Synthesis of the Elusive *bis*(4-carboxyphenylimino)acenaphthene Ligand and of its Palladium Dichloride Complex

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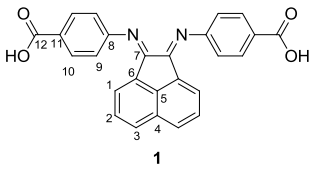
Abstract: The title *bis*-imine appears to be ideally suited to be employed in the preparation of MOFs and other advanced materials, but its synthesis has not been reported in the literature. The solution to the problems that likely originated this and the crystal structure of a palladium complex are reported.

Introduction

Nitrogen-donor ligands plays an important role in homogenous catalysis. Among the various class of N-ligands, *bis*-imines have been largely studied in combination with transition metals for a plethora of reactions. In this regards, our group has worked for many years on the synthesis of new and diverse types of *bis*-imines derived from the acenaphthenequinone scaffold (named R-BIAN in the literature).[1] In these compounds, the central acenaphthene moiety both imparts rigidity to the molecule and increases its stability against hydrolysis and central C-C bond rupture. These features have proved instrumental to get high activity and stability of the corresponding catalysts in a number of reactions, such as the selective semihydrogenation of alkynes[2] and allenes,[3] the allylic aminations of olefins by nitroarenes in the presence of CO,[4] the synthesis of pyrroles and oxazines from dienes, nitroarenes and CO,[5] and the reduction of nitroarenes to anilines by CO/H_2O[6]. In addition, they have shown to be useful in the field of olefin polymerization[7] and copolymerization[8] reactions, where other kind of *bis*-imines can also be applied.

A limit of all the catalytic systems cited above, lies in the difficulty in their separation and recycle at the end of the reaction. The problem is clearly an intrinsic disadvantage of homogeneous catalysts and to solve it, the whole area of supported catalysts has been developed. Different approaches have been used to immobilize homogeneous catalysts onto heterogeneous supports and gain the benefits of both. However, the exact structure of the catalytically active site becomes less defined in most cases. Metal-organic frameworks (MOFs) are a class of solids that can join the insolubility of inorganic supports with the molecular precise structure of single molecules. Initially reported examples employed MOFs in which the catalytically active centers were proposed to be the same metal atoms that played the role of nodes in the crystalline structure.[9] More recently, many ditopic "linkers" having different groups to coordinate the catalytically active metal and to bind to the metal-based node have been developed.[10] In this context, to the best of our knowledge, no MOF has been reported in the literature in which the linker contains a *bis*-imine as an additional coordination site. This is likely due to the fact that most *bis*-imines are flexible and the most stable conformation has the lone pairs on the two nitrogen atoms pointing in opposite directions, making the ligand unsuitable for chelation. Since carboxylic groups are known to be especially suited to generate stable MOFs,[11] a logical target for a bifunctional R-BIAN ligand suitable for the synthesis of a catalytically active MOF should be a molecule with free carboxy groups pointing in the proper directions.

Given what said above, it was an obvious choice to us to target the synthesis of the BIAN ligand **1**, named in the following HOOC-C_6H_4-BIAN (Scheme 1).



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Scheme 1. Structure and atoms numbering of HOOC-C_6H_4-BIAN (**1**).

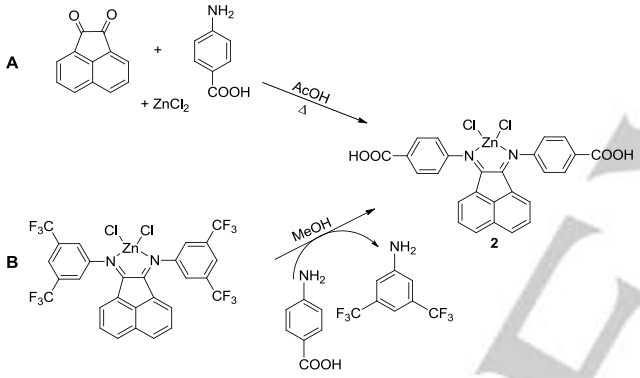
It is worth of note that the carboxylic moiety is also the functional group most commonly employed to link coordination compounds to TiO_2 and other supports used in optoelectronic applications. Thus **1** could be used for the preparation of advanced materials with applications in different fields. The optoelectronic properties of several Ar-BIAN complexes have already been described.[12]

