larger the reaction quantum yield. This expectation is consistent with the observation that the quantum yield is greatest in water, smaller in methanol, and smallest in acetone. The ligating ability of the solvents follows the same order. This mechanism does not specify the subsequent reactions of the nitrosyl radical. The associative attack by the solvent could displace NO from the coordination shell. Alternatively, a rapid radical reaction could occur between the coordinated solvent and the NO radical in close proximity. In both cases, the quantum yield is determined by the rate of the associative attack of the solvent on the metal.

The alternative mechanistic explanation of the reaction is dissociation of an NO radical to form a caged Fe(III)–NO pair. According to this mechanism, the quantum yield would be determined by the relative rate of either the scavenging of the NO or the diffusion of NO out of the cage relative to the rate of secondary recombination of the pair. The fate of the NO was not determined because of the low concentrations ($10^{-4}$–$10^{-5}$ M) at which the photoreactions were studied. Solubility limitations prevent us from exploring other solvents to distinguish between these mechanisms.

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**Registry No.** $[Fe(das)_2(NO)Cl](ClO_4)_2$, 36236-95-0; $[Fe(das)_2(NO)Br](ClO_4)_2$, 64070-48-0; $[Fe(das)_2(NO)I](ClO_4)_2$, 64070-46-8; $[FeCl_2(das)_2]^+$, 47511-84-2; $[FeBr_2(das)_2]^+$, 47511-80-8; $[FeI_2(das)_2]^+$, 64070-44-6.

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# A Resin-Bound Vanadyl Catalyst for the Epoxidation of Olefins

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Oxovanadium(IV) was incorporated on a sulfonic acid (sodium form) ion-exchange resin, and this system was found to catalyze the epoxidation of a variety of cyclic and acyclic olefins in the reaction of the olefin with *tert*-butyl hydroperoxide. The yields of epoxides formed were far greater than those catalyzed in the same reaction with the homogeneous catalyst $VO(acac)_2$, and selectivities toward the epoxide were 100%. Various factors enhancing and diminishing the yields were investigated, and longevity experiments on the catalyst showed that it could be recycled several times without noticeable decrease in activity. Experiments were carried out on various steps of the mechanism of epoxidation proposed elsewhere for the homogeneously catalyzed reaction. It was found that the kinetic results on the heterogeneous catalyst are consistent with the mechanism proposed for the homogeneous system.

## Introduction

In a series of papers by Gould and co-workers, several acetylacetonato complexes of transition metals were studied as catalysts for the oxidation of cyclohexene and other cyclic olefins.[1-5] In these studies, vanadyl ion was of primary interest as the catalytic species.

Increasing interest in polymer-anchored catalysis as well as the commercial importance of epoxidation of olefins prompted us to investigate various methods of incorporation of vanadyl ion onto an immobile support. To this end we have synthesized insoluble polymers containing oxovanadium(IV) attached to acetylacetone, ethylenediamine, and pyridine ligands, which will be reported in another paper.[6] This research is concerned with the incorporation of oxovanadium(IV) onto an ion-exchange resin, evaluation of the activity of the catalyst toward epoxidation, and mechanistic aspects of the reaction.

## Experimental Section

**Starting Materials.** Vanadyl sulfate and bis(acetylacetonato)oxovanadium(IV) were purchased from J. T. Baker and used as received. Aldrich supplied *tert*-butyl hydroperoxide, which was dried over molecular sieves and stored in the cold. Rexyn 101 (H), research grade, a sulfonic and ion-exchange resin of 40–100 mesh, was purchased from Fisher. All olefins were obtained from Aldrich, Eastman, or Chemical Samples; cyclic olefins were purified according to the method of Fusi et al.[7,8]

**Physical Methods and Analyses.** The epoxide products were identified by a comparison of their infrared and NMR spectral qualities, as well as gas chromatographic retention times, with those of authentic samples. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer whereas NMR spectra were obtained on a Varian A-60 spectrometer. Gas chromatography was performed on a Hewlett-Packard Model 5750-B research chromatography instrument equipped with a thermal conductivity detector, using helium as the carrier gas. The reference and sample columns were packed with 5% silicone rubber type UCC-982 (methylvinyl) on 80–100 mesh Chromosorb G support.

