Supplementary Material (ESI) for Chemical Communications


# Supporting Information

## Ligand Exchange Reactions in Cu(III) complexes: Mechanistic Insights by Combined NMR and DFT Studies

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## Experimental section

All cuprate samples were prepared by a method described by John et al.[1] The synthesis of the cuprate was directly done in $Et_2O$-$d_{10}$ to exclude protonated $Et_2O$. The protonated $Et_2O$ form the $^{13}C$-labelled MeLi solution was removed as much as possible before the addition to the Cu-salt suspension. Having the cuprate in hand it was cooled down to 170K and a solution MeI in DEE-$d_{10}$ was added depending on the synthesis. The amount of MeI was adjusted to the synthesis of the cuprate solution.

(1) John, M.; Auel, C.; Behrens, C.; Marsch, M.; Harms, K.; Bosold, F.; Gschwind, R. M.; Rajamohanan, P. R.; Boche, G. *Chem. Eur. J.* **2000**, *6*, 3060-3068.

## NMR Data Collection and Processing

The NMR spectra were recorded on a Bruker Avance 600 spectrometer equipped with a 5mm broadband triple resonance Z-gradient probe.

$^{1}H,^{13}C$ HMBC measurements were carried out with a standard Bruker pulse program using 32 number of scans, 16 dummy scans, TD(F2) = 16k and TD(F1) = 400 with a relaxation delay of 2s. The processing parameters were TD(F1) = 1k and TD(F2) = 1k. The temperatures for all measurements were controlled by a Bruker BVTE 3900 temperature unit.

