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Gas-Phase Synthesis, Submillimeter Spectra, and Precise Structure of Monomeric, Solvent-Free CuCH$_3$

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Abstract: The most-studied organocopper, methylcopper (CH$_3$Cu), has been synthesized for the first time as a monomer, free of other ligands or coordinated solvent, and detected using millimeter-wave rotational spectroscopy. The molecule was created in the gas phase by the reaction of copper vapor and several different precursors, including CH$_4$ and tetramethylsilane. An obvious symmetric top pattern was observed, indicative of C_{3v} symmetry. For confirmation, rotational spectra of four isotopically substituted species, $^{65}Cu^{12}CH_3$, $^{63}Cu^{12}CD_3$, $^{63}Cu^{13}CH_3$, and $^{65}Cu^{13}CH_3$, were recorded as well, following large-scale syntheses of specifically labeled precursors. From this data set, accurate spectroscopic constants and a structure for CH$_3$Cu were derived. The $r_m^{(2)}$ geometry shows the shortest alkyl carbon–copper(I) bond length known (1.8809 Å) and a rather large H–C–H angle in the methyl group (109.88°). The measured rotational and distortion constants are well reproduced by QCISD calculations. This study should allow further refinement of theoretical calculations on methylcopper and other organocopper derivatives, which are valuable synthetic intermediates in organic chemistry.

Introduction

The bonding of a carbanion to a metal affects the structure and reactivity of the carbon fragment in extremely useful ways. For example, whereas organolithium or -magnesium reagents add to conjugated enones in a 1,2-fashion, organocopper compounds are textbook reagents for achieving 1,4-addition.[1-4] This remarkable difference in reactivity, controlling the regioselectivity of carbon–carbon bond formation, was first reported in 1941 by Kharasch and Tawney using a catalytic amount of copper.[5,6] It could be said that the discovery of these and other useful reactions of organocopper compounds spurred the development of organometallic chemistry as a tool for organic chemists. Copper is a cheap, relatively nontoxic metal, and the continuing relevance of organocopper chemistry is highlighted by uses in catalysis of carbon–heteroatom bond formation,[7] carbene transfer,[8,9] and recent revelations about the role of various additives in conjugate addition.[10]

Although the first recorded attempt at making an organocopper was Buckton's use of diethylzinc on CuCl in the 1850s,[11] it was not until 1923 that impure samples of phenylcopper were reported,[12] and it was not until 1952 that samples of alkylcoppers were made by the group of Gilman.[13] The explosive nature of solid alkylcoppers and solution instability above −15 °C were noted first by early workers.[13-18] Initial attempts at making more stable complexes by adding ligands were disappointing,[19] but later workers succeeded by adding several phosphines[17,20-22] or, more recently, rigid diynes.[23-25] Clearly, however, obtaining

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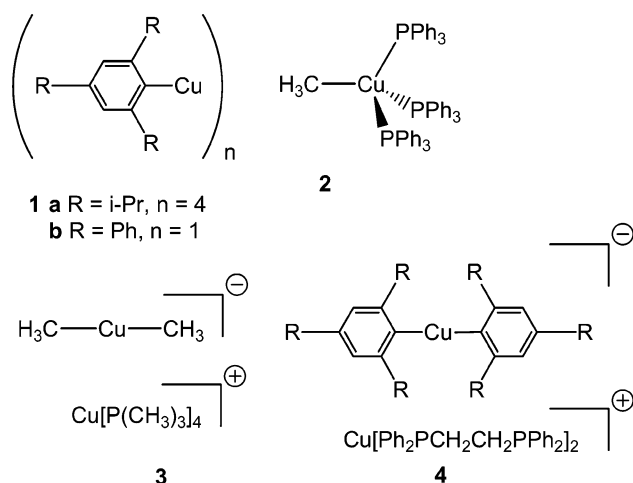(25) Stein, T.; Lang, H. *J. Organomet. Chem.* **2002**, *664*, 142–149.

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Scheme 1

1 **a** R = i-Pr, n = 4
  b R = Ph, n = 1

structural data on methylcopper or other organocoppers free of solvents or ligands was expected to be possible only with difficulty, by unusual synthetic methods. In fact, as far as we are aware, the only likely synthesis of monomeric methylcopper reported to date is as a minor photoproduct at 12 K in a methane matrix containing copper atoms.[26]

