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Nature of the Active Catalyst in the Rhodium Complex Catalyzed Reduction of Nitric Oxide by Carbon Monoxide

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Ethanolic solutions of dichlorodicarbonylrhodium(I) anion containing aqueous acid catalyze the reduction of nitric oxide by carbon monoxide under mild conditions according to eq 1.[1]

$$2NO + CO \rightarrow N_2O + CO_2 \quad (1)$$

Recently, we have reported a study which defines the co-catalytic role of water in this catalytic process.[2] In order to gain a further understanding of this mechanistically complicated reaction, a knowledge of the catalytically active species in solution is essential. In this context, the anion $[RhCl_2(CO)_2]^-$, whether generated in situ or introduced as the salt of a noninteracting cation, functions simply as the catalyst precursor.[3] The catalytically active species has previously been proposed as a mixed carbonylnitrosylrhodium complex since at room temperature it is maintained in the reaction solution only under a mixture of NO and CO.[1,4] Upon exposure to CO alone, the catalytically active species re-forms the $[RhCl_2(CO)_2]^-$ catalyst precursor, while under NO alone it forms an anionic rhodium nitrosyl (vide infra) which can also serve as a catalyst precursor under catalytic conditions. To date the active catalyst has steadfastly resisted all attempts at isolation. We now report the characterization of this species in solution and tentatively formulate it as a rhodium(III) carbonyl dinitrosyl with both nitrosyl ligands bent.

Experimental Section

Reacting solutions of the active catalyst were prepared in a hood by bubbling a 2:1 mixture of nitric oxide and carbon monoxide through a solution, supported on the frit of a Schlenk filter tube, of $(AsPh_4)[RhCl_2(CO)_2]$ (0.5 mmol) or $[RhCl(CO)_2]_2$ (0.25 mmol) in 25 mL of dry ethanol to which 0.1 mL (for IR spectra) or 0.25 mL of concentrated HCl had been added. The characteristic dark olive green color of the active catalyst was completely developed within 30 min. The complexes $(AsPh_4)[RhCl_2(CO)_2]$ and $[RhCl(CO)_2]_2$ were prepared by literature methods;[5] on dissolution in HCl solution the dimer forms the $[RhCl_2(CO)_2]^-$ anion.[6]

Ultraviolet and visible spectra of solutions of the catalyst and catalyst precursors were recorded on a Cary 118 spectrophotometer using a flow cell as described previously.[1] Infrared spectra were obtained on a Perkin-Elmer 467 spectrophotometer. While the IR spectrum was being scanned, the reacting catalyst solution was agitated under NO and CO in a 10-mL syringe and simultaneously injected into the lower port of a solution IR cell through a flexible Teflon syringe needle. The upper cell port led to a nitrogen-flushed ballast flask. The reference cell contained the catalyst solvent (ethanol + HCl). Because this solvent necessarily contained water, calcium fluoride cells (0.1 mm) were used.

Low-temperature ESR spectra were obtained on a JEOL 3BSX X-band ESR spectrometer. Samples were prepared by injecting a solution of the active catalyst into a NO/CO-filled capillary, which was immediately cooled in a dry ice bath and then removed only momentarily in order to seal the capillary. The spectrometer cavity was maintained at −65 °C while the spectrum was sought. The sample solutions showed no signs of decomposition before or after insertion into the cavity.

Two salts of the red rhodium nitrosyl complex were prepared by generating the green active catalyst from $[RhCl(CO)_2]_2$ followed by reaction with nitric oxide alone. After the reaction was judged complete (~15 min), excess NO was flushed from the solution with nitrogen. The solution was then transferred by syringe to an ethanol solution of a slight excess of either Ph_4AsCl or Me_4NCl under nitrogen. The precipitate was filtered in air and washed with ethanol and ether. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Micro-Analysis, Inc., Wilmington, Del.

