Stability-inducing strain: application to the synthesis of alkyl-BIAN ligands (alkyl-BIAN = bis(alkyl)acenaphthenequinonediimine)†

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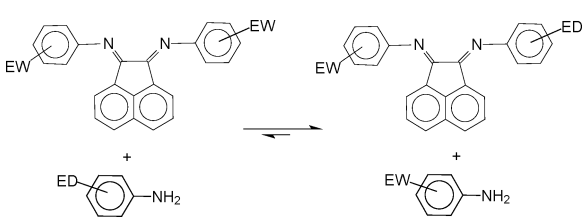
Received (in Durham, UK) 15th February 2006, Accepted 8th May 2006
First published as an Advance Article on the web 6th June 2006
DOI: 10.1039/b602257j

Ring strain is normally associated with increased reactivity and decreased stability of the strained molecule. However, we report here some examples in which the presence of a strained ring causes a stabilization of the molecule, allowing the isolation of some members of a class of otherwise unstable compounds. Alkyl-BIAN (alkyl-BIAN = bis(alkyl)acenaphthenequinonediimine) ligands have been elusive for 70 years. We have investigated the reason for earlier failures and identified it as an isomerization of the initially formed C=N double bond. This isomerization is driven by a release of ring strain in the five-membered ring of the acenaphthene moiety. The use of amines in which the $-NH_2$ group is bound to a quaternary carbon atom cannot be employed to avoid the isomerization because these amines are too sterically encumbered to react at all. However, the use of amines in which the amino group is bound to a strained ring solves the problem, because the isomerization would cause an even larger strain than the one that is released. Cyclopropylamine (Cypr-NH_2) is the ideal amine, no isomerization being observed at all. Cyclobutylamine (Cybu-NH_2) can also be employed, as well as amines in which the strain derives from the presence of a bi- o tri-cyclic system: 2-amino-*exo*-norbornane (Norb-NH_2) and 2-aminoadamantane (Ad-NH_2). The best synthetic procedure involves a transimination reaction from a [$ZnCl_2$(Ar-BIAN)] complex, where Ar contains electron-withdrawing groups, but the direct synthesis from acenaphthenequinone and the amine is also possible in the case of Cypr-BIAN. The structure of [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)][PF_6], [$ZnCl_2$(Cybu-BIAN)], [$ZnCl_2$(Norb-BIAN)] and [$NiBr_2$(Ad-BIAN)], has been determined by X-ray diffraction. Preliminary data indicate that Cypr-BIAN is a much stronger ligand than any Ar-BIAN compound.

Introduction

Compounds of the family Ar-BIAN (Ar-BIAN = bis(aryl) acenaphthenequinonediimine) (Scheme 1) have been known for sometime,[1,2] but have been brought to the general attention only in recent years by Elsevier and his group.[3] Since then, they have found widespread use as ligands especially for palladium, ruthenium and nickel and the corresponding complexes have been employed as catalysts for a wide variety of reactions.[4] For some of these syntheses, the use of the Ar-BIAN ligands was instrumental in achieving the high performance of the catalytic system. With respect to diimine ligands derived from glyoxal or related acyclic diketones, BIAN derivatives are more rigid, this rigidity both imposing the correct geometry for coordination and most of all imparting a high chemical stability both with respect to hydrolysis and rupture of the central C–C bond. The latter is a common problem with most diimine ligands and prevents their use as ligands for many catalytic systems when long catalyst lives are a requisite, as is always the case for industrial applications.

Until recently, ligands of this class were limited to those having two identical aryl rings, each of which could only bear electron-donating or mildly electron-withdrawing substituents. In previous works we have expanded the availability of Ar-BIAN ligands to those having strongly electron-withdrawing substituents on the aryl rings[5] and those bearing two different aryl groups.[6] However, BIAN derivatives having alkyl groups in place of aryl ones have not yet been reported. This is at first sight surprising since imines derived from alkylamines are generally even easier to prepare than those derived from arylamines and bis-alkylimine derivatives of diazabutadiene (R-DAB) are known and easily obtainable. By searching the literature, we found that the earliest



Scheme 1

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† Electronic supplementary information (ESI) available: Characterization data for all new compounds . See DOI: 10.1039/b602257j

investigations of the reactivity of acenaphthenequinone with aliphatic amines dates back 70 years.[7,8] Other works were published later,[9–12] but alkyl-BIAN derivatives were never obtained.[13] In general, a reaction always occurs, but mixtures of products are obtained and the desired bis-imine is never among them. The reactions of acenaphthenequinone with nitrogen nucleophiles have been recently reviewed.[14] A preliminary communication of part of the results here reported has been published.[15]

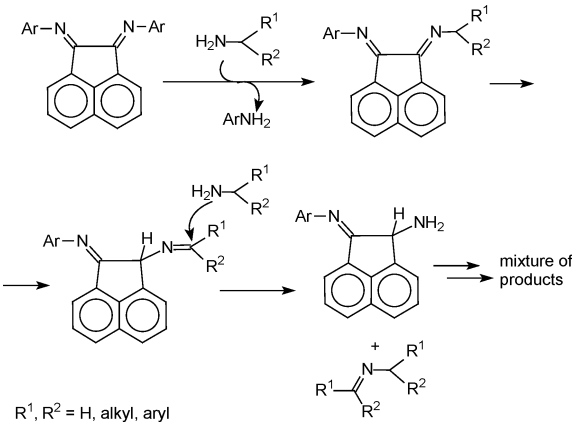
Results and discussion

Identification of the problem

The first possible reason for the failure of obtaining alkyl-BIAN derivatives we considered is the oxidizing power of the quinone itself. Aliphatic amines are oxidized more easily than aromatic ones and this fact may explain the different outcome of the reactions. To bypass the use of the quinone in conjunction with the aliphatic amine we employed the exchange reaction between a pre-synthesized Ar-BIAN and the alkyl amine. Such a kind of reaction, transimination, has been known for more than a century, although it is almost completely neglected in the recent literature.[16] The principle underlying this strategy is that Schiff bases in which the parent amine bears electron-withdrawing substituents are more easily hydrolyzed than those in which the amine bears electron-releasing groups. From a thermodynamic point of view, this implies that the equilibrium between two amines and the corresponding Schiff bases with the same quinone is shifted towards the side of the Schiff base of the more basic amine. We have recently employed this type of strategy to synthesize mixed Ar,Ar′-BIAN derivatives (Scheme 1).[6]

The reaction does not occur under mild conditions in the absence of a promoter, but proceeds easily in the presence of protic or Lewis acids, such as $ZnCl_2$. It should be noted that this transimination reaction can be effected under much milder conditions than the direct synthesis from the quinone, which requires refluxing in acetic acid. Thus it may be useful for the synthesis of BIAN ligands where the aryl moieties contain groups (*e.g.* chiral groups) which cannot withstand the harsh conditions of the direct synthesis from the quinone. Since alkylamines are always much more basic than arylamines, an exchange of the kind shown in Scheme 1 should easily proceed to completion in the case of any alkylamine.

