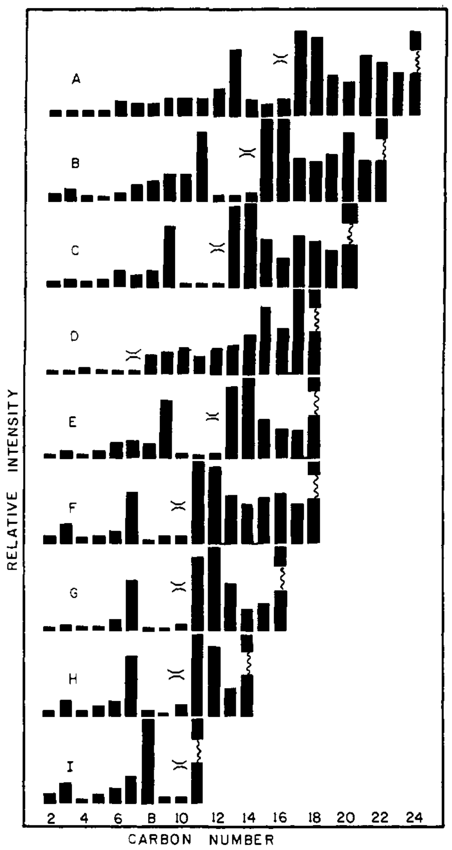

Figure 3. Bar graph representations of the CAD spectra of monounsaturated fatty acids (carbon one is the carboxylate terminus): (A) nervonic acid (*cis*-15-tetracosenoic acid); (B) erucic and brassidic acids (*cis*- and *trans*-13-docosenoic acids); (C) *cis*-11-eicosenoic acid; (D) petroselinic and petroselaidic acids (*cis*- and *trans*-6-octadecenoic acids); (E) *cis*- and *trans*-vaccenic acids (*cis*- and *trans*-11-octadecenoic acids); (F) oleic and elaidic acids (*cis*- and *trans*-9-octadecenoic acids); (G) palmitoleic and palmtolaidic acids (*cis*- and *trans*-9-hexadecenoic acids); (H) myristoleic acid (*cis*-9-tetradecenoic acid); (I) 10-undecenoic acid).

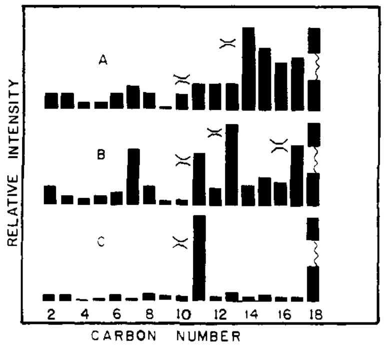

Figure 4. Bar graph representation of the CAD spectra of polyunsaturated and hydroxy fatty acids (carbon one is the carboxylate terminus): (A) linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid); (B) linolenic acid (*cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid); (C) ricinoleic acid (12-hydroxy-9-octadecenoic acid).

the alcohol functionality (α-cleavage).

The enhanced structural information obtained from dissociation reactions of negative ions compared to positive ions may be more general than for the fatty acids reported in this paper.[9] As a test, we are currently exploring the utility of this technique not only for more complex unsaturated acids but also for other unsaturated compounds. The mechanism of the CAD process is also under study.

Acknowledgment. This work was supported by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE 82-11164).

Registry No. Elaidic acid, 112-79-8; nervonic acid, 506-37-6; erucic acid, 112-86-7; brassidic acid, 506-33-2; *cis*-11-eicosenoic acid, 5561-99-9; *cis*-6-octadecenoic acid, 593-39-5; *trans*-6-octadecenoic acid, 593-40-8; *cis*-11-octadecenoic acid, 506-17-2; *trans*-11-octadecenoic acid, 693-72-1; oleic acid, 112-80-1; palmitoleic acid, 373-49-9; palmtolaidic acid, 10030-73-6; myristoleic acid, 544-64-9; 10-undecenoic acid, 112-38-9; linoleic acid, 60-33-3; linolenic acid, 463-40-1; ricinoleic acid, 141-22-0.

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[9] Specific fragmentation of fatty acid ester $(M - H)^-$ ions has also been recently reported: Bambagiotti, A. M.; Coran, S. A; Giannellini, V.; Vincieri, F. F.; Daolio, S.; Traldi, P. *Org. Mass Spectrom.* **1983**, *18*, 133-134.