# Increased formation of $Me_4Cu^-$ applying an excess of MeLi

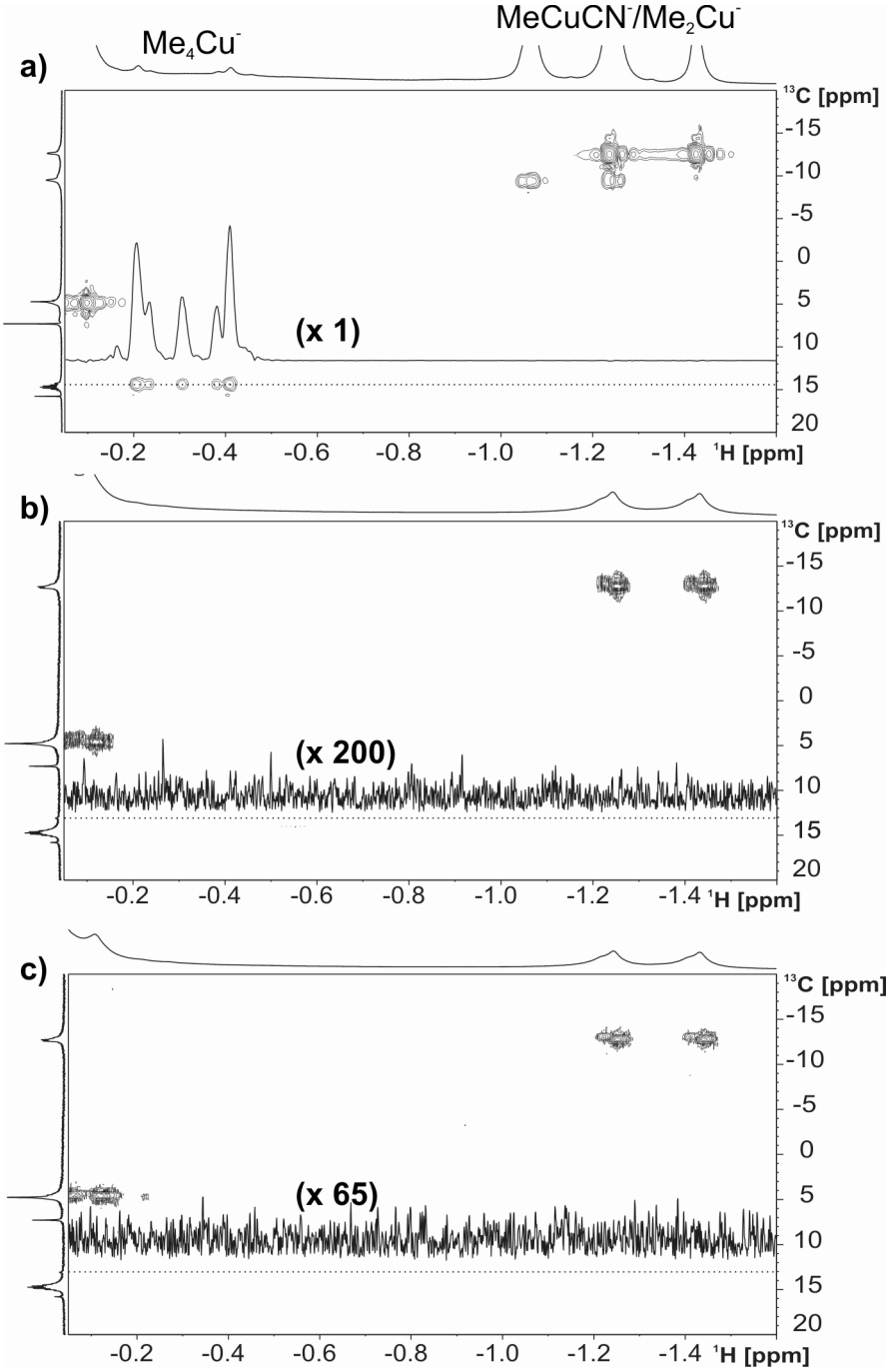


**Fig. S1** Sections of $^1H,^{13}C$ HMBC spectra at -63 °C in diethyl ether showing the signals of $Me_4Cu^-$, $MeCuCN^-$ and $Me_2Cu^-$. To visualize the increased concentration of $Me_4Cu^-$ in the sample with excess of MeLi, in addition, the row of the HMBC spectrum showing $Me_4Cu^-$ is presented as insert with their scaling factors given in brackets.
a) $Cu^{13}CN + 3\ ^{13}CH_3Li + CH_3I$
b) $Cu^{13}CN + 2\ ^{13}CH_3Li + CH_3I$ (number of scans identical to a)
c) $Cu^{13}CN + 2\ ^{13}CH_3Li + CH_3I$ (number of scans three times higher than in a)

# Analysis of the isotopic pattern of ethane in the reaction of $^{13}$C-labelled cyanocuprate converted with MeI and an excess of $^{13}$C-labelled MeLi

