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Hydrogenative Depolymerization of Nylons

Amit Kumar¹⁸, Niklas von Wolff², Michael Rauch¹, You-Quan Zou^{1‡}, Guy Shmul³, Yehoshoa Ben-David³, Gregory Leitus³, Liat Avram³, David Milstein^{1*}

¹Department of Organic Chemistry, ³Department of Chemical Research Support, The Weizmann Institute of Science, Rehovot 76100, Israel. ²Laboratoire d'Electrochimie Moléculaire, UMR 7591, CNRS/University of Paris, 75013 Paris, France.

ABSTRACT: The widespread crisis of plastic pollution demands discovery of new and sustainable approaches to degrade robust plastics such as nylons. Using a green and sustainable approach based on hydrogenation, in the presence of a ruthenium pincer catalyst at 150 °C and 70 bar H₂, we report here the first example of hydrogenative depolymerization of conventional, widely used nylons, and polyamides in general. Under the same catalytic conditions, we also demonstrate the hydrogenation of a polyurethane to produce diol, diamine and methanol. Additionally, we demonstrate an example where monomers (and oligomers) obtained from the hydrogenation process can be dehydrogenated back to a poly(oligo)amide of approximately similar molecular weight, thus completing a closed loop cycle for recycling of polyamides. Based on the experimental and DFT studies, we propose a catalytic cycle for the process that is facilitated by metal-ligand cooperativity. Overall, this unprecedented transformation, albeit at the proof of concept level, offers a new approach towards a cleaner route to recycling nylons.

INTRODUCTION

Nylons are commonly used plastics with a global market of more than 8 million tons per annum, and is being expected to grow at the rate of 2.2% reaching up to 10.4 million tons, equivalent to 47.0 billion USD by 2027.¹ Inevitably, the ubiquity of nylons and their nonbiodegradable nature have resulted in the increased land and ocean pollution posing a severe threat to our ecosystem.² Therefore, it is critical that efficient and sustainable technologies for the recycling of plastics such as nylons are developed. The current plastic recycling technologies are mostly based on mechanical recycling - converting one form of plastic to another by mechanical reprocessing (melting and re-extrusion): for example, converting plastic bottles to fibres. However, mechanical recycling produces poor quality of plastic and the number of times a plastic can be mechanically recycled is also limited.³ Distinct from mechanical recycling, chemical recycling involves depolymerization of a plastic to produce the monomer raw material from which the same virgin plastic can be made.³ Thus, only chemical recycling closes the loop of plastic production and is a sustainable mode of recycling. The reported chemical recycling methods for nylons are mainly based on pyrolysis, hydrolysis or aminolysis – all of which require harsh reaction conditions (such as temperatures \geq 250-300 °C).⁴ Other methods based on glycolysis or aminoglycolysis do not result in the efficient regeneration of nylons from the degraded polymers.5 Thus, development of new, efficient and sustainable methods to depolymerize nylons for the purpose of recycling are highly desirable.

Catalytic hydrogenation is an atom-economic, green and sustainable route for organic transformations as (a) it does not produce stoichiometric waste as in the case of conventional reducing agents and (b) hydrogen gas can potentially be produced from renewable

sources.⁶ In the past, we reported an efficient ruthenium pincer catalyst (1') for the hydrogenation of amides via C-N cleavage to form alcohols and amines (Figure 1.A.i).7 Several other homogeneous catalysts based on ruthenium,⁸⁻¹⁷ iron¹⁸⁻²¹ and manganese²² have also been reported for the hydrogenation of amides to form alcohols and amines.²³⁻²⁴ Additionally, we also reported acceptorless dehydrogenative coupling of alcohols and amines to form amides catalyzed by ruthenium pincer complex 2' (Figure 1.A.ii).²⁵ In this direction, Guan²⁶ and we²⁷ independently reported the synthesis of polyamides via dehydrogenative coupling of diols and diamines using the ruthenium pincer catalyst 2' (Figure 1.A.iii). In order to develop a closed loop cycle, we envisioned that it might be possible to achieve the very challenging catalytic hydrogenative depolymerization of polyamides to their monomers such as diols and diamines or amino alcohols (Figure 1.A.iv). Saito and coworkers have briefly mentioned an example of Ru-catalyzed hydrogenation of specialized, water soluble functionalized polyamides, although the structures of the polyamides and the hydrogenation products thereof were not reported.¹⁵ Hydrogenative depolymerization of polyesters and polycarbonates have also been reported earlier.²⁸ However, we are not aware of any report on the catalytic hydrogenation of conventional nylons such as nylon 6, nylon 66, nylon 12 or related polyamides in general which are highly robust and resistant to solvents. We report here our findings on the depolymerization of nylons using a ruthenium catalyzed hydrogenation process.

