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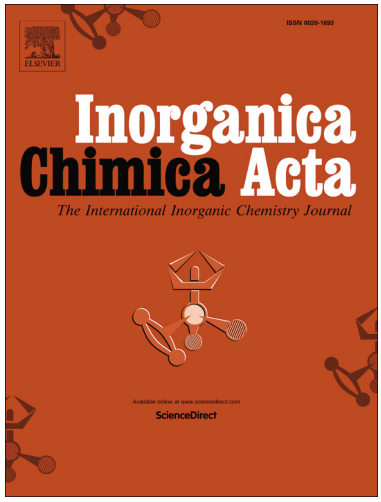

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A Chiral Ligand Accessible in One Step: Synthesis of *bis*-((R)-(+)-Bornyl)acenaphthenequinonediimine and of its Zinc and Nickel Complexes.

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Abstract

A new neutral chiral nitrogen ligand was obtained in one step from commercially available acenaphthenequinone and (R)-(+)-bornylamine. Use of titanium tetraisopropoxide is the key to obtain good yields of the condensed product. Ring strain in the bicyclic system helps in stabilizing the otherwise unstable Alkyl-BIAN type derivative, but is not enough to render the free ligand indefinitely stable. However, complexes of the ligand with the $ZnCl_2$ and $NiBr_2$ fragment were prepared and are stable. The single crystal X-ray structure of ((R)-(+)-Bornyl-BIAN)$NiBr_2$ has been determined.

Keywords: N-ligands; Schiff bases; Chiral ligands; Nickel; Zinc

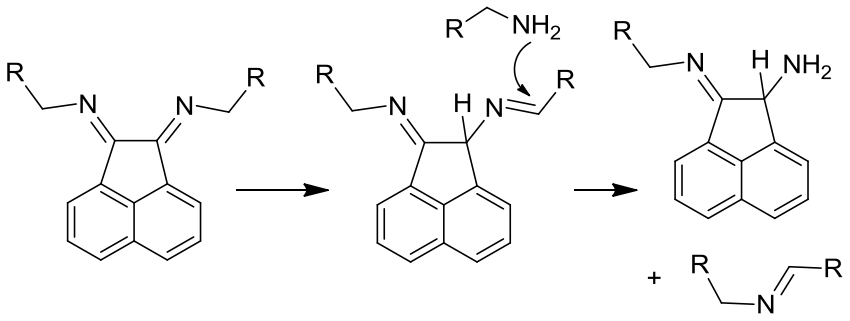
1. Introduction

Asymmetric catalysis is an area of growing importance. The field is dominated by phosphorus ligand, but nitrogen ligands have some strong points [1-5]. One is that the metal-to-nitrogen bond is shorter than the metal-to-phosphorus one and this can lead to a more efficient transfer of the asymmetric induction from the ligand to the catalytically active site. Another is that nitrogen ligands are usually much more resistant to oxidation than phosphines, making them the ligands of choice when dioxygen or peroxides are employed as reagents [6]. Most commonly employed chiral nitrogen ligands, such as bis-oxazolines, porphyrins or Salen derivatives are anionic. Indeed a weak point of neutral nitrogen ligands is that they are often quite labile. Loss of the ligand in solution is a problem even more serious in asymmetric catalysis than in traditional homogeneous catalysis because the ligand-free metal may not only deactivate, but even worse be still active and afford the racemic product. Thus, an excess, often a large excess, of the ligand has to be employed to stabilize the metal complex. This in turn implies that the ligand should be easily prepared at a low cost to be

of practical interest. Many neutral chiral ligands have been reported in the literature that have never been applied because their lengthy synthesis discouraged potential users.

