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Structures of Solvent-Free, Monomeric LiCCH, NaCCH, and KCCH[**]

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Organoalkali metal compounds are important reagents for introducing organic groups into organic and organometallic compounds in substitution or addition reactions.[1] For example, active ingredients in widely used oral contraceptives contain alkynyl groups that are introduced by the addition of alkali metal acetylides to steroidal ketones.[2] Organoalkali metal compounds show a pronounced tendency toward aggregation,[3] and alkali metal acetylides are no exception.[4, 5] The organic portion and co-ligand(s) (including solvent) influence reactivity and structure of the organoalkali metal compound dramatically, both in solution and in the solid state. An example of the structural changes induced by subtle variation of coligands is that whereas the crystallization of PhCCLi in the presence of tetramethylpropylenediamine gives dimeric units,[5e] similar treatment with the homologous tetramethylhexylenediamine gives tetrameric units.[5d] Such aggregated structures have provided the only experimental information about alkynyl–alkali metal bond lengths to date, but with one recent exception,[4d] the alkali metal acetylides

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[**] This research was supported by the U.S. National Science Foundation grants CHE 9531244 (to D.B.G. and L.M.Z.), AST 95-03274, and NASA grant NAGW 2989 (to L.M.Z.).

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

1433-7851/98/3719-2678 $ 17.50+.50/0

treated by theory have been in a monomeric, solvent-free state.[6] There is a clear trend toward longer metal–carbon bond lengths on increased solvation or oligomerization,[3] so direct comparison of experimental and theoretical data on alkynyl alkali metal compounds has been impossible. Notable approaches to monomeric alkyl or aryllithium compounds[7] have relied on large alkyl or aryl groups; such a strategy will probably not work for alkynyl compounds because the R group of RCCM is so far removed from the metal center M.

Here we report the first structural characterization of alkynyl alkali metal compounds in a monomeric state. The title molecules MCCH (M = Li, Na, K) are the simplest alkynyl derivatives of each metal, and thus are ideally suited for a direct comparison of experiment and theory. Each was made in a monomeric form in the absence of other ligands in the gas phase, and each structure was determined by millimeter/submillimeter spectroscopy, as was recently done for MCH_3 (M = Li, Na).[8] The experimental data[9] should allow further improvements in theoretical calculations, which in the case of the predicted values for the Li–C bond in LiCCH spread over the range 1.842 to 1.931 Å[6]

A direct absorption spectrometer in continuous-wave mode[10] was used to observe isotopomers of MCCH. Phase-locked Gunn oscillators with frequencies in the range 65–140 GHz were used as the radiation source. Schottky-barrier diode multipliers were used to double, triple, or quadruple the frequency to obtain an overall frequency range of 65–560 GHz. The reaction chamber was a double-pass cell with a length of 0.5 m. In the cell HCCH (30 mTorr) was treated with metal vapor (≤ 1 mTorr) to produce MCCH (M = Li, Na, K). Argon (30–50 mTorr) was used as a carrier gas for the metal and a direct current discharge (about 0.5 A at 200 V) was used to facilitate the reaction. The deuterium isotopomers MCCD for all three metals were studied by using DCCD.

The use of BrCCH[11] with Li gave such intense signals for the product that the two ^{13}C isotopomers $LiC^{13}CH$ and $Li^{13}CCH$ were observed. No discharge was required with BrCCH, and typically only a few mTorr of this precursor was required. Finally, ^6LiCCH was also measured by using Li enriched in ^6Li. To carry out a frequency measurement scans with a width of 5 MHz were made, both in decreasing and increasing frequency, and one to four pairs of such scans were then averaged. Linewidths varied from 200–1500 kHz in the frequency range 100–530 GHz, primarily because of modulation broadening, and typically 20–40 data points were taken over an absorption line. Gaussian functions were used to fit the data. Experimental accuracy of the frequencies is estimated to be ±50 kHz.

The alkali metal acetylides are linear molecules with $^1\Sigma$ ground electronic states, and the rotational quantum number is, therefore, J. No fine or magnetic hyperfine structure was observed, which is not unexpected because the alkali metal acetylides are closed-shell species. Nuclear-quadrupole interactions involving the metal nuclei were also not seen. However, the $J = 0 \rightarrow 1$ transitions, where this splitting is most likely to be resolved, were below the frequency range of the spectrometer.