RESULTS AND DISCUSSION

A major challenge in the chemical reactivity of nylons is their resistance to solvents and reagents due to the multiple, strong intermolecular hydrogen bonding interactions between the polymer chains. We started our



Figure 1.A. (i) Hydrogenation of amides via C–N cleavage to form alcohols and amines; (ii) dehydrogenative coupling of alcohols and amines to form amides; (iii) dehydrogenative coupling of diols and diamines to form polyamides and (iv) hydrogenation of polyamides via C–N cleavage to form monomers. **Figure 1.B**. Ruthenium complexes used in this study.

Table 1. Catalyst screening for the hydrogenative depolymerization of resins of nylon 6.



Entry	complex (2 mol%)	KOBu	conversion	Aminoalcohol selec- tivity (yield%)	Oligoamide detection (monomer:dimer:trimer)	remark
1	1	8 mol%	77%	24%	Yes (3:4:2)	No resins recovered
4	2	8 mol%	80%	26%	Yes (3:4:2)	No resins recovered
5	3	8 mol%	66%	16%	Yes (3:6:4)	No resins recovered
6	4	2 mol%	30%	Not detected	Yes	Resins recovered (broken)
7	5	2 mol%	22%	Not detected	Yes	Resins recovered (broken)
8	6	2 mol%	0%	Not detected	No	Resins recovered
9	7	0 mol%	0%	Not detected	No	Resins recovered
10	1'	0 mol%	22%	Not detected	Yes	Resins recovered (broken)
11	2'	0 mol%	18%	Not detected	Yes	Resins recovered (broken)

^aCatalytic conditions: Nylon 6 (117 mg, 1 mmol relative to the mol wt of the monomer), complex (0.02 mmol), KO^tBu (2-9 mg, 0.02-0.08 mmol) as specified, DMSO (2.5 mL), temperature 150 °C, reaction time 48 h and H₂ (70 bars). Conversion is based on the weight of soluble materials after hydrogenation (see SI). Monomer means aminoalcohol. The ratio of monomer:dimer:trimer has been estimated by the LC-MS. "Resins recovered" means complete recovery of resins with the shape and size intact. "Resins recovered (broken)" means that the resins were broken to small pieces after reaction.

