of the methylene bridge in the radical could take place with retention of configuration. This problem as well as the possible intermediacy of 7 during the rearrangement are presently under investigation.

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A Novel Intramolecular Exchange Reaction between Coordinated NO and NO_2 Groups in *cis*-$[Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2]$

Sir:

We wish to report a novel exchange reaction between coordinated NO and NO_2 groups. Although it is well known that a coordinated NO_2 group can be chemically converted to coordinated NO by treatment with acids or reducing agents,[1,2] to our knowledge, the direct interchange of coordinated NO_2 and NO has not heretofore been demonstrated. In our previous studies of the dithiocarbamate derivatives of the $\{FeNO\}^6$ and $\{FeNO\}^7$ groups,[3] we reported the preparation of $Fe(NO)(NO_2)(S_2CN(C_2H_5)_2)_2$ and demonstrated by proton NMR spectroscopy that it has cis geometry.[4] A subsequent structure determination by x-ray crystallography[5] has confirmed its cis geometry and has shown that the NO_2 group is attached to iron through the nitrogen atom.

The cis and trans isomers of the analogous complex, $Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2$, have now been prepared and their coordination geometries established by infrared and proton NMR spectroscopy. Isotopic substitution with ^{15}N shows that the NO_2 ligand is attached to iron through nitrogen in both cis and trans isomers (Table I). The trans isomer labeled with ^{15}NO (95%) is stable to isomerization below 5 °C and is readily prepared by reaction 1:

$$Fe(^{15}NO)(S_2CN(CH_3)_2)_2 + {}^{14}NO_2 \xrightarrow[CHCl_3]{-60\ ^\circ C} trans\text{-}[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] \quad (1)$$

Above 5 °C the trans isomer is converted to the cis isomer *with retention of the* ^{15}NO label (reaction 2):

$$trans\text{-}[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] \xrightarrow[CHCl_3]{>5\ ^\circ C} cis\text{-}[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] \quad (2)$$

The isomerization of trans to cis (reaction 2) is then succeeded by a slow exchange between the coordinated ^{15}NO and $^{14}NO_2$ groups of the cis isomer:

$$cis\text{-}[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2 \rightleftharpoons cis\text{-}[Fe(^{14}NO)(^{15}NO_2)(S_2CN(CH_3)_2)_2] \quad (3)$$

To establish the course of this unusual exchange reaction between coordinated NO and NO_2, reaction 3 has been studied at different concentrations in several solvents by monitoring the nitrosyl region of the infrared spectrum (Table II). The results of these kinetic studies show that the exchange of coordinated NO and NO_2 is first order in the cis isomer, is independent of solvent, and is independent of the concentration of either NO, NO_2, or NO_2^- for the range of concentrations studied. The fact that the rate of eq 3 is independent of the concentration of NO_2^- and of the donor properties of the solvent indicates that dissociative mechanisms in which iron-nitrogen bonds are cleaved heterolytically are not important. The requirement of cis geometry for exchange of the coordinated NO and NO_2 groups strongly suggests that an intramolecular process is responsible for reaction 3.

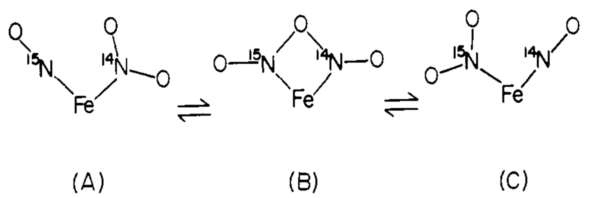

Figure 1. Proposed rate determining step for the exchange reaction between the NO and NO_2 groups of *cis*-$[Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2]$.

One intramolecular pathway that can be envisaged for the exchange of adjacent NO and NO_2 groups is shown in Figure 1. The rate determining step depicted in Figure 1 requires that there be no direct reaction of *cis*-$[Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2]$ with either free NO or free NO_2 which is faster than the reaction shown in Figure 1, in agreement with the observations that eq 3 is independent of the pressure of NO and NO_2 (Table II). However, to explore the possible exchange reactions of coordinated NO and NO_2 with free NO and NO_2, the rates of reactions 4-7 were also studied (Table II).

Table I. NO and NO_2 Vibrational Frequencies of *cis*- and *trans*-$Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2$ and Their ^{15}N Derivatives

Compound	ν_{NO} (CHCl$_3$)	ν_{NO} (KBr)	ν_{NO_2} (KBr)	ν_{NO_2} (KBr)	δ_{NO_2} (KBr)
cis-$Fe^{14}NO(S_2CNMe_2)_2{}^{14}NO_2$	1857	1835	1382	1305	812
cis-$Fe^{15}NO(S_2CNMe_2)_2{}^{15}NO_2$	1821	1802	1352	1282	804
trans-$Fe^{14}NO(S_2CNMe_2)_2{}^{14}NO_2$	1866	1840	1386	1275	760
trans-$Fe^{14}NO(S_2CNMe_2)_2{}^{15}NO_2$	1866	1840	1355	1255	754
trans-$Fe^{15}NO(S_2CNMe_2)_2{}^{14}NO_2$	1829	1804	1385	1275	760

Table II. Rate Data for the Exchange Reaction between the NO and NO_2 Groups of *cis*-$[Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2]$

Solvent	Temp, °K	Concn × 10^3	$10^4\ k_{obsd}$ s^{-1}	$t_{1/2}$, min
$CHCl_3$	295	2.5	1.28	45
$CHCl_3$	295	3.3	1.20	48
$CHCl_3$	285	2.5	0.55	102
CH_3CN	295	2.5	1.15	50
$CHCl_3$ + NO[a]	295	2.5	1.37	42
$CHCl_3$ + NO_2[b]	295	2.5	1.44	40
$CHCl_3$	295	25.0	1.28	45

