of the metal into three- and four-membered rings occurs only with great difficulty. Indeed, while we have been able to find several examples in the literature of square-planar complexes containing both η^2-dppe and η^2-L (η^2-L being a main-group ligand forming a three-membered ring with the metal),[10] we have been unable to locate any corresponding complexes with dppm. Moreover, we have demonstrated the synthetic utility of the constraint of the three-membered ring of η^2-cyclenphosphoranide in the synthesis of a dppm-supported heterobimetallic derivative. This feature may be of general use if other three-membered rings and/or other metals show the same behavior.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Robert A. Welch Foundation, and Southern Methodist University (Seed Grant) for generous financial support. We thank Mr. Harold Isom for help in the synthesis of cyclenPH and Dr. J. P. Fackler for helpful dicussions.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates for 5 and 6 (8 pages). Ordering information is given on any current masthead page.

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Reactivity of Gas-Phase Copper(I) with Octyne Isomers

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The decompositions of adducts of gas-phase Cu(I) and octyne isomers occur in both tandem and Fourier transform mass spectrometers. Three reactive fragmentations take place for the adducts: hydride abstraction to eliminate copper(I) hydride, propargylic insertion to expel olefins, and remote functionalization to eliminate primarily ethene and hydrogen. A comparison of the abundances of product ions produced in each spectrometer indicates that remote functionalization is a low-energy process, whereas hydride abstraction has the highest energy requirement. The propargylic insertion reaction requires intermediate energy with respect to the other two processes. Second-order reaction rate constants indicate that Cu(I) reacts very efficiently (one of every 2 collisions) with 1- and 3-octyne, but less so with 2- and 4-octyne (one of every 20 collisions).

Introduction

Alkynes are known to be highly reactive with transition metals, and their interactions have been well studied over the last 50 years.[1] Investigation of reactions such as the oligomerization of alkynes catalyzed by transition metals began during World War II with the work of Reppe,[2] but the mechanisms by which these and other metal/alkyne interactions occur are still not well understood. Mass spectrometry is an excellent tool for clarifying gas-phase metal ion–molecule reaction mechanisms because it combines simple, efficient adduct ion formation with sensitive adduct and fragment ion detection. Furthermore, the fragment ions produced by metastable decompositions in a mass spectrometer are indicative of an adduct's lowest energy decomposition pathways.

Gas-phase transition metal ion activation of hydrocarbon C–H and C–C bonds has been demonstrated for many systems by using various mass spectrometric techniques[3] such as tandem mass spectrometry (MS/MS),[4] Fourier transform mass spectrometry (FTMS) and ion cyclotron resonance (ICR) spectrometry,[5] as well as ion beam spectrometry.[6] In many cases, the gas-phase metal ion–molecule interaction involves an oxidative addition

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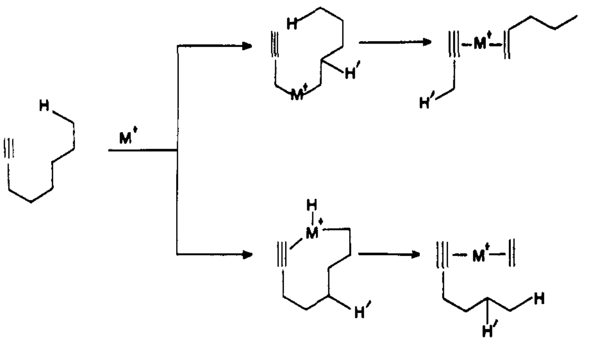
mechanism originally proposed by Allison and Ridge.[7] Adhering to this mechanism, a metal ion interacts with a functional group such as a double bond and then inserts into an allylic or propargylic C–C bond (eq 1). Transfer of a β-hydrogen ensues first to the metal center to generate a π-bound ligand and then to the remaining σ-bound ligand to transform it to a π-bonded moiety. The more weakly bound ligand subsequently detaches,[8] either spontaneously or upon activation.



(1)

(2)

There is a second pathway, remote functionalization (eq 2),[3b,g,4g,9] whereby the metal ion initially anchors to a functional group of an organic molecule and then oxidatively adds to a terminal C–H bond to form a metallacycle. Oxidative addition to a terminal C–H bond was observed for Mn(I) with 4-octyne[4e] and Fe(I) with alkanenitriles.[4g] Transfer of a β-hydrogen from the organic entity to the metal center may occur next, followed by reductive elimination of H_2 (not shown). Alternatively, the metal may cleave the β or, to a lesser extent, the γ C–C bond to generate a labile π-bonded olefin.

A recent study of the reactivity of Cu(I) with alkanes by Armentrout and co-workers[10] suggests that a third reactive pathway, heterolytic cleavage, may occur for systems involving Cu(I) if sufficient energy is added to the system. The Cu(I) reactions with alkanes yield mostly CuH and Cu(alkyl) as neutral fragments, along with modest abundances of CuH^+ and $Cu(CH_3)^+$. The authors suggested, as a possible reaction mechanism, that heterolytic cleavage occurs to form intermediate species such as $(H–Cu)–R^+$ and $H^+–(Cu–R)$ rather than the insertion product $H–Cu^+–R$. Were oxidative addition a plausible mechanism, more CuH^+ and $Cu(CH_3)^+$ fragment ions would be expected. Heterolytic cleavage was also suggested as the reactive pathway for Pd(I) with alkanes[11] as well as Fe(I) and Co(I) with silyl-substituted amines.[41]

Table I. Ionization Energies of Selected Compounds

compound	ionization energies,[a] eV
toluene	8.82
1-octyne	9.95 ± 0.02
2-octyne	9.31 ± 0.02
3-octyne	9.52 ± 0.02
4-octyne	9.20 ± 0.02

[a] Ionization energies are from ref 34.

It has been generally presumed that Cu(I) is unable to participate in oxidative addition reactions because its first and second electron promotion energies are high. Gas-phase Cu(I) acts in accord with this supposition in many reactions. For example, Cu(I) was shown to form only association complexes with propene,[12] to bind weakly with isobutane,[13] and to be inert with alkanes under the nearly thermal conditions of ion cyclotron resonance spectrometry.[14] In the reactions of Cu(I) with phenyl halides, only complexation products were observed.[15]

Several examples of more vigorous Cu(I) reactivity are also found in the literature. As discussed above, Cu(I) reacts via a heterolytic cleavage mechanism with alkanes in ion beam experiments in which translational energy is added to overcome endothermicity.[10] Insertion into C–C and C–H bonds of alkanes was also observed for sputtered copper(I) ions.[16] A dissociative attachment mechanism, which requires the organic molecule to contain a heteroatom, was suggested to explain the reactivity of Cu(I) with esters and ketones,[17] alkyl halides,[18] and alcohols.[19] The operation of an ion/dipole mechanism[3g,4g] was found in the reaction of Cu(I) with isopropyl isocyanate,[20a] butyl isothiocyanate,[20b] and α-substituted butaneisonitriles.[20c] Oxidative addition by Cu(I), however, was cited to explain activation of O–H bonds[21] and O–NO bonds.[22] Allylic insertion into alkenes by Cu(I)[23] is analogous to the reactivity of Fe(I)[24] with olefins.

