SUPPORTING INFORMATION

Amidation of Saturated C–H Bonds Catalyzed by Electron-Deficient Ruthenium and Manganese Porphyrins. A Highly Catalytic Nitrogen Atom Transfer Process

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General. All reactions were performed under an argon atmosphere. The solvents were purified by standard procedures. $PhI(OAc)_2$ (Aldrich), amides NH_2R (Aldrich, R = Ts, Ns, SO_2Me, $COCF_3$), and hydrocarbon substrates (Lancaster) were all the best products from the commercial vendors. *N*-Tosyliminophenyliodinane (PhI=NTs),[1] complexes **1**[2] and **2**[3] were prepared by the literature methods. ^1H NMR spectra were obtained on a Bruker DPX-300 FT-NMR spectrometer (300 MHz) and the chemical shifts (δ ppm) are reported relative to tetramethylsilane (TMS). Mass spectra were recorded on a Jasco spectrometer.

General Procedure for Complex 1 or 2-Catalyzed Amidation of Hydrocarbons with PhI=NTs. A solution of substrate (0.15 mmol) in dry dichloromethane (4 mL) was added through syringe into a Schlenk flask containing complex **1** or **2** (0.002 mmol) and molecular sieves (4 Å, 50 mg). The mixture was stirred at room temperature for 10 min, then treated with PhI=NTs (0.30 mmol) and maintained at 40 °C for 2 h. After the mixture was cooled to room temperature, the molecular sieves were filtered off and washed with CH_2Cl_2. The filtrate and washings were evaporated to dryness and the product was purified by column chromatography (silica gel 230–400 mesh; *n*-hexane:EtOAc = 6:1 as eluent).

General Procedure for Complex 2-Catalyzed Amidation of Hydrocarbons with $PhI(OAc)_2$ and NH_2R. To a well-stirred suspension of molecular sieves (4 Å, 50 mg) in dry dichloromethane (4 mL) containing complex **2** (0.002 mmol) at room temperature was added the substrate (0.20 mmol) by means of a syringe. After 10 min, NH_2R (0.30 mmol) and $PhI(OAc)_2$ (0.25 mmol) were added and the mixture was stirred at 40 °C for 2 h. The solution was then filtered and the products were separated and purified by column chromatography (silica gel 230–400 mesh; *n*-hexane:EtOAc = 6:1 as eluent).

***N*-(*p*-Toluenesulfonyl)-1-aminoindan.** mp 141–142 °C; MS *m/z* 287 (M^+); HRMS *m/z* (M^+) calcd for $C_{16}H_{17}NO_2S$ 287.0980, found 287.0972; ^1H NMR ($CDCl_3$) δ 7.82 (d, 2H, *J* = 7.96 Hz, Ar-H), 7.33 (d, 2H, *J* = 8.02 Hz, Ar-H), 7.07–7.26 (m, 4H, Ar-H), 4.82 (d, 1H, *J* = 6.91 Hz, NH), 4.69 (s, 1H, CH-N), 2.85–2.95 (m, 1H, CH_2-H_a), 2.68–2.79 (m, 1H, CH_2-H_b), 2.46 (s, 3H, CH_3), 2.28–2.39 (m, 1H, CH_2'-H_a), 1.68–1.81 (m, 1H, CH_2'-H_b).

***N*-(*p*-Toluenesulfonyl)-2-aminotetrahydrofuran.** mp 124–125 °C; MS *m/z* 241 (M^+); ^1H NMR ($CDCl_3$) δ 7.79 (d, 2H, *J* = 8.24 Hz, Ar-H), 7.27 (d, 2H, *J* = 8.21 Hz, Ar-H),

5.49 (d, 1H, J = 8.80 Hz, NH), 5.31–5.37 (m, 1H, CH-N), 3.67–3.72 (m, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.72–2.22 (m, 4H, CH_2).

***N*-(*p*-Toluenesulfonyl)-3-amino-1,2-dihydronaphthalene.** mp 130–131 °C; MS *m/z* 299 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.73 (d, 2H, J = 8.11 Hz, Ar-H), 7.30 (d, 2H, J = 8.21 Hz, Ar-H), 7.00–7.21 (m, 4H, Ar-H), 6.47 (d, 1H, J = 9.38 Hz, C*H*=CH), 5.72 (t, 1H, J = 4.85, 4.89 Hz, CH=C*H*), 4.58 (d, 1H, J = 8.89 Hz, NH), 4.10–4.15 (m, 1H, CH-N), 2.87–2.91 (m, 2H, CH_2), 2.45 (s, 3H, CH_3).

