

Synthesis of Ar-BIAN Ligands (Ar-BIAN = Bis(aryl)acenaphthenequinonediimine) Having Strong Electron-Withdrawing Substituents on the Aryl Rings and Their Relative Coordination Strength toward Palladium(0) and -(II) Complexes

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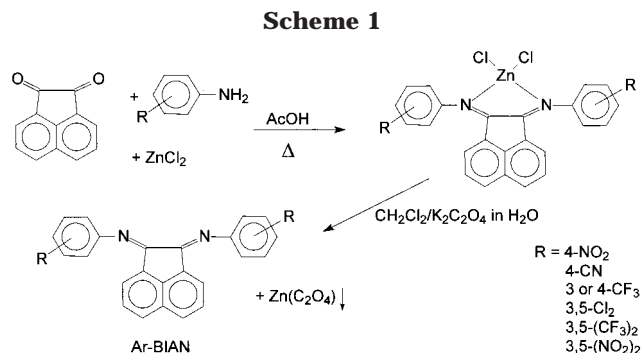
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The synthesis of Ar-BIAN ligands (Ar-BIAN = bis(aryl)acenaphthenequinonediimine) having strong electron-withdrawing substituents on the aryl ring is reported. Most of these derivatives had escaped isolation in a pure form up to now. A quantitative scale of coordination strength of the newly synthesized ligands in the complexes Pd⁰(L)(DMFU) (DMFU = dimethylfumarate) and Pd^{II}(L)(OAc)₂ has been measured. The series also includes some previously known Ar-BIAN ligands, phenanthroline, bipyridine, and Ph-DAB (Ph-DAB = diphenyldiazabutadiene). A good correlation is observed for the Ar-BIAN ligands between the Hammett σ constants of the substituents of the aryl group and the relative binding constant with respect to Ph-BIAN. The values for the ρ constant for the Pd(L)(DMFU) and Pd(L)(OAc)₂ series are respectively -1.57 and -3.44 , indicating that electron-rich ligands bind more strongly in both series, but the effect is much stronger in the Pd(II) series. The observed effect is relevant to the question of the effective oxidation state of palladium in the Pd(L)(DMFU) complex. Phenanthroline and bipyridine are stronger ligands than any Ar-BIAN compound, whereas Ph-DAB is the weakest ligand of all. The sterically hindered 2,6-Prⁱ₂C₆H₃-BIAN binds less strongly than its basicity would suggest.

Introduction

Compounds of the family Ar-BIAN (Ar-BIAN = bis(aryl)acenaphthenequinonediimine) (Scheme 1) have been known for some time,^{1,2} but have been brought to general attention only in recent years by Elsevier and his group.³ Since then, they have found widespread use as ligands for palladium, ruthenium, and nickel and the corresponding complexes have been employed as catalysts for a wide variety of reactions, such as alkene hydrogenation,⁴ polymerization,⁵ aziridination,⁶ and cyclopropanation,⁶ alkene-CO copolymerization,⁷ alkyne coupling in the presence of halogens or organic halides and tin compounds⁸ or just tin compounds,⁹ selective



hydrogenation of alkynes to alkenes,¹⁰ allylic aminations of olefins by nitroarenes in the presence of CO,^{11,12} the synthesis of pyrroles and oxazines from dienes, nitroarenes, and CO,¹² the reduction of nitroarenes to anilines by CO/H₂O,¹³ the cross-coupling reaction between organic halides and organomagnesium, -zinc, and -tin reagents,¹⁴ the Suzuki–Miyaura cross coupling,¹⁵

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the synthesis of 4-quinolones and 2,3-dihydroquinolones from 2'-nitrochalcones and CO,^{16,17} and the synthesis of indoles from *o*-nitrostyrenes and CO.^{17,18} For some of these syntheses, the use of the Ar-BIAN ligands was instrumental to achieving high performances of the catalytic system. With respect to most diimine ligands, 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 ligand for many catalytic systems when long catalyst lives are a requisite, as is always the case for industrial applications.

