

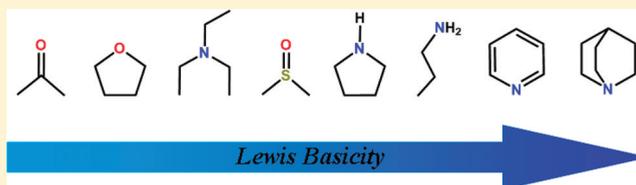
A Lewis Basicity Scale in Dichloromethane for Amines and Common Nonprotogenic Solvents Using a Zinc(II) Schiff-Base Complex as Reference Lewis Acid

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S Supporting Information

ABSTRACT: A consistent, reliable scale of Lewis basicity in dichloromethane for 26 bases, involving amines and nonprotogenic solvents, is presented. A Lewis acidic Zn^{II} Schiff-base complex, involving formation of stable 1:1 adducts is used as reference acid. Evaluation of binding constants is achieved from spectrophotometric titrations, by the least-squares nonlinear regression of multiwavelength spectrophotometric data. This Lewis basicity scale represents a unique set of data reflecting the actual Lewis basicity with respect this “real world” Lewis acidic species. The comparison of present Lewis basicity scale with data reported in the literature indicates that while for the involved solvents their relative basicity is scarcely affected by the reference Lewis acid, in contrast for sterically encumbered amines the Lewis basicity seems to be dependent from the reference species. Thus, Lewis basicity is governed by the steric hindrance at the donor atom and involves very different relative basicities than those predicted considering typical reference Lewis acids. This is expected to have a major involvement in the organic synthesis and catalysis, given the sterically encumbered nature of commonly involved Lewis acidic organometallic complexes.



1. INTRODUCTION

The Lewis theory of acids and bases represents one of most important concepts of modern chemistry, as it allows rationalizing most of the general chemical behavior of these involved species. The Lewis acidity/basicity can be defined as the capability of a species to accept/donate a lone pair of electrons, with formation of an acid–base adduct.¹ It can be referred in the gas-phase or in solvent media; however, its evaluation in solvent media is certainly of relevance for the effective properties and chemical behavior of a species in solution.

The acid/base strength, either in the gas-phase or in solution, cannot be determined by a direct measurement; therefore, it is indirectly referred to the bond strength of the formed adduct. To this end, a variety of methods, including optical UV/vis, IR absorption, fluorescence emission, NMR spectroscopy, electrical conductance, calorimetry, etc. can be found in the literature.^{2,3} Nevertheless, not always the acid–base adduct bond strength deduced from these methods correlates with the Lewis base/acid strength and, hence, to the Lewis acidity/basicity.

Another drawback associated with Lewis acidity/basicity is the choice of the reference Lewis base/acid, to achieve reliable acidity/basicity scales. Actually, as the Lewis acidity/basicity is a relative concept, there are in principle as many possible Lewis basicity scales as there are Lewis acids. It therefore turns out that the definition of a reliable scale of general validity still represents an unsolved issue.²

Although various attempts can be found in the literature about methods capable to establish reliable Lewis basicity scales, two main approaches are commonly involved to estimate Lewis basicity for solvents: the donor number (DN) first

developed by Gutmann in the early seventies,⁴ and reviewed by Jensen in 1978,⁵ and a Lewis basicity scale deduced by Maria, Gal et al. in 1985.⁶ The DN is a quantitative measure of the Lewis basicity and is defined as the negative enthalpy for the 1:1 adduct formation between SbCl₅, used as reference acid, and a Lewis base, both in a dilute solution in the noncoordinating 1,2-dichloroethane solvent. Analogously, Maria, Gal et al. established a solvent Lewis basicity scale in dichloromethane for various nonprotogenic solvents by measuring calorimetrically their enthalpies of complexation with boron trifluoride, representing the archetypical Lewis acid. A further relevant scale of basicity involving diiodine or 1-iodoacetylenes has been compiled by Laurence et al.⁷ in eighties. More recently, an extensive scale of hydrogen bond basicity involving 4-fluorophenol as reference acid, has been developed by Graton, Laurence et al.⁸ However, unlike the previous examples, the resulting hydrogen-bonded complexes can be considered as a special case of Lewis acid–base interactions.²