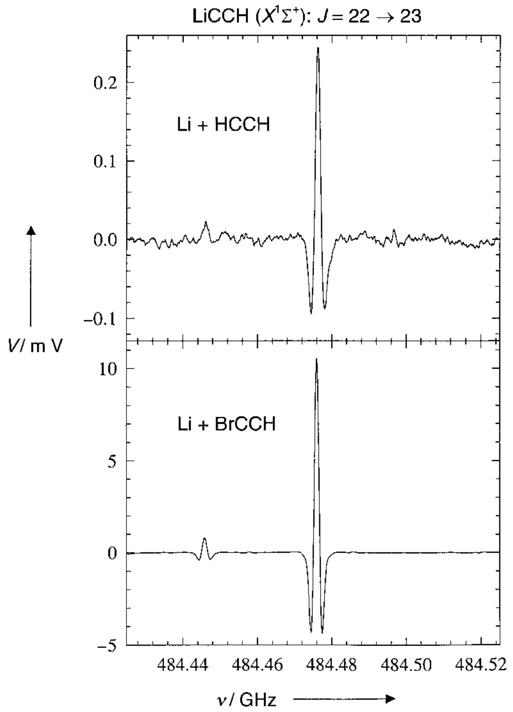

Figure 1. Top: Typical spectrum ($J = 22 \rightarrow 23$) for LiCCH made from Li and HCCH with a direct current discharge. Bottom: The same transition observed for LiCCH from the reaction of Li and BrCCH. The signal-to-noise ratio is much lower using BrCCH, and no discharge was necessary.

A typical spectrum of LiCCH is shown in Figure 1, which presents the $J = 22 \rightarrow 23$ transition of this species. The top part of the figure shows the spectrum of LiCCH made from HCCH, whereas the lower part shows that of LiCCH made from BrCCH, which clearly produced much stronger signals. The molecular constants shown in Table 1 were derived by using a $^1\Sigma$ Hamiltonian. To fit the data within experimental uncertainty,[12] the rotational constant B_o, the first-order centrifugal distortion constant D_o, and second order distortion parameter H_o were needed for each isotopomer. However, only B_o was needed to determine the moment of inertia and hence the structure. From the structure the bond lengths r_{CM}, r_{CC}, and r_{CH} were calculated, and the values are listed in Table 2.

Table 1. Molecular constants (in MHz) for MCCH isotopomers.[a]

Species	B_o	D_o	$10^7\ H_o$
LiCCH	10544.0909(45)	0.011373(14)	0.27(12)
^{6}LiCCH	11545.322(12)	0.013054(13)	–
LiC^{13}CH	10287.534(33)	0.010714(72)	–
Li^{13}CCH	10539.046(12)	0.011241(11)	–
LiCCD	9622.8736(92)	0.0086047(69)	–
NaCCH	4510.116(10)	0.0028240(46)	0.0363(70)
NaCCD	4181.180(84)	0.002282(25)	0.025(25)
KCCH	2970.8168(31)	0.0017560(13)	0.1310(22)
KCCD	2764.999(14)	0.0013966(21)	0.0497(11)

[a] The errors quoted in parentheses are based only on the errors in the statistical analysis (3σ).

The C–H bond lengths for NaCCH and KCCH were assumed to be 1.06 Å and the other two lengths were deter-

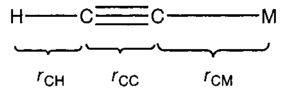

Table 2. Comparison of experimental and calculated bond lengths (in Å) in MCCH (M = Li, Na, K).