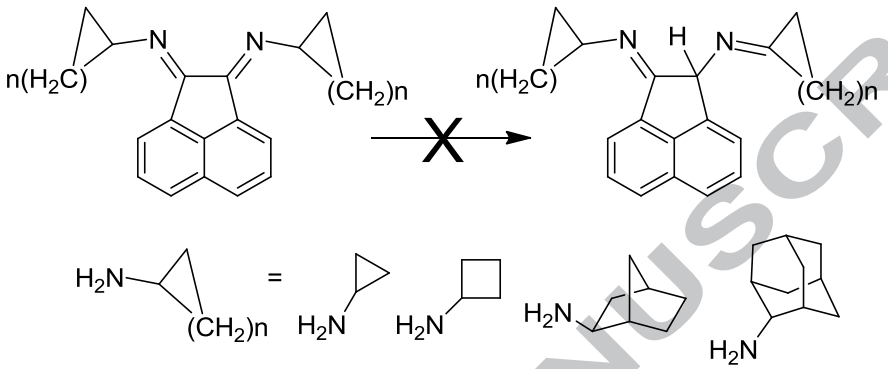
Bis-imines are among the most easily synthesized neutral nitrogen ligands, but the flexible nature of most of them makes such compounds of little use in asymmetric catalysis. Bis-imines derived from acenaphthenequinone (generally referred as R-BIAN ligands) are not only more rigid, but also even chemically more stable because their cyclic nature prevents the breaking of the central C-C bond of the di-imine moiety, which can be a problem in some cases [7]. R-BIAN compounds have been employed as ligands in a variety of catalytic systems. Although many of these papers focus on olefin polymerization [8-12] and copolymerization [13-18] reactions, it should be stressed that there are some systems in which the use of R-BIAN ligands is instrumental in obtaining high activities and selectivities, such as the selective semihydrogenation of alkynes [19] and allenes [20], the allylic aminations of olefins by nitroarenes in the presence of CO [21-23], the synthesis of pyrroles and oxazines from dienes, nitroarenes and CO [24], and the reduction of nitroarenes to anilines by CO/H_2O [25-27]. In these cases, no other kind of ligand affording comparable results. Many of the aforementioned reactions and additionally others for which R-BIAN ligands have been successfully employed, would surely benefit from an easy availability of a chiral ligand of the same family. For example, this would surely hold for the cross-coupling reaction of organic halides with organomagnesium, -zinc, and –tin reagents [28-31] and the Suzuki-Miyaura cross coupling [32]. It should be reminded that R-BIAN compounds have also been employed to synthesize robust and rigid N-heterocyclic carbenes [33-37] and the interest in chiral ligands of this kind is also strong. Finally, R-BIAN ligands can also be reduced to give stable hydrogenated compounds that can be used as anionic ligands [38, 39], widening the opportunities for their use in enantioselective reactions.

Most often, R-BIAN derivatives employed in catalytic reactions have aryl groups attached to the nitrogen atoms. However, until recently the only Ar-BIAN derivatives available in a chiral form [40] were prepared employing chiral anilines whose enantiomers had been separated by chiral semipreparative HPLC [41], a technique that cannot be employed on a synthetically useful scale. Only very recently a chiral Ar-BIAN derivative was prepared whose chirality derives from a menthyl group attached to the aniline ring and thus requires no separation of the enantiomers [42]. Aliphatic amines are widely available in a chiral form, but Alkyl-BIAN compounds are generally not stable. Several years ago, we showed that the reason for this instability is an isomerization of the C=N double bond, which paves the way to the attack of another amine molecule to initiate a series of further reactions (Scheme 1). The reason for the efficient isomerization, which is not usually observed for bis-imines derived from non-cyclic di-aldehydes or di-ketones, was identified in the release of ring strain of the central five-membered ring of the acenaphthene moiety, whose carbon atoms are all sp^2 hybridized [43, 44].



Scheme 1

A solution to this problem was found by the use of alkyl amines in which the amino group is directly bound to a ring strained system. In this way the ring strain released on the acenaphthene ring would be counterbalanced by an even stronger strain increase on the amine ring in the isomerized product and the process does not occur (Scheme 2)



Scheme 2

The obvious choice for a ring-strained amine is cyclopropyl amine, which indeed worked perfectly to give a molecule (Cypr-BIAN) that is stable in solution up to at least 170 °C. Other ring strained amines include cyclobutylamine (Cybu-NH_2), the bicylic *exo*-2-aminonorbornane (Norb-NH_2) and the tricyclic 2-aminoadamantane (Ad-NH_2) [43, 44]. However, it should be mentioned that the free ligands obtained from these other amines are not stable for long. Their $ZnCl_2$ complexes could be obtained by transimination of $ZnCl_2$(3,5-$(CF_3)_2C_6H_3$-BIAN) with the corresponding amine and were indefinitely stable. Once the metal was removed by treating the complex with potassium oxalate, decomposition occurred within minutes for Cybu-BIAN, hours for Norb-BIAN and a couple of days for Ad-BIAN. This instability is not an absolute limit to the use of the ligands because we proved that it is possible to synthesize complexes with other metals by fast zinc decomplexation immediately followed by addition of the different metal salt.

