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Nickel-catalysed addition of dialkylzinc reagents to *N*-phosphinoyl- and *N*-sulfonylimines

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This paper is dedicated to Professor K. P. C. Vollhardt on occasion of his 60th anniversary

Abstract—A catalytic amount of a nickel complex (0.1–5.3 mol %) extraordinarily increases the reaction rate of the addition of dialkylzinc reagents to *N*-(diphenylphosphinoyl)- or *N*-(benzenesulfonyl)imines. The reaction of imines derived from both aromatic and aliphatic aldehydes with various dialkylzinc reagents in the presence of several nickel complexes gives the expected addition products in most cases in 1 h and in very good yields. In general, the formation of reduction by-products was not an important side reaction. The process represents a great improvement, with regard to the reaction rate and the yield of the addition products, in comparison with the reactions performed in the absence of the nickel catalyst, and reaction times are much shorter than the ones reported so far using other catalysts.

1. Introduction

The addition of organometallic reagents to imines is a valuable method for the preparation of primary and secondary amines,[1,2] which are very interesting from both the synthetic and the biological point of view. However, this method presents some problems due to the low electrophilic character of the C=N bond and to the tendency of basic reagents to abstract protons α to the imine leading to tautomerization to the corresponding enamines. The electrophilicity of the imine can be enhanced by introducing an electron-withdrawing group attached to the nitrogen atom, such as the phosphinoyl or the sulfonyl group, among others. *N*-Phosphinoylimines[3] are very attractive since the phosphinoyl group can easily be removed from the addition product under mild reaction conditions leading to the free amines.[4] *N*-Sulfonylimines[5] are also very useful substrates, since they are slightly more reactive than *N*-phosphinoylimines, but the deprotection of the sulfonamide products can sometimes be problematic. Both *N*-phosphinoyl- and *N*-sulfonylimines have found a variety of synthetic applications, including asymmetric processes.[2,5] On the other hand, the susceptibility to α-deprotonation can be diminished by using less basic nucleophiles, such as boranes, stannanes, cuprates or dialkylzinc reagents. Among them, the latter are very useful nucleophiles since organozinc reagents[6] bearing several functional groups can easily be prepared,[7] and can lead to polyfunctionalised organic compounds. However, the reaction of *N*-phosphinoyl- or *N*-sulfonylimines with dialkylzincs is very slow, leading to low yields of addition products in very long reaction times. For *N*-phosphinoylimines, improved reaction rates and much higher yields have been observed by using some additives like β-aminoalcohols,[4,8] iminoalcohols,[9] hydroxyoxazolines[10] and copper[11] or zirconium[12] complexes, rendering the addition reactions into stereoselective processes. In the case of *N*-sulfonylimines, β-aminoalcohols[13] and copper[14] or rhodium[15] complexes have also shown to be efficient in catalysing the addition of organozinc reagents. We have recently started testing nickel complexes as catalysts for several nucleophilic addition reactions and we found that a catalytic amount of nickel acetylacetonate greatly accelerates the addition of dialkylzinc reagents to both aromatic and aliphatic aldehydes.[16] As an extension of that study, in this paper we report our results on the use of several nickel complexes to catalyse the addition of dialkylzincs to *N*-(diphenylphosphinoyl)- and *N*-(benzenesulfonyl)-imines.

2. Results and discussion

Since we have demonstrated the usefulness of $Ni(acac)_2$ to catalyse the addition of dialkylzinc reagents to aldehydes,[16] we decided to test the same complex for the addition to activated imines. *N*-(diphenylphosphinoyl)benzaldimine and diethylzinc were chosen as model substrate and nucleophilic

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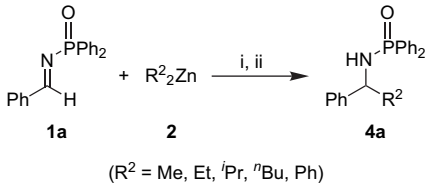
reagent, respectively, in order to start our study. Gratifyingly, the reaction of imine **1a** with an excess of diethylzinc (1:2.2 molar ratio) and a catalytic amount of $Ni(acac)_2$ (1:0.05 molar ratio) in acetonitrile at 0 °C for 1 h led, after hydrolysis, to the expected addition product **4aa** in 81% yield (Scheme 1 and Table 1, entry 1). As a mode of comparison, the same reaction in the absence of the nickel catalyst gave only a 11% yield of the addition product **4aa** after stirring for 48 h at room temperature (Table 1, entry 15). We then decided to test some other nickel complexes in order to look for the best catalyst. $NiCl_2$ and $NiBr_2$ were as efficient as $Ni(acac)_2$, giving the addition product in similar yields in 1 h under the same reaction conditions (Table 1, entries 2 and 3). However, $NiCO_3$ did not show the same acceleration effect: after stirring the reaction between **1a** and diethylzinc in the presence of 5 mol % of $NiCO_3$ for three days at room temperature, only 29% of the addition product was obtained (Table 1, entry 4), the major product being the one resulting from reduction of the C=N bond (60% yield; Table 1, entry 4). This reduction product was also detected in minor amounts in the reactions with the other nickel(II) complexes [2% with both $Ni(acac)_2$ and $NiBr_2$ and 13% with $NiCl_2$] and it is probably formed via β-hydride transfer from diethylzinc (or a generated ethylnickel complex) to the imine.[17] The nickel(0) complex $Ni(COD)_2$ was also tested and a 83% of the addition product was obtained (Table 1, entry 5), the reaction being as fast as the ones catalysed by the nickel(II) complexes (Table 1, entries 1–3). This result suggests that there is a mechanistic difference between this reaction and the nickel-catalysed addition of dialkylzinc reagents to aldehydes,[16,18] since we found that in that case $Ni(COD)_2$ was not acting as a catalyst.[16] Although the yield obtained with $Ni(COD)_2$ was slightly higher than the one obtained with $Ni(acac)_2$, we decided to use the latter in the next experiments, since it is more easily handled and inexpensive.



