Probing Cyanocuprates by Electrospray Ionization Mass Spectrometry

*Aliaksei Putau and Konrad Koszinowski**

*Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 5 – 13,
81377 München, Germany*

Supporting Information

Table of Contents

1.) Anion-mode ESI mass spectra recorded with the TSQ 7000 instrument (Figures S1 – S4)	S2
2.) Characterization of the HCT ion trap (Figures S5 – S8)	S4
3.) Comparison of measured and simulated isotope patterns (Figures S9 – S10)	S6
4.) Additional anion-mode ESI mass spectra of $\text{LiCuR}_2\cdot\text{LiCN}$ solutions (Figures S11 – S15)	S7
5.) Additional anion-mode ESI mass spectra of $\text{LiCu}(\text{Me})\text{R}\cdot\text{LiCN}$ solutions (Figures S16 – S26)	S10
6.) Additional anion-mode ESI mass spectra of $\text{LiCuR}(\text{CN})$ solutions (Figures S27 – S33)	S16
7.) Additional cation-mode ESI mass spectra of $\text{LiCuR}_2\cdot\text{LiCN}$ solutions (Figures S34 – S38)	S20
8.) Additional cation-mode ESI mass spectra of $\text{Li}_{0.8}\text{CuR}_{0.8}(\text{CN})$ solutions (Figures S39 – S44)	S23
9.) Mass spectra of mass-selected $\text{Li}_{n-1}\text{Cu}_n\text{R}_{2n}^-$ anions and their fragment ions (Figures S45 – S56)	S26
10.) Mass spectra of mass-selected $\text{Li}_{n-1}\text{Cu}_n\text{Me}_{2n-x}\text{R}_x^-$ anions and their fragment ions (Figures S57 – S72)	S32
11.) Mass spectra of mass-selected cyanide-containing cuprate anions and their fragment ions (Figures S73 – S100)	S40

1.) Anion-mode ESI mass spectra recorded with the TSQ 7000 instrument

Figure S1. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^n\text{Bu}_2\cdot\text{LiCN}$ in THF, measured with the TSQ 7000 instrument.

Figure S2. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^n\text{Bu}(\text{CN})$ in THF, measured with the TSQ 7000 instrument, a = $\text{Cu}(\text{CN})_2^-$, b = $\text{Cu}^n\text{Bu}(\text{CN})^-$, c = $\text{Cu}_2^n\text{Bu}(\text{CN})_2^-$, d = $\text{LiCu}_2^n\text{Bu}_2(\text{CN})_2^-$, e = $\text{LiCu}_3^n\text{Bu}_2(\text{CN})_3^-$.

Figure S3. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCuPh}_2\cdot\text{LiCN}$ in THF, measured with the TSQ 7000 instrument.

Figure S4. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCuPh}(\text{CN})$ in THF, measured with the TSQ 7000 instrument.

2.) Characterization of the HCT ion trap

Figure S5. Ratio of the signal intensities of $\text{Li}_2\text{Cu}_3^n\text{Bu}_6^-$ and Cu^nBu_2^- produced by ESI of a 25 mM solution of $\text{LiCu}^n\text{Bu}_2 \cdot \text{LiCN}$ in THF as a function of the voltage of the capillary exit (other parameters: $V(\text{Oct 1 DC}) = -5$ V, $V(\text{Oct 2 DC}) = -1.7$ V, trap drive level of 20).

Figure S6. Ratio of the signal intensities of $\text{Li}_2\text{Cu}_3^n\text{Bu}_6^-$ and Cu^nBu_2^- produced by ESI of a 25 mM solution of $\text{LiCu}^n\text{Bu}_2 \cdot \text{LiCN}$ in THF as a function of the voltage of the first transfer octopole (other parameters: $V(\text{capillary exit}) = -20$ V, $V(\text{Oct 2 DC}) = -1.7$ V, trap drive level of 20).

Figure S7. Ratio of the signal intensities of $\text{Li}_2\text{Cu}_3^n\text{Bu}_6^-$ and Cu^nBu_2^- produced by ESI of a 25 mM solution of $\text{LiCu}^n\text{Bu}_2 \cdot \text{LiCN}$ in THF as a function of the voltage of the second transfer octopole (other parameters: $V(\text{capillary exit}) = -20$ V, $V(\text{Oct 1 DC}) = -12$ V, trap drive level of 20).

