Supplementary Material (ESI) for Chemical Communications

For Electronic Supplementary Information

Synthesis of novel palladium OCN-pincer complexes: Unprecedented sequential C(sp3)-H activation and aerobic oxidation in the reaction of *N*,*N*-dialkyl-3-[(*N*,*N*-dimethylamino)methyl]-2-iodoanilines with $Pd_2(dba)_3$

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Experimental details	2
Characterization data of compounds **2c**, **4a,c-d**, **5a-d**, **9** and **10**	2-4
X-ray crystallographic data of **5a**	5-11

General procedure for the synthesis of palladium OCN-pincer complexes

To a stirred solution of haloaniline **3** (0.1 mmol) and Et_3N (0.5 mmol) in dry benzene (6 mL) were added PPh_3 (0.1 mmol) and $Pd_2(dba)_3$ (0.055 mmol). The solution was stirred at room temperature under O_2 (supplied from a toy balloon) for 9 h. The solvent was removed *in vacuo* and the residue was purified by 'flash'chromatography (SiO_2, from CH_2Cl_2 to 95:5 CH_2Cl_2/MeOH).

Palladium complex 2c. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (t, *J* = 7.5 Hz, 6H), 1.43 (m, 2H), 2.38 (m, 2H), 3.10 (s, 6H), 3.47 (m, 4H), 4.08 (s, 2H), 6.47 (d, *J* = 8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 8 and 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 10.9 (CH_3), 16.5 (CH_2), 55.1 (CH_3), 72.4 (CH_2), 74.8 (CH_2), 115.0 (CH), 122.3 (CH), 124.1 (CH), 147.3 (C), 152.4 (C), 167.4 (C). Anal. Calcd for $C_{15}H_{25}IN_2Pd$ (466.7)·CH_2Cl_2: C, 34.84; H, 4.93; N, 5.08. Found: C, 34.85, H, 4.97; N, 5.03.

3-[(*N*,*N*-Dimethylamino)methyl]-*N*-methylaniline (4a). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.31 (s, 6H), 2.84 (s, 3H), 3.44 (s, 2H), 6.54 (dm, *J* = 8 Hz, 1H), 6.60-6.68 (m, 2H), 7.14 (t, *J* = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 30.8 (CH_3), 44.8 (CH_3), 64.1 (CH_2), 111.5 (CH), 113.3 (CH), 118.3 (CH), 129.1 (CH), 137.8 (C), 149.4 (C).

3-[(*N*,*N*-Dimethylamino)methyl]-*N*-propylaniline (4c). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.99 (t, *J* = 7.2 Hz, 3H), 1.63 (sex, *J* = 7.2 Hz, 2H), 2.25 (s, 6H), 3.08 (t, *J* = 7.2 Hz, 2H), 3.36 (s, 2H), 6.47-6.65 (m, 3H), 7.11 (t, *J* = 7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 11.7 (CH_3), 22.8 (CH_2), 45.4 (CH_3), 45.8 (CH_2), 64.6 (CH_2), 111.4 (CH), 113.4 (CH), 118.0 (CH), 129.0 (CH), 139.7 (C), 148.5 (C).

***N*-Benzyl-3-[(*N*,*N*-dimethylamino)methyl]aniline (4d).** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 6H), 3.37 (s, 2H), 4.33 (s, 2H), 6.54 (dm, *J* = 7.8 Hz, 1H), 6.60-6.70 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.24-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 45.2 (CH_3), 48.4 (CH_2), 64.4 (CH_2), 111.6 (CH), 113.7 (CH), 118.6 (CH), 127.2 (CH), 127.5 (CH), 128.6 (CH), 129.1 (CH), 139.4 (C), 139.5 (C), 148.2 (C).

Palladium complex 5a. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.11 (s, 6H), 3.62 (s, 3H), 4.04 (s, 2H), 6.91 (d, *J* = 8 Hz, 1H), 6.97 (dd, *J* = 7.4 and 0.8 Hz, 1H), 7.22 (dd, *J* = 8 and 7.4 Hz, 1H), 7.93 (s, 1H). **5a** was not sufficiently soluble for ^{13}C NMR studies. MS (FAB^+): m/z 297 (M^+-I). Anal. Calcd for $C_{11}H_{15}IN_2OPd$ (424.6): C, 31.12; H, 3.56; I, 29.89; N, 6.60. Found: C, 31.17, H, 3.51; I, 30.29; N, 6.27. Crystallization from CH_2Cl_2 afforded crystals suitable for X-ray analysis.

