

Catalytic Hydrogenation of Polyurethanes to Base Chemicals: From Model Systems to Commercial and End-of-Life Polyurethane Materials

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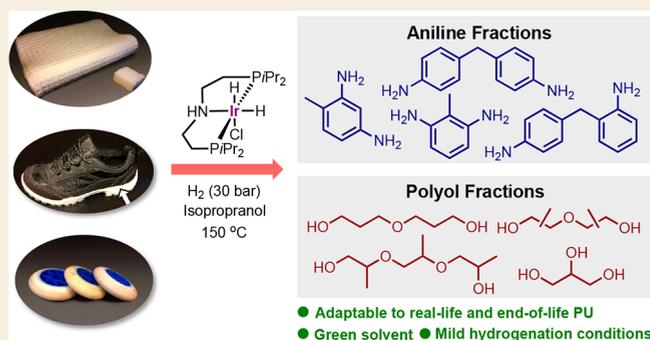
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Supporting Information

ABSTRACT: Polyurethane (PU) is a highly valued polymer prepared from diisocyanates and polyols, and it is used in everyday products, such as shoe soles, mattresses, and insulation materials, but also for the construction of sophisticated parts of medical devices, wind turbine blades, aircrafts, and spacecrafts, to name a few. As PU is most commonly used as a thermoset polymer composed of cross-linked structures, its recycling is complicated and inefficient, leading to increasing PU waste accumulating every year. Catalytic hydrogenation represents an atom-efficient means for the deconstruction of polyurethanes, but so far the identification of an efficient catalyst for the disassembly of real-life and end-of-life PU samples has not been demonstrated. In this work, we reveal that a commercially available catalyst, Ir-^{iPr}MACHO, under 30 bar H₂ and 150–180 °C, is a general catalyst for the effective hydrogenation of the four cornerstones of PU: flexible solid, flexible foamed, rigid solid, and rigid foamed, leading to the isolation of aromatic amines and a polyol fraction. For the first time, a variety of commercial PU materials, including examples of foams, inline skating wheels, shoe soles, and insulation materials, has been deconstructed into the two fractions. Most desirable, our reaction conditions include the use of isopropyl alcohol as a representative of a green solvent. It is speculated that a partial glycolysis at the surface of the PU particles is taking place in this solvent and reaction temperatures in the presence of catalytic amounts of base. As such a more efficient hydrogenation of the solubilized PU fragments in isopropyl alcohol becomes possible. As the isolated anilines are precursors to the original isocyanate building blocks, and methods for their conversion are well-known, the work reported in this paper provides a realistic indication of a potential circular plastic economy solution for PU. Preliminary experiments were also undertaken applying Mn-^{iPr}MACHO for the deconstruction of a commercial flexible PU foam. Although successful, more forcing conditions were required than those when applying Ir-^{iPr}MACHO.

KEYWORDS: polyurethane, polymer deconstruction, catalytic hydrogenation, diamines, polyols, iridium, manganese



INTRODUCTION

Today, there is an unprecedented need to reduce our waste generation, carbon footprint, and dependency on fossil fuels worldwide, and here plastics are of particular interest.^{1,2} In 2018, the annual production of plastics amounted to a stunning 359 million tons, of which Europe accounted for 61.8 million tons. In the same year, 29.1 million tons of plastic waste were collected in Europe, but only 32.5% was targeted for recycling. From the remaining fraction, ~25% was landfilled, while the rest of the plastic waste stream was sent for energy recovery through incineration.^{3,4} To establish a circular plastic economy, this plastic recycling challenge must be turned into an opportunity. The technology is already present for many thermoplastics including poly(ethylene terephthalate), polyethylene, and polypropylene (to name a

few), whereby high-value nonvirgin raw materials are made from plastic waste.^{5,6} For thermoset plastics, the degree of recycling is lagging behind, as similar recycling technologies are absent for this class of materials.^{7–9} The difference in the ease of recycling lies in the chemical nature of thermoplastics and thermoset plastics. On the one hand, waste thermoplastics can be melted and molded into new products, leading to some degree of recycling.¹⁰ Thermosets, on the other hand, are

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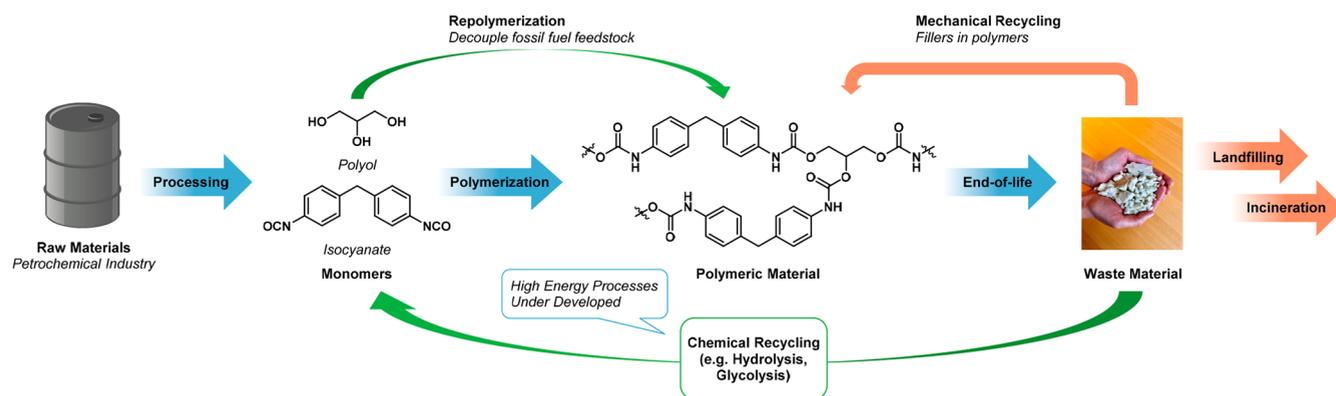


Figure 1. Schematic representation of the PU industry. Polyols are represented by glycerol, and isocyanates are represented by 4,4'-MDI.

composed of a cross-linked polymeric structure devoid of a melting point, thereby eliminating similar recycling strategies as for the thermoplastic materials.

