

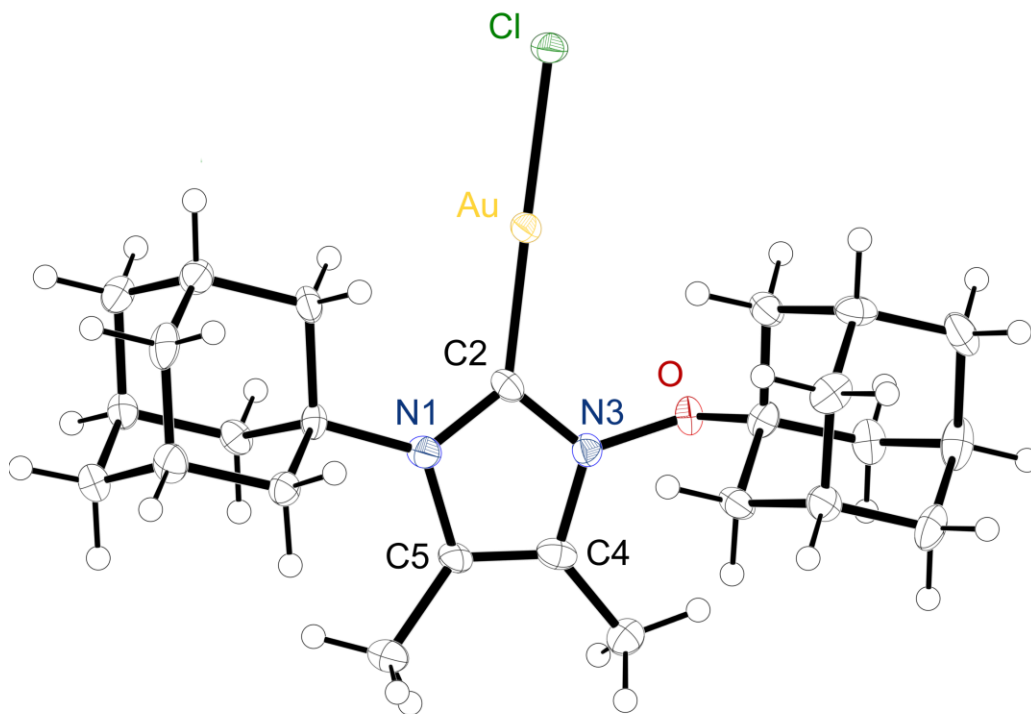
N-Alkoxyimidazolyliidines (NOHCs): A new class of highly nucleophilic carbenes

Vladyslav Bakhonskyi

Seminar talk

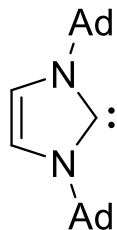
August 6th, 2021

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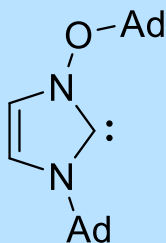


Arduengo carbene

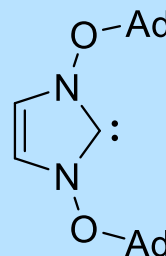


1

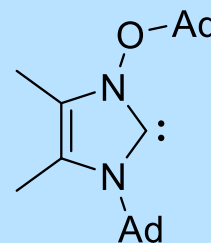
NOHCs



2

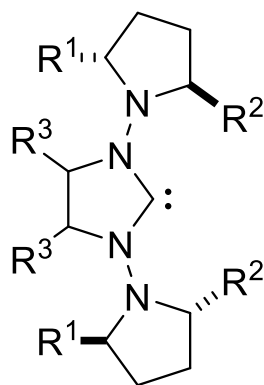


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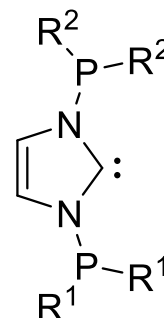
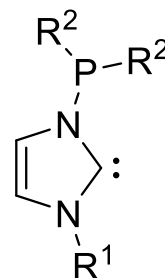