Palladium complex 5b. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.04 (s, 6H), 3.61 (s, 3H), 4.02 (s, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.97 (dd, *J* = 7.2 and 1 Hz, 1H), 7.21 (dd, *J* = 8.2 and 7.2 Hz, 1H), 7.96 (s, 1H). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.80 (s, 6H), 3.54 (s, 3H), 4.03 (s, 2H), 6.97 (dd, *J* = 7.2 and 0.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4 and 7.2 Hz, 1H), 8.20 (s, 1H). ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ 38.0 (CH_3), 54.0 (CH_3), 73.8 (CH_2), 113.2 (CH), 119.7 (CH), 126.4 (CH), 133.7 (C), 135.0 (C), 150.3 (C), 160.8 (CH). IR (film) 1622 cm^{-1}. MS (FAB^+): m/z 297 (M^+-Br). Anal. Calcd for $C_{11}H_{15}BrN_2OPd$ (377.6): C, 34.99; H, 4.00; Br, 21.16; N, 7.42. Found: C, 35.04, H, 3.95; Br, 20.86; N, 7.09.

Palladium complex 5c. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (t, *J* = 7.5 Hz, 3H), 1.83 (sex, *J* = 7.5 Hz, 2H), 3.09 (s, 6H), 4.02 (t, *J* = 7.5 Hz, 2H), 4.03 (s, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.93 (dd, *J* = 7.5 and 0.8 Hz, 1H), 7.20 (dd, *J* = 8.1 and 7.5 Hz, 1H), 8.04 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 10.9 (CH_3), 21.5 (CH_2), 51.5 (CH_2), 55.8 (CH_3), 73.9 (CH_2), 112.2 (CH), 118.9 (CH), 125.8 (CH), 131.4 (C), 137.6 (C), 149.5 (C), 158.5 (CH). Anal. Calcd for $C_{13}H_{19}IN_2OPd$ (452.6): C, 34.50; H, 4.23; N, 6.19. Found: C, 34.78, H, 4.26; N, 5.84.

Palladium complex 5d. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.10 (s, 6H), 4.01 (s, 2H), 5.25 (s, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.88 (dd, *J* = 7.2 and 0.9 Hz, 1H), 7.02 (dd, *J* = 8.1 and 7.2 Hz, 1H), 7.20-7.40 (m, 5H), 8.15 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 53.7 (CH_2), 55.9 (CH_3), 74.1 (CH_2), 113.4 (CH), 119.1 (CH), 125.8 (CH), 125.9 (CH), 128.3 (CH), 129.3 (CH), 132.0 (C), 134.3 (C), 137.5 (C), 149.4 (C), 159.4 (CH). Anal. Calcd for $C_{17}H_{19}IN_2OPd$ (500.6): C, 40.78; H, 3.83; N, 5.60. Found: C, 40.56, H, 3.93; N, 5.49.

Palladium complex 9. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.10 (s, 6H), 4.06 (s, 2H), 5.27 (s, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.88 (dd, *J* = 7.2 and 0.9 Hz, 1H), 7.02 (dd, *J* = 8.1 and 7.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.22-7.37 (m, 5H), 7.43 (m, 1H), 7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.7 (CH_3), 55.8 (CH_2), 74.1 (CH_2), 115.7 (CH), 119.2 (CH), 125.5 (CH), 125.9 (CH), 127.6 (CH), 127.7 (CH), 128.6 (CH), 129.0 (CH), 131.2 (CH), 134.2 (C), 134.3 (C), 135.4 (C), 137.9 (C), 148.7 (C), 169.0 (C).

