SUPPORTING INFORMATION FOR

CO_2 as a C_1-building block for the catalytic methylation of amines

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Supplementary catalytic results

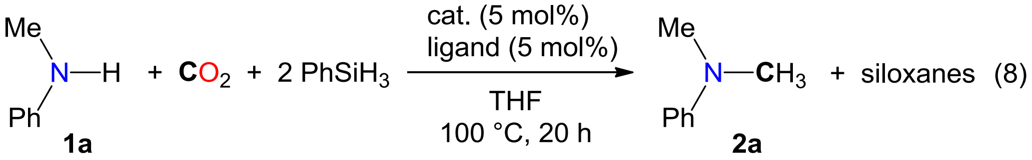

Table S1. Zinc-catalyzed methylation of N-methylaniline (**1a**) to N,N-dimethylaniline (**2a**), as depicted in Eq. 8.

Entry	Catalyst [mol%]	Ligand [mol%]	Yield [%][a]
1	$CuCl_2$ (5)	–	< 1
2	$Cu(OTf)_2$ (5)	–	< 1
3	$Cu(acac)_2$ (5)	–	< 1
4	$Cu(OAc)_2$•H_2O (5)	–	< 1
5	$Cu(OH)_2$ (5)	–	< 1
6	$FeCl_2$ (5)	–	< 1
7	$Fe(SO_4)$•$7H_2O$ (5)	–	< 1
8	$Fe(acac)_2$ (5)	–	< 1
9	$Fe(OAc)_2$ (5)	–	< 1
10	$Fe(BF_4)_2$•$6H_2O$ (5)	–	< 1
11	$Zn(acac)_2$•xH_2O (5)	–	2
12	$Zn(OAc)_2$ (5)	–	< 1
13	$Zn(SO_4)$•$7H_2O$ (5)	–	< 1
14	$ZnCl_2$ (5)	pyridine (10)	< 1
15	$ZnCl_2$ (5)	1,10-phenantroline (5)	4
16	$ZnCl_2$ (5)	tetramethylethylenediamine (5)	< 1

[a] Determined by GC/MS

Kinetic profile of the conversion of 1a to 2a and 3a

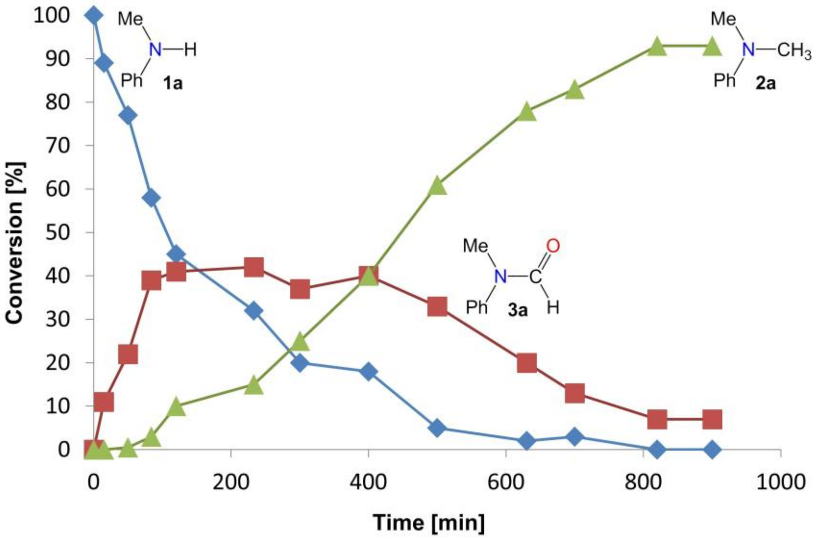

Figure S1. Kinetic profile of the zinc-catalyzed methylation of N-methylaniline (**1a**) to N,N-dimethylaniline (**2a**). Reaction conditions: In a glovebox, an NMR tube, equipped with a J. Young valve, is charged successively with **IPr**$ZnCl_2$ (3.3 mg, 0.0063 mmol, 5 mol%), d_8-THF (300 µL), **1a** (13.5 µL, 0.125 mmol, 1 equiv.) and $PhSiH_3$ (31.0 µL, 0.250 mmol, 2 eq). The reaction mixture is then exposed to a CO_2 atmosphere (1 bar) and the tube is sealed and heated in an oil bath (100 °C). The reaction is monitored by ^1H NMR over 20 h.

Experimental details

General considerations

All reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 60 ºC before use. All NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent impurities. Elemental analyses were performed at the CNRS facility in Gif-Sur-Yvette (France). Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLB^{TM}-ms fused silica capillary column (30 m x 0.25 mm x 0.25 µm). Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. Celite (Aldrich), alumina (Brockman I, Aldrich) and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Tetrahydrofuran (THF), d_8-Tetrahydrofuran (d_8-THF) and d_6-Benzene were dried over a sodium(0)/benzophenone mixture and distilled before use. Carbon dioxide was purchased from Messer in a 5.5 purity gas bottle. **IPr**, **s-IPr**, **IMes** and **s-IMes** were synthesized according to the method described by Arduengo[1] and used as the free bases. **I^{t}Bu** was synthesized by deprotonation of the corresponding imidazolium salt **I^{t}Bu**HCl,[2] using potassium *tert*-butoxide.

