

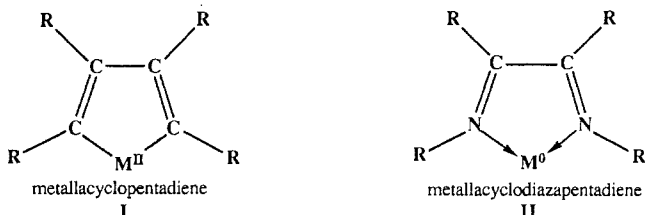
Synthesis, Electronic Structure, and Reactivity of Metallacyclotetraazapentadienes

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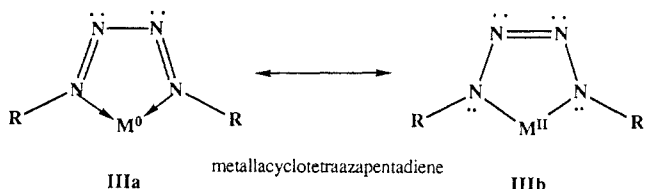
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Metallacyclopentadiene complexes I are important intermediates, as well as isolable products, formed by coupling reactions of acetylenes at transition-metal centers.¹ They generally possess localized C=C bonds



with little π -back-bonding from the metal into the metallacycle π^* orbitals.² Metallacyclodiazapentadiene (or diimine) complexes II are also well-known and usually have been formed by trapping of the metastable free ligand by low-valent transition metals.³ Phenanthroline and bipyridine can be regarded as resonance-stabilized diazabutadiene ligands.⁴ Although the C=N bonds in II usually are localized, π -back-donation from transition-metal d orbitals into the ligand π system is thought to be important.³ For example, $(OC)_4Mo[N(R)=C(R)C(R)=N(R)]$ complexes form stable 19-electron radical anions on one-electron reduction, whereas $Mo(CO)_6$ does not.^{4,5} Metal and nitrogen hyperfine splittings observed in the EPR spectra of these complexes suggest delocalization of the odd electron between the Mo d π and diazabutadiene π^* orbitals.

Over a decade ago we became interested in the properties of the metallacyclotetraazapentadiene fragment, which can exist in either resonance form IIIa or IIIb. Given the presence of four highly electronegative

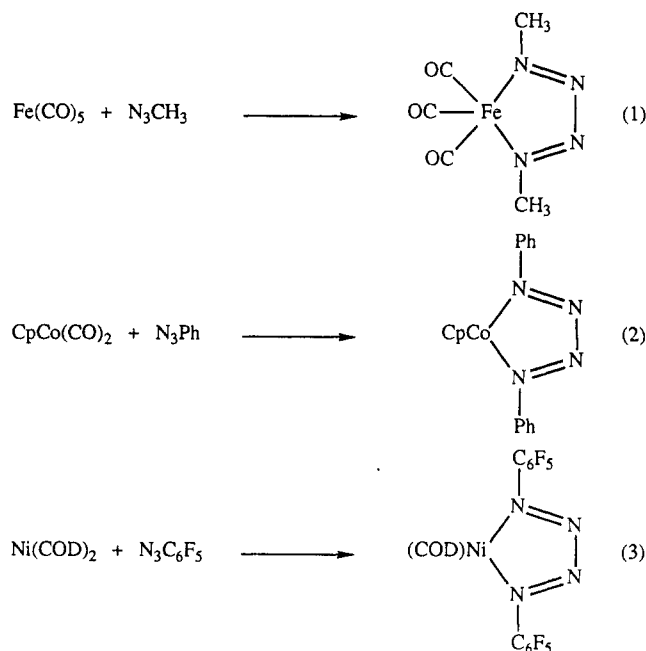


N atoms in the ring, it seemed likely that these compounds would possess low-lying metallacycle π^* orbitals, which might play an important role in their redox properties, photochemistry, and electronic structure. In this Account the synthesis, structure, bonding, and reactivity of compounds that contain ligand system III will be compared to those of complexes that contain

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ligand systems I and II. This provides an opportunity to study the relationship between π -back-bonding and the structural, reactivity, and physical properties of unsaturated metallacycles.

Synthesis of Tetraazabutadiene Complexes. In contrast to the general synthetic routes available for I and II, the preparation of ligand system IIIa or IIIb is more problematic. The free neutral ligand is unstable,⁶ and the dianion was unknown as an alkali metal or alkaline-earth salt, except for a multistep vacuum line synthesis of $Li_2[Me_3SiNN=NNSiMe_3]$.⁷ Tetraazabutadiene complexes were initially observed as products from the reaction between organic azides and low-valent-metal complexes (eqs 1-3).⁸⁻¹⁰



The mechanism for their formation, originally suggested by Stone,¹⁰ proceeds as in eq 4. We view this as

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 509-512.

(2) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* 1979, 3, 39.

(3) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* 1982, 21, 151.

(4) (a) Kaim, W.; Olbrich-Deussner, B. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; pp 173-200.

(b) Dessy, R. E.; Bares, L. A. *Acc. Chem. Res.* 1972, 1, 95.

(5) tom Dieck, H.; Franz, K. D.; Hohmann, F. *Chem. Ber.* 1975, 108, 163.

