

A Comparative Investigation of Aryl Isocyanides Chemisorbed to Palladium and Gold: An ATR-IR Spectroscopic Study

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The nature of the bonding interactions between aryl isocyanides and gold and palladium surfaces was investigated using attenuated total reflection infrared (ATR-IR) spectroscopy. The experiments were conducted by evaporating a film of either palladium or gold onto a ZnSe internal reflection element (IRE). The studies reveal that aryl isocyanides form only σ -bonded species when coordinated to gold and that these species are bonded relatively weakly to the gold surface, evidenced by their ready removal when subjected to ultrasound (sonication). In contrast, aryl isocyanides form at least two distinct types of species when bonded to a palladium surface: one effectively σ -bonded, as with gold, but much more tenaciously, and the other species bonded strongly to the surface by a σ/π synergistic interaction. The presence of π back-donation from the palladium surface into the isocyanide π system provides a rationale for the observation that barriers to conduction are lower when diisocyanides bridge palladium electrodes than when diisocyanides or dithiols bridge gold electrodes.

Introduction

Carbon monoxide is among the most studied of molecules coordinated to metal surfaces, due principally to the unique nature of the metal–ligand bond and the characteristic infrared signature of the carbonyl stretching vibration.¹ Isocyanides have often been discussed as carbon monoxide analogues since they are effectively isoelectronic with CO. While both molecules coordinate to transition-metal centers via a σ/π “synergistic” bonding scheme, isocyanides are generally better σ -donors and are therefore capable of coordination to transition metals in a variety of oxidation states. Isocyanides also display a characteristic infrared signature due to the C–N stretching vibration, and it is somewhat surprising that they have received only modest attention as surface probes. Early studies centered around the chemisorption of methyl isocyanide to a number of metals in UHV. Energy electron loss spectroscopy (EELS) of methyl isocyanide on Ni(111) by Friend, Muettterties, and Gland revealed a substantial decrease in the C–N stretching frequency, from 2166 cm^{-1} in the gas phase to 1710 cm^{-1} in the chemisorbed molecule.² These shifts were in the same range as those for complexes such as $\text{Ni}_4(\text{CNC}(\text{CH}_3)_3)_4(\mu_3\text{-}\eta^2\text{-CNCH}_3)_3$,³ leading the authors to conclude that an uprightly bridge-bonded η^1 species was the predominant entity on the surface. EELS studies of methyl isocyanide on Rh(111) by Semancik, Haller, and Yates similarly indicated that an upright bridge-bonded species existed at lower coverages, which converted to a species with a C–N stretching frequency of 2170 cm^{-1} at increased coverages.⁴ More recently, Trenary and co-workers have reported the formation of carbyne intermediates from the decomposition of methyl

isocyanide on Pt(111).⁵ We recently reported the results of a RAIRS spectroscopy study in UHV of methyl isocyanide adsorbed on Pd(111), in which a group theoretical analysis of methyl C–H vibrational modes indicated the possibility of an η^1 species at higher coverages.⁶ Chemisorbed aryl isocyanides have been studied almost exclusively on gold, chiefly by Angelici and Kubiak.⁷ Alkyl and aryl isocyanides on gold both experience C–N frequency stretching shifts to higher energies, indicative of an η^1 σ -bonded species.

A distinct advantage of aryl isocyanides over carbon monoxide is that they are capable of a multitude of substitutions on the aromatic ring, including a second isocyanide which will allow for the coupling of transition-metal complexes to metallic surfaces. We have recently shown that aromatic diisocyanides behave as conductive bridges between palladium and gold electrodes, with lower barriers to conduction than arylidithiol analogues coordinated to the same electrodes.⁸ These studies reveal that the barrier to conduction is substantially lower between palladium electrodes than it is between gold electrodes.

The sensitivity of aryl isocyanide ligands to differences in bonding is well-documented.⁹ The lone pair on carbon, chiefly involved in metal–ligand σ bonding, is antibonding with respect to the C–N bond, and delocalization away from the ligand results in an increase in the C–N stretching frequency. π donation from the metal centers into the ligand LUMO, either from the populated d orbitals

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on metal atoms or bulk metal Fermi levels, results in the population of ligand orbitals that are antibonding with respect to the C–N bond, resulting in a subsequent decrease in C–N stretching frequencies. Thus, infrared spectroscopy is an ideal probe for investigation of the nature of the metal–ligand bond. The results reported here clearly illustrate the differences between isocyanide–gold and isocyanide–palladium bonding and provide a plausible explanation for the differences in conductivity between the two types of electrode surfaces.

