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Hafnium-Catalyzed Direct Amide Formation at Room Temperature

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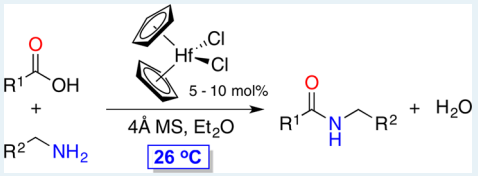
Supporting Information

ABSTRACT: Herein, the first example of a metal-catalyzed protocol for direct amidation of nonactivated carboxylic acids at ambient temperature (26 °C) is presented. The mild reaction conditions give rise to high yields of a range of amides in reaction times as short as 90 min, employing a commercial hafnium complex, $[Hf(Cp)_2Cl_2]$, as catalyst. Amino acids are transformed into their corresponding amides without racemization, and the catalyst displays full selectivity for the amidation of carboxylic acids over esters. Electronic properties of the carboxylic acids were found to have a strong influence on the rate of the amidation reaction, and the need for a balanced amount of molecular sieves was observed to be highly important for optimal reaction outcome.



KEYWORDS: *hafnium, amidation, carboxylic acid, Lewis acids, catalysis*

INTRODUCTION

The amide bond is found in a wide variety of chemical products such as pharmaceuticals, agrochemicals, and polymers, and products containing the functionality are synthesized on a multiton scale every year. Nature uses enzymes to form amides and peptides from carboxylic acids and amines in a catalytic fashion, generating water as the only byproduct. However, this green reaction has proved complicated to mimic for the synthetic chemist and only a limited number of catalytic protocols for the transformation is known.[1,2] To date, the most common way to form amides synthetically from carboxylic acids is via activation of the carboxylic acid, either by a coupling reagent[3] or by the formation of an acid chloride (the Schotten−Baumann reaction), followed by aminolysis of the activated carboxylic derivative. This fact was clearly illustrated in a survey performed by three major pharmaceutical companies, which showed that 93% of all N-acylations in the synthesis of 128 drug candidates were carried out by stoichiometric activation of the carboxylic acid.[4] Despite the efficiency of these methods, the stoichiometric activation is waste intensive and introduces extra steps to the synthesis, along with the need for additional purifications. These issues are circumvented by the use of catalysis. Amide formation avoiding poor atom economy reagents was highlighted as a key research area by the ACS Green Chemistry Institute Pharmaceutical Roundtable in 2005,[5] and the need for further development in the field is great.

Amides can be formed from several classes of starting materials, including esters, aldehydes, alcohols, and nitriles.[6] The use of carboxylic acids as starting materials in direct amidations is generally considered to be the most challenging, due to the possibility of salt formation between the acid and the amine upon mixing. This problem can be overcome by performing reactions at elevated temperature (generally around 160 °C), at which moderate to good yields of amides are obtained. The efficiency of direct thermal amidation has been shown to be highly substrate dependent,[7−11] and the high temperatures typically required are not suitable for highly functionalized or sensitive substrates. Hence, catalysis is an attractive alternative to enable atom-economical formation of amides from carboxylic acids and amines under milder conditions. The two main classes of synthetic catalysts for direct amidation are boronic acids and esters along with Lewis acidic metal complexes. In the first class, boric acid[12,13] as well as substituted arylboronic acids[14−16] have been used as catalysts. These protocols all require elevated reaction temperatures (generally 85−110 °C), with the exception of *o*-iodophenylboronic acid[17,18] and 2-furanylboronic acid,[19] which are the only synthetic amidation catalysts active at 25 °C. In addition, water formed in the reaction needs to be removed in order to obtain good yields of the amide products, most commonly by azeotropic distillation or the use of molecular sieves. In the second class of catalysts, complexes based on e.g. titanium,[20−22] zirconium,[9,23,24] zinc,[25,26] and iron[27] have been reported. Similar to the case for the boron-based catalysts, the metal-catalyzed protocols all require elevated temperatures and an efficient removal of water.