Electron spin resonance spectra were recorded on a Strand Magnion-Varian hybrid spectrometer; polymer-bound species were run neat at room temperature.

Analyses of vanadium content on the beads were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Concentrations of hydroperoxide were determined by the authors by placing samples into an acidified KI solution and then titrating the liberated $I_3^-$ with a standard sodium thiosulfate solution.

**Preparation of the Catalyst.** Commercial ion-exchange resin, Fisher Rexyn 101 (H), of particle size 40–100 mesh, was placed in a chromatography column and converted to the sodium form by washing with NaOH solution until the washings were basic. The material was washed with distilled $H_2O$ until the excess base was removed and then treated with $VOSO_4$ solution until the effluent was deep blue. Finally, the beads were washed with water until the washings were colorless. The dried beads may show varying vanadium content from batch to batch depending on the concentration of the $VOSO_4$ solution and other factors; the maximum amount of vanadium incorporated on the beads in this work was 9.99%.

To gain information relative to the nature of vanadyl ion on the sulfonate resin, a weighed quantity of $VOSO_4$ was passed through the beads ($Na^+$ form). After the beads were washed well with distilled water, the sulfate ion was precipitated from the wash as $BaSO_4$, filtered, dried, and weighed. Vanadyl ion was precipitated as the hydroxide. Of the initial sulfate ion, 91.3% was recovered, but only 18.2% of the initial vanadyl ion was detected.

**Epoxidation of Olefins.** The epoxidations of a variety of olefins were all carried out in a similar manner; therefore, only the reaction of cyclohexene will be given in detail. A 25-mL, three-neck flask was fitted with a condenser, a thermometer, and a serum cap. The top of the condenser was fitted with a gas adapter, which was in turn connected to an oil bubbler. Into the flask was placed an amount of polymer-supported catalyst to contain $1.2 \times 10^{-4}$ mol of V, a stir bar, 10 mL of cyclohexene which also served as the solvent, and 2 mL (0.02 mol) of *tert*-butyl hydroperoxide. After the flask was flushed with $N_2$, the serum cap was fitted and the reaction mixture was heated at 80 °C by means of an oil bath controlled by a thermoregulator. The temperature was maintained for 6 h, whereupon three 1-mL aliquots were removed from the reaction mixture. One aliquot was analyzed for peroxide remaining in the solution, and the other portions were used to determine the yield of cyclohexene oxide formed. This was carried out by gas chromatography after the aliquot was treated with triphenylphosphine (5.0 g, 0.02 mol) in acetone to remove the unreacted hydroperoxide.

The yield of epoxides may be expressed in two ways. Since the olefin is added in excess and functions also as the solvent, the yield is based on the amount of *tert*-butyl hydroperoxide added or consumed. Yields based on oxidant added initially can be misleading, since it was found that some oxidant decomposition occurred in competition with the epoxidation reactions. The methods of calculating yield are defined as follows:

$$\text{yield (oxidant added initially)} = \text{o.i.} = \frac{\text{mol of product formed}}{\text{mol of oxidant (initial)}} \times 100$$

$$\text{yield (oxidant consumed)} = \text{o.c.} = \frac{\text{mol of product formed}}{\text{mol of oxidant (initial)} - \text{mol of oxidant (final)}} \times 100$$

Table I presents data, including conditions and yields, for the olefins oxidized in this work.

**Studies on the Active Catalyst.** It was observed that in the epoxidation reactions listed in Table I, the catalyst beads change color early in the reaction from blue to red. The red color persists only for a short time, whereupon the beads take on a yellow appearance which lasts throughout the course of the reaction. The same changes in color were noted by Gould[1] for $VO(acac)_2$ in the corresponding homogeneous reactions.