The synthesis of this ligand is apparently trivial, but it proved to be more difficult than expected. A direct procedure to **1** has not been reported in the literature yet, although we are aware of one case in which an iridium complex of **1** has been described. However, the complex was not obtained starting from the free

ligand, but a complex having methyl ester groups on the ligand was first isolated and the ester was subsequently hydrolyzed while the ligand remained coordinated.[13] Although the synthesis was successful, this is clearly not a general strategy because *bis*-imines are themselves prone to hydrolysis and the procedure would result in decomposition of the ligand in many cases.

Results and Discussion

The most general procedure to prepare a wide variety of Ar-BIAN derivatives consists in preparing the [(Ar-BIAN)$ZnCl_2$] complex by reacting acenaphthenequinone and the desired amine in acetic acid in the presence of dry $ZnCl_2$,[14] followed by zinc removal. The zinc salt both acts as a Lewis acid and helps shifting the condensation equilibrium to the right by forming a complex insoluble in acetic acid.[1g] The method usually gives a pure compound that is soluble enough in $CDCl_3$ to record a ^1H NMR spectrum in this solvent. For the preparation of **1**, the reaction in Scheme 2A was repeated several times by changing the reactant ratios, the reaction time and the washing procedure, but an analytically pure compound was never obtained.



Scheme 2. Synthesis of [(HOOC-C_6H_4-BIAN)$ZnCl_2$] (**2**): A) by direct condensation; B) by transimination.

In general, some acetic acid seems to remain in the product. Heating the solid in acetic acid reproducibly afforded a solid with an elemental analysis closely matching that expected for a 1:1 complex: AcOH ratio. The same ratio was confirmed by ^1H NMR analyses. Suspending the complex in THF allowed to remove all acetic acid, but some THF remained in the solid instead, as evidenced again by NMR. However, NMR data were apparently not consistent with the formation of a complex only contaminated by solvent molecules. The complex is insoluble in most NMR solvents due to the strong interactions between carboxylic groups of different molecules and is only well soluble in DMF and DMSO. A typical ^1H NMR spectrum of the product of the reaction in DMSO-d^6 is shown in Figure 1.

The spectrum clearly shows the presence of some solvent molecules in the aliphatic region and of the carboxylic proton at almost 13 ppm. The most intense signals in the aromatic region are typical for compounds of the expected type. However, the minor signals have no obvious explanation. A COSY spectrum showed that the additional signals couple to each other, but not to the main signals, supporting the idea that they are due to a different species.

Despite all different variations in the synthetic procedure, the "impurities" were always present in approximately the same amount. This feature made us to think that the two species may be in equilibrium with each other. However, the only equilibrium that may reasonably occur for this complex involves the deprotonation of the carboxy group by dimethyl sulfoxide. Acid-base equilibria are usually fast on the NMR timescale, but can be relatively slow in DMSO, so that separate signals for H_2O and HDO can be observed in this solvent. Thus two sets of signals for the protonated and deprotonated species may be observed.

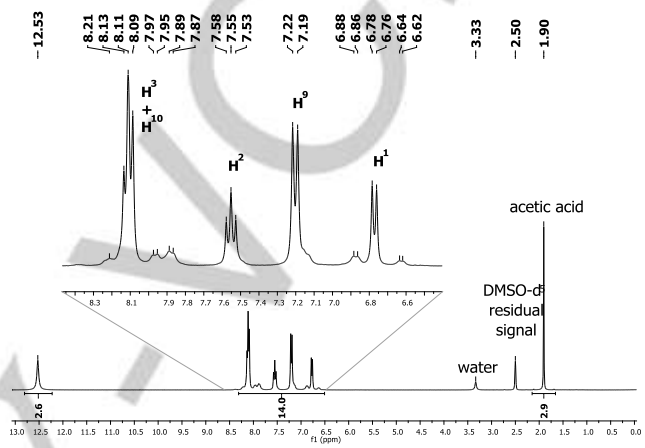


Figure 1. ^1H NMR spectrum of crude **2** in DMSO-d^6.