Experimental Section

Reagents. Isocyanides (*p*-CN(C₆H₄)R, R = NO₂, OCH₃, CH₃, F, CF₃, CN; *p*-CN(C₆H₂(CH₃)₂)NC; and *p*-CN(C₆(CH₃)₄)NC) were prepared by literature methods¹⁰ and were either sublimed or separated prior to use. Distillation of solvents and purification of nitrogen were performed by established methods, detailed elsewhere.¹¹

Attenuated Total Reflectance Infrared Spectroscopy. ATR experiments were carried out using a Harrick twin parallel mirror reflection attachment with a liquid sampling cell. A single-pass parallelepiped 45° ZnSe crystal with seven reflections was used. Infrared spectra were acquired on a Thermo-Nicolet Nexus 870 FTIR using a DTGS KBr detector at 4 cm⁻¹ resolution for 1000 scans. All ATR experiments were acquired with the contributions of the crystal and film subtracted in conjunction with the background.

Preparation of Metal Films for the Adsorption of Isocyanides. Films were deposited on one surface of an internally reflecting ZnSe crystal in a CVE 301 FR evaporator equipped with a liquid nitrogen-cooled diffusion pump maintaining a base pressure of 1 × 10⁻⁶ Torr. Palladium (99.95%, Alfa Aesar) films were deposited at a rate of approximately 1.25 nm/s by applying a current increased incrementally at 7 A/min to a maximum current of 70 A, maintaining a minimum pressure of 1 × 10⁻⁶ Torr. Gold (99.99% Premion, Alfa Aesar) films were deposited at a rate of 1.5 nm/s by applying a current increased incrementally at 20 A/min to a maximum current of 50 A, maintaining a pressure of 3 × 10⁻⁶ Torr. A new palladium film was deposited for each experiment.

Adsorption of Isocyanides on Metal-Coated Internal Reflection Elements. Isocyanides in toluene (20–40 mM) were allowed to react with the metal film in the ATR liquid sampling cell under nitrogen. The total reaction time was generally 4 h, with an in situ spectrum collected after 2 h to verify continued purity of the isocyanide in bulk. After 4 h, the isocyanide solution was removed, and the metal film was washed with copious amounts of toluene, followed by hexanes, and then allowed to dry under a dry nitrogen purge for 10 min. During this process the intensity of the isocyanide peak was monitored for change to determine that only adsorbed species remained. After all spectroscopic indications of residual isocyanide on the surface were negative, the isocyanide metal-coated film was washed an additional time, followed by sonication in toluene for 30 min.

Ultrahigh-Vacuum Experiments. Experiments were carried out in a stainless steel, ultrahigh-vacuum chamber operating at a base pressure of 1 × 10⁻¹⁰ Torr following bakeout, as detailed in previous work.¹² The sample was mounted on a carousel-geometry manipulator allowing for resistive heating to 2000 K or cooling to 80 K by thermal contact with a liquid nitrogen-filled reservoir. Temperature-programmed desorption data were generally collected using a heating rate of ~10 K/s, and desorbing species were detected using a Dycor quadrupole mass spectrometer interfaced to a PC, allowing five masses to be monitored sequentially during the same desorption sweep. In some cases, however, a faster heating rate of 20 K/s was employed to detect species desorbing at higher temperatures. The sample was dosed

Table 1. Maximum Film Thicknesses for Gold and Palladium Films in the Infrared Spectral Region¹⁸

metal	penetration depth ^a (700 cm ⁻¹), Å	penetration depth ^a (4000 cm ⁻¹), Å
gold	137	120
palladium	210	164

^a $I(z) = I(0)e^{-\alpha z}$ with $\alpha = 4\pi k/\lambda$, k = the imaginary component of the index of refraction, and λ = the wavelength. The penetration, z , is found when $I(z)/I(0) = e^{-1}$.

via a tube, which minimized background contamination and dosing of the supports. The stainless steel dosing source was coupled with a turbo pump operating at the high-speed setting, maintaining a base pressure of 1 × 10⁻⁹ Torr. The sample could be pumped via the turbo pump immediately prior to dosing, allowing for 1,4-diisocyanobenzene at room temperature to yield a dosing pressure of 4 × 10⁻¹⁰ Torr directly from the vial to the sample. Additionally, the entire source could be baked under vacuum to remove any impurities from the stainless steel walls. This gave a pressure enhancement compared with the background pressure of ~100. To further minimize spurious signals, the mass spectrometer was enclosed in a shroud with a 1 cm diameter hole in the front. The sample was cleaned using a standard procedure which consists of heating at 1000 K in ~4 × 10⁻⁸ Torr of oxygen and then annealing at 1200 K in vacuo to remove any remaining oxygen.

Sonication Experiments. The internal reflectance element (IRE) was suspended in a Teflon basket in 200 mL of distilled toluene (Na, benzophenone; reagent grade, Fischer) and sonicated in a Fisher Scientific FS140 sonicator for 30 min prior to and following film depositions. Additional sonications were executed where noted in the text in various solvents and for extended time intervals.

