# **Electronic Supplementary Information**

for

# Bis(imino)pyridine Complexes of the First Row Transition Metals: Alternative Methods of Activation

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The ligands  $\{2,6-[RN=C(CH_3)]_2\}C_5H_3N$  (R = 2,6-<sup>i</sup>Pr<sub>2</sub>Ph, 2-MePh) and transition metal halide salts were purchased from Strem, tris(pentafluorophenyl)borane and triethylaluminium from Aldrich, trityl tetrakis(pentafluorophenyl)borate from Albemarle, and MMAO-3A<sup>1</sup> and TEA from Akzo Nobel; all materials were used as received. The ligands  $\{2,6-[PhN=C(CH_3)]_2\}C_5H_3N^{2.3}$  and 4,5-bis-(arylimino)-1,2,3,4,5,6,7,8-octahydro-acridine (aryl = Ph, *o*-Tol),<sup>4</sup> trityl *tetrakis*(perfluorophenyl)aluminate<sup>5</sup> and the metal complexes **1a-e**,<sup>4,6</sup> **2a-c**,<sup>7</sup> **3a-c**<sup>8</sup> and **4a-c**<sup>2a,8</sup> were all prepared by literature procedures or slight modifications thereof. Solvents were procured from Aldrich, purified using an Innovative Technologies Solvent Purification System, and de-oxygenated prior to use. All operations were conducted under inert atmosphere using an argon filled glovebox and standard Schlenk techniques. Elemental analyses were performed by the Science Technical Support Unit of London Metropolitan University.





#### **Preparation of tricyclic N3 ligands:**

Synthetic route for the preparation of tricyclic ligands:



Acetic anhydride (17.36 g, 170 mmol) was added to a mixture of benzaldehyde and octahydroacridine at RT. The mixture was then heated under reflux at 140°C under N<sub>2</sub> atmosphere for 22 h. The mixture was then allowed to cool to RT then cooled to 0°C, upon returning the mixture to RT a yellow precipitate was formed. The later was washed with copious amounts of ethanol to give a white solid (5.12 g, 66%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{\rm H}$  1.91-1.99 (2 H, m, CH<sub>2</sub>), 2.93 (2 H, t, J = 6.1, CH<sub>2</sub>), 3.01 (2 H, m, CH<sub>2</sub>), 7.32-7.58 (10 H, m, Ph), 8.23 (1 H, s, CH);  $\delta_{\rm C}$  23.0 (CH<sub>2</sub>), 28.1 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 126.2, 126.7, 128.1, 129.7, 131.4, 135.8, 138.2 (Ph), 137.6 (C=C), 150.1 (C=C). Elemental analysis calculated for C<sub>27</sub>H<sub>25</sub>N: C: 89.21; H: 6.93; N: 3.85, found C: 89.25; H: 6.89; N: 3.88.



Benzyledene (2.50 g, 6.88 mmol) was dissolved in DCM (150 mL) at RT. The mixture was the purged with oxygen then cooled to -78°C. To this was connected an indicator. [Prepared from 2.5 g potassium iodide, 25 mL water and 25 mL acetic acid]. After 2 minutes the ozone generator was turned on and the mixture purged with ozone and continuously stirred. After 50 min - 1.2 h, the mixture turned slightly blue, it was then allowed to react until a persistent blue color was observed. At this point the

generator was turned off and the mixture purged with oxygen for 10 min (until the blue color disappeared). Dimethyl sulfide (3.0 mL) was added [solution turned slightly yellow] and the cold bath removed. Stirring was continued overnight, the reddish solution was then concentrated. The residue was washed with hot hexane ( $2 \times 20$  mL), then diluted with DCM (60 mL). This was then washed with NaOH(aq) ( $2 \times 20$  mL). Combined DCM layers were dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The residue was the purified over silica gel eluting with DCM, EtOAc (4:1) to give the desired product as an off-white solid (900 mg, 61%). The product was purified by crystallization from hot toluene (then allowed to reach RT, then store in a freezer at -18°C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  2.19 (2 H, m, CH<sub>2</sub>), 2.81 (2 H, t, J = 5.9, CH<sub>2</sub>), 3.06 (2 H, t, J = 6.1, CH<sub>2</sub>), 7.63 (1 H, s, CH);  $\delta_{\rm C}$  22.3 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 39.7 (CH<sub>2</sub>), 138.9 (CH), 143.5 (C), 147.5 (C), 195.1 (C=O). Elemental analysis calculated for C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub>: C: 72.54; H: 6.09; N: 6.51, found C: 72.60; H: 6.00; N: 6.51.



