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.

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

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

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

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

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.

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

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

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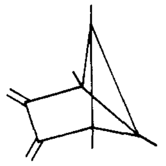
Novel Rhodium-Catalyzed Additions of Carbon Monoxide to Reactive Dienes and Enones with Formation of Five-Membered Rings

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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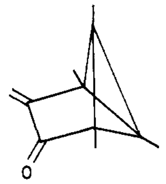

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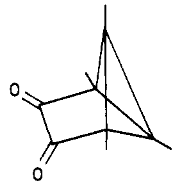

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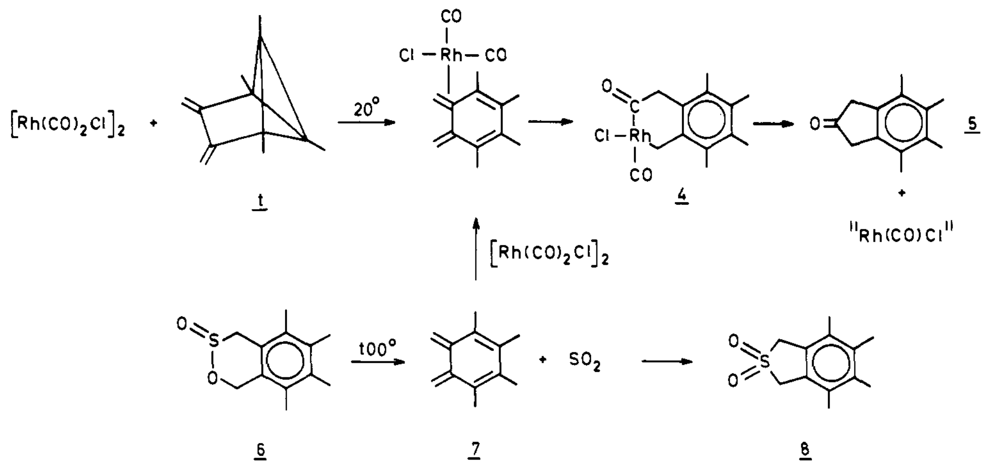
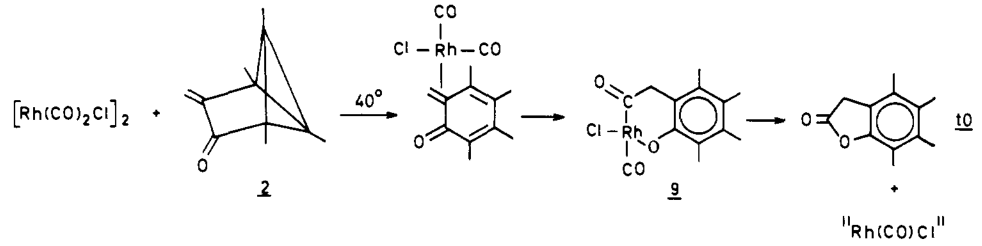
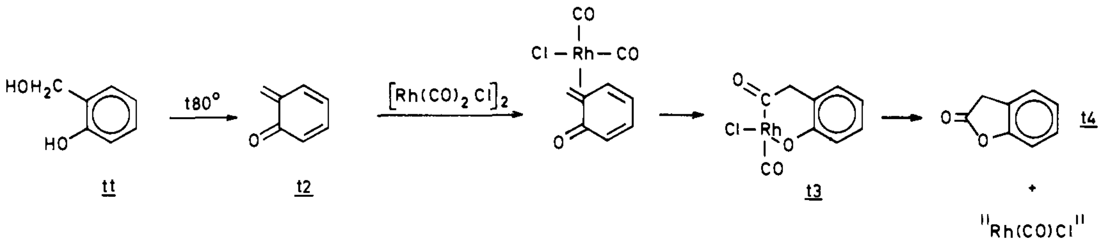
diene **1** (0,160 g, 1,000 mmole) reacted within 2 h in a benzene or chloroform solution (2.0 ml) with $[Rh(CO)_2Cl]_2$ of which 1 equiv (0.194 g, 0.500 mmol) was needed for a complete conversion. On examining the product it was found that besides a rearrangement of the bicyclobutane moiety a CO-insertion 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





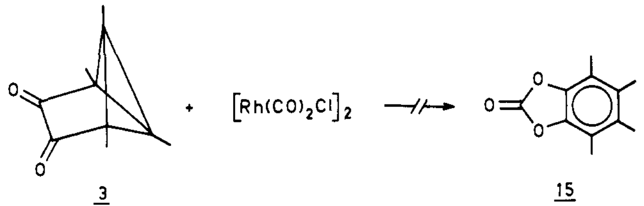


($CDCl_3$ solution) δ 2.28 and 2.37 (both apparent singlets of equal area). Due to the low intensity the methylene signals could not unambiguously be detected.[8] A comparison with literature data[2a,9] allows us to assign structure **4** to the intermediate (possibly in polymeric form; compare ref 2a).

