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Half-sandwich Ni(II) complexes bearing enantiopure bidentate NHC-carboxylate ligands: efficient catalysts for the hydrosilylative reduction of acetophenones†

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Chiral nickel complexes containing NHC-carboxylate chelate ligands derived from the (*S*)-isomeric form of amino acids have been synthesised from the corresponding imidazolium salt and nickelocene. The presence of the carboxylate on the *N*-side arm of the heterocycle results in the competing formation of mixtures of mono- and bis-NHC complexes (*i.e.*, [Ni(η^5-Cp)(κ^2-*C*,*O*-NHC)] and [Ni(κ^2-*C*,*O*-NHC)$_2$]), both of which retain the (*S*)-configuration of the stereogenic center and which can be separated by chromatography. Both the 18e$^-$ and 16e$^-$ complexes are found to be very stable and cannot be interconverted. The composition of the resulting mixtures depends mainly on the entity of the amino acid residue and, of more practical interest, on the reaction conditions. Thus, microwave heating and MeCN as a solvent favor the formation of the half-sandwich nickel complexes, rather than the bis-NHC compounds. Some of the [Ni(η^5-Cp)(κ^2-*C*,*O*-NHC)] complexes turn out to be among the best nickel catalysts for the hydrosilylative reduction of *p*-acetophenones described to date, although without chiral induction, in the absence of activating additives and under mild catalytic conditions.

Introduction

The superb expansion of N-heterocyclic carbene (NHC) chemistry that followed the seminal isolation of a stable crystalline carbene by Arduengo three decades ago,[1–3] continues to provide new breakthroughs at a remarkable rate, with great recent advances of interest for a broad research domain.[4] Indeed, their impact in organometallic chemistry means that this type of ligand can be considered to form part of the select and small group of versatile and broadly catalytically useful ligands that also includes cyclopentadienyls or phosphines.

Amongst other major fields in which the properties of NHCs have found great practical importance,[2–4] catalysis stands out as perhaps the most well-known.[4,5] The widespread use of second- and third-row transition metals in many catalytic processes, ranging from C–H activation and cross-coupling reactions to olefin metathesis, has concentrated the development of NHC chemistry on platinum group and heavier coinage metals, thus resulting in new generations of improved catalysts for many of these reactions.[3,6] More recently, and coinciding with the increasing awareness regarding the preferred use of 3d earth-abundant metals instead of less sustainable precious metals, much attention has been focused on the study of NHC complexes of metals such as Fe, Co, Ni or Cu.[7] Given that they are more readily available and less toxic than their heavier counterparts, the specific features of first-row metals (stabilization of lower oxidation states and coordination numbers, frequent higher reactivity and tendency to form radicals, *etc.*) open up novel mechanistic possibilities that allow new synthetic transformations. In particular, nickel has offered interesting perspectives in recent years, for instance by exhibiting an extraordinary ability to bind and activate unsaturated molecules or to promote challenging cross-coupling reactions.[8]

Within the realm of NHC-nickel compounds,[7b,9] NHC/cyclopentadienyl hybrid complexes of formula [Ni(Cp)(NHC)X] comprise a predominant class. The first examples thereof were reported by Cowley and Jones,[10] followed by others from the groups of Shen and Nolan, who started to explore their use as catalysts.[11] Pietrzykowsk, Royo, and Buchowicz, and co-workers,[12] have also published widely in this field, with the

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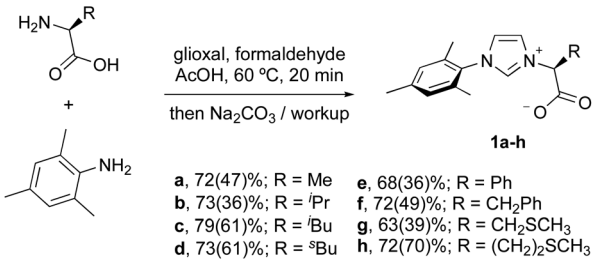
research team of Ritleng and Chetcuti being perhaps the most prolific.[13] This topic was reviewed by Buchowicz in 2019.[14]

Despite the considerable number of [Ni(Cp)(NHC)X] complexes reported to date, to the best of our knowledge only a few have been obtained as either racemic mixtures of chiral compounds containing Cp-NHC chelate ligands,[12c,15] or enantiopure compounds tethering stereogenic centers on the *N*-side arm (Chart 1).[16] We have recently detected the formation of a complex of this type, bearing a chiral κ^2-*C*,*O* bidentate NHC-carboxylate ligand with an arm derived from (*S*)-valine, as a byproduct (Chart 1).[17]

After deciding to investigate complexes of a similar nature, herein we disclose the synthesis and characterization of a family of nickel complexes containing NHC-carboxylate chelate ligands, namely [Ni(η^5-Cp)(κ^2-*C*,*O*-NHC)], which have been obtained enantiomerically pure by using NHCs based on the (*S*)-isomeric form of amino acids, and the catalytic behavior thereof in the hydrosilylation of phenones.

