Nickel and Cyclopropane Reactions and Photochemistry Using Matrix-Isolation FTIR Spectroscopy. Nickelacyclobutane Synthesis and Photofragmentation

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The reactions between atomic nickel and cyclopropane in cryogenic matrices have been investigated. Atomic nickel was observed to insert spontaneously into a carbon–carbon bond of cyclopropane and form a four-membered unligated metallacycle, nickelacyclobutane. Visible photolysis induced metathesis of this metallacycle through Ni–C and C–C bond cleavages, resulting in a methylenenickel ethylene π complex, $CH_2Ni(C_2H_4)$. With UV irradiation this π complex underwent activation of one of the C–H bonds of ethylene and rearranged to vinylnickel methyl, $C_2H_3NiCH_3$. $C_2H_3NiCH_3$ decomposed and released methane upon extended UV photolysis. Experimental results with cyclopropane-d_6 paralleled those of the undeuteriated system, except $CD_2Ni(C_2D_4)$ was stable and underwent no further reactions or decomposition with UV irradiation.

Introduction

Transition metal/hydrocarbon interactions have received considerable attention in recent years, particularly in an attempt to establish their roles in synthetic and catalytic reactions. The reactions of transition-metal complexes with strained alkane ring systems have been extensively studied. The activation of cyclopropanes by transition metals often results in oxidative addition of a carbon–carbon bond to the metal, forming a four-membered metallacyclobutane.[1] This type of reaction has been implicated in organic processes such as the metal-assisted conversion of substituted cyclopropanes to olefins and the palladium-catalyzed ring opening of cyclopropanes.[2,3] Metallacyclobutanes have also been proposed as intermediates in alkene polymerization, olefin metathesis, cyclopropanation reactions, and retrocarbene additions of cyclopropanes.[4-8]

Substituted metallacyclobutanes have been isolated and characterized.[9-14] Zeise's dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$, reacts with cyclopropanes to yield stable platinacyclobutanes which can be isolated for further studies.[10] The rearrangement and reactivity of these isolated metallacyclobutanes depend on a number of factors such as steric considerations, ligand electronegativities, and solvent interactions.[11-14]

To eliminate solvent and ligand effects Beauchamp et al.[15] studied gas-phase reactions of cyclopropane and metal ions in an ion beam apparatus. He generated metal carbene ions and determined their bond dissociation energies. Kinetically excited manganese,[16] cobalt,[17,18] and nickel ions[15] reacted with cyclopropane to produce the corresponding metal carbene ions, presumably through the decomposition of the intermediate metallacycles. Interestingly, kinetically excited iron ions were unreactive with respect to metal carbene formation.[17]

Matrix-isolation studies were initiated in this laboratory to synthesize an intermediate metallacycle from the reaction of a metal atom and cyclopropane. Previously, preliminary studies of iron and cyclopropane have indicated the formation of a methyleneiron ethylene π complex, presumably through an intermediate metallacycle.[19] In studies of nickel and cyclopropane, reported here, it was observed that the unligated metallacycle nickelacyclobutane was spontaneously produced when nickel atoms and cyclopropane were cocondensed in an argon matrix at 12 K. Metathesis of nickelacyclobutane occurred through Ni–C and C–C bond cleavages and produced methylenenickel ethylene π complex, $CH_2Ni(C_2H_4)$, with $\lambda \geqslant 500$ nm irradiation. Upon UV photolysis $CH_2Ni(C_2H_4)$ underwent C–H bond activation and rearranged to vinylnickel methyl, $C_2H_3NiCH_3$. $C_2H_3NiCH_3$ decomposed with additional UV irradiation and released methane. The first microsynthesis, isolation, and subsequent decomposition of an unligated nickelacyclobutane are presented here.

