Electronic Supporting Information (ESI) Application of the π -accepting ability parameter of *N*-heterocyclic carbene ligands to their iridium complexes for Signal Amplification By Reversible Exchange (SABRE)

Bram J. A. van Weerdenburg,^a Nan Eshuis,^a Marco Tessari,^a Floris P. J. T. Rutjes,^a and Martin C. Feiters,*^a

^a Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

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S1 General procedures

Unless stated otherwise, all experimental procedures were performed under an atmosphere of either nitrogen or argon using standard Schlenk line techniques or an mbraun Unilab glovebox. General solvents for synthetic chemistry were dried using an mbraun SPS 800 solvent purification system and were degassed prior to use. Chemicals were purchased from commercial vendors: (chloro-1,5-cyclooctadiene iridium(I) dimer, and 1,3-bis[2,6-bis(1-ethylpropyl)phenyl]imidazolium chloride from Strem Chemicals; pyridine, 1,3-diisopropylimidazolium tetrafluoroborate, selenium pellets ~ 2 mm, methanol- d_4 from Sigma Aldrich, 1,3-diisopropylimidazolinium tetrafluoroborate from TCI, CDCl₃ from Cambridge Isotope Laboratories). All chemicals were used as supplied. R_f values are obtained using thin layer chromatography (TLC) with silica gel-coated plates (Merck 60 F254) with the indicated solvent mixture. Column chromatography was carried out using ACROS silica gel (0.035-0.070 mm, and ca 6 nm pore diameter). Bench grade solvents were used for crystallization of samples for X-ray diffraction analysis. NMR spectra for compound analysis were recorded on a Bruker Advance III 400 MHz machine. ¹H and ¹³C NMR spectra were referenced to the residual solvent signals.⁷⁷Se NMR spectra were referenced internally to (PhSe)₂. Chemical shifts are given in parts per million (ppm) and coupling constants are reported as J-values in Hertz. For the assignment of the peaks the following abbreviations are used; s = singlet, d = doublet, spt = septet, m = multiplet. Highresolution mass spectra were recorded on a JEOL AccuTOF JMS-T100CS (ESI). [Ir(Cl)(CO)₂(NHC)] complexes were used to determine the buried volume and TEP as described previously.^{1, 2} The buried volume of the IPent ligand was determined based on the [Se(IPent)] complex.³ The δ_{Se} were acquired from S. V. C. Vummaleti *et al.*³ with exception of [Se(Im/Pr)] and [Se(SIm/VPr)]. The SABRE experiment with [Ir(Cl)(COD)(IPent)] was performed manually as described earlier.^{4,5}

S2 Overview of experimental data and ligand properties

No	Abbreviation	breviation Ligand	%V _{Bur}	$v_{CO(avg)}$ (cm ⁻¹)	⁷⁷ δSe (CDCl ₂)	Max S.E. ^a	Exchange rate (s ⁻¹) Py ^b	
				()	(;)		Rate	Error ^c
2	SImNPr ₂	γ^{N}	28.5	2024.5	-19	43	4.5	0.18
3	ImNPr ₂	$\gamma N = N + \gamma N + $	26.4	2024.1	63	72	1.6	0.07
4	Icy		27.1	2023.0	-22	18	4.3	0.6
5	SIMes		32.7	2024.6	110	369	49	5.6
6	IMes		31.6	2023.1	27	680	9.0 ^b	0.31
7	SIPr	<u>E</u> N <u></u> NE	35.7	2024.9	190	103	116	9
8	IPr	É nõn É	33.6	2023.9	90	125	34	2.3
9	IPent	$ \begin{array}{c} Et \\ \downarrow \\ \downarrow \\ \downarrow \\ \downarrow \\ Et \end{array} \begin{array}{c} Et \\ Et \end{array} \begin{array}{c} Et \\ Et \\ Et \end{array} \begin{array}{c} Et \\ Et \end{array} \end{array} $	n.d.	2021.6	101	_ d	n.d. ^e	
	ItBu ^f	YN.WK	35.5	2022.3	183	11	3.2	0.4

Table S1: Overview of experimental data and ligand properties

^a Max. S.E. = Maximal Signal Enhancement, ^b Measurement at 298 K; ^c Fitting error in Origin; ^d No signal enhancement was observed, indicating that the exchange rate is in this case too fast for polarisation transfer to pyridine ^e The bound pyridine signal is only observable at low temperatures (<10 °C) indicating a much higher exchange rate than that of the other reported catalyst.^f The reactivity of this complex is low and only trace amounts of active complex were formed.