Scheme 1. *Reagents and conditions*: (i) Ni complex **3**, solvent, *T*. (ii) NH_4Cl (aq).

Table 1. Preparation of compound **4aa** (R^2=Et) by a nickel-catalysed addition of diethylzinc to imine **1a** under optimised reaction conditions

Entry	Nickel complex		Solvent	*T* (°C)	Time (h)	Product
	3	Mol %				Yield (%)[a,b]
1	$Ni(acac)_2$	5	MeCN	0	1	81 (2)
2	$NiCl_2$	5	MeCN	0	1	77 (13)
3	$NiBr_2$	5	MeCN	0	1	80 (2)
4	$NiCO_3$	5	MeCN	0–20	72	29 (60)
5	$Ni(COD)_2$	5	MeCN	0	1	83 (7)
6	$Ni(acac)_2$	5	THF	0	1	76 (11)
7	$Ni(acac)_2$	5	CH_2Cl_2	0	1	59 (32)
8	$Ni(acac)_2$	5	PhMe	0	1	76 (18)
9	$Ni(acac)_2$	2	MeCN	0	1	83
10	$Ni(acac)_2$	1	MeCN	0	1	78
11	$Ni(acac)_2$	0.5	MeCN	0	1	86
12	$Ni(acac)_2$	0.1	MeCN	0	1	89
13	$Ni(acac)_2$	0.1	MeCN	−30	1	89
14	$Ni(acac)_2$	0.1	PhMe	−78	26	20[c]
15	—	—	MeCN	0–20	48	11[d]

[a] Isolated yield after column chromatography (silica gel, hexane/acetone) based on the starting imine **1a**. The isolated compound **4aa** was always ≥95% pure (GC and/or 300 MHz ^1H NMR).
[b] In brackets, yields of the corresponding reduction products.
[c] The reaction was not complete. A significant amount of the starting material was detected in the crude mixture.
[d] The reaction was not complete. A significant amount of the starting material was detected in the crude mixture, together with 37% of the reduction product.

Next, we studied the effect of the solvent. The addition of diethylzinc to the imine **1a** in the presence of 5 mol % of $Ni(acac)_2$ was performed in acetonitrile, THF, dichloromethane and toluene. The addition product **4aa** was obtained in 81, 76, 59 and 76% yields, respectively (Table 1, entries 1 and 6–8), together with variable amounts of the corresponding reduction product (2% in MeCN, 11% in THF, 32% in CH_2Cl_2 and 18% in PhMe; Table 1, entries 1 and 6–8). From these results, it is clear that acetonitrile is the solvent of choice, since it gives the highest yield of the addition product and the smallest amount of the reduction by-product.

The effect of the amount of the nickel catalyst on the increase of the rate of the addition reaction was also explored. The reaction of imine **1a** with diethylzinc in acetonitrile at 0 °C was performed in the presence of variable amounts of $Ni(acac)_2$, namely 2, 1, 0.5 and 0.1 mol %. In all cases, the reaction was finished in 1 h and the addition product **4aa** was isolated in 83, 78, 86 and 89% yield, respectively (Table 1, entries 9–12). It is remarkable that even such a low amount of nickel catalyst as 0.1 mol % can effectively promote the addition reaction, giving a slightly higher yield than the reaction in the presence of 5 mol % of $Ni(acac)_2$ (Table 1, entry 1). The reaction in the presence of 0.1 mol % of $Ni(acac)_2$ was repeated at −30 °C and no difference in reaction rate was observed: after 1 h, the starting material had disappeared and the addition product was obtained in 89% yield (Table 1, entry 13). In an attempt to further decrease the temperature, the same reaction was performed at −78 °C, but in toluene instead of acetonitrile, due to freezing of the reaction medium with the latter solvent. In this case, the reaction was much slower: after stirring for 26 h at −78 °C, the hydrolysis of the reaction gave only 20% of the addition product (Table 1, entry 14), together with some unreacted imine, benzaldehyde and diphenylphosphinic amide. The latter two products derive from the hydrolysis of part of the starting imine **1a**.

We then focused on the possibility of using other dialkylzinc reagents. Commercially available Me_2Zn, $^iPr_2Zn$ and $^nBu_2Zn$ reacted with *N*-(diphenylphosphinoyl)benzaldimine **1a** in the presence of 5 mol % of $Ni(acac)_2$ at 0 °C, giving the corresponding addition products **4ab**–**4ad** in 1 h in very good yields (Scheme 1 and Table 2, entries 2–4). The addition of commercially available diphenylzinc was also attempted, but without success. However, when the phenyl transfer reaction was tried by using a mixture of triphenylborane and diethylzinc as the phenyl source,[19] the expected addition product **4ae** was obtained in 1 h in 58% yield (Table 2, entry 5).