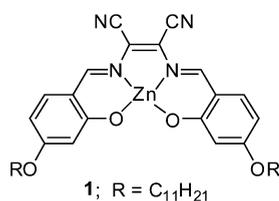
Without bringing into question about the reliability of these basicity scales, they cannot be considered of general validity, as they generally refer to less sterically encumbered reference Lewis acids. On the other hand, a Lewis basicity scale of more general validity should necessarily be referred also to “real-world”, sterically encumbered, Lewis acids, such as most acidic organometallics involved in organic synthesis and catalysis,⁹ excluding of course frustrated Lewis pairs.¹⁰

Received: August 3, 2011

Published: September 28, 2011

Tetracoordinated Zn^{II} complexes, in particular Schiff-base derivatives, are Lewis acidic species^{11,12} capable to saturate their coordination sphere by coordinating a large variety of neutral substrates such as alcohols, carbonyls, and nitrogen-based donor Lewis bases,^{12,13} including various anions.¹⁴

The objective of this contribution is to use for the first time the Lewis acidic Zn^{II} Schiff-base complex, **1**, as reference acid, to build up a reliable Lewis basicity scale in dichloromethane for amines and common nonprotogenic solvents, including ethanol, in the “real world” of most Lewis acidic species. Evaluation of binding constants has been achieved from spectrophotometric titrations, upon formation of **1**·base adducts, in a low-polarity, nonprotogenic solvent medium such as dichloromethane, by the least-squares nonlinear regression of multiwavelength spectrophotometric data.¹⁵



2. RESULTS AND DISCUSSION

2.1. Method. According to the IUPAC definition of the Lewis basicity¹ as “the thermodynamic tendency of a substance to act as a Lewis base”, the development of suitable methods whose “comparative measures of this property are provided by the equilibrium constants for Lewis adduct formation for a series of Lewis bases with a common reference Lewis acid,” become compulsory to achieve reliable basicity scales.

Additionally, some requirements in choosing the reference Lewis acid and the solvent medium should be fulfilled in order to design a suitable method, spectroscopic in our case, which correlates with the base strength and, hence, the Lewis basicity.

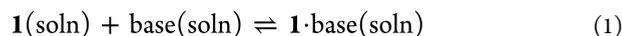
The reference acid should be a sufficient strong Lewis acid, capable to react with most common bases. It should form defined 1:1 adducts, without side reactions, always involving the same spectroscopic variations, thus avoiding specific effects on the acid–base adduct bond strength and, hence, on the Lewis basicity. In other terms, the adduct formation should be not family dependent. A suitable solvent should ensure adequate solubility for the acid/base and the formed adduct and, most important, it should not be involved in specific solvation effects.

It has recently reported that the amphiphilic Zn^{II} Schiff base complex **1** in solution of dichloromethane (DCM) upon addition of a coordinating species, i.e. a Lewis base, leads to the formation of **1**·base (1:1) adducts and involves substantial optical variations. As this process occurs because of the axial coordination to the Zn^{II} ion, it is expected to be sensitive upon Lewis basicity of the coordinating species.¹²

Given its strong Lewis acidic character, hence fast to react with any base in solution of nonprotogenic solvents, dichloromethane in our case, complex **1** fulfils the primary requirement to be an appropriate reference Lewis acid. Moreover, the formation of defined 1:1 adducts, without side reactions, always involving the same UV/vis optical absorption variations, independent from the Lewis base (*vide infra*), avoids specific effects on the acid–base adduct bond strength, and hence upon the Lewis basicity.

Binding constants are then achieved by the least-squares nonlinear regression of multiwavelength spectrophotometric

titrations data,¹⁵ upon formation of the (1:1) **1**·base adducts, involving the following equilibrium:



Therefore, according to the Lewis basicity definition,¹ the calculated binding constants upon eq 1 can properly be related to the relative Lewis basicity of the involved species.

The use of the Zn^{II} complex **1** as reference Lewis acid would allow a better estimation of the Lewis basicity of most Lewis acidic species.⁹ Actually, the complex **1**, in addition to be a sufficient strong Lewis acid leading to stable adducts with any common Lewis base, is a sufficiently hindered molecule so that the formation of adducts will be influenced even of the steric hindrance of the base. Therefore, relative basicity values deduced from this reference Lewis acid will reflect the actual, i.e., effective, basicity with respect this “real world” Lewis acidic species.

