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Gold Metal-Catalyzed Reactions of Isocyanides with Primary Amines and Oxygen: Analogies with Reactions of Isocyanides in Transition Metal Complexes

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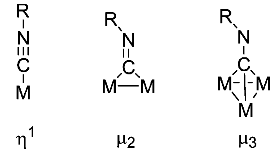
Abstract: Despite its generally poor catalytic properties, bulk gold metal is observed to catalyze reactions of isocyanides ($C\equiv N-R$) with primary amines (H_2N-R') and O_2 to give carbodiimides ($R-N=C=N-R'$) at room temperature and above. Detailed infrared reflection absorption spectroscopic (IRRAS) and kinetic studies show that the reaction occurs by initial η^1-adsorption of the isocyanide on the Au surface, which activates the isocyanide to attack by the amine. This attack is the rate-determining step in the catalytic cycle and has characteristics very similar to those of amine reactions with coordinated isocyanides in transition metal complexes. However, the metallic Au surface provides a pathway involving O_2 to give the carbodiimide product whereas homogeneous metal ion catalysts give formamidines [$HC(=NR)(NHR')$].

Introduction

Organic isocyanides ($R-N\equiv C$) adsorb on the surfaces of the following metals: nickel,[1] rhodium,[2] palladium,[3] platinum,[4] silver,[5] and gold in different forms (film,[6] powder,[7] or nanoparticles[8]). Some modes of isocyanide adsorption on these different metals are shown in Scheme 1. On Au and Ag, η^1 is the observed $C\equiv N-R$ adsorption mode.[9,10] The bonding interaction between Au and the isocyanide primarily involves σ donation of the lone pair of electrons from carbon to gold. Bulk gold metal is a very poor π donor, as evidenced by its very weak interaction with carbon monoxide,[11] which suggests that there is little if any π back-donation from the metal to the isocyanide.

Scheme 1. Modes of Isocyanide Adsorption on Metal Surfaces



Diisocyanides, $C\equiv N-R-N\equiv C$, with a flexible alkyl carbon chain (R), adsorb to the gold surface through both isocyano groups.[7d,12,13] On the other hand, when R is a rigid aromatic unit and the isocyano groups are *para* to each other, only one isocyano group adsorbs.[7a,9,14] The free NC group has been used to bond other molecules,[15] metal clusters,[16] nanoparticles,[14,17] and to form multilayers on gold surfaces.[13] The adsorption of 1,4 phenylenediisocyanide on gold nanoparticles is of special interest because the diisocyanide is proposed to bind to two different nanoparticles, with potential applications as a molecular wire.[8a, 8b]

Despite the large number of studies of adsorbed isocyanides on gold surfaces, there are no reports of reactions of adsorbed

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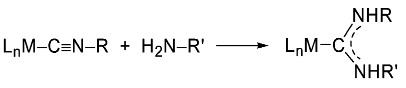
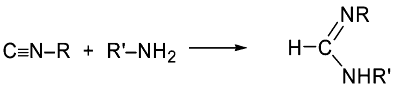
isocyanides or attempts to determine whether these molecules are activated to react when adsorbed to gold; however, the addition of a hydrogen atom to the nitrogen atom of $C{\equiv}N{-}CH_3$ adsorbed on Pt(111) has been reported.[4a,4b] It is well-known that η^1-coordinated isocyanides in transition metal complexes are activated to attack by nucleophiles such as amines (eq 1) and alcohols.[18−20]



$$L_nM{-}C{\equiv}N{-}R + H_2N{-}R' \longrightarrow L_nM{-}C(NHR)(NHR') \qquad (1)$$

An indicator of the susceptibility of such isocyanide ligands to nucleophilic attack is the magnitude of the increase of the $N{\equiv}C$ infrared stretching frequency, $\nu(NC)$, of the coordinated isocyanide as compared to that of the free $R{-}N{\equiv}C$ molecule. A value of $\Delta\nu(NC) = \nu(NC)_{coord} - \nu(NC)_{free}$ greater than 40 cm^{-1} in some systems indicates that a coordinated isocyanide is capable of reacting with nucleophilic agents such as amines.[19,20] Diaminocarbene complexes resulting from such a reaction have been isolated for complexes of Pt, Pd, Au, Ag, and Fe.[19,20] Isocyanide complexes of Au(I) and Au(III) that have been reported to undergo such reactions are $(C_6F_5)(p\text{-}CH_3C_6H_4N{\equiv}C)Au$,[21] $(p\text{-}CH_3C_6H_4N{\equiv}C)AuCl$,[22] $[(RN{\equiv}C)_2Au]^+$ ($R = C_6H_{11}$, $p\text{-}CH_3C_6H_4$),[23] and $(C_6F_5)_3(p\text{-}CH_3C_6H_4N{\equiv}C)Au$.[24] The isocyanide ligand in the gold clusters $[Au_8(PPh_3)_7(CNR)]$ (R = *tert*-butyl; *i*-propyl) also reacts with primary amines to form diaminocarbene cluster complexes.[25] The adsorption of isocyanides on metallic gold surfaces is also accompanied by an increase in $\nu(NC)$ to give $\Delta\nu(NC)$ values[7a,9] between 55 and 90 cm^{-1}, which suggests that adsorbed isocyanides should be susceptible to attack by nucleophiles.