Experimental Section

A recent publication contained a detailed description of the matrix-isolation apparatus interfaced to a vacuum IBM IR-98 Fourier transform infrared spectrometer.[20] An alumina crucible

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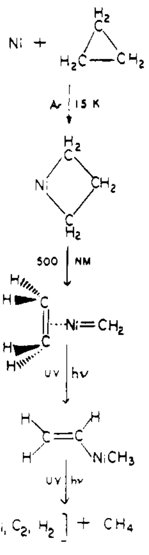
Table I. FTIR Frequencies (cm^{-1}) Measured for Cyclopropane and Cyclopropane-d_6 in Solid Argon[a]

vibrational mode	C_3H_6	C_3D_6
ν_1, CH_2 or CD_2 s-stretch	3038 (R)	2236 (R)
ν_2, CH_2 or CD_2 scissors	1479 (R)	1274 (R)
ν_3, ring stretch	1188 (R)	956 (R)
ν_4, CH_2 or CD_2 twist	1124.8	747.8
ν_5, CH_2 or CD_2 wag	1063.1	883.5
ν_6, CH_2 or CD_2 a-stretch	3091.8	2329.4
ν_7, CH_2 or CD_2 rock	864.7	611.8
ν_8, CH_2 or CD_2 s-stretch	3016.6	2208.3
ν_9, CH_2 or CD_2 scissors	1434.3	1068.1
ν_{10}, CH_2 or CD_2 wag	1025.0	891.2
ν_{11}, ring deformation	875.3	714.4
ν_{12}, CH_2 or CD_2 a-stretch	3082 (R)	2329 (R)
ν_{13}, CH_2 or CD_2 twist	1188 (R)	940 (R)
ν_{14}, CH_2 or CD_2 rock	739 (R)	528 (R)

[a] Frequencies for Raman-active modes of C_3H_6(g) and C_3D_6(g) were obtained from ref 22.

Scheme I



containing nickel metal (Mackay, 99.5%) was enclosed in a tantalum furnace (Fansteel Metals). Nickel vapors were obtained by resistively heating the tantalum furnace over the range 1150–1450 °C, as determined by a microoptical pyrometer (Pyrometer Instrument Co.). A quartz crystal microbalance was used to determine the rates of deposition of nickel, cyclopropane (Matheson, 99.0% min.), and argon (Matheson, 99.9998%). The concentration of nickel was varied from 0 to 16 parts per thousand argon, while the concentration of cyclopropane was varied from 0 to 10 parts per thousand.

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

Experiments were also conducted involving the deposition and photochemical behavior of cyclopropane-d_6 (MSD Isotopes, 98.0% min.) with nickel in excess argon under similar conditions.

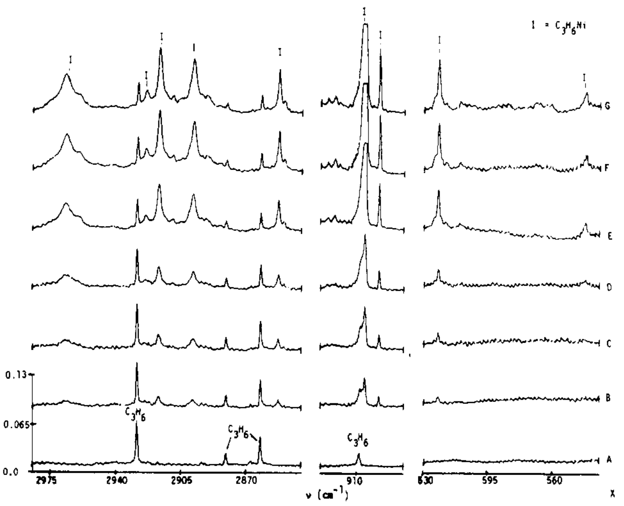


Figure 1. FTIR spectra for Ni + C_3H_6 reaction products with C_3H_6:Ar ≈ 5.0:1000 and various Ni concentrations: A, 0.0; B, 0.6; C, 1.3; D, 2.3; E, 5.1; F, 11.7; and G, 16.0 per 1000 Ar.