Palladium complex 10. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (t, *J* = 7.2 Hz, 3H), 1.60 (sex, *J* = 7.2 Hz, 2H), 3.09 (s, 6H), 4.05 (t, *J* = 7.2 Hz, 2H), 4.09 (s, 2H), 6.95 (m, 2H), 7.21 (dd, *J* = 8.1 and 7.5 Hz, 1H), 7.40-7.60 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 10.8 (CH_3), 21.3 (CH_2), 53.3 (CH_2), 55.6 (CH_3), 74.1 (CH_2), 115.0 (CH), 119.3 (CH), 125.6 (CH), 128.3 (CH), 128.8 (CH), 131.2 (CH), 133.3 (C), 134.4 (C), 138.8 (C), 148.7 (C), 168.8 (C).

X-ray Structure Determination of OCN-pincer complex 5a (SOIC8A)

The structure was solved by Direct methods, using the SHELXS97 computer program (Sheldrick, G.M., (1997), SHELXS. A computer program for crystal structure determination. Univ. Göttingen, Germany) and refined by full-matrix least-squares method with the SHELXL97 computer program (Sheldrick, G.M., (1997), SHELXL. A computer program for crystal structure determination. Univ. Göttingen, Germany), using 3767 reflections. The function minimized was $\sum$ w | $|Fo|^2$ - $|Fc|^2$ $|^2$, where w = $[\sigma^2(I) + (0.0496 P)^2]^{-1}$, and P = ($|Fo|^2$ + 2 $|Fc|^2$)/3, f, f' and f'' were taken from International Tables of X-Ray Crystallography (International Tables of X-Ray Crystallography, (1974), Ed. Kynoch press, Vol. IV, pp 99-100 and 149). 3H atoms were located from a difference synthesis and 12H atoms were computed and refined using a riding model. The temperature factor of H atoms was 1.2 time the equivalent displacement of atom linked to H. The final R(on F) factor was 0.032, wR(on $|F|^2$) = 0.071 and goodness of fit = 0.996 for all observed reflections. Number of refined parameters was 157. Max. shift/esd = 0.00, Mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.809 and - 0.660 $eÅ^{-3}$, respectively.

Table S1. Crystal data and structure refinement for **5a** (SOIC8A).

Identification code	soic8a
Empirical formula	$C_{11}H_{15}IN_2OPd$
Formula weight	424.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/a$
Unit cell dimensions	a = 10.190(8) Å b = 11.219(3) Å c = 11.646(2) Å β = 100.37(3) deg
Volume	1309.6(11) $Å^3$
Z, Calculated density	4, 2.153 Mg/m^3
Absorption coefficient	3.756 mm^{-1}
F(000)	808
Crystal size	0.1 x 0.1 x 0.2 mm
Theta range for data collection	2.54 to 29.96 deg.
Limiting indices	-14<=h<=14, 0<=k<=15, 0<=l<=16
Reflections collected / unique	3977 / 3767 [R(int) = 0.0509]
Completeness to theta = 29.96	98.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3767 / 0 / 157
Goodness-of-fit on F^2	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0705
R indices (all data)	R1 = 0.0411, wR2 = 0.0737
Largest diff. peak and hole	0.809 and -0.660 e. $Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for SOIC8A.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd	1984(1)	5454(1)	7716(1)	39(1)
I	1213(1)	3128(1)	7318(1)	61(1)
O	1133(2)	5477(2)	9165(2)	49(1)
N(1)	2849(2)	5680(2)	6241(2)	50(1)
N(2)	991(2)	7511(2)	9443(2)	44(1)
C(1)	2339(3)	7154(2)	7919(2)	41(1)
C(2)	1826(3)	7921(2)	8632(2)	43(1)
C(3)	2054(3)	9166(3)	8587(3)	57(1)
C(4)	2868(4)	9594(3)	7829(3)	66(1)
C(5)	3427(4)	8842(3)	7143(3)	62(1)
C(6)	3183(3)	7625(3)	7192(2)	48(1)
C(7)	3779(3)	6710(3)	6468(3)	56(1)
C(8)	3585(4)	4638(4)	5889(4)	79(1)
C(9)	1758(3)	6005(3)	5271(3)	61(1)
C(10)	762(3)	6368(2)	9641(2)	47(1)
C(11)	362(3)	8393(3)	10109(3)	59(1)

Table S3. Bond lengths [Å] and angles [deg] for SOIC8A.