However, when we reacted [$ZnCl_2$(Ar-BIAN)] (Ar = 3,5-$Cl_2C_6H_3$, 4-$O_2NC_6H_4$, 3,5-$(CF_3)_2C_6H_3$, 4-MeC_6H_4) with several alkylamines (RNH_2, R = Cy, Bn, *n*-Bu) at 60 °C (the reaction did not proceed at RT) mixtures of products were obtained, which never contained any detectable amount of the desired alkyl-BIAN. At least one of the by-products is air sensitive, as indicated by a rapid color change when the reaction mixture after a reaction run under a dinitrogen atmosphere was exposed to the air. The identification of some of these products, whose amounts vary when different substrates are employed, is discussed in the following, but a product that is always present and clearly identifiable in the GC-MS spectrum of the solution after the reaction of a generic amine $R^1R^2CHNH_2$ is the imine $R^1R^2C{=}NCHR^1R^2$. The

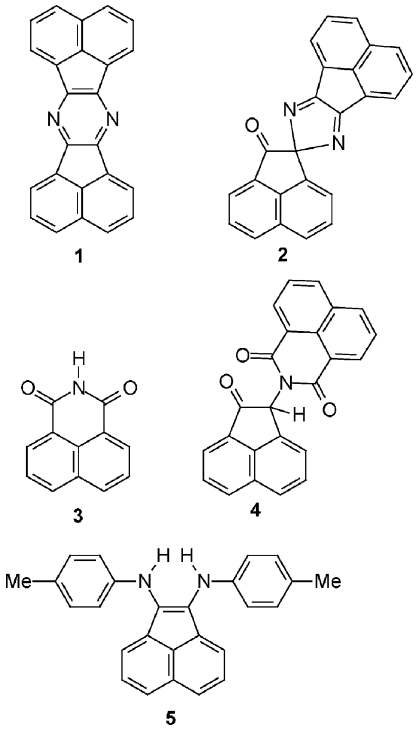


Scheme 2

only reasonable explanation for the formation of these imines is that transimination initially affords the desired $C{=}N{-}CHR^1R^2$ moiety, but this then isomerizes to $CH{-}N{=}CR^1R^2$ and the so formed iminic carbon is involved in a second transimination reaction with the alkylamine to afford the observed $R^1R^2CH{-}N{=}CR^1R^2$ (Scheme 2).

While the work was in progress, we became aware of a series of papers describing early explorations of the reactions of acenaphthenequinone with ammonia[10,17] or aliphatic amines.[9,10] The authors of these papers also observed the formation of *N*-benzyl-benzylideneimine when reacting benzylamine with acenaphthenequinone and proposed an analogous isomerization step. They also proposed that the isomerization was followed by a hydrolysis reaction by the water formed during the reaction between the quinone and benzylamine. Condensation of the so formed benzaldehyde with excess benzylamine would complete the reaction. Transimination reactions were not considered as an alternative, although, in the light of our results, they may also play a role. Tsuge and Tashiro also succeeded in identifying the main acenaphthene-derived product under their conditions as **1** (Scheme 3). Compounds **2–4** were also identified after reactions of acenaphthenequinone with aliphatic amines or ammonia.[9,10,17]

Mass spectral analysis of the solids obtained from our reactions after evaporation of all volatiles also showed the presence of peaks attributable to products **1–4**, although under our conditions **1** was never the dominant product and either **2** or **3** always prevailed. Moreover, the chromatographic separation over alumina (and under a dinitrogen atmosphere) of the product mixture after a reaction performed between [$ZnCl_2$(4-MeC_6H_4-BIAN)] and benzylamine also allowed us to identify compound **5** (Scheme 3) among the products. We had earlier obtained this kind of "reduced BIAN" and its independent synthesis and characterization will be reported in a forthcoming paper. This compound is air sensitive and is oxidized to Tol-BIAN in about one hour when dissolved, or in a few seconds if pure oxygen is bubbled through the solution. Since this process is associated with a color change from blue-violet to orange, the formation of **5** may explain the color change previously mentioned, although other air sensitive compounds may also be present. The formation of **2** from



Scheme 3

the available reagents requires an oxidation to occur at some stage. When the reaction is performed under dinitrogen, Ar-BIAN themselves clearly act as hydrogen acceptors in a quinone–hydroquinone type way. To the best of our knowledge, formation of **5** or related compounds is unprecedented, apart from our unpublished studies. They may find application as components of easily tunable reversible redox-active couples. Minor amounts of other compounds were also isolated or observed by GC-MS, for which only tentative structures can be proposed. Since it was not our aim to characterize all of the numerous by-products of these reactions, the nature of these compounds was not investigated any further. The important point is that the isomerization reaction is the starting point of all following transformations and the reason for the failure to obtain the alkyl-BIAN derivative. Ar-BIAN compounds cannot give this reaction and are thus stable.

The most obvious way of avoiding this isomerization would be to employ an amine lacking any hydrogen atom on the carbon atom α to nitrogen. However, all attempts to condense *tert*-butylamine or 1-aminoadamantane with acenaphthenequinone either directly or by a transimination procedure failed. No reaction was observed with acenaphthenequinone even under drastic conditions. Transimination also did not occur under mild conditions and when we attempted to effect the exchange of 1-aminoadamantane with [$ZnCl_2$(3,5-$Cl_2C_6H_3$-BIAN)] under drastic conditions (160 °C, in an autoclave), the initial Ar-BIAN was liberated and a colorless solid was isolated, showing no signals in the aromatic region of its ^{1}H NMR spectrum and having an elemental analysis close to the one calculated for [$ZnCl_2$(1-aminoadamantane)$_2$]. Thus, this kind of amine appears to be too sterically hindered to form alkyl-BIAN derivatives and this strategy cannot be employed to solve the problem. A deeper understanding of the source of the problem is needed.

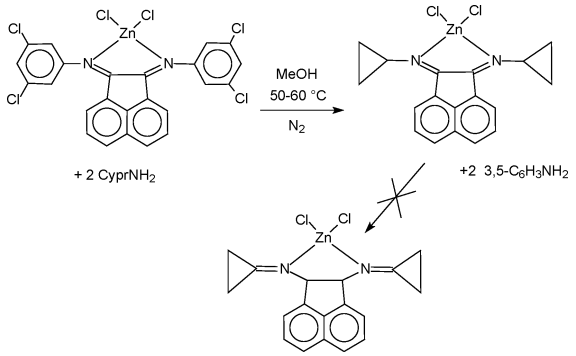
Solution of the problem

An isomerization of the kind shown in Scheme 2 can in principle occur during the synthesis of most imines, but is apparently not a problem in the synthesis of R-DAB (R-DAB = dialkyldiazabutadiene) or related ligands, most likely because during the isomerization the conjugation between the two double bonds is lost and the process is thus thermodynamically unfavorable. In the case of benzylamine, conjugation of the isomerized double bond with the phenyl group may limit this enthalpy increase, but this does not appear to be a major point in the reactions of acenaphthene derivatives, since *n*-$BuNH_2$ and $CyNH_2$ behaved in the same way as benzylamine and lack this possible stabilization.

We deemed the reason for the high efficiency of the isomerization reaction under examination is to be found in the strain of the five-membered ring of all BIAN-type ligands (and even of the parent quinone). Five-membered rings are usually little strained because the ideal angle for a sp^3 hybridized atom (109.5°) is very close to that of a regular pentagon (108°), although repulsion between the substituents deforms the ideal geometry. However, all five carbon atoms of the nitrogen-bearing ring of a BIAN ligand are sp^2 hybridized and the ideal angle for a sp^2 carbon is 120°, a very unfavorable situation, also taking into account that this ring has no aromatic stabilization. Isomerization of the imine double bond rehybridizes one (or two, if the process occurs on both imine groups) of the ring carbons from sp^2 to sp^3, thus partly releasing this hybridization-induced ring strain. The energy gain so obtained apparently overwhelms the loss due to the interruption of the conjugation between the two double bonds.[18]

If we are correct in identifying strain release as the initial cause of the isomerization, than the solution is to employ an amine such that isomerization would eventually lead to a "total" final strain even higher than the one that is released. The ideal amine from this point of view is cyclopropylamine, since isomerization would generate an sp^2 carbon atom on a three-membered ring and this is very unfavorable for what we mentioned before on ideal angles. It should be noted that ring strain is a complex phenomenon[19–23] and other contributions apart from the bond angles must be considered for a quantitative treatment of the problem. However, a simplified approach is sufficient for most of the points discussed in this paper. The approach was successful and the desired complex was obtained by transimination without any detectable amount of isomerized product or of compounds deriving from ring opening of the three-membered ring (Scheme 4).

