One-Pot, One-Step Precatalysts Through Mechanochemistry

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General Methods: All reactions were carried out under air, at ambient temperature (20-22 °C, 44-53% relative humidity). Cobalt(II)chloride hexahydrate, zinc(II)chloride, zinc(II)bromide, diacetylpyridine (1) and anilines 2a-d were purchased from TCI America; p-toluenesulfonic acid monohydrate (TsOH) and chloroform-d (CDCl₃) were purchased from Acros Organics; nickel(II)chloride hexahydrate and copper(II)chloride dihydrate were purchased from Alfa Aesar; manganese(II)chloride tetrahydrate, iron(II)chloride tetrahydrate and MgSO₄ were purchased from Strem Chemicals. All reagents were used as received. Solvents were purchased from Fisher Scientific and used without any further purification. Mechanochemical synthesis was conducted with a SPEX® 8000M high-energy ball mill utilizing 3 x 5 mL stainless steel Smartsnap[™] grinding jars from Form-Tech Scientific housed in a custom aluminum holder (see Fig. 1). Scale-up was conducted on the same mill, in a 65 mL SPEX® 8007 stainless steel grinding jar. NMR samples for timed reactions (Fig. 2) were filtered through Fisher Scientific basix™ 0.2 µm PTFE syringe filters. All NMR spectra were acquired on either a Bruker Avance III HD 400 MHz or Bruker Avance III 500 MHz spectrometer, and processed with Mestrelab's MestReNova 10.0 software. Spectra were referenced to residual CHCl₃ (¹H δ 7.26, ¹³C δ 77.36)¹ and DMSO (¹H δ 2.50, ¹³C δ 39.51)². Mass spectra were acquired on a Bruker EVOQ Qube® Triple Quad using electrospray ionization (ESI). Samples were prepared by serial dilutions to afford 2 ppm concentrations in 1 mL methanol:water (51:49). Elemental analysis (C,H,N) was conducted by Galbraith Laboratories, inc., Knoxville, TN USA.

Mechanochemical Synthesis – **time trials and Zn-species:** In a steel vial, diacetylpyridine **1** 0.0012 mol (200 mg) was mixed with 0.0038 mol of aniline **2a-c**, 10 mg of p-toluenesulfonic acid monohydrate (TsOH), and 200 mg MgSO₄ with (4) 3.175 mm 440c stainless steel balls. The reaction vessel was sealed, and allowed to react under continuous milling for 30-240 mins. When complete an aliquot of the slurry or powder was measured by ¹H NMR spectroscopy, and the % composition was determined by the integration of peaks in the aromatic region (Figures S1-4). To monitor formation of ligand and organometallic, a trial identical to that of **2c** was repeated with the addition of 0.0009 mol (128 mg) of ZnCl₂. A species tentatively assigned as **3c-ZnCl₂** was quantified by the low-intensity but generally well-resolved doublets of the imine-bound para-anisidine signals (¹H NMR CDCl₃; δ , ppm *ca*. 7.5 and 7.0) of the ligand.

Single-crystal X-ray crystallography: Single crystals of the compounds were selected under a microscope and mounted atop a glass fiber or a Mitegen Cryoloop. Intensity data were collected on a Bruker D8 Quest diffractometer equipped with TRIUMPH curved-crystal monochromator, a fine-focus X-ray tube producing Mo K α radiation (λ = 0.71073) and a Photon 100 CMOS detector operating in Shutterless mode at ambient temperature. Frames were collected with APEX3 Suite and integrated with Bruker SAINT software package available within APEX3.³ Absorption effects were corrected using the multi-scan method (SADABS).⁴ Structures were solved by intrinsic phasing methods with ShelXT⁵ and refined with ShelXL⁶ using full-matrix least square minimization on the Olex2⁷ GUI. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were refined as riding models. 2-methoxyaniline in **4d-ZnCl**₂ was disordered and was modeled using the PART instruction available within SHELXL. The data quality of **4b-MnCl**₂ was poor owing to weakly diffracting thin needles (0.23 x 0.02 x 0.03 mm³) and as a result, the *R*_{int} value was over 45%. In addition, the solvent CH₂Cl₂ could not be modeled satisfactorily and its electron density was removed by using 'Solvent Mask' command within Olex2. Molecular graphics were drawn using CrystalMaker 9⁸ or Olex2.