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investigation by searching for a solvent that would (a) be capable of 2 dissolving nylon 6 and (b) be compatible with Ru pincer complexcatalyzed hydrogenation. We have previously reported that complex 1 (Figure 1.B) in the presence of two (or more) equivalents (relative to 1) of base is a highly active catalyst for the hydrogenation of esters 6 and amides.²⁹⁻³⁰ Under the catalytic conditions using 1 (2 mol%), KO^tBu (8 mol%), H₂ (60 bar), for 48 h at 135 °C, we screened sev-8 eral solvents (2.5 mL) for the catalytic hydrogenation of nylon 6 (1 9 mmol, commercial resins of size 2-3 mm, $Mw = \sim 10,000$). As ruthenium PNN complexes react with acids, resulting in their deactivation 10 as catalysts,³¹ we avoided using acids such as formic acid or acetic 11 acid as solvents even though they are known to dissolve nylons. No 12 conversion of nylon 6 was observed when toluene, THF, 1,4-diox-13 ane, water or DMF were used under the catalytic conditions de-14 scribed above and resins of nylon 6 were completely recovered un-15 reacted, presumably due to the insolubility of nylon 6 in these sol-16 vents (Table S1, see SI). We then employed DMSO as a solvent as it 17 can dissolve nylon 6 at elevated temperature $(40\,\mathrm{g\,per}\,100\,\mathrm{mL}\,\mathrm{at}\,130\,\mathrm{mL})$ 18 °C).³² In addition to the ability of solubilizing nylons, DMSO has 19 also been claimed as an environmentally friendly solvent as it can be 20 prepared from renewable sources, exhibits lower toxicity compared 21 to several other polar solvents and is biodegradable.³³ Because of 22 such unique properties, coupled with low cost, DMSO has been uti-23 lized in several industrial processes as a solvent or reagent.³³ Encour-24 agingly, in case of DMSO solvent, a mixture of a solution and a white 25 precipitate was obtained at the end of the hydrogenation, suggestive 26 of a partial solubilization or degradation of nylon 6. Indeed, analysis 27 of the reaction mixture by GC revealed the formation of 6-amino-1-28 hexanol in 14% yield. Additionally, some other signals suggestive of oligomers were observed by GC. HR-ESI-MS and MALDI-TOF 29 spectrometry as well as NMR spectroscopy confirmed the presence 30 of 6-amino-1-hexanol and oligoamides (dimer-tetramer). Addition-31 ally, Diffusion Ordered Spectroscopy (DOSY) showed that the av-32 erage size of the formed oligoamides is approximately three times 33 than that of 6-amino-1-hexanol. The conversion of nylon was deter-34 mined by measuring the weights of the solid reaction mixture before 35 and after the reaction, as nylon 6 has no solubility in DMSO at room 36 temperature (see SI for details). Based on this method, the conver-37 sion of nylon 6 was determined to be 65%. Additional solvents such 38 as anisole, hexamethylphosphoramide (HMPA), 1-butyl-3-methyl 39 imidazolium octyl sulfate (BMIm-OctSO₄), diglyme and meta cre-40 sol were also screened under the same catalytic conditions (Table 41 S1, see SI) but we did not obtain any better results than when using 42 DMSO. 43

Further, we optimized the catalytic conditions by varying base loading, temperature, pressure, reaction time, ruthenium complexes (see Table 1) and additives such as water, molecular sieves and Lewis acids (see SI for the Table of optimization). Best results were obtained using 1 or 2 (2 mol%), KO^tBu (8 mol%), 70 bar of H_2 and 150 °C (oil bath temperature) for 48 h, which resulted in 77% conversion of nylon 6 (resins) and formation of 6-amino-1-hexanol in 24-26% yield (Table 1 and Table 2, entry 1), the remaining being oligomers (dimer-tetramer). Since complexes 1 and 2 exhibited

comparable catalytic activity (Table 1), we used complex 1 for further studies as it is relatively easy to synthesize compared to complex 2.

One of the reasons for the lower yield of 6-amino-1-hexanol could be catalyst deactivation over time. Hence, in order to achieve better yields of 6-amino-1-hexanol, we attempted sequential hydrogenation of nylon 6. After the first hydrogenation in DMSO under the optimized catalytic conditions, 2 mol% of complex 1 and 8 mol% of KO^tBu were added back to the mixture and the autoclave was pressurized with 70 bar of H₂ and heated at 150 °C for another 72 h. Following both hydrogenation steps, 99% of nylon 6 was depolymerized to form 6-amino-1-hexanol (37%) and a mixture of oligoamides (Table 2, entry 1^b, see SI, section 9). We found that if not for a matter of solubility, then THF or 1,4-dioxane are better solvents than DMSO for hydrogenation of amides using complex 1 (see SI, section 14.4). Thus, we developed an additional approach in which after the first step of hydrogenation, we distilled off the DMSO and added 1,4-dioxane along with complex 1 (2 mol%), KO^tBu (8 mol%) and H_2 (70 bar) and the autoclave was heated at 150 °C for additional 72 h. Interestingly, this resulted in a higher yield of 6-amino-1-hexanol (48%) although a lower conversion of nylon 6 (80%) was observed compared to the aforementioned process when DMSO was used for both the steps, presumably due to a lower solubility of nylon 6 in dioxane (Table 2, entry 1^c, see SI, section 9).

