dissociates prior to reductive elimination.[14] In the absence of a Lewis acid, a lower bound of about 27 kcal/mol on $\Delta G^{\ddagger}$ (45 °C) for the overall reductive elimination of dichloromethane is suggested by the kinetic studies of the decomposition of **6** in CD_2Cl_2, as compared with $\Delta G^{\ddagger}$ (31 °C) = 23.4 kcal/mol for the overall C–H reductive elimination from *cis*-$Rh(H)(PMe_3)_2(CH_2COCH_3)Cl$.[14]

According to this model, ligands such as PEt_3 decrease the rate of reductive elimination by intercepting the intermediate, cationic $16e^-$ species. Apparently, this species reacts readily with a variety of simple two-electron donors to give $18e^-$ species which, like **6**, do not diretly give C–H reductive elimination. At room temperature and in the presence of a Lewis acid, the effective barrier for C–H reductive elimination from **6** is greatly reduced while the barrier to Ir–C/N–C bond breaking remains relatively large. The observation of exclusive C–H reductive elimination from **6** in the presence of $TlPF_6$ and PEt_3 at room temperature suggests that PEt_3 binds reversibly to the cationic, intermediate $16e^-$ complex. The differing effects of THF and CH_2Cl_2 are probably due to the greater ability of THF to support a charged species.

In summary, a new approach to the synthetically important amination of olefins has been demonstrated. For this purpose, the various steps envisioned to be involved in such a transformation were individually discovered and elaborated in a catalytic cycle. The major steps involved are N–H oxidative addition, reaction of the resulting amido hydride complex with an olefin to form an azometallacycle, and finally C–H reductive elimination, resulting in cis addition of aniline to the exo face of norbornylene.

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Supplementary Material Available: APT, 2D $^1H/^{13}C$ correlation, 2D NOESY, and COSY NMR spectra of **7**, tables of anisotropic temperature factors and structure factor amplitudes for complex **6**, crystal structure of $[Ir(PEt_3)_2(H)]_2(\mu\text{-}NHPh)(\mu\text{-}OH)(\mu\text{-}Cl)]Cl^{12}$ including tables of atomic coordinates, thermal parameters, and distances and angles (14 pages); listing of structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

Mechanism of the Oxidation of CO by $PtCl_4^{2-}$. An Investigation into the Nature of the Intermediates by Isotopic Labeling

K. S. Sun and C. H. Cheng*

Contribution from the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China.

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Abstract: The oxidation of CO by $PtCl_4^{2-}$–$CuCl_2$ in the presence of ^{18}O-enriched water produces CO_2 of which the ^{18}O distribution indicates that statistically 1.5 of the 2 oxygens are derived from water. During the reaction, $PtCl_3(CO)^-$ may be isolated by quenching with $(AsPh_4)^+Cl^-$. This monocarbonyl species undergoes oxygen exchange with ^{18}O-enriched water reaching isotopic equilibrium within 5 min at ambient temperature. Under a ^{13}CO atmosphere, a solution of $PtCl_3(CO)^-$ yields CO_2 of which the ^{13}C abundance reveals that half the CO_2 comes from gaseous CO and the other half is from $PtCl_3(CO)^-$. These results strongly imply that $PtCl_3(CO)^-$ reacts with gaseous CO to give $PtCl_2(CO)_2$ prior to CO_2 formation. The rapid oxygen exchange of $PtCl_3(CO)^-$ with water and the irreversible attack of $PtCl_2(CO)_2$ by water to give CO_2 are proposed to explain the observation that statistically 1.5 of the 2 oxygens in CO_2 are from water. Isotopic analysis of the CO_2 produced from the reaction of ^{13}CO with $PtCl_3(CO)^-$ in ^{18}O-enriched aqueous solution demonstrates that one oxygen in $[^{13}C]$carbon dioxide is originally from water, while both oxygens in $[^{12}C]$carbon dioxide are derived from water. This double-labeling experiment further confirms the results obtained from ^{18}O and ^{13}C labeling studies. A detailed mechanism based on the results of these isotopic labeling studies is proposed.