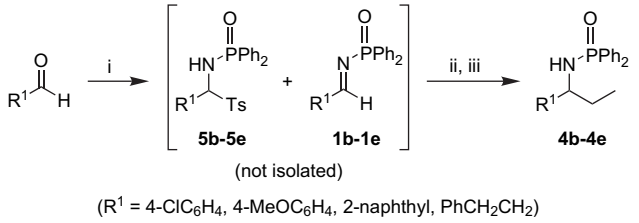
Next, we investigated the versatility of our procedure concerning the substrate. Although imine **1a** could be prepared

Table 2. Preparation of compounds **4** by a Ni(acac)$_2$-catalysed addition of dialkylzinc reagents to *N*-(diphenylphosphinoyl)imines **1** in acetonitrile at 0 °C

Entry	Imine			Nickel complex	Time (h)	Product	
	No.	R^1	R^2	Mol %		No.	Yield (%)[a]
1	**1a**	Ph	Et	5	1	**4aa**	81
2	**1a**	Ph	Me	5	1	**4ab**	85
3	**1a**	Ph	^{i}Pr	5	1	**4ac**	92
4	**1a**	Ph	^{n}Bu	5	1	**4ad**	80
5	**1a**	Ph	Ph[b]	5	1	**4ae**	58
6	**1b**[c]	4-ClC$_6$H$_4$	Et	2.6[d]	2	**4b**	43[e]
7	**1c**[c]	4-MeOC$_6$H$_4$	Et	5.3[d]	17	**4c**	50[e]
8	**1d**[c]	2-Naphthyl	Et	5.3[d]	13	**4d**	29[e]
9	**1e**[c]	PhCH$_2$CH$_2$	Et	5	1	**4e**	80

[a] Isolated yield after column chromatography (silica gel, hexane/acetone) based on the starting imine **1**. All isolated compounds **4** were ≥95% pure (GC and/or 300 MHz ^{1}H NMR).
[b] Phenylzinc species were generated in situ by reaction between triphenylborane and diethylzinc.
[c] Imine generated in situ (see text and experimental part).
[d] The mol % of Ni(acac)$_2$ is based on the starting amount of *P,P*-diphenylphosphinic amide.
[e] Isolated yield after column chromatography (silica gel, hexane/acetone) based on the starting amount of *P,P*-diphenylphosphinic amide.

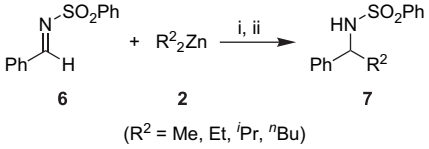
by reaction of benzaldehyde with diphenylphosphinic amide in the presence of titanium tetrachloride following the literature procedure[20] and could be isolated in pure form, we found some problems when the same method was applied to the synthesis of imines **1b–1e**. In all cases, the expected imines were formed in very small amounts and they could not be purified neither by recrystallisation nor by column chromatography on deactivated silica gel. Fortunately, imines **1b–1e** could be generated in situ from their corresponding sulfinic acid adducts **5** (Scheme 2), which were readily prepared by mixing the corresponding aldehydes with diphenylphosphinic amide and *p*-toluenesulfinic acid in Et$_2$O.[21] In all of these reactions, a white precipitate was slowly formed, which was filtered and washed with Et$_2$O. For the reactions with 4-chlorobenzaldehyde, 4-methoxybenzaldehyde and 2-naphthaldehyde, ^{1}H NMR of the white solid showed that it was a mixture of the expected adducts **5b–5d** and the corresponding imines **1b–1d**. Since both compounds **5** and **1** were expected to yield the same addition product by reaction with diethylzinc, the solid mixtures were used in the addition reactions without purification. When the mixture of **5b** and **1b**, derived from *p*-chlorobenzaldehyde, was treated with an excess of diethylzinc in the presence of 2.6 mol % of Ni(acac)$_2$ (based on the starting amount of *P,P*-diphenylphosphinic amide) in acetonitrile at 0 °C, the expected product **4b** was obtained in 2 h in 43% yield (Scheme 2 and Table 2, entry 6). The addition to electron-rich imines was slower, but increasing the amount of the nickel catalyst up to 5.3 mol % (based on the starting amount of *P,P*-diphenylphosphinic amide) and stirring for a longer time, the mixtures **5c+1c** and **5d+1d** gave the addition products **4c** and **4d** in 50 and 29% yields, respectively, after stirring at 0 °C for 17 and 13 h, respectively (Table 2, entries 7 and 8). It must be noted that the yields of products **4b–4d** are referred to the starting amounts of *P,P*-diphenylphosphinic amide. Since in the formation step of the adducts the amounts of solid that precipitated were 54% (for **5b**), 78% (for **5c**) and 47% (for **5d**) of the expected amounts (assuming that only the adducts had been formed), the actual yields of the addition reactions with diethylzinc are much higher. We were delighted to see that our methodology was also applicable to imines derived from aliphatic aldehydes. Imine **1e** was generated in situ by reaction of the corresponding adduct **5e** (obtained in pure form by a literature procedure[21]) with diethylzinc and it gave the addition product in a reaction time of only 1 h at 0 °C using 5 mol % of Ni(acac)$_2$ (Table 2, entry 9). To the best of our knowledge, this is the fastest addition reaction of diethylzinc to an aliphatic *N*-(diphenylphosphinoyl)imine that has ever been reported.