(6) Moore, D. S.; Robinson, S. D. *Adv. Inorg. Chem. Radiochem.* 1986, 30, 1.

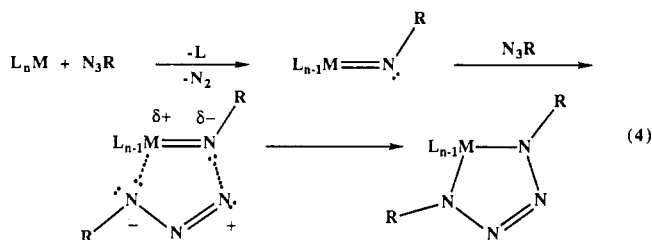
(7) Wiberg, N.; Bayer, H.; Vasisht, S. K. *Chem. Ber.* 1981, 114, 2658.

(8) Dekker, M.; Knox, G. R. *Chem. Commun.* 1967, 1243. Doedens, R. J. *Ibid.* 1968, 1271.

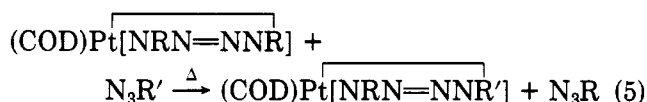
(9) Otsuka, S.; Nakamura, A. *Inorg. Chem.* 1968, 7, 2542.

(10) Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1972, 1805.

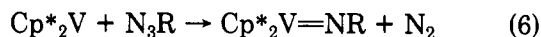
an example of the 1,3-dipolar cycloaddition of an organic azide to an unsaturated metal–nitrogen bond.



Such 1,3-dipolar addition reactions have ample precedent in organic reaction chemistry.¹¹ Evidence for the thermal reversibility of the ring-closure step is suggested by the observation of intermolecular exchange reactions (e.g., eq 5).¹² Often the metal nitrene species

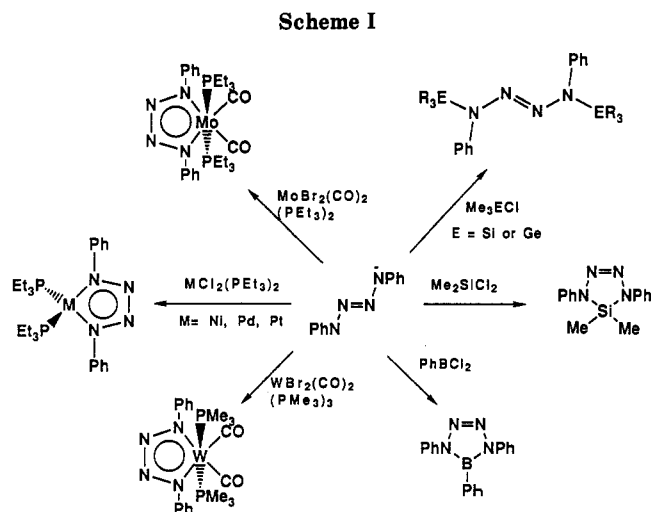


formed by addition of N_3R to a metal center undergoes other reactions, such as CO insertion or H atom abstraction from solvent.⁸ For electron-deficient early-transition-metal complexes, the $M=NR$ species may be stable, as shown in eq 6.¹³ So far the tetraazabutadiene ligand has only been observed for d^n metals with $n \geq 6$. This may reflect the need for metal π -donation to stabilize the N_4R_2 ligand relative to a metal–nitrene complex and free organic azide.

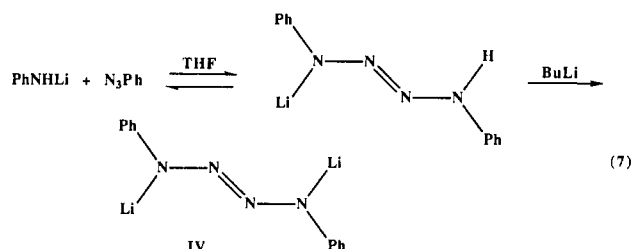


One problem with this synthetic approach is revealed by the mechanism of eq 4. The intermediate metal–nitrene species, generated by addition of the first mole of azide, can be highly reactive and undergo competing reactions. For example, in eq 2 we have observed organic isocyanates as byproducts of the reaction.¹³ The reaction of eq 1 yields a ureylene-bridge dinuclear iron carbonyl as the major product,⁸ in addition to the desired tetraazabutadiene complex. We therefore sought a route to $LiN(R)N=N(R)Li$ as an alternative reagent for the synthesis of metal tetraazabutadienes.

