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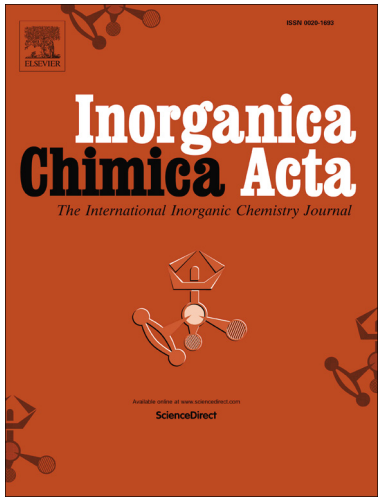

Research paper

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Synthesis and characterization of N,N-chelate manganese complexes and applications in C–N coupling reactions

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Abstract Bidentate NN-ligands have been derived from the reaction between aldehydes and 2-(aminomethyl)pyridine. The treatment of these ligands with $Mn(CO)_5Br$ gave complexes that are highly bench stable. The complexes were characterized by various analytical and spectral methods. Single-crystal XRD of complex **Mn-2** was performed, which indicates an octahedral geometry around the metal center. The complexes efficiently catalyze the *N*-alkylation of anilines with alcohols under optimized reaction conditions.

Keywords: Manganese; Non-pincer ligand; C–N Coupling reactions; Phosphine free; Amines; X-Ray structure

1. Introduction:

Nitrogen-containing compounds such as amines and imines are important building constituents for bioactive molecules, pharmaceuticals, herbicides, and dyestuffs[1]. The development of sustainable routes for the construction of C-N bonds is of substantial interest for synthetic chemists. The traditional methods for their synthesis involve the substitution of alkyl halides, triflates, tosylates, and mesylates with amines[2]. However, over-alkylation, as well as the formation of copious waste, limits the applicability of these methods. An alternate pathway employs the reductive amination with aldehydes, ketones, and carboxylic acids[1e, 3] in the presence of stoichiometric hydride transfer agents. However, this also suffers from low functional group tolerance and generation of substantial metal waste.

Of late, the borrowing hydrogen (BH) methodology, also known as hydrogen auto-transfer[2a, 4] employing suitable metal catalyst, have been developed as a greener and atom economical way to synthesize alkylated amines. This three-step technique can be achieved in one pot utilizing the readily available, cheap and less noxious alcohols as starting materials and therefore gained recognition in the perspective of sustainable development. In this process, initially, the alcohol is dehydrogenated to aldehyde, followed by condensation with an amine to generate the imine. Hydrogenation of the imine by the hydrogen borrowed in the preliminary step yields the saturated amine. In 1981, Grigg[5] and Watanabe[6] group individually reported Rh- and Ru- catalyzed synthesis of *N*-alkylated amines based on this borrowing hydrogen strategy for the first time. Nevertheless, the methods suffered from the lack of product selectivity as both secondary and tertiary amines formed under such harsh conditions (≥ 180^{o}C). Over the past few decades, a diverse range of homogeneous and heterogeneous catalysts based on noble metals Ru[4a, 4c, 7], Rh[7s], Ir[7m, 8], Pd[7m, 9], Pt[4d, 10], Ta[11], Au[12] have been synthesized and utilized efficiently for C-N bond formation. However, due to the toxicity, sparse availability, and high-cost, numerous efforts have been made for the replacement of these precious metals by their lower congeners. Indeed, significant progress has been achieved with Fe[13], Co[7m, 14], Ni[4d, 7m, 15] and Mn[4e, 16], Cu[17] based catalysts for C–N bond formation reactions. In this context, the groups of Feringa[13a], Barta[13a, 13c, 15c], Saito (Fe catalyst), Beller[4e, 16a], Milstein[4e, 18] (Mn catalyst), Zheng[14a], Kempe[14b, 16d] (Co, Mn catalyst) have made prominent contribution.

After iron and titanium, manganese is the third most abundant transition metal in Earth's crust and is less toxic and economically amiable. It envisioned as a potential replacement for its higher congeners. Milstein[18] and co-workers utilized a PNP-pincer based manganese catalyst for coupling of amines with alcohols which yielded aldimines. Pioneering work in the field of *N*-alkylation with manganese catalyst was demonstrated by Beller[16a] and co-workers, using an Mn(I)-PNP pincer based catalyst. After that, in 2017, Kirchner[19] and Sortais[16b] groups also reported phosphine based PNP-pincer manganese complexes for *N*-alkylation of primary amines. Although these phosphine-based catalyst systems have achieved immense success in this field, the toxicity, high cost, and operational difficulties demand other alternative ligand systems. In 2018, Balaraman *et al*.[16e] reported in-situ generated manganese catalyst with pincer NNN and salen based ligands for this transformation.