Pd-C(1)	1.948(3)
Pd-O	2.031(2)
Pd-N(1)	2.083(2)
Pd-I	2.7405(7)
O-C(10)	1.235(3)
N(1)-C(9)	1.481(4)
N(1)-C(8)	1.486(4)
N(1)-C(7)	1.488(4)
N(2)-C(10)	1.331(3)
N(2)-C(2)	1.455(4)
N(2)-C(11)	1.474(4)
C(1)-C(2)	1.363(4)
C(1)-C(6)	1.414(4)
C(2)-C(3)	1.418(4)
C(3)-C(4)	1.400(5)
C(3)-H(3)	0.98(3)
C(4)-C(5)	1.356(6)
C(4)-H(4)	1.00(4)
C(5)-C(6)	1.391(4)
C(5)-H(5)	0.92(4)
C(6)-C(7)	1.522(5)
C(7)-H(7)	0.9700
C(7)-H(7A)	0.9700
C(8)-H(8)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(9)-H(9)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(10)-H(10)	0.9300
C(11)-H(11)	0.9600
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(1)-Pd-O	89.11(9)
C(1)-Pd-N(1)	83.32(10)
O-Pd-N(1)	172.26(9)
C(1)-Pd-I	173.86(8)
O-Pd-I	90.04(6)
N(1)-Pd-I	97.32(7)
C(10)-O-Pd	126.43(18)
C(9)-N(1)-C(8)	109.3(3)
C(9)-N(1)-C(7)	108.1(3)
C(8)-N(1)-C(7)	108.9(3)
C(9)-N(1)-Pd	106.73(17)
C(8)-N(1)-Pd	116.2(2)
C(7)-N(1)-Pd	107.41(18)
C(10)-N(2)-C(2)	124.0(2)
C(10)-N(2)-C(11)	116.7(2)
C(2)-N(2)-C(11)	119.4(2)
C(2)-C(1)-C(6)	118.0(3)
C(2)-C(1)-Pd	127.52(19)
C(6)-C(1)-Pd	114.4(2)

C(1)-C(2)-C(3)	121.1(3)
C(1)-C(2)-N(2)	121.9(2)
C(3)-C(2)-N(2)	117.0(3)
C(4)-C(3)-C(2)	118.7(3)
C(4)-C(3)-H(3)	109(2)
C(2)-C(3)-H(3)	132(2)
C(5)-C(4)-C(3)	121.2(3)
C(5)-C(4)-H(4)	112(3)
C(3)-C(4)-H(4)	126(3)
C(4)-C(5)-C(6)	119.3(3)
C(4)-C(5)-H(5)	117(2)
C(6)-C(5)-H(5)	123(2)
C(5)-C(6)-C(1)	121.6(3)
C(5)-C(6)-C(7)	123.1(3)
C(1)-C(6)-C(7)	115.3(3)
N(1)-C(7)-C(6)	108.5(2)
N(1)-C(7)-H(7)	110.0
C(6)-C(7)-H(7)	110.0
N(1)-C(7)-H(7A)	110.0
C(6)-C(7)-H(7A)	110.0
H(7)-C(7)-H(7A)	108.4
N(1)-C(8)-H(8)	109.5
N(1)-C(8)-H(8A)	109.5
H(8)-C(8)-H(8A)	109.5
N(1)-C(8)-H(8B)	109.5
H(8)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(1)-C(9)-H(9)	109.5
N(1)-C(9)-H(9A)	109.5
H(9)-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
H(9)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
O-C(10)-N(2)	128.7(2)
O-C(10)-H(10)	115.7
N(2)-C(10)-H(10)	115.7
N(2)-C(11)-H(11)	109.5
N(2)-C(11)-H(11A)	109.5
H(11)-C(11)-H(11A)	109.5
N(2)-C(11)-H(11B)	109.5
H(11)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5

