Taming Monomeric $[Cu(\eta^6\text{-}C_6H_6)]^+$ Complex with Silylene

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Content:

S1. Experimental Section:

All experiments were carried out under an atmosphere of dry argon or in vaccuo using standard Schlenk technique and in a dinitrogen filled MBRAUN MB 150-G1 glovebox. The solvents used were purified by MBRAUN solvent purification system MB SPS-800. The starting materials **1** and **4** were prepared as reported in the literature.[1] All other chemicals purchased from Aldrich were used without further purification. ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded with Bruker 400 MHz spectrometer, using $CDCl_3$ and CD_2Cl_2 as solvent with an external standard ($SiMe_4$ for ^{1}H, ^{13}C and ^{29}Si and trifluorotoluene for ^{19}F). Mass spectra were recorded using AB Sciex, 4800 plus MALDI TOF/TOF.

Synthesis of 2:

30 mL CH_2Cl_2 was added to a 100 mL Schlenk flask containing mixture of **1** (0.281g, 0.25 mmol), $AgSbF_6$ (0.171g, 0.5 mmol) and C_6Me_6 (0.081 g, 0.5 mmol). After overnight stirring, AgBr was separated out from the reaction mixture by filtration and colorless block shaped crystals were observed in CH_2Cl_2-pentane mixture at 0 °C. Yield: 0.280g (64%). Mp: 130 °C (decomposition). ^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ 0.20 (*s*, 9H, Si*Me₃*), 0.27 (*s*, 9H, Si*Me₃*), 1.06 (*s*, 18H, C*Me₃*), 2.34 (*s*, 18H, C_6*Me₆*), 7.31-7.36 (*m*, 1H, Ph), 7.42-7.56 (*m*, 4H, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, CD_2Cl_2, 298 K): δ 4.59 (Si*Me₃*), 5.15 (Si*Me₃*), 17.59 (*C₆*Me₆), 31.54 (C*Me₃*), 54.61 (*C*Me₃), 126.11, 127.92, 128.47, 128.87, 129.89, 130.56, 131.32 (Ph-*C*), ppm. ^{29}Si{^{1}H} NMR (79.495 MHz, $CDCl_3$, 298 K): δ 7.83 (*Si*Me₃), 7.09 (*Si*Me₃), 0.02 (*Si*N($SiMe_3$)₂). ^{19}F{^{1}H} NMR (376.49 MHz, $CDCl_3$, 298K): δ -176.70 (br) ppm. MALDI: *m/z* $[C_{33}H_{59}N_3Si_3Cu]^+$: 482.47 $[M-C_6Me_6]^+$. Anal Calcd: C, 44.97; H, 6.75; N, 4.77. Found: C, 44.89; H, 6.64; N, 4.82.

Synthesis of 3:

$AgSbF_6$ (0.171g, 0.5 mmol) was dissolved in CH_2Cl_2 (15 mL) and added to the solution of **1** (0.280g, 0.25 mmol) in benzene (15 mL). It was stirred overnight at room temperature. After that, AgBr was separated out from the reaction mixture by filtration and reduced the volume to 15 mL and kept it at 0 °C. Colorless block shaped crystals suitable for X-ray analysis were observed after one day. Yield: 0.260 g (65 %). Mp: 112 °C (decomposition). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.24 (*s*, 9H, Si*Me₃*), 0.39 (*s*, 9H, Si*Me₃*), 1.15 (*s*, 18H, C*Me₃*), 7.22-7.32

