

FTIR Matrix Isolation Studies of the Reactions of Atomic and Diatomic Nickel with Acetylene in Solid Argon. The Photosynthesis of Nickel Vinylidene

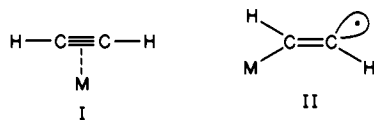
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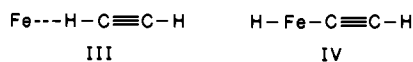
Abstract: The reactions between atomic nickel and acetylene have been investigated in argon matrices at 12 K with Fourier-transform infrared spectroscopy. At very low concentrations of nickel and acetylene the nickel atom forms a π complex with the triple bond of acetylene. This π complex photorearranges upon visible photolysis with $\lambda \geq 400$ nm to give nickel vinylidene, NiCCH₂. Photolysis with ultraviolet light causes the reversal of this reaction. Isotopic studies with C₂D₂, C₂HD, ¹³C₂H₂, and ¹²C¹³CH₂ support these findings. The FTIR spectrum of a dinickel-acetylene π complex obtained at higher nickel concentrations has also been identified. The bond order of acetylene has been reduced to two in both Ni(C₂H₂) and Ni₂(C₂H₂), as evidenced from the big shift in the carbon-carbon stretching frequency. No photochemistry was observed in the case of the dinickel reaction.

The interactions of transition-metal atoms with small unsaturated organic molecules such as acetylene have received considerable attention. Surface studies and cluster chemistry provide insight into bond cleavage and rearrangement in organometallic syntheses and transition-metal catalysis. The matrix isolation technique is an additional method for study of transition metal-acetylene interactions.

There are a number of plausible structures for metal-acetylene complexes. Adduct I, a π -coordinated structure consistent with the Dewar-Chat-Duncanson scheme of bonding,^{1,2} is predicted for manganese-acetylene adducts with use of ab initio calculations.³ This π complex has been reported for copper and gold atoms.^{4,5} A "pseudo" or extremely weak π complex has been reported for silver cocondensed with acetylene. However, the gas-phase reaction of silver and acetylene generated a radical of the vinyl form II.⁴ This vinyl form II was also observed for gold and aluminum in matrices of high acetylene concentration.^{5,6} The bonding patterns for these metals were determined by matrix isolation electron spin resonance studies. Ab initio calculations on the silver and copper systems^{7,8} and infrared/UV-vis spectroscopic data for the copper-acetylene adduct⁸ further supported the assigned structures.



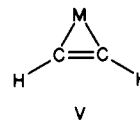
Our group has recently observed III, a transition metal hydrogen bonded to an alkyne, when iron was cocondensed with acetylene in an argon matrix.⁹ Upon UV photolysis, the iron atom inserted into a C-H bond of acetylene to give the ethynyliron hydride IV.



Nickel has played an important role in catalytic and organometallic chemistry, as, for example, in hydrogenation reactions.^{10,11} Reaction intermediates on nickel surfaces and in organometallic clusters have been investigated. Ultraviolet photoemission spectroscopy (UPS) and temperature programmed thermal desorption spectroscopy have been employed to investigate the chemical reactions of acetylene with Ni(100), Ni(110),¹² and Ni(111) surfaces.¹³ The chemisorption of acetylene on a Ni(111) surface has also been studied by high resolution electron energy loss spectroscopy (HREELS),¹⁴ ab initio MO calculations,¹⁵ and the Hartree-Fock-Slater LCAO method.¹⁶ These studies have

provided insight into the relative energy levels and bonding models for adsorbed hydrocarbon fragments, i.e., H, C, CH, CH₂, CCH, and C₂H₂ on nickel surfaces.

Matrix isolation studies by Ozin and co-workers generated a nickel atom-acetylene adduct to which they assigned the bonding pattern I, based on infrared and UV-vis spectroscopic data as well as SCF-X α -SW molecular orbital calculations.⁸ We were interested in the photochemistry of this nickel atom-acetylene adduct. When we codeposited nickel and acetylene in an argon matrix at 12 K, the FTIR spectrum of Ni(C₂H₂) is characteristic of the bonding pattern V. V can be viewed as an extreme case of π -complexation in which the triple bond of acetylene has been reduced to a double bond. This mode of bonding has been assigned to the LiC₂H₂ molecule in matrix isolation studies on the basis of infrared spectroscopy.¹⁷



Upon photolysis with visible light ($\lambda \geq 400$ nm) the nickel-acetylene adduct V undergoes bond cleavage and rearrangement to give the metal vinylidene VI. Gold vinylidene in an adamantane matrix at 77 K¹⁸ and sodium vinylidene in an argon matrix¹⁹ have been observed with use of ESR spectroscopy. We report here the

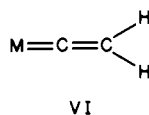
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Table I. Infrared Frequencies (cm⁻¹) Measured for ^{12/13}C₂H₂ and C₂HD in Solid Argon

vibrational mode	^{12/13} C ₂ H ₂	vibrational mode	C ₂ HD
ν_1 , CH s-stretch	3366.1	ν_1 , CH stretch	3341.1
ν_2 , C≡C stretch		ν_2 , C≡C stretch	1856.6
ν_3 , CH a-stretch	3290.0	ν_3 , CD stretch	2586.6
ν_4 , CH s-bend		ν_4 , CH bend	683.6
ν_5 , CH a-bend	735.7	ν_5 , CD bend	519.5
		$2\nu_4$	1350.6
$\nu_4 + \nu_5$	1329.4	$\nu_4 + \nu_5$	1204.8
		$2\nu_5$	1018.5

first identification of a metal vinylidene by FTIR matrix isolation spectroscopy.



Acetylenes typically uniformly bind in a μ_2 - η^2 fashion in dinuclear metal complexes to give an M₂C₂ tetrahedral core structure in which the acetylenic C≡C bond length is substantially increased.²⁰ In our present studies we isolated a dinickel acetylene complex, Ni₂(C₂H₂), in which the C≡C bond of acetylene has been reduced to a double bond.

Experimental Section

A matrix isolation apparatus interfaced to a vacuum IBM IR-98 Fourier-transform infrared spectrometer was used in these studies. This apparatus is described in detail in a recent publication.²¹ A tantalum furnace enclosing an alumina crucible containing nickel metal was resistively heated. Nickel vapors were obtained over the temperature range 1150–1450 °C, as measured by a microoptical pyrometer (Pyrometer Instrument Co.). The rates of deposition of nickel (Mackay, 99.5%), acetylene (Big Three Industries, A.A., 99.6% min), and argon (Matheson, 99.9998%) were determined by a quartz crystal microbalance. The concentration of nickel was varied from 0 to 20 parts per thousand of argon, while the concentration of acetylene was varied from 0 to 10 parts per thousand. In other concentration studies involving acetylene, the concentration of acetylene ranged to as high as 100 parts per thousand. In experiments involving molecular hydrogen (Matheson, 99.9%) the rate of hydrogen deposition was adjusted by a leak valve in concordance with ionization gauge readings.