PTSA (a few crystals) was added to a solution of the tricyclic diketone (500 mg, 2.32 mmol) and aniline (469 mg, 4.87 mmol) in EtOH at RT. The mixture was heated to 80°C for 16 h, resulting in a brick red solution. EtOH was removed under reduced pressure, and the resultant oil dissolved in DCM. This was washed with ( $3 \times 50$  mL) 10% bicarbonate solution in water. The organics were collected, treated with MgSO<sub>4</sub> and volatiles removed *in vacuo*. This gave a brick red solid (548 mg, 65%).

Elemental analysis calculated for  $C_{25}H_{23}N_3$ : C: 82.16; H: 6.34; N: 11.50, found C: 82.20; H: 6.27; N: 11.41.



The reaction was undertaken following the procedure described above, using tricyclic diketone (500 mg, 2.32 mmol), *ortho*-toluidine (522 mg, 4.87 mmol) and few crystals of PTSA in EtOH. This gave the product as brick red solid (589 mg, 65%). Elemental analysis calculated for  $C_{27}H_{27}N_3$ : C: 82.41; H: 6.92; N: 10.68, found C: 82.57; H: 6.86; N: 10.56.

#### **Preparation of complexes:**



A THF solution (40 mL) of N3<sup>Ph</sup> ligand (750 mg, 2.39 mmol) and FeBr<sub>2</sub> (492 mg, 2.28 mmol) was stirred at RT for 1 h. Et<sub>2</sub>O was added (60 mL) to fully precipitate the product, which was collected by filtration, washed with Et<sub>2</sub>O (2 × 20 mL) and dried *in vacuo* to leave a deep purple powder (1.170 g, 97%).



A THF solution (50 mL) of N3<sup>Tol</sup> ligand (416 mg, 1.22 mmol) and FeBr<sub>2</sub> (250 mg, 1.16 mmol) was stirred at 50°C for 16 h. After cooling, Et<sub>2</sub>O was added (100 mL) to fully precipitate the product, which was collected by filtration, washed with Et<sub>2</sub>O (2 × 20 mL) and dried *in vacuo* to leave a blue-purple powder (607 mg, 94%).



A THF solution (40 mL) of N3<sup>Dipp</sup> ligand (453 mg, 0.94 mmol) and FeBr<sub>2</sub> (193 mg, 0.89 mmol) was heated at  $60^{\circ}$ C for 18 h. The THF was reduced *in vacuo* to a minimum volume and Et<sub>2</sub>O added to precipitate the product, which was recovered by filtration and dried *in vacuo* to leave a deep blue powder (618 mg, 99%).



A mixture of *cyclic*-N3<sup>Ph</sup> ligand (300 mg, 0.82 mmol) and FeCl<sub>2</sub> (104 mg, 0.82 mmol) in *n*-butanol (50 mL) was heated to 80°C for 16 h, resulting in a dark brown solution. The *n*-butanol was removed *in vacuo* and the resultant solid washed with ether (3 × 20 mL) to give the desired product as a brown solid (387 mg, 96%). Magnetic moment,  $\mu_{eff}$  3.89.



Prepared as **1d**, but with *cyclic*-N3<sup>Tol</sup> ligand (559 mg, 1.42 mmol) and FeCl<sub>2</sub> (179 mg, 1.42 mmol). This gave the product as a black solid (613 mg, 83%). Magnetic moment,  $\mu_{eff}$  4.81.



A THF solution (100 mL) of N3<sup>Ph</sup> ligand (1.050 g, 3.35 mmol) and (THF)<sub>3</sub>VCl<sub>3</sub> (1.192 g, 3.19 mmol) was stirred at 50<sup>o</sup>C for 18 h. After cooling the solid was collected by filtration, washed with Et<sub>2</sub>O (2 × 20 mL) and dried *in vacuo* to leave a purple-black powder (1.192 g, 77%).



