New Insight into the Structure of Organocuprate π-Complexes by Determination of ^{13}C,^{13}C Coupling Constants

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The past two decades have witnessed remarkable developments concerning the use of organocuprates as tools in synthetic organic chemistry,[1] particularly in stereoselective synthesis.[2] Whereas the 1,4-addition to enones and enoates is still the most important reaction of cuprates,[1,2] the synthetic potential of conjugate cuprate additions has recently been extended by the 1,6- and 1,8-addition reactions to 2-en-4-ynoates and 2,4-dien-6-ynoates, respectively, which open a versatile access to richly functionalized allenes.[3] From the mechanistic point of view, these reactions exhibit striking similarities: in all cases, π-complexes of the cuprate at the C–C double bond adjacent to the carbonyl function are formed, as has been shown by different groups[4] for 1,4-addition and by us[5] for 1,6- and 1,8-addition reactions. The structural assignment of these π-complexes is based on the chemical shifts observed in their ^{13}C-NMR spectra: coordination of a copper atom with the π-system induces large upfield shifts for the resonances of the C–C double bond, whereas an interaction of a lithium atom of the cuprate cluster with the carbonyl oxygen atom causes small downfield shifts of the carbonyl resonances.[4-6] These investigations, however, are unsatisfactory with regard to two problems: (i) it is difficult to draw conclusions about the bonding situation (bonding order, hybridization) of the complexed Michael acceptor from chemical shifts and (ii) no information about the structure of the cuprate part of the π-complexes could be obtained. In view of these difficulties and of the importance of the π-complex formation for the mechanism and consequently the stereoselectivities of conjugate cuprate additions, we sought to gain additional information about the structure of cuprate π-complexes by determination of ^{13}C,^{13}C coupling constants, since these are known to be very sensitive toward the bonding situation.[7] To the best of our knowledge, no investigations of this type have been reported so far.[8]

Toward this end, we synthesized three ^{13}C-labeled 2-en-4-ynoates **1** with labels at C-2, C-3, and C-5, respectively, and converted them into the π-complexes **2** by treatment with lithium di-*tert*-butylcyanocuprate (t-$Bu_2Cu(CN)Li_2$) in THF as described earlier.[5] The $^{1}J_{C,C}$ coupling constants for the starting enyne were determined independently by an INADEQUATE experiment using the unlabeled material; the values found (see Figure 1) are in the expected range.[7] A comparison of the ^{13}C,^{13}C coupling constants of π-complex **2** with those of the uncomplexed enyne shows that the coupling between C-2 and C-3 decreases considerably from 74 to 51 Hz upon π-complex formation, whereas all other $^{1}J_{C,C}$ constants remains virtually unchanged (see Figure 1). This finding proves unambigously that *the cuprate is coordinated to the C–C double bond of 2-en-4-ynoate **1**, whereas no interaction with the π-system of the triple bond is taking place.*

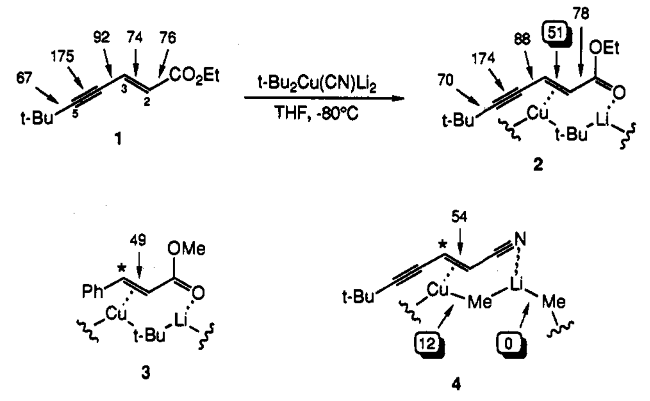

Figure 1. ^{13}C-labeled π-complexes examined in this work ($^{1}J_{C,C}$ coupling constants given in hertz).