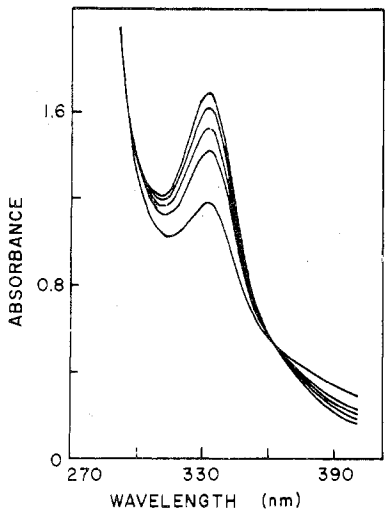

Figure 1. UV–visible absorption spectrum of the active catalyst re-forming the $[RhCl_2(CO)_2]^-$ precursor. A 0.628 mM solution of $(AsPh_4)[RhCl_2(CO)_2]$ in EtOH–HCl was stirred under CO/NO (4:1), sealed in a flow cell, and monitored for 2 h. The maximum which grows in at 332.5 nm (ϵ 3.06 × 10^3 M^{-1} cm^{-1}) is characteristic of $[RhCl_2(CO)_2]^-$.

Results and Discussion

In order to establish that only a single rhodium species is present to significant concentrations in the green, catalytically active solutions formed from $[RhCl_2(CO)_2]^-$, a visible–UV spectrophotometric study was carried out. A dilute solution (0.628 mM) of the carbonyl anion in a reaction flask was charged with CO/NO in a 4:1 ratio and sealed in a flow cell several hours later. When the visible–UV spectrum of the solution was recorded periodically over a 2-h period, a gradual increase in the absorbance of $[RhCl_2(CO)_2]^-$ at 332.5 nm accompanied by a decrease in the longer wavelength absorbance of the active catalyst was observed with a clear isosbestic point at 360 nm. This is shown in Figure 1. The isosbestic point is identical with that observed previously[1] by charging a dilute solution of the red nitrosyl catalyst precursor under CO and monitoring the spectrum over time. Thus only a single predominant species exists in the green, catalytically active solutions whether generated from $[RhCl_2(CO)_2]^-$ or from the red nitrosyl complex.

The infrared solution spectrum of the catalytically active species could not be obtained using a sealed solution cell. While the catalyst can be maintained indefinitely at room temperature under a mixture of NO and CO, it is not stable in the conventional sense but is continuously consuming NO and CO in the catalytic cycle, resulting in a steady-state concentration of the active catalyst. Depletion of either NO or CO in the solution breaks the catalytic cycle and prevents regeneration of the catalytically active species. For example, it was observed that in a standard IR cell a 0.02 M catalyst solution initially saturated with NO and CO exhibits significant decomposition within about 10 s. This observation precluded using a closed solution cell for obtaining an infrared spectral characterization of the active catalyst and led to the design and employment of a simple flow cell system for this purpose. With this system, the residence time of the catalyst solution in the IR cell was kept to well under 10 s, the NO and CO in solution was not depleted, and the spectrum of the active catalyst thus was measured in the range 2700–1500 cm^{-1}. The spectrum is shown in Figure 2(a). The active catalyst shows only three bands in this range, at 2095, 1715, and 1680 cm^{-1}, assignable to one ν_{CO} and two ν_{NO} vibrations, respectively. The other two absorptions in the spectrum at

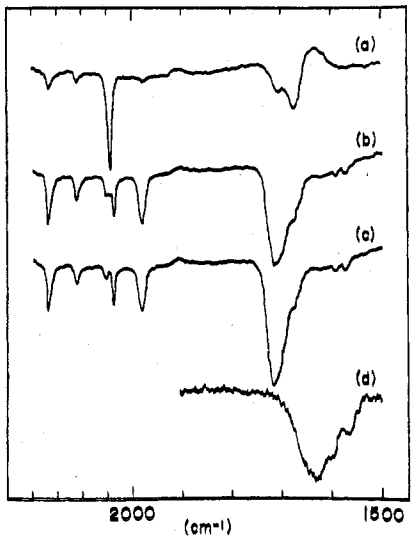

Figure 2. (a) Infrared spectrum of the active catalyst in solution. (b) Spectrum of solution ca. 1 min after flow is stopped. (c) Spectrum after 5 min—later spectra of solution showed no change. (d) Spectrum of NMe_4^+ salt of red rhodium nitrosyl (KBr pellet).

2340 and 2230 cm^{-1} are due respectively to the CO_2 and N_2O products of the catalytic reaction. Consequently, we formulate the active catalyst as a rhodium carbonyl dinitrosyl complex. The spectrum also indicates complete conversion of $[RhCl_2(CO)_2]^-$ to the active catalyst from the absence of carbonyl stretches characteristic of this catalyst precursor.

