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Supporting Information

Advancing Homogeneous Catalysis for Parahydrogen-Derived Hyperpolarisation and its NMR Applications

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A range of SABRE active complexes with different NHC auxiliary ligands have been reported (see Figure 12 and 13 of the manuscript) which exhibit a variety of steric and electronic properties. These can be quantified by use of % Buried Volumes (%BurV) or Tolman Electronic Parameters (TEP) respectively (Table S1). We provide here a comparison of the different %BurV and TEP parameters for IMes-derived ligands used in SABRE hyperpolarisation experiments.

Table S1: Summary of electronic and steric properties of SABRE polarisation transfer catalysts with a variety of NHC ligands.

No.	Abbreviation	R_1	R_2	R_3	R_4	R_5	TEP /cm^{-1}	BurV /%	Ref.
5	IMe	CH_3	H	CH_3	-	-	2054.1[¤]	26.3[¤]	[48]
6	Im*N*Pr$^i_2$	$CH(CH_3)_2$	H	$CH(CH_3)_2$	-	-	2050.4[%]	26.4[@]	[154],[155]
7	ImMe_2*NP*r$^i_2$	$CH(CH_3)_2$	CH_3	$CH(CH_3)_2$	-	-	2049.6[¤]	38.4[¤]	[48]
8	ItBu	^{t}Bu	H	^{t}Bu	-	-	2048.9[%]	35.5[@]	[155]
9	Icy	Cyclohexyl	H	Cyclohexyl	-	-	2049.5[%]	27.1[@]	[154],[155]
					-	-	2049.6[¤]	27.4[¤]	[48]
10	Iad	Adamantyl	H	Adamantyl	-	-	2048.3[%]	36.1[@]	[155]
11	-	Ph	H	CH_3	-	-	-	-	[163]
12	-	Mesityl	H	CH_3	-	-	-	-	[163]
13	-	Mesityl	H	CH_2Ph	-	-	-	-	[163]
14	-	Mesityl	H	CH_2CH_2Ph	-	-	-	-	[163]
15	SIm*N*Pr$^i_2$	$CH(CH_3)_2$	H	$CH(CH_3)_2$	-	-	2050.8[%]	28.5[@]	[154],[155]
16	ipr-NHC	Mesityl	H	$CH(CH_3)_2$	-	-	-	-	[156]
17	Si-NHC	Mesityl	H	$(CH_2)_3Si(OEt)_3$	-	-	-	-	[156]
18	tzNHC	Mesityl	CH_3	Ph	-	-	-	-	[156]
19	CAAC-NHC	$CH(CH_3)_2$	-	-	-	-	-	-	[156]
20	IMes	CH_3	H	CH_3	H	H	2049.6[%]	31.6[@]	[154],[155]
							2049.6[#]	31.6	[153]
							2050.7[¤]	36.5[¤]	[48]
21	-	CH_3	H	H	H	H	2050.5[#]	30.5	[153]
22	-	H	H	CH_3	H	H	2050.6[#]	31.6	[153]
23	-	H	H	CH_2CH_3	H	H	2049.8[#]	31.7	[153]
24	IPr	H	H	$CH(CH_3)_2$	H	H	2050.1[#]	32.6	[153]
							2050.2[%]	33.6[@]	[154],[155]
							2051.5[¤]	44.5[¤]	[48]
25	-	H	CH_3	H	H	H	2049.6[#]	30.5	[153]
26	-	CH_3	CH_3	H	H	H	2048.9[#]	30.5	[153]
27	-	F	H	CH_3	H	H	2051.4[#]	31.7	[153]
28	-	Cl	H	CH_3	H	H	2051.7[#]	31.7	[153]
29	-	Br	H	CH_3	H	H	2051.9[#]	31.7	[153]
30	-	I	H	CH_3	H	H	2051.9[#]	31.7	[153]
31	-	CO_2Me	H	CH_3	H	H	2052.2[#]	31.8	[153]
32	-	OTf	H	CH_3	H	H	2053.2[#]	31.8	[153]
33	-	OAc	H	CH_3	H	H	2051.3[#]	31.7	[153]
34	-	Ph	H	CH_3	H	H	2050.4[#]	31.7	[153]
35	-	^{t}Bu	H	CH_3	H	H	2049.6[#]	31.7	[153]
36	-	OMe	H	CH_3	H	H	2049.3[#]	31.5	[153]
37	-	NMe_2	H	CH_3	H	H	2047.6[#]	31.6	[153]
38	-	CH_3	H	CH_3	CH_3	CH_3	2047.2[#]	31.4	[153]
39	-	CH_3	H	CH_3	CH_2CH_3	CH_2CH_3	2047.8[#]	31.6	[153]
40	-	CH_3	H	CH_3	Cl	Cl	2052.8[#]	31.7	[153]
41	-	CH_3	H	CH_3	Br	Br	2052.4[#]	31.8	[153]
42	-	Cl	H	CH_3	Cl	Cl	2054.9[#]	31.8	[153]
43	-	H	H	$CH(Et)_2$	H	H	2048.3[%]	-	[154]
44	-	CH_3	H	CH_3	NMe_2	H	-	-	[212]
45	SIMes	CH_3	H	CH_3	H	H	2050.8[%]	32.7[@]	[154],[155]
							2051.5[¤]	36.9[¤]	[48]
46	SIPr	H	H	$CH(CH_3)_2$	H	H	2051.1[%]	35.7[@]	[154],[155]
							2052.2[¤]	47.0[¤]	[48]
47-51	-	-	-		-	-	-	-	[161]-[163]

[¤]These values were calculated using density functional theory involving $[Ni(CO)_3(NHC)]$ and were originally reported in Ref. no. [151]
[%]Ref. no. [154] presented average infrared carbonyl stretching frequencies ($\nu_{CO,av}$) of $[Ir(NHC)(CO)_2Cl]$. TEP values were calculated from these in our work according to the established equation TEP = $0.847\nu_{CO,av}$ + 336 consistent with other works.[152,153]
[@]These values were calculated in Ref. no. [155] from X-ray crystal structures of $[Ir(NHC)(CO)_2Cl]$ reported in Ref. no. [152].
[#]Values determined from average infrared carbonyl stretching frequencies ($\nu_{CO,av}$) of $[Ir(NHC)(CO)_2Cl]$

Note that reference numbers correspond to those that appear in the main manuscript