We are interested in exploring the occurrence of these reactive pathways for systems involving Cu(I) and octynes and comparing the results with other metal ion systems. Gas-phase oxidative addition reactions between octynes and Fe(I)[4a,9] as well as between 4-octyne and Cr(I),[25] Mn-

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(I),[26] and Co(I), Ni(I), and Cu(I)[27] were previously documented. We continue the investigation of the reactivity of Cu(I) in this study of isomeric and deuterium-labeled octynes. The strategy for this study is to use tandem mass spectrometry to observe metastable ion decompositions and Fourier transform mass spectrometry to examine the details of the bimolecular reaction between the metal ion and each octyne. Although metastable ion decomposition characteristics do not differentiate systems that are closely related and have similar structures, these characteristics are significantly distinctive for the Cu^+/octyne complexes and indicate dissimilar structures.

Experimental Procedures

Tandem Mass Spectrometry Experiments. Tandem mass spectrometry (MS/MS) experiments were performed on a Kratos MS-50 triple analyzer of EBE geometry[28] equipped with an Ion Tech saddle field FAB gun operated at 1 mA and 6 kV. In a typical experiment, the octyne was admitted to a high-pressure FAB source (CI-FAB)[29] to a pressure sufficient to give products with copper(I). Copper ions were ablated by the fast argon beam from a bare copper probe tip situated inside the source where reactions with specific octyne isomers occurred to form adducts. The metastable decompositions of the adduct ion of interest, selected by MS-1 (EB), were monitored with MS-2 (E).

Fourier Transform Mass Spectrometry Experiments. Experiments aimed at understanding the kinetics of the adduct formation were performed on a custom-built Fourier transform (FT) mass spectrometer[30] interfaced to a Nicolet-2000 data system. The FT mass spectrometer was operated at a magnetic induction of 1.2 T, and a 5.08-cm cubic cell was used. Copper(I) ions were produced by laser desorption[31] from a metal probe tip by using the fundamental wavelength (1064 nm) of a Quanta Ray Nd-YAG DCR-2 laser (Mt. View, CA). Each neutral hydrocarbon was introduced to the cell in separate experiments via a Varian leak valve to a pressure of 2×10^{-7} Torr (uncorrected), as measured by a Bayard-Alpert ionization gauge situated near the cell. A trap voltage of 1 V was used to minimize ion evaporation.[32]

The reaction kinetics were monitored by varying the reaction time prior to the detection pulse. For these experiments, the density of the neutral molecule was determined from the well-characterized reaction of $C_7H_7^+$ with toluene.[33] A filament producing 30-eV electrons over a 3-ms beam time was employed. The density of toluene at an ionization gauge reading of 1.5×10^{-6} Torr was calculated to be 6.7×10^9 molecules/cm^3. Reaction rate constants for the Cu(I) interacting with the octyne isomers were calculated by assuming that the octynes and toluene have similar ionization cross sections and, thus, similar ionization gauge responses. This is a reasonable assumption because the compounds have ionization energies that are within 1 eV of each other (see Table I).[34] Because the ionization energy of toluene is less than the ionization energies of the octynes, however, the calculated rate constants for the reactions of Cu(I) and the individual octyne isomers are upper limits.

Reagents. Toluene and the alkynes were purchased from Wiley Organics or Aldrich Chemicals and were used without further purification other than subjecting them to multiple freeze–pump–thaw cycles to eliminate noncondensable gases. The synthesis of the deuterated octynes was reported previously.[35]

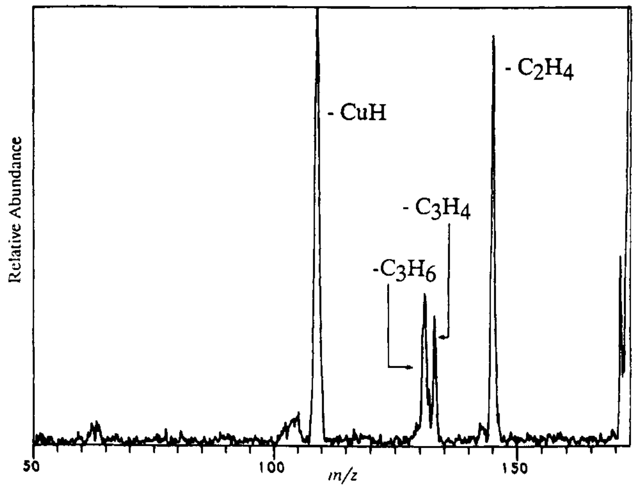
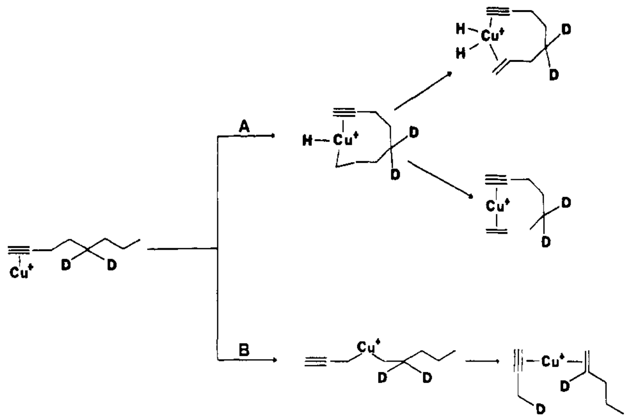


Figure 1. Metastable ion decomposition spectrum of [Cu^+/1-octyne].

Scheme I



Results and Discussion

Metastable Ion Mass Spectrometry Experiments. The adducts of Cu(I) and the octyne isomers undergo rich metastable ion decompositions. Losses of C_2H_4, $H^{\bullet}$, H_2, and CuH are common. Distinctive losses such as that of C_4H_8 from the [Cu^+/2-octyne] and [Cu^+/4-octyne] adducts also occur. The mechanisms leading to the formation of these various fragments will be discussed in the following paragraphs.

[Cu^+/1-Octyne]. The [Cu^+/1-octyne] adduct undergoes parallel losses of CuH, H_2, $H^{\bullet}$, and C_2H_4 (Figure 1). The losses of CuH and C_2H_4 are the most facile and occur to nearly the same extent. Losses of C_3H_6 and C_3H_4 occur to a lesser extent.

The reaction pathways leading to the various decompositions can be elucidated from the spectrum of the adduct of Cu(I) and [5,5-$^2H_2$]-1-octyne. Deuterium incorporation into the departing ethene and propene neutral molecules is not observed for this labeled adduct. Thus, one interaction of Cu(I) with 1-octyne must occur so as to keep the CD_2 unit intact. The remote functionalization mechanism, shown as path A in Scheme I, satisfies this requirement. An alternative to C–C cleavage is transfer of a β-hydrogen to the metal center. This pathway leads to subsequent elimination of H_2.