Table I. Oxidation of Olefins by *tert*-Butyl Hydroperoxide[a]

| Olefin | *T*, °C | Time, h | o.i. | o.c. |
|---|---|---|---|---|
| Cyclohexene | 80 | 6 | 34 | 74 |
| | 40 | 6 | 13 | |
| | 60 | 6 | 19 | |
| | 60 | 4 | 14 | 45 |
| | 60 | 8 | 18 | 46 |
| | 60 | 12 | 18 | 47 |
| | 60 | 24 | 21 | 47 |
| | 60 | 35 | 25 | 49 |
| 1-Methylcyclohexene | 80 | 6 | 9 | 28 |
| 1,2-Dimethylcyclohexene | 80 | 6 | 0 | 0 |
| Cycloheptene | 80 | 6 | 13 | 39 |
| Cyclooctene | 80 | 6 | 31 | 78 |
| | 40 | 6 | 10 | 15 |
| | 60 | 6 | 17 | 23 |
| | 100 | 6 | 34 | 39 |
| 1-Hexene | 60 | 6 | 11 | 17 |
| *cis*-2-Hexene | 80 | 6 | 21 | |
| *trans*-3-Hexene | 60 | 6 | 21 | 39 |
| 1-Octene | 80 | 6 | Trace | Trace |
| 2,4,4-Trimethyl-1-pentene | 80 | 6 | 26 | 38 |
| 2,4,4-Trimethyl-2-pentene | 80 | 6 | 7 | 10 |
| *cis*-3-Methyl-2-hexene | 60 | 6 | 15 | 23 |
| *cis*-3-Methyl-2-hexene | 80 | 6 | 14 | 19 |

[a] All reactions were catalyzed by an amount of beads containing $2 \times 10^{-4}$ mol of V.

Table II. Catalyst Longevity Study in the Oxidation of Cyclohexene

| | Yield, % | |
|---|---|---|
| Experiment[a] | o.i. | o.c. |
| 1 | 19 | |
| 2 | 34 | 34 |
| 3 | 13 | 33 |
| 4 | 18 | 42 |
| 5 | 19 | 41 |

[a] Conditions: 10 mL of cyclohexene, 2 mL of *tert*-butyl hydroperoxide, 60 °C, 6 h, $1.2 \times 10^{-4}$ mol of vanadium.

In order to gain information about the nature of the red intermediate, a saturated solution of $VO(acac)_2$ in cyclohexene was prepared and treated with an excess of *tert*-butyl hydroperoxide. A second solution of the reactants and catalyst was prepared by reverse addition in order to ensure good mixing of the two. After several seconds of standing at room temperature, the solutions turned red whereupon they were quickly frozen in liquid nitrogen and studied by ESR. For both frozen solutions, the ESR spectra were identical.

A third solution of $VO(acac)_2$ and *tert*-butyl hydroperoxide in cyclohexene was prepared and allowed to stand at room temperature. The red color changed to yellow in a few seconds, and the yellow solution was subjected to ESR spectrometry.

**Longevity of the Catalyst.** The epoxidation of cyclohexene was carried out in the manner described at 80 °C for 6 h, using an amount of beads to contain $2 \times 10^{-4}$ mol of vanadium. After that time, the catalyst was filtered from solution, dried, and used again in a second reaction under identical conditions. This process was repeated five times; the data are shown in Table II.

**Rate Studies.** In an effort to compare mechanistic aspects of the heterogeneous catalyst with those reported by Gould[1] for the homogeneous reaction, rate data were compiled, following the appearance of product as a function of time. Whereas it is not possible to know precisely the percent of active sites in the heterogeneous catalyst, these studies assume that the total number of active sites varies directly with the amount of heterogeneous catalyst added. Thus, a reaction mixture containing $4 \times 10^{-4}$ mol of vanadium is assumed to contain twice the number of active sites as $2 \times 10^{-4}$ mol of vanadium. This assumption is used in lieu of concentration of catalyst.