Figure S8. Ratio of the signal intensities of $\text{Li}_2\text{Cu}_3^n\text{Bu}_6^-$ and Cu^nBu_2^- produced by ESI of a 25 mM solution of $\text{LiCu}^n\text{Bu}_2 \cdot \text{LiCN}$ in THF as a function of the trap drive level (other parameters: $V(\text{capillary exit}) = -20$ V, $V(\text{Oct 1 DC}) = -16$ V, $V(\text{Oct 2 DC}) = -1.7$ V).

3.) Comparison of measured and simulated isotope patterns

Figure S9. Comparison of observed (black) and simulated (red) isotope patterns for Cu^nBu_2^- .

Figure S10. Comparison of observed (black) and simulated (red) isotope patterns for $\text{Li}_2\text{Cu}_3^n\text{Bu}_6^-$.

4.) Additional anion-mode ESI mass spectra of $\text{LiCuR}_2 \cdot \text{LiCN}$ solutions

Figure S11. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCuEt}_2 \cdot \text{LiCN}$ in THF.

Figure S12. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^n\text{Bu}_2 \cdot \text{LiCN}$ in THF.

Figure S13. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^s\text{Bu}_2 \cdot \text{LiCN}$ in THF.

Figure S14. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^f\text{Bu}_2 \cdot \text{LiCN}$ in THF.

Figure S15. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCuPh}_2 \cdot \text{LiCN}$ in THF, a = $\text{LiCu}_2\text{Ph}_3(\text{CN})^-$.

5.) Additional anion-mode ESI mass spectra of $\text{LiCu}(\text{Me})\text{R}\cdot\text{LiCN}$ solutions

Figure S16. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}(\text{Me})\text{Et}\cdot\text{LiCN}$ in THF.

Figure S17. Section from the anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}(\text{Me})\text{Et}\cdot\text{LiCN}$ in THF.

Figure S18. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}(\text{Me})^{\text{d}}\text{Bu}\cdot\text{LiCN}$ in THF, a = $\text{LiCu}_2\text{Me}(\text{OH})^{\text{d}}\text{Bu}_2^-/\text{LiCu}_2(\text{OH})_2^{\text{d}}\text{Bu}_2^-$, b = $\text{Li}_2\text{Cu}_3\text{Me}_5^{\text{d}}\text{Bu}^-$, c = $\text{Li}_2\text{Cu}_3\text{Me}_4^{\text{d}}\text{Bu}_2^-$, d = $\text{Li}_2\text{Cu}_3\text{Me}_3^{\text{d}}\text{Bu}_3^-$, e = $\text{Li}_2\text{Cu}_3^{\text{d}}\text{Bu}_6^-$.

Figure S19. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}(\text{Me})^{\text{t}}\text{Bu}\cdot\text{LiCN}$ in THF, a = $\text{LiCu}_2\text{Me}_2^{\text{t}}\text{Bu}_2^-$.

Figure S20. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}(\text{Me})\text{Ph}\cdot\text{LiCN}$ in THF, $\text{a} = \text{Cu}(\text{Me})\text{Ph}^-$, $\text{b} = \text{Li}_2\text{Cu}_3\text{Me}_5\text{Ph}^-$, $\text{c} = \text{LiCu}_2(\text{Me})\text{Ph}_3^-$.

Figure S21. Anion-mode ESI mass spectrum of a 1:1 mixture of 25 mM solutions of $\text{LiCuMe}_2\cdot\text{LiCN}$ and $\text{LiCuEt}_2\cdot\text{LiCN}$ in THF.

Figure S22. Section from the anion-mode ESI mass spectrum of a 1:1 mixture of 25 mM solutions of $\text{LiCuMe}_2\cdot\text{LiCN}$ and $\text{LiCuEt}_2\cdot\text{LiCN}$ in THF.

Figure S23. Anion-mode ESI mass spectrum of a 1:1 mixture of 25 mM solutions of $\text{LiCuMe}_2\cdot\text{LiCN}$ and $\text{LiCu}^n\text{Bu}_2\cdot\text{LiCN}$ in THF, $a = \text{Li}_2\text{Cu}_3\text{Me}_4^n\text{Bu}_2^-$, $b = \text{Li}_2\text{Cu}_3\text{Me}_3^n\text{Bu}_3^-$.