***N*-(*p*-Toluenesulfonyl)-1-amino-1-(2-naphthyl)ethane.** mp 152–155 °C; MS *m/z* 325 (M^+), 310 ($M^+ - CH_3$); HRMS *m/z* (M^+) calcd for $C_{19}H_{19}NO_2S$ 325.1137, found 325.1136; ^{1}H NMR ($CDCl_3$) δ 7.41–7.76 (m, 8H, Ar-H), 7.18–7.22 (dd, 1H, J = 1.76, 1.77 Hz, Ar-H), 7.03 (d, 2H, J = 8.00 Hz, Ar-H), 4.93 (d, 1H, J = 6.91 Hz, NH), 4.59–4.68 (m, 1H, CH-N), 2.24 (s, 3H, Ar-CH_3), 1.51 (d, 3H, J = 6.86 Hz, CH*CH*$_3$).

***N*-Methylsulfonyl-1-aminoindan.** ^{1}H NMR ($CDCl_3$) δ 7.40–7.26 (m, 4H, Ar-H), 4.94–5.02 (m, 1H, CH-N), 4.57 (d, 1H, J = 8.58 Hz, NH), 3.07 (s, 3H, CH_3), 2.97–3.06 (m, 1H, CH_2-H_a), 2.81–2.91 (m, 1H, CH_2-H_b), 2.59–2.69 (m, 1H, CH_2'-H_a), 1.88–2.00 (m, 1H, CH_2'-H_b).

The spectral data of the other *N*-substituted amides are identical with those reported previously.[4–6]

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Table S1. Crystal Data and Structure Refinement for Complex **2**·$4CH_2Cl_2$

empirical formula	$C_{44}H_8ClF_{20}N_4Mn·4CH_2Cl_2$
formula weight	1402.64
T, K	293(2)
λ, Å	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	18.017(3)
b, Å	18.017(3)
c, Å	8.389(1)
α, deg	90.000(3)
β, deg	90.000(4)
γ, deg	90.000(4)
V, Å^3	2723.1(7)
Z	2
F(000)	1380
density (calcd), Mg/m^3	1.713
abs coeff, mm^{-1}	0.790
index ranges	$-23 \le h \le 23$, $-23 \le k \le 23$, $0 \le l \le 10$
no. of reflns collected	12179
no. of independent reflns	12157
abs correction	SADABS
max / min transmission	0.947 / 0.921
refinement method	full-matrix least-squares on F^2
data / restraints / parameters	12157 / 0 / 740
final R indices ($I > 2\sigma(I)$)	$R1 = 0.0688$, w$R2 = 0.2605$
goodness-of-fit on F^2	1.128
largest diff. peak / hole, eÅ^{-3}	0.905 / −0.639

