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Isocyanide Ligands Adsorbed on Metal Surfaces: Applications in Catalysis, Nanochemistry, and Molecular Electronics[†]

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Knowledge of the coordination chemistry and reactivity of isocyanide ligands in transition-metal complexes forms the basis for understanding the adsorption and reactions of isocyanides on metal surfaces. In this overview, we explore reactions (often catalytic) of isocyanides adsorbed on metal surfaces that reflect their patterns of reactivity in metal complexes. We also examine applications of isocyanide adsorption to the stabilization of metal nanoparticles, the functionalization of metal electrodes, and the creation of conducting organic−metal junctions in molecule-scale electronic devices.

I. Introduction

Aryl and alkyl isocyanides ($C{\equiv}NR$) are a well-studied family of ligands typically found in coordination and organometallic complexes of the transition metals.[1−7] They bind strongly in these complexes whether the oxidation state of the metal is high (e.g., 2+ and 3+) or low (e.g., 1− and 2−). In recent years, studies have shown that they also bind strongly to the surface of various metals. In a recent review,[8] we summarized the different ways that isocyanides bind to metal surfaces. Depending on the metal, the form of the metal (powder, film, single crystal, or nanoparticle), the surface coverage, and the specific isocyanide, the isocyanide may be coordinated to one, two, or three metal atoms as inferred from spectroscopic studies. Assignments of adsorption modes on metal surfaces are based on known binding modes in transition-metal complexes (Figure 1).

In my (R.J.A.) lecture at the Spring 2007 American Chemical Society meeting at which the ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry was presented, I described our studies of the adsorption and catalytic reactions of isocyanides on gold metal surfaces, which are of special interest because gold metal (except for gold nanoparticles) is a poor catalyst of a variety of other reactions. Of course, it is the binding of isocyanides to the metal surface that activates them to react and to be converted catalytically to various organic products. It is the purpose of this paper to summarize these and other reactions of isocyanides that occur on metal surfaces. Also, we describe how the adsorption of isocyanide ligands on metal surfaces contributes to other fields of science: the stabilization of metal nanoparticles, the creation of biomolecular sensors, and the design of molecular electronic devices. Throughout the discussion, we emphasize the properties of isocyanide ligands in metal complexes that make them useful in understanding their bonding and reactivity on metal surfaces.

II. Reactions of Isocyanides Adsorbed on Metal Surfaces

In this section are described reactions of isocyanides that occur as a result of their adsorption on a metal surface. In these studies, the adsorbed isocyanide and surface-bound

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Bob Angelici was born in 1937 in Rochester, MN. He received his B.S. degree in 1959 from St. Olaf College and his Ph.D. in 1962 from Northwestern University under the direction of Fred Basolo. He was an NSF Postdoctoral Fellow with Ernst O. Fischer at the University of Munich in 1962−1963. He joined the faculty at Iowa State University (ISU) in 1963, where he was subsequently promoted to Associate (1968), Full (1971), and Distinguished (1988) Professor. He was chair of the Chemistry Department from 1977 to 1981 and received several teaching awards from ISU and the State of Iowa. He was author of the inorganic laboratory text *Synthesis and Technique in Inorganic Chemistry*. In addition to presenting many invited lectures, he was honored as an Alfred P. Sloan Fellow and recipient of the St. Olaf Alumni Achievement Award. His selection for the American Chemical Society (ACS) Award for Distinguished Service in the Advancement of Inorganic Chemistry (2007) is the occasion for this present paper. He was chair of the Organometallic Subdivision of the ACS Division of Inorganic Chemistry (DIC) and chair of the DIC in 1985. His research has been directed primarily at the synthesis and reactivity of transition-metal complexes containing novel ligands such as CS, CP^-, carbene, carbyne, unsaturated fatty acids, thiophenes, and curved carbon surfaces. Most recently, his research has focused on applications of principles derived from organometallic chemistry to catalytic reactions of organic ligands adsorbed on metal surfaces, especially gold.

Mihaela Lazar was born in the city of Ocna Mures, Romania, in 1968. She attended Babes-Bolyai University in Cluj Napoca, where she received her License degree in chemistry. In 1994, she joined the National Institute for R&D on Isotopic and Molecular Technologies in Cluj Napoca, where she is currently a Scientific Researcher. Her research has focused primarily on heterogeneous catalytic reactions of hydrogen (hydrogenation, hydrogen spillover, and hydrogen production and storage) and catalytic H/D isotopic exchange for the preparation of deuterated compounds. During the year 2005−2006, she joined Angelici's group, where she investigated catalytic reactions of isocyanides on gold metal.

reaction intermediates are typically characterized by a variety of surface science techniques whose acronyms are used in the discussion and are defined in Table 1.

A. Decomposition of Isocyanides on Metal Surfaces. Although gold is the most common metal substrate for isocyanide adsorption studies, no investigations of the thermal decomposition of isocyanides on gold have been reported. On the Ag(311) surface of a single crystal of silver, CH_3NC is proposed to adsorb through its carbon in an upright orientation (η^1; Figure 1) at high CH_3NC coverage, but at low coverage, it is in a tilted or "lying-down" configuration; assignments to these modes of adsorption are based on HREELS and ESDIAD studies.[9] Molecular CH_3NC is the only gas-phase product detected when CH_3NC/Ag(311) is heated under ultrahigh-vacuum conditions. However, the low-coverage "lying-down" species desorbs at a somewhat higher temperature (185 K) than the η^1 species (160 K). No decomposition products (H_2, HCN, or N_2) were observed.

RAIRS investigations of CH_3NC on Pd(111) at low temperatures (80 K) suggest that it exists in two forms depending on the surface coverage: the μ_2-η^1:η^1(N) mode is proposed at low coverage, while the η^1 mode is favored at high coverage.[10] High-coverage CH_3NC/Pd(111) samples desorb CH_3NC at 125 K. As the temperature is increased further, a new adsorption mode, μ_2-η^1:η^1, appears and persists up to a temperature of above 400 K. Then, above 450 K, decomposition of CH_3NC to HCN and H_2 was detected by mass spectrometry. The TPD spectra exhibit a single peak at 495 K for this decomposition. These transformations of CH_3NC on Pd(111) are summarized in Scheme 1.

Transmission IR studies show that palladium supported on Al_2O_3 adsorbs CH_3NC in three forms (Figure 1) at 190 K: η^1 (2180 cm^{-1}), "bridge linear" (2050 cm^{-1}), and bent η^1 (1850 cm^{-1}).[11] As the sample is heated from 190 to 352 K, the 2180 and 2050 cm^{-1} peaks decrease in intensity while the 1850 cm^{-1} peak increases and a new peak at 1980 cm^{-1} develops. As the sample is heated to 500 K, the η^1-bonded CH_3NC desorbs from the surface. Also, the following products of CH_3NC decomposition are detected: H_2, HCN, and "mass 38". Neither CH_4 nor NC−CN was detected.

On Rh(111), CH_3NC adsorbs at 90 K in two forms, which were characterized by HREELS: η^1 (2170 cm^{-1}) and one in which CH_3NC bridges two or three metal atoms (1710 cm^{-1}).[12] As the temperature of CH_3NC/Rh(111) is increased, TPD and MS studies show that H_2 desorbs with peaks at 420 and 500 K. A desorption peak for HCN is observed at 500 K. The desorption of N_2 at 790 K indicates that nitrogen is among the most strongly bound species on the surface. However, the form of the nitrogen is not known because AES indicates that carbon is also present on the surface.