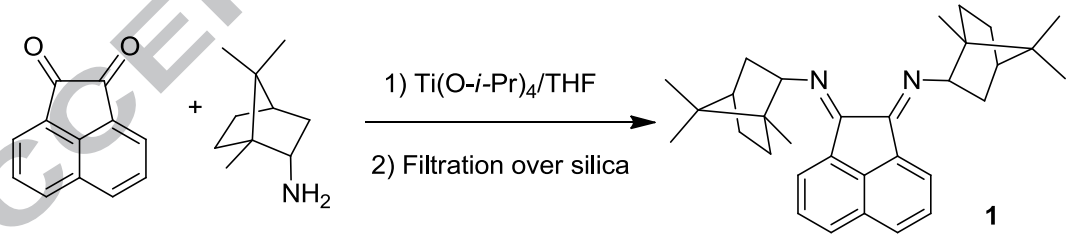
The discovery of this rare case in which ring strain induces stability in a product rather than instability led us to prepare the first chiral BIAN derivatives available in synthetically useful amounts. Cyclopropyl amines derived from commercially available and enantiomerically pure β-pinene were used to this aim [45]. Although the procedure does not involve any separation of enantiomers, it still requires four synthetic steps and a delicate chromatographic separation of the four diasteroisomers that are formed. Here we report a one-step synthesis of a chiral Alkyl-BIAN derivative obtained from an amine commercially available as a single enantiomer. It should be recalled that Alkyl-BIAN ligands coordinate more strongly than any Ar-BIAN compound and more strongly even than phenanthroline [45-47]. This is an important point in view of the lability problem of neutral nitrogen ligands mentioned above.

Results and Discussion

1.1. Synthesis of (R)-(+)-Bornyl-BIAN

Among chiral amines that are commercially available at a convenient price, only (R)-(+)-bornylamine features an amino group directly bound to a strained ring [48]. Use of bornyl amine had been considered since the beginning of our work on chiral Alkyl-BIAN synthesis. However, attempts made by direct reaction of acenaphthenequinone with the amine in the presence of $ZnCl_2$ [49] or by the transimination strategy developed in our laboratories to prepare mixed Ar,Ar'-BIANs [50] had either failed or given only very small amounts of the desired product. The negative results are likely due to the strong steric hindrance of the bornyl groups. In the meanwhile we have discovered that Ti(O-*i*-Pr)$_4$ is a much better reagent to promote the condensation of acenaphthenequinone with sterically hindered alkyl amines than $ZnCl_2$ [45] and this led us to reconsider the use of bornylamine.

Acenaphthenequinone and (R)-(+)-bornylamine were reacted at RT in THF with Ti(O-*i*-Pr)$_4$ for 48 h. The product obtained at this stage is likely a titanium complex of the final BIAN derivative, or a mixture of complexes of the same. When zinc complexes of BIAN ligands are concerned, we have shown many years ago that treating a CH_2Cl_2 solution of the ligand with aqueous potassium or sodium oxalate is the most effective way of removing the metal [22, 26, 46]. In our paper on the synthesis of the pinene-derived Alkyl-BIAN ligands, we had found that in the case of titanium, the method was only partly effective and a further elution through a short silica gel column was necessary to remove even the last traces of metal. In the present work, we decided to skip the treatment with potassium oxalate, since the filtration over silica appeared to be effective in removing all the coordinated titanium (Scheme 3).



Scheme 3. Synthesis of (R)-(+) Bornylamine derived BIAN ligand (**1**).

