

Alkynes and Metal Atoms

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Introduction

In recent years, there has developed an intense interest in the reaction chemistry of metal atoms and vapors. Actually, studies which were concerned with the reactivity of photoexcited mercury atoms date from the 1920s¹ and include reports of the photosensitized polymerization of acetylene by mercury vapor. Organic molecules of all types have been investigated by using a variety of main-group and transition metal atoms.² The breadth of investigation includes areas from gas-phase kinetic studies³ to low-temperature matrix isolation experiments^{4,5} and multigram synthetic-scale organometallic reactions.^{5,6}

In general, the reactions of alkynes with metal atoms for synthetic purposes have only been intermittently investigated. Early reviews^{2,7,8} were able to cover much of the subject in a few paragraphs or did not mention it at all. However, as this review attempts to show, the reaction chemistry of alkynes with metal atoms and vapors is a broad area with much current interest and with a great deal of multidisciplinary facets, including materials science, catalysis, and organometallic chemistry.

The discussion of metal atom-alkyne chemistry which follows has been organized according to the groups of the periodic table, beginning with the main-group metals, followed by the transition metals. No detailed discussions of specific experimental techniques have been included, except when necessary for clarity, since most methods are thoroughly described in general reviews³⁻⁷ or in the primary articles themselves. The-

oretical studies of metal atom interactions with alkynes, often conspicuously absent from review articles of metal atom chemistry, have been included here to underscore the multidisciplinary nature of this subject and to amplify the usefulness of close ties between the experimental and theoretical approaches to metal atom reactivity.

Although the discussion is organized on the basis of groups of the periodic table, the naming of the groups is the subject of considerable confusion. For example, depending upon the source document, group IIIA includes boron, aluminum, gallium, indium, and thallium (common U.S. usage through the 1970s) or scandium, yttrium, lanthanum, and actinium (IUPAC usage since 1970). Because the literature is replete with examples of both, the element must be specified to ensure accuracy. Both the American Chemical Society and IUPAC, through their nomenclature committees, have acted to resolve the difficulty. In 1983, ACS recommended notation using groups 1 through 18, eliminating the Roman numerals and the designations A and B. IUPAC is considering similar notation in its revision of the "Nomenclature of Inorganic Chemistry". Following this approach, aluminum (group IIIA or IIIB) will become 13 (carbon becoming 14, nitrogen 15, chromium 6 or 6d, oxygen 16; the last digit will preserve some measure of continuity or familiarity with the existing literature).

The Main-Group Metals

Li, Na, K, Rb, Cs, Fr (Group 1)

Margrave and co-workers⁹ have reported that lithium cocondensed with acetylene in low-temperature matrices forms species attributable to Li(HC₂H) and Li₂(HC₂H) complexes. An additional preliminary report by Hauge and Margrave¹⁰ indicated that alkali metal atoms cocondensed with acetylene formed charge-transfer complexes of the type [M]⁺[HC₂H]⁻, where M = Li, Na, K, or Cs. Infrared spectra of the matrices showed that a 12% change in $\nu(\text{C-H})$ occurred upon complexation (3290 cm⁻¹ for free acetylene, 2900 cm⁻¹ for the complex) which was independent of the alkali metal vaporized.

Recently, Kasai¹¹ has reported the matrix isolation study of the interaction of sodium atoms with acetylene in argon matrices. With matrices containing concentrations of approximately 0.1% sodium atoms and 1% acetylene, three distinct reaction stages could be distinguished at 4 K with electron spin resonance (ESR) as a probe. The first stage, a purple matrix, was seen immediately after deposition and consisted solely of a quartet ESR signal, split by matrix effects, due to matrix isolated sodium atoms (²³Na, 100% natural



Robert W. Zoellner was born in central Wisconsin in 1956 and grew up near the small town of Stratford. He is married to Barbara J. Moore. He was graduated with a B.Sc. degree in chemistry from St. Norbert College, DePere, WI, in 1978. While an NSF Undergraduate Research Participant with Professor Klabunde at the University of North Dakota, during the summer of 1977, he was introduced to the synthetic and catalysis-related aspects of metal atom chemistry, and he began his graduate work there in 1978. In 1979, he moved with Professor Klabunde's research group to Kansas State University and received the Ph.D. degree from there in 1983. His continuing interests in organometallic synthesis led him to accept a post-doctoral position with Dr. James M. Burlitch at Cornell University, investigating the reactivity of mercury-cobalt clusters. He is currently at l'Université d'Aix-Marseille as an NSF/CNRS Visiting Scientist, collaborating with Professor Michel Chanon on the applications of electron-transfer activation to metal atom reactivity.



Kenneth J. Klabunde was born in Madison, WI, in 1943 and grew up in the Madison area and later Davenport, IA. He is married and has three children. He graduated from Augustana College in 1965, where he learned to appreciate nontraditional research areas and was thus attracted to Donald Burton's fluorocarbon research group at the University of Iowa (Ph.D. 1969) and later to Phil Skell's carbon vapor research program at Penn State (postdoctoral 1970). His first position was at the University of North Dakota in 1970. There he established research programs in metal atom-vapor chemistry, reactive small-molecule chemistry, metal oxide surface chemistry, and general catalysis. In 1979 he moved to Kansas State University as Professor and Chemistry Department Head and is continuing his research efforts. In recent years he has become involved in industrial-academic relations especially regarding cooperative research efforts.

abundance, $I = 3/2$). After irradiation with "red" light ($\lambda > 5800 \text{ \AA}$), stage two was observed, in which electron transfer between isolated sodium atoms and acetylene

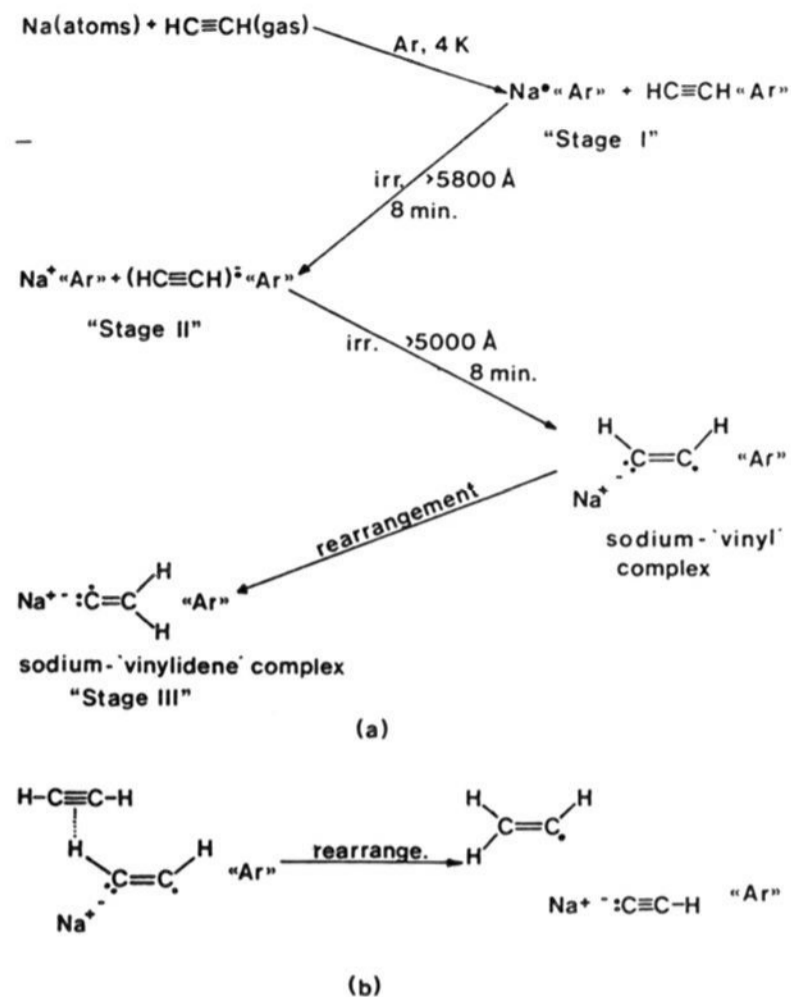


Figure 1. Sodium atom-acetylene reactions in low-temperature matrices. Reactions which are associated with low acetylene concentration ($\sim 1\%$) matrices are depicted in (a), while those additional reactions associated with higher acetylene concentration ($\sim 4\%$) matrices are depicted in (b). The symbol Ar denotes a species which is isolated in an argon matrix. (Adapted from ref 11.)

molecules had occurred. (The matrix remained purple.) The acetylene radical anion produced exhibited no ESR signal, presumably because it is a $^2\Pi$ radical, and thus is too orbitally broadened to be detected. Finally, irradiation with "yellow" light ($\lambda > 5000 \text{ \AA}$) produced a colorless matrix with an ESR spectrum composed of a triplet (coupling constant $57.5 \pm 0.5 \text{ G}$; 2 H) of quartets (coupling constant $12.3 \pm 0.3 \text{ G}$; Na). This spectrum was apparently due to a vinylidene-sodium complex, produced by the rearrangement of an undetected intermediate sodium-"vinyl" complex (see Figure 1a).

In matrices with acetylene concentrations of approximately 4%, acetylene dimers formed and reacted with sodium atoms to ultimately produce vinyl radicals (see Figure 1b). Intermediate concentrations of acetylene produced matrices containing mixtures of both the high- and the low-concentration species.

A series of articles¹² which report the results of non-empirical (MO-LCAO-SCF; STO-4GF minimum basis) theoretical studies of acetylene complexes of alkali metal cations has recently been published. The following conclusions were drawn: The energy of complex formation was in the order $(\text{C}_2\text{H}_2)\text{H}^+ \gg (\text{C}_2\text{H}_2)\text{Li}^+ > (\text{C}_2\text{H}_2)\text{Na}^+$, with the stability of a bridged type of structure (a nonclassical structure, or π -complex) being greatest for $(\text{C}_2\text{H}_2)\text{Na}^+$ while an open structure (a classical structure, or vinyl complex) was most stable for $(\text{C}_2\text{H}_2)\text{H}^+$. The LUMO energy levels were calculated to be in the order $\text{C}_2\text{H}_2 > (\text{C}_2\text{H}_2)\text{Na}^+ > (\text{C}_2\text{H}_2)\text{Li}^+ > (\text{C}_2\text{H}_2)\text{H}^+$, and the electron density transfer from the acetylene to the cationic center was in the order $\text{H}^+ > \text{Li}^+ > \text{Na}^+$.^{12a}

Extension of the calculations to include $(C_2H_2)K^+$ determined that with respect to decomposition to the free cation plus acetylene the order of stability of the complexes is $(C_2H_2)Li^+ \gg (C_2H_2)Na^+ \sim (C_2H_2)K^+$ and that the complexation energy arises primarily from electrostatic forces for $(C_2H_2)Na^+$ (57%) while for $(C_2H_2)Li^+$ and $(C_2H_2)K^+$ the energy is derived primarily from orbital interactions (71% and 63%, respectively).^{12b} Calculations performed on di- and triacetylene complexes showed that the $(C_2H_2)-M^+$ bond strength decreases only slightly when additional acetylene molecules are complexed to the cation and that the complexes $(C_2H_2)_2M^+$ ($M = Li, Na, K$) and $(C_2H_2)_3Li^+$ were stable with respect to decomposition either to the cation plus acetylene or to an acetylene molecule plus a monoacetylene complex.^{12c} Additional calculational methods for $(C_2H_2)Li^+$ have also confirmed the results outlined above.^{12d}

In an energy-transfer experiment, Hertel and Reiland¹³ investigated the interaction of excited-state sodium atoms ($3^3P_{3/2}$) with acetylene and substituted ethylenes. A supersonic (1350 m/s) beam of sodium atoms was crossed with a molecular beam from a capillary array,¹⁴ and the colliding species were examined. It was found that 40–80% of the available energy was transferred to the organic molecule and that the major interaction was with the unsaturated portion of the molecule. The unsaturated molecules quenched the excited-state sodium atoms in much the same manner as do diatomics, indicating that the primary interaction pathway involved the unsaturated portion of the molecule, independent of the remainder of the molecule.