The conversion of CO to CO_2 assisted by metal complexes is a basic process in several important reactions. These include the water–gas shift reaction,[1] the Reppe-modified hydroformylation,[2] the reduction of aromatic nitro compounds by carbon monoxide,[3] the hydrogenation of olefins by carbon monoxide and water,[4] the reduction of metal ions by carbon monoxide,[5] and the reduction of nitric oxide or nitrous oxide by carbon monoxide.[6,7] Nevertheless, there are only a few examples in the literature[8] concerning the mechanism of the production of CO_2 from coordinated CO

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Table I. Experimental and Calculated Isotopic Abundance of Carbon Dioxide from the ^{18}O Labeling Study

	reactn time, min	A_{44}	A_{46}	A_{48}	n
exptl	10	0.658	0.309	0.0218	1.56
	30	0.672	0.297	0.0201	1.50
	50	0.669	0.298	0.0221	1.52
calcd[a,b]		0.679	0.284	0.0253	1.49

[a] These values were calculated from eq 1–4. [b] The relative isotopic distributions of water used are A_{18} (H_2O) = 0.775 and A_{20} ($H_2{}^{18}O$) = 0.225.

groups. These mechanistic studies clearly established that metal hydroxycarbonyl, formed via the attack of water or hydroxide ion at a coordinated CO group, is an important intermediate in the formation of CO_2 from CO. The results had led to the synthesis of several hydroxycarbonyl complexes,[9] which in many cases were shown to evolve CO_2 on heating. Despite these efforts toward the elucidation of the mechanism of CO_2 formation, some important features of the process remain unsolved. In this paper we report the results of our studies on the mechanism of the reduction of $PtCl_4^{2-}$ by CO using isotopic labeling. The investigation provides valuable new insights into the process of CO_2 formation.

Experimental Section

Spectroscopic Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 580 and a BOMEM DA 3.002 Fourier transform spectrometer in 0.10-mm CaF_2 solution cells. Analysis of gaseous samples was performed on a Varian Aerograph Model 3700 gas chromatograph with thermal conductivity detector in conjunction with a Shimadzu Model Chromatopac C-R1A microprocessor. A Pressure-Lok gas syringe obtained from Precision Sampling Corp. was used for sampling gas mixtures. Separation of CO from air and CO_2 was performed on a molecular sieve 5A column; a Porapak-Q column was used to separate CO_2 from diatomic gases. Helium was employed as the carrier gas for these analyses. Mass spectral data were obtained on a Jeol JGC-20K/JMS-D100 GC/MS system; the isotopic compositions of CO_2, CO, and H_2O were determined by measuring the ratios of the corresponding peak heights. All experiments were carried out at 29 ± 0.5 °C unless otherwise mentioned.

Materials. The following compounds were obtained from the indicated suppliers: K_2PtCl_4 (Strem), $CuCl_2{\cdot}2H_2O$ (Merck), CuCl (Fluka), HCl (Merck), CO (Matheson), CO enriched to 99% or 90% in ^{13}C (Stohler Isotope), H_2O enriched to 50% in ^{18}O (Cambridge Isotope). All these compounds were used without further purification.

Reduction of Cu^{2+} by CO Catalyzed by K_2PtCl_4. Experiment 1. The reaction vessel used for the catalytic reaction consisted of a 32-mL 14/20 single-neck round-bottomed side-arm flask. The side arm was connected to a three-way stopcock with one end attached to a vacuum pump and the other used for addition of carbon monoxide or stoppered with a septum for gas sampling. To the reaction vessel was added K_2PtCl_4 (0.0467 g, 0.113 mmol), $CuCl_2{\cdot}2H_2O$ (0.192 g, 1.126 mmol), CuCl (0.0557 g, 0.563 mmol), LiCl (0.0788 g, 1.859 mmol), hydrochloric acid (0.50 mL, 0.72 M), and H_2O (0.50 mL). The reaction vessel was quickly connected to a mercury manometer via a ground-glass adapter and was evacuated. The system was flushed with carbon monoxide three times before being filled with 500 Torr of the gas. The solution was magnetically stirred at 29 °C. The gas mixture above the solution was sampled and analyzed on a GC; 131 Torr of CO_2 was produced in 1 h.

Isotopic Labeling Studies. ^{18}O Labeling Study. Experiment 2. The same reaction conditions and procedures as in Experiment 1 were employed, except that water (0.50 mL) containing ~50% ^{18}O was used. At intervals the gas mixture was sampled by a gas syringe; these samples were injected into a GC/MS for analysis of the isotopic distribution of carbon monoxide and carbon dioxide. The results are shown in Table I. The ^{18}O content of aqueous solution was also analyzed in the mass spectrometer; 22.5% ^{18}O enrichment was found.

