## **Supporting Information File**

## Dehydrogenation of amines in aryl-amine functionalized pincer-like nitrogen-donor redox non-innocent ligands *via* ligand reduction on Ni(II) template

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Figure S1. <sup>1</sup>H NMR Spectrum of compound A in CDCI<sub>3</sub>



Figure S2. <sup>13</sup>C NMR Spectrum of compound **A** in CDCI<sub>3</sub>



Figure S3. <sup>1</sup>H NMR Spectrum of compound **B** in d<sub>6</sub>-DMSO



Figure S4. <sup>13</sup>C NMR Spectrum of compound **B** in CDCI<sub>3</sub>



Figure S5. <sup>1</sup>H NMR Spectrum of HL<sup>a</sup> in CDCI<sub>3</sub> [N-H proton shown in inset]



Figure S6. <sup>13</sup>C NMR Spectrum of HL<sup>a</sup> in d<sub>6</sub>-DMSO







Figure S8. <sup>13</sup>C NMR Spectrum of HL<sup>b</sup> in d<sub>6</sub>-DMSO



Figure S9. <sup>1</sup>H NMR Spectrum of HL<sup>c</sup> in CDCI<sub>3</sub>(s-acetone)



Figure S10.  $^{13}\text{C}$  NMR Spectrum of  $\text{HL}^{c}$  in d\_6-DMSO



Figure S11. Full-range ESI-MS spectrum of the Compound A in acetonitrile



Figure S12. Full-range ESI-MS spectrum of Compound B in acetonitrile



Figure S13. Full-range ESI-MS spectrum of the ligand HL<sup>a</sup>



Figure S14. Full-range ESI-MS spectrum of the ligand  $\rm HL^{b}$ 



Figure S15. Full-range ESI-MS spectrum of the ligand HL<sup>c</sup>



Figure S16. ORTEP representation and atom numbering schemes for the complex 2 in 50% probability level



Figure S17. Optimized structure of the ligand HL<sup>a</sup>



Figure S18. Optimized structure of the ligand  $\rm HL^{c}$ 



Figure \$19. Optimized structure of the complex 1



Figure S20. Optimized structure of the complex 3



Figure S21. Optimized structure of the complex 6



Figure S22. Reaction with NaO<sup>t</sup>Bu



Figure S23. <sup>1</sup>H NMR Spectrum of L<sup>x</sup> in CDCI<sub>3.</sub>

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Figure S24. <sup>13</sup>C NMR Spectrum of L<sup>x</sup> in CDCl<sub>3.</sub>







Figure S26. <sup>13</sup>C NMR Spectrum of L<sup>y</sup> in CDCl<sub>3</sub>.



**Figure S27.** Full-range ESI-MS Spectrum of the ligand **L**<sup>x</sup> in acetonitrile.



**Figure S28**. Full-range ESI-MS Spectrum of the ligand L<sup>y</sup> in methanol.



Figure S29. ORTEP representation and atom numbering schemes for the complex 8 in the 50% probability level.



Figure S30. Optimized structure of the ligand L<sup>x</sup>



Figure S31. Optimized structure of Complex 7



Figure S32. Optimized structure of Complex 9



Figure S33:  $\alpha$ -MOs of the Complex 7.



Figure S34:  $\beta$ -MOs of the Complex 7.











HOMO-1



LUMO+2









номо







Figure S36:  $\beta$ -MOs of the Complex 8.



номо

HOMO-1

номо-2



LUMO

LUMO+1

Figure S37:  $\alpha$  -MOs of the Complex 9.



номо

HOMO-1

номо-2



LUMO

LUMO+1

Figure S38:  $\beta$  -MOs of the Complex 9.



Figure S39: UV-vis spectra of HL<sup>a</sup>, L<sup>x</sup> and complex 1, 3, 7 and 9.



Figure S40. Cyclic voltammogram of the complex 7 and 9 in acetonitrile.



Figure S41. ORTEP representation and atom numbering schemes for the complex 10 in the 50% probability level.



Figure S42. UV-vis spectra of the complex 12 in CH<sub>3</sub>CN.



Figure S43. ORTEP representation and atom numbering schemes for the complex 12 in the 50% probability level.



Figure S44: IR Spectrum of Zn(OH)<sub>2</sub>.



Figure S45: IR Spectrum of [Cp<sub>2</sub>Co]OH.

## Table S1. Crystallographic Data Table of the Complexes 2, 8, 10, and 12.

	2	8	10	12
CCDC no.	1887736	1964891	1887741	1887743
empirical formula	$C_{20}H_{20}CI_2N_4Ni$	$C_{20}H_{18}CI_2N_4Ni$	$C_{18} H_{14} I_2 N_4 Ni$	$C_{18}H_{14}CI_2N_4$ Ni
formula wt.	445.99	443.99	598.82	415.92
crystal system	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
space group	P-1	Pbca	P2 <sub>1</sub> /n	Pbca
<i>a</i> (Å)	9.0074(5)	13.3625(2)	10.3761(6)	13.7101(8)
b (Å)	9.9859( <i>6</i> )	14.1391(2)	15.2932(9)	14.8189(6)
<i>c</i> (Å)	11.7946( <i>6</i> )	20.0908(2)	11.9597(7)	17.3058(8)
$\alpha$ (deg)	87.050( <i>4</i> )	90.00	90.00	90.00
<i>6</i> (deg)	75.671( <i>5</i> )	90.00	95.1020(10)	90.00
γ (deg)	71.025( <i>5</i> )	90.00	90.00	90.00
Cell Volume	971.54(10)	3795.83(9)	1890.29(19)	3516.0(3)
R-factor	5.66	2.71	2.88	3.58
Ζ	2	8	4	8
Т (К)	100.00(10)	100.00(10)	293.15 (10)	100.00(10)
$\mu$ (mm <sup>-1</sup> )	4.064	4.161	4.301	1.415
$\rho_{calcd}(g \text{ cm}^{-3})$	1.525	1.554	2.104	1.572
F (000)	460.0	1824.0	1136.0	1696.0
28 range (deg)	7.74 to 132.5	10.12 to 132.42	4.34 to 50.00	4.68 to 52.74
Data/restraints/ parameters	3350/0/250	3308/0/246	3321/0/220	3598/0/226
$R_{1}, WR_{2}[1 >= 2\sigma(1)]$	0.0566,0.1561	0.0271, 0.0747	0.0288,0.0694	0.0358,0.0894
$R_1$ , $wR_2$ (all data)	0.0581,0.1580	0.0281, 0.0755	0.0322,0.0709	0.0470,0.0976
$GOF$ on $F^2$	1.062	1.057	1.127	1.056
largest difference in peak and hole(e Å $^{-3}$ )	0.93,-0.99	0.27/-0.35	0.73,-0.75	0.40,-0.32