Be, Mg, Ca, Sr, Ba, Ra (Group 2)

The only reports of synthetic-scale metal vapor–alkyne reactions with these metals have been from the laboratories of Skell. In the codeposition of thermally produced, ground-state ($1S$) magnesium atoms with ammonia and but-2-yne mixtures, an 87% yield of *trans*-but-2-ene was produced upon warmup of the matrix,¹⁵ presumably proceeding via the mechanism outlined in Figure 2. In a blank reaction, a mixture of ammonia and but-2-yne condensed on a previously deposited magnesium film produced less than 5% but-2-ene. Arc-produced, excited-state (metastable $3P$) magnesium atoms deposited with mixtures of ammonia and but-2-yne produced only a 28% yield of *trans*-but-2-ene, presumably due to competition between ammonia and but-2-yne for reaction with the more reactive excited-state magnesium atoms. (Some confusion about whether the *cis*- or *trans*-alkene was the product exists,^{8,16} but the original report¹⁷ clearly states that the *trans* isomer was the product.)

Swope and Schaefer¹⁸ have performed a theoretical investigation of the interaction of beryllium atoms with acetylene. They found that ground-state beryllium atoms ($1S$) exhibited no bonding interactions with acetylene but that the excited state ($3P$) of $3B_2$ symmetry will form a bond of 19.1 kcal/mol at a distance of 1.771 Å. (The excited states with $3B_1$ and $3A_1$ symmetry exhibited no bonding interactions.) The strongest bonding interaction (30.0 kcal/mol at 2.032 Å) arose from the beryllium cation (Be^+ , ground state

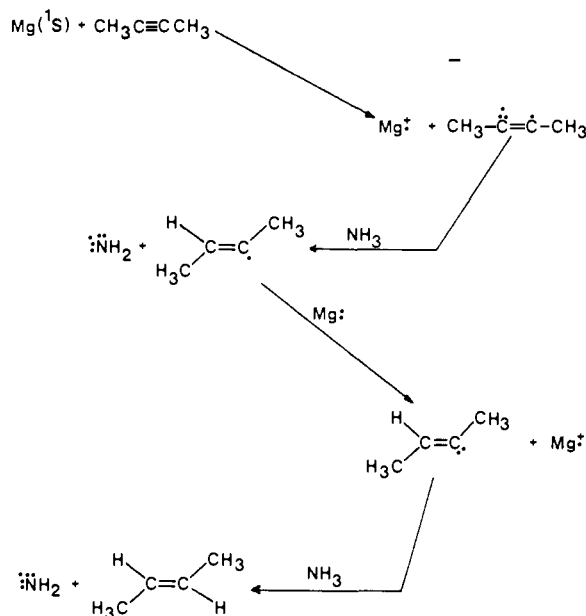


Figure 2. The proposed mechanism for the reaction of thermally produced magnesium atoms with ammonia–but-2-yne mixtures. (Adapted from ref 15.)

$2^2S, 2^2A_1$ symmetry) interacting with acetylene. Similar results were found for ethylene–beryllium interactions.

In a short communication, Bleekrode and vanBenthem¹⁹ describe a determination of the absolute cross section for the quenching of the $Mg(3s3p\ 1P_1)$ state in the gas phase using various quencher molecules. Their value for the acetylene cross section, σ_Q , was $90 \times 10^{-16} \text{ cm}^2$, with an estimated error of 25%. Breckenridge and Umemoto²⁰ have redetermined σ_Q to be $(55.7 \pm 2.1) \times 10^{-16} \text{ cm}^2$ at 426 K, corrected for temperature differences. The more recent experiments show that the quenching reaction is entrance channel controlled (i.e., deactivation occurs at practically every collision) and that for acetylene, the pathway is most likely electronic to vibrational energy transfer. No evidence for hydride abstraction (MgH formation) was found for the acetylene-quenched reaction.

Al, Ga, In, Tl (Group 13)

Little synthetic-scale work with these elements has been reported. Skell and Wolf²¹ report the reactions of aluminum atoms with propyne and but-2-yne, followed by hydrolysis (with D_2O) of the nonvolatile reaction products, and the volatiles listed in Table I were identified. The hydrolysis products from the reaction of but-2-yne and aluminum atoms were much less complex: only *cis*- and *trans*-but-2-ene in a 2:1 ratio were found. The authors suggest the reactions proceed via addition of aluminum to the alkyne, forming aluminumcycloalkenes and 1,2-dialuminoalkenes, but that some aluminum substitution for hydrogen also occurs. No mention of the formation of alkyne polymerization products was made.

A preliminary communication by Kasai and co-workers²² describes the matrix isolation study of the reaction of aluminum and gallium atoms with acetylene. Recently, the aluminum atom reaction was reported in detail by Kasai²³ with expanded analysis and studies of additional photoinduced matrix reactions. Conden-

TABLE I. Products of the Cocondensation Reaction of Propyne and Aluminum Atoms after D₂O Hydrolysis^a

product	amt, mmol	%						
		<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₅	
propene	1.07	3	43	53	1			
propyne	0.63	35	61	4				
allene	0.075	1	83	16				
propane	0.030	2	5	33	36	20	4	
hydrogen	0.034		11	89				
methane	0.055	mol ^b	nd ^b	nd ^b	nd ^b	nd ^b	nd ^b	

^a Adapted from ref 19. ^b Not determined.

TABLE II. Hyperfine Coupling Tensors and *g* Values for the Matrix Isolated Aluminum Atom/Acetylene Adducts^a

	adduct formed					
	upon deposition			after irradiation		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
<i>g</i>	2.0050	2.0023	2.0023	2.0023	2.0023	2.0023
Al, G	85 ± 1	92	78	70 ± 1	60 ± 1	50 ± 1
H _a , ^b G	25	20	15	26 ± 5	26 ± 5	26 ± 5
H _b , ^b G	55	55	55	56 ± 1	56 ± 1	56 ± 1

^a Adapted from ref 23. ^b See Figure 3 for the postulated structures of these adducts.

sation of aluminum atoms with perdeuterioacetylene in a neon matrix resulted in a purple matrix with an ESR spectrum consisting solely of a clearly resolved sextet due to the hyperfine interaction of aluminum (²⁷Al, 100% natural abundance, *I* = 5/2). Condensation of aluminum atoms with normal acetylene produced a spectrum complicated by additional hyperfine interactions, which on close examination were determined to be due to two nonequivalent protons. Irradiation of either matrix with visible light ($\lambda > 4000 \text{ \AA}$) brought about a gradual change, ultimately producing a spectrum similar in appearance to that observed before irradiation but with different hyperfine coupling constants (see Table II). The author suggests that the photoconversion results from *cis*-*trans* isomerization of a vinyl-type adduct of an aluminum atom with acetylene (see Figure 3a). It was not determined whether the initial form was *cis* or *trans*.

A theoretical investigation of three possible isomers of the aluminum-acetylene adducts (see Figure 3b) by Schaefer and co-workers²⁴ determined the aluminum-carbon bond energy for the vinylidene-type adduct and the *cis*- and *trans*-vinyl-type structures. The bond strength for both the *cis*- and *trans*-vinyl structures were approximately the same, 8.2 and 9.0 kcal/mol, respectively, while that for the vinylidene structure was 20.0 kcal/mol. The barrier between an acetylene and a vinylidene structure is approximately 8 kcal/mol. However, in the presence of aluminum, the conversion should be exothermic, while, for the isolated molecule, the acetylene to vinylidene conversion is endothermic.

Baney²⁵ has performed similar calculations.

Ge, Sn, Pb (Group 14)

The only synthetic-scale experiments for atoms of these elements are those carried out by Klabunde and co-workers using the metal atom cocondensation technique.²⁶⁻²⁸ Germanium codeposited with hexafluorobut-2-yne upon warming yielded a polymer of approx-

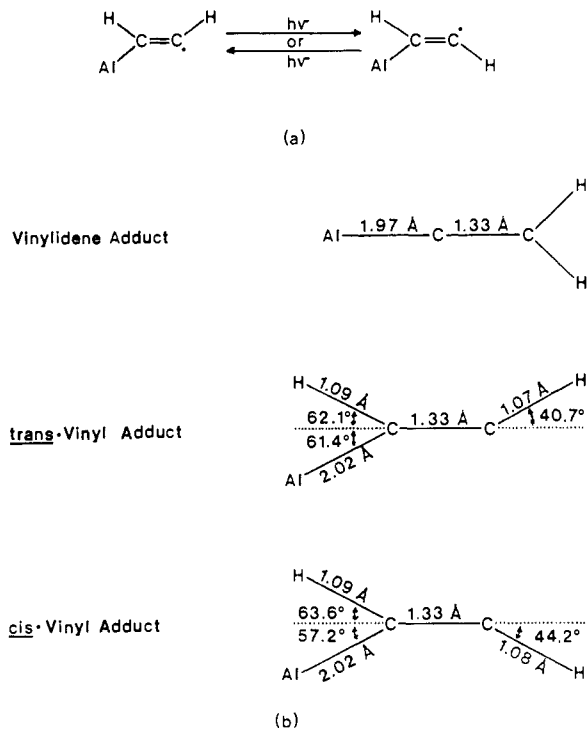


Figure 3. Aluminum-acetylene adducts. The photoconversion of the *cis* to the *trans* adduct (or vice versa) is depicted in (a). (Adapted from ref 23.) The structures of the possible adduct isomers as determined by Schaefer and co-workers are shown in (b). (Adapted from ref 24.)

imately 3:2 metal to ligand stoichiometry containing residual acetone solvate. Tin vapor reacted with hexafluorobut-2-yne similarly, forming dark brown acetone-soluble material. While these reaction products were initially acetone soluble, continuous decomposition ultimately led to formation of insoluble material. Germanium cocondensed with but-2-yne and propyne yielded high polymers insoluble in all common laboratory solvents.²⁶

When either germanium or tin atoms were cocondensed with acetylene, high molecular weight, very insoluble polymers, containing incorporated metal atoms, were formed.^{27,28} These polymers are of a nonstoichiometric but reproducible (i.e., (C₂H_{2.75}Ge_{0.72})_x and (C₂H_{2.60}Sn_{0.70})_x) composition, exhibit slight paramagnetism (as evidenced by broad ESR spectra), and are extremely air sensitive. Conductivity studies indicated that under pressed-powder conditions, the polymers behaved as insulators. Lead atoms cocondensed with acetylene under similar conditions did not form polymers.