^{13}C Labeling Study. Experiment 3. The reaction in Experiment 1 was allowed to proceed for 2.5 h. The system was cooled to 0 °C, evacuated, charged with N_2, and then stirred at room temperature for 5 min. The cooling–pumping process was repeated twice to remove all the CO ligand of the Cu^+ ions.[10] To the system was added 200 Torr of ^{13}C-enriched carbon monoxide (~99%) and 550 Torr of N_2. The solution was stirred at 29 °C. The gas mixture was sampled and analyzed by GC/MS at various reaction time; the ratio of $^{13}CO_2$ to $^{12}CO_2$ obtained and the isotopic content of the gaseous carbon monoxide are presented in Table II.

Table II. Experimental and Calculated Isotopic Abundance of Carbon Dioxide from the ^{13}C Labeling Study

	reactn time, min	A_{44}	A_{45}	A_{28}	A_{29}
exptl	10	0.515	0.485	0.025	0.975
	30	0.470	0.530		
	60	0.436	0.564		
calcd[a]		0.507	0.493		

[a] The calculated values were obtained from eq 5 and 6.

^{18}O and ^{13}C Double-Labeling Study. Experiment 4. The reaction in Experiment 2 was allowed to proceed for 1 h. The system was degassed thoroughly following the procedure described in Experiment 3. To the system was added 200 Torr of enriched carbon monoxide (~90% ^{13}C) and 550 Torr of nitrogen gas. The system was then stirred at 29 °C. The gas mixture was sampled and analyzed by GC/MS at various reaction times to determine the isotopic distributions of carbon dioxide and carbon monoxide. The results are displayed in Table III.

Isolation of $(AsPh_4)[PtCl_3(CO)]$ from the Catalyst Solution. The reaction in Experiment 1 was allowed to proceed for 1 h. To the solution was added 0.127 g of $(AsPh_4)^+Cl^-{\cdot}HCl{\cdot}2H_2O$ in 2.5 mL of water. The precipitate was collected and washed with 2-propanol to yield 0.0499 g of $(AsPh_4)[PtCl_3(CO)]$ (62% yield). The product was identified by comparing its IR and UV–vis spectra with those of an authentic sample prepared by a method reported previously.[7b,11]

Data Treatment

In Table I, the number of oxygen atoms derived from water in a CO_2 molecule was calculated according to eq 1 in which A_{46},

$$n = 2[(A_{46}/2) + A_{48}]/[A_{20}/(A_{18} + A_{20})] \qquad (1)$$

A_{48}, A_{20}, and A_{18}, are the relative isotopic abundances of $CO^{18}O$, $C^{18}O^{18}O$, $H_2{}^{18}O$, and H_2O, respectively; the subscripts denote the relative molecular masses.

Values of A_{44}, A_{46}, and A_{48} in Table I were calculated according to eq 2–4, assuming that of the two oxygens in CO_2 statistically

$$A_{44} = \tfrac{1}{2}(A_{28}A_{18}) + \tfrac{1}{2}(A_{18})^2 0.989 \qquad (2)$$

$$A_{46} = \tfrac{1}{2}[(A_{30}A_{18}) + (A_{28}A_{20})] + A_{18}A_{20}0.989 \qquad (3)$$

$$A_{48} = \tfrac{1}{2}(A_{30}A_{20}) + \tfrac{1}{2}(A_{20})^2 0.989 \qquad (4)$$

1.5 are derived from water, in which A_{30}, A_{28}, and 0.989 are the natural abundances of $^{12}C^{18}O$, $^{12}C^{16}O$, and ^{12}C, respectively. $A_{30} = 0.002$ and $A_{28} = 0.987$ are actually employed for these calculations.

The theoretical values of A_{44} and A_{45} in Table II were calculated from eq 5 and 6; A_{28} and A_{29} are the relative isotopic abundance

$$A_{45} = A_{29}/2 + 0.011/2 \qquad (5)$$

$$A_{44} = 1 - A_{45} \qquad (6)$$

of ^{12}CO and ^{13}CO in the gas phase. These calculations were performed according to an ideal model of reaction in which half the CO_2 comes from gaseous CO and the other half is derived from $PtCl_3(CO)^-$ (see Results and Discussion). The ^{13}C and ^{12}C contents in $PtCl_3(CO)^-$ were assumed to be the same as the natural abundance of these isotopes, i.e., 0.011 and 0.989, respectively.