Reactions between isocyanides and primary amines to give formamidines (eq 2) are sometimes *catalyzed* by metal ions.



$$C{\equiv}N{-}R + R'{-}NH_2 \longrightarrow H{-}C({=}NR)(NHR') \qquad (2)$$

Such is the case for group 11 and 12 metals (Cu^+, Ag^+, Zn^{2+}, Cd^{2+}, and Hg^{2+}). It was proposed that these catalytic reactions proceed by a mechanism that involves initial coordination (η^1) of the isocyanide to the metal ion followed by attack of the amine on the isocyanide carbon atom, and then elimination of the product formamidine.[22] For Au(I) and Au(III) complexes, the formamidine is liberated from the diaminocarbene complex only upon displacement by other ligands such as PPh_3 or CN^-.[26]

In the present study, we sought to determine whether isocyanides adsorbed on bulk gold metal are activated to react with primary amines as is observed for isocyanide ligands in metal complexes. Additional goals were to explore the possibility that diaminocarbene groups are detectable on the gold surface, to determine whether formamidine or some other products are formed in the reactions, and to determine whether reactions of isocyanides and primary amines are catalyzed by gold metal, even though bulk gold metal is known to be a poor catalyst; however, it is noted that supported gold nanoparticles are very active catalysts.[27,28] Through these investigations, we sought to understand the similarities and differences between reactions of isocyanides in transition metal complexes and on bulk gold metal surfaces.

Experimental Section

Except where stated otherwise, all experiments were performed in air, at room temperature. The isocyanides *n*-butyl isocyanide (*n*-BuNC), 1,1,3,3-tetramethylbutyl isocyanide (TMBNC), and cyclohexyl isocyanide (CyNC) were purchased from Sigma Aldrich and Strem Chemicals and kept in a freezer at −20 °C. (Although isocyanides have a penetrating odor, the quantities used in these studies were so small that odors were avoided by performing all manipulations and reactions in the hood. Glassware was washed with KOH/ethanol solutions. Gold films containing adsorbed isocyanides have a slight odor when handled outside the hood.) The amines *n*-dodecylamine (*n*-$DoNH_2$), cyclohexylamine ($CyNH_2$), benzylamine ($BzNH_2$), obtained from Sigma Aldrich, and *n*-butylamine (*n*-$BuNH_2$) obtained from Alfa Aesar, were used as received. The solvents 1,2-dichloroethane (DCE), ethanol (EtOH) and hexane are spectrophotometric grade and were obtained from Sigma Aldrich.

Gold Substrate Preparation. The gold films were prepared on glass slides (25 mm/75 mm) by physical vapor deposition. First, a 15 nm Cr layer was deposited and then 300 nm of gold.[29] Evaporation and deposition were performed in a cryopumped E306A Edwards Coating System, maintaining the pressure during evaporation below 7×10^{-6} Torr and a deposition rate of 0.2 nm/s. Gold slides were stored in dry air, in a desiccator. The gold powder was prepared from $HAuCl_4$ by reduction with hydroquinone according to a published procedure[30] and had a surface area of 0.35 m^2/g and a particle diameter of approximately 1 μm.[7a] The gold powder was washed with methanol in a Soxhlet extractor for 24 h and dried in air in the oven at 110 °C for 1 h.

Gold Surface Cleaning. Clean gold surfaces for isocyanide monolayer formation were obtained by treating previously used gold substrates with "piranha" solution (a 3:1 mixture of concentrated H_2SO_4 and 30% aqueous H_2O_2; CAUTION: Add H_2SO_4 to H_2O_2, manipulate carefully and neutralize everything with Na_2CO_3 immediately after finishing the experiment). The gold slides were placed in 50 mL of freshly prepared "piranha" solution for 5 min. Then the slides were washed thoroughly with deionized water and methanol and dried in an oven at 125 °C for 2 h. The gold powder was cleaned in a similar manner using our previously published method.[7c] Both the gold film and the gold powder, when treated in this way, gave clean surfaces that exhibited no absorption peaks in their IR spectra.[7c] Such cleaned Au surfaces adsorbed isocyanide like the freshly prepared Au substrates.

Monolayer Preparation. Monolayers were formed by immersing the gold slides for 24 h into 50 mL of 5 mM isocyanide solution in DCE. Upon removal from the isocyanide solution, the slides were rinsed

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with ethanol for 5 s, to remove the unadsorbed isocyanide, and dried in an air flow for about 10 s. The following procedure was used to create an isocyanide monolayer on gold powder:[7c] 1 mL of 5 mM isocyanide solution in DCE was added to a Pyrex test tube containing 1.00 g of gold powder. The test tube was capped with a Teflon-lined screw cap, shaken for 30 s, and then allowed to settle for 24 h. The isocyanide solution was decanted, and the gold powder was allowed to dry in air for 24 h.

Infrared Reflection Absorption Spectroscopy (IRRAS). IRRAS measurements were performed on a Nicolet 850 FT-IR spectrometer with a liquid nitrogen cooled HgCdTe detector and *p*-polarized light incident at 82°. During the analysis, the spectrometer was purged with nitrogen. The spectra were collected by referencing 512 sample scans to 512 reference scans at a resolution of 2 cm^{-1} with Happ−Genzel apodization and reported as $-\log(R/R_0)$, where R is the reflectivity of the sample and R_0 is the reflectivity of the reference. The reference was a monolayer of *n*-octadecanethiol prepared on the same type of gold slide by immersing the slide for 12 h in a 1 mM solution of *n*-octadecanethiol in ethanol.[31,32] The spectra were processed to remove absorptions due to traces of water and CO_2 and baseline corrected using OMNIC software.

Reactions of Adsorbed Isocyanides on Au with Amines. A gold slide prepared with adsorbed isocyanide on its surface, as described above, was placed in 25 mL of a 5 mM amine solution in hexane for a specific period of time in air. Then the slide was removed from the solution, rinsed in an ethanol flow for 3 s, dried in a nitrogen flow for 30 s, and placed directly in the IRRAS spectrophotometer for the spectral measurements.

