Stabilisation of Carbonyl Free Amidinato-Manganese(II) Hydride Complexes: "Masked" Sources of Manganese(I) in Organometallic Synthesis

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SUPPORTING INFORMATION

(7 Pages)

Contents

1. Synthesis of [{(Priso)Mn(μ-Br)}$_2$}]

A solution of K[Priso][1] (1.20 g, 2.3 mmol) in THF (20 cm^3) was added to a suspension of $MnBr_2$ (480 mg, 2.2 mmol) in THF (40 cm^3) at -80 °C. The reaction mixture was warmed to room temperature and stirred overnight. All volatiles were removed *in vacuo* and the residue was extracted with hexane (60 cm^3). The resultant pale yellow solution was concentrated to 30 cm^3 and cooled to -30 °C overnight to give colourless crystals of [{(Priso)Mn(μ-Br)}$_2$}]. Concentration of the supernatant and cooling to -30 °C yielded a second crop of the compound (861 mg, 63 %). M.p. = 58-70 °C; μ_{eff} (C_6D_6) = 6.40 μ_B; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = -13.29 (v. br), -12.12 (v. br), -5.07 (v. br), 4.43 (v. br), 15.00 (v. br), 19.18 (v. br) ppm; IR (ATR) ν = 3366 (m), 2173 (vs), 1610 (vs), 1582 (s), 1455 (m), 1433 (m), 1393 (w), 1276 (m), 1255 (m), 1177 (m), 1154 (m), 1124 (s), 1109 (m), 1045 (m), 933 (m), 871 (m), 798 (s), 755 (vs) cm^{-1}; MS (EI), *m*/*z* (%): 420.3 (PrisoH$^+$, 100); elemental analysis calc. for $C_{62}H_{96}Br_2Mn_2N_6$: C: 62.31 %, H: 8.10 %, N: 7.03 %; found: C: 62.42 %, H: 8.18 %, N: 7.13 %.