4

O-R wingtip substituents

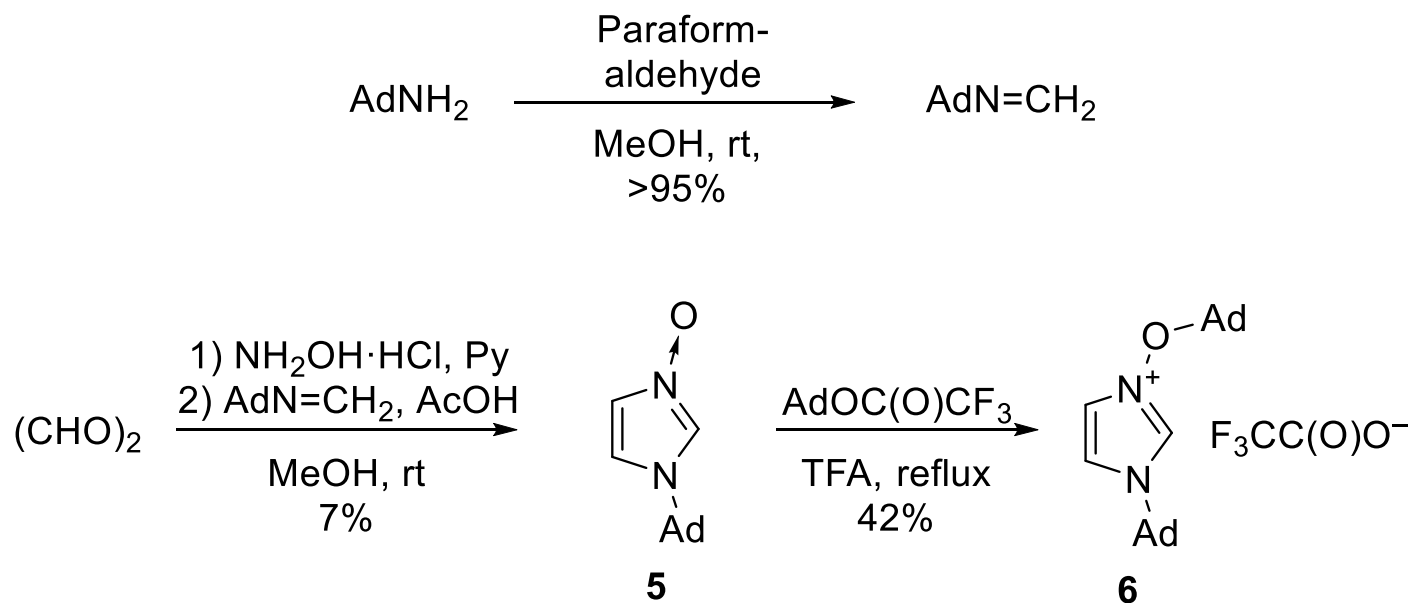


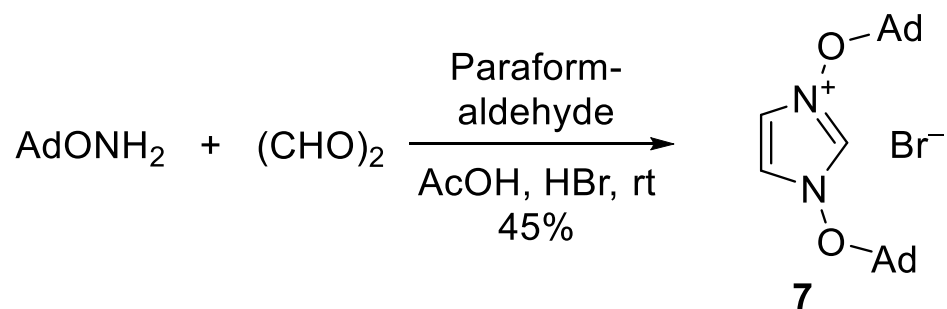
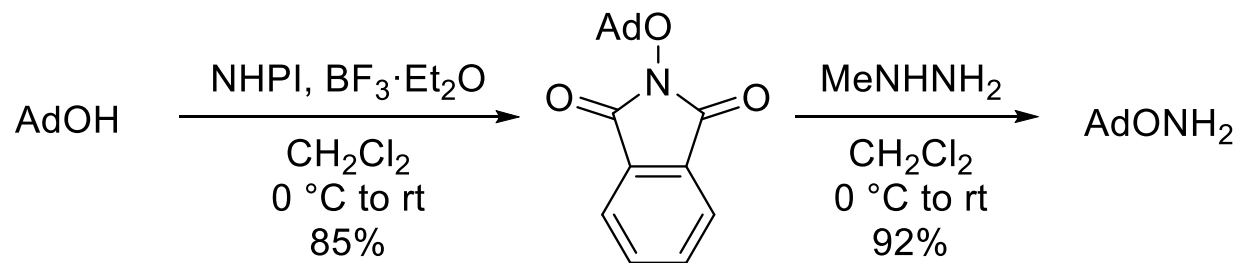
I, N-R₂ wingtip substituents