(*m*, 1H, Ph), 7.33-7.43 (*m*, 2H, Ph), 7.46 (*s*, 6H, C_6H_6) 7.47-7.69 (*m*, 2H, Ph) ppm. $^{13}C\{^1H\}$ NMR (100.613 MHz, $CDCl_3$, 298 K): δ 3.51 (Si*Me₃*), 4.87 (Si*Me₃*), 30.72 (C*Me₃*), 53.91 (*C*Me₃), 126.55, 126.67, 126.92, 127.82, 129.23, 129.86, 130.08 (Ph-*C*), 168.91 (N*C*N) ppm. $^{29}Si\{^1H\}$ NMR (79.495 MHz, $CDCl_3$, 298 K): δ 7.65 (*Si*Me₃), 7.21 (*Si*Me₃), 4.41 (*Si*N(SiMe₃)₂). $^{19}F\{^1H\}$ NMR (376.49 MHz, $CDCl_3$, 298K): δ -173.64 (br) ppm. MALDI: *m/z* $[C_{27}H_{47}N_3Si_3Cu]^+$: 482.84 $[M-C_6H_6]^+$. Anal Calcd: C, 40.68; H, 5.94; N, 5.27. Found: C, 40.57; H, 6.05; N, 5.37.

Synthesis of 5:

30 mL CH_2Cl_2 was added to a 100 mL Schlenk flask containing mixture of **4** (0.266g, 0.5 mmol), $AgSbF_6$ (0.171g, 0.5 mmol) and C_6Me_6 (0.081 g, 0.5 mmol). After overnight stirring, AgBr was separated out from the reaction mixture by filtration and it was crystallized in saturated CH_2Cl_2 solution. Yield: 0.300g (70%). Mp: 175 °C (decomposition). ^1H NMR (400 MHz, $CDCl_3$, 298K): δ 1.10 (*dd*, 24H, *J*= 9.7, 6.9 Hz, $CH(CH_3)_2$), 1.80 (*s*, 18H, C_6Me_6), 2.20-2.30 (*m*, 4H, $CH(CH_3)_2$), 7.29 (*d*, 4H, *J*= 7.8 Hz, Ph), 7.52 (*t*, 2H, *J*= 7.8 Hz, Ph) ppm. $^{13}C\{^1H\}$ NMR (100.613 MHz, $CDCl_3$, 298 K): δ 16.21, 22.81, 23.19, 27.67, 123.34, 123.54, 128.27, 129.82, 133.62, 144.34, 175.90 ppm. $^{19}F\{^1H\}$ NMR (376.49 MHz, $CDCl_3$, 298K): δ -174.02 (br) ppm. MALDI: *m/z* $[C_{39}H_{54}N_2Cu]^+$: 613.43 $[M]^+$. Anal Calcd: C, 55.10; H, 6.40; N, 3.30. Found: C, 55.22; H, 6.60; N, 3.24.

Synthesis of 6:

$AgSbF_6$ (0.171g, 0.5 mmol) was dissolved in CH_2Cl_2 (15 mL) and added to the solution of **4** (0.266g, 0.5 mmol) in benzene (15 mL). After overnight stirring, AgBr was separated out from the reaction mixture by filtration and reduced the volume to 15 mL and kept it at 0°C. Colorless block shaped crystals suitable for X-ray analysis was observed after one day. Yield: 0.275g (72%). Mp: 228°C (decomposition). ^1H NMR (400 MHz, CD_2Cl_2, 298K): δ 1.14 (*dd*, 24H, *J*= 8.9, 7.0 Hz, $CH(CH_3)_2$), 2.25-2.32 (*m*, 4H, $CH(CH_3)_2$), 7.11 (*br*, 4H, C_6H_6), 7.18 (*s*, 2H, C_6H_6), 7.31 (*d*, 4H, *J*= 7.8 Hz, Ph), 7.53 (*t*, 2H, *J*= 7.8 Hz, Ph) ppm. $^{13}C\{^1H\}$ NMR (100.613 MHz, CD_2Cl_2, 298 K): δ 23.01, 23.68, 27.94, 123.62, 123.68, 130.25, 133.13, 144.74 ppm. $^{19}F\{^1H\}$ NMR (376.49 MHz, $CDCl_3$, 298K): δ -173.64 (br) ppm. MALDI: *m/z* $[C_{33}H_{42}N_2Cu]^+$: 451.19 $[M -C_6H_6]^+$. Anal Calcd: C, 51.74; H, 5.53; N, 3.66. Found: C, 51.62; H, 5.40; N, 3.57.