To 1.00 g of gold powder with isocyanide adsorbed on the surface was added 1 mL of 5 mM amine solution in hexane in air. The test tube was capped, and the contents were stirred with a magnetic bar for 5 min in the case of *n*-$BuNH_2$ and for 10 min for the rest of the amines. A sample of this solution was analyzed by GC-MS to identify the reaction products R−N═C═N−R′

GC-MS Analyses. These analyses were performed on a Micromass GCT gas chromatograph mass spectrometer from Waters Corporation, Beverly, MA. The instrument includes an Agilent 7683 series autosampler, an Agilent 6890 gas chromatograph, and a Micromass time-of-flight mass spectrometer. Instrument control, data acquisition, and data processing used a Compaq Deskpro PC workstation with a Windows XP operating system. The application software was MassLynx 4.0 from Waters. The computerized libraries include the NIST 2002 from the National Institute of Standards and Technology (147 198 entries), and the Wiley Registry of Mass Spectral Data, 7th Edition, from John Wiley & Sons, Inc. (329 171 entries). A Varian VS-5MS capillary column (30 m length, 0.25 mm internal diameter, 0.25 μm film thickness, 5% phenyl, 95% methyl silicone polymer) was used to determine product yields. The GC analysis conditions were as follows: carrier gas (He); mode (constant flow); initial column temperature (40 °C); temperature program: time at initial temperature (2 min)/heating rate (15 °C/min)/final temperature (280 °C).

Kinetic Studies of the Reaction between *n*-BuNC, *n*-$BuNH_2$, and O_2 Catalyzed by Gold Powder. In a 10 mL round-bottom flask was placed 1.00 g of clean gold powder. A mixture of *n*-BuNC, *n*-$BuNH_2$, and *n*-decane in hexane solution was added to the gold. *n*-Decane was the internal standard for quantitative GC analysis. The flask was thermostated at the desired temperature using an oil bath. The experiments were performed in air at room temperature and 60 °C with continuous stirring with a stirbar. One set of experiments was made with 0.5 mM isocyanide, and the amine concentration was varied from 5 to 50 mM. Another experiment was made with 4.5 mM isocyanide and 45 mM amine. For all experiments, the total solution volume was 3.0 mL. The reaction was monitored by periodically removing a sample of the reaction solution and analyzing it by GC using the experimental conditions described above and standard solutions of *n*-BuNC and Bu^t−N═C═N−Bu^t for quantitation of the *n*-BuNC and Bu^n−N═C═N−Bu^n present in the reaction solutions. The rate of the reaction of 0.5 mM *n*-BuNC with 50 mM *n*-$BuNH_2$ under a pure O_2 atmosphere at 60 °C was the same as the same reaction performed under an air atmosphere, and the yield (68%) of Bu^n−N═C═N−Bu^n was nearly the same as that (76%) achieved under an air atomosphere. When the same reaction was performed under an argon atmosphere, the reaction gave small amounts of the Bu^n−N═C═N−Bu^n product, but only 4% of the *n*-BuNC had reacted after 2 h, whereas 100% of the isocyanide reacted after the same time when the reaction was conducted in air or O_2. The small amount of reaction observed under argon was presumably due to adventitious oxygen. These results show that O_2 is a reactant in these reactions.

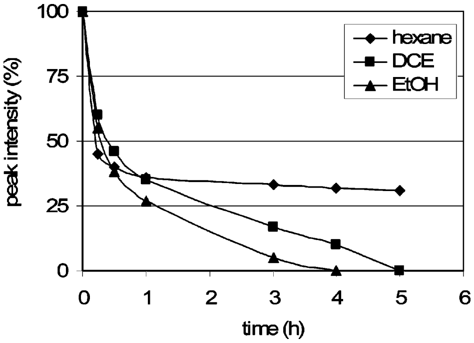

Figure 1. Decrease of the ν(NC) peak intensity of *n*-BuNC adsorbed on a Au film with time, upon immersion in solvents. On the *y* axis is the percent of the peak intensity expressed as $(I/I_0) \times 100$, where I_0 is the initial intensity of the peak and I is the peak intensity at time t.

Results and Discussion

Adsorption/Desorption of Isocyanides on Gold Films. IRRAS spectra of isocyanide monolayers on gold slides, formed by placing the slides in 50 mL of 5 mM isocyanide in DCE for 24 h at room temperature, showed a strong ν(NC) absorption at 2200−2225 cm^{-1}. In this region of the spectra, no other peaks of the analyzed molecules are present. On the gold film, the ν(NC) absorptions shift to higher wavenumbers as compared with those of the free isocyanides. For example, the ν(NC) value for *n*-BuNC in DCE is 2148 cm^{-1}, whereas that for *n*-BuNC adsorbed on gold film is 2224 ± 1 cm^{-1}. Values of ν(NC) for the free and adsorbed isocyanide for the other two isocyanides used in this study are: TMBNC, 2133 cm^{-1} (in DCE), 2205 cm^{-1} (adsorbed); CyNC, 2140 cm^{-1} (in DCE), 2216 cm^{-1} (adsorbed). The IRRAS spectra show that the isocyanide monolayers on the Au film are stable for at least 2 or 3 weeks, if the gold slides are kept in a desiccator (in air) at room temperature.

To determine the stability of the *n*-BuNC isocyanide monolayer toward desorption in a solvent, the Au slides were placed in 25 mL of hexane at room temperature. Periodically the slides were removed from the hexane, rinsed with ethanol, dried in an N_2 flow, and the IRRAS spectra were recorded. The decrease in intensity of the ν(NC) peak was used to determine the approximate rate at which the isocyanide was removed from the surface. By repeated immersions of the slide in hexane, it was possible to determine an approximate rate for the desorption process (Figure 1). During the desorption, the ν(NC) value of the remaining adsorbed isocyanide shifts to higher values (for example, 2225 cm^{-1} initially, but 2232 cm^{-1} after ∼40% of

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2the *n*-BuNC had been removed); this shift suggests that there are different types of adsorption sites on the gold surface. Within the first minute, approximately 55% of the adsorbed *n*-BuNC is removed from the surface. After that, slow desorption removes another 10% in approximately 2 h, whereas the remaining 35% does not desorb even after 9 h (Figure 1). These IRRAS and rate of desorption studies indicate that there are two categories of adsorbed *n*-BuNC: (1) weakly adsorbed with ν(NC) = 2225 cm^{-1} and (2) strongly adsorbed with ν(NC) = 2232 cm^{-1}.