The positions of the bands in the infrared spectrum offer further insight into the nature of the active catalyst. While both nitrosyl stretching frequencies are in the region of ambiguity for determining nitrosyl bonding mode,[4,8,9] the value of ν_{CO} is relatively high and characteristic of a rhodium(III) carbonyl species.[10,11] Since the ambiguity regarding nitrosyl bonding mode involves bent coordination vs. linear coordination to a low oxidation state metal ion and since the carbonyl stretch provides direct evidence of the Rh oxidation state, the ambiguity in the present case is resolved. Both nitrosyl ligands in the active catalyst are bent and the complex is best formulated as $[RhCl_2(CO)(NO^-)_2]^-$.

By standard electron-counting formalisms in which NO^- is a 1-electron donor, this complex is a 16-electron species. Examples of pentacoordinate Rh^{III}–NO^- complexes have been reported in the literature, and a number of them such as $RhCl_2(NO)(PPh_3)_2$[12] and $RhCl(NO)(ppp)^+$ [13] have been structurally studied. An alternative possibility is that the active catalyst is solvated to form a six-coordinate 18-electron species. Lability of the coordinated solvent molecule must be relatively high since it has previously been determined that the rate-determining step of the catalytic cycle involves CO attack on the active catalyst.[1] Binuclear formulations of the active catalyst have been eliminated through kinetic studies[1] which have established a first-order dependence on metal ion concentration.

In order to verify that the active catalyst and not a decomposition product was being observed in the infrared spectrum, the decomposition of the active species was monitored by allowing the solution to stand in the infrared cell while repeatedly scanning the spectrum. The spectrum of the decomposing catalyst solution is shown in Figure 2(b) while that of the decomposed solution is in Figure 2(c). None of the bands that developed correspond to bands in the initial spectrum. In addition, the initial spectrum of the active catalyst could be reproduced by reestablishing the flow of catalyst solution through the cell. The only readily identifiable decomposition product is $[RhCl_2(CO)_2]^-$.[7] Also evident are a rhodium(III) carbonyl, possibly $[RhCl_5(CO)]^{2-}$,[14] from the band at 2110 cm^{-1},[10,11] and at least one nitrosyl species, evident from the broad band centered at 1710 cm^{-1}.

The low-temperature ESR spectrum of the active catalyst in solution is consistent with the formulation of the catalyst as a dinitrosyl complex since no paramagnetism was detected. This spectrum was obtained using a sealed sample maintained at dry ice temperatures (−78 °C prior to placement in the ESR cavity, −65 °C in the cavity). At these temperatures, the rate of catalysis is dramatically slowed and catalyst solutions show no sign of decomposition for days. A consideration of possible carbonylnitrosylrhodium complexes reveals that mononitrosyls such as $[RhCl_2(CO)_2(NO)]^-$ and $[RhCl_2(CO)(NO)]^-$ are odd-electron species and will be paramagnetic, while dinitrosyls such as $[RhCl_2(CO)(NO)_2]^-$ or $[RhCl_2(CO)(NO)_2(S)]^-$ (S = solvent) will be diamagnetic. No paramagnetism was detected in fresh solutions of the active catalyst prepared under a number of NO:CO gas ratios, nor was any signal detected from older catalyst solutions kept at dry ice temperature or from decomposed catalyst solutions.

While the active catalyst generated under catalytic conditions is not stable, an alternate preparation has resulted in a surprisingly stable catalyst solution which will last for hours even in the absence of NO and CO. The catalyst precursor in this preparation is the $AsPh_4^+$ salt of the anionic red rhodium nitrosyl formed by the action of NO alone on the active catalyst as generated from $[RhCl_2(CO)_2]^-$. The stable solution of the green active catalyst is prepared by reacting this rhodium nitrosyl in anhydrous acidic ethanol under CO alone. This is achieved by adding a benzene or toluene solution of *p*-toluenesulfonic acid, dried by distilling off the azeotrope, to a slurry of the rhodium nitrosyl in dry ethanol and passing CO over the mixture for about 15 min. The infrared spectrum of the resulting green solution shows a mixture, in roughly equal proportions, of the catalyst and $[RhCl_2(CO)_2]^-$. Under CO the active catalyst decomposes slowly to $[RhCl_2(CO)_2]^-$ while under N_2 it yields a red solution. The slow decomposition of the active catalyst in these solutions may well be an autocatalytic reaction promoted by the formation of water through acid-induced coupling of nitrosyl ligands followed by decomposition to $N_2O + H_2O$. That water promotes the decomposition of the catalytically active species was demonstrated by adding it to the stable green solution and observing an instantaneous color change to red. Thus, stabilization of the active catalyst may be achieved at room temperature under completely anhydrous conditions.