Husain and co-workers have published kinetic studies of the gas-phase reactions of lead²⁹ and tin³⁰ atoms with acetylene in various buffer gases. Ground-state lead (6 ³P₀) was generated from Pb(C₂H₅)₄ and ground-state tin (5 ³P₀) from Sn(CH₃)₄ by low-energy pulsed irradiation and were monitored photoelectrically in absorption by time-resolved attenuation of resonance radiation from a microwave-powered atomic flow lamp. Metal-acetylene π -complexes were suggested as the species responsible for the decay of the absorption of the ground-state atom. The third-order rate constants (metal + acetylene + buffer gas) are listed in Table III.

TABLE III. Third-Order Rate Constants for the Gas-Phase Reactions of Tin and Lead with Acetylene^a

M	Sn (5^3P_0) $k^M_{C_2H_2}$, cm ² molecule ⁻² s ⁻¹	Pb (6^3P_0) $k^M_{C_2H_2}$, cm ² molecule ⁻² s ⁻¹
He	$(1.1 \pm 0.3) \times 10^{-29}$	$(1.3 \pm 0.2) \times 10^{-33}$
N ₂		$(2.6 \pm 0.3) \times 10^{-33}$
CO ₂		$(3.9 \pm 0.3) \times 10^{-33}$
CH ₄		$(5.3 \pm 0.6) \times 10^{-33}$
SF ₆		$(4.5 \pm 0.5) \times 10^{-33}$

^a Adapted from ref 29 and 30.TABLE IV. Third-Order Rate Constants for the Gas-Phase Reactions of Antimony and Bismuth with Acetylene^a

M	Sb ($5^4S_{3/2}$) $k^M_{C_2H_2}$, cm ² molecule ⁻² s ⁻¹	Bi ($6^4S_{3/2}$) $k^M_{C_2H_2}$, cm ² molecule ⁻² s ⁻¹
He	$(9.4 \pm 0.1) \times 10^{-33}$	$(1.1 \pm 0.1) \times 10^{-33}$
N ₂	$(1.0 \pm 0.1) \times 10^{-32}$	$(7.4 \pm 0.2) \times 10^{-33}$
SF ₆	$(1.2 \pm 0.1) \times 10^{-32}$	$(6.5 \pm 0.4) \times 10^{-33}$

^a Adapted from ref 31 and 32.

Sb, Bi (Group 15)

Husain and co-workers have published the only reports of reactions of these atoms with alkynes in their kinetic studies of the gas-phase reactions of antimony³¹ and bismuth³² atoms with acetylene in various buffer gases. Ground-state antimony ($5^4S_{3/2}$) was generated from Sb(CH₃)₃, and ground-state bismuth ($6^4S_{3/2}$) was generated from Bi(CH₃)₃. The third-order rate constants for these reactions are listed in Table IV.

Po (Group 16)

There are no reports of metal atom-alkyne studies for this radioactive metalloid.

The Transition Metals

Cu, Ag, Au (Group 11 (11d))

There is one report of synthetic-scale experiments of alkyne reactions with the metals of this group.²⁶ In the codeposition of hexafluorobut-2-yne with copper or gold atoms, moderately stable, darkly colored complexes with undetermined stoichiometry were formed. The gold complex, simply formulated as Au_x(CF₃C₂CF₃)_y, exhibited an infrared absorption band at 1725 cm⁻¹ which was tentatively assigned as $\nu(C\equiv C)$. Both the copper and gold complexes decomposed over several hours in solution at room temperature, forming metal particles or mirrors and the alkyne cyclotrimer, hexakis(trifluoromethyl)benzene.

Various groups have reported matrix isolation studies of group 11 metals with acetylene and other alkynes. Kasai and co-workers³³ have communicated their investigation of the reaction of copper atoms with acetylene in low-temperature matrices. A more complete account of this study also describes the reaction of silver atoms with acetylene.³⁴ The electron spin resonance spectrum (at 4 K) of an argon matrix containing 0.1% copper atoms and 2% acetylene exhibits three distinct sets of resonances. Matrix isolated copper atoms (a mixture of two isotopes, ⁶³Cu, 69% natural abundance,

TABLE V. Electron Spin Resonance Parameters for the Acetylene Adducts and Complexes of Copper, Silver,^a and Gold^b

Cu(π -HC ₂ H)	$g_{\parallel} = 2.015 \pm 0.002$ $g_{\perp} = 1.982 \pm 0.002$	$A_{\parallel} = 4111 \pm 5$ MHz $A_{\perp} = 4053 \pm 5$ MHz $ A_H \leq 5$ G
Cu(π -HC ₂ H) ₂	$g_{\parallel} = 1.997 \pm 0.002$ $g_{\perp} = 1.997 \pm 0.002$	$A_{\parallel} \approx 0$ $A_{\perp} = 190 \pm 14$ MHz $ A_H = 28$ G
Ag \cdots (HC ₂ H) ^c	$g = 2.000 \pm 0.001$	$a = 1753 \pm 1$ MHz
Ag \cdots (HC ₂ H) ₂ ^c	$g = 1.999 \pm 0.001$	$A = 1657 \pm 1$ MHz
Ag \cdots (HC ₂ H) _{≥3} ^c	$g = 1.997 \pm 0.001$	$A = 1611 \pm 1$ MHz
Ag(σ -HC ₂ H)	$g_1 = 2.015 \pm 0.002$ $g_2 = 2.002 \pm 0.002$ $g_3 = 1.991 \pm 0.002$	$A_1 = 125 \pm 5$ G $A_2 = 135 \pm 5$ G $A_3 = 123 \pm 5$ G $A_{H\alpha} = 30$ G $A_{H\beta} = 50$ G
Au(π -HC ₂ H)	$g_x = 1.977 \pm 0.002$ $g_y = 2.003 \pm 0.002$ $g_z = 1.856 \pm 0.002$	$A_x = 1845 \pm 2$ MHz $A_y = 1888 \pm 2$ MHz $A_z = 1844 \pm 2$ MHz
Au(σ -HC ₂ H)	$g = 2.002 \pm 0.006$	$A_{Au} = 617 \pm 28$ MHz $A_{Ca} = 224 \pm 28$ MHz $A_{H\alpha} = 70 \pm 14$ MHz $A_{H\beta} = 140 \pm 28$ MHz

^a Adapted from ref 34. ^b Adapted from ref 36. ^c Isolated silver atoms in a matrix have $g = 1.9998 \pm 0.0001$ and $A = 1.809.5 \pm 0.2$ MHz.³⁵

$I = 3/2$ and ⁶⁵Cu, 31% natural abundance, $I = 3/2$) account for the first set. Because of the relative magnitudes of the spectrometer frequency and the intrinsic zero-field splitting of the copper nuclei, each copper isotope exhibited only two resonances (rather than the four expected due to the nuclear spin quantum number of $3/2$), one of which corresponds to a nuclear spin transition and the other corresponding to an electron spin transition.³⁵

The remaining two sets of resonances are ascribed to copper-acetylene complexes. In order to determine the stoichiometry of the complexes, the concentration of acetylene in the matrices was varied while the copper atom concentration was held constant. At low acetylene concentrations (0.3%), the resonances due to copper atoms increased, the second set remained approximately constant, and the third set decreased dramatically. In matrices containing high acetylene concentrations (10%), no resonances due to copper atoms were detected, the second set of resonances decreased, and the third set of resonances became very intense. These concentration studies indicated that the second set of resonances could be assigned to a monoacetylene complex and the third set to a multiacetylene complex, with the bis(acetylene) stoichiometry a likely formulation. The monoacetylene complex resonances were two quartets of unequal intensity, due to hyperfine interactions with the two copper isotopes. No proton coupling was observed, indicating that the unpaired electron was in an orbital primarily localized on copper. The resonances associated with the multiacetylene complex were a quartet of quintets. This multiplicity indicated coupling to a copper atom and to four equivalent protons and allowed this complex to be assigned the bis(acetylene) stoichiometry. The ESR parameters for these complexes, and for the silver complexes discussed below, are found in Table V.

When silver atoms are isolated in low-temperature inert-gas matrices, their ESR spectrum consists of two sets of sharp doublets due to the two isotopes of silver

TABLE VI. Spectroscopic Data for the Copper/Acetylene Adducts^a

assignment ^b	Cu(¹² C ₂ H ₂)	Cu(¹³ C ₂ H ₂)	Cu(¹² C ₂ H ₂) ₂	Cu(¹³ C ₂ H ₂) ₂
Infrared Spectra, cm ⁻¹				
$\nu(\text{C-H})$	3040		2928	
$\nu(\text{C-H})$			2856	
$\nu(\text{C}\equiv\text{C})$	1870	1812	1850	1784
$\nu(\text{C-Cu})$	380		420	
Ultraviolet Spectra, nm				
6a ₁ → 3b ₂	440		460	
5a ₁ → 6a ₁	315			
2b ₁ → 6a ₁				
4a ₁ → 6a ₁				
2b ₂ → 6a ₁				
5a ₁ → 3b ₂	273			
2b ₁ → 3b ₁			230	
4a ₁ → 3b ₂				
2b ₂ → 3b ₂				

^a Adapted from ref 37. ^b Infrared assignments are by analogy to assignments of vibrations of acetylene gas; ultraviolet assignments are from the SCF-X α -SW molecular orbital schemes and apply only to the monoacetylene complex.

(¹⁰⁷Ag, 51% natural abundance, $I = 1/2$, and ¹⁰⁹Ag, 49% natural abundance, $I = 1/2$). The hyperfine coupling constant for isolated silver atoms can vary as much as 5%, depending upon the gas used as the matrix material.³⁵ The ESR spectrum of an argon matrix containing silver atoms (0.1%) and acetylene (0.1% to 20%) exhibited two sets of resonances, neither of which could be ascribed to a bona fide silver-acetylene complex. One set of resonances was definitely due to isolated silver atoms, but the other set was composed of three sets of doublets with slightly different silver hyperfine coupling constants and was concentration dependent. Because of the small change in coupling constants when compared to isolated silver atoms, these resonances were assigned as acetylene-silver pseudocomplexes, symbolized as Ag...(HC_2H)_n. Through concentration studies, the stoichiometries of the three sets of doublets were assigned as $n = 1$, $n = 2$, and $n \geq 3$.³⁴ These pseudocomplexes may be the low-temperature matrix analogue of gaseous van der Waals molecules or may be due to a matrix site effect.

