Supporting Information

Facile and reversible double dearomatization of pyridines in non-phosphine Mn
complexes with N,S-donor pyridinophane ligand

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I. Experimental Details

**General Specifications.** All manipulations unless stated otherwise were performed using Schlenk or glovebox techniques under dry argon atmosphere. Anhydrous solvents were dispensed from an MBRAUN solvent purification system and degassed prior to use. Anhydrous deuterated solvents were purchased from Eurisotop and stored over 4Å molecular sieves. All chemicals unless noted otherwise were purchased from major commercial suppliers (TCI, Sigma-Aldrich and Nacalai Tesque) and used without purification.

**Instrumentation.** NMR spectra were measured on JEOL ECZ600R 600MHz and JEOL ECZ400S 400 MHz. The following abbreviations are used for describing NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sept, septet; m, multiplet; br, broad; Ar−H, aromatic proton; quaternary, quat. Residual solvent peaks or internal standard was used as a reference for chemical shifts in $^2$H NMR spectra. Electrospray Ionization Mass Spectrometry (ESI-MS) measurements were performed on a Thermo Scientific ETD apparatus using MeOH or MeCN as a solvent for injection. Elemental analyses were performed using an Exeter Analytical CE440 instrument. Solid-state FT-IR spectra were measured using Agilent Cary 630 with ATR module in an argon filled glovebox. The following abbreviations are used for describing FT-IR spectra: s (strong), m (medium), w (weak), br (broad). UV-vis spectra were recorded on an Agilent Cary 60 spectrophotometer.

2,11-dithia[3,3](2,6)pyridinophane (N2S2) ligand was prepared according to a literature procedure.$^1$
II. Synthesis and characterization of complexes

Synthesis of \([\text{Mn(CO)}_2(\text{N2S2})]\text{Br} ([1]\text{Br})\):

206.0 mg (0.751 mmol) of N2S2 ligand and 200.2 mg (0.729 mmol, 0.97 equiv.) of Mn(CO)5Br were combined in a flame dried Schlenk flask inside a glove box and 10 mL toluene was added to give a yellow suspension. Subsequently, 1 mL methanol was added to the reaction mixture to yield a clear solution. The flask was taken outside the glove box and heated at 80 °C for 24 hours and then cooled inside the glove box to room temperature. The solution was then filtered through a celite pad. The filtrate obtained was evaporated under reduced pressure to yield a yellow solid which was washed thrice with copious amounts of diethyl ether (~15 mL) and then dried to produce [1]Br. Yellow crystals were grown by by vapor diffusion of ether into a 1:1 dichloromethane and methanol mixture of the complex. Yield: 330 mg (95 %).

\(^1\)H NMR (400 MHz, 25 °C, DMSO-\(d_6\)): \(\delta 7.74\) (t, \(3J_{HH} = 7.8\) Hz, \(p-H_{Py}\), 2H), 7.47 (d, \(3J_{HH} = 7.8\) Hz, \(m-H_{Py}\), 4H), 4.90 (d, \(2J_{HH} = 18.0\) Hz, Py-\(CH_2\)-N, 4H), 4.79 (d, \(2J_{HH} = 18.0\) Hz, Py-\(CH_2\)-N, 4H). \(^{13}\)C NMR (151 MHz, 25 °C, DMSO-\(d_6\)): \(\delta 225.6\) (CO), 159.0 (quat. \(C_{Py}\)), 137.2 (\(p-C_{Py}\)), 121.4 (\(m-C_{Py}\)), 49.1 (Py-\(CH_2\)-N). Anal. Calcd. for MnC\(_{16}\)H\(_{14}\)N\(_2\)S\(_2\)O\(_2\)Br: C, 41.30; H, 3.03; N, 6.02. Found: C, 41.41; H, 3.03; N, 6.03.

UV-vis, \(\lambda\), nm (\(\epsilon\), M\(^{-1}\) cm\(^{-1}\)), \(\text{CH}_2\text{Cl}_2\text{-MeOH (1:1)}\): 225 (27900), 259 (17900), sh 282 (7960), 342 (7560), sh 366 (7160).

FT-IR (ATR, solid): \(\nu 2935\) (m), 2880 (m), 1935 (s), 1864 (s), 1593 (m), 1567 (m), 1457
(s), 1426 (m), 1398 (br), 1384 (br), 1156 (br), 905 (w), 858 (s), 778 (s), 668 (s) cm$^{-1}$.

ESI-HRMS ($m/z$): calculated for $[\text{C}_{16}\text{H}_{14}\text{MnN}_{2}\text{O}_{2}\text{S}_{2}]^+$, ([M-Br]$^+$, $z = 1$): 384.9872;

Found: 384.9868.
Figure S1. $^1$H NMR (400 MHz) spectrum of complex [1]Br in DMSO-$d_6$ at 25 °C.
Figure S2. $^{13}$C NMR (151 MHz) spectrum of complex [1]Br in DMSO-$d_6$ at 25 °C.
Figure S3. UV-Vis absorbance spectra for complex [1]Br in a dichloromethane: methanol mixture (1:1).

Figure S4. ATR FT-IR transmittance spectra of complex [1]Br.
Synthesis of $[\text{K(THF)}_3][(\text{N}_2\text{S}_2\text{**})\text{Mn(CO)}_2] \ (2)$ from $[1]\text{Br}$:

42.0 mg (0.090 mmol) of $[1]\text{Br}$ was weighed out in a scintillation vial inside a glove box and 5 mL THF was added to give a yellow suspension. 22.1 mg (0.198 mmol, 2.2 equiv.) of KO'Bu was weighed out in another vial and added in one portion to the yellow suspension. The solution immediately turned into deep orange color and was stirred for 30 minutes. After 30 minutes, the solution was filtered through a layer of celite and a clear orange solution was obtained that was characterized as $2$. A THF solution of the compound is stable at -30 °C for about 2 days but if solvent is evaporated, the orange solid starts to decompose immediately and turns black within minutes. Hence, isolated yield of the compound could not be calculated, however, NMR shows complete conversion. All subsequent yields were based upon the parent compound used in the reaction. Yellow crystals were grown by vapor diffusion of pentane into a THF-$d_8$ solution of $2$ at -30 °C overnight. Complex $2$ is stable in THF solution at -30 °C for several weeks and in the solid state for at least several hours (see Section IV).

$^1$H NMR (600 MHz, -30 °C, THF-$d_8$): 6.13 (dd, $^3J_{HH} = 7.1, 8.1$ Hz, $p$-$H_{Py}$, 2H), 5.74 (d, $^3J_{HH} = 8.3$ Hz, $m$-$H_{Py}$, 2H), 5.37 (d, $^3J_{HH} = 6.5$ Hz, $m$-$H_{Py}$, 2H), 3.44 (2 doublets, $^2J_{HH} = 14.7$ Hz, Py-$CH_2$-$N$, 4H), 3.38 (s, Py-$CH$-$N$, 2H). tert-Butanol is a by-product of the reaction giving a singlet at $\delta$ 1.13 ($\text{CH}_3$, tBu) and a broad peak at $\delta$ 10.6 (br s, OH). $^{13}$C NMR (151 MHz, -30 °C, THF-$d_8$): $\delta$230.5 (CO), 166.2 (quat. $C_{Py}$), 156.9 (quat. $C_{Py}$),
129.6 (p-C\(_2\)H\(_5\)), 109.6 (m-C\(_2\)H\(_5\)), 99.6 (m-C\(_2\)H\(_5\)), 63.8 (Py-CH-N), 60.0 (Py-CH\(_2\)-N).