Results and Discussion

Characterization of Thin Films Deposited on ZnSe Infrared Elements. The substrate metal films absorb infrared radiation, and it was therefore necessary to limit their thicknesses to ca. 10–20 nm, depending on the infrared absorptivity of the metal. Table 1 gives maximum penetration depths at the wavelength limits of the experiment. The evaporation of both metals yielded a continuous film, ascertained by conductivity experiments, with palladium films significantly more resistive than gold films. Figure 1 shows typical $I(V)$ plots for deposited films of both metals. However, the films were still amorphous with many imperfections, particularly in the case of palladium, where the film formed puddles observable with a scanning electron microscope (SEM). Because of these imperfections, it was necessary to establish that the isocyanides did not form chemisorbed species on the ZnSe crystal itself. Each isocyanide studied was exposed to a clean ZnSe surface in an experiment which duplicated the conditions of adsorption to metal films. In all cases no residual isocyanide peaks were observed in the infrared spectra in these control experiments. Film thicknesses were adjusted empirically in order to obtain a conducting film thick enough to guarantee that surface selection rules would be obeyed (i.e., enough atoms to allow for the creation of a dipole image), while still allowing for the observation of adsorbed species.

Comparison of 1,4-Diisocyanobenzene Adsorbed on Palladium vs Gold. In 1984, Avery and Matheson proposed three possible modes of coordination to metal surfaces, illustrated in Scheme 1 as modes I, III, and IV.¹³ On the basis of our observations of isocyanide transition metal complexes, in which coordination to a single metal

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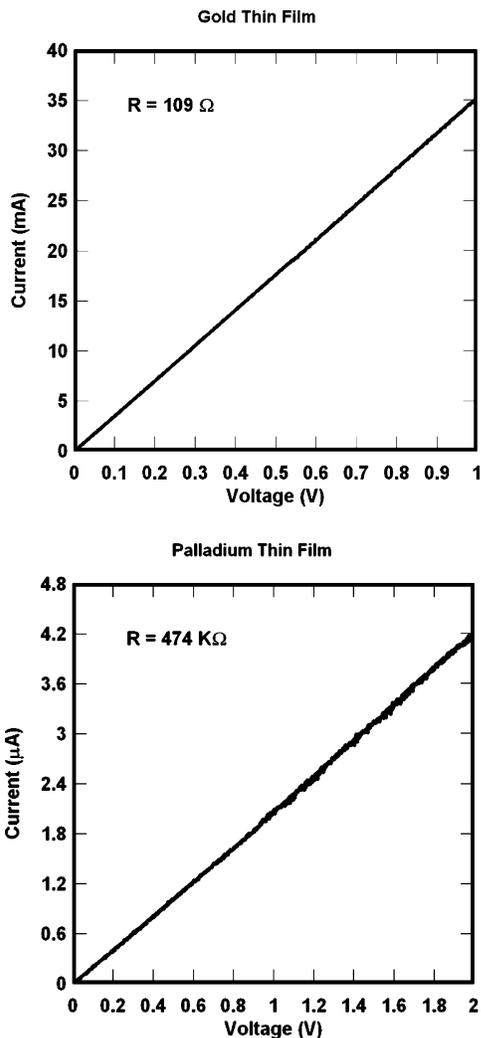
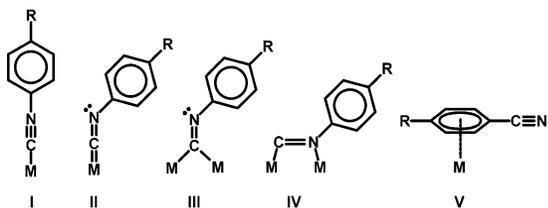


Figure 1. Typical $I(V)$ plots for deposited gold and palladium films.

Scheme 1. Possible Modes of Binding of Isocyanides to Metal Surfaces



atom can also result in significant bending of the aryl isocyanide due to strong π donation from the metal, mode II in Scheme 1 is also possible. Finally, on the basis of the tendency for aromatic species to form $\eta^6 \pi$ -bonded species, the mode illustrated as mode V in Scheme 1 is also a possibility. The ATR-IR spectra of 1,4-diisocyanobenzene on gold and palladium are illustrated in Figures 2 and 3, respectively. The ligand spectrum on gold is entirely consistent with that observed by Angelici et al.^{7a} Two C–N stretching frequencies are observed: one for the coordinated end of the isocyanide and the other for the “free” end. The uncoordinated end of the molecule experiences only a small (5 cm^{-1}) shift, compared to the spectrum of the ligand in solution, while the coordinated end experiences a significant shift of 43 cm^{-1} to a higher frequency, indicative of a strong polarization of lone pair electron density into the metal, since the lone pair density is antibonding with respect to the C–N bond. This shift is

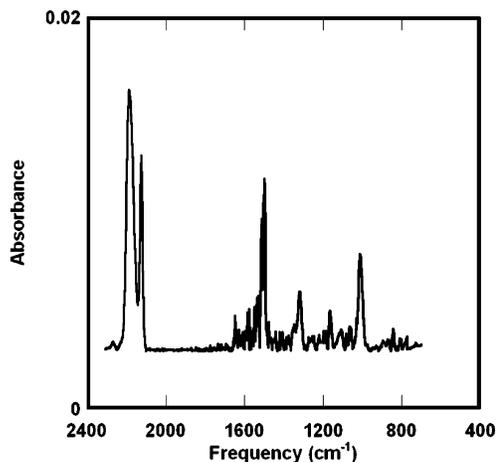


Figure 2. ATR-IR spectrum of 1,4-diisocyanobenzene adsorbed on a gold film.