Synthesis of IPrZnCl$_2$

A 25 mL flask was charged with a stir bar, $ZnCl_2$ (48.4 mg, 0.355 mmol), **IPr** (138 mg, 0.355 mmol) and toluene (15 mL). The resulted suspension was heated to 70 °C for 2 h, and then cooled to room temperature. The volatiles were removed under reduced pressure at 50 °C, to provide **IPr**$ZnCl_2$ as an off-white solid (259 mg, >99 %).

Anal. Calcd for $C_{27}H_{36}Cl_2N_2Zn$: C, 61.78; H, 6.91; N, 5.34; Found C, 62.09; H, 6.93; N, 5.28; **^{1}H NMR** (d_6-benzene): 7.4-7.05 (5H, m); 6.45 (2H, s); 2.89 (4H, bs); 1.55 (12H, bs); 1.00 (12H, bs); **^{13}CNMR** (d_6-benzene): 144.1; 132.6; 128.7; 126.3; 125.8; 122.5; 27.0; 24.0; 21.4; **^{1}H NMR** (d_8-THF, 298 K) : δ 7.58 (2H, s); 7.43 (2H, m): 7.31 (4H, m); 2.76 (4H, s, J = 7Hz); 1.34 (12H, d, J = 7Hz); 1.12 (12H, d, J = 7Hz).

Typical procedure for the catalytic methylation of amines to N-methylamines and determination of the product distributions

The typical procedure is detailed for the conversion of N-methylaniline (**1a**) to N,N-dimethylaniline (**2a**) using **IPr**$ZnCl_2$ as catalyst. Under inert atmosphere (Ar), an NMR tube, equipped with a J. Young valve, is charged successively with **IPr**$ZnCl_2$ (3.3 mg, 0.0063 mmol, 5 mol%), d_8-THF (0.3 mL), N-methylaniline (**1a**) (13.5 µL, 0.125 mmol, 1 eq), and phenylsilane (31.0 µL, 0.250 mmol, 2 eq). The reaction mixture is exposed to a CO_2 atmosphere (1 bar) and the tube is sealed and heated in an oil bath (100 °C) for 20 h. The corresponding N,N-dimethylaniline (**2a**) is identified and the distribution of nitrogen containing compounds is determined by ^{1}H NMR in $CDCl_3$ and GC/MS using biphenyl as an internal standard.

^{1}H NMR and **^{13}C NMR** of the following methylated products **2b,**[3] **2e (11f)**,[4] **2f,**[5] **2g (11g)**, [6]**2h (11d)**,[7] **2i**,[8] **2j**,[9], **3b (10d)**,[10], **3c**, [11]**3d**,[10] **3e (10f)**, [12] **3f**, [13] **3j**, [14] **5e**,[15] **5f**,[16] **6d**,[17] **6e**,[18] **6f**,[19] **9e**,[20] **9h**,[21] **9i**,[22] **10a**,[23] **10b**,[24] **10e**, [10] **11a**,[25] **11e**,[26] **11h**,[27] **11i**,[28] are identical to reported data.

^{1}H NMR and **^{13}C NMR** of the following products were compared with commercial samples purchased from Aldrich: **1a (9c), 2a (11c), 2c, 2d, 3a (10c), 3g (10g), 5a, 5b, 5c, 5d, DMF, TMA, 6a, 6b, 6c, 9b, 9d, 9g, 11b.**

Synthesis of N,N-dimethylaniline (2a) by catalytic methylation of N-methylaniline (1a) using CO_2 and $PhSiH_3$

Under inert atmosphere (Ar), a 16 mL J. Young Schlenk flask, equipped with a magnetic stir bar and a J. Young valve is charged successively with **IPr**$ZnCl_2$ (26.4 mg, 0.0500 mmol, 5.0 mol%), THF (3.0 mL), N-methylaniline (**1a**) (108 µL, 1.00 mmol, 1 eq), and phenylsilane (248 µL, 2.00 mmol, 2 eq). The reaction mixture is exposed to a CO_2 atmosphere (1 bar) and the tube is sealed and heated in an oil bath (100 °C) for 20 h and then allowed to cool to 25 °C. CH_2Cl_2 (5.0 mL) is then added. An aqueous solution of HCl (2x10 mL, 1.0 M) is added and the aqueous phase is collected. The pH of the solution is then adjusted to 12 using K_2CO_3 as a base and Et_2O (2x10 mL) is utilized to extract the free amine **2a**. The organic phase is collected and dried over Na_2SO_4. Et_2O is removed under reduced pressure to afford analytically pure **2a** as a light yellow oil. Average isolated yield over three runs: 81 %, 98.1 mg. Elemental Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56; Found: C, 78.93; H, 9.26; N, 11.27.