*tert*-Butanol is a by-product of the reaction giving two peaks in \(^{13}\)C NMR at \(\delta\) 66.6 (C(CH\(_3\))-OH), 33.7 (C(CH\(_3\))-OH).

UV-vis, \(\lambda\), nm (\(\epsilon\), M\(^{-1}\) cm\(^{-1}\)), THF: 211 (43200), 294 (28200), 322 (25800), 438 (4480), sh 493 (1790).

FT-IR (ATR, solid): \(\nu\) 3795 (w), 3693 (w), 3052 (m), 2951 (w), 2880 (m), 2234 (m), 2090 (m), 1889 (s), 1801 (s), 1597 (s), 1517 (s), 1475 (s), 1418 (s), 1383 (s), 1286(s), 1247 (s), 1158 (s), 1095 (m), 1023 (s), 969 (s), 872 (s), 833 (s), 746 (s), 720 (s), 679 (s) cm\(^{-1}\).

ESI-MS could not be determined accurately due to high air and moisture sensitivity of 2.
Figure S5. $^1$H NMR (600 MHz) spectrum of complex 2 in THF-$d_8$ at -30 °C. Peaks of $t$BuOH by-product are marked by as asterisk.
Figure S6. $^{13}$C NMR (151 MHz) spectrum of complex 2 in THF-$d_8$ at -30 °C. Peaks of 'BuOH by-product are marked by an asterisk.
Figure S7. $^1$H-$^1$H COSY spectrum of complex 2 in THF-$d_8$ at -30 °C.
Figure S8. $^1$H-$^{13}$C HMQC spectrum of complex 2 in THF-$d_8$ at -30 °C.
Figure S9. UV-Vis absorbance spectrum for complex 2 in THF.

Figure S10. ATR FT-IR transmittance spectrum of complex 2.
Synthesis of $[\text{Mn(CO)}_2(\text{N}_2\text{S}_2)]\text{Br}$ (1[Br]) from 2:

![Chemical structure](image)

Compound 2 was prepared from 42.0 mg (0.090 mmol) of [1]Br and 22.1 mg (0.198 mmol, 2.2 equiv.) of KOtBu in THF. To the orange solution, 680 μL of 33% HBr in acetic acid (0.225 mmol, 3.2 equivalents) was added using a microsyringe. The solution upon complete addition of acid turned yellowish in color. The solution was then evaporated to give a yellow solid identified as 1[Br]. Crystals of [1]Br could be re-grown from vapor diffusion of hexane into the dichloromethane solution of the yellow compound. Yield: 36 mg (86%). NMR is identical to the complex obtained as described above from N2S2 and Mn(CO)5Br.

Synthesis of $[\text{Mn(CO)}_2(\text{N}_2\text{S}_2)]\text{Cl}$, [1]Cl, from 2:

![Chemical structure](image)

Compound 2 was prepared from 42.0 mg (0.090 mmol) of [1]Br and 22.1 mg (0.198 mmol, 2.2 equiv.) of KOtBu in THF. To the orange solution, 8.5 μL of 1M hydrogen chloride in diethyl ether (0.225 mmol, 3.2 equivalents) was added using a microsyringe. The solution immediately turned cloudy and reddish and upon complete addition of acid turned yellowish in color. The solution was stirred for 15 minutes and concentrated under vacuum. Dichloromethane and methanol (9:1) was added to dissolve the solid and
the solution was filtered out through a celite pad to remove KCl and the filtrate was evaporated to dryness to yield [1]Cl as a yellow solid. Yellow crystals were grown by vapor diffusion of diethyl ether into a dichloromethane solution of [1]Cl. Yield: 34 mg (89%).

\(^1\)H NMR (600 MHz, 25 °C, DMSO-d\(_6\)): \(\delta 7.74 \ (t, \ 3J_{HH} = 7.8 \ Hz, \ p-H_{Py}, \ 2H)\), 7.48 (d, \(3J_{HH} = 7.7 \ Hz, \ m-H_{Py}, \ 4H)\), 4.94 (d, \(2J_{HH} = 18.0 \ Hz, \ Py-CH_2-N, \ 4H)\), 4.80 (d, \(2J_{HH} = 18.0 \ Hz, \ Py-CH_2-N, \ 4H)\).

\(^{13}\)C NMR (151 MHz, 25 °C, DMSO-d\(_6\)): \(\delta 226.1 \ (CO), \ 159.5 \ (quat. \ C_{Py}), \ 137.7 \ (p-C_{Py}), \ 122.0 \ (m-C_{Py}), \ 49.6 \ (Py-CH_2-N)\). Anal. Calcd. for MnC\(_{16}\)H\(_{14}\)N\(_2\)S\(_2\)O\(_2\)Cl:

- C, 45.67; H, 3.35; N, 6.66. Found: C, 45.12; H, 3.30; N, 6.53.

UV-vis, \(\lambda, \) nm (\(\epsilon, \) M\(^{-1}\) cm\(^{-1}\)): CH\(_2\)Cl\(_2\):MeOH (1:1): 225 (42080), 258 (24400), sh 280 (10950), 336 (10550), sh366 (9750).

FT-IR (ATR, solid): \(\nu 2932 \ (w), \ 1949 \ (s), \ 1868 \ (s), \ 1592 \ (br), \ 1570 \ (br), \ 1455 \ (w), \ 1417 \ (w), \ 1276 \ (w), \ 1166 \ (w), \ 769 \ (w), \ 757 \ (w) \ cm\(^{-1}\).\)

ESI-HRMS (m/z): calculated for [C\(_{16}\)H\(_{14}\)MnN\(_2\)O\(_2\)S\(_2\)]\(^+\) ([M-Cl]\(^+\), \(z = 1\)): 384.9872; Found: 384.9866.
Figure S11. $^1$H NMR (600 MHz) spectrum of complex [1]Cl in DMSO-$d_6$ at 25 °C.
Figure S12. $^{13}$C NMR (151 MHz) spectrum of complex [1]Cl in DMSO-$d_6$ at 25 °C.
Figure S13. UV-Vis absorbance spectrum for complex [1]Cl in CH₂Cl₂:MeOH (1:1).

Figure S14. ATR FT-IR transmittance spectrum of complex [1]Cl.
Synthesis of \([\text{Mn(CO)}_2(\text{N}_2\text{S}_2)](\text{HCOO})\) ([1]HCOO) from 2:

Compound 2 was prepared from 42.0 mg (0.090 mmol) of [1]Br and 22.1 mg (0.198 mmol, 2.2 equiv.) of KOtBu in THF. To the orange solution, 11.9 \(\mu\)L of formic acid (0.315 mmol, 3.5 equiv.) was added using a microsyringe. The solution was stirred for 15 minutes and concentrated under vacuum. Dichloromethane was added to dissolve the solid and the solution was filtered out through a celite pad. The yellow filtrate was evaporated to dryness to yield [1]HCOO as a yellow solid. Yellow crystals were grown by vapor diffusion of hexane into a dichloromethane solution of [1]HCOO. Yield: 38 mg (97%). [1]HCOO can be also obtained by adding 2.2 equiv. of formic acid to 2. But addition of 3.5 equivalents helps in crystallization where the counter ion is hydrogen bonded to a neutral formic acid molecule.