Methyl isocyanide is proposed to be bonded through both the C and N atoms (η^2) to the Ni(111) surface on the basis of HREEL studies.[13] With heating to 300 K, no desorption of CH_3NC occurs.[14] However, as the temperature is increased, H_2 is released at 390 K, HCN is detected at 490 K, and N_2 is observed at 770 K. These are the same gases, and they appear in the TPD in the same order, as observed in the TPD of CH_3NC on Rh(111) (see above). However, the authors propose different modes of CH_3NC adsorption and decomposition on the Ni(111) and Rh(111) surfaces.

Benzyl isocyanide ($PhCH_2NC$) is proposed to adsorb on Cu(111) at 160 K in a bent η^1 bonding mode at low coverage

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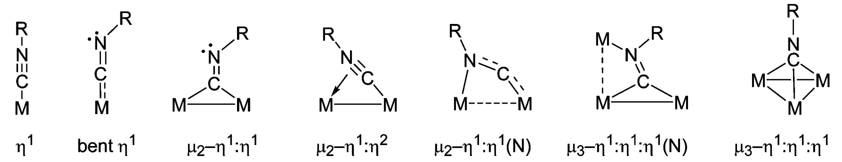
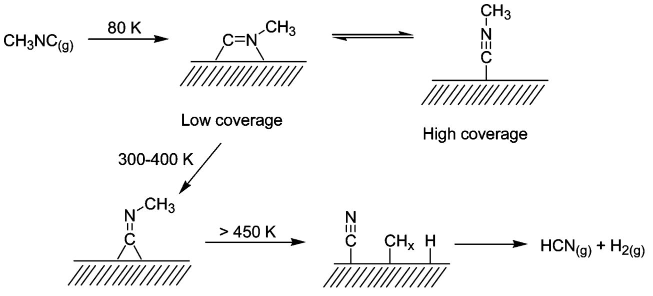


Figure 1. Known modes of isocyanide coordination to one, two, and three metals in compounds whose structures have been established by X-ray diffraction investigations.[8]

Table 1. Acronyms for Techniques Used in the Study of Isocyanide Adsorption and Reaction on Metal Surfaces

AES	auger electron spectroscopy
AFM	atomic force microscopy
ATR-IR	attenuated total reflection infrared spectroscopy
DRIFT	diffuse reflectance infrared Fourier transform spectroscopy
ESDIAD	electron-stimulated desorption ion angular distribution
FTIR	Fourier transform infrared spectroscopy
GATR	grazing-angle attenuated total reflectance infrared spectroscopy
HREELS	high-resolution electron energy loss spectroscopy
LEED	low-energy electron diffraction
OE	optical ellipsometry
PM-IRRAS	polarization-modulated infrared reflection absorption spectroscopy
RAIRS	reflection−absorption infrared spectroscopy
SERS	surface-enhanced Raman Scattering
SNIFTIRS	subtractively normalized interfacial Fourier transform infrared spectroscopy
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
TPD	temperature-programmed desorption
UPS	ultraviolet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy

Scheme 1. Methyl Isocyanide Adsorption and Decomposition on the Pd(111) Surface[10]



but a μ_2-η^1:η^1 bridging mode at high coverage, based on XPS and UPS studies.[15] In TPD investigations, the $PhCH_2NC$ desorbs intact at 247, 285, 340, and 455 K. Between 250 and 600 K, there is a broad and weak desorption of H_2, while toluene desorbs over essentially the same range (280−600 K). HCN is liberated in two peaks at higher temperatures (550 and 640 K). No cyanogen $(CN)_2$ is detected. The results suggest that $PhCH_2NC$ undergoes C−H bond cleavage below 280 K while C−CN cleavage occurs about 270 K, in order to account for the formation of toluene. Although H and CN form on the surface at temperatures as low as 270, HCN is not desorbed until 550 and 600 K. When annealed at 850 K, the surface retains amorphous carbon.

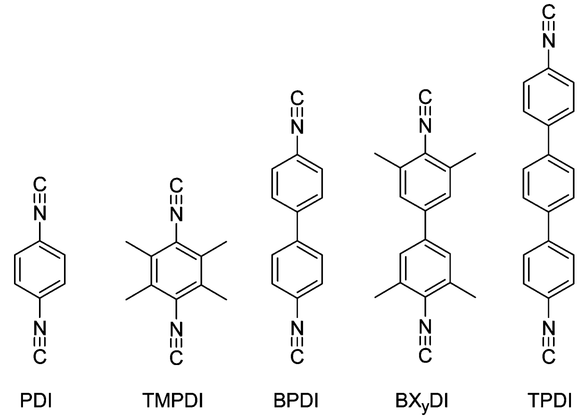


Figure 2. Structures of aryl diisocyanides.

B. Oxidation of Isocyanides on Metal Surfaces. Although studies specifically directed at oxidizing isocyanides (RN≡C) to isocyanates (RN=C=O) have not been reported, such oxidations have been observed as side reactions in studies of isocyanides adsorbed on metal surfaces. PM-IRRAS and GATR investigations[16] of the diisocyanides in Figure 2 adsorbed on gold films show a ν(NC) band at 2170−2190 cm^{-1}, which was assigned to an isocyanide group that is η^1-coordinated to the metal surface. On palladium films, the same diisocyanides show a band at 1980−2000 cm^{-1}, which was assigned to the adsorbed isocyanide group, but its coordination mode was not definitively assigned. A second band was observed in spectra of the diisocyanides adsorbed on both gold and palladium at 2114−2121 cm^{-1}. This band was shifted only 2−9 cm^{-1} as compared to the free diisocyanide ligand and was therefore assigned to the uncoordinated isocyanide group in the adsorbed diisocyanide ligand. A third band on both gold and palladium was broad (2270−2279 cm^{-1}), and its intensity varied depending on the treatment of the monolayer. With heated at 60 °C or "illumination" in air (but not in N_2), this peak intensity increased substantially. These results were interpreted to mean that the *uncoordinated* isocyanide group was oxidized by air to the isocyanate group (NCO).

When a self-assembled monolayer (SAM) of $C_6H_5C{\equiv}CC_6H_4C{\equiv}CC_6H_4NC$ (OPE-NC) on a gold film (~200 nm of gold deposited on a silicon substrate) was exposed to the laboratory environment,[17] oxidation of isocyanide to isocyanate was detected in the appearance of the isocyanate band at ~2270 cm^{-1}. Exposure to a pure O_2 or N_2 atmosphere did not produce the 2270 cm^{-1} band, but an ozone (O_3) atmosphere produced a considerable amount

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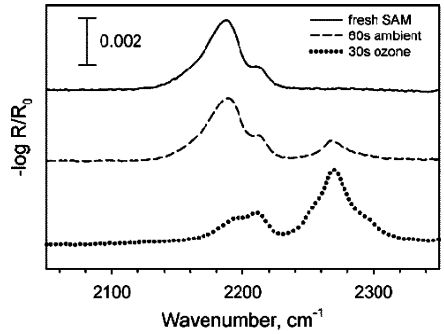