2.2. Binding Constants. The complex **1** represents a suitable Lewis acidic system capable of axially coordinating Lewis bases. This binding interaction leads to formation of stable 1:1 adducts, as established by Job’s plot analysis (see the Supporting Information),¹⁶ ¹H NMR spectroscopy, and ESI mass spectrometry.¹² As representative examples, the structure of some **1**·base adducts is reported in the Supporting Information. Moreover, this process is accompanied by appreciable optical absorption variations, therefore it has been investigated on a quantitative ground by means of spectrophotometric titrations, followed by an accurate data analysis¹⁵ to get binding constants. Calculated binding constants for the **1**·base adducts are reported in Table 1.

Table 1. Calculated Binding Constants for the **1**·base Adducts

	Lewis base	log K
2	quinuclidine	6.73 ± 0.03
3	pyridine	6.67 ± 0.03
4	isopropylamine	6.66 ± 0.01
5	<i>n</i> -butylamine	6.35 ± 0.02
6	ethylmethylamine	6.31 ± 0.07
7	propylamine	6.30 ± 0.04
8	<i>tert</i> -amylamine	6.21 ± 0.01
9	piperidine	6.18 ± 0.02
10	isoquinoline	5.92 ± 0.02
11	pyrrolidine	5.8 ± 0.1
12	dimethylethylamine	5.75 ± 0.03
13	diethylamine	5.48 ± 0.02
14	tropane	4.59 ± 0.01
15	quinoline	4.50 ± 0.01
16	DMSO	4.20 ± 0.01
17	DMF	3.55 ± 0.01
18	triethylamine	3.45 ± 0.01
19	diisopropylamine	3.30 ± 0.01
20	aniline	3.08 ± 0.01
21	triisopropylamine	2.89 ± 0.02
22	di- <i>tert</i> -amylamine	2.75 ± 0.02
23	THF	2.46 ± 0.01
24	ethanol	1.83 ± 0.02
25	tris-(2-ethylhexyl)amine	1.61 ± 0.01
26	acetonitrile	1.32 ± 0.03
27	acetone	1.18 ± 0.02

Spectrophotometric titrations of 10 μM DCM solutions of **1** were performed using DCM solutions of the Lewis bases 2–27

as titrants. As representative example, the titration with pyridine is reported in Figure 1. Spectrophotometric titrations of other

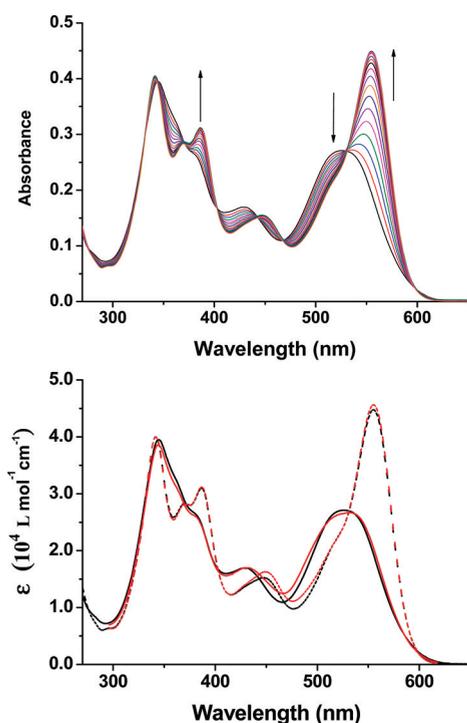


Figure 1. UV/vis absorption (top) titration curves of **1** ($10 \mu\text{M}$ solution in DCM) with addition of pyridine. The concentration of pyridine added varied from 0 to $18.0 \mu\text{M}$. Comparison (bottom) of experimental (black lines) UV/vis absorption spectra for **1** (—) and **1**·pyridine adduct (---) with calculated values (red lines).

prototype bases are reported as Supporting Information. Optical absorption spectra upon titration indicate some absorbance changes in the UV/vis region with the existence of multiple isosbestic points, and an appreciable increase of the absorbance in the region between 530 and 600 nm. Spectrophotometric titrations of all investigated Lewis bases, upon reaching the saturation point, show almost identical optical absorption changes in the region $>330 \text{ nm}$, in terms of intensity, λ_{max} values, and isosbestic points, thus indicating that the coordination of the Lewis base to the Zn^{II} atom similarly affects the low-lying electronic states of **1**. In other terms the formation of **1**·base adducts is not family dependent. Moreover, the existence of multiple isosbestic points in optical absorption spectra upon titration is in agreement with the formation of defined 1:1 adducts.