The reactants were codeposited in excess argon onto a polished rhodium-plated copper surface maintained at 12 K by use of a closed-cycle helium refrigerator. After a 30-min deposition, the matrix block was rotated 180° and an infrared spectrum was measured over the range 4000–500 cm⁻¹. Matrices were typically irradiated after deposition. A medium-pressure 100-W Hg lamp was employed in the photolysis experiments. A water Pyrex filter with Corning long-pass 500- and 400-nm cutoff filters and a band filter, 360 ≥ λ ≥ 280 nm, were used during wavelength-dependent photolysis studies.

Carbon-13 enriched acetylene (Prochem Isotopes, 75% isotopic purity), deuterated acetylene (MSD Isotopes, 99.0% isotopic purity), carbon-12, carbon-13 acetylene (MSD Isotopes, 97.6% isotopic purity), and monodeuterated acetylene were also deposited with nickel in excess argon in similar experiments. The monodeuterated acetylene was prepared by using a modified version of a previously reported synthesis.¹⁷ This synthesis involved adding a mixture of 70% D₂O (Sigma, 99.8% isotopic purity) and 30% H₂O dropwise to a solution of CaC₂ (J.T. Baker, technical grade) in dry, air-free THF (J.T. Baker, 99% min.) with use of standard Schlenk-line techniques. The C₂HD was passed through molecular sieves, collected, and used without further purification.

Results

The Fourier-transform infrared spectra were obtained for ^{12/13}C₂H₂ and C₂HD in solid argon at 12 K for reference purposes. The measured frequencies are reported in Table I. Acetylene has a tendency to "dimerize", or, more specifically, two molecules of acetylene tend to align and interact with each other in the argon matrix.²² Thus, the acetylene concentration was kept very low

(one part per thousand of argon) in order to minimize or eliminate the formation of (C₂H₂)₂.

Ni(C₂H₂) and NiCCH₂ Complexes. When nickel and acetylene were cocondensed in an argon matrix, adduct bands appeared mainly in the 1800–500-cm⁻¹ region of the infrared spectrum. Upon photolysis with λ ≥ 400 nm, photoproduct peaks grew in as the adduct bands decreased in intensity. Adduct peaks may be shifted only slightly from the uncomplexed reactants and may indeed fall too close to the reactant peaks to be distinguishable. To avert the possibility of overlooking an infrared band, subtraction plots were computed. These subtraction plots, in which spectra obtained before photolysis were subtracted from spectra measured after photolysis, also afforded better identification of the adduct and photoproduct peaks and demonstrated that the nickel-acetylene adduct is a precursor to the photoproduct.

Both adduct and photoproduct absorption bands were located in two major regions of the infrared spectrum: 1700–1550 and 900–500 cm⁻¹. Figure 1 contains the FTIR difference spectra of these regions for the adducts and photoproducts of the Ni/C₂H₂, Ni/^{12/13}C₂H₂, and Ni/¹³C₂H₂ systems. The negative peak at 1647.4 cm⁻¹ is in the region characteristic of ν(C≡C) stretching. This peak is assigned to the nickel-acetylene complex spontaneously formed upon deposition. This assignment is further supported by the negative peak at 1568.6 cm⁻¹ for the Ni/¹³C₂H₂ π complex. The isotopic shift observed in the Ni/^{12/13}C₂H₂ system is to a higher frequency of 1692.4 cm⁻¹. This unexpected result will be discussed in a later section.

Bands were also observed for the nickel-acetylene π complex in the 900–600-cm⁻¹ region. This region is the C–H deformation region for transition metal-acetylene π complexes. These bands are shown in Figure 2 and are assigned to in-plane and out-of-plane C–H bending modes.

Figure 1 also shows the presence of peaks at 1635.0 and 1623.8 cm⁻¹ for the photolysis product. These peaks were shifted to 1586.6 and 1575.8 cm⁻¹, respectively, when ¹³C₂H₂ was used. A carbon-13 isotopic shift close to 50 cm⁻¹ is characteristic of the ν(C≡C) stretching mode. The presence of four peaks for the ^{12/13}C₂H₂ system indicates the carbons are inequivalent in the photolysis product. The inequivalency of the carbon atoms in the photolysis product is also shown in the ρ_w(CH₂) wagging region, 900–700 cm⁻¹. Two peaks with very small shifts were observed in the mixed isotopic study. This isotopic pattern is typical of an unresolved quartet.

The equivalency of the hydrogens in the photolysis product is evident in Figure 2. There is only one peak due to the CHD wagging mode for the monodeuterated nickel/acetylene photoproduct. Its frequency is roughly halfway between that observed for the nickel photoproducts of C₂D₂ and C₂H₂. Isotopic shifts of approximately 70 cm⁻¹ were measured. Nickel vinylidene is proposed to be this photoproduct with two inequivalent carbon atoms and two equivalent hydrogen atoms.

Figure 3 contains spectra from a wavelength-dependent reversible photolytic study of nickel cocondensed with acetylene in an argon matrix. The infrared bands associated with the nickel-acetylene π complex are present before photolysis. Upon photolysis with λ ≥ 400 nm, however, these adduct peaks decreased as new bands assigned to nickel vinylidene gradually grew in. Figure 3 shows this spectral change for the ρ_w(CH₂) wagging and the ν(C≡C) stretching regions. Upon photolysis with UV (360 nm ≥ λ ≥ 280 nm), the vinylidene peaks decreased as the π-complex infrared bands reappeared. However, a repeated photolysis with λ ≥ 400 nm resulted in the reverse occurrence in which the vinylidene peaks again increased in intensity as the π-complex peaks were reduced. Thus, the reaction is shown to be photo-reversible. Note that the infrared band at 1678.8 cm⁻¹ is observed before photolysis which indicates the spontaneous formation of a small amount of nickel vinylidene.

