Synthetic, reactivity, and physical studies of metal tetraazadiene complexes, vanadocene nitrene complexes, and tetrazene anions are described. A serendipitous discovery of a novel isocarbonyl complex is also discussed. Keywords: Molecular Orbitals, Molecular Structure, Magnetic Susceptibility, Molecular Energy Levels.
The chemistry of tetraazadiene complexes containing the \( (n-C_{5}H_{5})Co \) fragment has been elucidated. A series of complexes have been prepared\(^1\) according to eqn 1

\[
(n-C_{5}H_{5})Co(CO)_{2} + N_{3}R \rightarrow \text{Complex}
\]  

Extrusion of \( N_{2} \) takes place photochemically according to the mechanism of eqn 2, sketched below.

This is one of the few cases\(^2\) where formation of a metal bisnitrene has been observed. The reactivity is remarkable since all the aryl derivatives prepared in eqn 1 undergo this reaction and we have documented C-H, C-F, and C-C bond breaking in these systems.

Molecular orbital calculations\(^3\) (Figure 1) showed that these complexes should contain a low-lying \( \pi^* \) orbital \((21a')\) associated with the Co-N\(_4\) \( \pi \) system.
It seemed possible that this empty butadiene like \( \pi^* \) MO could accept an electron. Cyclic voltammetric and Coulometric experiments\(^3\) revealed a reversible one-electron reduction to 19-electron tetraazadiene species. The reduction potentials were \(-1.53, -1.01, -0.71, -0.97, \) and \(-1.31 \) V vs. NHE for the \( \text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_6\text{F}_5, 2,4-\text{F}_2\text{C}_6\text{H}_3 \) and \(2,6-\text{Me}_2\text{C}_6\text{H}_3\) derivatives respectively. Thus the complexes reduce more readily than \((n-\text{C}_5\text{H}_5)\text{Co(CO)}_2\), \((-1.95 \text{ V vs. NHE})\) and that reflects the exceptional \( \pi \)-acceptor ability of the \( \text{N}_4\text{R}_2 \) group. The 19-electron anions were also characterized by EPR spectroscopy which was consistent with the proposed formulation of the acceptor orbital (Figure 2).
The great sensitivity of the reduction potentials to the substituents, \( R \), and the presence of Co hyperfine splitting in the EPR spectra suggest that the acceptor orbital is delocalized over both the ligand and metal. Recently the pentamethyl-cyclopentadienyl (\( \text{Cp}^* \)) analogues have been prepared in our laboratories according to eqn 3.

\[
(r,-C_5Me_5)Co(C_2H_4)_2 + 2N_3R \longrightarrow \begin{array}{c}
\text{Cp}^* \\
\end{array}
\]

(3)
The analogous reaction of eqn 1 did not yield tetraazadiene complex, but RNCO and \([(\text{n-C}_5\text{Me}_5)\text{Co(\mu-CO)}\)]\(_2\) were isolated as the only products. The mechanism shown in Scheme I may account for this behavior.

**Scheme I:**

\[
\begin{align*}
\text{Cp}^*\text{Co(CO)}_2 + \text{N}_3\text{R} & \xrightarrow{-\text{CO}} \text{Cp}^*\text{Co(CO)(N(R)N}_2) \\
\xrightarrow{-\text{N}_2} \text{Cp}^*\text{Co(CO)(NR)} & \rightarrow \text{Cp}^*\text{Co(RNCO)} \\
\xrightarrow{\text{CO}} \frac{1}{2} \text{[Cp Co(\mu-CO)]}_2 & + \text{RNCO}
\end{align*}
\]

To prevent rapid CO insertion into the Co-N bond we used the ethylene complex (eqn 3). It is hoped that the bulky pentamethyl complex will stabilize the dinitrene intermediate of eqn 2 and permit trapping with substrates (e.g., C\(_2\)H\(_4\), C\(_2\)Ph\(_2\)).

The preceding studies provide models for decomposition reactions of energetic azides that are catalyzed by metal complexes. There are few examples\(^4\) of reactions between organic azides and early transition metal organometallic complexes. We were interested to see whether the same kinds of products (e.g., tetraazadienes and nitrenes) found in late transition metal chemistry\(^5\) are present in early metal systems. Reactive 15-electron and 17-electron complexes of vanadium (\(\text{n-C}_5\text{H}_5\))\(_2\text{V}, \) (\(\text{n-C}_5\text{Me}_5\))\(_2\text{V}, \) and \(\text{V(CO)}_6\) were selected for study.\(^6\) In every case rapid evolution of \(\text{N}_2\) occurred upon addition of the organic azides (\(\text{RN}_3, R = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_6\text{F}_5, 2,6-\text{Me}_2\text{C}_6\text{H}_3, \text{biphenyl}, \text{SiMe}_3, \text{SiPh}_3, \text{CPh}_3, \) and neopenetyl). The cleanest reactions occurred between (\(\text{n-C}_5\text{Me}_5\))\(_2\text{V}\) and \(\text{RN}_3\) (\(R = \text{aryl}\)),
eqn 4.