The almost identical absorptivity values upon comparison of experimental vs calculated optical absorption data for **1** and **1**·base adduct (see Figure 1 and the Supporting Information), indicate the goodness of the least-squares nonlinear regression of multiwavelength spectrophotometric titration data.

2.3. Lewis Basicity. From binding constants for the **1**·base adducts reported in Table 1, it is possible drawing some general trends about relative basicity of the involved species. Within acyclic amines, with exception of the less sterically encumbered secondary ethylmethylamine, primary amines always represent the strongest bases. On the other hand, the basicity of secondary and tertiary amines apparently does not show a regular trend, except if we consider amines having the same alkyl substituent, in this case secondary amines are stronger bases than tertiary

amines. Thus, diethylamine is a stronger Lewis base than triethylamine, and diisopropylamine is stronger than triisopropylamine. Among alicyclic amines, the trend is opposite: the tertiary quinuclidine is a stronger base than the secondary piperidine or pyrrolidine. The tropane is the weaker base within this series.

In general, present data indicate a relative order of the Lewis basicity for acyclic amines, primary $>$ secondary $>$ tertiary, in agreement with the Lewis basicity deduced from the relative enthalpies of formation for some amineborane adducts,¹⁷ or by competition experiments using $\text{B}(\text{Me})_3$ as reference acid,¹⁸ although gas-phase basicities indicate the opposite.^{19,20} This order is, however, inverted, tertiary $>$ secondary \approx primary (acyclic), in the case of alicyclic amines, with exception of tropane, being a bicyclic tertiary amine but having a *N*-methyl.

These comparisons suggest that the relative Lewis basicity of involved aliphatic amines, with respect to the reference Lewis acid **1**, is governed by steric effects, and can be attributed to poorer overlap of orbitals because of the additional steric constraints in the case more encumbered species.²¹ In fact, the less sterically crowded primary amines show the highest, almost unchanging binding constants. The progressively lower binding constant for secondary and tertiary amines parallels the increasing steric hindrance at the nitrogen amine atom. Alicyclic amines, possessing a reduced sterical hindrance, exhibit larger binding constant values. Thus piperidine possesses a binding constant comparable to the ethylmethylamine, the latter of which being the least sterically encumbered species within the series secondary acyclic amines. Finally, quinuclidine, representing the least sterically encumbered tertiary amine,²² exhibits the largest binding constant value, even with respect to primary amines (Table 1). An analogous trend for the relative binding ability of tertiary amines has recently been found in the formation of zinc-salophen amine adducts.^{13b}

The secondary alicyclic piperidine and pyrrolidine amines offer the opportunity for a further comparison, being the former a stronger base. This is in agreement with a larger Lewis basicity predicted on theoretical ground for cyclic amines, and can be related to degree of pyramidalization around the nitrogen donor atom.²³ The larger pyramidalization angle of pyrrolidine leads to a larger *s*-character of the nitrogen lone pair orbital and, hence, to a weaker Lewis basicity.

Prototype heterocyclic amines were also considered. Again, within this series of amines the order of relative basicity, pyridine $>$ isoquinoline $>$ quinoline, can be related to the increasing steric hindrance at the heterocyclic nitrogen. Note that, pyridine is a stronger Lewis base than triethylamine, although gas-phase basicities indicate the opposite.² However, it has been demonstrated that pyridine can displace trimethylamine from $\text{Me}_3\text{N}\cdot\text{BMe}_3$.²⁴ Again, the steric repulsion favor the less encumbered pyridine adduct over the triethylamine analogue.²¹

Among the involved solvents, calculated binding constants indicate that DMSO and DMF are stronger Lewis bases than acyclic tertiary amines and encumbered secondary amines, whereas acetonitrile and acetone represent the weakest bases within the investigated series.

2.4. Comparison with Literature Lewis Basicity Scales. Present Gibbs energy for the **1**·base adducts can useful be compared with relevant scales reported in the literature,^{4–7} although the latter refer to the Lewis affinity,² as they involve enthalpy measurements for the adduct formation.