RESULTS AND DISCUSSION

We have previously reported on the use of titanium and zirconium complexes in catalytic amounts for the formation of

Scheme 1. Hafnium-Catalyzed Direct Amidation of Phenylacetic Acid and Benzylamine

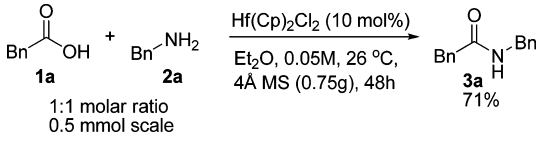


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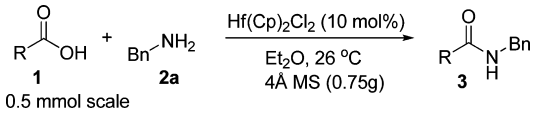
Table 1. Evaluation of Reaction Mixture Concentration

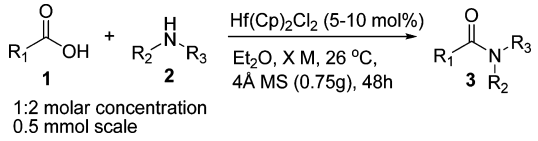


entry	amide	carboxylic acid	[acid] (M)	amt of amine (equiv)	reaction time (h)	isolated yield (%)
1	**3a**	phenylacetic acid	0.05	1	24	38
2	**3a**	phenylacetic acid	0.05	1.5	24	56
3	**3a**	phenylacetic acid	0.05	2	24	81
4	**3a**	phenylacetic acid	0.1	2	24	86
5	**3a**	phenylacetic acid	0.2	2	24	81
6	**3a**	phenylacetic acid	0.4	2	24	84
7	**3b**	valeric acid	0.05	2	48	17
8	**3b**	valeric acid	0.1	2	48	76
9	**3b**	valeric acid	0.2	2	24	80
10	**3b**	valeric acid	0.4	2	24	85
11	**3b**	valeric acid	0.05	2	96	63
12	**3b**	valeric acid	0.05	4	48	75

primary, secondary, and tertiary amides.[22−24] A range of differently substituted amides were formed in good yields, using a catalyst loading of 2−20 mol % and a reaction temperature ranging between 70 and 120 °C. The latter is a significant drawback for the amidation of sensitive substrates, and we were therefore interested to find a milder catalytic protocol which would enable the formation of amides even at room temperature. We set out to evaluate different Lewis acidic metal complexes in catalytic amounts for the direct amidation of phenylacetic acid (**1a**) (see the Supporting Information for a complete list of complexes and solvents screened). The sandwich complex bis(dicyclopentadienyl)hafnium dichloride was identified as the most active catalyst, giving rise to 71% isolated yield of the amide formed from phenylacetic acid (**1a**) and benzylamine (**2a**) after 48 h in diethyl ether (Scheme 1). Molecular sieves were added to scavenge water formed in the reaction and to prevent the hydrolytically unstable catalyst from decomposing.[28] The amount of molecular sieves is important for the reaction outcome, and 0.75 g of activated powdered 4 Å sieves was found to be optimal for the transformation of 0.5 mmol of carboxylic acid into amide (vide infra).

The amount of amine **2a** was found to be important for the reaction outcome. Increasing the amount of amine resulted in a significant improvement of the yield of amide product **3a** after 24 h reaction time (Table 1, entries 1−3). The standard conditions were hence set to a 2:1 molar ratio of amine to carboxylic acid. Optimizing the reaction conditions with regard to the concentration of the reaction mixture, we found significant differences between structurally different acids. In the amidation of phenylacetic acid (**1a**) with benzylamine, the acid concentration had little effect on the outcome of the

