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A Metal Atom Model for the Oxidation of Carbon Monoxide to Carbon Dioxide. The Gold Atom–Carbon Monoxide–Dioxygen Reaction and the Gold Atom–Carbon Dioxide Reaction

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By cocondensing Au atoms with equimolar mixtures of $^{12}C^{16}O/^{16}O_2$ at 10 K, a single compound (I) is generated which at 30–40 K acts as a precursor for $^{12}C^{16}O_2$. Infrared studies of $^{13}C^{16}O/^{16}O_2$, $^{12}C^{16}O/^{18}O_2$, and $^{12}C^{16}O/^{13}C^{18}O/^{16}O_2/^{16}O^{18}O/^{18}O_2$ isotopic mixtures cocondensed with Au atoms establish that I is best formulated as monocarbonylgold(II) peroxyformate (see structure of species I). The breakdown of this novel metallocycle to CO_2 is monitored by infrared spectroscopy using $^{13}C^{16}O/^{16}O_2$ and $^{12}C^{16}O/^{18}O_2$ mixtures, from which it can be deduced that cleavage of the peroxy group is the primary step leading to CO_2 production. Infrared and UV–vis studies of the fragmentation of I during careful warm-up experiments reveal the existence of an intermediate II which is best formulated as monocarbonylgold(II) oxide, (OC)AuO. The identification of II favors a two-step fragmentation process of I rather than a concerted reductive elimination of two molecules of CO_2 from I. In order to gain an insight into (i) the elimination of CO_2 from II, (ii) the importance of the tautomeric form $Au(\pi\text{-}CO_2)$ as a resonance contributor to II, and (iii) the possible existence of labile carbon dioxide gold complexes among the $Au/CO/O_2$ reaction products, the Au/CO_2 cocondensation reaction was also made the subject of investigation. An attempt is made to interrelate the results of the Au atom based oxidation reactions of the present study with actual heterogeneous oxidations of CO to CO_2.

Introduction

In searching for metal atom based oxidation models of actual heterogeneous catalytic oxidation processes, we recently investigated the silver catalyzed oxidation of ethylene to ethylene oxide[1] and CO to CO_2[1,2] on a single silver atom site. In both instances a single reaction intermediate was identified and characterized to be $[(C_2H_4)Ag]^+O_2^-$ and $[(OC)Ag]^+O_2^-$, respectively.[1,2] Although these complexes might at first glance be regarded as likely candidates for localized bonding models of the surface intermediates involved in the actual oxidation processes,[3] neither complex, during warm-up, acted as a precursor for the oxidation product. In view of the negative nature of these experiments, other metal atom based oxidation systems were sought.

We discovered that on moving to gold atoms, oxidation processes could be induced and observed even at 10 K. In this paper we present our findings for the Au atom based oxidation of CO to CO_2, as well as spectroscopic evidence for a labile monocarbon dioxide complex, $Au(CO_2)$.

Experimental Section

Monatomic gold was generated by directly heating a thin tungsten rod (0.025 in.) around the center of which was wound gold wire (0.005 in). The gold metal (99.99%) was supplied by Imperial Smelting Co., Toronto. Research grade $^{16}O_2$ (99.99%) and $^{12}C^{16}O$ (99.99%) were supplied by Matheson of Canada, $^{16}O_2/^{18}O_2$, $^{16}O_2/^{16}O^{18}O/^{18}O_2$ isotopic mixtures by Miles Laboratories, and $^{12}C^{16}O/^{13}C^{16}O$, $^{12}C^{16}O/^{13}C^{18}O$ isotopic mixtures by Prochem. The furnace used for the evaporation of the metals has been described previously.[4] The rate of gold atom deposition was continuously monitored using a quartz crystal microbalance.[5] In the infrared experiments, matrices were deposited on either a NaCl or CsI plate cooled to 10 K by means of an Air Products Displex closed cycle helium refrigerator. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. UV–vis spectra were recorded on a Varian Techtron instrument in the range 190–900 nm, the sample being deposited on a NaCl optical plate.

Results and Discussion

Before presenting the results of the $Au/CO/O_2$ reaction, we will briefly recall some of the pertinent facts for the individual Au atom/CO[6] and Au atom/O_2[7] reactions. The results for the new system Au/CO_2 will follow.