In Table III, the quantities A_{44}, A_{45}, A_{46}, A_{47}, A_{48}, A_{49}, A_e, A_o, n_e, and n_o were calculated from eq 7–16. The values of A_{29}, A_{28},

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Table III. Experimental and Calculated Isotopic Abundance of Carbon Dioxide from the ^{18}O and ^{13}C Double-Labeling Study[a,b]

	A_{44}	A_{46}	A_{48}	A_e	n_e	A_{29}	A_{28}	A_{20}	A_{18}
exptl	0.317	0.206	0.0513	0.574	2.15	0.885	0.115	0.250	0.750
calcd[c]	0.321	0.200	0.0309	0.552	1.90				

	A_{45}	A_{47}	A_{49}	A_0	n_0
exptl	0.328	0.0890	0.0081	0.425	0.99
calcd[c]	0.335	0.113	0.00057	0.449	1.02

[a] A_{29} and A_{28} are the average relative isotopioc abundances of $^{13}C^{16}O$ and $^{12}C^{16}O$, respectively, in the gas phase at the beginning and the end of the experiment, and A_{20} and A_{18} are the relative isotopic abundances of $H_2{}^{18}O$ and $H_2{}^{16}O$ in the solvent. [b] Reaction time 5 min. [c] The calculated values were obtained from eq 7-16.

A_{20}, and A_{18} used in the calculations were obtained experimentally and are listed in Table III.

$$A_{45} = (A_{29}/2)A_{18} + (0.011/2)(A_{18})^2 \tag{7}$$

$$A_{47} = (A_{29}/2)A_{20} + (0.002/2)A_{18}A_{29} + 2(0.011/2)A_{18}A_{20} \tag{8}$$

$$A_{49} = (0.002/2)A_{29}A_{20} + (0.011/2)(A_{20})^2 \tag{9}$$

$$A_{44} = 0.989(A_{18})^2/2 + (A_{28}/2)A_{18} \tag{10}$$

$$A_{46} = 0.989A_{18}A_{20} + (A_{28}/2)A_{20} + (0.002)(A_{28}/2)A_{18} \tag{11}$$

$$A_{48} = 0.989(A_{20})^2/2 + (0.002)(A_{28}/2)A_{20} \tag{12}$$

$$A_e = A_{44} + A_{46} + A_{48} = 1 - A_o \tag{13}$$

$$A_o = A_{45} + A_{47} + A_{49} = A_{29}/2 + 0.011/2 \tag{14}$$

$$n_e = 2[(A_{46}/2) + A_{48}]/\{[A_{20}/(A_{18} + A_{20})]A_e\} \tag{15}$$

$$n_o = 2[(A_{47}/2) + A_{49}]/\{[A_{20}/(A_{18} + A_{20})]A_o\} \tag{16}$$

Results and Discussion

It is known that Pt(II) species are readily reduced by carbon monoxide to platinum metal or to platinum carbonyl clusters.[12] In the presence of oxidant, the reduced platinum complex is reoxidized to Pt(II).[13] All the experiments on CO oxidation described in this paper were carried out in an aqueous K_2PtCl_4–$CuCl_2$–CuCl–HCl–LiCl system, which resembles that for the catalytic reduction of nitric oxide by carbon monoxide.[7b] Under the conditions shown in Experiment 1 the system catalytically produced 131 Torr of CO_2 in 1 h at ambient temperature corresponding to 1.91 turnovers/platinum atom per h. In the reaction, the Pt(II) species is reduced by CO to a Pt(0) intermediate, which is then reoxidized by $CuCl_2$ to Pt(II). Consequently, the net reaction for the catalysis is

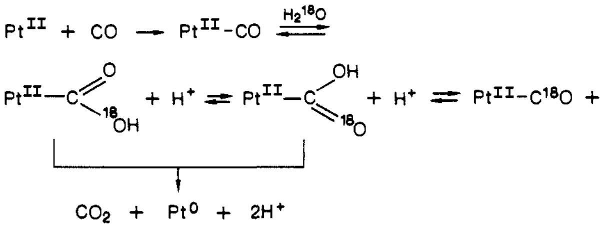
$$CO + 2CuCl_2 + H_2O \rightarrow CO_2 + 2CuCl_2^- + 2H^+ \tag{17}$$