\[
(n-C_5Me_5)_2V + N_3R \rightarrow V≡N-R
\]

\[R = C_6H_6, 2,6-Me_2C_6H_3, \text{o-biphenyl}\]

One of the compounds has been characterized by X-ray crystallography (Figure 3) in collaboration with Dr. Rheingold of the University of Delaware. The linear \(V-N-R\) geometry poses fundamental questions concerning the electron donor nature of the \(N-R\) group. If the nitrene group acts as a 4-electron donor then the complex is a 19-electron species. Early metal complexes rarely exceed the 19-electron configuration. EPR spectra verify the doublet ground state for the nitrene compounds. Analysis of the hyperfine splitting (Figure 4) shows that the electron is delocalized over both the vanadium and nitrogen atoms. Structural evidence for the electron rich nature of the molecule exists in the slipping of the \(n^5-C_5Me_5\) rings toward an allyl-ene \(n^3\) coordination geometry. Three of the \(V-C\) bonds in the \(C_5\) ring are 0.17Å shorter than the other two. Vanadocene undergoes a similar reaction with aryl azides to form paramagnetic nitrene complexes (from EPR characterization). These compounds are quite sensitive and defy isolation. We are presently defining the reactivity of the \(V=N-R\) group in these systems. If we can find reactions where the \(N-R\) group is transferred to organic substrates then we would have the basis for a catalytic cycle to transfer an \(N-R\) group from \(N_3R\) to substrates such as olefins.

Bulky azides, \(N_3R'\), where \(R'\) forms a stable radical, exhibit a second mode of reaction\(^6\) (eqn 5).
Figure 3: Molecular Structure of (η-C₅(CH₃)₅)₂VN[2,6-(CH₃)C₆H₃] as Determined by Single Crystal X-ray Diffraction. Only the Nonhydrogen Atoms are Shown.
Figure 4: Simulated and measured EPR spectra of \( \text{Cp}^2\text{YNX} \).
Our initial idea in these experiments was to use the steric bulk of the \((\eta^5\text{C}_5\text{Me}_5)\) ligands and \(R'\) to direct \(N_3R'\) to the metal via the remote nitrogen as shown in Scheme II.

Scheme II:

\[
\begin{align*}
\text{a)} \quad & \text{C}_{2}^*V + N_3R' \quad \rightarrow \quad \text{C}_{2}^*V + N_3N=N=N-N-R' \\
\text{b)} \quad & \text{C}_{2}^*V + N_3R \quad \rightarrow \quad \text{C}_{2}^*V + N_3N = N-R
\end{align*}
\]

\(R' = \text{bulky} \quad R = \text{not bulky}\)

If binding of azide occurred as in reaction 'a' then we would have the first example of a complexed organic azide. In most reactions where \(N_3R\) adds to metal complexes the initial binding is thought to occur as in reaction 'b'. This latter structure readily explains loss of \(N_2\) to yield nitrene species. What we learned from the reactions with \(N_3\text{SiMe}_3\), \(N_3\text{SiPh}_3\), and \(N_3\text{CPh}_3\) was that binding of azide, as in Scheme II 'a' could occur; however, the one-electron reducing
properties of \( \text{Cp}_2\text{V} \) lead to homolysis of the \( \text{N}-\text{R} \) bond to produce \( \text{R}^' \) and \( \text{Cp}_2\text{VN}_3 \). The presence of \( \text{R}^' \) was suggested by isolation of \( \text{R}^'_2 \) from reaction solutions. In support of the mechanism for steric control for this reaction we note that unhindered \( \text{Cp}_2\text{V} \) and hindered \( \text{N}_3\text{SiPh}_3 \) yield \( \text{Cp}_2\text{V}(\text{NSiPh}_3) \) when combined.