Figure 3. RAIRS spectra of $C_6H_5C{\equiv}CC_6H_4C{\equiv}CC_6H_4NC$ on a gold film after exposure to an ambient laboratory atmosphere (middle line) and to O_3 (bottom line).[17]

of isocyanate within 30 s (Figure 3). Thus, it appears that it is O_3 in laboratory air that causes the oxidation of OPE-NC to isocyanate, which is probably attached to the surface via only weak physisorption forces. An XPS study of the oxidized SAM established the presence of oxygen on the surface (an increase in the O 1s band after exposure to ambient conditions), which is consistent with isocyanate formation on the gold surface. Similar experiments performed with the same gold substrate but with $CH_3(CH_2)_{17}NC$ and other *alkyl isocyanide* SAMs showed *no* evidence for the formation of isocyanates. This difference in reactivities of the alkyl and aryl isocyanides could be explained by polarity or conjugation effects or by a higher packing density of the alkyl isocyanide monolayer. In view of the results reported in this study, it seems likely that oxidation of the diisocyanide SAMs discussed above[16] is also caused by O_3 in the laboratory atmosphere. Although there appear to be no reports of the *catalytic* oxidation of isocyanides on metal surfaces, the reaction of *t*-BuNC with O_2 to give *t*-BuNCO is catalyzed in solution by several transition-metal complexes [$RhCl(PPh_3)_3$, $Co(COD)_2$, and $Ni(COD)_2$, where COD = 1,5-cyclooctadiene].[18] Studies of the $Ni(COD)_2$-catalyzed reaction suggest that peroxo complex $(t\text{-BuNC})_2NiO_2$ is an intermediate that reacts with excess *t*-BuNC to give *t*-BuNCO and the $(t\text{-BuNC})_4Ni$ active catalyst.[18,19]

C. Polymerization of Isocyanides on Metal Surfaces. Alkyl diisocyanides, $CN(CH_2)_nNC$, adsorb on gold surfaces through either one or both isocyanide groups via the η^1 bonding mode.[8] From methanol solutions, low concentrations (1.0×10^{-3} M) of 1,6-diisocyanohexane (DICH) adsorb on *gold films* (~200 nm of gold on a glass substrate) through both isocyanide groups.[20] However, at concentrations higher than 5×10^{-3} M, only one isocyanide group binds to the surface. Under these conditions, the adsorbed molecules and isocyanide in solution react to give a polymeric isocyanide, also known as a poly(iminomethylene), $-N{=}C{<}$. The formation of a polyisocyanide on the gold surface was indicated by the appearance of a new peak in the RAIRS spectra in the 1580−1680 cm^{-1} region, which was assigned to the $\nu(-N{=}C{<})$ stretching mode.

The isocyanide concentration in solution is an important factor in determining the rate of the polymerization process. An appreciable amount of the DICH polymer forms on gold substrates after being placed in 0.1 M DICH solutions for as little as 4 h, but the amount of poly(DICH) formed on the gold substrate in 0.001 M DICH solutions is insignificant even after 5 days. At high concentrations of DICH, the majority of the DICH molecules on the metal surfaces are bound through only one isocyanide group, leaving uncoordinated isocyanide functionalities at the monolayer film−dosing solution interface. It was proposed that the proximity of these groups to each other and the high concentration of DICH in solution were important for the formation of poly(DICH). The highly concentrated, exposed isocyanide groups at the monolayer−solution interface presumably act as nucleation sites for the formation of the polymers.

A SAM consisting of $C_6H_5C{\equiv}CC_6H_4C{\equiv}CC_6H_4NC$ (OPE-NC) adsorbed on a palladium film (175 nm of palladium deposited on a silicon substrate)[17] exhibits a broad band in the reflectance IR spectrum at ~1970 cm^{-1}, which was inconclusively assigned to the bent η^1, μ_2-η^1:η^1, or μ_3-η^1:η^1:η^1 bonding mode. Upon exposure to the laboratory atmosphere, the 1970 cm^{-1} band intensity decreased while new peaks appeared in the 1570−1670 cm^{-1} region. These changes indicate the formation of a poly(iminomethylene) ($-N{=}C{<}$) resulting from the polymerization of the isocyanide groups. It was estimated that 89% of the isocyanide was converted to polymer after 72 h of exposure to laboratory conditions. The polymerization of OPE-NC on palladium differs from the oxidation of OPE-NC on gold and diisocyanides (Figure 2) on palladium and gold (see section IIB), which give isocyanates when exposed to the laboratory atmosphere.

On copper metal thin films that had been exposed to air for ~5 min, both PDI[21] (Figure 2) and $CN(CH_2)_6NC$ (DICH)[22] undergo polymerization at room temperature. On the other hand, 2,5-dimethylphenyl isocyanide on Cu(111) is proposed to be adsorbed in two forms (η^1- and bridge-bonded), but neither polymerizes nor decomposes under UHV conditions up to 800 K; it simply desorbs from the surface.[23] Thus, it appears that polymerization of isocyanides on metal surfaces is favored by exposure to air.

Although the mechanism for the polymerization of isocyanides on palladium metal is not known, it is evident that air promotes the reaction. A variety of transition-metal complexes also catalyze the polymerization of isocyanides.[24,25] Palladium(II) complexes with Pd−C bonds are highly active[26] and are proposed to function by allowing sequential isocyanide insertions into Pd−C bonds, a well-

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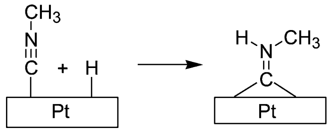
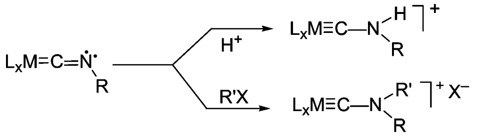
Scheme 2. Reaction of Methyl Isocyanide with Hydrogen on Pt(111)[30,31]



known reaction in organometallic systems.[27] On the other hand, the catalytic activity of nickel complexes, like palladium films (see above), depends on the presence of O_2, which is involved in the proposed catalytic cycle.[19]

D. Reactions of Isocyanides on a Gold Electrode. A monolayer of 1,8-diisocyanooctane, $CN(CH_2)_8NC$, η^1-bonded through one isocyanide group, on a gold electrode[28] in an aqueous K_2SO_4 (0.1 M) solution was stable between the potentials +0.7 and −1.0 V. Within this range, the ν(NC) value in SNIFTIR spectra of the adsorbed isocyanide decreases as the potential becomes more negative. Outside of these potentials, the ν(NC) band disappears, indicating that the isocyanide layer is no longer present on the gold surface. No new SNIFTIR peaks for products were detected. The most likely products are the corresponding formamide (RNHCHO) or carbon dioxide at positive potentials, and it is suggested that amines (RCH_2NH_2) are the most likely products at negative potentials. However, neither of these products was detected because peaks corresponding to the ν(C=O) and ν(N−H) vibrations were obscured by absorptions of the water solvent.

E. Reactions of Electrophiles and Nucleophiles with Isocyanides Adsorbed on Metal Surfaces. It is well-known that isocyanide ligands in transition-metal complexes are activated to react with electrophiles or nucleophiles depending on the electron-richness of the metal center. When the metal is in a low oxidation state and its associated ligands are electron-donating, the isocyanide ligand can be protonated or alkylated as shown in eqs 1 and 2.[29] Examples of isocyanide ligands that are known to react in this way are



(1)

(2)

found in the following complexes: *trans*-[ReCl(C≡NR)(dppe)$_2$], where dppe = $Ph_2PCH_2CH_2PPh_2$ and *trans*-[M(C≡NR)$_2$(dppe)$_2$], where M = Mo or W.