Although Cu(I) appears as a reaction product in eq 17, its presence greatly accelerates the reaction particularly at the beginning of the catalysis. For example, in the absence of CuCl, the activity of the catalyst system decreases by approximately 1 order of magnitude giving only 3 Torr of CO_2 in 10 min compared to 33 Torr of CO_2 in the presence of CuCl. The enhancement of CO_2 production by CuCl is closely related to the function of Cu(I) as a CO carrier, which absorbs gaseous CO and transfers it to the Pt(II) species (eq 18 and 19). Evidence for Cu(I) as a CO carrier as well as the effect of the Cl^- ion concentration on the CO_2 production has been presented in our recent paper.[7b]

$$Cu^I + CO \rightarrow Cu^I(CO) \tag{18}$$

$$Pt^{II} + Cu^I(CO) \rightarrow Pt^{II}\text{–}CO + Cu^I \tag{19}$$

^{18}O Labeling Experiment. In an investigation of the role of water in the oxidation of carbon monoxide to carbon dioxide in the platinum-catalyzed reaction (eq 17), ^{18}O-enriched water ($H_2{}^{18}O$:$H_2{}^{16}O$ = 22.5:77.5) was employed as the solvent. The observed isotopic distribution of carbon dioxide analyzed by GC/MS is displayed in Table I. A comparison of the average ^{18}O abundance with that in the solvent clearly indicates that ca. 75% of the oxygen atoms in carbon dioxide statistically come from the water solvent. In other words, the number of oxygen atoms in a carbon dioxide molecule originally from the solvent (denoted hereafter by *n*) is 1.5 within experimental error. It is noteworthy that under the same conditions, there is no incorporation of ^{18}O into the gaseous carbon monoxide. Furthermore, the oxygen exchange between gaseous carbon dioxide and water was found to be less than 2.9% in 0.5 h in agreement with the results reported earlier.[8c] The observed value of *n* for CO_2 reveals that the hydroxycarbonyl intermediates in reaction 20 exhibit a substantial tendency for back-reaction relative to decarboxylation, which leads to the CO_2 product. In the reduction of NO by CO catalyzed by $Rh(CO)_2Cl_2^-$, $H_2{}^{18}O$ labeling studies showed that the CO_2 product contains only one oxygen that is derived from water.[8c] There appears to have been no other investigation of the isotopic distribution of oxygen in the formation of CO_2 from coordinated CO and water. Related oxygen exchange reactions between carbonyl groups of $M(CO)_6^+$,[14] $M(CO)_5L^+$,[15] $M(CO)_4L_2^+$[16] (M = Mn and/or Re), $Fe(CO)_5$,[17] and $H_2{}^{18}O$ have been observed as cited.



(20)

An interesting aspect of this ^{18}O labeling study is the observation that nearly one and a half of the two oxygens (*n* = 1.5) in the carbon dioxide product are derived from the oxygen of water. However, whether this is coincidentally the result of competition between the back-reaction and decarboxylation of the hydroxycarbonyl intermediate shown in eq 20 or whether there is a particular mechanistic implication for the present reaction remains uncertain. Attempts to explain the results of this ^{18}O labeling study have led us to perform several new isotopic labeling experiments, which have provided the following notable observations.

Characterization of the Intermediate. During the course of the catalytic oxidation of carbon monoxide to carbon dioxide, the $PtCl_4^{2-}$ anion incorporates a CO molecule to form a species that exhibits a CO absorption at 2118 cm^{-1}. The carbonyl complex isolated by quenching the reaction with $(AsPh_4)^+Cl^-$ was identified as $(AsPh_4)^+[PtCl_3(CO)]^-$ by comparing its IR and UV-vis spectroscopic data with those of an authentic sample.[7b,11]

^{13}C Labeling Study. To determine the role of $PtCl_3(CO)^-$ in the CO_2 product process, a ^{13}C isotope labeling experiment was

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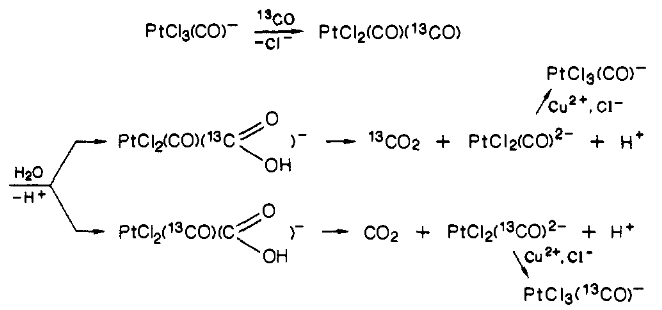
Scheme I