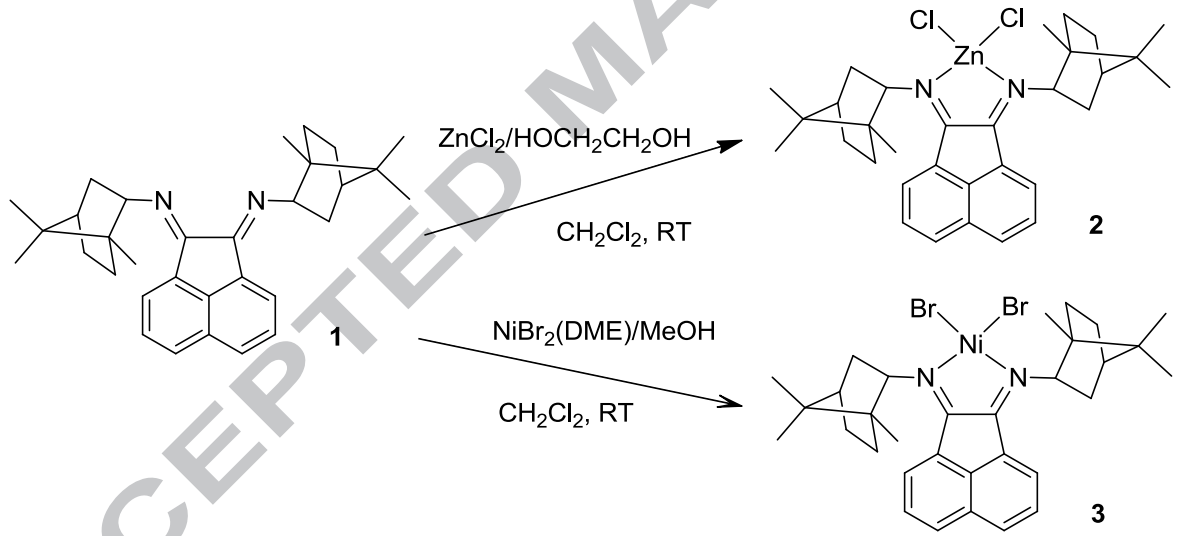
The procedure was successful and after the filtration over silica (see the experimental part for details), the ligand **1** was obtained as a light orange solid in a fair yield (60%).

As expected based on the structural similarity between **1** and Norb-BIAN, the free ligand is unstable (decomposes in few hours) and for this reason it is necessary to stabilize it by complexation to a metal. $ZnCl_2$ and $NiBr_2$ were chosen to this aim. The former because several R-BIAN complexes with this metal salt have been characterized and may be used for comparison and the latter because of the importance of Ni/Ar-BIAN complexes as catalysts for olefin

polymerization, the catalytic reaction for which R-BIAN derivatives have been most deeply investigated.

1.2. Synthesis of ((R)-(+)-Bornyl-BIAN)$ZnCl_2$ (2) and ((R)-(+)-Bornyl-BIAN)$NiBr_2$ (3)

Most of the solvents in which zinc chloride is well soluble, water or strongly coordinating solvents like DMSO, efficiently compete with nitrogen ligands for coordination to the metal and would not be a good choice to prepare the target complex. Methanol only slightly dissolve $ZnCl_2$, but ethylene glycol dissolves it well and can be employed to our aim. Unfortunately, (R)-(+)-Bornyl-BIAN is not soluble in it. Thus, we chose to run the reaction in a biphasic system ethylene glycol/methylene chloride. In this way, ((R)-(+)-Bornyl-BIAN)$ZnCl_2$ (**2**) remained in the CH_2Cl_2 phase and could be separated and purified by crystallization from hexane. The isolated yield of the purified material was low (21 %), but it should be stressed that our aim at this stage was not to maximize the yield, but to obtain pure products that could be thoroughly characterized. The obtained compound was indeed analytically pure and all ^{1}H and ^{13}C NMR signals could be attributed by bi-dimensional NMR techniques (see experimental).