Ni₂(C₂H₂) and Ni(C₂H₂)₂ Complexes. The formation of nickel/acetylene adducts of varying nuclearity, specifically Ni₂(C₂H₂) and Ni(C₂H₂)₂, was also investigated. The stoichiometry

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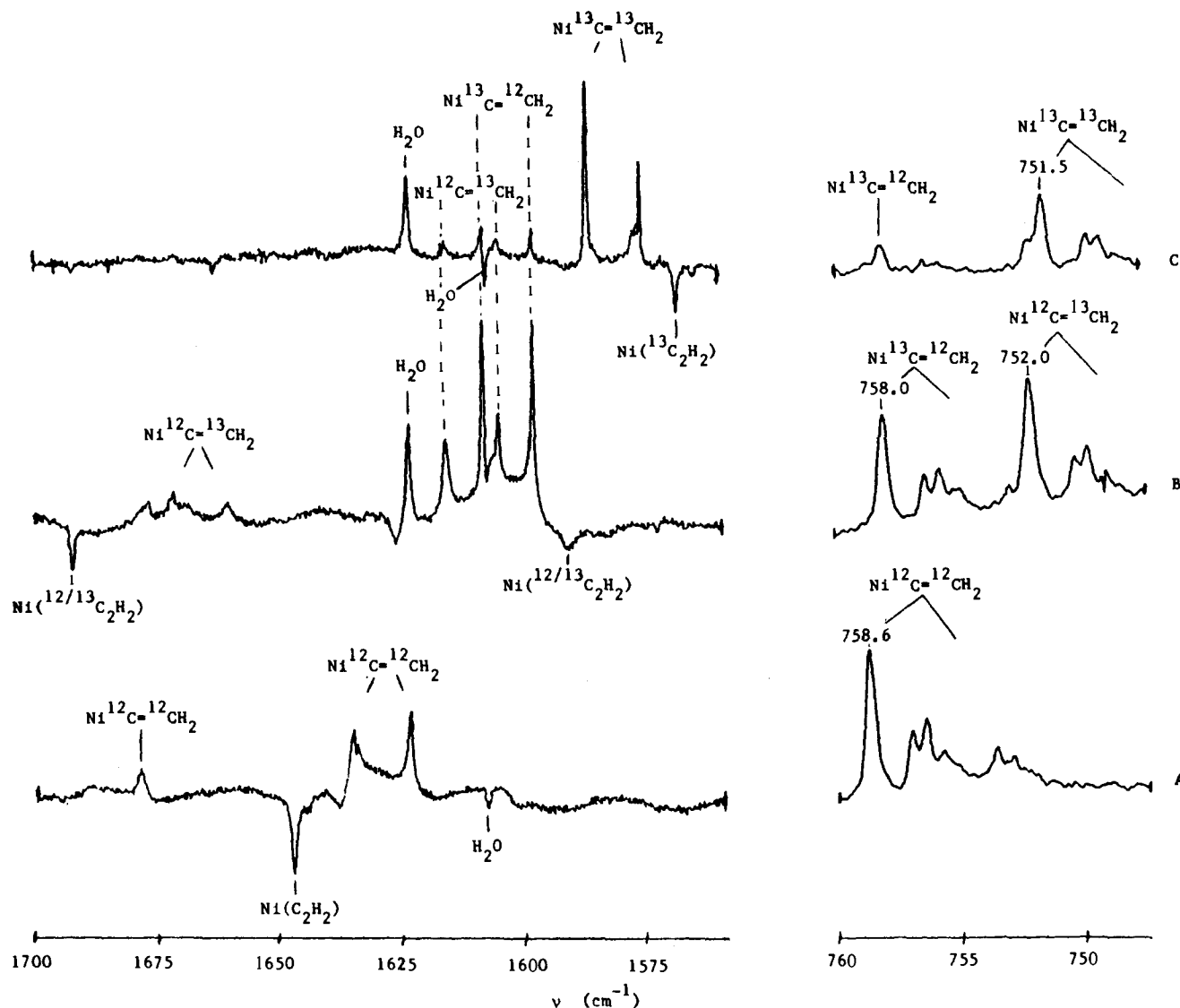


Figure 1. An isotopic study. FTIR difference spectra ($X - Y$) of the $C=C$ stretching and $C-H$ deformation regions of adducts and photoproducts of nickel acetylene: (X) after 30 min of photolysis with $\lambda \geq 400$ nm; and (Y) after deposition, no photolysis. Molar ratio of $Ni:C_2H_2:Ar \sim 5:1:1000$: (A) Ni with C_2H_2 in Ar; (B) Ni with $^{12/13}C_2H_2$ in Ar; and (C) Ni with $^{13}C_2H_2$ in Ar.

of these nickel/acetylene complexes was determined from nickel and acetylene concentration studies. Figure 4 is representative of a typical metal concentration study from which infrared bands due to the dinickel monoacetylene adduct can be deduced. The nickel concentration was varied between 0 and 20 parts per thousand of argon while the acetylene concentration was held constant at 1 part per thousand. Peaks appeared at 1647.4 and 1638.4 cm^{-1} at low concentrations of nickel. These peaks increased with increasing nickel concentration until their rate of growth slowed when the molar ratio of nickel to argon reached ~ 5 parts per thousand. At this concentration new adduct peaks appeared and increased at 1688.9, 1675.1, and 1639.7 cm^{-1} . These new peaks were assigned to a dinickel acetylene adduct. Their frequencies are in the infrared region characteristic of the $\nu(C=C)$ stretching mode.

Upon prolonged photolysis, the $Ni_2(C_2H_2)$ peaks slowly disappeared. No new peaks grew in, indicating that dinickel acetylene adduct possibly photodissociated.

The results of an acetylene concentration study are depicted in Figure 5. The nickel concentration was maintained at ~ 2.5 parts per thousand of argon while the acetylene concentration was varied from ~ 1 to ~ 100 parts per thousand. Infrared bands due to the mononickel acetylene concentration adduct appeared at low acetylene concentrations and increased with increasing acetylene concentrations. Peaks at 1705.4, 1699.9, and 1696.9 cm^{-1} appeared at $C_2H_2:Ar \sim 5:1000$ and increased with increasing C_2H_2

concentration. These new frequencies, in the carbon-carbon stretching region characteristic of a transition metal-acetylene π complex, were assigned to the mononickel bis(acetylene) complex $Ni(C_2H_2)_2$. Both UV and visible photolyses enhanced the formation of bis(acetylene) nickel, similar to behavior observed with the bis(acetylene) iron system.⁹

Interactions of $NiCCH_2$ and H_2 . Nickel and acetylene were codeposited in excess argon with $\lambda \geq 400$ nm irradiation during a 30-min deposition in a typical matrix isolation experiment. Photolysis during deposition rather than after deposition enhanced photoproduct formation, a commonly observed effect. When nickel and acetylene were cocondensed under the same conditions but with the addition of H_2 , the intensity of bands assigned to nickel vinylidene was decreased by half. In nickel/acetylene matrix isolation studies with no photolysis, experiments were performed under identical conditions except for the addition or absence of hydrogen. A decrease in intensity observed in the peaks associated with the π complex indicates its formation is also inhibited by the presence of hydrogen. No formation of an Ni/C_2H_4 complex was observed.

Discussion

Nickel/acetylene reaction products of varying stoichiometries were isolated in argon matrices at 12 K. Table II summarizes all peak assignments, both before and after photolysis, of frequencies measured from Fourier-transform infrared spectra.