Polyurethane (PU) is most commonly used as a thermoset plastic. The polymer is constructed from two monomeric building blocks (denoted isocyanates and polyols), which form the polymeric networks with interchain cross-linkages.¹¹ PU exists in a myriad of different forms, including elastomers, adhesives, and rigid, flexible, and molded foams (to name a few).^{12–14} Here, the polymeric property lies in the chemical and morphological structure of PU. These can easily be tailored through the choice of polyol, isocyanate, and additives like blowing agent, fillers, etc. Because of PU's versatile form, it is found in an astonishing number of every day products including footwear, furniture, refrigerators, and freezers but also in sophisticated high-end utilities such as wind-turbine blades, medical devices, and as key components in aircrafts and spacecrafts.¹⁵ With an annual PU production of more than 16 million tons globally, this polymer is the sixth most-used plastic worldwide. Taking into consideration the number of applications for PU, it comes as no surprise that the amount of PU waste increases each year.¹⁶ PU waste covers end-of-life products, postconsumer waste, and off-cuts from slabstock manufacturing, with the latter reaching as much as 15–20% with regard to the final PU product.^{8,17} As current technologies make PU recycling difficult, and since PU cannot undergo remolding, landfilling or incineration are the common ways for PU waste disposal (Figure 1). Since the majority of PU products are composed of lightweight foams, the transportation of these end-of-life products are highly uneconomical and far from sustainable. Furthermore, energy recovery through incineration must be performed carefully in order to avoid the liberation of toxic compounds, including carbon monoxide and hydrogen cyanide. Moreover, PU foams often contain flame retardants, which further complicates energy recovery.¹⁸

The recycling of waste PU can be divided into mechanical and chemical methods as described below (see Figure 1 for a schematic representation of the PU industry). In mechanical recycling, solid PU waste is ground down into powder or granules, which can be used as fillers in other materials or directly as substrates for subsequent processes.¹⁹ Shreddings of flexible foams can become rebound materials upon regluing under heat and pressure. While these approaches offer a second life, generally the polymer product is of lower value compared to the original PU material. Another tactic to PU recycling involves a chemical intervention, often denoted as

tertiary recycling. By reversing the polymerization, it is possible to create building blocks for new virgin PU materials, which decouples the formation of new monomers from the normal fossil fuel feedstock production.

Among the different chemical recycling methods, hydrolysis, aminolysis, and glycolysis are perhaps the most important for PU. In fact, only the latter is economically feasible, and therefore, it represents the only technology applied on an industrial scale.^{8–16} For hydrolysis, PU is reacted with water at elevated temperatures in combination with a basic catalyst. This provides a stream of the corresponding amine, polyol, and CO₂. The process is often deemed uneconomical due to the high energy input and excess water removal after the reaction. For aminolysis, ammonia or aliphatic amines are reacted with PU waste, providing a urea and a polyol fraction.²⁰ In glycolysis, the PU waste is reacted with a diol at elevated temperatures. This creates a new polyol fraction that can be used for the preparation of new PU products upon polymerization with added isocyanates.^{21,22}

Another, emerging and innovative, chemical recycling approach involves catalytic protocols,^{23,24} whereby a transition-metal catalyzed hydrogenation offers an atom-economical approach to the deconstruction of PU.²⁵ Furthermore, hydrogen gas can be produced from either a steam reforming of biobased resources or the electrolysis of water, and as such this method could provide a greener alternative to common chemical recycling methods.²⁶ Recent developments have shown that other plastics, including polyesters, polycarbonates, poly(ethylene terephthalate), and poly(lactic acid), all can be deconstructed by this catalytic methodology.^{27–34}

For polyurethane, two recent papers from Milstein et al. and Schaub et al. demonstrate that the deconstruction of model PU resins and technical-grade PU is possible (Scheme 1).^{35,36} However, in order to test catalyst efficiency, it would be more interesting to investigate the deconstruction of real-life and end-of-life PU samples, the molecular complexity of which is substantially more challenging because of the interchain cross-linkages.

In this paper, we disclose the first general procedure for the efficient deconstruction of a number of polyurethane products to base chemicals applying a catalytic hydrogenation setup under broadly applicable reaction conditions with a commercially available Ir complex (Scheme 1). Characteristic for our reaction conditions, compared to previous efforts, is the use of milder reaction conditions and the adaptability of a green and inexpensive solvent for the effective deconstruction of this class of polymers. With the presented methodology, the four

Scheme 1. Catalytic Hydrogenation of PU Resins (Milstein), Technical-Grade PU (Schaub), and End-of-Life-Cycle PU (This Work)