Molecule	Source	M–C	C–C	C–H	Ref.
LiCCH	exp.[a]	1.888	1.226	1.061	this work
LiCCH	exp.[b]	1.888	1.227	1.062	this work
LiCCH	STO-4G	1.862	1.213	1.070	[6b]
LiCCH	SS[c]	1.921	1.219	1.056	[6b]
LiCCH	SS+d[c]	1.931	1.208	1.056	[6b]
LiCCH	INDO	1.842	1.220[d]	1.099[d]	[6c]
NaCCH	exp.[a]	2.221	1.217	1.06[d]	this work
NaCCH	RCCSD(T)	2.23	1.23	1.07	[6e]
KCCH	exp.[a]	2.540	1.233	1.06[d]	this work

[a] Millimeter spectroscopy; r_o structure (see text). [b] Millimeter spectroscopy; r_s structure (see text). [c] SS = Gaussian split-shell basis set, SS+d = same with carbon 3d orbitals. [d] Assumed value.

mined directly from the moments of inertia I_o of the two isotopomers studied, MCCH and MCCD, that is, from the r_o structure. For the lithium analogue, every atom was substituted. Unfortunately, the ^{13}C atom nearest the lithium atom in LiCCH was found to be very close to the center of mass, and, therefore, Li^{13}CCH was not used in the calculations. However, sufficient substitutions were still available for LiCCH that both r_s and r_o structures could be determined. The r_s structures are thought to result in better estimates of the true bond lengths because effects of zero-point vibrations largely cancel in this method.[13] In fact, the estimated accuracies for r_s bond lengths are ±0.0005 Å, as opposed to ±0.005 Å for r_o bond lengths.[13] On the other hand, the effects of vibration are not too critical if the molecules are fairly rigid, as the acetylides certainly are. Experimental verification comes from the similar values of r_o and r_s bond lengths for LiCCH shown in Table 2.

The carbon–metal bond lengths appear to be the shortest ones known for organoalkali metal compounds of each metal. The three main factors responsible for this are probably the small size and the sp hybridization of the organic portion, and the solvent-free, monomeric nature of each species. The closest precedents among organolithium compounds would be the following three monomers: gas-phase CH_3Li (C–Li distance 1.959 Å),[8] gas-phase $LiCH(SiMe_3)_2$ (2.03(6) Å),[4b] and a solid-phase aryllithium featuring an ether ligand (2.017(7) Å).[4a] Our experimental results for the C–C and C–H bond lengths compare well with those predicted from ab initio calculations. However, for the relatively well-studied LiCCH the predicted Li–C bond lengths ranged from 1.842 to 1.931 Å,[6] whereas our results set this length at 1.888 Å. On the other hand, our experimental value for the Na–C length in NaCCH is only 0.01 Å shorter than an ab initio result.[6e] Differences in bond lengths in experimental or theoretical r_e and experimental r_o structures such as ours are typically on the order of 0.01 Å or less,[14] and as discussed above, r_s structures are even better. Thus, the differences between our experimental data and calculated values should allow refinement of calculations involving the highly electropositive alkali metals in MCCH and other organoalkali compounds.[15]

Received: April 6, 1998 [Z11688IE]
German version: *Angew. Chem.* **1998**, *110*, 2824–2827

Keywords: alkali metals · alkynes · gas-phase chemistry · rotational spectroscopy

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A Coordination-Induced 1,4→1,2-Quinonediimine Isomerization[**]

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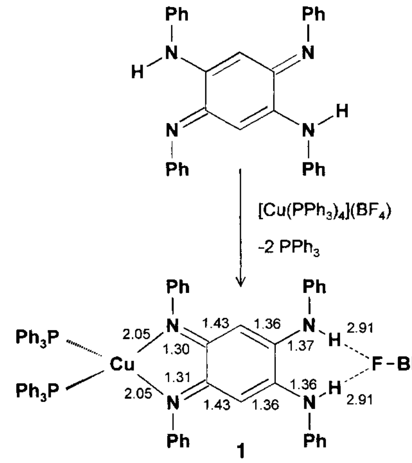
Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

Azophenine (2,5-diamino-1,4-benzoquinonediimine, ap) is a long known *para*-quinonoid compound, which can be obtained in various ways from aniline.[1] Although azophenine bears a close similarity to the increasingly used bis-chelate ligand family derived from 2,5-dihydroxy-1,4-benzoquinone[2] its coordination chemistry has hitherto remained unexplored.[3] This is all the more surprising since metal complexes of quinonoid compounds with O and N donor functionalities have been much studied recently for reasons of their unusual electronic structures (with sometimes ambiguous oxidation state formulations),[4] their potential uses in molecular biology,[5] and their possible occurrence in enzymes.[6] In particular, copper-dependent amine oxidases show an interaction between the redox-active metal center and a functionalized "topaquinone" ligand present as a modified tyrosine side chain.[7–9] Since this topaquinone ligand reacts with amine substrates to form quinoneimine intermediates,[6, 8, 9] we set out to treat copper compounds with the bifunctional azophenine ligand.