Table S2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex **2**·4CH_2Cl_2. U(eq) = One Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	y	z	U(eq)
Mn(1)	-2500(1)	2500(1)	-2516(1)	37(1)
Cl(1)	-2502(1)	2499(1)	-5448(1)	58(1)
F(1)	-1625(1)	5159(1)	389(3)	94(1)
F(2)	-1283(2)	6613(1)	380(3)	110(1)
F(3)	-1232(2)	7355(1)	-2395(4)	121(1)
F(4)	-1534(2)	6647(1)	-5165(3)	118(1)
F(5)	-1921(1)	5200(1)	-5152(3)	95(1)
F(6)	151(1)	1627(1)	397(3)	95(1)
F(7)	1607(1)	1284(2)	389(3)	115(1)
F(8)	2353(1)	1255(2)	-2400(3)	121(1)
F(9)	1646(1)	1544(2)	-5167(3)	122(1)
F(10)	201(1)	1923(1)	-5144(3)	98(1)
F(11)	-3073(1)	-201(1)	-5128(3)	97(1)
F(12)	-3468(2)	-1650(1)	-5159(3)	121(1)
F(13)	-3755(2)	-2351(1)	-2383(4)	123(1)
F(14)	-3719(1)	-1611(1)	368(3)	111(1)
F(15)	-3377(1)	-162(1)	393(3)	96(1)
F(16)	-5204(1)	3075(1)	-5116(3)	94(1)
F(17)	-6640(1)	3456(2)	-5145(3)	113(1)
F(18)	-7350(1)	3757(2)	-2366(3)	121(1)
F(19)	-6600(1)	3723(2)	369(3)	112(1)
F(20)	-5155(1)	3377(1)	397(3)	95(1)
N(1)	-1541(1)	3050(1)	-2365(3)	41(1)
N(2)	-1945(1)	1538(1)	-2357(3)	41(1)
N(3)	-3464(1)	1945(1)	-2365(3)	42(1)
N(4)	-3055(1)	3463(1)	-2358(3)	43(1)
C(1)	-2005(2)	4330(2)	-2348(4)	44(1)
C(2)	-1446(2)	3816(2)	-2353(4)	48(1)
C(3)	-659(2)	3976(2)	-2329(4)	60(1)
C(4)	-291(2)	3338(2)	-2354(4)	56(1)
C(5)	-830(2)	2752(2)	-2352(4)	46(1)
C(6)	-676(2)	1996(2)	-2343(4)	47(1)
C(7)	-1194(2)	1439(2)	-2338(4)	48(1)
C(8)	-1023(2)	665(2)	-2325(4)	56(1)
C(9)	-1662(2)	289(2)	-2341(4)	55(1)
C(10)	-2246(2)	827(2)	-2356(4)	46(1)
C(11)	-2999(2)	679(2)	-2351(4)	42(1)
C(12)	-3559(2)	1190(2)	-2330(4)	47(1)
C(13)	-4339(2)	1010(2)	-2320(4)	61(1)
C(14)	-4702(2)	1660(2)	-2346(4)	60(1)
C(15)	-4169(2)	2253(2)	-2346(4)	47(1)
C(16)	-4325(2)	2995(2)	-2357(4)	45(1)
C(17)	-3815(2)	3548(2)	-2353(4)	47(1)
C(18)	-3979(2)	4333(2)	-2307(4)	61(1)
C(19)	-3335(2)	4709(2)	-2352(4)	56(1)
C(20)	-2750(2)	4162(2)	-2361(4)	45(1)
C(21)	-1786(2)	5134(2)	-2392(4)	49(1)
C(22)	-1626(2)	5507(2)	-1025(4)	61(1)

C(23)	-1442(2)	6257(2)	-953(5)	70(1)
C(24)	-1408(2)	6620(2)	-2386(6)	84(2)
C(25)	-1573(2)	6264(2)	-3841(5)	80(2)
C(26)	-1765(2)	5539(2)	-3787(5)	63(1)
C(27)	126(2)	1778(2)	-2385(4)	53(1)
C(28)	508(2)	1618(2)	-1001(4)	60(1)
C(29)	1243(2)	1434(2)	-916(5)	72(1)
C(30)	1619(2)	1427(2)	-2327(6)	98(2)
C(31)	1279(2)	1577(2)	-3803(5)	79(2)
C(32)	544(2)	1762(2)	-3770(5)	62(1)
C(33)	-3218(2)	-133(2)	-2404(4)	50(1)
C(34)	-3230(2)	-546(2)	-3790(5)	62(1)
C(35)	-3425(2)	-1274(2)	-3800(5)	79(2)
C(36)	-3585(2)	-1627(2)	-2411(6)	82(2)
C(37)	-3570(2)	-1266(2)	-979(5)	69(1)
C(38)	-3373(2)	-509(2)	-1021(5)	63(1)
C(39)	-5133(2)	3217(2)	-2385(4)	53(1)
C(40)	-5546(2)	3230(2)	-3771(4)	62(1)
C(41)	-6277(2)	3424(2)	-3797(5)	71(1)
C(42)	-6611(2)	3579(2)	-2386(6)	84(2)
C(43)	-6257(2)	3558(2)	-961(5)	69(1)
C(44)	-5506(2)	3378(2)	-1000(5)	64(1)
C(45)	-4004(3)	1353(3)	3260(7)	146(3)
Cl(2)	-4250(1)	1966(1)	1814(2)	155(1)
Cl(3)	-4618(1)	651(1)	3550(2)	151(1)
C(46)	-3647(3)	3999(3)	3209(7)	139(2)
Cl(4)	-4348(1)	4619(1)	3535(2)	151(1)
Cl(5)	-3034(1)	4250(1)	1829(2)	157(1)
C(47)	995(3)	6357(3)	-3209(7)	136(2)
Cl(7)	755(1)	6963(1)	-1827(2)	156(1)
Cl(6)	381(1)	5648(1)	-3526(2)	149(1)
C(48)	-1369(3)	987(3)	-6755(7)	161(3)
Cl(8)	-645(1)	382(1)	-6463(2)	152(1)
Cl(9)	-1967(1)	750(1)	-8179(2)	156(1)