The pseudocomplexes of acetylene and silver were prepared under conditions which did *not* allow vapor-phase contact between acetylene molecules and silver atoms. Under conditions which allowed vapor-phase contact *before* deposition, a vinyl-type silver-acetylene complex formed, similar to the aluminum-acetylene adduct mentioned earlier, and can be detected by ESR techniques. This result is in contrast to the results for the reaction of copper atoms with acetylene, where a π -complex formed regardless of experimental conditions.

The matrix isolation study of gold atoms with acetylene has also been reported by Kasai.³⁶ In argon matrices containing gold atoms and 10% acetylene, three sets of signals were observed, one of which corresponds to matrix-isolated gold atoms. Concentration studies and experiments utilizing perdeuterated acetylene allowed the assignment of the remaining sets of resonances to a monoacetylene π -complex of gold and to a gold-acetylene σ -adduct such as was seen with silver atoms, described above. These results are also summarized in Table V.

Ozin and co-workers,³⁷ using ultraviolet and infrared spectroscopy as probes, have investigated the reaction

of copper atoms with acetylene in low-temperature matrices. Their infrared data, supported by labeled acetylene studies, confirm the assignment of the copper-acetylene complexes as the mono- and bis(acetylene) stoichiometries. The experimentally determined ultraviolet data and bonding schemes were probed by the SCF-X α -SW molecular orbital method,³⁷ and the theoretical results were found to be in agreement with the predictions based upon ESR data.³⁴ The infrared and ultraviolet data are presented in Table VI.

A report by Howard, Mile, and co-workers³⁸ describes another investigation of the reactions of copper, silver, and gold with acetylene, using electron spin resonance as a probe. In contrast to the reports of Kasai and co-workers and Ozin and co-workers, however, this article describes the use of adamantane or cyclohexane as the matrix material and employs a somewhat unusual type of low-temperature matrix apparatus, the rotating cryostat.^{39,40}

The rotating cryostat, neglecting the technical aspects, is a rotatable metal drum, filled with liquid nitrogen, and surrounded by vacuum. Ports have been arranged in the outer vacuum chamber through which substrates and metal atoms can be introduced. Since the inner drum rotates, a layering effect occurs which gives excellent substrate/metal mixing without any gas-phase interactions.³⁹ A possible drawback of this method involves the use of electron spin resonance as a probe, since the matrix must be scraped into an ESR tube under vacuum at low temperature, and this transfer involves some mechanical difficulties.^{39b}

In the experimental setup used by Howard and Mile,³⁸ the temperature of the matrix was approximately 77 K, and this (comparatively) high temperature might allow different reactions to occur than were found in those experiments carried out at 4 K. For copper atoms and acetylene in an adamantane matrix, however, only the mono- and bis(acetylene) π -adducts were produced, again supporting the work of Kasai and Ozin.

The codeposition of silver atoms with acetylene in an adamantane matrix was found to give a silver-vinyl complex with an ESR spectrum similar to that of Kasai.³⁴ However, Kasai produced the silver-vinyl complex through a gas-phase reaction prior to condensation, while no such interaction is possible in the rotating

TABLE VII. Atom/Alkyne Complexes in Adamantane and Cyclohexane Matrices^a

complex ^b	matrix	decompn temp, K	<i>g</i> -factor	coupling constants, G
Cu(π -HC ₂ H) ^c	C ₁₀ H ₁₆ ^d	100		$a_{Cu} = 1479$ $a_{Cu'} = 1434$ $a_{Cu''} = 1368$ $a_{Cu'''} = 1218$ $A_{ } = \sim 0$ $A_{\perp} = 67 \pm 5$ $A_H = 29 \pm 3$ $a_{Cu} = 133.7$ $a_H = 45.1$ $a_{Ag} = 150.5$ $a_{H\beta} = 51.1$ $a_{H\alpha} = 28.7$ $a_C = \sim 55'$ $a_{Ag} = 109.6$ $a_H = 46.3$ $a_{Au} = 386.5$ $a_H = 19.7$ $a_C = \sim 55'$ $a_{Au} = 224.1$ $a_{H\alpha} = 20$ $a_{H\beta} = 41.5$ $a_{Au} = 189.1$ $a_H = 45.6$ $a_{Au} = 107$
Cu(π -HC ₂ H) ₂	C ₁₀ H ₁₆	>160	$g_{ } = 2.0019 \pm 0.002$ $g_{\perp} = 2.0019 \pm 0.002$	
Cu(σ -CH=CC ₆ H ₅)	C ₆ H ₁₂ ^e		2.0019	
Ag(σ -CH=CH)	C ₁₀ H ₁₆	123	1.9988	
Ag(σ -CH=CC ₆ H ₅)	C ₆ H ₁₂		2.0014	
Au(σ -C=CH ₂)	C ₁₀ H ₁₆	>100 K	1.9938	
Au(σ -CH=CH)	C ₁₀ H ₁₆	~ 77 K	1.9938	
Au(σ -CH=CC ₆ H ₅) (trans)	C ₆ H ₁₂		1.997	
Au(σ -CH=C ₆ H ₅) (cis)	C ₆ H ₁₂		1.997	

^a Adapted from ref 38. ^b Monoisotopic copper (⁶³Cu), and monoisotopic silver (¹⁰⁷Ag) were used in these studies. Gold is naturally monoisotopic (¹⁹⁷Au, 100% natural abundance, $I = 3/2$). ^c Trapped in four different sites in the matrix; hence the four unique coupling constants. ^d Adamantane. ^e Cyclohexane. ^f Coupling to ¹³C determined through depositions using ¹³C₂H₂ and ¹³C₂D₂.

cryostat. This matrix reaction is most likely due to the additional thermal energy in a 77 K matrix not available at 4 K.

Gold atoms also react with acetylene in an adamantane matrix to form a gold-vinyl complex, but the major product of the reaction is a gold-vinylidene species [Au(C=CH₂)], which is fluxional at 77 to 100 K. Phenylacetylene was also used as a reactant in cyclohexane matrices. All group 11 atoms formed vinyl-type complexes at the β -carbon (to the phenyl ring). The complexes with copper and silver are probably trans, with no cis form being produced. Both cis and trans forms were detected in the gold/phenylacetylene co-deposition. Data for all of these adamantane- or cyclohexane-matrix-formed complexes has been listed in Table VII.

Cohen and Basch⁴¹ have performed ab initio SCF calculations on the mono- and bis(acetylene)-silver complexes, using a relativistic effective core potential (RECP) for silver. Their geometry optimization results indicated that both stoichiometries form stable, isolable complexes but that the acetylene-silver interaction is much stronger in the monoacetylene complex. Some of the relevant parameters are as follows:

	$R(C-C)$ Å	$R(C-H)$ Å	$R(Ag-C)$ Å	$\angle(HCC)$
Ag(HC ₂ H)	1.298	1.086	2.278	37.5°
Ag(HC ₂ H) ₂	1.230	1.055	2.496	14.6°
free HC ₂ H	1.202	1.054		0°

A theoretical study by Itoh and Kunz,⁴² utilizing Hartree-Fock molecular orbital calculations, has been performed to investigate the interaction of a copper atom with acetylene. The purpose of this study was to compare the theoretical results with ultraviolet photoelectron spectral (UV-PES) data for acetylene adsorbed on copper. The theoretical calculations qualitatively explained the experimental UV-PES data.

Zn, Cd, Hg (Group 12 (12d))

Klabunde and co-workers²⁶ report the only synthetic scale metal atom-alkyne reactions within this group. When zinc atoms were cocondensed with hexafluorobut-2-yne, there was no apparent reaction, nor could any products be isolated and characterized.

Excited-state mercury atoms have been shown to polymerize acetylene in the gas phase. Bates and Taylor,⁴³ using the 2536.7-Å line of a mercury arc to excite mercury vapor, found that acetylene was rapidly polymerized, but mixtures which contained hydrogen as well as acetylene showed no hydrogenated products. Rideal⁴⁴ and Melville⁴⁵ investigated the rates, mechanisms, and products of the mercury-photosensitized polymerization of acetylene. Since mercury was continually being depleted during the process, an initial mercury-acetylene complex (possibly a mercury-vinyl-type free-radical structure, since the experimental rates indicated free-radical mechanisms were operative) was postulated. The average polymer chain length was independent of acetylene pressure (mercury vapor pressure was held constant, light intensity, or initial rate of reaction). A temperature dependence was found for chain length, however. At 20 °C, the average chain length was 10 acetylene units; this increased to 100 units at 250 °C (the maximum) and decreased to 50 units at 500 °C.

Jungers and Taylor⁴⁶ compared the rate of acetylene polymerization to that of acetylene-*d*₂ under mercury-photosensitized conditions. They found a 30% greater rate for HC₂H polymerization when compared to DC₂D. The demonstration of nitric oxide inhibition of the polymerization by LeRoy and Steacie⁴⁷ gives more support to a radical mechanism for the reaction. In addition, they measured the quantum yield of the reaction (in the absence of nitric oxide) to be 4.5 ± 1.2 and found a small temperature coefficient (25 °C to 300 °C) of about 3.7 in the rate.

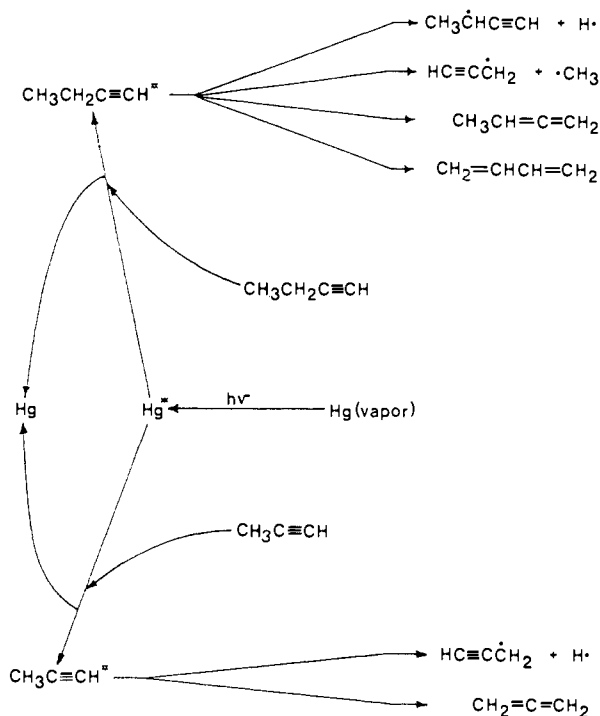


Figure 4. Mercury-photosensitized decomposition pathways for but-1-yne and propyne. (Adapted from ref 54.)