Equally striking is the fact that structural data on organo-copper complexes in general and alkylcoppers in particular are sparse.[27] However, several trends can be discerned. As with other more polar organometallics such as organoalkalis,[28–30] the vast majority of organocoppers RCu are aggregated,[23,27,31] though this tendency is lower for organocuprates R_2Cu^-. A wide variety of fascinating structures of varying nuclearity is obtained, and even small changes in the structure of the aryl ligand lead to large changes in structure of the copper compound: for example, compound **1a** is a tetramer in the solid,[32] whereas **1b** is one of the few monomers known.[33] Solvation[34] and solubility play unpredictable roles: for example, mesitylcopper has been isolated in tetrameric and pentameric forms by changing solvent.[35] Moreover, a 1:1 molar ratio of Cu and alkyl or aryl ligand R does not guarantee the existence of neutral $RCuL_n$, as shown by contrasting the crystal structures of **2**, which is a monomer with one methyl group on copper,[22] with the structures of **3**[36] and **4**,[37] which are ionic cuprates featuring two methyl or aryl groups on one copper atom and none on the other.

Because of intense synthetic interest in organocoppers, a number of workers have calculated several structures for

methylcopper and related simple species such as the dimeth-ylcuprate ion $[(CH_3)_2Cu]^-$. Copper−carbon bond lengths of 1.85−2.16 Å have been predicted, depending on the theo-retical approach.[38–53] Meanwhile, for isolable methylcopper species, all of which bear several added ligands, solid-phase X-ray diffraction data show C−Cu distances of 1.935−2.043 Å.[22,24,36,54–56] One general goal of our research, of which this report is an example, is to make and spectroscopically characterize fundamentally interesting low-coordinate organo-metallics in the gas phase, free of aggregation and solvation, to provide benchmark structural data of high precision for calcula-tions. Herein we report these experimental data and improved ab initio calculations of methylcopper.

Experimental Section

The spectrum of CH_3Cu was measured using millimeter-wave direct absorption techniques. These data were taken using one of the Ziurys group spectrometers, which is described in detail elsewhere.[57] The system uses Gunn oscillator/Schottky diode multiplier combinations as frequency sources, which cover the range 65−650 GHz. The radiation is launched from a scalar feedhorn and is passed through a free-space gas cell using a series of Teflon lenses and a polarizing grid. The cell is a double-pass system, containing a Broida-type oven. The radiation is detected by an InSb hot electron bolometer. The source is frequency-modulated, and the signal from the bolometer is processed by a lock-in amplifier at 2*f*; therefore, a second-derivative spectrum is obtained.

Methylcopper was first synthesized by the reaction of copper vapor, produced in the Broida oven, and methane (20 mTorr) using a dc discharge of 1 A at 50 V. The species was produced continuously and flowed through the reaction cell under nonequilibrium conditions. Argon was used as a carrier gas (10 mTorr) and was added from beneath the oven to entrain the metal vapor. It was also flowed over the Teflon lenses that seal the ends of the reaction chamber (20 mTorr), to prevent coating of these optics. Because alkyl group transfer from alkyllead compounds to copper(I)[14,58] was known, and because of our prior success at making organoalkalis using tetramethyltin,[59,60] methylcopper

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was also made using the tin compound, primarily as a chemical test. In this case, 10 mTorr of precursor was used, and no dc discharge was needed. As an additional confirmation, a third reactant, tetramethylsilane, was used (10 mTorr). Tetramethylsilane is thus a proven methyl group donor, with the advantages that it is considerably cheaper and less toxic than tetramethyl tin. (Although there are reports of activated copper(0) species reacting with alkyl halides by some sort of oxidative addition process,[61] we were unable to use iodomethane as a precursor for methylcopper. The main problem was severe contamination by other, unknown spectral features.)

To create the deuterated and ^{13}C isotopomers of CuCH$_3$, CD$_3$Si-(CH$_3$)$_3$ and ^{13}CH$_3$Si(CH$_3$)$_3$ were employed as precursor materials. About 10 mTorr of reactant was used in each case, and no dc discharge was required. These species could also be created with CD$_4$ or ^{13}CH$_4$, but with a significantly lower signal-to-noise ratio. Both deuterium- and carbon-13-labeled versions of tetramethylsilane had to be made. Syntheses for both compounds were known in the literature, but existing preparations were unsatisfactory for our work, for various reasons: either no or very few experimental details were given, or very small quantities had been made, in some cases as mixtures of isotopomers, for example, as products of quenching organometallic complexes with deuterated materials.[62−69] Procedures to make large quantities of isotopomers CD$_3$Si(CH$_3$)$_3$ and ^{13}CH$_3$Si(CH$_3$)$_3$ were therefore developed and are detailed fully in the Supporting Information. The copper isotopomers were observed in their natural abundances of ^{63}Cu/^{65}Cu = 69.1:30.9.[70]

Precise transition frequencies were measured by averaging pairs of scans taken in increasing and decreasing frequency. Typically, one or two signal-averaged pairs were necessary for measurements of ^{63}CuCH$_3$, and two to eight pairs for the other isotopomers and the vibrational state spectra. The line profiles were fit to a Gaussian shape to determine the center frequency, as well as line widths, which varied from 950 to 1800 kHz over the range of 313−543 GHz. The experimental error is estimated to be ±70 kHz.