Scheme 2. *Reagents and conditions*: (i) Ph$_2$P(O)NH$_2$, *p*-MeC$_6$H$_4$SO$_2$H, Et$_2$O, 20 °C, then filtrate. (ii) Et$_2$Zn (1.7–3.3 equiv), Ni(acac)$_2$ (2.6–5.3 mol %), MeCN, 0 °C. (iii) NH$_4$Cl (aq).

Unfortunately, the application of the same methodology to ketimines was unsuccessful. The *N*-(diphenylphosphinoyl)-imine derived from acetophenone was prepared and submitted to the reaction with diethylzinc in the presence of 10 mol % of Ni(acac)$_2$. No addition product was detected after stirring for 24 h at room temperature, the unaltered starting imine being recovered.

Having established the usefulness of our methodology to the addition of dialkylzinc reagents to *N*-(diphenylphosphinoyl)imines, we decided to apply it to another type of activated imines, *N*-sulfonylimines. Commercially available *N*-(benzenesulfonyl)benzaldimine **6** was treated with an excess of diethylzinc (1:2.2 molar ratio) and a catalytic amount of Ni(acac)$_2$ (1:0.05 molar ratio) in acetonitrile at 0 °C for 1 h and, after hydrolysis, the expected addition product **7a** was obtained in 80% yield (Scheme 3 and Table 3, entry 1). In order to compare with the non-catalysed reaction, the addition of diethylzinc to **6** was repeated in the absence of the nickel catalyst. In this case, after 24 h at room temperature, 40% of the product **7a** was obtained, together with 8% of the product resulting from reduction of the imine[17,22] (Table 3, entry 2). Both reactions were also performed in toluene instead of acetonitrile and a significant increase in the amount of the reduction by-product was observed (Table 3, entries 3 and 4). The improvement in yield obtained in this solvent was much higher than the one obtained with acetonitrile: while the nickel-catalysed reaction gave a 83% yield of the addition product **7a** in 1 h (Table 3, entry 3), the non-catalysed reaction afforded only 6% of **7a**, together with 59% of the reduction product (Table 3, entry 4). As it was the



Scheme 3. *Reagents and conditions*: (i) Ni complex **3**, solvent, *T*. (ii) NH$_4$Cl (aq).

Table 3. Preparation of compounds **7** by a nickel-catalysed addition of dialkylzinc reagents to *N*-(benzenesulfonyl)benzaldimine **6**

Entry	R^2	Nickel complex		Solvent	*T* (°C)	Time (h)	Product	
		3	Mol %				No.	Yield (%)[a,b]
1	Et	$Ni(acac)_2$	5	MeCN	0	1	**7a**	80 (2)
2	Et	—	—	MeCN	0–20	24	**7a**	40 (8)
3	Et	$Ni(acac)_2$	5	PhMe	0	1	**7a**	83 (14)
4	Et	—	—	PhMe	0–20	24	**7a**	6 (59)
5	Et	$Ni(COD)_2$	5	MeCN	0	1	**7a**	67 (19)
6	Me	$Ni(acac)_2$	5	PhMe	0	1	**7b**	83
7	^{i}Pr	$Ni(acac)_2$	5	PhMe	0	1	**7c**	24 (73)
8	^{i}Pr	$Ni(acac)_2$	5	MeCN	0	1	**7c**	27 (31)
9	^{n}Bu	$Ni(acac)_2$	5	PhMe	0	1	**7d**	48 (41)

[a] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting imine **6**. All isolated compounds **7** were ≥95% pure (GC and/or 300 MHz ^{1}H NMR).
[b] In brackets, yields of the corresponding reduction products.

case with the *N*-(diphenylphosphinoyl)imines, the nickel(0) complex $Ni(COD)_2$ was also an efficient catalyst for the addition reaction, although the yield of product **7a** was lower than the one obtained with $Ni(acac)_2$ (Table 3, entry 5).

We then tested some other dialkylzinc reagents for the addition to the sulfonylimine **6** using 5 mol % of $Ni(acac)_2$ as catalyst. Me_2Zn gave the expected addition product **7b** in 83% yield after 1 h at 0 °C (Table 3, entry 6). When imine **6** was treated with $^iPr_2Zn$ in toluene at 0 °C, after stirring for 1 h only 24% of the addition product **7c** was formed, the major product being *N*-benzylbenzenesulfonamide (Table 3, entry 7). This reaction was repeated in acetonitrile in order to try to improve the yield of the addition product, but a disappointing 27% yield of **7c** was obtained (Table 3, entry 8). $^nBu_2Zn$ gave a moderate yield of 48% of **7d** together with 41% of the reduction product (Table 3, entry 9). According to these results, it seems that *N*-sulfonylimines are more prone to undergo reduction than *N*-phosphinoylimines when treated with the combination dialkylzinc-$Ni(acac)_2$, especially with sterically congested dialkylzinc reagents.

It is interesting to note that, to the best of our knowledge, although several reports have been published concerning the addition of diethylzinc to *N*-tosylimines and other arene substituted *N*-arenesulfonylimines, no addition to *N*-(benzenesulfonyl)imines has been reported in the literature. Therefore, this is the first time that the addition of dialkylzinc reagents to such type of imines has been described.