The reactions were conducted in a manner similar to that described earlier for the oxidation of cyclohexene, with the exception that the capacity of the flask was 100 mL, and the volumes of cyclohexene and *tert*-butyl hydroperoxide were increased to 40 and 8 mL, respectively, to minimize the concentration effects upon sample withdrawal. The temperature throughout the reactions was 80 ± 0.1 °C, and the temperature was controlled by a thermoregulator. Quantities of cyclohexene oxide were determined by gas chromatography using durene as the internal standard, and *tert*-butyl hydroperoxide was determined by titration. The results, given in Tables

**Table III.** Appearance of Cyclohexene Oxide with Time for 0.20 mmol of Vanadium

| Time, h | mmol of epoxide | mmol of oxidant remaining |
|---|---|---|
| 1 | 0.31 | |
| 2 | 0.59 | 18.8 |
| 3 | 0.80 | |
| 4 | 1.17 | 17.4 |
| 5 | 1.30 | |
| 6 | 1.50 | 17.1 |
| 8 | 1.90 | |
| 12 | 2.42 | |
| 18 | 2.81 | |
| 20 | 2.40 | 15.2 |
| 24 | 3.05 | |
| 27 | 3.48 | 13.0 |

**Table IV.** Appearance of Cyclohexene Oxide with Time for 0.40 mmol of Vanadium

| Time, h | mmol of epoxide | mmol of oxidant remaining |
|---|---|---|
| 1 | 0.56 | 18.9 |
| 1.5 | 1.00 | 18.0 |
| 2 | 2.06 | 15.9 |
| 4 | 2.48 | 15.1 |
| 7 | 3.36 | 13.3 |
| 12 | 3.83 | 12.3 |
| 24 | 5.88 | 8.2 |

**Table V.** Appearance of Cyclohexene Oxide with Time for 2.0 mmol of Vanadium

| Time, h | mmol of epoxide | mmol of oxidant remaining |
|---|---|---|
| 2 | 2.84 | 14.3 |
| 4 | 3.64 | 12.7 |
| 6 | 4.34 | 11.3 |
| 8 | 5.19 | 9.6 |
| 24 | 7.84 | 4.3 |
| 29 | 10.2 | Trace |

III–V are the average of at least two runs each; the average deviation in the measurements of the quantities of epoxide produced was 3.4%, the greatest spread being ±5.5%.

## Results and Discussion

The most striking feature in this work is the remarkable increase in the catalytic activity of resin-bound vanadyl ion compared to those in other systems. The homogeneous catalyst, VO(acac)$_2$, promoted yields of cyclohexene oxide in the 10–12% range (based on oxidant consumed). Vanadyl ion, anchored to a polystyrene support through acetylacetonate or ethylenediamine ligands, gave yields of cyclohexene oxide up to 26%, roughly a twofold increase over the homogeneous system. However, with vanadyl ion immobilized on the sulfonated ion-exchange resin, yields of up to 74% of cyclohexene oxide were realized.

It should be noted that the yields of cyclohexene oxide using the homogeneous catalyst VO(acac)$_2$ were determined in this work using conditions identical to those employed for the resin-bound system. Under certain reaction conditions (closed tube under vacuum), quantitative yields of the epoxide may be obtained, based on oxidant consumed.[9] Furthermore, Gould[1] has reported that using vanadyl octoate as the catalyst, yields of 95–100% of cyclohexene oxide were obtained at conversions of up to 90% of the hydroperoxide.

A second, major advantage of the heterogenized catalyst over the homogeneous counterpart is in the ease of recovering and reuse of the catalyst. Whereas the VO(acac)$_2$ is not recoverable from epoxidation reactions, vanadyl anchored to the sulfonated resin may be recovered by filtration and reused many times before a significant decrease in activity is apparent. The results in Table II show that the yields of cyclohexene oxide after five runs with the same catalyst are essentially the same as the first run. It should be noted that the variation in yields (o.i.) in Table II, particularly for runs 2 and 3, is reproducible.

Table I shows that the catalyst is versatile in that several different types of olefins can be oxidized in good yields. In general, cyclic olefins are more susceptible to oxidation than acyclic alkenes. Substitution of one olefinic hydrogen by a methyl group results in a decrease in yield of epoxide, and doubly substituted olefins are inert to oxidation. No particular difference is noted between the ease of oxidation of terminal and internal olefins.