Table 2. Substrate Scope



entry	amide	acid	amine	amt of Hf (mol %)	[acid] (M)	isolated yield (%)
1	**3a**	phenylacetic acid	benzylamine	5	0.1	87[a]
2	**3b**	valeric acid	benzylamine	5	0.4	76
3	**3c**	Boc-Gly-OH	benzylamine	5	0.1	83
4	**3d**	Z-Gly-OH	benzylamine	5	0.2	88
5	**3e**	Boc-Ala-OH	benzylamine	5	0.2	87[b]
6	**3f**	Boc-Met-OH	benzylamine	5	0.1	96[b]
7	**3g**	Boc-Leu-OH	benzylamine	5	0.1	81[b]
8	**3h**	Boc-Pro-OH	benzylamine	5	0.1	88[b]
9	**3i**	Boc-Trp-OH	benzylamine	5	0.4	73[b]
10	**3j**	cyclohexanecarboxylic acid	benzylamine	10	0.4	76/87[c]
11	**3k**	benzoic acid	benzylamine	10	0.4	52/80[c]
12	**3l**	cinnamic acid	benzylamine	10	0.4	60[c]
13	**3m**	trichloroacetic acid	benzylamine	10	0.05	76
14	**3n**	dichloroacetic acid	benzylamine	10	0.05	92[d]
15	**3o**	chloroacetic acid	benzylamine	10	0.05	79
16	**3p**	phenylacetic acid	pentylamine	5	0.1	90
17	**3q**	phenylacetic acid	dodecylamine	5	0.1	90
18	**3r**	phenylacetic acid	cyclohexylamine	10	0.2	79
19	**3s**	phenylacetic acid	2-thiophenemethylamine	10	0.05	83
20	**3t**	phenylacetic acid	(*R*)-phenylethylamine	10	0.4	78[b]
21	**3u**	phenylacetic acid	1,4-dioxa-8-azaspiro[4.5]decane	10	0.1	81
22	**3v**	phenylacetic acid	4-methoxybenzylamine	10	0.05	82
23	**3w**	phenylacetic acid	4-chlorobenzylamine	10	0.05	86
24	**3x**	phenylacetic acid	4-fluorobenzylamine	10	0.05	95

[a]24 h reaction time. [b]>99% ee determined by HPLC (AD column 90/10 *i*-hex/*i*PrOH). [c]4 equiv of amine. [d]90 min reaction time.

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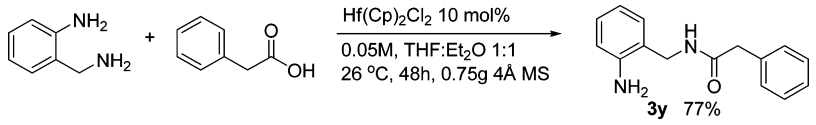
Scheme 2. Selective Monoacylation of a Diamine: Aromatic Amine Remains Unchanged



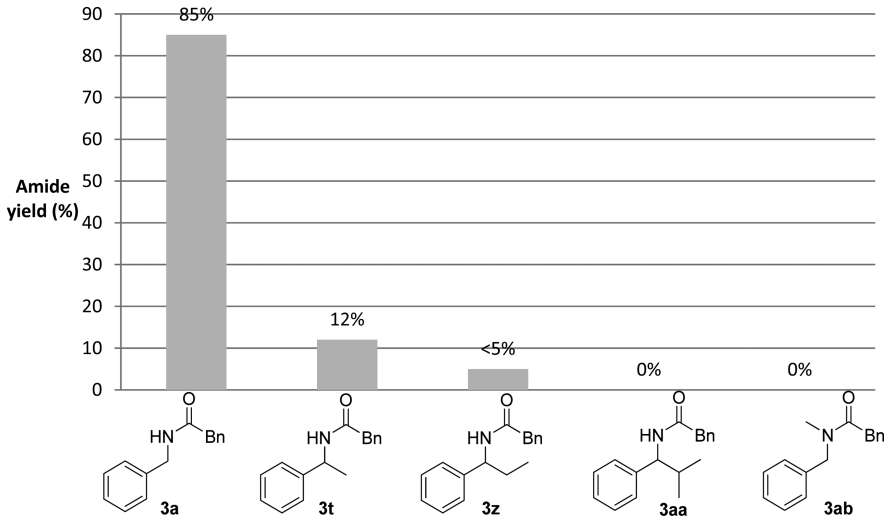


Figure 1. Steric hindrance in the amine affecting the reaction outcome. Reaction conditions: phenylacetic acid (0.5 mmol), amine (1.0 mmol), $Hf(Cp)_2Cl_2$ (10 mol %), Et_2O (10 mL), 4 Å MS (powder, 0.75 g), 26 °C, 48 h.