Synthesis of trimethylamine (TMA) by catalytic methylation of dimethylammonium dimethylcarbamate (7) using CO_2 and $PhSiH_3$

Under inert atmosphere (Ar), a 16 mL J. Young Schlenk flask, equipped with a magnetic stir bar and a J. Young valve is charged successively with **IPr**$ZnCl_2$ (26.4 mg, 0.0500 mmol, 5.0 mol%), THF (3.0 mL), dimethylammonium dimethylcarbamate (**7**) (64 µL, 0.050 mmol, 0.5 eq), and phenylsilane (384 µL, 3.00 mmol, 3 eq). The reaction mixture is exposed to a CO_2 atmosphere (1 bar) and the tube is sealed and heated in an oil bath (100 °C) for 72 h and then allowed to cool to 25 °C. CH_2Cl_2 (5.0 mL) is then added. An aqueous solution of HCl (2x10 mL, 1.0 M) is added and the aqueous phase is collected. The volatiles are then removed under reduced pressure to afford TMA as its ammonium chloride salt (given the low boiling point of free TMA (2 °C), TMA was isolated as TMA•HCl). Average isolated yield over three runs: 93 %, 88.9 mg. Elemental Anal. Calcd for $C_3H_{10}ClN$: C, 37.70; H, 10.55; N, 14.66; Found: C, 37.49; H, 10.52; N, 14.57.

Synthesis of N,N-dimethylaniline (2a and 11c) by catalytic bis-methylation of aniline (8c) using CO_2 and $PhSiH_3$

Under inert atmosphere (Ar), a 16 mL J. Young Schlenk flask, equipped with a magnetic stir bar and a J. Young valve is charged successively with **IPr**$ZnCl_2$ (26.4 mg, 0.0500 mmol, 5.0 mol%), THF (3.0 mL), aniline (**8c**) (91.0 µL, 1.00 mmol, 1 eq), and phenylsilane (248 µL, 2.00 mmol, 2 eq). The reaction mixture is exposed to a CO_2 atmosphere (1 bar) and the tube is sealed and heated in an oil bath (100 °C) for 72 h and then allowed to cool to 25 °C. CH_2Cl_2 (5.0 mL) is then added. An aqueous solution of HCl (2x10 mL, 1.0 M) is added and the aqueous phase is collected. The pH of the solution is then adjusted to 12 using K_2CO_3 as a base and Et_2O (2x10 mL) is utilized to extract the free amine **11c**. The organic phase is collected and dried over Na_2SO_4. Et_2O is removed under reduced pressure. The residue is purified by flash chromatography on silica gel (0.069-0.200 mm, standard grade) using a mixture of n-pentane and ethyl acetate (98:2) as the eluent and the N,N-dimethylaniline **2a** is then collected as an analytically pure light yellow oil. Average isolated yield over three runs: 61 %, 73.9 mg. Elemental Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56; Found: C, 79.03; H, 9.25; N, 11.34.

^{1}H NMR and **^{13}C NMR** of the following methylated products **2b,**[29] **2e (11f)**,[30] **2f,**[31] **2g (11g)**, [32]**2h (11d)**,[33] **2i**,[34] **2j,**[35], **3b (10d),**[36], **3c,** [37]**3d,**[10] **3e (10f),** [38]**3f,** [39] **3j,** [40] **5e**,[41] **5f**,[42] **6d**,[43] **6e**,[44] **6f**,[45] **9e**,[46] **9h**,[47] **9i**,[48] **10a**,[49] **10b**,[50] **10e,** [10] **11a**,[51] **11e**,[52] **11h**,[53] **11i**,[54] are identical to reported data.

^{1}H NMR and **^{13}C NMR** of the following products were compared with commercial samples purchased from Aldrich: **1a (9c), 2a (11c), 2c, 2d, 3a (10c), 3g (10g), 5a, 5b, 5c, 5d, DMF, TMA, 6a, 6b, 6c, 9b, 9d, 9g, 11b.**

Kinetic data

General procedure for the determination of k_{obs}(2). In a glovebox, an NMR tube, equipped with a J. Young valve, is charged successively with **IPr**$ZnCl_2$ (3.3 mg, 0.0063 mmol, 5 mol%), d_8-THF (300 µL), the corresponding *para*- or *meta*-substitued N-methylaniline **1** (0.125 mmol) and a large excess of phenylsilane (155 µL, 1.25 mmol, 10 eq). The reaction mixture is exposed to a CO_2 atmosphere (1 bar) and the tube is sealed and heated in an oil bath (100 °C). The rate data are determined by monitoring the formation of **2** as a function of time by integration of the N–CH_3 groups resonance in the ^1H NMR spectrum of the crude mixture. The reactions followed first-order kinetics through at least 30 % conversion.

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