Results and discussion

NHC-ligand precursors **1a–h** were obtained as zwitterionic forms by adapting the multicomponent and straightforward synthesis reported by Baslé and Mauduit for **1b** (Scheme 1). The one-pot procedure is described to be efficient for a non-symmetrical *N*,*N*-substitution pattern of NHCs tethering a carboxylic function, which are otherwise inaccessible, in which the use of cheap and available enantiopure amino acids gives access to chiral imidazolium derivatives, as demonstrated with the isolation of hexafluorophosphate salts of protonated **1a–c**,



Scheme 1 Synthesis of chiral zwitterionic imidazolium salts **1a–h**, and their corresponding selectivity (isolated yield) %.

the corresponding for R = ^{t}Bu, and dipolar ion **1b**.[18] Gratifyingly, we found this strategy to be successful beyond the involvement of alkyl α-functionalized amino acids (R = Me (**a**), ^{i}Pr (**b**), ^{i}Bu (**c**), ^{s}Bu (**d**)), and widened the scope to aromatic (R = Ph (**e**), Bn(**f**)) and sulfide (R = CH_2SMe (**g**), $(CH_2)_2SMe$ (**h**)) functional groups. The selectivity for the desired hetero-disubstituted salts **1a–h**, as opposed to formation of their two possible homo-disubstituted counterparts, is above the statistically expected value (63–79%; established by ^{1}H NMR inspection of the crude reaction mixture) and in the range of those reported by Baslé and Mauduit, with some general improvement in yield (up to 70%) after workup to isolate the zwitterions.

The procedure first described by Cowley[10b] was tested for the synthesis of the nickel complexes (method A, scheme in Table 1). Thus, the 1 : 1 acid-base reaction between zwitterions **1** and nickelocene in warm acetonitrile led to monocarbene complexes **2** when starting from alanine (**1a**), phenylglycine (**1e**), methylcysteine (**1g**) and methionine (**1h**) derivatives (entries 1, 11, 17 and 19, respectively; Table 1). In contrast, imidazolium salts containing valine (**1b**), leucine (**1c**) and isoleucine (**1d**) residues gave the excepted compounds **2b–d** together with different amounts (10–32%, according to ^{1}H-NMR spectra of the crude reaction mixtures) of the corresponding biscarbenes **3b–d** (entries 3, 6 and 9), whilst no reaction was observed with the phenylalanine compound **1f** after several days (entry 12). The synthesis was also tested with **1b**, **1c** and **1f** in THF as solvent. In this case, the selectivity changed to give **3b** as a single product (entry 4) and a greater proportion of **3c** (entry 7 *vs.* 6), whereas **1f** remained unreactive in this solvent (entry 13).

The group of Nolan has considered that the strong Ni–Cl bond formed in the reaction of $NiCp_2$ with imidazolium chlorides for the synthesis of [Ni(Cp)(NHC)Cl] complexes, must act as a significant driving force leading to product.[11b] For complexes **2** and **3** the thermodynamics must comprise the formation of strong Ni–O linkages instead, and the additional stabilization provided by the formation of six-membered metallocycles after the chelating coordination of the bidentate NHC ligands.

At this point, it should be noted that an excess of **1** or $NiCp_2$, or the addition of NaX (X = Cl, Br; 1–5 equiv.) as a source of anionic halide ligand in an attempt to form Na[Ni

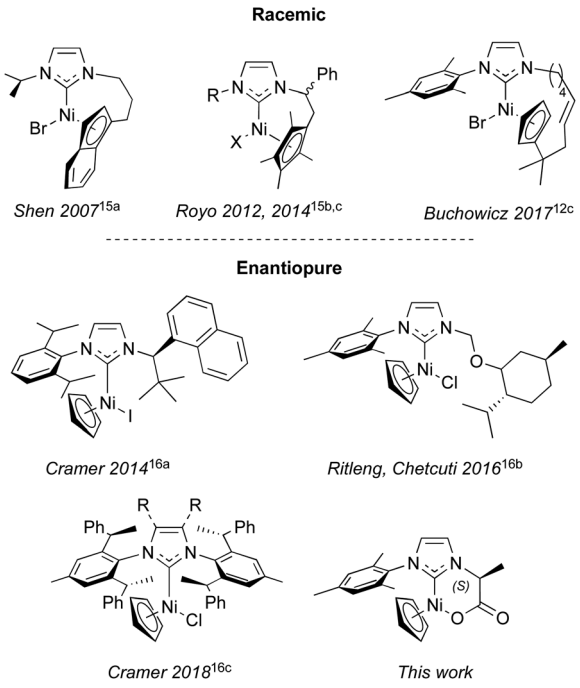
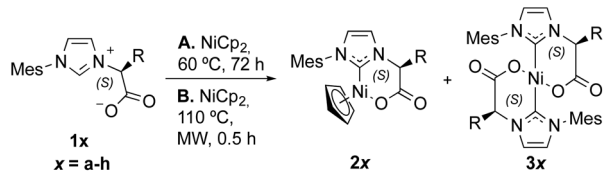


Chart 1

Table 1 Synthesis of nickel complexes **2** and **3** bearing chiral NHC ligands[a]