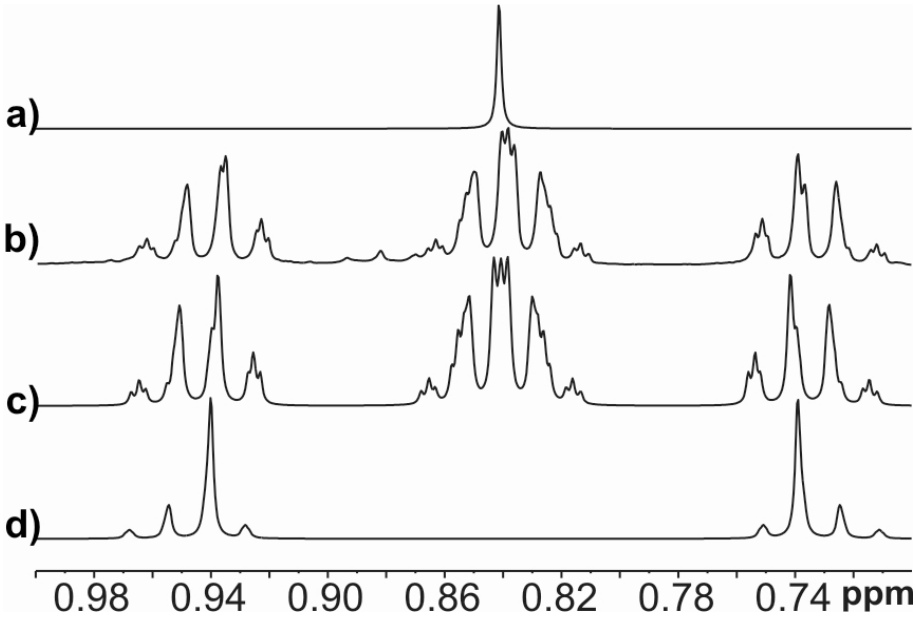


**Fig. S2** Simulated $^{1}$H spectra of a) $H_3C$-$CH_3$, c) $H_3C$-$^{13}CH_3$ and d) $H_3{}^{13}C$-$^{13}CH_3$ in comparison with b) the experimental spectrum of the resulting products of $^{13}$C-labelled cyanocuprate converted with MeI and an excess of $^{13}$C-labelled MeLi.

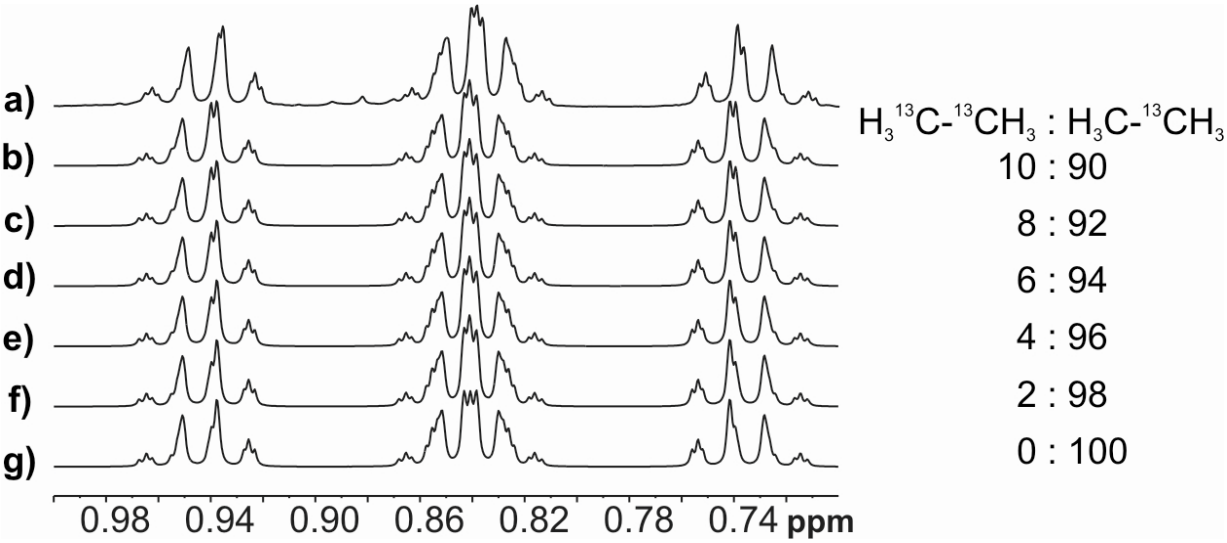


**Fig. S3** a) Experimental spectrum of the resulting products of the $^{13}$C-labelled cyanocuprate converted with MeI and an excess of $^{13}$C-labelled MeLi in comparison with b-g) the simulated $^{1}$H spectra of different mixtures of $H_3{}^{13}C$-$CH_3$ and $H_3{}^{13}C$-$^{13}CH_3$ (ratios given aside).

## DFT functional Calculations

All calculations were done using the GAUSSIAN 03 package.[2] All geometry optimisations were performed with the DFT-method and the B3LYP hybrid functional, using SDD for copper, iodine and gold and 6-31+G(d) for all other atoms. Local minima have zero and transition states (TS) have one and only one imaginary frequency. The intrinsic reaction coordinate (IRC) analysis[3-5] was carried out to confirm that stationary points are smoothly connected to each other. All energies used throughout are zero-point corrected and calculated for the gas-phase.

(2) Gaussian 03, R. C.; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr., T. V.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, a. J. A.; Gaussian, I., Wallingford CT, 2004.
(3) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363-368.
(4) Gonzalez, C.; Schlegel, H. B. J. *Chem. Phys.* **1989**, *90*, 2154-2161.
(5) Gonzalez, C.; Schlegel, H. B. J. *Phys. Chem.* **1990**, *94*, 5523-5527.