Results and Discussion

Spectrum. The spectrum of CuCH$_3$ was found while searching for another species, CuC, while reacting copper with methane in a dc discharge. A classical symmetric top pattern was observed after scanning for 95 GHz under these chemical conditions. The pattern of a close-shell symmetric top can be described by the following equation:

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2$$
$$\text{for } J \to J+1 \quad (1)$$

Here, B is the rotational constant, D_J and D_{JK} are the centrifugal distortion constants, J is the rotational quantum number, and K is the projection of J along the symmetry axis. For a symmetric top, $J \geq K$, such that for $J = 0$, $K = 0$, for $J = 1$, $K = 1$ and
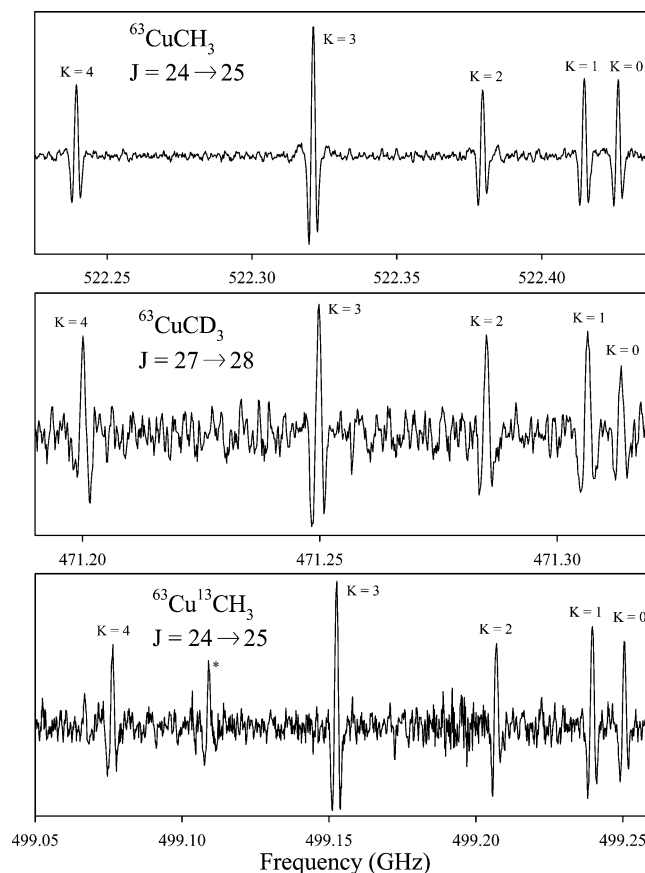
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Figure 1. Representative spectra of rotational transitions of ^{63}CuCH$_3$ ($J = 24 \to 25$), ^{63}CuCD$_3$ ($J = 27 \to 28$), and ^{63}Cu^{13}CH$_3$ ($J = 24 \to 25$) near 522, 471, and 499 GHz, respectively, in the ground ($v = 0$) vibrational state. The symmetric top progression of K components is readily visible in each spectrum. (The line marked by an asterisk is unidentified.) These data are composites of 2−3 scans, each about 1 min in duration and covering 100 MHz.

0, for $J = 2$, $K = 2$, 1, and 0, etc. Selection rules for the strong electric dipole transitions require $\Delta J = \pm 1$, $\Delta K = 0$, and a nonzero dipole moment. Therefore, every rotational transition $J \to J + 1$ consists of "K-ladder" structure, namely, multiple K components corresponding to $K = 0, 1, 2, 3, ...$ These K components follow a distinct pattern in frequency with a relative spacing of 1:3:5:7....The rotational pattern of a given molecule that is a symmetric top is thus easily recognized. The top panel of Figure 1, which shows the rotational spectrum of the $J = 24 \to 25$ transition of CuCH$_3$, clearly illustrates this pattern.