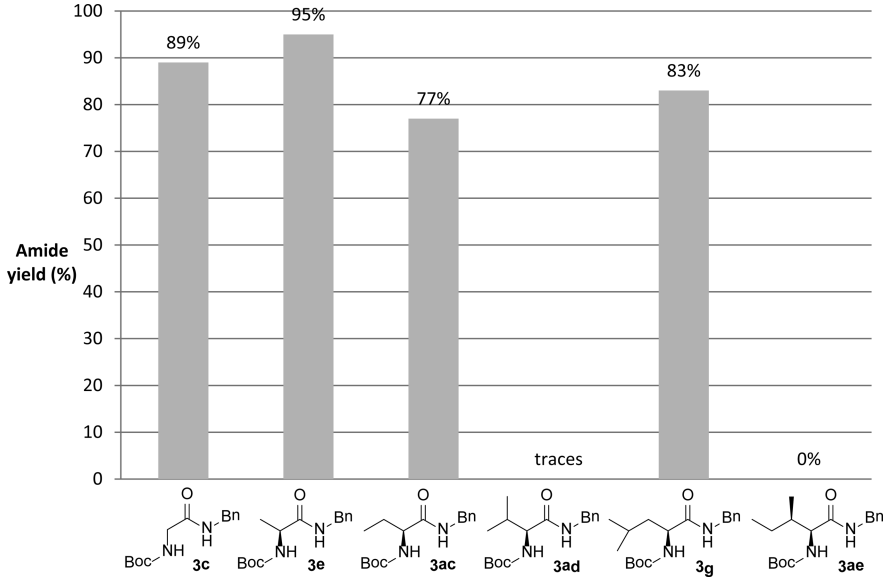
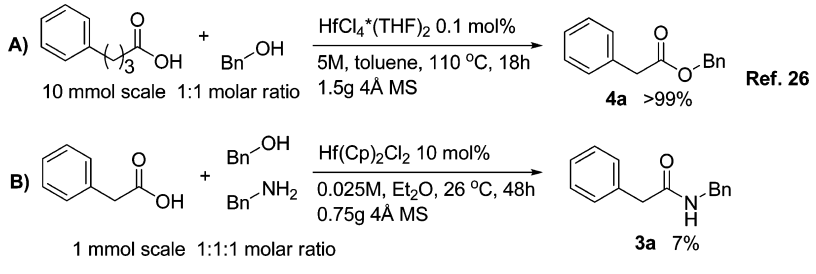


Figure 2. Steric hindrance in the β position in the carboxylic side chain of the amino acid heavily affecting the reaction outcome. Reaction conditions: carboxylic acid (0.5 mmol), benzylamine (1.0 mmol), $Hf(Cp)_2Cl_2$ (10 mol %), Et_2O (10 mL), 4 Å MS (powder, 0.75 g), 26 °C, 48 h.

Scheme 3. Ester Formation Catalyzed by Hf(IV) at High Reaction Temperatures (A) but Not at Room Temperature (B)



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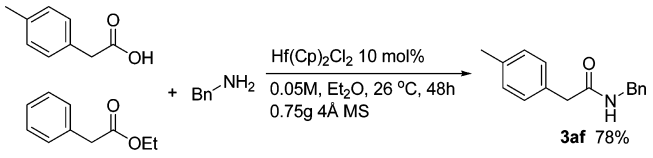
Scheme 4. Competition Experiment between an Ester and a Carboxylic Acid Showing That the Catalyst Is Fully Selective toward Amidation of the Acid



0.5 mmol scale 1:1:4 acid:ester:amine

reaction (Table 1, entries 3–6). However, in the corresponding amidation of valeric acid, the acid concentration effectively influenced the isolated yield of amide **3b** (Table 1, entries 7–10). It was also found that a high yield of amide **3b** could be obtained at an acid concentration of 0.05 M when the reaction time was prolonged (Table 1, entry 11), as well as when a larger excess of the amine was used (Table 1, entry 12).

With this knowledge at hand, we investigated the scope of the hafnium-catalyzed direct amidation protocol at room temperature. The reaction conditions were optimized for each substrate with respect to catalyst loading and molar concentration. A reaction time of 48 h was chosen as standard to allow even slow-reacting substrates to reach a high conversion. It should be noted, however, that several substrates are fully converted long before this time, some already after 90 min (Table 2, entry 14). Moreover, it was found that the catalyst loading could be decreased from 10 to 5 mol % for a number of substrates. A further decrease in catalyst loading resulted in lower isolated yields, and a control experiment without the hafnium complex present did not give rise to any product. Vigorous stirring and freshly activated molecular sieves were in all cases crucial for an efficient reaction outcome. The substrate evaluation presented in Table 2 shows that several substrates work well under the catalytic conditions. No racemization was detected in the amino acid amide products (Table 2, entries 5–9) after the reaction. Protection groups such as Boc (*tert*-butylcarbonyloxy) (Table 2, entries 3 and 5–9) and Cbz (benzylcarbonyloxy) (Table 2, entry 4) are stable under the reaction conditions. Benzoic acid and cinnamic acid were converted into their corresponding benzylamides in moderate to good yields (Table 2, entries 11 and 12). These substrates are particularly interesting, since conjugated acids are known to react poorly in catalytic direct amidation, unless elevated reaction temperatures are used.[15,18,22] In addition, sterically demanding carboxylic acids and amines were successfully transformed into the corresponding amides (Table 2, entries 10 and 18). Good yields were also obtained using both electron-rich and electron-poor benzylamines (Table 2, entries 22–24) as well as electron-poor carboxylic acids (Table 2, entries 13–15). Of the latter, amide **3o** is of special interest, since the α-halo substituent can easily serve as a handle for further synthetic manipulations. In addition, amide **3e** was synthesized on a 5 mmol scale in a round-bottomed flask and was isolated in 77% yield (1.2 g) after extractive workup and column chromatography.