In a series of STM studies performed on gold films that were prepared in the same way as those described in the present work, Porter et al. demonstrated that the Au surface of evaporated films, with a predominant Au(111) component, has a "rolling hills" topography with a high step density.[31,32] The surface can be modeled as densely packed arrays of hemispheres on which about 55% of the surface atoms are located on terraces and 45% on step edges. For alkanethiol monolayers, the molecules adsorbed on step sites are more strongly bonded than those on the terrace sites. Our isocyanide desorption results are consistent with approximately 55% of the sites (terrace sites) being weakly adsorbing; the *n*-BuNC molecules adsorbed on these sites are quickly desorbed in the first minutes of immersion in hexane. Our previous DRIFT (diffuse reflectance IR Fourier transform) spectroscopic investigations[7c] of the adsorption of isocyanides on gold powder also showed two types of adsorption regimes, as characterized by ν(NC) values of 2225 cm^{-1} at saturation coverage and 2233 cm^{-1} for strongly adsorbed *n*-BuNC; these values are the same as those for *n*-BuNC on gold film as described above. For Au powder, approximately 30% was weakly adsorbed, whereas 70% of the isocyanide (*n*-BuNC and $C_{18}H_{37}NC$) was strongly adsorbed. The difference between 70% strongly adsorbed isocyanide on gold powder and 45% on gold film is likely due to differences in surface topography of these two forms of gold.

Two other solvents, DCE and EtOH, were used in studies of the desorption of *n*-BuNC from Au film. These polar solvents remove *all* of the adsorbed isocyanide from the Au surface within about 5 h (Figure 1). In these cases, an inflection in the plot occurs at the point where approximately 60% of the isocyanide is removed from the surface. The weakly adsorbed molecules are desorbed in a few minutes, followed by slower desorption of the remaining isocyanide within about 5 h. The ν(NC) value of adsorbed molecules shifts from 2225 cm^{-1} in the initial monolayer to 2234 cm^{-1} after 60% of the *n*-BuNC is removed with DCE; this shift is from 2224 to 2229 cm^{-1} with EtOH. Thus, in all of the isocyanide desorption experiments, the strongly adsorbed isocyanide has a higher ν(NC) value, which is consistent with the observation in transition metal complexes in which a greater σ donation of the isocyanide to a metal center is correlated with a higher ν(NC) value;[19] this greater σ-donation typically occurs in complexes where the metal has a higher positive charge.

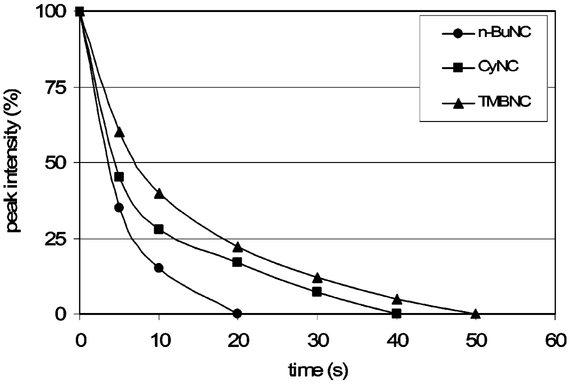


Figure 2. Decrease of the ν(NC) peak intensity of isocyanides adsorbed on gold slides immersed in 5 mM *n*-$DoNH_2$/hexane solutions.

Table 1. Rates of Isocyanide Removal from RNC/Au Film in Amine/Hexane Solutions

isocyanide	amine	$t_{1/2}$ (s)	$t'_{1/2}$ (s)	amine pK_a
n-BuNC	hexane	50	–	
	n-$BuNH_2$	3	5	10.62
	n-$DoNH_2$	3.5	6.5	10.63
	$CyNH_2$	9	22	10.64
	$BzNH_2$	13	87	9.34
CyNC	hexane	70	–	
	n-$BuNH_2$	5	17	10.62
	n-$DoNH_2$	4	13	10.63
	$CyNH_2$	11	28	10.64
	$BzNH_2$	16	60	9.34
TMBNC	hexane	100	–	
	n-$BuNH_2$	7	10	10.62
	n-$DoNH_2$	7.5	17	10.63
	$CyNH_2$	12	27	10.64
	$BzNH_2$	8	20	9.34

Reaction/Desorption of Isocyanides on Au Films in Amine Solutions in Air. In a series of experiments, gold slides with an isocyanide monolayer on the surface were immersed in 25 mL of 5 mM amine in hexane solution for a specific period of time, in air, at room temperature. After being removed from solution, the slide was rinsed with ethanol for 3 s, dried in a N_2 flow, and placed in the IR spectrometer for analysis. After being immersed in the amine solution for 10 s, the ν(NC) peak intensity decreased drastically. Figure 2 presents the change in ν(NC) intensity when a slide containing an adsorbed isocyanide is immersed in 5 mM *n*-$DoNH_2$ solution. For *n*-BuNC, after only 20 s of immersion, the ν(NC) adsorption peak completely disappeared. For CyNC and TMBNC, the ν(NC) intensity is zero after 40 and 50 s, respectively. Similar results were obtained with all amines (*n*-$BuNH_2$, $CyNH_2$, and $BzNH_2$) used in this study.

