Supporting Information

Superbasic Amidine Monodentate Ligands in *fac*-[Re(CO)$_3$(5,5′-Me$_2$bipy)(Amidine)]BF$_4$ Complexes: Dependence of Amidine Configuration on the Remote Nitrogen Substituents

Theshini Perera, Frank R. Fronczek, Patricia A. Marzilli,

*and Luigi G. Marzilli**

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

E-mail: lmarzil@lsu.edu

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Figure S2. Depictions of several amidine complex cations with the $\{Re(CO)_3\}^+$ core positioned in the same orientation. (a) $[Re(CO)_3(5,5'\text{-}Me_2bipy)(Z\text{-}HNC(CH_3)NH_2)]BF_4$ (**7**); (b) $[Re(CO)_3(5,5'\text{-}Me_2bipy)(E'\text{-}HNC(CH_3)NHCH(CH_3)_2)]BF_4$, (**2**); and (c) $[Re(CO)_3(5,5'\text{-}Me_2bipy)(E'\text{-}HNC(CH_3)NHC(CH_3)_3)]BF_4$ (**4**). Figure illustrates that the amidine ligand is oriented differently in these products.

Figure S3. Depiction of stacking of the phenyl ring of the amidine moiety (gold) above one ring of the bipyridine ligand (green) in $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH_2C_6H_5)]BF_4$ (**5**) in the solid state.

Figure S4. ROESY spectrum of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) in acetonitrile-d_3 at 25 °C, showing NOE peaks.

Figure S5. NOE (top) and COSY (bottom) cross-peaks in ROESY and COSY spectra of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) in acetonitrile-d_3 at 25 °C.

Figure S6. ROESY spectrum of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]BF_4$ (**2**) in $CDCl_3$ at 25 °C, showing negative EXSY cross-peaks (circled) and NOE peaks.

Figure S7. Starting with the structure of the *E′* isomer of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHCH(CH_3)_2)]^+$ (**2**), *E*, *Z*, and *Z′* isomer models were constructed by using Chem3D Pro software. Rotations were performed to create short N3H-to-CH(isopropyl) nonbonded distances. Nonbonded distances were measured by using Mercury software, and all structures are illustrated as space-filling models by using this software. The closest N3H-to-CH(isopropyl) distances found were 2.18, 4.18, 4.39 and 3.51 Å for the *E′*, *E*, *Z*, and *Z′* isomers, respectively. Note that in the *Z′* isomer the isopropyl group would clash with atoms in the equatorial plane defined by the 5,5′-Me_2bipy ligand. It is evident that, while this distance is favorably long in both the *E′* and *E* isomers, in the *E* isomer the isopropyl group would be rather close to the methyl group on the amidine carbon. This proximity can lead to clashes as the size of the R group increases.

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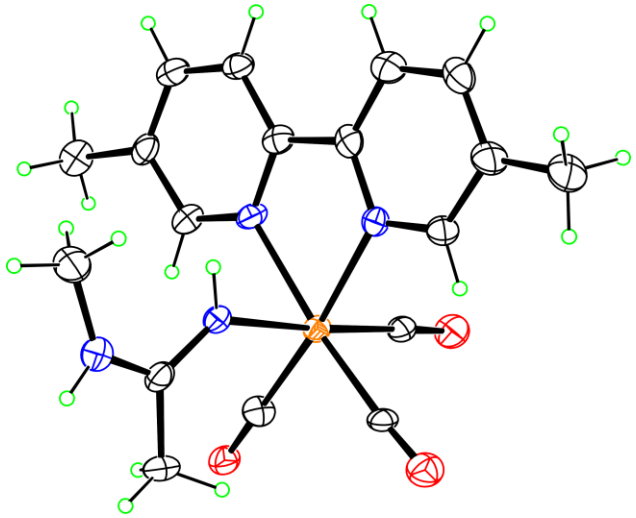