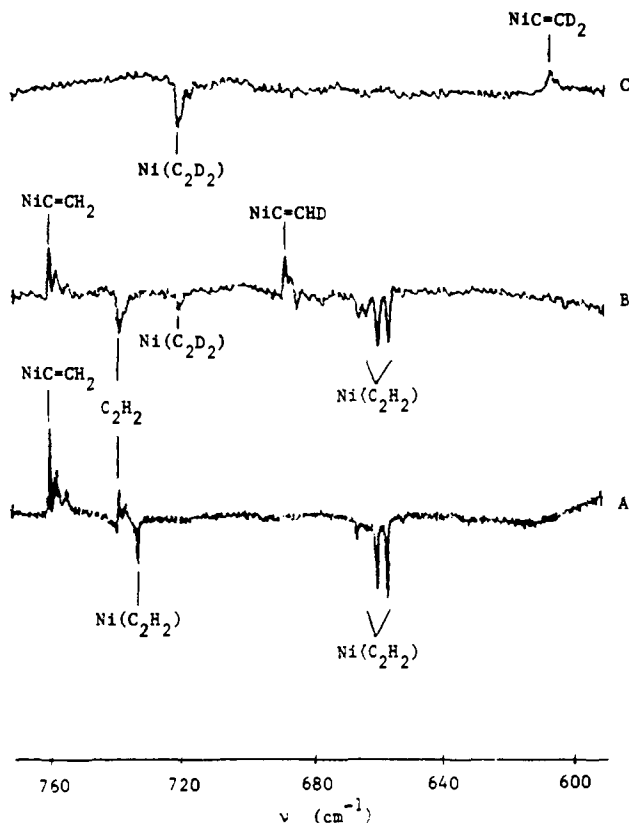


Figure 2. An isotopic study. FTIR difference spectra ($X - Y$) of the C-H deformation region of adducts and photoproducts of nickel acetylene: (X) after 30 min of photolysis with $\lambda \geq 400$ nm; and (Y) after deposition, no photolysis. Molar ratio of Ni:C₂H₂:Ar \sim 5:1:1000: (A) Ni with C₂H₂ in Ar; (B) Ni with C₂HD in Ar; and (C) Ni with C₂D₂ in Ar.

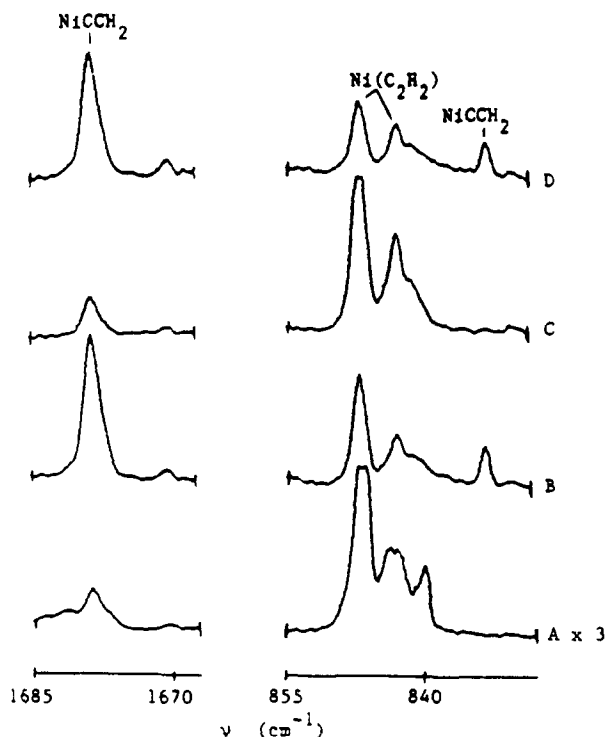


Figure 3. A reversible photolysis study. The C=C stretching and C-H deformation regions of nickel/acetylene products. Molar ratio of Ni:C₂H₂:Ar \sim 5.0:4.2:1000: (A) no photolysis; (B) $\lambda \geq 400$ nm, 0.5 h; (C) $360 \text{ nm} \geq \lambda \geq 280$ nm, 0.5 h; and (D) $\lambda \geq 400$ nm, 0.5 h.

I. Nickel/Acetylene Complexes. Ni(C₂H₂) Complex. The interaction between monoatomic nickel and an acetylene molecule

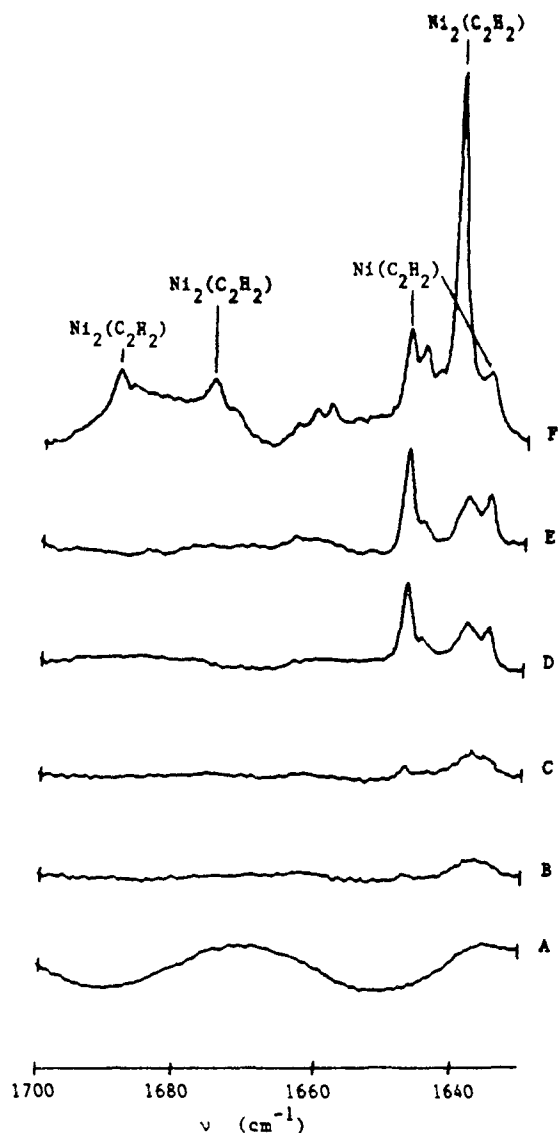


Figure 4. A nickel concentration study. Molar ratio of C₂H₂:Ar \sim 1.1:1000. Molar ratio of Ni:1000 Ar: (A) 0.0, (B) 0.55, (C) 1.0, (D) 5.0, (E) 9.7, and (F) 20.6.

in an argon matrix was found to be through the π system of acetylene. A reduction from a triple to a double bond of the alkyne was measured. Isotopic studies established the equivalency of both the hydrogen and carbon atoms and provided support for our assigned structure V for the Ni(C₂H₂) π complex. Table III lists the frequencies and vibrational mode assignments for this complex.