Since [$ZnCl_2$(Cypr-BIAN)] is almost insoluble in methanol, simple filtration of the suspension after the reaction gave the complex in essentially quantitative yield. Washing with hot methanol afforded the analytically pure yellow complex in a 95% isolated yield. The free ligand can then be obtained by treating the zinc complex with sodium or potassium oxalate in a CH_2Cl_2–H_2O biphasic system, following the protocol already described by us for Ar-BIAN derivatives.[5] However,



Scheme 4

since Cypr-BIAN is more strongly coordinated to $ZnCl_2$ than any of the Ar-BIAN ligands, use of a saturated solution of oxalate is advisable, instead of only a slight excess over stoichiometry. The free ligand is obtained as a colorless, analytically pure solid in an 80% isolated yield.

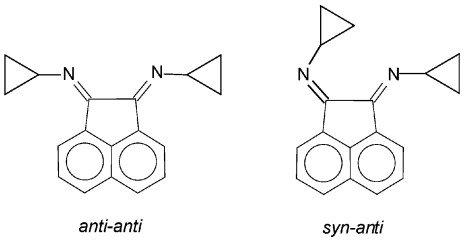
That the isomerization and not the experimental conditions is responsible for previous failures to obtain alkyl-BIAN derivatives is indicated by the fact that Cypr-BIAN can be obtained almost quantitatively even from the quinone and the amine in the presence of molecular sieves (in methanol, at 60 °C, in a closed vessel), although some product is lost in the purification (see the Experimental section). The presence of $ZnCl_2$ is not required.

The colorless nature of Cypr-BIAN is noteworthy. All Aryl-BIAN ligands are colored, the color ranging from yellow for the derivatives with electron-withdrawing substituents to red for 4-$MeOC_6H_4$-BIAN and acenaphthenequinone itself is yellow.

Much has been written about strained systems in organic chemistry.[19–24] Strained systems are generally considered to be more reactive than their non-strained analogues and this increase in reactivity is employed as a synthetic tool. The present is a very rare case in which strain is employed to inhibit an unwanted decomposition which occurs with any unstrained group. It should be noted that it has long been known that SN1 substitution reactions on cyclopropyl derivatives are slower than those on unstrained molecules.[25] However, we are not aware of any case in which this effect has been developed into a synthetic tool to prepare otherwise unstable molecules.

The ^{1}H NMR spectrum of the [$ZnCl_2$(Cypr-BIAN)] complex (in $CDCl_3$) shows a symmetrical structure. In particular, the =N–C*H* protons give a unique signal (an apparent septuplet, implying that the coupling constants to the four CH_2 cyclopropyl protons are very similar). Once the ligand is decomplexed, two isomers are observable in solution, one of which maintains the symmetrical structure, whereas the other shows two different signals for the =N–C*H* protons and for the protons of the two halves of the acenaphthene moiety. In general, two isomers can exist in solution for diimine compounds of this kind, the *syn–anti* and the *anti–anti* ones (Scheme 5).

In the case of Ar-BIAN ligands, the *syn–anti* isomer is usually not present or is present only in small amount,[3,6] but the related compounds derived from camphorquinone show both isomers.[3] Moreover, isomerization appears to be easy for



Scheme 5

Ar-BIAN derivatives, but is very slow for Cypr-BIAN, taking days at room temperature to reach equilibrium. The two isomers are even detected as two peaks in the GC-MS analysis, despite the fact that they are eluted at 250 °C. Both peaks show in the mass spectrum the same parent peak and very similar fragmentation patterns. The slower *syn–anti* isomerization rate of alkyl-substituted Schiff bases with respect to aryl-substituted ones has precedents.[26] The ratio between the two isomers after the decomplexation varied from preparation to preparation in an unpredictable way, but the *syn–anti* isomer always predominated (typically in a roughly 2 : 1 ratio). In one case we obtained the pure *syn–anti* isomer, which then isomerized to a mixture of the isomers even in the solid state over several weeks, but we never observed the *anti–anti* isomer pure from the other isomer. The assignments of all the signals in the ^{1}H NMR spectrum of the mixture of the two Cypr-BIAN isomers (except for the individual resonances of the CH_2 protons of the cyclopropyl rings) was possible by COSY and NOESY experiments and the results are reported in Table S1 (ESI†), together with other relevant NMR data.

Despite the fact that the presence of two cyclopropyl rings may be supposed to allow for new decomposition pathways based on the opening of these strained rings, Cypr-BIAN is extremely stable. When a methanol solution of this ligand was heated at 170 °C for 2 h (a 10 bar CO pressure was also applied to avoid the boiling of the solvent) a light red color developed, but the ^{1}H NMR spectrum of the residue after solvent evaporation only showed the presence of the starting material, with just a small change in the relative amount of the *syn–anti* and *anti–anti* isomers being detected, indicating that decomposition is negligible even under these forcing conditions.

We have recently introduced a method to measure the relative coordination strength of a chelating nitrogen ligand based on the position of an equilibrium reaction in which the tested ligand displaces Ph-BIAN from a complex.[5,6,27] When we applied our protocol, employing [Pd(Ph-BIAN)(DMFU)] (DMFU = dimethylfumarate) and [Pd(3,5-$Me_2C_6H_3$-BIAN)$(OAc)_2$] as representative complexes, very slow reactions were observed relative to those of previously tested ligands. While exchange reactions of [Pd(Ph-BIAN)(DMFU)] are usually complete in less than 1 h at RT, the exchange reaction with Cypr-BIAN continued to evolve for at least two days (eqn (1)).

$$\mathrm{Pd(Ph\text{-}BIAN)(DMFU)} + \mathrm{Cypr\text{-}BIAN} \underset{20\,^\circ\mathrm{C}}{\overset{\mathrm{CDCl_3}}{\rightleftharpoons}} \mathrm{Pd(Cypr\text{-}BIAN)(DMFU)} + \mathrm{Ph\text{-}BIAN} \quad (1)$$

During such a long time, a small amount of decomposition products was observed, so that a reliable K_{eq} value cannot be

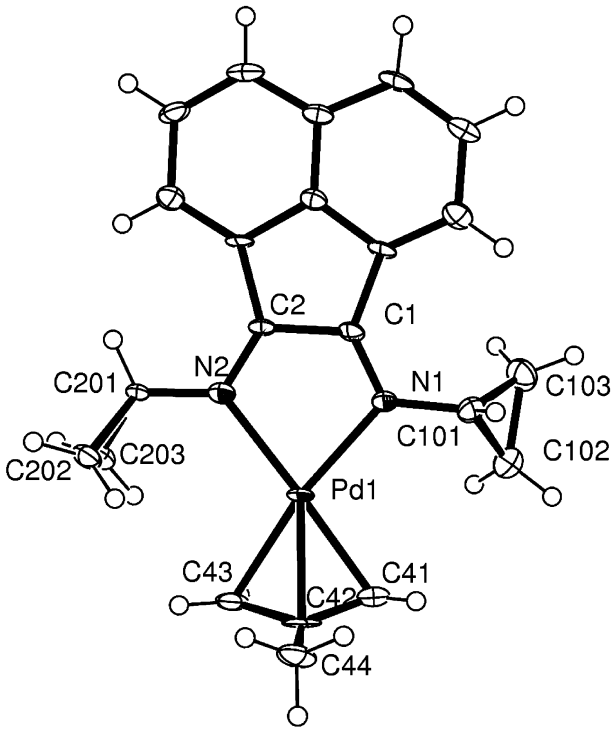


Fig. 1 ORTEP drawing of the cationic part of [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)][PF_6]. Ellipsoids are shown at the 50% probability level.