A THF solution (150 mL) of N3<sup>Tol</sup> ligand (793 mg, 2.32 mmol) and (THF)<sub>3</sub>VCl<sub>3</sub> (826 mg, 2.21 mmol) was stirred at 50<sup>o</sup>C for 18 h. After cooling, the THF volume was reduced to ~50 mL *in vacuo*, and the solid recovered by filtration, washed with Et<sub>2</sub>O (2 × 20 mL) and dried *in vacuo* to leave a deep purple powder (1.050 g, 95%).



A THF solution (70 mL) of N3<sup>Ph</sup> ligand (511 mg, 1.63 mmol) and (THF)<sub>3</sub>CrCl<sub>3</sub> (593 mg, 1.58 mmol) was stirred at 50°C for 18 h. Et<sub>2</sub>O was added (60 mL) to fully precipitate the product, which was collected by filtration, washed with Et<sub>2</sub>O (2 × 20 mL) and dried *in vacuo* to leave a green powder (390 mg, 52%).



A THF solution (150 mL) of N3<sup>Tol</sup> ligand (846 mg, 2.48 mmol) and (THF)<sub>3</sub>CrCl<sub>3</sub> (884 mg, 2.36 mmol) was stirred at 50°C for 18 h. After cooling, the THF volume was reduced to ~50 mL *in vacuo*, and the solid recovered by filtration, washed with Et<sub>2</sub>O (2 × 20 mL) and dried *in vacuo* to leave a green powder (1.026 g, 87%).



A THF solution of N3<sup>Dipp</sup> (300 mg, 0.62 mmol) and (THF)<sub>3</sub>CrCl<sub>3</sub> (233 mg, 0.62 mmol) was stirred at RT for 16 h. The THF was reduced *in vacuo* to a minimum volume and Et<sub>2</sub>O added to precipitate the product, which was recovered by filtration and dried *in vacuo* to leave a green solid (398 mg, 99%). Magnetic moment,  $\mu_{eff}$  3.51.



A THF solution (100 mL) of N3<sup>Ph</sup> ligand (558 mg, 1.78 mmol) and CoCl<sub>2</sub> (220 mg, 1.69 mmol) was stirred at 60°C for 18 h. Et<sub>2</sub>O was added (100 mL) to fully precipitate the product, which was collected by filtration, washed with Et<sub>2</sub>O (2 × 20 mL) and dried *in vacuo* to leave a sage green colored powder (682 mg, 91%).



An mixture of CoCl<sub>2</sub> (304 mg, 2.34 mmol) and N3<sup>Tol</sup> (800 mg, 2.34 mmol) in *n*-butanol (50 mL) was heated to 117°C for 4 h to give a green solution. After cooling to RT, the *n*-butanol was removed by filtration and the green solid washed with diethyl ether (2 × 30 mL). The solid was dried *in vacuo* to give the product as a lime green solid (1.081 g, 98%). Magnetic moment  $\mu_{eff}$  4.61.



A THF solution (100 mL) of N3<sup>Dipp</sup> (300 mg, 0.622 mmol) and CoCl<sub>2</sub> (80 mg, 0.622 mmol) was heated at 60°C for 16 h. Following filtration and dying, the product was obtained as a tan colored solid (369 mg, 97%). Magnetic moment,  $\mu_{eff}$  4.73.