In order to confirm whether it is indeed possible for $[Rh(CO)_2Cl]_2$ to react with a reactive diene like **7** to give **5**, the sulfinic ester **6** obtained from the SO_2 addition to diene **1**[10] was heated in *o*-dichlorobenzene at 100 °C in the presence of 2 equiv of $[Rh(CO)_2Cl]_2$. Together with sulfone **8**, the CO-insertion product **5** was formed in a 67% yield as judged from the areas of the absorptions at δ 3.43 (s, $-COCH_2-$, **5**) and δ 4.27 (s, $-SO_2CH_2-$, **8**). The formation of the CO-insertion product **5** by itself is not in our opinion compelling evidence for the intermediacy of an *o*-xylylene in the reaction between diene **1** and $[Rh(CO)_2Cl]_2$. The presence of **5** merely proves the ability of the Rh-complex to add its CO to a highly reactive diene. It cannot be excluded that in the reaction from **1** to **5** the Rh-complex adds to one of the olefinic bonds, with subsequent intramolecular isomerization of the bicyclobutane moiety.

Enone **2** (0.162 g, 1.000 mmol) reacts with $[Rh(CO)_2Cl]_2$ in a similar manner as diene **1**, although at a lower rate. In this case the conversion to 2[3*H*]-4,5,6,7-tetramethylbenzofuranone (**10**),[11] isolated in 87% yield[8] (0.166 g, 0.874 mmol), is complete within 4 h at 40 °C and is postulated to occur via **9** (not observed by ^1H NMR). In a separate experiment it was shown that *o*-benzoquinone methide **12**, prepared by pyrolysis of *o*-hydroxybenzyl alcohol **11**[12] at 180 °C in the presence of 2 equiv of $[Rh(CO)_2Cl]_2$ afforded to a small extent 2[3*H*]-benzofuranone (**14**)[13] (isolated in a 12% yield).

Diketone **3** did not react with $[Rh(CO)_2Cl]_2$ to the corresponding carbonate **15**. After heating in refluxing benzene for 10 days, the diketone was recovered unchanged.[14]



Finally, it was shown that the observed reactions can be made catalytic. When the reaction between $[Rh(CO)_2Cl]_2$ and diene **1** was carried out in a benzene solution using a catalytic amount of the Rh-complex (5 mol %) under a CO pressure of 40 atm at 20 °C for 2 days, product **5** was isolated in 90% yield. Under similar conditions (40 atm, 40 °C during 4 days) the same holds for enone **2**; compound **10** was isolated in 88% yield.

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(6) Compound **5** was purified by column chromatography (Al_2O_3/hexane). ^1H NMR ($CDCl_3$; 35 °C) δ 2.16 (s, 6 H), 2.20 (s, 6 H), and 3.43 (s, 4 H); ^{13}C NMR ($CDCl_3$; 35 °C; δ relative to internal Me_4Si; noise decoupled) δ 15.4, 16.3, 43.5, 129.1, 133.2, 133.3, and 182.5; Ir (Nujol mull)1750 cm^{-1}; MS:M^+ peak at *m/e* 188. Anal. Calcd for $C_{13}H_{16}O$: C, 82.95; H, 8.57. Found: C, 83.01; H, 8.56. Mp 148.5–149.5 °C.

(7) Using different samples of $[Rh(CO)_2Cl]_2$ the yields of isolated products in the stoichiometric experiments varied from 65 to 90% in the case of **5** and from 30 to 87% in the case of **10.** The reason for this difference is unknown to us. The catalytic processes using CO pressure, however, always afforded almost quantitative yields of **5** and **10.**

(8) The evolution of some free CO was also observed (ir 2270 cm^{-1}). The presence of an absorption at 1850 cm^{-1} remains unexplained.

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(11) Isolation and purification by column chromatography (Al_2O_3/hexane). ^1H NMR ($CDCl_3$; 35 °C) δ 2.16 (s, 6 H), 2.18 (s, 6 H), 3.60 (s, 2 H); ^{13}C NMR ($CDCl_3$ 35 °C; δ relative to internal Me_4Si; noise decoupled) δ 15.6, 16.0, 16.5, 17.0, 33.3, 116.7, 119.0, 120.5, 129.6, 130.3, 135.9, and 174.7; ir (Nujol mull): 1800 cm^{-1}; MS: M^+ peak at *m/e* 190. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.82; H, 7.50. Mp 143.5–144.5 °C.

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Structure Elucidation with Lanthanide-Induced Shifts. The Use of Bound Shifts and High-Symmetry Substrates

Sir:

Nuclear magnetic resonance spectroscopy has become a basic and essential structural tool during the past 20 years. Hinckley's discovery[1] of lanthanide-induced shifts (LIS), which are a function[1,2] of molecular geometry, suggested the possibility that the NMR technique might develop into a liquid state structure elucidation method as powerful as solid-state crystallographic techniques. Unfortunately, this possibility has not yet been realized.[3,4] We report here an experimental and computational approach which we believe represents a major advance in the use of LIS as a rigorous method for structure determination. Not only do we obtain experimental NMR data which are in excellent agreement with molecular structure, but we can now for the first time accurately predict the LIS behavior of a substrate independently of the experimental data for a particular compound. Since no adjustable parameters are involved, the comparison between calculated and experimental LIS provides a far more accurate and reliable assessment of a proposed structure than has been available previously.