S2 Synthesis of [Ir(Cl)(COD)(IPent)]

The procedure of Pompeo *et al.*⁶ was slightly adjusted. To a suspension of the 1,3-Bis[2,6-bis(1-ethylpropyl)phenyl]imidazolium chloride (0.42 mmol, 1.0 eq) in THF, KOtBu (1.2 eq., 1.0 M solution in THF) was added. The mixture was stirred for approximately 10 minutes till the solution becomes clear, where after the iridium dimer [Ir(COD) (μ -Cl)]₂ (0.21 mmol, 0.5 eq.) was added. The mixture was stirred at room temperature for approx. 6 hours. Next; silica was added and the solvent evaporated. The residue was dry-loaded on a column and run with EtOAc/heptane 1/4. The desired fractions were collected and evaporated, where after the product was recrystallized with THF/pentane. The product was obtained in 84% yield (295 mg) as a yellow/orange solid (R_f =0.72, EtOAc/heptane 1/4).

¹H NMR (400 MHz, CDCl₃) δ 7.40 (t, J = 7.8 Hz, 2H), 7.19 (d, J = 7.6 Hz, 4H), 6.96 (s, 2H), 4.17 (m, 2H), 2.93 (m, 2H), 2.67 (br. s, 4H), 1.95 (br. S, 2H), 1.86-173 (m, 6H), 1.64-1.58 (m, 2H), 1.48-1.53 (m, 10H), 1.38-1.30 (m, 2H), 1.11-1.18 (m, 2H), 1.03 (t, J = 7.2 Hz, 12H), 0.74 (t, J = 7.5 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 179.7, 137.5, 128.6, 124.9, 124.5, 82.7, 51.4, 41.2, 33.3, 28.8, 28.2, 26.6, 12.6, 10.9, (reported signal at 144.4 was not observed). The spectral data are in accordance with earlier reported values.⁶

S3 General procedure for the synthesis of [Se(NHC)] complexes

Safety note: selenium and organoselenium compounds are highly toxic, and should be handled with care. The following literature procedure was used:³ the NHC salt (ca. 50 mg, weighed accurately), excess selenium (ca. 30 mg, pellets were grinded before use) and a stirrer bar were added to a Schlenk tube and purged with nitrogen. Next, dry degassed THF (0.75 mL) and KOtBu (1.2 equiv. 1.0M solution in THF) were added via the septum and the resulting suspension was stirred at room temperature overnight. The solvent was evaporated and the resulting residue was suspended in DCM (ca. 2 mL) and filtered through a pad of celite. The pad was washed with further DCM (ca. 2 mL). The DCM was evaporated and the residue was washed with pentane (3 x ca. 1 mL).

Synthesis of [Se(ImNPr)]

Following the above described procedure, the product was obtained as an offwhite solid in 62% yield (30.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 1.40 (d, *J* = 6.74 Hz, 12 H) 5.30 (spt, *J* = 6.70 Hz, 2 H) 6.92 (s, 2 H), ¹³C NMR (100 MHz, CDCl₃) δ 153.0 (C, carbene), 115.3 (CH=CH), 50.4 (CH), 22.0 (CH₃), ⁷⁷Se NMR (76 MHz, CDCl₃) δ -19.02 (s). HRMS (ESI⁺) calcd for C₉H₁₇N₂Se [M+H]⁺ 233.0557, found 233.0560. A crystal of X-ray quality was obtained after recrystallisation by slow vapor diffusion with DCE/pentane. The structure is deposited in the CDCC database: 1402867.

Synthesis of [Se(SIm/VPr)]

Following the above described procedure, the product was obtained as an offwhite solid in 71% yield (34.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 1.20 (d, *J* = 6.79 Hz, 12 H) 3.48 (s, 4 H) 5.08 (spt, *J* = 6.70 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 178.8 (C, carbene) 49.0 (CH), 41.4 (CH₂-CH₂), 19.4 (CH₃), ⁷⁷Se NMR (76 MHz, CDCl₃) δ 63.41 (s). HRMS (ESI⁺) calcd for C₉H₁₉N₂Se [M+H]⁺ 235.0714, found 235.0720.

S4 NMR spectra of [Se(Im/Pr)] ¹<u>H NMR of [Se(Im/Pr)] in CDCl₃ @ 400 MHz</u>







JMOD(APT) ¹³C NMR of [Se(Im/Pr)] in CDCl₃ @100 MHz



S5 NMR spectra of [Se(SIm/Pr)] ¹<u>H NMR of [Se(SIm/Pr)] in CDCl₃ @ 400 MHz</u>



¹³C NMR of [Se(SImNPr)] in CDCl₃ @ 100 MHz



JMOD(APT) ¹³C NMR of [Se(SIm/VPr)] in CDCl₃ @ 100 MHz







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