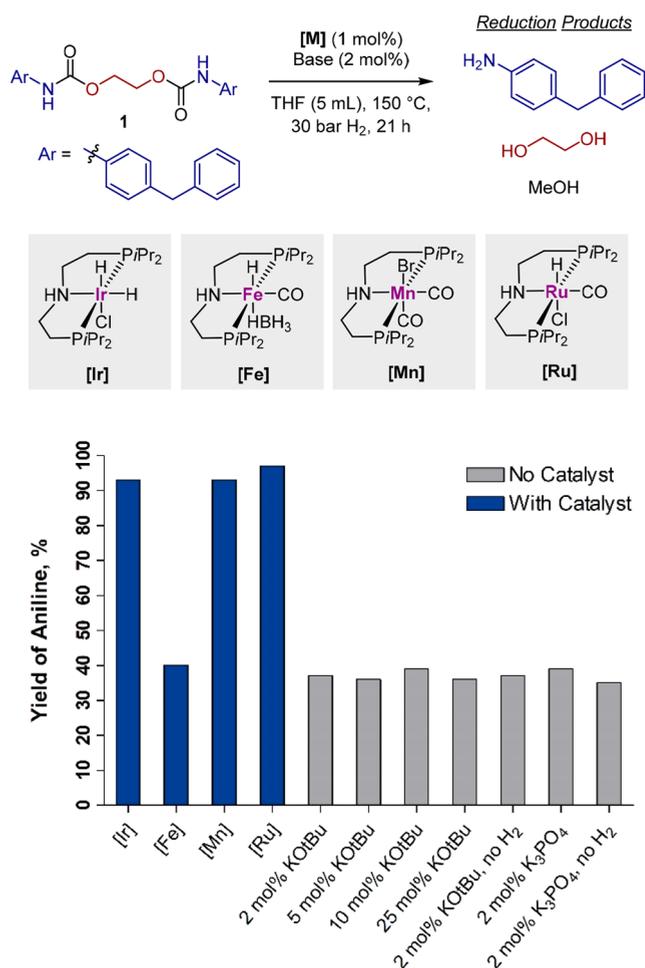
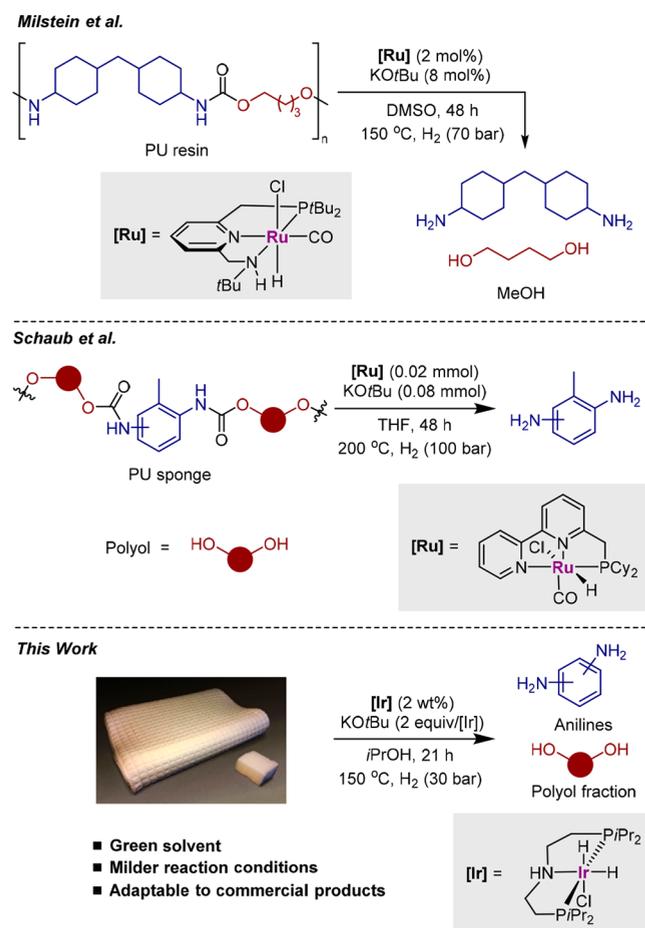


Figure 2. All reactions were performed in 30 mL autoclaves using 0.5 mmol of **1**. Conversions are based on the average of two experiments and determined using ¹H NMR spectroscopy with mesitylene as an internal standard. See the [Supporting Information](#) for full details.

cornerstones of PU (flexible solid, flexible foamed, rigid solid, and rigid foamed) can all be deconstructed with an isolation of the aromatic amines and a polyol fraction. Real-life and end-of-life PU samples, including examples of foams, shoe soles, insulation materials, and others, can be deconstructed for the first time applying this catalytic hydrogenation approach. As the isolated anilines are precursors to the isocyanate building blocks and, therefore, can be regenerated to the original isocyanates, a potential viable circular plastic economy loop is reported.

RESULTS AND DISCUSSION

Our initial studies evolved around the catalytic hydrogenation of model substrate **1** using the commercially available catalyst Ir-ⁱPrMACHO-HCl (Figure 2).³⁷ Much to our delight, the corresponding aniline was obtained in a 93% yield based on an analysis of the ¹H NMR spectrum using 1 mol % [Ir] and 2 mol % KOtBu at 150 °C in tetrahydrofuran (THF) as solvent and with 30 bar H₂ for 21 h. To evaluate the direct role of the transition metal for the catalytic hydrogenation of the carbamate functionality, we prepared the corresponding Fe-, Mn-, and Ru-ⁱPrMACHO complexes using literature procedures (see the [Supporting Information](#)). As can be seen from Figure 2, the Ir-, Mn-, and Ru-ⁱPrMACHO complexes all gave quantitative and comparable conversions for the hydrogenation of a simple PU model system, dicarbamate **1**, to

the corresponding aniline fragment, whereas Fe-ⁱPrMACHO proved to be more sluggish. Ethylene glycol and methanol were also noted in the ¹H NMR spectrum of the reaction mixture after the reaction completion, although their quantities were not measured. Lowering the hydrogen pressure or reaction temperature only led to reduced yields of the different reduction products for the three most active complexes (see the [Supporting Information](#) for full optimization studies with the dicarbamate **1**). In order to test if alternative pathways for PU deconstruction could be operating, the catalyst was omitted to investigate whether the addition of base alone was enough to promote the formation of anilines. Regardless of the base amount (e.g., 2-, 5-, 10-, or 25 mol %) or type of base, an almost similar conversion of ~37% to the corresponding aniline was noted. Furthermore, no conversion was observed in the absence of base (Table S1, [Supporting Information](#)). As such, a catalytic base-promoted pathway in addition to the catalytic hydrogenation of the carbamate group is operating under these reaction conditions. A possible scenario could be the base-promoted deprotonation of the carbamate followed by an isocyanate formation. Under the catalytic hydrogenation conditions, the isocyanate is possibly reduced directly to the aniline.