Shida and co-workers⁴⁸ investigated the *products* of the mercury-photosensitized polymerization of acetylene. Specifically, they determined the conditions necessary for the production of benzene. In their reactions, 29% of the acetylene underwent cyclotrimerization to benzene; the overall quantum yield was 4.8 when the benzene was included and 4.3 without the inclusion of benzene in the product. The rate of acetylene cyclotrimerization was proportional to acetylene pressure and light intensity at pressures up to about 30 torr and independent thereafter. Tsukada and Shida⁴⁹ also proposed a mechanism for the production of benzene from acetylene (i.e., free-radical vs. excited-state molecule initiation of reaction). However, their explanation of their results was questioned,^{50a} and their own analysis of their data was subsequently withdrawn.^{50b}

Callear and Hedges⁵¹ also investigated the mercury-photosensitized reactions of acetylene and detected HgH in the product mixtures, with a measured quantum yield of 0.18 ± 0.007 .

Evidence for the existence of a (initially thought to be *trans*) triplet-state acetylene formed through energy transfer from the photoinduced excited-state of mercury atoms was reported by Burton and Hunziker.^{52,53} Observation of a spectral region not examined in the earlier report⁵² gave added support for the triplet-state acetylene. A band at $\sim 1.35 \mu\text{m}$ corresponding to the $1^3A_2-1^3B_2$ electronic transition of *cis*-bent acetylene⁵³ was observed which corresponded well with theoretical calculations of the state. The *trans* configuration was ruled out as a possibility because of this observation.

Kebarle⁵⁴ has extended the reactions of photoexcited mercury atoms to other alkynes. By use of a flow system (helium carrier gas at 10 torr; substrate pressure at 2×10^{-3} torr) connected to a mass spectrometer, the products of the reaction between excited-state mercury atoms and but-1-yne and propyne were examined. The

TABLE VIII. Competitive quenching of Cd($^5\text{P}_1$) by alkynes^a

compound	rate ^b
<i>cis</i> -but-2-ene	(1.00)
acetylene	1.03 ± 0.03
acetylene- <i>d</i> ₂	0.94 ± 0.10
propyne	1.24 ± 0.09
vinylacetylene	1.25 ± 0.02

^a Adapted from ref 56b. ^b Relative to the isomerization of *cis*- to *trans*-but-2-ene, set arbitrarily at 1.00.

primary decomposition pathways for these molecules are illustrated in Figure 4.

As early as 1943, measurements of the absolute cross section for the quenching of the 5^3P_1 state of cadmium, by Steacie and LeRoy,⁵⁵ were reported. It should be noted, however, that this earlier value, $22.0 \times 10^{-16} \text{cm}^2$, differs by a factor of π from later values for the quenching cross section due to a change in convention for reporting quenching cross sections.³

Tsunashima and co-workers,⁵⁶ using a competitive quenching method, examined the quenching of excited-state cadmium atoms at $270 \pm 1^\circ\text{C}$ with various alkynes, compared to the *cis* to *trans* isomerization of *cis*-but-2-ene by excited-state cadmium atoms. Their results, relative to a value of 1.00 for *cis*-but-2-ene, can be found in Table VIII and compare well with those of Steacie and LeRoy.⁵⁵ In the quenching of cadmium atoms produced in the flash photolysis of $(\text{CH}_3)_2\text{Cd}$, Young and co-workers⁵⁷ found that acetylene, in a bath gas of methane, caused a decay rate of $(62 \pm 13) \times 10^7 \text{L mol}^{-1} \text{s}^{-1}$ at 27°C and at 275°C a decay rate of $410 \times 10^7 \text{L mol}^{-1} \text{s}^{-1}$.

Breckenridge and Malmin⁵⁸ report a study of the quenching of cadmium $5s5p^1\text{P}_1$ with various molecules. They find that with unsaturated molecules, quenching to the $^1\text{S}_0$ state competes with the singlet to triplet conversion, $^1\text{P}_1$ to $^3\text{P}_{2,1,0}$, and that deactivation occurs at essentially every encounter (entrance-pathway control). For acetylene, the branching ratio (singlet to triplet conversion) is 0.9, and the normal statistical ratios for $^3\text{P}_{2,1,0}$ (5:3:1, or 55.6%, 33.3%, 11.1%) is skewed toward $^3\text{P}_1$ and $^3\text{P}_0$ ($36 \pm 2\%$, $14 \pm 1\%$, or 2.6:3.6:1). This is postulated to result from the formation of long-lived complexes which approach truly statistical distributions of vibrational, rotational, translational, and electronic energies.

Sc, Y, Lanthanides, Actinides (Group 3 (3d))

Group 3 and its subgroups have been combined in one section to facilitate discussion and due to the dearth of reports concerning alkyne reactions with these metals. Of course, the radioactivity of promethium, actinium, and the actinides makes these elements difficult to work with, although some investigations have been performed.⁵ On the other hand, scandium, yttrium, lanthanum, and the lanthanides, sometimes referred to as the "rare earths", are neither truly rare nor expensive.⁵⁹ Such "common" metals as molybdenum, silver, and lead are present in the earth's crust in smaller quantities than is cerium, the most abundant lanthanide, and even the least abundant lanthanide, thulium, is far more abundant than gold.

The only reports of metal vapor-alkyne reactions of these metals have originated in the laboratories of Ev-

ans and co-workers.⁶⁰⁻⁶² Cocondensation of erbium atoms with hex-3-yne at -196°C ultimately produces three products, distinguished by their solubility in either pentane, toluene, or tetrahydrofuran (THF). The compounds are all paramagnetic, exhibit an intense charge-transfer absorption extending from beyond the ultraviolet to the near infrared, and have similar, but not identical, infrared spectra, with absorptions at approximately 1875 and 1790 cm^{-1} , which have been tentatively assigned as the $\nu(\text{C}\equiv\text{C})$ of a coordinated alkyne. All three products analyze with the empirical formula $[\text{ErC}_9\text{H}_{15}]_n$; molecular weight data indicate that the toluene-soluble compound has $n = 2$ and the THF-soluble compound has $n = 10$.^{60,61}

Hydrogenation studies, using the erbium-hex-3-yne complexes as catalysts, were also performed.^{60,61a} The pentane-soluble and toluene-soluble complexes, in neat hex-3-yne, hydrogenated hex-3-yne to *cis*-hex-3-ene in 97% yield, at a rate of 0.2 to 0.4 turnover per min. When THF was used as a solvent, the THF-soluble complex also hydrogenated hex-3-yne to hex-3-ene, although at a lower rate (0.0021 turnover per min), and also hydrogenated hex-3-ene to hexane at a rate of 0.0002 turnover per min.

The cocondensation of samarium and ytterbium with hex-3-yne yielded THF-soluble complexes with 1:1 empirical formulas and with similar infrared spectra ($\nu(\text{C}\equiv\text{C})$ for " $\text{SmC}_6\text{H}_{10}$ " at 1865 and 1754 cm^{-1} and for " $\text{YbC}_6\text{H}_{10}$ " at 1860 and 1765 cm^{-1}).^{60,61a} The cocondensation of lanthanum with hex-3-yne, and of erbium with diphenylacetylene, was mentioned without further elaboration.^{61a}

Evans and co-workers^{61b} also report the cocondensation reactions of lanthanides with terminal alkynes. The complexes isolated from the reaction of ytterbium, samarium, or erbium with hex-1-yne were postulated to be oligomeric alkynide hydrides with empirical formulas of approximately 2:3 metal:alkyne stoichiometry. These complexes exhibited low rates of hydrogenation activity.

A recent brief review by Evans⁶² is an overview of work from his laboratory concerning lanthanide metal vapor chemistry. In addition to a discussion of lanthanide atom-alkyne reactions, the results of lanthanide metal vapor reactions with alkenes and with cyclopentadiene are discussed and proposed mechanisms evaluated.

Tl, Zr, Hf (Group 4 (4d))

There are no reports of metal atom-alkyne reactions for these metals.

V, Nb, Ta (Group 5 (5d))

There are no reports of metal atom-alkyne reactions for these metals.

Cr, Mo, W (Group 6 (6d))

An early report by Skell and co-workers⁶³ described the reactions of chromium atoms with alkynes. Only the cyclotrimers of the alkynes were observed in the product workup, i.e., but-2-yne cyclotrimerized to hexamethylbenzene, but-1-yne to 1,2,4- and 1,3,5-trisubstituted benzene, and pent-1-yne to 1,2,4- and 1,3,5-tri-*n*-propylbenzene. No bis(arene)chromium complexes

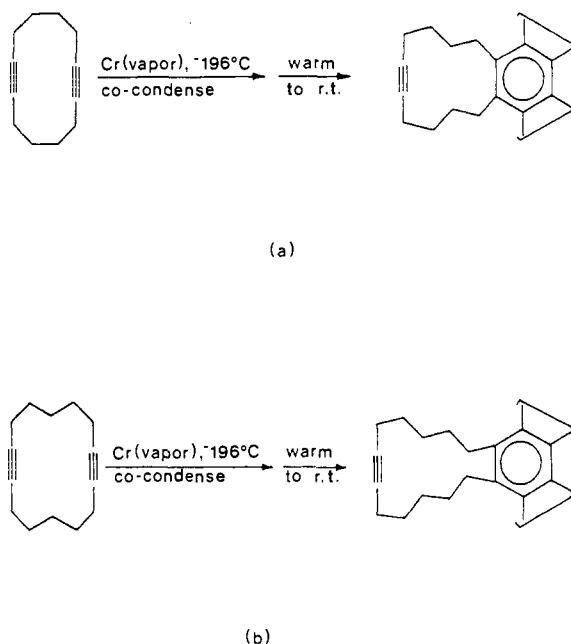


Figure 5. Chromium atom cyclotrimerization reactions: (a) cyclododeca-1,7-diyne; (b) cyclotetradeca-1,8-diyne. (Adapted from ref 64.)

could be isolated, although an insoluble green solid remained in the reactor after workup, and the reactions were not catalytic.

Gladysz and co-workers⁶⁴ have cocondensed cyclic diynes with chromium atoms with the expectation of a template synthesis of cyclophanes. When either cyclododeca-1,7-diyne or cyclotetradeca-1,8-diyne was cocondensed with chromium atoms, however, only one triple bond of the diyne took part in the cyclotrimerization and no cyclophanes were formed (see Figure 5).