To test this hypothesis, a series of NMR spectra were recorded while adding increasing amounts (1, 3, 5, 10 equiv. with respect to the complex) of triethylamine (Figures S1 and S2, Supporting Information).

The aliphatic region of the spectrum (Figure S2a) immediately makes it clear that the idea that the proton exchange may be slow in this system is wrong, at least when a base is present. The intensity of the signals for the CH_3 and CH_2 protons increases as the amine amount increases, as it should obviously be, whereas the position of the signals moves at the same time from a position intermediate to that expected for $[HNEt_3]^+$ to one closer to that of non-protonated Et_3N (0.93 and 2.43 ppm in DMSO-d_6)[15] but two sets of signals for the two forms of the base are not observed. The signal for the residual hydrogen atoms of DMSO is stable at 2.50 ppm, further proving that DMSO is not involved in any protonation equilibrium. As far as the signals of the BIAN molecule are concerned, the one that is most affected is that due to the aryl protons closer to the amino group, followed by that of the aryl protons closer to the carboxy group. Among the signals of the acenaphthene moiety, the H^1 protons are affected to a small extent, whereas the position of the other signals is virtually unchanged. Most importantly, the signals for the "impurities" also resent of the presence of the base in a similar way, but never disappear or merge with those of the main species, indicating that the two are not connected by a simple protonation-deprotonation equilibrium. This conclusion will also be relevant in the following, when another hypothesis will be presented.

To test if the different signals were due to a different aggregation of the molecules in solution, such as the reversible formation of dimers or higher aggregates, a DOSY experiment was made,

employing a solution of [(4-$MeOC_6H_4$.BIAN)$ZnCl_2$] as a surely "monomeric" reference with a similar molecular volume in a coaxial tube. Only one species was observed, with a molecular volume similar to that of the reference, implying that aggregation equilibria are also not the cause for the observation of the other set of signals.

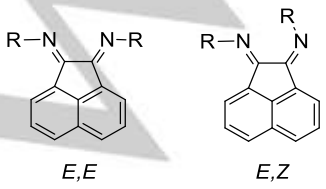
To test if the problem of the presence of a second compound could be solved by a different synthetic strategy, we employed the transimination reaction between another BIAN complex and aminobenzoic acid (Scheme 2B). Such strategy takes advantage of the solubility of [(3,5-$(CF_3)_2C_6H_3$-BIAN)$ZnCl_2$] in methanol, where most related complexes are insoluble, and of the tendency of more electronrich amines to replace amines with strongly electronwithdrawing groups.[1e] The synthesis was successful, but the usual extra signals were still present.

At this stage, we decided to proceed with the removal of the coordinated zinc anyway, in the hope that the problem would not be present in the free ligand.

It was originally reported that free Ar-BIAN can be obtained by refluxing the zinc complex in ethanol in the presence of Na_2CO_3.[14a, 14c] However, hydrolysis of the ligand can occur when electronwithdrawing groups are present on the aryl groups. Years ago, we developed a more efficient protocol to this aim, which involves suspending the complex in CH_2Cl_2 and treating with a potassium oxalate aqueous solution. Zinc is either precipitated as zinc oxalate or remain dissolved in the aqueous phase as $[Zn(C_2O_4)_2]^{2-}$, while the free ligand dissolves in the organic phase.[1g, 4b, 6c] This has now become the standard procedure in the literature. However, in the present case the complex was completely insoluble in CH_2Cl_2 and the method could not be applied as such. The lowest polarity solvent in which the complex is soluble is DMF, which however is miscible with water, so that a biphasic protocol cannot be operated with this solvent only. To overcome to this problem, we performed a series of test under different condition employing a DMF/CH_2Cl_2 mixture, which is partly, miscible with water, followed by a series of extractions and back extractions with $CHCl_2$ and water. The best procedure (See Experimental) reproducibly afforded a product whose elemental analysis is indicative of compound containing chlatrated water, in a mol ratio ligand/water = 3:1.

