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Electronic Supplementary Information for:

Reactivity variance between the stereoisomers of saturated N-heterocyclic carbenes on gold surfaces

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Figure S1. ¹H NMR spectrum of 1 in CDCl₃.



Figure S2. ¹³C NMR spectrum of 1 in CDCI₃.



Figure S3. IR spectrum of 1.



Figure S4. DART HRMS spectrum of 1.



Figure S5. ¹H NMR spectrum of 2 in CD₂Cl₂.



Figure S6. ¹³C NMR spectrum of 2 in CD₂Cl₂.



Figure S7. IR spectrum of 2.



Figure S8. DART HRMS spectrum of 2.



Figure S9. ¹H NMR spectrum of 3a in CD₂Cl₂.



Figure S10. ¹³C NMR spectrum of 3a in CD₂Cl₂.



Figure S11. ¹H-¹³C HSQC spectrum of **3a** in CD₂Cl₂.



Figure S12. IR spectrum of 3a.



Figure S13. MALDI HRMS spectrum of 3a.



Figure S14. ¹H NMR spectrum of **3b** in CD₃CN.



Figure S15. ¹³C NMR spectrum of **3b** in CD₃CN.



Figure S16. $^{1}H-^{13}C$ HSQC spectrum of **3b** in CD₃CN.



Figure S17. ¹⁹F NMR spectrum of **3b** in CD₃CN.



Figure S18. ³¹P NMR spectrum of 3b in CD₃CN.



Figure S19. IR spectrum of 3b.



Figure S20. MALDI HRMS spectrum of 3b.



Figure S21.¹H NMR spectrum of 4a in CD₂Cl₂.



Figure S22. ¹³C NMR spectrum of 4a in CD₂Cl₂.



Figure S23. ¹H–¹³C HSQC spectrum of 4a in CD₂Cl₂.



Figure S24. IR spectrum of 4a.



Figure S25. MALDI HRMS spectrum of 4a.



Figure S26. ¹H NMR spectrum of 4b in CD₃CN.



Figure S27. ¹³C NMR spectrum of 4b in CD₃CN.



Figure S28. ¹H-¹³C HSQC spectrum of 4b in CD₃CN.



Figure S29. ^{19}F NMR spectrum of 4b in CD₃CN.



Figure S30. ³¹P NMR spectrum of 4b in CD₃CN.



Figure S31. IR spectrum of 4b.



Figure S32. MALDI HRMS spectrum of 4b.



Figure S33. ¹H NMR spectrum of 5 in CD₃CN.



Figure S35. ¹H–¹³C HSQC spectrum of 5 in CD₃CN.

10

9

8

7

11

12

6 f1 (ppm) 4

5

3

2

1

0

- 110 - 120 - 130 - 140 - 150 - 150 - 160 - 170 - 180



Figure S37. ³¹P NMR spectrum of 5 in CD₃CN



Figure S38. IR spectrum of 5.



Figure S39. MALDI HRMS spectrum of 5.



Figure S40. ¹H NMR spectrum of 6-CO₂ in CD₂Cl₂.



Figure S41. ¹³C NMR spectrum of $6-CO_2$ in CD_2CI_2 .



Figure S42. IR spectrum of 6-CO₂.



Figure S43. ¹H NMR spectrum of 7-CO₂ in CD₂Cl₂.



Figure S44. ¹³C NMR spectrum of 7-CO₂ in CD₂Cl₂.



Figure S45. IR spectrum of 7-CO₂.



Figure S46. ¹H NMR spectrum of 8-CO₂ in CDCl₃.



Figure S47. ¹³C NMR spectrum of 8-CO₂ in CDCl₃.



Figure S48. IR spectrum of 8-CO₂.



Figure S49. UV-Vis spectrum of AuNPs.





Figure S50. TEM image of 60 ± 10 nm citrate-capped AuNPs.



Figure S51. SERS spectra obtained upon depositing **6**, **7**, and **8** onto gold mirror which was sandwiched with 60 nm gold-nanoparticles. The presence of an intense feature at ~1000 cm⁻¹, likely arising from phenyl ring vibrational modes, illustrates adsorption of the ligand.

The SERS spectra for NHCs on gold can reveal significant information about the binding mode, but most previous studies have employed benzimidazole style NHCs.¹⁻³ Our aspiration was that the stereochemical differences between **6** and **7** would be clearly visible spectroscopically. Notably, each spectrum has a dominant peak at ~1000 cm⁻¹ and a smaller band at ~1020 cm⁻¹. Similar features were observed in SERS of thiol ligands with phenyl rings. ^{4, 5}Therefore, these features likely arise from phenyl ring vibrational modes. The SERS spectrum for **8** has a much weaker absolute intensity and shows two peaks, the aforementioned one near 1000 cm⁻¹ and an additional one at ~1290 cm⁻¹. Since the selection rules for SERS are highly surface sensitive and strongly favor normal modes perpendicular

to the surface,⁶⁻⁸ slight differences in ligand binding yield massive changes in the SERS spectra. Considering the similarity of the SERS spectra, we conclude that NHCs **6**, **7**, and **8** adopt very similar conformations on the surface and, in each case, that the ligand adsorbs to the gold surface. We speculate that the appearance of a new feature in SERS of 8 at 1290 cm⁻¹ may arise from the unsaturated imidazolium ring or, perhaps, differences in surface orientation on the surface. Critically, these SERS measurements have been augmented by computational modeling to elucidate the most-likely binding geometry (vide infra).