[a] Mole ratio of complex:NO = 1:1. [b] Mole ratio of complex:NO_2 = 1:1.

$$\textit{cis}\text{-}[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{14}NO \xrightarrow[CHCl_3]{22\ °C} \textit{cis}\text{-}[Fe(^{14}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{15}NO \quad (4)$$

$$\textit{cis}\text{-}[Fe(^{14}NO)(^{15}NO_2)(S_2CN(CH_3)_2)_2] + {}^{14}NO \xrightarrow[CHCl_3]{22\ °C} \textit{cis}\text{-}[Fe(^{14}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{15}NO \quad (5)$$

$$\textit{cis}\text{-}[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{14}NO_2 \xrightarrow[CHCl_3]{22\ °C} \textit{cis}\text{-}[Fe(^{14}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{15}NO_2 \quad (6)$$

$$\textit{cis}\text{-}[Fe(^{14}NO)(^{15}NO_2)(S_2CN(CH_3)_2)_2] + {}^{14}NO_2 \xrightarrow[CHCl_3]{22\ °C} \textit{cis}\text{-}[Fe(^{14}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{15}NO_2 \quad (7)$$

Reactions 4-7 do take place but none was faster than eq 3. More importantly, however, reactions 4-7 occur at the same rate as eq 3. These facts suggest that B may be an intermediate which either reverts to the six-coordinate complexes A and C or possibly dissociates forming N_2O_3 ($NO + NO_2$) and $Fe(S_2CN(CH_3)_2)_2$ with the position of equilibrium lying well on the side of B. Species B should be accessible because the $\{FeNO\}^6$ group is well known to undergo nucleophilic attack,[1,6] and coordinated NO_2 groups are reasonably good nucleophiles. Thus an intramolecular attack by the oxygen atom of the coordinated NO_2 group on the adjacent NO group corresponds to the rate determining step shown in Figure 1. However, the structure of crystalline *cis*-$[Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2]$ shows that the plane of the NO_2 group is perpendicular to the FeNO bond.[5] Consequently the geometry of B cannot be easily attained in the solid state, which accounts for the lack of exchange in solid samples of *cis*-$[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2]$ upon storage for 3 months.

Additional evidence for the importance of B in the reactions of *cis*-$[Fe(NO)(NO_2)(S_2CN(CH_3)_2)_2]$ is provided by exchange studies of the trans isomer with free NO. Reactions 8 and 9 were found to be fast (15 min), but *did not* lead to exchange of the coordinated NO_2 group.

$$\textit{trans}\text{-}[Fe(^{15}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{14}NO \xrightarrow[CHCl_3]{5\ °C} \textit{trans}\text{-}[Fe(^{14}NO)(^{14}NO_2)(S_2CN(CH_3)_2)_2] + {}^{15}NO \quad (8)$$

$$\textit{trans}\text{-}[Fe(^{14}NO)(^{15}NO_2)(S_2CN(CH_3)_2)_2] + {}^{14}NO \xrightarrow[CHCl_3]{5\ °C} \text{no observable reaction} \quad (9)$$

The process outlined in Figure 1 is essentially an oxygen atom transfer reaction between two adjacent coordinated ligands which effects no net chemical changes except for the scrambling of the ^{15}N isotope. However, similar oxygen atom transfer reactions between coordinated NO_2 and CO may also be possible and could account for the ease with which $Ni(NO_2)_2(PEt_3)_2$ is converted to $Ni(NO)(NO_2)(PEt_3)_2$ by CO.[2]

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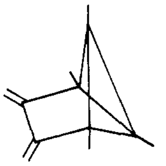
Novel Rhodium-Catalyzed Additions of Carbon Monoxide to Reactive Dienes and Enones with Formation of Five-Membered Rings

Sir:

Although many reactions have been reported[1] between transition metal complexes and organic substrates containing π-bonds (e.g., olefins) and strained saturated systems (e.g., bicyclobutanes), the number of catalytic CO-insertions leading to cyclic species is small.[2] To our knowledge there is no report concerning the transition metal catalyzed CO-insertion into dienes and enones leading to cyclic molecules. We herewith present this novel type of reaction.

In view of known transition metal complex promoted rearrangements of bicyclobutanes,[3] diene **1**,[4] enone **2**,[5] and diketone **3**[5] were treated with $[Rh(CO)_2Cl]_2$. At room temperature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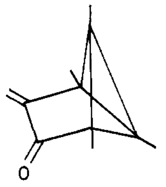

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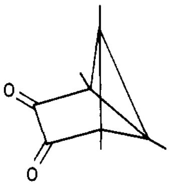

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diene **1** (0.160 g, 1.000 mmole) reacted within 2 h in a benzene or chloroform solution (2.0 ml) with $[Rh(CO)_2Cl]_2$ of which 1 equiv (0.194 g, 0.500 mmol) was needed for a complete conversion. On examining the product it was found that besides a rearrangement of the bicyclobutane moiety a CO-insertion had taken place, leading to the 4,5,6,7-tetramethylindan-2-one, **5**, which was isolated in 90% yield (0.170 g, 0.904 mmol).[6,7]

The question as to which mechanistic route is followed in this process is not an easy one to answer; however, a few data are at hand. By studying the reaction between **1** and $[Rh(CO)_2Cl]_2$ using ir and ^1H NMR techniques, a transient species (present up to 10% according to ^1H NMR) was observed: ir 1700 and 2050 cm^{-1} ($CDCl_3$ solution) and ^1H NMR