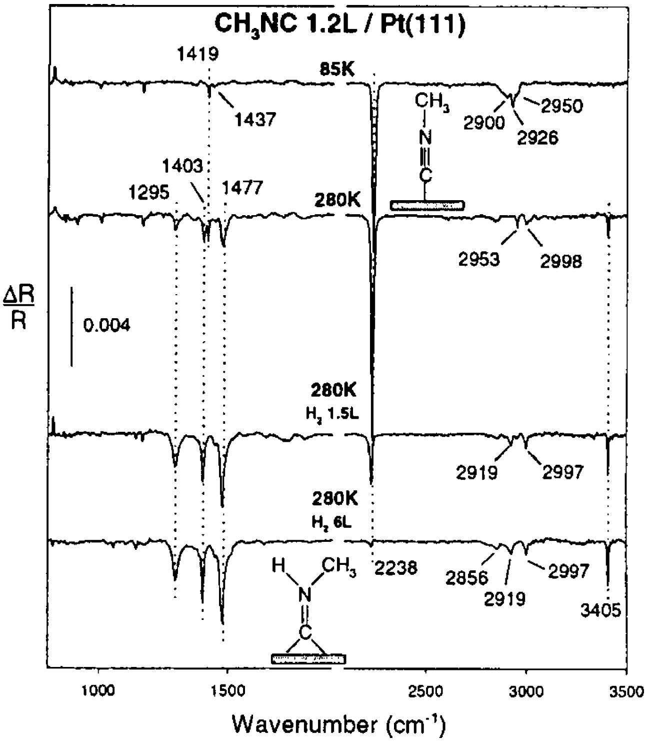


Figure 4. RAIRS spectra following exposure of Pt(111) at 85 K to 1.2 L (1 L = 1 × 10^{-6} Torr s) of methyl isocyanide with subsequent heating to 280 K (top two spectra) and exposure to H_2 of the sample at 280 K followed by cooling back to 85 K, where the spectra were obtained (bottom two spectra).[30,31]

In a reaction that resembles somewhat the electrophilic addition of H^+ to an electron-rich isocyanide ligand (eq 1), CH_3NC adsorbed on a Pt(111) crystal[30−33] reacts at 280 K with hydrogen on the surface to form the methylaminocarbyne $CNHCH_3$ group (Scheme 2), which is stable on the surface up to 370 K.

This is the only example of a reaction of an isocyanide on a metal surface in which a reactant adds at the isocyanide N atom. Identification of the methylaminocarbyne group on the Pt(111) surface was based on the following RAIRS studies.[30,31] The observation of an intense peak at 2238 cm^{-1} in low-coverage experiments of CH_3NC on Pt(111) at 85 K shows that under these conditions only the on-top (η^1) form of the adsorbed isocyanide is present (Figure 4). At higher coverage, an additional ν(NC) peak is observed at 1748 cm^{-1}, which indicates a reduction in the CN bond order and was assigned to the bent-bridged (μ_2-η^1:η^1) form. After annealing at 280 K and exposure of a low-isocyanide coverage surface to H_2, a decrease in the intensity of the ν(NC) band of the on-top (η^1) adsorbed molecule was observed. The ν(NC) peak corresponding to the bent-bridge (μ_2-η^1:η^1) species undergoes only a small decrease in the intensity but shifts to lower wavenumbers (from 1748 to 1716 cm^{-1}). The reaction of η^1 CH_3NC with H_2 also produces an entirely new species on the surface, $CNHCH_3$, with ν(NC) at 1477 cm^{-1} and ν(NH) at 3405 cm^{-1}. The low ν(NC) value suggests that the C≡N bond is weakened to give a CN bond order between 1 and 2, which is characteristic of an iminium species. The isocyanide reaction with H_2 does not take place at isocyanide exposures higher than 2 L regardless of the H_2 exposure. This result can be explained by assuming that the reaction takes place between adsorbed isocyanide and adsorbed H_2,

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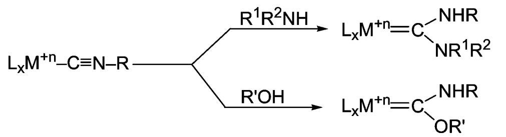
and at higher coverages where the bent-bridge species (μ_2-η^1:η^1) is formed, the H_2 is displaced from the surface. It is also consistent with the suggestion that empty sites around isocyanide are required for the reaction to occur and that such sites would be less available at high isocyanide coverages.

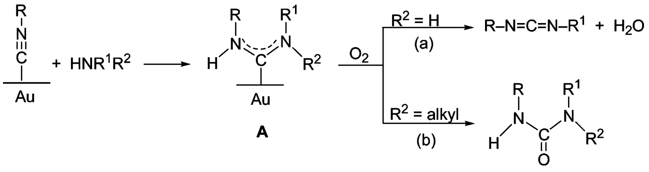
In contrast to reactions (eqs 1 and 2) of electrophiles with isocyanides in electron-rich metal complexes, nucleophiles attack the carbon of isocyanide ligands in electron-poor complexes, often those in which the metal is in a positive oxidation state.[34−36] Amines and alcohols/alkoxides are among the most studied nucleophiles in reactions with isocyanide complexes (eqs 3 and 4). In order for the isocyanide to be activated to attack by these nucleophiles, the metal must be sufficiently positive that it increases the ν(N≡C) wavenumber of the isocyanide by at least 40 cm^{-1} as compared with the free isocyanide, which means that there is relatively little π-back-bonding from the metal to the isocyanide ligand.[35] Such increases in ν(N≡C) are known for isocyanides in complexes of palladium(II), platinum(II), and silver(I) and many other metals. In principle, isocyanides that experience a similar increase in ν(N≡C) when adsorbed on a metal surface should also be susceptible to nucleophilic attack.



$$L_xM^{+n}{-}C{\equiv}N{-}R \xrightarrow{R^1R^2NH} L_xM^{+n}{=}C(NHR)(NR^1R^2) \qquad (3)$$

$$L_xM^{+n}{-}C{\equiv}N{-}R \xrightarrow{R'OH} L_xM^{+n}{=}C(NHR)(OR') \qquad (4)$$

Scheme 3. Mechanism for the Gold-Catalyzed Reaction of Isocyanides (C≡NR) with Primary and Secondary Amines and O_2[39,41]



In fact, isocyanides adsorbed on many metals have ν(N≡C) values that are more than 40 cm^{-1} higher than those of the free isocyanide.[8] We chose to study reactions of isocyanides adsorbed on gold metal because the metal is not oxidized in air, which means that the surface Au atoms are in the zero oxidation state only.[37] Isocyanides easily adsorb on different forms of gold (film, powder, and nanoparticles) with ν(N≡C) values 50−80 cm^{-1} higher than those of the free isocyanides.[8,38] To determine whether or not isocyanides adsorbed on gold react with nucleophiles as they do in metal complexes, a gold film (∼300 nm of Au on glass) with adsorbed n-BuNC was placed in a hexane solution of n-BuNH$_2$.[39] The ν(N≡C) intensity of the adsorbed isocyanide in the RAIRS spectrum decreased rapidly and completely disappeared after 20 s, indicating that the adsorbed isocyanide is no longer present on the gold surface. The process is slower if the amine is less basic or more sterically bulky than n-BuNH$_2$. There was no evidence in the infrared spectrum of the resulting gold film for diaminocarbene groups =C(NH-n-Bu)(NHR) (eq 3), which are expected to give a ν(NC=N) absorption near 1480−1600 cm^{-1}.[40] In fact, no new peaks appeared in the RAIRS spectrum, indicating that the product of the reaction of the adsorbed isocyanide with the amine must have desorbed from the surface. In order to identify the product, n-BuNC was adsorbed on 1.0 g of gold powder (which has a much larger surface area and therefore more adsorbed n-BuNC than on the gold film). The reaction of this powder with n-BuNH$_2$ gave a sufficient amount of the product that it could be identified by gas chromatography (GC)−mass spectrometry (MS) as the carbodiimide n-BuN=C=N-n-Bu. Some of n-BuNC desorbed from the gold powder without reacting, but it too was converted to the carbodiimide product when the reaction mixture was allowed to stir for a longer time or was heated to 60 °C. This meant that the reaction of n-BuNC with n-BuNH$_2$ to form n-BuN=C=N-n-Bu was *catalyzed* by gold metal. The two H atoms in the n-BuNH$_2$ reactant apparently combined with O_2 to give H_2O, as the reactions were conducted in air or in an O_2 atmosphere. When the reaction was performed under an argon atmosphere, no carbodiimide product was formed. Therefore, the complete gold-catalyzed reaction is represented by eq 5.