\(^1\)H NMR (600 MHz, 25 °C, DMSO-\(d_6\)): \(\delta\) 8.32 (brs, HCOO, 1 H), 7.74 (t, \(^3\)J\(_{HH}\) = 7.6 Hz, \(p\)-H\(_{\text{Py}}\), 2H), 7.47 (d, \(^3\)J\(_{HH}\) = 7.7 Hz, \(m\)-H\(_{\text{Py}}\), 4H), 4.91 (d, \(^2\)J\(_{HH}\) = 18.0 Hz, Py-CH\(_2\)-N-, 4H), 4.79 (d, \(^2\)J\(_{HH}\) = 18.0 Hz, Py-CH\(_2\)-N-, 4H). \(^{13}\)C NMR (151 MHz, 25 °C, CD\(_2\)Cl\(_2\)): \(\delta\) 225.3 (CO), 166.6 (HCOO), 158.9 (quat. C\(_{\text{Py}}\)), 137.6 (p-C\(_{\text{Py}}\)), 122.4 (m-C\(_{\text{Py}}\)), 50.4 (Py-CH\(_2\)-N).

Anal. Calcd. for MnC\(_{17}\)H\(_{15}\)N\(_2\)S\(_2\)O\(_2\).HCOO:C, 45.48; H, 3.39; N, 5.89. Found: C, 45.28; H, 3.51; N, 5.86.

UV-vis, \(\lambda\), nm (\(\epsilon\), M\(^{-1}\) cm\(^{-1}\)) (CH\(_2\)Cl\(_2\)): 225 (30600), 258 (20500), sh 281 (9300), 337 (8200), sh 367 (7600).
FT-IR (ATR, solid): \( \nu \) 2961 (w), 2909 (w), 1948 (s), 1874 (s), 1667 (br), 1588 (m), 1459 (m), 1407 (br), 1303 (w), 1166 (w), 918 (w), 862 (w), 787 (br), 746 (m) cm\(^{-1}\).

ESI-HRMS \((m/z)\): calculated for \([C_{16}H_{14}MnN_{2}O_{2}S_{2}]^{+}\) ([M-HCOO]\(^{+}\), \(z = 1\)): 384.9872; Found \(C_{16}H_{14}MnN_{2}O_{2}S_{2}\): 384.9871.
Figure S15. $^1$H NMR (600 MHz) spectrum of complex [1]HCOO in DMSO-$d_6$ at 25 °C.
Figure S16. $^{13}$C NMR (151 MHz) spectrum of complex [1]HCOO in CD$_2$Cl$_2$ at 25 °C.
Figure S17. UV-Vis absorbance spectrum for complex [1]HCOO in CH$_2$Cl$_2$:MeOH (1:1).

Figure S18. ATR FT-IR transmittance spectra of complex [1]HCOO.
Synthesis of [Mn(CO)$_2$(N$_2$S$_2^*$)] (3) from 2 using HCl:

![Chemical reaction diagram]

Compound 2 was prepared from 42.0 mg (0.090 mmol) of [1]Br and 22.1 mg (0.198 mmol, 2.2 equiv.) of KO'Bu in THF. To the orange solution, 100 μL of 1M hydrogen chloride in diethyl ether (0.100 mmol, 1.11 equiv.) was added using a micro syringe. The solution immediately turned cloudy and reddish. The solution was stirred for 15 minutes and filtered through a plug of celite and the filtrate was evaporated to dryness to yield a red solid. The red solid was again re-dissolved in benzene and filtered to give a red solution that was concentrated to produce 3 as a red powder. Red crystals were grown by vapor diffusion of pentane into a benzene solution of 3. Yield: 29.4 mg (84%). Caution! Benzene is a known carcinogenic and can be replaced by toluene during the synthesis but 3 is less soluble in toluene and so larger volumes of toluene is needed.

The transformation of 3 from 2 can be done with 1-1.11 equiv. HBr or formic acid instead of HCl using the same procedure.

Synthesis of [Mn(CO)$_2$(N$_2$S$_2^*$)] (3) from 2 using aq. ammonia:

![Chemical reaction diagram]

Compound 2 was prepared from 42.0 mg (0.090 mmol) of [1]Br and 30.4 mg (0.271 mmol, 2.2 equiv.) of KO'Bu in THF. To the orange solution, 100 μL of 1M hydrogen chloride in diethyl ether (0.100 mmol, 1.11 equiv.) was added using a micro syringe. The solution immediately turned cloudy and reddish. The solution was stirred for 15 minutes and filtered through a plug of celite and the filtrate was evaporated to dryness to yield a red solid. The red solid was again re-dissolved in benzene and filtered to give a red solution that was concentrated to produce 3 as a red powder. Red crystals were grown by vapor diffusion of pentane into a benzene solution of 3. Yield: 29.4 mg (84%). Caution! Benzene is a known carcinogenic and can be replaced by toluene during the synthesis but 3 is less soluble in toluene and so larger volumes of toluene is needed.

The transformation of 3 from 2 can be done with 1-1.11 equiv. HBr or formic acid instead of HCl using the same procedure.
mmol, 3 equiv.) of KOtBu in THF. To the yellowish orange solution, aqueous ammonia (28%) (15 μL, 0.36 mmol, 4 equiv.) was added using a microsyringe. The solution immediately turned reddish. The solution was stirred for 15 minutes and filtered through a plug of celite and the filtrate was evaporated to dryness to yield a red solid 3 which was confirmed by NMR.

\(^1\)H NMR (600 MHz, -30 °C, THF-\(d_8\)): \(\delta\) 7.55 (vt, \(3^J_{HH} = 7.5\) Hz, \(p-\text{H}_{Py}\), 1H), 7.41 (d, \(3^J_{HH} = 7.6\) Hz, \(m-\text{H}_{Py}\), 1H), 7.32 (d, \(3^J_{HH} = 7.2\) Hz, \(m-\text{H}_{Py}\), 1H), 6.27 (dd, \(3^J_{HH} = 8.7\) Hz, 6.5 Hz, \(p-\text{H}_{Py}\), 1H), 5.84 (d, \(3^J_{HH} = 8.7\) Hz, \(m-\text{H}_{Py}\), 1H), 5.63 (d, \(3^J_{HH} = 6.5\) Hz, \(m-\text{H}_{Py}\), 1H), 4.67 (d, \(2^J_{HH} = 16.8\) Hz, Py-\(CH_2\)-N, 1H), 4.28 (d, \(2^J_{HH} = 16.8\) Hz, Py-\(CH_2\)-N, 1H), 4.17 (d, \(2^J_{HH} = 16.8\) Hz, Py-\(CH_2\)-N, 1H), 4.05 (d, \(2^J_{HH} = 16.8\) Hz, Py-\(CH_2\)-N, 1H), 3.84 (d, \(2^J_{HH} = 16.8\) Hz, Py-\(CH_2\)-N, 1H), 3.54 (s, Py-\(CH\)-N, 1H).