## Energies and Cartesians Coordinates of Stationary Points

**MeLi•$(OMe_2)_3$**
SCF Done: E(RB+HF-LYP) = -512.564881634 A.U. after 6 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 1 | 0 | -0.788842 | 1.055813 | 2.975777 |
| 2 | 6 | 0 | -0.013699 | 0.350495 | 2.609524 |
| 3 | 1 | 0 | 0.940869 | 0.768948 | 2.991726 |
| 4 | 1 | 0 | -0.172692 | -0.571035 | 3.208609 |
| 5 | 3 | 0 | -0.009230 | 0.090102 | 0.544882 |
| 6 | 8 | 0 | -1.754444 | -0.669118 | -0.217108 |
| 7 | 8 | 0 | 1.527804 | -1.051062 | -0.164216 |
| 8 | 8 | 0 | 0.247165 | 1.786007 | -0.598593 |
| 9 | 6 | 0 | -2.644681 | -1.140739 | 0.796707 |
| 10 | 1 | 0 | -2.287121 | -0.718958 | 1.736989 |
| 11 | 1 | 0 | -2.621108 | -2.239059 | 0.846667 |
| 12 | 1 | 0 | -3.671606 | -0.808215 | 0.585589 |
| 13 | 6 | 0 | -2.062628 | -1.170125 | -1.507584 |
| 14 | 1 | 0 | -1.352353 | -0.725630 | -2.209189 |
| 15 | 1 | 0 | -3.085236 | -0.891173 | -1.802781 |
| 16 | 1 | 0 | -1.970413 | -2.266303 | -1.537504 |
| 17 | 6 | 0 | 1.457705 | 2.433948 | -0.208502 |
| 18 | 1 | 0 | 2.261919 | 1.704748 | -0.322852 |
| 19 | 1 | 0 | 1.404413 | 2.750317 | 0.841118 |
| 20 | 1 | 0 | 1.650163 | 3.303090 | -0.854469 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 6 | 0 | -0.882101 | 2.649506 | -0.482113 |
| 22 | 1 | 0 | -0.763319 | 3.524916 | -1.137201 |
| 23 | 1 | 0 | -1.010923 | 2.978334 | 0.557745 |
| 24 | 1 | 0 | -1.757457 | 2.074620 | -0.790040 |
| 25 | 6 | 0 | 2.178410 | -1.839037 | 0.833273 |
| 26 | 1 | 0 | 1.781452 | -1.505683 | 1.793466 |
| 27 | 1 | 0 | 3.266060 | -1.680660 | 0.795223 |
| 28 | 1 | 0 | 1.961940 | -2.906709 | 0.681156 |
| 29 | 6 | 0 | 1.951469 | -1.349209 | -1.484145 |
| 30 | 1 | 0 | 1.423643 | -0.667368 | -2.155326 |
| 31 | 1 | 0 | 1.711429 | -2.389572 | -1.751174 |
| 32 | 1 | 0 | 3.035824 | -1.196367 | -1.591802 |

**$Me_2O$**

SCF Done: E(RB+HF-LYP) = -155.033688970 A.U. after 7 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.000000 | 0.587561 | 0.000000 |
| 2 | 6 | 0 | 1.177331 | -0.195661 | 0.000000 |
| 3 | 1 | 0 | 1.233901 | -0.836130 | -0.895388 |
| 4 | 1 | 0 | 1.233901 | -0.836130 | 0.895389 |
| 5 | 1 | 0 | 2.023631 | 0.495986 | 0.000000 |
| 6 | 6 | 0 | -1.177331 | -0.195661 | 0.000000 |
| 7 | 1 | 0 | -1.233901 | -0.836130 | -0.895388 |
| 8 | 1 | 0 | -2.023631 | 0.495986 | 0.000000 |
| 9 | 1 | 0 | -1.233901 | -0.836130 | 0.895388 |