Previous attempts to stabilize the active catalyst by the addition of triphenylphosphine (L) to the ethanol solutions containing aqueous acid were unsuccessful in yielding a mixed nitrosyl carbonyl compound and instead produced a mixture of $Rh(NO)Cl_2L_2$, $RhCl(CO)L_2$, and an unidentified carbonyl containing species (ν_{CO} ~1940 cm^{-1}).[1,12] This mixture of products precluded using phosphine addition to the stable solution of the active catalyst and quantitative analysis of the evolved gases as a means of determining catalyst stoichiometry.

The red anionic rhodium nitrosyl which serves as precursor to the stable green catalyst solution has been prepared with several cations. The infrared spectrum of the NMe_4^+ salt in a KBr pellet, shown in Figure 1(d), has a broad unresolved band centered at 1630 cm^{-1}. Therefore this complex is not identical with the nitrosyl species formed by the decomposition of the catalyst in the absence of reactant gases. This complex had been tentatively characterized as $[RhCl_2(NO)_2]^-$ through the stoichiometry of its formation,[1] but analysis of the $AsPh_4^+$ and the NMe_4^+ salts indicates a more complex formulation,[15] which we have not been able to define. Efforts to obtain analytically pure samples of this intriguing complex and crystals suitable for a structure determination are continuing.

In summary, the catalytically active species is best formulated as a rhodium(III) carbonyl dinitrosyl complex in which both nitrosyl ligands are bent. The catalyst reacts with NO to form a complex anionic rhodium nitrosyl, which in turn can serve as the catalyst precursor and which under anhydrous conditions with CO yields a relatively stable solution of the catalyst.

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Registry No. $[RhCl_2(CO)(NO)_2]^-$, 61752-34-9; $(AsPh_4)[Rh_2(NO)_2Cl_4]$, 61867-72-9; $(NMe_4)_2[Rh_2(NO)_2Cl_5]$, 61867-73-0; $(AsPh_4)[RhCl_2(CO)_2]$, 13986-82-8; $[RhCl(CO)_2]_2$, 14523-22-9; nitric oxide, 10102-43-9.

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(15) The analytical results, though not good, are best fit by the empirical formulas $(AsPh_4)[Rh_2(NO)_2Cl_4]$ and $(NMe_4)_2[Rh_2(NO)_2Cl_5]$. Anal. Calcd for $(AsPh_4)[Rh_2(NO)_2Cl_4]$, $C_{24}H_{20}AsCl_4N_2O_2Rh_2$: C, 36.44; H, 2.55; Cl, 17.93; N, 3.54. Found: C, 37.69; H, 2.80; Cl, 18.46; N, 3.37. Calcd for $(NMe_4)_2[Rh_2(NO)_2Cl_5]$, $C_8H_{24}Cl_5N_4O_2Rh_2$: C, 16.25; H, 4.09; Cl, 29.98; N, 9.47. Found: C, 17.94; H, 4.62; Cl, 31.73; N, 9.28. The species are diamagnetic.

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Stereoselective Binding of Optically Active Amino Acids by Nickel(II) and Copper(II) Complexes of *N*-Carboxymethyl-β-(2-pyridyl)-L-α-alanine

