Soc., Chem. Commun.* 1978, 126. [g] Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1975, *97*, 4808. [h] Foster, M. S.; Beauchamp, J. L. *Ibid.* 1975, *97*, 4814. [i] Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* 1976, *15*, 665. [j] Corderman, R. R. Ph.D. Thesis, California Institute of Technology, 1977. [k] Evans, S.; Green, J. C.; Orchard, A. F.; Saito, T.; Turner, D. W. *Chem. Phys. Lett.* 1969, *4*, 361. [l] Lloyd, D. R.; Schlag, E. W. *Inorg. Chem.* 1969, *8*, 2544. [m] Hubbard, J. L.; Lichtenberger, D. L. *Ibid.* 1980, *19*, 1388. [n] Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* 1975, *29*, 113. [o] Lichtenberger, D. L.; Fenske, R. F. *Inorg. Chem.* 1974, *13*, 486. [p] Hall, M. B. *J. Am. Chem. Soc.* 1975, *97*, 2057. [q] Efraty, A.; Huang, M. H. A.; Weston, C. A. *Inorg. Chem.* 1975, *14*, 2796. [r] Distefano, G. *J. Res. Natl. Bur. Stand., Sect. A* 1970, *74*, 233. [s] Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* 1976, *98*, 50. [t] Rabalais, J. W.; Werme, L. O.; Bergmath, T.; Karlsson, L.; Hussain, M.; Seigbahn, K. *J. Chem. Phys.* 1972, *57*, 1185. [u] Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* 1962, 3653. [v] This compound has not been studied; however, $(C_5H_5)Mn(CO)_3$,[t] $(Et_4C_5H)Mn(CO)_3$,[u] and $(Et_5C_5)Mn(CO)_3$[w] protonate at the metal. [w] Lokshin, B. V.; Ginzburg, A. G.; Setkina, V. N.; Kursanov, D. N.; Nemirovskaya, I. B. *J. Organomet. Chem.* 1972, *37*, 347. [x] Curphey, T. J.; Santer, J. O.; Rosenblum, M.; Richards, J. H. *J. Am. Chem. Soc.* 1960, *82*, 5249. [y] Cerichelli, G.; Illuminati, G.; Ortaggi, G.; Giuliani, A. M. *J. Organomet. Chem.* 1977, *127*, 357. [z] Turner, G. K.; Kläui, W.; Scotti, M.; Werner, H. *Ibid.* 1975, *102*, C9.

hybridization of the metal center which result in weaker bonds with increasing oxidation state. This concept is not unfamiliar to most chemists; a Co(I)/Co(III) couple, but not a Co(III)/Co(V) couple, is prevalent in catalysis.

Connor[1] has also noted a decrease in bond energy with increasing oxidation state; he gives as an example the average metal–chlorine bond strengths in $MoCl_n$ and WCl_n, $n = 4–6$.

In this context, NO appears to have the same effect as a σ-bonding ligand; protonation on the cyclopentadienyl ring, rather than on the metal, of the cyclopentadienyl–chromium and –nickel complexes is interpreted as evidence of a weaker metal–hydrogen bond for these compounds as well.

Although this hypothesis generally seems valid, an exception is $D[(CO)_5MnCH_3^+–H]$ = 67 kcal/mol compared to $D[(CO)_5MnH^+–H]$ = 87 kcal/mol; in this instance ligand variation has a striking effect on the bond strength.

(4) Although $D[(CO)_5MnH^+–H]$ is a very strong 87 kcal/mol, the second metal–hydrogen bond is very weak (reaction 2). These

$$(CO)_5MnH_2^+ \xrightarrow{87\ \text{kcal/mol}} (CO)_5MnH^+ + H \xrightarrow{23\ \text{kcal/mol}} (CO)_5Mn^+ + 2H \quad (2)$$

data give the reductive elimination of H_2 from $(CO)_5MnH_2^+$, 6 kcal/mol endothermic.[10] We expect this disparity between the first and second bond energies is a general result with dihydrides for which the unsaturated species (in this case $(CO)_5Mn^+$) has a singlet ground state.

(5) For main-group hydrides the bond energy in the ion is typically 10–15 kcal/mol stronger than in the isoelectronic neutral.[11] The ions $(CO)_5FeH^+$ and $(CO)_4NiH^+$ are isoelectronic with $(CO)_5MnH$ and $(CO)_4CoH$, for which metal–hydrogen bond energies of 57[5]–64[4] and 55[6,8]–58[7] kcal/mol have been estimated. For the transition metals the bond energies will depend heavily on the geometry and orbital hybridization at the metal. For example, $(CO)_4Ni^+$ is expected to be of nearly tetrahedral geometry, with the radical electron of predominantly d character. Although $(CO)_4Co$ may have a similar structure, several theoretical and experimental studies have suggested that $(CO)_4Co$ could be of C_{3v} geometry, with the radical electron of substantial s–p character.[12] These differences may cause changes in the bond energy between ion and neutral of such magnitude that comparisons or predictions between them are difficult to make at this point.

---

(10) Stevens, A. E.; Beauchamp, J. L., submitted for publication.

(11) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417.

(12) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. Pensak, D. A.; McKinney, R. J. *Ibid.* **1979**, *18*, 3407 and references therein.

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°).

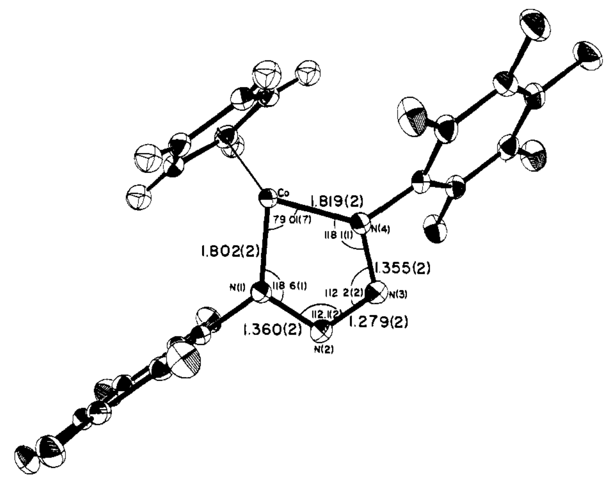
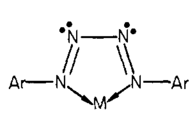


Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)Co((C_6F_5)N_4(C_6F_5))$. Selected distances (Å) and angles (deg) are shown. Thermal ellipsoids are drawn at the 50% probability level.

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 = $p\text{-}FC_6H_4$, 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. 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, β = 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