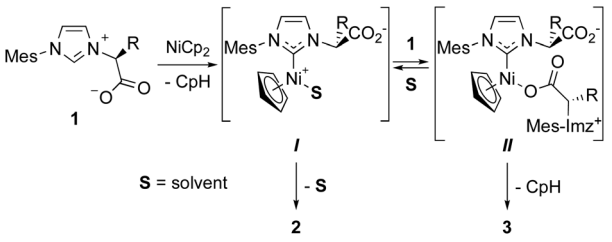
R = Me (**a**), ^{i}Pr (**b**), ^{t}Bu (**c**), ^{s}Bu (**d**), Ph (**e**), CH_2Ph (**f**), CH_2SCH_3 (**g**), $(CH_2)_2SCH_3$ (**h**)

Entry	1	R	Solvent	Method	Selectivity 2 : 3[b]	Yield (%) 2/3[c]
1	**1a**	Me	MeCN	**A**	100 : 0	43/—
2	**1a**	Me	MeCN	**B**	100 : 0	68/—
3[d,e,f]	**1b**	^{i}Pr	MeCN	**A**	68 : 32	37/25
4	**1b**	^{i}Pr	THF	**A**	0 : 100	—/44
5	**1b**	^{i}Pr	MeCN	**B**	85 : 15	40/19
6	**1c**	^{i}Bu	MeCN	**A**	72 : 28	56/0
7	**1c**	^{i}Bu	THF	**A**	67 : 33	29/20
8	**1c**	^{i}Bu	MeCN	**B**	100 : 0	86/—
9	**1d**	^{s}Bu	MeCN	**A**	90 : 10	41/5
10	**1d**	^{s}Bu	MeCN	**B**	81 : 19	54/15
11	**1e**	Ph	MeCN	**A**	100 : 0	30/—
12	**1f**	CH_2Ph	MeCN	**A**	— : —	—/—
13	**1f**	CH_2Ph	THF	**A**	— : —	—/—
14	**1f**	CH_2Ph	MeCN	**B**	63 : 37	nd
15[g]	**1f**	CH_2Ph	MeCN	**B**	87 : 13	46/12
16	**1f**	CH_2Ph	THF	**B**	25 : 75	25/30
17	**1g**	CH_2SMe	MeCN	**A**	100 : 0	68/—[h]
18	**1g**	CH_2SMe	MeCN	**B**	100 : 0	72/—[h]
19	**1h**	$(CH_2)_2SMe$	MeCN	**A**	100 : 0	69/—[h]
20	**1h**	$(CH_2)_2SMe$	MeCN	**B**	100 : 0	51/—[h]

[a] Reactions 1 : 1 with 1 mmol of **1** and $NiCp_2$ in 40 mL of solvent for Method A, or 0.8 mmol of **1** and $NiCp_2$ in 4 mL for Method B. [b] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture and based on **1**. [c] Purified/separated by column chromatography using AcOEt as eluent and based on **1**. [d] Selectivity **2 : 3** = 39 : 91 at r.t. [e] Selectivity **2b : 3b** = 75 : 25 in 100 instead of 40 mL of solvent. [f] Selectivity **2b : 3b** = 85 : 15 adding **1b** in three portions. [g] Reaction time 1 h. [h] Purified by washing with cold Et_2O.

$(Cp)(NHC^-)Cl]$ (or $Na_2[Ni(NHC^-)_2Cl_2]$),[19] barely affect the **2 : 3** ratio of the product mixture. Moreover, and unexpectedly, no intermolecular ligand exchange leading to **3b** and $NiCp_2$ is observed upon heating isolated **2b** in MeCN, and no reaction between **2b** (or **2c**) and **1b** (or **1c**) to form the biscarbene takes place in MeCN or THF at 65 °C after several days.

The formation of biscarbene complexes by abstraction of the acidic proton of two imidazolium species by both cyclopentadienyl ligands in $NiCp_2$ has been documented to occur only in the presence of a second equivalent or excess of carbene precursor.[20] The tendency to form biscarbene complexes **3** must be attributed to the presence of the carboxylate group in **1** and its coordinating and chelating capabilities. The set of outcomes observed here suggests the participation of transient species such as **I** and **II** depicted in Scheme 2. Thus, deprotonation of **1** by a η^5-Cp ligand and bonding of the carbene carbon to the metal center results in 18-electron species with a coordination site occupied by solvent **S** or η^2-cyclopentadiene (**I**), or by a second ion **1** coordinated as an anionic ligand *via* the carboxylate moiety (**II**). Chelation by



Scheme 2 Transient species proposed for the formation of **2** and **3**.

intramolecular substitution of **S** in **I**, or double chelation accompanied by deprotonation of the κ-*O*-imidazolium ligand and elimination of the second C_5H_6 ring in **II**, must irreversibly lead to complexes **2** or **3**, respectively. More-branched R groups in **1b**, **1c** and **1d** hinder chelation, thereby favoring the shift to species **II**, whereas the better coordinating properties and higher polarity of acetonitrile compared to THF are likely to stabilize species **I** and hinder that shift. The scarce effect of an excess of **1** or $NiCp_2$ in the products ratio **2 : 3** is explained by the fact that none of the reactants are fully soluble under the reaction conditions and by the irreversible formation of the complexes. Moreover, the reaction of entry 3 carried out in solution by using 100 mL of MeCN rises the selectivity **2b : 3b** from 68 : 32 (entry 3) to 75 : 25 (entry 3[e]), and reaches the maximun towards the formation of **2b** (85%, entry 3[f]) by adding **1b** in portions every 24 h to the nickelocene suspension.