Srimani et al. have developed NNS-Mn complexes for the C–N bond formation reaction [16f]. Very recently, Ke *et al*.[16h] developed N-heterocyclic carbene based Mn catalyst for *N*-alkylation of anilines with alcohols.

Our group also reported manganese catalyzed olefination of heteroaryl moieties[20], and sulfones[21], α-alkylation of ketones[22], and nitriles[23], and hydroboration of carboxylic acids[24] with different homogeneous manganese catalysts. Maintaining our focus on homogeneous manganese catalysis, herein, we are reporting the synthesis of two phosphine-free bidentate non-pincer manganese complexes and their applications in selective *N*-alkylation of amines with alcohols. The developed method requires very low catalyst loading (2 mol%) to achieve the complete conversion to the product without the necessity for functional group manipulations. In the viewpoint of environmental concern, this method is sustainable as water is forming as the only byproduct.

2. Experimental

2.1. General

All commercially available chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, TCI, and Avra Synthesis and used without further purification. Non-halogen containing solvents were dried over calcium hydride. THF was dried over sodium/benzophenone and distilled under argon atmosphere. The solvents were degassed with argon and stored over activated 4 Å molecular sieves. Merck pre-coated TLC plates (silica gel 60 F254 0.25mm) were used for thin-layer chromatographic (TLC) analysis and spots were visualized by UV light (254nm), $KMnO_4$, and under I_2. FT-IR spectra were collected on Bruker ATR and Perkin-Elmer FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded using Bruker mass spectrometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using Bruker (^{1}H: 500 MHz, ^{13}C: 126 MHz) and JEOL (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer employing $CDCl_3$ as solvent and peaks are reported as δ (ppm) with reference to the resonance of the solvent. Coupling constant (*J*) values are reported in Hz. Multiplicity patterns are stated as follows: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet).

Crystal of **Mn-2** was mounted on glass fibers and data were collected at 100 K using an AGILENT SUPERNOVA SINGLE CRYSTAL XRD diffractometer. Graphite monochromated Cu-Kα radiation (λ = 1.54184 Å) was used throughout. The absorption corrections were done by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structure was solved by direct methods using the program SHELXS. Refinements and all other calculations were carried out using SHELXL-97. The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. Atomic scattering factors were incorporated in the computer programs.

2.2. Synthesis of ligands

L1-3: [25] The ligands were prepared according to the following modified procedures. Aldehyde (2.0 mmol) and 2-(aminomethyl)pyridine (2.1 mmol) are mixed in methanol, and then sodium sulfate (2.5 mmol) was added. The reaction mixture was stirred at 35 °C for 12 h and then filtered. To the filtrate was added $NaBH_4$ (4.0 mmol) and heated at 45 °C for 1 h. The solvent was removed under vacuum resulting in a white paste. The organic part was extracted with DCM and purified using flash column chromatography. The ligands were obtained as a yellow oil. The spectral data resembles that reported in the literature[25].

L4: A solution of N-(2-(methylthio)benzyl)-1-(pyridin-2-yl)methanamine (**L1**) (0.5 mmol) in dry THF (3 ml) was cooled to 0 °C and NaH (1.5 equiv.) was added in one portion. The resulting mixture was stirred at that temperature for 30 mins and methyl iodide (1.5 equiv.) was added dropwise. The solution was warmed to room temperature and stirred overnight during which the color changed from yellow to orange. The reaction was quenched with water, the organic part was extracted with EtOAc and purified using flash column chromatography. Yield: 65%. Selected **IR** (ATR, cm^{-1}): 1568, 1550, 1450, 1416, 1226, 1055, 1016, 957, 863, 736, 669. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.64 (td, *J* = 7.7, 1.7 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 3.8 Hz, 2H), 7.15 – 7.06 (m, 2H), 3.73 (s, 2H), 3.68 (s, 2H), 2.47 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.1, 148.9, 139.0, 137.2, 136.6, 129.8, 127.8, 125.7, 124.6, 123.3, 122.0, 63.7, 60.5, 42.2, 16.2. **HRMS:** Calculated for [$C_{15}H_{19}N_2S^+$; $[M+H]^+$] 259.1263, found 259.1264.

2.3. Synthesis of manganese (I) complexes

Mn 1 and **Mn-2:** To a solution of the ligand (1 equiv.) in dry THF (0.05 M) was added $Mn(CO)_5Br$ (1.05 equiv.) under argon atmosphere. The resulting yellow colored solution was heated at 90 °C for 3h, during which time the color changes to dark orange or brown. The solution was cooled to ambient temperature, and the solvent was removed under vacuum. The resulting orange or yellow residue was washed with hexane and dried under vacuum to yield the complexes as orange or yellow-colored solid. Single crystals for the complexes were obtained by slow diffusion of diethyl ether into a saturated solution of the complex in THF.