**CP1**

SCF Done: E(RB+HF-LYP) = -1134.88630484 A.U. after 8 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 1 | 0 | 4.804038 | 0.179295 | 1.367932 |
| 2 | 6 | 0 | 3.861348 | -0.076711 | 1.900031 |
| 3 | 1 | 0 | 4.040145 | -1.076201 | 2.349273 |
| 4 | 1 | 0 | 3.807466 | 0.618673 | 2.763107 |
| 5 | 3 | 0 | 2.140180 | -0.013532 | 0.679157 |
| 6 | 8 | 0 | 2.253065 | 1.574693 | -0.648369 |
| 7 | 8 | 0 | 2.163424 | -1.506307 | -0.781244 |
| 8 | 6 | 0 | 2.673173 | 2.745822 | 0.039471 |
| 9 | 1 | 0 | 3.440099 | 2.427722 | 0.748458 |
| 10 | 1 | 0 | 1.832539 | 3.199665 | 0.584433 |
| 11 | 1 | 0 | 3.084852 | 3.481973 | -0.670728 |
| 12 | 6 | 0 | 1.190705 | 1.813862 | -1.562785 |
| 13 | 1 | 0 | 0.945336 | 0.852695 | -2.018886 |
| 14 | 1 | 0 | 1.509790 | 2.526635 | -2.341129 |
| 15 | 1 | 0 | 0.305325 | 2.199400 | -1.043299 |
| 16 | 6 | 0 | 1.468618 | -2.699367 | -0.437519 |
| 17 | 1 | 0 | 0.474605 | -2.402625 | -0.101082 |
| 18 | 1 | 0 | 1.988569 | -3.229919 | 0.374176 |
| 19 | 1 | 0 | 1.390381 | -3.363111 | -1.313538 |
| 20 | 6 | 0 | 3.503564 | -1.744417 | -1.187599 |
| 21 | 1 | 0 | 3.522905 | -2.380305 | -2.088552 |
| 22 | 1 | 0 | 4.077385 | -2.220937 | -0.381417 |
| 23 | 1 | 0 | 3.947594 | -0.771813 | -1.407129 |
| 24 | 17 | 0 | -0.316098 | 0.088658 | 1.246509 |
| 25 | 29 | 0 | -2.387269 | -0.021244 | 0.152812 |

| | | | | | |
|---|---|---|---|---|---|
| 26 | 6 | 0 | -2.508414 | 1.964525 | -0.057417 |
| 27 | 1 | 0 | -1.789172 | 2.432486 | 0.623350 |
| 28 | 1 | 0 | -3.522166 | 2.326396 | 0.160911 |
| 29 | 1 | 0 | -2.262529 | 2.227156 | -1.096873 |
| 30 | 6 | 0 | -2.481839 | -2.012453 | 0.325698 |
| 31 | 1 | 0 | -1.846155 | -2.316040 | 1.164632 |
| 32 | 1 | 0 | -2.099545 | -2.454791 | -0.606288 |
| 33 | 1 | 0 | -3.508225 | -2.367893 | 0.485033 |
| 34 | 6 | 0 | -4.066097 | -0.129793 | -0.825925 |
| 35 | 1 | 0 | -4.183786 | 0.735022 | -1.483608 |
| 36 | 1 | 0 | -4.848816 | -0.128469 | -0.058978 |
| 37 | 1 | 0 | -4.104950 | -1.061446 | -1.396312 |