We tentatively ascribe the lack of reactivity of **1f** to conformational issues, with the α-benzyl group deterring deprotonation at the 2-position of the heterocycle by the η^5-Cp ring. Indeed, clear correlations between that C–H group and the benzyl protons are observed in the NOE spectrum of **1f** (see ESI†).

In an attempt to improve these syntheses, we applied the protocol reported by Navarro replacing conventional heating with microwave heating at 110 °C and using shorter reaction times (method B, scheme in Table 1).[21] Most of the reactions went to completion in just 30 min, resulting in the formation of monocarbenes **2** and providing cleaner reaction mixtures from which higher yields were generally attained (entries 2, 5, 8, 10, 14–16, 18 and 20). To our delight, even the elusive imidazolium **1f** reacts under these conditions, although the conversion (50% for entry 14) required a longer time to complete (60 min, entry 15), and biscarbene **3f** is again favored in THF (entry 16).

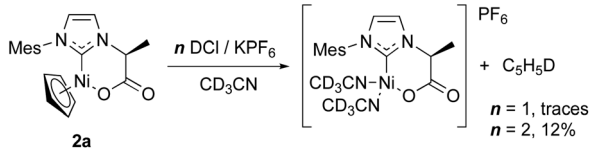
Salts **1** are soluble in water, dmso, CH_2Cl_2, MeOH, to some extent in MeCN, and insoluble in Et_2O, toluene or alkanes. In addition, **1g,h** are slightly soluble in THF. The metal complexes **2** and **3** are all soluble in polar solvents, in Et_2O, THF, and toluene, insoluble in alkanes, and only **2g,h** are soluble in water (and sparingly soluble in THF). Zwitterionic compounds **1** are stable when exposed to air in solution and in the solid state, although they must be stored under an inert atmosphere given their hygroscopic nature. The 18- (**2**) and 16-electron (**3**) nickel complexes are stable as solids under air for months, but

noticeable decomposition is observed in solutions exposed to air after a month.

Experiments with DCl have been carried out to test the robustness of the monocarbene complexes. The instantaneous and quantitative acidolysis and substitution of the Cp ligand by acetonitrile molecules has been reported for related half-sandwich κ^2-*C*,*C*-alkyl-NHC nickel complexes.[22] In contrast, the same test, comprising the addition of one equivalent of DCl to a solution of **2a** and KPF_6 in CD_3CN, hardly affects the mixture, and only traces of free monodeuterated cyclopentadiene are detected by ^1H NMR spectroscopy after 1 h, irrespective of whether the addition is performed at low (−78 °C) or at room temperature (Scheme 3). Moreover, with two equivalents of DCl, only a 12% yield of Cp-D is observed after 1 h, thus confirming the stability of the complex.

Compounds **1d–h** exhibit the NMR spectroscopic features observed for $[(\mathbf{1a–c})H]^+$ BF_4^- or **1b**,[18] with different resonances due to the different R substituents in the acetate side arm. Thus, the $^1H/^{13}C$ signals for the CH at the 2-,4-, and 5-Imz positions are observed at around 9.4/137, 7.9/123, and 7.8/122 ppm, respectively, and in the range 4.3–4.9/64–71 ppm for the corresponding nuclei at the stereogenic center, although that proton is more deshielded (δ = 5.9) for **1e** with R = Ph. The NMR spectra show the peak corresponding to the carbene carbon at around 156 ppm for complexes **2**, except for **2f** (δ = 137), which is shielded by the benzyl group, and at 160 ppm for bis-NHC compounds **3**, whereas for [Ni(Cp)(NHC)Cl] complexes this signal appears above 166 ppm.[10b,11b] The resonances for most of the characteristic nuclei also shift upon complex formation and coordination of the carbene ligands to nickel (*e.g.*, δ for $^1H/^{13}C$ for 4- and 5-Imz at around 7.8/124 and 7.3/123 ppm for **2**, and δ 7.5/122 and 7.2/123 for **3**, respectively, but at 7.1/130 and 7.0/129 for **2f**, thus pointing to the proximity of the Bn and the Imz rings). The proton and carbon at the chiral center are observed in the range (δ 4.3–4.7/60–71 for **2** and 3.9–4.6/62–70 for **3**), with the proton more deshielded for **2e** (δ 5.9) with R = Ph. The cyclopentadienyl ring signals appear at 4.7 (^1H) and 91 (^{13}C) ppm for complexes **2**, and the carboxylic carbon shifts to 171 ppm for **2** and **3**. It should also be noted that the methylthio group in **2g,h** resonates at 2.2 (^1H) and 15 (^{13}C) ppm, almost the same values found for precursors **1g,h** (δ 2.1 and 14 respectively), thus denoting the absence of an interaction between this donor group and the metal center in solution.