Au Atom–Carbon Monoxide Reactions. In the inert gas matrices, Ne through to Xe, two compounds, namely (OC)Au(CO) and Au(CO),[6] have been generated and characterized. In pure CO matrices, a lattice stabilized isocarbonyl–carbonyl isomer (OC)Au(OC) was identified.[6]

Au Atom–Dioxygen Reactions. Compared to the other members of group 1B,[1,8] gold atom cocondensation reactions with O_2 were suprisingly simple in that they led to a single "green" product, $Au(O_2)$, whether the reaction was performed in pure O_2 or inert gas/O_2 mixtures.[7] Dioxygen isotope substitution experiments using $^{16}O_2/^{16}O^{18}O/^{18}O_2$ scrambled mixtures favored a side-on bonded O_2 in $Au(O_2)$. However, the oxidation state of the metal in this dioxygen complex could not be ascertained. In brief, the dioxygen stretching frequency indicated superoxide character for the O_2 moiety and formally gold oxidation state I. On the other hand the UV–vis data for this "green" complex argued in favor of either gold(0) or gold(II) rather than gold(I).

Au Atom–Carbon Dioxide Reactions. Despite the current interest in transition metal–carbon dioxide complexes which can catalytically fix CO_2,[9] one finds that metal atom/CO_2 reactions per se have not hitherto received much attention. Besides an erroneous report of binary Ni/CO_2 complexes[10a] (the reality of which has recently been reappraised[10b]) and a recent claim to have synthesized $Ag(CO_2)$,[11] little else is known about metal atom/CO_2 chemistry.

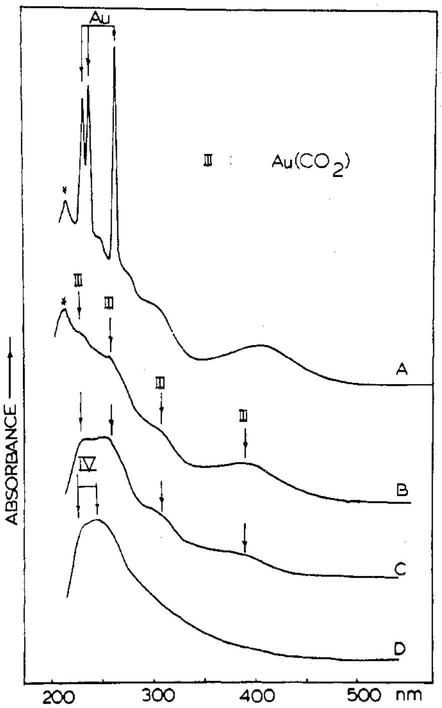
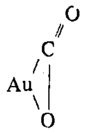


Figure 1. The UV–vis spectra obtained on cocondensing Au atoms with $CO_2/Ar \simeq 1/10$ mixtures at (A) 10 K, and (B)–(D) after matrix warm-up to 20, 30, and 40 K (the asterisk depicts an instrumental artifact).

Therefore in order to appreciate the subtleties of the $Au/CO/O_2$ cocondensation reaction, it was necessary to establish the fate of Au atoms in the presence of CO_2 under matrix conditions. The UV–vis spectrum obtained on cocondensing Au atoms with $CO_2/Ar \simeq 1/10$ mixtures at 10 K is shown in Figure 1A. Aside from the sharp atomic lines of isolated Au atoms observed on deposition, four new broad absorptions are seen at 240, 260, 310, and 394 nm (a situation very similar to that recently discovered for $Ag(CO_2)$[11]). Carbon dioxide concentration experiments and warm-up studies indicate that these four absorptions belong to a single species (III). Warming these matrices to 20–30 K (Figure 1B) simply causes the Au atomic lines to steadily decrease in intensity eventually leaving the four new absorptions as the only observable spectral features (Figure 1C). Further warming of these matrices to 40 K causes simplification to a spectrum displaying only two resolvable absorptions at roughly 230 and 280 nm (species IV, Figure 1D). At 45 K this spectrum decays to zero, signifying decomposition of species IV. These data point to the existence of an extremely labile $Au(CO_2)$ complex (III) that transforms at roughly 30–40 K to species IV which at 45 K probably breaks up to CO_2 and Au_n.