Mn-4: Following the procedure described for **Mn-1** to **2** a orange colored solid was formed. THF (0.05 M) was added to the orange solid and the light-yellow precipitate was formed. The aliquot was decanted, and the precipitate was washed with THF (2 times), dried under vacuum.

Mn-1 The complex was synthesized following the above-mentioned procedure in 90% yield as yellow solid. **Mp**: 76-78 °C, Selected **IR** (CH_2Cl_2, cm^{-1}): 3045, 2928, 2860, 2025 (s, ν_{CO}), 1962 (ν_{CO}), 1913 (ν_{CO}), 1605, 1478, 1429, 1088, 751, 697. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.00 (s, *o*-**H** of Py 1H), 7.73 (br s, 1H), 7.53 – 6.93 (m, 6H), 5.10 – 4.72 (m,-NHC**H**$_2$Py, 1H), 4.69 – 4.35 (m, -NHC**H**$_2$Py, 1H), 4.17 [br s,-NHC**H**$_2$(*o*-SMeC$_6$H$_4$), 1H], 3.97 [s, -NHC**H**$_2$(*o*-SMeC$_6$H$_4$), 1H], 2.53 (s,-SC**H**$_3$, 3H). [Py = Pyridyl]. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 222.9, 221.4, 221.1, 158.9, 153.8, 138.4, 138.2, 133.6, 130.8, 129.8, 127.1, 125.7, 124.7, 121.3, 58.6, 56.9, 16.2. **HRMS**: Calculated for [$C_{17}H_{16}MnN_2O_3S$; [M – Br]$^+$] 383.0262, found 383.0188.

Mn-2 The complex was synthesized following the procedure mentioned above in 91% yield as orange solid. **Mp**: 140 – 142 °C. Selected **IR** (ATR, cm^{-1}): 3190, 2888, 1991 (s, ν_{CO}), 1903 (s, ν_{CO}), 1852 (s, ν_{CO}), 1589, 1427, 1048, 971, 763, 681. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.99 (br s, *o*-**H** of Py, 1H), 7.78 (br s, 1H), 7.36 (br s, 2H), 4.43 (s, -NHC**H**$_2$Py, 1H), 3.96 (s, -NHC**H**$_2$Py, 1H), 3.75 (s, -NHC**H**$_2$Cy, 1H), 3.22 (s, -NHC**H**$_2$Cy, 1H), 2.99 (s,-N**H**, 1H), 1.79 (br s, 6H), 1.45 – 0.74 (m, 7H). [Py = Pyridyl, Cy = Cyclohexyl]. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 222.8, 221.3, 221.1, 158.9, 153.8, 138.2, 124.8, 121.2, 63.4, 58.1, 35.5, 31.2, 29.9, 26.2, 25.7, 25.55. **HRMS**: Calculated for [$C_{16}H_{20}MnN_2O_3$; [M – Br]$^+$] 343.0854, found 343.0836.

Mn-4 The complex was synthesized following the procedure mentioned above in 70% yield as yellow solid. Selected **IR** (ATR, cm^{-1}): 2001 (ν_{CO}), 1909 (ν_{CO}), 1897 (ν_{CO}), 1591, 1446, 1427, 1283, 946, 846, 761, 747, 669. **HRMS**: Calculated for [$C_{18}H_{18}MnN_2O_3S$; [M – Br]$^+$] 397.0419, found 397.0420.

2.4. Synthetic procedure for N-alkylation of amines with alcohols

In a 10 mL screw-capped vial was placed 2.0 mol% of manganese(I) catalyst, 40 mol% of the base, 0.1 mL of toluene, 0.4 mmol of alcohol and 0.2 mmol of amine under argon atmosphere. The reaction mixture was heated at 140 °C for 24 h in an oil bath. The reaction mixture was then cooled at ambient temperature, quenched with water, and the organic layers were extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated. The product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane as eluent.

3. Results and discussions

3.1. Synthesis and characterization of manganese(I) complexes

The secondary amine-based ligands (**L1-3**) were prepared by the reductive amination of 2-(aminomethyl)pyridine with aldehydes, 2-(methylthio)benzaldehyde, cyclohexyl carboxaldehyde, and benzaldehyde, respectively (**Scheme 1**). The ligand **L4** was synthesized by the substitution of N-H proton by a methyl group using methyl iodide. The N,N-chelate Mn(I) complexes (**Mn-1**, **Mn-2** and **Mn-4**) were synthesized by treating a solution of amine-based ligands in THF with $MnBr(CO)_5$ at 90 °C for 3 h in 1:1.05 M ratio (**Scheme 1**). The manganese complexes were obtained in 90, 91 and 97% yields, respectively and are highly stable in air. For characterization of these complexes, analytical, spectroscopic methods (IR, ^{1}H, ^{13}C NMR, and HRMS) were employed. X-ray crystallography for **Mn-1** and **Mn-2** are described below. The reaction of **L3** with $Mn(CO)_5Br$ resulted in a mixture of compounds, which shows broad ^{1}H NMR spectra. At present, we are unable to purify and characterize it.

