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Catalytic Hydrogenation of Urea Derivatives and Polyureas

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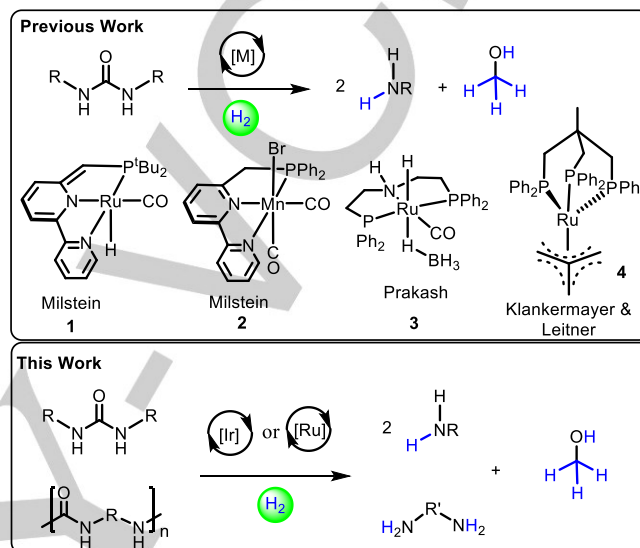
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Abstract: We present here the catalytic hydrogenation of various urea derivatives to amines and methanol. The reaction is catalyzed by a ruthenium or an iridium Macho pincer complex and produces amine and methanol in very good to excellent yields. Moreover, we also expand this concept to demonstrate the first example of the hydrogenative depolymerization of polyureas to produce diamines and methanol in moderate yields.

The development of a cost-effective and sustainable integrated approach for the capture of CO₂ and its conversion to methanol lies at the heart of the methanol economy as proposed by Olah and Prakash.^[1] The dominant CO₂ capture technology involves the reaction of CO₂ with amines to form carbamate or urea derivatives. Efficient hydrogenation of such carbamate or urea derivatives to methanol with the regeneration of amines can present alternative technology for the transformation of CO₂ to methanol. However, the hydrogenation of urea derivatives is the most challenging of all carbonyl bonds due to their low polarizability.^[2] As a matter of fact, urea derivatives have been used as solvents in hydrogenation reactions.^[3,4] Till date, only two catalysts (**1**, **2** Scheme 1), both from the Milstein group have been reported for hydrogenation of urea derivatives with broad substrate scopes.^[5–7] Prakash,^[8] and Leitner and Klankermayer^[9] have also utilized ruthenium-based catalysts (**3**, **4** Scheme 1) for the hydrogenation of urea derivatives. However, only a single substrate (diphenyl urea) has been hydrogenated using catalysts **3**, and **4**. Considering the significance and difficulty level associated with this reaction, it is important to explore new catalysts for the efficient hydrogenation of urea derivatives to methanol and amines.

Additionally, the expansion of this concept to the hydrogenative depolymerisation of polyureas can present a new technology for the chemical recycling of polyureas.^[10] We have recently discovered a new methodology for the synthesis of a broad range of polyureas from the ruthenium catalysed dehydrogenative coupling of diamines and methanol.^[11] Development of the reverse reaction i.e. hydrogenative depolymerisation of polyureas to methanol and diamines will therefore enable the circular economy of recycling of polyureas. Although several methods (e.g. pyrolysis, solvolysis, aminolysis, and glycolysis)^[12] have been investigated for the chemical recycling of plastics, reports on chemical recycling of polyureas are scarce. For example, Deng has reported degradation of polyureas by reacting them with urea and alcohol in the presence of a CuO-ZnO catalyst to form dicarbamates.^[13] Matsumoto has utilized supercritical CO₂ to hydrolyse polyureas to form amines.^[14] Although the approach of catalytic hydrogenation has been utilized for the depolymerisation of various plastics such as polyesters,^[15–17] polycarbonates,^[15,16,18–20] nylons,^[21,22] and polyurethanes,^[21–23] there has been no report on the hydrogenative depolymerisation of polyureas despite a significant output in the area of homogeneous catalytic hydrogenation.^[24–30]



Scheme 1. Previously reported catalysts for the hydrogenation of urea derivatives and the work described herein on the catalytic hydrogenation of urea derivatives and polyureas.