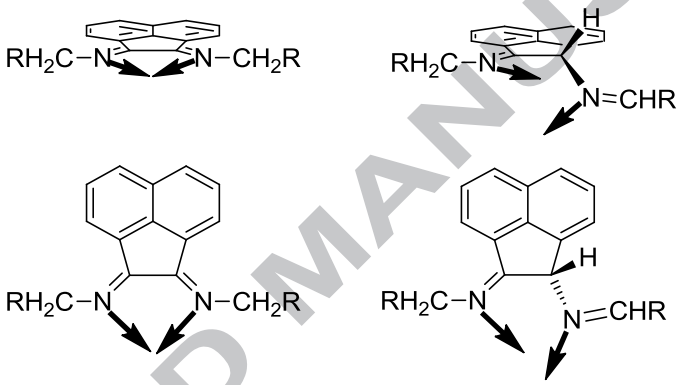


Scheme 4. Synthesis of complexes **2** and **3**

The most convenient starting material to generate $NiBr_2$ complexes is its dimethoxyethane solvate, $NiBr_2$(DME). The latter is well soluble in methanol and a solution of the solvate in this solvent was reacted with a CH_2Cl_2 solution of the ligand. The final product, **(**(R)-(+)-Bornyl-BIAN)$NiBr_2$ (**3**) (36 % yield. Again no attempt was made to improve this yield) is paramagnetic, so no NMR characterization can be given, but diffusion of hexane into a CH_2Cl_2 solution of it allowed the growing of crystals suitable for a single crystal X-ray diffraction analysis and the results are described in the next paragraph.

Both **2** and **3** are indefinitely stable, at least in the solid state. Since we have never discussed the reason for the higher stability of the complexes with respect to the free ligands, it is worth to do it now. Chelation to the metal requires the two lone pairs on the nitrogen atoms to converge with an angle around 90° and to a point not too distant from the nitrogen atoms themselves. Though the

angles made by the two C=N double bonds connected to a five-membered ring are not ideal from this point of view, the two lone pairs still converge quite well, which is not surprising given the number of stable R-BIAN complexes known (Scheme 5, left). However, if one of the two C=N double bond is isomerized, the two lone pairs will diverge (Scheme 5, right). Although not immediately evident from a two dimensional drawing, any 3D model shows that even if the isomerized N=CHR moiety is rotated around the C-N single bond, the two lone pairs become at best almost parallel, but no rotation can led them to converge at a close distance. This implies that isomerization of the ligand should be accompanied by the breaking of one of metal-nitrogen bonds, making the process less thermodynamically favored. This extra stabilization of the Alkyl-BIAN ligands when coordinated plays an essential role when the ring-strain effect of the alkyl groups is not by itself strong enough. Note anyway that when no ring strain is present, coordination to zinc is not enough to stabilize the ligand [43, 44].



Scheme 5. Front and top view of a generic Alkyl-BIAN (left) and of its isomerized form (right) with arrows indicating the directions in which the lone pairs on the nitrogen atoms point.

1.3. Crystal structure of ((R)-(+)-Bornyl-BIAN)$NiBr_2$ (3)

Compound **3** crystallizes in the chiral space group $P2_1$ in a 1:1 ratio with dichloromethane, which occupies, in an ordered way, the interstitial sites of the crystal. Whereas no crystallographic symmetry is possible in $P2_1$, the complex shows a pseudo-C_2 symmetry with a root mean square deviation of 0.22 Å from the symmetrized geometry (see Figure 1). The BIAN skeleton is deformed from ideal planarity; in fact the acenaphthene plane is inclined by ca 9º with respect to the plane of N-Ni-N atoms and it is not exactly perpendicular with respect to the Br-Ni-Br plane (ca. 80º). This distortion does not affect the pseudo-C_2 symmetry, which is in fact compatible with this rotation and in particular does not modify the bonding in the imino group of the BIAN. The coordination of BIAN to the metal is rather symmetric (N1-Ni = 2.010(9) Å and N2-Ni = 2.024(10) Å) and the C-N distances are also rather similar (1.31(1) Å and 1.29(1) Å), at least within the relatively low precision of the model, which is due to the crystal quality. In the Supplementary Material, crystallographic details, atomic positions and distances are provided.