In search of a more representative PU model, we explored the catalytic hydrogenation of a structurally simple polyur-

ethane prepared from the polymerization of an equimolar amount of dipropylene glycol (isomeric mixture) and methylene diphenyl isocyanate (MDI) (a mixture of 4,4'-MDI and 2,4'-MDI) (PU-1). In the preparation of PU-1, 10 wt % of zeolite was added to remove the moisture for suppressing the formation of urea bonds, which may result from the decomposition of isocyanates to anilines in the presence of water. To ease the chemical analysis, a gas chromatography (GC) method was devised for distinguishing the free methylenedianiline (MDA) from the mixture. As such, the catalytic activity was assessed based on the formation of free anilines as compared to the amounts of isocyanates added (see the Supporting Information for full data). Prior to using the polymeric material, the sample was ground to a fine powder to enhance the solubility and increase the overall surface area. In the catalytic hydrogenation of PU-1 with 2 wt % of Ir-^{iPr}MACHO, 2 equiv of base per catalyst, and 30 bar H₂ at 150 °C in THF, a 61% conversion to free anilines was observed based on the GC analysis of the crude reaction mixture (Table 1, entry 1). Contrary to the results obtained

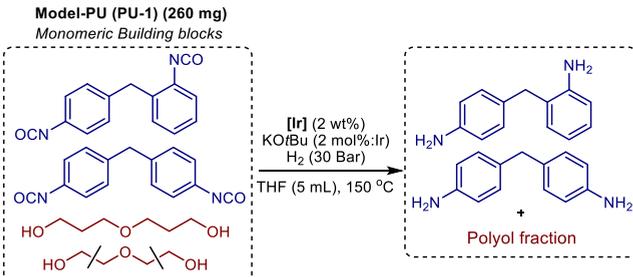
(entry 6), whereas dimethyl sulfoxide (DMSO) (entry 7), which was the solvent of choice in the report by Milstein et al.,³⁵ resulted in an almost complete shutdown of the catalytic activity, with only a 6% yield of the aniline mixture.

A number of alternative solvents were screened for the catalytic deconstruction of PU-1. Among those, isopropyl alcohol, which is considered to be a green solvent,³⁸ proved to be superior and led to an 83% conversion to anilines (entry 8 and the Supporting Information). Substituting the base for Cs₂CO₃ provided a 61% yield of the free anilines, while K₃PO₄ was comparable to KO^tBu pushing the aniline yield up to 85% (entries 8–10). While the change from KO^tBu only provided a slight increase in the overall output, the system proved to be more consistent with K₃PO₄ as the base. Increases in the catalyst loading, temperature, hydrogen pressure, or amount of base all resulted in a similar conversion to the free aniline (entries 11–14). When the effect of the catalyst loading was investigated, we noticed that a lower conversion to the anilines was observed using only 1 wt % [Ir], but a higher turnover could be obtained by increasing the amount of base (see the Supporting Information for details). This information proved crucial when the catalytic system was applied on more difficult PU samples.

With the optimized conditions in hand (2 wt % [Ir], 2 equiv of K₃PO₄ per [Ir], 30 bar H₂, 150 °C in 5 mL of *i*PrOH), it was possible to isolate an isomeric mixture of 4,4'- and 2,4'-MDA (1:1.3) in an 86% yield and the polyol fraction in a 90% yield from PU-1 (Figure 3). From a visual inspection of the crude reaction mixture, it was observed that most of the original solid was in solution. Possibly small amounts of a remaining insoluble material were the potassium phosphate and the zeolite used for the synthesis of the polymer. After purification via flash column chromatography, the formation of different formanilides could be detected. This could account for the remaining aniline fraction. As such, this outcome suggests that the formanilides could represent intermediates in the mechanism of PU hydrogenation, whereby an initial reduction of the carbon–oxygen bond precedes the carbon–nitrogen bond cleavage. This would also indicate that formanilide is a precursor to methanol. From the GC-mass spectrometry (MS) analyses of the crude product mixtures, MeOH could be detected and calculated for all plastics used throughout this study (see the Supporting Information for full results).

Next, the polyurethane sample PU-2, in which dipropylene glycol has been replaced by propylene glycol (PPG200), was tested. Much like PU-1, the sample was ground prior to use, and since no drying agent was added, the crude reaction mixture was completely homogeneous after the 21 h reaction time. To promote the original PU polymerization, a catalytic amount of triethylenediamine had been added. However, this proved not to be an issue for the hydrogenation, and under the optimized reaction conditions, a satisfying 87% isolated yield of a 4,4'- and 2,4'-MDA (1:1.3) mixture and a 71% yield of the polyol were obtained. From here, the methodology was tested on more representative PU samples, in which extensive cross-linkage is normally present. For PU-3, where glycerol was added as a cross-linker and used as the polyol together with dipropylene glycol (isomeric mixture), an 80% isolated yield of a 4,4'- and 2,4'-MDA (1:1.9) isomeric aniline mixture and a 51 wt % yield of the original polyol fraction could be isolated after the reaction. Here, the addition of 5 equiv of K₃PO₄ per [Ir] and a slight increase in temperature from 150 to 160 °C

Table 1. Optimization of the Catalytic Hydrogenation of PU-1^a



entry	deviations from standard cond	aniline ^b [%]
1	none	61%
2	Fe- ^{iPr} MACHO instead of [Ir]	12%
3	Mn- ^{iPr} MACHO instead of [Ir]	25%
4	Ru- ^{iPr} MACHO instead of [Ir]	53%
5	no catalyst	0%
6	dioxane instead of THF	47%
7	DMSO instead of THF	6%
8	<i>i</i> PrOH instead of THF	83%
9	<i>i</i> PrOH and Cs ₂ CO ₃	61%
10	<i>i</i> PrOH and K ₃ PO ₄	85% (86%) ^c
11	<i>i</i> PrOH, K ₃ PO ₄ and 3 wt % [Ir]	86%
12	<i>i</i> PrOH, K ₃ PO ₄ and 160 °C	77%
13	<i>i</i> PrOH, K ₃ PO ₄ and 40 bar H ₂	83%
14	<i>i</i> PrOH and K ₃ PO ₄ (4 equiv per [Ir])	80%

^aAll reactions were performed in a 30 mL autoclave fitted with a poly(tetrafluoroethylene) inlay using 260 mg of ground PU-1. Results are based on the average of two experiments. ^bGC-MS was used to determine the amount of the 4,4'-diamine and 2,4'-diamine. See the Supporting Information for full details. ^cIsolated yields.