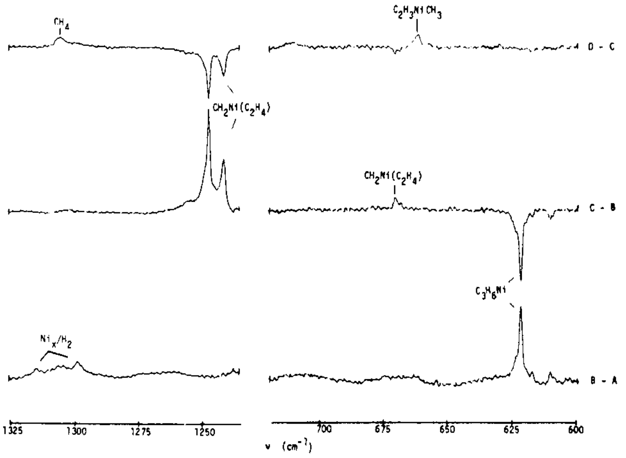


Figure 2. A photolysis study showing FTIR difference spectra of Ni/C_3H_6 products and photoproducts (molar ratio of Ni:C_3H_6:Ar ≈ 3.5:4.6:1000; period of photolysis = 15 min): A, no nickel; B, no photolysis; C, λ ≥ 500 nm; D, 360 nm ≥ λ ≥ 280 nm. The peaks at 1314.0 and 1298.0 cm^{-1} are due to reactions of nickel with residual molecular hydrogen in the vacuum system.[21]

Results

The Fourier transform infrared spectra of C_3H_6 and C_3D_6 in solid argon in the region between 4000–500 cm^{-1} were obtained for reference purposes. Table I contains the measured frequencies and their mode assignments.

The reactions and photochemistry of nickel atoms and cyclopropane in an argon matrix are summarized in Scheme I. The photochemical behavior and frequency assignments of the species in Scheme I are given here. A detailed description of the basis for these peak assignments is given in the Discussion.

Figure 1 depicts results obtained from a typical nickel concentration study. When nickel was cocondensed with cyclopropane in an argon matrix, new product peaks appeared at low nickel concentrations and increased steadily with increasing nickel concentration. These peaks, labeled as I in Figure 1, were assigned to a mononickel mono(cyclopropane) product identified as nickelacyclobutane.

A typical representation of subtraction plots used to elucidate peak assignments is given in Figure 2. The lowest spectrum in Figure 2 is a plot of cyclopropane in argon subtracted from a plot of nickel and cyclopropane in argon. Peaks associated with the mononickel mono(cyclopropane) product nickelacyclobutane are readily distinguishable.

Upon irradiation with λ ≥ 500 nm the peaks assigned to nickelacyclobutane disappeared as new peaks appeared.

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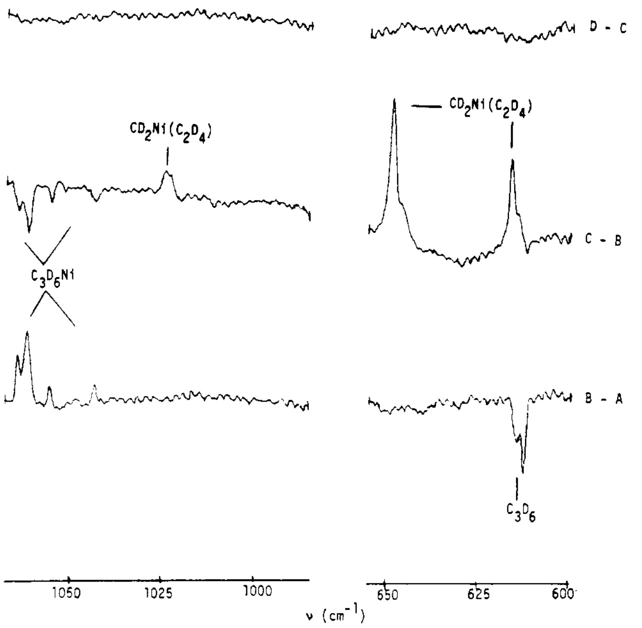

Figure 3. A photolysis study showing FTIR difference spectra of Ni/C_2D_6 products and photoproducts (molar ratio of $Ni:C_3D_6:Ar$ ≈ 8.6:6.0:1000; period of photolysis = 15 min): A, no nickel; B, no photolysis; C, $\lambda \geq 500$ nm; D, 360 nm $\geq \lambda \geq$ 280 nm.

The frequencies corresponding to these peaks have been assigned to methylenenickel ethylene π complex $CH_2Ni(C_2H_4)$. Irradiation with UV photolysis resulted in a disappearance of the peaks associated with $CH_2Ni(C_2H_4)$ and a concomitant growth of a new set of frequencies. The spectrum of the UV photoproduct was assigned to a vinylnickel methyl species, $C_2H_3NiCH_3$. Upon extended photolysis the peaks associated with $C_2H_3NiCH_3$ decreased and methane was produced.