Treatment of azophenine with [Cu(PPh$_3$)$_4$](BF$_4$) in acetone (or dichloromethane) results in the spontaneous formation of the copper(I) complex [Cu(PPh$_3$)$_2$(ap)](BF$_4$) (**1**, Scheme 1).[10] The complex is highly soluble in acetone, dichloromethane, and alcohols, but insoluble in hydrocarbons. Any remaining azophenine could be removed by column chromatography. Treatment of ap with two equivalents of [Cu(PPh$_3$)$_4$](BF$_4$) also yielded the mononuclear complex and not a dinuclear compound.

Single crystals of **1** were obtained from a solution of acetone/pentane and were analyzed by crystallography.[11] They were found to contain three equivalents of acetone as supported by elemental analysis and ^{1}H NMR spectroscopy. Refinement of the molecular structure (Figure 1) revealed two quite remarkable structural features of **1**:



Scheme 1. Synthesis of **1** from ap. The general bond pattern in **1** and selected bond lengths [Å] are shown.

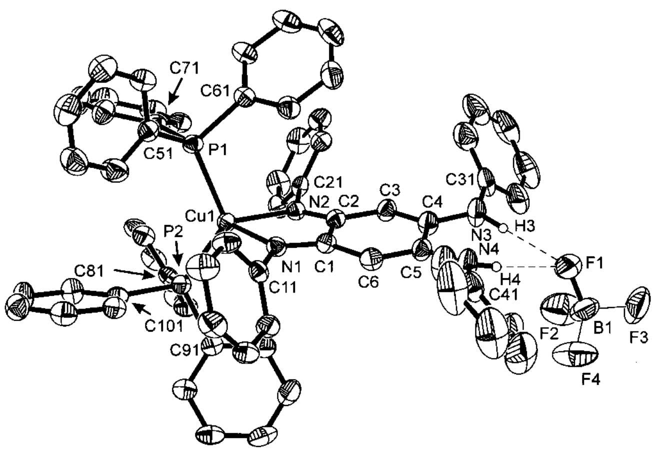


Figure 1. View of the structure of **1** in the crystal. Selected bond lengths [Å] and bond angles [°]: Cu1–N1 2.052(4), Cu1–N2 2.054(4), Cu1–P2 2.2439(13), Cu1–P1 2.2571(13), N1–C1 1.307(5), N2–C2 1.300(5), N3–C4 1.368(6), N4–C5 1.364(6), C1–C6 1.430(6), C1–C2 1.483(6), C2–C3 1.426(6), C3–C4 1.357(6), C4–C5 1.486(6), C5–C6 1.360(6); N1-Cu1-N2 79.18(14), N2-Cu1-P2 115.90(11), N2-Cu1-P1 104.88(11), C1-N1-Cu1 114.5(3), N1-Cu1-P2 111.57(11), N1-Cu1-P1 114.42(11), P2-Cu1-P1 122.62(5), C2-N2-Cu1 114.5(3).

1) The tetracoordinate copper(I) center is bound in a chelate fashion by two *o*-quinonediimine N-donor centers; the C=N bond lengths (standard deviation ≤0.006 Å) and the general bond pattern within the six-membered ring are summarized in Scheme 1. Clearly, there has been an isomerization from the usually more stable *para*-quinonediimine state[12] to the higher energy *ortho* form to allow the formation of a chelate complex between the π electron-rich metal and a strongly π-accepting[4b,c, 13] *o*-quinonediimine ligand.[14] This situation results in the occurrence of a metal-to-ligand charge transfer (MLCT) absorption of the complex at 525 nm (Figure 2); the long-wavelength intraquinone transition of the free ligand at 390 nm is slightly shifted to 395 nm in the complex.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagen Foundation, and the Fonds der Chemischen Industrie. We thank Dr. K.-W. Klinkhammer for helpful suggestions, and T. Sixt and T. Scheiring for assistance.