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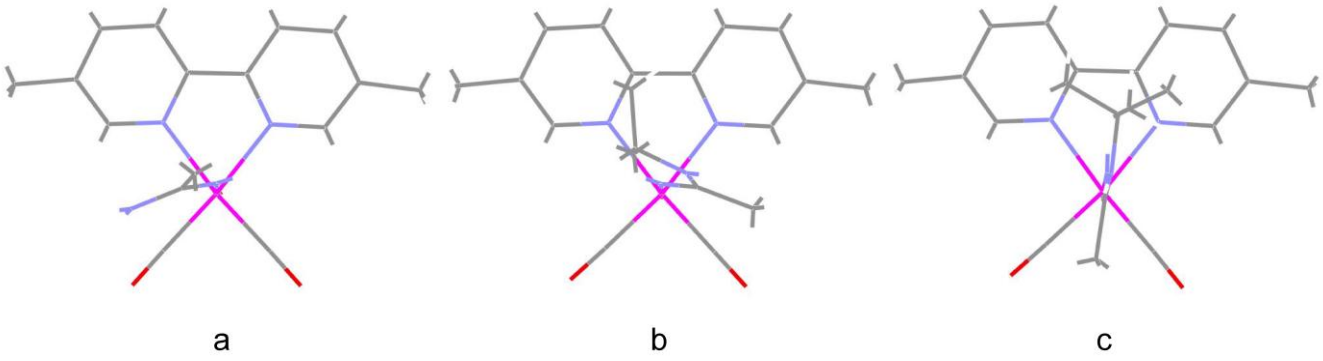

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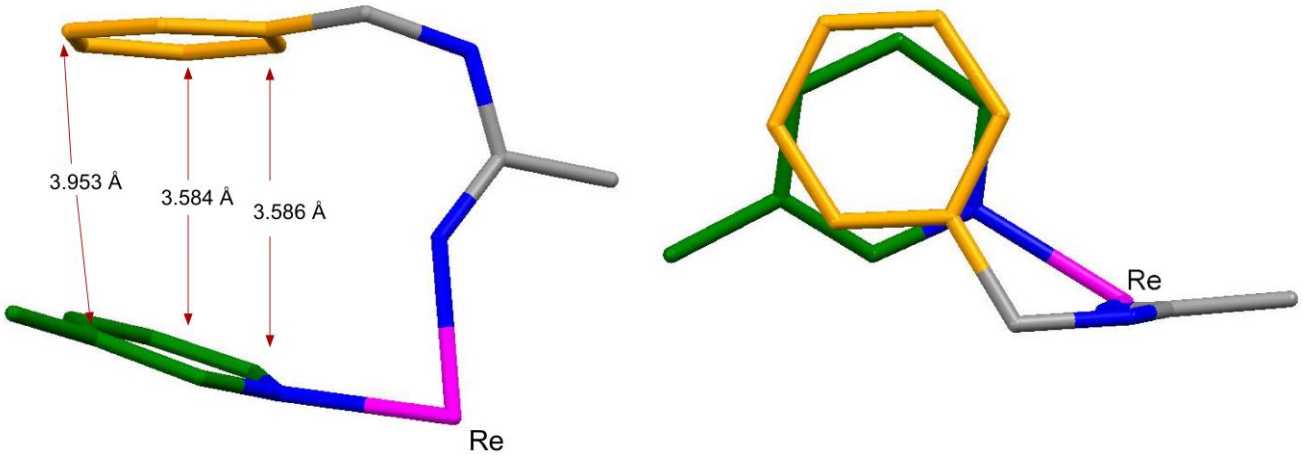