As it was the case with the *N*-(diphenylphosphinoyl)ketimines, the application of our methodology to *N*-(benzenesulfonyl)-ketimines was unsuccessful. The *N*-(benzenesulfonyl)imine derived from acetophenone was prepared and submitted to the reaction with diethylzinc in acetonitrile in the presence of 10 mol % of $Ni(acac)_2$. No addition product was detected after stirring for 48 h at room temperature. The starting imine was recovered unchanged.

Concerning a possible reaction mechanism, the fact that the addition reaction to both *N*-(diphenylphosphinoyl)imines and *N*-(benzenesulfonyl)imines is very fast with nickel(II) as well as nickel(0) complexes suggests that the mechanism could be similar in both cases. We assume that a nickel(0) species could be the real catalyst. The nickel(II) complexes could be reduced to nickel(0) species by the action of the dialkylzinc reagent.[23] The rapid change in colour that is observed in the reaction medium from green [corresponding to $Ni(acac)_2$] to black after a few drops of the dialkylzinc reagent have been added could support this hypothesis. Coordination of the imine to these nickel(0) species could facilitate the attack of the dialkylzinc reagent to the imine carbon atom, leading to a fast addition reaction.

Finally, we have performed the $Ni(acac)_2$-catalysed addition of diethylzinc to imines **1a** and **6** in the presence of several chiral β-aminoalcohols in order to try to get some enantioselectivity in the process. The reaction rates were not affected by the presence of the chiral ligands, but almost racemic products have been obtained so far. Further efforts to develop an asymmetric version of this addition reaction are currently underway in our laboratories.

3. Conclusion

In conclusion, we have reported here a very efficient procedure to effect the addition of dialkylzinc reagents to both *N*-(diphenylphosphinoyl)- and *N*-(benzenesulfonyl)imines in short times and under mild reaction conditions. The use of a catalytic amount of a nickel(II) or a nickel(0) complex causes an extraordinary increase in the reaction rate and leads to very good yields of the addition products in reaction times as short as 1 h. The methodology is applicable to imines derived from both aromatic and aliphatic aldehydes, but it is not successful for ketimines. Several dialkylzinc reagents and phenylzinc species can be employed with good results. $Ni(acac)_2$ has been shown to be a very convenient catalyst, since it is inexpensive and an amount of it as low as 0.1 mol % can be used without loosing efficiency.

4. Experimental

4.1. General

All moisture sensitive reactions were carried out under an argon atmosphere. Commercially available anhydrous MeCN (≥99.9%, water content ≤0.005%, Acros), THF (99.9%, water content ≤0.006%, Acros), CH_2Cl_2 (≥99.5%, water content ≤0.005%, Fluka), toluene (≥99.7%, water content ≤0.005%, Fluka) and Et_2O (≥99.8%, water content ≤0.005%, Fluka) were used as solvents in the reactions. All the aldehydes needed for the synthesis of imines **1**

were commercially available and liquid ones were distilled before use. Solid aldehydes and commercially available *P,P*-diphenylphosphinic amide, sodium *p*-toluenesulfinate, *N*-(benzenesulfonyl)benzaldimine **6**, $Ni(acac)_2$, $NiCl_2$, $NiBr_2$, $NiCO_3$ and $Ni(COD)_2$ were used without further purification. Imine **1a** was prepared according to a literature procedure[20] and it was obtained in pure form by column chromatography on silica gel previously deactivated by treatment with triethylamine. Dialkylzinc reagents were used as their commercially available solutions in toluene or heptane (Aldrich, Fluka). Phenylzinc species were generated in situ by reaction between triphenylborane and diethylzinc.[19] All glassware was dried in an oven at 100 °C and cooled to room temperature under argon before use. Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm, 240–400 mesh). Thin layer chromatography (TLC) was performed on precoated silica gel plates (Merck 60, F254, 0.25 mm); detection was done by UV_{254} light; R_f values are given under these conditions. Melting points (mp) are uncorrected and were measured on a Reichert thermovar apparatus. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-300 spectrometer using $CDCl_3$ as solvent and, as internal references, tetramethylsilane (TMS) for ^1H NMR and $CDCl_3$ for ^{13}C NMR; chemical shifts are given in δ (ppm) and coupling constants (J) in Hertz. ^{13}C NMR assignments were made on the basis of DEPT experiments. Infrared (FTIR) spectra were obtained on a Nicolet 510 P-FT spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector.

4.2. Nickel-catalysed addition of dialkylzinc reagents to imine 1a. Preparation of products 4aa–4ad. General procedure

The commercially available solution of the dialkylzinc reagent in toluene (for dimethyl-, diethyl- and diisopropylzinc) or heptane (for dibutylzinc) (1.1 mmol of R^2_2Zn) was dropwise added during ca. 5 min to a stirred mixture of the imine **1a** (153 mg, 0.5 mmol) and the corresponding amount of the nickel complex **3** in the desired solvent (3 mL) under argon at the required temperature (see Tables 1 and 2 for details). After stirring for the time indicated in Tables 1 and 2, the reaction was hydrolysed with an aqueous saturated solution of NH_4Cl (5 mL). Water (5 mL) was added and the mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with brine (5 mL), being then dried (Na_2SO_4). After filtration and evaporation of the solvents, the crude residue was purified by column chromatography (silica gel, hexane/acetone), giving products **4aa**–**4ad** in the yields indicated in Tables 1 and 2. Compounds **4aa** and **4ab** were characterised by comparison of their physical and spectroscopic data with the ones reported in the literature.[4] For the rest of the products, **4ac** and **4ad**, their corresponding physical and spectroscopic data follow.