Figure S1. ¹H NMR spectra in CDCl₃ for the mechanochemical reaction of **1** and **2a** as a function of time. *Each* measurement represents a discreet sample terminated at the note 30 minute intervals; time 0 = 1 alone.



Figure S2. ¹H NMR spectra in CDCl₃ for the mechanochemical reaction of **1** and **2b** as a function of time. *Each* measurement represents a discreet sample terminated at the note 30 minute intervals; time 0 = 1 alone.



Figure S3. ¹H NMR spectra in CDCl₃ for the mechanochemical reaction of **1** and **2c** as a function of time. *Each* measurement represents a discreet sample terminated at the note 30 minute intervals; time 0 = 1 alone.



Figure S4. ¹H NMR spectra in CDCl₃ for the mechanochemical reaction of **1**, **2c** and ZnCl₂ as a function of time. *Each* measurement represents a discreet sample terminated at the note 30 minute intervals, samples 90-240 min. are run in duplicate; time $0 = \mathbf{1}$ alone. Note: shift in peak positions are attributed to extensive H-bonding between the various mixture components.



Figure S5. %composition determined by ¹H NMR spectra in $CDCl_3$ for the mechanochemical reaction of **1** and **2a** (A), **2b** (B), **2c** (C) and **2c** + $ZnCl_2$ (D) as a function of time. *Color coding is referenced in Scheme S1.*



Scheme S1. . Formula for the mechanochemical synthesis of (i) **3(a-c)** and **4(a-c)**, and (ii) **3c**, **4c**, and ultimately **4c**-**ZnCl**₂ with proposed **3c-ZnCl**₂ as minor component. *Color coding correlates to Figure 5S*.



Figure S6. (A) Concentration of **1** as a function of free volume vs time, (B) $\ln[1]$ vs time, and concentration of **4** as a function of free volume vs time for reactions involving **2a**, **2b**, **2c**, and **2c** + ZnCl₂. * = **4c-ZnCl**₂ in the case of **2c** + ZnCl₂.

Mechanochemical Synthesis – **4c-ZnCl**₂ & **4d-ZnCl**₂: A similar protocol as described in the time-screening trials (*see above*) was followed for the formation of **4c-ZnCl**₂, with 0.0009 mol (128 mg) of ZnCl₂ added to the reaction mixture. This protocol was again repeated for analogous species **4d-ZnCl**₂. When milling was complete, the powder/slurry was washed with minimal toluene, then the powder allowed to sit in minimal dichloromethane to solubilize, extract and separate product from MgSO₄. The intensely colored solution was concentrated *in-vacuo* and allowed to precipitate overnight at -25 °C. The powders were isolated by filtration, and dried to remove residual solvent. Both bright yellow powders were isolated in 76% (349 mg **4c-ZnCl**₂) and 73% (335 mg **4d-ZnCl**₂) yield. Products were identified by NMR, elemental analysis (EA), ESI-MS, and single-crystal X-ray diffraction measurements. Single crystals suitable for analysis were grown by slow diffusion of hexanes into a saturated solution of CH₂Cl₂ (**4c-ZnCl**₂) or CDCl₃ (**4d-ZnCl**₂) at -25 °C. Synthesis of **4c-ZnCl**₂ was scaled-up 5 x: **1** 0.006 mol (1000 mg) was mixed with 0.019 mol of **2c**, 0.0047 mol (640 mg) of ZnCl₂, 50 mg of p-toluenesulfonic acid monohydrate (TsOH), and 600 mg MgSO₄ with (4) 12.7 mm ss balls and milled for 4 h continuously on a SPEX[®] 8000M mill (18 Hz). The isolated yield over one single crop was 78% (1.87 g).

2,6-Bis{1-[(4-methoxyphenyl)imino]ethyl}pyridine zinc chloride (4c-ZnCl₂) ¹H NMR (500 MHz, CDCl₃; δ, ppm) 8.36 (t, ³J_{H-H} = 7.8 Hz, 1H, py_p-H), 8.15 (d, ³J_{H-H} = 7.9 Hz, 2H, py_m-H), 7.35 (d, ³J_{H-H} = 8.5 Hz, 4H, Ph_m-H), 6.94 (d, ³J_{H-H} = 8.5 Hz, 4H, Ph_o-H), 3.81 (s, 6H, O-CH₃), 2.53 (s, 6H, N=C(CH₃)). ¹³C{¹H} NMR (125 MHz, CDCl₃; δ, ppm) 160.42 (C_q), 158.33 (C_q), 149.57 (C_q), 143.21 (C_q), 138.74 (C_q), 125.20 (Ar-CH), 123.86 (Ar-CH), 114.26 (Ar-CH), 55.47 (O-CH₃), 16.98 (N=C(CH₃)). EA predicted C 54.20%, H 4.55%, N 8.24%, observed C 53.71%, H 4.26%, N 8.12%, m/z [M+1] 508.05. See Figure S10 for X-ray structure.