\(^{13}\)C NMR (151 MHz, -30 °C, THF-\(d_8\)): \(\delta\) 228.7 (CO), 228.1 (CO), 166.5 (quat. \(C_{Py}\)), 162.6 (quat. \(C_{Py}\)), 160.5 (quat. \(C_{Py}\)), 152.9 (quat. \(C_{Py}\)), 135.9 (\(p-C_{Py}\)), 130.6 (\(p-C_{Py}\)), 123.4 (\(m-C_{Py}\)), 120.8 (\(m-C_{Py}\)), 111.3 (\(m-C_{Py}\)), 100.6 (\(m-C_{Py}\)), 64.6 (Py-\(CH\)-N-), 60.1 (Py-\(CH_2\)-N), 52.2 (Py-\(CH_2\)-N), 47.5 (Py-\(CH_2\)-N).

UV-vis, \(\lambda\), nm (\(\epsilon\), M\(^{-1}\) cm\(^{-1}\)), THF: 214 (7860), 261 (244), 329 (3400), sh 368 (120), 436 (50) sh 498 (20).

FT-IR (ATR, solid): \(\nu\)3844 (w), 3759 (w), 3676 (w), 3055 (m), 2913 (br), 2235 (m), 2081 (br), 1914 (s), 1834 (s), 1605 (s), 1517 (s), 1476 (s), 1403 (s), 1293 (s), 1253 (s), 1169 (s), 1107 (s), 1046 (s), 1023 (s), 976 (s), 909 (m), 866 (s), 841 (s), 779 (m), 742 (s), 723 (s), 669 (s) cm\(^{-1}\).
Figure S19. $^1$H NMR (600 MHz) spectrum of complex 3 (made from 2 using aqueous ammonia) in THF-$d_8$ at -30 °C. Peaks of $^t$BuOH and adventitious H$_2$O are marked with as asterisk.
Figure S20. $^{13}$C NMR (151 MHz) spectrum of complex 3 (made from 2 using aqueous ammonia) in THF-$d_8$ at -30 °C. Peaks of $^t$BuOH by-product are marked with an asterisk.
Figure S21. $^1$H-$^1$H COSY spectrum of complex 3 in THF-$d_8$ at -30 °C.
Figure S22. $^1$H-13C HMOC spectrum of complex 3 in THF-$d_8$ at -30 °C.
Figure S23. DEPT-135 NMR spectrum of complex 3 in THF-\textit{d}_8 at -30 °C.
Figure S24. UV-Vis absorbance spectrum for complex 3 in THF.

Figure S25. ATR FT-IR transmittance spectrum of complex 3.
**Synthesis of [Mn(CO)$_2$(N2S2*)] (3) from 2 using H$_2$O:**

![Chemical structure]

Compound 2 was prepared from 42.0 mg (0.090 mmol) of [1]Br and 30.4 mg (0.271 mmol, 3 equiv.) of KO'Bu in THF. To the yellowish orange solution, 1.6 μL of deionized H$_2$O (0.090 mmol, 1 equiv.) was added using a microsyringe. The solution immediately turned reddish. The solution was stirred for 15 minutes and filtered through a plug of celite and the filtrate was evaporated to dryness to yield a red solid 3 which was confirmed by NMR.

**Stability of 3 in the presence of excess of water**

![Chemical structure]

Compound 2 was prepared from 20.0 mg (0.043 mmol) of [1]Br and 14.5 mg (0.129 mmol, 3.0 equiv.) of KO'Bu in THF. To the yellowish orange solution, 10 μL of degassed D$_2$O (0.55 mmol, 13 equiv.) was added using a microsyringe. The solution immediately turned reddish. The solution was stirred for 15 minutes and filtered through a plug of celite and the filtrate was directly used for the NMR characterization.

Even in the presence of 13 equiv. of D$_2$O, $^1$H NMR spectrum indicates that complex 3 is still a major species selectively formed in solution; with H/D exchange being observed in CH/CH$_2$ arms (Figure S27, bottom).

When 50 equivalents of water were added in an analogous reaction (from 10 mg [1]Br, 7.3 mg of KO'Bu and 19 μL of deionized H$_2$O), *in situ* $^1$H NMR spectrum shows...
significantly broadened signals of the aromatic peaks and CH₂/CH arms likely due to fast proton exchange between CH₂/CH position. However, when solvents were quickly removed by evaporation under vacuum and the solid residue was redissolved in THF-d₈, ¹H NMR spectrum shows complex 3 as the major species (Figure S27, top).
**Figure S26.** $^1$H NMR (600 MHz) spectrum of complex 3 (made from 2 using H$_2$O (1.0 equiv.) at 25 °C). tBuOH and H$_2$O peaks are denoted by asterisk.
Figure S27. $^1$H NMR spectrum of complex 3 made from 2 using 13 equiv. of D$_2$O at 25 °C (bottom, maroon) and complex 3 obtained by reacting 2 with 50 equiv. of H$_2$O followed by evaporation (top, blue-green). $^t$BuOH peak is denoted by asterisk.
III. Deuterium labeling experiments

**Reaction of 2 and DBr:** Compound 2 was prepared from 10.0 mg (0.022 mmol) of [1]Br and 7.7 mg of KO\textsubscript{t}Bu (0.069 mmol, 3.2 equiv.) in THF. To the orange solution, 4.8 μL of 45% DBr in D\textsubscript{2}O (5.5 M, 0.32 mmol, 15 equiv.) was added using a micro syringe. The solution immediately turned cloudy and reddish and upon complete addition of acid turned yellowish in color. The solution was stirred for 15 minutes, then evaporated to dryness, washed with copious amount of hexane, dried under vacuum and redissolved in DMSO. Yield: 8.8 mg (88%).

\(^2\text{H}\) NMR (600 MHz, 25 °C): \(\delta\) 4.98, 4.78 (br m, Py-(H/D)\textsubscript{2}-N).

\(^1\text{H}\) NMR (600 MHz, 25 °C, DMSO-\textsubscript{d}6): \(\delta\) 7.74 (t, \(^3\)\text{J}\text{HH} = 7.7 Hz, \text{p-}H\text{Py}, 2H), 7.48 (d, \(^3\)\text{J}\text{HH} = 7.7 Hz, m-\text{HPy}, 4H), 4.99 (d, \(^2\)\text{J}\text{HH} = 19.5 Hz, Py-\text{CH}\text{2}-N, \text{1.28H}), 4.78 (d, \(^2\)\text{J}\text{HH} = 19.5 Hz, Py-\text{CH}\text{2}-N, \text{1.34H}). \(^{13}\text{C}\) NMR (151 MHz, 25 °C, DMSO-\textsubscript{d}6): \(\delta\) 225.6 (CO), 158.9 (quat. C\text{Py}), 137.1 (p-C\text{Py}), 121.5 (m-C\text{Py}), 48.8, 48.7, 48.6 and 48.5 (Py-CH\text{2}-N).

\(^2\text{H}\) NMR spectrum of product obtained by reaction of 2 with DBr shows two broadened peaks present at the same chemical shifts as CH\textsubscript{2} peaks in \(^1\text{H}\) NMR spectrum of [1]Br in the same solvent. \(^1\text{H}\) spectrum of the product shows decreased integration intensity for peaks of CH\textsubscript{2} groups due to deuterium incorporation (relaxation delay of 10 s was used); 67% of D incorporation was obtained under these conditions. \(^{13}\text{C}\) spectrum also shows splitting of methylene carbon signal from deuterium. HRMS analysis shows multiple incorporation of deuterium atoms: the most intense peak appears at m/z 390.0182 corresponding to incorporation of at least 5 deuterium atoms, while for the product in the absence of D incorporation, the most intense peak at m/z 384.9872 is expected.
Figure S28. $^2$H NMR (92 MHz) spectrum of complex [1]Br obtained by reaction of 2 with DBr (DMSO, 25 °C).
Figure S29. $^1$H NMR (600 MHz) spectrum of [1]Br obtained by reaction of 2 with DBr (DMSO-$d_6$ at 25 °C).
Figure S30. $^{13}$C NMR (151 MHz) spectrum in DMSO-$d_6$ at 25 °C. Peak of CH$_2$ group is broadened due to splitting from D.
Figure S31. HRMS of [1]Br obtained by reaction of 2 with DBr.