Figure 3 contains subtraction plots for a photolysis study of nickel and cyclopropane-d_6. The appearance of peaks assigned to nickelacyclobutane-d_6 concurrent with the disappearance of peaks associated with cyclopropane-d_6 is apparent from the plot of a C_3D_6/Ar spectrum subtracted from a $Ni/C_3D_6/Ar$ spectrum. Peaks formed from $\lambda \geq 500$ nm irradiation of nickelacyclobutane-d_6 were assigned to $CD_2Ni(C_2D_4)$. $CD_2Ni(C_2D_4)$ was quite stable and did not decompose with UV irradiation, even after an extended period of photolysis.

Discussion

Scheme I summarizes the reactions and photochemistry of nickel and cyclopropane cocondensed in an argon matrix. Comparison of observed frequencies with known frequencies of similar compounds, isotopic studies, photochemical behavior of peaks assigned to specific complexes, and most plausible intermediates and pathways support this proposed reaction sequence.

Table II summarizes the observed frequencies assigned to nickelacyclobutane and nickelacyclobutane-d_6. Although the frequencies for an unligated metallacyclobutane are unknown, frequencies for gas-phase cyclobutane and cyclobutane-d_8 have been measured and are included in Table II as a basis for comparison. One notes substantial correlation between the various modes of cyclobutane and the product species, particularly for the CH_2 stretching and ring deformation modes. The set of frequencies at 833.8, 831.2, and 827.6 cm^{-1} observed for the deuteriated case did not have any correlating features in the undeuteriated system. These frequencies could possibly be due to ring stretching, reported as 882 cm^{-1} for cyclobutane-d_8. Thus, frequency comparisons substantiate the identification of the mononickel mono(cyclopropane) product as nickelacyclobutane. In addition, major support for the assignment of a metallacycle to the mononickel mono(cyclopropane) product is implied by the formation of $CH_2Ni(C_2H_4)$ with $\lambda \geq 500$ nm irradiation, precisely the expected decomposition product resulting from metathesis of nickelacyclobutane.

Table II. FTIR Frequencies (cm^{-1}) Measured for Cyclobutane,[a] Nickelacyclobutane,[b] Nickelacyclobutane-d_6,[b] and Cyclobutane-d_8,[b] in Solid Argon

approx type of vibrational mode	C_4H_8	C_3H_6Ni	C_3D_6Ni	C_4D_8
CH_2 or CD_2 stretch	2987	2966.9	2232.0	2242
		2916.8	2166.4	
	2897	2898.3	2162.8	
	2878	2852.0	2120.6	
CH_2 or CD_2 scissor	1447		1060.9	1078
			1055.1	
CH_2 or CD_2 wag	1257		1042.8	1048
ring stretch			833.8	882
			831.2	
			827.6	
ring deformation	926	926.1	766.3	746
		922.3		
ring deformation	898	905.9	727.8	734
		898.2	724.9	
			723.2	
CH_2 rock	627	621.9		
		617.6		
		610.6		
NiC stretch		542.1		

[a] Frequencies for C_4H_8(g) and C_4D_8(g) were obtained from ref 22. [b] Only frequencies of the most intense peaks are listed.

The oxidative addition of cyclopropanes to metal centers to produce a metallacycle involves C–C rather than C–H bond activation and cleavage. Cyclopropane has the strongest C–H bonds of any alkane, 106.3 kcal/mol.[23] The C–C bonds are very weak and should be susceptible to metal insertion. The relief of ring strain produced by ring opening has been claimed to be the major driving force for these reactions.[14] The exact mechanisms of cyclopropane ring opening have been extensively studied. Two mechanisms have been proposed for the palladium-induced ring opening of cyclopropanes: edge activation of a carbon–carbon bond resulting in retention of stereochemistry and corner activation producing stereochemical inversion.[3] In a theoretical study of the cyclopropane ring opening by a ligand-free palladium(0) atom, the calculated energy for palladacyclobutane is 6 kcal/mol higher than for palladium and cyclopropane.[24] The edge metalation has an energy barrier of 17 kcal/mol, approximately half the magnitude of the barrier for corner metalation. However, ligated palladium(II) complexes were found to change drastically the reaction barriers and favor corner activation.[25] This suggests that attack by an unligated nickel atom is most likely directed at the C–C bond, rather than at a corner carbon.