3.2. Spectroscopy studies

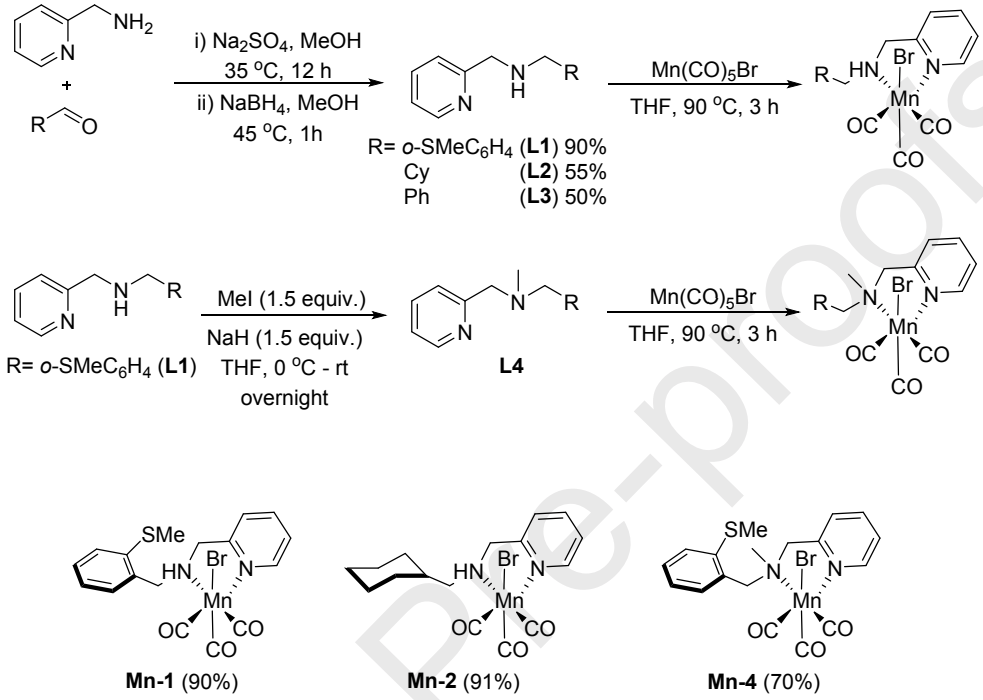
In the IR spectra of the manganese(I) complexes three bands characteristic to terminal ν_{CO} was observed. For **Mn-1**, three strong bands distinctive to ν_{CO} appeared at 2025 cm^{-1}, 1962 and 1913 cm^{-1}. However, for **Mn-2**, one of the three bands corresponding to ν_{CO} was observed at 2023 cm^{-1} and the other two bands observed at 1926, and 1907 cm^{-1} overlapped with each other. The three carbonyl stretching frequencies for **Mn-4** were observed at 2001, 1909, 1897 cm^{-1}. Vibrations corresponding to the presence of aliphatic and aromatic bonds also appeared in normal positions. The IR spectra of the three complexes thus confirm the bidentate binding mode of the secondary amine-based ligands to the metal center.

The ^{1}H NMR spectra of the complexes show downfield chemical shifts in comparison to the free ligand. The singlets that observed at 3.91 and 3.93 ppm corresponding to the -C**H**$_2$-NH-C**H**$_2$- protons in **L1** shifted to downfield 5.10 – 4.72 (m, 1H), 4.69 – 4.35 (m, 1H), 4.17 (br s, 1H), 3.97 (s, 1H) ppm in the complex (**Mn-1**) due to the coordination of the nitrogen atom to Mn(I), also their splitting pattern is changed due to the presence of diastereotopic -C**H**$_2$- protons in the complex. Signals characteristic to the aromatic proton of pyridine ring at 8.55 ppm also shifted to 9.00 ppm suggesting deshielding upon the coordination of pyridine nitrogen to Mn(I). The ^{13}C NMR spectra are also conclusive about the composition of the complex. For the uncoordinated ligands, the peaks corresponding to -**C**H$_2$-NH-**C**H$_2$- were observed at 54.8 and 51.5 ppm. Upon coordination and complex formation, these signals showed a downfield shift to 58.6 and 56.9 ppm. The signals due to the aromatic carbons also changed considerably from that of free ligand. These shifts are very much conclusive about the coordination of ligands and the formation of the complex. The signals for terminal C≡O carbon atoms for **Mn-1**.was observed at 222.9, 221.4, and 221.1ppm.