The HRMS (ESI/TOF$^+$) spectra of the new compounds **1** show the ion $[M + H]^+$ as the most intense peak in all cases, and this peak is often accompanied by cation $[M + Na]^+$ always



Scheme 3 Resistance of **2a** to acidolysis by DCl.

Table 2 Specific rotations $[\alpha]_D^{20}$ determined for salts **1**, and complexes **2** and **3**[a]

x=	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
1*x*	+35	−16	+43	+61	+1	−60	−10	+20
2*x*	−169	−553	−450	−598	−7	−574	−8	−423
3*x*		−220	−106	−284		−278		

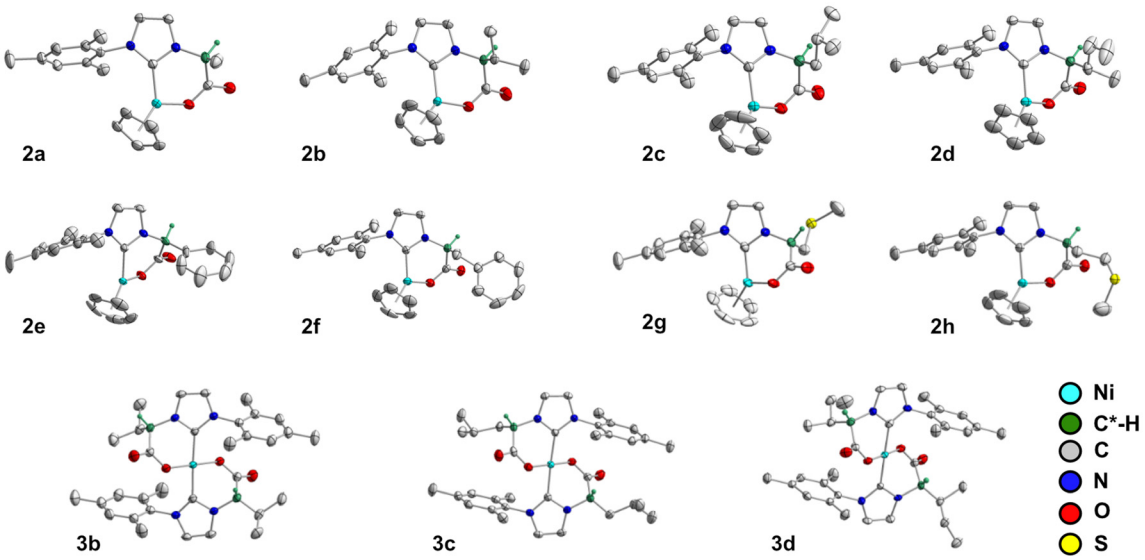
[a] $[\alpha]_D^{20}$ determined in EtOH; $C \simeq 0.1$ g/100 mL.

matching the calculated isotopic patterns. Most of the monocarbene complexes **2** afford very high specific rotation values in ethanol (Table 2).

Further structural insights have been gained by X-ray analysis of single crystals for complexes **2a–h** and biscarbenes **3b–d** (Table 3). The NHC ligands coordinate to the nickel center in a κ^2-*C*,*O*-chelating mode, retaining the (*S*)-configuration of the starting amino acids. In other words, no epimerization takes place during the formation of heterocycles **1** or during metalation to form enantiopure complexes **2** and **3**. The absolute configuration for **2g** is unique because, given this retention, the positions at the stereogenic center (H atom and R group) are exchanged relative to the other structures, as corresponds to the (*S*)-enantiomer and the CIP descriptors with R = CH_2SMe. The coordination geometry of all monocarbenes **2** is trigonal planar considering the Cp ring centroid, the carbene and the coordinated oxygen atom (sum of bond angles 360°), with a narrow bond angle for the chelating donor atoms (*ca.* 92°) in the range (90–96°) found in the crystal structure of neutral and cationic [Ni(Cp)(NHC)] moieties bearing a κ^2-*E*,*C*-carbene six-membered chelate ligand (E = S,[23] C,[24] or *N*[25]). The Ni–carbene bond lengths are in the lower limit of the range found for [Ni(Cp)(NHC)Cl] and related complexes, whereas the C–Ni–Cp(c) bond angles are, in general, wider.[10b,11b] The structures of **3b–d** resemble that found for the palladium equivalent of **3c**, namely square-planar complexes with a *trans* arrangement of the carbene ligands.[17] The *trans* influence of the carbenes can be seen from the longer Ni–C bond lengths than for monocarbenes **2**. The NHC moiety is tilted to the coordination plane of the metal in all cases (27–33° for **2a–h**, 35–9° for **3b–d**), and is almost coplanar in the biscarbene complexes (deviations of 5–15°).