Similar results were obtained for π-complexes **3**[9] (formed by treatment of 3-[^{13}C]methyl cinnamate with t-$Bu_2Cu(CN)Li_2$ in THF) and **4**[10] (from (E)-3-[^{13}C]-6,6-dimethyl-2-hepten-4-ynenitrile and $Me_2CuLi{\cdot}LiI$ in CD_2Cl_2/Et_2O), respectively. Comparison of the chemical shifts of the free Michael acceptors with those of these π-complexes shows in all cases the characteristic behavior mentioned above, i.e., drastic upfield shifts for the signals of C-2/C-3 and small downfield shifts for C-1.[9,10] As found earlier for **1**/**2**,[5] the resonances for the C–C triple bond of enynenitrile **4** are shifted together upon π-complexation, but their average shows no characteristic upfield or downfield shift. In the NMR spectra of complex **3**, two species are observed, a behavior that might be due to the presence of geometric isomers of dimeric or larger clusters;[5] however, ^{13}C,^{13}C coupling constants could only be determined for the major species. Thus, for **3** a value of $^{1}J_{2,3} = 49$ Hz was found; the corresponding coupling constant for uncomplexed methyl cinnamate is $^{1}J_{2,3} = 72$ Hz. Analogously, the value for $^{1}J_{2,3}$ decreases from 77 to 54 Hz upon formation of π-complex **4**;[11] here, only one species is observed in the NMR spectra. Although there are small differences between

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(3) (a) Krause, N. *Chem. Ber.* **1990,** *123,* 2173–2180. (b) Krause, N. *Chem. Ber.* **1991,** *124,* 2633–2635. (c) Arndt, S.; Handke, G.; Krause, N. *Chem. Ber.* **1993,** *126,* 251–259. (d) Krause, N.; Arndt, S. *Chem. Ber.* **1993,** *126,* 261–263. (e) Krause, N. *Liebigs Ann. Chem.* **1993,** 521–525. (f) Handke, G.; Krause, N. *Tetrahedron Lett.* **1993,** *34,* 6037–6040. (g) Haubrich, A.; van Klaveren, M.; van Koten, G.; Handke, G.; Krause, N. *J. Org. Chem.* **1993,** *58,* 5849–5852.

(4) (a) Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1985,** *282,* 133–144. (b) Lindstedt, E.; Nilsson, M.; Olsson, T. *J. Organomet. Chem.* **1987,** *334,* 255–261. (c) Ullenius, C.; Christenson, B. *Pure Appl. Chem.* **1988,** *60,* 57–64. (d) Christenson, B.; Olsson, T.; Ullenius, C. *Tetrahedron* **1989,** *45,* 523–534. (e) Bertz, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.* **1989,** *111,* 8276–8277. (f) Sharma, S.; Oehlschlager, A. C. *Tetrahedron* **1991,** *47,* 1177–1184.

(5) Krause, N. *J. Org. Chem.* **1992,** *57,* 3509–3512.

(6) A differentiation between the two possible bonding types in these organometallic species (π-complex or metallacyclopropane) can be made with a simple chemical test: hydrolysis of the cuprate π-complexes provides the starting olefins; if a metallacyclopropane were present, hydrolysis should give the corresponding alkane.

(7) (a) Marshall, J. L. *Carbon–Carbon and Carbon–Proton NMR Couplings*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Thieme: Stuttgart, 1984; pp 493–512.

(8) Observation of ^{13}C,^{13}C couplings in cyanocuprates: Bertz, S. H. *J. Am. Chem. Soc.* **1991,** *113,* 5470–5471.

(9) ^{13}C-NMR chemical shifts (δ, ppm) and ^{13}C,^{13}C coupling constants (J, Hz) follow. 3-[^{13}C]Methyl cinnamate ($CDCl_3$ as solvent and internal standard [$\delta = 77.05$]): $\delta = 117.9$ (C-2), 134.5 (C-4), 144.9 (C-3), 167.4 (C-1); $^{1}J_{2,3} = 72$, $^{1}J_{3,4} = 56$. π-Complex **3** (THF as solvent and internal standard [$\delta = 26.5$], –80 °C): $\delta = 60.2$ (C-2), 69.7 (C-3), 145.8 (C-4), 174.3 (C-1); $^{1}J_{2,3} = 49$, $^{1}J_{3,4} = 55$.

(10) ^{13}C-NMR chemical shifts (δ, ppm) and ^{13}C,^{13}C coupling constants (J, Hz): (E)-3-[^{13}C]-6,6-Dimethyl-2-hepten-4-ynenitrile ($CDCl_3$ as solvent and internal standard [$\delta = 77.05$]): $\delta = 28.4$ (C-6), 30.4 ($C(CH_3)_3$), 75.9 (C-4), 107.2 (C-2), 111.0 (C-5), 117.2 (C-1) 132.0 (C-3); $^{1}J_{2,3} = 77$, $^{1}J_{3,4} = 93$, $^{2}J_{3,5} = 12$. π-Complex **4** (CD_2Cl_2 as solvent and internal standard [$\delta = 53.5$], –80 °C): $\delta = -10.7$ (d, $J = 12$, Me-metal), –5.1 (s, Me-metal), 27.5 (C-6), 28.8 (C-2), 30.6 ($C(CH_3)_3$, 42.4 (C-3), 80.8 (C-4), 90.8 (C-5), 125.0 (C-1); $^{1}J_{2,3} = 54$, $^{1}J_{3,4} = 90$, $^{2}J_{3,5} = 12$.