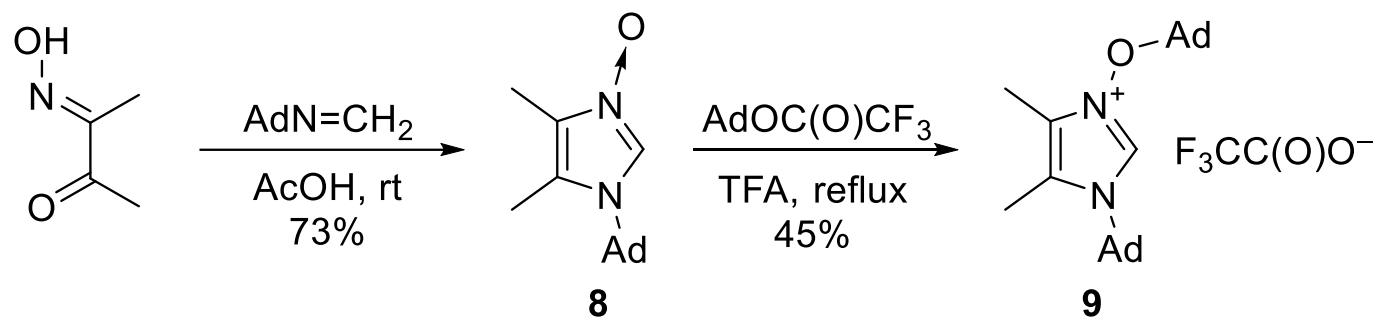


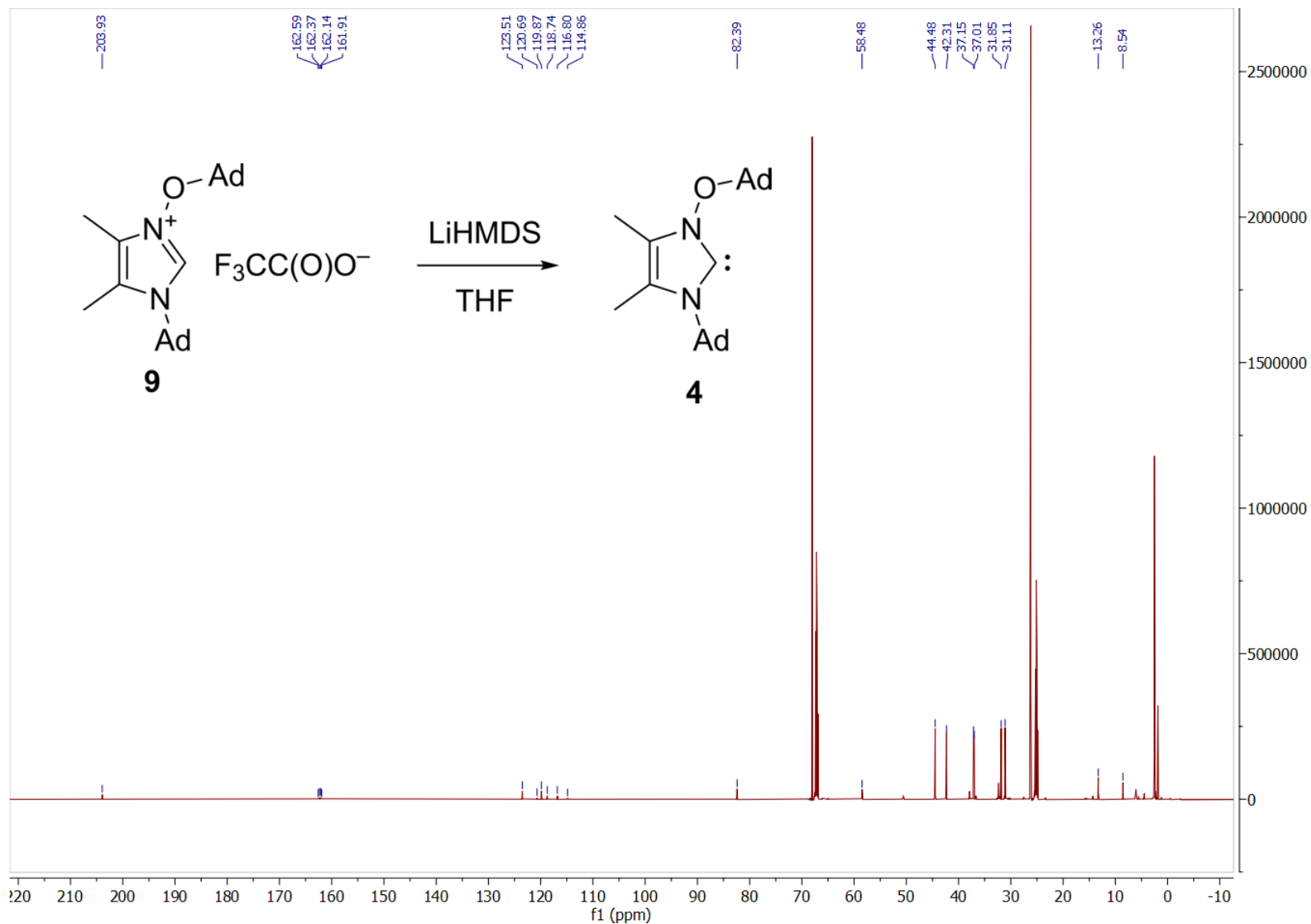
II, P-R₂ wingtip substituents

1. M. Alcarazo, S. J. Roseblade, E. Alonso, R. Fernandez, E. Alvarez, F. J. Lahoz, J. M. Lassaletta, *J. Am. Chem. Soc.* **2004**, 126, 13242-13243. 2. Y. Hoshimoto, T. Kinoshita, M. Ohashi, S. Ogoshi, *Angew. Chem. Int. Ed.* **2015**, 54, 11666-11671. 3. A. P. Marchenko, H. N. Koidan, A. N. Hurieva, I. I. Pervak, S. V. Shishkina, O. V. Shishkin, A. N. Kostyuk, *Eur. J. Org. Chem.* **2012**, 2012, 4018-4033. 4. A. P. Marchenko, H. N. Koidan, A. N. Huryeva, E. V. Zarudnitskii, A. A. Yurchenko, A. N. Kostyuk, *J. Org. Chem.* **2010**, 75, 7141-7145. 5. P. Nägele, U. Herrlich, F. Rominger, P. Hofmann, *Organometallics* **2012**, 32, 181-191.