S2. Crystal Data and Structure Refinements for 2, 3, 5, and 6: Single crystals of suitable size, coated with paraffin oil was mounted for all the complexes. Crystal data for all the complexes were collected on a Bruker Smart Apex Duo diffractometer at 100 K using Mo Kα radiation (λ = 0.71073 Å). Collected data were integrated by using SAINT and then absorption correction was done by multi-scan method using SADABS program. All the structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 (SHELXL-2014/6). CCDC No.: **2** (1540046), **3** (1540047), **5** (1547791) and **6** (1547792).

	2	**3**	**5**	**6**
Chemical formula	$C_{36}H_{56}CuF_6N_3SbSi_3$	$C_{33}H_{59}CuF_6N_3SbSi_3$	$C_{40}H_{56}Cl_2CuF_6N_2Sb$	$C_{33}H_{42}CuF_6N_2Sb$
Formula weight	914.39	881.39	935.08	766.00
Temperature	100(2)	100(2)	100(2)	100(2)
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1/n$	$P\,2_1/c$	$P\,2_1/n$	$P\,2_1/c$
a	14.617(7) Å	13.605(4) Å	10.506(5) Å	13.3555(16) Å
b	14.759(7) Å	14.057(4) Å	20.813(9) Å	13.9173(16) Å
c	21.243(10) Å	21.790(8) Å	20.439(9) Å	18.181(2) Å
α	90°	90°	90°	90°
β	107.874(10)°	107.833(9)°	104.289(7)°	102.245(3)°
γ	90°	90°	90°	90°
Volume	4361(4) Å^3	3967(2) Å^3	4176.4(18) Å^3	3302.4(7) Å^3
Z	4	4	4	4
Density (calculated)	1.393 g/cm^3	1.476 g/cm^3	1.487 g/cm^3	1.541 g/cm^3
Absorption coefficient	1.242 mm^{-1}	1.363 mm^{-1}	1.341 mm^{-1}	1.521 mm^{-1}
F(000)	1876	1816	1912	1552
Theta range for data collection	2.44 to 25.25°	2.44 to 25.25°	2.24 to 25.25	2.26 to 25.25°
Index ranges	-17<=h<=17 -17<=k<=17	-16<=h<=16 -16<=k<=16	-12<=h<=12 -24<=k<=24	-16<=h<=16 -16<=k<=16

	-25<=l<=25	-26<=l<=26	-24<=l<=24	-21<=l<=21
Reflections collected	77830	182758	142079	104497
Independent reflections	7893[R(int)=0.1631]	7182[R(int)=0.1797]	7557[R(int)=0.1114]	5981[R(int)=0.1502]
Coverage of independent reflections	99.9%	99.9%	99.9%	99.9%
Function minimized	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2
Data/ restraints/ parameters	7893/ 18/ 451	7182/ 0/ 442	7557/ 0/ 483	5981/ 0/ 396
Goodness-of-fit on F2	1.009	1.094	1.034	1.027
Δ/ σ max	0.001	0.012	0.001	0.001
Final R indices	5006 data; [I>2σ(I)] *R*1= 0.0586, w*R*2= 0.1179	4904 data; [I>2σ(I)] *R*1= 0.0382, w*R*2= 0.0642	5835 data; [I>2σ(I)] *R*1= 0.0362, w*R*2= 0.0760	4129 data; [I>2σ(I)] *R*1= 0.0516, w*R*2= 0.0932
	all data, *R*1= 0.1162, w*R*2= 0.1441	all data, *R*1= 0.0834, w*R*2= 0.0772	all data, *R*1= 0.0587, w*R*2= 0.0861	all data, *R*1= 0.0958, w*R*2= 0.1086
Largest diff. peak and hole	1.218 and -0.860 eÅ^{-3}	0.817 and -0.657 eÅ^{-3}	1.309 and -0.601 eÅ^{-3}	1.001 and -0.937 eÅ^{-3}
R. M. S deviation from mean	0.127 eÅ^{-3}	0.111 eÅ^{-3}	0.091 eÅ^{-3}	0.108 eÅ^{-3}