Figure S24. Anion-mode ESI mass spectrum of a 1:1 mixture of 25 mM solutions of $\text{LiCuMe}_2 \cdot \text{LiCN}$ and $\text{LiCu}^s\text{Bu}_2 \cdot \text{LiCN}$ in THF, a = $\text{Li}_2\text{Cu}_3\text{Me}_5^s\text{Bu}^-$, b = $\text{Li}_2\text{Cu}_3\text{Me}_4^s\text{Bu}_2^-$, c = $\text{Li}_2\text{Cu}_3\text{Me}_3^s\text{Bu}_3^-$, d = $\text{Li}_2\text{Cu}_3^s\text{Bu}_6^-$.

Figure S25. Anion-mode ESI mass spectrum of a 1:1 mixture of 25 mM solutions of $\text{LiCuMe}_2 \cdot \text{LiCN}$ and $\text{LiCu}^t\text{Bu}_2 \cdot \text{LiCN}$ in THF, a = $\text{LiCu}_2\text{Me}_2^t\text{Bu}_2^-$.

Figure S26. Anion-mode ESI mass spectrum of a 1:1 mixture of 25 mM solutions of $\text{LiCuMe}_2 \cdot \text{LiCN}$ and $\text{LiCuPh}_2 \cdot \text{LiCN}$ in THF, a = $\text{Cu}(\text{Me})\text{Ph}^-$, b = $\text{Li}_2\text{Cu}_3\text{Me}_5\text{Ph}^-$.

6.) Additional anion-mode ESI mass spectra of LiCuR(CN) solutions

Figure S27. Anion-mode ESI mass spectrum of a 25 mM solution of LiCuEt(CN) in THF, a = $\text{Cu}_3\text{Et}_2\text{Bu}(\text{CN})_2^-$, b = $\text{Li}_2\text{Cu}_3\text{Et}_3(\text{CN})_3^-$, c = $\text{Li}_2\text{Cu}_3\text{Et}_6^-$, d = $\text{LiCu}_4\text{Et}_3\text{Bu}(\text{CN})_3^-$, e = $\text{Li}_2\text{Cu}_5\text{Et}_4\text{Bu}(\text{CN})_4^-$. The presence of Cu(+2)-containing species with butyl substituents is inferred from fragmentation experiments. The butyl moieties possibly originate from carbometalation of ethene, which supposedly results from β -hydrogen elimination of ethyllithium or -copper species.

Figure S28. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^n\text{Bu}(\text{CN})$ in THF, $a = \text{Li}_2\text{Cu}_3^n\text{Bu}_3(\text{CN})_3^-$.

Figure S29. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^t\text{Bu}(\text{CN})$ in THF, $a = \text{LiCu}_2^t\text{Bu}_3(\text{CN})^-$, $b = \text{Li}_2\text{Cu}_3^t\text{Bu}_3(\text{CN})_3^-$.

Figure S30. Anion-mode ESI mass spectrum of a 25 mM solution of LiCuPh(CN) in THF.

Figure S31. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.8}\text{CuMe}_{0.8}(\text{CN})$ in THF, a = $\text{Cu}_2\text{Me}_2(\text{CN})^-$, b = $\text{Li}_2\text{Cu}_3\text{Me}_6^-$, c = $\text{Li}_2\text{Cu}_3\text{Me}_3(\text{CN})_3^-$.

Figure S32. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.5}\text{CuMe}_{0.5}(\text{CN})$ in THF, a = $\text{Cu}_2\text{Me}_2(\text{CN})^-$, b = $\text{Li}_2\text{Cu}_3\text{Me}_6^-$, c = $\text{Li}_2\text{Cu}_3\text{Me}_3(\text{CN})_3^-$.

Figure S33. Anion-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^s\text{Bu}_2 \cdot \text{LiCN}$ in THF after brief exposure to air.

7.) Additional cation-mode ESI mass spectra of $\text{LiCuR}_2 \cdot \text{LiCN}$ solutions

Figure S34. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{LiCuEt}_2 \cdot \text{LiCN}$ in THF.

Figure S35. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^n\text{Bu}_2 \cdot \text{LiCN}$ in THF.