Topographical analysis of the steric maps of the ligands, obtained by uploading the crystal structures data to Cavallo's SambVCa application,[26] reveals a higher steric pressure of the NHC in **2a–h** (%V_{Bur} = 44–47, Table 4) than for the IMes ligand in the reference compound [Ni(Cp)(IMes)Cl] (36%, calculated using the same set of structural parameters).[27] The average %V_{Bur} for NHCs in biscarbenes **3b–d** lies below the lower limit of that range (43 ± 2%), in agreement with the slightly longer Ni–C(NHC) bond distances. The asymmetry of the carbene ligands results in high disparities in quadrant occupancies, although they are relatively constant for all structures. According to the defined coordinates for complexes **2** (Table 4), the difference in %V_{Bur} between the least- (NW = 25 ± 3%) and the most-encumbered (NE = 69 ± 4%) quadrants contrasts with the

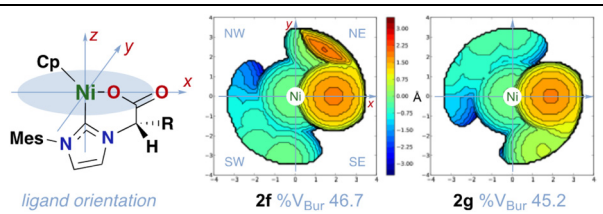
Table 3 ORTEP representation and selected bond lengths (Å) and angles (°) for the chiral nickel compounds [Ni(Cp)(NHC)] **2a–h** and [Ni(NHC)$_2$] **3b–d**[a]



	Ni–C	Ni–O	Ni–Cp(c)	C–Ni–O	C–Ni–Cp(c)	O–Ni–Cp(c)
2a	1.851(3)	1.887(2)	1.753	92.6(1)	137.0	130.4
2b	1.860(3)	1.882(2)	1.767	92.8(1)	137.0	130.2
2c	1.858(4)	1.882(3)	1.758	92.1(1)	138.4	129.6
2d	1.860(4)	1.876(3)	1.767	91.6(2)	137.9	130.3
2e	1.858(5)	1.873(4)	1.766	92.1(2)	139.5	128.4
2f	1.860(3)	1.888(2)	1.758	92.6(1)	136.4	130.9
2g	1.851(3)	1.889(2)	1.757	91.9(1)	134.6	133.5
2h	1.857(3)	1.889(2)	1.757	92.6(1)	137.9	129.5
	Ni–C	Ni–O		C–Ni–O	C–Ni–C′	O–Ni–O′
3b	1.90(1)[b]	1.87(1)[b]		90(2)[b]	177.3(1)	178.8(1)
3c	1.91(1)[b]	1.855(3)[b]		90(1)[b]	176.9(1)	177.3(1)
3d	1.90(2)[b]	1.869(4)[b]		90(2)[b]	178.8(2)	178.5(2)

[a] Only the hydrogen atom at the stereogenic centers is included; the remainder are omitted for clarity. [b] Averaged values.

Table 4 Steric maps for the NHC ligands in complexes **2f** and **2g**, and total % of buried volume (%V_{Bur}) values and %V_{Bur} per quadrant determined from crystal structures of **2a–h**[a]



%V_{Bur}	2a	2b	2c	2d	2e	2f	2g	2h
Total	44.1	45.0	45.2	45.2	46.8	46.7	45.2	46.2
SW	39.2	41.4	41.9	40.3	40.5	40.5	23.4	40.5
NW	22.4	24.8	23.8	23.0	28.5	24.1	39.1	23.3
NE	65.2	65.8	66.2	66.8	67.4	73.0	50.9	71.6
SE	49.7	48.0	48.9	50.8	50.8	49.2	67.2	49.4

[a] %V_{Bur} values were calculated with the metal at the center of the sphere with a radius of 3.5 Å. Bondi radii scaled by 1.17, mesh spacing of 0.1. H atoms were excluded.[26]

uniform steric map for IMes in the reference compound (36 ± 3% in all quadrants).[27] Similar asymmetric pockets can be seen for the ligands in complexes **3**, and the least- and most-hindered quadrants for **2g** turn to be SW (23%) and SE (67%), respectively, due to the absolute configuration thereof (compare the figures for **2f** and **2g** in Table 4).

Having successfully synthesized the nickel compounds, we envisioned their use in catalytic reduction reactions of ketones, namely acetophenone derivatives, by hydrosilylation followed by hydrolysis. This procedure complements the traditional reduction of carbonyl functionalities and avoids the hazards and often poor selectivity of classic reducing reagents (*e.g.*, alkali metals and metal hydrides),[28] the use of catalysts based on expensive precious metals,[29] and the need for high-pressure hydrogenation reactors. Indeed, efficient first-row transition metal catalysts for hydrosilylative reductions have emerged recently,[30] although, for nickel, only a limited number of catalysts for this reaction are known,[31] most of which are either of the pincer[32] or the [Ni(Cp)(NHC)X] type.[15b,16b,23,25b,33,34]

Good performance in the hydrosilylative reduction of aldehydes has been reported for all these catalysts, although most of them showed low (or no) catalytic activity with ketones. Inspired by the results reported by Royo,[15b] Chetcuti and Ritleng[16b,23,25b,33] and Albretch[34] in the hydrosilylation of carbonyl compounds with [Ni(Cp)(NHC)X] complexes, we decided to test ketones using complexes **2** and **3** as catalysts. After some preliminary testing to optimize the reaction with acetophenone as a model substrate (see ESI†), the conditions selected were those summarized in Table 5. Conversions to the secondary alcohol (*i.e.*, 1-phenylethanol) were high in 0.5–1.5 h (Table 5, entries 1, 4, 7, 10, 13 and 16), except for complexes **2g,h**, which contain a methylthio group (entries 19 and 22), and the biscarbene **3b** (entry 25), for which significant conversions required much longer reaction times (>20 h).