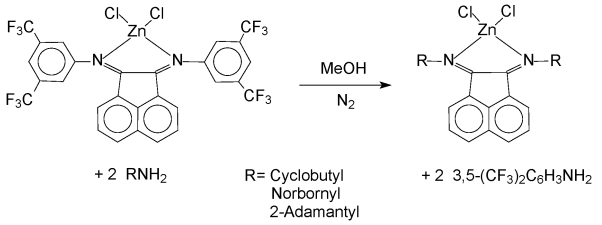
given. However, a lower limit $K_{eq} > 200$ can be estimated, which makes Cypr-BIAN a much stronger ligand than any Ar-BIAN compound ($0.077 \leq K_{eq} \leq 6.85$) and stronger even than phenanthroline ($K_{eq} = 66.4$).[5] In the case of [Pd(3,5-$Me_2C_6H_3$-BIAN)$(OAc)_2$], the reaction was so slow that not even an approximate value can be given. The slow reaction rate is only partly due to the presence of the *syn–anti* form, which needs to isomerize to the *anti–anti* form to coordinate the metal, because even the latter reacts slowly. Thus the new ligand appears to be thermodynamically very strong, but kinetically slow, two features that must be taken into account in planning its possible applications.[28]

A palladium π-allyl complex of Cypr-BIAN, [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)][PF_6], has been synthesized and its structure was determined through single crystal X-ray diffraction‡ (Fig. 1, see below for further discussion).[15]

Other amines

Now that "hybridization induced strain" has been identified as both the cause and a possible remedy for the instability of "usual" alkyl-BIAN compounds, other molecules can be designed which may be stable, keeping in mind that strained rings can be present not only in 3 or 4-membered cycles, but also in bi- or tricyclic molecules. To test the feasibility of this approach we selected three commercially available amines, cyclobutylamine (Cybu-NH_2), *exo*-2-aminonorbornane

‡ CCDC reference numbers 243009, 278714–278716. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602257j



Scheme 6

(Norb-NH_2, bicyclic) and 2-aminoadamantane (Ad-NH_2, tricyclic). Initial attempts employing the direct reaction of acenaphthenequinone with the amine in the presence of molecular sieves, under the same conditions successfully applied to the synthesis of Cypr-BIAN, were disappointing. Although the desired product was formed, isomerization processes analogous to those observed for unstrained amines also occurred in a competitive way. Transimination from [$ZnCl_2$(3,5-$Cl_2C_6H_3$-BIAN)], as employed for Cypr-BIAN, also failed to give pure compounds, at least in part because the low solubility of this complex requires long reaction times. However, during our studies on the synthesis of mixed Ar,Ar′-BIANs, we had found that [$ZnCl_2$(3,5-$(CF_3)_2C_6H_3$-BIAN)] is a more convenient starting material for transimination reactions, being both more activated and much more soluble in methanol than its chlorinated analogue.[6] By using this complex as a reagent, [$ZnCl_2$(alkyl-BIAN)] complexes could be obtained in high yields and purities by simple filtration of the reaction mixture for all of the three mentioned amines (Scheme 6).

The X-ray crystal structures of [$ZnCl_2$(Cybu-BIAN)] and [$ZnCl_2$(Norb-BIAN)] have been solved and are shown in Figs. 2 and 3, respectively.‡ They are described in a later paragraph. The structure of [$ZnCl_2$(Ad-BIAN)] was also solved, but due to the poor crystal quality, it is not reported. A few structural

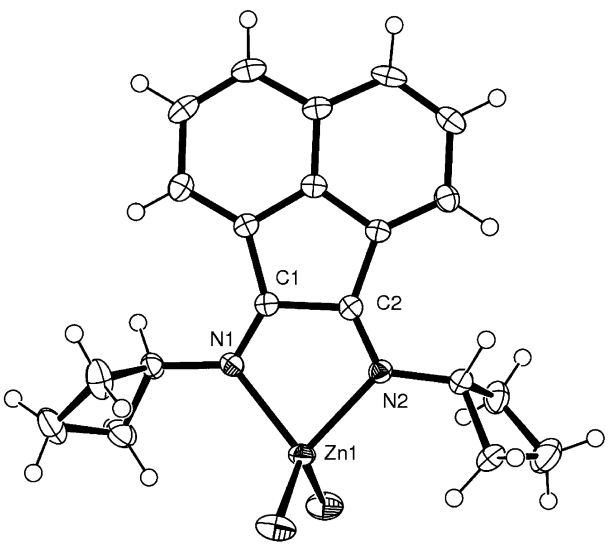


Fig. 2 ORTEP drawing of [$ZnCl_2$(Cybu-BIAN)]. Ellipsoids, for non-H atoms, are drawn at the 50% probability level.

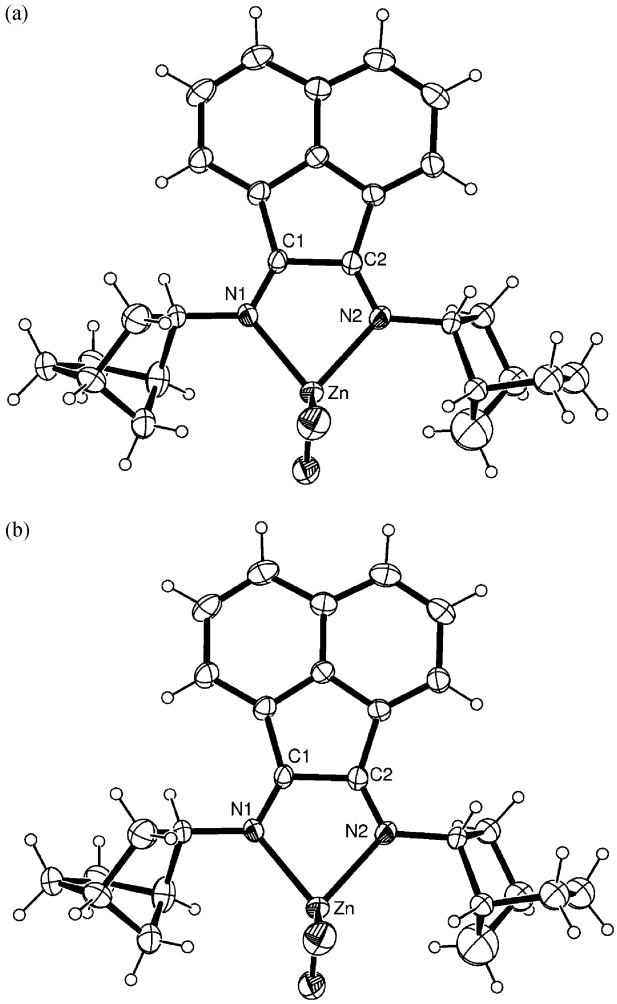


Fig. 3 (a) ORTEP drawing of [$ZnCl_2$(*meso*-Norb-BIAN)]. Ellipsoids are drawn at the 30% probability level. (b) ORTEP drawing of [$ZnCl_2$(R-Norb-BIAN)]. Ellipsoids are drawn at the 30% probability level.

features of this compound are mentioned in the Experimental section.

The free ligands can be obtained from the corresponding zinc complexes with the same procedure described for Cypr-BIAN, however, contrary to Cypr-BIAN, they are not indefinitely stable in solution. Cybu-BIAN is the least stable and starts to decompose in solution after a few minutes. A red color initially develops and then disappears in a few hours. GC-MS analysis immediately after decomplexation shows the presence of a peak with the expected m/z value as the overwhelmingly dominating product, but this peak gradually fades and after a few hours it completely disappears. Several new peaks are observed, the dominant one being attributable to naphthalimide on the basis of its fragmentation path. The condensation product of $CybuNH_2$ with cyclobutylketone is also observed, which was not initially present and indicates that the usual isomerization has occurred.