In the case of the diiodine adducts, however, a comparison with Gibbs energy is possible (Figure 2) from available literature data.²⁵ It shows a roughly linear correlation for most of the

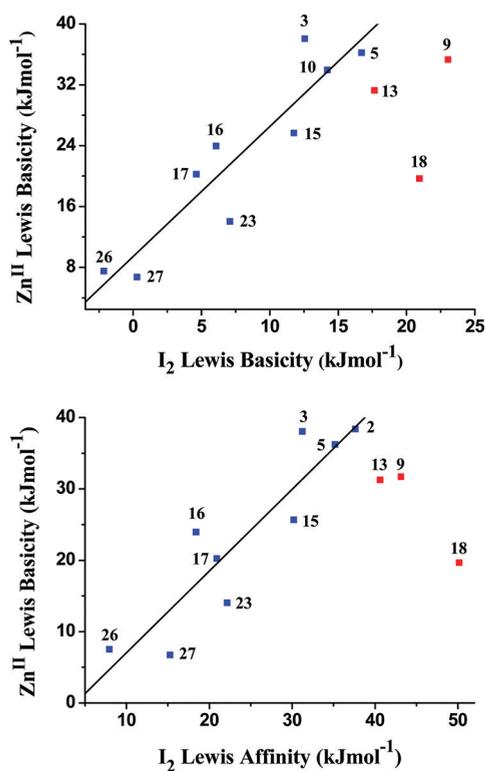


Figure 2. Comparison of Lewis basicity for 1-base adducts and diiodine Lewis basicity (top) or diiodine Lewis affinity (bottom). Diiodine data are from ref 25. Masked data (marked in red) are not included in the linear fit.

involved bases, with Gibbs energy for the 1-base adducts approximately twice than those found for diiodine adducts, thus indicating a stronger acid–base interaction in the former case. A clear divergence of this rough linearity is observed in the case of triethylamine, representing the most encumbered species among the bases involved in this comparison and, to a lesser amount, for the secondary amines 9 and 13. It, therefore, turns out that these amines exhibit a lower Lewis basicity with the reference acid 1 than that with the less sterically encumbered reference Lewis diiodine acid. An essentially analogous trend is observed on comparing Gibbs energy for the 1-base adducts with the enthalpy of formation for the diiodine analogues (Figure 2). Again, triethylamine strongly deviates from the approximate linearity for the other bases. Note, however, that these comparisons should necessarily be considered just qualitative as the literature data²⁵ refer to measurements in various laboratories, using different conditions and different data refinement.

The comparison of the Gibbs energy for the 1-base adducts with available data from the SbCl₅⁴ and BF₃⁶ Lewis affinity scales, the latter of which represents a homogeneous set of values, allows for a further assessment of present Lewis basicity scale. In both cases, linearity is apparent for involved solvents (Figure 3), whereas departure from linearity is evident for triethylamine and for isopropylamine. In particular, present data indicate a lower Lewis basicity for these aliphatic amines with respect that predicted considering SbCl₅ or BF₃ as reference acids. Again, it can be related to the greater steric hindrance at the nitrogen atom for these aliphatic amines.

In summary, the comparison of present Lewis basicity scale with data reported in the literature indicates that although the relative basicity for the involved solvents representing less

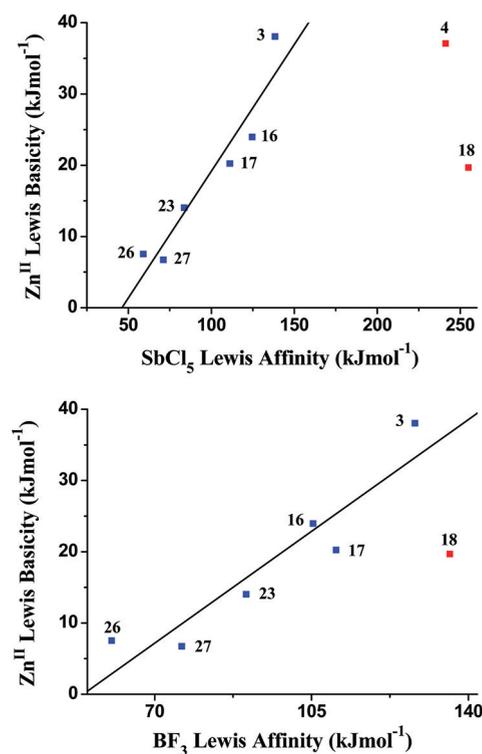


Figure 3. Comparison of Lewis basicity for 1-base adducts and SbCl₅ Lewis affinity (top) or BF₃ Lewis affinity (bottom). SbCl₅ and BF₃ data are from refs 4 and 6, respectively. Masked data (marked in red) are not included in the linear fit.

sterically encumbered species is scarcely affected by the reference Lewis acid, for sterically encumbered amines, the Lewis basicity seems to be dependent from the reference acid. Actually, the reference Lewis acidic Zn^{II} complex 1 involves very different relative Lewis basicities than those expected considering the less sterically encumbered SbCl₅, BF₃, or I₂ reference species. Thus, even the DMSO solvent is expected to be more basic than triethylamine, the latter of which is commonly considered as a strong base. On the other hand, THF possesses Lewis basicity comparable to that of various encumbered acyclic tertiary amines.