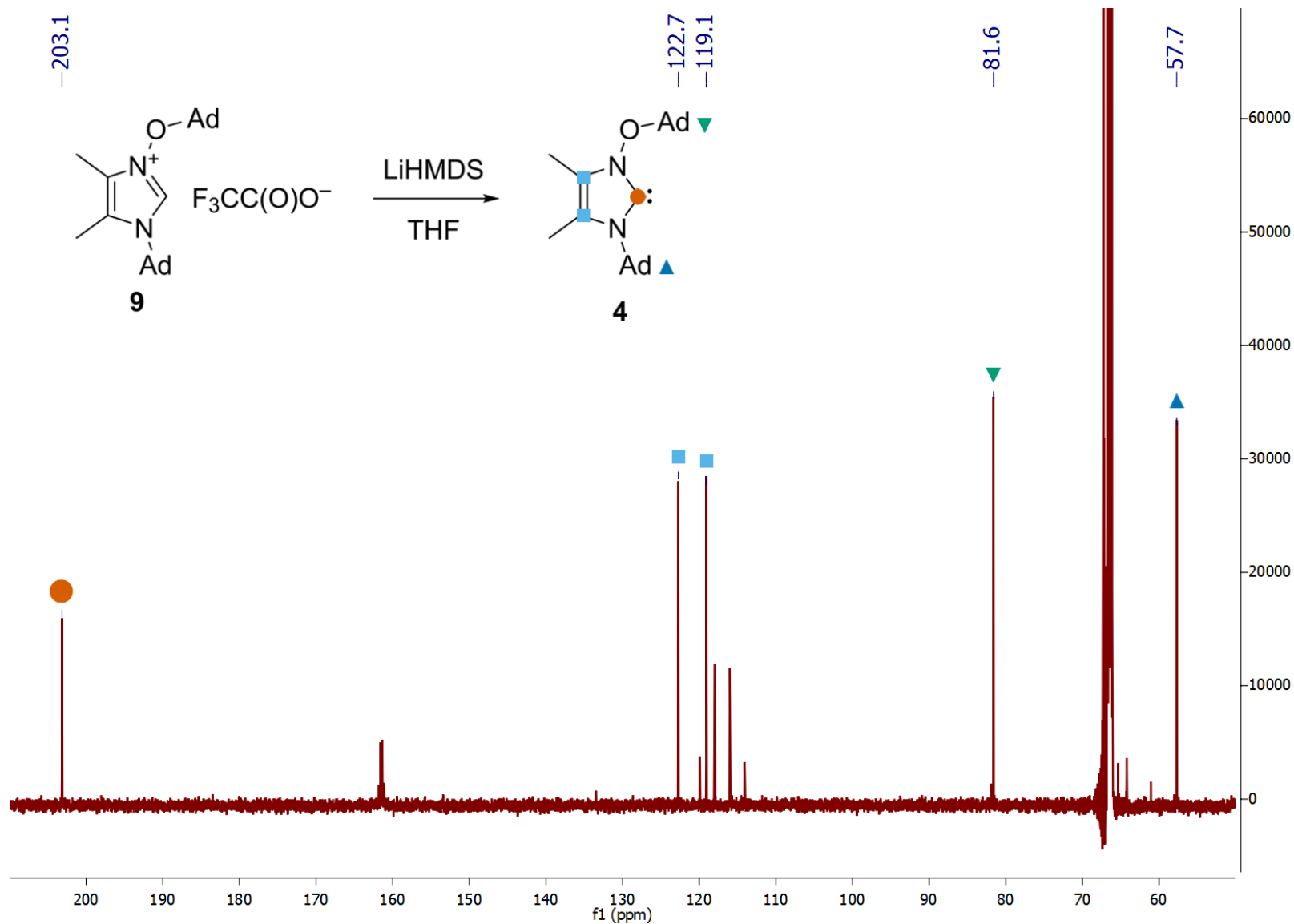




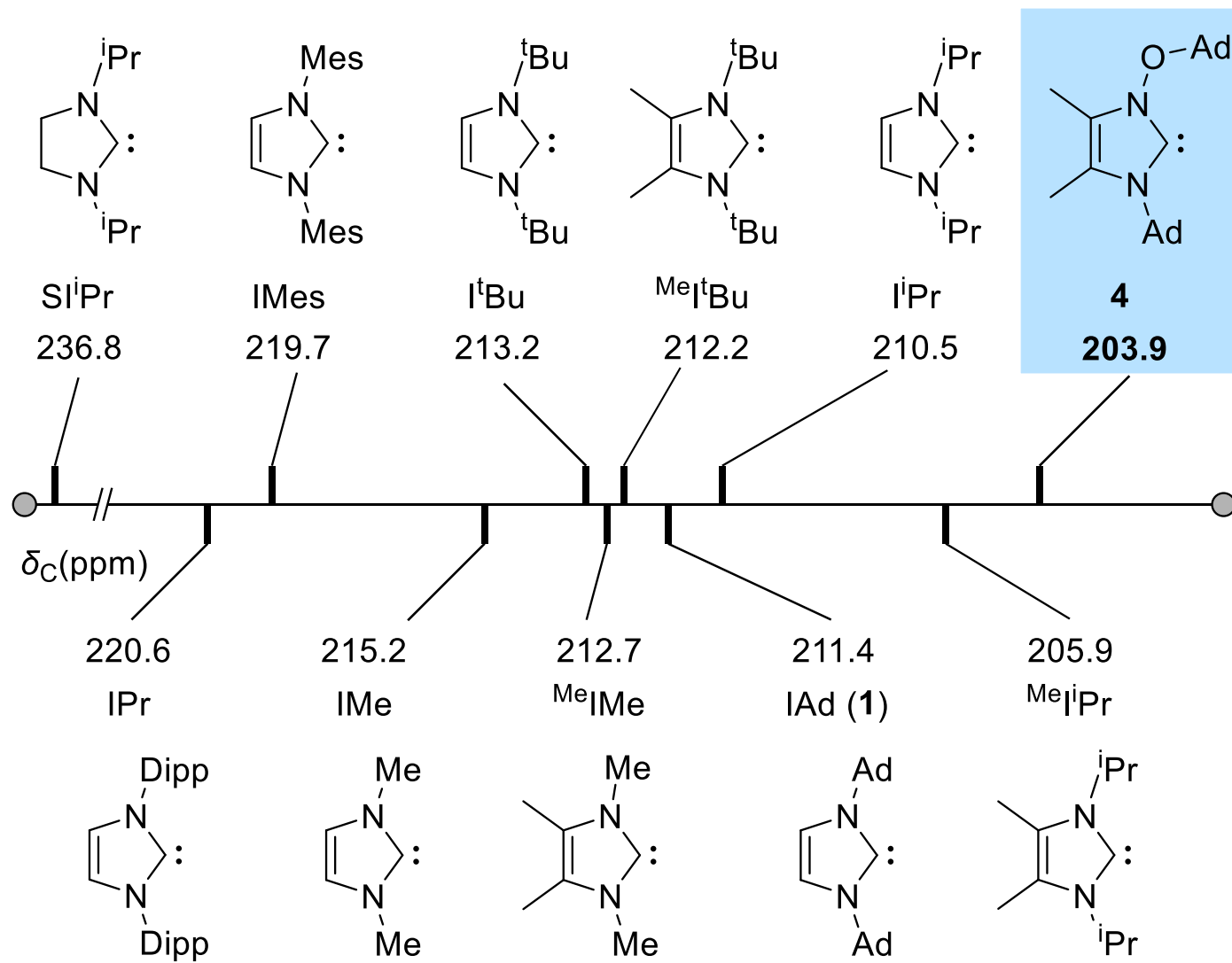


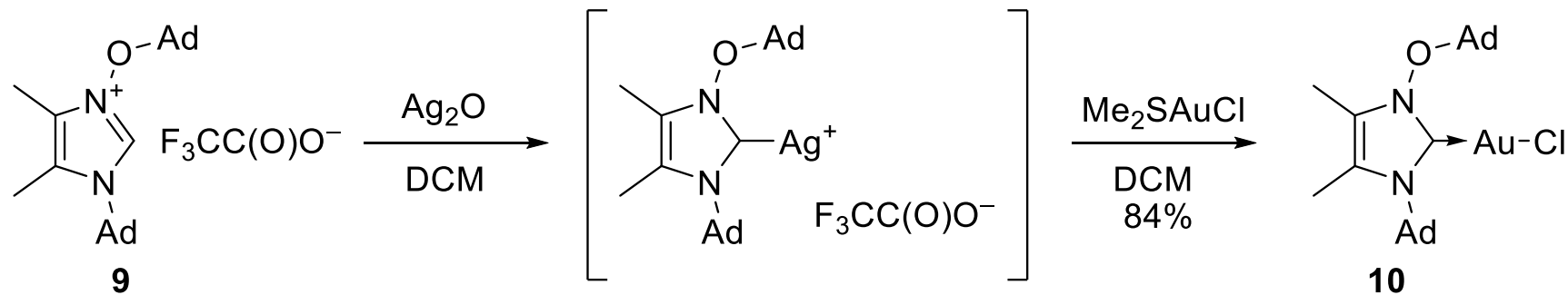


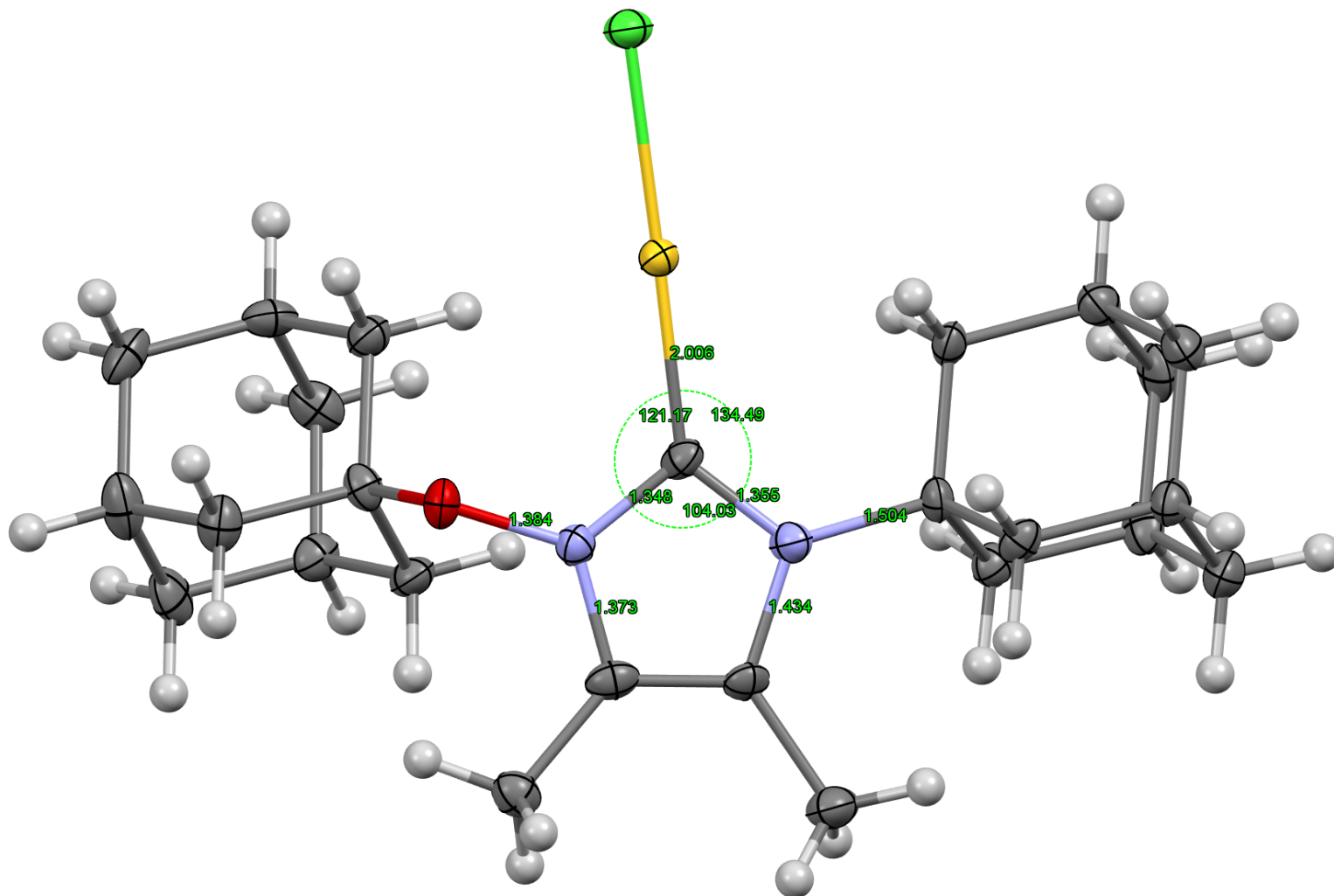