Despite the utility of these ligands, only Ar-BIAN compounds having electron-releasing or moderately electron-withdrawing groups on the aryl ring have been reported in the literature. Among those reported, the one having the most electron-withdrawing substituent is 4-CF₃C₆H₄-BIAN^{5b} (p*K*_a of 4-CF₃C₆H₄NH₃⁺ = 2.75;¹⁹ all p*K*_a values quoted in the following are measured in water at 25 °C), which was synthesized by refluxing acenaphthenequinone and 4-CF₃C₆H₄NH₂ in toluene with a Dean–Stark apparatus for 5 days.²⁰ The same procedure failed to afford the corresponding ligand with a 4-nitro group (p*K*_a of 4-NO₂C₆H₄NH₃⁺ = 1.00²¹). The ZnCl₂ or NiBr₂ complexes of the latter can be obtained if the corresponding salts are present in the reaction mixture (acetic acid as solvent),^{1–3} but previous attempts to liberate the free ligand from the templating metal by refluxing the complex with ethanolic K₂CO₃ (for ZnCl₂) or treating it with sodium cyanide (for NiBr₂) led to extensive hydrolysis.^{1,3}

Most of the catalytic systems previously mentioned are sensitive to the electron-donating or -withdrawing power of the substituents on the aryl ring, and electron-withdrawing substituents are beneficial in some cases, for example in the technologically important polymerization of ethylene by nickel catalysts.^{5b} In this paper we report that simply applying our previously reported^{11b} protocol for the liberation of Ar-BIAN ligands from ZnCl₂ allows the effective synthesis (without hydrolysis) not only of 4-NO₂C₆H₄-BIAN but also of other BIANS that are even more electron-poor, such as the derivative having two nitro groups in the 3 and 5 positions (Scheme 1). In some cases, a modification of the previously reported procedure for the synthesis of the ZnCl₂ complex was required, which is also discussed. It should be noted that chelating diimine ligands having strong electron-withdrawing groups on the aryl rings are very

rare molecules, even if the field is not limited to the BIAN skeleton.

Given the high importance that bidentate chelating nitrogen ligands have gained in homogeneous catalysis,²¹ it is surprising that very little quantitative information exists on their relative binding strength to transition metals. Several papers, especially in the older literature, have been devoted to phenanthroline (Phen) and bipyridine (Bipy) complexes,²² but all of the available data were measured in aqueous solution, where protonation of the ligand becomes important. Thus this information is difficult to transfer to the low- to medium-polarity, often anhydrous, solvents commonly employed for catalytic reactions. The effect of steric hindrance on the identity of the most stable complex has been examined for some R-DAB complexes,²³ but electronic effects were not investigated. To the best of our knowledge, no quantitative binding strength scale exists for chelating nitrogen ligands toward a transition metal and in an organic solvent. We have thus managed to measure such a scale for our new ligands, together with others already known in the literature, and the results are also reported here.

Results and Discussion

Synthesis of Ar-BIAN Ligands with Ar = 4-NO₂C₆H₄–, 4-NCC₆H₄–, 3,5-Cl₂C₆H₃–, 3,5-(NO₂)₂-C₆H₃–. The ZnCl₂ complexes of the ligands having the 4-NO₂–, 4-CN–, 3,5-Cl₂–, and 3,5-(NO₂)₂– substituents on the aryl group of the starting aniline (the p*K*_a values for the corresponding anilinium salts are respectively 1.00,²⁴ 1.74,²⁵ 2.37,²⁶ and 0.229²⁷) can be easily synthesized by the known procedure employing the reaction of a 15% molar excess of the aniline with acenaphthenequinone and an almost 3-fold molar excess of ZnCl₂ in refluxing acetic acid.^{2,3} The desired complex precipitates in high yields from the hot solution that is filtered while hot. During this work we have noted that the excess aniline is partly transformed into the corresponding acetanilide by reaction with the solvent. Especially the derivative of 3,5-dichloroaniline is slightly soluble and partly coprecipitates. To remove these impurities it is convenient to suspend the precipitate in hot acetic acid for at least 15 min and filter it again, rather than simply washing it with hot acetic acid, as originally reported. The formation of acetanilides has other important consequences and will be further discussed below.