In a kinetics study, Gould proposed a mechanism for the oxidation of cyclohexene by VO(acac)$_2$. It was of interest to investigate certain aspects of the mechanism for the resin-bound catalyst to determine whether parallels existed between the homogeneous and heterogeneous reactions. Two features of the proposed mechanism were investigated: inhibiting effect of *tert*-butyl alcohol, and the oxidation state of the active catalyst.

According to the mechanism proposed by Gould, the oxidation of cyclohexene is strongly inhibited by the presence of *tert*-butyl alcohol which is the by-product. To test the inhibitory nature of the alcohol, several experiments were conducted with added amounts of *tert*-butyl alcohol of 10, 5, 2, and 1 mL. In all cases, no product was detected at times up to 24 h in those systems to which *tert*-butyl alcohol had been added.

A second aspect of Gould's mechanism that was investigated in this work was the activation of the catalyst, i.e., the conversion of V(IV) to V(V), which was proposed to be rapid and irreversible in the presence of *tert*-butyl hydroperoxide. An unequivocal method of determining an oxidation state change on vanadium from IV to V is by ESR spectrometry, since the signal arising from the d$^1$ configuration of VO$^{2+}$ will disappear as the diamagnetic V(V) is produced.

ESR spectra were recorded on the frozen, red-colored intermediate and also on the yellow solution. An analogous oxidation of vanadyl ion by hydrogen peroxide has been reported,[10] and an intermediate consisting of a vanadium(V) complex with a paramagnetic ligand was detected by ESR spectrometry. On the basis of a *g* value greater than 2.0023 and the observed narrow line width superimposed on the eight-line vanadyl spectrum, it was speculated that the nature of the intermediate was the radical OVOO$^{2+}\cdot$. Therefore, it was expected that the red species might also show free-radical behavior in the ESR spectrum. However, only a spectrum arising from a vanadium(IV) species was observed, although the signals were much weaker than those of VO(acac)$_2$ in a comparably concentrated solution. Possibly, the red substance is a mixture of vanadium(IV) and -(V) species with the hydroperoxide functioning as a ligand. No evidence was obtained for any free-radical species in the frozen state.

The yellow solution was also investigated by ESR techniques; the spectrum indicated that the species was diamagnetic. Thus, our studies on the homogeneous system are in accord with Gould's proposal for the rapid and irreversible generation of the vanadium(V) species as the active catalyst.

ESR spectral studies were also carried out on the immobilized vanadyl catalyst before and after a 6-h reaction in the oxidation of cyclohexene. In both cases the spectra were recorded at room temperature on the neat, dried catalyst, and in both cases the spectra were identical (see Figure 1). It should be pointed out that although the catalyst beads show transient colors during the course of the reaction from blue to red to yellow, the recovered catalyst, after drying in an oven at 50 °C for 4 h, shows a blue color very nearly the same as that of the initial catalyst.

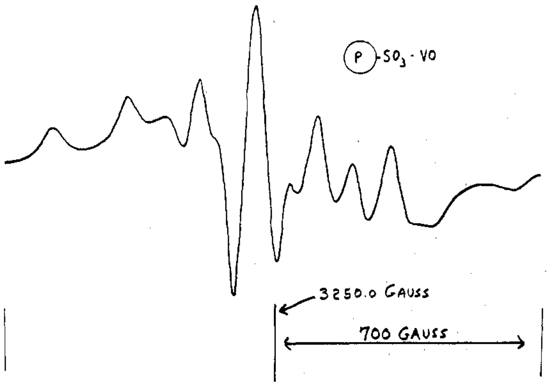

**Figure 1.** First-derivative ESR spectrum of the resin-bound $VO^{2+}$ catalyst before and after a 6-h oxidation reaction.