$$n\text{-BuNC} + n\text{-BuNH}_2 + \frac{1}{2}O_2 \xrightarrow{Au} n\text{-BuN}{=}C{=}N\text{-}n\text{-Bu} + H_2O \qquad (5)$$

At 60 °C in a hexane solvent under an air atmosphere and stirring with 1.0 g of gold powder, n-BuNC (1.7×10^{-2} mmol) and n-BuNH$_2$ (17×10^{-2} mmol) reacted for 90 h to give a 73% yield of n-BuN=C=N-n-Bu. Mixed carbodiimides RN=C=NR′ were obtained when relatively low concentrations of a variety of isocyanides (C≡NR) were reacted with a variety of primary amines (R′NH$_2$).

Kinetic studies[39] of the gold powder-catalyzed reaction (eq 5) of n-BuNC and n-BuNH$_2$ at 60 °C in hexane show that the rate is first-order in the concentration of n-BuNH$_2$ and is independent of the O_2 concentration/pressure. These results suggest the mechanism presented in Scheme 3, reaction a. The isocyanide first adsorbs on the gold surface; as in metal complexes (eq 3), this makes the isocyanide susceptible to nucleophilic attack by the amine. This is the rate-determining step in the reaction. The resulting isocyanide−amine adduct then rearranges to a diaminocarbene group **A** (as occurs in metal complexes), which reacts with O_2 to give the carbodiimide and H_2O. Because the overall reaction rate does not depend on the O_2 concentration, the

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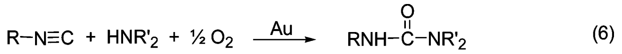
Table 2. Gold Metal-Catalyzed Reactions[a] of *n*-BuNC with Secondary Amines and O_2[41]

NHR'_2	HN-*n*-Pr_2	HN-*n*-Pr_2[b]	piperidine	morpholine	HN-*n*-Pr_2[c]
urea yield (%)	44	38	51	22	19

[a] Reaction conditions: *n*-butyl isocyanide (2.0 mM), 80 mM amine, gold powder (1.0 g), O_2 (~1.0 L at ~1 atm), at 60 °C in 5 mL MeCN for 24 h. [b] Air instead of O_2. [c] 1,1,3,3-Tetramethyl-*n*-butyl isocyanide (2.0 mM).

initial amine attack must be slow as compared with the reaction of the diaminocarbene **A** with O_2.

For reactions of isocyanides with secondary amines (HNR'_2), it is still possible for the amine to attack an adsorbed isocyanide, but the resulting diaminocarbene intermediate **A** (Scheme 3) cannot react with O_2 to give a carbodiimide product. Therefore, the reactions of isocyanides with secondary amines in the presence of gold powder must take a different pathway and, in fact, give substituted ureas (eq 6).[41] The reactions were performed under the same conditions (60 °C, hexane or MeCN solvent, 1.0 g of gold powder) as those used with the gold-catalyzed reactions of isocyanides with *primary* amines (eq 5). The reaction rate was slightly less than first-order in the amine and substantially less than first-order in the O_2 concentration. The rate of the catalyzed reaction depends also on the steric and electronic properties of the amines. The urea product yields obtained after 24 h of reaction of *n*-BuNC with different secondary amines under a standard set of conditions (60 °C, MeCN solvent, 1 atm O_2, 1.0 g gold powder) are presented in Table 2. Both the steric and electronic properties of the amines have predictable effects on the reaction rates. The lower rate with a more bulky isocyanide (last entry in Table 2) could reflect a lower isocyanide coverage on the gold surface or a reduced rate of amine attack on the adsorbed bulky isocyanide.



$$R{-}N{\equiv}C + HNR'_2 + \tfrac{1}{2}O_2 \xrightarrow{Au} RNH{-}\overset{O}{\overset{\|}{C}}{-}NR'_2 \qquad (6)$$

The mechanism proposed for the reaction of isocyanides with secondary amines (Scheme 3, reaction b) is related to that proposed for the analogous reaction with primary amines (Scheme 3, reaction a). The first step in both of these mechanisms is amine attack on an adsorbed isocyanide to give an isocyanide−amine adduct, which rearranges to the diaminocarbene intermediate **A**. The rate of this attack plays a major role in influencing the overall rate of catalysis. After the initial attack, the resulting diaminocarbene **A** reacts with O_2 by two different pathways depending on whether the amine is a secondary or primary amine (Scheme 3, reactions a and b). The diaminocarbene **A** formed from the secondary amine reacts with O_2 to cleave the Au−C bond with formation of urea. The gold metal surface must play a role in cleaving the metal−diaminocarbene bond, but O_2 is known not to adsorb on bulk gold in detectable amounts at room temperature.[37] So, it is presumably the strongly electron-donating ability of the diaminocarbene group **A** that makes the gold sufficiently electron-rich to react with O_2.

In contrast to the reactions of diaminocarbene intermediates **A** derived from secondary amines that lead to urea products, intermediates **A** derived from primary amines react with O_2 by transferring two of its H atoms to O_2 to give H_2O and carbodiimide products. It is not clear why intermediate **A** formed from primary amines prefers to give a carbodiimide rather than a urea product.

While we have cited precedents (eq 3) in the organometallic literature for the attack of amines on isocyanides adsorbed on metal surfaces (Scheme 3), there are no precedents for reactions of diaminocarbene ligands in transition-metal complexes with O_2 that model the proposed reactions of intermediate **A** (Scheme 3) with O_2. In fact, metal complexes that act as oxidation catalysts often contain diaminocarbene ligands because they do not react with oxidizing agents.[42]

III. Other Applications of Isocyanides Adsorbed on Metal Surfaces

A. Nanoparticle Stabilization. Because they form strong bonds with metal surfaces and are conveniently studied by IR spectroscopy, isocyanides are good ligands for the stabilization and functionalization of colloidal transition metals. They have therefore been used to prepare stable nanoparticles that can be handled like simple chemical compounds (dissolved in solvents and precipitated as solids). Such nanoparticles of platinum metal were prepared by first reducing H_2PtCl_6 with $NaBH_4$ in the presence of $[(n\text{-octyl})_4N]Br$ to give lightly stabilized platinum nanoparticles, which were reacted with dodecyl isocyanide, $CH_3(CH_2)_{11}NC$.[43] The resulting isocyanide-stabilized platinum nanoparticles were isolated by precipitation as a black solid from an ethanol solution upon cooling to −20 °C. The black solid is soluble in nonpolar solvents such as toluene. TEM studies show the solid to be a homogeneous dispersion of particles with 1−3 nm diameters and a well-defined crystalline structure with a face-centered-cubic structure in the metallic core of 2.0 ± 0.4 nm. FTIR spectra of the dodecyl isocyanide-coated platinum particles show a ν(NC) value for the adsorbed isocyanide at 2218 cm^{-1} (approximately 70 cm^{-1} higher than that for the free isocyanide). This ν(NC) value lies between those found for isocyanides in platinum(II) and platinum(0) complexes.[43]