For **Mn-2,** similar shifts and change in splitting patterns observed in the ^{1}H NMR spectra. For free ligands the signal

due to the presence of -C**H**$_2$-NH-C**H**$_2$- protons were shifted from 3.87 (s, 2H) and 2.47 (d, J = 6.6 Hz, 2H) to 3.96 (s, 1H), 3.75 (s, 1H), 3.22 (s, 1H), 2.99 (s, 1H) indicative of nitrogen coordination. Signals due to the coordination of the pyridine nitrogen atom also shifted to downfield 8.98 ppm from 8.53 ppm. In ^{13}C NMR spectra, the expected signals for three-terminal C≡O bonds observed at 222.8, 221.3, and 221.1 ppm. The two carbon atoms adjacent to nitrogen exhibited signals at 56.5 and 55.5 ppm in the free ligand, whereas in the complex they shifted at 63.4 and 58.1 ppm, respectively due to deshielding upon coordination of nitrogen. Aromatic carbons also showed considerable shift upon complex formation.

All these spectral data are indicative of coordination of nitrogens in bidentate fashion to manganese(I) center and formation of distinct complexes.



Scheme 1 Synthesis of manganese (I) complexes

3.3. Crystal structure of manganese(I) complexes

The crystals of **Mn-1** & **Mn-2** suitable for X-ray diffraction were obtained by the slow diffusion of diethyl ether into a saturated solution of the complexes in THF.

The **Mn-1** complex was crystallized as a monoclinic crystal system with space group $P2_1/c$. The single crystal X-ray diffraction experiment was performed at 293K. The ORTEP diagram is given in **Figure 1**. A five-membered ring formed from the coordination of Mn(I) to the nitrogen atoms of the **L1** ligand and the nitrogen atoms occupy two equatorial sites around Mn(I). The geometry of the complex around the Mn(I) ion is distorted octahedron. Two terminal carbonyl groups are occupying the two other equatorial site *trans* to the nitrogen atoms. Other carbonyl and the bromide coordinates Mn(I) linearly, perpendicular to the equatorial plane.

Dark orange crystals of **Mn-2** approximate dimensions 0.5×0.5×0.3 mm were isolated, and the single-crystal X-ray diffraction experiment was performed at 100 K. The ORTEP diagram is given in **Figure 2**. The complex was crystallized in a monoclinic system with space group $P2_1/c$. The structure resembles with that of **Mn-1.**

The structure refinement parameters selected bond angles, and bond lengths are summarized in **Table 1** to **4.**