The time required for the disappearance of the ν(NC) peak is very short compared with that in the desorption experiments with the hexane solvent only (Figure 1). The faster rate of isocyanide removal from the surface in the presence of the amine may be due to a reaction of the adsorbed isocyanide with the amine and/or an amine promoted desorption of the isocyanide; these possibilities are discussed in detail in the next section. In Figure 2, it can be seen that there are two different parts of the process. In the first part, the ν(NC) peak intensity decreases rapidly; this is followed by a slower decrease to zero. This behavior also indicates the existence of two types of isocyanides and adsorption sites on the gold surface, as was observed in the solvent desorption studies (Figure 1).

Table 1 summarizes semiquantitative rate data for the removal of the isocyanides from the gold film in the presence of amines. The third column presents the time ($t_{1/2}$) in which half of the initial amount of adsorbed isocyanide is removed from the surface, which is the time at which the ν(NC) peak intensity I is half that of the initial I_0. Considering that approximately 45% of the total isocyanide is strongly bonded to the surface, column

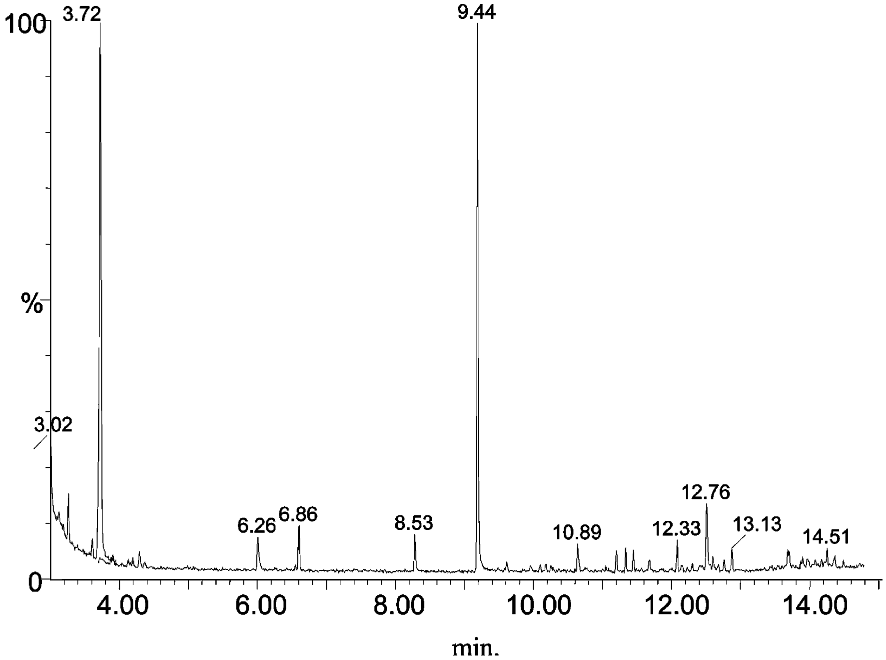


Figure 3. GC chromatogram of the solution from the reaction of *n*-BuNC adsorbed on powdered gold with *n*-$BuNH_2$. The peak at 3.72 min is *n*-BuNC, whereas that at 9.44 min is *n*-Bu-N=C=N-*n*-Bu.

four presents the time ($t'_{1/2}$) at which half of this strongly adsorbed isocyanide is removed from the surface; thus, $t'_{1/2}$ was obtained by plotting I/I_0 versus time considering an I/I_0 value of 0.45 as the starting point and measuring $t'_{1/2}$ at $I/I_0 = 0.225$. There are several general trends that are evident in the data in Table 1. For the same isocyanide, the rate of the process (both $t_{1/2}$ and $t'_{1/2}$) is influenced by the nature of the amine. It is faster for those amines with a linear carbon chain (*n*-$BuNH_2$ and *n*-$DoNH_2$) and slower for the more bulky amines ($CyNH_2$ and $BzNH_2$). The slower rates for $BzNH_2$, as compared with $CyNH_2$, are probably due to its lower basicity/nucleophilicity. For reactions using the same amine (e.g., *n*-$BuNH_2$) but different adsorbed isocyanides, the rates decrease (*n*-BuNC > CyNC > TMBNC) as the bulkiness of the isocyanide increases, which is consistent with a lower accessibility of bulky isocyanides to attack by the amine.

In these studies, there is no IRRAS evidence in the ν(N−H) region (3100−3500 cm^{-1}) for adsorbed amine on the gold surface, even in the absence of isocyanide. Also, there is no evidence for a diaminocarbene group (see eq 1) on the surface; such a species should give a ν(N−C=N) absorption near 1550 cm^{-1}, which is characteristic of diaminocarbene groups in transition metal complexes.[19] Likewise, there is no IR band in the region ∼2130 cm^{-1} that is characteristic of an adsorbed carbodiimide (R−N=C=N−R) product. Because of their low concentrations, it was not possible to detect desorbed R−N≡C or reaction products in the Au film immersion solutions.