**TS1**

SCF Done: E(RB+HF-LYP) = -1134.87649990 A.U. after 9 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 29 | 0 | -1.912119 | -0.048872 | -0.047769 |
| 2 | 6 | 0 | -1.875615 | -2.042889 | -0.159832 |
| 3 | 1 | 0 | -0.941936 | -2.345570 | -0.647468 |
| 4 | 1 | 0 | -2.726301 | -2.415848 | -0.747854 |
| 5 | 1 | 0 | -1.922060 | -2.459657 | 0.854523 |
| 6 | 6 | 0 | -2.158205 | 1.928632 | 0.084088 |
| 7 | 1 | 0 | -1.259554 | 2.411292 | -0.316338 |
| 8 | 1 | 0 | -2.306623 | 2.217012 | 1.133128 |
| 9 | 1 | 0 | -3.030315 | 2.245546 | -0.505372 |
| 10 | 6 | 0 | -3.775963 | -0.220590 | 0.529497 |
| 11 | 1 | 0 | -4.355299 | -0.240631 | -0.400306 |
| 12 | 1 | 0 | -4.063061 | 0.639134 | 1.139330 |
| 13 | 1 | 0 | -3.907913 | -1.154621 | 1.080633 |
| 14 | 17 | 0 | -0.068324 | 0.211577 | -1.821935 |
| 15 | 6 | 0 | -0.031477 | -0.174374 | 2.131064 |
| 16 | 1 | 0 | -0.169284 | -1.235320 | 2.411374 |
| 17 | 1 | 0 | 0.822378 | 0.200244 | 2.741371 |
| 18 | 1 | 0 | -0.919784 | 0.362316 | 2.500417 |
| 19 | 3 | 0 | 0.941240 | 0.016402 | 0.267890 |
| 20 | 8 | 0 | 2.299951 | 1.605023 | 0.345222 |
| 21 | 8 | 0 | 2.427689 | -1.458728 | 0.054122 |
| 22 | 6 | 0 | 3.051572 | 1.828003 | -0.838512 |
| 23 | 1 | 0 | 3.835665 | 2.582995 | -0.660363 |
| 24 | 1 | 0 | 2.398039 | 2.153094 | -1.658983 |
| 25 | 1 | 0 | 3.511733 | 0.873836 | -1.104183 |
| 26 | 6 | 0 | 1.638600 | 2.777157 | 0.809858 |
| 27 | 1 | 0 | 1.027127 | 2.475066 | 1.661554 |
| 28 | 1 | 0 | 0.987090 | 3.191083 | 0.028820 |
| 29 | 1 | 0 | 2.377817 | 3.535829 | 1.115808 |
| 30 | 6 | 0 | 2.135350 | -2.517163 | -0.851370 |
| 31 | 1 | 0 | 1.683806 | -2.058502 | -1.732706 |
| 32 | 1 | 0 | 1.418529 | -3.222045 | -0.407168 |
| 33 | 1 | 0 | 3.059337 | -3.054904 | -1.120974 |
| 34 | 6 | 0 | 2.908128 | -1.917325 | 1.309093 |
| 35 | 1 | 0 | 2.164077 | -2.557792 | 1.802151 |
| 36 | 1 | 0 | 3.079818 | -1.034785 | 1.928178 |
| 37 | 1 | 0 | 3.850499 | -2.475571 | 1.180891 |