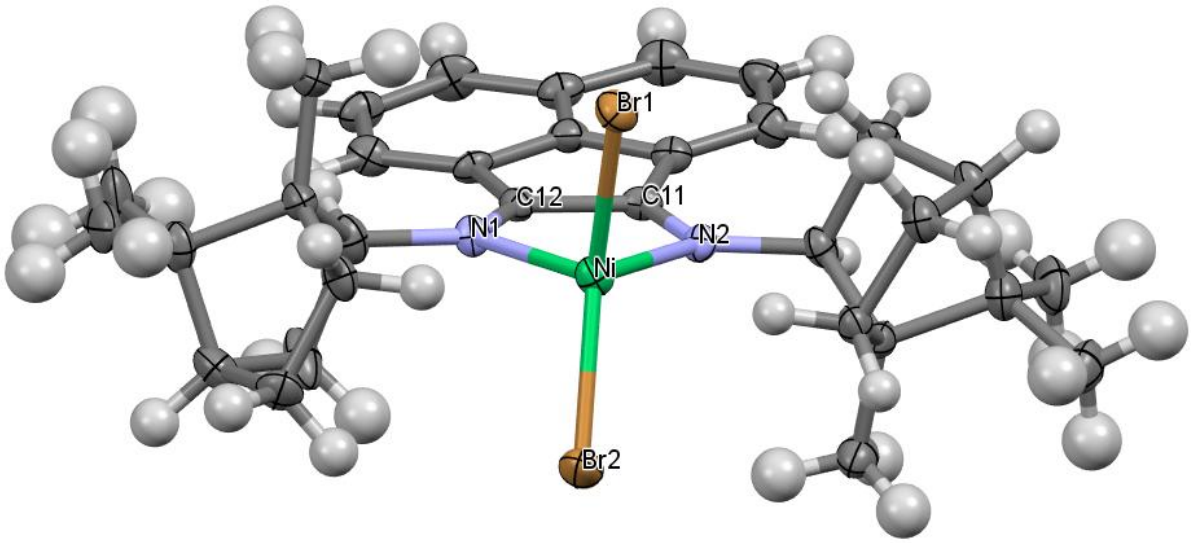


Figure 1. Molecular geometry of compound **3** as obtained from single crystal X-ray diffraction. Ellipsoids represent the probability volume of each atom, drawn at 50% level). Some relevant atomic labels are shown.

2. Conclusions

In this paper we reported on the synthesis of new neutral chiral nitrogen ligand in one step from commercially available starting materials and obtained the corresponding the $ZnCl_2$ and $NiBr_2$ complexes. Although the ligand is not stable in the free form, it is stable long enough to generate the aforementioned complexes, which are indefinitely stable, and likely many others. The crystal structure of the Ni derivative clearly confirms the formation of such complex, featuring a pseudo-C_2 symmetry. Titanium tetraisopropoxyde was confirmed to be the reagent of choice to obtain the diimine from acenaphthene quinone and sterically hindered alkyl amines. This compound is commercially available even in multiliter bottles and at a cheap price. So it is very well suited to be used even on a large scale.

3. Experimental section

3.1. Methods and materials

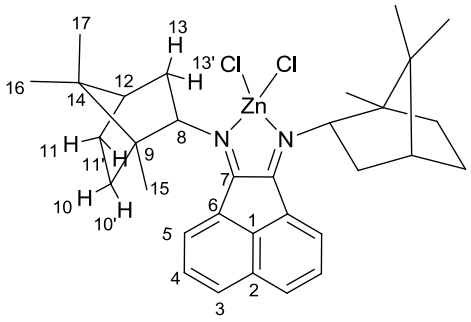
All the syntheses were performed under a dinitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2 and Et_3N were distilled over CaH_2 and stored under a dinitrogen atmosphere. THF and hexane were distilled over sodium/benzophenone ketyl and stored under a dinitrogen atmosphere. Ethylene glycol was degassed by three pump/thaw cycles and stored under dinitrogen. $CDCl_3$ was passed over basic alumina, degassed and kept over activated 4 Å molecular sieves under a dinitrogen atmosphere. $NiBr_2$(DME) was prepared as reported in the literature [51]. $ZnCl_2$ was dried by heating it under vacuum and was subsequently stored under nitrogen. All other reagents were purchased form Sigma Aldrich and used without further purification. All glassware and magnetic stirring bars were kept in an oven at 125 °C overnight and let to cool under vacuum before use. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 300 or on a Bruker Avance DRX 400. Chemical shifts are reported in ppm relative to TMS. Elemental analyses were performed on a Perkin Elmer 2400 CHN elemental analyzer.

3.2. Synthesis of Bornyl-BIAN (1).

In an oven dried Schlenk flask acenaphthenequinone (127.2 mg, 0.7 mmol) and (R)-(+)bornylamine (301.2 mg, 2 mmol) were dissolved in THF (15 mL) and Ti(O-*i*Pr)$_4$ (575 µL, 2.1 mmol) was added while stirring. After a few hours, the color of the solution had changed from yellow to purple. The mixture was stirred at room temperature for 48 hours. The solution was then evaporated and the crude filtered through a short column of silica gel (hexane/AcOEt = 8:2 + 2% of triethylamine). Titanium compounds and unreacted bornylamine are not eluted under these conditions. After evaporation of the solvent, the ligand was obtained as a light orange solid in 60% yield. The product is only stable for a short time. Thus, it was immediately used in the subsequent complexation reactions without further purification.