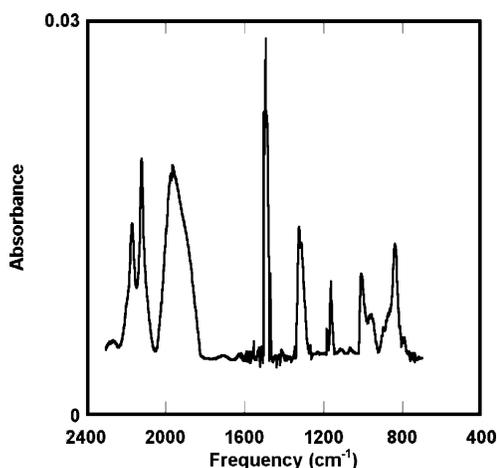


Figure 3. ATR-IR spectrum of 1,4-diisocyanobenzene adsorbed on a palladium film.

often balanced in isocyanides by compensatory π donation from the metal center,¹⁴ but this is clearly not the case here. It is reasonable to conclude that the NC–Au bond is essentially “ σ ” in character, with little, if any, π coupling with the metal. Tentative spectral assignments for chemisorbed 1,4-diisocyanobenzene on gold are given in Table 2, made by comparison to the spectrum of free 1,4-diisocyanobenzene and assuming that the symmetry of the ligand–metal species is unperturbed from D_{2h} ; these assignments are consistent with bonding mode I.

The spectrum of 1,4-diisocyanobenzene on palladium is remarkably different! The 2120 cm^{-1} band for the uncoordinated isocyanide moiety occurs at the same place as it does for the molecule coordinated to gold, but a strong peak is also observed at 1960 cm^{-1} , characteristic of isocyanide coordination to metals with a dominant π back-donation contribution from the metal.¹⁵ In contrast to the case of the isocyanide coordinated to gold, there is apparently substantial π coupling with the metal when 1,4-diisocyanobenzene chemisorbs to palladium. Bonding modes IV and V are ruled out for spectra obtained on both metals, since surface selection rules would preclude the intense bands observed from dipoles parallel to the surface. On the basis of molecular analogues, it is likely that pairing

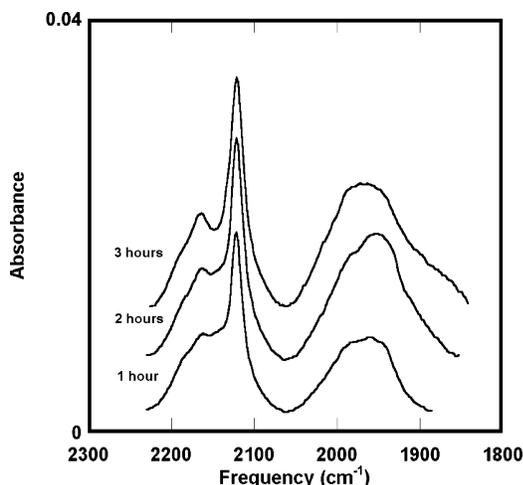
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Table 2. Tentative Assignment of Vibrational Frequencies for 1,4-Diisocyanobenzene Adsorbed on Gold and Palladium

CNPhNC			CNPhNC on Au			CNPhNC on Pd		
freq (cm ⁻¹)	assignt	sym (<i>D</i> _{2h})	freq (cm ⁻¹)	assignt	sym (<i>D</i> _{2h})	freq (cm ⁻¹)	assignt	sym (<i>C</i> _s)
			2170	$\nu_{\text{CN}}(\sigma)^*$	a'(x)	2170	$\nu_{\text{CN}}(\sigma)^*$	a'(x)
2127	ν_{CN}	b _{3u} (x)	2122	$\nu_{\text{CN}}(\text{free})$	a'(x)	2120	$\nu_{\text{CN}}(\text{free})$	a'(x)
						1960	$\nu_{\text{CN}}(\sigma\pi)^*$	a'(x)
1503	ν_{ring}	b _{2u} (y), b _{3u} (x)	1511	ν_{ring}	a'(x), (y)	1505	ν_{ring}	a'(x), (y)
1483	ν_{ring}	b _{2u} (y), b _{3u} (x)	1497	ν_{ring}	a'(x), (y)	1495	ν_{ring}	a'(x), (y)
1286	ν_{ring}	b _{3u} (x)	1319	ν_{ring}	a'(x)	1317	ν_{ring}	a'(x)
1183	δ_{ring}	b _{3u} (x)	1166	δ_{ring}	a'(x)	1156	δ_{ring}	a'(x)
1028	δ_{ring}	b _{2u} (y), b _{3u} (x)	1008	δ_{ring}	a'(x), (y)	1008	δ_{ring}	a'(x), (y)
851	ν_{CN}	b _{3u} (x)	841	ν_{CN}	a'(x)	843	ν_{CN}	a'(x)