**CP2**

SCF Done: E(RB+HF-LYP) = -1134.92455705 A.U. after 9 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 29 | 0 | -2.718215 | -0.044376 | 0.157558 |
| 2 | 6 | 0 | -4.677411 | -0.045688 | -0.156602 |
| 3 | 1 | 0 | -4.844226 | -0.426396 | -1.175666 |
| 4 | 1 | 0 | -5.123333 | 0.953938 | -0.070361 |
| 5 | 1 | 0 | -5.168481 | -0.729386 | 0.549349 |
| 6 | 6 | 0 | -2.718315 | 1.946924 | -0.015239 |
| 7 | 1 | 0 | -3.311718 | 2.255555 | -0.888098 |
| 8 | 1 | 0 | -1.709918 | 2.378315 | -0.094234 |
| 9 | 1 | 0 | -3.202419 | 2.355873 | 0.885130 |
| 10 | 6 | 0 | -2.767937 | -2.037366 | 0.284900 |
| 11 | 1 | 0 | -2.690778 | -2.296255 | 1.352180 |
| 12 | 1 | 0 | -1.905392 | -2.480806 | -0.235088 |
| 13 | 1 | 0 | -3.691370 | -2.473378 | -0.119113 |
| 14 | 6 | 0 | -0.736513 | -0.079921 | 0.479057 |
| 15 | 1 | 0 | -0.313808 | -0.099494 | -0.537655 |
| 16 | 1 | 0 | -0.433371 | -0.976384 | 1.036543 |
| 17 | 1 | 0 | -0.410818 | 0.825336 | 1.008716 |
| 18 | 3 | 0 | 1.686165 | -0.070277 | 0.402464 |
| 19 | 17 | 0 | 3.239728 | -0.487828 | 1.972954 |
| 20 | 8 | 0 | 2.115479 | 1.718699 | -0.472935 |
| 21 | 8 | 0 | 2.101195 | -1.363654 | -1.144514 |
| 22 | 6 | 0 | 2.737187 | 2.689557 | 0.366741 |
| 23 | 1 | 0 | 3.413413 | 3.325056 | -0.225844 |
| 24 | 1 | 0 | 3.296894 | 2.131749 | 1.120392 |
| 25 | 1 | 0 | 1.978617 | 3.320754 | 0.852146 |
| 26 | 6 | 0 | 1.308124 | 2.293236 | -1.493808 |
| 27 | 1 | 0 | 0.900334 | 1.470561 | -2.084252 |
| 28 | 1 | 0 | 1.916669 | 2.946669 | -2.138216 |
| 29 | 1 | 0 | 0.478740 | 2.869577 | -1.062714 |
| 30 | 6 | 0 | 1.656211 | -2.690734 | -0.866438 |
| 31 | 1 | 0 | 0.592698 | -2.630116 | -0.628754 |
| 32 | 1 | 0 | 2.204408 | -3.107413 | -0.010688 |
| 33 | 1 | 0 | 1.800669 | -3.331003 | -1.749929 |
| 34 | 6 | 0 | 3.481741 | -1.319105 | -1.497634 |
| 35 | 1 | 0 | 4.103299 | -1.675446 | -0.666863 |
| 36 | 1 | 0 | 3.722816 | -0.273486 | -1.699925 |
| 37 | 1 | 0 | 3.659525 | -1.924788 | -2.400136 |

**$LiCl•(OMe_2)_3$**

SCF Done: E(RB+HF-LYP) = -932.976896813 A.U. after 12 cycles

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 17 | 0 | 0.003482 | 0.882891 | 2.259162 |
| 2 | 8 | 0 | -1.647813 | -0.998481 | -0.201492 |
| 3 | 8 | 0 | 1.644403 | -1.003460 | -0.202886 |
| 4 | 8 | 0 | 0.002712 | 1.588489 | -1.130556 |
| 5 | 6 | 0 | -2.451683 | -1.403286 | 0.912393 |
| 6 | 1 | 0 | -2.062692 | -0.872869 | 1.783543 |
| 7 | 1 | 0 | -2.375413 | -2.489781 | 1.060491 |
| 8 | 1 | 0 | -3.501979 | -1.131109 | 0.737709 |
| 9 | 6 | 0 | -2.039008 | -1.604305 | -1.424306 |
| 10 | 1 | 0 | -3.086056 | -1.364672 | -1.660325 |
| 11 | 1 | 0 | -1.925119 | -2.697254 | -1.375177 |
| 12 | 1 | 0 | -1.393211 | -1.204210 | -2.209961 |
| 13 | 6 | 0 | 2.445779 | -1.414073 | 0.910691 |
| 14 | 1 | 0 | 2.060479 | -0.881330 | 1.782054 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | 1 | 0 | 3.497806 | -1.148794 | 0.735870 |
| 16 | 1 | 0 | 2.362289 | -2.500090 | 1.058429 |
| 17 | 6 | 0 | 2.030754 | -1.611779 | -1.426034 |
| 18 | 1 | 0 | 1.388735 | -1.205392 | -2.211564 |
| 19 | 1 | 0 | 1.907302 | -2.703723 | -1.377776 |
| 20 | 1 | 0 | 3.079919 | -1.381067 | -1.661447 |
| 21 | 6 | 0 | -1.180235 | 2.377438 | -0.968739 |
| 22 | 1 | 0 | -1.203114 | 3.181427 | -1.717796 |
| 23 | 1 | 0 | -1.221711 | 2.798075 | 0.043600 |
| 24 | 1 | 0 | -2.031639 | 1.710886 | -1.120218 |
| 25 | 6 | 0 | 1.188673 | 2.373200 | -0.969820 |
| 26 | 1 | 0 | 1.214233 | 3.176377 | -1.719654 |
| 27 | 1 | 0 | 2.037528 | 1.703306 | -1.120875 |
| 28 | 1 | 0 | 1.232061 | 2.794529 | 0.042131 |
| 29 | 3 | 0 | 0.000437 | 0.070331 | 0.199855 |