Isocyanide-stabilized nanoparticles of palladium were prepared by a method similar to that for platinum.[44] First, $PdCl_2(NCCH_3)_2$ was reduced with $NaBEt_3H$ in a tetrahydrofuran solvent in the presence of $[(n\text{-octyl})_4N]Br$. After the addition of *n*-octyl isocyanide, a black powder precipitated upon addition of methanol. TEM studies of the isocyanide-stabilized palladium show the average diameter of the particles to be 2.1 ± 0.7 nm. FT-IR spectra of the nanoparticles showed three IR peaks that were assigned to η^1-bonded (2156 cm^{-1}), doubly bridged (~1964 cm^{-1}), and

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triply bridged (~1611 cm^{-1}) isocyanides. In the XPS, the binding energies of the palladium electrons are similar to those reported for metallic palladium. The Pd−CNR interface protects the surface against oxidation, keeping the surface in a zero oxidation state. An especially interesting property of these isocyanide-stabilized palladium nanoparticles is their ability to absorb H_2. At 100 °C and hydrogen pressures between 0 and 10 MPa, the nanoparticles absorb H_2 completely within a few seconds. The H_2 storage capacity is about the same as that of bulk palladium, ~0.6 wt %, but the H_2 absorption rate is much faster than that of bulk palladium. The isocyanide-stabilized palladium nanoparticles also exhibit good recyclability through four absorption−desorption cycles.

Nanoparticles of gold and silver were stabilized by 4-biphenyl isocyanide (BPNC)[45] and benzyl isocyanide (BZI).[46] The gold nanoparticles were prepared by reacting a citrate-stabilized nanocolloid of gold with the isocyanide ligands. The silver nanoparticles were generated from $AgNO_3$ by reaction with $NaBH_4$ followed by the addition of isocyanide. The average diameters of the BPNC/Au and BPNC/Ag nanoparticles were 17 and 10 nm, respectively. Their SERS spectra show ν(NC) peaks at 2187 (for Au) and 2177 cm^{-1} (for Ag), which are higher than that (2125 cm^{-1}) of the free BPNC ligand, which suggests that the isocyanide is η^1-bonded on both metals. SERS spectra of the BZI-stabilized nanoparticles also exhibit ν(NC) bands, 2215 (for Au) and 2206 cm^{-1} (for Ag), that are higher than those for the free BZI (2151 cm^{-1}).

The diisocyanide 4,4′-biphenyl diisocyanide (BPDI; Figure 2) was used to stabilize gold nanoparticles with a diameter of approximately 17 nm.[47] During their preparation, when the concentration (5×10^{-3} M) of the BPDI was much higher than that required for monolayer coverage, two ν(NC) peaks were observed in the Raman spectrum (Figure 5). The highest wavenumber peak at 2185 cm^{-1} was assigned to the η^1-coordinated NC group, while a 2123 cm^{-1} band was assigned to the uncoordinated NC group because its ν(NC) value is very similar to that of free BPDI (2124 cm^{-1}). However, when the BPDI concentration was reduced to 5×10^{-6} M, the 2123 cm^{-1} peak completely disappeared while the 2185 cm^{-1} band remained. This suggested that, at low concentrations of BPDI, both of the NC groups in BPDI are coordinated to gold nanoparticles, by linking two particles.

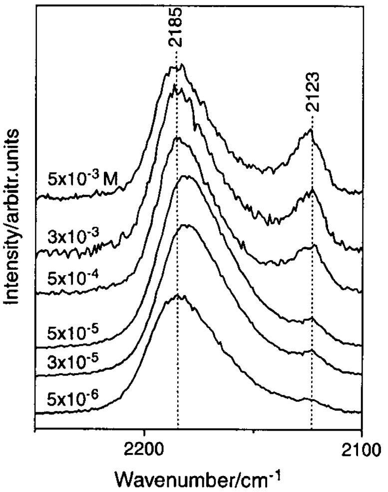

Figure 5. ν(NC) region between 2250 and 2100 cm^{-1} in SERS spectra of BPDI/Au nanoparticles prepared with concentrations of BPDI from 5×10^{-6} to 5×10^{-3} M.[47]

Using different concentrations of citrate in the reduction of $HAuCl_4$, nanoparticles of different mean diameters (14, 23, 40, 57, and 97 nm) were prepared with the adsorbed diisocyanide 1,4-phenylene diisocyanide (PDI; Figure 2).[48] In studies of these gold nanoparticles using a range of PDI concentrations and nanoparticle sizes, it was possible to determine from the relative intensities of the ν(NC) bands for the coordinated (2180 cm^{-1}) and uncoordinated NC groups (2129 cm^{-1}), whether the PDI was coordinated through only one NC group or through two NC groups to two different nanoparticles. For the smaller nanoparticles (14, 23, and 40 nm), both isocyanide groups coordinate to separate nanoparticles when the PDI concentration is low (~10^{-7} M), but as the PDI concentration is increased to 10^{-4} M, only one of the isocyanide groups is bound to the gold nanoparticles. These trends in concentration are similar to those observed in studies of BPDI discussed in the previous paragraph.

On the other hand, the effect of the PDI concentration on the larger nanoparticles (57 and 97 nm) is somewhat different. At low concentrations (10^{-7} M) of PDI, both isocyanide groups are coordinated. As the concentration is increased to 10^{-6} and 10^{-5} M, the appearance of the 2129 cm^{-1} band suggests that PDI coordinates through only one NC group. However, as the PDI concentration is increased even further to 10^{-4} M, the 2129 cm^{-1} peak again disappears, which suggests that both NC groups again coordinate to gold nanoparticles. The authors discuss possible reasons for this unexpected diisocyanide bridging of large nanoparticles at high concentrations of PDI.[48]

B. Selective Adsorption on Different Regions of a Metal Surface. In order to create surfaces with a particular spacial distribution (or pattern) of adsorbed ligands, various research groups have taken advantage of the fact that gold metal has a higher affinity for thiols than for isocyanides, while platinum has a higher affinity for isocyanides. In one study,[49] rod-shaped colloidal particles of about 200 nm in length were prepared with end sections that were metallic gold, while the middle section was platinum. When the Au−Pt−Au rods were allowed to react with a hexane solution of *n*-BuNC, *n*-BuNC adsorbed on both the gold and platinum sections of the rods (Figure 6). When these *n*-BuNC-covered rods were reacted with 2-mercaptoethylamine (MEA), the isocyanides were largely displaced by the thiol from the gold sections but not from the platinum. To

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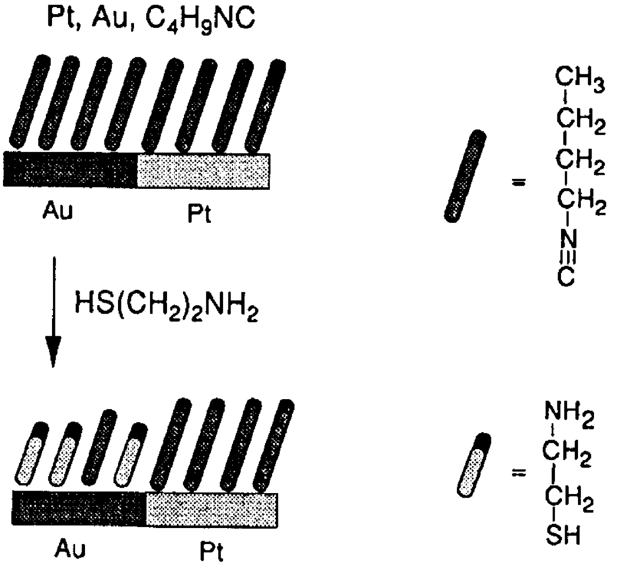

Figure 6. Controlled spacial distribution of isocyanides and thiols on platinum and gold.[49]

demonstrate that only the gold sections contained MEA, the rods were treated with Rhodamine B isothiocyanate, which reacted with the terminal amino group of the adsorbed MEA. Fluorescence microscopy of the nanorods showed fluorescence from only the end gold sections, which confirmed the selective adsorption of MEA on the gold sections. The authors suggest that such selective functionizations of nanoparticles may be used to prepare specific 2-D and 3-D assemblies of metallic particles.