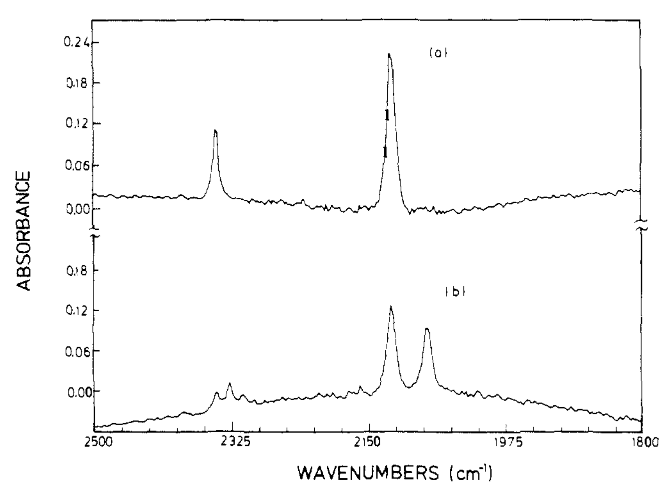


Figure 1. IR spectra of $PtCl_3(CO)^-$ in the carbonyl region: (a) in $CuCl_2$-CuCl-HCl-H_2O solution; (b) in ^{18}O-enriched $CuCl_2$-CuCl-HCl-H_2O solution ($H_2{}^{16}O$:$H_2{}^{18}O$ = 65.6:34.4). The concentration of the platinum species is 75.0 mM in either system. The absorptions near 2350 cm^{-1} arise from carbon dioxide dissolved in the solutions.

performed. First, the K_2PtCl_4-$CuCl_2$-CuCl-HCl-LiCl system was allowed to react with CO of natural isotopic abundance for 1 h to generate $PtCl_3(CO)^-$. The system was evacuated, and the unreacted CO and CO_2 produced were then removed completely. $PtCl_3(CO)^-$ was found to remain in the solution through this removal process as indicated by the IR spectrum of the solution. ^{13}C-enriched CO was then introduced into the system for further reaction. Analysis of the isotopic distribution of the CO_2 product after various periods gave the results shown in Table II. The presence of substantial amounts of $^{12}CO_2$ and $^{13}CO_2$ in the gaseous products unambiguously establishes that the CO in both the gaseous phase and $PtCl_3(CO)^-$ is involved in the process of formation of CO_2. Moreover, the observed ratio $^{13}CO_2$:$^{12}CO_2$ = 0.48:0.52 at 10 min as compared to the calculated value of 0.49:0.51 unequivocally shows that half the CO_2 product is derived from CO in the gas phase and the other half comes from $PtCl_3(CO)^-$. The data required for the calculations include the relative abundance of ^{13}CO and ^{12}CO in the gas phase and in $PtCl_3(CO)^-$. The relative isotopic abundance of CO in the gas phase was obtained directly from GC/MS measurement while the ^{13}CO abundance in $PtCl_3(CO)^-$ was assumed to be the same as the natural abundance of ^{13}C isotope. The equations employed for the calculation are presented in the Experimental Section. Apparently, the results of this ^{13}C labeling study cannot be interpreted in terms of a mechanism involving $PtCl_3(CO)^-$ as the intermediate for reaction with water to release CO_2. A correct mechanism must explain the observation that free CO and coordinated CO in $PtCl_3(CO)^-$ are equally probable to be converted to CO_2. Scheme I provides a mechanism that can fully account for the observations. The initial step is substitution of ^{13}CO for one chloride in $PtCl_3(CO)^-$ to give a dicarbonyl species with two structurally equivalent carbonyl groups. Water attack at either carbonyl to give a hydroxycarbonyl intermediate is followed by the decarboxylation of the species to produce $^{13}CO_2$ and $^{12}CO_2$ in a 1:1 ratio. The reduced platinum species is reoxidized by Cu^{2+} to $PtCl_3(*CO)^-$ (*C = ^{12}C or ^{13}C), leading to a catalytic production of carbon dioxide. However, further reaction of $PtCl_3(*CO)^-$ with gaseous ^{13}CO and subsequently with water should yield carbon dioxide with its ^{13}C abundance much higher than the calculated value of 0.49. In Table II, the observed ^{13}C content of carbon dioxide gradually increases with reaction time in agreement with this expectation.

While the correct geometry of the dicarbonyl compound is unknown, a previous study[18] indicates that the substitution reaction of $PtCl_3(CO)^-$ takes place initially at the chloride trans to the carbonyl group due to the strong trans effect of the latter. However, the trans dicarbonyl isomer rearranges rapidly to the thermodynamically more stable cis structure even at ambient temperature. Regardless whether the structure is trans or cis, the dicarbonyl species on reacting with water would produce equal amounts of $^{13}CO_2$ and $^{12}CO_2$ if the isotope effect is negligible The failure to detect the dicarbonyl species, the observation of $PtCl_3(CO)^-$ in the catalyst solution, and the results of the ^{13}C labeling experiment strongly imply that the substitution reaction of $PtCl_3(CO)^-$ with CO to produce the dicarbonyl compound is the rate-determining step of the overall reaction. Attack of water at the dicarbonyl species to yield the hydroxycarbonyl and the subsequent decarboxylation of the latter should be rapid relative to the substitution reaction.