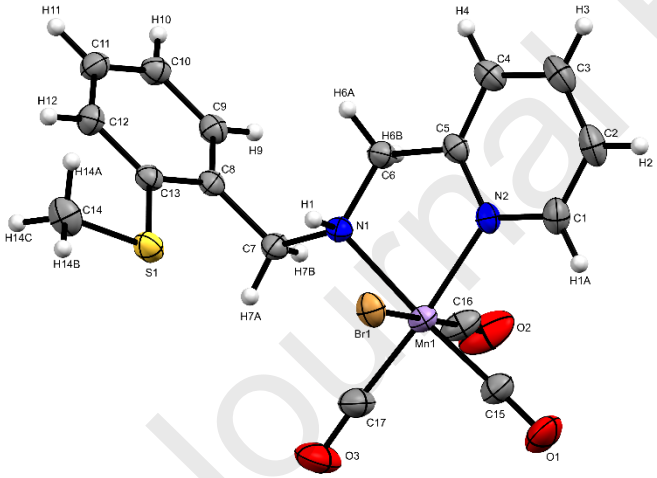


Figure 1 ORTEP diagram of **Mn-1[26]**

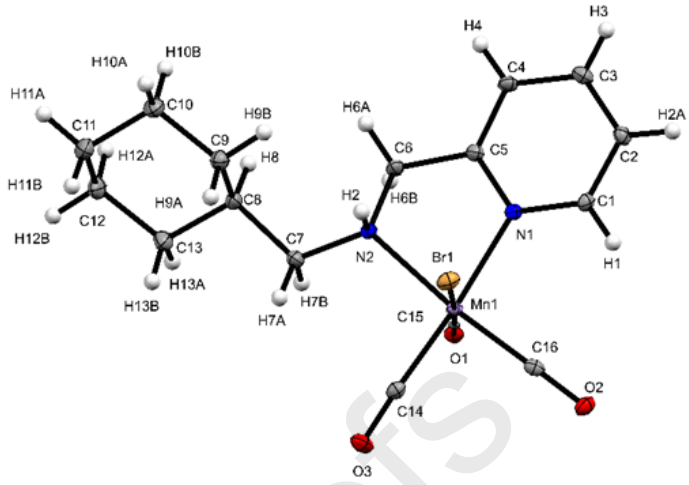


Figure 2 ORTEP diagram of **Mn-2[27]**

Table 1 Crystal data and structure refinement parameters for **Mn-1**

*Complex **Mn-1***	
Empirical formula	$C_{17}H_{16}BrMnN_2O_3S$
Formula weight	463.23
Temperature(K)	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	10.7643(2)
b(Å)	13.4050(3)
c(Å)	13.3946(2)
β(°)	96.471(2)
Volume(Å)^3	1920.47(6)
Z	4
Density (calculated) (g/cm^3)	1.602
Absorption coefficient (mm^{-1})	9.199
F(000)	928.0
Scan range for data collection(°)	8.26 to 132.86
Index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $15 \le l \le 12$
Reflections collected	17531
Independent reflections	3360 [R_{int} = 0.0430, R_{sigma} = 0.0249]
Data/restraints/parameters	3360/0/227
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0308, wR_2 = 0.0846
Final R indexes [all data]	R_1 = 0.0339, wR_2 = 0.0878

Table 2 Selected bond lengths and bond angles of **Mn-2.**

Interatomic distances (Å)			
Mn(1)-Br(1)	2.5232(5)	Mn(1)-C(15)	1.798(3)
Mn(1)-N(1)	2.099(2)	Mn(1)-C(16)	1.803(3)
Mn(1)-N(2)	2.059(2)	Mn(1)-C(17)	1.812(4)
Bond angles(°)			
N(2)-Mn(1)-Br(1)	86.16(6)	C(16)-Mn(1)-N(1)	94.59(12)
N(1)-Mn(1)-Br(1)	85.88(6)	C(16)-Mn(1)-C(15)	90.05(15)

N(1)-Mn(1)-N(2)	79.31(8)	C(16)-Mn(1)-C(17)	91.68(19)
C(15)-Mn(1)-Br(1)	89.46(11)	C(17)-Mn(1)-Br(1)	88.55(13)
C(15)-Mn(1)-N(2)	95.65(14)	C(17)-Mn(1)-N(2)	173.54(14)
C(15)-Mn(1)-N(1)	173.34(13)	C(17)-Mn(1)-N(1)	96.62(13)
C(16)-Mn(1)-Br(1)	179.45(13)	C(17)-Mn(1)-C(15)	88.00(16)
C(16)-Mn(1)-N(2)	93.64(15)		

Table 3 Crystal data and structure refinement parameters for **Mn-2**.

*Complex **Mn-2***	
Empirical formula	$C_{16}H_{20}BrMnN_2O_3$
Formula weight	423.19
Temperature (K)	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	18.2446(3)
b (Å)	7.42000(10)
c (Å)	13.1500(2)
β (°)	96.652(2)
Volume (Å)^3	1768.20(5)
Z	4
Density (calculated) (g/cm^3)	1.590
Absorption coefficient (mm^{-1})	8.847
F(000)	856.0
Scan range for data collection (°)	12.9 to 133.08
Index ranges	$-21 \le h \le 18$, $-8 \le k \le 8$, $-15 \le l \le 15$
Reflections collected/ unique, R_{int}	15731 3090, 0.0401, 0.0260
Data/restraints/parameters	3090/0/208
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	$R_1 = 0.0283$, $wR_2 = 0.0735$
Final R indexes [all data]	$R_1 = 0.0294$, $wR_2 = 0.0743$

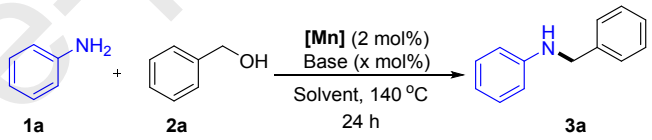
Table 4 Selected bond lengths and bond angles of **Mn-2.**

Interatomic distances (Å)			
Mn(1)-Br(1)	2.5243(5)	Mn(1)-C(15)	1.853(3)
Mn(1)-N(1)	2.046(2)	Mn(1)-C(16)	1.797(3)
Mn(1)-N(2)	2.090(2)	Mn(1)-C(14)	1.819(3)
Bond angles(°)			
N(2)-Mn(1)-Br(1)	85.63(6)	C(16)-Mn(1)-N(1)	95.45(10)
N(1)-Mn(1)-Br(1)	88.29(6)	C(16)-Mn(1)-C(15)	93.10(11)
N(1)-Mn(1)-N(2)	79.07(8)	C(16)-Mn(1)-C(14)	88.51(11)
C(15)-Mn(1)-Br(1)	176.37(7)	C(14)-Mn(1)-Br(1)	88.96(8)
C(15)-Mn(1)-N(2)	90.75(9)	C(14)-Mn(1)-N(2)	96.80(10)
C(15)-Mn(1)-N(1)	91.15(9)	C(14)-Mn(1)-N(1)	175.20(10)
C(16)-Mn(1)-Br(1)	90.53(8)	C(14)-Mn(1)-C(15)	91.34(11)
C(16)-Mn(1)-N(2)	173.38(10)		