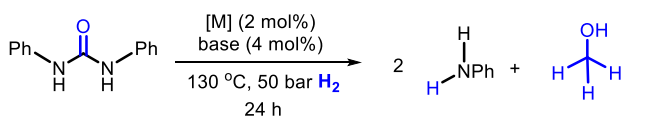
We started our investigation by optimizing catalytic conditions for the hydrogenation of diphenylurea. The hydrogenation reaction was studied using catalysts **5–10** (2 mol%) in the presence of KO^tBu (4 mol%) at 50 bar of H₂ and 130 °C in THF. The analysis of the reaction outcome by the ¹H NMR spectroscopy, and GC-MS revealed that the best yield (85% yield of aniline, and 80% yield of methanol) was observed using the iridium-Macho pincer catalyst **9** (Table 1, entry 5). N-methylaniline was obtained as a side-product in a ~15% yield. Ru-Macho pincer complex **5** also resulted in a similar yield of aniline (80%, entry 1), and methanol (72%). No reaction was observed using Gusev's Ru-SNS catalyst **6** under this catalytic condition (entry 2). Interestingly, hydrogenation of diphenyl urea (1 mmol) using the non-pincer catalyst **7** resulted in a high yield of aniline (70%, 1.4 mmol), however, poor selectivity towards methanol (~40%, 0.4 mmol) was observed with the concomitant formation of N-methyl aniline in ~60% yield (~0.6 mmol, entry 3). Remarkably, the Milstein's RuPNN catalyst **8** resulted in the formation of aniline and methanol in 80%, and 75% yields respectively (entry 4). No reaction was obtained in the case of Ru(PPh₃)₃(H)(Cl)(CO) (**10**, entry 6) suggestive of the important role of metal-ligand cooperation. Changing the solvent from THF to toluene, using complex **5** resulted in a lower yield presumably because of the lower solubility of diphenylurea in toluene (entry 7). Using 1,4-dioxane or anisole as solvents resulted in relatively lower yields of methanol and aniline in comparison to that of THF (Table 1, entry 8, 9). A much lower selectivity of methanol was obtained when KOH was used as a base with the concomitant formation of the by-product N-methylaniline (entry 10), whereas good

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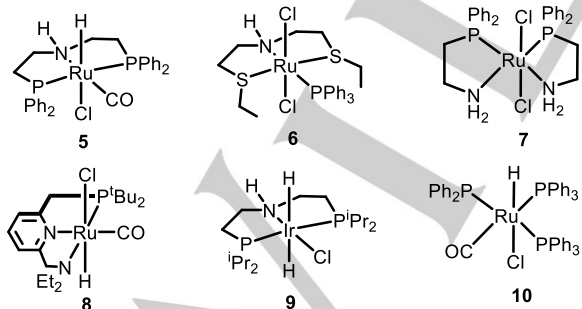
yields of aniline and methanol were obtained in the case of K_3PO_4 (entry 11). Interestingly, lowering the base loading to 2 mol% while keeping the remaining conditions the same, resulted in a lower yield of methanol and aniline (entry 12). This is suggestive of a dual role of base: (a) to generate the coordinatively unsaturated ruthenium complex (catalytically active species) by the N-H deprotonation and concomitant abstraction of chloride ligand from the precatalyst **5**, and

(b) to assist in the hydrogenation process by enabling facile decomposition of a hemiaminal intermediate as suggested earlier for the hydrogenation of amides.^[22] Moreover, increasing the base loading to 10 mol% resulted in a poor selectivity of methanol (20%), with the remaining product observed as the N-methyl aniline (entry 13). No conversion of diphenyl urea was observed when the catalysis

Table 1. Optimization of catalytic conditions for the hydrogenation of diphenylurea.^a



Entry	Pre catalyst	Base	Solvent	Conversion	Aniline	Methanol
1.	5	KO ^t Bu	THF	100%	80%	72%
2.	6	KO ^t Bu	THF	0%	0%	0%
3.	7	KO ^t Bu	THF	100%	70%	40%
4.	8	KO ^t Bu	THF	98%	80%	75%
5.	9	KO ^t Bu	THF	100%	85%	80%
6.	10	KO ^t Bu	THF	0%	0%	0%
7.	5	KO ^t Bu	toluene	50%	40%	38%
8.	5	KO ^t Bu	1,4-dioxane	99%	70%	52%
9.	5	KO ^t Bu	anisole	65%	52%	38%
10.	5	KOH	THF	99%	60%	20%
11.	5	K_3PO_4	THF	88%	75%	70%
12. ^b	5	KO ^t Bu	THF	60%	55%	50%
13. ^c	5	KO ^t Bu	THF	100%	50%	20%
14. ^d	-	KO ^t Bu	THF	0%	0%	0%
15. ^e	5	-	THF	0%	0%	0%



^aCatalytic conditions: diphenylurea (1 mmol), complex **5-10** (0.02 mmol), base (0.04 mmol), solvent (2 mL), H_2 (50 bar), 130 °C, 24 h. ^b0.02 mmol KO^tBu was used. ^c0.1 mmol KO^tBu was used. ^dNo KO^tBu was used. ^eNo metal-complex was used. Products were detected by the GC-MS and their yields were calculated by the ¹H NMR spectroscopy using 1,1'-diphenylethane as the internal standard. The conversion was determined by the GC-MS.