Figure S7. ¹H (*left*) and ¹³C (*right*) NMR spectra in CDCl₃ for **4c-ZnCl₂**.

2,6-Bis{1-[(2-methoxyphenyl)imino]ethyl}pyridine zinc chloride (4d-ZnCl₂) ¹H NMR (500 MHz, CDCl₃; δ, ppm) 8.36 (t, ³*J*_{*H*-H} = 7.9 Hz, 1H, py_p-H), 8.16 (d, ³*J*_{*H*-H} = 7.9 Hz, 2H, py_m-H), 7.79 (d, ³*J*_{*H*-H} = 7.8 Hz, 2H, Ph_m-H), 7.21 (t, ³*J*_{*H*-H} = 7.8 Hz, 2H, Ph_m-H), 7.04 (t, ³*J*_{*H*-H} = 7.6 Hz, 2H, Ph_p-H), 6.98 (d, ³*J*_{*H*-H} = 8.2 Hz, 2H, Ph_o-H), 3.79 (s, 6H, O-CH₃), 2.37 (s, 6H, N=C(CH₃)). ¹³C{¹H} NMR (125 MHz, CDCl₃; δ, ppm) 163.12 (C_q), 149.18 (C_q), 143.24 (C_q), 134.89 (C_q), 127.42 (Ar-CH), 125.36 (Ar-CH), 124.49 (Ar-CH), 121.33 (Ar-CH), 112.28 (Ar-CH), 56.26 (O-CH₃), 17.46 (N=C(CH₃)). EA predicted C 54.20%, H 4.55%, N 8.24%, observed C 52.90%, H 4.68%, N 7.92%, m/z [M+Na] 530.04. See Figure S11 for X-Ray structure.



Figure S8. ¹H (*left*) and ¹³C (*right*) NMR spectra in CDCl₃ for 4d-ZnCl₂.