The infrared value for the $\nu(\text{C}=\text{C})$ mode of Ni(^{12/13}C₂H₂) is shifted to a higher frequency. This unexpected result may be interpreted in terms of a coupling between the $\nu(\text{C}=\text{C})$ mode and an overtone of a $\nu(\text{C}-\text{H})$ deformation mode.

π complexes of acetylene with gold,⁵ copper,^{4,8} lithium,¹⁷ and nickel⁸ in cryogenic matrices have been reported. Literature values for the $\nu(\text{C}=\text{C})$ stretching frequencies of acetylene and its metal complexes follow: C₂H₂, 1973.8 cm⁻¹; Cu(C₂H₂), 1870 cm⁻¹; Li(C₂H₂), 1655 cm⁻¹; and Ni(C₂H₂), 1729 cm⁻¹. We measured a frequency of 1647.4 cm⁻¹ for our Ni(C₂H₂) π complex. This frequency is in close proximity to the value of 1629 cm⁻¹ for the $\nu(\text{C}=\text{C})$ stretching of ethylene²³ and demonstrates considerable weakening of the C \equiv C bond in the π complex. Thus, there is considerable Ni d_z electron transfer into an antibonding π^* orbital of C₂H₂. This implies a strengthening of and considerable covalent character in the Ni-C bonds of the π complex, structure V.²⁴

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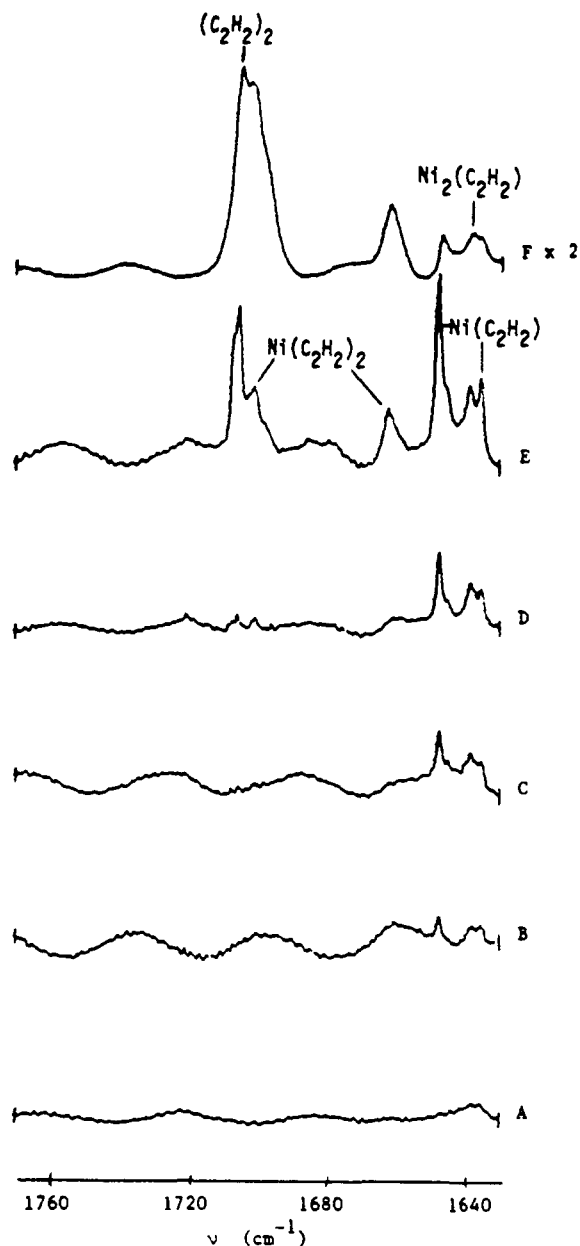


Figure 5. An acetylene concentration study. Molar ratio of Ni:Ar \sim 2.4:1000. Molar ratio of C_2H_2 :1000 Ar: (A) 1.3, no Ni; (B) 1.3; (C) 2.6; (D) 5.0; (E) 23.8; and (F) 94.2.

Studies of organometallic complexes containing nickel and an acetylene ligand provide additional insight into our proposed structure for the nickel-acetylene π complex. The electronic structures of zerovalent nickel π complexes such as $Ni(HC\equiv CH)(HNC)_2$ and $Ni(C_6H_5C\equiv CC_6H_5)(t-BuNC)_2$ have been investigated with the INDO method.²⁴ These side-on coordinated nickel-acetylene complexes favor a square-planar geometry. The increments in $C\equiv C$ bond lengths reflect the net effects of σ donation and π back-donation; bond length increases linearly with increasing donation. The greater the extent of back-donation of electrons from nickel to acetylene, the greater the Ni—C covalent bond strength and the weaker and more elongated the $C\equiv C$ bond. Thus, the substantially lengthened $C\equiv C$ bond in the $Ni(C_2H_2)_2$ π complex indicates strong Ni—C bonds and correlates well with our proposed structure V.

$Ni(C_2H_2)_2$ Complex. A bis(acetylene)-nickel complex was formed at high acetylene concentrations. The observed FTIR frequencies are reported in Table II. These frequencies are in

Table II. Infrared Measured Frequencies (cm^{-1}) for Nickel/Acetylene Products in Solid Argon

assignment	Ni/ C_2H_2	Ni/ $^{12/13}C_2H_2$	Ni/ $^{13}C_2H_2$	Ni/ C_2HD	Ni/ C_2D_2
A. Before Photolysis					
$Ni(C_2H_2)_2$	1705.4	1677.5	1648.0		
$Ni(C_2H_2)_2$	1699.9	1671.7	1642.2		
$Ni(C_2H_2)_2$	1696.9	1670.4	1639.3		
$Ni_2(C_2H_2)$	1688.9				
$Ni_2(C_2H_2)$	1675.1				
$Ni(C_2H_2)_2$	1661.1				
$Ni(C_2H_2)$	1647.4	1692.4	1568.6	1582.6	1540.6
$Ni_2(C_2H_2)$	1639.7				
$Ni(C_2H_2)$	1638.4	1590.7	1560.3	1573.1	1531.9
$Ni(C_2H_2)$	1634.8		1558.6	1571.5	1529.3
$Ni(C_2H_2)$	847.3	842.3	836.7	833.1	718.6
$Ni(C_2H_2)$	843.2	837.7	831.9	829.5	715.0
$Ni(C_2H_2)$				827.6	
$Ni(C_2H_2)$	840.3	834.8	828.9	824.9	
$Ni(C_2H_2)_2$	778.3	773.3	768.5		
$Ni(C_2H_2)$				736.7	
$Ni(C_2H_2)$	730.9	729.5	728.5	675.9	506.2
$Ni(C_2H_2)$				521.2	
$Ni(C_2H_2)$	658.1	657.2	655.1		548.4
$Ni(C_2H_2)$	655.0	652.4	651.2		542.9
$Ni(C_2H_2)$	548.6	539.9	533.8	521.2	507.4
$Ni(C_2H_2)$	545.3	536.1	529.7	525.3	503.3
$Ni(C_2H_2)$	539.6	531.3	525.8		
B. After Photolysis					
$NiCCH_2$	2983.5	2980.0	2977.3		
$NiCCH_2$	2889.1	2887.6	2886.9		
$NiCCH_2$	1678.8	1671.8		1642.6	1626.2
$NiCCH_2$		1660.8		1634.4	1618.0
$NiCCH_2$	1635.0	1616.1	1586.6	1629.6	1613.2
$NiCCH_2$		1608.5			1575.6
$NiCCH_2$	1623.8	1605.3	1575.8		1556.7
$NiCCH_2$		1598.2			
$NiCCH_2$	1522.3	1520.4	1507.6		1438.9
$NiCCH_2$	1517.9	1516.1	1503.7		
$NiCCH_2$	1511.3	1509.5	1496.3		1431.9
$NiCCH_2$	833.6	828.5	821.0		
$NiCCH_2$		827.1			
$NiCCH_2$	758.6	758.0	751.5	686.8	606.3
$NiCCH_2$		752.0			
$NiCCH_2$	756.4	755.8	749.1	684.8	
$NiCCH_2$		749.7			
$NiCCH_2$	753.3	752.9	746.1	682.0	
$NiCCH_2$		746.7			