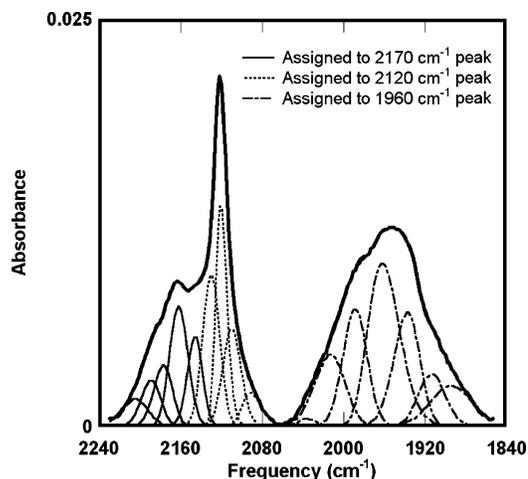
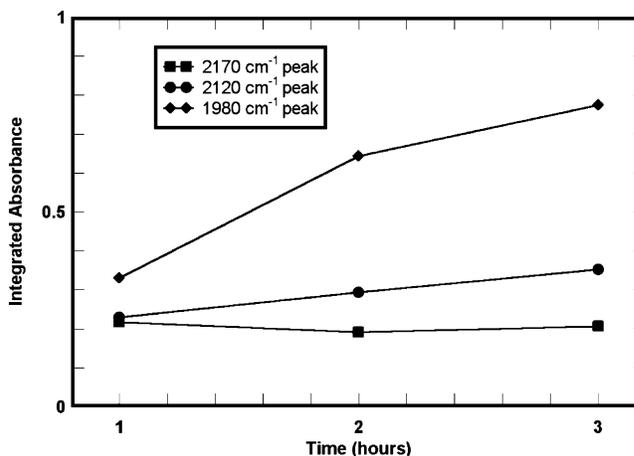
^a σ indicates that the isocyanide species is bonded to the surface primarily through σ donation, while $\sigma\pi$ indicates a species with substantial additional π back-bonding.

**Figure 4.** ATR-IR spectra of 1,4-diisocyanobenzene adsorption on a palladium film at specific exposure times.

effects cause the π -bonded isocyanide on palladium to be bent,¹⁶ making bonding modes II or III the most likely.

In addition to this new band, there is also an intense band at 2170 cm⁻¹, effectively identical to that observed in the spectrum of the molecule adsorbed to gold. The only scheme that would allow for a single species to produce such a spectrum would be one in which one isocyanide was coordinated to the surface at a site conducive to σ/π bonding, while the other end coordinated to another site on the surface with " σ -only" bonding. A more likely alternative is that there is more than one distinct type of isocyanide species bonded to the surface. Because the uncoordinated end of the isocyanide would not be likely to experience significantly different perturbations from either mode of coordination, the 2120 cm⁻¹ band would be expected to arise from the overlap of the bands from the free NC group of both species. To test this hypothesis, an experiment was conducted in which the formation of the chemisorbed isocyanide on palladium was observed as a function of time.

Adsorption of 1,4-Diisocyanobenzene on Palladium as a Function of Time. In this experiment the isocyanide solution was purged from the ATR cell at specific intervals, spectra were collected, and then the isocyanide solution was reintroduced. Figure 4 shows the spectra obtained in the experiment. To determine relative peak intervals, the spectra were fit with a set of 16 log-normal functions, using simplex optimization to generate the best least-squares fit, allowing the position, maximum value, width, and degree of skewness of the log-normal

**Figure 5.** Log-normal deconvolution a typical time-dependent spectrum. Observed and calculated spectra lie on top of one another and are virtually indistinguishable.**Figure 6.** Relative integrals for each of the major absorbance bands as a function of time of exposure to the isocyanide solution based on log-normal deconvolution.

functions to vary.¹⁷ The integrals of the log-normals corresponding to each peak were then summed to provide an overall value for the peak integral. Figure 5 illustrates the results of this deconvolution for the $t = 2$ h spectrum in Figure 4. The breadth of the observed peaks and the need to use multiple log-normal functions to obtain the best fit indicates the strong likelihood that each peak consists of several similar surface species—which would be expected on an amorphous film. Figure 6 is a plot of the relative integrals for each of the peaks as a function

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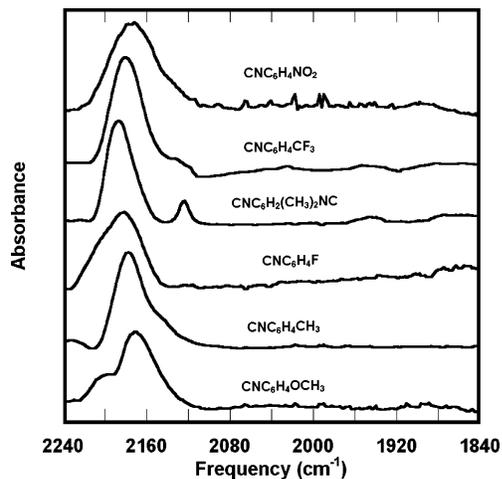


Figure 7. ATR-IR spectra of various para-substituted aryl isocyanides adsorbed on a gold film.