Isotope labeling \( ^{14}\text{N}/^{15}\text{N} \) studies for \( \text{Cp}_2\text{VNP} \) (\( \text{Cp}^* = \text{n-C}_5\text{(CH}_3)_5 \), \( \text{Ph} = \text{C}_6\text{H}_5 \)) suggest assignment of the \( \text{V-N} \) vibrational stretch to a peak at 934 cm\(^{-1} \) and the \( \text{N-C} \) stretch to a peak at 1330 cm\(^{-1} \) in the infrared spectra. This assignment for the \( \text{V-N} \) stretch lies below the range (1100-1300 cm\(^{-1} \)) generally accepted for metal nitrene or imido complexes. Because of the high degree of coupling and because of the weak intensity of the \( \text{V-N} \) band, assignments of \( \text{M-N} \) stretching frequencies in other metal nitrene complexes should be made cautiously. We proposed a range of 850-1150 cm\(^{-1} \) for \( \text{M-N} \) stretches in nitrene complexes.

Exploratory studies of the reactions between \( \text{N}_3\text{R} \) and \( \text{V(CO)}_6 \) failed to produce any well defined products; however, a serendipitous discovery emerged. In view of the one-electron reducing ability of \( \text{(n-C}_5\text{Me}_5)_2\text{V} \), mentioned above, and the one-electron oxidizing ability of \( \text{V(CO)}_6 \) we combined the two reagents. The product was the novel complex, (Figure 5) \( \text{(n-C}_5\text{Me}_5)_2\text{V(=OC)V(CO)}_5 \), the first species containing a linear \( \text{M-O-C-M} \) unit. Isocarbonyl bridged species are of extreme importance as models for the activation of \( \text{CO} \). In this context, we performed \( \text{X}\alpha \) calculations that explained the unusual magnetic properties (Figure 6, a triplet from 5-300 K) we found for the complex. Two \( \text{v}_{\text{E}}\text{-adiacene localized orbitals} \) are accidentally degenerate and led to a \( ^3\text{B}_1 \) ground state. Although the attraction between \( \text{(n-C}_5\text{Me}_5)_2\text{V}^+ \) and \( \text{(OC)V(CO)}_5^- \) is primarily electrostatic a \( \text{t}_{2\text{g}} \) \((p) \) orbital localized on \( \text{V(CO)}_6^- \) was found to delocalize onto the \( \text{(n-C}_5\text{Me}_5)_2\text{V}^+ \) fragment.
The synthesis and metallation reactions of tetrazenes have also been studied during the grant period. Our goal here was to synthesize an unsymmetrical tetrazene that contained two removable protecting groups. A good yield of 1,4-dibenzoyl-1,4-diphenyltetrazene was obtained (30% overall yield) by the sequence of reactions shown in Scheme III.

**Scheme III:**

\[
\begin{align*}
\text{Ph}N\equiv & N\text{H} + \text{OCPh} \rightarrow \text{Ph}N\equiv\text{CPh}_2 \\
1) & \text{BuLi} (-78^\circ\text{C}), \text{PhCOCl} \\
2) & \text{PhCOCl} \\
\text{Ph}N\equiv & \text{CPh}_2 \rightarrow \text{HCl} \\
\text{Ph}N\equiv & \text{CPh}_2 \\
\text{Ph}N\equiv & \text{CPh}_2 \\
\text{Ph} & = \text{C}_6\text{H}_5 \\
\end{align*}
\]

Attempts to remove the benzoyl protecting groups with K(O-t-Bu), BuLi, MeLi, NaNH$_2$, DIBAL, KH, and MeMgI led to fragmentation or reduction to a tetrazane. The most interesting process was fragmentation with the carbanion reagents according to Scheme IV.
This mechanism best explains the PhN₃, PhBzNH, and Me₂C(OH)Ph products that are the observed reaction products. The key step is fragmentation of the delocalized tetrazene anion into phenyl azide and PhBzN⁻. Unfortunately, this thwarted our efforts to prepare the 1,4-dilithiotetrazene. The lack of existing methodology for N-N bond forming reactions led us to explore a new way to accomplish this transformation.

The reaction between phenyl azide and non resonance stabilized amido ions NHR (R = H, Ph, 2,6-Me₂C₆H₃) has led to a novel synthesis of tetrazene anions (eqn 6).

\[
\text{Ph-N=N=N + NaNHR} \rightarrow \text{Ph-N=N=N-R} 
\]  

(eqn 6)
This reaction is the reverse of the fragmentation seen in Scheme IV. Deprotonation of the green monoanion occurs on addition of BuLi to yield an orange dianion. Both the mono and dianions can be quenched with methyl iodide to yield Ph(Me)N=N=NPh(H) and Ph(Me)N=N=NPh(Me) when R = Ph. We are presently optimizing conditions for this one step synthesis of tetrazenes and exploring reactions of the tetrazene anions with metal complexes.
References


6) a) Osborne, J.H.; Rheingold, A.L.; Trogler, W.C., in press.


10) Maciejewski, M.L.; Trogler, W.C., to be submitted.
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