Such assemblies were prepared from metallic plates (10−30 μm) in which the top and bottom faces consisted of platinum metal, while the sides were gold.[50] In a treatment very similar to that used with the Au−Pt−Au nanoparticle rods (Figure 6),[49] the plates were treated with *n*-BuNC, which covered both the gold and platinum surfaces. Then, treatment with 6-mercaptohexanoic acid displaced the isocyanide from the gold sides but not from the platinum faces. The *n*-BuNC groups on the platinum faces made these surfaces hydrophobic, while the gold surfaces on the sides were hydrophilic due to the carboxylic acid groups. Hydrophilic interactions between the $-CO_2H$ groups gave a 2-D assembly of the plates, while hydrophobic interactions between the *n*-Bu groups on the faces caused the plates to stack in multilayers.

C. Isocyanide-Derivatized Nanoparticles as Sensors. The intensities of ν(NC) bands in SERS spectra of isocyanide ligands adsorbed on silver (or gold) are dramatically enhanced by a factor of approximately 10^6 as compared with those in normal Raman spectra. The ability to detect by SERS spectroscopy small amounts of an isocyanide adsorbed on silver nanoparticles was used[51] to detect avidin, which is a tetrameric protein that has symmetric biotin-binding pockets positioned in pairs on opposite faces of the protein. These pockets have a very strong binding affinity ($K \sim 10^{13}$) for biotin. Taking advantage of these properties, an avidin sensor was constructed that consists of a silver plate that forms a SAM (by adsorption through the carboxylic acid group) with *N*-(+)-biotinyl-6-aminocaproic acid (BACA). Separately, silver nanoparticles (~15 nm in diameter) were derivatized with a mixture of BACA and cyclohexyl isocyanide (CHIC). In the absence of avidin, the BACA/CHIC/Ag nanoparticles do not bind to the silver plates. However, if avidin is present, it binds (Figure 7) to the biotinyl groups anchored on both the silver plate and the BACA/CHIC/Ag nanoparticles. SERS spectra of the silver plates then show a strong ν(NC) band for the isocyanide at 2209 cm^{-1}. Therefore, the isocyanide ligand on the silver nanoparticle acts as a very sensitive marker or reporter for avidin. The narrow and intense ν(NC) band in a region of the vibrational spectrum that does not overlap with vibrations of biological molecules makes the isocyanide-derivatized silver nanoparticles sensitive detectors of avidin.

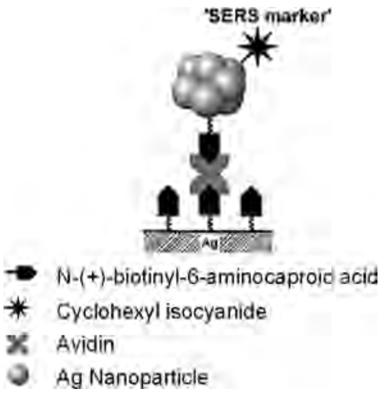

Figure 7. Isocyanide-derivatized silver nanoparticles as detectors of avidin.[51]

D. Metal Complexes Tethered to Metal Surfaces through Isocyanide Ligands. When PDI (Figure 2) adsorbs to a metal through one of its NC groups,[8] the uncoordinated NC group is still capable of binding to other species such as a metal complex. In one example, a gold film covered with PDI was reacted[52] with $Re(CO)_3(bipy)(OTf)$, where bipy = 2,2′-bipyridyl and $OTf^- = CF_3SO_3^-$. RAIRS spectra of the resulting film showed that the ν(NC) band of the uncoordinated NC group at 2122 cm^{-1} had disappeared, which implied that the $Re(CO)_3(bipy)^+$ group had coordinated to it with displacement of the OTf^- ligand, but the tethered complex was not characterized further. A more detailed study showed that a trinuclear nickel complex $Ni_3(dppm)_3(I)^+$, where dppm = $Ph_2PCH_2PPh_2$, binds to the isocyano group of the 4-isocyanothiophenol, HSC_6H_4NC, ligand;[52,53] in this case, the attachment to the gold is through the sulfur.

A more thorough characterization of a PDI-tethered metal complex was reported for a ruthenium phthalocyanine (Pc) complex.[54] During the reaction of a PDI-covered gold film with $Ru(Pc)(NCPh)_2$, the ν(NC) bands of the *adsorbed* (2176 cm^{-1}) and *uncoordinated* NC groups (2122 cm^{-1}) of PDI

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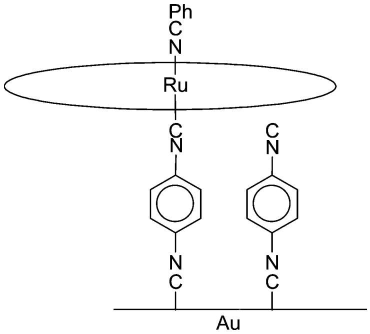

Figure 8. Ruthenium phthalocyanine complex anchored through the diisocyanide PDI on gold metal.[54]

diminished substantially in intensity while new bands at 2155 and ~2100 cm^{-1}, assigned to the gold-adsorbed NC and ruthenium-coordinated NC groups, respectively, appeared. Ellipsometry and XPS investigations of the tethered system were consistent with a representation (Figure 8) in which the Ru(Pc)(NCPh) unit is bound to the isocyano group while one benzonitrile ligand remains coordinated to the ruthenium. From XPS studies, it was estimated that the ratio of PDI [not bound to Ru(Pc)(NCPh)] to Ru(Pc)(NCPh) was 12, which is consistent with a close packing arrangement of the large Ru(Pc) units standing over a close-packed SAM of PDI. It was suggested that the labile PhCN ligands on the tethered complex could be substituted to give multilayer assemblies.

E. Nanoparticle-Decorated Metal Electrodes Using Isocyanides. With the goal of creating a more catalytically active electrode surface,[55] nanoparticles of platinum were attached to gold and platinum electrodes by dropping a platinum sol onto the metal surfaces and allowing the substrate to dry. These nanoaggregate electrodes were then immersed in an ethanol solution of 2,6-dimethylphenyl isocyanide. Their SERS spectra showed ν(NC) bands that were assigned to isocyanide groups adsorbed on the gold substrate (2166 cm^{-1}) and to isocyanide groups adsorbed on the platinum nanoaggregates [2166 (η^1), 2124 (μ_2-η^1:η^1), and 1997 cm^{-1} (μ_3-η^1:η^1:η^1)]. All of these ν(NC) values increased by 41−54 cm^{-1}/V as the potential on the nanoaggregate platinum electrodes was increased from −0.6 to +0.2 V. To date, there appear to be no reports of electrocatalysis with these nanoaggregate electrodes.