Once this pattern was observed, the precursor was then switched to tetramethyltin. The signals increased significantly. A third precursor, tetramethylsilane, was then tried, and again the pattern was reproduced. Turning off the oven and thus removing copper vapor caused the signals to immediately disappear. Therefore, the spectra had to arise from a polar, symmetric top species containing copper and a functional group common to the three species CH$_4$, tetramethyltin, and tetramethylsilane. The only likely species satisfying these criteria is CH$_3$Cu. Further evidence was then obtained by scanning an additional 47 GHz, where other symmetric top patterns were found that were identified as arising from the less abundant copper isotopomer, ^{65}CuCH$_3$, as well as the $v_3 = 1$ vibrational state of ^{63}CuCH$_3$, the lowest excited state of the Cu−C stretch. Spectral intensities of the two copper isotopomers had the expected ratio of 69.1:30.9, reflecting the natural abundance

Table 1. Spectroscopic Constants for CH$_3$Cu ($\tilde{X}^1A_1$)[a]

| | ^{63}CuCH$_3$ | | ^{65}CuCH$_3$ | | ^{63}CuCD$_3$ | ^{63}Cu^{13}CH$_3$ | ^{65}Cu^{13}CH$_3$ |
	$v=0$	$v_3=1$	$v=0$	$v_3=1$	$v=0$	$v=0$	$v=0$
B	10468.98018(67)	10383.2318(30)	10409.46177(74)	10324.5387(31)	8432.0966(27)	10003.7957(29)	9943.7840(34)
D_J	0.01636715(66)	0.0163995(25)	0.01618776(71)	0.0162223(26)	0.0100695(14)	0.0150333(22)	0.0148562(27)
D_{JK}	0.236052(14)	0.26992(35)	0.233389(20)	0.26506(45)	0.12790(15)	0.21979(17)	0.21647(69)
H_{JK}	$1.625(12) \times 10^{-6}$	$3.74(28) \times 10^{-6}$	$1.599(18) \times 10^{-6}$	$3.40(36) \times 10^{-6}$	$7.40(80) \times 10^{-7}$	$1.52(12) \times 10^{-6}$	$1.04(54) \times 10^{-6}$
H_{KJ}	$1.3187(62) \times 10^{-5}$	$-1.096(68) \times 10^{-4}$	$1.2987(93) \times 10^{-5}$	$-1.28(11) \times 10^{-4}$	$4.4(1.5) \times 10^{-6}$	$1.15(17) \times 10^{-5}$	
L_{JK}		$3.08(47) \times 10^{-8}$		$3.27(79) \times 10^{-8}$			
L_{KKJ}		$-5.49(21) \times 10^{-7}$		$-1.57(79) \times 10^{-7}$			
rms	0.023	0.025	0.018	0.029	0.030	0.026	0.033

[a] In MHz; errors are 3σ in the last quoted decimal places.
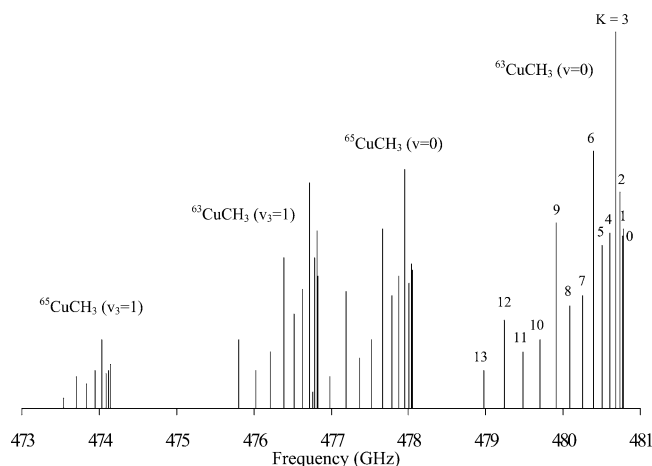

Figure 2. Stick spectrum of the experimentally observed $J = 22 \rightarrow 23$ transition of CH$_3$Cu, showing the pattern exhibited by the various isotopomers in their $v = 0$ and $v_3 = 1$ states, and illustrating their relative intensities.

ratio of ^{63}Cu/^{65}Cu.[70] All of these patterns were found to repeat themselves on a regular basis that indicated a rotational constant corresponding to a molecule with a molecular weight of one copper atom and one methyl group only. (The rotational constant is inversely proportional to the corresponding moment of inertia of a given species.[70,71])

As definitive confirmation, and to obtain an accurate structure, rotational spectra of CuCD$_3$ and Cu^{13}CH$_3$ were measured as well. To find the spectrum of CuCD$_3$, a 15 GHz range of frequency space was continuously scanned. After these measurements, the transition frequencies of the ^{13}C isotopomer were predicted with sufficient accuracy that the spectra of both ^{63}-Cu^{13}CH$_3$ and ^{65}Cu^{13}CH$_3$ were found quite readily (within 50 MHz of the predictions).