^{13}C NMR of NOHC 4



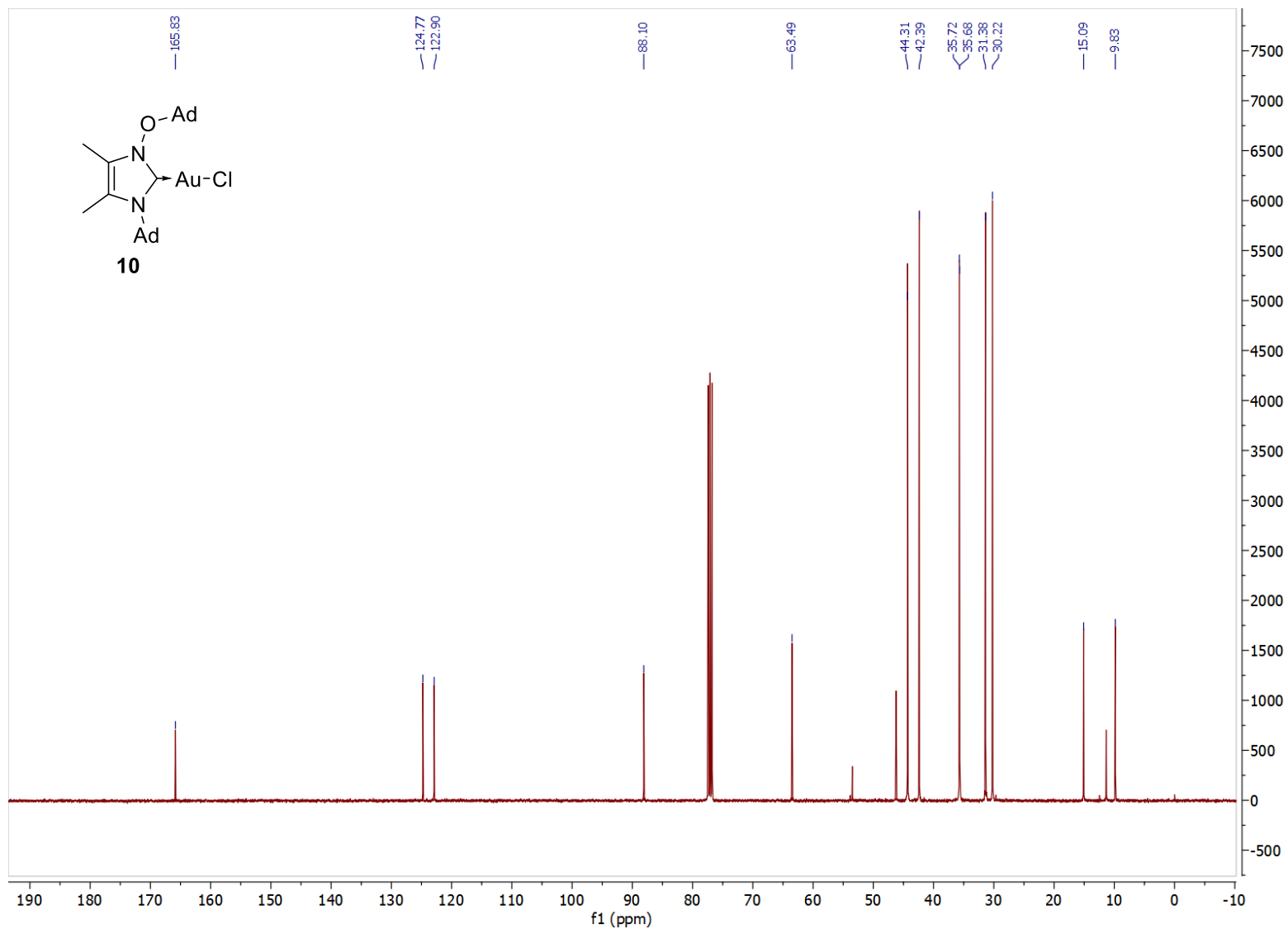
Comparison of ^{13}C NMR chemical shifts between novel 4 and known carbenes.



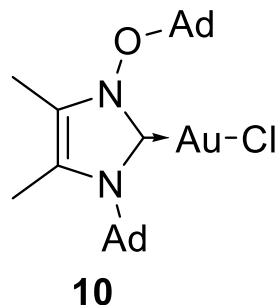