It is difficult with the UV–vis data above to make an a priori assignment of III to an Au(0) or an Au(II) monocarbon dioxide complex, $Au(CO)_2$. However, the corresponding infrared data[14] are helpful in that they show the presence of a weakly perturbed CO_2 molecule in compound III which is not the situation to be expected for a Au(II) oxidative-addition product,



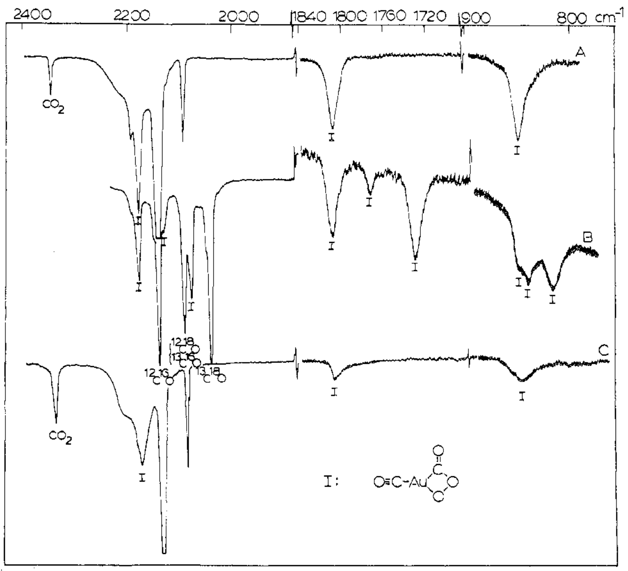


Figure 2. The matrix infrared spectra observed on depositing Au atoms with (A) $^{12}C^{16}O/^{16}O_2 \simeq 1/1$, (B) $^{12}C^{16}O/^{13}C^{18}O/^{16}O_2/^{16}O^{18}O/^{18}O_2 \simeq 1/1/1/2/1$ matrices at 10 K, and (C) the same as (A) but after warm-up to 30 K (note that the commercially available $^{12}C^{16}O/^{13}C^{18}O$ mixtures contain about 7–10% of $^{12}C^{18}O/^{13}C^{16}O$).

Table I. The Infrared Spectra of the Products of the Au Atom/CO/O_2 Cocondensation Reaction

$CO/O_2 \simeq 1/1$ (10 K)	Assignment	
	Mode	Species
2190 wsh[a]	ν(C≡O)	II
2176 s[a]	ν(C≡O)	I
1807 w	ν(C=O)	I
850 w	ν(C−O)	I
448 w	ν(Au=O) or	II
416 w	ν(Au−C)	II
356 mbr	ν(Au−O) or ν(Au−C)	I

[a] Depending on the deposition conditions, these two bands could occur in the frequency ranges 2190–2180 and 2180–2170 cm^{-1}, respectively.

One is therefore forced to conclude that although CO_2 complexation to Au is quite apparent in the UV–vis spectrum of III, the nature of the gold–carbon dioxide interaction must be very weak, probably somewhere between that of a genuine coordination compound and a van der Waals complex, with the Au oxidation state close to zero.

Although a second species IV can be observed spectroscopically on warming III to 40 K, its chemical composition or structure cannot be ascertained from the data of the present study. Further work will be required to clarify this point.

Au Atom–CO–O_2 Reactions. When Au atoms are cocondensed with $^{12}C^{16}O/^{16}O_2 \simeq 1/1$ mixtures at 10 K, the infrared spectrum shown in Figure 2A is obtained. Besides the absorptions of free $^{12}C^{16}O$ (and $^{12}C^{18}O/^{13}C^{16}O$ in natural abundance) in the matrix, together with a trace amount of $^{12}C^{16}O_2$ at 2344 cm^{-1} (formed in the metal–CO–O_2 deposition process), *seven* new absorptions were observed and are listed in Table I.

These spectra are particularly interesting as they show no evidence for either of the parent compounds, $Au(CO)_{1,2}$ or $Au(O_2)$. The species responsible for the new absorptions in Figure 2A decompose on warming to 30 K with the concomitant production of CO_2 (Figure 2C). At 40 K, a roughly 300% increase in the absorbance of the $^{12}CO_2$ line was observed. The warm-up experiments also indicate that the bands observed at 2176, 1807, 850, and 356 cm^{-1} belong to a single species I, while those at 2190, 448, and 416 cm^{-1} belong to a second species II. Of the two, species I disappears first at about 30–35 K with species II following at about 40–45 K (see later).