Table S3. Bond Lengths (Å) and Angles (°) for Complex **2**

Mn(1)-N(1)	1.996(2)	Mn(1)-N(3)	2.009(2)
Mn(1)-N(2)	2.006(2)	Mn(1)-N(4)	2.006(2)
Mn(1)-Cl(1)	2.4595(11)	F(1)-C(22)	1.342(4)
F(2)-C(23)	1.320(5)	F(3)-C(24)	1.360(4)
F(4)-C(25)	1.309(5)	F(5)-C(26)	1.327(4)
F(6)-C(28)	1.338(4)	F(7)-C(29)	1.305(4)
F(8)-C(30)	1.359(4)	F(9)-C(31)	1.322(5)
F(10)-C(32)	1.340(4)	F(11)-C(34)	1.314(4)
F(12)-C(35)	1.328(5)	F(13)-C(36)	1.339(4)
F(14)-C(37)	1.318(4)	F(15)-C(38)	1.340(4)
F(16)-C(40)	1.316(4)	F(17)-C(41)	1.308(4)
F(18)-C(42)	1.368(4)	F(19)-C(43)	1.310(4)
F(20)-C(44)	1.332(4)	N(1)-C(2)	1.389(4)
N(1)-C(5)	1.388(4)	N(2)-C(7)	1.365(4)
N(2)-C(10)	1.391(4)	N(3)-C(12)	1.372(4)
N(3)-C(15)	1.386(4)	N(4)-C(20)	1.375(4)
N(4)-C(17)	1.378(4)	C(1)-C(20)	1.375(4)
C(1)-C(2)	1.368(4)	C(1)-C(21)	1.503(4)
C(2)-C(3)	1.449(4)	C(3)-C(4)	1.327(5)
C(4)-C(5)	1.435(4)	C(5)-C(6)	1.389(4)
C(6)-C(7)	1.370(4)	C(6)-C(27)	1.499(4)
C(7)-C(8)	1.427(4)	C(8)-C(9)	1.335(4)
C(9)-C(10)	1.432(4)	C(10)-C(11)	1.382(4)
C(11)-C(12)	1.366(4)	C(11)-C(33)	1.515(4)
C(12)-C(13)	1.443(4)	C(13)-C(14)	1.340(5)
C(14)-C(15)	1.436(5)	C(15)-C(16)	1.367(4)
C(16)-C(17)	1.355(4)	C(16)-C(39)	1.511(4)
C(17)-C(18)	1.444(4)	C(18)-C(19)	1.344(5)
C(19)-C(20)	1.443(4)	C(21)-C(26)	1.379(5)
C(21)-C(22)	1.360(5)	C(22)-C(23)	1.392(5)
C(23)-C(24)	1.370(6)	C(24)-C(25)	1.410(6)
C(25)-C(26)	1.353(5)	C(27)-C(32)	1.385(5)
C(27)-C(28)	1.380(5)	C(28)-C(29)	1.367(5)
C(29)-C(30)	1.364(6)	C(30)-C(31)	1.408(6)
C(31)-C(32)	1.366(5)	C(33)-C(34)	1.381(5)
C(33)-C(38)	1.372(5)	C(34)-C(35)	1.358(5)
C(35)-C(36)	1.359(6)	C(36)-C(37)	1.367(6)
C(37)-C(38)	1.409(5)	C(39)-C(44)	1.372(5)
C(39)-C(40)	1.381(5)	C(40)-C(41)	1.362(5)
C(41)-C(42)	1.357(6)	C(42)-C(43)	1.357(6)
C(43)-C(44)	1.391(5)	C(45)-Cl(3)	1.696(5)
C(45)-Cl(2)	1.699(6)	C(46)-Cl(5)	1.663(5)
C(46)-Cl(4)	1.709(5)	C(47)-Cl(7)	1.651(6)
C(47)-Cl(6)	1.712(5)	C(48)-Cl(9)	1.665(6)
C(48)-Cl(8)	1.718(5)		