The measured laboratory frequencies for the five isotopomers of CH$_3$Cu are listed in the Supporting Information, Table S1. CH$_3$Cu is a closed-shell symmetric top species with C_{3v} symmetry, and thus has a $^1A_1$ ground state. Each energy level is thus defined by J and K quantum numbers. As Table S1 shows, a total of 10 rotational transitions was measured in the ground vibrational state for ^{63}CuCH$_3$ and ^{65}CuCH$_3$, and five each for ^{63}CuCD$_3$, ^{63}Cu^{13}CH$_3$, and ^{65}Cu^{13}CH$_3$, for $K = 0$ up to, at most, $K = 13$. Table S2 lists the five rotational transitions recorded for ^{63}CuCH$_3$ and ^{65}CuCH$_3$ in their $v_3 = 1$ state, in which the Cu–C stretching mode has been excited by one quantum. The ^{63}Cu and ^{65}Cu isotopomers were measured in their

natural abundance ratio of 69.1:301.9 for both carbon species. On the other hand, the signal-to-noise ratio for the deuterium isotopomer was not large enough to see a spectrum of ^{65}CuCD$_3$.

Figure 1 shows spectra of representative rotational transitions of ^{63}CuCH$_3$ ($J = 24 \rightarrow 25$), ^{63}CuCD$_3$ ($J = 27 \rightarrow 28$), and ^{63}Cu^{13}CH$_3$ ($J = 24 \rightarrow 25$) near 522, 471, and 499 GHz, respectively, arising from the ground vibrational state. The K components are separated in frequency by a 1:3:5:7 ratio, as usually seen for a prolate symmetric top. The $K = 3n$ (ortho) components have twice the intensity of the $K \neq 3n$ (para) components, due to spin statistics of the three hydrogens of the methyl group. Figure 2 shows a stick spectrum of the $J = 22 \rightarrow 23$ transition of ^{63}CuCH$_3$ and ^{65}CuCH$_3$ in their $v = 0$ and $v_3 = 1$ states. This plot presents the actual frequencies and relative intensities of the two vibrational states, and illustrates the expected pattern for a prolate symmetric top with C_{3v} geometry.

Analysis. For each isotopomer of CH$_3$Cu, a separate fit was performed for each observed vibrational state (the $v = 0$ and, when available, the $v_3 = 1$ state), using an effective Hamiltonian employing rotational and centrifugal distortion parameters and the nonlinear least-squares routine SPFIT.[72] The spectroscopic constants thus ascertained for CH$_3$Cu are presented in Table 1. All the parameters are well determined, and the rms of each fit lies in the range 18–33 kHz. Furthermore, the ground vibrational states for all five isotopomers of CH$_3$Cu required only the fourth- and sixth-order centrifugal distortion constants D_J, D_{JK}, H_{JK}, and H_{KJ} for a good fit.

In contrast, the $v_3 = 1$ data for both ^{63}CuCH$_3$ and ^{65}CuCH$_3$ needed the eighth-order distortion parameters L_{JK} and L_{KKJ} in order to achieve the same accuracy. The higher degree of distortion of this state is likely due to rotation–vibration effects. Some transitions were not included in the final data fit, for the following reasons. Some lines were blended with those of other isotopomers, and thus were excluded; the $K = 6$ components of the $v_3 = 1$ state of ^{63}CuCH$_3$ were not included as well. This particular set of K components could only be fit with residuals near 200 kHz—about a factor of 10 higher that other K components, including those with $K \geq 7$. This unusual effect is likely a result of perturbations by energy levels of another vibrational state.[73]

Structure. By measuring the rotational spectrum of five isotopomers of CH$_3$Cu, a very accurate structure could be determined from the rotational constants. The r_0 and $r_m^{(1)}$ structures were determined by a nonlinear least-squares fit to the moments of inertia using the STRFIT program.[74] Kraitchman's equations were used to calculate an r_s structure, as well,

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Table 2. Metrical Parameters for CH_3Cu and Other Relevant Organocopper Complexes