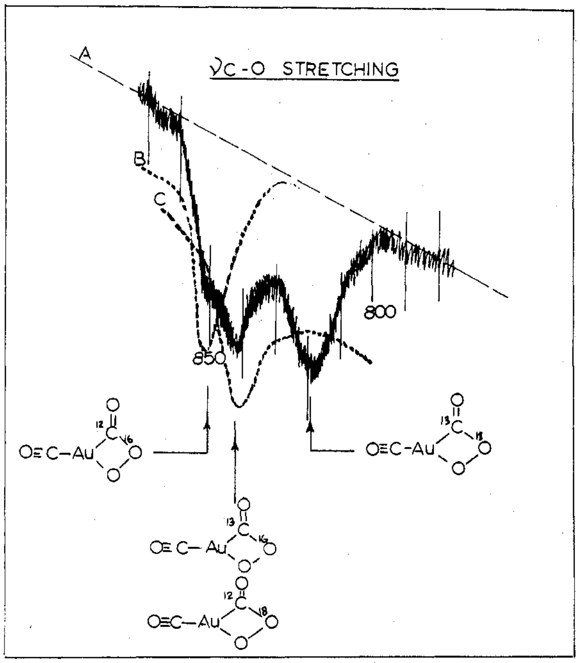
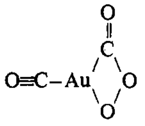


Figure 3. The same as Figure 2B but showing (A) the 870–780-cm^{-1} region under expanded conditions and (B) and (C) the corresponding region but using $^{12}C^{16}O/^{16}O_2 \simeq 1/1$ and $^{12}C^{16}O/^{18}O_2 \simeq 1/1$ mixtures.

Species I. Certain features of the spectrum of species I are most informative. The observation of a carbonyl stretching mode (2176 cm^{-1}) at a frequency above that of free $^{12}C^{16}O$ (2138 cm^{-1}) points to the presence of a CO group coordinated to an oxidized gold center. Gold concentration experiments demonstrate that species I is mononuclear.[13] We can therefore eliminate the possibility that the 1807-cm^{-1} absorption is associated with a bridging CO group. A carboxylic type >C═O group is therefore implied by the presence of the 1807-cm^{-1} absorption while the 850-cm^{-1} absorption indicates the presence of either a peroxidic O–O or a C–O grouping.

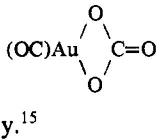
The stoichiometry and nature of species I was established from a combination of Au atom (a) $^{12}C^{16}O/^{13}C^{16}O/^{16}O_2$, (b) $^{12}C^{16}O/^{18}O_2$, (c) $^{12}C^{16}O/^{13}C^{16}O/^{16}O_2/^{16}O^{18}O/^{18}O_2$, and (d) $^{12}C^{16}O/^{13}C^{18}O/^{16}O_2/^{16}O^{18}O/^{18}O_2$ isotopic substitution experiments. A typical trace for the latter mixture is shown in Figures 2B and 3, from which the characteristic isotope patterns of a monocarbonyl grouping, a monocarboxylic type >C═O grouping, and a vibrational mode involving the motion of a *single* oxygen atom, that is, a C–O grouping, can be discerned (Table II).

Taken together, the vibrational data point to a monocarbonylgold(II) peroxyformate species:



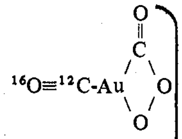
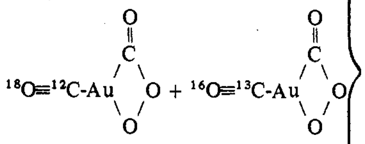
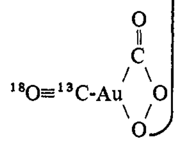
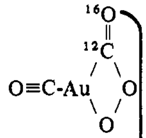
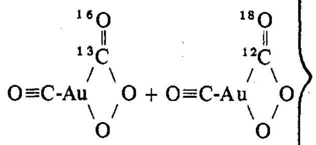
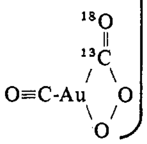
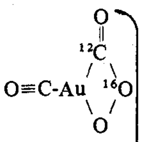
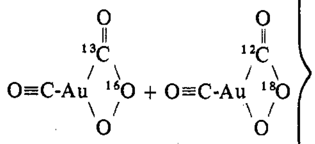
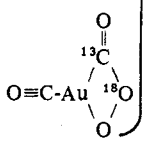
I