N(1)-Mn(1)-N(3)	172.72(10)	N(1)-Mn(1)-N(2)	89.61(10)
N(3)-Mn(1)-N(2)	89.79(10)	N(1)-Mn(1)-N(4)	89.92(10)
N(3)-Mn(1)-N(4)	89.71(10)	N(2)-Mn(1)-N(4)	172.36(10)
N(1)-Mn(1)-Cl(1)	93.76(8)	N(3)-Mn(1)-Cl(1)	93.52(8)
N(2)-Mn(1)-Cl(1)	93.81(8)	N(4)-Mn(1)-Cl(1)	93.83(8)
C(2)-N(1)-C(5)	105.8(2)	C(2)-N(1)-Mn(1)	126.8(2)
C(5)-N(1)-Mn(1)	127.3(2)	C(7)-N(2)-C(10)	105.5(2)
C(7)-N(2)-Mn(1)	127.5(2)	C(10)-N(2)-Mn(1)	126.92(19)
C(12)-N(3)-C(15)	106.4(2)	C(12)-N(3)-Mn(1)	127.12(19)

C(15)-N(3)-Mn(1)	126.5(2)	C(20)-N(4)-C(17)	107.2(2)
C(20)-N(4)-Mn(1)	126.31(19)	C(17)-N(4)-Mn(1)	126.3(2)
C(20)-C(1)-C(2)	124.7(3)	C(20)-C(1)-C(21)	117.8(3)
C(2)-C(1)-C(21)	117.4(3)	C(1)-C(2)-N(1)	125.6(3)
C(1)-C(2)-C(3)	125.9(3)	N(1)-C(2)-C(3)	108.6(3)
C(4)-C(3)-C(2)	108.4(3)	C(3)-C(4)-C(5)	107.5(3)
N(1)-C(5)-C(6)	124.3(3)	N(1)-C(5)-C(4)	109.8(3)
C(6)-C(5)-C(4)	125.9(3)	C(7)-C(6)-C(5)	125.6(3)
C(7)-C(6)-C(27)	117.7(3)	C(5)-C(6)-C(27)	116.7(3)
N(2)-C(7)-C(6)	125.3(3)	N(2)-C(7)-C(8)	109.9(3)
C(6)-C(7)-C(8)	124.7(3)	C(9)-C(8)-C(7)	108.1(3)
C(8)-C(9)-C(10)	106.8(3)	C(11)-C(10)-N(2)	124.2(3)
C(11)-C(10)-C(9)	126.2(3)	N(2)-C(10)-C(9)	109.6(3)
C(12)-C(11)-C(10)	126.5(3)	C(12)-C(11)-C(33)	117.3(3)
C(10)-C(11)-C(33)	116.3(3)	N(3)-C(12)-C(11)	125.2(3)
N(3)-C(12)-C(13)	110.1(3)	C(11)-C(12)-C(13)	124.7(3)
C(14)-C(13)-C(12)	106.2(3)	C(13)-C(14)-C(15)	108.9(3)
N(3)-C(15)-C(16)	125.4(3)	N(3)-C(15)-C(14)	108.4(3)
C(16)-C(15)-C(14)	126.2(3)	C(17)-C(16)-C(15)	125.5(3)
C(17)-C(16)-C(39)	117.3(3)	C(15)-C(16)-C(39)	117.2(3)
C(16)-C(17)-N(4)	126.2(3)	C(16)-C(17)-C(18)	125.6(3)
N(4)-C(17)-C(18)	108.2(3)	C(19)-C(18)-C(17)	108.4(3)
C(18)-C(19)-C(20)	106.7(3)	N(4)-C(20)-C(1)	126.3(3)
N(4)-C(20)-C(19)	109.4(3)	C(1)-C(20)-C(19)	124.3(3)
C(26)-C(21)-C(22)	116.6(3)	C(26)-C(21)-C(1)	122.5(3)
C(22)-C(21)-C(1)	120.8(3)	F(1)-C(22)-C(21)	121.0(3)
F(1)-C(22)-C(23)	114.5(3)	C(21)-C(22)-C(23)	124.5(3)