3.4. Catalytic N-alkylation of amines

The preliminary catalytic exploration started using aniline **1a** and benzyl alcohol **2a** as the model substrate and **Mn-1** as the catalyst (Table 3). The treatment of aniline (2 equiv.) with benzyl alcohol (1 equiv.) in the presence of 2 mol% **Mn-1** and 40 mol% of *t*-BuOK as a base at 140 °C resulted in full conversion of benzyl alcohol and after aqueous workup and column chromatography we have isolated 91% yield of the desired amine (Table 3, entry 1). Decreasing the amount of alcohol, however, decreases the yield of **3a** (Table 3, entry 2). The catalytic activity of the catalyst **Mn-2** was found to be significantly lower than that of **Mn-1** under the same condition, and 40% **3a** was obtained (Table 3, entry 3). Interestingly, the use of **Mn-4** as a catalyst resulted in 18% yield of the desired product (Table 3, entry-4). This indicated the operation of N-H proton assisted bifunctional mechanism. Utilization of more polar solvents such as *t*-AmOH, THF, or under neat condition greatly affects the reaction outcome (Table 3, entry 5-7). The reaction was also found sensitive to the nature of base. The use of *t*-BuONa, *t*-BuOLi, KOH, and Cs_2CO_3 resulted in lower yields of **3a** under identical conditions (Table 3, entry 8-11). Decreasing the base loading, reaction time, and reaction temperature decreases the yield (Table 3, entry 12-15). Notably, the *N*,*N*-dialkylation was not observed during the reaction. The control experiment demonstrated that in the absence of Mn-catalyst or base only traces of the desired product was obtained (Table 3, entry 16-17).

Table 3 Reaction optimization



1a **2a** **3a**

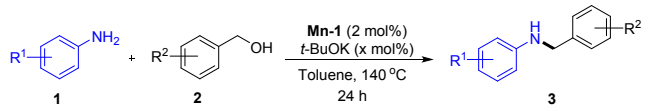
Entry	Catalyst	Solvent	Base (mol%)	**3a**[b] (%)
1	**Mn-1**	Toluene	*t*-BuOK (40 mol%)	91
2[c]	**Mn-1**	Toluene	*t*-BuOK (40 mol%)	37[d]
3	**Mn-2**	Toluene	*t*-BuOK (40 mol%)	40[d]
4	**Mn-4**	Toluene	*t*-BuOK (40 mol%)	18[d]
5	**Mn-1**	*t*-AmOH	*t*-BuOK (40 mol%)	55[d]
6	**Mn-1**	THF	*t*-BuOK (40 mol%)	Trace[d]
7	**Mn-1**	Neat	*t*-BuOK (40 mol%)	12[d]
8	**Mn-1**	Toluene	*t*-BuONa (40 mol%)	37[d]
9	**Mn-1**	Toluene	*t*-BuOLi (40 mol%)	Trace[d]
10	**Mn-1**	Toluene	KOH (40 mol%)	55[d]
11	**Mn-1**	Toluene	Cs_2CO_3 (40 mol%)	Trace[d]
12	**Mn-1**	Toluene	*t*-BuOK (20 mol%)	45[d]
13	**Mn-1**	Toluene	*t*-BuOK (10 mol%)	20[d]
14[e]	**Mn-1**	Toluene	*t*-BuOK (40 mol%)	67[d]
15[f]	**Mn-1**	Toluene	*t*-BuOK (40 mol%)	25[d]
16	**Mn-1**	Toluene	-	Trace[d]
17	-	Toluene	*t*-BuOK (40 mol%)	Trace[d]

Reaction conditions: [a]catalyst (2 mol%), Base (x mol%), Solvent (2M), alcohol (0.4 mmol), amine (0.2 mmol) at 140 °C for 24 h under argon. [b]Isolated yields. [c] alcohol (1.5 equiv.). [d]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [e]18 h. [f]120 °C.

To check the applicability of the developed manganese catalyzed C-N bond-forming protocol, we have tested *N*-alkylation of different substituted amines with differently substituted alcohols employing **Mn-1** as the model

catalyst, and the results are summarized in Table 4. Initially, the N-alkylation of substituted aniline with substituted alcohols was inspected. Electron-rich aromatic alcohols such as 4-methoxybenzyl alcohol (**2b**), and piperonyl alcohol (**2c**) reacted smoothly with aniline **1a** under the standard reaction condition to deliver the corresponding secondary amines **3b**,**c** in 65% and 70% yields, respectively. Benzylic alcohols containing halogens such as chloro (**2d**), and bromo (**2e**) were also found to be suitable coupling partner delivering the products **3d**,**e** in good yields with the complete retention of the halogen functionality thus enabling potential future functionalization. Interesting, the steric effect of the *ortho*-substituted impart negligible effect on the reaction outcome. Likewise, biphenyl methanol (**2f**) yielded the adduct **3f** in 80% yield. Substrate containing strongly electron-withdrawing trifluoromethyl group (**2g**) was also well-tolerated, and the alkylated amine **3g** was isolated in 60% yield. Pyridine containing heteroaromatic alcohol (**2h**) was also found to be a viable coupling partner delivering the adduct **3h** 60% yield. Anilines with electron-donating as well as withdrawing substituents (**1b-d**) could also be converted to the *N*-benzylated amines **3i-k** with similar efficiency.