Clearly a peroxymetallocycle of this type could act as a source of CO₂ at cryogenic temperatures, whereas elimination of CO₂ from a monocarbonylgold(II) carbonate complex



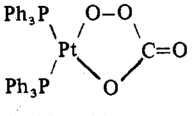
would be far less likely.[15]

Table II. Infrared Isotopic Frequencies for Species I

Freq, cm^{-1}	Assignment	
2176		
2126		ν(C≡O)
2076		
1807		
1769		ν(C=O)
1732		
850		
840		ν(C–O)
820		

The formation of I in Au/CO/O₂ cocondensations may be rationalized in a number of ways, the most attractive of which involves an $(OC)_2Au(O_2)$ intermediate. Subsequent insertion of CO into the gold–dioxygen linkage of this complex could lead to species I. The rearrangement of I to a monocarbonylgold(II) carbonate complex is unlikely to occur under very low temperature conditions.

It is worth noting here, that the reaction which we have proposed as a route to I is not an unprecedented occurrence. For example, CO₂ is known to insert into the platinum–dioxygen linkage of $(Ph_3P)_2Pt(O_2)$[12] to yield the peroxycarbonate species shown below



in which ν(C═O) and ν(C—O) modes have been assigned to

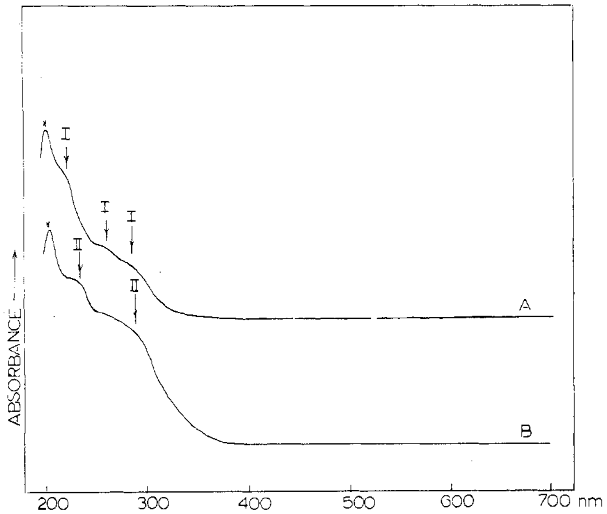


Figure 4. The UV-vis spectra obtained on cocondensing Au atoms with $^{12}C^{16}O/^{16}O_2 \simeq 1/1$ mixtures at (A) 10 K and (B) after warm-up to 30-40 K. (The asterisk depicts an instrumental artifact.)

Table III. The UV-Vis Spectra[a] of the Products of the Au Atom/CO_2 and Au Atom/CO/O_2 Cocondensation Reactions

CO_2/Ar (1/10)		Species assignment	CO/O_2 (1/1)		Species assignment
10 K	40 K		10 K	40 K	
			220		I
				230	II
	235	IV			
240		III			
	246	IV			
			255		I
260		III			
			280		I
				283	II
310		III			
394		III			

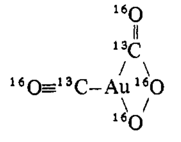
[a] Wavelength scale quoted in nm.

infrared bands at 1678 and 978 cm^{-1}, respectively[12] (cf. 1807 and 850 cm^{-1} for species I). We note also the occurrence of ν(PtO) modes at 387 and 305 cm^{-1} for the peroxycarbonate in a region similar to the ν(Au—O) and/or ν(Au—C) modes of species I (Table I).

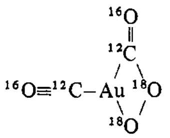
The UV-vis spectrum of species I was also investigated and a typical trace is shown in Figure 4 and Table III. Included in Table III for the purposes of comparison are the data for Au(CO_2) (III). The spectral differences between I and III are quite apparent and will be referred to later, when the mode of decomposition of I is considered.

Carbon Dioxide Production. With the prior knowledge that species I can act as a source of CO_2 on warming to 30-43 K, one can devise specific isotope labeling experiments to determine the mode of fragmentation of I.