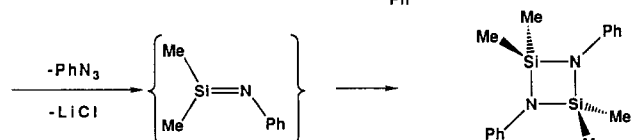
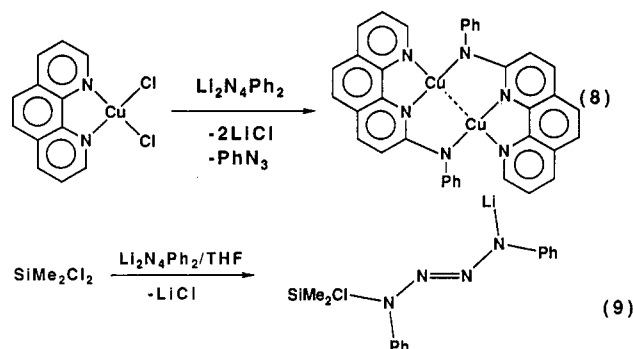
Similar to the known^{15a} addition of carbanions to organic azides, we found^{15b} that basic nitrogen anions could add to phenyl azide as shown in eq 7. Deprotonation of the intermediate species produced reagent IV as an isolable solid, which proved useful for the synthesis of both main-group^{15,16} and transition-metal tetraaza compounds^{17,18} as shown in Scheme I. The reaction of eq 7 provides an alternative to Fischer's classic synthesis¹⁹ of the tetrazene skeleton by oxidative



coupling of unsymmetrical hydrazines. A limitation of the reaction is the leaving ability of the azide ion. The coupling reaction of eq 7 does not proceed well with methyl or trimethylsilyl azide substrates, which are susceptible to S_N2 displacement with amide anions.



Another reactivity sometimes observed with IV is fragmentation to generate PhN_3 and an NPh^{2-} equivalent.^{20,21} Thus in eqs 8 and 9 a presumed monomeric nitrene–metal or nitrene–silyl species dimerizes by insertion into a C–H bond²¹ and by cycloaddition,¹⁶ respectively. For eq 9 the conditions were similar to those from the analogous reaction reported in Scheme I; however, toluene was used as solvent for the $SiMe_2Cl_2$ reaction in Scheme I.



Structure and Bonding in Tetraazabutadiene Complexes. Metallacyclopentadiene complexes I generally exhibit two localized carbon–carbon double bonds. Theoretical calculations² predict that the empty

(11) Huisgen, R. *J. Org. Chem.* 1976, 41, 403.

(12) Overbosch, P.; van Koten, G.; Vrieze, K. *J. Chem. Soc., Dalton Trans.* 1982, 1541.

(13) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* 1985, 107, 7945.

(14) Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.* 1981, 209, 407.

(15) (a) Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* 1981, 103, 2483. (b) Lee, S. W.; Miller, G. A.; Campana, C. F.; Maciejewski, M. L.; Trogler, W. C. *J. Am. Chem. Soc.* 1987, 109, 5050.

(16) Miller, G. A.; Lee, S. W.; Trogler, W. C. *Organometallics* 1989, 8, 738.

(17) Lee, S. W.; Miller, G. A.; Campana, C. F.; Trogler, W. C. *Inorg. Chem.* 1988, 27, 1215.

(18) Lee, S. W.; Trogler, W. C. *Organometallics* 1990, 9, 1470.

(19) Fischer, E. *Justus Liebigs Ann. Chem.* 1878, 190, 67.

(20) Lee, S. W.; Trogler, W. C. *Inorg. Chem.* 1990, 29, 1099.

(21) Lee, S. W.; Trogler, W. C. *Inorg. Chem.* 1990, 29, 1659.

Table I
Structural and Electrochemical Data for Tetraazabutadiene and Tetrazene Compounds

compound	M—N, ^a Å	N—N, ^a Å	N=N, Å	ϕ , ^b deg	$E^{\circ/c}$
<i>trans</i> -Ph(SiMe ₃)NN=NNPh(SiMe ₃) ¹⁶	1.781 (1)	1.394 (2)	1.254 (3)	—	—
<i>trans</i> -Ph(GeMe ₃)NN=NNPh(GeMe ₃) ¹⁶	1.912 (3)	1.377 (3)	1.260 (4)	—	—
Me ₃ Si[N(Ph)N=NN(Ph)] ¹⁶	1.755 (1)	1.392 (1)	1.267 (2)	90	—
CpCo[N(C ₆ F ₅)N=NN(C ₆ F ₅)] ^{27,28}	1.811 (8)	1.358 (3)	1.279 (2)	—	-0.71
(MePh ₂ P) ₂ Ni[N(Ph)N=NN(Ph)] ¹⁷	1.876 (5)	1.353 (7)	1.321 (11)	33	—
(Et ₃ P) ₂ Ni[N(Ph)N=NN(Ph)] ²²	1.883 (9)	1.36 (2)	1.28 (2)	33	-1.60
(Et ₃ P) ₂ Pd[N(Ph)N=NN(Ph)] ¹⁷	2.05 (1)	1.38 (1)	1.26 (1)	15	-1.77
(Et ₃ P) ₂ Pt[N(Ph)N=NN(Ph)] ¹⁷	2.00 (2)	1.40 (2)	1.32 (2)	14	-2.55
(OC) ₂ (Ph ₃ P) ₂ Mo[N(Ph)N=NN(Ph)] ¹⁸	2.086 (8)	1.33 (1)	1.33 (1)	8	—
(OC) ₂ (Et ₃ P) ₂ Mo[N(Ph)N=NN(Ph)] ¹⁸	2.076 (4)	1.348 (5)	1.283 (8)	10	-1.40
(OC) ₂ (Ph ₃ P) ₂ W[N(Ph)N=NN(Ph)] ¹⁸	2.06 (2)	1.39 (3)	1.27 (3)	16	—
(OC) ₂ (Me ₃ P) ₂ W[N(Ph)N=NN(Ph)] ¹⁸	2.11 (3)	1.37 (5)	1.24 (5)	31	-1.94