The cocondensation of bis(trimethylsilyl)acetylene with chromium atoms has been reported^{65a} to produce an involatile green solid which, on treatment with CO, yields complexes that were formulated as *trans*-bis- $[\eta^2\text{-bis}(\text{trimethylsilyl})\text{acetylene}]\text{tetracarbonylchromium}$ and bis- $[\mu^2\text{-bis}(\text{trimethylsilyl})\text{acetylene}]\text{hexacarbonyldichromium}$. These compounds readily decomposed to $\text{Cr}(\text{CO})_6$ and nonvolatile solids.

Zaitseva and co-workers^{66a} reported the reaction of chromium atoms with diphenylacetylene in a synthetic scale^{66b} metal atom reactor. In their reaction, chromium atoms (0.5 g/h flux) were cocondensed with a 0.8 M solution of diphenylacetylene in decane, flash vaporized into the reactor. Three organochromium compounds were isolated from the reaction mixture: $[\text{bis}(2\text{-phenylethynyl})-\eta^6\text{-benzene}]\text{chromium}$ (0.7% yield), $[(2\text{-phenylethynyl})-\eta^6\text{-benzene}](\text{hexaphenyl})-\eta^6\text{-benzene}\text{chromium}$ (0.5% yield), and bis(hexaphenyl)- $\eta^6\text{-benzene}\text{chromium}$ (2% yield). Two organic products, hexaphenylbenzene and 1,2,3,4-tetraphenyl-1,3-butadiene, were also identified in the product mixture.

The chromium atom-alkyne reactions reported by Skell and co-workers⁶³ and Gladysz and co-workers⁶⁴ suggested that no more than *three* alkynes could coordinate to a chromium atom at *any one time* during a metal atom reaction, hence the production of cyclotrimers (benzenes) but not bis(arene)chromium complexes. The synthesis of bis(hexaphenyl)- $\eta^6\text{-benzene}\text{chromium}$ by Zaitseva and co-workers^{66a} is in direct

contrast to the earlier investigations. In the case of the reaction of chromium atoms with diphenylacetylene, then, the evidence seems to point to the possibility of coordinating up to six alkynes or their derivative equivalents to one chromium atom *at the same time*.

Mn, Tc, Re (Group 7 (7d))

Simons and Lagowski⁶⁷ have reported that manganese atoms cocondensed with pent-2-yne gave no detectable reaction or product, while phenylacetylene and hex-1-yne gave 1,2,4-trisubstituted benzenes and cyclooctatetraenes of undetermined substitution patterns. Some polymer was also isolated from the manganese-hex-1-yne reaction, but no metal-containing products could be isolated from these reactions.

When manganese atoms were cocondensed with acetylene, followed by attempted trapping with trifluorophosphine during warmup, no manganese-containing products could be isolated.²⁷

Fe, Ru, Os (Group 8 (8d))

Iron atoms have been cocondensed with alkynes and, contrary to the results found for manganese, metal-containing complexes were isolated.⁶⁷ The reaction of pent-2-yne with iron atoms produced an oligomer (1,2,4,7-tetramethyl-3,5,6,8-tetraethylcyclooctatetraene) and a red oil with a composition, determined by high-resolution mass spectrometry, of $\text{Fe}(\text{pent-2-yne})_5$. Products of similar stoichiometry were isolated from the reactions of but-2-yne and methylphenylacetylene with iron atoms. Propyne, however, gave only non-iron-containing polymers. These reactions are summarized in Figure 6.

Recently, Simons and Lagowski^{68a} have reported an investigation of the reactions illustrated in Figure 6 and, in addition, the reaction of iron atoms with hex-3-yne.

The iron complexes isolated from the reactions of iron atoms with alkynes exhibited stoichiometries of $\text{Fe}(\text{alkyne})_5$ by high-resolution mass spectrometry. Stoichiometries such as these could indicate a number of different structural possibilities, including π -bound alkynes, three- or five-member metallacycles, cyclobutadienes, cyclooctatetraenes, or combinations of these structures. In order to determine the actual structure, the spectral data being inconclusive, X-ray crystallography was necessary.

Crystallographic quality crystals of the "Fe(but-2-yne)₅" product and the "Fe(hex-3-yne)₅" product were grown by thermal gradient vacuum sublimation. Transparent yellow crystals of the iron-but-2-yne complex, structurally analyzed by X-ray diffraction,^{68b} were determined to be the unexpected product decamethylferrocene! Analogously, the transparent yellow platelets of the iron-hex-3-yne complex were found to be decaethylferrocene. The preparation of substituted ferrocenes from the reaction of iron atoms with alkynes formally requires the rearrangement of two-and-one-half alkyne ligands into a five-membered ring.^{68a} This rearrangement may have occurred via an alkyne-bis-(metallacycle)iron complex, where the iron atom inserts into the carbon-carbon triple bond, yielding a bis(carbyne) complex. The system could then rearrange to the bis(substituted-cyclopentadienyl)iron complex. Another plausible pathway is for a carbyne-iron insertion into a coordinated cyclobutadiene moiety, again pro-

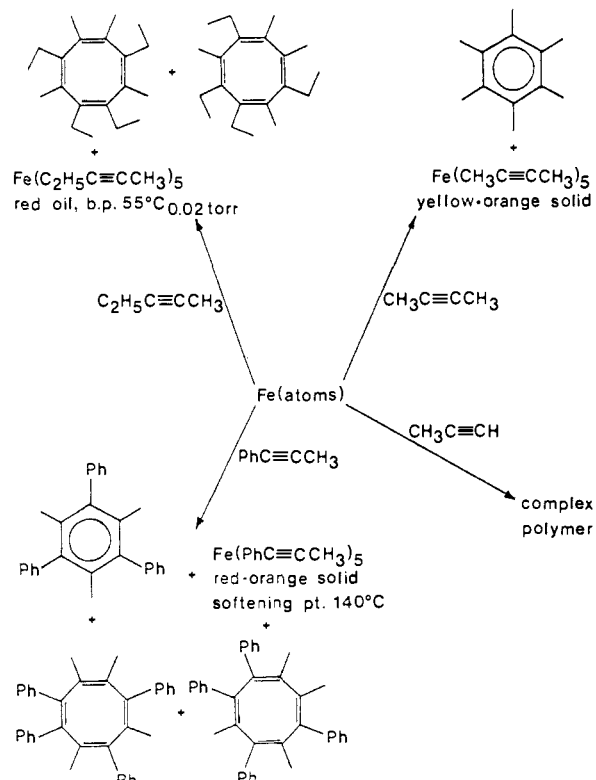


Figure 6. Reactions of iron atoms with alkynes. (Adapted from ref 67.) The products originally identified as $\text{Fe}(\text{alkyne})_5$ have been determined to be bis(substituted-cyclopentadienide)iron complexes.^{68a}

ducing a five-membered ring system.

A report that the cocondensation of iron atoms with (trimethylsilyl)acetylene, followed by reaction with CO, yields the cluster $\text{Fe}_3(\text{CO})_9(\text{alkyne})$ has been made.^{65a} Additionally, the reaction of iron atoms with bis(trimethylsilyl)acetylene^{65b} is reported to give a solid of variable stoichiometry, i.e., $\text{Fe}(\text{alkyne})_{1.8-4.0}$. Reaction of CO with this solid produces $[(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{C}-\text{H}_3)_3]\text{Fe}(\text{CO})_4$.

When iron atoms were cocondensed with acetylene, followed by the addition of PF_3 during warmup, no iron-acetylene complexes could be isolated.²⁷ Only small amounts of $\text{Fe}(\text{PF}_3)_5$ were observed.⁶⁹

The theoretical study of Itoh and Kunz⁴² of the interactions of selected metal atoms with acetylene to explain the UV-PE spectra of adsorbed acetylene on metal surfaces includes iron atoms. In the case of iron atoms, however, the theoretical results did not correlate well with the experimental data.

Sneddon and co-workers⁷⁰ have communicated results which demonstrate the versatility of the metal atom cocondensation technique. The reaction of iron atoms with but-2-yne, pentaborane(9) or hexaborane(10), and toluene yielded metallacarborane clusters identified as $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe}[(\text{CH}_3)_2\text{C}_2]\text{B}_4\text{H}_4$, $[\eta^6\text{-C}_6(\text{CH}_3)_6]\text{Fe}[(\text{CH}_3)_4\text{C}_4]\text{B}_3\text{H}_3$, and $[\eta^6\text{-C}_6\text{H}_5\text{CH}_3]\text{Fe}[(\text{CH}_3)_4\text{C}_4]\text{B}_3\text{H}_3$. Note that in the first two products, cyclotrimerization of the alkyne has occurred, while in each product the alkyne is an integral part of the carborane cluster.^{70a}

Co, Rh, Ir (Group 9 (9d))

The cobalt atom mediated cyclotrimerization of phenylacetylene with alkyl cyanides has been reported.^{65b} When these compounds are cocondensed with

cobalt atoms (a "tricondensation"), 1,2,4- and 1,3,5-triphenylbenzenes and 3,5-, 3,6-, 4,5-, and 4,6-diphenyl-2-alkylpyridines are produced.

The reaction of cobalt atoms with three substances, cyclopentadiene, but-2-yne, and pentaborane(9), co-condensed simultaneously, produces (albeit in low yields) three cobaltacarboranes, one of which is a new isomeric form of a known dicobaltacarborane. The compounds identified were a monocobalt cluster, $[2,3-(\text{CH}_3)_2-1,2,3-(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_4\text{H}_4]$, and two di-cobalt clusters, $[2,3-(\text{CH}_3)_2-1,7,2,3-(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_3\text{H}_3]$ and $[2,3-(\text{CH}_3)_2-1,7,2,5-(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_5]$, the latter of which was the new isomeric form of the $\text{Co}_2\text{C}_2\text{B}_5\text{H}_5$ cluster.^{70b}

In an extension of their "multiple-condensation" reactions, Freeman^{71a} and Sneddon and co-workers^{71b} have investigated the condensation of cobalt atoms with cyclopentadienes and alkynes as simultaneous reactants. The number of possible complexes from reactions such as these, and the inherent separation difficulties associated with them, makes the isolation and characterization of the 15 (!) complexes these researchers report quite an achievement. All compounds were identified spectroscopically and by high-resolution mass spectrometry.

The major products of the cyclopentadiene-alkyne-cobalt vapor cocondensation reactions were categorized⁷¹ as (a) complexes containing ligands resulting from alkyne dimerization or trimerization, usually accompanied by hydrogen addition, so as to produce alkene-derivative ligands, (b) multinuclear clusters which contain alkyne ligands, (c) complexes containing ligands resulting from cyclopentadiene-alkyne cycloadditions, and (d) complexes containing ligands resulting from cyclopentadiene-alkyne simple additions. All complexes contained the $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$ moiety. The types of products formed suggested $(\eta^5\text{-C}_5\text{H}_5)\text{CoH}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$ as intermediates in product formation, and reaction pathways incorporating these intermediates were postulated.