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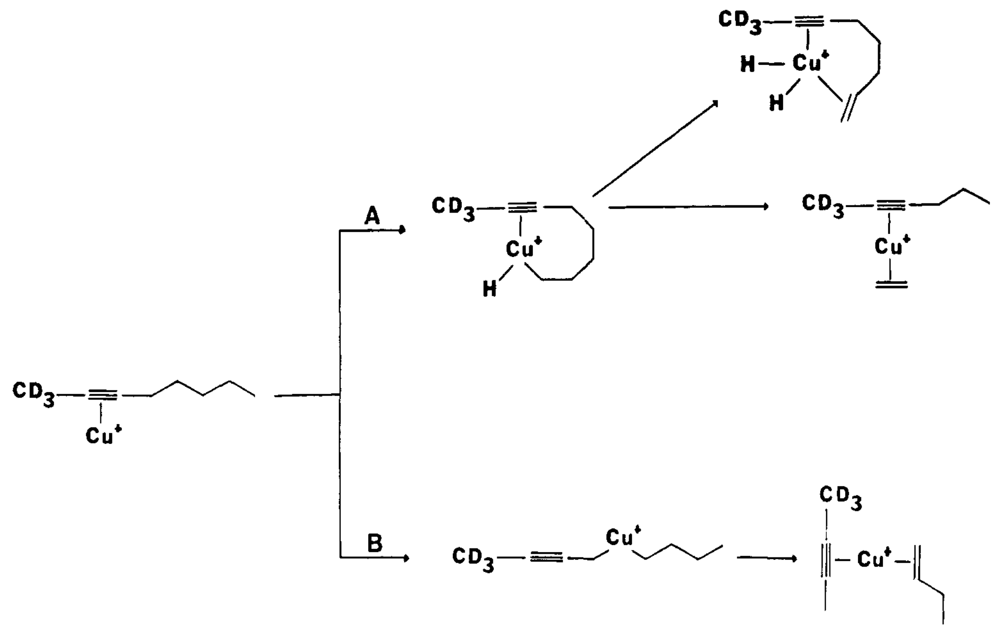
Scheme II



We cannot arbitrarily rule out a small fraction of $C_3H_2D_2$ loss because the product would overlap with the product formed upon elimination of C_3H_6. The propene-loss product, however, is approximately the same percentage of all products in the spectra of the labeled and unlabeled complexes. Therefore, we assume that the loss of the isobaric $C_3H_2D_2$ species is minor, at best, and does not contribute to the peak representing the loss of C_3H_6.

Incorporation of two deuteriums into the C-5 position of 1-octyne causes the loss of C_3H_4 from the unlabeled adduct to shift to the loss of C_3H_3D from the labeled adduct. Thus, the C-5 position is involved in this fragmentation pathway. The propargylic insertion mechanism depicted in Scheme I (path B) fits these observations.

Deuterium labeling of the C-5 position of 1-octyne also shows that the losses of CuH versus CuD occur in the ratio of 1.36. The abundance of the CuD loss product is higher than is expected for arbitrary abstraction of one deuterium from among 14 possible abstraction candidates. This increased propensity for CuD loss suggests that the loss of CuH proceeds primarily via selective abstraction of an internal rather than a terminal hydride. The implications of these data are discussed later.

[Cu$^+$/2-Octyne]. Metastable decomposition of the [Cu$^+$/2-octyne] adduct is dominated by the loss of CuH. A second facile loss is that of C_4H_6 (see Figure 2).

An understanding of the pathways that form these ions is gained from the metastable ion spectrum of [Cu$^+$/[*1,1,1*-$^2H_3$]-2-octyne]. Neutral, unlabeled ethene is lost from the isotopically labeled adduct. A likely explanation is that ethene is formed and then eliminated via the remote functionalization mechanism illustrated in Scheme II (path A). An analogous reaction was observed for [Fe$^+$/2-octyne], which loses ethene and H_2.[36] The deuterium-labeled carbon is isolated from the tail end of the octyne molecule into which the metal ion inserts. Thus, deuterium incorporation into the labile ethene cannot occur. Loss of H_2 probably takes place via the remote functionalization mechanism because H_2 is still eliminated when the isotopomer is used as the reagent.

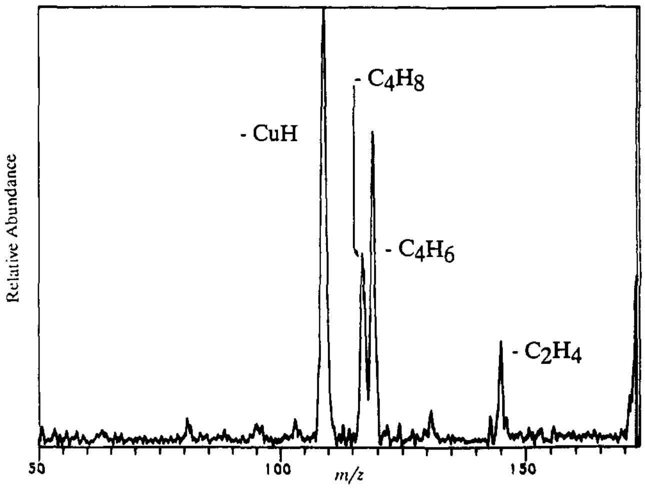


Figure 2. Metastable ion decomposition spectrum of [Cu$^+$/2-octyne].

Labeling the C-1 position provides evidence for the reactive pathway that leads to elimination of C_4H_6 from unlabeled [Cu$^+$/2-octyne]. Loss of the corresponding $C_4H_3D_3$ species occurs from the deuterium-labeled adduct, whereas the loss of C_4H_8 from [Cu$^+$/2-octyne] remains as C_4H_8 from [Cu$^+$/[*1,1,1*-$^2H_3$]-2-octyne] species. These observations can be understood if the interaction occurs via the propargylic insertion pathway outlined in Scheme II (path B). Transfer of a β-hydrogen from one ligand to the metal followed by transfer to the second ligand generates another π-bound ligand, which can exist as either a 1,2-butadiene species or 2-alkyne entity, depending on which position receives the incoming hydrogen. An analogous situation pertains to the reactions of Fe(I) with octynes.[4a]

From an initial analysis of the decomposition products of [Cu$^+$/2-octyne], one might assume that the C-1 position is a mere bystander in the reaction. We see no evidence for deuterium exchange between ligands to distribute the label to different decomposition products. Indications of a more complex interaction, however, come from a comparison of the abundances of the observed products. From the [Cu$^+$/2-octyne] adduct, the loss of the C_4H_6 ligand occurs 1.6 times more readily than the loss of the C_4H_8 ligand. Loss of $C_4H_3D_3$ occurs as readily as loss of C_4H_8 from the deuterium-labeled adduct, however. Thus, some type of interaction must occur between Cu(I) and the