**Reaction of 2 and DCl:** Compound 2 was prepared from 10.0 mg (0.022 mmol) of [1]Br and 7.7 mg (0.069 mmol, 3.2 equiv.) in THF. To the orange solution, 1.3 μL of 9.3 M DCl in D2O (0.32 mmol, 15 equiv.) was added using a microsyringe. The solution immediately turned cloudy and reddish and upon complete addition of acid, turned yellowish in color. The solution was stirred for 15 minutes, then evaporated to dryness, washed with copious amount of diethyl ether and hexane and redissolved in DMSO. Yield: 8.0 mg (88%).

$^2$H NMR (600 MHz, 25 °C, DMSO): δ 4.94, 4.77 (br m, Py-$\text{CH}_2$-N).

$^1$H NMR (600 MHz, 25 °C, DMSO-$d_6$): δ 7.76 (t, $^3J = 7.8$ Hz, $p$-$\text{H}_{\text{Py}}$, 2H), 7.50 (d, $^3J = 7.8$ Hz, $m$-$\text{H}_{\text{Py}}$, 4H), 5.01 (d, $^2J = 19.2$ Hz, Py-$\text{CH}_2$-N, 1.67H), 4.81 (d, $^2J = 19.2$ Hz, Py-$\text{CH}_2$-N, 1.77H). $^{13}$C NMR (151 MHz, 25 °C, DMSO-$d_6$): δ 225.8 (CO), 159.1 (quat.
$C_{Py}$), 137.3 ($p$-$C_{Py}$), 121.6 ($m$-$C_{Py}$), 49.2, 49.1, 49.06, 49.0, 48.9, 48.8 and 48.6 (Py-$CH_2$N).

$^2$H NMR spectrum of product obtained by reaction of 2 with DCl shows two peaks present at the same chemical shifts as CH$_2$ peaks in $^1$H NMR spectrum of $[1]$Cl in the same solvent. $^1$H spectrum of the product shows decreased integration intensity for peaks of CH$_2$ groups due to deuterium incorporation (relaxation delay of 10 s was used) 57% of D incorporation was obtained under these conditions. $^{13}$C spectrum also shows splitting of methylene carbon signal from deuterium. HRMS analysis shows multiple incorporation of deuterium atoms: several peaks appear between m/z 384.9867 and 390.0188, while for the product in the absence of D incorporation, the most intense peak at m/z 384.9872 is expected.
Figure S32. $^2$H NMR (92 MHz) spectrum of complex [1]Cl obtained by reaction of 2 with DCl (DMSO, 25 °C).
Figure S33. $^1$H NMR (600 MHz) spectrum of complex [1]Cl obtained by reaction of 2 with DCl (DMSO-$d_6$, 25 °C).
**Figure S34.** $^{13}$C NMR (151 MHz) spectrum of complex [1]Cl obtained by reaction of 2 with DCl (DMSO-$d_6$, 25 °C). Broadening of C(H/D)$_2$ group is due to coupling from D.
Figure S35. HRMS of [1]Cl obtained by reaction of 2 with DCl.

Reaction of 2 and HCOOD: Compound 2 was prepared from 10.0 mg (0.022 mmol) of [1]Br and 7.7 mg of KOtBu (0.069 mmol, 3.2 equiv.) in THF. To the orange solution, 12.2 μL of formic acid-O-D, HCOOD, (0.32 mmol, 15 equiv.) was added using a microsyringe. The solution immediately turned cloudy and reddish and upon complete addition of acid, turned yellowish in color. The solution was stirred for 15 minutes, evaporated to dryness, washed with copious amount hexane and redissolved in DMSO. Yield: 9.0 mg (97%).

$^2$H NMR (600 MHz, 25 °C, DMSO): δ 4.86 and 4.72 (br m, Py-C(H/D)$_2$-N).

$^1$H NMR (600 MHz, 25 °C, DMSO-d$_6$): 8.34 (br s, HCOO, 6H), 7.74 (br m, p-Hp$_2$, 2H), 7.48 (br m, m-H$_2$Py, 4H), 4.93 (d, $^2$J$_{HH}$= 19.3 Hz, Py-CH$_2$-N, 1.51H), 4.78 (d, $^2$J$_{HH}$ = 19.3 Hz, Py-CH$_2$-N, 1.64H). $^{13}$C NMR (600 MHz, 25 °C, DMSO-d$_6$): δ 225.6 (CO), 165.4
(HCOO), 158.9 (quat. C<sub>py</sub>), 137.2 (p-C<sub>py</sub>), 121.5 (m-C<sub>py</sub>), 49.1, 49.0, 48.96, 48.9, 48.8 and 48.7 (Py-CH<sub>2</sub>-N).

<sup>2</sup>H NMR spectrum of product obtained by reaction of 2 with HCOOD shows two peaks present at the same chemical shifts as CH<sub>2</sub> peaks in <sup>1</sup>H NMR spectrum of [1](HCOO) in the same solvent. <sup>1</sup>H spectrum of the product shows decreased integration intensity for peaks of CH<sub>2</sub> groups due to deuterium incorporation (in the absence of D incorporation, integration intensity is close to 8; relaxation delay of 10 s was used); 61% of D incorporation was obtained under these conditions. <sup>13</sup>C spectrum also shows splitting of methylene carbon signal from deuterium. HRMS analysis shows multiple incorporation of deuterium atoms: several intense peaks appear between m/z 384.9869 and 390.0023, while for the product in the absence of D incorporation, the most intense peak at m/z 384.9872 is expected.
Figure S36. $^1$H NMR (92 MHz) spectrum of [1]HCOO obtained by reaction of 2 with HCOOD (DMSO, 25 °C).
Figure S37. $^1$H NMR (600 MHz) spectrum [1]HCOO obtained by reaction of 2 with HCOOD (DMSO-$d_6$, 25 °C).
Figure S38. $^{13}$C NMR (151 MHz) spectrum of [1]HCOO obtained by reaction of 2 with HCOOD (DMSO-$d_6$, 25 °C).
Figure S39. HRMS of [1]HCOO obtained by reaction of 2 with HCOOD.

Synthesis of partially deuterated [Mn(N2S2²⁻)(CO)₂] (3) from 2 using D₂O: Compound 2 was prepared from 20.0 mg (0.043 mmol, 1 equiv.) of [1]Br and 15.0 mg KOtBu (0.133 mmol, 3 equiv.) in THF. To the orange solution, 5 µL D₂O in excess (0.279 mmol, 6.5 equiv.) was added using a micro syringe. The reaction mixture immediately turned into dark red clear solution. The solution was stirred for 15 minutes and was further used for the NMR characterization without purification.

Based on NMR, deuterium incorporation occurs in all CH/CH₂ positions in complex 3.