In order to explore the generality of this depolymerization reaction, we attempted the hydrogenation of other nylons. A powder form of commercial nylon 6 (Mw~11,000) was also depolymerized (85% conversion) under the optimized catalytic conditions (1, 2 mol% and KO^tBu 8 mol%, 70 bar of H₂ and at 150 °C) to produce 6amino-1-hexanol in 32% yield, the remainder being oligomers as observed for the hydrogenation of nylon 6-resins. Under the same catalytic conditions, but using complex 2, a slightly better yield of 6amino-1-hexanol (36%) was observed (Table 1, entry 2). Interestingly, when a catalytic combination of 2 (5 mol%) and KO^tBu (20 mol%) was used for 72 h, maintaining the remaining conditions, 99% conversion of nylon 6 was observed and 6-amino-1-hexanol was detected in 55% yield based on GC analysis, the rest being the oligomers (Table 1, entry 2^d). The products were also confirmed by the HR-ESI-MS and NMR spectroscopy. LC-ESI-MS was used to estimate the amount of formed oligomers, showing a ratio of monomer, dimer and trimer of 3:4:2 (see SI for yields of the formed oligomers estimated by the LC-ESI-MS).

Given the satisfactory result of the hydrogenative depolymerization of nylon 6, we explored the hydrogenation of other polyamides. Commercial resins of Nylon 12 (purchased from Sigma Aldrich) were also hydrogenated using the optimized catalytic condition to obtain a mixture of 12-aminododecan-1-ol and smaller oligomers (dimer and trimer, Table 2, entry 3). Additionally, we also prepared some polyamides using the dehydrogenative coupling route reported earlier by us²⁷ and then attempted to depolymerize them. Under the optimized catalytic conditions, 60% conversion of nylon 66 was observed and 1,6-hexane diol and hexamethylene diamine were detected in 20% and 25%

Table 2. Substrate scope for the catalytic hydrogenative depolymerization of polyamides^a

Entry	Polymer	Form	Mol Wt	Conversion	Selectivity (yield of amino alcohols, diols/diamines)
1.		resins	10,000	77% 99% ^b 80% ^c	24% 37% ^b 48% ^c
2.		powder	11,000	85% 99% ^d	36% 55% ^d
3.	$\left\{ \overset{P}{\overset{O}}{\overset{O}{\overset{O}}{\overset{O}}{\overset{O}}{\overset{O}{\overset{O}}}}{\overset{{\bullet}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	resins ^e	-	80%	30%
4.		powder	3500	60%	20% (diol) 25% (diamine)
5.		powder	1500	99%	80% (diol) 85% (diamine)
6.	$\left[\begin{array}{c} & & \\ & $	powder	4500	80%	42% (diol) 45% (diamine)
7.		powder	2500	95%	75% (diol) 74% (diamine)
8. r		powder	1500	95%	77% (diol) 82% (diamine)
9. H	I I I I I I I I I I I I I I I I I I I	resins ^e	-	90%	70% (diol) 66% (diamine)

^aCatalytic conditions: Polyamide (1 mmol relative to the molecular weight of the monomer), complex **1** (0.02 mmol), KO'Bu (0.08 mmol), DMSO (2.5 mL), H₂ (70 bar), temperature 150 °C and reaction time 48 h. ^bTwo sequential hydrogenation steps both in DMSO (*vide supra*). ^cTwo sequential hydrogenation steps first in DMSO and second in 1,4-dioxane (*vide supra*). ^d**2** (0.05 mmol) and KO'Bu (0.2 mmol), 72 h, remaining conditions as above^a. ^eMolecular weight could not be determined.

yields, respectively (entry 4). A low molecular weight polyamide prepared by the dehydrogenative coupling of 1,4- phenylenedimethanol and 1,4-phenylenedimethanamine was hydrogenated to afford 80% diol and 85% diamine (entry 5). Some other synthesized poly(oligo)amides with the combination of aliphatic and aromatic parts were also successfully hydrogenated to produce diols and diamines (entries 6-8). Further, we extended this concept to the hydrogenation of polyurethanes that is also a commonly used plastic and can be prepared from CO₂.³⁴ Thus, hydrogenation of polyurethanes (to diols, diamines and methanol) are beneficial not only for the recycling purpose but also for the indirect conversion of CO_2 to methanol. Under the same catalytic conditions (Table 1, entry 9), using complex **1** (2 mol%) and KO'Bu (8 mol%), commercial resins of a polyurethane were hydrogenated to afford 1,4-butanediol (70%), 4,4'-methylenebis(cyclohexan-1-amine) (66%) and methanol (45%). With the recent growth in the notion of circular chemistry (economy),³⁵ we also demonstrated, as a proof of concept that the catalytic hydrogenation/dehydrogenation process can be utilized

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for the development of closed loop cycle for the polyamide synthesis/degradation. The monomers and oligomers obtained (after removal of DMSO) from the reaction mixture described in Table 1, entry 5 were refluxed in 1,4-dioxane solvent containing complex **5** (1 mol%) and KO'Bu (1 mol%) for 48 h to produce the corresponding polyamide of 1600 mol. wt., similar to that used for hydrogenation (entry 5, also see SI, section 13).