4.2.1. *N*-(2-Methyl-1-phenylpropyl)-*P,P*-diphenylphosphinic amide (4ac).[11c] White solid; R_f 0.38 (ethyl acetate); mp 166 °C; ν (KBr) 3443 (NH), 3088, 3060, 3028, 1503 (HC═C), 1165 cm^{-1} (P═O); δ_H 0.82, 1.01 (3H each, 2d, J=6.9 Hz each, 2×Me), 1.90–2.11 (1H, m, C*H*Me), 3.33 (1H, m, NH), 3.80–3.99 (1H, m, CHN), 7.00–7.11, 7.15–7.54, 7.59–7.73 and 7.77–7.91 (2H, 9H, 2H and 2H, respectively, 4m, ArH); δ_C 19.2, 19.3 (2×Me), 35.7 (d, J=4.3 Hz, *C*HMe), 61.3 (CN), 126.8, 126.9, 128.0, 128.1, 128.2, 128.4, 128.5, 131.7, 131.8, 131.9, 132.6, 132.7, 142.9 (d, J=3.9 Hz) (ArC); *m/z* 349 (M^+, <1%), 307 (22), 306 (100), 201 (50).

4.2.2. *P,P*-Diphenyl-*N*-(1-phenylpentyl)phosphinic amide (4ad).[9] White solid; R_f 0.63 (ethyl acetate); mp 167 °C; ν (KBr) 3126 (NH), 3055, 3022, 3000, 1591 (HC═C), 1100 cm^{-1} (P═O); δ_H 0.79 (3H, t, J=6.9 Hz, Me), 0.99–1.32 [4H, m, Me(CH_2)$_2$], 1.73–1.87, 1.89–2.02 (1H each, 2m, CH_2CN), 3.11–3.27 (1H, m, NH), 4.07–4.21 (1H, m, CHN), 7.06–7.55, 7.68–7.80 and 7.81–7.91 (11H, 2H and 2H, respectively, 3m, ArH); δ_C 13.9 (Me), 22.4, 28.2 [Me(*C*H$_2$)$_2$], 39.5 (d, J=3.7 Hz, *C*H$_2$CN), 55.8 (CN), 126.4, 127.0, 128.2, 128.3, 128.4, 128.45, 128.5, 131.75, 131.8, 131.9, 132.5, 132.6, 143.9 (d, J=5.4 Hz) (ArC); *m/z* 363 (M^+, <1%), 307 (21), 306 (100), 201 (46).

4.3. Nickel-catalysed phenyl transfer reaction to imine 1a. Preparation of product 4ae

Diethylzinc (0.91 mL of a 1.1 M solution of diethylzinc in toluene, 1.0 mmol) was dropwise added to a solution of triphenylborane (66 mg, 0.25 mmol) in toluene (1 mL) at room temperature.[19] After stirring for 30 min at that temperature, the resulting solution was dropwise transferred via syringe during ca. 5 min to a stirred mixture of the imine **1a** (76 mg, 0.25 mmol) and $Ni(acac)_2$ (3.3 mg, 0.013 mmol) in toluene (1 mL) under argon at 0 °C. After stirring for 1 h, the reaction was hydrolysed with an aqueous saturated solution of NH_4Cl (5 mL). Water (5 mL) was added and the mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with brine (5 mL), being then dried (Na_2SO_4). After filtration and evaporation of the solvents, the resulting residue was purified by column chromatography (silica gel, hexane/acetone), affording product **4ae** in 58% yield. The corresponding physical and spectroscopic data for compound **4ae** follow.

4.3.1. *P,P*-Diphenyl-*N*-(diphenylmethyl)phosphinic amide (4ae).[24] White solid; R_f 0.47 (ethyl acetate); mp 166 °C; ν (KBr) 3170 (NH), 3062, 3049, 3022, 1598 (HC═C), 1194 cm^{-1} (P═O); δ_H 3.61–3.78 (1H, m, NH), 5.44 (1H, t, J=10.8 Hz, CHN), 7.09–7.58 and 7.67–7.98 (15H and 5H, respectively, 2m, ArH); δ_C 58.8 (CN), 127.4, 127.6, 127.7, 128.5, 128.6, 128.7, 132.1, 132.2, 132.3, 132.4, 134.4, 143.3 (d, J=4.4 Hz) (ArC); *m/z* 383 (M^+, <1%), 307 (21), 306 (100), 201 (55).