3. CONCLUSIONS

The use of the Lewis acidic Zn^{II} complex 1 has successfully allowed the achievement of a consistent, reliable scale of Lewis basicity for amines and nonprotogenic solvents. It represents a unique set of data reflecting the actual Lewis basicity with respect this “real world” Lewis acidic species.

The comparison of present Lewis basicity scale with data reported in the literature indicates that although the relative basicity of the involved solvents is scarcely affected by the reference Lewis acid, for sterically encumbered amines, the Lewis basicity seems to be dependent from the reference species. Actually, even if SbCl₅, BF₃, or I₂ are considered good reference Lewis acids, they represent simple model systems given their less sterically encumbered nature. In these cases, relative Lewis basicities take into account almost exclusively for electronic effects alone,²⁶ but not for sterical effects, which significantly contribute to the actual basicity of a species.

For the present reference Lewis acidic Zn^{II} complex 1, Lewis basicity is governed by the steric hindrance at the donor atom and involves very different relative basicities than those

predicted considering typical reference Lewis acids. Thus, even the DMSO solvent is more basic than triethylamine, commonly considered as a strong base, whereas THF possesses Lewis basicity comparable to that of various encumbered acyclic tertiary amines. This is expected to have a major involvement in the organic synthesis and catalysis, given the sterically encumbered nature of commonly involved Lewis acidic organo-metallic complexes.

Modeling calculations for 1•base adducts in fluctuating polar solvent remains a challenge for the future, for example, by using QM/MM methodology²⁷ to generalize the present Lewis basicity scale to other solvent media.

4. EXPERIMENTAL SECTION

4.1. Physical Measurements and General Procedures.

Optical absorption spectra were recorded at 25 °C with a UV–vis–NIR spectrophotometer. Titrations were performed using a 1 cm path length cuvette equipped with a magnetic stirrer. Typically, to record a UV–vis spectrum the base was delivered by a precision buret.

4.2. Determination of the Binding Constants. The stoichiometry of the 1•base adducts was initially determined by the mole ratio²⁸ and Job's plot¹⁶ methods. Both methods indicate the presence of 1:1 1•base adducts. However, since the above methods are not sensitive enough to reveal the presence of minor species that may accompany the formation of the 1:1 adducts, the speciation of the systems was carried out resorting to multiwavelength and multivariate treatments of the spectral data, by using two different softwares, i.e., SPECFIT²⁹ and HYPERQUAD.¹⁵ However, under the actual experimental conditions of spectrophotometric titrations, the system indicates the presence of only two absorption species. Spectrophotometric data were collected over the range 270–650 nm for all the investigated Lewis bases. These data were initially analyzed by the software SPECFIT, which makes use of a multiwavelength and multivariate treatment of spectral data, combining a chemometric analysis (factor analysis and evolving factor analysis)³⁰ with a nonlinear least-squares minimization procedure. However, as the data compression procedure used by SPECFIT might introduce some distortion into the data, for this reason, the data were double checked by using the HYPERQUAD program, which follows a different strategy to deduce the number of light absorbing species, by adopting a procedure that eliminates the accumulation of errors inherent in the matrix compression procedure.³¹ Furthermore, HYPERQUAD is able to refine simultaneously the data from different titration measurements.^{31a} At least three replicate titrations data were refined for each base. Therefore, data reported in Table 1 refer to those achieved by the HYPERQUAD program. However, the binding constants values obtained by using the two different software packages gave, within the standard deviations, almost equal values.

■ ASSOCIATED CONTENT

● Supporting Information

Job's plot analysis, optimized structure of 1•base adducts, additional spectrophotometric titration data. This material is available free of charge via the Internet at <http://pubs.acs.org>

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■ ACKNOWLEDGMENTS

This research was supported by the MIUR and PRA (Progetti di Ricerca di Ateneo).

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