Table 2. Substrate scope for the hydrogenation of urea derivatives.^a

Entry	Substrate	Conversion	Amine	Methanol
1.		99%	85%	80%
2.		99%	87%	82%
3.		99%	95%	94%
4.		99%	85%	79%
5.		99%	88% ^b	64%
6.		95%	76%	65%
7.		90%	88%	57%
8.		94%	73%	60%
9.		0%	0%	0%
10.		0%	0%	0%

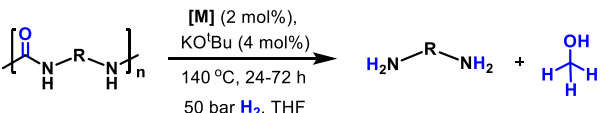
^aCatalytic conditions: urea derivative (1 mmol), **9** (0.02 mmol), KO^tBu (0.04 mmol), THF (2 mL), H_2 (50 bar), 130 °C, 24 h. ^bCombined yield of both the amine. Products were detected by the GC-MS and their yields were calculated by the ¹H NMR spectroscopy using 1,1'-diphenylethane as the internal standard. The conversion was determined using the GC-MS.

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was performed just in the presence of KO^tBu (in the absence of a metal-catalyst, entry 14) or just in the presence of the complex **5** (in the absence of a base, entry 15) suggesting that both a metal complex (e.g. **5,7-9**) and a base (e.g. KO^tBu) are essential for the catalysis.

Upon optimization of catalytic conditions for the hydrogenation of diphenyl urea, we employed this methodology for the hydrogenation of other urea derivatives. Under the catalytic combination of 2 mol% of complex **9**, and 4 mol% KO^tBu, a wide range of urea derivatives were hydrogenated under 50 bar of H₂ (130 °C, 24 h) in THF to produce methanol and the corresponding amine in very good to excellent yields (Table 2, entries 1-8). N-methyl or N-formyl amines were also detected by the GC-MS and the ¹H NMR spectroscopy as minor side-products. This explains the slightly lower yield of methanol in comparison to the corresponding amines (Scheme 2). No conversion of cyclic ureas – N,N'-trimethyleneurea (entry 9), and 1,3-dimethyl-2-imidazolidinone (entry 10) were observed under the reaction conditions.

Table 3. Hydrogenative depolymerisation of Polyureas.^a

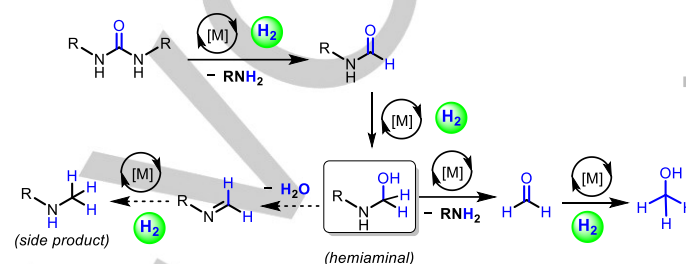


Entry	Substrate	Catalyst	Solvent	Conv.	Diamine	Methanol
1.		9	THF	45%	40%	27%
			Anisole	25%	23%	17%
			DMSO	50%	43%	34%
			THF	62%	60% ^b	41% ^b
2.		5	THF	40%	35%	20%
			THF	0%	0%	0%
3.		9	THF	0%	0%	0%
			THF	0%	0%	0%
5.		9	THF	38%	35% ^c	28% ^c
			THF	58%	51% ^b	43% ^b

^aCatalytic conditions: Polyurea (1 mmol), **9** or **5** (0.02 mmol), KO^tBu (0.04 mmol), solvent (2 mL), H₂ (50 bar), 140 °C, 24 h. ^bReaction time 72 h. ^cReaction time 36 h. Products were detected by the GC-MS and their yields were calculated by the ¹H NMR spectroscopy using 1,1'-diphenylethane as the internal standard.