^a For structures where the two M—N or N—N bond lengths were not required to be equivalent by crystal symmetry, the average values are given. ^b Angle ϕ measures the dihedral angle between the M—N—N=N—N planar ring and ML₂ ligand plane. For Mo and W, L = CO. ^c Reduction potential determined by cyclic voltammetry. Data in different solvents vs the Ag wire reference was placed on a common scale with the ferrocene/ferrocenium couple $E^{\circ} = 0.400$ V vs NHE as a standard (Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* 1980, 19, 2854).

π^* orbitals of the unsaturated ligand lie at too high an energy to act as π -acceptor orbitals. Ligand system II also usually conforms to a diene structure; however, a lengthening of the double bonds occurs by donation of $d\pi$ electron density from the metal into the empty π^* orbitals of the diazabutadiene ligand.^{3,6} The high electronegativity of the nitrogen ring atoms lowers the energy of these acceptor orbitals in comparison to I.

In contrast to the localized diene resonance forms dominant for I and II, the tetraazabutadiene complexes defy a simple description. Table I contains structural parameters from our work for a range of tetraaza compounds. The pattern of N—N bond lengths usually conforms to that expected for the monoene resonance form IIIb. We use the X-ray data¹⁶ for *trans*-Ph-(Me₃E)NN=NN(Ph)(EMe₃) (E = Si or Ge) to define an ideal N—N single bond length of 1.389 Å and a ideal N=N double bond length of 1.257 Å for an unstrained tetrazene. These values alter little in the cyclic main-group tetrazene Me₃Si[N(Ph)N=NN(Ph)], but a lengthening of the double bond and a shortening of the two single bonds occur for all the transition-metal compounds contained in Table I. In some complexes the N—N bonds become nearly equivalent.

Short metal–nitrogen bond lengths often occur as well. For example, in (PEt₃)₂Ni[N(Ph)N=NN(Ph)]²² the Ni—N bond is shorter than (Table I) the range (2.10–2.15 Å) known²³ for Ni^{II}–NH₃ bond lengths. The Co—N bond in CpCo[N(C₆F₅)N=NN(C₆F₅)]²⁴ is significantly shorter than that of 1.960 (4) Å found in Co(NH₃)₆^{3+,25}. The comparisons are even more remarkable when one considers that the Ni(0) and Co(I) character of the tetraazabutadiene complexes should result in an increase of the metal radii. All this data

agrees with a description of a metal–tetraazabutadiene bonding intermediate between the two limiting resonance forms shown for III. Although one might be tempted to invoke additional resonance forms that involve M—N multiple bonding, they lead to 20-electron structures in these systems. The problem resembles the flexible redox properties shown by 1,2-dithioketones or 1,2-diquinones, where the assignment of oxidation state becomes a moot issue.

For the octahedral Mo and W compounds¹⁸ shown in Table I, we prefer a description for electron-counting purposes where the tetraazabutadiene is viewed as a neutral ligand (IIIa) with strong π -acceptor character, since the complexes can then be classified as normal 18-electron octahedral d⁶ systems. If one viewed the diazabutadiene as a dianion bound to Mo^{II} and W^{II}, then the complexes would be coordinatively unsaturated 16-electron systems. These compounds, however, fail to add two-electron donors. On the other hand, the structural data in Table I are most easily rationalized in the context of resonance form IIIb.

The Ni, Pd, and Pt complexes¹⁷ might at first be regarded as 16-electron square-planar M²⁺ compounds, which are well-known for these metals. This satisfying description is spoiled by the deviation of the MN₄ plane from a coplanar geometry with the two phosphine ligands by as much as 33° for the nickel complex. Even the Pt complex differs significantly from the square-planar structure characteristic of Pt(II). Although the diamagnetic nickel complex might be viewed as more nearly a tetrahedral Ni(0) complex, the pattern of N—N bond lengths again more closely resembles resonance form IIIb. These conflicting observations underscore the inherent difficulty in describing the redox state of the tetraazabutadiene ligand with a single resonance form.

Molecular Orbital Models and One-Electron-Reduced Tetraazabutadiene Complexes. In Figure 1 we show the valence orbitals for the tetraazabutadiene ligand in its monoene resonance form, as found¹⁶ in X α calculations for H₂Si[N(H)N=NN(H)] in C_{2v} symmetry. Since the two π orbitals b₁ and 1a₂ are occupied along with the b₁ π^* orbital, the net π bond order is 1.

(22) Lee, S. W.; Trogler, W. C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1990, 46, 900.

(23) Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G. W., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 5, pp 70–75.

(24) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *J. Am. Chem. Soc.* 1981, 103, 192.

(25) Figgis, B. N.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* 1979, 32, 417.