The most stable of the three new compounds is Ad-BIAN. After a $CDCl_3$ solution of this compound had been left to stand overnight at RT, a red color developed, but the ^1H NMR spectrum was indistinguishable from that of the freshly prepared, colorless, solution, indicating that the highly colored decomposition product had been formed only in very small amounts. This relative stability allowed the attribution of the most characteristic ^1H NMR signals by bidimensional spectroscopy. As for Cypr-BIAN, two isomers were detected, but in this case the *syn–anti* isomer strongly prevailed and only a small amount of the *anti–anti* isomer could be detected. Norb-BIAN appears to have an intermediate stability, but its decomposition in solution was fast enough that an unequivocal attribution of its numerous ^1H NMR signals could not be achieved.

The reason for the stability of the complexes and instability of the free ligands has not been investigated in depth, but apparently coordination induces an additional thermodynamic preference for the initial compound with respect to the isomerized one. This is most likely due to geometric constraints. Indeed, isomerization of only one C=N bond of any alkyl-BIAN ligand would increase the distance between the two nitrogen atoms, making the chelation less effective. A concerted isomerization of both C=N double bonds, on the other hand, is statistically unlikely.

The reason for the low stability of Cybu-BIAN may appear surprising, but it is in line with other results reported in the literature. No data are available for the cyclobutylamine–cyclobutylimine couple, but the data on the methylcyclobutane–methylenecyclobutane and methylcyclopropane–methylenecyclopropane couples show that the introduction of an sp^2 hybridized carbon atom in the four-membered ring causes an increase in strain energy much lower than in the case of the three-membered one.[21,22]

The decomposition of the free ligands in solution is not an absolute limit to their applicability. Indeed, it is possible to coordinate the free ligand to a new metal immediately after the decomplexation, before it has the time to rearrange. This approach was tested by treating a freshly prepared Ad-BIAN solution with [$NiBr_2$(DME)] (DME = dimethoxyethane), obtained by suspending $NiBr_2 \cdot 2H_2O$ in dimethoxyethane and refluxing it in the presence of trimethylorthoformate, as reported in the literature.[29] By this way, [$NiBr_2$(Ad-BIAN)] was obtained in fair unoptimized yields. The paramagnetic nature of the complex prevented its characterization by NMR, but single crystals of it were grown and its structure solved by X-ray diffraction (Fig. 4). The $NiBr_2$ moiety has been selected because nickel complexes with sterically hindered bis-imines as ligands are active catalysts for ethylene polymerization.[30]

Even if Norb-BIAN is less stable than Ad-BIAN the following experiment was performed. The complex [$ZnCl_2$(Norb-BIAN)] was decomplexed in the usual way and the obtained solution was immediately evaporated to dryness. The solid was redissolved in methanol and to this solution was added a solution of $ZnCl_2$ in ethylene glycol. A solid immediately started to precipitate, whose ^1H NMR spectrum was indistinguishable from that of the starting complex, showing that no contamination had occurred in the process. Complex [$ZnCl_2$(Norb-BIAN)] was isolated in a 72% yield with respect to its initial amount, indicating that Norb-BIAN can also be employed in the synthesis of other complexes, provided reaction times are short.

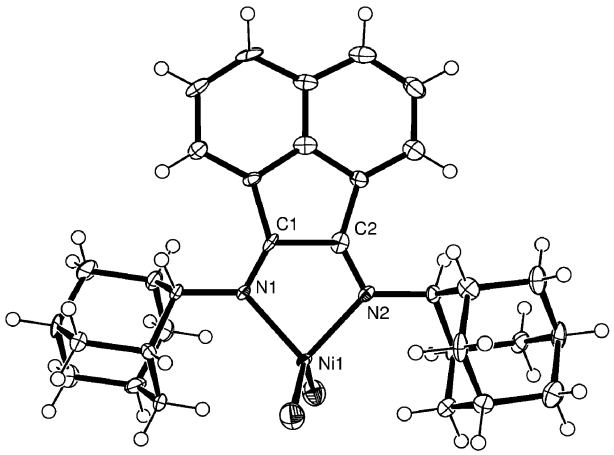


Fig. 4 ORTEP drawing of [$NiBr_2$(Ad-BIAN)]. Ellipsoids are drawn at the 50% probability level.

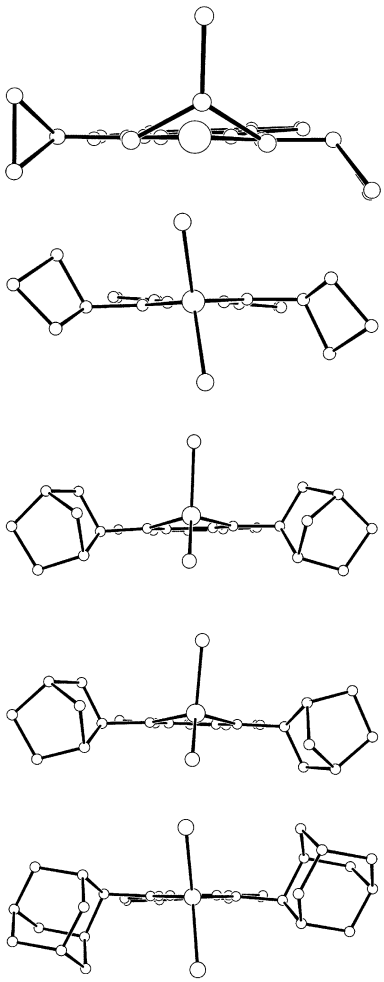


Fig. 5 A view perpendicular to the acenaphthene planes for all the complexes characterized by single crystal X-ray diffraction. From top to bottom: [Pd(Cypr-BIAN)(C_4H_7)][PF_6], [$ZnCl_2$(Cybu-BIAN)], [$ZnCl_2$(*meso*-Norb-BIAN)], [$ZnCl_2$(R-Norb-BIAN)], and [$NiBr_2$(Ad-BIAN)]. This allows one to grasp the "non-orthogonality" of the MX_2 planes and the C_s/C_2 pseudo-symmetries of the molecules. Note also the envelope arrangement of the metallacyclopentane ring (Zn–N1–C1–C2–N2) in [$ZnCl_2$(Norb-BIAN)].

Structural characterization of the complexes

The crystal structures of [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)][PF_6], [$ZnCl_2$(Cybu-BIAN)], [$ZnCl_2$(Norb-BIAN)] and [$NiBr_2$(Ad-BIAN)][CH_2Cl_2] have been determined by single crystal X-ray diffraction (see Figs. 1–4).‡

The geometry of [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)]$^+$ (Fig. 1) is clearly different from the other molecules and comparable, instead, with the previously reported Ar-BIAN Pd(allyl) complexes,[6] sharing with them some structural features: the plane of the three allylic carbons is not perpendicular to the acenaphthene (67.3° here); the methyl substituent at the central atom of the allylic group is bent towards the metal; the two external carbons of the allyl group lie approximately on the same plane as the BIAN (see also Fig. 5). The coordination at the metal is quite distorted from a regular square plane (the N1–Pd1–N2 angle is 79.5(2)°, C41–Pd1–C43 is 68.0(2)°) also because of the short Pd–C42 distance (2.160(5) Å).

In the Zn and Ni complexes, the coordination at the metal is approximately tetrahedral, although the MX_2 (M = Zn, Ni; X = Cl, Br) and the acenaphthene planes are not strictly orthogonal and the X–M–X and N–M–N angles significantly deviate from the ideal 109° (much larger the former, much smaller the latter). The distortion from symmetry is due to the conformations adopted by the alkyl substituents which affect the coordination of the halogens at the metal site. In principle, we could expect four possible conformations of the bulky alkyl groups that could be accommodated: (a) on the side of the metal, (b,c) above or below the acenaphthene plane (this distinction holds only for the Pd(allyl) complex); (d) on the side of the BIAN skeleton. Conformation d is quite unlikely because the rigidity of the BIAN would not allow such a high steric hindrance and, in fact, it is not observed even for the smaller groups.