The present ^{13}CO labeling experiment appears to be an excellent method for determining the number of carbonyl groups in the active species that is responsible for CO_2 formation and that cannot be directly observed. The conventional method for determining the active species requires kinetic measurements to obtain the reaction order of CO_2 formation with respect to the CO pressure and spectroscopic measurements to characterize the species in solution.

Oxygen Exchange of $PtCl_3(CO)^-$. Although the results of this ^{13}C labeling study exclude $PtCl_3(CO)^-$ as the species directly responsible for CO_2 formation in the catalytic oxidation of CO, its carbonyl group rapidly undergoes oxygen exchange with water. As depicted in Figure 1a, the CO absorption of $PtCl_3(CO)^-$ appears at 2118 cm^{-1}. Addition of $H_2{}^{18}O$ to the solution rapidly leads to the formation of $PtCl_3(C^{18}O)^-$ of which the carbonyl group absorbs at 2072 cm^{-1} (Figure 1b). The isotopic equilibrium between H_2O and $PtCl_3(CO)^-$ is reached in less than 5 min at ambient temperature.

This oxygen scrambling process is at least 1 order of magnitude more rapid than the CO_2 formation from the platinum system (vide supra). Consequently, we expect that $PtCl_3(CO)^-$ is sufficiently long-lived to undergo complete oxygen scrambling with H_2O before it further reacts with gaseous CO to give $PtCl_2(CO)_2$ and subsequently with water to yield CO_2. As a result, in ^{18}O-enriched water, one of the carbonyls of $PtCl_2(CO)_2$, originally coordinated to $PtCl_3(CO)^-$, is in isotopic equilibrium with the aqueous solvent. The attack of this carbonyl by labeled water would lead to the formation of CO_2 of which the ^{18}O enrichment is the same as that of the aqueous solvent. However, this path accounts for only half the CO_2 product. Water attack at the second carbonyl of $PtCl_2(CO)_2$ leads to the formation of the other half of CO_2. To explain the observation that on the average 1.5 of the 2 oxygens in CO_2 is from water (Table I), the second carbonyl in $PtCl_2(CO)_2$ should not exchange oxygen with water so that the value of n for the CO_2 produced from this carbonyl group is equal to one. This can be achieved only when water attack at $PtCl_2(CO)_2$ is an irreversible process.

^{13}C and ^{18}O Double-Label Study. In an effort to further distinguish the two structurally identical, but historically different, carbonyl groups in $PtCl_2(CO)_2$, a double-labeling study was performed. The experimental conditions and procedure were the same as those for the ^{13}C labeling study except that ^{18}O-enriched water was employed as the solvent. The observed and calculated isotopic compositions of carbon dioxide are presented in Table III. The overall $^{13}CO_2$ (A_o) to $^{12}CO_2$ (A_e) ratio of 0.425:0.574, as compared to the calculated value of 0.449:0.552, further sup-

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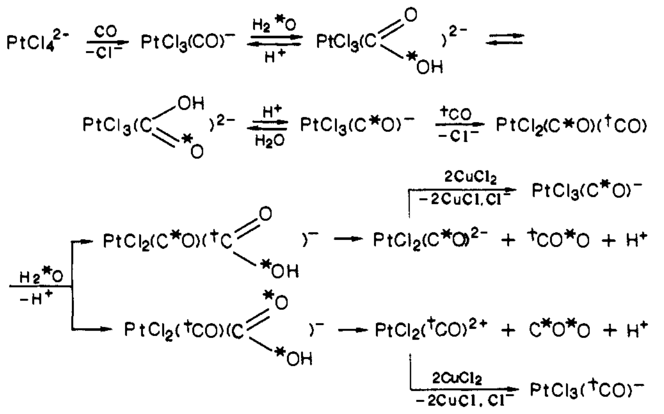
Scheme II



ports the notion that half the carbon dioxide is derived from gaseous CO and the other half from $PtCl_3(CO)^-$. In addition, the isotopic distribution data exhibit a significant difference in ^{18}O content between $^{13}CO_2$ and $^{12}CO_2$. The values of n, obtained from the ^{18}O isotopic distribution data and eq 15 and 16, are 0.99 for $^{13}CO_2$ and 2.15 for $^{12}CO_2$, respectively. These results again lead us to conclude that the CO group in $PtCl_2(CO)_2$ originally from $PtCl_3(CO)^-$ is sufficiently long-lived to reach complete isotopic equilibrium with water before attack by water. On the contrary, the carbonyl group derived from the gaseous CO in the dicarbonyl species does not exchange oxygen with water at all, presumably due to the irreversible attack of water at $PtCl_2(CO)_2$. For comparison the calculated n values based on this model are 1.02 and 1.90 for $^{13}CO_2$ and $^{12}CO_2$, respectievly. The results obtained from this double-labeling experiment may be summarized according to eq 21.