the $\nu(C\equiv C)$ stretching region and indicate an additional acetylene molecule has π -complexed to a nickel atom.

Ozin and co-workers have reported infrared and UV-vis spectra for $Ni(C_2H_2)$ and $Ni(C_2H_2)_2$ π complexes isolated in argon and krypton matrices at 15 K.⁸ Their frequency assignments for the $Ni(C_2H_2)$ and $Ni(C_2H_2)_2$ complexes in argon matrices are included in Table II as a basis for comparison. We propose that their $Ni(C_2H_2)$ π complex is actually the bis(acetylene) complex $Ni(C_2H_2)_2$ since their experiments were performed at very high acetylene concentrations (C_2H_2 :Ar \sim 1:10–100). As shown in Figure 1, the only peaks in the 1770–1630- cm^{-1} region at low C_2H_2 concentrations are those we have assigned to the mononickel acetylene π complex. The bis(acetylene)-nickel peaks are apparent at higher acetylene concentrations.

$Ni_2(C_2H_2)$ Complex. The presence of peaks in the double bond region of the infrared spectrum of the dinickel-acetylene complex provides some information for possible structures of the dinickel complex in which the triple bond has been reduced to a double bond. Most dinuclear metal-acetylene complexes have carbon-carbon bond lengths between 1.31 and 1.38 Å, characteristic of a double bond.^{20,25} Single-crystal X-ray diffraction data for $(\eta^5-C_5H_5Ni)_2CH\equiv CH$ give a " $C\equiv C$ " bond distance of 1.341 (6)

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Table III. Infrared Frequencies (cm⁻¹) for the Nickel Acetylene π -Complex Isotopomers in Solid Argon^a

approximate type of vibrational mode	Ni(C ₂ H ₂)	Ni(^{12/13} C ₂ H ₂)	Ni(¹³ C ₂ H ₂)	Ni(C ₂ HD)	Ni(C ₂ D ₂)
CH stretch	(3112) ^b				
asymmetric C=C stretch	(1729) ^c				
	1647.4	1692.4	1568.6	1582.6	1540.6
	1638.4	1590.7	1560.3	1573.1	1531.9
	1634.8		1558.6	1571.5	1529.3
in-plane CH or CD s-bend	847.3	842.3	836.7	833.1	718.6
	843.2	837.7	831.9	829.5	715.0
				827.6	
	840.3	834.8	828.9	824.9	
			736.7		
out-of-plane CH or CD a-bend	730.9	729.5	728.5	675.9	548.4
				521.2	542.9
in-plane CH or CD bend	658.1	657.2	655.1		506.2
	655.0	652.4	651.2		
Ni-C stretch	(570/560)				
	548.6	539.9	533.8	525.3	507.4
	545.3	536.1	529.7	521.2	503.3
	539.6	531.3	525.8		

^aFrequencies in parentheses were obtained from ref 8. ^bSuspected band overlap of Ni(C₂H₂)_{1,2} in ν (CH) region. ^cOzin reported a frequency of 1760 cm⁻¹ for Ni(C₂H₂)₂ in an argon matrix.

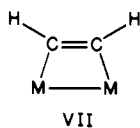
Table IV. Infrared Frequencies (cm⁻¹) for the Nickel Vinylidene Photolysis Product

approximate type of vibrational mode	CCH ₂ ^a	NiCCH ₂	Ni ¹² C ¹³ CH ₂	Ni ¹³ C ¹³ CH ₂	NiCCHD	NiCCD ₂
CH ₂ or CD ₂ a-stretch	3312	2983.5	2980.0	2977.3		
CH ₂ or CD ₂ s-stretch	3217	2889.1	2887.6	2886.9		
C=C stretch	1719	1635.0	1616.1	1586.6	1642.6	1626.2
			1605.3			
		1623.8	1608.5	1575.8	1629.6	1618.0
			1598.2			
CH ₂ scissors	1289					
CH ₂ or CD ₂ rock ^b	422	833.6	828.5	821.0		
			827.1			
CH ₂ or CD ₂ wag ^b	800	758.6	758.0	751.5	686.8	606.3
			752.0			
		756.4	755.8	749.1	684.8	
			749.7			
		753.3	752.9	746.1	682.0	
		746.7				

^aCalculated frequencies (cm⁻¹) for the ground state of vinylidene were obtained from ref 32. ^bThese are tentative assignments based on relative peak intensities.