from the hydrogenation of dicarbamate **1**, Fe-, Mn-, and Ru-^{iPr}MACHO were all inferior with respect to the aniline formation (entries 1–4). While a base-promoted cleavage of the polyurethane model was observed, a similar experiment, where catalyst was omitted in the hydrogenation of PU-1, produced no free aniline according to a GC analysis of the crude product mixture (entry 5). When THF was exchanged for dioxane, a 47% conversion to the free anilines was noted

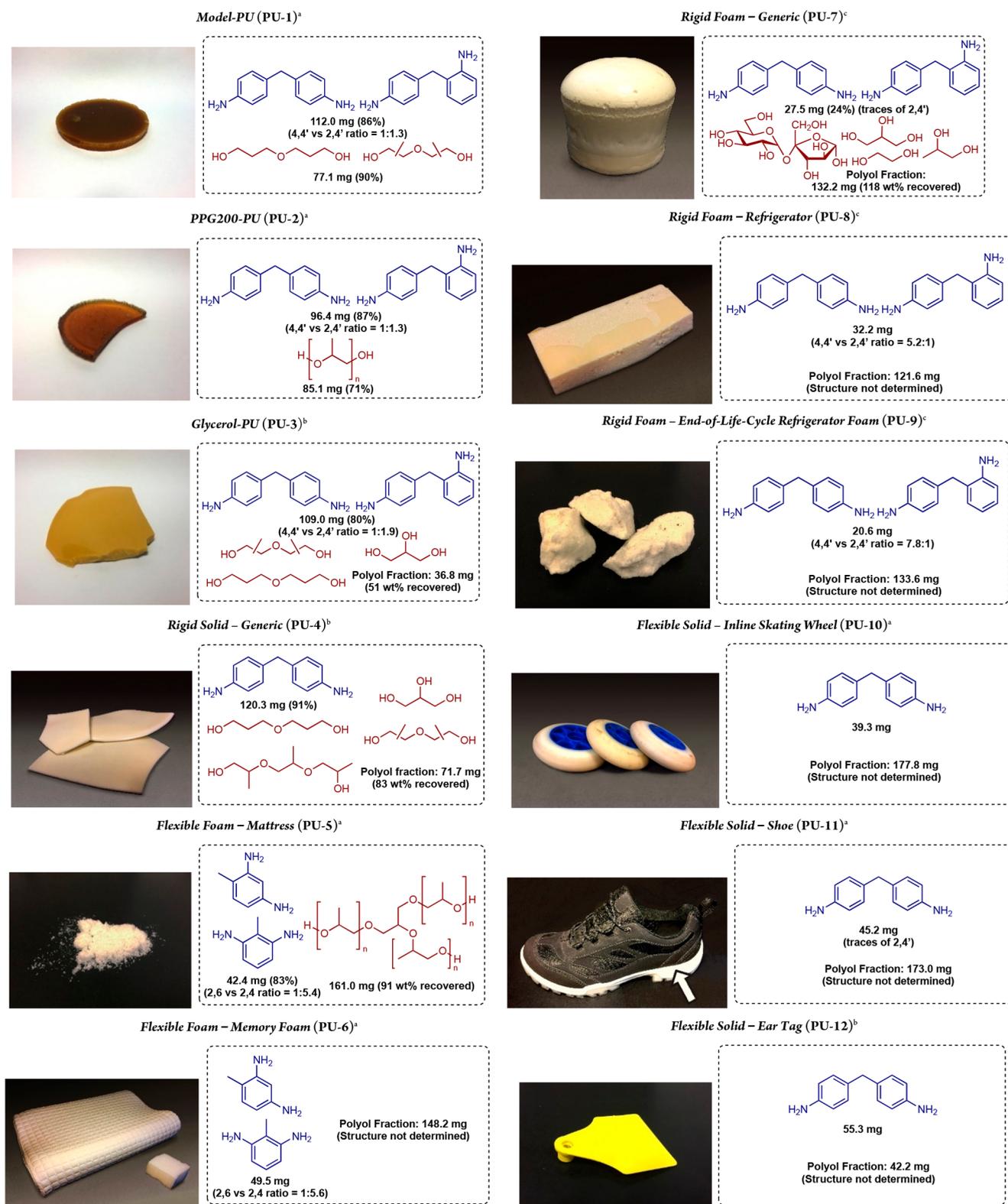


Figure 3. Hydrogenation of PU samples, consumer products, and end-of-life foams PU1–PU12. All reactions were performed in a 45 mL autoclave fitted with a 30 mL poly(tetrafluoroethylene) inlay using 260 mg of ground plastic, 2 wt % of Ir-*i*-Pr-MACHO, and 30 bar H₂ in *i*PrOH (5 mL). Yields reported as an average of two experiments. ^a 2 equiv of K₃PO₄ per [Ir] catalyst at 150 °C. ^b 5 equiv of K₃PO₄ per [Ir] catalyst and 160 °C. ^c 5 equiv of K₃PO₄ per [Ir] catalyst and 180 °C.

improved the isolated yield of the aniline fraction from 16% to 80% and the polyol fraction from 15.7 to 36.8 mg as a mixture of glycerol and dipropylene glycol.

For even more challenging substrates, we were pleased to see that a rigid solid PU material worked under the relatively mild cleavage conditions. The hydrogenation of the rigid solid polyurethane PU-4, which is composed of both glycerol and

tripropylene glycol as cross-linkers, dipropylene glycol, and 4,4'-MDI, resulted in a 91% isolated yield of the 4,4'-MDA, and 83 wt % of the original polyol was obtained. Much like the previous polyurethane, PU-3, a slight increase in the base amount and in temperature proved crucial, as the yield of 4,4'-MDA could be increased from 43% to 91%, while the polyol fraction gave a modest improvement in its isolation from 66.6 to 71.7 mg. The positive effect of a slight increase in base, combined with isopropyl alcohol and the reaction temperatures, can possibly be reasoned by a partial glycolysis of this difficult PU under these conditions, with a subsequent liberation of PU fragments into the solvent. The hydrogenation of these fragments would undoubtedly be more facile.