Identification of $CH_2Ni(C_2H_4)$ as the metathesis product of nickelacyclobutane was provided by comparison of the

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Table III. FTIR Frequencies (cm^{-1}) Measured for Methylenenickel Ethylene π Complex, Methylenenickel,[a] Ethylene Nickel Monoxide π Complex[b] and Ethylene Nickel π Complex[c] in Solid Argon

approx type of vibrational mode	$CH_2Ni(C_2H_4)$	$Ni{=}CH_2$	$NiO(C_2H_4)$	$Ni(C_2H_4)$
C=C stretch	1515.8 1514.3		1516.3	1468.0
CH_2 scissors (ethylene)	1246.8 1241.0		1244.1	1165.8
CH_2 wag (methylene)	795.5 784.2	791.9		
Ni–C stretch (methylene)	670.9	696.2		

approx type of vibrational mode	$CD_2Ni(C_2D_4)$	$Ni{=}CD_2$	$NiO(C_2D_4)$
CD_2 stretch (ethylene)	2215.6		2225.7
CD_2 stretch (methylene)	2158.9	2133.0	
C=C stretch	1365.6		1365.6
CD_2 scissors (methylene)	1023.3	993.6	
CD_2 scissors (ethylene)	954.6		955.3
Ni—C stretch (methylene)	648.5	641.7	
CD_2 wag (methylene)	615.9	627.0	

[a] Reference 26. [b] Reference 27. [c] Reference 28.

Scheme II

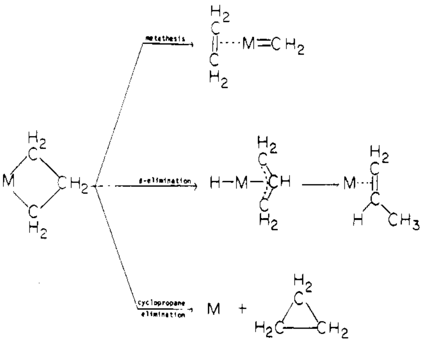

Table IV. FTIR Frequencies (cm^{-1}) Measured for Vinylnickel Methyl, Methylnickel Hydride,[a] and Vinylnickel Hydroxide[b] in Solid Argon

approx type of vibrational mode	$C_2H_3NiCH_3$	$HNiCH_3$	C_2H_3NiOH
CH_3 stretch	2933.9 2875.3	2950.5 2861.0	
CH_3 deformation	1163.0 1143.6	1139.0 1120.3	
CH_2 wag	937.7		937.7
CH_3 rock	661.9	642.7	

[a] Reference 26. [b] Reference 27.

measured frequencies with observed frequencies of similar compounds. This is shown in Table III. The C=C stretching and CH_2 scissoring of ethylene in $CH_2Ni(C_2H_4)$, at 1514.3 and 1246.8 cm^{-1}, respectively, were in excellent agreement with that observed for ethylene in $NiO(C_2H_4)$, 1516.3 and 1244.1 cm^{-1}. Both sets of frequencies were shifted to higher frequencies than observed in $Ni(C_2H_4)$, indicating an expected stronger π interaction between Ni and C_2H_4 for the latter species. The CH_2 wagging frequency in methylenenickel, $NiCH_2$, is seen to be within 4 cm^{-1} of that assigned to the methylene wagging in $CH_2Ni(C_2H_4)$.

Stretching frequencies were observed for both the ethylene and methylene moieties of $CD_2Ni(C_2D_4)$ at 2215.6 and 2158.9 cm^{-1}, respectively, and are very similar to the frequencies of 2225.7 and 2158.9 cm^{-1} for $NiO(C_2D_4)$ and $NiCD_2$. The C=C stretching frequency for $CD_2Ni(C_2D_4)$, 1365.6 cm^{-1}, was virtually identical with that of $NiO(C_2D_4)$. The CD_2 scissoring of the ethylene moiety and the Ni–C stretching in $CD_2Ni(C_2D_4)$ were within 10 cm^{-1} of the corresponding frequencies in $NiO(C_2D_4)$ and $NiCD_2$.