In another approach to anchoring nanoparticles on a gold metal electrode,[28] a gold disk was immersed in a toluene solution of 1,8-diisocyanooctane [$CN(CH_2)_8NC$, DICO]. After rinsing with toluene, reflectance infrared studies using the SNIFTIRS technique showed the presence of both adsorbed isocyanide (2213 cm^{-1}) and free isocyanide (2147 cm^{-1}) groups. When this DICO-derivatized gold electrode was immersed in a toluene solution of platinum nanoparticles, ν(NC) bands for the adsorbed and free isocyanide groups remained in the spectrum, as expected for the nanostructured film shown in Figure 9. A ν(NC) band for the isocyanide bound to the platinum nanoparticles was expected at 2218 cm^{-1}, but it would overlap with the 2213 cm^{-1} band of the isocyanide adsorbed on the gold. To show unequivocally the presence of the tethered platinum nanoparticles, the electrode was reacted with CO. The SNIFTIRS spectrum then showed a ν(CO) band at 2072 cm^{-1}, which is characteristic of CO adsorbed on platinum nanoparticles.

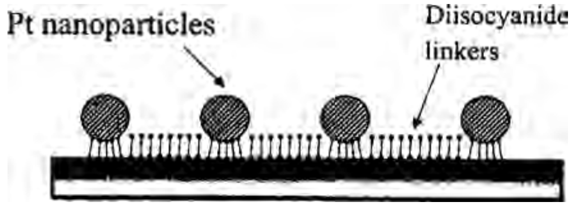

Figure 9. Representation of a nanostructured film consisting of platinum nanoparticles anchored through a diisocyanide (DICO) to a gold surface.[28]

F. Isocyanide−Metal Junctions in Molecular Electronic Devices. There is considerable interest in creating molecular-scale electronic components such as wires, diodes, switches, and memories.[56] These components often require the attachment of a conducting organic molecule to a metal surface. Such metal−organic junctions must have low impedance and high stability. A mismatch between the Fermi level of the metal and the highest occupied molecular orbital or lowest unoccupied molecular orbital of the organic molecule will lead to a high impedance. Because so little is known about the conducting properties of these junctions, initial studies have involved relatively well-characterized monolayers of organic thiols or isocyanides on gold metal.[57] Investigations of the conducting properties of these systems typically use conducting-probe STM, but the measurements are often difficult to reproduce and depend on details of the experimental procedures.[58] Many of the initial studies sought to determine whether thiols or isocyanides provide the most conducting and stable junctions. Results of recent studies indicate that $PhC{\equiv}CC_6H_4NC$ and PhC_6H_4NC adsorbed on gold electrodes are approximately an order of magnitude more conducting than their thiol analogues, $PhC{\equiv}CC_6H_4S-$ and PhC_6H_4S-.[59] Even the saturated *n*-decyl isocyanide $CH_3(CH_2)_9NC$ is more conducting than *n*-decylthiol $CH_3(CH_2)_9SH$, although both had much lower conductances than the unsaturated molecules. In contrast to the higher conductances of isocyanides as compared with thiols in the above studies, Ph−NC and 2-naphthyl−NC were reported to be *less* conducting than their thiol analogues, Ph−SH and 2-naphthyl−SH, on gold electrodes.[60] Complicating the picture even further is the finding that PDI (Figure 2) and its thiol analogue, 1,4-HSC_6H_4SH, have comparable conductances on gold electrodes.[61] The conductances of PDI and 1,4-HSC_6H_4SH are also similar on platinum electrodes,

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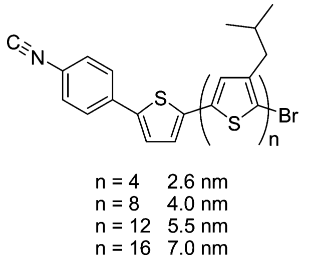

Figure 10. Structures of oligothiophene isocyanides of different chain lengths.[63]

but their conductances on platinum were an order of magnitude higher than those on gold. These differences in conductance on platinum and gold were rationalized by differences in the density of states at the Fermi level for the two metals.[62] However, it might be noted that the modes of PDI adsorption on gold and platinum are quite different,[8] which might contribute to the different conductances of their isocyanide−metal junctions. On gold, PDI adsorbs only by the η^1 mode, but on platinum, three modes of adsorption are present: η^1, 2-fold, and 3-fold bridging modes.

In another investigation, $C_6H_5C{\equiv}CC_6H_4C{\equiv}CC_6H_4NC$ (OPE-NC) was adsorbed on Au(111) and Pd(111) surfaces.[17] As noted in section IIB, OPE-NC on Au(111) is oxidized to the isocyanate in a laboratory environment (due to the presence of O_3), which disrupts contact with the gold surface. On the other hand, the OPE-NC interface was somewhat more stable on palladium, although it does undergo degradation by polymerization but somewhat more slowly (see section IIC). Conducting-probe STM measurements on the OPE-NC/Pd system showed that the conductance decreased by 2 orders of magnitude over an 18 h time period. It was estimated that $\sim$50% of the OPE-NC SAM had polymerized during this time, which reasonably accounts for the decrease in conductance. It is possible that isocyanide degradation occurs during conductance measurements on other isocyanide SAMs as well.

For the purpose of creating a system with a molecular *semiconductor* attached to a metal, a series of oligothiophene isocyanides (Figure 10) were adsorbed on platinum electrodes.[63] Characterization of the isocyanide SAMs by IR and XPS showed that the oligothiophenes were linked to the platinum surface through the isocyanide group, and it was estimated that the oligothiophene chain was tilted $\sim$41° from the surface normal. In an extension of these studies, molecular wires consisting of oligothiophenylethyne diisocyanides (Figure 11) were adsorbed through the isocyanide group to platinum metal electrodes.[64] Electrochemical oxidation of these molecules induces a geometric change in the organic chain, which gives them on/off switching properties that are potentially useful in molecular field effect transistors.

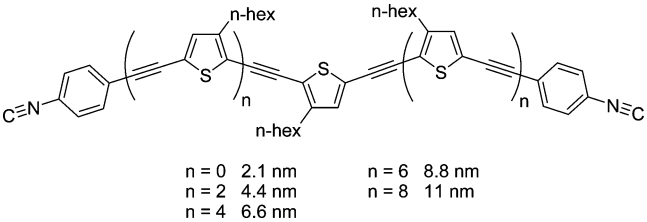

Figure 11. Oligothiophenylethyne diisocyanides of different chain lengths.[64]

IV. Conclusions

Although isocyanide ligands are well-known to coordination and organometallic chemists, it is only in recent years that they have attracted the attention of others who have a need to attach organic molecules to metal surfaces. There are several properties that make them useful for such applications. Their ability to act as both σ donors and π acceptors allows them to bond to surfaces of metals with a broad range of orbital energies. Another very useful property is their prominent ν(NC) absorption (especially in SERS spectra) in a region of the infrared spectrum that makes it easy to monitor transformations of the isocyanide group and to act as a detector of other species associated with it. In addition, the unsaturated and presumably conducting nature of the $C{\equiv}N-$ group makes it not only a linking group ("alligator clip") to a metal surface but also an electronic conductor in molecular electronic devices. Because of this combination of properties, it is likely that isocyanides will be examined in many other future applications.

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