2. IR spectra of 2 and II

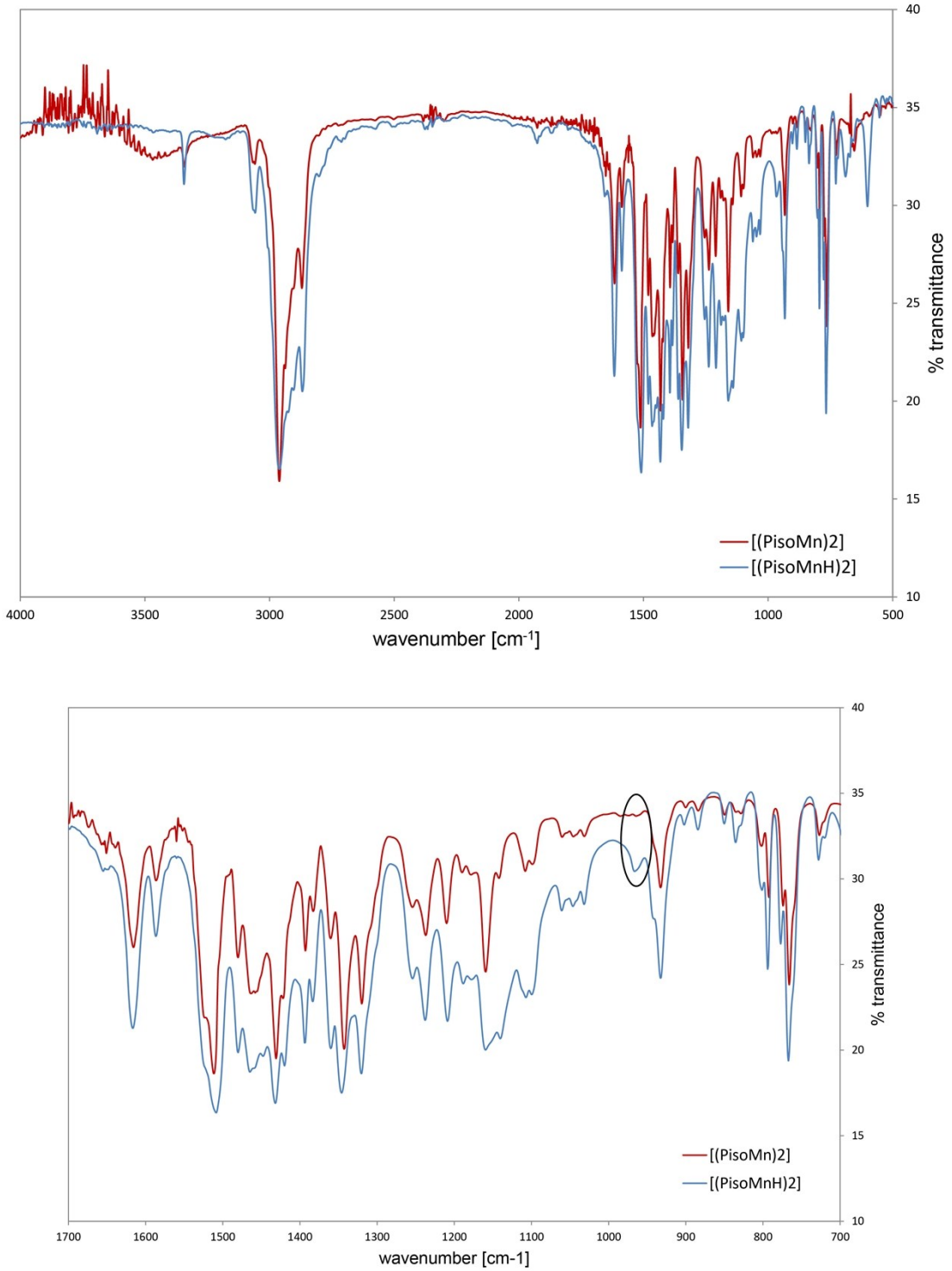

Figure S1. IR spectra (KBr disks) of compounds **2** and **II**. Full spectra (top) and zoom from 1700-700 cm^{-1} (bottom). The tentatively assigned Mn-H stretching band is circled.

3. X-ray Crystallography

Table S1. Summary of Crystallographic Data for **2**, **4**-**6**, [Mn(Piso")$_2$] **1S** and [{(Priso)Mn(μ-Br)}$_2$] **2S**

	2	**4**·(hexane)$_{0.75}$	**5**	**6**	**1S**·(hexane)$_{2.25}$	**2S**·(hexane)
empirical formula	$C_{58}H_{88}Mn_2N_4$	$C_{205.5}H_{226.5}Mn_3N_6$	$C_{33}H_{43}MnN_2O_4$	$C_{58}H_{86}Mn_2N_4O_2$	$C_{147.5}H_{173.5}MnN_4$	$C_{68}H_{110}Br_2Mn_2N_6$
formula weight	951.20	2945.25	586.63	981.19	2057.34	1281.32
crystal system	triclinic	trigonal	triclinic	triclinic	triclinic	monoclinic
space group	*P*-1	*P*-3*c*1	*P*-1	*P*-1	*P*-1	$P2_1/n$
a (Å)	10.3891(4)	22.945(2)	9.5137(4)	10.2505(4)	17.7667(4)	12.3353(6)
b (Å)	10.6635(4)	22.945(2)	10.4772(5)	10.6927(4)	19.5336(5)	19.0705(10)
c (Å)	14.1219(6)	40.907(3)	17.1114(8)	14.2503(6)	20.8577(5)	15.5764(8)
α (deg.)	108.980(3)	90	85.869(4)	105.002(3)	72.130(2)	90
β (deg)	102.353(3)	90	83.117(4)	103.792(3)	67.919(2)	101.664(2)
γ (deg.)	105.950(3)	120	67.869(4)	106.646(4)	78.661(2)	90
vol (Å^3)	1340.99(9)	18651(3)	1567.89(12)	1360.52(9)	6356.9(3)	3588.5(3)
Z	1	4	2	1	2	2
ρ (calcd) (g.cm^{-3})	1.178	1.049	1.243	1.198	1.075	1.186
μ (mm^{-1})	0.510	0.251	0.459	0.507	0.154	1.505
F(000)	514	6306	624	528	2223	1360
T (K)	123(2)	123(2)	150(2)	123(2)	123(2)	123(2)
reflections collected	9006	67838	10159	9780	97371	22314