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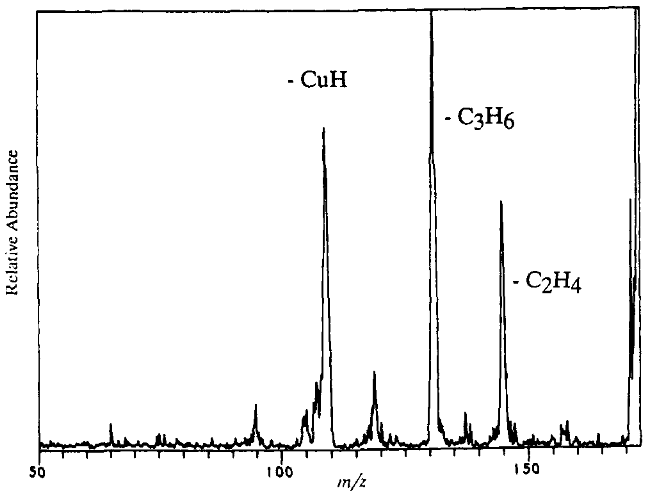
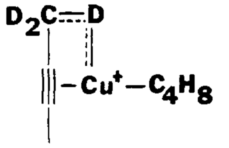


Figure 3. Metastable ion decomposition spectrum of [Cu^+/3-octyne].

hydrogen or deuterium attached to the C-1 position, and that interaction must be stronger for CuD than for CuH. The interaction may involve a three-center two-electron bond as is depicted by structure 1 in which hydrogen would



1

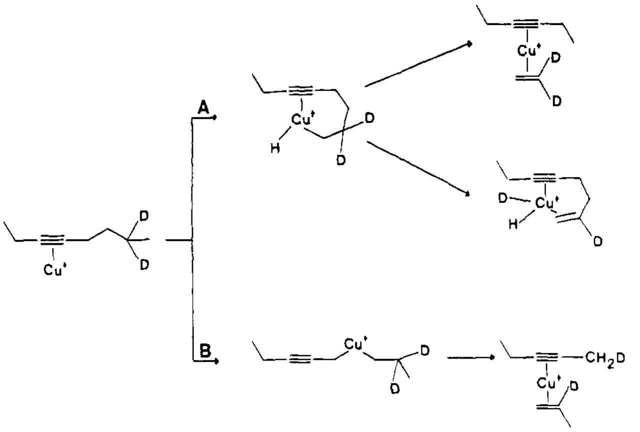
act as a bridge between copper and carbon. Three-center two-electron bonds also occur between Cu(I) and low molecular weight diatomic gases such as H_2 and D_2.[37] Hydrogen transfer to the C_4H_8 ligand does not occur on the time frame of our experiments.

It is possible that the C_4H_6 loss from the unlabeled species shifts to both $C_4H_4D_2$ and $C_4H_3D_3$ losses from the labeled adduct. In that case, the ion produced by elimination of $C_4H_4D_2$ would overlap with that produced by loss of C_4H_8. The abundance of the C_4H_8 loss product, however, is nearly identical (within ±10% relative abundance) to that formed from the unlabeled adduct, indicating that the loss of $C_4H_4D_2$ is minor at best.

In an earlier study of [Fe^+/2-octyne], it was suggested that decomposition of the adduct to form $FeC_4H_6^+$ occurs in part as a result of dehydrogenation of $FeC_4H_8^+$.[9] If dehydrogenation occurs from $CuC_4H_8^+$ to form $CuC_4H_6^+$ in a parallel process with simple expulsion of the C_4H_6 ligand, we would expect to observe formation of both $CuC_4H_6^+$ and $CuC_4H_3D_3^+$ from the deuterium-labeled adduct. Only $CuC_4H_3D_3^+$ is formed, however. Thus, the reaction of Cu(I) with 2-octyne is not identical to that of Fe(I), but the differences are subtle.

The predominant decomposition pathway of the [Cu^+/2-octyne] adduct, loss of CuH, appears to be mainly unaffected by the deuteration of one terminus of the organic entity. Loss of CuH from the deuterium-labeled adduct occurs 10 times more readily than loss of CuD, but only one-third as readily as would be expected if all CH and CD positions were equivalent with respect to Cu(I) reactivity. This observation supports the suggestion that Cu(I) has a greater affinity for internally located hydrides than for terminal hydrides. The affinity is not so great to preclude abstraction when the terminal hydride is in a sterically favorable position, such as occurs when Cu(I) is anchored to the triple bond of 2-octyne.

Scheme III



[Cu^+/3-Octyne]. The metastable ion decompositions of the [Cu^+/3-octyne] adduct occur mainly by competitive losses of C_3H_6, CuH, and C_2H_4 (see Figure 3). Information illuminating the decomposition of [Cu^+/3-octyne] is obtained from the decomposition of [Cu^+/[7,7-$^2H_2$]-3-octyne]; deuterated ethene, $C_2H_2D_2$, is lost from this adduct. These data are consistent with ethene loss via the remote functionalization pathway, as shown in Scheme III (path A).

The [Cu^+/[7,7-$^2H_2$]-3-octyne] adduct also eliminates C_3H_5D via a mechanism that must involve cleavage of the C-7–D bond. Propargylic insertion of Cu(I) into the C-5–C-6 bond leads to β-deuterium transfer from the C-7 position (see Scheme III, path B). Loss of C_3H_5D would also result by first inserting the (complexed) Cu^+ ion in the C-7–D bond followed by β C–C bond cleavage. A distinction between these mechanistic variants is not possible yet. Whether the C_5H_8 ligand exists as a 2-pentyne or a 1,2-pentadiene is determined by the site that receives the transferred hydrogen. If the mechanism for Fe(I) pertains for the Cu(I) system, both ligand structures will be formed.[4a]

Elimination of C_4H_6 from [Cu^+/3-octyne] to give a $CuC_4H_8^+$ species shifts to elimination of C_4H_5D from the deuterium-labeled adduct to give $CuC_4H_7D^+$. This loss is unusual for 3-octyne and more characteristic of a 2-octyne complex. One possibility is a metal-initiated isomerization of the 3-octyne to a 2-octyne entity. The labeling results, however, do not support this. Another possibility is the insertion by Cu(I) into the C-7–D bond by a process similar to that in the initial step of the remote functionalization mechanism. Deuterium is then transferred to the triple bond. At this point, the pathway deviates from that of conventional remote functionalization. Cleavage of the C-4–C-5 bond occurs, rather than cleavage of the C-6–C-7 bond, and leads to a [$(C_4H_5D)Cu(C_4H_7D)$]$^+$ species.