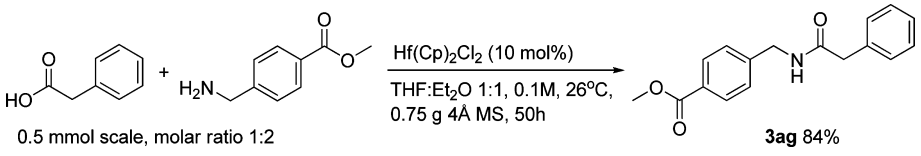
Anilines are poor nucleophiles in comparison to aliphatic amines and need high reaction temperatures in order to work successfully in direct amidations.[15,20,29] All attempts to use even the electron-rich *p*-anisidine in the amidation of phenylacetic acid **1a** failed using hafnium catalysis. However, the poor reactivity of anilines under optimized reaction conditions enabled the selective acylation of the nonaromatic amine of 2-aminobenzylamine, as illustrated in Scheme 2. In contrast, aliphatic diamines (*e.g.* *p*-xylylenediamine and 1,3-diaminopropane) are incompatible with the reaction conditions and result in no product formation when they are mixed with phenylacetic acid. In addition, ammonia (NH_3 in THF, 0.4 M) failed to form the corresponding phenylacetamide.

Although the cyclic amine 1,4-dioxa-8-azaspiro[4.5]decane works well in the amidation reaction (Table 2, entry 21), secondary acyclic amines fail as coupling partners, which is in line with what has previously been reported for boronic acid catalysis at room temperature.[17,18] The reason for this is not clear, but the increased steric hindrance might play a role. The results from the condensation of a series of benzylamines with phenylacetic acid under identical reaction conditions are shown in Figure 1. As can be seen, increasing the size of the substituents on the amine lead to a dramatic drop in isolated amide yield. Whereas optimizations of the reaction conditions could circumvent this steric effect and enable a reasonable yield for amide **3t** (Table 2, entry 20), other amines such as the secondary *N*-methylbenzylamine remained unreactive and failed to form the desired amide **3ab**.

Increasing the steric hindrance in a series of carboxylic acids did not affect the reaction outcome in the same way (Figure 2). Interestingly, a significant change in reactivity was only seen when the β position of the amino acid was doubly substituted, as in the case of Boc-protected valine (**3ad**) and isoleucine (**3ae**), and in these cases the reaction did not proceed at all. Despite various attempts to optimize the reaction conditions for the formation of amide **3ad**, no product was formed. The failure of this substrate to react can possibly be explained by steric interactions, which hinder the acid to adopt an appropriate binding mode to hafnium in order to enable amidation.

In addition to direct amidation of carboxylic acids, group IV metal complexes are known to catalyze other transformations of carboxylic derivatives. For example, Yamamoto and co-workers have shown that $HfCl_4 \cdot 2THF$ and $Hf(OtBu)_4$ catalyze the esterification of carboxylic acids with alcohols in refluxing toluene with excellent yields (Scheme 3, reaction A).[30] In addition, Collins et al. recently demonstrated that both intra- and intermolecular esterifications can be performed using $Hf(OTf)_4$ as a catalyst in refluxing toluene.[31] However, when we used the hafnocene complex under the reaction conditions optimized for amidation, no esterification between phenylacetic acid and ethanol was observed. Instead, the catalyst was

Scheme 5. Amidation of Phenylacetic Acid with the Amino Ester Methyl (4-Methylamino)benzoate