^{13}C NMR of NOHC-AuCl complex



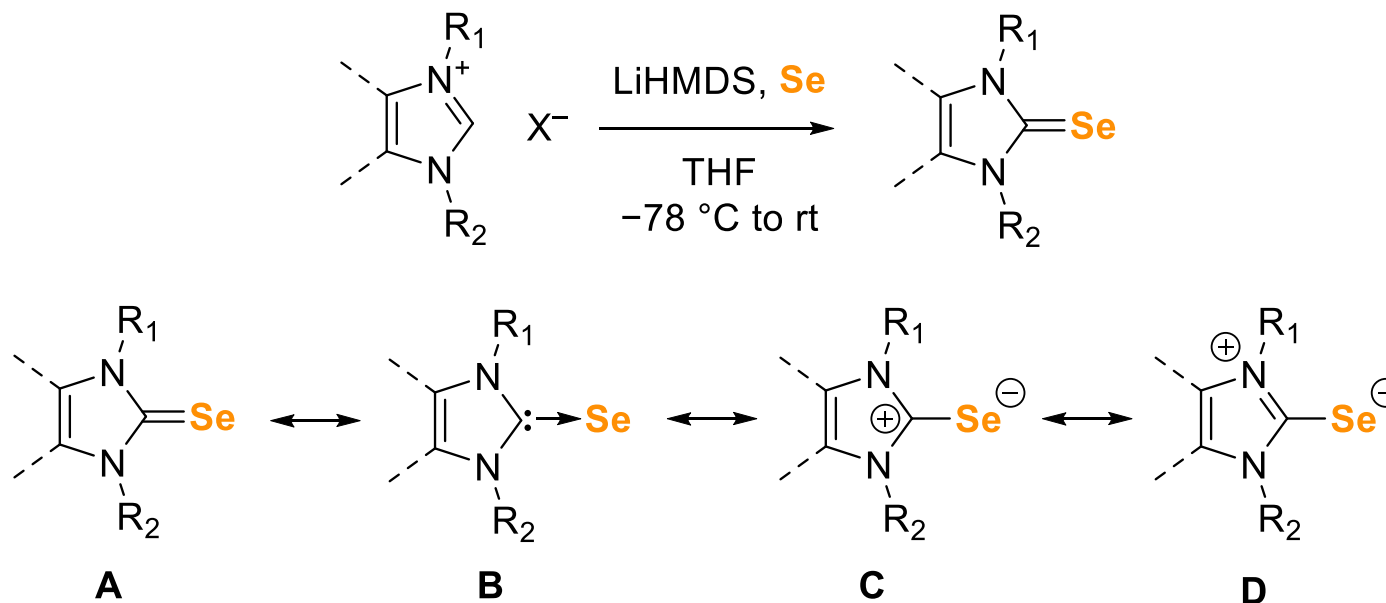
Comparison of ^{13}C NMR chemical shifts between **10** and known NHC-AuCl complexes.