To determine whether the four-carbon chain on one side of the triple bond is important to this interaction, we acquired the metastable ion spectra of the Cu(I) adducts of 2-heptyne and 4-nonyne. Both organic molecules have a four-carbon chain attached to one side of the triple bond. Were cleavage of the bond adjacent to the triple bond and rearrangement of the organic entity to occur for [Cu^+/2-heptyne] as described above for the 3-octyne system, we would expect to find evidence for elimination of C_4H_8 or C_3H_4. Similarly, elimination of C_4H_8 or C_5H_8 would be expected from the [Cu^+/4-nonyne] adduct. The only loss to be observed, however, is a small elimination of C_4H_8 from [Cu^+/4-nonyne]. Thus, the mechanism does not appear to be affected by the length of the carbon chain and remains unclear.

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[37] Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* 1986, 90, 6576.

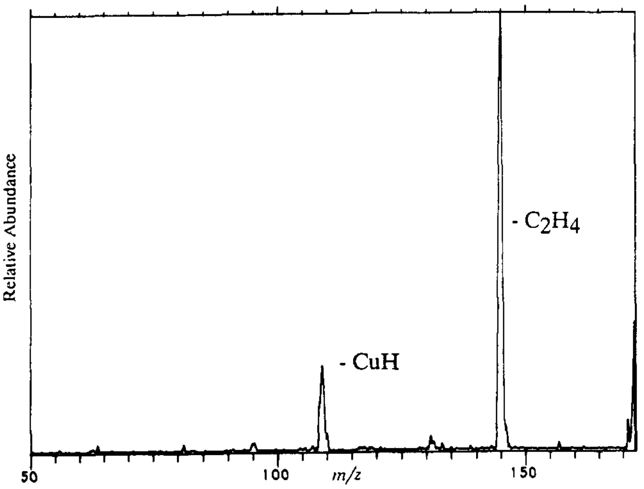


Figure 4. Metastable ion decomposition spectrum of [Cu$^+$/4-octyne].

Analogous interactions do not take place with the other [Cu$^+$/octyne] systems studied here, but a similar process may occur for the [Fe$^+$/3-octyne]$^+$ system.[4a] Both $FeC_4H_8^+$ and $FeC_4H_6^+$ are observed, but of the two, the $FeC_4H_6^+$ species is 10 times more abundant.

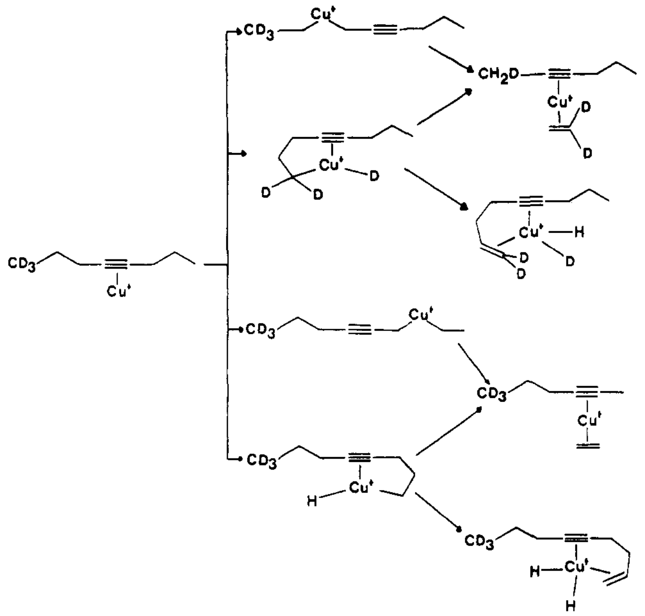
The [Cu$^+$/[7,7-$^2H_2$]-3-octyne] adduct gives loss of CuH and CuD; elimination of CuD is favored by a factor of 1.6. This is more evidence for the preference of abstraction of internal hydrides by Cu(I). Because abstraction of deuteride is so facile here, even though two of eight internally bonded sites are occupied by D, the proximity of the deuteride must be a factor in the abstraction.

[Cu$^+$/4-Octyne]. The [Cu$^+$/4-octyne] adduct presents a strikingly simple metastable ion spectrum (Figure 4), even when compared to the spectra obtained for the other Cu(I) adducts investigated here. The spectrum provides little insight into the pathways of fragment formation. The metastable ion spectrum of [Cu$^+$/[*1,1,1*-$^2H_3$]-4-octyne] also provides no additional clarification. The labeled adduct generates ions resulting from parallel losses of C_2H_4 and $C_2H_2D_2$ [kinetic isotope effect (k_H/k_D) of 1.43]. These losses do not distinguish the propargylic insertion mechanism from the remote functionalization pathway (see Scheme IV).

The minor loss of C_3H_6 occurs along with the loss of C_2H_4 by means of the remote functionalization mechanism for the adducts of Cu(I) and the other isomeric octynes. Roughly equivalent losses of C_3H_6 and $C_3H_3D_3$ occur from [Cu$^+$/[*1,1,1*-$^2H_3$]-4-octyne]. It is possible that these losses may occur similarly to the cleavage of the bond adjacent to the triple bond in the 3-octyne system discussed above. The losses are more consistent with reaction via the remote functionalization pathway and, thus, are suggestive that remote functionalization occurs to some extent for the 4-octyne system, also.

In a recent study[27] of 4-octyne complexes with several first-row transition metal ions, the rate-determining step for the elimination of C_2H_4 from [Cu$^+$/4-octyne] was determined. Loss of ethene from the adduct was not associated with a kinetic isotope effect. Instead, a small isotope effect (k_H/k_D = 1.93) pertains to the initial C–H bond activation. The size of the isotope effect is consistent with propargylic insertion via a bent transition structure. We observe a smaller isotope effect (k_H/k_D = 1.43) for C–H bond activation: this value is comparable to those reported for other first-row transition metal ions. The deviation does not dispute the conclusion that the elimination of ethene proceeds via a propargylic insertion mechanism, but we suggest that a small amount of remote functionalization mechanism cannot be ruled out.

Scheme IV



Fourier Transform Mass Spectrometry Experiments. The Fourier transform mass spectrometry experiments with the [Cu$^+$/octyne] adducts were performed primarily to investigate the kinetics of adduct formation, but they also yielded structural and mechanistic information that complements that obtained by using tandem mass spectrometry. This aspect of the FTMS work will be discussed briefly here and in the section that follows.

Products of the three mechanistic pathways (propargylic insertion, remote functionalization, and hydride abstraction) are also seen in the FTMS experiments. One major difference between the decompositions in the FT and the tandem spectrometers is that, in the FTMS experiment, losses of H$^\bullet$ and H_2 do not occur to a detectable extent. The abundances of the other remote functionalization products are less in the FTMS experiment than those formed via metastable ion decompositions (see Figure 5[38]). The relative abundances of the propargylic insertion products remain nearly the same as in the tandem experiments, however.