4.4. Nickel-catalysed addition of diethylzinc to adducts 5b–5d. Preparation of products 4b–4d. General procedure[21]

A representative experimental procedure for the preparation of **4b** follows. *p*-Toluenesulfinic acid was prepared by dissolving sodium *p*-toluenesulfinate in hot 10% (v/v) hydrochloric acid (the resulting pH must be lower than 3). After cooling to 4 °C, the white crystals that appeared were filtered and dried under vacuum. 4-Chlorobenzaldehyde (0.32 mL, 2.8 mmol) was added to a suspension of *P,P*-diphenylphosphinic amide (402 mg, 1.9 mmol) and *p*-toluenesulfinic acid

(437 mg, 2.8 mmol) in anhydrous Et_2O (16 mL) at room temperature. The mixture was stirred for 15 h, during which time a white precipitate was slowly formed. The solution was filtered and the white solid was washed with anhydrous Et_2O (10 mL) and dried under vacuum. The weight of this solid was 496 mg. Its ^1H NMR showed that it was a mixture of the expected adduct **5b** and the corresponding imine **1b**, which was used in the addition reaction with diethylzinc without purification. Diethylzinc (3.0 mL of a 1.1 M solution in toluene, 3.3 mmol) was dropwise added during ca. 5 min to a stirred mixture of the white solid obtained before (496 mg) and $Ni(acac)_2$ (13 mg, 0.05 mmol) in MeCN (6 mL) under argon at 0 °C. After stirring for 2 h, the reaction was hydrolysed with an aqueous saturated solution of NH_4Cl (5 mL). Water (5 mL) was added and the mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with brine (5 mL), being then dried (Na_2SO_4). After filtration and evaporation of the solvents, the crude residue was purified by column chromatography (silica gel, hexane/acetone), giving product **4b** in 43% overall yield (based on the starting *P*,*P*-diphenylphosphinic amide). Following a similar procedure but using 0.10 mmol of $Ni(acac)_2$ and stirring the reactions with diethylzinc for the time indicated in Table 2, products **4c** and **4d** were isolated in 50 and 29% overall yields, respectively. Compound **4b** was characterised by comparison of its physical and spectroscopic data with the ones reported in the literature.[4] For the rest of the products, **4c** and **4d**, their corresponding physical and spectroscopic data follow.

4.4.1. *N*-[1-(4-Methoxyphenyl)propyl]-*P*,*P*-diphenylphosphinic amide (4c).[25] White solid; R_f 0.32 (ethyl acetate); mp 173 °C; ν (KBr) 3208 (NH), 3060, 3044, 3039, 1618, 1509 (HC═C), 1105 cm^{-1} (P═O); δ_H 0.77 (3H, t, J=7.5 Hz, *Me*CH_2), 1.70–2.10 (2H, m, CH_2), 3.18–3.40 (1H, br s, NH), 3.79 (3H, s, MeO), 3.97–4.16 (1H, m, CHN), 6.81, 7.08 (2H each, 2d, J=7.6 Hz each, 4×ArH), 7.26–7.54 and 7.67–8.00 (6H and 4H, respectively, 2m, 10×ArH); δ_C 10.6 (*Me*CH_2), 32.4 (d, J=4.4 Hz, CH_2), 55.2 (MeO), 56.6 (CN), 113.7, 127.6, 128.1, 128.3, 128.4, 131.6, 131.7, 131.9, 132.4, 132.6, 135.6 (d, J=5.5 Hz), 158.5 (ArC); *m*/*z* 366 (M^++1, <1%), 365 (M^+, 2), 337 (22), 336 (100), 202 (14), 201 (83), 165 (10), 164 (89), 77 (18).

4.4.2. *N*-[1-(2-Naphthyl)propyl]-*P*,*P*-diphenylphosphinic amide (4d).[13b] White solid; R_f 0.29 (ethyl acetate); mp 105 °C; ν (KBr) 3127 (NH), 3040, 3026, 3012, 1598 (HC═C), 1114 cm^{-1} (P═O); δ_H 0.81 (3H, t, J=7.4 Hz, Me), 1.88–2.17 (2H, m, CH_2), 3.27–3.46 (1H, m, NH), 4.21–4.34 (1H, m, CHN), 7.21–7.30, 7.32–7.57 and 7.65–7.93 (2H, 8H and 7H, respectively, 3m, ArH); δ_C 10.6 (Me), 32.3 (d, J=4.0 Hz, CH_2), 57.3 (CN), 124.5, 125.5, 125.7, 126.1, 127.6, 127.8, 128.2, 128.3, 128.4, 128.5, 131.65, 131.7, 131.75, 131.8, 131.9, 132.5, 132.6, 132.7, 133.2, 140.7 (d, J=5.4 Hz) (ArC); *m*/*z* 386 (M^++1, 2%), 385 (M^+, 6), 357 (25), 356 (100), 202 (16), 201 (89), 185 (13), 184 (83), 154 (13), 77 (17).

4.5. Nickel-catalysed addition of diethylzinc to adduct 5e. Preparation of product 4e

Sulfinic acid adduct **5e** was prepared in pure form according to a literature procedure.[21] Diethylzinc (3.0 mL of a 1.1 M solution in toluene, 3.3 mmol) was dropwise added during ca. 5 min to a stirred mixture of the adduct **5e** (490 mg, 1.0 mmol) and $Ni(acac)_2$ (13 mg, 0.05 mmol) in MeCN (6 mL) under argon at 0 °C. After stirring for 1 h, the reaction was hydrolysed with an aqueous saturated solution of NH_4Cl (5 mL). Water (5 mL) was added and the mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with brine (5 mL), being then dried (Na_2SO_4). After filtration and evaporation of the solvents, the crude residue was purified by column chromatography (silica gel, hexane/acetone), affording product **4e** in 80% yield. Compound **4e** was characterised by comparison of its physical and spectroscopic data with the ones reported in the literature.[21]

4.6. Nickel-catalysed addition of dialkylzinc reagents to *N*-sulfonyl imine 6. Preparation of products 7a–7d. General procedure