Mechanochemical Synthesis – screening transition metal complexes: In a steel vial 300 mg of $MX_2(H_2O)_n$ (X = CI: M = Cu, n = 2; M = Mn, Fe, n = 4; M = Co, Ni, n = 6; M = Zn, n = 0, X = Br) was mixed with 1.2 mol equiv. diacetylpyridine 1, 3 mol equiv. of aniline 2a-c, 10 mg of p-toluenesulfonic acid monohydrate (TsOH), and 200 mg MgSO₄ with (4) 3.175 mm 440c stainless steel balls. The reaction vessel was sealed, and allowed to react under continuous milling for 8 h. When complete, the powder/slurry was washed with minimal hexanes or toluene (for 2c), then the powder allowed to sit in minimal dichloromethane to solubilize, extract and separate product from MgSO₄. The intensely colored solution was concentrated in-vacuo and allowed to precipitate overnight at -25 °C. The powders were isolated by filtration, and dried to remove residual solvent. Isolated yields and corresponding colors are as follows: 4a-CuCl₂ (727 mg, 82%, yellow); 4c-CuCl₂ (760 mg, 85%, orange); 4a-ZnBr₂ (460 mg, 58%, yellow); 4a-NiCl₂ (504 mg, 80%, amber); 4b-MnCl₂ (555 mg, 70%, pale orange); 4c-MnCl₂ (613 mg, 81%, orange); 4b-CoCl₂ (505 mg, 76%, green); 4b-FeCl₂ (625 mg, 79%, dark blue). Products were identified by elemental analysis (EA), ESI-MS, and when suitable single crystals could be grown, single-crystal X-ray diffraction measurements. Single crystals suitable for analysis were grown by slow diffusion of hexanes into a saturated solution of product in CH₂Cl₂ at -25 °C. Diamagnetic Zn-based species 4b-ZnBr₂ was further confirmed by ¹H and ¹³C NMR. Due to the purification process (reprecipitation/crystallization from CH2Cl2), EA results for 4b-MnCl2 and 4b-ZnBr2 are indicative of solvent incorporation. 4c-CuCl₂ predicted C 54.39%, H 4.56%, N 8.27%, observed C 53.85%, H 4.89%, N 8.04%, m/z [M+Na] 529.04; 4a-CuCl₂ predicted C 59.58%, H 5.40%, N 8.34%, observed C 58.28%, H 5.24%, N 7.78%, m/z [M+1] 503.098; 4a-NiCl₂ isolated as [4a-NiCl₂]₂[CH₂Cl₂]₁ predicted C 56.55%, H 5.21%, N 7.76%, observed C 56.94%, H 5.29%, N 7.59%, m/z [M+H] 497.8; 4c-MnCl, predicted C 55.33%, H 4.64%, N 8.42%, observed C 54.94%, H 5.10%, N 8.49%, m/z [M+1] 499.062; **4b-MnCl₂** isolated as [4b-MnCl₂]₃[CH₂Cl₂]₁ predicted C 59.51%, H 5.79%, N 7.62%, observed C 59.93%, H 6.07%, N 7.76%, m/z [M+1] 523.2; **4b-CoCl₂** predicted C 61.49%, H 5.92%, N 7.97%, observed C 62.38%, H 6.34%, N 7.55%, m/z [M+1] 527.135; **4b-FeCl**, predicted C 61.85%, H 5.96%, N 8.01%, observed C 62.21%, H 5.94%, N 7.43%, m/z [M+1-Cl,THF_{adduct}] 561.209. 4a-ZnBr₂ isolated as [4b-ZnBr₂]₂[CH₂Cl₂]₁ predicted C 48.07%, H 4.43%, N 6.60%, observed C 47.74%, H 4.29%, N 6.64%, m/z [M+Na] 613.98, ¹H NMR (400 MHz, DMSO; δ, ppm) 8.47 (d, ³J_{HH} = 7.8 Hz, 2H, py_m-H), 8.12 (t, ³J_{H-H} = 7.9 Hz, 1H, py_p-H), 7.09 (d, ³J_{H-H} = 7.4 Hz, 4H, Ph_m-H), 6.92 (t, ³J_{H-H} = 7.1 Hz, 2H, Ph_p-H), 2.18

(s, 6H, N=C(CH₃)), 1.97 (s, 12H, Ph_o-CH₃) 13 C{¹H} NMR (125 MHz, DMSO; δ, ppm) 167.10 (C_q), 155.03 (C_q), 148.89 (C_q), 138.25 (C_q), 128.30 (Ar-CH), 125.15 (Ar-CH), 123.35 (Ar-CH), 122.74 (Ar-CH), 18.04 (Ph_o-CH₃), 16.74 (N=C(CH₃)).



Figure S9. (A) ¹H and (B) ¹³C NMR spectra in CDCl₃ of 4a-ZnBr₂.

	4c-ZnCl ₂ (CCDC# 1948354)	4d-ZnCl ₂ (CCDC# 1948355)	4c-MnCl₂ (CCDC# 1948358)
Empirical formula	$C_{24}H_{25}CI_4N_3O_2Zn$	$C_{31}H_{33}CI_5N_4O_3Zn$	$C_{23}H_{23}CI_2MnN_3O_2$
Formula weight	594.64	752.23	499.28
Temperature/K	296	296	296
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	<i>P</i> 2 ₁ /n	P21/c
a/Å	16.398(3)	13.123(1)	9.499(2)
b/Å	16.137(3)	18.312(1)	16.286(3)
c/Å	20.361(3)	14.510(1)	15.947(3)
α/°	90	90	90
β/°	90	98.320(2)	103.854(3)
γ/°	90	90	90
Volume/Å ³	5387.6(2)	3450.0(4)	2395.4(7)
Z	8	4	4
$\rho_{calc}g/cm^3$	1.466	1.448	1.384
μ/mm ⁻¹	1.335	1.137	0.798
F(000)	2432.0	1544.0	1028.0
Crystal size/mm ³	$0.26 \times 0.19 \times 0.16$	$0.21 \times 0.15 \times 0.08$	0.22 × 0.13 × 0.07
Radiation	ΜοΚα (λ = 0.71073)	ΜοΚα (λ = 0.71073)	ΜοΚα (λ = 0.71073)
20 range for data collection/°	5.922 to 52.742	5.926 to 52.902	5.826 to 49.608
Index ranges	-21 ≤ h ≤ 21, -20 ≤ k ≤ 20, -25 ≤ l ≤ 25	$-16 \le h \le 16$, $-22 \le k \le 22$, $-18 \le l \le 18$	-11 ≤ h ≤ 11, -19 ≤ k ≤ 19, -18 ≤
Reflections collected	61770	72553	28491
Independent reflections	5505 [R_{int} = 0.0616, R_{sigma} = 0.0300]	7076 [R _{int} = 0.0423, R _{sigma} = 0.0258]	4119 [R _{int} = 0.2177, R _{sigma} = 0.1587]
Data/restraints/parameters	5505/0/311	7076/0/475	4119/0/272
Goodness-of-fit on F ²	1.058	1.015	1.027
Final R indexes [I>=2σ (I)]	R ₁ = 0.0493, wR ₂ = 0.1346	$R_1 = 0.0432$, $wR_2 = 0.0995$	$R_1 = 0.0845$, $wR_2 = 0.1436$
Final R indexes [all data]	R ₁ = 0.0711, wR ₂ = 0.1476	$R_1 = 0.0667$, $wR_2 = 0.1106$	R ₁ = 0.1955, wR ₂ = 0.1809
Largest diff. peak/hole / e Å-3	0.70/-0.38	0.56/-0.57	0.47/-0.29