S3. Deduction of hapticities in 5 and 6

The Cu-C(arene) bond distance should be <2.50 Å to be considered for hapticity count. [*Angew. Chem., Int. Ed.,* 2015, **54**, 3088]

For **5**: Cu1-C21 2.678(4), Cu1-C20 2.715(4), Cu1-C19 2.894(4). As these bond distances are are >2.50 Å, they were not considered for hapticity count.

For **6**: Cu1-C28 2.456(6), Cu1-C31 2.621(5), Cu1-C33 2.813(6), Cu1-C32 2.892(6).

One Cu1-C28 2.456(6) distance is less than 2.50 Å, however, the difference from the coordinating Cu-C bond distances [Cu1-C29 2.129(6); Cu1-C30 2.217(5)] is quite large. Hence, the hapticity count is difficult for such cases. We have therefore used the method given in *Organometallics,* 2014, **33**, 6660-6668.

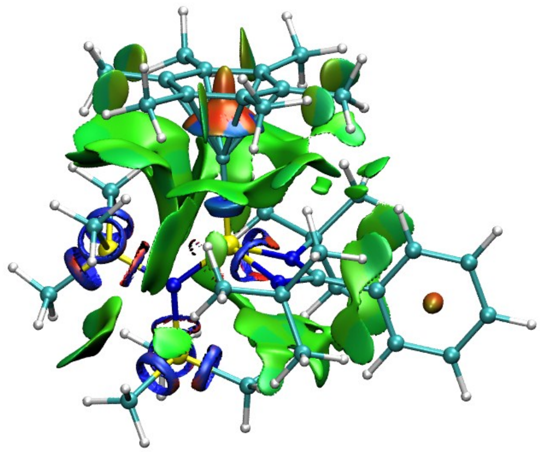
It can be deduced from the values of the distance ratios of the three shortest Cu-C_{arene} distances ($d_1 < d_2 < d_3$), p_1 (d_2/d_1) and p_2 (d_3/d_1)

η1 coordination: $\rho1 \approx \rho2 \gg 1$

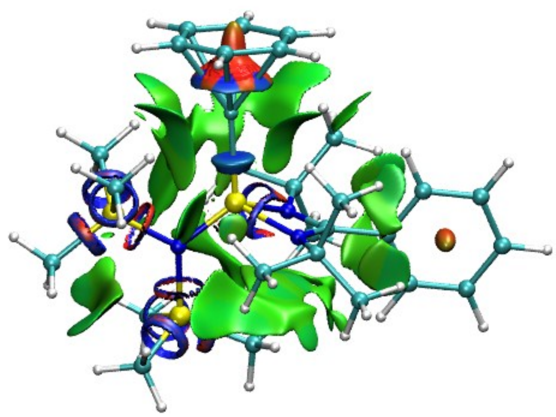
η3 coordination, (we expect the three M−C bond distances to be approximately equivalent) $\rho1 \approx \rho2 \approx 1$

η2 coordination, for which $d1 \approx d2 < d3$, $\rho2 > \rho1 \approx 1$.