Intrigued by the catalytic activity of the ruthenium pincer complexes 1 and 2 for the hydrogenation of polyamides, we explored the mechanism of the hydrogenative depolymerization process. The excellent ability of DMSO to disrupt the hydrogen bonding in amides and peptides was reported earlier using NMR spectroscopy and DFT studies.^{36,37} We found that using complex 1 (2 mol%) and KO^tBu (8 mol%), only a trace amount of DMSO gets hydrogenated under 70 bar of H₂ in THF (150 °C, 24 h). We detected Me₂S only in a trace quantity under the reaction conditions of hydrogenation of nylons using DMSO as solvent. These experiments indicate that complex 1 is not a good catalyst for the hydrogenation of DMSO, availing the catalyst for the hydrogenation of polyamides in DMSO as solvent. Additionally, reaction of complex 1 with 4 equivalents of KO^tBu in DMSO-d6 shows formation of a doubly-deprotonated anionic complex A reported by us earlier in THF.³⁰The ¹H NMR spectrum in DMSO-d6 exhibited a hydride signal $\left[\delta -18.19 \left(d, {}^{2}J_{H,P}\right)\right]$ 27.0 Hz, 1H)] very close to that observed in THF-d8 [δ -18.45 (d, ${}^{2}J_{H,P} = 28.0 \text{ Hz}, 1\text{H})$ where the hydride is located *trans* to a vacant coordination site (Scheme 1.i).³⁰ This indicates that DMSO is likely not coordinated to the ruthenium center, making the vacant coordinate site available for the hydrogenation reaction.

In order to gain further mechanistic insight, we studied the reaction of nylon 6 (powder form, Mw = 11,000) with the *in situ* prepared complex A in DMSO-d6 using variable temperature NMR spectroscopy (Scheme 1.ii). No reaction was observed when the temperature was gradually increased from 298 K to 360 K, but interestingly at 400 K, the hydride signal in the ¹H NMR spectrum completely disappeared and the corresponding ³¹P{¹H} NMR spectrum showed a mixture of species. This might indicate insertion of one of the carbonyl groups of nylon 6 into the Ru-H bond. Addition of H₂ (5 bar) to the same NMR tube at 298 K resulted in the formation of multiple ruthenium hydride species in the ¹H NMR spectrum featured by broad signals at δ -5.56, -5.78, -10.30 and -11.34. The signals at δ -5.56, -5.78 agree well with the ruthenium *trans* dihydride complex **C** that was independently prepared by the reaction of complex 1 with KO^tBu and H₂ (Scheme 1.i, hydride signals at δ -4.73 (d, ²*J*_{H,P} = 14.9 Hz) and -5.12 (d, ${}^{2}J_{H,P}$ = 17.6 Hz) in THF-d8 and at δ -5.23 $(d, {}^{2}J_{H,P} = 15.7 \text{ Hz})$ and -5.42 $(d, {}^{2}J_{H,P} = 16.0 \text{ Hz})$ in DMSO-d6). The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture after addition of H_{2} also showed a mixture of complexes, including a signal at δ 123.9, very close to that of complex C (δ 123.5 in THF-d8, δ 122.93 in DMSO-d6).

A similar observation was made upon reaction of complex **A** with N-benzyl benzamide (see SI, section 14.4). We also studied the reactivity of complex **A** with a diamide (Scheme 1.iii). Reaction of an *in situ* prepared complex **A** in THF or toluene-d8 with N1,N2-bis(4methoxybenzyl)oxalamide (4 equivalents) resulted in the formation of a mixture of complexes (See SI, section 14.5). Interestingly, a single crystal obtained from this reaction mixture revealed a diruthenium complex **B** (see SI, Figure S56) featuring N-H activation of both the amide groups. Significantly, both the C=O groups of the two amide moieties were found to coordinate to the two ruthenium centers, opening the amine side-arm of the pincer ligand. Hemilability of the amine-side arms in case of PNNH pincer complexes of ruthenium and manganese were proposed a few times in catalytic (de)hydrogenation reactions.^{29,38-40} Notably, this is the first crystal structure providing direct evidence for the hemilability of a PNNH pincer complex relevant to catalysis. The size of complex **B** as a dimer was also confirmed in the solution by DOSY NMR spectroscopy.