Two types of labeling experiments proved to be most informative. To begin with, compound I was synthesized from $^{13}C^{16}O/^{16}O_2$ mixtures and the ^{13}C labeled complex shown below was produced:



On warming this complex to 30-40 K, decomposition ensued with the concomitant production of $^{13}CO_2$. During these warm-up experiments, the absorbance of the band associated with a trace impurity of $^{12}C^{16}O_2$ did not increase, proving that the $^{13}C^{16}O_2$ originated from species I. By preparing the ^{18}O peroxy labeled compound shown below



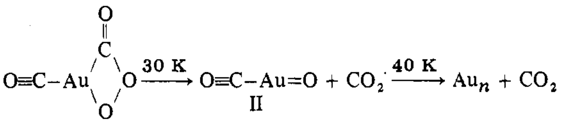
from Au atom/$^{12}C^{16}O/^{18}O_2$ cocondensations, one is able to establish that $^{18}O-^{18}O$ bond cleavage is the primary step leading to CO_2 production during the decomposition of I. This is seen from a roughly 100% increase in the absorbance of the band associated with the $^{12}C^{16}O^{18}O$ molecule, while the relative absorbances of the trace quantities of $^{12}C^{16}O_2$ and $^{12}C^{18}O_2$ (formed on deposition) remain essentially constant.

Species II. On warming the matrix containing I to 40-45 K the UV-vis spectrum of I (Figure 4A) transforms to the spectrum shown in Figure 4B and Table III. The species giving rise to these UV absorptions in II is probably a reaction intermediate formed after the elimination of a molecule of CO_2 from I. The corresponding infrared data for this intermediate is relatively simple, showing a *high* frequency carbonyl stretching mode at roughly 2190 cm^{-1} and low frequency modes at 448/416 cm^{-1}. Further warming of species II to 40-45 K causes additional growth in the absorbance of CO_2 with gradual loss of II. At these temperatures species I has completely decomposed, implying that II is also a precursor of CO_2.

A $^{12}C^{16}O/^{13}C^{16}O/^{16}O_2$ isotopic substitution experiment was performed under conditions which favored the presence of species II. The infrared spectrum of II displayed an isotopic pattern characteristic of a monocarbonyl. The high frequency of the CO stretching mode of II, above that of free CO (2138 cm^{-1}), favors the presence of CO coordinated to oxidized gold.

Taken together, this series of observations point to the existence of a *two-step* fragmentation process for species I, through the intermediacy of species II, the latter being probably best formulated at monocarbonylgold(II) oxide, (OC)AuO.

We are therefore led to believe that the reaction sequence shown below is a reasonable description of the fragmentation of I to produce CO_2:



I

With the prior knowledge that species III is transformed to IV in the temperature range at which II decomposes, and since it is difficult to discern the presence of IV in the midst of II, we cannot eliminate the possible intermediacy of III or IV in the decomposition of II. We note, however, that II can be considered to be a tautomeric form of species III, Au(CO_2), described earlier. New experiments, however, will be required if one is to elucidate the exact nature of III and its warm-up product IV.

Acknowledgment. We wish to thank the National Research Council of Canada, the Atkinson Foundation, and Liquid Carbonic for financial support. D.M. is most grateful to the NRCC for a scholarship.

Registry No. I, 62006-64-8; II, 62006-65-9; Au, 7440-57-5; CO, 630-08-0; O_2, 12185-07-8; CO_2, 124-38-9; ^{13}C, 14762-74-4; ^{18}O, 14797-71-8.

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(14) Labeling experiments using $^{12}CO_2$/$^{13}CO_2$/Ar isotopic mixtures confirmed that weak absorptions in the 1600-cm^{-1} region were associated with trace amounts of H_2O rather than coordinated CO_2.

(15) Note, that had I been the carbonate, then both the symmetric and asymmetric ν(C—O) stretching modes should have been observed[12] in the 1250–800 cm^{-1} region.

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Synthesis and Characterization of Reactive Intermediates in the Palladium Atom–Ethylene System, $(C_2H_4)_nPd$ (where n = 1, 2, or 3)

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The cocondensation of Pd atoms with C_2H_4 and C_2H_4/inert gas matrices at 15 K is shown to provide a direct and efficient route to binary palladium ethylene complexes of the form $(C_2H_4)_nPd$ (where n = 1, 2, or 3). The complexes were identified and characterized by infrared and UV–vis spectroscopy coupled with ethylene concentration studies, warm-up experiments, and $^{13}C_2H_4$ and $^{12}C_2H_4$/$^{13}C_2H_4$ isotopic substitution. Extended Hückel molecular orbital calculations are performed for all three complexes and prove to be a useful aid toward understanding the origin of and observed trends in their UV charge-transfer spectra. Comparisons between the $(C_2H_4)_nPd$ complexes and the analogous $(C_2H_4)_nNi$ complexes are briefly discussed. The suitability of $(C_2H_4)Pd$ as a localized bonding model for the π-complexed form of ethylene chemisorbed onto palladium is also considered.