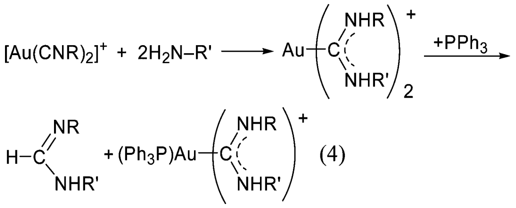
Reaction/Desorption of Isocyanide on Au Powder in Amine Solutions. Because the amount of desorbed isocyanide and/or product was too small to be detected by GC-MS in Au film experiments, we performed a series of experiments using gold powder, which has a larger surface area than gold film: 3×10^{-1} m^2/g for gold powder[7a] and 3×10^{-3} m^2/slide (calculated from refs 31 and 32). So, one gram of gold powder is capable of adsorbing 100 times as much isocyanide as a gold slide. This larger amount of isocyanide, combined with the ability to use a smaller volume of solution, allowed us to determine the product(s) formed when isocyanides adsorbed on gold powder were reacted with primary amines. The isocyanide was first adsorbed on 1.00 g of gold powder by immersing it in a 5.00 mM isocyanide solution in DCE.[7c] After decanting the solution and air-drying, the RNC/Au powder was immersed in 1 mL of a 5 mM amine solution in hexane, and the mixture was stirred for 5 min in the case of *n*-$BuNH_2$ and for 10 min for the other amines. According to the Au film studies, all of the isocyanide should be removed from the gold surface during these times (Figure 2). The solution was analyzed by GC-MS to identify the free isocyanide and/or reaction product. For the reaction of adsorbed *n*-BuNC with *n*-$BuNH_2$, the GC chromatogram (Figure 3) shows two new peaks (beside those of amine and solvent) with retention times (t_R) of 3.72 and 9.44 min. These two peaks were identified as *n*-BuNC (at 3.72 min) and *N*,*N*′-dibutylcarbodiimide (at 9.44 min) by comparing their mass spectra with those of known compounds in the computer libraries described in the Experimental Section. The *n*-BuNC was also identified by comparing its GC-MS spectrum to that of an authentic sample. On the basis of this product identification, the reaction of the adsorbed *n*-BuNC with *n*-$BuNH_2$ is described by eq 3

$$n\text{-BuNC} + n\text{-BuNH}_2 + \text{O}_2 \rightarrow \text{Bu}^n\text{−N=C=N−Bu}^n + \text{“H}_2\text{O”} \quad (3)$$

The observation of *n*-BuNC in the GC chromatogram (Figure 4) shows that some of the isocyanide simply desorbs from the surface, without reacting with the amine. To determine whether the desorbed isocyanide reacts with amine in solution, we reacted a 0.5 mM solution of *n*-BuNC with 5 mM *n*-$BuNH_2$ in hexane, in the absence of gold. GC-MS studies of this solution showed no evidence for *N*,*N*′-dibutylcarbodiimide after 5 days of stirring at room temperature. This result is consistent with an earlier report that stated that aliphatic isocyanides do not react with primary amines in the absence of a catalyst even at temperatures as high as 120 °C.[33] Thus, in the present studies, the reaction between the isocyanide and the amine must occur on the gold.

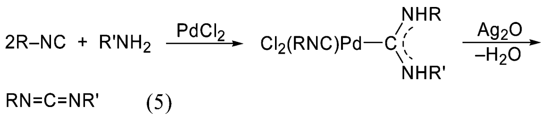
Similar GC-MS analyses of solutions obtained from reactions of other adsorbed isocyanides and amines were also performed for the following reactants: (1) n-BuNC and n-DoNH$_2$; (2) n-BuNC and BzNH$_2$; (3) CyNC and CyNH$_2$; (4) CyNC and n-BuNH$_2$. In all cases, the GC-MS spectra showed two new peaks, further identified to be the desorbed isocyanide and the corresponding carbodiimide R$-$N$=$C$=$N$-$R′, where the R and R′ groups originated from the reacting isocyanide and amine.

The carbodiimide reaction product is surprising because isocyanide ligands in metal complexes react with amines to form diaminocarbene complexes (eq 1), and in some cases the carbene ligand can be displaced as the formamidine (eq 4).[26a]



(4)

As noted in the Introduction (eq 2), some metal ions *catalyze* the reaction of isocyanides with amines to give formamidines. However, there are no catalytic reactions of isocyanides and amines to give carbodiimides. Although a reaction (eq 5) of a Pd diaminocarbene complex with Ag$_2$O gives a carbodiimide,[34] the Ag$_2$O reactant makes this a reaction that is very different than the reactions of isocyanides adsorbed on gold metal in the current study.



(5)

Reactions of n-BuNC with n-BuNH$_2$ and O$_2$ Catalyzed by Gold Metal. In the previous section we showed that a reaction takes place on the Au surface between *preadsorbed* isocyanide and amine in solution. To determine whether gold *catalyzes* the reaction of isocyanides with amines, we performed a series of experiments in which clean Au powder (1.00 g) was stirred with a solution of n-BuNC (0.5 mM), n-BuNH$_2$ (5 mM), and 0.10 mg of decane (internal standard) in hexane at room temperature (20 °C) in air. Periodically, the solution was analyzed by GC to determine the quantities of isocyanide and carbodiimide product. The initial amount of isocyanide was selected to be similar to that used in previous experiments, which would give saturation coverage of the gold powder at room temperature[7b] (1.6×10^{-3} mmol n-BuNC). For other experiments, the initial concentration of isocyanide was increased by a factor of approximately 10. In every case, the amine concentration was 10 times that of the isocyanide. As shown in Table 2, the reactions were much faster at 60 than at 20 °C, and the yield of Bu$^n-$N$=$C$=$N$-$Bu^n was higher (70−73%) at 60 °C. In addition to the Bu$^n-$N$=$C$=$N$-$Bu^n carbodiimide, di-N,N'-n-butylurea was identified as a minor product in the GC-MS spectra of all of the reaction solutions. Unidentified products with higher molecular weights (>300) were also observed.

Table 2. Isocyanide Conversion and Product Yield for the Au-Catalyzed Reaction of n-BuNC with n-BuNH$_2$

exp	n-BuNC (mmol)	T (°C)	C^a (%)	η^b (%)	$t_{1/2}{}^c$ (h)
1	1.6×10^{-3}	20	97	42	72
2	17×10^{-3}	20	98	47	120
3	1.6×10^{-3}	60	100	70	5
4	17×10^{-3}	60	100	73	40

[a] Conversion after: 8 days for (1), 19 days for (2), 12 h for (3), and 90 h for (4). [b] Yield of carbodiimide. [c] Time at which the conversion is 50%.