0.5 mmol scale, molar ratio 1:2

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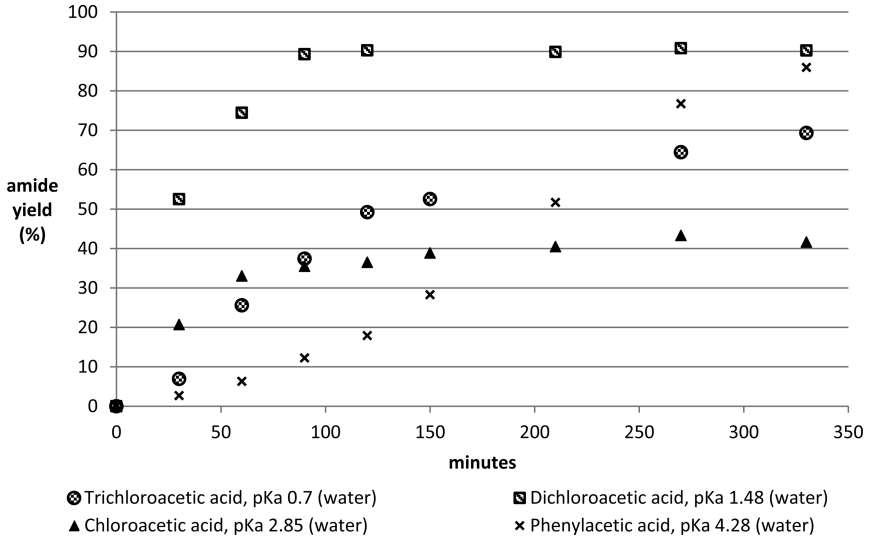

Figure 3. Reaction profiles for four different carboxylic acids with different pK_as. Reaction conditions: carboxylic acid (0.5 mmol), benzylamine (1.0 mmol), $Hf(Cp)_2Cl_2$ (10 mol %), Et_2O (10 mL), 4 Å MS (powder, 0.75 g), 26 °C, 48 h. Yields were determined by ^{1}H NMR.

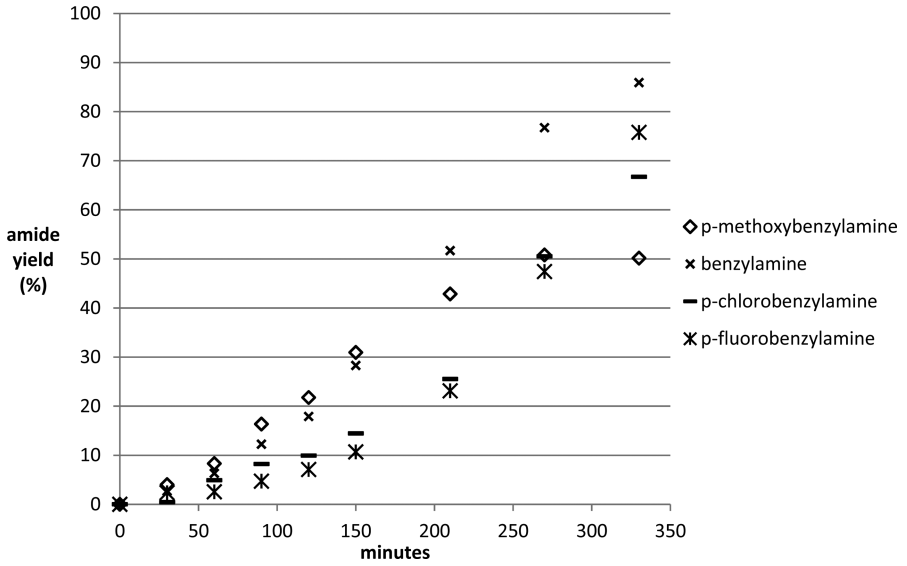

Figure 4. Reaction profiles of phenylacetic acid reacted with differently substituted benzylamines. Reaction conditions: phenylacetic acid (0.5 mmol), amine (1.0 mmol), $Hf(Cp)_2Cl_2$ (10 mol %), Et_2O (10 mL), 4 Å MS (powder, 0.75 g), 26 °C, 48 h. Yields determined by ^{1}H NMR.

inhibited by the presence of alcohol, which was further demonstrated in a competition experiment between benzylamine and benzyl alcohol, resulting in only 7% product with full chemoselectivity for the amide **3a** (Scheme 3, reaction B). Interestingly, this reactivity is the opposite of that described for $Hf(OTf)_4$, which was found to be fully selective for esterification over amidation.[31] The low tolerance of $Hf(Cp)_2Cl_2$ toward free hydroxyl groups under the reaction conditions explain why Boc-Ser-OH, Boc-Tyr-OH, and mandelic acid failed to form their correspondning benzylamides.