Table 4 Coupling of anilines with alcohols



1 2 3

Entry	Amine	Alcohol	N-alkylated amine[a,b]
1	**1a**	**2a**	**3a**, 91%
2	**1a**	**2b**	**3b**, 65%
3	**1a**	**2c**	**3c**, 70%[c]
4	**1a**	**2d**	**3d**, 98%
5	**1a**	**2e**	**3e**, 72%[c]
6	**1a**	**2f**	**3f**, 80%[c]
7	**1a**	**2g**	**3g**, 60%[c]
8	**1a**	**2h**	**3h**, 60%[c]
9	**1b**	**2a**	**3i**, 72%[c]
10	**1c**	**2a**	**3j**, 74%[c]
11	**1d**	**2a**	**3k**, 50%[c]

[a]Reaction conditions: **Mn-1** (2 mol%), *t*-BuOK (40 mol%), toluene (2 M), alcohol (0.4 mmol), amine (0.2 mmol) at 140 °C under argon. [b]Isolated yields. [c] 1 equiv. base is used.

4. Conclusion

We report the synthesis of three new manganese complexes **Mn-1-3** by the reaction of commercially available precursor $MnBr(CO)_5$ and readily made bidentate amine-based ligands. The complexes were well characterized using IR, NMR, and mass spectroscopic method. The molecular structure of the complexes **Mn-1,2** were determined by X-ray crystallography, which revealed that the complexes exists as a distorted octahedron around

manganese ion where the ligand binds the Mn center through bidentate fashion. The catalysts are highly air-stable and easily handleable. The manganese complexes were established for catalytic *N*-alkylation of amines. The reaction parameters were optimized, and **Mn-1** was found to be most effective. The developed method showed excellent functional group tolerance and is a sustainable and atom economical way to secondary amines.

Declaration of Competing Interest

There are no conflicts to declare.

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Appendix A: Supplementary materials

Electronic supplementary information (ESI) available: Detailed experimental procedures, analytical data, and NMR spectra of compounds and complexes. Crystallographic data for **Mn-1**, CCDC1948389 and **Mn-2**, CCDC 1948387 can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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[26] CCDC-1948389. Contains the supplementary crystallographic data.

[27] CCDC-1948387. Contains the supplementary crystallographic data.

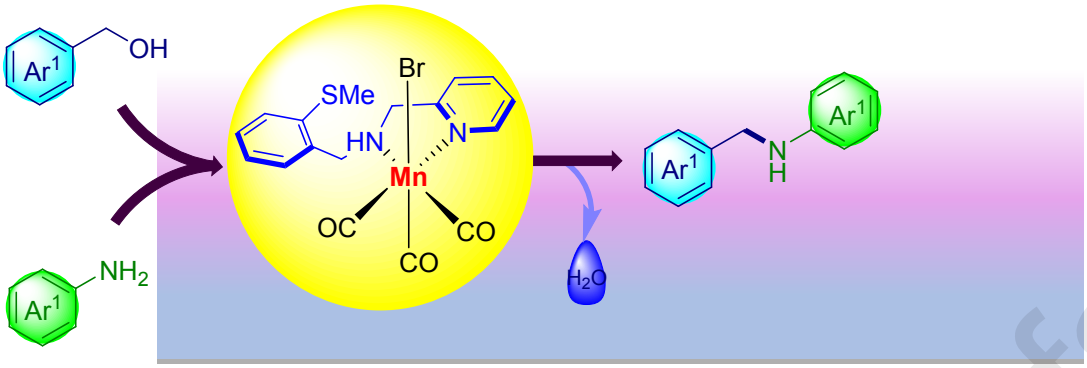
Author statement

Kuhali Das: Conceptualization, Methodology, Investigation, Writing- Original draft preparation, **Amol Kumar**: Investigation, Methodology. **Akash Jana**: Investigation, Methodology. **Biplab Maji**: Conceptualization, Supervision, Writing- Original draft preparation, Writing- Reviewing and Editing, Funding acquisition

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Highlights:

- Highly bench stable phosphine free N,N-chelate Mn(I) complexes have been synthesized.
- Characterization by analytical and spectral methods propose distorted octahedral geometry around manganese.
- The single-crystal XRD experiment confirms the proposed geometry.
- N-alkylation reactions could be performed efficiently with the phosphine-free manganese(I) catalyst.
- Good functional group tolerance observed for the C-N coupling reactions.