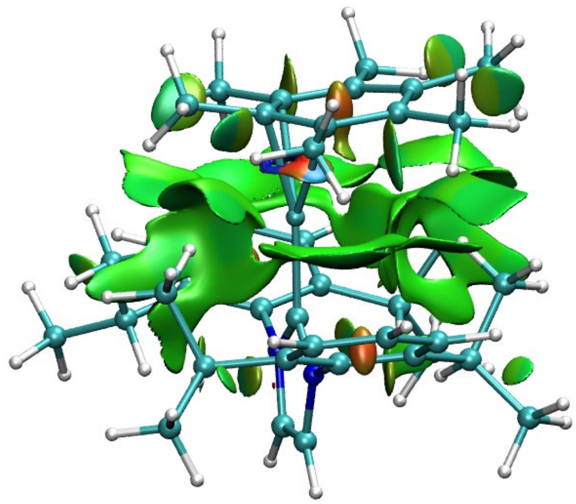
S4. **NCI plots** of **2**, **3**, **5** and **6**.



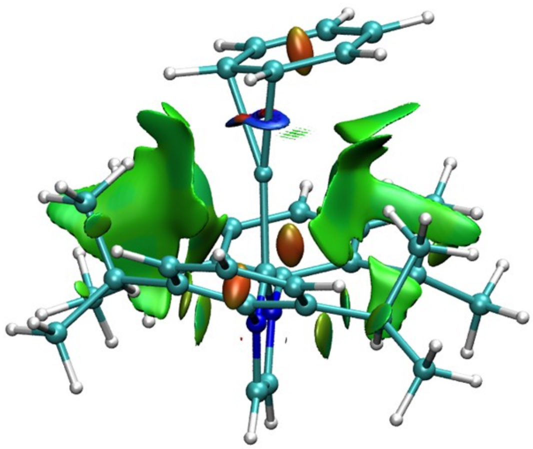
2



3



5



6

S5. Cartesian coordinates of the four structures (**2**, **3**, **5** and **6**) characterized as real minima of the corresponding potential energy surfaces.

2

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 C   -13.839974   -27.024876    -3.296973
 C   -15.464877   -28.873660    -3.260955
 C   -16.163156   -22.185511    -0.514172
 C   -14.680936   -27.936760    -3.982614
 C   -13.839555   -26.991307    -1.877480
 C   -12.922086   -26.143998    -4.112519
 C   -15.444915   -28.854402    -1.844053
 C   -16.253130   -19.993251     0.497906
 C   -14.588062   -27.955489    -1.155522
 C   -14.922364   -20.118542     0.892667
 C   -17.670055   -24.788060     0.645696
 C   -16.834505   -23.276190    -1.265141
 C   -14.828564   -22.309187    -0.117682
 C   -13.023226   -25.948640    -1.145363
 C   -14.685487   -27.935514    -5.492393
 C   -14.641357   -22.781776    -3.487757
 C   -19.947205   -22.507053    -1.988565
 C   -16.875389   -21.023690    -0.204291
 C   -14.211034   -21.278141     0.584149
 C   -16.633770   -21.262100    -3.788396
 C   -14.466926   -28.087494     0.345370
 C   -19.269893   -28.266685    -2.745239
 C   -16.164711   -22.720580    -3.688870
 C   -18.334103   -26.171626     0.551693
 C   -16.262670   -29.903280    -4.026300
 C   -18.280306   -26.927791    -5.394054
 C   -16.529597   -23.466936    -4.981935
 C   -16.287765   -29.813867    -1.035776
 C   -16.307249   -24.940186     1.340630
 C   -21.767038   -24.890042    -1.600739
 C   -21.304522   -23.636274    -4.422743
 C   -21.197397   -26.947090    -4.674101
 C   -18.574205   -23.833019     1.437823
Cu   -16.006426   -26.693625    -2.576251
 H   -16.809513   -19.092978     0.734532
 H   -14.440014   -19.315339     1.438873
 H   -14.276490   -23.211894    -0.353214
 H   -17.908542   -20.922723    -0.516325
 H   -13.175429   -21.379509     0.890229
 H   -11.991250   -26.276320    -0.985070
 H   -13.448057   -25.717776    -0.170783
 H   -12.987856   -25.012577    -1.700227
 H   -13.816898   -28.473963    -5.886753
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H	-14.643381	-26.922229	-5.892026
H	-15.573444	-28.405230	-5.905539
H	-14.332287	-23.809838	-3.290868
H	-14.316440	-22.156444	-2.656889
H	-14.125408	-22.434264	-4.386288
H	-19.214319	-21.969544	-2.589778
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H	-17.703967	-21.206454	-3.996562
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H	-13.618858	-27.538370	0.746029
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H	-18.307119	-28.253467	-2.232967
H	-19.363519	-29.225358	-3.264118
H	-17.687030	-26.885393	0.032763
H	-19.283567	-26.124735	0.014611
H	-18.532618	-26.561336	1.551751
H	-15.639600	-30.383737	-4.783081
H	-17.113165	-29.451399	-4.541011
H	-16.645298	-30.694187	-3.388076
H	-17.230125	-26.890038	-5.102370
H	-18.455051	-26.092612	-6.079190
H	-18.440765	-27.849101	-5.963221
H	-17.610775	-23.487647	-5.135453
H	-16.170160	-24.500262	-4.958929
H	-16.074571	-22.972732	-5.842273
H	-17.185215	-30.123834	-1.563575
H	-16.615576	-29.364804	-0.098904
H	-15.725050	-30.718309	-0.781154
H	-15.858466	-23.977355	1.580723
H	-15.622196	-25.490408	0.693172
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H	-22.117586	-25.875743	-1.914874
H	-22.648647	-24.248293	-1.503356
H	-22.097231	-24.313046	-4.742768
H	-20.567375	-23.581508	-5.229815
H	-21.751090	-22.641553	-4.327460
H	-21.339103	-26.288200	-5.532304
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H	-21.307055	-27.973908	-5.040199
H	-19.569490	-23.773849	0.993005
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H	-18.686374	-24.188835	2.464972
H	-13.471959	-25.389431	-4.680267
H	-12.371220	-26.745682	-4.838956