Next, consumer products including mattresses and memory foam pillows were tested, as flexible foam constitutes one of the largest proportions of PU products and one of the cornerstones of polyurethane. Pleasingly, the Ir-catalyzed hydrogenation of the flexible foam from a mattress (PU-5) resulted in an 83% isolation of the aniline fraction consisting of 2,6- and 2,4-toluenediamine (TDA) in a 1:5.4 mixture and a polyol fraction consisting of a 91 wt % sample of the original 3000 MW propoxylated glycerol. A matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analysis of the latter fraction revealed the polyol had not undergone degradation (see the Supporting Information). PU-5 was produced from a generic recipe, in which additives comprising of water, triethylenediamine, stannous octoate, and a silicon-based stabilizer were added. Pleasingly, all of these components in the polyurethane proved compatible with the hydrogenation conditions, which underlines the robustness of the catalytic process.

A brand-new memory foam pillow was thereafter subjected to the reaction conditions. Here, chunks of the memory foam (PU-6) were removed, dried, and added to an autoclave without further manipulations. Under the optimized reaction conditions, a 260 mg sample of PU-6 furnished 49.5 mg of an isomeric mixture of 2,6- and 2,4-TDA (1:5.6), while 148.2 mg of a fraction containing polyols was isolated, which was not further characterized. As the original composition of the PU is unknown, yields cannot be calculated for the polyol or the aniline fractions. While these masses were comparable to the isolated yields from PU-5, it was observed that the reaction mixture was fairly cloudy after the hydrogenation step, which is explained by the presence of a filler in the polyurethane. We did not characterize the structure of this filler.

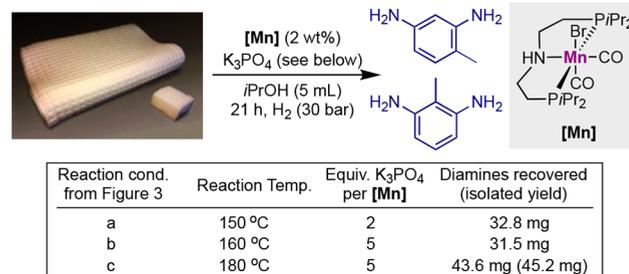
While the catalytic deconstruction of the flexible foam PUs proved efficient under the developed reaction conditions, the shift into rigid foams proved to be more challenging. Initially, the rigid foam PU-7 produced from a generic recipe based on highly cross-linking alcohols such as propoxylated sucrose was tested. At standard conditions, 8.1 mg of the aniline fraction (7%) could be obtained, while the polyol fraction amounted to 149.5 mg. The high mass obtained for the polyol fraction was a result of the incomplete hydrogenation of the PU sample. The polyol fraction still contained substantial amounts of the original 4,4'-MDI tethered to the different polyols. Increasing both the base amount to 5 equiv of K_3PO_4 per [Ir] and the reaction temperature from 150 to 180 °C improved the reaction slightly, leading to a 24% isolated yield of diamines, while the polyol fraction decreased from 149.5 to 132.2 mg. Much as in the previous experiment, an incomplete hydrogenation was observed from the polyol fraction isolated.

Continuing with another rigid foam, we examined the catalytic hydrogenation of an insulation foam from a refrigerator. This polyurethane (PU-8) necessitated forcing reaction conditions for its deconstruction. By increasing the reaction temperature to 180 °C and the base amount to 5 equiv of K_3PO_4 per [Ir], 32.2 mg of an isomeric mixture of 2,4'- and 4,4'-MDA (1:5.2) and 121.6 mg of a polyol fraction could be separated. To further test the utility of the developed methodology, a PU mixture from a scrap facility, where refrigerators are being recycled, was subjected to hydrogenation. The PU sample (PU-9) contained metal particles and other plastic fragments from the shredding process, which was not separated from the test sample. Nonetheless, the same conditions as applied to PU-8 were applicable for PU-9, and 20.6 mg of an isomeric mixture of 2,4'- and 4,4'-MDA (1:7.8) along with 133.6 mg of a polyol fraction could be isolated. Analyzing the polyol fraction by ^{31}P NMR spectroscopy, we observed that the sample contained a phosphorus compound as well, which could originate from a flame retardant used as an additive in the foam.

Lastly, examples of the flexible solid PU cornerstone were tested. Here, an inline skating wheel and a shoe were used, where parts of the outer rim of the wheel (PU-10) and shoe sole (PU-11) were shredded into finer particles and thereafter separately hydrogenated under the optimized reaction conditions. To our delight, both PU-10 and PU-11 could be deconstructed under these mild conditions generating a homogeneous reaction mixture from which 39.3 and 45.2 mg of 4,4'-MDA could be isolated, respectively, from PU-10 and PU-11 (traces of 2,4'-MDA). Alongside the diamine, 177.8 mg of the polyol fraction could be obtained from PU-10, whereas PU-11 led to an isolation of 173.0 mg of a polyol fraction, the structures of which were not further characterized. Finally, an ear tag used for tagging domestic livestock (PU-12) and also representing a flexible solid PU was tested. Slightly more forcing conditions compared to those used for PU-10 and PU-11 were used, as the temperature had to be increased to 160 °C, and the base amount was likewise increased to 5 equiv of K_3PO_4 per [Ir]. However, this small change in the reaction conditions was enough to push the free aniline formation from 28.1 to 55.3 mg of pure 4,4'-MDA and the polyol fraction from 45.8 to 42.2 mg.