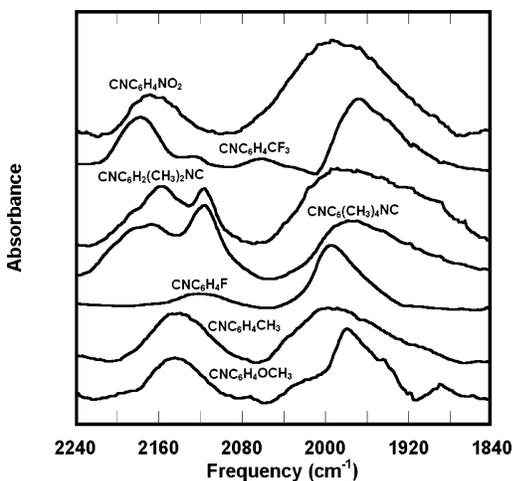


Figure 8. ATR-IR spectra of various para-substituted aryl isocyanides adsorbed on a gold-palladium film.

of time of exposure to the isocyanide solution. It is immediately clear that these bands correspond to independent species since changes in their intensities are independent. The intensity of the band corresponding to the σ/π -bonded species increases significantly, while the band resulting from the σ -bonded species sharpens, its integrated intensity remaining essentially constant with time. The sharpening appears to be the result of a diminution of the intensity of the lower wavelength contributors in the 2170 cm^{-1} band, suggesting that the some of the species which initially bond primarily through σ donation to the surface eventually find sites where they are able to π bond. This also suggests that the σ/π species is thermodynamically more stable.

Comparison of Para-Substituted Isocyanides Adsorbed on Palladium vs Gold. To further test the surface-bonding model described above, a series of para-substituted isocyanides were chemisorbed to gold and palladium in the same manner as described for 1,4-diisocyanobenzene. The ATR-IR spectra of these isocyanides adsorbed on a gold film are shown in Figure 7. In all cases the only absorbance(s) observed in the CN stretching region occur at higher frequencies than the uncoordinated isocyanide, which can be seen at 2170 cm^{-1} in the spectrum of $\text{CNC}_6\text{H}_2(\text{CH}_3)_2\text{NC}$, the dimethyl analogue of $\text{CNC}_6\text{H}_4\text{NC}$. Thus, it appears clear that the mode of coordination of isocyanides to gold surfaces is through a NC-Au bond that is principally " σ " in character.

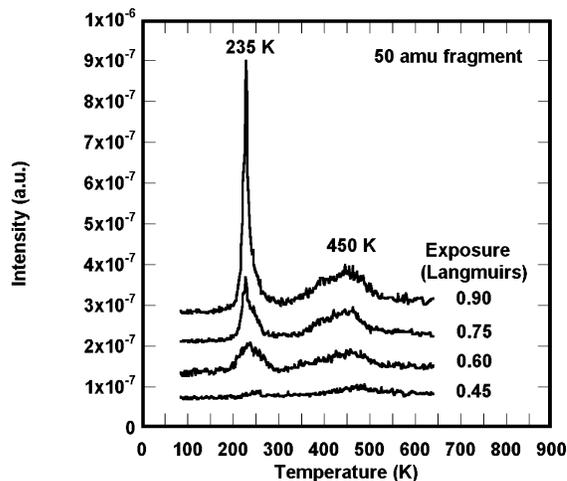


Figure 9. Temperature-programmed desorption spectra collected at 50 amu as a function of 1,4-diisocyanobenzene exposure on Pd(111) using a heating rate of 10 K/s .

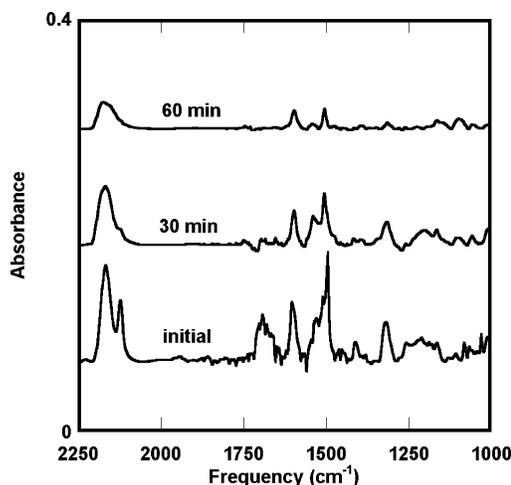


Figure 10. ATR-IR spectra of 1,4-diisocyanobenzene chemisorbed on gold at a series of times of exposure to sonication conditions.