H	-12.182106	-25.631126	-3.504006
N	-16.868723	-23.432600	-2.595998
N	-17.508310	-24.316232	-0.749327
N	-19.174650	-25.286928	-3.045548
Si	-17.567996	-25.144218	-2.411448
Si	-20.509528	-24.123088	-2.779921
Si	-19.471470	-26.814704	-3.933269

3

C	-22.855824	17.396611	1.527478
C	-24.050357	22.278252	1.877667
C	-23.684904	21.992847	0.553616
C	-24.675811	21.803741	-0.422206
C	-26.032837	21.900874	-0.074972
C	-26.399383	22.183138	1.251918
C	-25.406866	22.373143	2.228481
C	-19.154555	18.001061	1.095387
C	-22.762904	18.434924	-1.429495
C	-18.664544	16.695199	1.100673
C	-21.402930	17.158077	1.357925
C	-24.594151	14.682167	2.268427
C	-23.182231	15.943170	-1.363114
C	-25.102629	17.554235	-1.452207
C	-20.912726	15.849883	1.357918
C	-27.233935	14.610024	0.788081
C	-28.348669	18.804500	0.542073
C	-29.389878	16.986816	2.739822
C	-22.997573	18.005782	4.032057
C	-27.791843	19.405491	3.549811
C	-27.127896	14.834188	3.897725
C	-22.455950	19.445120	4.093447
C	-19.544606	15.621631	1.231610
C	-21.919958	17.010865	4.485529
C	-24.222722	17.886959	4.952025
C	-20.520829	18.233697	1.227033
C	-23.684739	17.320419	-0.907529
Cu	-25.155966	20.314239	1.300685
H	-23.286471	22.417877	2.631922
H	-22.638785	21.913215	0.285494
H	-24.395489	21.583472	-1.444434
H	-26.797146	21.754792	-0.827424
H	-27.445260	22.240407	1.523724
H	-25.689323	22.580940	3.252676
H	-18.472535	18.837710	0.989518
H	-17.599594	16.515282	1.003177
H	-21.596564	15.016641	1.473397
H	-19.166746	14.605218	1.238563
H	-20.901374	19.248906	1.212888