While the commercially available Ir-^{iPr}MACHO proved efficient for the depolymerization of all four cornerstones of

Scheme 2. Mn-^{iPr}MACHO Catalyzed Hydrogenation of a Commercial Polyurethane Sample (PU-6)^a



^aReactions were performed in a 30 mL autoclave fitted with a poly(tetrafluoroethylene) inlay using 260 mg of ground PU-6. Results are based on an average of two experiments. GC-MS was used to determine the amount of 2,6- and 2,4-toluenediamine. See the Supporting Information for full details.

polyurethane, the usage of iridium comes with certain drawbacks including high price and low abundance. As such, preliminary experiments with Mn-^{iPr}MACHO were undertaken to verify if a commercial PU sample, namely, PU-6, could be depolymerized with a catalyst based on a less-expensive earth-abundant metal (Scheme 2). The three different reaction conditions applied in Figure 3 were attempted. As compared to the results obtained for the deconstruction of PU-6 using Ir-^{iPr}MACHO at 150 °C (see Figure 3), performing the same reaction with Mn-^{iPr}MACHO led to 32.8 mg of the free diamines (see the Supporting Information for full details). Nonetheless, an increase in the reaction temperature to 180 °C and a slight increase in base loading provided more reproducible results and with an increased efficiency with respect to the depolymerization of PU-6, as 45.2 mg of the diamines could be isolated after column chromatography.

CONCLUSIONS

In summary, we have reported on the first general procedure for the deconstruction of polyurethane materials and products. Real-life and end-of-life PU samples can be transformed back into their base chemicals applying a catalytic hydrogenation approach, thus representing a potential viable circular plastic economy for PU. Our studies demonstrate that the commercially available Ir-^{iPr}MACHO complex is effective for performing hydrogenations of samples from all four cornerstones of polyurethane (flexible solid, flexible foamed, rigid solid, and rigid foamed) under broadly applicable reaction conditions with the isolation of the polyol and aniline fractions. This is exemplified by the disassembly of pillow foam, end-of-life refrigerator foam, inline skating wheels, and of shoe sole polyurethane, in which the corresponding monomers can be isolated and potentially reused for the formation of new PU material. Moreover, best results were achieved when the hydrogenations were performed in the green solvent, isopropyl alcohol. We hypothesize that the combination of a partial glycolysis and the subsequent catalytic hydrogenation of PU fragments in solution is a possible reason for the success of this PU deconstruction methodology. As hydrogen can be produced from biobased resources or the electrolysis of water, there is an anticipation that this polymer disassembly approach can pave the way toward a cost-efficient recycling of PU. Initial efforts also demonstrated that a metal complex based on manganese revealed interesting activity with respect to the catalytic deconstruction of one of the PU samples. Further work is now in progress to improve the efficiency of such manganese-based catalysts for PU hydrogenation as well as other catalysts comprising of benign and earth-abundant transition metals and to test these on the deconstruction of all four cornerstones of PU plastics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.1c00050>.

Experimental details of the catalytic hydrogenations, GC-MS data, MALDI and NMR spectral data (PDF)

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Notes

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REFERENCES

- (1) Keijer, T.; Bakker, V.; Slootweg, J. C. Circular Chemistry to Enable a Circular Economy. *Nat. Chem.* **2019**, *11* (3), 190–195.
- (2) Hong, M.; Chen, E. Y.-X. Chemically Recyclable Polymers: a Circular Economy Approach to Sustainability. *Green Chem.* **2017**, *19* (16), 3692–3706.
- (3) Plasticseurope: Plastics—The Facts 2019. https://www.plasticseurope.org/download_file/force/3183/181 (accessed 2021-01-20).
- (4) Plasticseurope: The Circular Economy for Plastics—A European Overview. https://www.plasticseurope.org/download_file/force/3259/181 (accessed 2021-01-20).