Furthermore, group IV metal complexes were reported by Porco and co-workers to catalyze the aminolysis of esters to form amides.[32] The authors present results with up to 95% yield of the amide product at room temperature in THF, using 10 mol % of $Zr(OtBu)_4$ and 10 mol % of 1-hydroxy-1-azabenzotriazole (HOAt) as catalysts. However, the ester functionality was found to be inert under the hafnium-catalyzed conditions and only starting material was recovered when ethyl phenylacetate was mixed with 2 equiv of benzylamine under the standard conditions. This chemoselectivity was further confirmed in a competitive experiment between ethyl phenylacetate, *p*-tolylacetic acid, and benzylamine, which resulted in full selectivity for the amidation of the carboxylic acid and 78% isolated yield of amide **3af** (Scheme 4).

The inertness of esters under the hafnium-catalyzed amidation conditions suggested that this functionality can act as a protecting group for additional carboxylic acid groups present in the substrates. Gratifyingly, the concept proved successful, as demonstrated in the reaction between methyl 4-(aminomethyl)benzoate and phenylacetic acid, which resulted in 84% isolated yield of amide **3ag** with the ester functionality untouched (Scheme 5).

It has previously been demonstrated that the pK_a of the carboxylic acid is of importance for the reaction outcome for both uncatalyzed and catalyzed direct amidations.[8] Comparing

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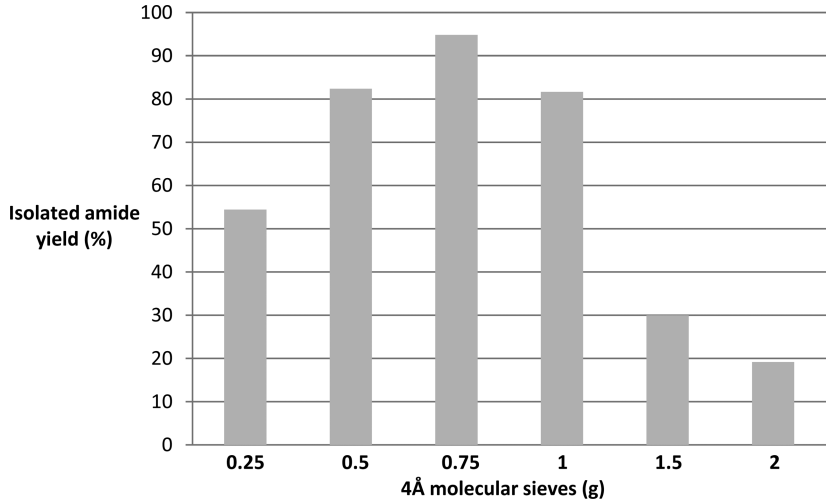

Figure 5. Dependence of the reaction outcome on the amount of molecular sieves present in the reaction mixture. Reaction conditions: phenylacetic acid (0.5 mmol), benzylamine (1.0 mmol), $Hf(Cp)_2Cl_2$ (10 mol %), Et_2O (10 mL), 4 Å MS (powder, 0.75 g), 26 °C, 48 h.

three carboxylic acids with different pK_as, Whiting and co-workers showed that bromoacetic acid (pK_a 2.69 in water) did not react to form amide products under either thermal or boric or *o*-iodophenylboronic acid catalysis during 48 h of reaction time in toluene (120 or 50 °C), whereas phenylbutyric acid (pK_a 4.76) reacted to form amides with a series of amines. Benzoic acid (pK_a 4.19) demonstrated a reactivity between the other two. These results were in contrast to those reported by Loupy and co-workers, who did not find any strong correlations between reactivity and pK_a for the thermal direct amidation at 150 °C under microwave irradiation.[33] Similarly, no correlation between pK_a and product yield was seen in the hafnium-catalyzed amidation reaction. As demonstrated in Table 2 (entries 1 and 13−15), high yields of the corresponding benzyl amides were obtained after 90 min to 48 h from four different carboxylic acids with pK_as (H_2O) ranging between 0.7 and 4.3, indicating that the pK_a does not have a significant effect on the thermodynamics of the reaction. However, the pK_a of the carboxylic acid is of importance for the reaction kinetics. As can be seen in Figure 3, the three chloride-containing acids form amide products at a higher rate in comparison to phenylacetic acid during the first 90 min. Interestingly, dichloroacetic acid is the fastest to react and forms the corresponding benzyl amide in an NMR yield of around 90% after only 90 min, a yield confirmed by workup and isolation of the product (Table 2, entry 14). This observation suggests that there are two counteracting effects at play, which need to be balanced. On the one hand, a high electron-withdrawing capacity of the substituents on the carboxylic acid makes the carbonyl carbon more electrophilic and hence more susceptible for attack from the amine. On the other hand, the high acidity of strong acids is likely to protonate the amine to a greater extent, thereby effectively decreasing the concentration of the nucleophile.