H	-23.085706	19.402009	-1.035187
H	-22.803905	18.478342	-2.520580
H	-21.723976	18.273413	-1.143267
H	-24.056978	14.876526	1.341060
H	-24.680662	13.595987	2.375891
H	-23.990541	15.043188	3.102073
H	-22.175705	15.741583	-0.995550
H	-23.153301	15.897896	-2.454449
H	-23.845752	15.150099	-1.011345
H	-25.808629	16.820616	-1.058447
H	-25.105042	17.474632	-2.540800
H	-25.466352	18.551904	-1.189358
H	-28.235931	15.013349	0.625183
H	-27.338166	13.528050	0.918366
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H	-27.546277	19.436573	0.155795
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H	-28.519226	18.012475	-0.193595
H	-29.549578	16.100388	2.123792
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H	-26.944129	20.076514	3.397703
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H	-26.700231	13.873908	4.202622
H	-28.208496	14.698934	3.840204
H	-21.589266	19.567433	3.441637
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H	-23.942818	18.110870	5.983160
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5

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C	-6.470765	-49.136612	2.543252
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C	-14.988412	-49.532885	3.034713
C	-8.563330	-49.895242	1.312046
C	-12.965200	-50.075438	1.592420
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C	-12.967057	-50.852441	6.652960
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C	-15.650354	-49.494573	4.261018
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C	-7.103983	-51.414130	7.107790
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N	-9.535593	-50.710660	3.917702

6

C	6.083847	38.826709	-9.762372
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C	6.590231	36.639245	-9.995363

C	3.669903	38.740824	-10.226428
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C	5.008587	40.653740	-12.686423
C	3.639262	38.961901	-13.990056
C	3.298842	38.276603	-7.739967
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C	2.168695	37.670516	-6.897394
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C	11.028821	38.901610	-8.714191
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C	9.347098	38.470123	-10.408815
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C	9.882024	37.718858	-12.789963
C	8.716690	39.929440	-12.332273
C	7.737805	38.232448	-6.898300
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C	7.618992	39.535872	-6.090182
C	4.659990	42.908537	-8.858580
C	5.894895	42.468935	-8.335993
C	7.067795	42.602518	-9.112993
C	6.995088	43.194035	-10.391363
C	5.774578	43.641136	-10.880291
C	4.607261	43.493310	-10.117301
Cu	6.234753	40.659074	-9.355623
H	4.505430	36.057891	-10.500185
H	7.228451	35.771828	-10.002305
H	0.918422	39.487972	-8.408665
H	0.243231	40.432270	-10.575720
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H	5.055619	38.527940	-12.460355
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H	8.036610	42.389162	-8.670512
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H	3.658633	43.841149	-10.510030

H	5.482612	40.870413	-11.727146
H	4.299574	41.460219	-12.892111
H	5.782106	40.672065	-13.458007
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H	3.098777	38.013156	-13.951988
H	4.402660	38.884790	-14.768469
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H	4.862259	39.779622	-7.545894
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H	8.094564	36.103770	-6.552982
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H	7.427336	40.390595	-6.746660
H	8.533467	39.752098	-5.533073
H	6.798929	39.471751	-5.371524
N	4.970904	38.128008	-10.087670
N	7.073473	37.907126	-9.708604

S6. **Computational details**.

