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platinum(III) species disappears and strongly acidic protons are generated, formed in a redox process involving oxidation of water.

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Supplementary Material Available: Tables of positional parameters and anisotropic temperature factors for **1*** and equations of planes, deviations of atoms, and dihedral angles for **1*** and figures showing EPR spectra of **2a** and **2c** (4 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Notes

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Homogeneous Catalytic Reduction of Nitric Oxide by Olefin in the Presence of Palladium(II) Chloride

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The catalytic reduction of NO by CO, NH_3, H_2, or hydrocarbons over a heterogeneous system[1] has been investigated in an effort to find suitable ways to remove these pollutants in automobile emission. Similar attempts to reduce NO by using homogeneous catalysts also led to the development of several successful catalyst systems. To date, however, only the reduction of NO by CO[2-8] and by NH_3[9] has been reported. In the present paper, we describe the reduction of NO by olefin catalyzed by a soluble $PdCl_2$ system (reaction 1) under mild conditions. This

$$2NO + RCH{=}CH_2 \rightarrow N_2O + RCOCH_3 \tag{1}$$

catalytic reaction is the first one using hydrocarbons for NO removal homogeneously. In addition, it also appears to be a useful method for making organic carbonyl compounds from olefins.

In choosing an appropriate catalyst system for reaction 1, we were attracted to the $PdCl_2$–$CuCl_2$ system in view of the fact that $PdCl_2$ is known to oxidize olefin to ketone or aldehyde[10] and the $PdCl_2$–$CuCl_2$ system is found to catalyze the reduction of NO by CO.[5] A simple catalyst system was obtained consisting of $PdCl_2$ and $CuCl_2$ dissolved in water. The catalysis of reaction 1 takes places at ambient temperature under an initial NO pressure of less than 1 atm. While quantitative analysis of each component was performed on gas chromatographs, the identities of the organic products were verified by comparing their IR ^1H NMR, and mass spectra with those of authentic samples. The quantitative data of several reaction runs are summarized in Table I, and changes of reactants and products vs time for the reaction of NO with ethylene are displayed in Figure 1.

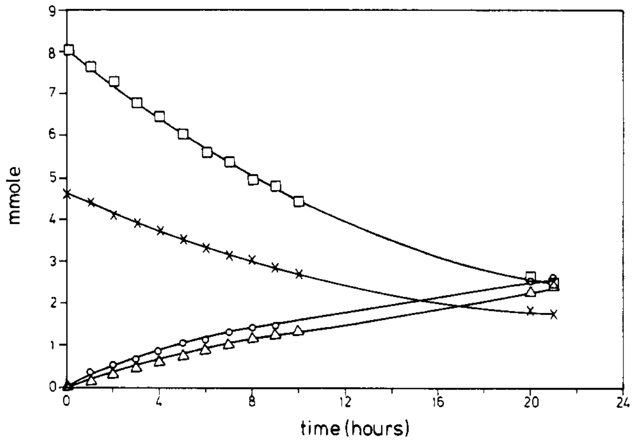

Figure 1. Change of compositions as a function of time for the catalytic reduction of NO by ethylene using the $PdCl_2$–$CuCl_2$–H_2O system at 19 °C: nitric oxide (□); ethylene (×); nitrous oxide (△); acetaldehyde (○).

The stoichiometry for the catalysis of reaction 1 by the $PdCl_2$–$CuCl_2$–H_2O system is indicated by the relative ratio of NO and olefin consumed and N_2O and carbonyl compound produced, shown in Table I. The rate of catalysis at ambient temperature corresponds to 0.384, 0.255, 0.298, and 0.190 (turnovers/h)/palladium ion on the basis of N_2O produced for ethylene, propylene, 1-butene, 1-hexene, respectively (runs I–IV). These terminal olefins were converted exclusively to the corresponding 2-ketones. No other organic product was detected by GC. Notable here is that the reaction NO with an internal olefin such as cyclohexene is extremely slow under reaction conditions similar to those for terminal olefin. In the absence of $CuCl_2$, $PdCl_2$ in a mixture of DMSO and water (9:1 v/v) is also effective for the catalysis of reaction 1. No palladium precipitation was observed under the conditions used. Quantitative data of the reactions catalyzed by the system are shown in Table I (runs V–VIII). Surprisingly, other solvent mixtures such as acetonitrile–water and DMF–water exhibit much smaller activities for the catalysis (runs IX and X).