²H NMR (600 MHz, 25 °C, THF with additive of THF-d₈ as a internal standard): δ 4.60, 4.18, 4.07, 3.83 (br m, Py-C(H/D)₂-N). Broad peak at 2.69 ppm is from OH.

¹H NMR (600 MHz, -30 °C, THF-d₈): δ 7.56 (vt, ³JHH = 7.4 Hz, p-HPy, 1H), 7.42 (d, ³JHH = 7.4 Hz, m-HPy, 1H), 7.33 (d, ³JHH = 7.3 Hz, m-HPy, 1H), 6.27 (dd, ³JHH = 8.8, 6.5 Hz, p-HPy, 1H), 5.83 (d, ³JHH = 8.8 Hz, m-HPy, 1H), 5.62 (d, ³JHH = 6.5 Hz, m-HPy, 1H),
4.68 (m, $^2J_{HH} = 19.9$ Hz, Py-C($H/D$)$_2$-N, 0.17H), 4.27 (m, $^2J_{HH} = 18.4$ Hz, Py-C($H/D$)$_2$-N, 0.21H), 4.16 (m, $^2J_{HH} = 19.5$ Hz, Py-C($H/D$)$_2$-N, 0.19H), 3.84 (m, $^2J_{HH} = 17.9$ Hz, Py-C($H/D$)$_2$-N, 0.20H), 3.53 (m, Py-C($H/D$)-N, 0.26H).

$^{13}$C NMR (151 MHz, -30 °C, THF-$d_8$): $\delta$ 166.2 (quat. C$_{py}$), 162.3 (quat. C$_{py}$), 160.2 (quat. C$_{py}$), 152.6 (quat. C$_{py}$), 135.7 (p-C$_{py}$), 130.4 (p-C$_{py}$), 123.2 (m-C$_{py}$), 120.7 (m-C$_{py}$), 111.1 (m-C$_{py}$), 100.3 (m-C$_{py}$), 64.33-63.9 (Py-C($H/D$)-N, multiplet due to C-D splitting), 59.9-59.4 (Py-C($H/D$)$_2$-N, multiplet due to C-D splitting), 51.8-51.5 (Py-C($H/D$)$_2$-N, multiplet due to C-D splitting), 47.2-46.9 (Py-C($H/D$)$_2$-N, multiplet due to C-D splitting).

$^2$H NMR spectrum of product obtained by reaction of 2 with D$_2$O shows peaks present at the same chemical shifts as CH and CH$_2$ peaks in $^1$H NMR spectrum of 3 in the same solvent. $^1$H spectrum of the product shows decreased integration intensity for peaks of CH$_2$ groups due to deuterium incorporation (80% D incorporation based on integration).

$^{13}$C spectrum also shows splitting of methylene carbon signal from deuterium. HRMS analysis shows multiple incorporation of deuterium atoms. the most intense peak appears at m/z 391.0181 corresponding to incorporation of at least 6 deuterium atoms, while for the product in the absence of D incorporation, the most intense peak at m/z 384.9872 is expected

**Other H/D exchange experiments**

No H/D exchange was observed when isolated complex [1]Br or [1]HCOO were reacted with 3.2 equiv. of DBr or 6.0 equiv. of HCOOD, respectively, for 2 days.

No H/D exchange was also observed in free ligand under analogous conditions.
Figure S40. $^1$H NMR (92 MHz) spectrum of complex 3 after addition of D$_2$O (THF-$d_8$ as an internal standard) at 25 °C.
Figure S4. $^1$H NMR (600 MHz) spectrum of complex 3 in THF-$d_8$ after addition of D$_2$O at -30 °C.
Figure S4. $^{13}$C NMR (151 MHz) spectrum of complex 3 in THF-$d_8$ after addition of D$_2$O at -30 °C.
Figure S43. $^1$H-$^1$H COSY spectrum of complex 3 in THF-$d_8$ after addition of D$_2$O at -30 °C.
Figure S44. $^1$H-$^{13}$C HMQC spectrum of complex 3 in THF-$d_8$ after addition of D$_2$O at -30 °C.
Figure S45. HRMS of complex 3 after addition of D$_2$O.
IV. Stability and reactivity tests

Typical procedure for synthesis of 2 from [1]Br using various bases

[1]Br (10 mg or 20 mg) was weighed out in a scintillation vial inside a glove box and 1.0-1.5 mL THF-$d_8$ was added to give a yellow suspension. Base (3.2 equiv. if not indicated otherwise) was weighed out and added in one portion to the yellow suspension. The solution immediately turned yellowish orange and was stirred for 15 minutes. The reaction mixture was filtered through a layer of celite and to give a clear solution of 2. The internal standard 1,3,5-trimethoxybenzene was added to the reaction mixture and $^1$H NMR was measured in THF-$d_8$ before evaporation; the peak of complex 2 at 5.40 ppm was integrated against the peak of internal standard at 6.03 ppm. The reaction mixture was then evaporated and kept under high vacuum in the glove box. After the indicated time intervals, the solids were redissolved in THF-$d_8$ and $^1$H NMR was recorded to estimate the stability of complex 2 by integration against internal standard and comparison with the value obtained before evaporation. The NMR spectra showing complex obtained immediately, and stored under vacuum for the indicated periods of time are shown in Figures S46-50.

When complex 2 obtained by reaction with KHMDS was redissolved in THF-$d_8$ after evaporation for 1 h, small amount of precipitate was present, which was separated by filtration and redissolved in DMSO-$d_6$, however, the NMR of the precipitate showed that the major component resembled doubly dearomatized complex 2.
In the reaction with NaOMe, the resulting solution was deep red and only the mono-deprotonated species 3 observed by NMR.

In a reaction with n-BuLi, formation of 2 or 3 has not been observed and an unidentified product was present in the reaction mixture.

**Table S1. Stability of complex 2.**

<table>
<thead>
<tr>
<th>Base</th>
<th>Amount of 2 (% of the amount present before evaporation) remaining after evaporation or storage in the solid state for an indicated period of time.</th>
<th>1h</th>
<th>6h</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOtBu</td>
<td></td>
<td>98%</td>
<td>98%</td>
</tr>
<tr>
<td>NaHMDS</td>
<td></td>
<td>98%</td>
<td>84%</td>
</tr>
<tr>
<td>LiHMDS</td>
<td></td>
<td>96%</td>
<td>90%</td>
</tr>
<tr>
<td>KHMDS</td>
<td></td>
<td>49%</td>
<td>31%</td>
</tr>
</tbody>
</table>
| KH (in oil)|                                                                                                                                        | 84%| >50% decomposition (peaks are broadened; new resonances appear)
Figure S46. $^1$H NMR spectra (THF-$d_8$, 25 °C) of 2 obtained by reaction with KOtBu before and after evaporation.
Figure S47. $^1$H NMR spectra (THF-$d_8$, 25°C) of 2 obtained by reaction with NaHMDS before and after evaporation.
**Figure S48.** $^1$H NMR spectra (THF-$d_8$, 25 °C) of 2 obtained by reaction with LiHMDS before and after evaporation.
Figure S49. $^1$H NMR spectra (THF-$d_8$, 25 °C) of 2 obtained by reaction with KHMDS before and after evaporation.
**Figure S50.** $^1$H NMR spectra (THF-$d_8$, 25 °C) of 2 obtained by reaction with KH before and after evaporation.
Reactivity tests

Complex 2 generated in situ by addition of 3-3.5 equiv. of ‘BuOK was tested in high pressure hydrogenation of acetophenone at 70 bar H₂, transfer hydrogenation of acetophenone from ‘PrOH at 70 °C, dehydrogenation of benzyl alcohol and hydration of terminal alkynes in THF-H₂O (20:1 v/v) mixture.