F(2)-C(23)-C(24)	120.1(3)	F(2)-C(23)-C(22)	124.0(4)
C(24)-C(23)-C(22)	115.9(4)	F(3)-C(24)-C(23)	118.7(4)
F(3)-C(24)-C(25)	119.1(4)	C(23)-C(24)-C(25)	122.2(4)
F(4)-C(25)-C(26)	123.4(4)	F(4)-C(25)-C(24)	118.9(3)
C(26)-C(25)-C(24)	117.7(4)	F(5)-C(26)-C(21)	118.9(3)
F(5)-C(26)-C(25)	118.0(3)	C(21)-C(26)-C(25)	123.1(4)
C(32)-C(27)-C(28)	115.5(3)	C(32)-C(27)-C(6)	123.3(3)
C(28)-C(27)-C(6)	121.1(3)	F(6)-C(28)-C(29)	115.0(3)
F(6)-C(28)-C(27)	119.7(3)	C(29)-C(28)-C(27)	125.3(3)
F(7)-C(29)-C(30)	118.4(3)	F(7)-C(29)-C(28)	125.6(3)
C(30)-C(29)-C(28)	116.0(4)	C(29)-C(30)-F(8)	121.7(4)
C(29)-C(30)-C(31)	123.0(4)	F(8)-C(30)-C(31)	115.3(4)
F(9)-C(31)-C(32)	120.8(4)	F(9)-C(31)-C(30)	122.3(3)
C(32)-C(31)-C(30)	116.8(4)	F(10)-C(32)-C(31)	118.9(3)
F(10)-C(32)-C(27)	117.8(3)	C(31)-C(32)-C(27)	123.3(4)
C(34)-C(33)-C(38)	116.3(3)	C(34)-C(33)-C(11)	123.3(3)
C(38)-C(33)-C(11)	120.3(3)	F(11)-C(34)-C(35)	120.5(3)
F(11)-C(34)-C(33)	117.4(3)	C(35)-C(34)-C(33)	122.0(4)
F(12)-C(35)-C(36)	119.0(4)	F(12)-C(35)-C(34)	120.9(4)
C(36)-C(35)-C(34)	120.1(4)	F(13)-C(36)-C(35)	121.3(4)
F(13)-C(36)-C(37)	117.0(4)	C(35)-C(36)-C(37)	121.7(4)
F(14)-C(37)-C(36)	121.6(3)	F(14)-C(37)-C(38)	122.0(3)
C(36)-C(37)-C(38)	116.4(4)	F(15)-C(38)-C(33)	121.3(3)
F(15)-C(38)-C(37)	115.3(3)	C(33)-C(38)-C(37)	123.4(3)
C(44)-C(39)-C(40)	116.5(3)	C(44)-C(39)-C(16)	121.0(3)
C(40)-C(39)-C(16)	122.4(3)	F(16)-C(40)-C(41)	119.6(3)
F(16)-C(40)-C(39)	117.9(3)	C(41)-C(40)-C(39)	122.5(3)
F(17)-C(41)-C(42)	121.5(3)	F(17)-C(41)-C(40)	120.5(3)
C(42)-C(41)-C(40)	118.0(4)	C(43)-C(42)-C(41)	123.6(3)
C(43)-C(42)-F(18)	117.0(4)	C(41)-C(42)-F(18)	119.4(4)
F(19)-C(43)-C(42)	121.5(3)	F(19)-C(43)-C(44)	122.2(3)
C(42)-C(43)-C(44)	116.3(4)	F(20)-C(44)-C(39)	120.8(3)

F(20)-C(44)-C(43)	116.2(3)	C(39)-C(44)-C(43)	123.0(4)
Cl(3)-C(45)-Cl(2)	114.7(3)	Cl(5)-C(46)-Cl(4)	115.1(3)
Cl(7)-C(47)-Cl(6)	115.7(3)	Cl(9)-C(48)-Cl(8)	115.5(3)