Scheme 1. (i) Reaction of complex 1 with KO'Bu and H_2 , formation of complexes A and C; (ii) reaction of complex A with nylon 6 and H_2 ; (iii) reaction of complex 1/KO'Bu with the diamide N1,N2-bis(4-methoxybenzyl)oxalamide.

To get further insights into the mechanism, we employed DFT ωB97M-V/def2calculations the at TZVPP/RIJCOSX/SMD//M06-L/def2TZVP/GD3/W06 level of theory. We suggest that the first step involves deprotonation of the precatalyst 1 at the benzylic position of the ligand P-arm to generate the dearomatized complex **D** (as observed experimentally).³⁰ In depth experimental thermodynamic analysis showed that for a similar PNP-Ru complex, the dearomatized form can be in equilibrium with different Lewis or Brønsted acids to undergo reversible re-aromatization.41 From a computational point of view the amido N-H bond of a simple test amide seems not to be acidic enough to generate higher concentrations of **F** (+9.1 kcal/mol) nor to be a good chelate (E, +9.6 kcal/mol), in contrast to recent findings involving formamides.⁴² On the other hand, other deprotonated species such as N-arm dearomatized D' (+5.9 kcal/mol) or N-H deprotonated D" (-0.3 kcal/mol) should be accessible under the employed reaction conditions.

Our calculations suggest that the hydrogenation reaction proceeds via two connected catalytic cycles involving the dearomatized complex **D** and the *trans* dihydride complex **C** formed upon hydrogen activation of **D**. Importantly, although the reaction is run at high temperature, which was shown to disfavor the H₂-splitting thermodynamics,⁴¹ formation of the dihydride species **C** is energetically downhill (-9.7 kcal/mol). This emphasizes the importance of relatively high pressures to generate high concentrations of **C** in this challenging amide hydrogenation. Previously reported experimental and theoretical studies implicate an important role of proton relays and solvation for this step.⁴³⁻⁴⁵



Scheme 2. Proposed mechanism for the hydrogenation of amides using DFT calculations.

As the reaction proceeds, both alcohols and amines are generated and are very likely involved in this step. Although not rate-determining and over-simplified, we wish to emphasize that we find the lowest barriers for H₂-splitting from **D'** (**TS1A**, 19.4 kcal/mol), with the test amide not acidic/basic enough to facilitate this step (TS1B, 26.2 kcal/mol). In the first catalytic cycle, hydrogen activation step is followed by the hydrogenation of amide bond by the trans dihydride complex C to form hemiaminal and regeneration of the dearomatized complex D. Given the experimental evidence for ligand hemilability in the presence of the diamide in **B** (Scheme 1.iii), we probed if this would be a viable pathway for amide hydrogenation. However, we find a stepwise Noyori-type mechanism to be more favorable with hydride transfer (TS2A1, 24.1 kcal/mol) preceding proton transfer from the N-H group (TS2A2, 21.4 kcal/mol). Indeed, hydride transfer via ligand hemilability is around 9 kcal/mol higher in energy (**TS2B**, 33.0 kcal/mol).

An intriguing aspect of amide hydrogenation is the fate of the intermediate hemiaminal. We calculate its dissociation to the amine and aldehyde to be strongly favorable ($\Delta G = -7.1 \text{ kcal/mol}$). A common notion is thus, that the hemiaminal dissociates easily as also implied by a mechanistic proposal by Sanford and co-workers.⁴⁶ Similarly, Prakash and co-workers could not detect any hemiaminal intermediate during CO2 hydrogenation via formamides.⁴⁷ In contrast, recent work from the Bernskoetter group indicates that hemiaminal dissociation is kinetically hindered and relies on proton-relay catalysis to occur readily.⁴⁸ This is in agreement with earlier DFT calculations from the same group, highlighting the TOF-limiting nature of this step, that is facilitated either by the employed iron complex, or via proton-relay by a solvent/reactant molecule.49 We were thus interested how these observations translate to our system. Again, the test amide seems not to be acidic enough to serve as efficient protonrelay for the generation of the labile zwitterion (TS3D1, 43.1 kcal/mol). Interestingly, for Fe and for Mo-complexes in the absence of alcohols,⁵⁰ a C-N bond cleavage might be promoted via an N-coordinated intermediate. In our case, such a pathway can be