Preparation and Structural Characterization of Acetylene(2,2′-dipyridylamine)copper(I) Tetrafluoroborate[†]

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Cuprous complexes with ethylene and acetylene have been of interest for many years. These complexes are, in general, unstable (to loss of C_2H_4 and C_2H_2) and only poorly characterized.[1-3] Our interest in this area arises from the proposed role of copper in the binding of the plant hormone ethylene to its receptor site.[4] Although the effects of ethylene on virtually every phase of plant development (germination, growth, flowering, fruit ripening, senescence, and abscission) are well established, the site of ethylene action remains unknown.[4,5] Binding and inhibition studies suggest that a copper ion may be involved.[4,5] We reported recently the synthesis and first structural characterization of stable Cu(I)-ethylene complexes, which established that the coordination chemistry of Cu(I)-monoolefin complexes is consistent with the

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[†] Contribution No. 3211.

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proposed role of copper as the receptor site of ethylene in plants.[6] In this communication, we present our initial results on the synthesis and first structural characterization of a Cu(I) complex with acetylene, $[Cu(NHpy_2)(C_2H_2)]BF_4$ (I), where $NHpy_2$ = 2,2′-dipyridylamine. Such complexes are of interest for several reasons. Acetylene binds competitively with ethylene and will induce the ethylene effect, although a significantly higher concentration is needed.[5] The characterization of I lends additional support for the role of copper by demonstrating that mononuclear $Cu(I)-C_2H_2$ complexes, which are stable to loss of acetylene, can be prepared and structurally characterized. The tight binding of ethylene and acetylene shown by I and the complexes previously reported by us is characteristic of the native systems.[7] Complex I is also of interest from an inorganic perspective because it demonstrates an unusual mode of coordination for Cu(I) ions with acetylene; this chemistry is dominated by the formation of Cu(I)–acetylide complexes, rather than by the formation of complexes analogous to those with monoolefins.[3,6]

The acetylene complex I was prepared by the procedure outline in eq 1. Addition of acetylene to a methanol solution of $[Cu(CH_3CN)_4]BF_4$[8] produced a deep red solution, to which the ligand was added slowly as a powder. The reaction mixture was then filtered under nitrogen and concentrated with acetylene. A white crystalline material was obtained by vapor diffusion of diethyl ether into this methanol solution at room temperature under nitrogen. Elemental analysis[9] and infrared and proton NMR spectral data are consistent with the indicated formulation for I. There is a weak band in the infrared spectrum at 1795 cm^{-1} assignable to the coordinated acetylene molecule. This value is 179 cm^{-1} lower than the C≡C stretching band for free acetylene (1974 cm^{-1}).[10] The proton NMR spectrum has a peak at 5.21 ppm (relative to tetramethylsilane) assigned to the acetylene protons. The compound appears to be indefinitely stable under an inert atmosphere in the solid state at room temperature and can be dissolved in acetylene-free solvents without significant decomposition, as evidenced by the lack of decomposition products in the NMR spectrum.

$$[Cu(CH_3CN)_4]BF_4 + C_2H_2 \xrightarrow[\text{methanol}]{} \xrightarrow[\text{NHpy}_2]{} [Cu(NHpy_2)(C_2H_2)]BF_4 \quad (1)$$

Crystals of I suitable for diffraction were grown from a methanol–diethyl ether solution at room temperature. The compound crystallizes in the monoclinic space group $C2/c$ with four molecules per unit cell of dimensions a = 10.140 (2) Å, b = 17.782 (4) Å, c = 7.852 (1) Å, and β = 105.34 (1)° at −100 °C. Intensity data were collected on a Syntex P3 diffractometer. The structure was solved by direct methods and Fourier methods. After convergence of the non-hydrogen portion of the molecule, all hydrogen atoms were located in a Fourier difference synthesis and refined satisfactorily. The structure was then refined by full-matrix least-squares refinement of 119 variables to an R index of 0.046 and R_w of 0.044 for 1259 independent reflections with $F_o^2 > 2\sigma(F_o^2)$. The structure consists of a three coordinate Cu(I) cation, which is shown in Figure 1, and a BF_4 anion that is well separated from the cation; the shortest Cu–F distance is 4.839 (2) Å. The geometry about the Cu(I) ion, which is coordinated to two pyridyl nitrogen atoms and an acetylene molecule, is trigonal planar.