Klabunde and co-workers²⁶ report that the cocondensation reaction of hexafluorobut-2-yne with cobalt atoms results in the formation of low-valent complexes, stable at room temperature, which were susceptible to decomposition to metal particles and hexakis(trifluoromethyl)benzene.

The cocondensation of cobalt atoms with acetylene, followed by the addition of PF_3 , did not yield isolable cobalt-containing complexes.²⁷ This result was similar to that found for manganese atoms under the same reaction conditions.

The molecular orbital calculations of Itoh and Kunz⁴² for the interaction of a cobalt atom with acetylene compared well with the experimental UV-PES data for acetylene adsorbed on a cobalt surface.

Ni, Pd, Pt (Group 10 (10d))

The technique of ion cyclotron resonance (ICR) has recently been employed by Staley and co-workers⁷² to demonstrate that unipositive, two-ligand metal complexes, in the gas phase, exhibited the trans influence⁷³ as manifested in thermodynamic properties (i.e., gas-phase metal-ligand bond strengths).^{72a} Their data for nickel ions included results for gas-phase acetylene complexes. In the ideal case of a two-ligand complex

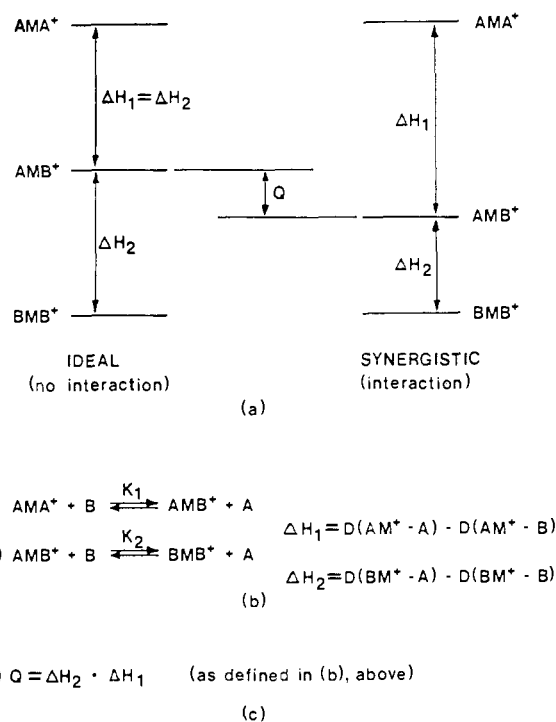


Figure 7. Stabilization energies for two-ligand, unipositive, gas-phase metal complexes. (a) Ideal vs. interacting complexes with reactions defined in (b). The deviation from ideal behavior is defined in (c). (Adapted from ref 72.)

in which no trans influence is manifested, the enthalpies (ΔH_1 and ΔH_2) in Figure 7a,b will be equal, since there will be no interaction between the two ligand sites on the metal ion. If, however, there is some site interaction which causes a synergistic enhancement of the mixed species AMB^+ when compared to AMA^+ and BMB^+ , the enhancement can be measured as a deviation Q (defined in Figure 7c) of the relative enthalpy for AMB^+ from the ideal value.

Data for the gas-phase complexes $(\text{HC}_2\text{H})_2\text{Ni}^+$, $(\text{HC}_2\text{H})\text{Ni}(\text{CH}_2=\text{C}=\text{CH}_2)^+$, and $(\text{CH}_2=\text{C}=\text{CH}_2)_2\text{Ni}^+$ (i.e., $\text{A} = \text{HC}_2\text{H}$ and $\text{B} = \text{CH}_2=\text{C}=\text{CH}_2$ in Figure 7) yielded a value of 0.14 kcal/mol for Q and a total enthalpy change for the exchange of both ligands, $D(\text{M}^+ - 2\text{B}) - D(\text{M}^+ - 2\text{A})$, of 0.19 kcal/mol.^{72a} The data, along with information for a large number of other pure and mixed gas-phase complexes, were combined to form a table of relative bond dissociation energies, using $\delta D(\text{Ni}^+ - 2\text{HC}_2\text{H})$ as a defined zero. The table has an inherent accuracy of ± 0.2 kcal/mol and is internally consistent, although no absolute values could be assigned.

The ICR studies of nickel ions represent a major new direction for metal atom-alkyne chemistry. However, the remainder of the discussion within this group concerns neutral metal atoms.

Itoh and Kunz⁴² have also used their ab initio molecular orbital calculations to investigate the interaction of a nickel atom with acetylene. Their results correlated well with the ultraviolet photoelectron spectral data for acetylene adsorbed on nickel surfaces, which was the goal of their study. Through the use of GVB-CI calculations, Upton and Goddard⁷⁵ determined the structure of an acetylene-nickel adduct. Their calculated planar, symmetrical structure had nickel-carbon distances of 2.01 Å, a carbon-carbon distance of 1.21 Å, carbon-hydrogen distances of 1.058 Å, and a car-

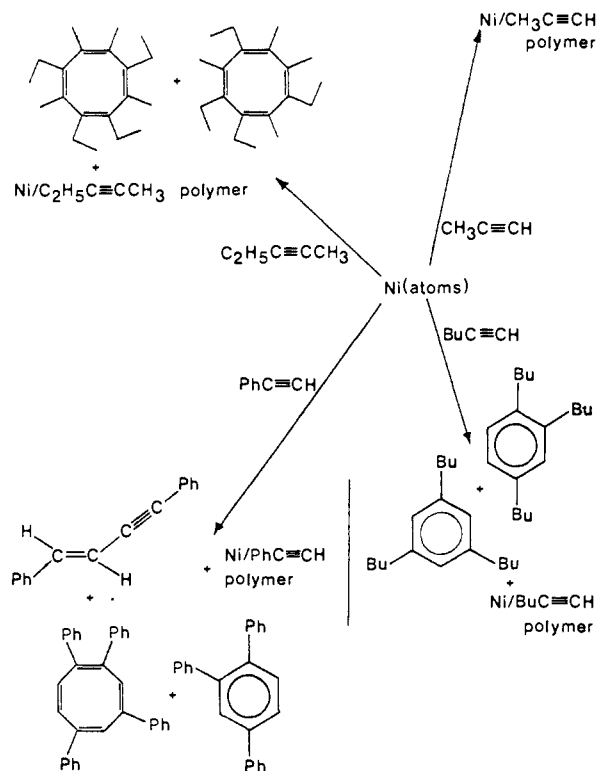


Figure 8. Reactions of nickel atoms with alkynes. (Adapted from ref 67.)

bon-hydrogen bend-back angle of only 5° . This indicated that only a small amount of orbital distortion occurred in the acetylene molecule upon complexation with a nickel atom.

The earliest report of synthetic-scale metal atom-alkyne reactions in this group is by Skell and co-workers.⁷⁶ They mention in a brief report that terminal alkynes cocondensed with nickel atoms are cyclotrimerized to 1,2,4- and 1,3,5-trialkylbenzenes.

Simons and Lagowski⁶⁷ have reported detailed studies of nickel atom-alkyne reactions, and their results are illustrated in Figure 8. The major product in all reactions was a black, poorly characterized nickel-containing polymer mixture, and, with the exception of the nickel-propyne reaction, dimers, trimers, and tetramers of the reactant alkyne were also isolated.

The metal-alkyne polymers mentioned above have been shown to be alkyne oligomerization and arene hydrogenation catalysts.^{67,77} In the nickel-propyne polymer catalyzed oligomerization of propyne, a novel linear trimer of propyne (4,6-dimethylhepta-4(Z),6-dien-2-yne) was the major product, rather than the expected 1,2,4- and 1,3,5-trimethylbenzenes. (Table IX is a summary of the catalytic data.) The nickel-alkyne polymers were also found to catalytically hydrogenate benzene to cyclohexane and methyl benzoate to methyl cyclohexanecarboxylate, but acetophenone could only be hydrogenated to 1-phenylethanol.

Klabunde and co-workers²⁶ have investigated the cocondensation reactions of nickel, palladium, and platinum atoms with hexafluorobut-2-yne. If CO was added to the cold matrix formed from the cocondensation of nickel atoms and hexafluorobut-2-yne, the known⁷⁸ cluster $\text{Ni}_4(\text{CO})_4(\text{CF}_3\text{C}_2\text{CF}_3)_3$ was formed in high yield. A volatile substance could also be isolated, which converted to the cluster upon standing, and was

TABLE IX. Alkyne Oligomerization by Nickel-Alkyne Polymers^a

catalytic system ^b	substrate alkyne ^c	% dimer	% trimer	% tetramer
Ni/propyne	phenylacetylene ^d	0	20	50
	pent-2-yne ^e	0	45	55
	acetylene	0	2	98
Ni/pent-2-yne	phenylacetylene ^e	2	60	20
	pent-2-yne ^f	0	100	0
	acetylene	0	100	0

^a Adapted from ref 67 and 77. ^b Indicates the source of the black, nickel containing catalyst, but not the stoichiometry or structure of the catalyst. ^c Reactions run in neat alkyne except for acetylene, which was in cyclohexane solution at 1 atm pressure of acetylene. ^d 30% polymer also produced. ^e 12% polymer also produced. ^f No reaction.

identified as the known⁷⁸ mononickel complex $(\text{CO})_2\text{-Ni}(\text{CF}_3\text{C}_2\text{CF}_3)$. Palladium atoms reacted with hexafluorobut-2-yne in a similar manner, producing in high yield the hitherto unknown palladium cluster $\text{Pd}_4(\text{C}-\text{O})_4(\text{CF}_3\text{C}_2\text{CF}_3)_3$. A volatile monopalladium analogue of $(\text{CO})_2\text{Ni}(\text{CF}_3\text{C}_2\text{CF}_3)$ was not identified in these reactions.

In the absence of CO addition, cocondensation reactions of these metals led to less easily characterizable complexes. Nickel atoms cocondensed with hexafluorobut-2-yne formed an acetone-soluble complex which analyzed with a 1:1:1 nickel: $\text{CF}_3\text{C}_2\text{CF}_3$:acetone stoichiometry. With palladium a product whose molecular weight and elemental analysis indicated a formula of $\text{Pd}(\text{CF}_3\text{C}_2\text{CF}_3)_2$ was formed. Platinum atoms cocondensed with hexafluorobut-2-yne formed only poorly characterized, highly colored complexes.

The cocondensation of dimethyl acetylenedicarboxylate (dmadc) with nickel atoms led to the formation of a nickel-alkyne complex with the empirical formula $(\text{dmadc})_3\text{Ni}_2$.⁷⁹ The properties of this complex suggested that it is polymeric in the solid state and oligomeric in acetone solution; molecular weight data in acetone solution, when extrapolated to infinite dilution, gave a molecular weight which corresponded closely to the unit empirical formula. Hexamethyl benzenehexacarboxylate and a low molecular weight alkyne polymer containing traces of nickel could also be isolated from the metal atom reaction products.