The ESR data suggest either that the catalytically active species is $VO^{2+}$, and not V(V), for the resin-bound system or that the oxidation state change on the metal is reversible. However, it is also possible that only a tiny fraction of the vanadium sites are catalytically active, and the spectrum obtained after reaction merely arises from the inactive sites. If this latter possibility is correct, then the resin-bound catalyst which shows about a sixfold increase in activity over the homogeneous system is actually far more active than that, since the reaction would be promoted by considerably fewer catalytic sites.

We are not yet in a position to differentiate among the possible explanations; the answer must await further studies on the active form of the catalytic species.

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**Registry No.** *tert*-Butyl hydroperoxide, 75-91-2; cyclohexene, 110-83-8; 1-methylcyclohexane, 591-49-1; 1,2-dimethylcyclohexene, 1674-10-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *trans*-3-hexene, 13269-52-8; 1-octene, 111-66-0; 2,4,4-trimethyl-1-pentene, 107-39-1; 2,4,4-trimethyl-2-pentene, 107-40-4; *cis*-3-methyl-2-hexene, 10574-36-4; $VO^{2+}$, 20644-97-7.

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# Organometallic Nitrosyl Chemistry. 4.[1] Additional Reactions of Nitrosyl Chloride with Neutral Carbonyl Complexes

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Nitrosyl chloride exhibits a number of different reaction modes during its reactions with monomeric and dimeric neutral carbonyl complexes of transition metals. From its reaction with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ under controlled conditions, the organometallic compounds $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$, and $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ can be obtained. (The latter complex can also be prepared by treating $[(\eta^5\text{-}C_5H_5)Cr(NO)(OCH_2CH_3)]_2$ in benzene with gaseous HCl.) In contrast, the analogous $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo or W) compounds react with ClNO in a 1:2 stoichiometry to produce $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ in comparable yields, but both of these products form intractable solids in the presence of an excess of ClNO. The cobalt complexes $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and $Co(CO)_3(NO)$ are both converted to $[Co(NO)_2Cl]_2$ by novel reactions with nitrosyl chloride, and (arene)$M(CO)_3$ (M = Mo or W) compounds form the polymeric $[M(NO)_2Cl_2]_n$ species via labile $M(CO)_2(NO)_2Cl_2$ intermediates under identical experimental conditions. Nitrosyl chloride apparently behaves as a nitrosonium salt in its reaction with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ since the $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]^+$ cation is the principal product isolated, but it simply cleaves $Mn_2(CO)_{10}$ to yield the inert $Mn(CO)_5Cl$. Possible pathways leading to the formation of all products are presented.

## Introduction

We recently reported[2] that the stoichiometric reaction of nitrosyl chloride with weakly nucleophilic metal carbonyl anions provides a convenient means of synthesizing neutral nitrosyl compounds such as $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ (M = Cr, Mo, or W), $W(CO)_4(NO)Cl$, $Mn(CO)_4(NO)$, and $Fe(CO)_2(NO)_2$ in reasonable yields. Further reactions between ClNO and the neutral carbonyl-containing compounds readily lead to neutral chloronitrosyl complexes in most instances. However, in some cases unexpected products result. For instance, when $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ is treated with ClNO, a minor product is $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl_2]_2$, whose appearance, we believe,[2] reflects the fact that ClNO exists in solution as part of the equilibrium

$$2ClNO \rightleftharpoons 2NO + Cl_2$$

In other words, solutions of nitrosyl chloride may exhibit reactions that can be attributed to any of the chemical entities present in the above equilibrium. Even when nitrosyl chloride reacts as such with neutral carbonyl complexes, a number of different reaction modes can be envisaged for it. Among these are (1) displacement of ligands capable of donating a total of four electrons to a metal in a coordinatively saturated complex, (2) complete displacement of a hydrocarbon ligand regardless of the number of electrons that it formally donates to the metal, and (3) formal reaction as a nitrosonium salt with only $NO^+$ being coordinated to the metal center. This paper describes new reactions between ClNO and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo, or W), $Co(CO)_3(NO)$, $(\eta^5\text{-}C_5H_5)Co(CO)_2$, (arene)$M(CO)_3$ (M = Mo or W), or $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, reactions which typify these reaction modes.

## Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to reported procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled,