

# Efficient Palladium/1,10-Phenanthroline-Catalyzed Reductive Carbonylation of Mono- and Dinitroarenes to Urethanes in Phosphonium Salt Ionic Liquids

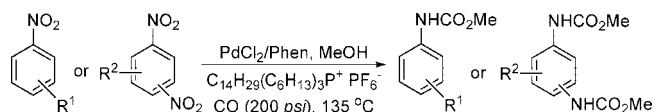
Qian Yang,<sup>†</sup> Al Robertson,<sup>‡</sup> and Howard Alper<sup>\*†</sup>

Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5, Canada, and Cytec Canada, Inc., 9061 Garner Road, Niagara Falls, Ontario L2E 6S5, Canada

howard.alper@uottawa.ca

Received September 8, 2008

## ABSTRACT



The highly reactive and selective reductive carbonylation of mono- and dinitroarenes to the corresponding mono- and diurethanes was carried out in the presence of a PdCl<sub>2</sub>/Phen catalytic system, using PSIL110[C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>PF<sub>6</sub><sup>-</sup>] as the ionic liquid under mild reaction conditions. No cocatalyst is required.

Some mono- and diurethanes are useful agriculture chemicals and pesticides. They are also valuable precursors for isocyanates, which are important intermediates for the manufacture of commercially important materials, such as high-performance plastics, polyurethane foams, elastomers, coatings, and adhesives. The conventional production of isocyanates involves the reduction of nitro compounds to amines, followed by reaction with phosgene. Since highly toxic phosgene is used and large amounts of corrosive HCl are produced during this procedure, efforts have been made to develop alternative, phosgene-free processes.<sup>1,2</sup> A promising approach is the direct preparation of urethanes by the reductive carbonylation of nitro compounds with carbon

monoxide in the presence of transition-metal catalysts, followed by conversion to isocyanates.<sup>2,3</sup> This type of reaction has been studied extensively during the last three decades. In many cases, large amounts of corrosive Lewis and Brønsted acids and/or a base were needed as cocatalysts to achieve good results. The volatility and toxicity of these acids may cause serious environmental problems. Furthermore, most of the reactions usually require high carbon monoxide pressures. Therefore, there is a need to develop new methods involving greener reaction conditions such as solvents.

Ionic liquids (ILs) have recently attracted considerable attention as environmentally friendly reaction media because

<sup>†</sup> University of Ottawa.

<sup>‡</sup> Cytec Canada, Inc.

(1) Oxidative Carbonylation: (a) Zhang, X.; Lu, S. *Synth. Commun.* **2007**, 37, 3291. (b) Orejon, A.; Castellanos, A.; Salagre, P.; Castillon, S.; Claver, C. *Can. J. Chem.* **2005**, 83, 764. (c) Shi, F.; Peng, J.; Deng, Y. *J. Catal.* **2003**, 219, 372. (d) Kim, H. S.; Kim, Y. J.; Lee, H.; Park, K. Y.; Lee, C.; Chim, C. S. *Angew. Chem., Int. Ed.* **2002**, 41, 4300. (e) Shi, F.; Deng, Y. *Chem. Commun.* **2001**, 443. (f) Valli, V. L. K.; Alper, H. *Organometallics* **1995**, 14, 80. (g) Leung, T. W.; Dombek, B. D. *J. Chem. Soc., Chem. Commun.* **1992**, 205. (h) Halligudi, S. B.; Bhatt, K. N.; Khan, M. M. T. *J. Mol. Catal.* **1991**, 68, 261. (i) Alper, H.; Hartstock, F. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1141.

(2) Reductive carbonylation: (a) Paul, F. *Coord. Chem. Rev.* **2000**, 203, 269, and references cited therein. (b) Cenini, S.; Ragaini, F. *Catalytic Reductive Carbonylation of Organic Nitro Compounds*; Kluwer Academic: Dordrecht, 1997, and references cited therein. (c) Tafesh, A. M.; Weiguny, J. *Chem. Rev.* **1996**, 96, 2035, and references cited therein.

(3) (a) Wang, X.; Li, P.; Yuan, X.; Lu, S. *J. Mol. Catal. A: Chem.* **2006**, 253, 261. (b) Wang, X.; Ling, G.; Xue, Y.; Lu, S. *Eur. J. Org. Chem.* **2005**, 1675. (c) Skupinska, J.; Karpinska, M.; Ołówek, M. *Appl. Catal. A: Gen.* **2005**, 284, 147. (d) Skupinska, J.; Karpinska, M.; Ołówek, M.; Kasprzycka-Guttman, T. *Cent. Eur. J. Chem.* **2005**, 3, 28. (e) Skupinska, J.; Karpinska, M. *Appl. Catal. A: Gen.* **2004**, 267, 59. (f) Skupinska, J.; Karpinska, M.; Wachowski, L.; Hofman, M. *React. Kinet. Catal. Lett.* **2004**, 82, 311.

of their low volatility, nonflammability, capability to dissolve various organic and inorganic compounds, and potentially recyclable properties. Imidazolium-based ionic liquids are most commonly used as these alternative solvents.<sup>4</sup> In recent years, phosphonium salt ionic liquids (PSILs) have been the subject of some publications. They have higher thermal stability than the nitrogen-based ILs. McNulty and co-workers and others recently described several different reactions in PSILs, and good to excellent results were obtained.<sup>5</sup> To our knowledge, there is only one publication on the reductive carbonylation of nitrobenzene that was carried out with imidazolium-based ionic liquids as cocatalysts and ethanol as the solvent.<sup>6</sup>

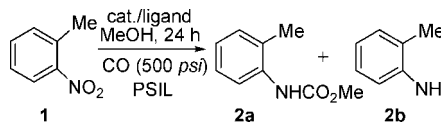
Herein, we report our results on the highly reactive and selective reductive carbonylation of mono- and dinitroarenes to the corresponding mono- and diurethanes in good yields and selectivities, using PdCl<sub>2</sub>/Phen (Phen: 1,10-phenanthroline) as the catalytic system and PSIL110 [C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>PF<sub>6</sub><sup>-</sup>] as the reaction medium.

We investigated the reductive carbonylation of nitroarenes in PSILs with ruthenium and/or palladium transition-metal catalysts. The reductive carbonylation of 2-nitrotoluene in the presence of methanol was chosen as the model reaction, and the reaction was effected under different conditions. The results are presented in Table 1.

We first examined PdCl<sub>2</sub>/Ru<sub>3</sub>(CO)<sub>12</sub>/2,2'-bipy as the catalytic system and ran the reactions in different PSILs in order to determine the optimal phosphonium salt-based ionic liquid for the reaction (Table 1, entries 1–4).<sup>7</sup> We found that with the PSILs as reaction media, the reaction could occur at lower carbon monoxide pressure (500 psi) than that reported in a number of other publications, but yields and selectivities were moderate.

According to the literature, palladium(II) with Phen is also a very effective catalytic system for the reductive carbonylation of nitroarenes.<sup>8</sup> Therefore, we ran the reaction in PSIL109[C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>NTf<sub>2</sub><sup>-</sup>] with PdCl<sub>2</sub>/Phen as the catalytic system (Table 1, entry 7). The product yield increased from 51% to 83%, and selectivity increased from

**Table 1.** Reductive Carbonylation of 2-Nitrotoluene with Different Catalytic Systems in Various PSILs<sup>a</sup>



entry	catalytic systems	PSIL <sup>b</sup>	yield <sup>c</sup> (%)	sel (%) (2a:2b)
1	PdCl <sub>2</sub> /Ru <sub>3</sub> (CO) <sub>12</sub> /2,2'-bipy	109	51	82:18
2	PdCl <sub>2</sub> /Ru <sub>3</sub> (CO) <sub>12</sub> /2,2'-bipy	101	31	47:53
3 <sup>d</sup>	PdCl <sub>2</sub> /Ru <sub>3</sub> (CO) <sub>12</sub> /2,2'-bipy	101	48	81:19
4 <sup>d</sup>	PdCl <sub>2</sub> /Ru <sub>3</sub> (CO) <sub>12</sub> /2,2'-bipy	110	72	58:42
5	Ru <sub>3</sub> (CO) <sub>12</sub> /2,2'-bipy	109	63	84:16
6 <sup>e</sup>	PdCl <sub>2</sub> /2,2'-bipy	109	16	100:0
7	PdCl <sub>2</sub> /Phen	109	83	96:4
8 <sup>f</sup>	PdCl <sub>2</sub> /Phen	101	ND	ND
9	Ru <sub>3</sub> (CO) <sub>12</sub> /Phen	109	69	87:13
10	Ru <sub>3</sub> (CO) <sub>12</sub>	109	36	68:32
11	PdCl <sub>2</sub> /Phen	110	92	100:0

<sup>a</sup> Reaction conditions: **1** (2 mmol), cat. (0.1 mmol), ligand (0.2 mmol), MeOH (30 mmol), 135 °C, 24 h. <sup>b</sup> PSIL101: C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>Cl<sup>-</sup>. PSIL109: C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>NTf<sub>2</sub><sup>-</sup>. PSIL110: C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>PF<sub>6</sub><sup>-</sup>. <sup>c</sup> Isolated yield. <sup>d</sup> CO (1000 psi), 150 °C. <sup>e</sup> Significant starting material remained after 24 h. <sup>f</sup> ND = Not determined, many products.

82:18 to 96:4. When the reaction was carried out in PSIL101 [C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>Cl<sup>-</sup>], the desired product was obtained in trace quantities with nearly all of the starting material recovered after 24 h (Table 1, entry 8). When Ru<sub>3</sub>(CO)<sub>12</sub>/Phen or Ru<sub>3</sub>(CO)<sub>12</sub> was used as the catalytic system, both the yield and selectivity decreased (Table 1, entries 9 and 10). We were pleased to learn that when the reaction was run in PSIL110 as the ionic liquid **2a** was isolated in 92% yield and no amine byproduct was detected (Table 1, entry 11).

In order to try to improve the reaction efficiency, the reductive carbonylation of *p*-nitrotoluene **3** was carried out

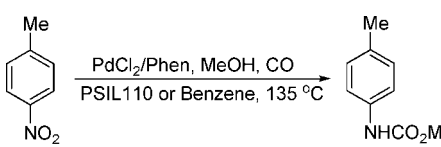
(4) (a) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459. (b) Wilkes, J. S. *Green. Chem.* **2002**, *4*, 73. (c) Dupont, J.; De Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667. (d) Sheldon, R. A. *Chem. Commun.* **2001**, 2399. (e) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772. (f) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391. (g) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.

(5) (a) Cao, H.; McNamee, L.; Alper, H. *J. Org. Chem.* **2008**, *73*, 3530. (b) McNulty, J.; Nair, J. J.; Robertson, A. *J. Org. Lett.* **2007**, *9*, 4575. (c) McNulty, J.; Cheekoori, S.; Bender, T. P.; Coggan, J. A. *Eur. J. Org. Chem.* **2007**, *9*, 1423. (d) McNulty, J.; Nair, J. J.; Cheekoori, S.; Larichev, V.; Capretta, A.; Robertson, A. *J. Chem.—Eur. J.* **2006**, *12*, 9314. (e) Vygodskii, Y. S.; Shaplov, A. S.; Lozinskaya, E. I.; Filippov, O. A.; Shubina, E. S.; Bandari, R.; Buchmeiser, M. R. *Macromolecules* **2006**, *39*, 7821. (f) McNulty, J.; Cheekoori, S.; Nair, J. J.; Larichev, V.; Capretta, A.; Robertson, A. *J. Tetrahedron Lett.* **2005**, *46*, 3641. (g) McNulty, J.; Capretta, A.; Cheekoori, S.; Clyburne, J. A. C.; Robertson, A. *J. Chim. Oggi* **2004**, *22*, 13. (h) Gerritsma, D. A.; Robertson, A. J.; McNulty, J.; Capretta, A. *Tetrahedron Lett.* **2004**, *45*, 7629. (i) Ramani, A.; Earle, M. J.; Robertson, A. *J. PCT Int. Appl.* **2003**, *24*. (j) McNulty, J.; Capretta, A.; Wilson, J.; Dyck, J.; Adjabeng, G.; Robertson, A. *J. Chem. Commun.* **2002**, 1986. (k) Karodia, N.; Guise, S.; Newlands, C.; Andersen, J.-A. *Chem. Commun.* **1998**, 2341. (l) Kaufmann, D. E.; Nouroozian, M.; Henze, H. *Synlett* **1996**, 1091.

(6) Shi, F.; He, Y.; Li, D.; Ma, Y.; Zhang, Q.; Deng, Y. *J. Mol. Catal. A: Chem.* **2006**, *244*, 64.

(7) Valli, V. L. K.; Alper, H. *J. Am. Chem. Soc.* **1993**, *115*, 3778.


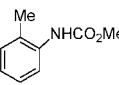

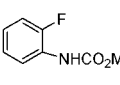

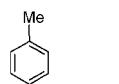

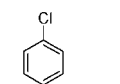

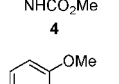

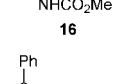

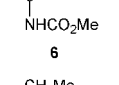

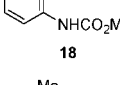

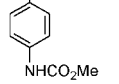

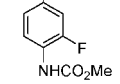

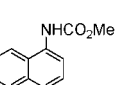

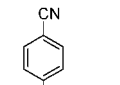
**Table 2.** Reductive Carbonylation of *p*-Nitrotoluene Catalyzed by PdCl<sub>2</sub>/Phen with Different Catalyst Loadings and CO Pressures<sup>a</sup>



entry	cat. loading (mol %)	sol <sup>b</sup>	pressure (psi)	time (h)	yield <sup>c</sup> (%)
1	5	IL110	500	24	96
2	5	IL110	200	24	93
3	2	IL110	200	48	91
4	2	IL110	200	24	92
5	1	IL110	200	24	89
6	5	benzene	200	48	9

<sup>a</sup> Reaction conditions: **3** (2 mmol), MeOH (30 mmol), 24 h. <sup>b</sup> PSIL110: C<sub>14</sub>H<sub>29</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>P<sup>+</sup>PF<sub>6</sub><sup>-</sup>, 2.0 g. <sup>c</sup> Isolated yield.

**Table 3.** Reductive Carbonylation of Various Mononitroarenes Catalyzed by PdCl<sub>2</sub>/Phen in PSIL110<sup>a</sup>

nitroarene	product	yield(%) <sup>b</sup>	nitroarene	product	yield(%) <sup>b</sup>
		89			87
		89			96
		88			95
		91			79
		92			90
		91			84

<sup>a</sup> Reaction conditions: nitroarene (2 mmol), PdCl<sub>2</sub> (0.02 mmol), Phen (0.04 mmol), MeOH (30 mmol), CO (200 psi), 135 °C, 24 h, PSIL110: 2.0 g. <sup>b</sup> Isolated yield.

using reduced catalyst loadings and lower carbon monoxide pressures. The results are listed in Table 2.


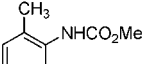

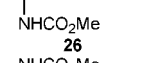

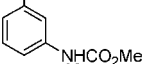

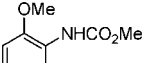

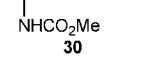

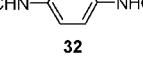

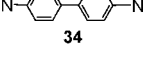

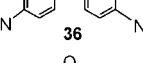

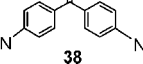

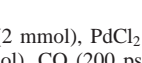



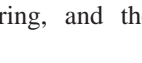
The results in Table 2 indicate that decreasing the pressure of carbon monoxide from 500 psi to 200 psi has almost no effect on the yield of **4** (Table 2, entries 1–2).

When the catalyst loading was reduced to 2 or 1 mol %, the product was still formed in 89–92% yield (Table 2, entries 3–5). However, when the reaction was carried out in 12 mL of dry benzene with 5 mol % of PdCl<sub>2</sub>/Phen as the catalyst, the desired product was obtained in only 9% isolated yield after 48 h reaction time (Table 2, entry 6).

To investigate the scope of this reaction, we carried out the reductive carbonylation reaction for other mononitroarenes with various electron-donating and electron-withdrawing

(8) (a) Gasperini, M.; Ragaini, F.; Cenini, S.; Gallo, E.; Fantauzzi, S. *Appl. Organomet. Chem.* **2007**, *21*, 782. (b) Gasperini, M.; Ragaini, F.; Remondini, C.; Caselli, A.; Cenini, S. *J. Organomet. Chem.* **2005**, *690*, 4517. (c) Ragaini, F.; Gasperini, M.; Cenini, S. *Adv. Synth. Catal.* **2004**, *346*, 63. (d) Ragaini, F.; Cognolato, C.; Gasperini, M.; Cenini, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 2886. (e) Gasperini, M.; Ragaini, F.; Cenini, S.; Gallo, E. *J. Mol. Catal. A: Chem.* **2003**, *204–205*, 107. (f) Paul, F.; Fischer, J.; Ochsenbein, P.; Osborn, J. A. C. R. *Chimie* **2002**, *5*, 267. (g) Gallo, E.; Ragaini, F.; Cenini, S.; Demartin, F. *J. Organomet. Chem.* **1999**, *586*, 190. (g) Wehman, P.; Kaasjager, V. E.; de Lange, W. G. J.; Hartl, F.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 3751.