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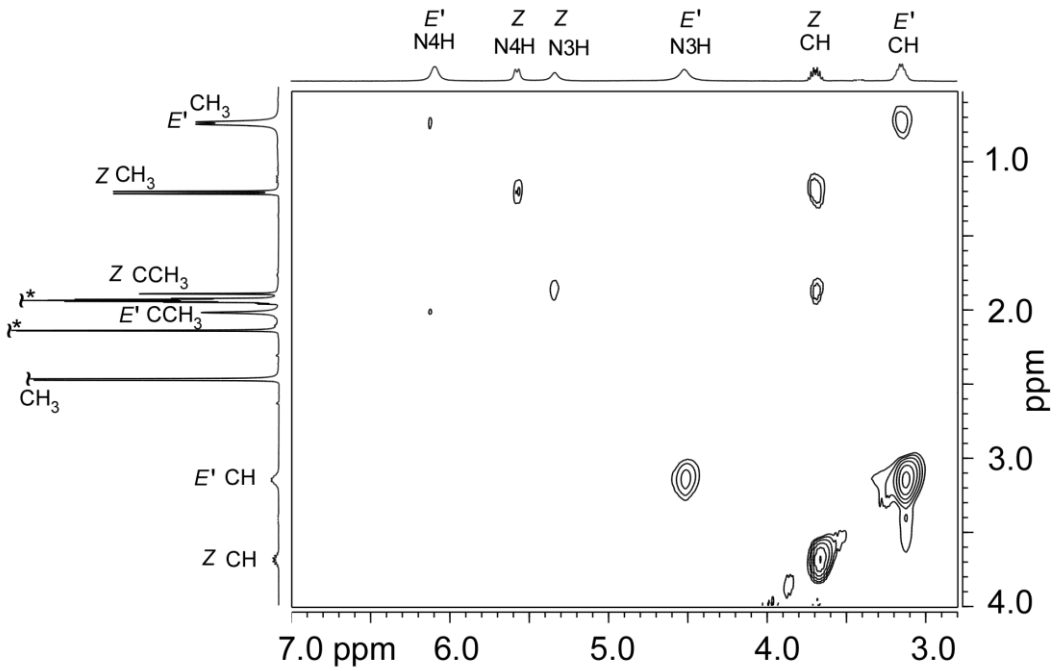

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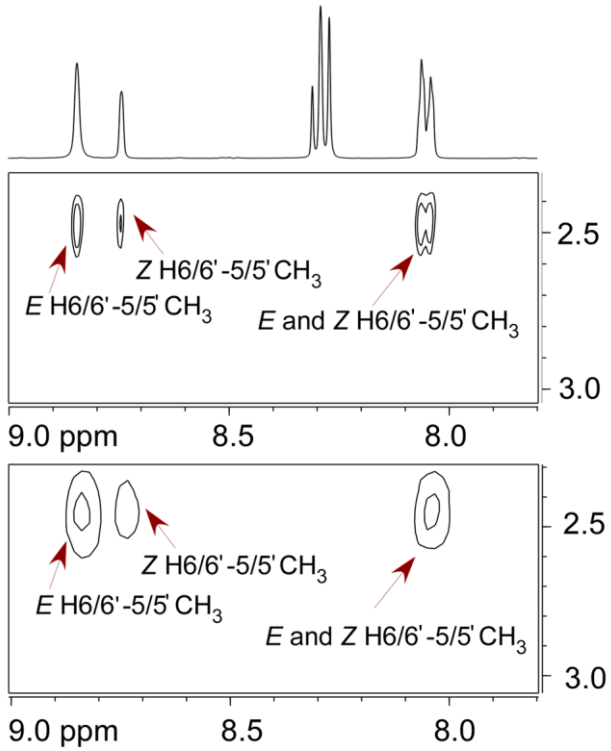