The most facile process in the FTMS experiment for all the adducts except [Cu$^+$/4-octyne] is the generation of a $C_8H_{13}^+$ species by elimination of CuH. The process generates 87% of the products from the [Cu$^+$/1-octyne] adduct. The abundance of $C_8H_{13}^+$ from the other adducts is less than from [Cu$^+$/1-octyne], but it does not decrease smoothly as the triple bond is moved from the C-1 position to the C-4 position. The data (see Figure 5) from both experimental techniques support the proposition that internally bonded hydrogens are preferred for abstraction by the metal ion. The [Cu$^+$/1-octyne] adduct provides 10 possible sites for hydride abstraction, whereas the other adducts provide only 8. The hydride abstraction process for the [Cu$^+$/4-octyne] adduct is reduced owing to competition by the low energy and high probability of the

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[38] To generate Figure 5, the ion abundances of all products attributed to a specific decomposition pathway from each individual adduct were summed and divided by the abundance of all products of all pathways. As discussed above, we are unable to determine the specific abundance contributions of the remote functionalization and propargylic insertion mechanisms to the decomposition of [Cu$^+$/4-octyne]. Ethene elimination from the complex is attributed to propargylic insertion by other workers.[27] Thus, all ethene elimination from [Cu$^+$/4-octyne] is attributed to the propargylic insertion pathway.

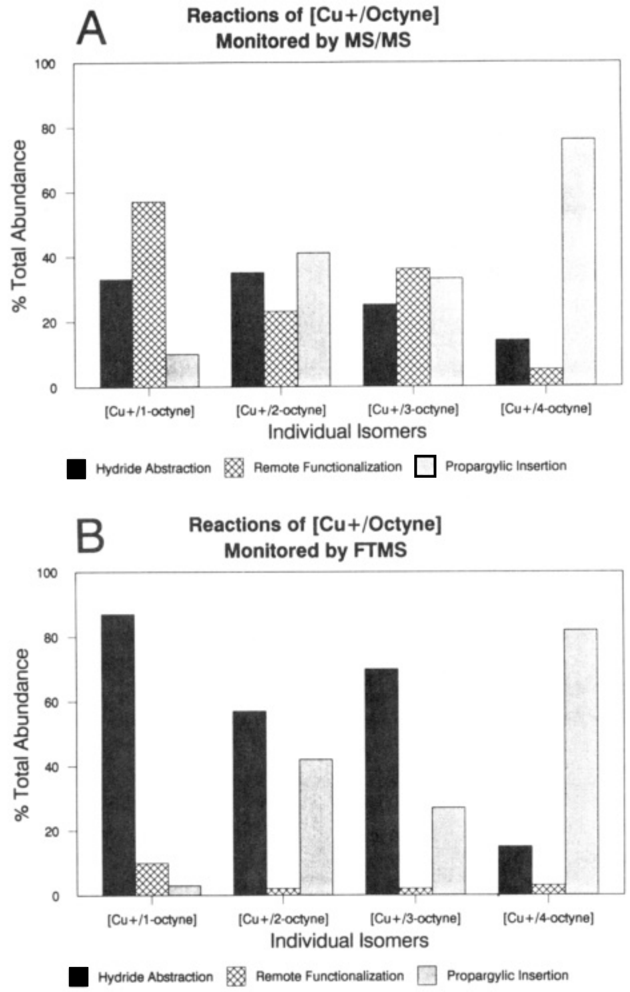

Figure 5. Abundances of products of reactive pathways as observed by using (A) MS/MS or (B) FTMS.

Table II. Reaction Rate Constants for [Cu$^+$/Octyne] Adducts

adduct	k', s^{-1}	k, cm^3/(molecules·s)
[Cu$^+$/1-octyne]	0.68	7.6×10^{-10}
[Cu$^+$/2-octyne]	0.072	8.1×10^{-11}
[Cu$^+$/3-octyne]	0.81	9.0×10^{-10}
[Cu$^+$/4-octyne]	0.10	1.1×10^{-10}

propargylic insertion reaction.

The FTMS experiments also provide insight into the kinetics of adduct formation. A plot of the depletion of Cu(I) over time is depicted for the [Cu$^+$/3-octyne] species in Figure 6. The exponential decay of the Cu(I) signal is in accord with pseudo-first-order reaction kinetics. Similar kinetic behavior pertains to formation of the other [Cu$^+$/octyne] adducts, and the pseudo-first-order rate constants as well as the second-order rate constants are given in Table II.

The rate constants for the formation of the [Cu$^+$/2-octyne] and [Cu$^+$/4-octyne] adducts are nearly 1 order of magnitude smaller than those for formation of [Cu$^+$/1-octyne] and [Cu$^+$/3-octyne]. The latter two reactions have rate constants that are nearly identical. Part of the difference is the channel for CuH elimination. The [Cu$^+$/1-octyne] and [Cu$^+$/3-octyne] adducts both undergo facile eliminations of CuH, whereas the other two adducts do so to a lesser extent.

The Langevin capture rate constants for the [Cu$^+$/octyne] adducts are also presented in Table II. The polarizability values for the octynes, necessary for the calculation of the capture rate constants, were obtained by using

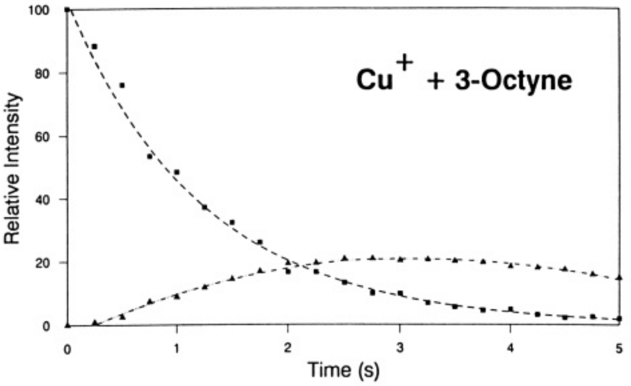

Figure 6. Depletion of the Cu$^+$ signal (■) and increase in the [Cu$^+$/3-octyne] signal (▲) with respect to time.

the method of Le Fevre.[39] The results indicate that the rapid reactions of the [Cu$^+$/1-octyne] and [Cu$^+$/3-octyne] systems occur approximately for one of every two collisions. The two less reactive systems are approximately 1 order of magnitude less efficient.

Comparison of FTMS and Metastable Ion Spectrometry Results. Differences in the experimental conditions of FTMS and MS/MS account for the different product distributions (see Figure 5 for a comparison). These differences are most readily apparent when a comparison of the remote functionalization and hydride abstraction products is made.

Elimination of CuH is the dominant decomposition of the intermediate formed in the FT mass spectrometer cell. The process is significantly diminished for all adducts except [Cu$^+$/4-octyne] in the tandem mass spectrometry experiment. In the FT cell, the intermediate possesses the full energy released when Cu(I) bonds to the octyne. No collisional stabilization occurs in the low-pressure environment. On the other hand, the metastable ion decompositions in the tandem mass spectrometer are of intermediates that are stabilized by collisions with excess octyne acting as a bath gas. Remote functionalization, which accounts for less than 10% of the products from individual adducts in the FTMS experiment, is now a facile process (see Figure 5). One remote functionalization channel, elimination of H_2, disappears completely in the FTMS experiments. The internal energy of the metastably decomposing adducts is low, just sufficient to cause fragmentation, and only the most stable products are formed. Thus, remote functionalization is the lowest energy process of the three.