In addition, reaction of in situ generated 2 in THF-d₈ under ca. 3 bar H₂ in a pressure NMR tube did not produce any new product or gave evidence of N₂S₂** ligand protonation, and complex 2 remained stable at RT. Attempted stoichiometric reaction with phenylacetylene or aniline (3 equiv.) in THF-d₈ did not show any products that could result from protonation of the N₂S₂** ligand with C-H bond of phenylacetylene or N-H bond of aniline, respectively, at RT.
V. X-ray structure determination details

The X-ray diffraction data for the single crystals were collected on a Rigaku XtaLab PRO instrument (κ-goniometer) with a PILATUS3 R 200K hybrid pixel array detector using MoKα (0.71073 Å) radiation monochromated by means of multilayer optics. The performance mode of a MicroMax™-003 microfocus sealed X-ray tube was 50 kV, 0.60 mA. The diffractometer was equipped with a Rigaku GN2 system for low temperature experiments. Suitable crystals of appropriate dimensions were mounted on loops in random orientations. Preliminary unit cell parameters were determined with three sets of a total of 10 narrow frame scans. The data were collected according to recommended strategies in an ω-scan mode. Final cell constants were determined by global refinement of reflections from the complete data sets using the Lattice wizard module. Images were indexed and integrated with “smart” background evaluation using the CrysAlisPro data reduction package (1.171.39.20a, Rigaku Oxford Diffraction). Analysis of the integrated data did not show any decay. Data were corrected for systematic errors and absorption using the ABSPACK module: Numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The GRAL module and the ASSIGN SPACEGROUP routine of the WinGX suite were used for analysis of systematic absences and space group determination.

The structures were solved by the direct methods using SHELXT-2018/2 and refined by the full-matrix least-squares on $F^2$ using SHELXL-2018/3, which uses a model of atomic scattering based on spherical atoms. Calculations were mainly performed using the WinGX-2018.3 suite of programs. Non-hydrogen atoms were refined anisotropically.
The positions of the hydrogen atom H41 of formic acid in the crystals of [1]HCOO and H11 and H27 of doubly dearomatized complex 2 and mono-deprotonated complex 3 were determined by difference Fourier maps, and these atoms were refined isotropically. The other hydrogen atoms were inserted at the calculated positions and refined as riding atoms. All the compounds studied have no unusual bond lengths and angles.

Compound [1]HCOO crystallizes as a solvate with formic acid (1:1) (Figure S53). Interestingly, in the case of compound 2 a 1D polymeric structure is formed along the shortest axis 0a by means of cation(K+)…π(N2S2**) interactions and coordination bonds K+…O (Figure S55).

The disorder, if present, was resolved using free variables and reasonable restraints on geometry and anisotropic displacement parameters. It is noteworthy that in the case of 3 the apparent geometry of the ligand is averaged over two forms with either C11 or C27 arm being deprotonated.

Molecular structures of the investigated complexes in the crystalline phase as well as accepted partial numbering are presented as ORTEP diagrams in Figures S51–S56.


C16H14MnN2O2S21+ Br1−, bright yellow needle (0.250 × 0.049 × 0.043 mm3), formula weight 465.26; monoclinic, I2/a (No. 15), a = 17.4339(6) Å, b = 11.9674(3) Å, c = 18.4715(7) Å, β = 117.847(5)°, V = 3407.5(2) Å³, Z = 8, Z' = 1, T = 101(2) K, dcalc = 1.814 g cm⁻³, μ(MoKα) = 3.376 mm⁻¹, F(000) = 1856; Tmax/mini = 1.000/0.461; 27368 reflections were collected (2.110° ≤ θ ≤ 30.314°, index ranges: −22 ≤ h ≤ 24, −15 ≤ k ≤ 16, −25 ≤ l ≤ 22), 4504 of which were unique, Rint = 0.0670, Re = 0.0385; completeness to θ of 25.242° 99.8%. The refinement of 217 parameters with no restraints converged to R1 = 0.0260 and wR2 = 0.0679 for 4098 reflections with I > 2σ(I)
and \( R_1 = 0.0297 \) and \( wR_2 = 0.0692 \) for all data with \( S = 1.049 \) and residual electron density, \( \rho_{\text{max/min}} = 0.693 \) and \(-0.614 \, \text{e} \, \text{Å}^{-3}\). The crystals were grown by vapor diffusion of diethyl ether into a DCM/MeOH (1:1) solution.

**Crystallographic data for [1]Cl.**

C16H14MnN2O2S2^{1+} Cl^{-}, yellow plate (0.329 × 0.078 × 0.048 mm\(^3\)), formula weight 420.80; monoclinic, \( I2/a \) (No. 15), \( a = 18.1969(3) \, \text{Å}, \ b = 12.35882(16) \, \text{Å}, \ c = 16.6861(3) \, \text{Å}, \ \beta = 117.826(2)^\circ, \ V = 3318.66(12) \, \text{Å}^3, \ Z = 8, \ Z' = 1, \ T = 93(2) \, \text{K}, \ d_{\text{calc}} = 1.684 \, \text{g cm}^{-3}, \ \mu(\text{MoK} \alpha) = 1.220 \, \text{mm}^{-1}, \ F(000) = 1712; \ T_{\text{max/min}} = 1.000/0.707; \) 45115 reflections were collected \((2.078^\circ \leq \theta \leq 30.872^\circ, \text{index ranges}: \ -26 \leq h \leq 25, \ -17 \leq k \leq 17, \ -24 \leq l \leq 23), \) 4895 of which were unique, \( R_{\text{int}} = 0.0331, \ R_o = 0.0154; \) completeness to \( \theta \) of 25.242° 99.9%. The refinement of 217 parameters with no restraints converged to \( R_1 = 0.0235 \) and \( wR_2 = 0.0642 \) for 4539 reflections with \( I > 2\sigma(I) \) and \( R_1 = 0.0258 \) and \( wR_2 = 0.0652 \) for all data with \( S = 1.035 \) and residual electron density, \( \rho_{\text{max/min}} = 0.633 \) and \(-0.448 \, \text{e} \, \text{Å}^{-3}\). The crystals were grown by vapor diffusion of diethyl ether into a dichloromethane solution.

**Crystallographic data for [1]HCOO.**

C16H14MnN2O2S2^{1+} CHO2^{1-} \times CH2O2, yellow plank (0.116 × 0.102 × 0.043 mm\(^3\)), formula weight 476.39; monoclinic, \( P2_1/n \) (No. 14), \( a = 8.46572(14) \, \text{Å}, \ b = 14.8583(2) \, \text{Å}, \ c = 15.3199(2) \, \text{Å}, \ \beta = 98.6737(15)^\circ, \ V = 1905.00(5) \, \text{Å}^3, \ Z = 4, \ Z' = 1, \ T = 93(2) \, \text{K}, \ d_{\text{calc}} = 1.661 \, \text{g cm}^{-3}, \ \mu(\text{MoK} \alpha) = 0.952 \, \text{mm}^{-1}, \ F(000) = 976; \ T_{\text{max/min}} = 1.000/0.779; \) 59612 reflections were collected \((2.597^\circ \leq \theta \leq 32.353^\circ, \text{index ranges}: \ -12 \leq h \leq 12, \ -22 \leq k \leq 22, \ -22 \leq l \leq 22), \) 6441 of which were unique, \( R_{\text{int}} = 0.0369, \ R_o = 0.0208; \) completeness to \( \theta \) of 25.242° 99.9%. The refinement of 266 parameters with 1 restraint converged to \( R_1 = 0.0269 \) and \( wR_2 = 0.0753 \) for 5437 reflections with \( I > \)
2σ(I) and $R_1 = 0.0337$ and $wR_2 = 0.0782$ for all data with $S = 1.091$ and residual electron density, $\rho_{\text{max/min}} = 0.581$ and $-0.435$ e Å$^{-3}$. The crystals were grown by vapor diffusion of hexane into a dichloromethane solution.