	Cu–C, Å	C–H, Å	H–C–H, deg	method	ref
CH_3Cu	1.8841(2)[a]	1.091(2)[a]	110.07(8)[a]	r_0	this work
	1.8817(1)[a]	1.0923(2)[a]	110.02(3)[a]	r_s	this work
	1.8799(1)[a]	1.0914(3)[a]	110.02(3)[a]	$r_m^{(1)}$	this work
	1.8809(1)[b]	1.0851(1)[b]	109.88(2)[b]	$r_m^{(2)}$	this work
	ca. 2.2[c]	nd	nd	estimated from IR	14
	1.9911	1.0853	108.9	RHF/6-21G	38
	1.86	nd	nd	HFS/STO-TZ	39
	1.936	fixed	110.1	MCPF/[8s 4p 3d 3d]+	40
	2.161	nd	nd	HF/3-21G-ECP(SZ)	41−44
	2.040	nd	nd	HF/3-21G-ECP(DZ)	
	1.921	1.096	110.0	CCSD(T)/DZP	46
	2.005	nd	nd	HF/3-21G	48
	2.005			HF/6-31G(d)	
	1.923			MP2/6-31+G(d)	
	1.970	nd	nd	HF/6-31G(d)-RECP	49
	1.866			MP2/6-31G(d)-RECP	
	1.927	nd	nd	B3LYP/LANL2DZ	50
	1.853	1.099	111.2	LSD/TZ2P	51
	1.902	1.098	111.0	BP/TZ2P	
	1.923	1.095	111.3	BLYP/TZ2P	
	1.921	1.089	111.3	B3LYP/TZ2P	
	1.848−1.868	nd	108.8−108.9	HF, various sets	52
	1.824		108.8	HF, basis incl f orbitals	
	1.912	nd	nd	B3LYP/6-31++G(d,p)	53
	1.904	1.091	109.8	CCSD(T)/Roos aug-TZ	88
	1.8725	1.0915	108.11	QCISD/6-311G(d,p)	this work
$[(CH_3)_2Cu]^-$	1.927	1.115	106.2	LDF(Dmol)	47
	1.917	1.114	106.2	LDF(Dgauss)	
CH_3Cu derivatives					
$CH_3Cu(PPh_3)_3$	2.043(12)			X-ray	22
$CH_3Cu(\eta^2\text{-alkyne})_2$	1.966(2)			X-ray	24
$[(CH_3)_2Cu]^-$ derivatives					
$[(CH_3)_2Cu]^-$ $[Li(12\text{-crown-}4)_2]^+$	1.935(8)			X-ray	54
3 $[(CH_3)_2Cu]^-$	1.94(1)			X-ray	36
$[(CH_3)_2Cu]^-$ $[Li(dme)_3]^+$	1.929(3), 1.937(3)			X-ray	56
$[CH_3-Cu-PtBu_2]^-$	1.940(4)			X-ray	55
1b (monomer)	1.890(6)			X-ray	33
1a (tetramer)	1.958(7), 2.018(7)			X-ray	32
$[2,4,6\text{-}(t\text{-Bu})_3C_6H_2)Cu(SMe_2)$	1.916(1)			X-ray	97

[a] Uncertainties are 1 standard deviation. [b] The uncertainties in the $r_m^{(2)}$ structure were derived from a nonlinear least-squares fit to the moments of inertia. The data do not fit to an exact solution. [c] Not clear if sample was monomeric.

assuming the center of mass condition.[71] The center of mass condition was used to calculate the z distance of the deuterium atoms from the center of mass. (The D substitution could only determine the y distance.) An $r_m^{(2)}$ geometry was additionally calculated. Here there are five parameters to be determined, and five isotopomers were measured. Hence, an exact solution is determined in this case.

The $r_m^{(2)}$ structure is thought to be the most accurate because it takes into account the effects of zero-point vibrations by modeling the mass dependence of the moment of inertia.[75] Therefore, it is usually closest to the equilibrium structure, which is the common product of theoretical calculations. In contrast, an r_0 geometry does not change with isotopic substitution, and thus is directly calculated from the B_0 rotational constants. It therefore amounts effectively to a completely vibrationally averaged structure. In the case of the r_s geometry, a "substitu-

tion" structure is calculated in which changes in the center of mass are considered with isotopic variation.[71] It is thought to compensate for some of the vibrational effects. An $r_m^{(1)}$ geometry corrects for only some of the mass dependence of the moments of inertia, and hence is inferior to the $r_m^{(2)}$ calculation.[75] The four geometries determined for CH_3Cu are shown in Table 2.

Calculations. Previous computational studies of CH_3Cu had not specifically sought to predict the ground-state spectroscopic properties with high precision. All but those by Bauschlicher and co-workers[40,46] had been carried out at the relatively low-level HF, MP2, and DFT levels, and rotational constants predicted from these structures vary by more than 25%. Furthermore, the previous CCSD(T) calculations employed a basis set chosen to predict the relative energies of the electronic states at the expense of geometric precision.[46] Calculations were therefore deemed appropriate in the present study to determine whether the spectroscopic constants derived from the rotational spectrum can be reliably predicted ab initio. From among several levels of theory available with the Gaussian 98[76] and Gamess[77] quantum chemistry suites, QCISD[78] was found to offer fairly fast optimization and consistent accuracy when comparing computed equilibrium geometries and experimental r_s structures for ZnCN,[79] NiCN,[80] and CuCN.[81] With the extended 6-311G-