$$\delta_{\text{C}} = 165.8$$

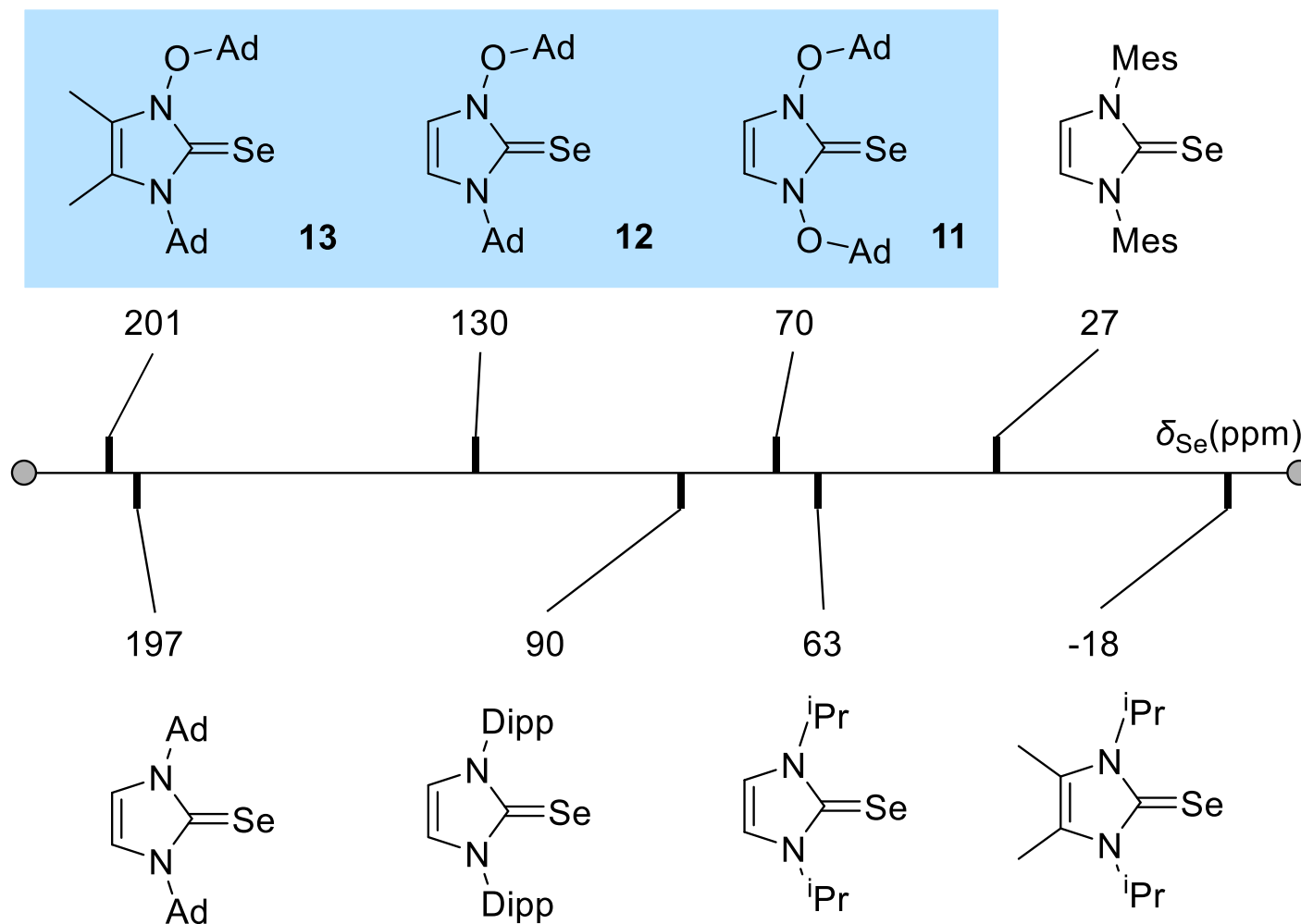
Table 1. ^{13}C NMR Data for [Au(NHC)Cl] Complexes