In [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)]$^+$, the two cyclopropyls adopt conformations a and c (C201–C203 and C101–C103, respectively, see Fig. 1). Because they afford different instabilities at the metal (conformation a produces more hindrance), the Pd–N2 distance is significantly longer than Pd–N1 (2.156(4) *vs.* 2.106(4) Å), that induces, in turn, an asymmetric coordination of the allyl group (Pd–C43 is 2.144(5) Å, while Pd–C41 is 2.099(5) Å).

In both [$ZnCl_2$(Cybu-BIAN)] and [$NiBr_2$(Ad-BIAN)] the alkyl groups adopt the intermediate a/b and a/c conformations leading to pseudo C_2 geometries (the root mean square deviations from ideal symmetry are 0.12 and 0.14 Å, respectively). This causes severe distortion from orthogonality of the MX_2 and acenaphthene planes (79.4° and 86.7°, respectively), as evident from Fig. 5. An even larger deviation from orthogonality (*ca.* 73°) is observed for [$ZnCl_2$(Ad-BIAN)], whose structure (quite similar to that of $NiBr_2$ analogue) is however not reported here, because the low quality of crystals did not allow refinement of a satisfactory model (see also experimental details). Due to the pseudo two-fold arrangements, no particular distortion is observed for the BIAN–metal coordinations, which respect the ideal symmetry, see Table 1.

Table 1 Comparison of selected geometrical parameters in the four complexes whose structures were characterized by X-ray diffraction. M = Pd, Zn or Ni. X = Cl, Br. Standard uncertainties are reported in parentheses

	[Pd(Cypr-BIAN)(C_4H_7)][PF_6]	[$ZnCl_2$(Cybu-BIAN)]	[$ZnCl_2$(Norb-BIAN)]	[$NiBr_2$(Ad-BIAN)]
M–N1	2.106(4) Å	2.081(2) Å	2.093(5) Å	2.035(5) Å
M–N2	2.156(4) Å	2.085(2) Å	2.096(5) Å	2.035(5) Å
M–X1	—	2.218(7) Å	2.224(2) Å	2.349(1) Å
M–X2	—	2.214(8) Å	2.194(2) Å	2.346(1) Å
N1–C1	1.287(6) Å	1.282(3) Å	1.279(7) Å	1.267(8) Å
N2–C2	1.295(6) Å	1.278(3) Å	1.270(7) Å	1.289(8) Å
C1–C2	1.496(7) Å	1.526(3) Å	1.530(8) Å	1.530(9) Å
N1–C101	1.443(6) Å	1.466(3) Å	1.488(7) Å	1.489(8) Å
N2–C201	1.414(6) Å	1.457(3) Å	1.473(7)[a] Å	1.490(8) Å
N1–M–N2	79.5(2)°	81.73(8)°	81.4(2)°	84.4(2)°
X1–M–X2	—	119.61(3)°	116.27(8)°	130.52(5)°
BIAN–MX1X2[b]	—	79.5°	86.4°	85.5°

[a] The two disordered norbornyl groups bound to N2 are modeled sharing the pivotal carbon atom. [b] The angle between the plane of the acenaphthene and that formed by the metal and the two bonded halides. No standard uncertainty is available for this parameter.

A separate discussion is necessary for [$ZnCl_2$(Norb-BIAN)]. The starting amine is chiral but not enantiomerically resolved, therefore two kinds of complexes can be produced: one chiral (having (*R*,*R*) or (*S*,*S*) pairs of stereocenters in the alkyl groups) and one *meso* (*R*,*S*). Surprisingly, the only crystalline species identified is actually a mixture of the two forms (present in almost the same amount in the single crystal used for the X-ray analysis). Because the asymmetric unit contains a single molecule, a disorder is implied in the crystal structure, where one of the two norbornyl is modeled by two distinct and chirally opposed groups (each having *ca.* 50% occupancy). Because the phase is centrosymmetric, the actual content is approximately 50% *meso*, 25% (*R*,*R*) and 25% (*S*,*S*). Both the *meso* and the chiral forms adopt conformations of type a for the norbornyl groups, which implies an almost C_s symmetry for the *meso* complex (r.m.s. deviations of 0.18 Å) but a non-symmetric conformation for the chiral species (quite far from the idealized C_2 symmetry) because the metallacyclopentane ring (Zn–N1–C1–C2–N2) has an envelope type conformation, see Fig. 5. This is probably due to some intermolecular interactions impinging asymmetrically on the $ZnCl_2$ moiety (for example, four C–H–Cl contacts shorter than 2.9 Å are found for one of the two Cl atoms but not for the other). A molecular justification would be less convincing given that the same geometry is shared by both forms without any evidence of disorder at the metal site.

The conformations adopted by all the alkyl groups are influenced not just by the balance of intramolecular steric repulsions but also by the crystal packings. In [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)]$^+$ the cyclopropyl C201–C203 cannot assume the conformation c (the most stable in an isolated molecule) because it is hampered by a symmetry related molecule, while in solution (at RT) the compound appears to be symmetric on the ^{1}H NMR timescale. In the other complexes, the room available for the alkyl group is larger (for example, [$NiBr_2$(Ad-BIAN)] co-crystallizes with CH_2Cl_2 solvent) and therefore the most stable conformations are always observed.

Inspecting Table 1, we can appreciate that the C1–C2, N1–C101 and N2–C201 bonds of [Pd(Cypr-BIAN)(η^3-$CH_2C(CH_3)CH_2$)]$^+$ are somewhat outlying. However, an investigation of the Cambridge Structural Database[31] shows that shorter distances of substituents at a cyclopropyl carbon are quite common; in particular, in C(cyclopropyl)–N=C moieties the mean C(cyclopropyl)–N distance is 1.442(5) Å, quite in agreement with our observation. This is certainly caused by the weaker C–C bond within the cyclopropyl ring, responsible for a slight elongation of the N1–C1 and N2–C2 bonds and a shortening of C1–C2. Anyway, it is quite clear that in the Pd(Cypr-BIAN) system more extensive conjugation occurs with respect to BIANs bearing the other, less strained, (poly)rings.

Details of the X-ray single crystal diffraction analyses are reported in the experimental section and are summarized in Table 2.

Conclusions

In this work we have shown that strained systems can impart stability, instead of instability, when included in a more complex system in cases where the decomposition would generate an additional strain in the already strained moiety. This principle is clearly not limited to the synthesis of alkyl-BIAN compounds and not even to organic chemistry in general. For example, many transition metal alkylamido and alkoxo complexes are unstable because of easy β-hydrogen elimination. Use of strained amines and alcohols should inhibit this last reaction and may constitute an entrance to a new chemistry of this type of complex. Attempts in this direction are in progress. Chiral substituted cyclopropylamines have also been reported in the literature and attempts are also in progress to prepare their corresponding chiral BIAN ligands.