(73) A plausible origin of the perturbation is an interaction with high-K lines of the molecule excited to $v = 1$ in the lowest-frequency degenerate bend, predicted from our calculations to lie only about 80 cm⁻¹ above the Cu–C stretching mode. The contribution of vibrational angular momentum in the bending state causes one K manifold to increase in energy as $A(K^2 - K)$ rather than as AK^2, and at $K = 6$ this difference allows the stretching state to accrue roughly 60 cm⁻¹ more energy than the bend, causing the two K manifolds to become similar in energy and perturbations between them likely to become observable.
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Table 3. Comparison of Experimentally Determined Geometries of CH₃X Molecules

molecule	structure	r(X–C) (Å)	r(C–H) (Å)	θ(H–C–H) (°)	ref	χ_A for X[a]
CH₃Li	partial r_s	1.961(5)	1.122(5)	107.2(1)	59	0.771
CH₃Na	r_0	2.299	1.091[b]	107.3	59	0.934
CH₃K	r_s	2.633(5)	1.135(5)	107.0(1)	59	0.760
CH₃Ca	r_0	2.349(13)	1.100[b]	105.6(2.8)	98	0.991
CH₃Mg	r_0	2.102(2)	1.105[b]	108.163	99	1.316
CH₃Cu	r_0	1.8841(2)	1.091(2)	110.07(8)	this work	1.749
	r_s	1.8817(1)	1.0923(2)	110.02(3)	this work	
	$r_m^{(1)}$	1.8799(1)	1.0914(3)	110.02(3)	this work	
	$r_m^{(2)}$	1.8809(1)	1.0851(1)	109.88(2)	this work	
CH₃I	r_e	2.133(2)	1.085(3)	111.3(4)	100	2.487
CH₃Br	r_e	1.933(2)	1.086(3)	111.2(4)	100	2.686
CH₃Cl	r_e	1.778(2)	1.086(4)	110.7(7)	100	2.960
CH₃F	r_0	1.3890(8)	1.0947(11)	110.3(1)	101	3.938
	r_e	1.383(1)	1.087(1)	110.2(1)	102	

[a] Electronegativity values, determined in ref 53. [b] Assumed value.

(d,p) basis set[82] using the Wachters−Hay metal functions as implemented by Raghavachari and Trucks,[83−85] the QCISD equilibrium geometries overestimate the M−C bond lengths by 0.002−0.016 Å, and the C−N bond length by 0.011−0.026 Å. These tests were carried out prior to comparison of the CH₃Cu calculations against experiment. A relatively low-lying triplet electronic state causes small differences between the unrestricted and restricted QCISD calculations for CH₃Cu. Based on their superior predictive quality in simpler open-shell systems with comparable spin contamination,[86,87] unrestricted calculations were used in the present work.

The ¹A₁ CH₃Cu geometry was optimized and the harmonic frequencies were calculated. The equilibrium geometry predicted at the UQCISD/6-311G(d,p) level significantly improves the Cu−C bond length over previous calculations. There is a 1.8° error in the predicted HCH bond angle, which corresponds to only a 0.2% shift in the predicted rotational constants. The UQCISD/6-311G(d,p) rotational constants for all observed CH₃-Cu isotopomers lie within 0.5% of the $r_m^{(2)}$ values. It is not entirely straightforward to improve the computed geometry further. An additional CCSD(T) calculation[88] using a triple-ζ Roos basis set[89] was carried out in the course of review of this

paper, and improves on the previous CCSD(T) geometry by reducing the Cu−C bond length to 1.904 Å, leaving a 2% discrepancy between the predicted and observed B_e values. That remaining discrepancy may arise from neglect of relativistic terms in the Hamiltonian; we find those terms account for a 0.017 Å reduction in Cu−C bond length at the MCSCF level.[90]

The Cu−C stretch has the lowest predicted harmonic vibrational constant, $\omega_e = 586$ cm⁻¹. The lowest predicted bending frequency is nearby, at 667 cm⁻¹, but the impact of any hydrogen motion on the moments of inertia is small enough that a pseudodiatomic analysis remains reasonable for estimating some dynamical features of the spectrum. From the computed stretching frequency, the distortion constant D_J is predicted by a typical Morse oscillator analysis[91] to be 15.1 kHz for the most abundant isotopomer, in fair agreement with the observed value of 16.4 kHz.