complex	solvent	$\delta_{\text{C}}(\text{Au}-\text{C}(1))$	$\delta_{\text{C}}(\text{NHC})$	ref	solvent	$\Delta\delta_{\text{C}}$	$\delta_{\text{C}}(\text{NHC}\cdot\text{HCl})^a$	solvent	$\Delta\delta_{\text{C}}$
[Au(IMes)Cl] (10)	CDCl_3	173.4	219.7	17	C_6D_6	46.3	134.76	$\text{DMSO}-d_6$	38.6
[Au(SIMes)Cl] (11)	CDCl_3	195.0	243.8	18	C_6D_6	48.8	160.2	$\text{DMSO}-d_6$	34.8
[Au(IPr)Cl] (12)	CD_2Cl_2	175.1	220.6	18	C_6D_6	45.5	132.22	$\text{DMSO}-d_6$	42.9
[Au(SIPr)Cl] (13)	CDCl_3	196.1	244.0	18	C_6D_6	47.9	160.0	$\text{DMSO}-d_6$	36.1
[Au(IPrMe)Cl] (14)	CDCl_3	166.0	207.9	19	C_6D_6	41.9			
[Au(IMe)Cl] (15)	CD_2Cl_2	168.4	213.7	19	C_6D_6	45.3			
[Au(ICy)Cl] (16)	CD_2Cl_2	168.0	210.1	20	C_6D_6	42.1	134.51	$\text{DMSO}-d_6$	33.5
[Au(IAd)Cl] (17)	CD_2Cl_2	166.3	211.4	17	C_6D_6	45.1	132.11	$\text{DMSO}-d_6$	34.2
[Au(ITPh)Cl] (18)	CDCl_3	167.8					135.26	$\text{DMSO}-d_6$	32.5
[Au(ItBu)Cl] ^b	CDCl_3	168.2	213.2	21	C_6D_6	45.0	132.7	$\text{DMSO}-d_6$	35.5
[Au(Me ₂ -imy)Cl] ^c	$\text{DMSO}-d_6$	169	213.7	22	C_6D_6	44.7			
$\text{Ni}(\text{CO})_3(\text{IMes})$	C_6D_6	198.73	219.7	17	C_6D_6	20.97	134.76	$\text{DMSO}-d_6$	64.0
$\text{Ni}(\text{CO})_3(\text{SIMes})$	C_6D_6	220.40	244.0	18	C_6D_6	23.6	160.2	$\text{DMSO}-d_6$	60.2
$\text{Ni}(\text{CO})_3(\text{IPr})$	C_6D_6	198.21	220.6	18	C_6D_6	22.39	132.22	$\text{DMSO}-d_6$	66.0
$\text{Ni}(\text{CO})_3(\text{SIPr})$	C_6D_6	223.16	244.0	18	C_6D_6	20.84	160.0	$\text{DMSO}-d_6$	63.2
$\text{Ni}(\text{CO})_3(\text{ICy})$	C_6D_6	199.48	210.1	20	C_6D_6	10.62	134.51	$\text{DMSO}-d_6$	65.0

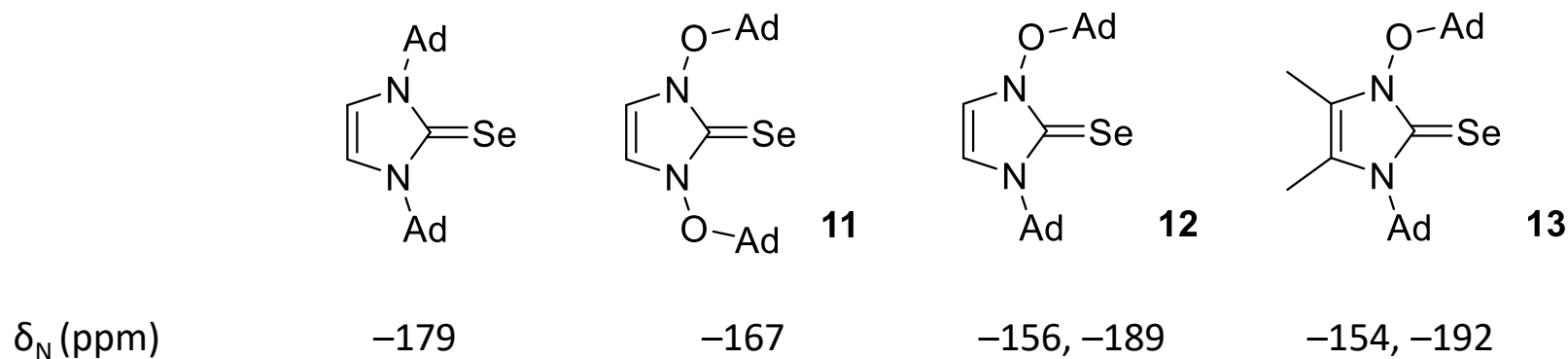


^{77}Se NMR downfield shift: π -acceptor ability

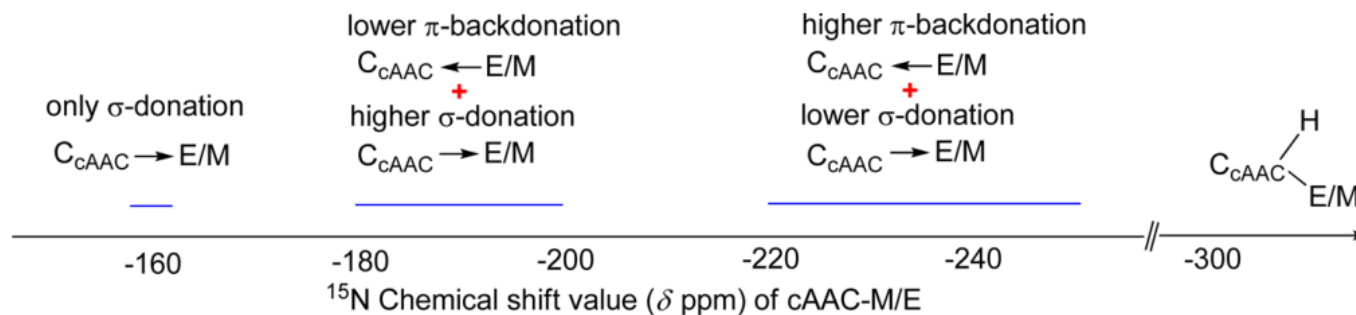
Comparison of ^{77}Se NMR chemical shifts between NOHCSe and known carbene adducts.



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H.W. Roesky *et al.*:





- First synthesis of free 3-alkoxyheterocyclic carbene;
- Synthesized free NOHC has the most upfield ^{13}C NMR shift of literature known imidazolylienes;
- The structure of isolated NOHC-AuCl complex shows clear influence of alkoxy moiety on imidazolylidene geometry;
- ^{77}Se and ^{15}N NMR measurements of NOHC-Se adducts point at strong σ -donor properties, while somewhat lowering π -acidity.



- Synthesis of NOHC-metal complexes and investigation of possible applications;
- Testing the NOHC analogues to commercially available ligands (IMes, IPr, *etc.*) in common reactions as ligands and organocatalysts;
- Further investigation of NOHC properties.

Acknowledgments



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