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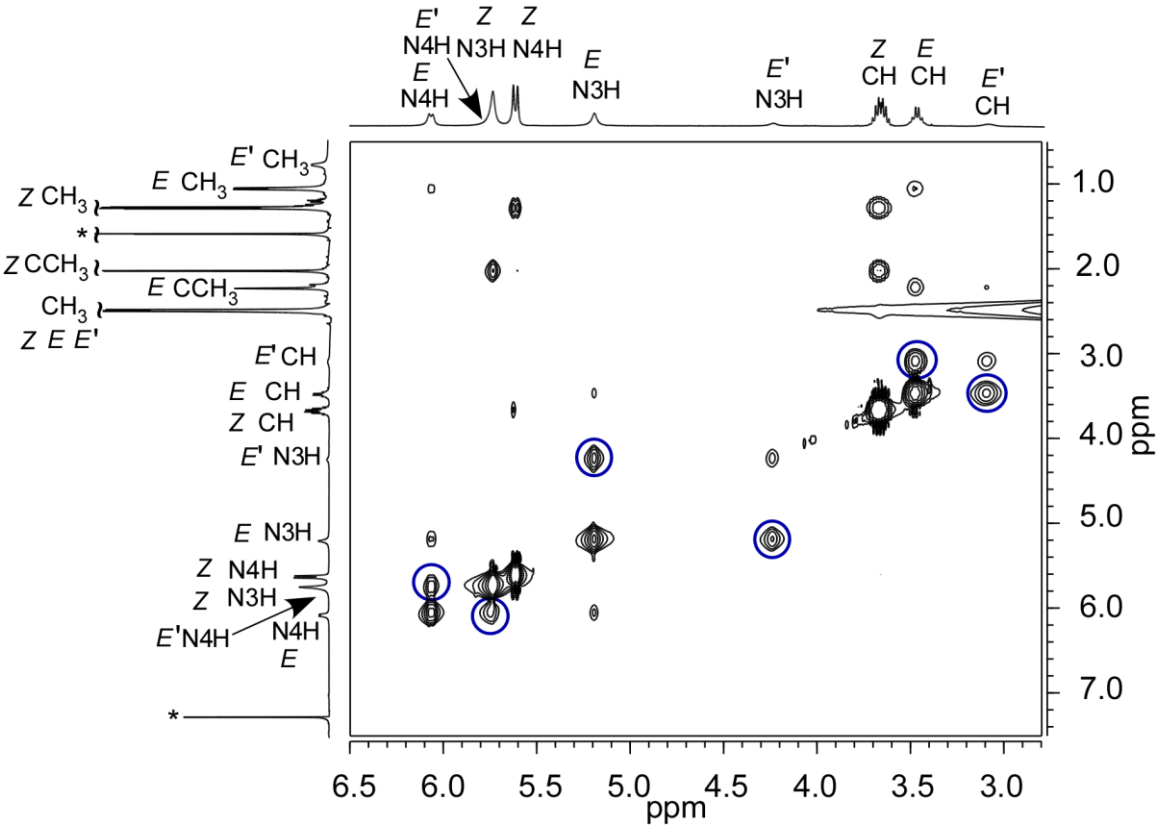