- (5) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use and Fate of all Plastics Ever Made. *Sci. Adv.* **2017**, *3* (7), e1700782.
- (6) Rahimi, A.; Garcia, J. M. Chemical Recycling of Waste Plastics for New Materials Production. *Nat. Rev. Chem.* **2017**, *1* (6), 0046.
- (7) Eling, B.; Tomović, Ž.; Schädler, V. Current and Future Trends in Polyurethanes: An Industrial Perspective. *Macromol. Chem. Phys.* **2020**, *221* (14), 2000114.
- (8) Simón, D.; Borreguero, A. M.; de Lucas, A.; Rodríguez, J. F. Recycling of Polyurethanes from Laboratory to Industry, a Journey Towards the Sustainability. *Waste Manage.* **2018**, *76*, 147–171.
- (9) Vollmer, I.; Jenks, M. J. F.; Roelands, M. C. P.; White, R. J.; Harmelen, T.; Wild, P.; Laan, G. P.; Meirer, F.; Keurentjes, J. T. F.; Weckhuysen, B. M. Beyond Mechanical Recycling: Giving New Life to Plastic Waste. *Angew. Chem., Int. Ed.* **2020**, *59* (36), 15402–15423.
- (10) Ignatyev, I. A.; Thielemans, W.; Vander Beke, B. Recycling of Polymers: A Review. *ChemSusChem* **2014**, *7* (6), 1579–1593.
- (11) Engels, H.-W.; Pirkel, H.-G.; Albers, R.; Albach, R. W.; Krause, J.; Hoffmann, A.; Casselmann, H.; Dormish, J. Polyurethanes: Versatile Materials and Sustainable Problem Solvers for Today's Challenges. *Angew. Chem., Int. Ed.* **2013**, *52* (36), 9422–9441.
- (12) Gama, N. V.; Ferreira, A.; Barros-Timmons, A. Polyurethane Foams: Past, Present, and Future. *Materials* **2018**, *11* (10), 1841.
- (13) Chattopadhyay; Raju, K. V. S. N. Structural Engineering of Polyurethane Coatings for High Performance Applications. *Prog. Polym. Sci.* **2007**, *32* (3), 352–418.
- (14) Furtwengler, P.; Averous, L. Renewable Polyols for Advanced Polyurethane Foams from Diverse Biomass Resources. *Polym. Chem.* **2018**, *9* (32), 4258–4287.
- (15) Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R. Polyurethane types, Synthesis and Application – a Review. *RSC Adv.* **2016**, *6* (115), 114453–114482.
- (16) Kemon, A.; Piotrowska, M. Polyurethane Recycling and Disposal: Methods and Prospects. *Polymers* **2020**, *12* (8), 1752.
- (17) Kiss, G.; Rusu, G.; Peter, F.; Tănase, I.; Bandur, G. Recovery of Flexible Polyurethane Foam Waste for Efficient Reuse in Industrial Formulations. *Polymers* **2020**, *12* (7), 1533.
- (18) Chattopadhyay, D. K.; Webster, D. C. Thermal Stability and Flame Retardancy of Polyurethanes. *Prog. Polym. Sci.* **2009**, *34* (10), 1068–1133.
- (19) Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and Chemical Recycling of Solid Plastic Waste. *Waste Manage.* **2017**, *69*, 24–58.
- (20) Datta, J.; Kopczyńska, P. From Polymer Waste to Potential Main Industrial Products: Actual State of Recycling and Recovering. *Crit. Rev. Environ. Sci. Technol.* **2016**, *46* (10), 905–946.
- (21) Zia, K. M.; Bhatti, H. N.; Ahmad Bhatti, I. Methods for Polyurethane and Polyurethane Composites, Recycling and Recovery: A Review. *React. Funct. Polym.* **2007**, *67* (8), 675–692.
- (22) Datta, J.; Blazek, K.; Włoch, M.; Bukowski, R. A New Approach to Chemical Recycling of Polyamide 6.6 and Synthesis of Polyurethanes with Recovered Intermediates. *J. Polym. Environ.* **2018**, *26* (12), 4415–4429.
- (23) Garcia, J. M. Catalyst: Design Challenges for the Future of Plastic Recycling. *Chem.* **2016**, *1* (6), 813–819.
- (24) Kosloski-Oh, S. C.; Wood, Z. A.; Manjarrez, Y.; de los Rios, J. P.; Fieser, M. E. Catalytic Methods for Chemical Recycling or Upcycling of Commercial Polymers. *Mater. Horiz.* **2021**, DOI: 10.1039/D0MH01286F.
- (25) Cabrero-Antonino, J. R.; Adam, R.; Papa, V.; Beller, M. Homogeneous and Heterogeneous Catalytic Reduction of Amides and Related Compounds using Molecular Hydrogen. *Nat. Commun.* **2020**, *11* (1), 3893.
- (26) Zainzinger, V. Trying to Making Green Hydrogen Work in Europe. *C&EN* **2020**, *98* (23), 20–22.
- (27) Han, Z.; Rong, L.; Wu, J.; Zhang, L.; Wang, Z.; Ding, K. Catalytic Hydrogenation of Cyclic Carbonates: A Practical Approach from CO₂ and Epoxides to Methanol and Diols. *Angew. Chem., Int. Ed.* **2012**, *51* (52), 13041–13045.
- (28) Krall, E. M.; Klein, T. W.; Andersen, R. J.; Nett, A. J.; Glasgow, R. W.; Reader, D. S.; Dauphinais, B. C.; McIlrath, S. P.; Fischer, A. A.; Carney, M. J.; Hudson, D. J.; Robertson, N. J. Controlled Hydrogenative Depolymerization of Polyesters and Polycarbonates Catalyzed by Ruthenium(II) PNN Pincer Complexes. *Chem. Commun.* **2014**, *50* (38), 4884–4887.
- (29) Fuentes, J. A.; Smith, S. M.; Scharbert, M. T.; Carpenter, I.; Cordes, D. B.; Slawin, A. M. Z.; Clarke, M. L. On the Functional Group Tolerance of Ester Hydrogenation and Polyester Depolymerisation Catalysed by Ruthenium Complexes of Tridentate Aminophosphine Ligands. *Chem. - Eur. J.* **2015**, *21* (30), 10851–10860.
- (30) Westhues, S.; Idel, J.; Klankermayer, J. Molecular Catalyst Systems as Key Enablers for Tailored Polyesters and Polycarbonate Recycling Concepts. *Sci. Adv.* **2018**, *4* (8), eaat9669.
- (31) Kumar, A.; Janes, T.; Espinosa-Jalapa, N. A.; Milstein, D. Manganese Catalyzed Hydrogenation of Organic Carbonates to Methanol and Alcohols. *Angew. Chem., Int. Ed.* **2018**, *57* (37), 12076–12080.
- (32) Zubar, V.; Lebedev, Y.; Azofra, L. M.; Cavallo, L.; El-Sepelgy, O.; Rueping, M. Hydrogenation of CO₂-Derived Carbonates and Polycarbonates to Methanol and Diols by Metal-Ligand Cooperative Manganese Catalysis. *Angew. Chem., Int. Ed.* **2018**, *57* (41), 13439–13443.
- (33) Stadler, B. M.; Hinze, S.; Tin, S.; Vries, J. G. Hydrogenation of Polyesters to Polyether Polyols. *ChemSusChem* **2019**, *12* (17), 4082–4087.
- (34) Dahiya, P.; Gangwar, M. K.; Sundararaju, B. Well-Defined Cp*Co(III)-Catalyzed Hydrogenation of Carbonates and Polycarbonates. *ChemCatChem* **2021**, *13* (3), 934–939.
- (35) Kumar, A.; von Wolff, N.; Rauch, M.; Zou, Y.-Q.; Shmul, G.; Ben-David, Y.; Leitius, G.; Avram, L.; Milstein, D. Hydrogenative Depolymerization of Nylons. *J. Am. Chem. Soc.* **2020**, *142* (33), 14267–14275.
- (36) Zhou, W.; Neumann, P.; Al Batal, M.; Rominger, F.; Hashmi, A. S. K.; Schaub, T. Depolymerization of Technical Grade Polyamide 66 and Polyurethane Materials via Hydrogenation. *ChemSusChem* **2020**, DOI: 10.1002/cssc.202002465.
- (37) Clarke, Z. E.; Maragh, P. T.; Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid, K. A Family of Active Iridium Catalysts for Transfer Hydrogenation of Ketones. *Organometallics* **2006**, *25* (17), 4113–4117.
- (38) Alfonsi, K.; Colberg, J.; Dunn, P. J.; Fevig, T.; Jennings, S.; Johnson, T. A.; Kleine, H. P.; Knight, C.; Nagy, M. A.; Perry, D. A.; Stefaniak, M. Green Chemistry Tools to Influence a Medicinal Chemistry and Research Chemistry Based Organisation. *Green Chem.* **2008**, *10* (1), 31–36.