The ligand after decomplexation is still insoluble in most solvents, slightly soluble in THF and well soluble only in DMF and DMSO, so that NMR studies were again performed in the last solvent.

Quite surprisingly, the ^{1}H NMR spectrum of the free ligand is virtually indistinguishable from that of the zinc complex, "impurities" included. Coordination to zinc would be expected to shift all signals, even if a shift so small to be undetectable is not impossible. In the case of the free ligand, however, the presence of a second series of signals can have a different explanation, that would not be possible for the complex, that is the presence of two isomers, *E,E* and *E,Z* (Scheme 3), often called in the literature *anti-anti* and *syn-anti.*



Scheme 3. Isomers of non-coordinated R-BIANs.

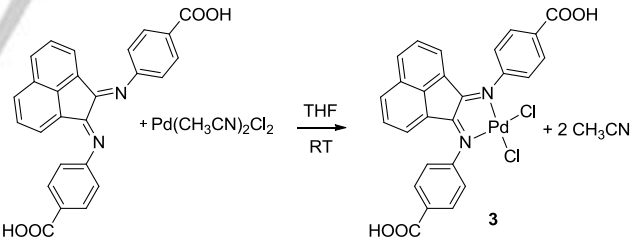
In most cases, the *E,E* isomer is the only observable one in solution for Ar-BIANs,[16] but in some cases a minor amount of the other isomer is also detectable. Interconversion of the two isomers is slow at room temperature on the ^{1}H NMR timescale.

To test if the two isomers may be responsible for the two sets of signals, a variable temperature ^{1}H NMR study was undertaken. The spectra at increasing temperature show indeed a coalescence of the signals of the two isomers, which is almost complete at 120 °C (see the Supporting Information). A ^{1}H NMR spectrum recorded at RT after the higher temperature series was identical to the starting one, proving that the coalescence of the signals is not due to a decomposition process.[17]

At this stage, we suspected that the reason for the almost coincidence of the spectra of the complexes and decomplexed ligand may simply be that they are indeed the same species and DMSO is a strong enough ligand for zinc to displace the BIAN ligand from it. To prove this unequivocally, we run a second series of spectra at different temperatures on the zinc complex. A comparison of the two series shows that the room temperature spectrum and all those at higher temperature are identical to the first series of spectra. Such a correspondence cannot be coincidental. Indeed, DMSO displaces the BIAN ligand from zinc and the "impurities" that could not be eliminated are simply the *E,Z* isomer. Such a behavior was not expected because DMSO has been employed as solvent for many other studies of different BIAN complexes and we are not aware that such a displacement has been reported before.[18]

The observed NMR signals were therefore assigned to specific protons by bidimensional NMR experiments. Integration of the NMR signals also allowed determining that the *E,E*/*E,Z* ratio in DMSO solution at RT is 80:20.

With the ligand in our hands, we prepared its $PdCl_2$ complex, **3**, by reacting a solution of **1** in THF with a solution of [$Pd(CH_3CN)_2Cl_2$] in the same solvent (Scheme 4).



Scheme 4. Synthesis of [(HOOC-C_6H_4-BIAN)$PdCl_2$] (**3**).

The complex was characterized by NMR and by X-ray diffraction on a single crystal obtained by slow diffusion of diethyl ether vapors into a DMF solution of the complex. In this case, no displacement of palladium from the ligand by DMSO was observed, at least over several hours, and the NMR signals are clearly shifted downfield upon palladium coordination.

The complex co-crystallizes with DMF and diethyl ether and all crystals were found to be twinned. The crystal structure belong to the *triclinic* P-1 space group and the twinning occurs along a diagonal (0 1 -1) direction with respect to the standard orientation settings chosen for the structure solution. Nevertheless, the quality of the crystal structure determination is quite good which enables a pretty accurate analysis of the molecular geometry.