and 37.4 kcal/mol, respectively). On the other hand, C-N bond cleavage via O-coordination (TS3A, 30.7 kcal/mol), positions the leaving amido group for protonation by the side-arm CH₂-group, as observed also for the reverse reaction in a PNP-Ru complex.⁴² Although significantly lower in energy than the other explored pathways, it would still be linked to an energetic span of around 40 kcal/mol. Anionic alkoxide species are amenable to expel very weak leaving groups (e.g. hydrides in the case of alcohol dehydrogenation).⁵¹ As amines are poor leaving groups, it might be suggested that basic conditions will favor C-N bond cleavage. This is at least in qualitative agreement with the above reported example of Beller's anionic Mo-alkoxo complex,⁵⁰ that can deprotonate the hemiaminal and facilitate subsequent C-N cleavage via H-bonding, or the example from the Bernskoetter group where the strongly basic co-catalyst TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) generates the highest catalytic activity.⁴⁸ In another Ru-catalyzed amide hydrogenation system, basic conditions were needed to promote C-N cleavage.⁵² Finally, an analogy to the cleavage to the hemiaminal might be the scission of C-N bonds in oxaziridines, which was shown to be base-catalyzed.53 In our case, indeed excess KO^tBu is needed for a successful turnover. Moreover, as the reaction proceeds, the reaction medium will become more basic. The generated amines and alcohols could further provide a stabilizing H-bond network. A preliminary surface scan of the potassium salt of the hemiaminal showed that in the absence of an H-bonding network, the C-N cleavage is uphill in energy but without any sizeable transition state (see SI). Clearly a more profound analysis, possibly involving explicit solvation, would be needed to assess with certainty the true nature of the C-N bond cleaving transition state in such amide hydrogenation reactions.

clearly ruled out due to very high barriers (TS3B and TS3C, 39.7

Finally, the aldehyde from the decomposition of hemiaminal gets hydrogenated by C to form alcohol and regenerates the dearomatized complex D", that would again be in rapid equilibrium with D.

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CONCLUSION

In conclusion, we report here the hydrogenative depolymerization of conventional nylons such as nylon 6, other polyamides and a polyurethane. The reaction is catalyzed by ruthenium pincer complexes using DMSO as a solvent which plays a critical role in the process, by disrupting the hydrogen bonding of the polyamide and at the same time remaining uncoordinated to the metal-center, thus allowing the catalysis to occur. We also demonstrate an example where the diols and diamines obtained from the hydrogenative depolymerization process are used to synthesize the original polyamide via a ruthenium catalyzed dehydrogenative coupling process, thus closing the loop of polyamide production. DFT calculations confirm the important role of metal-ligand cooperativity where the hydrogenation of amide bonds take place via an outer-sphere mechanism. Methods for chemical recycling of nylons have been reported earlier, however this is the first time that a process based on hydrogenation, which is a green, sustainable and atom-economic reaction, has been used to depolymerize conventional and robust nylons such as nylon 6. We believe that this unprecedented transformation, although not at a practical level yet, provides a new promising direction aimed at the highly desirable depolymerization of waste nylons, as well as hydrogenation of other polyamides.

ASSOCIATED CONTENT

Supporting Information. Supporting information is available free of charge via the Internet at http://pubs.acs.org. Experimental details of catalytic hydrogenation, mechanistic studies, NMR, GC, ESI-MS and X-ray data, and computational details, Crystallographic data for **B**.

AUTHOR INFORMATION

Corresponding Author

* <u>david.milstein@weizmann.ac.il</u>

Present Addresses

⁸School of Chemistry, University of St. Andrews, KY169ST, UK; [†]Department of Chemistry, University of Cambridge, CB21EW, UK.

Notes

The authors declare no competing financial interest.

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