Table S4. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex $2 \cdot 4CH_2Cl_2$. The Anisotropic Displacement Factor Exponent Takes the Form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn(1)	27(1)	28(1)	58(1)	-2(1)	-1(1)	1(1)
Cl(1)	58(1)	58(1)	57(1)	0(1)	-1(1)	3(1)
F(1)	111(2)	78(2)	91(2)	-14(1)	-5(1)	-27(1)
F(2)	125(2)	82(2)	124(2)	-40(2)	-8(2)	-34(2)
F(3)	130(2)	40(1)	193(3)	3(2)	-25(2)	-31(1)
F(4)	149(2)	77(2)	129(2)	48(1)	-21(2)	-31(2)
F(5)	136(2)	67(2)	83(2)	2(1)	-32(1)	-12(2)
F(6)	84(2)	115(2)	88(2)	5(1)	-9(1)	28(1)
F(7)	84(2)	133(2)	127(2)	15(2)	-47(1)	35(2)
F(8)	35(1)	137(2)	192(3)	16(2)	2(1)	35(1)
F(9)	74(2)	153(2)	139(2)	26(2)	49(1)	30(2)
F(10)	70(2)	138(2)	86(2)	25(2)	1(1)	20(2)
F(11)	142(2)	73(2)	77(2)	-9(1)	26(1)	-15(2)
F(12)	165(2)	70(2)	127(2)	-45(2)	21(2)	-28(2)
F(13)	128(2)	33(1)	207(3)	-1(2)	14(2)	-35(1)
F(14)	129(2)	75(2)	128(2)	36(1)	17(2)	-31(2)
F(15)	109(2)	81(2)	97(2)	8(1)	1(1)	-30(1)
F(16)	68(2)	130(2)	85(2)	-29(2)	-14(1)	14(2)
F(17)	78(2)	138(2)	123(2)	-18(2)	-35(1)	23(2)
F(18)	38(1)	126(2)	198(3)	-21(2)	1(2)	32(1)
F(19)	79(2)	128(2)	128(2)	-10(2)	34(1)	32(2)
F(20)	74(2)	115(2)	95(2)	-7(2)	5(1)	26(1)
N(1)	27(1)	33(1)	63(2)	1(1)	-4(1)	5(1)
N(2)	27(1)	30(1)	65(2)	1(1)	4(1)	-4(1)
N(3)	34(1)	27(1)	64(2)	-7(1)	4(1)	-1(1)
N(4)	30(1)	27(1)	72(2)	-1(1)	-6(1)	-1(1)
C(1)	31(2)	33(2)	70(2)	-2(2)	-6(2)	4(1)
C(2)	46(2)	33(2)	64(2)	3(2)	-5(2)	-10(2)
C(3)	35(2)	43(2)	102(3)	4(2)	-4(2)	-17(2)
C(4)	34(2)	43(2)	92(3)	7(2)	3(2)	-2(2)
C(5)	28(2)	32(2)	77(2)	0(2)	0(2)	5(1)
C(6)	32(2)	38(2)	71(2)	6(2)	-4(2)	1(2)
C(7)	33(2)	40(2)	70(2)	3(2)	-2(2)	1(2)
C(8)	38(2)	41(2)	90(3)	5(2)	3(2)	12(2)
C(9)	43(2)	34(2)	88(3)	-3(2)	10(2)	8(2)
C(10)	38(2)	29(2)	71(2)	4(2)	5(2)	2(2)
C(11)	37(2)	28(2)	62(2)	0(2)	6(2)	-2(1)
C(12)	32(2)	35(2)	74(2)	-2(2)	-3(2)	-9(2)
C(13)	43(2)	41(2)	99(3)	-9(2)	5(2)	-3(2)
C(14)	32(2)	47(2)	102(3)	-18(2)	1(2)	-11(2)
C(15)	28(2)	35(2)	77(2)	-6(2)	4(2)	-1(2)
C(16)	30(2)	33(2)	71(2)	-5(2)	-1(2)	1(1)
C(17)	36(2)	35(2)	69(2)	-2(2)	-1(2)	2(2)
C(18)	38(2)	40(2)	105(3)	-9(2)	-8(2)	11(2)
C(19)	37(2)	30(2)	102(3)	1(2)	-10(2)	2(2)
C(20)	30(2)	29(2)	75(2)	-3(2)	-4(2)	0(1)
C(21)	27(2)	37(2)	85(2)	-5(2)	-8(2)	-3(2)
C(22)	48(2)	49(2)	86(3)	15(2)	3(2)	-6(2)