unique reflections	4953	11566	6112	5334	24925	8196
R_{int}	0.0229	0.1588	0.0343	0.0442	0.0405	0.0614
R1 indices [$I>2\sigma(I)$]	0.0543	0.0873	0.0544	0.0471	0.0613	0.0736
*w*R2 indices (all data)	0.1503	0.2598	0.1364	0.0902	0.2003	0.1432
Largest peak and hole (e/Å^3)	0.85 , -0.57	0.94, -0.35	0.90, -0.37	0.35, -0.42	1.55, -0.37	0.70, -0.62
CCDC No.	1436857	1436859	1436860	1436861	1436856	1436858

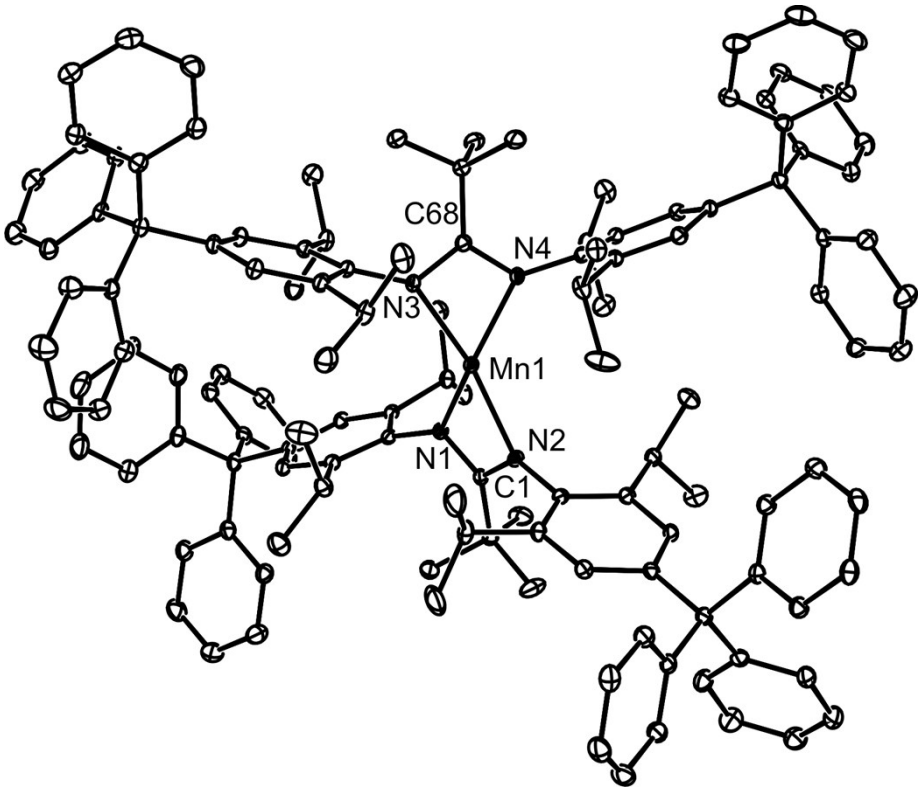

Figure S2. Thermal ellipsoid (25%) drawing of [Mn(Piso")$_2$] **1S**. Hydrogen atoms omitted. Selected bond distances (Å) and angles (°): Mn(1)-N(4) 2.0974(18), Mn(1)-N(1) 2.1010(18), Mn(1)-N(2) 2.1708(18), Mn(1)-N(3) 2.1806(19), N(1)-C(1) 1.349(3), N(2)-C(1) 1.341(3), N(3)-C(68) 