The electronic nature of the amine also affects the reaction outcome. As previously mentioned, anilines are not suitable as coupling partners, likely due to the low electron density of the aromatic nitrogen. On comparison of a series of differently substituted benzylamines, both electron-rich and electron-poor analogues as reaction partners with phenylacetic acid resulted in high amide yields (Table 2, entries 1 and 22−24). Analogous to the results for the carboxylic acids, the thermodynamics of the reaction is not strongly affected by the pK_a of the amines. However, comparing the reaction profiles (Figure 4), one can see that the initial rates of the halo-substituted amines are somewhat lower and display a more pronounced sigmoidal shape in comparison to the two more electron rich amines. Interestingly, the most electron rich species, *p*-methoxybenzylamine, is not significantly faster in comparison to the unsubstituted benzylamine, which might be explained by the relatively small difference in basicities among the examined amines (Figure 4).

Furthermore, water was found to play an important role in the hafnium-catalyzed direct amidation of carboxylic acids. Figure 5 shows a chart of the isolated yield of amide **3a**, where the reactions were run with different amounts of powdered molecular sieves, all other parameters being equal. As can be seen, a maximum in isolated yield after 48 h is reached at 0.75 g of molecular sieves for a reaction of 0.5 mmol of carboxylic acid. A decrease as well as an increase in the amount of molecular sieves resulted in a lower product yield. This observation points toward a dual role of water in the reaction. On the one hand, group IV metal complexes are known to be hydrolytically unstable[28] and molecular sieves are likely required in the reaction vessel to prevent water formed in the condensation to decompose the catalyst and/or reactive intermediates in the catalytic cycle. On the other hand, the presence of some water seems to be needed for an efficient reaction, possibly by partially hydrolyzing the metal complex to form the active catalyst in a fashion similar to what was proposed by Shteinberg and co-workers for a titanium-based amidation catalyst.[34,35] Hall and co-workers have recently suggested that molecular sieves might act as a reversible reservoir of water, which they speculate enhances the catalytic activity of *o*-iodophenylboronic acid in direct amidations at room temperature,[18] and it is not unlikely that the molecular sieves play an analogous role in the hafnium-catalyzed amidation reaction.

The nature of direct amidation has previously been described to be governed by several different factors such as stability of the ammonium carboxylate salts, the pK_as of the carboxylic acids, and the balance between amine nucleophilicity and basicity.[8] These factors, together with the concentration dependence observed for several substrates (vide supra), point toward a complex sequence of coupled equilibria

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governing the hafnium-catalyzed amidation. In addition, the amount of water appears to play an important role in the outcome of the amidation reaction. Mechanistic studies of group IV metal catalyzed direct amidation are ongoing, and the results from these studies will be communicated in due time.

CONCLUSIONS

The development of mild and environmentally friendly processes for the effective formation of amides is of great interest to chemists in both industry and academia. The mild method presented herein is the first example of a hafnium-catalyzed protocol for the direct amidation of nonactivated carboxylic acids. The method gives rise to high yields of a range of differently substituted amides in reaction times as short as 90 min. Additionally, the protocol is the first example of a metal-catalyzed amidation process performed at ambient temperature, and the full conservation of enantiomeric purity of the asymmetric starting materials is a testimony to the mildness of the reaction conditions. The catalyst is highly selective toward amidation of carboxylic acids over esters, enabling the latter to function as protecting groups for additional carboxylic acid moieties present in the substrates. The reaction outcome was shown to be affected by the amount of activated molecular sieves present and the concentration of the reaction mixture, as well as the steric and electronic nature of the substrates.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00385.

Experimental procedures and spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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