Electronic Supplementary Information (ESI)

Copper-Diphosphine Complex Catalysts for *N*-Formylation of Amines under 1 atm of Carbon Dioxide with Polymethylhydrosiloxane

Ken Motokura, Naoki Takahashi, Daiki Kashiwame, Sho Yamaguchi, Akimitsu Miyaji and Toshihide Baba*

Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan

Experimental procedures

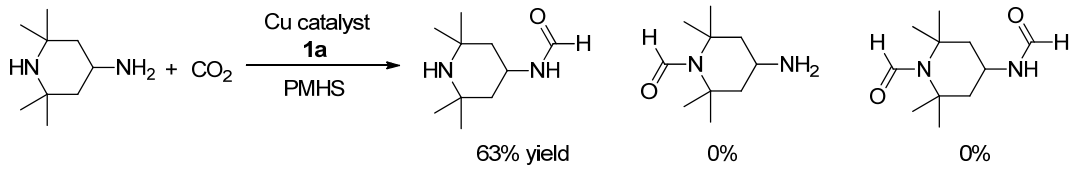
Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ with a Bruker AVANCE 400 spectrometer operating at 400 and 100.61 MHz, respectively. A Shimadzu QP5000 instrument equipped with a DB-1 column was used for GC-MS analysis.

$Cu(OAc)_2{\cdot}H_2O$ (Cu content >99.99%) was purchased from Aldrich Inc. Polymethylhydrosiloxane (PMHS) was purchased from WAKO Pure Chemicals (FW: *ca.* 1900). Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., or Aldrich Inc. *p*-Xylene or mesitylene was used as an internal standard.

Typical Procedure for Formylation of Amines under CO_2 with PMHS

Into a glass reactor equipped with a CO_2 balloon were placed $Cu(OAc)_2{\cdot}H_2O$ (Cu: 1.0×10^{-3} mmol), 1,2-bis(diisopropylphosphino)benzene (**1a**, P: 3.0×10^{-3} mmol), piperidine (1.4 mmol), PMHS (0.211 g, Si-H: 3.2 mmol), and 1,4-dioxane (5.0 mL). The resulting mixture was stirred vigorously at 80 ^{o}C for 5 h. ^{1}H NMR analysis of the reaction mixture showed a 98% yield of *N*-formylpiperidine. Formamide products were identified by comparison with reported ^{1}H NMR and GC-MS data. Yield and conversion were determined using a $CDCl_3$ solution of the reaction mixture by the internal standard technique. Mesitylene or 1,3,5-triisopropylbenzene was used as an internal standard. The products were confirmed by the comparison of their GC-MS spectra, and/or ^{1}H and ^{13}C NMR spectra with those of authentic data.

Regioselective Formylation (Table 2, entry 14)



Into a glass reactor equipped with a CO_2 balloon were placed $Cu(OAc)_2 \cdot H_2O$ (Cu: 1.0×10^{-3} mmol), 1,2-bis(diisopropylphosphino)benzene (**1a**, P: 1.0×10^{-2} mmol), 2,2,6,6-tetramethylpiperidin-4-amine (1.4 mmol), PMHS (0.211 g, Si-H: 3.2 mmol), and 1,4-dioxane (5.0 mL). The resulting mixture was stirred vigorously at 80 ^{o}C for 24 h. ^{1}H NMR analysis using a $CDCl_3$ solution of the reaction mixture showed a 63% yield of regioselective formylated product. Other forymalated products were not detected in either ^{1}H NMR or GC-MS. The resulting reaction mixture was purified over a column of silica gel (C200) and eluted (ethyl acetate --> acetone) to give the isolated product. The product was identified by MS, ^{1}H NMR, ^{13}C NMR, and ^{1}H-^{1}H COSY NMR spectroscopy (Figure S1).