**Table 4.** Reductive Carbonylation of Dinitroarenes Catalyzed by PdCl<sub>2</sub>/Phen in PSIL110<sup>a</sup>

entry	dinitroarene	cat. loading (mol %)	product	yield(%) <sup>c</sup>
1 <sup>b</sup>		5		83
2		5		85
3		2		78
4		5		79
5		2		76
6		5		77
7		5		82
8		2		73
9		5		75
10		2		70
11		2		88
12		2		86

<sup>a</sup> Reaction conditions: dinitroarene (2 mmol), PdCl<sub>2</sub> (2 or 5 mol %), Phen (4 or 10 mol %), MeOH (60 mmol), CO (200 psi), 135 °C, PSIL110: 2.0 g, 24 h. <sup>b</sup> CO (500 psi). <sup>c</sup> Isolated yield.

substituents on the aromatic ring, and the results are summarized in Table 3.

The results in Table 3 show that by the use of PdCl<sub>2</sub>/Phen as the catalytic system and PSIL110 as the ionic liquid, the reductive carbonylation of mononitroarenes proceeded well with both electron-donating and electron-withdrawing substituents on the aromatic ring, affording urethanes in 79–96% yields. No amine byproduct was detected in these reactions.

The reductive carbonylation of dinitro aromatics to commercially more important diisocyanates or diurethanes is more challenging because of their reduced reactivity compared to the mononitroarenes.<sup>9</sup> To investigate the applicability of the above reaction system for the reductive carbonylation of dinitroarenes, several dinitro substrates were subjected to the reaction with PdCl<sub>2</sub>/Phen as the catalytic system and PSIL110 as the reaction medium (Table 4).

First, 2, 4-dinitrotoluene reacted with carbon monoxide and methanol in the presence of 5 mol % of PdCl<sub>2</sub> and 10 mol % of Phen at 135 °C and 200–500 psi in 2.0 g of PSIL110 for 24 h. The product, dimethyl 4-methyl-1, 3-phenylenediurethane, was obtained in 83–85% isolated yield (Table 4, entries 1–2). Reduction of the catalyst loading

to 2 mol % lowered the urethane yield from 85% to 78% (Table 4, entry 3). Several other dinitroarenes were subjected to these reaction conditions, and the diurethanes were isolated in 70–88% yields (Table 4, entries 4–12).

For the reductive carbonylation of dinitroarenes, we used 1, 3-dinitrobenzene under the same reaction conditions in  $(C_4H_9)_4P^+Br^-$ ,  $(C_4H_9)_4P^+Cl^-$ ,  $(C_8H_{17})_4P^+Br^-$ , and  $C_{14}H_{29}(C_4H_9)_3P^+Cl^-$ , but the reactions were much less efficient and only traces of product could be detected. When  $C_2H_5(C_4H_9)_3P^+OP(O)(OC_2H_5)_2$  was used as the reaction medium, the desired product was formed in 71% isolated yield.

---

(9) (a) Gasperini, M.; Ragaini, F.; Cazzaniga, C.; Cenini, S. *Adv. Synth. Catal.* **2005**, *347*, 105. (b) Santi, R.; Romano, A. M.; Panella, F.; Mestroni, G.; Santi, A. S. O. *J. Mol. Catal. A: Chem.* **1999**, *144*, 41. (c) Islam, S. M.; Mal, D.; Palit, B. K.; Saha, C. R. *J. Mol. Catal. A: Chem.* **1999**, *142*, 169. (d) Wehman, P.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1996**, 217. (e) Reddy, N. P.; Masdeu, A. M.; M.; Ali, B. E.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 863.

In summary, the reductive carbonylation of mono- and dinitroarenes was carried out in the presence of the  $PdCl_2/Phen$  catalytic system, using PSIL110 as the ionic liquid. Important advantages of this reaction system include high yields, excellent selectivities for the urethanes, and the possibility of carrying out the reaction at considerably low carbon monoxide pressures. In addition, no cocatalyst is required for the reaction.

**Acknowledgment.** We are grateful to Cytec Canada, Inc. and to the Natural Sciences and Engineering Research Council for support of this work.

**Supporting Information Available:** Detailed experimental procedures and spectral data for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL802096X