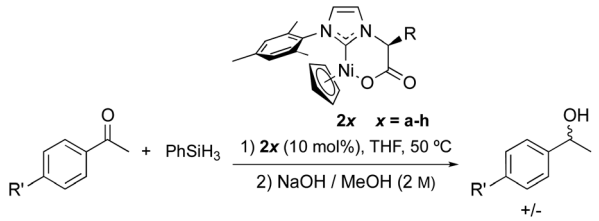
The activities found for **2a–f**, with an average TOF (TOF_{av}) of up to 20 h^{-1} (entries 7 and 16), are better than those reported for the reference catalysts in the same transformation: [Ni(Cp*-NHC^{Me})O^{t}Bu] (85% conversion, 2 mol%, 24 h, 100 °C in toluene, TOF_{av} = 2 h^{-1}),[15b] [NiCp(IMes)Cl] (97%, 5 mol%, $NaHBEt_3$ 5 mol%, 17 h, 25 °C in THF, TOF_{av} = 1 h^{-1}),[33] [NiCp(NHC^{py})]Br (99%, 2 mol%, KO^{t}Bu 2 mol%, 24 h, 100 °C in toluene, TOF_{av} = 2 h^{-1});[25b] or for the most active pincer nickel complexes reported to date [Ni(L)H] (L = bis(phosphino)boryl PBP-ligand) (99%, 5 mol%, 6 h, 70 °C in C_6D_6, TOF_{av} = 3 h^{-1}),[32d] [Ni{NHC-$(CH_2PPh_2)_2$}$(SPh)_2$] (98%, 2.5 mol%, 8 h, 70 °C in toluene, TOF_{av} = 5 h^{-1}).[32f] It should be noted that the significant conversions obtained in shorter reaction times with complexes **2a–f** are obtained at a relatively low temperature and without the need for any additive/activator. For instance, the reaction catalyzed by **2c** (2 mol%) in toluene at 100 °C gives 99% conversion in 1 h, with an increased TOF_{av} of 48 h^{-1} (see ESI†).

The reduction of *para*-chloro and -methoxy acetophenone was also tested. Complexes **2a,d,e,f** are somewhat less active in the presence of the electron-withdrawing group, requiring longer reaction times for similar conversions (entries 2, 11, 14 and 17 *vs.* 1, 10, 13 and 16), whereas the other catalysts (**2b,c**) show similar activities as with acetophenone (entries 5 and 8 *vs.* 4 and 7). Lower activities are observed with *p*-methoxyacetophenone in all cases, with significant conversions only after reaction for 21–24 h (entries 3, 6, 12 and 15 *vs.* 1, 4, 10 and 13) except for complexes **2c,f** (entries 9 and 18 *vs.* 7 and 16), which complete the reaction in only 1.5 h.

Given the solubility of complexes containing the thioether functionality in water, we checked the hydrosilylative reduction of *p*-chloroacetophenone with **2h** in water (rest of conditions as in Table 5, entry 23) and compared the outcome with the performance of **2c** in aqueous solution (other conditions as in entry 8). Despite the very low water-solubility of the latter, the conversion is, once again, higher (93%) than for **2h** (72%) after reaction for 7 h. As such, the behavior summarized in Table 5 for complexes **2g,h** cannot be attributed to their poor solubility in THF. The presence of hemilabile groups based on *N*- or *S*-coordinated donor atoms in related NiCp(NHC) complexes has been associated with high TOF values in the hydrosilylation of aldehydes as a result of a protecting effect on the catalytic species in the resting state.[23,34] In this case, the presence of the additional pendant donor group in complexes **2g,h** appears to hamper the catalysis.

Chiral-HPLC determinations indicate a racemic composition for the resulting secondary alcohols. We also observed the darkening of all catalytic solutions with time. Ritleng and Chetcuti have explained the lack of chiral induction in this reaction using a D-menthyl-functionalized [Ni(Cp)(NHC)Cl] complex, suggesting a distant location away from the metal center of the chiral group.[16b] The same authors have found evidence for the formation of nickel nanoparticles (NiNPs) under the harsh reaction conditions necessary for a [Ni(Cp-NHC^{py})]Br complex to be active against acetophenone.[25b] We have ruled out the formation of NiNPs during the catalysis under our milder conditions because none were observed in any field inspected by TEM in samples from solutions of the reactions performed with **2c**. Moreover, the catalytic reaction with **2f** was found to be unchanged by the addition of a few drops of