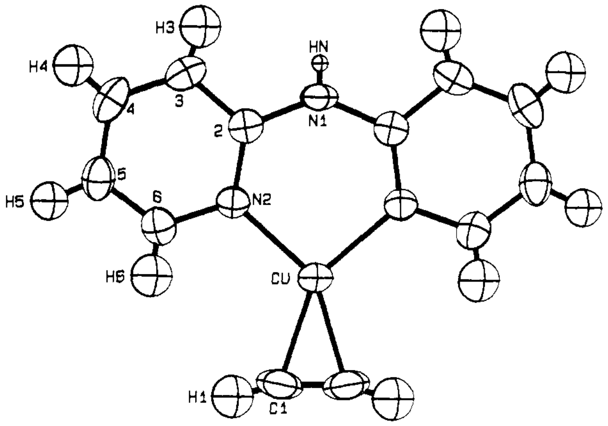

Figure 1. The molecular structure of the cationic portion of $[Cu(NHpy_2)(C_2H_2)]BF_4$. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Cu–N2, 1.968 (3); Cu–C1, 1.971 (4); C1–C1′, 1.188 (11). Selected bond angles (degrees): N2–Cu–N2′, 96.8 (2); N2–Cu–C1, 114.1 (2); C1–Cu–C1′, 35.1 (3).

Two important results emerge from this initial study. Firstly, the coordination chemistry of this complex is similar to that observed for Cu(I)–monoolefin complexes, which have been structurally characterized.[6,11] Importantly, the corresponding ethylene complex, $[Cu(NHpy_2)(C_2H_4)]^+$, appears to have the same structure, on the basis of analytical and spectroscopic data.[12] Trigonal-planar geometry appears to be the preferred geometry for such Cu(I) complexes, although tetrahedral complexes can be prepared with the proper choice of ligands.[3h,6] Secondly, coordination to the Cu(I) ion has virtually no effect on the carbon–carbon bond length of the bound C_2H_2 molecule: 1.188 (11) Å vs. 1.204 Å for free acetylene.[13] A similar result was observed for the effect of Cu(I) coordination to ethylene in the $Cu(I)-C_2H_4$ complexes reported previously by us[6] as well as in the recently reported Cu(I)–diphenylacetylene complexes.[3g] These results suggest that for both acetylene and ethylene σ-bonding is the important interaction with Cu(I) ions, whereas π-backbonding, a key part of the bonding interaction for other d^{10} metal ethylene and acetylene complexes, does not appear to be important.[14]

This study demonstrates that $Cu(I)-C_2H_2$ complexes have the same properties (stability, geometrical preferences, and bonding interactions with Cu(I) ions) as the Cu(I)–ethylene complexes reported by us[6] and additionally provides support for the proposed role of copper in the ethylene effect. The ethylene analogues (propylene, acetylene, carbon monoxide, and other terminally unsaturated compounds[4,5]) bind competitively with ethylene and presumably have the same mode of action. If copper is indeed the binding site for ethylene in plants, it is expected that cuprous ion will form stable complexes with all of the biologically active olefins and acetylenes as well as carbon monoxide. There are now examples of well-characterized Cu(I) complexes with all three of these types of small molecules (CO, C_2H_4 and other monoolefins,[6] and acetylene).

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(9) Anal. Calcd for $C_{12}H_{11}BCuF_4N_3$: C, 41.47; H, 3.19; N, 12.09; Cu, 18.28. Found: C, 41.65; H, 3.33; N, 12.26; Cu, 18.62.

(10) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 387.

(11) (a) Thompson, J. S.; Whitney, J. F., manuscript submitted for publication. (b) The complex $Cu(HBpz_3)(C_6H_{10})\cdot CuCl$ crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions a = 9.951 (3) Å, b = 11.737 (3) Å, c = 9.130 (2) Å, α = 100.51 (2)°, β = 115.80 (2)°, and γ = 79.15 (2)° at −100 °C. Least-squares refinement of 306 variables has led to a value of the conventional R index (on F) of 0.026 and R_w of 0.027 for 3582 reflections having $F_o^2 > 2\sigma(F_o^2)$. The geometry about one of the Cu(I) ions, which is coordinated to two pyrazole nitrogen atoms and a cyclohexene molecule, is trigonal planar, whereas the geometry about the second Cu(I) ion, which is coordinated to a pyrazole nitrogen atom and a chloride ion, is linear.

(12) (a) Thompson, J. S.; Whitney, J. F., manuscript in preparation. (b) The complex $[Cu(NHpy_2)(C_2H_4)]ClO_4$ was prepared from $Cu(ClO_4)_2\cdot 6H_2O$ and Cu metal in a manner analogous to that described for I. The NMR spectrum has a peak at 4.70 ppm assignable to the ethylene protons. Anal. Calcd for $C_{12}H_{13}ClCuN_3O_4$: C, 39.79; H, 3.62; N, 11.60. Found: C, 39.74; H, 3.53; N, 11.44.

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Acknowledgment. The technical assistance of R. M. Swiatek, C. W. Dietrich, and L. Lardear is gratefully acknowledged.