Figure S36. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^s\text{Bu}_2\cdot\text{LiCN}$ in THF.

Figure S37. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{LiCu}^t\text{Bu}_2\cdot\text{LiCN}$ in THF.

Figure S38. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{LiCuPh}_2 \cdot \text{LiCN}$ in THF, a = $\text{Li}_3(\text{CN})_2(\text{THF})_2^+$, b = $\text{Li}(\text{THF})_3^+$, c = $\text{Li}_2\text{CN}(\text{THF})(^n\text{Bu}_2\text{O})^+$. $^n\text{Bu}_2\text{O}$ stems from the PhLi solutions used for the preparation of $\text{LiCuPh}_2 \cdot \text{LiCN}$.

8.) Additional cation-mode ESI mass spectra of $\text{Li}_{0.8}\text{CuR}_{0.8}(\text{CN})$ solutions

Figure S39. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.8}\text{CuEt}_{0.8}(\text{CN})$ in THF.

Figure S40. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.8}\text{Cu}^n\text{Bu}_{0.8}(\text{CN})$ in THF.

Figure S41. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.8}\text{Cu}^s\text{Bu}_{0.8}(\text{CN})$ in THF.

Figure S42. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.8}\text{Cu}^t\text{Bu}_{0.8}(\text{CN})$ in THF.

Figure S43. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.8}\text{CuPh}_{0.8}(\text{CN})$ in THF.

Figure S44. Cation-mode ESI mass spectrum of a 25 mM solution of $\text{Li}_{0.8}\text{Cu}^s\text{Bu}_{0.8}(\text{CN})$ in Et_2O . The Cu(+2)-containing ion is shown in red.

9.) Mass spectra of mass-selected $\text{Li}_{n-1}\text{Cu}_n\text{R}_{2n}^-$ anions and their fragment ions

Figure S45. Mass spectrum of mass-selected $\text{LiCu}_2\text{Me}_4^-$ ($m/z = 193$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V).

Figure S46. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_6^-$ ($m/z = 293$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V).

Figure S47. Mass spectrum of mass-selected CuEt_2^- ($m/z = 121$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V).

Figure S48. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Et}_6^-$ ($m/z = 377$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V).

Figure S49. Mass spectrum of mass-selected Cu^nBu_2^- ($m/z = 177$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.25$ V).

Figure S50. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3^n\text{Bu}_6^-$ ($m/z = 545$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.23$ V).

Figure S51. Mass spectrum of mass-selected Cu^sBu_2^- ($m/z = 177$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.25$ V).

Figure S52. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3^s\text{Bu}_6^-$ ($m/z = 545$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.20$ V).

Figure S53. Mass spectrum of mass-selected Cu^tBu_2^- ($m/z = 177$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.25$ V).

Figure S54. Mass spectrum of mass-selected $\text{LiCu}_2^t\text{Bu}_4^-$ ($m/z = 361$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V).

Figure S55. Mass spectrum of mass-selected $\text{LiCu}_2\text{Ph}_4^-$ ($m/z = 441$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.20$ V).

Figure S56. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Ph}_6^-$ ($m/z = 665$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.20$ V).

10.) Mass spectra of mass-selected $\text{Li}_{n-1}\text{Cu}_n\text{Me}_{2n-x}\text{R}_x^-$ anions and their fragment ions

Figure S57. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3(\text{Me})\text{Et}_5^-$ ($m/z = 363$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.29$ V), a = $\text{Cu}(\text{Me})\text{Et}^-$, b = $\text{Cu}_2(\text{Me})\text{Et}_2^-$.

Figure S58. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_2\text{Et}_4^-$ ($m/z = 349$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.29$ V), a = $\text{Cu}(\text{Me})\text{Et}^-$, b = $\text{Cu}_2(\text{Me})\text{Et}_2^-$.

Figure S59. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_3\text{Et}_3^-$ ($m/z = 335$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.29$ V), a = $\text{Cu}(\text{Me})\text{Et}^-$, b = $\text{Cu}_2\text{Me}_2\text{Et}^-$.

Figure S60. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_4\text{Et}_2^-$ ($m/z = 321$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.29$ V), a = Cu_2Me_3^- , b = $\text{Cu}_2\text{Me}_2\text{Et}^-$.