As with 1,4-diisocyanobenzene, all isocyanides exhibit a markedly different spectrum when coordinated to palladium, as illustrated in Figure 8. In all cases a strong and relatively broad band is observed at frequencies substantially lower than those of the uncoordinated isocyanide, indicating the presence of a significant metal-to-ligand π component in the bonding. In addition, another large band is observed at frequencies higher than those of the free isocyanide, again implying that another species, bonded primarily through σ donation, is present on the palladium surface.

Temperature-Programmed Desorption of CN-PhNC on Pd(111). The observed lower stretching frequencies for the N-C bond upon coordination of the isocyanide group to palladium suggests a strong synergistic bonding interaction with the palladium surface. To quantify this, a temperature-programmed desorption (TPD) study of CNPhNC on Pd(111) was undertaken. Figure 9 shows the results of this study. The only desorbed species observed was molecular 1,4-diisocyanobenzene (128 amu) and its mass spectral fragments. No other decomposition was observed. The 50 amu fragment was monitored due to its increased sensitivity in our mass spectrometer. The multilayer desorbs at 235 K, while the chemisorbed species desorbs at 450 K. Assuming that desorption is a first-order process with a preexponential

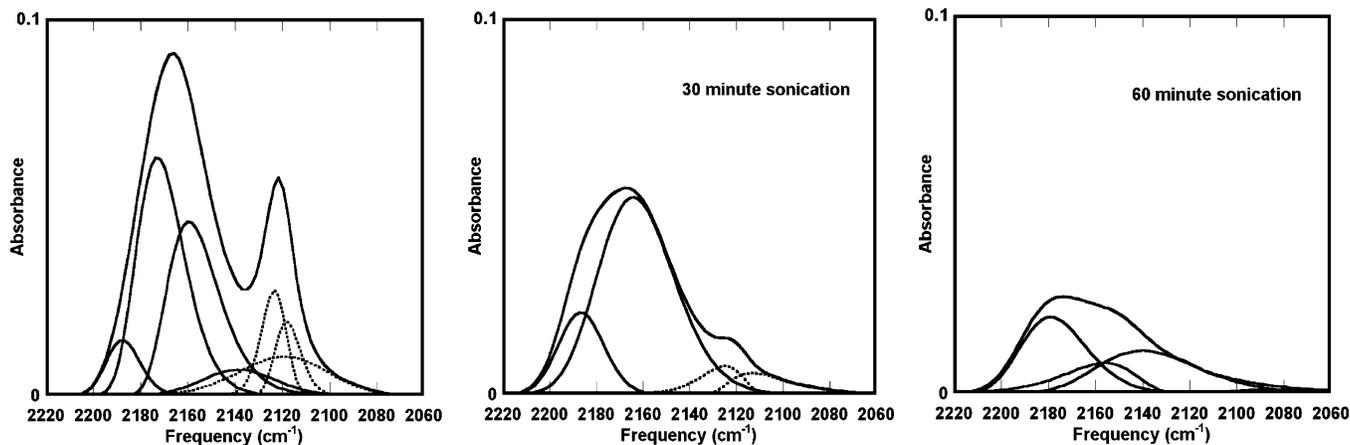


Figure 11. Log-normal deconvolution of IR absorption bands in the C–N stretching region for 1,4-diisocyanobenzene chemisorbed on gold at 0, 30, and 60 min of exposure to sonication conditions. Observed and calculated spectra lie on top of one another and are virtually indistinguishable.

factor of $1 \times 10^{13} \text{ s}^{-1}$ and a heating rate of 10 K/s, the desorption activation energy is 113 kJ/mol,¹⁸ indicating a strong Pd–CNR bonding interaction. In previous work we observed that methyl isocyanide underwent surface decomposition in similar TPD experiments.⁶ 1,4-Diisocyanobenzene does not exhibit similar behavior, attesting to the increased stability from electron delocalization in aromatic isocyanides.

Assessment of Surface–Ligand Interactions of Para-Substituted Isocyanides Adsorbed on Palladium vs Gold: Susceptibility to Removal by Sonication. These studies arose from attempts to clean the surface of the films on the ATR crystal in an ultrasonic bath containing either toluene or THF. Qualitatively, it was noted that we were able to remove the isocyanide completely from the gold films after several washings, while the ligands remained firmly attached to the palladium film. We therefore undertook a more systematic investigation, monitoring the spectra of the species coordinated to the ATR crystal as a function of time in the ultrasonic bath.