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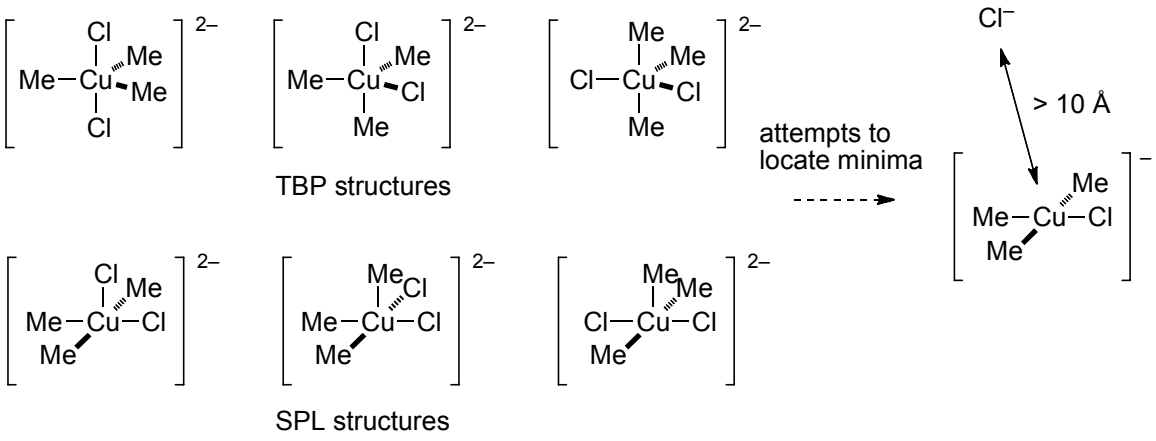
## Attempted Study of Intramolecular Isomerization of Organocopper(III) Complex

In order to probe the possibility of the pseudorotation mechanism for the isomerization of organocopper(III) complexes, geometry optimization of dianionic Cu(III) complex $[Me_3CuCl_2]^{2-}$ was carried out starting from a series of possible pentacoordinate (i.e., trigonal bipyramidal (TBP) and square pyramidal (SPL)) structures as shown below. However, none of such structures was located as a stationary point, and all the attempts uniformly led to dissociation into a square-planar $[Me_3CuCl]^-$ complex and a chloride anion (closest distance > 10 Å). In addition, inclusion of a lithium cation into the below computational model did not give a pentacoordinate Cu(III) complex as well. Thus, geometry optimization led to the formation of a complex between $[Me_3CuCl]^-$ and LiCl, where the Cl atom of the former and the Li atom of the latter electrostatically interact with each other (i.e., the Cl atom of LiCl does not interact with the Cu atom). Note also that attempts to locate a pentacoordinate Cu(III) complex of $[Me_4CuCl]^-$ led to dissociation into square-planar $[Me_4Cu]^-$ and a chloride anion. Because none of pentacoordinate Cu(III) complexes existed as a local minimum, we concluded that the classical pseudorotation mechanism is unlikely to operate in the organocopper(III) reactions.




We also examined the possibility of unimolecular isomerization of a tetracoordinate Cu(III) complex. Thus, trigonal pyramidal (TP) and tetrahedral (Th) structures of $[Me_3CuCl]^-$ were calculated assuming that they are either intermediates or transition states for the *cis*/*trans* isomerization of the square-planar structure. However, the attempts to locate them as local minima and as TSs uniformly led to the square-planar structure and the TS for reductive elimination of ethane, respectively.