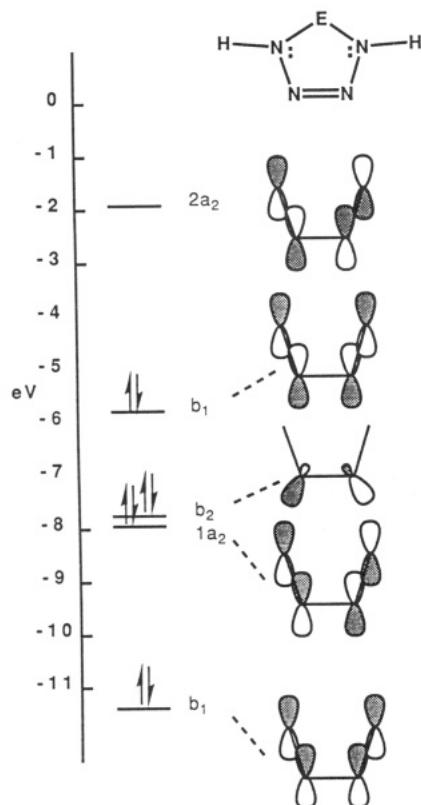


Figure 1. Orbital energies from SCF-X α -DV calculations of $\text{H}_2\text{Si}[\text{N}(\text{H})\text{N}=\text{NN}(\text{H})]$, adapted from ref 16, were used to illustrate the four frontier π orbitals and the available b_2 lone-pair orbital (the a_1 lone pair lies at much lower energies) expected for the IIIb resonance form of the tetraazabutadiene ligand.

When this formal dianionic ligand binds to a CpCo^{2+} or $(\text{OC})_3\text{Fe}^{2+}$ fragment, X α calculations show^{26,27} that the highest occupied b_1 orbital delocalizes onto the metal (31a' for $(\text{OC})_3\text{Fe}[\text{N}(\text{H})\text{N}=\text{NN}(\text{H})]$ and 28a' for $\text{CpCo}[\text{N}(\text{H})\text{N}=\text{NN}(\text{H})]$) by use of an appropriate π symmetry metal orbital. This metal-nitrogen covalent π bonding removes electron density from the π^* b_1 orbital of the tetraene fragment. The nodal symmetry of this orbital requires a shortening of two N-N bonds and a lengthening of the unique N-N bond as it depopulates. This explains the bond-length changes noted in the previous section. We could have arrived at an equivalent description by considering neutral $(\text{OC})_3\text{Fe}$ or CpCo fragments donating π electron density into the empty b_1 π^* orbital of a neutral diene resonance form of the ligand. In either picture the MN_4 ring comprises a six-electron π -metalloaromatic²⁶ ring. Thus the structural differences observed among metallacycles I-III can be attributed to variations in the energy of the b_1 π^* orbital. As one substitutes the more electronegative N for C on proceeding from I to III, the increased stability of the b_1 π^* orbital results in its increased fractional occupation.

Another feature in Figure 1, which is supported by photoelectron spectral studies²⁶ of $(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$, is the presence of a b_2 lone-pair orbital

on the remote nitrogen atoms of the ring. The basicity of the lone-pair electrons permits their reversible complexation by BF_3 and by hydrogen bonding to protic solvents as noted later.

One consequence of the frontier orbital interaction between the ligand b_1 π^* orbital and a $d\pi$ metal orbital of appropriate symmetry is the formation of two molecular orbitals, one occupied and one empty. We will refer to the occupied orbital as metallacycle π (even though derived from ligand π^*) and the unoccupied orbital as metallacycle π^* . In X α calculations for $(\text{OC})_3\text{Fe}[\text{N}(\text{H})\text{N}=\text{NNH}]$ ²⁶ and $\text{CpCo}[\text{N}(\text{H})\text{N}=\text{NNH}]$ ²⁷ the covalent metallacycle π^* orbital was calculated to be the lowest unoccupied molecular orbital (LUMO). The presence of this low-lying metallacycle π^* orbital is evident by the reversible one-electron-reduction processes observed (Table I) for these compounds. The covalent nature of the metallacycle π^* orbital was confirmed by EPR spectroscopic and electrochemical studies²⁸ of $\text{CpCo}[\text{N}(\text{R})\text{N}=\text{NN}(\text{R})]$. Thus, the EPR spectra were anisotropic (for $\text{R} = \text{CH}_3$, $g_1 = 2.161$, $g_2 = 2.022$, and $g_3 = 1.967$) with appreciable ^{59}Co hyperfine splittings ($A_1 = 121$ G, $A_2 = 17$ G, and $A_3 = 30$ G) indicative of a radical with significant metal d character. However, the reduction potentials, E° vs NHE in CH_3CN , showed a remarkable sensitivity to the nature of the tetraazabutadiene R group (C_6F_5 , -0.71 V; $2,4\text{-F}_2\text{C}_6\text{H}_3$, -0.97 V; C_6H_5 , -1.01 V; $2,6\text{-Me}_2\text{C}_6\text{H}_3$, -1.31 V; CH_3 , -1.53 V), which emphasizes the ligand character of the electron-acceptor orbital. One-electron

reduction of $\text{trans}(\text{OC})_2(\text{PEt}_3)\text{Mo}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]$ produces a radical anion whose solution EPR spectrum shows a $g = 2.0215$ resonance with a phosphorus hyperfine splitting, A_p , of 55.6 G.¹⁸ Phosphorus hyperfine splittings in the analogous diazabutadiene complexes, $(\text{OC})_2(\text{PBu}_3)_2\text{Mo}[\text{N}(t\text{-Bu})=\text{CHCH}=\text{N}(t\text{-Bu})]$ with $A_p = 45.0$ G and $(\text{OC})_2(\text{PBu}_3)_2\text{Mo}(2,2'\text{-bipyridine})$ with $A_p = 23.6$ G, have been taken as a measure^{4b,5} of the π -acceptor ability of the diimine ligand. Since A_p for the tetraazabutadiene ligand significantly exceeds the values for both the diimine complexes, it suggests a superior π -acceptor ability for the tetraazabutadiene ligand.