Figure 10 shows the results of the effects of sonication on 1,4-diisocyanobenzene chemisorbed on gold. The isocyanide species begin to desorb from the surface almost immediately, and after 30 min the relative peak intensities have diminished significantly. It is interesting to note that the relative intensity of the band corresponding to the uncoordinated end of the ligand decreases more rapidly than that for the coordinated end. Figure 11 illustrates the deconvolution of these bands using log-normal functions. The integrals for the bands corresponding to the coordinated and free ends of the isocyanide for the spectrum prior to sonication are 1.77 and 0.57, respectively, essentially 3:1. After 30 min of sonication the same integrals reduce to 1.38 and 0.18, a ratio of 7.6:1. Thus, a substantial amount of the initial ligand has desorbed from the surface, and the signal due to the uncoordinated end of the isocyanide has almost disappeared after 30 min; it is completely lost after 60 min of sonication. In addition, the band corresponding to the coordinated end broadens—apparently due to the bonding of species at different sites on the surface. It is possible here that sonication results in the migration of ligands to sites on the surface where the orientation of the C–N bond with respect to the surface has changed and/or both ends have become bonded—perhaps at step or kink sites. A change in the bonding mode is also possible (e.g., mode I

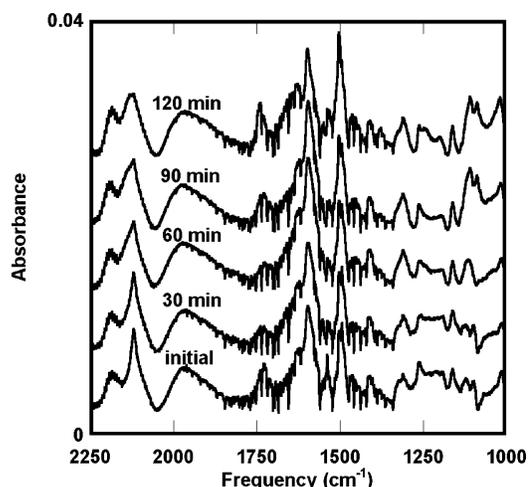


Figure 12. ATR-IR spectra of 1,4-diisocyanobenzene chemisorbed on palladium at a series of times of exposure to sonication conditions.

transforming to mode II or mode III); however, this seems far less likely, since gold is a notoriously poor π donor, as evidenced by the very weak interaction between bulk gold and carbon monoxide.²⁰ There are also no major shifts in coordinated CN stretching frequencies which would be expected from such a transformation. All of the isocyanides in this study behaved similarly.

The sonication of 1,4-diisocyanobenzene coordinated to palladium exhibits markedly different behavior. Figure 12 shows the results of sonication over a 120 min period of time. The bands from the species coordinated largely through σ donation and the band due to the uncoordinated isocyanide broaden slightly, indicating the possibility of some surface rearrangement, perhaps analogous to that observed with gold. The species coordinated to the surface with a strong π component remains essentially unchanged, indicative of a robust surface–ligand bond. Furthermore, unlike isocyanides on gold, 1,4-diisocyanobenzene, as well as all of the other isocyanides in this study, could not be removed from the surface by sonication. Thus, not only is the σ/π -bonded species more strongly coordinated to

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palladium than gold, but the species bonded chiefly through σ donation is also more strongly bound.

Conclusions

Infrared spectroscopy of isocyanides coordinated to thin films of gold and palladium demonstrates clearly that the nature of the metal–CN bond is qualitatively and quantitatively quite different between the two metals. While gold is an excellent conductor, it is also the noblest of noble metals—it does not yield its electron density to external agents with ease. Thus, it is not surprising that it is a poor π donor. Bonding to a gold surface is therefore generally “ σ ” in character, with the bonding ligand supplying the charge density necessary to form the ligand–surface bond. The ATR-IR studies here clearly support this concept. All of the isocyanides studied showed clear evidence of charge polarization of the ligand lone pair into the metal, with little, if any, evidence for π back-donation from the metal. In general, gold does not participate in this mode of bonding with a great degree of tenacity, and the strength of the isocyanide–gold bond is weak enough to be broken under sonication conditions.

The palladium–isocyanide interactions stand in sharp contrast to this. Not only is the bonding to the palladium surface more vigorous in general, but it is considerably more complex. The ATR experiments indicate that at least two distinct types of surface-bound species are formed on the palladium surface. One species is chiefly σ -bonded, as

in the case of the gold/isocyanide, but the bonding is much more tenacious than with gold; sonication conditions are insufficient to desorb these species from the palladium surface. Even more importantly, there is a second surface species which is bonded through σ -donation from the ligand and π back-donation from metal. This interaction is effectively unperturbed by sonication.

As stated in the Introduction, we reported earlier that aryl diisocyanides exhibit lower barriers to conduction than do aryldithiols when serving as bridges between palladium and gold electrodes. In that study we also observed that the lowest barriers were exhibited when the isocyanides bridged palladium electrodes. The results described here provide a plausible rationale for these observations, since aryldithiols are constrained to a bonding mode chiefly “ σ ” in nature, while isocyanides can behave as π acids. Only on the palladium surface does this π bonding interaction play a major role, and it is apparent that Pd–CN synergistic bond is a major factor in lowering the barrier to electron transfer.

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