$$PtCl_4^{2-} \xrightarrow[-Cl^-]{CO} PtCl_3(CO)^- \xrightarrow[H_2{}^{18}O]{{}^{13}CO} {}^{13}CO^{18}O + C^{18}O^{18}O\ (1:1) \qquad (21)$$

Mechanism. The labeling studies described in this paper have uncovered detailed mechanistic information that is difficult to obtain by other methods for the oxidation of CO to CO_2 catalyzed by a $PtCl_4^{2-}$–CuCl–$CuCl_2$ system. On the basis of these results, a detailed mechanism for the catalytic reaction is proposed and is depicted in Scheme II. An interesting aspect of this mechanism is that $PtCl_3(CO)^-$ undergoes oxygen scrambling with water rapidly with negligible decomposition to give carbon dioxide, but the reverse is true for $PtCl_2(CO)_2$. The divergence in the rate of decarboxylation for the two platinum species may be understood in terms of the difference in ability to stabilize low oxidation state metal complexes between a carbonyl group and a chloride ligand. The decarboxylation of $PtCl_3(COOH)^{2-}$ (eq 22) is not favored

$$PtCl_3(COOH)^{2-} \rightarrow PtCl_3^{3-} + CO_2 + H^+ \qquad (22)$$

$$PtCl_2(CO)(COOH)^- \rightarrow PtCl_2(CO)^{2-} + CO_2 + H^+ \qquad (23)$$

because of the inability of Cl^- to stabilize Pt(0) in the presumed product of $PtCl_3^{3-}$. On the other hand, the presence of a carbonyl group in $PtCl_2(CO)(COOH)^-$ facilitates the decarboxylation of the species (eq 23) by decreasing the electron density in the transition state through back-donation. The recent results of an investigation[19] of the stability of hydroxycarbonyl complexes are in accord with our observation that strong π-acid ligands accelerate decomposition to give CO_2.

Conclusion

The results of our ^{13}C labeling study have unambiguously established that $PtCl_2(CO)_2$ is the species that reacts with water to give CO_2 in the present catalysis even though the dicarbonyl is not directly observed. In addition, the ^{18}O and double-labeling experiments have shown that the two structurally equivalent, but historically different carbonyl groups in $PtCl_2(CO)_2$ may be distinguished. On reacting with water, one carbonyl gives CO_2 product of which all oxygens come from water, while the other carbonyl yields CO_2 with only one oxygen derived from water. The ^{13}C experiment appears to be a new and powerful method for determining the number of carbonyl groups in the active species, while ^{18}O and double-labeling experiments are very useful in elucidating the paths for CO_2 formation.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this research.

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Nitrogen Atom Activation: The Influence of Porphyrin Ring Structure on the Kinetics of the Reaction of Trifluoroacetic Anhydride with Nitrido Manganese(V) Porphyrins

Lawrence A. Bottomley* and Frank L. Neely

Contribution from the School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400. Received February 25, 1988

Abstract: The kinetics of the reaction of (porphyrin)Mn(N) (where the porphyrin was octaethylporphyrin, Baldwin's capped porphyrin or one of several substituted tetraphenylporphyrins) with selected substituted acetic anhydrides to form the corresponding nitrenoid Mn porphyrin complex were determined under pseudo-first-order conditions. This reaction is the rate-determining first step in the nitrogen atom activation and transfer sequence that uses nitrido Mn porphyrins to convert olefins to the corresponding aziridines. The apparent rate constants, which varied over three orders of magnitude, were dependent upon porphyrin ring basicity, acetic anhydride substituent, and the steric environment about the nitrido–Mn reaction center.

The chemistry of high-valent metalloporphyrins has been actively pursued since the discovery that these materials are capable of oxidizing water.[1-3] Recently, workers in the field have focused their attention on the reactivity of oxo iron and oxo manganese porphyrins, models of the active site of cytochrome P-450.[4-12]

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