The Metallacycle π^* Orbital and Low-Lying Electronic States. One feature characteristic of transition-metal tetraazabutadiene complexes is the presence of an intense (ϵ of 2000–7000 $\text{M}^{-1}\text{cm}^{-1}$) electronic absorption at low energy (400–600 nm), as seen in Table II. We have assigned this absorption to the metallacycle $\pi \rightarrow$ metallacycle π^* electric dipole-allowed transition.^{26–29} Often weaker absorptions ($\epsilon < 600$ $\text{M}^{-1}\text{cm}^{-1}$) lie at energies below this transition, which can be attributed to excitations from filled d orbitals into the metallacycle π^* orbital. From the data in Table II several patterns emerge. For the CpCo complexes with CH_3 or $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3$ substituents on nitrogen, one-electron reduction to the radical anion shifts the transition to higher energy (longer λ). For the complexes containing the sterically unhindered C_6H_5 or C_6F_5 substituents, which can conjugate with the metallacycle π^* system, the transition shifts to lower energy in the

(26) Trogler, W. C.; Johnson, C. E.; Ellis, D. E. *Inorg. Chem.* **1981**, *20*, 980.

(27) (a) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *Organometallics* **1982**, *1*, 732. (b) Gross, M. E.; Ibers, J. A.; Trogler, W. C. *Organometallics* **1982**, *1*, 530.

(28) Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144.

(29) Johnson, C. E.; Trogler, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6352.

Table II
Metallacycle $\pi \rightarrow$ Metallacycle π^* Electronic Absorptions
in Transition-Metal Tetraazabutadiene Complexes^{17,18,26-28}

complex	λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)
$\text{CpCo}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	428 (7650)
$\text{CpCo}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]^-$	407 (2080)
$\text{CpCo}[\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{NN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]$	445 (5450)
$\text{CpCo}[\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{NN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]^-$	403 (2300)
$\text{CpCo}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]$	471 (7520)
$\text{CpCo}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]^-$	569 (2300)
$\text{CpCo}[\text{N}(2,6\text{-F}_2\text{C}_6\text{H}_3)\text{N}=\text{NN}(2,6\text{-F}_2\text{C}_6\text{H}_3)]$	467 (7720)
$\text{CpCo}[\text{N}(2,6\text{-F}_2\text{C}_6\text{H}_3)\text{N}=\text{NN}(2,6\text{-F}_2\text{C}_6\text{H}_3)]^-$	539 (1890)
$\text{CpCo}[\text{N}(\text{C}_6\text{F}_5)\text{N}=\text{NN}(\text{C}_6\text{F}_5)]$	467 (6740)
$\text{CpCo}[\text{N}(\text{C}_6\text{F}_5)\text{N}=\text{NN}(\text{C}_6\text{F}_5)]^-$	533 (1720)
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	467 (2650)
$(\text{OC})_2[\text{P}(\text{OMe})_3]\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	471 (3060)
$(\text{OC})_2(\text{PMe}_3)\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	495 (2550)
$(\text{OC})_2(\text{PPh}_3)\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	500 (2100)
$(\text{OC})[\text{P}(\text{OMe})_3]_2\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	461 (2230)
$(\text{OC})(\text{PMe}_3)_2\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	482 (2060)
$(\text{OC})(\text{PPh}_3)_2\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	515 (1600)
$[\text{P}(\text{OMe})_3]_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	518 (1940)
$(\text{PPh}_2\text{Me})_2\text{Ni}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]$	440 (2300)
$(\text{PEt}_3)_2\text{Pd}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]$	612 (1700)
$(\text{PEt}_3)_2\text{Pt}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]$	473 (1800)
<i>trans</i> - $(\text{OC})_2(\text{PMe}_3)_2\text{W}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]$	366 (4200)
<i>trans</i> - $(\text{OC})_2(\text{PEt}_3)_2\text{Mo}[\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{NN}(\text{C}_6\text{H}_5)]$	416 (5800)

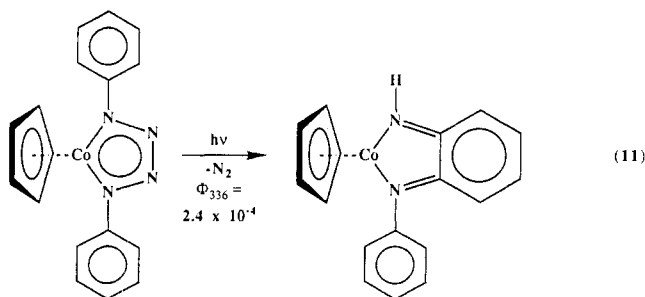
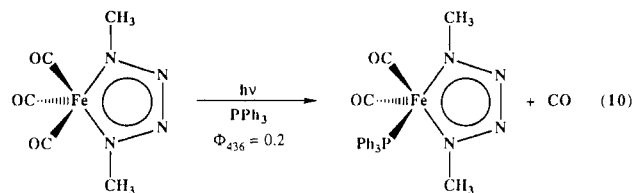
radical anion. This suggests a greater π -conjugation in the electron-rich anion than in the neutral species, and this helps rationalize the large substituent effect on redox potentials noted in the preceding section.