Given the steric demands of the remote functionalization transition state, the rate of occurrence will likely increase only slowly with internal energy. Elimination of CuH, however, is a kinetically simple reaction with a higher energy requirement than that of remote functionalization, and thus, it occurs most readily from the higher energy species. The propargylic insertion mechanism is intermediate in energy requirements and is only slightly affected with respect to the other two pathways as the internal energy of the adduct changes.

Preliminary results obtained by collisionally activating the adducts indicate that propargylic insertion increases whereas remote functionalization decreases with increasing adduct internal energy. These trends lend support to the above conclusions concerning the energy requirements of the various decomposition processes.

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[39] Le Fevre, R. J. W. In *Advances in Physical Chemistry*; Gold, V., Ed.; Academic Press: London, 1965.

Other Mechanistic Considerations. The copper(I) cation exhibits strong reactivity with the octyne isomers, particularly with the 1- and 3-isomers. Most organic compounds containing heteroatoms form only condensation products with Cu(I),[40] but this is not the case for Cu(I) interacting with the octynes, as well as with alkenes and other alkynes. Three distinct reaction pathways are evident: propargylic insertion, remote functionalization, and hydride abstraction. Propargylic insertion and remote functionalization also occur in the reactions of Cr(I), Mn(I), and Fe(I) with 4-octyne.[9,25,26,41] Interestingly, whereas hydride abstraction to form a stable MH species is significant for [Cu$^+$/octyne] adducts, the pathway is not observed in the Cr(I) system and contributes to only a minor extent in the Fe(I) and Mn(I) systems. Thus, our discussion of the reactivity of Cu(I) begins with hydride abstraction.

Hydride Abstraction. Armentrout and co-workers[10] suggested that Cu(I) reacts with alkanes via a heterolytic cleavage mechanism that leads to abstraction of H$^-$ or R$^-$. An analogous mechanism was also proposed to explain the reactivity of Pd(I) with alkanes[11] and Au(I) with alkanes, alkenes, and alkyl halides.[42] Both Cu(I) and Pd(I) have high hydride affinities (221 ± 4[10] and 232 kcal/mol,[11] respectively), but the values are slightly less than those of various R$^+$ species (230–280 kcal/mol).[10] The Cu cation, therefore, is able to abstract H$^-$ and form a neutral copper species in an exothermic process as shown in eq 3.

$$\mathrm{Cu^+ + R{-}H \rightarrow (H{-}Cu){-}R^+ \rightarrow CuH + R^+} \qquad (3)$$

Armentrout and co-workers[10] suggested that two electrons from a C–H or C–C bond are donated into the empty 4s Cu(I) orbital, forming a stable intermediate with a three-center two-electron bond. The intermediate, held together by acid/base interactions, decomposes via a low-energy alkyl ion loss. Our experiments with labeled octynes indicate that abstraction of internal rather than terminal hydrides is preferred. In this way, stable secondary carbocations are formed, at least initially. Additionally, internal C–H bonds are approximately 3 kcal/mol weaker than terminal C–H bonds. Another contributing factor is the ionization energy of the alkyl fragments.

These factors, however, are not sufficient to explain why hydride abstraction occurs to such a large extent when M$^+$ = Cu$^+$ compared to when M$^+$ = Fe$^+$,[4a,9] Mn$^+$,[25] or Cr$^+$.[26] Other factors specific to Cu(I) must play a part. One is the formation of the stable species, copper(I) hydride, which has a stable electron configuration with a pair of electrons in a σ-bonding orbital and a closed 3d^{10} shell. Other metal ion hydrides have empty d orbitals and, thus, would be less stable than CuH. Also, the bond dissociation energy for (Cu–H)[43] is significantly greater than the D^0(M–H) values given for other first-row transition metals, other than Ni. The ionization energy (IE) of CuH (9.4 ± 0.2 eV) is also higher by at least 1 eV than those of other transition metal hydrides (the IE of FeH, for example, is 7.7 ± 0.2 eV). Therefore, it can be understood that hydride abstraction is predominant for decomposition of the [Cu$^+$/octyne] systems but occurs to little or no extent for adducts of octynes with Fe(I),[4a,9] Cr(I),[26] Mn(I),[25] and Ni(I).[27]

Oxidative Addition Mechanisms. The experiments strongly suggest that Cu(I) undergoes oxidative addition into propargylic C–C and terminal C–H bonds of alkynes. This behavior[20] of Cu(I), which is much like that of Fe(I), a metal ion well-known to exhibit oxidative addition activity,[44] is unexpected. How does Cu(I), with high first and second promotion energies (2.8 and 8.7 eV, respectively[45]) insert into C–C and C–H bonds?

One answer to this puzzling question may lie in the initial anchoring of the metal ion to the triple bond. Interaction of Cu(I) with π bonds occurs according to the Dewar–Chatt–Duncanson model[46] by donating electron density from a filled d orbital to the empty π^* orbital on the alkyne. Electron density is also donated from the filled π orbital of the alkyne into the empty Cu(I) 4s orbital. The extent of this interaction depends on the electron affinity (EA) and promotion energy (PE) of the metal. For Cu(I), with high PE and moderate EA (7.72 eV),[45] electron donation from the metal is less significant than electron acceptance by the metal. The newly ligated Cu(I) has a lower overall PE than the bare metal ion because the net shift in electron density is toward the metal. Recent theoretical studies indicate that electron donation from d orbitals of Cu$^+$ in complexes with CO[47] or propyne[48] is negligible.

Generally, ligands that donate electron density to a metal lower its PE and EA. Conversely, the PE and EA will be raised when the metal donates more electron density to the ligands than it receives. For the Cu(I)/octyne systems, the PE is lowered sufficiently to allow Cu(I) to participate in oxidative addition. Oxidative addition is further facilitated by the weakening of the bonds in the organic entity near the interaction site by the shift in electron density.

There are reasonably smooth trends for how the two oxidative addition pathways (i.e., propargylic insertion and remote functionalization) trade off as the position of the triple bond is varied. Remote functionalization, which is facile only under the conditions of the MS/MS experiment (i.e., for ions of low internal energy), occurs most readily for the 1-octyne adduct and least for the 4-octyne adduct. This is due to the long alkyne chain of 1-octyne, which allows an interaction between the terminal CH and the metal anchored at the triple bond. The 2- and 3-octyne isomers show intermediate reactivity.

The most reactive isomer for propargylic insertion is 4-octyne whereas 1-octyne is least reactive. The high reactivity of 4-octyne is attributed to the two internal propargylic bonds that, when subjected to oxidative addition, ultimately produce substituted alkenes and alkynes (or 1,2-dienes).

The only other complete metal ion/octyne data set is for interactions with Fe(I).[4a,9] The data for that system

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[40] See, however: Reference 20.

[41] Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898.