The H$_2$O product of this reaction (eq 3) could not be positively identified in the reaction solutions by GC-MS. Although it was possible to identify H$_2$O in water-saturated hexane solutions, the H$_2$O peak in the GC chromatogram of these solutions was only marginally distinguishable from that of the background. The extremely low solubility of water in hexane is well-documented.[35] Although H$_2$O could not be positively identified as a product of the reaction, it seems to be the most likely product of the reaction of O$_2$. However, it is possible that the two hydrogen atoms released from the amine in the reaction (eq 3) combine with O$_2$ *and* some of the isocyanide or amine to give other products. The involvement of O$_2$ in the reaction is essential because Bu$^n-$N$=$C$=$N$-$Bu^n is not formed in the reaction of n-BuNC and n-BuNH$_2$ in the absence of O$_2$.

The presence of both the carbodiimide and water in the product solution suggests the possibility that they could react to form N,N'-di-n-butylurea. As noted above, small amounts of N,N'-di-n-butylurea are observed in the reaction solutions. However, this small amount is not sufficient to account for all of the H$_2$O that would be produced in the reaction. To determine whether a carbodiimide and H$_2$O could react under the conditions (Table 2) of reaction 3, amounts of H$_2$O (0.030 mmol, 0.54 μL) and Bu$^t-$N$=$C$=$N$-$Bu^t (0.030 mmol) comparable to those produced in the Au-catalyzed reaction (eq 3) were stirred in 20 mL of hexane. Even after 48 h at room temperature, there was no decrease in the amount of Bu$^t-$N$=$C$=$N$-$Bu^t, which indicates that it is unlikely that N,N'-di-n-butylurea would form under the conditions in Table 2, assuming that Bu$^n-$N$=$C$=$N$-$Bu^n and Bu$^t-$N$=$C$=$N$-$Bu^t have similar reactivities. This lack of reaction between Bu$^t-$N$=$C$=$N$-$Bu^t and H$_2$O may be due to the very low solubility of water in hexane.

On the basis of the present studies and previous investigations of reactions of isocyanide ligands in metal complexes with amines (eq 1), we propose the mechanism in Scheme 2 for the Au-catalyzed reactions of isocyanides with primary amines to form carbodiimides. Initially, the isocyanide adsorbs to a Au atom on the surface, which creates a more positive isocyanide carbon atom,[10] making it susceptible to attack by nucleophiles. Attack of the amine on this carbon (step 1) leads to intermediate **a**, which can transfer both hydrogen atoms to the gold surface while releasing the carbodiimide product (step 2). Alternatively, one of the NH$_2$ hydrogen atoms in intermediate **a** can migrate to the other nitrogen to give a diaminocarbene intermediate **b** (step 3) comparable to diaminocarbene complexes formed in

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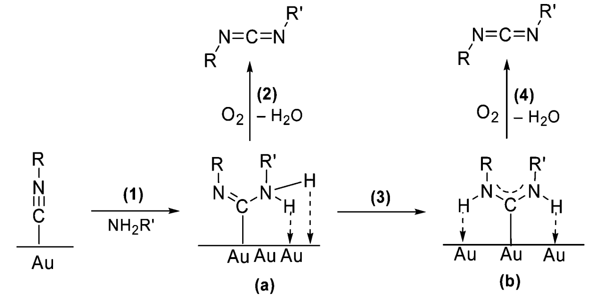
(33) Saegusa, T.; Ito, Y. *Isonitrile Chemistry*, Ugi, I., Ed.; Academic Press: New York, 1971; p 67.

(34) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1975**, *40*, 2981.

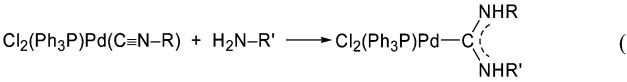
(35) IUPAC−NIST Solubility Database. NIST Standard Reference Database 106: http://srdata.nist.gov/solubility/sol_detail.asp?sys_ID=37_252.

Scheme 2. Mechanism for the Au-Catalyzed Reaction of Isocyanides (R−N≡C) with Primary Amines (H_2NR') and O_2



reactions of isocyanide metal complexes with amines (eq 1). This intermediate **b** could form the carbodiimide product by transferring the two N−H hydrogen atoms to the gold surface (step 4). Both carbodiimide-producing steps (2 and 4) are proposed to involve transfer of the two hydrogen atoms to oxygen to give H_2O. Because the rate of reaction 3 is the same in air and in pure O_2, the participation of O_2 in the overall reaction must occur after the rate-determining step. This means that we have no information about the details of steps 2 or 4. An unlikely pathway for steps 2 and 4 involves the formation of free H_2; bulk gold powder is reported[27,36] to catalyze the reaction of H_2 and O_2 at a significant rate only at temperatures above 130 °C. It might be noted that supported gold *nanoparticles* catalyze the reaction of H_2 and O_2 to give H_2O_2 even below room temperature.[37,38]

IRRAS studies of the gold film did not reveal a ν(N−C═N) absorption for intermediate (**b**) or (**a**); however, it is possible that their absorptions are too weak to be observed. If it is assumed that these intermediates are not present in significant concentration, it means that the intermediate is rapidly converted to product and that step 1, amine attack on the adsorbed isocyanide, is the rate-controlling step in the catalysis. A kinetic study[20,39] of amine attack on the isocyanide ligand in $Cl_2(Ph_3P)Pd(C{\equiv}N{-}R)$ (eq 6) shows that the reaction follows a rate law,



$$Cl_2(Ph_3P)Pd(C{\equiv}N{-}R) + H_2N{-}R' \longrightarrow Cl_2(Ph_3P)Pd{-}C\begin{matrix}NHR\\ NHR'\end{matrix} \qquad (6)$$

R = $MeOC_6H_4$, MeC_6H_4 or Ph; R' = $MeOC_6H_4$, MeC_6H_4, Ph, and ClC_6H_4

Rate = $k[Cl_2(Ph_3P)Pd(CNR)]\ [H_2NR']$, which is first order in the amine concentration. It was also noted that the rates of reaction increase as the basicity of the amine increases from p-$ClC_6H_4NH_2$ to p-$MeOC_6H_4NH_2$. If the rate-determining step in the Au-catalyzed reaction (eq 3) were amine attack on the adsorbed isocyanide (step 1 in Scheme 2), the overall rate of conversion of isocyanide to the carbodiimide product should also be first order in the amine concentration.