3.3.Synthesis of (Bornyl-BIAN)$ZnCl_2$ (2).

In a Schlenk flask, anhydrous $ZnCl_2$ (48.2 mg, 0.4 mmol) was dissolved in ethylene glycol (3 mL). The ligand (54.8mg, 0.1 mmol) dissolved in CH_2Cl_2 (0.5 mL) was then added. The mixture was stirred at room temperature for 12 hours. The ethylene glycol was then separated and the chlorinated phase was washed with distilled water and dried over sodium sulfate. The suspension was filtered and the solution evaporated under vacuum to yield 81.8 mg of a dark yellow solid, which is mostly composed by the desired product, but also contains some impurities. The latter was purified by recrystallization in hexane affording 15 mg (0.03 mmol) of the complex. Yield = 21%. ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): δ = 8.24 (d, *J* = 7.7 Hz, 2H, H5), 8.20 (d, *J* = 8.5 Hz, 2H, H3), 7.85 (t, *J* = 7.8 Hz, 2H, H4), 5.26 – 5.14 (m, 2H, H8), 2.95 – 2.73 (m, 2H, H10‘), 2.63 – 2.45 (m, 2H, H13), 2.21 -2.08 (m, 2H, H13‘), 1.99 – 1.76 (m, 6H, H12, H11 and H11‘), 1.68 – 1.47 (m, 2H, H10), 1.16 (s, 6H, H17), 0.99 (s, 6H, H16), 0.89 ppm (s, 6H, H15). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C): δ = 164.8 (C6), 143.5 (C), 131.7 (C3), 131.5 (C), 128.8 (C4), 126.9 (C), 126.5 (C5), 68.7 (C8), 53.7 (C), 50.0 (C), 45.1 (C12), 36.0 (C13), 29.1 (C10), 28.4 (C11), 19.9 (C16), 19.3 (C17), 15.1 ppm (C15). Elem. anal. calcd. for $C_{32}H_{40}Cl_2N_2Zn$: C, 65.26; H, 6.85; N, 4.76%; found: C, 65.56; H, 6.99; N, 4.65%



3.4. Synthesis of (Bornyl-BIAN)$NiBr_2$.

In a Schlenk flask, a solution of the ligand (55.8 mg, 0.12 mmol) in distilled dichloromethane (10 mL) was added, under nitrogen, to a solution of $NiBr_2$(DME) (47 mg, 0.15 mmol) in distilled methanol (5 mL). The resulting solution was stirred at room temperature for 24 hours. The precipitation of a white solid occurred. This was separated by centrifugation and the solution dried in *vacuo* affording a light brown solid. The solid was dissolved in the minimum amount of CH_2Cl_2 and the solution was layered with hexane. A crystalline material was isolated (30.1 mg, 4.5 10^{-2} mmol, 36 % yield). Some of the obtained crystals were suitable for an X-ray diffraction analysis.

3.5. Single crystal X-ray diffraction.

A crystal of compound **3** was mounted in air at ambient conditions and measured on a Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated Mo Kα radiation (λ = 0.71073 Å) and Al filtered [52]. The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of reflections in the range $1.8 < \theta < 28.2°$. A total of 857 frames were collected using ω scans, with 20+20 seconds exposure time, a rotation angle of 1.0° per frame, a crystal-detector distance of 65.0 mm, at T = 173(2) K. Data reduction was performed using the CrysAlisPro program [53]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in CrysAlisPro was applied. The measured unit cell dimensions are: a = 10.9426(2) Å; b = 13.3077(3) Å; c = 11.2608(3) Å; β = 97.709(2)°; Volume = 1624.99(6) $Å^3$. Z = 2; Density = 1.545 g/cm^3; Absorption coefficient = 3.246 mm^{-1}. The structure was solved by direct methods using SHELXT [54], which revealed the positions of all non-hydrogen atoms of the title compound. The non-hydrogen atoms were refined anisotropically. All H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom. Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(Fo^2 - Fc^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the SHELXL-2014/74 program [54]. The final agreement indices were: $R_1 = 0.0661$, $wR_2 = 0.1640$ for $I > 2\sigma(I)$ and $R_1 = 0.0841$, $wR_2 = 0.1820$ for all data. Oher data collection and refinement parameters are given in Supplementary Material.