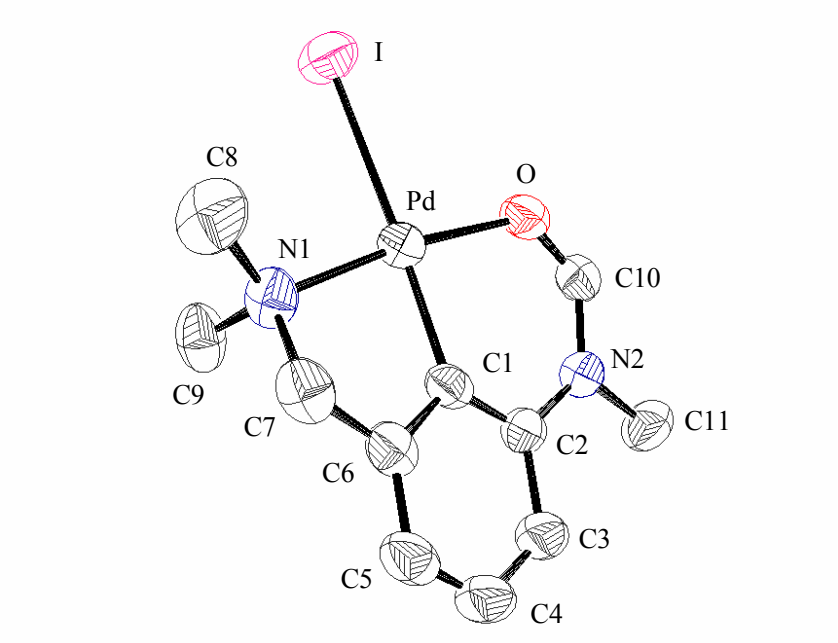
Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for SOIC8A. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	35(1)	40(1)	41(1)	2(1)	8(1)	0(1)
I	71(1)	44(1)	72(1)	-9(1)	25(1)	-7(1)
O	65(1)	41(1)	45(1)	7(1)	20(1)	2(1)
N(1)	40(1)	63(2)	51(1)	-5(1)	19(1)	-8(1)
N(2)	48(1)	42(1)	41(1)	-2(1)	5(1)	-3(1)
C(1)	41(1)	41(1)	38(1)	9(1)	0(1)	-4(1)
C(2)	45(1)	42(1)	38(1)	2(1)	-3(1)	-10(1)
C(3)	66(2)	46(2)	53(2)	4(1)	-3(1)	-16(1)
C(4)	79(2)	50(2)	64(2)	8(2)	1(2)	-25(2)
C(5)	64(2)	64(2)	52(2)	15(2)	-6(1)	-27(2)
C(6)	40(1)	59(2)	42(1)	8(1)	-4(1)	-14(1)
C(7)	39(1)	76(2)	54(2)	6(1)	12(1)	-13(1)
C(8)	67(2)	86(3)	95(3)	-13(2)	46(2)	7(2)
C(9)	51(2)	90(2)	45(1)	-5(2)	11(1)	-16(2)
C(10)	55(2)	47(1)	38(1)	4(1)	11(1)	-4(1)
C(11)	72(2)	48(2)	61(2)	-12(1)	19(2)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for SOIC8A.

	x	y	z	U(eq)
H(7)	3906	7063	5735	67
H(7A)	4640	6447	6886	67
H(8)	4294	4426	6516	94
H(8A)	3951	4838	5210	94
H(8B)	2984	3977	5714	94
H(9)	2091	6012	4551	74
H(9A)	1424	6781	5412	74
H(9B)	1051	5431	5222	74
H(10)	256	6221	10215	56
H(11)	596	9182	9900	71
H(11A)	670	8271	10930	71
H(11B)	-590	8301	9933	71
H(3)	1880(30)	9820(30)	9100(30)	53(9)
H(4)	3200(40)	10430(30)	7800(40)	78(12)
H(5)	4050(40)	9160(30)	6750(40)	66(11)



Molecular structure of **5a** (ORTEP view). H atoms are omitted for clarity. Selected bond distances (Å) and angles (º): Pd-C1 = 1.948 (3), Pd-N1 = 2.083 (2), Pd-O = 2.031 (2), Pd-I = 2.7405 (7), C1-Pd-N1 = 83.32 (10), C1-Pd-O = 89.11 (9), N1-Pd-I = 97.32 (7), O-Pd-I = 90.04 (6)