Table 3. Au-Catalyzed Reaction of *n*-BuNC with *n*-$BuNH_2$ in Hexane at 60 °C

	amine concentration (mM)				
	5	12.4	24.8	37.5	50
k_{obs} (h^{-1})	0.13	0.34	0.72	1.07	1.39
$t_{1/2}$ (h)	5.25	2.01	0.96	0.64	0.49
η (%)[a]	70	78	74	76	76

[a] Yield at end of reaction.

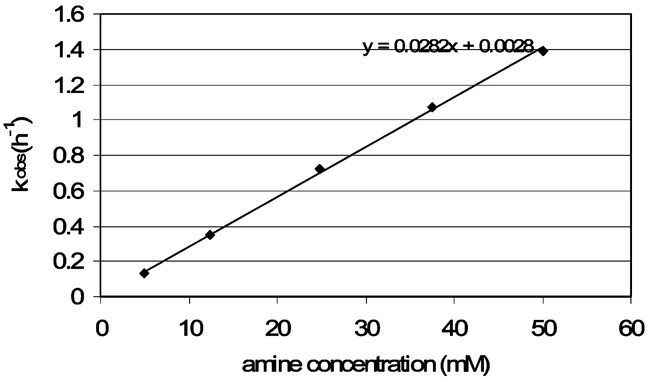


Figure 4. Plot of k_{obs} vs [*n*-$BuNH_2$] for the Au-catalyzed reaction of *n*-BuNC with *n*-$BuNH_2$ at 60 °C in hexane.

To examine the amine concentration dependence of this reaction (eq 3), a series of experiments was performed in which 1.6 × 10^{-3} mmol of *n*-BuNC in 3 mL of hexane was reacted with excess amine (10−100 amine/isocyanide ratio) in the presence of 1.00 g of Au powder at 60 °C in air. The large excess of amine allows one to obtain pseudo first-order rate constants (k_{obs}) from plots of ln[*n*-BuNC] vs time, where k_{obs} = k[*n*-$BuNH_2$] (Table 3). The plot of k_{obs} vs [*n*-$BuNH_2$] is linear (Figure 4) demonstrating that the reaction is first order in the amine concentration and that the overall rate law in the presence of 1.00 g Au powder is Rate = k[*n*-BuNC][*n*-$BuNH_2$]. This rate law, and especially the first order dependence on the amine concentration, supports the proposal that step 1 in the mechanism (Scheme 2) is rate-determining. In studies of the removal of *n*-BuNC from a gold film upon reaction with amines in hexane solution, it was observed (Table 1) that the less sterically bulky and more basic amines removed the isocyanide more rapidly. This is also consistent with amine attack (step 1) being the rate-determining step. Because the steps beyond step 1 occur rapidly, it is not possible to define the subsequent steps that lead to the carbodiimide product. However, these results indicate that the initial step in the Au-catalyzed reaction of isocyanide with amines is very similar to that of isocyanide reactions in transition metal complexes.

Conclusions

Except for supported nanosized particles,[27,28] gold metal is generally a poor catalyst. However, we find that Au particles of even 1 μm size catalyze reactions of isocyanides with primary amines and O_2 to form carbodiimides (eq 3) at room temperature. IRRAS and DRIFT studies show that isocyanides adsorb in an η^1 fashion (Scheme 1) onto the surfaces of Au films and powders and are thereby activated to react with amines. An indication of this activation is the ~75 cm^{-1} increase in the isocyanide ν(NC) value upon adsorption. Previous studies suggest that an increase in ν(NC) greater than 40 cm^{-1} upon coordination in a metal complex is sufficient to activate an isocyanide to attack by amines to give a diaminocarbene ligand (eqs 1 and 6). As for reactions of metal complex−coordinated isocyanides, the Au-catalyzed reaction of isocyanides is first

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(36) Benton, A. F.; Elgin, J. C. *J. Am. Chem. Soc.* **1927**, *49*, 2426.

(37) Landon, P.; Collier, P. J.; Papworth, A. J.; Kiely, C. J.; Hutchings, G. J. *Chem. Commun.* **2002**, 2058.

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order in the amine concentration, which suggests that amine attack on an adsorbed isocyanide is the rate-determining step in the overall mechanism (Scheme 2). Although the initial activation of isocyanide to amine attack is common to both the Au-catalyzed reaction and reactions of isocyanides in metal complexes, the Au-catalyzed reaction (eq 3) gives a carbodiimide product whereas the homogeneous metal-ion-catalyzed reaction (eq 2) gives a formamidine. It is apparently the ability of hydrogen atoms to transfer to the Au surface and/or to the O_2 that leads to the carbodiimide product, a pathway that is not available to the metal-ion-catalyzed reaction. These investigations highlight the commonality of key steps in reaction mechanisms of organometallic complexes and heterogeneous catalysts that nevertheless lead to different products.

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Supporting Information Available: IRRAS spectra of isocyanides on Au-film. GC-MS spectra of carbodiimide products ($R-N=C=N-R'$). Rate plots for reactions of *n*-BuNC with *n*-$BuNH_2$ under atmospheres of air, O_2, and Ar. This material is available free of charge via the Internet at http://pubs.acs.org.

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