During the catalysis of reaction 1 by the $PdCl_2$–$CuCl_2$–H_2O system, the reaction solution exhibited an absorption at 425 nm in the UV–vis spectrum. This band is close to the absorption at 421 nm for a pure $PdCl_2$ solution.[11] There is no evidence for the coordination of olefin or NO to the palladium. To understand further the features of catalysis by $PdCl_2$–$CuCl_2$–H_2O, several control experiments were carried out, leading to the following observations. (i) No catalysis takes place in the absence of $PdCl_2$. (ii) A reaction solution with 0.59 M LiCl present has only 82% of the catalytic activity in its absence. (iii) The presence of 0.55

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Table I. Results of the Catalytic Reduction of NO by Olefins[a]

run	solvent	temp, °C	react consumed, mmol		product, mmol	
			NO	olefin	N_2O	carbonyl
I	H_2O	25	4.30	2.33 (ethylene)	2.17	2.08 (acetaldehyde)
II	H_2O	20	3.09	1.31 (propylene)	1.44	1.37 (acetone)
III	H_2O	24	3.71	1.68 (1-butene)	1.68	1.60 (2-butanone)
IV	H_2O	19	2.08	1.16 (1-hexene)	1.07	1.05 (2-hexanone)
V	DMSO/H_2O[b]	25	4.17	2.07 (ethylene)	1.67	1.72 (acetaldehyde)
VI	DMSO/H_2O[b]	20	2.15	0.82 (propylene)	0.79	0.79 (acetone)
VII	DMSO/H_2O[b]	24	2.73	1.17 (1-butene)	1.17	1.21 (2-butanone)
VIII	DMSO/H_2O[b]	19	1.80	0.92 (1-hexene)	0.83	0.80 (2-hexanone)
IX	DMF/H_2O[b]	27	2.98	0.94 (ethylene)	0.48	0.94 (acetaldehyde)
X	CH_3CN/H_2O[b]	27	1.60	0.88 (ethylene)	0.38	0.87 (acetaldehyde)
XI[c]	H_2O[c]	25		2.62 (ethylene)		2.38 (acetaldehyde)

[a] Each catalyst solution was prepared according to the procedure described in the text. Reaction time = 10 h. A systematic error of 5% is estimated for each run. [b] The ratio of organic solvent to water is 9:1 (v/v). [c] The reaction conditions are the same as those in run I except that NO is replaced by Ar.

M H^+ decreases the activity to 22% of that in its absence. (iv) Omission of $CuCl_2$ reduces the solubility of $PdCl_2$ and leads to a decrease in catalytic activity and precipitation of palladium metal, but high concentrations of $CuCl_2$ (>0.59 M) inhibit the catalysis; e.g. at 1.17 M $CuCl_2$, the rate is 80% of that at 0.59 M $CuCl_2$. (v) In the absence of NO, the conversion of ethylene to acetaldehyde occurs at approximately the same rate as in the presence of NO (run XI).

On the basis of the foregoing observations and the established chemistry of Wacker type reactions,[10] the following reactions are proposed to account for the oxidation of olefins and the reduction of NO.