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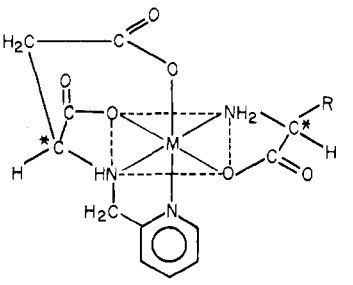
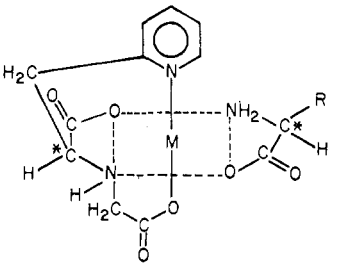
Previously we reported[2] the stereoselective binding of optically active amino acids by Ni(II) and Cu(II) complexes of *N*-(2-pyridylmethyl)-L-aspartic acid (*N*-pyr-L-Asp). The stronger preference of these complexes for L-amino acidates was rationalized by assuming that the resulting complex had geometry I. In this structure the L-amino acidates (as shown) would bind normally because the bulky R group would not encounter significant crowding from the carboxylate donor trans to the pyridine. On the other hand, the R group of D-amino acidates (where R and H interchange positions from the L form) would crowd the large pyridyl group thereby reducing the interaction between D-amino acidates and the metal ion.



I

For the purpose of testing this model further, we have synthesized a ligand *N*-carboxymethyl-β-(2-pyridyl)-L-α-alanine (Cm-L-Pyala) in which the pyridyl and carboxylate groups are essentially interchanged from those in *N*-pyr-L-Asp. By assuming a structure similar to I, we would expect Cm-L-Pyala^{2-} and an L-amino acidate to coordinate as follows:



II

In this case, steric crowding between the R side chain and the pyridyl group should reduce binding of the L-amino acidates as compared to their D enantiomers. Thus, the selectivity should be just the reverse of that found in the M(*N*-pyr-L-Asp) complexes.

The strength of the binding of D- and L-amino acidates (A^-) in these Cm-L-Pyala complexes was determined by measuring constants for the following equilibria:

$$(\text{Cm-L-Pyala})M + \text{L-}A^- \rightleftarrows (\text{Cm-L-Pyala})M(\text{L-A})^- \quad (K_L) \qquad (1)$$

$$(\text{Cm-L-Pyala})M + \text{D-}A^- \rightleftarrows (\text{Cm-L-Pyala})M(\text{D-A})^- \quad (K_D) \qquad (2)$$

The results of these studies are reported herein.

Experimental Section

Preparation of *N*-Carboxymethyl-β-(2-pyridyl)-L-α-alanine, Cm-L-PyalaH$_2$. Racemic β-(2-pyridyl)-α-alanine (PyalaH)) was prepared as described previously.[3] It was resolved by precipitation of L-Pyala-*d*-tartrate with *d*-tartaric acid as reported.[3] However, instead of using $HgCl_2$ to remove L-Pyala from the diastereomeric salt, 10.0 g (31.5 mmol) of L-Pyala-*d*-tartrate was dissolved in 100 ml of hot water. The resulting solution was passed through a column of 150 ml of Bio-Rad AG-3 weakly basic ion exchange resin in the basic form. The L-PyalaH was eluted with approximately 1 L of hot water. (Ninhydrin tests were negative on later fractions.) Evaporation of the solution yielded L-PyalaH which was recrystallized from 80% ethanol to give 4.65 g (89%).

The 4.65 g (28 mmol) of L-PyalaH was neutralized in 42 ml of water to pH 10 with 5 M LiOH. Separately, 4.67 g (32.8 mmol) of bromoacetic acid was dissolved in a minimum volume of water (~5 ml) and brought to pH 6 at 0 °C with 5 M LiOH. To the stirred L-Pyala solution at 60 °C was added slowly the bromoacetic acid solution. The pH 10 of the solution was maintained by adding 5 M LiOH as required. When the pH ceased changing (after ~30 min), the pH was reduced to 3 with concentrated HCl. After evaporation under reduced pressure, an oil remained. It was dissolved in 95% ethanol; after a few hours at room temperature solid Cm-L-PyalaH$_2$ precipitated. Recrystallization from hot methanol gave 3.0 g (48%) of Cm-L-PyalaH$_2$. It had a melting point of 178–180 °C and $[\alpha]_D^{25}$ +36.4 (*c* 0.35, H_2O). Anal. Calcd for $C_{10}H_{12}N_2O_4 \cdot 1.5H_2O$: C, 47.8; H, 6.01; N, 11.1. Found: C, 48.2; H, 6.14; N, 11.21. The proton NMR spectrum of Cm-L-PyalaH$_2$ in D_2O shows the following peaks: δ 7.85–8.90 multiplet, pyridine H's; δ 4.05–4.32 doublet of doublets,