1.334(3), N(4)-C(68) 1.354(3), N(1)-Mn(1)-N(2) 62.14(7), N(4)-Mn(1)-N(3) 61.95(7), N(2)-C(1)-N(1) 110.13(19), N(3)-C(68)-N(4) 110.05(19).

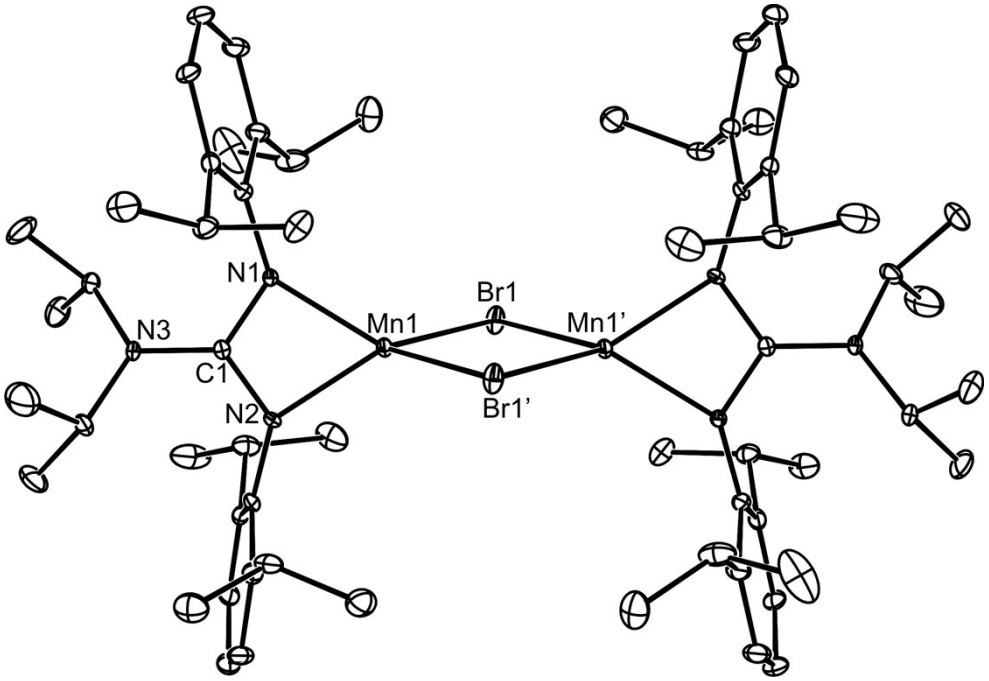

Figure S3. Thermal ellipsoid (25%) drawing of [{(Priso)Mn(μ-Br)}$_2$] **2S**. Hydrogen atoms omitted. Selected bond distances (Å) and angles (°): Br(1)-Mn(1) 2.5438(8), Mn(1)-N(2) 2.078(3), Mn(1)-N(1) 2.085(3), Mn(1)-Br(1)' 2.5387(8), N(1)-C(1) 1.355(5), N(2)-C(1) 1.348(5), N(3)-C(1) 1.383(5), Mn(1)'-Br(1)-Mn(1) 85.08(2), N(2)-Mn(1)-N(1) 64.46(13), Br(1)'-Mn(1)-Br(1) 94.92(2), N(2)-C(1)-N(1) 110.5(3). Symmetry operation: ' -x+1, -y+1, -z.

4. References

1. G. Jin, C. Jones, P. C. Junk, K.-A. Lippert, R. P.Rose, A. Stasch, *New J. Chem.*, 2009, **33**, 64.