The initial nickel/cyclopropane reaction leads to a metallacyclobutane which may decompose by three basic routes as shown in Scheme II.[29] The first pathway, metathesis, involves C–C breakage of the ring and subsequent metal carbene olefin π complex formation. This mode of decomposition has been implicated as an intermediate step in several catalytic processes.[5-7] A second decomposition pathway, β-elimination, involves an intermediate metal hydride π-complexed to a propyl moiety which subsequently undergoes a hydride shift and propene elimination. Although the conversion of cyclopropane to propene is 8 kcal/mol exothermic[23] and η^3-allyl metal hydride complexes have been isolated from oxidative addition of cyclopropane to iridium complexes,[30] this pathway requires cleavage of a C–H bond rather than a C–C bond in the metallacycle. Cyclobutane has C–H bond strengths of 96.5 kcal/mol, whereas the C–C bonds are substantially weaker at 70–80 kcal/mol and are therefore the thermodynamically preferred sites of breakage.[23]

β-Elimination has been induced in organometallic complexes by removing electron density on the metal with such factors as strongly electron-withdrawing ligands or electronegative solvents.[30-32] However, in the absence of ligand or solvent effects, metathesis should be favored relative to β-elimination. The major product observed from kinetically excited cobalt ions and cyclopropane was the metal carbene, in approximately 85–90% yield. The other observed species accounted for less than 10% of the total products and were characteristic of highly endothermic processes, probably resulting from C–H bond cleavage.[18]

Thus, the decomposition of nickelacyclobutane to $CH_2Ni(C_2H_4)$ in our experiments is not surprising. The detection of frequencies associated with the metal carbene species in the nickelacyclobutane product provides conclusive evidence for metathesis rather than β-elimination as the decomposition process.

The third mode of decomposition, reductive elimination of cyclopropane, is a thermoneutral process. Cyclopropane elimination is a forbidden reaction for a metal in d^0–d^4 state, yet is allowed for a metal in d^6 state.[33] This correlates with a general pattern of predominant metathesis for low d electron counts and cyclopropane elimination without metathesis for d^6 complexes.[34] Also, cyclopropane elimination is more common for first-row transition metals, due to the increased metal carbon bond strengths as one progresses down the periodic table. Reductive elimination of cyclopropane could possibly be occurring with $\lambda \geq 500$ nm irradiation, but the major reaction is clearly the irreversible transformation to the nickel carbene species complexed to ethylene.

Peaks assigned to $CH_2Ni(C_2H_4)$ decreased with UV irradiation as peaks appeared in the CH_3 stretching, deformation, and rocking regions. These frequencies and their mode assignments are contained in Table IV. CH_3

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stretching, deformation, and rocking frequencies observed for hydridonickel methyl are also included in Table IV and further substantiate the presence of a methyl group. This was also indirect evidence of an $NiCH_3$ group, as no frequency was observed in the Ni–C stretching region. The CH_2 wagging frequency, 937.7 cm^{-1}, was identical with that observed for the vinyl group in vinylnickel hydroxide, C_2H_3NiOH, and corroborated the presence of a vinyl group. We have thus assigned the structure of vinylnickel methyl, $C_2H_3NiCH_3$, to this UV product.

Upon extended UV photolysis, the peaks assigned to $C_2H_3NiCH_3$ decreased and methane was produced. The other decomposition product(s), having a total empirical formula of C_2H_2Ni, is (are) unknown. Possible candidates would be $NiCCH_2$ and $Ni(C_2H_2)$. Nickel and acetylene have been shown to form an $Ni(C_2H_2)$ π complex which rearranged to $NiCCH_2$, nickel vinylidene, with $\lambda \geqslant 400$ nm irradiation.[35] $NiCCH_2$ was unstable in UV irradiation and photoreverted to the nickel acetylene π complex. However, the absence of frequencies assignable to either an $Ni(C_2H_2)$ π complex or $NiCCH_2$ with the disappearance of $C_2H_3NiCH_3$ suggests a different photofragmentation product. One possibility is the production of nickel carbide and hydrogen. The infrared spectrum of nickel carbide has not been measured and could be quite difficult to detect.