$$Pd^{2+} + RCH{=}CH_2 + H_2O \rightarrow Pd^0 + RCOCH_3 + 2H^+ \quad (2)$$

$$Pd^0 + 2NO + 2H^+ \rightarrow Pd^{2+} + N_2O + H_2O \quad (3)$$

$$Pd^0 + 2Cu^{2+} \rightarrow Pd^{2+} + 2Cu^+ \quad (4)$$

$$2Cu^+ + 2NO + 2H^+ \xrightarrow{Pd^{2+}} 2Cu^{2+} + N_2O + H_2O \quad (5)$$

The formation of organic carbonyl compounds probably takes place via coordination of olefin, nucleophilic attack of H_2O at the olefin, and the subsequent rearrangement of the (β-hydroxyalkyl)palladium species. An evidence for the formation of Pd^0 species from reaction 2 is the observation of inactive palladium precipitation generated by introducing olefin into a $PdCl_2$–DMSO–H_2O or a $PdCl_2$–$CuCl_2$–H_2O solution. A pathway for N_2O production is likely through the oxidation of Pd^0 by NO (reaction 3). Support for this reaction comes from the observation that $PdCl_2$–DMSO–H_2O effectively catalyzes reaction 1 without leading to precipitation of Pd metal. Alternatively, the Pd^0 from reaction 2 may be oxidized by Cu^{2+} to give Pd^{2+} and Cu^+ (reaction 4). Further reaction of Cu^+ with NO catalyzed by Pd^{2+} yields N_2O (reaction 5). This process has been verified and proposed to account for formation of N_2O in the reduction of NO by CO using $PdCl_2$–$CuCl_2$.[5] For the present $PdCl_2$–DMSO–H_2O system, reaction 3 appears to be the only pathway for N_2O formation due to the absence of $CuCl_2$, while for the $PdCl_2$–$CuCl_2$–H_2O system N_2O formation is occurring at least in part via reactions 4 and 5 in view of the observation of a Pd precipitate if $CuCl_2$ is absent during the catalysis. However, because some catalytic activity still exists in the initial period in the absence of $CuCl_2$, the mechanism via reaction 3 can not be excluded for the $PdCl_2$–$CuCl_2$–H_2O system.

Experimental Section

Spectroscopic Measurements. NMR spectra were measured on a Varian EM-390 spectrophotometer. IR spectra were recorded on a Perkin-Elmer Model 781 instrument in 0.05-mm CaF_2 solution cells. Mass spectral data were obtained on a JEOL JGC-20K/JMS-D100 GC/MS system. Solution UV–vis spectra were measured on a Perkin-Elmer Lambda 5 spectrophotometer. Quantitative analysis of NO, N_2O, and CH_2CH_2 gases was performed on a Varian Aerograph Model 3700 gas chromatograph with TCD detector. A molecular sieve column was used for separating NO from other components, while a Porapak-Q column was employed to separate N_2O or CH_2CH_2 from other gases.[4] Other organic compounds were analyzed on a Shimadu Model GC-8A instrument with a FID detector. A Carbopac column (80/100) containing 0.19% picric acid was used for analyzing propene and 1-butene; a column consisting of 10% Carbowax 20 M on Chromosorb W HP (80/100) was employed for analyzing 1-hexene, 2-hexanone, acetaldehyde, acetone, and 2-butanone.

Materials. The following compounds were obtained from the indicated suppliers: $PdCl_2$ (Strem); $CuCl_2\cdot 2H_2O$, LiCl (Merck); NO, N_2O, CH_2CH_2, propene, 1-butene (Matheson); 1-hexane, DMSO (Aldrich); 2-butanone, 2-hexanone, acetone (Merck). All these compounds were used without further purification.

Reduction of NO by Olefin Catalyzed by $PdCl_2$. The reaction vessel used for the catalytic reaction was a 300-mL 24/40 single-neck round-bottomed side-arm flask. The side arm was connected to a three-way stopcock and one end attached to a vacuum pump and the other used for addition of gases or stoppered with a septum for gas sampling. To the reaction vessel was added $PdCl_2$ (0.100 g, 5.64×10^{-4} mol), $CuCl_2\cdot 2H_2O$ (2.00 g, 1.17×10^{-2} mol), and water (20.0 mL). The vessel was connected to a mercury manometer via a ground-glass adapter and was evacuated. The system was flushed once with NO and was then filled with 500 Torr of NO and 250 Torr of olefin. In the case of liquid olefin, an amount equal to $^1/_2$ molar equiv of NO was syringed into the vessel. The solution was magnetically stirred at ambient temperature. The solution and the gas mixture were sampled and analyzed on a GC from time to time. The results are presented in Table I and in Figure 1. The organic product was separated from the solution either by distillation or by extraction with $CHCl_3$.

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