Experimental

General procedures

The synthesis of the ligands was generally performed under a dinitrogen atmosphere, but the decoordination reactions were always performed in air. Methanol was dried over $Mg(OMe)_2$ and distilled before use in the transimination reactions. [$ZnCl_2$(3,5-$Cl_2C_6H_3$-BIAN)] and [$ZnCl_2$(3,5-$(CF_3)_2C_6H_3$-BIAN)] were prepared as previously described.[5] [Pd(Ph-BIAN)(DMFU)][32] and [Pd(3,5-$(CH_3)_2C_6H_3$-BIAN)$(OAc)_2$],[5] and [$NiBr_2$(DME)] were synthesized as reported in the literature.[29] [Pd(Cypr-BIAN)(η^2-$CH_2C(CH_3)CH_2$)][PF_6] was

Table 2 Crystallographic data for the four crystalline systems investigated by X-ray diffraction analysis[a]

Compound	[Pd(Cypr-BIAN)(C_4H_7)][PF_6][b]	[$ZnCl_2$(Cybu-BIAN)]	[$ZnCl_2$(Norb-BIAN)]	[$NiBr_2$(Ad-BIAN)][CH_2Cl_2]
Molecular formula	[$C_{22}H_{23}N_2Pd$][PF_6]	[$C_{20}H_{20}Cl_2N_2Zn$]	[$C_{26}H_{28}Cl_2N_2Zn$]	[$C_{31}H_{36}Br_2N_2Ni$][CH_2Cl_2]
Temperature	120(2) K	120(2) K	298(2) K	150(2) K
Wavelength	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 8.6005(14) Å	a = 7.2312(8) Å	a = 9.3088(6) Å	a = 11.321(1) Å
	b = 13.217(2) Å	b = 16.204(2) Å	b = 15.4380(9) Å	b = 11.743(1) Å
	c = 18.918(3) Å	c = 15.981(2) Å	c = 15.9947(9) Å	c = 13.758(1) Å
				α = 103.925(2)°
	β = 91.575(4)°	β = 91.205(2)°	β = 99.803(2)°	β = 108.377(2)°
				γ = 108.885(2)°
Volume	3149.65(7) Å^3	1872.1(4) Å^3	2265.0(2) Å^3	1518.0(2) Å^3
Reflections for unit cell	1024	1024	1024	1024
Z, calculated density	4, 1.75 g cm^{-3}	4, 1.507 g cm^{-3}	4, 1.480 g cm^{-3}	2, 1.645 g cm^{-3}
Absorption coefficient	1.002 mm^{-1}	1.602 mm^{-1}	1.337 mm^{-1}	3.474 mm^{-1}
Crystal size	0.4 × 0.2 × 0.1 mm	0.2 × 0.2 × 0.1 mm	0.1 × 0.1 × 0.05 mm	0.1 × 0.1 × 0.05 mm
Crystal color	Yellow	Yellow	Yellow	Yellow
Diffractometer	SMART CCD	SMART CCD	SMART CCD	SMART CCD
No. of frames, time per frame	2400, 30 s	1800, 20 s	1800, 30 s	2400, 30 s
θ range of the data collection	1.8 to 35.7°	2.5, 30.2°	2.4, 23.3	1.7, 23.3°
Reflections collected/ unique	20 251/3804	18 167/5132	19 002/3258	13 979/4360
R_{int}	0.0669	0.0507	0.0885	0.0662
Data/restraints/parameters	3804/0/302	5132/0/226	3258/28/305	4360/0/361
Goodness-of-fit on F^2	1.09	1.00	1.060	1.022
Final R indices	R_1 = 0.0467,	R_1 = 0.0377,	R_1 = 0.0486,	R_1 = 0.0469,
[$I > 2\sigma(I)$]	wR_2 = 0.1179	wR_2 = 0.0760	wR_2 = 0.1100	wR_2 = 0.1080
Largest diff. peak and hole	1.3 and −1.9 e Å^{-3}	0.40 and −0.47 e Å^{-3}	0.52 and −0.45 e Å^{-3}	0.73 and −0.93 e Å^{-3}

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(mean)|/\Sigma F_o^2$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GoF $= \{S/(n-p)\}^{1/2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. [b] This structure has already been described in the preliminary communication of this work (CDS REF CODE YANKUU).[15]

prepared by the same procedure previously described for related complexes with other BIAN ligands.[6] All other organic reagents were commercial products and were used as received. Equilibration experiments for the determination of the relative coordination strength of Cypr-BIAN were performed as previously described,[5,27] integrating the ^{1}H NMR signal for the proton on the carbon atom α to the nitrogen one of the free (both isomers) and coordinated Cypr-BIAN. NMR spectra were recorded under N_2 on a Bruker Advance 300 DPX, operating at 300 MHz for ^{1}H, at 75 MHz for ^{13}C and at 282 MHz for ^{19}F, at 20 °C. The ^{1}H NMR signals of the compounds described in the following have been attributed by COSY and NOESY techniques. Assignments of the resonances in ^{13}C NMR spectra were made using the APT pulse sequence and HSQC technique, at 20 °C. IR spectra were recorded on a Bio-Rad FTS-7 spectrophotometer. GC-MS analyses were performed on a Shimadzu GCMS-QP5050A instrument, equipped with an Equity 5 column. Elemental analyses and mass spectra of high boiling substances were recorded in the analytical laboratories of Milan University.

Characterization data for all new compounds are reported in the ESI.†

Synthesis of Cypr-BIAN

(a) By transimination. Given the low boiling point of cyclopropylamine (49–50 °C) and the absence of any reaction at room temperature, the reaction had to be performed either in an autoclave, under 10 bar N_2, or, more conveniently in a vessel closed with a Teflon valve, of the kind commonly employed to store dry deuterated solvents. A 1.5 molar excess of cyclopropylamine over the stoichiometric amount is sufficient to shift completely the reaction towards the side of the cyclopropyl derivative. To a 50 cm^3 vessel, as described above, was added [$ZnCl_2$(3,5-$Cl_2C_6H_3$-BIAN)] (1.00 g, 1.65 mmol). The flask was evacuated and filled with dinitrogen three times after which cyclopropylamine (0.35 cm^3, 4.96 mmol) and dry methanol (20 cm^3) were added. The flask was closed and heated at 60 °C for 12 h in an oil bath. Both the starting and final complex are very little soluble in methanol, but the exchange was anyway complete in the given time. The yellow solid was collected by filtration in the air and was suspended in methanol at 50 °C to remove colored impurities, after which [$ZnCl_2$(Cypr-BIAN)] was collected by filtration again and dried *in vacuo* (623 mg, 95% yield).

The compound so obtained was suspended in CH_2Cl_2 (100 cm^3) in a separating funnel and a saturated sodium oxalate solution (20 cm^3) was added. Shaking was continued until the yellow foamy solid which initially formed at the interface completely dissolved. The organic phase was separated, dried with sodium sulfate and evaporated *in vacuo* to give the analytically pure colorless product (344 mg, 80% overall yield).

(b) By direct reaction of acenaphthenequinone and cyclopropylamine. To a 50 cm^3 vial with a Teflon valve, of the kind commonly used to store dry deuterated solvents, were added

acenaphthenequinone (547 mg, 3.00 mmol) and 3 Å molecular sieves (about 2.5 g). The vial was evacuated and filled with dinitrogen three times, after which cyclopropylamine (624 µl, 9.00 mmol) and dry methanol (20 cm^3) were added. The vial was closed and heated at 60 °C in an oil bath for 7 h with occasional swirling. Acenaphthenequinone was only partly soluble at the beginning of the reaction, but a clear yellow-orange solution was formed during the heating time. The solution was filtered by the aid of a cannula and the molecular sieves washed with methanol (2 × 5 cm^3). The combined solutions were evaporated *in vacuo*, the resulting solid was almost completely dissolved in refluxing heptane (20 cm^3) and the solution was filtered while hot by the aid of a cannula. Upon cooling the product precipitated out as almost colorless needles, which were collected by filtration and washed with cold hexane (2 × 3 cm^3). 524 mg, 2.01 mmol, 67.0% yield. The so obtained Cypr-BIAN is analytically pure and melts at the same temperature (111 °C) as the perfectly pure compound, but still contains very small amounts of impurities, as evidenced by a pale yellow color. A colorless material (with the same mp) can be obtained by a further recrystallization from heptane. The initial heptane solution and hexane washings were evaporated *in vacuo*. The yellow solid so obtained mostly contains additional Cypr-BIAN, but is not analytically pure. It is pure enough to be employed in most synthetic applications or can be recrystallized again to afford more analytically pure product.