Despite the molecule may feature a mirror or a twofold rotational symmetry, the molecule in the crystal is asymmetric (Figure 2).
The coordination at the Pd atom is square planar, with just minor deviations from perfect planarity (the plane containing the two Cl atoms and Pd is tilted by ca. 7° with respect to the entire BIAN skeleton or 5.4° with respect to the N-Pd-N plane). The conformation of the ligand is obviously *E,E* and the phenyl rings of the carboxylic groups are almost perpendicular to the BIAN plane (both featuring an angle of ca. 81°).

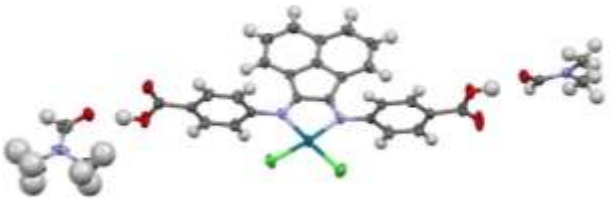


Figure 2. Ortep drawing of [**3**][DMF]$_2$[Et$_2$O]. The diethyl ether molecule is removed for clarity.

The relative conformation of the carboxylic groups is *anti*, which makes the molecular geometry pseudo-C_2, instead of pseudo-C_s. Both carboxylic groups form medium strength hydrogen bonds with the DMF molecules (the two O---O distances are 2.585(5) and 2.618(5) Å). On the other hand, the diethyl ether molecule is more weakly embedded in the crystal structure, lacking of any significant intermolecular interaction with the complex or the other co-crystallized molecules.
The Pd-Cl distances are 2.268(2) and 2.2269(2) Å, which is within the expected range for this kind of bonds.
The Pd-N distances (2.048(4) and 2.039(4) Å) are in keeping with typical BIAN coordination ranges. The same holds true for the C-N (1.288(6) and 1.287(6) Å) and C-C (1.494(7)) distances, in agreement with the electronic configurations reported above.

Conclusion

The apparently trivial synthesis of **1** presents several problems that justify why this ligand has not been reported previously despite its obvious interest. Solution of these problems allowed proving that its complexes can be obtained in a pure form and can be employed as starting materials for the preparation of catalytically active ditopic MOFs or other advanced materials for optoelectronic applications. The latter indeed is also a field in which BIAN ligand with carboxy groups may find applications, especially taking into consideration that techniques to get BIAN ligands with two different aryl groups are known [1e].

Supporting Information Summary

Details for the experimental procedures, 1D and 2D NMR spectra and crystallographic data are included in the supporting information

Acknowledgements

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Keywords: bis-imine • ditopic ligand • bridging ligand; coordination compound • palladium

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[16] The relative stability can be different for Alkyl-BIAN ligands, where the *E,Z* isomer may prevail see ref. 1b, 1c and J.A. Moore, K. Vasudevan, N.J. Hill, G. Reeske, A.H. Cowley, *Chem. Commun*., **2006**, 2913-2915.

[17] Although no decomposition was observed on the timescale of the NMR experiment, prolonged heating of the ligand in dry DMSO caused its decomposition with formation of acenaphthenequinone and a compound whose ^{1}H NMR signals are consistent with those expected for the sulfonylimine $Me_2S{=}NC_6H_4COOH$. We did not study this process in more detail, but prolonged heating in DMSO is discouraged.

[18] It may be surmised that since DMSO removes zinc from the ligand, no need exists for adding a complexing agent to get the free ligand. However, attempts to precipitate the ligand from the DMSO solution also containing $ZnCl_2$ by the addition of either water or isopropanol resulted in the precipitation of a material that does contain zinc and that is insoluble even in DMSO. Whether this material is a MOF or not is under investigation, but it is clear that displacement of zinc from the BIAN ligand by DMSO is easily reversible.

Entry for the Table of Contents

Some tricky problems in the synthesis of the BIAN derivative having two carboxy groups have been solved and a reproducible procedure is reported, which paves the way to the use of the ligand for many advanced applications in material construction and surface-grafted complex preparation. The crystal structure of a palladium complex shows that the carboxy groups have the proper orientation for the applications they were designed for.