The commercially available solution of the dialkylzinc reagent in toluene (for dimethyl-, diethyl- and diisopropylzinc) or heptane (for dibutylzinc) (2.2 mmol of R^2_2Zn) was dropwise added during ca. 5 min to a stirred mixture of the imine **6** (245 mg, 1.0 mmol) and $Ni(acac)_2$ (13 mg, 0.05 mmol) in the desired solvent (1.5 mL) (see Table 3 for details) under argon at 0 °C. After stirring for 1 h, the reaction was hydrolysed with an aqueous saturated solution of NH_4Cl (5 mL). Water (5 mL) was added and the mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with brine (5 mL), being then dried (Na_2SO_4). After filtration and evaporation of the solvents, the crude residue was purified by column chromatography (silica gel, hexane/ethyl acetate), giving products **7a–7d** in the yields indicated in Table 3. The corresponding physical and spectroscopic data for compound **7a–7d** follow.

4.6.1. *N*-(1-Phenylpropyl)benzenesulfonamide (7a).[26] White solid; R_f 0.30 (hexane/ethyl acetate: 4/1); mp 74 °C; ν (KBr) 3246 (NH), 3066, 3028, 3006, 1503 (HC═C), 1159 cm^{-1} (S═O); δ_H 0.79 (3H, t, J=7.5 Hz, Me), 1.58–1.91 (2H, m, CH_2), 4.22 (1H, q, J=7.4 Hz, CHN), 5.24–5.50 (1H, m, NH), 6.91–7.05, 7.06–7.17, 7.22–7.47 and 7.59–7.72 (2H, 3H, 3H and 2H, respectively, 4m, ArH); δ_C 10.4 (Me), 30.6 (CH_2), 59.9 (CN), 126.5 (2C), 126.9 (2C), 127.3, 128.3 (2C), 128.6 (2C), 132.1, 140.5, 140.6 (ArC); *m*/*z* 275 (M^+, <1%), 247 (16), 246 (100), 141 (25), 77 (35).

4.6.2. *N*-(1-Phenylethyl)benzenesulfonamide (7b).[27] White solid; R_f 0.20 (hexane/ethyl acetate: 4/1); mp 102 °C; ν (KBr) 3268 (NH), 3071, 3028, 3006, 1585 (HC═C), 1170 cm^{-1} (S═O); δ_H 1.43 (3H, d, J=7.1 Hz, Me), 4.38–4.59 (1H, m, CHN), 4.87–5.40 (1H, m, NH), 6.96–7.23, 7.28–7.54 and 7.67–7.80 (5H, 3H and 2H, respectively, 3m, ArH); δ_C 23.6 (Me), 53.7 (CN), 126.1 (2C), 127.0 (2C), 127.5, 128.5 (2C), 128.8 (2C), 132.3, 140.6, 141.8 (ArC); *m*/*z* 261 (M^+, <1%), 246 (56), 141 (40), 120 (41), 105 (21), 104 (11), 78 (12), 77 (100), 51 (27), 42 (16).

4.6.3. *N*-(2-Methyl-1-phenylpropyl)benzenesulfonamide (7c).[28] White solid; R_f 0.33 (hexane/ethyl acetate: 4/1); mp 102 °C; ν (KBr) 3252 (NH), 3066, 3028, 3017, 1585

(HC═C), 1159 cm^{-1} (S═O); δ_H 0.71, 0.95 (3H each, 2d, J=7.1 Hz each, 2×Me), 1.84–1.99 (1H, m, C*H*Me), 4.03 (1H, t, J=8.4 Hz, CHN), 5.28 (1H, d, J=8.4 Hz, NH), 6.84–6.97, 7.01–7.11, 7.19–7.41 and 7.53–7.67 (2H, 3H, 3H and 2H, respectively, 4m, ArH); δ_C 18.8, 19.4 (2×Me), 34.4 (*C*HMe), 64.2 (CN), 126.8 (2C), 126.9 (2C), 127.1, 128.1 (2C), 128.5 (2C), 132.0, 139.7, 140.5 (ArC); *m*/*z* 289 (M^+, <1%), 247 (16), 246 (100), 141 (24), 77 (33).

4.6.4. *N*-(1-Phenylpentyl)benzenesulfonamide (7d).[29]

White solid; R_f 0.40 (hexane/ethyl acetate: 4/1); mp 70 °C; ν (KBr) 3257 (NH), 3066, 3017, 1585 (HC═C), 1165 cm^{-1} (S═O); δ_H 0.78 (3H, t, J=7.0 Hz, Me), 0.97–1.32 [4H, m, $(CH_2)_2$Me], 1.55–1.85 (2H, m, CH_2CN), 4.28 (1H, q, J=7.2 Hz, CHN), 5.58 (1H, d, J=7.2 Hz, NH), 6.90–7.05, 7.06–7.17, 7.22–7.46 and 7.59–7.71 (2H, 3H, 3H and 2H, respectively, 4m, ArH); δ_C 13.8 (Me), 22.1, 27.9, 37.3 (3×CH_2), 58.4 (CN), 126.4 (2C), 126.9 (2C), 127.2, 128.3 (2C), 128.6 (2C), 132.0, 140.6, 140.8 (ArC); *m*/*z* 303 (M^+, <1%), 247 (16), 246 (100), 141 (24), 77 (35).

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