C(23)	57(2)	44(2)	107(3)	-15(2)	-8(2)	-6(2)
C(24)	60(3)	31(2)	161(4)	-4(2)	-13(3)	-11(2)
C(25)	68(3)	49(2)	121(3)	28(2)	-15(2)	-11(2)
C(26)	53(2)	43(2)	92(3)	5(2)	-16(2)	-6(2)
C(27)	27(2)	34(2)	97(3)	4(2)	-5(2)	-2(2)
C(28)	51(2)	48(2)	80(3)	-4(2)	4(2)	11(2)
C(29)	43(2)	78(3)	94(3)	4(2)	-2(2)	13(2)
C(30)	40(2)	65(3)	189(4)	-3(3)	-41(3)	21(2)
C(31)	38(2)	64(3)	136(3)	8(2)	33(2)	10(2)
C(32)	38(2)	56(2)	92(3)	12(2)	6(2)	6(2)
C(33)	24(2)	41(2)	85(2)	14(2)	4(2)	-2(2)
C(34)	60(2)	34(2)	93(3)	-12(2)	14(2)	-10(2)
C(35)	80(3)	56(3)	99(3)	-23(2)	11(2)	-3(2)
C(36)	72(3)	26(2)	146(4)	2(2)	11(3)	-15(2)
C(37)	62(2)	47(2)	98(3)	15(2)	15(2)	-9(2)
C(38)	55(2)	45(2)	88(3)	-13(2)	-2(2)	-7(2)
C(39)	42(2)	30(2)	85(2)	-5(2)	11(2)	4(2)
C(40)	47(2)	64(2)	74(2)	-15(2)	-4(2)	11(2)
C(41)	43(2)	74(3)	96(3)	-8(2)	-30(2)	11(2)
C(42)	32(2)	61(3)	158(4)	-14(3)	5(2)	10(2)
C(43)	33(2)	68(3)	105(3)	-10(2)	16(2)	10(2)
C(44)	53(2)	50(2)	90(3)	-6(2)	-11(2)	8(2)
C(45)	112(4)	119(4)	208(6)	25(4)	-61(4)	-48(3)
Cl(2)	147(1)	177(2)	140(1)	54(1)	-37(1)	-35(1)
Cl(3)	128(1)	132(1)	192(2)	8(1)	-22(1)	-66(1)
C(46)	96(4)	93(4)	228(6)	40(4)	22(4)	31(3)
Cl(4)	133(1)	130(1)	189(2)	18(1)	5(1)	63(1)
Cl(5)	176(1)	158(1)	137(1)	36(1)	52(1)	39(1)
C(47)	113(4)	115(4)	180(5)	-29(4)	51(3)	-42(3)
Cl(7)	149(1)	183(2)	136(1)	-57(1)	35(1)	-40(1)
Cl(6)	126(1)	130(1)	191(2)	-7(1)	17(1)	-64(1)
C(48)	142(4)	119(4)	221(6)	-77(4)	-57(4)	77(3)
Cl(8)	134(1)	133(1)	190(2)	-20(1)	-7(1)	68(1)
Cl(9)	181(2)	154(1)	133(1)	-37(1)	-50(1)	39(1)

Table S5. Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Complex **2**·$4CH_2Cl_2$.

	x	y	z	U(eq)
H(3A)	-446	4447	-2300	72
H(4A)	222	3281	-2370	68
H(8A)	-550	459	-2307	67
H(9A)	-1716	-224	-2343	66
H(13A)	-4549	539	-2301	73
H(14A)	-5214	1717	-2362	72
H(18A)	-4450	4542	-2254	74
H(19A)	-3278	5222	-2373	67
H(45A)	-3526	1141	2988	175
H(45B)	-3946	1621	4255	175
H(46A)	-3385	3919	4205	167
H(46B)	-3864	3528	2895	167
H(47A)	1471	6144	-2916	163
H(47B)	1064	6621	-4206	163
H(48A)	-1639	1036	-5760	193
H(48B)	-1166	1471	-7012	193