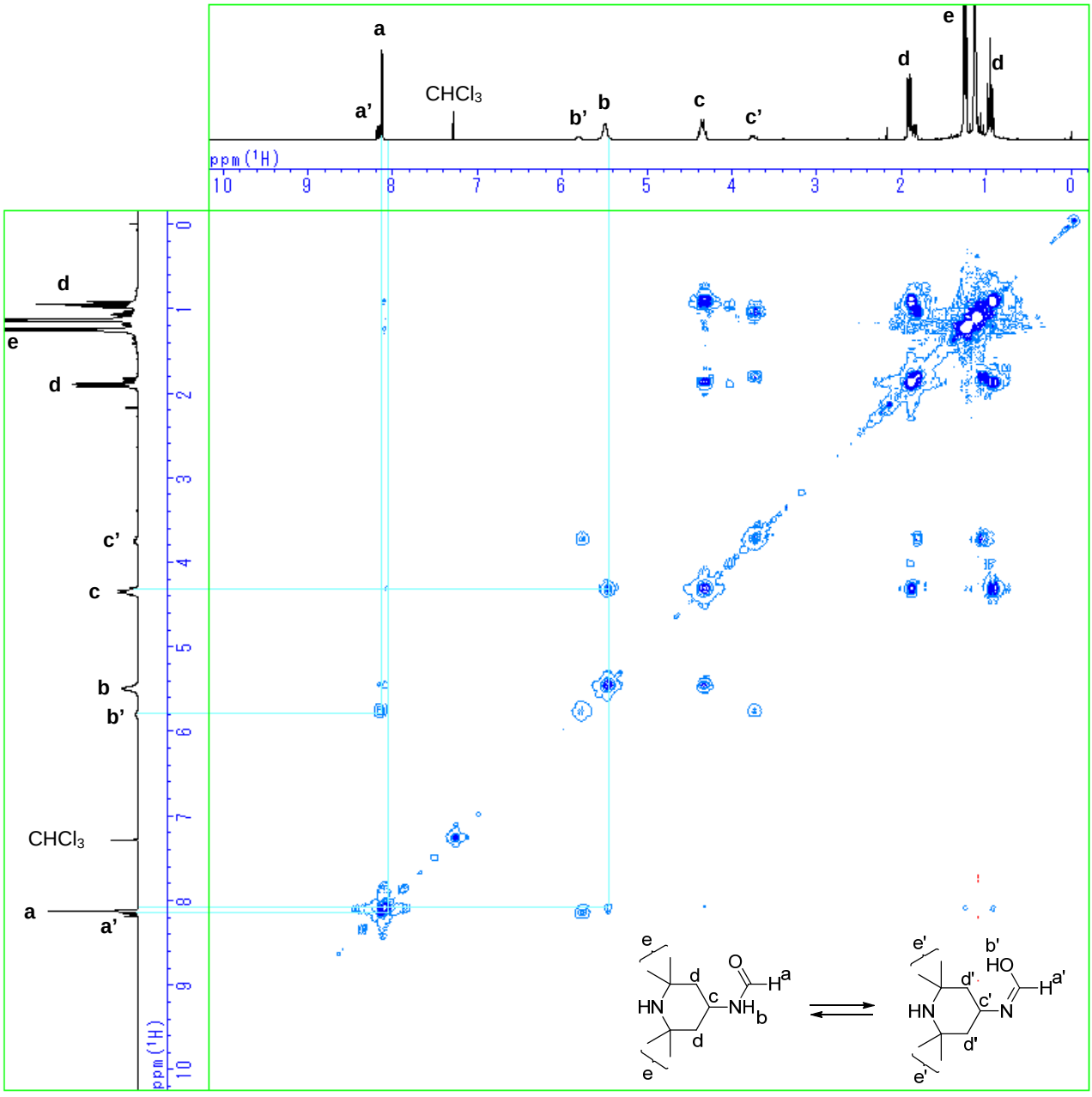


Figure S1 ^{1}H-^{1}H COSY analysis of the regioselective formylation product.

Table S1 List of Catalysts for Formylation of Amines with CO_2 and Hydrosilanes

Amine	Catalyst	CO_2 (atm)	Hydrosilane	Time / temp	TON	Ref
Piperidine	Cu-**1b**	1	PMHS	23 h / 80 ^oC	11700	***This***
Morpholine	Cu-**1b**	1	PMHS	22 h / 80 ^oC	9000	***Work***
Piperidine	TBD	1	$PhSiH_3$	24 h / 100 ^oC	20	[S1]
Morpholine	NHC	1	$PhSiH_3$, PMHS	1 h / rt	20 (TOF: 160 h^{-1})	[S2]
Piperidine	$Rh_2(OAc)_4$	1	$PhSiMe_2H$	2 h / 50 ^oC (hydrosilylation), 1 h / 50 ^oC (amide formation)	200	[S3]

Table S2 List of Catalysts for Formylation of Amines other than Dimethylamine with CO_2 and H_2

Amine	Catalyst	CO_2 (atm)	H_2 (atm)	Time / Temp	TON	Ref
Piperidine	$Na[HRu_3(CO)_{11}]$	60	60	24 h / 140 ^oC	850	[S4]
$NH(C_2H_5)_2$	Ru-silica-hybrid aerogel	180 (total)	180 (total)	-	(TOF: 18400 h^{-1})	[S5]
$NH(n\text{-}C_3H_7)_2$	$RuCl_2(dppe)_2$	276 (total)	55	5 h / 80 ^oC	110	[S6]
Piperidine	$RuCl_2(dppe)_2$	180 (total)	88	3 h / 100 ^oC	117780	[S7]
Morpholine	$RuCl_2(dppe)_2$	180 (total)	88	3 h / 100 ^oC	205200	
Morpholine	$RuCl_2(bspe)_2/SiO_2$	100 g (200 bar total)	80	20 h / 100 ^oC	3416	[S8]
Piperidine	$Fe(BF_4)_2$ / tetraphos	30	60	20 h / 100 ^oC	373	[S9]
Piperidine	$Co(BF_4)_2 \cdot 6H_2O$	30	60	20 h / 100 ^oC	1254	[S10]

References

[S1] C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat, *Angew. Chem. Int. Ed.* 2012, **51**, 187.
[S2] O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, T. Cantat, *J. Am. Chem. Soc.* 2012, **134**, 2934.
[S3] S. Itagaki, K. Yamaguchi, N. Mizuno, *J. Mol. Catal. A Chem.* 2013, **366**, 347.
[S4] G. Süss-Fink, M. Langenbahn, T. Jenke, *J. Organomett. Chem.* 1989, **368**, 103.
[S5] L. Schmid, M. Rohr, A. Baiker, *Chem. Commun.* 1999, 2303.
[S6] F. Liu, M. B. Abrams, R. T. Baker, W. Tumas, *Chem. Commun.* 2001,433.
[S7] L. Schmid, A. Canonica, A. Baiker, *Appl. Catal. A General* 2003, **255**, 23.
[S8] M. Rohr, M. Günther, F. Jutz, J.-D. Grunwaldt, H. Emerich, W. van Beek, A. Baiker, *Appl. Cata. A General* 2005, **296**, 238.
[S9] C. Fedesel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem. Int. Ed.* 2010, **49**, 9777.
[S10] C. Federsel, C. Ziebart, R. Jackstell, W. Baumann, M. Beller, *Chem. Eur. J.* 2012, **18**, 72.