Registry No. I, 86393-14-8; $[Cu(CH_3CN)_4]BF_4$, 15418-29-8; C_2H_2, 74-86-2; $NHpy_2$, 1202-34-2.

Supplementary Material Available: Tables of positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

A Titanium Vinylidene Route to Substituted Allenes

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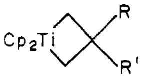
Received March 24, 1983

The unique structure and reactivity of allenes has prompted a long-term interest in these compounds by both synthetic and physical organic chemists.[2] In many cases, however, the synthesis of substituted allenes has proven difficult. Standard methods of allene synthesis include nucleophilic additions to propargyl halides[3] and acetates[4] and reductive cleavage of *gem*-dihalocyclopropanes.[5] These methods can lead to mixtures of the desired allene contaminated with the corresponding acetylenes, dienes, or other allenes.[6] Herein we report on a fundamentally different approach[7] for the preparation of a wide variety of di-, tri-, and tetrasubstituted allenes in good to excellent yield.

We have previously described the preparation and reactions of a variety of titanacyclobutanes of type **1**.[8] These metallacycles

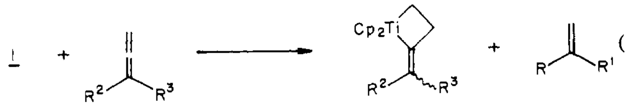


a) R = R' = CH_3
b) R = CH_3, R' = n-propyl

1

have been shown to undergo a variety of synthetically and catalytically useful reactions.[9] More recently **1a** has been employed in the high yield synthesis of regiochemically pure titanium enolates using acid chlorides as substrates.[10]

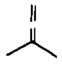
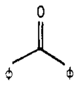
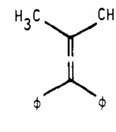
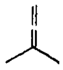
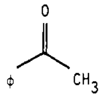
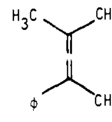
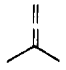
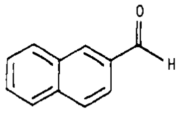
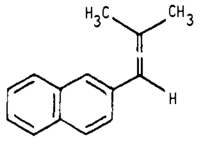
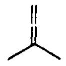
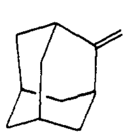
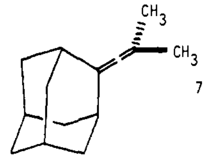
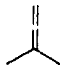
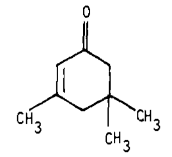
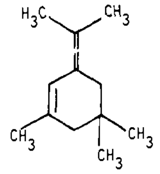
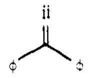
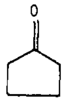
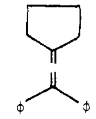
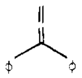
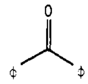
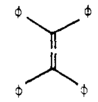
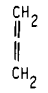
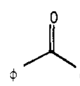
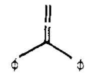
We have now found that the reaction of **1** with 1 equiv of a 1,1-disubstituted allene produces a quantitative yield (^1H NMR) of the new metallacycles **2** with the liberation of olefin (eq 1).[11]



2 (1)

In all cases these unsaturated metallacycles are obtained as the single regioisomer depicted as **2**. The structure of **2** has been assigned on the basis of ^1H and ^{13}C NMR data[12] and by their reaction chemistry.[13,14] When a benzene solution of **2** is treated with 1 equiv of a ketone for a period of 2-12 h at room tem-

Table I

starting allene	ketone	product allene[a]	yield, %[b]
			80[c]
			56
			53
			75
			55
			72
			56
			58[c]

[a] All compounds were characterized by ^1H and ^{13}C NMR.
[b] Isolated yields based on quantity of ketone used. [c] Ca. 3% 1,1-diphenylethylene was also isolated from this reaction.

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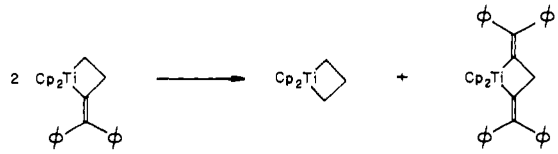
[11] Unsaturated metallacycles of type **2** appear to be thermally stable except in the case R = R' = Ph, where the following disproportionation occurs:



[12] For **2**, R = R' = CH_3: ^1H NMR (C_6D_6) δ 0.27 (m, 2 H), 1.80 (br s, 6 H), 2.6 (m, 2 H), 5.31 (s, 10 H); ^{13}C NMR $\{^1H\}$ (C_6D_6) δ -8.0, 22.1, 27.6, 66.7, 107.6, 124.6, 213.6.

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