 Table S1.
 X-ray crystallographic data.

	4a-NiCl ₂ (CCDC# 1948357)	4b-MnCl ₂ (CCDC# 1948356)	
Empirical formula	$C_{26}H_{29}Cl_4N_3Ni$	$C_{27}H_{31}Cl_2MnN_3$	
Formula weight	584.03	523.39	
Temperature/K	296	296	
Crystal system	orthorhombic	monoclinic	
Space group	Pna21	P21/n	
a/Å	17.253(2)	14.55(1)	
b/Å	14.716(1)	14.92(1)	
c/Å	22.123(2)	14.95(1)	
α/°	90	90	
β/°	90	107.55(3)	
γ/°	90	90	
Volume/ų	5616.7(8)	3093(5)	
Z	8	4	

ρ _{calc} g/cm ³	1.381	1.124
μ/mm ⁻¹	1.091	0.616
F(000)	2416.0	1092.0
Crystal size/mm ³	$0.335 \times 0.16 \times 0.07$	0.23 × 0.03 × 0.02
Radiation	ΜοΚα (λ = 0.71073)	ΜοΚα (λ = 0.71073)
20 range for data collection/°	5.776 to 52.742	5.718 to 49.422
Index ranges	$-21 \leq h \leq 21, -18 \leq k \leq 18, -27 \leq l \leq 27$	-17 ≤ h ≤ 10, -14 ≤ k ≤ 17, -16 ≤ l ≤ 17
Reflections collected	106974	16161
Independent reflections	11480 [$R_{int} = 0.0848$, $R_{sigma} = 0.0513$]	5261 [R _{int} = 0.4523, R _{sigma} = 0.6807]
Data/restraints/parameters	11542/1/625	5261/12/294
Goodness-of-fit on F ²	1.023	0.876
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0547$, $wR_2 = 0.1202$	$R_1 = 0.1202$, $wR_2 = 0.2561$
Final R indexes [all data]	$R_1 = 0.0947$, $wR_2 = 0.1394$	$R_1 = 0.3613$, $wR_2 = 0.3662$
Largest diff. peak/hole / e Å-3	0.49/-0.54	0.60/-0.68
Flack parameter	0.07(3)	N/A



Figure S10. X-ray structure of $4c-ZnCl_2$ with hydrogens and interstitial CH_2Cl_2 omitted for clarity showing atom labeling scheme. Thermal ellipsoids are drawn at 50% probability level.