(11) This was also found in the ^{1}H-NMR spectra of π-complex **4** (without ^{13}C-label): the resonances of 2-H and 3-H ($\delta = 5.60$, 6.46 in the free enyne) are shifted upfield upon π-complex formation ($\delta = 2.22$, 2.63), and the vicinal coupling constant decreases from $^{3}J_{2,3} = 16.2$ to 11.3 Hz.[8]

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the values of ${}^1J_{2,3}$ for the three complexes **2**–**4**, the decrease induced by formation of the π-complex is identical for all systems examined (ΔJ = 23 Hz). A comparison of these values of ${}^1J_{2,3}$ (49–54 Hz) with the C–C coupling constants observed for 1,3–butadiene (${}^1J_{1,2}$ = 68.6 Hz, ${}^1J_{2,3}$ = 53.7 Hz[7]) reveals that *the hybridization of this bond in the π-complexes is similar to that of a single bond connecting two carbon atoms with sp^2 hybridization.*[12] Interestingly, this bonding situation is also present in the allenyl enolate formed by 1,6-addition, where a single bond at C-2/C-3 is flanked by the allene moiety and the enolate double bond.

Intriguingly, the use of ^{13}C-labeled Michael acceptors provided also for the first time an insight into the cuprate part of a π-complex. In the ^{13}C-NMR spectra of π-complex **4** formed from (*E*)-3-[^{13}C]-6,6-dimethyl-2-hepten-4-ynenitrile and $Me_2CuLi{\cdot}LiI$, two resonances for methyl groups bound to copper and/or lithium were observed at $\delta = -5.1$ and -10.7, respectively; whereas the former is a singlet,[13] the latter shows a coupling with the labeled carbon atom with a coupling constant of J = 12 Hz! This means that *of the two different metal-bound methyl groups present in this π-complex, only one is close enough to the C–C double bond of the Michael acceptor to show a $^{13}C,^{13}C$ coupling.* This finding is in accordance with a representation of the cuprate part of this π-complex as in formula **4**; here, the methyl group between copper and lithium shows a coupling with C-3, whereas the second one attached to lithium does not. Connection of two or more of these entities over Me–Li–Me bridges might give dimeric or larger clusters of this type.[14,15] Interestingly, the coupling constant of 12 Hz in π-complex **4** is about half the values found by Bertz for the coupling between R and CN in cyanocuprates RCu(CN)Li (20–24 Hz),[8] indicating that the order of the π-bond between the olefin and the copper in **4** is about half that between CN and copper in RCu(CN)Li.

To summarize the results of this work, it has been found by determination of ^{13}C,^{13}C coupling constants that in π-complexes of enoates and 2-en-4-ynoates with organocuprates a complexation takes place at the C–C double bond but not at an adjacent triple bond; upon π-complexation, the bonding order of the C–C double bond is lowered considerably (hybridization of a single bond between two sp^2-hybridized carbon atoms). In the case of π-complex **4**, the observation of a coupling with only one of two spectroscopically different metal-bound methyl groups provided an insight into possible structures of the cuprate part of this complex.

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(12) For a tantalum alkene complex, a ^{13}C,^{13}C coupling constant of ${}^1J$ = 34 Hz was determined and interpreted in terms of a metallacyclopropane structure: Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773–9781.

(13) The singlet at $\delta = -5.1$ is not caused by free MeLi; for this, the following chemical shifts were determined (CD_2Cl_3 as solvent and internal standard [δ = 53.5], –80 °C): $\delta = -14.2$ (^{13}C-NMR), –1.99 (^{1}H-NMR).

(14) Free cuprates are usually dimeric: Van Koten, G. *J. Organomet. Chem.* **1990**, *400*, 283–301 and references cited therein.

(15) Analogous π-complexes with $Me_2CuLi{\cdot}LiI$ could not be obtained. Whereas **1** reacts rapidly with $Me_2CuLi{\cdot}LiI$ in Et_2O under 1,6-addition, no π-complex formation takes place in THF;[5] with methyl cinnamate and $Me_2CuLi{\cdot}LiI$, only suspensions containing a yellow precipitate (MeCu?) were obtained. In contrast to this, π-complex **4** is stable up to 0 °C; at higher temperatures, decomposition and *E*/*Z*-isomerization of the enyne takes place.[8]