Å for the acetylene ligand.²⁶ The infrared spectra of dinuclear metal-acetylene complexes provide further support for a trend toward double bond character. The measured frequencies 1526 and 1562 cm⁻¹ for [Ni₂{ μ_2 (η^2 -Me₃SiC₂SiMe₃)}(cod)₂] and [Ni₂{ μ_2 (η^2 -CF₃C₂CF₃)}(*t*-BuNC)₄], respectively, are in the ν (C=C) stretching region.²⁷

One possible mode of bonding in these dinuclear metal complexes is shown in VII, where the acetylene ligand binds parallel to the M-M bond. Examples of organometallic clusters exhibiting



this type of bonding are [Pt₂(PhC₂Ph)(cod)₂] (cod = cyclo-octadiene)²⁷ and [Rh₂{ μ_2 (η^1 -CF₃C₂CF₃)}(CO)₂(η^5 -C₅H₅)₂].²⁸

However, this dimetallacyclobutene structure is rarely observed. Typically, the acetylene ligand binds in a μ_2 - η^2 fashion to give an M₂C₂ quasitetrahedral structure with a substantially increased acetylenic C≡C bond length.²⁰ From orbital symmetry considerations, the M₂C₂ quasitetrahedral structure is preferred over the metallacyclobutene mode of bonding.²⁹

Further support for our proposed structure of a bridging acetylene perpendicular to the nickel-nickel axis is gained from organometallic clusters. Much literature exists on acetylene-dimetal clusters with neutral ligands in which the acetylene binds perpendicular to the metal-metal bond.^{20,26,29,30} In particular, the electron density map of (η^5 -C₅H₅Ni)₂CH≡CH portrays an acetylene ligand perpendicular to the metal-metal bond. The acetylene ligand is cis bent and a double bond exists between the two nickel atoms.²⁶ Thus, a plausible structure for the dinickel acetylene complex is as shown in structure VIII, although one cannot totally rule out the possibility of alternative structures. We have also proposed bonding as in VIII for matrix-isolated diiron acetylene.⁹

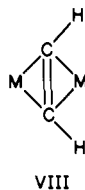
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II. Nickel Vinylidene. The identification of nickel vinylidene is based on isotopic studies which establish the equivalency of the hydrogen atoms and the inequivalency of the carbon atoms in the photolysis product. Upon examination of structures I–VI, only the vinylidene structure VI satisfies these criteria.

The nickel vinylidene assignment is further substantiated by vibrational mode assignments of FTIR frequencies, compiled in Table IV. The presence of two peaks in the $\nu(\text{C}=\text{C})$ stretching region can be attributed to either matrix site splitting or slightly different geometries of the nickel–vinylidene complex. Additional weak peaks at slightly higher frequencies in the $\nu(\text{C}=\text{C})$ stretching region for $\text{Ni}^{12}\text{C}^{12}\text{CH}_2$ and $\text{Ni}^{12}\text{C}^{13}\text{CH}_2$ are present in Figure 1. A reduced intensity for the sets of peaks assigned to these two isotopomers is also apparent. These effects most likely arise from a Fermi interaction of the combination mode due to the CH_2 scissors and the $\text{Ni}-\text{C}$ stretch with the $\text{C}=\text{C}$ stretch. The peak at 1678.8 cm^{-1} , clearly evident for the $\text{Ni}/\text{C}_2\text{H}_2$ system in Figures 1 and 3, is most likely due to this combination mode of the $\text{Ni}-\text{C}$ stretch and CH_2 scissors motion. Neither of these modes were directly observed, but their expected frequencies are such that their combination would produce a peak in this region.

Vibrational data obtained from photodetachment experiments converting the vinylidene anion $\text{H}_2\text{C}=\text{C}^-$ to the vinylidene radical $\text{H}_2\text{C}=\text{C}\cdot$ gave values of $1650 \pm 120\text{ cm}^{-1}$ for $\nu(\text{C}=\text{C})$ stretching and $1170 \pm 100\text{ cm}^{-1}$ for $\delta(\text{CH}_2)$ bending in the ground state of vinylidene.³¹ A summary of calculated frequencies for vinylidene by Carrington et al. is included in Table IV and further corroborates the presence of nickel vinylidene.³²

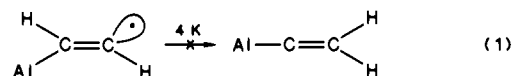
$\text{Ni}(\text{C}_2\text{H}_2)/\text{NiCCH}_2$ Interconversion. Extensive theoretical and experimental studies of acetylene/vinylidene isomerization have been reported. Theoretical studies employing ab initio calculations have estimated an average value of around 40 kcal/mol for the acetylene/vinylidene energy separation.^{33–36} The lifetime of ground-state singlet vinylidene is calculated as 10^{-11} s ,³⁵ comparing favorably to an experimental value of 10^{-10} s .³⁷ Excited-state triplet vinylidene radicals in vacuum-UV photolysis studies absorbed at 137.4 nm and had a lifetime of 0.1–250 μs .³⁸ The energy barrier for singlet vinylidene/acetylene rearrangement is estimated at 2–4 kcal/mol,³² compared to a barrier of about 50 kcal/mol for triplet vinylidene.³⁹ The relatively long lifetime of triplet vinylidene increases its susceptibility to chemical reactions and suggests it is the reactive state.⁴⁰ Laufer proposes that triplet vinylidene is the carrier in quenching of vinylidene radicals by helium.³⁸

Although vinylidene is less stable than acetylene, the vinylidene anion is more stable than the acetylene anion. The electron affinity of acetylene is -1.83 eV ; the addition of an electron to an antibonding π^* orbital of acetylene is unfavorable. In the vinylidene anion the added electron occupies the nonbonding $2b_2$ orbital which

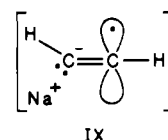
is vacant in singlet $\text{H}_2\text{C}=\text{C}$. The subsequent $\pi^*\text{CH}_2(1b_2)$ and $\pi^*\text{CH}_2(3b_2)$ orbital interactions are stabilizing and justify a positive electron affinity of 0.51 eV for vinylidene.⁴¹ Thus, the rearrangement of the acetylene anion to the vinylidene anion is quite reasonable. The considerable back-bonding occurring in the $\text{Ni}(\text{C}_2\text{H}_2)$ π complex could provide much electron density and anionic character to the $\text{HC}=\text{CH}$ molecule, subsequently lowering the $\text{HC}=\text{CH}^- \rightarrow ^-\text{CCH}_2$ energy barrier.

The addition of an electron to acetylene is energetically unfavorable. However, in rare gas matrices with electron-donating and electron-accepting molecules, photons of unexpectedly low energy induce electron transfer. These photons are several electron volts below the ionization potential of the donor. The cations and anions are effectively separated in the resulting matrix.⁴² In the synthesis of sodium vinylidene in an argon matrix Kasai proposed that photoirradiation with $\lambda \geq 580\text{ nm}$ produced a charge-transfer complex consisting of an isolated acetylene anion and sodium cation. Further irradiation with $\lambda \geq 500\text{ nm}$ resulted in rearrangement of $\text{Na}^+(\text{C}_2\text{H}_2)^-$ to sodium vinylidene.¹⁹

In matrix-isolation studies of the $\text{Al}/\text{C}_2\text{H}_2$ system Kasai observed the vinyl adduct II which exhibited photoinduced cis/trans isomerization.⁶ Ab initio SCF calculations predicted aluminum vinylidene is 12.5 kcal/mol more stable than vinyl aluminum.^{36,43} However, in rare gas matrices at 4 K the barrier height of 39.1 kcal/mol prevents vinyl/vinylidene isomerization, as in (1).