Table S2. Selected bond lengths (Å) and angles (°) for $4c\text{-}ZnCl_2.$

Zn1	Cl1		2.2427(11)
Zn1	Cl2		2.2382(11)
Zn1	N1		2.086(3)
Zn1	N2		2.264(3)
Zn1	N3		2.240(3)
Cl1	Zn1	N2	98.21(9)
Cl2	Zn1	Cl1	115.74(4)
Cl2	Zn1	N2	101.45(9)
Cl2	Zn1	N3	95.91(9)
N1	Zn1	Cl1	125.71(9)
N1	Zn1	Cl2	118.48(9)
N1	Zn1	N2	74.04(12)

N1	Zn1	N3	73.66(11)
N3	Zn1	Cl1	98.54(9)
N3	Zn1	N2	147.61(11)



Figure S11. X-ray structure of **4d-ZnCl**₂ with hydrogens and PART 2 of the disordered 2-methoxyaniline are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Zn1	Cl1		2.2515(8)
Zn1	Cl2		2.2309(8)
Zn1	N1		2.072(2)
Zn1	N2		2.245(2)
Zn1	N3		2.269(2)
Cl1	Zn1	N3	98.54(6)
Cl2	Zn1	Cl1	120.17(3)
Cl2	Zn1	N2	95.39(6)
Cl2	Zn1	N3	97.66(6)
N1	Zn1	Cl1	115.57(6)
N1	Zn1	Cl2	124.26(6)
N1	Zn1	N2	74.62(8)
N1	Zn1	N3	73.94(8)
N2	Zn1	Cl1	99.81(6)
N2	Zn1	N3	148.08(8)

Table S3. Selected bond lengths (Å) and angles (°) for 4d-ZnCl₂



Figure S12. X-ray structure of 4c-MnCl₂ with hydrogens omitted for clarity. Thermal ellipsoids at 50% probability.

Table S4. Selected bond lengths ((Å)) and	angles	(°)	for	4c-N	/InCl	2
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Mn1	Cl1		2.348(2)	
Mn1	Cl2		2.326(2)	
Mn1	N1		2.216(5)	
Mn1	N2		2.320(6)	
Mn1	N3		2.289(6)	
Cl2	Mn1	Cl1	114.36(8)	
N1	Mn1	Cl1	127.57(15)	
N1	Mn1	Cl2	118.02(15)	
N1	Mn1	N2	71.0(2)	
N1	Mn1	N3	71.2(2)	
N2	Mn1	Cl1	99.46(16)	
N2	Mn1	Cl2	103.16(15)	
N3	Mn1	Cl1	99.86(16)	
N3	Mn1	Cl2	98.22(15)	
N3	Mn1	N2	141.9(2)	



Figure S13. X-ray structure of **4a-NiCl₂** with hydrogens omitted for clarity. The asymmetric unit is shown on the left and the individual units are on the right. Thermal ellipsoids are drawn at 50% probability level.

Table S5. Selected bond lengths (Å) and angles (°) for 4a-NiCl₂.

Ni1	Cl1		2.260(3)
Ni1	Cl2		2.241(3)
Ni1	N1		1.975(6)
Ni1	N2		2.227(7)
Ni1	N3		2.205(7)
Ni2	Cl3		2.242(3)
Ni2	Cl4		2.261(3)
Ni2	N4		1.981(6)
Ni2	N5		2.214(7)
Ni2	N6		2.218(7)
Cl2	Ni1	Cl1	119.75(11)
N1	Ni1	Cl1	110.3(2)
N1	Ni1	Cl2	129.9(2)
N1	Ni1	N2	76.1(3)
N1	Ni1	N3	77.1(3)
N2	Ni1	Cl1	95.89(18)
N2	Ni1	Cl2	96.8(2)
N3	Ni1	Cl1	95.37(19)
N3	Ni1	Cl2	98.6(2)
N3	Ni1	N2	153.1(2)
Cl3	Ni2	Cl4	118.85(11)
N5	Ni2	N6	153.2(3)
N6	Ni2	CI3	96.8(2)
N6	Ni2	Cl4	95.68(19)



Figure S14. X-ray structure of **4b-MnCl₂** showing the atom labeling scheme with hydrogens omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table S6. Selected bond lengths (Å) and angles (°) for 4b-MnCl₂.

Mn1	Cl1		2.319(5)
Mn1	Cl2		2.363(6)
Mn1	N1		2.26(1)
Mn1	N2		2.32(1)
Mn1	N3		2.33(2)
Cl1	Mn1	Cl2	114.1(2)
Cl1	Mn1	N2	100.9(3)
Cl1	Mn1	N3	99.2(4)
N1	Mn1	Cl1	123.3(4)
N1	Mn1	Cl2	122.5(4)
N1	Mn1	N2	69.2(5)
N1	Mn1	N3	72.9(6)
N2	Mn1	Cl2	99.1(4)
N2	Mn1	N3	142.1(5)
N3	Mn1	Cl2	101.6(4)

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