**Crystallographic data for 2.**

C28H12D24KMnN2O5S2, light yellow plate (0.409 × 0.123 × 0.061 mm$^3$), formula weight 662.89; monoclinic, $P2_1/n$ (No. 14), $a = 9.3544(2)$ Å, $b = 16.4310(4)$ Å, $c = 19.2887(5)$ Å, $\beta = 94.431(2)^\circ$, $V = 2955.84(13)$ Å$^3$, $Z = 4$, $Z' = 1$, $T = 93(2)$ K, $d_{\text{calc}} = 1.490$ g cm$^{-3}$, $\mu(\text{MoK} \alpha) = 0.769$ mm$^{-1}$, $F(000) = 1336$; $T_{\text{max/min}} = 1.000/0.545$; 52162 reflections were collected (2.352° ≤ θ ≤ 27.000°, index ranges: $-11 \leq h \leq 11$, $-20 \leq k \leq 20$, $-24 \leq l \leq 24$), 6427 of which were unique, $R_{\text{int}} = 0.0572$, $R_o = 0.0322$; completeness to θ of 25.242° 99.9%. The refinement of 416 parameters with 211 restraints converged to $R_1 = 0.0460$ and $wR_2 = 0.1076$ for 5519 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0561$ and $wR_2 = 0.1123$ for all data with $S = 1.076$ and residual electron density, $\rho_{\text{max/min}} = 1.404$ and $-0.574$ e Å$^{-3}$. The crystals were grown by vapor diffusion of pentane into a THF-$d_8$ solution at −30 °C.

**Crystallographic data for 3.**

C16H13MnN2O2S2, red prism (0.110 × 0.053 × 0.037 mm$^3$), formula weight 384.34; monoclinic, $P2_1/c$ (No. 14), $a = 13.7117(3)$ Å, $b = 13.0041(2)$ Å, $c = 8.82065(19)$ Å, $\beta = 104.355(2)^\circ$, $V = 1523.69(6)$ Å$^3$, $Z = 4$, $Z' = 1$, $T = 94(2)$ K, $d_{\text{calc}} = 1.675$ g cm$^{-3}$, $\mu(\text{MoK} \alpha) = 1.150$ mm$^{-1}$, $F(000) = 784$; $T_{\text{max/min}} = 1.000/0.773$; 30423 reflections were collected (2.192° ≤ θ ≤ 28.997°, index ranges: $-18 \leq h \leq 18$, $-17 \leq k \leq 16$, $-11 \leq l \leq 11$), 3981 of which were unique, $R_{\text{int}} = 0.0392$, $R_o = 0.0220$; completeness to θ of 25.242° 99.9%. The refinement of 217 parameters with 1 restraint converged to $R_1 = 0.0477$ and $wR_2 = 0.1076$ for 3704 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0518$ and $wR_2 = 0.1088$ for
all data with $S = 1.312$ and residual electron density, $\rho_{\text{max/min}} = 1.102$ and $-0.648 \text{ e Å}^{-3}$.

The crystals were grown by vapor diffusion of pentane into a benzene solution.

Detailed information about crystal structure determination can be accessed via supplementary cif files. The crystallographic data for the investigated compounds have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1887964 ([1]Br), 1887965 ([1]Cl), 1887966 ([1]HCOO), 1887967 (2), and 1887968 (3). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
Figure S51. ORTEP at 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound [1]Br. Selected interatomic distances [Å]: Mn1–S1 2.2712(5), Mn1–S2 2.2609(5), Mn1–N1 2.0582(15), Mn1–N2 2.0572(14), Mn1–C1 1.7897(18), Mn1–C2 1.797(2).
Figure S52. ORTEP at 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound [1]Cl. Selected interatomic distances [Å]: Mn1–S1 2.2676(3), Mn1–S2 2.2646(3), Mn1–N1 2.0562(10), Mn1–N2 2.0541(10), Mn1–C1 1.7877(12), Mn1–C2 1.8025(13).
Figure S53. ORTEP at 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound [1]HCOO. Selected interatomic distances [Å]: Mn1–S1 2.2681(3), Mn1–S2 2.2705(3), Mn1–N1 2.0677(8), Mn1–N2 2.0660(8), Mn1–C1 1.7914(10), Mn1–C2 1.7884(10). Parameters of the H-bond O41–H41...O31 [Å, °]: O41–H41 0.925(16), H41...O31 1.620(16), O41...O31 2.5422(12), 〈O41–H41...O31 174(2).
Figure S54. ORTEP at 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound 2. Minor disordered components of THF ligands are omitted for clarity. Selected interatomic distances [Å]: Mn1–S1 2.2756(8), Mn1–S2 2.2867(7), Mn1–N1 2.044(2), Mn1–N2 2.049(2), Mn1–C1 1.767(3), Mn1–C2 1.779(3), C11–C12 1.384(4), C26–C27 1.367(4), C16–C17 1.499(4), C21–C22 1.508(4), S1–C11 1.737(3), S1–C21 1.820(3), S2–C17 1.825(3), S2–C27 1.752(3).
Figure S55. Fragments of packing of compound 2 demonstrating a 1D polymeric structure formed along the shortest axis 0a by means of cation(K$^+$)...π(N2S2**) interactions and coordination bonds (K$^+$...O). Minor disordered components of THF ligands are omitted for clarity. Some of the atoms are shown in a space-fill mode. Selected interatomic distances [Å]: O1–K1 2.733(2), Mn1...K1$^i$ 4.7368(7), N1...K1$^i$ 3.422(2), C13...K1$^i$ 3.424(3), C14...K1$^i$ 3.209(3), C15...K1$^i$ 3.103(3), C16...K1$^i$ 3.211(2), C25...K1$^i$ 3.246(3), C26...K1 3.202(3), C27...K1 3.451(3); symmetry operation $i$ ($x+1$, $y$, $z$).
Figure S56. ORTEP at 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound 3. Minor disordered component is shown by dash lines. Selected interatomic distances [Å]: Mn1–S1 2.2726(9), Mn1–S2 2.2866(9), Mn1–N1 2.051(2), Mn1–N2 2.056(2), Mn1–C1 1.782(3), Mn1–C2 1.784(3), C11–C12 1.444(4), C26–C27 1.441(4), C16–C17 1.507(4), C21–C22 1.494(5), S1–C11 1.784(3), S1–C21 1.816(3), S2–C17 1.823(3), S2–C27 1.784(3). The geometry is averaged over two forms with either C11 or C27 arm being deprotonated.
VI. References