Similarly, α was estimated computationally by carrying out a relaxed potential energy surface scan of the Cu−C bond length at the UQCISD level. The resulting curve was used to calculate wave functions and energies numerically,[92] again treating the methyl group as a single unit. Vibrationally averaged B values for the ground and $v_3 = 1$ states were calculated by the average value theorem, and the difference between these values is the ab initio value of α. The predicted value of 76 MHz falls within 15% of the experimental value. The ability of these calculations—using standard methods optimized here for MCN geometries—to accurately predict rotational, distortion, and vibration−rotation coupling constants in the present spectra bodes well for their application to rovibrational spectra of the ground electronic states of other small organo-transition metal compounds.

The 586 cm⁻¹ vibrational constant estimated for the Cu−C stretch is significantly larger than the 350 cm⁻¹ peak assigned to that mode in the matrix isolation spectrum.[26] Although the harmonic analysis of stretches overestimates frequencies by as much as 10%, the agreement of the measured and predicted distortion constant D_J in the present work suggests that the ab initio predicted frequency is relatively accurate, whereas a vibrational constant of 350 cm⁻¹ would predict a value for D_J over 40 kHz. The QCISD value is also consistent with the value of 516 cm⁻¹ obtained by the MCPF calculations of Bauschlicher et al.[40,46] Further support for a higher Cu−methyl stretching

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frequency is given by the known Cu−CH₂ stretching frequency of 614 cm⁻¹,[93] the lack of observed metal−methyl stretching frequencies below 400 cm⁻¹, even among third-row transition metal methyls such as Hg(CH₃)₂ and W(CH₃)₆,[93] and the original authors' tentativeness in assignment of the 350 cm⁻¹ band.

Metrical Parameters and Bonding. The Cu−C distance in monomeric methylcopper is determined to be 1.8799−1.8841 Å, depending on the analysis (Table 2). Since the $r_m^{(2)}$ geometry (Cu−C distance 1.8809 Å) is probably the most accurate (vide supra), it will be used for the following discussion. In comparing the Cu−C distance to the few known data for ligated methyl-copper species, it is clear that coordination of two other ligands lengthens the Cu−C distance by 0.086 Å, whereas three ancilliary ligands increase this by twice as much (0.16 Å). Related cuprates of general formula [CH₃CuR]⁻ represent species with only one ancilliary ligand, and here the distances between the Cu and methyl carbon are only 0.05−0.06 Å longer than in monomeric methylcopper. Thus, there is a smooth progression in metal−carbon bond length as one considers the series of mono- to tetracoordinate CH₃CuL$_n$. As far as we are aware, the copper−carbon bond of methylcopper is the shortest known for an alkylcopper(I) species, and the distance is even small for an *alkynyl*copper.[27]

The bond angles in the methyl ligand are of interest in connection with discussions of the effects of substituents X on the geometry of CH₃−X.[59,94] Among CH₃−X compounds in which X is a metal and for which precise experimental data exist, the H−C−H angle is rather large.[95] From Table 3 and our previous work,[59] it is clear that the size of an alkali metal (Li vs K) does not alter the angle to an experimentally significant extent. Our previous conclusion, both from the experimental data as well as considering theoretical literature from other workers,[94,96] was that the electronegativity of X plays the major role. A recent article[53] using theoretical calculations of molecular geometry offers a way to assign reasonable electronegativities χ_A to transition metals, as well as main-block elements; thus, Table 3 lists χ_A values. From the limited available data on metal-containing species, one can see that there appears to be some correlation between increasing electronegativity and increasing H−C−H angle, as predicted by others.[94,96] Interestingly, the reverse trend is seen for the haloalkanes. Further theoretical and experimental work (particularly on metal−methyl species) is needed to clarify this discrepancy.

Conclusions

The geometry of methylcopper determined here is the first such structure of a monomeric alkylcopper, as well as one of the very few available for methyl−metal species. Measurement of the pure rotational spectrum of this species using millimeter-wave direct absorption methods has made this determination possible. Efficient gas-phase synthesis of methylcopper occurred using both tetramethyltin and tetramethylsilane, but the lower toxicity of the latter encouraged its use, and efficient, detailed, large-scale syntheses of two isotopomers were developed. Methylcopper could also be made from methane, albeit in lower efficiency. The precise gas-phase structure of methylcopper allows comparisons with solid-phase structures of methylcopper complexes of higher coordination number, which feature longer metal−carbon bond lengths. More significantly, direct comparisons of experiment and theory are possible, here validating the use of ab initio methods in calculating geometries and spectroscopic constants with meaningful precision.

Supporting Information Available: Tables of observed rotational transitions for the five isotopomers studied; full details of the preparation of isotopically labeled tetramethylsilanes and their characterization; tables of *x*, *y*, and *z* coordinates for the computed structure of methylcopper; and data used in the estimation of the vibration−rotation coupling constant. This material is available free of charge via the Internet at http://pubs.acs.org.

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