We then attempted to utilize this method for the hydrogenative depolymerisation of polyureas. Gratifyingly, under the analogous conditions used for the hydrogenation of urea derivatives (Table 2), polyurea **PU1** (M_n = 5500) was depolymerised to produce 40% yield of 4,7,10-trioxa-1,13-tridecanediamine, and 27% yield of methanol (Table 3, entry 1). The use of anisole as a solvent resulted in a lower yield of diamine, and methanol whereas a higher yield was obtained in the case of DMSO. Moreover, increasing the reaction time to 72 h in THF also increased the yield of diamine and methanol to 60%, and

41% respectively (Table 3, entry 1). Utilizing the ruthenium analogue catalyst **5**, resulted in a slightly lower yield of diamine and methanol under the same catalytic conditions (entry 2). Hydrogenation of polyurea **PU2** (M_n = 2925) was not successful using either catalyst **9** or **5** and no methanol or p-xylenediamine was detected after the reaction time (entries 3,4, Table 3). **PU2** was completely recovered after completion of the reaction time. Under similar catalytic conditions, polyurea **PU3** (M_n = 4498) was also hydrogenated to produce 4,4'-methylenebis(cyclohexylamine) and methanol in up to 51%, and 43% yields respectively (Table 3, entry 5). No conversion of **PU1** was obtained when a control experiment was conducted without adding a catalyst (e.g. **9** and KO^tBu) while keeping the remaining condition the same as described in Table 3 (reaction time 24 h) confirming the necessity of external catalyst.



Scheme 2. Proposed pathway for the catalytic hydrogenation of urea derivatives.

Having demonstrated the hydrogenation of urea derivatives and polyureas, we carried some mechanistic investigations to understand the reaction pathway for the hydrogenation reaction. Analysis of the reaction mixture after hydrogenation of urea derivatives from Table 2 showed the presence of N-formamide and N-methylated amines by the ¹H NMR spectroscopy or the GC-MS (e.g. Figure S26, and S28). Interestingly, hydrogenation of formanilide under the catalytic conditions used for Table 2, entry 1, resulted in the formation of aniline and methanol in more than 90% yields. Formation of N-methyl aniline was also observed in ~5% yield. This suggests that the hydrogenation of urea derivatives to methanol and amines in the presence of complex **9** proceeds via a formamide intermediate. Based on the previous study,^[6] a proposed pathway for the catalytic hydrogenation of urea derivatives has been outlined in Scheme 2. Addition of the first equivalent of H₂ to a urea derivative results in the formation of a formamide intermediate with the concomitant release of an amine molecule. Further hydrogenation of the formamide intermediate results in the formation of a hemiaminal intermediate that could undergo transition-metal or base-assisted C-N cleavage^[22] to form another equivalent of amine and formaldehyde. Subsequent hydrogenation of formaldehyde produces methanol. The side-product N-methylamine could result from the dehydration of hemiaminal intermediate to form an imine followed by subsequent hydrogenation to produce N-methylamine. Hong has recently demonstrated that hydrogenation of N-benzyl formamide in the presence of the Ru-MachoBH catalyst (**3**) could form both benzylamine or N-methylbenzylamine as major products depending on the catalytic conditions (e.g. reaction temperature and the amount of methanol used as a solvent).^[31] The presence of methanol was found to facilitate the dehydration reaction possibly via a hydrogen-bonding interaction between methanol and the hydroxy group of the hemiaminal intermediate. We suspect that in our case, formation of N-methyl amine could result from a similar pathway.

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In conclusion, hydrogenation of urea derivatives and polyureas to produce (di)amines, and methanol in moderate to excellent yields using a ruthenium (**5**) or an iridium pincer complex (**9**) has been accomplished. Although, high yields for the hydrogenation of polyureas could not be achieved, this is the first demonstration of hydrogenative depolymerisation of polyureas, which we believe presents attractive opportunities for the closed-loop production/recycling of polyureas. Future work to improve the catalytic activity, and expansion of substrate scope, in particular using commercial polyurea waste is in progress.

Acknowledgements

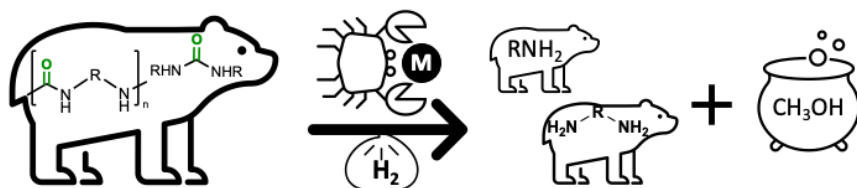
AK thanks the Leverhulme Trust for an early career fellowship. JL thanks the University of St. Andrews for the Undergraduate Research Assistantship. We thank the research group of Prof. Matt Clarke (School of Chemistry, University of St. Andrews) for assisting with lab equipment/facilities. We also thank Prof. Eli Zysman-Colman and Dr. Subeesh Madayanad Suresh (School of Chemistry, University of St. Andrews) for their help with the GC-MS.

Keywords: Catalysis • Hydrogenation • Pincer • Polyurea • Urea

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Hydrogenation of various urea derivatives and polyureas to amines/diamines and methanol using ruthenium and iridium Macho-pincer catalysts is reported herein. Considering that the reverse reaction has been reported before, the present study is of significance to the circular economy, methanol economy, and hydrogen economy (development of liquid hydrogen storage material).

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