In the iron carbonyl complexes a pattern emerges where substitution of CO by trivalent phosphorus donors shifts the metallacycle $\pi \rightarrow$ metallacycle π^* transition to lower energy. Since this substitution should increase electron density on the metal, it suggests that the metallacycle π orbital contains more metal d character (i.e., is destabilized more by CO substitution) than the metallacycle π^* orbital. This conclusion agrees with our preceding observation that ligand substituent effects in the CpCo system become magnified when the metallacycle π^* orbital is occupied. Finally, the results for the Ni, Pd, Pt, Mo, and W complexes in Table II show a smaller $\pi-\pi^*$ splitting for second-row-metal complexes than for analogous first- or third-row-metal complexes.

Photoreactivity of Metallacyclopentadiene Complexes. We have discussed photoreactivity in a comprehensive fashion elsewhere.³⁰ For completeness here we note that excitation of the metallacycle $\pi \rightarrow$ metallacycle π^* electronic transition can result in either metal-ligand bond cleavage (eq 10)²⁹ or extrusion of N_2 from the metallacycle^{13,31} to generate a highly reactive bisnitrene species (eq 11). Some photochemical reactions we observed for metallacyclopentadienes include metal-ligand bond homolysis and isomerization to η^4 -cyclobutadiene complexes, as well

(30) Trogler, W. C. *ACS Symp. Ser.* 1986, 307, 177.

(31) Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.* 1984, 23, 2968.



as photooxygenation to form 1,4-diketenes.³²

Thermal Reactivity of Tetraazabutadiene Complexes. Although tetraaza unsaturated compounds are expected to have a high energy content, the transition-metal-bound tetraazabutadiene ligand exhibits a reasonable stability. Thermal decomposition with the accompanying evolution of N_2 does not occur until 100–200 °C. The tetraazabutadiene ligand, however, greatly labilizes the metal center toward associative ligand substitution reactions as seen in a comparison of the reactivity of $\text{Fe}(\text{CO})_5$, $(\text{OC})_3\text{Fe}[\text{N}(\text{R})=\text{C}(\text{R}')\text{C}(\text{R}')=\text{N}(\text{R})]$ (for R = aryl, cyclohexyl, *t*-Bu), and $(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$.

Iron pentacarbonyl reacts predominantly by a first-order CO-dissociative mechanism with $k = 6 \times 10^{-11} \text{ s}^{-1}$ at 50 °C.³³ In contrast to this, 1,4-diaryl-2,3-dimethyltetraazabutadiene complexes, $\text{Fe}(\text{CO})_3(\text{DAB})$, react with nucleophiles solely by a second-order process.³⁴ The rate law is first order in both $\text{Fe}(\text{CO})_3(\text{DAB})$ and nucleophile. Activation parameters for the reaction between the 4-fluorophenyl derivative and PMe_3 in toluene solvent support the associative nature of this reaction (Table III). Carbon monoxide replacement rates depend on the nature of the nucleophile, and they increase in the series $\text{PPh}_3 < \text{P}(\text{OMe})_3 < \text{P}(n\text{-Bu})_3 < \text{PMe}_3$. This rate also increases when the π -acceptor ability of the DAB ligand increases (judged by the ν_{CO} stretching frequencies for the $\text{Fe}(\text{CO})_3$ fragment).

Thermal carbon monoxide substitution in $(\text{CO})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$ also proceeds readily to form monosubstituted products $(\text{OC})_2\text{LFe}(\text{N}_4\text{Me}_2)$ with L = PMe_3 , PMe_2Ph , PBu_3 , PEt_2Ph , $\text{P}(\text{OEt})_3$, $\text{P}(\text{OMe})_3$, PH_2Ph , $\text{P}(c\text{-Hx})_3$, PPh_3 , AsMe_3 , AsEt_3 , AsMe_2Ph , 4-CNpy, and Me_3CNC . Di- and trisubstituted products are also observed in the case of *tert*-butyl isocyanide. The substitution reaction obeys a second-order rate law that is first order in both $(\text{OC})_3\text{Fe}(\text{N}_4\text{Me}_2)$ and the en-

(32) Trogler, W. C.; Ibers, J. A. *Organometallics* 1982, 1, 536.

(33) Keeley, D. F.; Johnson, R. E. *J. Inorg. Nucl. Chem.* 1959, 11, 33. Shen, J.-K.; Gao, Y.-C.; Shi, Q.-Z.; Basolo, F. *Inorg. Chem.* 1989, 28, 4304.