All electronic structure calculations were performed with Gaussian09.[1] We used the B3LYP functional in all cases. The effect of the inclusion of Grimme's dispersion correction term (GD3) was evaluated. We have observed that at the DFT-D level we obtain Cu-Si and Cu-C(carbene) distances shorter than with simple DFT, the former being closer to the experimental ones. For instance, for **2**, the Cu-Si distance is 2.265 Å without dispersion and 2.206 Å with dispersion (experimental = 2.219 Å), and for **6**, the Cu-C distance is 1.908 without dispersion and 1.887 Å with dispersion (experimental = 1.886 Å). On the other side, there is no clear variation of the Cu-arene distance upon inclusion of the dispersion term. For **2**, the shortest Cu-C(arene) distance is 2.298 and 2.311 Å with and without dispersion, respectively, whereas for **6**, they are 2.105 and 2.086 Å with and without dispersion, respectively. It must be remarked that the inclusion of the dispersion term does not modify the hapticities in any case, which are well reproduced at the B3LYP and B3LYP-D3 levels.

The effect of the basis sets on the optimized geometries has been also evaluated. We have concluded that the use of a double-ζ basis set (6-31G*) for all atoms does not reproduce the experimental hapticities, which are obtained only by increasing the size of the basis set at the C and H atoms (6-311+G*). The most relevant bond lengths for both cases can be found in the table below. We have also optimized **6** with the 6-311+G* basis set for all atoms including Cu, but it could not be applied for **2**, **3** and **5** due to computational limitations.

	6-31G* all atoms			6-31G* (6-311+G* in C and H)			6-311+G* all atoms		
Comp.	Hapt.	Cu-Si/C	Cu-C(ar)	Hapt.	Cu-Si/C	Cu-C(ar)	Hapt.	Cu-Si/C	Cu-C(ar)
2	η^6	2.207	2.268	η^6	2.206	2.298	-	-	-
3	η^3	2.236	2.056	η^6	2.209	2.272	-	-	-
5	η^6	1.914	2.227	η^3	1.886	2.078	-	-	-
6	η^3	1.893	2.025	η^2	1.887	2.105	η^2	1.903	2.114

After these prospective calculations, all calculations reported in the article were done at the B3LYP-D3 level of theory. The 6-311+G * basis set was employed for C and H and 6-31G* for all other elements. Compounds **2**, **3**, **5** and **6** were characterized as true minima of the PES by vibrational analysis.

The NBO analysis was carried out by using the NBO 3.1 program as implemented in Gaussian09. Complex **6** was decomposed into three fragments (Cu + NHC ligand + C_6H_6) for the second order perturbation analysis, while complex **3** were decomposed into five fragments (SiCu + C_6H_6 + C_3H_9Si + C_3H_9Si + $C_{15}H_{23}N_2$).

NCI isosurfaces (s = 0.3 au) were obtained from promolecular densities by means of the NCIPLOT program.[2] "Atoms in Molecules" (AIM) analysis was done with the AIMAll software on the B3LYP electron density.[3]

The energy was decomposed by means of the second-generation absolutely localized molecular orbital energy decomposition analysis (ALMO-EDA)[4, 5] implemented in Q-Chem[6] 5.0 at the B3LYP-D3 level of theory with CP correction of the BSSE. The ALMO-EDA decomposes the intermolecular interaction energy into further several interactions, namely a frozen term, a polarization effect term and a charge transfer contribution ($\Delta E_{int} = \Delta E_{FRZ} + \Delta E_{Pol} + \Delta E_{CT}$). Physically, ΔE_{FRZ} contains three contributions that arise without any relaxation of the fragment orbitals: attractive dispersion (ΔE_{Disp}), Pauli repulsion (ΔE_{Pauli}) and permanent electrostatics (ΔE_{Elec}).[4]

S7. REFERENCES:

1. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
2. J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, **7**, 625-632.
3. AIMAll (Version 16.08.17), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2016 (aim.tkgristmill.com).
4. P. R. Horn, Y. Mao and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2016, **18**, 23067-23079.
5. P. R. Horn and M. Head-Gordon, *J. Chem. Phys.*, 2016, **144**, 084118.
6. Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell,

N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Mol. Phys.*, 2015, **113**, 184-215.