4. Supplementary material

Copies of ^{1}H NMR and ^{13}C NMR spectra, crystallographic material for compound **3.**

5. Acknowledgements

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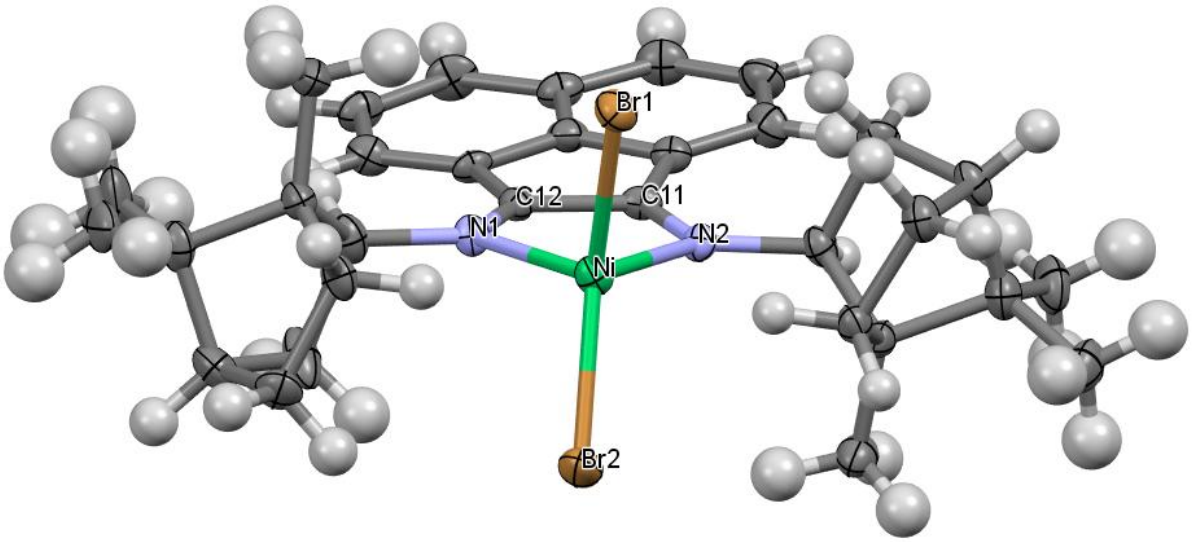

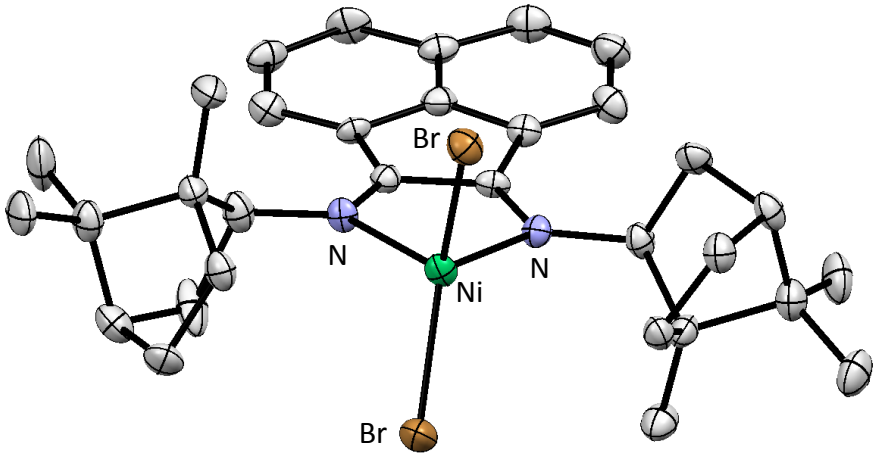

Highlights

- A new chiral chelating nitrogen ligand of the R-BIAN family is reported (BIAN = bis-iminoacenaphthene).
- The ligand is obtained in one step from commercially available and enantiomerically pure (R)-(+)-bornylamine.
- The free ligand is not indefinitely stable, but its complexes are.
- The single-crystal X-ray structure of ((R)-(+)-Bornyl-BIAN)$NiBr_2$ was determined.