Synthesis and decomplexation of [$ZnCl_2$(Cybu-BIAN)]

To a 100 cm^3 Schlenk flask under nitrogen were added [$ZnCl_2$(3,5-$(CF_3)_2C_6H_3$-BIAN)] (1.00 g, 1.35 mmol) and methanol (25 cm^3). The suspension was heated at 50 °C until all the complex dissolved, after which it was cooled to room temperature. CybuNH_2 (0.58 cm^3, 6.75 mmol) was added and the solution heated again at 45 °C. Precipitation of a yellow solid started after 15 min, but the reaction was run for 14 h at the same temperature. The analytically pure solid was separated by filtration on a Buckner funnel, washed with methanol (5 cm^3) and dried first in air and then under vacuum. 420 mg, 73.3% yield. Crystals suitable for the X-ray diffraction study were grown in air, dissolving the compound in hot (about 150 °C) nitrobenzene and letting the solution slowly cool in the oil bath.

To eliminate the $ZnCl_2$ moiety, the complex (50 mg, 0.118 mmol) was suspended in CH_2Cl_2 (10 cm^3) in a separating funnel. A saturated aqueous potassium oxalate solution (15 cm^3) was added and the biphasic mixture vigorously shaken until the solid completely dissolved. The organic phase was initially colorless, but after a few minutes took a violet color and after 1 h was colorless again. Analysis of the solution by GC-MS immediately after decomplexation only showed a peak associated with the mass of the intact Cybu-BIAN (m/z = 288).

Synthesis and decomplexation of [$ZnCl_2$(Norb-BIAN)]

The reaction was performed as described for [$ZnCl_2$(Cybu-BIAN)], starting from [$ZnCl_2$(3,5-$(CF_3)_2C_6H_3$-BIAN)] (1.33 g, 1.80 mmol), norbornylamine (1.03 cm^3, 8.99 mmol) and methanol (30 cm^3), heating at 45–50 °C for 16 h. 655 mg, 72% yield. Crystals suitable for the X-ray diffraction study were grown in air, dissolving the compound in hot (about 160 °C) nitrobenzene and letting the solution slowly cool in the oil bath.

To eliminate the $ZnCl_2$ moiety, the complex (100 mg, 0.198 mmol) was suspended in CH_2Cl_2 (20 cm^3) in a separating funnel. A saturated aqueous potassium oxalate solution (20 cm^3) was added and the biphasic mixture vigorously shaken until the solid completely dissolved. The organic phase was dried with Na_2SO_4, filtered and evaporated *in vacuo*. The initially colorless solution became violet during the evaporation. The obtained solid is dark violet. When the solid was redissolved in CH_2Cl_2 and the solution analyzed by GC-MS, a peak was observed corresponding to Norb-BIAN (m/z = 368), but accompanied by other peaks, including the Schiff base of norbornylamine with norbornanone (m/z = 203).

In another experiment, [$ZnCl_2$(Norb-BIAN)] (200 mg, 0.396 mmol) was treated as described above. The violet solid was dissolved in methanol (15 cm^3) under dinitrogen and a solution of $ZnCl_2$ (81.0 mg, 0.594 mmol) in ethyleneglycol (5 cm^3) was added to this. The solution was stirred at room temperature for 3 h, during which time a solid precipitated, whose ^{1}H NMR was identical to that of the starting [$ZnCl_2$(Norb-BIAN)] (144 mg, 72.0% yield).

Synthesis and decomplexation of [$ZnCl_2$(Ad-BIAN)]

To a 50 cm^3 Schlenk flask under dinitrogen was added 2-aminoadamantane hydrochloride (980 mg, 1.33 mmol), CH_2Cl_2 (10 cm^3) and methanol (10 cm^3). The latter was added in order to help the solubilization of the starting material, which was not completely soluble in CH_2Cl_2. Then CaH_2 (500 mg, 1.19 mmol) was also added and the mixture stirred at RT overnight. The obtained suspension was filtered with the aid of a cannula and the solution evaporated *in vacuo* in another Schlenk flask under dinitrogen. To this were added [$ZnCl_2$(3,5-$(CF_3)_2C_6H_3$-BIAN)] and methanol (20 cm^3). Heating at 50 °C was continued for 15 h, during which time a yellow precipitate formed, which was collected by filtration and washed with methanol (5 cm^3). 560 mg, 72.1% yield. Part of the solid was treated with $K_2C_2O_4$ as reported for [$ZnCl_2$(Norb-BIAN)]. The dark violet solid was stable enough to be characterized by ^{1}H NMR and mass spectrometry (see ESI†). It is worth noting that the compound turned back to colorless when dissolved in $CDCl_3$, although the solution was not stable for prolonged periods of time and became red after several hours.

Synthesis of [$NiBr_2$(Ad-BIAN)]

A sample of Ad-BIAN was prepared as described above, starting from [$ZnCl_2$(Ad-BIAN)] (132 mg, 0.226 mmol) and immediately dissolved in CH_2Cl_2 (20 cm^3) under dinitrogen. To a separate Schlenk flask under dinitrogen, were added [$NiBr_2$(DME)] (58.0 mg, 0.189 mmol) and methanol (5 cm^3). After the complex was dissolved, the Ad-BIAN solution was added to this flask and the solution stirred at room temperature for 5 h, during which time a brown solid precipitated, which was separated by filtration under dinitrogen and washed with methanol (5 cm^3), affording the analytically pure

compound. 46 mg, 37% yield. No attempt was made to improve the yield by further workup of the filtered solution. Crystals of [$NiBr_2$(Ad-BIAN)][CH_2Cl_2] suitable for the X-ray diffraction study were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex.

Single crystal X-ray analysis

The X-ray diffraction instrument used for the experiments described below was a Bruker SMART CCD 1000 diffractometer, equipped with an Oxford Cryosystem liquid-N_2 cryostream (600 series). The generator was working at 45 kV and 40 mA. Mo-Kα radiation from fine focus sealed tubes, 0.5 mm collimation, was used. All crystals were mounted in air on a glass fiber fixed on top of a goniometer head and then positioned in the goniometer center. Results of each data collection and crystal structure determination are given in Table 2.

The raw intensities, integrated with SAINT[33] were corrected for crystal anisotropies by SADABS[34] and a spherical absorption correction was then applied. Structures were solved using direct methods with SIR97[35] and refined with SHELX-97[36] (within the WINGX[37] package) based on full-matrix least squares against F^2. For [$ZnCl_2$(Norb-BIAN)] and [$NiBr_2$(Ad-BIAN)][CH_2Cl_2], the low intensity of high order data suggested the use of only reflections of resolution higher than 0.9 Å in the refinement. Anisotropic temperature factors were assigned to all atoms except hydrogens, which were always treated as riding on their carbon atoms. For [$ZnCl_2$(Norb-BIAN)], a disorder between two forms (the *meso* and the chiral one) was detected (see the text). Atoms involved in the disordered part of the structure were treated with isotropic thermal factors. One of the two norbornyl groups can in fact be modeled by applying the superposition of two chirally opposed groups, having relative occupancies of 55% and 45%.

The crystal form of [$NiBr_2$(Ad-BIAN)] contains solvent molecules of clathrated CH_2Cl_2 and no alternative pseudo-polymorph was detected during the X-ray analysis. The study of [$ZnCl_2$(Ad-BIAN)] revealed the much lower quality of the crystals, but could anyway afford some information (although we do not report the crystal structure because of the much poorer agreement factor, $R_1 \sim 0.16$). [$ZnCl_2$(Ad-BIAN)] crystallizes very likely without solvent molecules (the small empty volume found, 21 $Å^3$ per unit cell, is not enough to host solvent molecules). Therefore, the lattice constants of [$ZnCl_2$(Ad-BIAN)] correspond to a slightly modified triclinic unit cell that actually transforms into a monoclinic *C* centered cell (a = 13.741(2), b = 11.279(2), c = 18.488(3) Å, β = 107.616(6)°).

Acknowledgements

We thank S. Morelato for experimental assistance, Prof. S. Cenini for helpful discussion and the MIUR (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, PRIN 2005035123) for financial support.

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