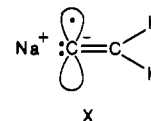
Thus the vinyl structure II may be a short-lived intermediate to the metal vinylidene structure VI. We may be producing a vinyl nickel intermediate which subsequently provides enough electron density and energy to cause isomerization to nickel vinylidene. Indeed, evidence indicates the acetylene/vinylidene barrier is reduced by a metal atom. As previously stated, the acetylene/vinylidene conversion is calculated to be 12.5 kcal/mol exothermic with the addition of an Al atom. A vinyl intermediate IX is proposed in the synthesis of matrix-isolated sodium vinylidene.¹⁹ Vinyl gold and gold vinylidene were both identified in



an adamantane matrix at 77 K, whereas only vinyl gold was observed in rare gas matrices at 4 K.^{18,5} The initially formed vinyl gold purportedly undergoes a rapid 1,2-hydrogen shift at 77 K. The higher temperature matrix could supply the energy necessary to cross the barrier for vinyl/vinylidene isomerization.

The photoreversibility between the nickel–acetylene π complex and nickel vinylidene is clearly established in Figure 3. The presence of the infrared band at 1678.8 cm^{-1} before photolysis indicates the spontaneous formation of a small amount of nickel vinylidene.

Structure. Theoretical calculations on acetylene/vinylidene isomerization were performed on vinylidene with a linear structure at the carbon bearing the unpaired electron.^{36,43} This is the case in the proposed structure for sodium vinylidene X. The Na–C “bond” is actually quite ionic, with sp hybridization of the carbon bearing the electron existing in a p orbital.¹⁹ ESR studies of gold



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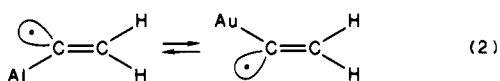
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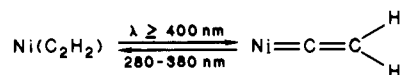
vinylidene indicate fluxional behavior as depicted in (2).¹⁸ The



Au-C bond contains less ionic character than the Na-C bond, yet Au prefers a lone electron configuration. Nickel vinylidene has equivalent hydrogens, and atomic nickel tends to form double bonds. We thus tentatively propose a linear structure for nickel vinylidene as in sodium vinylidene but with a Ni-C double bond. Unfortunately, the nickel-carbon stretching frequency was not detected in the present study.

Concluding Remarks

1. The first identification of a transition-metal vinylidene by Fourier-transform infrared spectroscopy has been reported. Nickel is shown to form a π complex with acetylene which photoreversibly rearranges to nickel vinylidene:



The implications of this acetylene/vinylidene interconversion are worth noting. Although an isolated acetylene/vinylidene reaction is endothermic, this same conversion becomes favorable in the presence of nickel, gold,¹⁸ sodium,¹⁹ and theoretically aluminum.³⁶ Other endothermic reactions such as methylcarbene/ethylene and methylnitrene/methylenimine rearrangements may become exothermic when complexed to a metal atom, cluster, or surface.^{43,44} Metal systems that open new reaction channels and effectively convert endothermic reactions to exothermic processes are invaluable in catalysis and surface chemistry.

2. The complexes $\text{Ni}(\text{C}_2\text{H}_2)_2$, $\text{Ni}(\text{C}_2\text{H}_2)_3$, and $\text{Ni}_2(\text{C}_2\text{H}_2)$ have been isolated in argon matrices. The acetylene donates electrons through the $\text{C}\equiv\text{C}$ π orbitals and is a π -acceptor through the $\text{C}\equiv\text{C}$ π^* orbitals in these complexes, classical Dewar-Chat-Duncanson bonding.

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Crystal and Molecular Structures of Double Macrocyclic Inclusion Complexes Composed of Cyclodextrins, Crown Ethers, and Cations

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Abstract: The crystal structures of γ -cyclodextrin-12-crown-4-LiSCN (3:3:1) inclusion complex ($\text{C}_{48}\text{H}_{80}\text{O}_{40}\cdot\text{C}_8\text{H}_{16}\text{O}_4\cdot\frac{1}{3}(\text{LiSCN})\cdot 7.7\text{H}_2\text{O}$) (1) and γ -cyclodextrin-12-crown-4-KCl (3:3:1) inclusion complex ($\text{C}_{48}\text{H}_{80}\text{O}_{40}\cdot\text{C}_8\text{H}_{16}\text{O}_4\cdot\frac{1}{3}(\text{KCl})\cdot 9\text{H}_2\text{O}$) (2) were determined by X-ray analyses. Crystals of 1 and 2 are isomorphous with space groups $P4_212$, $a = b = 23.75$ (2) Å, $c = 22.92$ (3) Å for 1 and $a = b = 23.842$ (2) Å, $c = 23.132$ (2) Å for 2. Three γ -cyclodextrins are stacked along the fourfold rotation axis forming a channel type structure, and each of them includes a 12-crown-4 molecule with similar orientation. Three 12-crown-4 molecules have the same C_4 ring conformations, and two of them form a 2:1 sandwich structure complex of (12-crown-4)₂-cation, which is included in the hydrophobic channel formed by two γ -cyclodextrins, while the third one is free from a cation.

Cyclodextrins (CDs) are truncated cone-shaped cyclic oligosaccharides composed of six, seven, or eight α -1,4-linked D-glucoses. They have hydrophobic cavities and primary hydroxyl groups on the narrow sides of macrocycles (head) and secondary hydroxyl groups on the other sides (tail). As they are able to form stable inclusion complexes with various organic compounds as guest molecules, they have received much attention as relatively low molecular weight models for biological macromolecules.^{1,2} Many structures of α -CD and β -CD complexes including hydrates were intensively investigated by the X-ray method. However, few X-ray studies on γ -CD complexes have been reported: two uncomplexed-hydrated γ -CDs^{3,4} and the γ -CD-propan-1-ol complex.⁵ In the γ -CD-propan-1-ol complex, the guest molecules, propan-

1-ol, are not located in the cavities of γ -CDs, so structures of the inclusion complexes of γ -CDs, especially the locations of guest molecules, have not been elucidated yet.

On the basis of space-filling models, Vögtle and Müller indicated that small crown ether and cryptand just fit into the conical cavity of γ -CD, and mixing of aqueous solutions of γ -CD and 12-crown-4 leads to crystallization of a 1:1 inclusion complex. They also showed that a few cation complexes of crown ethers and cryptands, such as the 12-crown-4-LiSCN complex, can form inclusion complexes with γ -CDs.⁶

In order to elucidate the interaction between hydrophobic cavities of γ -CDs and crown ethers having an ability to form cation complexes, the X-ray crystallographic study of γ -CD-12-crown-4 inclusion complex 3 was undertaken by us.⁷ According to this study, the γ -CDs include 12-crown-4 molecules by a 1:1 ratio, forming the novel double macrocyclic inclusion complexes, and these 12-crown-4 molecules have C_4 ring conformations, which

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