[42] Chowdhury, A. K.; Wilkins, C. L. *J. Am. Chem. Soc.* **1987**, *109*, 5336.

[43] (a) A summary of metal hydride bond dissociation energies may be found in the following work: Armentrout, P. B. In *Bonding Energetics in Organometallic Compounds*; Marks, T., Ed.; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990. (b) Reports of experimentally determined bond dissociation energies for CuH include (*i*) 61 ± 4 kcal/mol from: Reference 10. (*ii*) 60 ± 4 kcal/mol from: Kant, A.; Moon, K. A. *High Temp. Sci.* **1981**, *14*, 23; **1979**, *11*, 55. (c) A calculated value for the CuH bond dissociation energy is 67 kcal/mol from ref 19.

[44] Recent reviews of metal ion-molecule reactions provide summaries of the reactivity of Fe$^+$ with different types of molecules: (a) MacMillan, D. K.; Gross, M. L. In *Gas-Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum Publishing: New York, 1989. (b) Crekory, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Stenrück, N.; Süîrle, D.; Weiske, T.; Schwan, H. In *Organometallics in Organic Synthesis*; Werner, H., Erker, G., Eds.; Springer Verlag: Heidelberg, 1989; Vol. 2.

[45] Moore, C. E. *Atomic Energy Levels*; NRSDS-NBS 35; Washington, DC, 1971; Vol. I-III.

[46] (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

[47] Merchan, M.; Nebot-Gil, I.; Gonzalez-Luque, R.; Orti, E. *J. Phys. Chem.* **1987**, *87*, 1690.

[48] Andres, M. M.; Nebot-Gil, I.; Tomas, F. *J. Phys. Chem.* **1985**, *89*, 4769.

Organometallics **1992,** *11,* 2087–2098

do not correlate directly with the results discussed here, however, because the study of Fe(I) was of collisionally activated adducts. Of the three decomposition pathways for the Cu(I)/octyne adducts, hydride abstraction is not observed for Fe(I)/octynes, and propargylic insertion occurs more readily than remote functionalization. The percentage of propargylic insertion products increases as the triple bond is moved across the octyne skeleton, whereas the percentage of remote functionalization decreases.[49] This is similar to the trend observed for the Cu(I) systems.

Preliminary results obtained in this laboratory by collisional activation indicate that the [Cu^+/octyne] adducts need little additional energy to open a multiplicity of new reaction modes. Additional work with the collisionally activated decompositions of the adducts studied here should provide more insight into the interesting reactivity of Cu(I).

Acknowledgment. This work was supported by funds from the National Science Foundation (CHE-9017250), the Deutsche Forschungsgemeinschuft, and the Volkswagen-Stifung.

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(49) Only the products of the remote functionalization and propargylic insertion pathways were considered when the percent calculations were made.

General Route to the "Half-Open" Metallocenes C_5Me_5Ru(pentadienyl) and C_5Me_5Ru(diene)Cl. X-ray Structures of an Optically Active Half-Open Metallocene and of a Dimetallic Ruthenabenzene Complex

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Treatment of $[C_5Me_5RuCl_2]_n$ (1) with various acyclic and cyclic diolefins in the presence of zinc powder leads to the "half-open" metallocenes C_5Me_5Ru(pentadienyl), to C_5Me_5Ru(diolefin) chloro compounds, or to cationic complexes with an η^6 ligand, depending on the stereochemistry and substitution pattern of the starting diolefin. An X-ray crystallographic analysis of optically active C_5Me_5Ru(dimethylnopadienyl) (11; $[\alpha]_{589} = -250.6°$), which crystallizes from methanol in the monoclinic space group $P2_1$ with $a = 9.214$ (4) Å, $b = 17.593$ (8) Å, $c = 13.115$ (6) Å, $\beta = 101.55$ (4)°, and $Z = 4$, reveals the coordination of the C_5Me_5Ru moiety from the sterically less hindered side of the tricyclic ligand. The half-open metallocene $C_5Me_5Ru(2,4\text{-}C_7H_{11})$ (2; $2,4\text{-}C_7H_{11} = \eta^5$-2,4-dimethylpentadienyl) can be protonated with HBF_4, yielding $[C_5Me_5Ru(H)(C_7H_{11})]BF_4$, which has a dynamic structure on the NMR time scale. 2 can also be lithiated; the site of lithiation could be determined by quenching experiments with $MeOD/CH_3COOD$. 2 reacts with $[C_5H_5Ru(CH_3CN)_3]PF_6$ to yield the dimetallic complex $[C_5H_5Ru(\mu\text{-}2,4\text{-}C_7H_9)Ru(C_5Me_5)(CH_3CN)]PF_6$ (19). 19 crystallizes from propionic anhydride in the orthorhombic space group *Pnma*, with $a = 13.274$ (2) Å, $b = 11.865$ (2) Å, $c = 16.578$ (3) Å, and $Z = 4$ and displays an η^6 coordination of a ruthenabenzene unit to C_5H_5Ru. The substitution of the diolefin and/or chloro ligand in C_5Me_5Ru(2-methyl-(*E*)-pentadiene)Cl (7) in a range of solvents and under mild conditions is a rapid and facile process. Mono- and bidentate ligands (Br, CO, CH_3, $P(OMe)_3$, cod) substitute the diolefin, the chloro ligand, or both, depending on reaction conditions, to produce the complex $C_5Me_5RuL_2X$, $[C_5Me_5RuL_3]^+$, or $[C_5Me_5RuL_2L']^+$. All compounds are obtained in high yield and have been characterized by a combination of elemental analyses and spectroscopic methods (IR, ^1H and ^{13}C NMR, MS).

Introduction

The chemistry of "open" and "half-open" metallocenes, that is of metal complexes with pentadienyl ligands, was largely left unexplored for a long time, in contrast to the vigorous development in the chemistry of related cyclopentadienyl or allyl complexes. Recent research, however, confirmed earlier predictions on the stability of metal–pentadienyl compounds and their chemical and catalytic properties.[1,2] This is largely due to the work of Ernst and co-workers. Two general synthetic routes to such complexes emerged from their research, namely the metathetical pathway of reacting lithium, potassium, or tin pentadienyl derivatives with transition-metal halides and the reductive method employing either $RuCl_3 \cdot nH_2O$ or Na_2OsCl_6, zinc powder, and an appropriate diolefin ligand, based on the general procedure developed by Vitulli.[3]

Both methods are somewhat restricted, as the absence or presence of additional methyl substituents in the organic ligand very often is crucial for synthetic success,[2] and the handling of the pyrophoric and reactive alkali-metal pentadienyl derivatives requires considerable synthetic skill. The reductive route, on the other hand, suffers from unpredictable yields, possibly owing to the uncertain and variable nature of the commercial starting material

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(1) Ernst, R. D. *Acc. Chem. Res.* **1985,** *18,* 56.
(2) Ernst, R. D. *Chem. Rev.* **1988,** *88,* 1255.
(3) Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* **1980,** 1961.

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