Introduction

A promising chemical approach which is receiving increasing attention in the field of heterogeneous catalysis[1] involves the use of transition metal atoms for synthesizing localized bonding models of the chemisorbed state.[2] With a careful choice of reaction partners and experimental conditions one can, in principle, design a metal atom–ligand combination to simulate and study almost any adsorbate–adsorbent interaction of catalytic interest.[3,4]

Because olefins are involved in a large number of important heterogeneous catalytic reactions of industrial significance,[5] we chose initially to study the interactions between ethylene and group 8 metal atoms using cryochemical trapping techniques.

In a previous paper[6] we reported that by using Ni atom/C_2H_4 and C_2H_4/Ar matrix cocondensation reactions one can gain a synthetic route to the extremely labile reaction intermediates $(C_2H_4)Ni$ and $(C_2H_4)_2Ni$ as well as the known compound $(C_2H_4)_3Ni$.[7] These complexes were characterized by matrix infrared and UV–vis spectroscopy, coupled with nickel–ethylene concentration studies and warm-up experiments.

In this paper we have extended the technique to palladium atoms to determine whether binary ethylene complexes of palladium, like those of nickel, have an independent existence. By using a combination of ethylene concentration and matrix warm-up experiments, we have been able to definitely identify three $(C_2H_4)_nPd$ complexes, the highest stoichiometry of which is proven from $^{13}C_2H_4$ isotope labeling experiments to be $(C_2H_4)_3Pd$. A previous claim to have synthesized $(C_2H_4)_3Pd$ at 77 K,[7c,d] while effectively demonstrating the existence of a binary Pd/C_2H_4 complex, employed comparative infrared spectroscopic techniques for making a stoichiometric assignment, rather than isotopic labeling. In this paper we will demonstrate that the infrared technique without isotopic substitution is somewhat suspect, in that in a series of complexes $(C_2H_4)_nM$ the infrared peaks shift very little on increasing n or on changing M. On the other hand, we find that the metal-to-ligand charge transfer transitions (MLCT) in the UV spectra of $(C_2H_4)_n$ Pd are quite sensitive to variations in both n and M.

Experimental Section

Monatomic Pd vapor was generated by directly heating a 0.010 in. ribbon filament of the metal or 0.005 in. Pd ribbon wound on a W support with ac in a furnace similar to that described previously.[8] The palladium (99.99%) was supplied by McKay. Research grade $^{12}C_2H_4$ (99.99%) and Ar (99.99%) were supplied by Matheson of Canada and $^{13}C_2H_4$ (91%) by Prochem. The rate of Pd atom deposition was continuously monitored using a quartz crystal microbalance.[9]

In the infrared experiments, matrices were deposited onto a NaCl or CsI optical plate cooled to 15 K by means of an Air Products Displex closed cycle helium refrigerator. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. UV–vis spectra were recorded on a standard Varian Techtron in the range 190–900 nm, the sample being deposited onto a NaCl optical plate.

Extended Hückel calculations for $(C_2H_4)_{1,2,3}Pd$ were performed on an IBM 7094 computer.

Results and Discussion

Infrared Experiments. When Pd atoms are cocondensed with $^{12}C_2H_4/Ar \simeq 1/10$ mixtures at 15 K (using very low concentrations of Pd to eliminate complications due to cluster formation, Pd/Ar $\simeq 10^{-4}$),[10] aside from infrared absorptions belonging to free ethylene isolated in the Ar matrix (labeled E in all figures), a number of new absorptions were observed in the ν(CH), ν(C═C), $\delta(CH_2)$, and $\rho_w(CH_2)$ regions (Figure 1B) which are clearly associated with ethylene coordinated to palladium. Warm-up experiments performed in the range 10–45 K demonstrate that the set of new absorptions can be ascribed to *two* distinct species labeled III and II in Figure 1B and Table I. Of particular note is the fact that the absorptions labeled III occur at frequencies very close to those