(34) Chang, C.-Y.; Johnson, C. E.; Richmond, T. G.; Chen, Y.-T.; Trogler, W. C.; Basolo, F. *Inorg. Chem.* 1981, 20, 3167.

Table III
 Activation Parameters for the Reactions of Iron Diazabutadiene and Tetraazabutadiene Complexes in Toluene Solvent^{34,35}

compound	nucleophile	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol K)
$\text{Fe}(\text{CO})_5^a$	^{13}CO	40	18
$(\text{OC})_3\text{Fe}[\text{N}(4\text{-C}_6\text{H}_4\text{F})\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{N}(4\text{-C}_6\text{H}_4\text{F})]$	PMe_3	13.6	-35
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	PMe_3	6.9	-31
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	PBu_3	7.3	-39
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	PEt_3	7.3	-41
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	$\text{P}(\text{OMe})_3$	11.0	-35
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	$\text{CN}(t\text{-Bu})$	11.6	-35
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$	AsMe_3	13.3	-34
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]^b$	AsMe_3	9.8	-34
$(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]^b$	PPh_3	11.9	-39

^a From ref 33. ^b In methanol solvent.

tering ligand. In addition, the rate and activation enthalpy strongly depend on the ligand size and basicity (Table III). The rate of reaction increases markedly in alcohol solvents, which are capable of hydrogen bonding to the unsubstituted tetraazabutadiene nitrogens. In the presence of excess BF_3 , which forms a Lewis acid-base complex with the tetraazabutadiene ring nitrogens, the rate of substitution increases by a factor of 10^6 . These compounds are significantly more reactive than analogous diazabutadiene complexes. For example $(\text{OC})_3\text{Fe}[\text{N}(\text{Ph})\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{N}(\text{Ph})]$ and $(\text{OC})_3\text{Fe}[\text{N}(\text{CH}_3)\text{N}=\text{NN}(\text{CH}_3)]$ react with PMe_3 at 70 °C with second-order rate constants of $2.48 \text{ M}^{-1} \text{ s}^{-1}$ and $4.10 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively.³⁵

The activation energy data in Table III illustrate the mechanistic change from $\text{S}_{\text{N}}1$ (large ΔH^\ddagger and positive ΔS^\ddagger) for $\text{Fe}(\text{CO})_5$ to $\text{S}_{\text{N}}2$ (low ΔH^\ddagger and large negative ΔS^\ddagger) when the iron carbonyl complex contains diazabutadiene or tetraazabutadiene ligands. Although resonance from IIIa seems to explain the 18-electron ground-state structures for these compounds, the availability of an associative mechanism can be attributed to the importance of resonance form IIIb for stabilizing the electron-rich transition state in the ligand-substitution reactions of diazabutadiene as well as tetraazabutadiene complexes. If the iron center in these complexes is regarded as Fe(II) in the transition state, then the addition of nucleophile leads to an 18-electron transition state. A comparison to $\text{Fe}(\text{CO})_5$ suggests that although the additional two CO ligands are excellent π -acceptors, they cannot stabilize an electron-rich transition state as well as the diazabutadiene and tetraazabutadiene ligands with their flexible redox characteristics.

Conclusions. In this Account we have shown how the development of a nucleophilic coupling reaction between nitrogen anions and organic azides leads to a novel nonoxidative route to the tetraaza skeleton. Tetraazabutadiene metallacycles lie at an extreme pos-

ition among the series of five-membered-ring unsaturated metallacycles in their ability to accept electron density into the π^* orbital of the "diene ligand" fragment. A study of their structures, reactivities, and physical properties provides insight about the effects of π -back-bonding in unsaturated metallacycles.

First, we have shown how an oxidation-state ambiguity arises because of varying amounts of π -electron transfer and how no single resonance description (i.e., oxidation state) of the ligand can account for all the physical and reactivity properties observed. The creation of electron deficiency at the metal center can greatly accelerate nucleophilic attack there, and resonance form IIIb may play a key role in transition-state stabilization. Covalency in the metal $d\pi$ -tetraazadiene π^* interaction creates an occupied metallacycle π orbital and an empty metallacycle π^* orbital. While the ligand π^* character to the occupied orbital explains ground-state structural changes, the empty metallacycle π^* orbital accounts for the properties of the radical anions formed by one-electron reduction. The importance of the metallacycle π^* orbital is further evidenced by the low-energy electronic absorptions characteristic for these species and the photoreactivity when these transitions are excited. Our discussion has emphasized aspects of electronic structure and reactivity where π -bonding considerations are important. Other properties, such as electric-field gradients from NQR studies,³⁶ show little sensitivity to π -bonding changes in these metallacycles. While π -delocalization in carbocyclic unsaturated rings has been long recognized as having a dominant influence on their reactivity and physical properties, the importance of such delocalization in metallacycles is not as clear-cut. The work described herein suggests that the crucial factor will be the energy match between the metal $d\pi$ and diene fragment π^* orbitals.

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(35) Shi, Q. Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *Organometallics* 1982, 1, 1033.

(36) Miller, E. J.; Brill, T. B. *Inorg. Chem.* 1983, 22, 2392.