Figure S61. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3(\text{Me})^n\text{Bu}_5^-$ ($m/z = 503$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.21$ V).

Figure S62. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_2^n\text{Bu}_4^-$ ($m/z = 461$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.19$ V), a = $\text{LiH}_2\text{Cu}_2(\text{Me})^n\text{Bu}^-$.

Figure S63. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_3^n\text{Bu}_3^-$ ($m/z = 419$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.16$ V), $a = \text{Cu}(\text{Me})^n\text{Bu}^-$.

Figure S64. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_4^n\text{Bu}_2^-$ ($m/z = 377$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.34$ V), $a = \text{HCu}^n\text{Bu}^-$, $b = \text{Cu}(\text{Me})^n\text{Bu}^-$, $c = \text{Cu}_2\text{Me}_2^n\text{Bu}^-$, $d = \text{Li}_2\text{HCu}_3\text{Me}_4^n\text{Bu}^-$.

Figure S65. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_3^s\text{Bu}_3^-$ ($m/z = 419$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.17$ V).

Figure S66. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_4^s\text{Bu}_2^-$ ($m/z = 377$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V).

Figure S67. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_5^s\text{Bu}^-$ ($m/z = 335$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V), $a = \text{Li}_2\text{Cu}_2\text{Me}_4^s\text{Bu}^-$, $b = \text{Li}_2\text{HCu}_3\text{Me}_5^-$.

Figure S68. Mass spectrum of mass-selected $\text{LiCu}_2(\text{Me})^t\text{Bu}_3^-$ ($m/z = 319$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V), $a = \text{LiH}_2\text{Cu}_2(\text{Me})^t\text{Bu}^-$, $b = \text{HCu}_2^t\text{Bu}_2^-$.

Figure S69. Mass spectrum of mass-selected $\text{LiCu}_2\text{Me}_2^t\text{Bu}_2^-$ ($m/z = 277$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V), a = $\text{LiH}_2\text{Cu}_2\text{Me}_2^-$, b = $\text{HCu}_2(\text{Me})^t\text{Bu}^-$, c = $\text{Cu}_2(\text{Me})^t\text{Bu}_2^-$.

Figure S70. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_3\text{Ph}_3^-$ ($m/z = 479$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.17$ V).

Figure S71. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_4\text{Ph}_2^-$ ($m/z = 417$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.15$ V).

Figure S72. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_5\text{Ph}^-$ ($m/z = 355$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.27$ V).

11.) Mass spectra of mass-selected cyanide-containing cuprate anions and their fragment ions

Figure S73. Mass spectrum of mass-selected $\text{Cu}_2\text{Me}_2(\text{CN})^-$ ($m/z = 182$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V).

Figure S74. Mass spectrum of mass-selected $\text{LiCu}_2\text{Me}_2(\text{CN})_2^-$ ($m/z = 215$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.40$ V).

Figure S75. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Me}_3(\text{CN})_3^-$ ($m/z = 326$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V).

Figure S76. Mass spectrum of mass-selected $\text{Li}_3\text{Cu}_4\text{Me}_4(\text{CN})_4^-$ ($m/z = 437$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.13$ V).

Figure S77. Mass spectrum of mass-selected $\text{Cu}_2\text{Et}_2(\text{CN})^-$ ($m/z = 210$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V).

Figure S78. Mass spectrum of mass-selected $\text{LiCu}_2\text{Et}_2(\text{CN})_2^-$ ($m/z = 243$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V), a = $\text{LiCuEt}(\text{CN})_2^-$.

Figure S79. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Et}_3(\text{CN})_3^-$ ($m/z = 368$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.30$ V), $a = \text{Li}_2\text{Cu}_2\text{Et}_2(\text{CN})_3^-$, $b = \text{Li}_2\text{HCu}_3\text{Et}_2(\text{CN})_3^-$.

Figure S80. Mass spectrum of mass-selected $\text{Cu}_3\text{Et}_2(^n\text{Bu})(\text{CN})_2^-$ ($m/z = 356$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.25$ V).

Figure S81. Mass spectrum of mass-selected $\text{LiCu}_4\text{Et}_3^{\text{nBu}}(\text{CN})_3^-$ ($m/z = 481$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.16$ V).