The problems involved in structural interpretations of LIS are most easily discussed in terms of a simplified form of the pseudocontact equation[1-4] such as given below:

$$\Delta\delta_i = k(3\cos^2\theta_i - 1)/r_i^3 \qquad (1)$$

This is for a hypothetical lanthanide shift reagent (LSR) substrate complex such as illustrated in Figure 1. Thus, the induced shift, $\Delta\delta_i$, depends on: (1) r_i, the distance between the metal ion and the nucleus of interest, (2) θ_i, the angle subtended by the line connecting the metal ion and the observed nucleus and the line representing the LSR magnetic axis (assumed here to be equivalent to the bond between the lanthanide ion and the heteroatom X), and (3) a constant, k, which should be a characteristic property of the particular LSR.

The difficulty in applying eq 1 lies in the fact that, of the four parameters, only $\Delta\delta_i$ is measured directly; even here most workers have utilized relative shifts for LIS.[4-9] The problems associated with estimating values for r_i and θ_i can be seen in Figure 2, which illustrates the case of a complex with an alcohol. In order to obtain values of θ_i and r_i it is necessary to specify the geometric coordinates of both the metal ion and the observed nucleus relative to the oxygen atom. However, the bond length R_{LX} and the C–X–L bond angle are both unknown as is ω_L, the angle of rotation about the carbon-oxygen bond. Similarly, it may be difficult to specify the exact location of the observed proton. While bond angles and bond lengths for organic molecules can be estimated with reasonable accuracy,[10] one cannot ignore the different available conformations (i.e., the appropriate value or values of ω_H). Earlier workers have used a variety of unjustified simplifications and most commonly have treated these "constants" as variable parameters in their shift optimizations.[4]

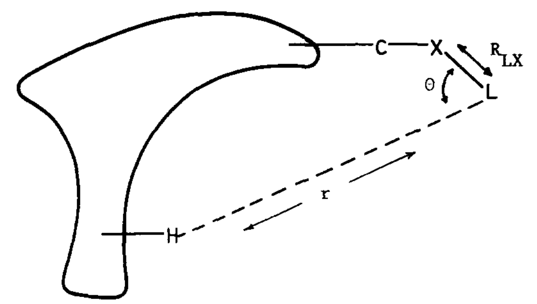


Figure 1. Representation of the geometric relationship between the lanthanide ion L and a hydrogen atom in terms of distance and angle from the magnetic axis for a complex of an organic substrate where X is the binding site.

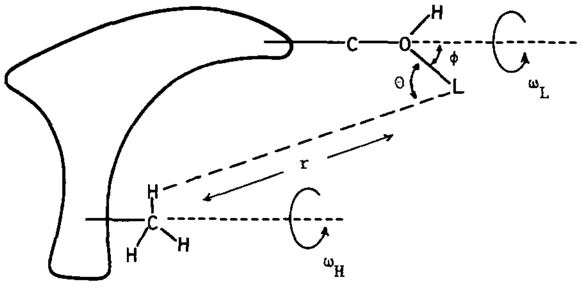
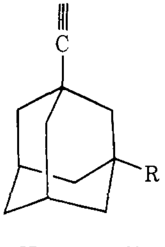
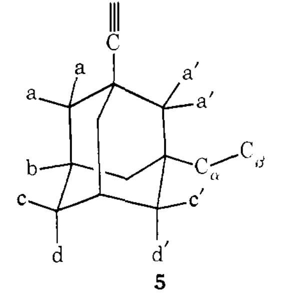


Figure 2. Representation of the geometric relationships in a complex of an alcohol in which conformational flexibility is available for both the lanthanide ion (ω_L) and for a hydrogen of interest on the organic substrate (ω_H).

We have attempted to overcome these difficulties by careful selection of substrates, observed shifts, and experimental and computational methods. In order to reduce uncertainty in the location of the lanthanide ion, we have turned to substrates in which the metal ion should lie on the line defined by the C–X bond; it is therefore possible to specify that $\phi = 0$; ω_L no longer has any relevance. Thus, three parameters have been reduced to one, and only the L–X bond distance (R_{LX}) need be considered. We have also attempted to reduce the other problem shown in Figure 2 (i.e., conformational mobility of the organic moiety as illustrated by ω_H) by turning to conformationally restricted molecules. We further decided to utilize substrates with a high degree of symmetry in order to simplify analyses of spectra and structural computations. The compounds which



1, R = H; **2**, R = CH_3
3, R = C_2H_5; **4**, R = *i*-C_3H_7



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