The stability of $CD_2Ni(C_2D_4)$ toward $\lambda \geqslant 400$ nm and UV irradiation indicates a strong kinetic isotope effect, as expected for a hydrogen shift. The photofragmentation of $CH_2Ni(C_2H_4)$ and production of methane both involve a hydrogen shift.

Conclusions

1. The isolation and characterization of the first unligated nickelacyclobutane have been accomplished by using matrix-isolation FTIR spectroscopy. C–C bond activation of cyclopropane, oxidative addition to a nickel atom, and metallacyclobutane formation have been demonstrated.

2. Nickelacyclobutane underwent metathesis to methylenenickel (ethylene) π complex with $\lambda \geqslant 500$ nm irradiation. The presence of a metal atom has been shown to lower the energy for the decomposition of cyclopropane to methylene and ethylene, a highly endothermic process requiring 92.0 kcal/mol.

3. With UV photolysis $CH_2Ni(C_2H_4)$ underwent C–H bond activation of ethylene and rearranged to vinylnickel methyl. $C_2H_3NiCH_3$ ultimately decomposed, releasing methane. The stepwise decomposition of an industrially significant molecule, cyclopropane, to methane has been accomplished at a single metal atom center at cryogenic temperatures.

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Registry No. C_3H_6, 75-19-4; C_3D_6, 2207-64-9; Ni, 7440-02-0; $CD_2Ni(C_2D_4)$, 114199-03-0; $CH_2Ni(C_2H_4)$, 114199-04-1; $C_2H_3NiCH_3$, 114199-05-2; nickelacyclobutane, 114199-01-8; nickelacyclobutane-d_6, 114199-02-9; methane, 74-82-8.

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Synthesis and Characterization of Neopentylgallium Compounds

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The series of neopentylgallium compounds, $Ga(CH_2CMe_3)_3$, $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)_2Br$, $Ga(CH_2CMe_3)Cl_2$, and $Ga(CH_2CMe_3)I_2$ have been prepared by very facile, high-yield routes, have been easily purified, and have been fully characterized. The new compound $Ga(CH_2CMe_3)_3$ is a nonpyrophoric liquid that exists as monomeric, three-coordinate gallium species in benzene solution. Cryoscopic molecular weight studies indicate that $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)Cl_2$, and $Ga(CH_2CMe_3)Br_2$ are dimeric in benzene solution. Consequently, it is noteworthy that an equimolar mixture of $[Ga(CH_2CMe_3)_2Cl]_2$ and $[Ga(CH_2CMe_3)Cl_2]_2$ does not undergo a rapid exchange reaction at room temperature as four ^1H NMR lines are observed. A comparison of the properties of the neopentyl- and [(trimethylsilyl)methyl]gallium derivatives suggest that the neopentyl group has larger steric effects and stronger electron-withdrawing properties than the corresponding (trimethylsilyl)methyl substituents.

Introduction

The utilization of compound semiconductors for electronic and optical devices can be related to the development of epitaxial growth techniques.[1] The technique of choice for preparing compound semiconductors such as GaAs, GaP, and GaSb is organometallic vapor-phase epitaxy or organometallic chemical vapor deposition. Since only a surprisingly few organogallium compounds, $GaMe_3$ and $GaEt_3$, are readily available as gallium sources, our research program has been directed toward the synthesis and characterization of new organogallium compounds. In order for a gallium compound to be a useful gallium source, the compound should be readily prepared and easily purified as well as be a volatile liquid with excellent thermal stability at room temperature. In this paper, we report the synthesis and characterization of a series of organogallium compounds that incorporate the neopentyl (CH_2CMe_3 = Np) group including $GaNp_3$, $GaNp_2Cl$, $GaNp_2Br$, $GaNpCl_2$, and $GaNpI_2$. These neopentylgallium derivatives are of chemical interest because the bulky neopentyl substituent with no β-hydrogen atoms might introduce unusual chemical properties. Furthermore, direct comparisons between corresponding neopentyl and

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