Figure S82. Mass spectrum of mass-selected $\text{Cu}_2^{\text{nBu}_2}(\text{CN})^-$ ($m/z = 266$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V), a = $\text{HCu}(\text{CN})^-$, b = $\text{H}_2\text{Cu}_2(\text{CN})^-$.

Figure S83. Mass spectrum of mass-selected $\text{LiCu}_2^n\text{Bu}_2(\text{CN})_2^-$ ($m/z = 299$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V).

Figure S84. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3^n\text{Bu}_3(\text{CN})_3^-$ ($m/z = 452$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.20$ V), a = $\text{Li}_2\text{Cu}_2^n\text{Bu}_2(\text{CN})_3^-$, b = $\text{Li}_2\text{HCu}_3^n\text{Bu}_2(\text{CN})_3^-$, c = $\text{Cu}_3^n\text{Bu}_3(\text{CN})_2^-$. The latter does not correspond to a fragment ion but instead results from imperfect mass selection.

Figure S85. Mass spectrum of mass-selected $\text{Li}_3\text{Cu}_4^n\text{Bu}_4(\text{CN})_4^-$ ($m/z = 605$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.15$ V), a = $\text{LiCu}_4^n\text{Bu}_4(\text{CN})_3^-$. The latter does not correspond to a fragment ion but instead results from imperfect mass selection.

Figure S86. Mass spectrum of mass-selected $\text{Cu}_2^s\text{Bu}_2\text{CN}^-$ ($m/z = 266$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V), a = $\text{HCu}(\text{CN})^-$, b = $\text{H}_2\text{Cu}_2(\text{CN})^-$.

Figure S87. Mass spectrum of mass-selected $\text{LiCu}_2^s\text{Bu}_2(\text{CN})_2^-$ ($m/z = 299$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V).

Figure S88. Mass spectrum of mass-selected $\text{LiCu}_3^s\text{Bu}_3(\text{CN})_2^-$ ($m/z = 419$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.17$ V).

Figure S89. Mass spectrum of mass-selected $\text{Cu}_2^t\text{Bu}_2(\text{CN})^-$ ($m/z = 266$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.40$ V), a = $\text{HCu}(\text{CN})^-$, b = $\text{H}_2\text{Cu}_2(\text{CN})^-$.

Figure S90. Mass spectrum of mass-selected $\text{LiCu}_2^t\text{Bu}_2(\text{CN})_2^-$ ($m/z = 299$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V).

Figure S91. Mass spectrum of mass-selected $\text{LiCu}_2^t\text{Bu}_3(\text{CN})^-$ ($m/z = 330$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.35$ V).

Figure S92. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3^t\text{Bu}_3(\text{CN})_3^-$ ($m/z = 452$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.20$ V).

Figure S93. Mass spectrum of mass-selected $\text{Li}_3\text{Cu}_4\text{tBu}_4(\text{CN})_4^-$ ($m/z = 605$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.15$ V).

Figure S94. Mass spectrum of mass-selected $\text{Cu}_2\text{Ph}_2(\text{CN})^-$ ($m/z = 306$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.45$ V).

Figure S95. Mass spectrum of mass-selected $\text{LiCu}_2\text{Ph}_2(\text{CN})_2^-$ ($m/z = 339$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.45$ V).

Figure S96. Mass spectrum of mass-selected $\text{Li}_2\text{Cu}_3\text{Ph}_3(\text{CN})_3^-$ ($m/z = 512$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.20$ V).

Figure S97. Mass spectrum of mass-selected $\text{Cu}_3^n\text{Bu}_3(\text{CN})_2^-$ ($m/z = 412$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.20$ V).

Figure S98. Mass spectrum of mass-selected $\text{LiCu}_4^n\text{Bu}_4(\text{CN})_3^-$ ($m/z = 565$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.17$ V).

Figure S99. Mass spectrum of mass-selected $\text{Cu}_3^s\text{Bu}_3(\text{CN})_2^-$ ($m/z = 412$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.17$ V).

Figure S100. Mass spectrum of mass-selected $\text{LiCu}_4^s\text{Bu}_4(\text{CN})_3^-$ ($m/z = 565$) and its fragment ions produced upon collision-induced dissociation ($V_{\text{exc}} = 0.17$ V).