LDI-MS data



Figure S52. LDI-MS pulsed ion extraction experiments performed on **7-Au** with a delay time of either 110 nanoseconds (**top spectra**) or 0 nanoseconds (**bottom spectra**).

LDI-MS pulsed ion extraction experiments were performed on **7-Au** with a delay time of either 110 nanoseconds (**top spectra**) or 0 nanoseconds (**bottom spectra**) between the laser pulse and subsequent ion extraction. If NHC **8** formed during LDI, then only NHC **7** should appear in the LDI-MS spectrum of **7-Au** when the delay time equals 0 nanoseconds, and a mixture of NHC **7** and **8** should appear in the LDI-MS spectrum when the delay time equals 110 nanoseconds. Instead, the resulting LDI-MS spectra illustrates that NHC **8** is present regardless of the delay time. These data illustrate that species observed in LDI-MS are not the result of the LDI process, e.g. reactions in the plume.



Figure S53. LDI-MS spectra collected for five different 7-Au samples.

The data suggests that NHC 8 clearly forms in each experiment as evidenced by the presence of $[(8)_2Au]^+$ and $[((8)(7)Au]^+$ in each spectrum. These results illustrate that the conversion of 7 to 8 is reproducible for **7-Au** samples. The bottom two spectra were acquired on gold mirrors with 100 nm of gold.

Computational data



Figure S54. (A) BEs of NHCs with optimized flat-lying geometry on Au clusters calculated with DFT. **(B)** BEs of NHCs when bound vertically on Au clusters calculated with DFT. BEs for flat-lying geometry (red) are energetically more favorable than vertical geometry (blue). For **7-Au**, the flat-lying geometry with backbone hydrogens pointing away from the surface is dominant.

Single crystal X-ray diffraction data

Compound	3b	4b	5
Empirical formula	C ₂₁ H ₂₇ F ₆ N ₂ P	C ₂₇ H ₃₃ F ₆ N ₂ P	$C_{21}H_{25}F_6N_2P$
Formula weight	452.41	530.52	450.40
Temperature/K	275.0	100.0	100.00
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> -1	P21/n
a/Å	10.3657(2)	8.8187(6)	8.7080(2)
b/Å	16.1664(3)	9.9208(8)	16.5031(4)
c/Å	13.9209(3)	15.7533(12)	15.1826(4)
a/°	90	97.668(3)	90
β/°	90.7850(10)	94.611(2)	99.1630(10)
γ/°	90	96.795(3)	90
Volume/Å ³	2332.59(8)	1349.82(18)	2154.03(9)
Z	4	2	4
ρ _{calc} g/cm ³	1.288	1.305	1.389
µ/mm ⁻¹	0.174	0.161	0.189
F(000)	944.0	556.0	936.0
Crystal size/mm ³	0.410 × 0.350 × 0.138	0.611 × 0.289 × 0.094	0.295 × 0.239 × 0.238
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
2θ range for data collection/°	4.668 to 53.462	4.602 to 52.744	4.936 to 54.198
Index ranges	-11 ≤ h ≤ 13, -20 ≤ k ≤ 20,	-10 ≤ h ≤ 11, -12 ≤ k ≤ 12,	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21,
	-17 ≤ ≤ 17	-19 ≤ I ≤ 19	-19 ≤ I ≤ 19
Reflections collected	48149	55042	44228
Independent reflections	9886 [R _{int} = 0.0642, R _{sigma} = 0.0629]	5518 [R _{int} = 0.0801, R _{sigma} = 0.0447]	$\begin{array}{l} 4738 \; [R_{\text{int}} = 0.0751, \\ R_{\text{sigma}} = 0.0364] \end{array}$
Data/restraints/parameters	9886/26/629	5518/62/532	4738/0/338
Goodness-of-fit on F ²	1.057	1.025	1.034
Final R indexes [I>=2σ (I)]	$R_1 = 0.0741,$ w $R_2 = 0.2201$	$R_1 = 0.0847,$ w $R_2 = 0.1976$	$R_1 = 0.0372,$ w $R_2 = 0.0931$
Final R indexes [all data]	$R_1 = 0.0802,$ $wR_2 = 0.2302$	$R_1 = 0.1020,$ $wR_2 = 0.2102$	$R_1 = 0.0429,$ w $R_2 = 0.0973$
Largest diff. peak/hole / e Å ⁻³	0.40/-0.27	0.36/-0.40	0.37/-0.32
Flack parameter	0.05(3)	n/a	n/a

Table S1. Single crystal structure parameters of compounds **3b**, **4b**, and **5**.

Table S2.	-C bond distance of carbon backbone and N-C-N bond angle of compounds 3b,
4b, and 5.	

Compound	C–C bond distance of	N–C–N bond angle (°)	
Compound	carbon backbone (Å)		
3b	1.570(7)	115.4(5)	
	1.559(6)	114.4(4)	
4b	1.565(9)	115.1(8)	
	1.563(6)	114.6(5)	
5	1.3640(18)	109.01(11)	

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