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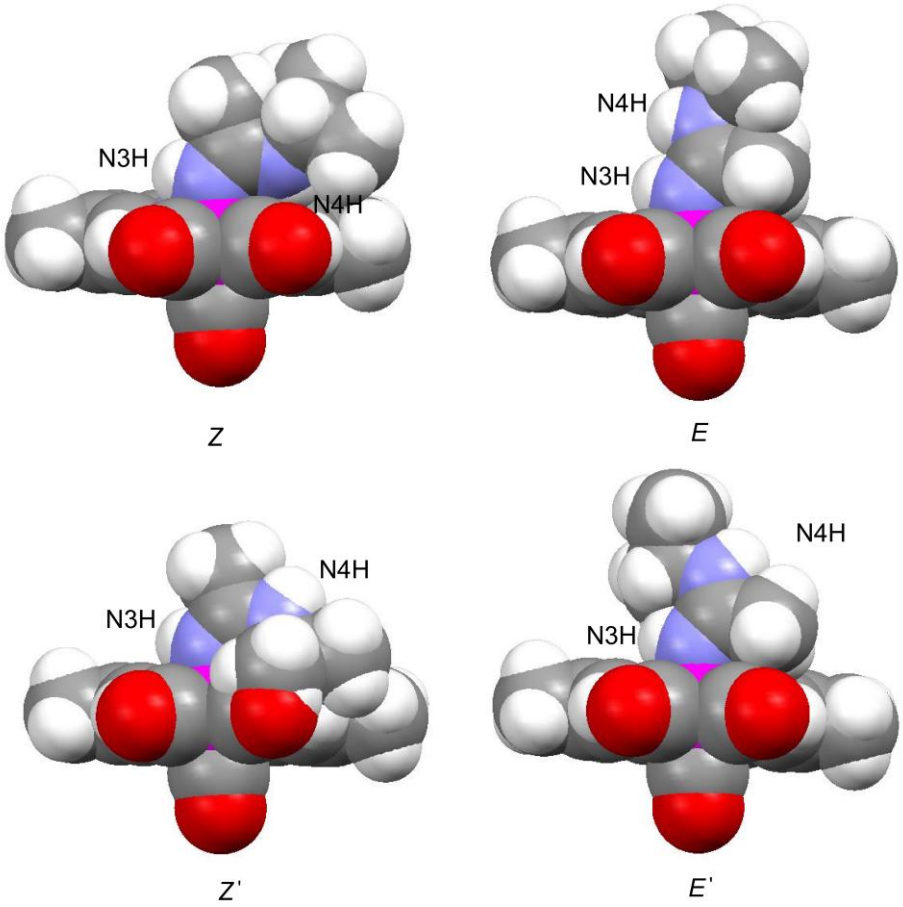

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R	isomer	N3H	N4H	CH_3 (formerly CH_3CN)	$N4CH_n$ [a]	H6/6′
			$CDCl_3$			
isopropyl (**2**)	*E′*	4.30	5.77	2.20	3.13	8.64
	E	5.22	6.07	2.23	3.50	8.62
	Z	5.76	5.61	2.03	3.67	8.55
isobutyl (**3**)	*E′*	4.37	6.05	2.22	2.46	8.68
	E	5.33	6.22	2.21		8.62
	Z	5.83	5.75	2.00	3.06	8.55
tert-butyl (**4**)	*E′*	4.26	5.57	2.25		8.68 [b]
	E	5.22	6.17	2.32		8.65
	Z	5.73	6.03	2.14		8.55
			CD_2Cl_2			
isopropyl (**2**)	*E′*	4.06	5.85	2.20	2.96	8.77
	E	5.11	5.96	2.24	3.51	8.69
	Z	5.15	5.69	1.99	3.69	8.64
isobutyl (**3**)	*E′*	4.15	6.09	2.20	2.81	8.76
	E		6.09	2.23	2.41	8.69
	Z	5.29	5.82	1.96	3.08	8.63
tert-butyl (**4**)	*E′*	4.28	5.57	2.19		8.78
	Z	4.32	6.10	2.10		8.63

[a] The $N4CH_n$ signals vary in multiplicity according to the R group. [b] Shoulder, some overlap.

Table S2. Distribution (%) of *E*, *E′*, and *Z* isomers of $[Re(CO)_3(5,5'\text{-}Me_2bipy)(HNC(CH_3)NHR)]BF_4$ at 25 °C

	$CDCl_3$			CD_2Cl_2			acetonitrile-d_3		DMSO-d_6	
R	*E′*	*E*	*Z*	*E′*	*E*	*Z*	*E′*	*Z*	*E′*	*Z*
isopropyl (**2**)	5	32	63	19	19	62	64	36	78	22
isobutyl (**3**)	7	29	64	21	17	62	65	35	80	20
tert-butyl (**4**)	15	28	57	53	*a*	47	82	18	87	13

[a] Not observed.