Silyl-substituted acetylenes have also been cocondensed with nickel atoms.⁸⁰ Bis(trimethylsilyl)acetylene (btmsa) yielded a series of extremely air-sensitive oligomeric nickel-alkyne complexes, formulated as $(\text{btmsa})_2\text{Ni}$, $(\text{btmsa})_3\text{Ni}_2$, etc. 1-(Trimethylsilyl)prop-1-yne yielded an air-sensitive, black crystalline powder whose elemental analyses indicated a 1:1 nickel:alkyne stoichiometry.

When nickel vapor is cocondensed with acetylene, followed by warmup in the presence of PF_3 as a trapping agent, no nickel-acetylene complexes could be isolated.²⁷ Small amounts of $\text{Ni}(\text{PF}_3)_4$ were found.⁶⁹

Matrix isolation techniques have also been used to examine nickel, palladium, and platinum atom reactions with alkynes. Ozin and co-workers³⁷ have used infrared and ultraviolet spectroscopy and theoretical calculations to identify the products of nickel-acetylene reactions in low-temperature matrices. Through the use of different matrix gases (argon, krypton, and pure acetylene) and concentration studies, the identity of two com-

TABLE X. Spectroscopic Data for the Nickel-Acetylene Adducts^a

assignment ^b	Ni(¹² C ₂ H ₂)	Ni(¹³ C ₂ H ₂)	Ni(¹² C ₂ H ₂) ₂	Ni(¹³ C ₂ H ₂) ₂
Infrared Spectra, cm ⁻¹				
$\nu(\text{C-H})$	3112 (Ar) ^c 3110 (Kr) ^d		3112 (Ar) 3130 (Kr)	
$\nu(\text{C}\equiv\text{C})$	1729 (Ar) 1734 (Kr)	1668 (Kr)	1760 (Ar) 1757 (Kr) 1760 (C) ^e 512 (Kr)	1700 (Kr)
$\nu(\text{Ni-C})$	570/560 (Ar) 572/556 (Kr)			
Ultraviolet Spectra, nm				
2b ₁ → 6a ₁ 5a ₁ → 6a ₁ 4a ₁ → 6a ₁	394			
2b ₂ → 6a ₁ 2b ₁ → 3b ₁ 5a ₁ → 3b ₂ 4a ₁ → 3b ₂		328		320
2b ₂ → 3b ₂				
1a ₂ → 2a ₂	256		240	

^a Adapted from ref 37. ^b Infrared assignments are by analogy to assignments of vibrations of other nickel-acetylene complexes; ultraviolet assignments are from the SCF-X α -SW molecular orbital schemes and apply only to the monoacetylene complex. ^c Argon matrix. ^d Krypton matrix. ^e Acetylene matrix.

TABLE XI. Infrared Spectra of the Alkyl-Alkyne Complexes of Nickel, Palladium, and Platinum Atoms^a

species	$\nu(\text{C}\equiv\text{C})$, cm ⁻¹	$\nu(\equiv\text{CH})$, cm ⁻¹
hex-1-yne	2118	3280
hex-1-yne/nickel	2011, 2044	3240
hex-1-yne/palladium	1902, 2031	3184, 3238
hex-1-yne/platinum	1817, 2034	3142, 3237
propargyl chloride	2132	3280
propargyl chloride/nickel	1968, 2030	3226
propargyl chloride/palladium	1933, 2076	3231
propargyl chloride/platinum	1821, 2025	3152

^a Adapted from ref 81.

plexes, Ni(HC₂H)_{1,2}, was established. Assignments of the ultraviolet spectrum of the monoacetylene complex were made based upon SCF-X α -SW calculations. The infrared and ultraviolet data are presented in Table X.

An early report of the interaction of nickel, palladium, and platinum atoms with hex-1-yne and propargyl chloride in alkyne matrices at -180 °C (93 K) by Aleksanyan and co-workers⁸¹ has been published. Their results are listed in Table XI. Note that in matrices containing metal atoms, *two* new bands appear, both assigned as $\nu(\text{C}\equiv\text{C})$. The authors suggest that the additional band may be due to alkynide formation, metal cluster complexes of alkynes, or to "weak" complexes.

Although the authors do not make any definite conclusions concerning the species responsible for the additional $\nu(\text{C}\equiv\text{C})$ band, some information can be derived from graphical analysis of the $\nu(\text{C}\equiv\text{C})$ absorptions (see Figure 9). As is readily apparent, the lower band of each absorption pair for each alkyne-metal series forms a very nearly linear relationship, exhibiting greater metal-alkyne interaction in the order Ni < Pd < Pt. The higher absorption band of each pair shows a more random change with the change of metal.

In the light of the work of Kasai and co-workers³⁴ concerning pseudocomplexes of silver atoms and acetylene, it is tempting to assign the lower band of the absorption pair to a bona fide metal-alkyne complex and the higher band to a pseudocomplex of the type M... (alkyne), using Kasai's symbolism. Metal cluster-alkyne complexes would be expected⁸² to exhibit a much greater shift in $\nu(\text{C}\equiv\text{C})$ frequency than the additional bands exhibit. However, metal-alkynide complexes⁸³

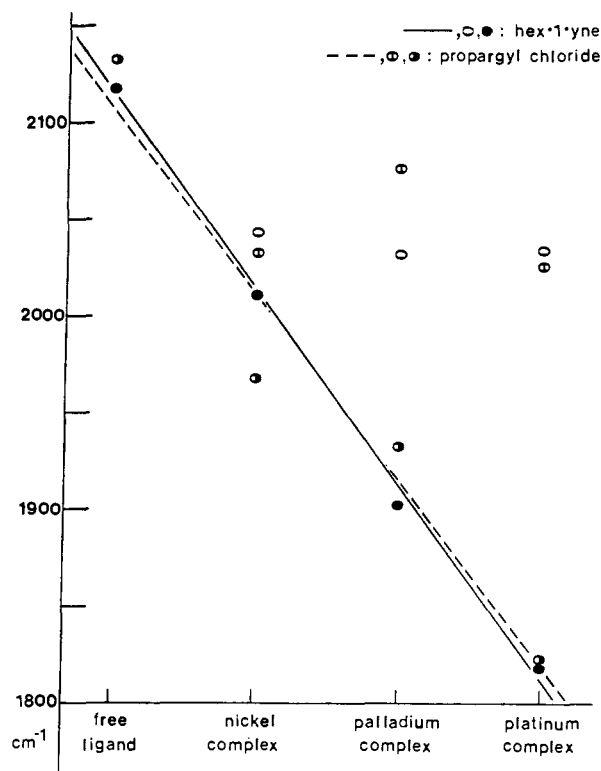


Figure 9. Carbon-carbon triple bond stretches of the alkyl-alkyne complexes of nickel, palladium, and platinum, graphically displayed. Solid symbols are the lower bands and open symbols are the higher bands of each absorption pair. The equations were calculated through linear-regression least-squares analysis of the lower absorption.

cannot be ruled out (no mention of the observation of $\nu(\text{M-H})$ was made).

Kuz'yants and Aleksanyan⁸⁴ have also reported a matrix isolation study of (trifluoromethyl)acetylene and hexafluorobut-2-yne and nickel, palladium, and platinum atoms. Their infrared spectral results are listed in Table XII. Interestingly, the observed $\nu(\text{C}\equiv\text{C})$ frequencies are in the order Ni < Pd < Pt, showing metal-alkyne interaction in the order Ni > Pd > Pt, the opposite to that found for alkyl-alkynes.⁸¹

Aleksanyan and Garkushna⁸⁵ report the matrix isolation study of acetylene with nickel, palladium, and

TABLE XII. Infrared Spectra of the fluoroalkyne Complexes of Nickel, Palladium, and Platinum Atoms^a

species	$\nu(\text{C}\equiv\text{C}), \text{cm}^{-1}$	$\nu(\text{C}\equiv\text{H}), \text{cm}^{-1}$
trifluoromethylacetylene ($\text{CF}_3\text{C}_2\text{H}$)	2172	3314
$\text{CF}_3\text{C}_2\text{H}/\text{nickel}$	1907	3223
$\text{CF}_3\text{C}_2\text{H}/\text{palladium}$	1935	3240
$\text{CF}_3\text{C}_2\text{H}/\text{platinum}$	2073	
hexafluorobut-2-yne ($\text{CF}_3\text{C}_2\text{CF}_3$)	2300	
$\text{CF}_3\text{C}_2\text{CF}_3/\text{nickel}$	1962	
$\text{CF}_3\text{C}_2\text{CF}_3/\text{palladium}$	1996, 2149	
$\text{CF}_3\text{C}_2\text{CF}_3/\text{platinum}$	2058, 2152	

^a Adapted from ref 84.**TABLE XIII. Infrared Spectra of the Acetylene Complexes of Nickel, Palladium, and Platinum Atoms^a**

cm^{-1}	Ni complex ^b	Pd complex ^c	Pt complex ^d
$\nu(\text{C}-\text{H})$	3154 (3150) 3104	3182 (3200) 3153 (3180)	3170 3122 3093 2974
$\nu(\text{C}=\text{C})$	1698 (1758) (1748)	1762 (1789) (1782) (1770)	1439
$\sigma(\text{C}-\text{H})$	963 (711)	(717)	
$\nu(\text{M}-\text{L})$	565 (478) (392)	416	

^a Adapted from ref 85. ^b Bands observed at deposition temperature of 20 K. Numbers in parentheses are bands observed after annealing matrix to 60 K. ^c Bands observed at deposition temperature of 20 K. Numbers in parentheses are bands observed after annealing matrix to 50 K. ^d No changes observed upon annealing.

platinum atoms in a matrix of acetylene at 20 to 150 K. When nickel atoms were cocondensed with acetylene, a characteristic light green matrix was formed; the matrices containing either palladium or platinum atoms were colorless.

The infrared spectral frequencies for these metal-acetylene matrices are listed in Table XIII. The results of Aleksanyan and Garkusha⁸⁵ for nickel do not agree with the results of Ozin and co-workers.³⁷ However, Ozin and co-workers operated at a matrix temperature of approximately 10 K, while Aleksanyan and Garkusha performed their experiments at higher temperatures. Warmup studies by Aleksanyan and Garkusha indicated the formation of new complexes in the nickel-acetylene and palladium-acetylene matrices, and these new complexes were stable to 60 and 50 K, respectively.⁸⁵

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- (73) In this regard, it should be noted that the trans "influence" is taken to refer to the influence of a ligand on the ground-state properties (i.e., bond distances, vibrational frequencies, etc.) of a ligand trans to the first ligand and is a thermodynamic property.⁷⁴ Being a thermodynamic property, the trans influence should also be exhibited in such properties as enthalpy of formation, etc.^{72a} The trans "effect", on the other hand, is a kinetic property usually associated with the effect of a ligand on the rate of substitution of a ligand trans to the first ligand.⁷⁴
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