Table 5 Hydrosilylation of acetophenones catalyzed by complexes **2**[a]



Entry	Catalyst	R	R′	*t* (h)	Conv. (%)[b]
1	**2a**	Me	H	0.5	97
2			Cl	1.5	97
3			MeO	1.5/24	76/97
4	**2b**	^{i}Pr	H	1.5	94
5			Cl	1.5	92
6			MeO	1/22.5	58/90
7	**2c**	^{i}Bu	H	0.5	99
8			Cl	0.5	96
9			MeO	1	94
10	**2d**	^{s}Bu	H	1.5	96
11			Cl	2.5	96
12			MeO	1/20.5	24/95
13	**2e**	Ph	H	1	98
14			Cl	2.5	94
15			MeO	1/21.5	55/98
16	**2f**	CH_2Ph	H	0.5	99
17			Cl	1.0	96
18			MeO	1.5	99
19	**2g**	CH_2SMe	H	1.5/21	2/38
20			Cl	1.5/21	3/62
21			MeO	1.5/21	0/18
22	**2h**	$(CH_2)_2SMe$	H	1.5/24	23/93
23			Cl	1.5/23	26/98
24			MeO	1.5/24	3/31
25	**3b**	^{i}Pr	H	22	87

[a] All reactions were carried out with 1.5 mmol of acetophenone derivative, 0.15 mmol of **2** (10 mol%) and 1.8 mmol of $PhSiH_3$ in dry THF (7.5 mL, [Ni] = 0.02 m) at 50 °C. The catalytic reactions were performed at least in duplicate and the reproducibility of the conversions measured is estimated at ±2%. [b] Conversions determined by GC-MS after methanolysis.

mercury at t = 40 min (conv. = 60% and 97% at t = 45 and 60 min, respectively) compared to the experiment without Hg (conv. = 62% and 96% at t = 45 and 60 min, respectively). Therefore, the total absence of enantioselectivity with complexes **2** is likely to be due to decoordination of the carboxylate from the 18 e^- metal center under the catalytic conditions, rather than to the participation of NiNPs with non-selective surfaces, thus resulting in a dangling NHC side-arm that is free to rotate. As such, in line with a recent proposal for a pincer nickel dithiolate complex,[32f] one possible reaction pathway involves silylation of the κ-*O*-carboxylate before it enters the catalytic cycle. Nevertheless, no detectable changes are observed in the ^{1}H NMR spectra of complex **2a** in the presence of *p*-chloroacetophenone or $PhSiH_3$ (1 equiv.) after 1 h at 50 °C in THF-d_8.

Since the catalysts do not degrade to nanoparticles, apparently operating under homogeneous conditions with discrete species, we tested the durability of **2c** by reloading with fresh *p*-chloroacetophenone and $PhSiH_3$ at the end of the reaction (Table 5, entry 8). Some catalyst depletion was observed, with the initial conversion (97% in 1.5 h, TOF_{av} = 6.5 h^{-1}) decreasing in the first (92% in 2.5 h, TOF_{av} = 3.5 h^{-1}) and second (85% in 4.5 h, TOF_{av} = 2 h^{-1}) reruns of the reaction.

Conclusions

In addition to expanding the procedure reported by Baslé and Mauduit for the preparation of chiral imidazolium derivatives by using amino acids functionalized with aromatic or thiolate groups, we have managed to synthesize, to the best of our knowledge, the first family of nickel complexes containing NHC-carboxylate chelate ligands. Moreover, since no epimerization takes place during either formation of the starting imidazolium salts **1** or during their nickelation, the complexes have been obtained as enantiomerically pure compounds. The reactions between **1** and nickelocene tend to form mixtures of mono- and bis-NHC complexes (*i.e.*, [Ni(η^5-Cp)(κ^2-*C*,*O*-NHC)] and [Ni(κ^2-*C*,*O*-NHC)$_2$]) due to the competing coordination capability of the carboxylate group, in ratios that depend on the reaction conditions. Thus, microwave heating accelerates the reactions and favors formation of the half-sandwich compounds in a polar and good coordinating solvent such as acetonitrile. All complexes were found to be very stable to air and moisture. In fact, mono-NHC complexes catalyze the hydrosilylation of chloroacetophenone in water. Some of the [Ni(η^5-Cp)(κ^2-*C*,*O*-NHC)] complexes turn out to be among the best nickel catalysts for the hydrosilylative reduction of *p*-acetophenones described to date. Moreover, no activating additives are required, and catalysis takes place under mild operational conditions. The lack of chiral induction during formation of the secondary alcohol points to decoordination of the κ-*O*-carboxylate before it enters the catalytic cycle.

The features of the new complexes demonstrate the potential of suitable ligands to impart improved catalytic performance to earth-abundant metal compounds.

Author contributions

J. S.-G.: investigation, conceptualization, validation, data curation. A. M.: resources, formal analysis, data curation. C. G.-A.: methodology, conceptualization, supervision, project administration, funding acquisition. J. C. F.: conceptualization, supervision, project administration, funding acquisition, writing – original draft. All authors contributed to the writing – review and editing process of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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