Complex	C %	Н %	N %
	calc. (found)	calc. (found)	calc. (found)
1a, C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> FeBr <sub>2</sub>	47.68 (47.52)	3.62 (3.53)	7.94 (7.82)
1b, C <sub>23</sub> H <sub>23</sub> N <sub>3</sub> FeBr <sub>2</sub>	49.59 (49.64)	4.16 (4.21)	7.54 (7.50)
1c, C <sub>33</sub> H <sub>43</sub> N <sub>3</sub> FeBr <sub>2</sub>	56.84 (56.91)	6.22 (6.31)	6.03 (5.96)
1d, C <sub>25</sub> H <sub>23</sub> N <sub>3</sub> FeCl <sub>2</sub>	61.00 (60.85)	4.71 (4.58)	8.54 (8.42)
1e, C <sub>27</sub> H <sub>27</sub> N <sub>3</sub> FeCl <sub>2</sub>	62.33 (62.26)	5.23 (5.13)	8.08 (8.06)
2a, C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> VCl <sub>3</sub>	53.59 (53.66)	4.07 (4.17)	8.93 (8.90)

## Elemental analysis data for complexes:

2b, C <sub>23</sub> H <sub>23</sub> N <sub>3</sub> VCl <sub>3</sub>	55.39 (55.46)	4.65 (4.78)	8.43 (8.36)
3a, C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> CrCl <sub>3</sub>	53.47 (53.54)	4.06 (4.20)	8.91 (8.80)
3b, C <sub>23</sub> H <sub>23</sub> N <sub>3</sub> CrCl <sub>3</sub>	55.27 (55.38)	4.64 (4.52)	8.41 (8.27)
3c, C <sub>33</sub> H <sub>43</sub> N <sub>3</sub> CrCl <sub>3</sub>	61.92 (61.79)	6.77 (6.62)	6.56 (6.43)
4a, C <sub>21</sub> H <sub>19</sub> N <sub>3</sub> CoCl <sub>2</sub>	56.91 (57.05)	4.32 (4.39)	9.48 (9.48)
4b, C <sub>23</sub> H <sub>23</sub> N <sub>3</sub> CoCl <sub>2</sub>	58.62 (58.64)	4.92 (4.91)	8.92 (8.96)
4c, C <sub>33</sub> H <sub>43</sub> N <sub>3</sub> CoCl <sub>2</sub>	64.81 (65.01)	7.09 (7.17)	6.87 (6.71)
[Ph <sub>3</sub> C][Al(O <sup>t</sup> Bu <sup>F</sup> ) <sub>4</sub> ]	34.73 (34.75)	1.25 (1.27)	- (-)

## Discussion on the relative rates and stability of the catalytic species for Table 1, Entries 1-5

Graphical representation of the ethylene uptake profiles for catalysis runs, Table 1, Entries 1-5.



Ethylene Oligomerisation with 1a (N3-Ph)FeBr2

As can be seen from the gas uptake profiles above, entries 1 and 4 employing 10 µmol of pre-catalyst show the quickest drop in rate as measured by ethylene uptake; these two runs showing exotherms of 110°C and 95°C respectively. In comparison entries 2 and 5 employing 5 µmol of precatalyst show a slower drop in rate as measured by ethylene uptake; these two runs showing exotherms of 50°C and 64°C respectively. Indeed during the first 15 minutes, for entries 2 and 5 it is noted that the absolute rate observed in g/min of ethylene is higher than for entries 1 and 4, even though the amount of pre-catalyst has been halved. In the case of entry 5, it appears that the catalyst has died after 20 min, however this is an artifact of the equipment used to measure the ethylene flow rate which has a lower detection threshold of 0.2 g/min, thus although the catalyst continues to consume ethylene the monitored flow appears as zero. The continued consumption of ethylene is verified by closing the inlet valve to the autoclave for a period of time and watching the pressure drop, re-opening the inlet valve then creates sufficient ethylene flow briefly to register on the flow meter again – as can be seen for example at  $\sim 27$  min. The time axis of the graph is truncated to 40 minutes for clarity, entries 4 and 5 in fact continuing to consume ethylene for 2 hours. The sharp spikes at the beginning of the runs are due to the large volumes of ethylene required to fill the autoclaves combined with changes in ethylene pressure due to the application of cooling to control the initial exotherms. For entry 3 a reasonably stable ethylene uptake is achieved only after 10 minutes due to temperature control, the exotherm never exceeding 40°C; the apparent loss of activity at 25 minutes is in fact due to the liquid level in the autoclave reaching the gas entrainment holes on the stirrer shaft, which greatly reduces the efficiency of ethylene entrainment into solution and in turn impacts upon the rate of catalysis.

#### References

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