The well-dried precipitate is then suspended in CH₂Cl₂, and an aqueous solution of sodium or potassium oxalate is added in a separating funnel. Shaking for a few minutes results in complete dissolution of the colored complex, with concomitant formation of colorless

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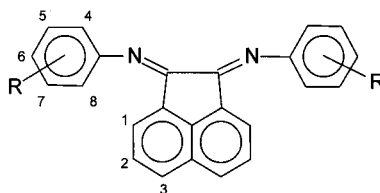
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Table 1. ^1H NMR Spectra of Ar-BIAN Ligands^a

R	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₈
4-CN	6.88 d (<i>J</i> = 7.2)	7.49 pst	8.02 d (<i>J</i> = 8.3)	7.24 d (<i>J</i> = 8.5)	7.81 d (<i>J</i> = 8.5)		= H ₅	= H ₄
4-NO ₂	6.93 d (<i>J</i> = 7.1)	7.50 pst	8.04 d (<i>J</i> = 8.2)	7.28 d (<i>J</i> = 8.3)	8.4 d (<i>J</i> = 8.3)		= H ₅	= H ₄
3-CF ₃	6.86 d (<i>J</i> = 7.2)	7.81 pst	7.98 d (<i>J</i> = 8.3)	7.57 d (<i>J</i> = 7.5) ^b	7.63 pst	7.35 d (<i>J</i> = 7.6) ^b		7.44 s
3,5-Cl ₂	7.03 d (<i>J</i> = 7.5)	7.54 pst	8.02 d (<i>J</i> = 8.3)	7.05 d (<i>J</i> = 1.9)		7.29 t (<i>J</i> = 1.9)		= H ₄
3,5-(CF ₃) ₂	6.89 d (<i>J</i> = 7.2)	7.52 pst	8.05 d (<i>J</i> = 8.3)	7.63 s		7.83 s		= H ₄
3,5-Me ₂ ^c	6.92 d (<i>J</i> = 6.9)	7.40 pst	7.9 d (<i>J</i> = 8.2)	6.75 s		6.9 s		= H ₄

^a Recorded in CDCl₃ at room temperature; 300 MHz. Values are in ppm relative to TMS, *J* values are in Hz. 3,5-(NO₂)₂C₆H₃-BIAN was too insoluble to allow recording of the ^1H NMR spectrum. ^b CF₃ group at position 7 in the drawing. Assignment was made by two-dimensional ^1H NMR (COSYDFTP), but the attribution of the H₄ and H₆ signals is not unequivocal and may be reversed. ^c In addition to the signals reported in the table, a singlet at δ 2.38 was observed for the methyl groups.

ZnCl₂O₄. Oxalate is preferred with respect to carbonate, as the former is less basic, but, at the same time, zinc oxalate is less soluble than zinc carbonate. The free ligand is isolated in a pure form from the CH₂Cl₂ layer. In general, no hydrolysis was observed, as indicated in particular by the absence of any absorption over 1700 cm⁻¹ in the IR spectrum of the free ligands. Only in the case of 3,5-Cl₂C₆H₃-BIAN was a small amount of the monoimine detected after decoordination. This impurity is present in a small amount and does not prevent employing the crude ligand in most cases. A complete purification can be achieved by column chromatography on silica. In the case of 3,5-(NO₂)₂C₆H₃-BIAN, not only its zinc complex but even the pure ligand was only slightly soluble in CH₂Cl₂. In this case decoordination was best preceded by an irradiation of the biphasic mixture by ultrasound (in an ultrasound cleaning bath) in order to disaggregate the solid particles at best. The ligand was finally recovered by filtration. It is only sparingly soluble in most solvents.

Synthesis of Ar-BIAN Ligands with Ar = 4-CF₃C₆H₄⁻, 3-CF₃C₆H₄⁻, 3,5-(CF₃)₂C₆H₃⁻. When the previously described protocol for the synthesis of ZnCl₂(Ar-BIAN) complexes is applied to 3-CF₃C₆H₄NH₂ (*pK*_a = 3.20¹⁹), an acceptable yield of 70% in the desired complex is still obtained, but with its 4 isomer (*pK*_a = 2.75¹⁹), the yields drop to about 40%, and with the 3,5-disubstituted aniline (*pK*_a = 1.15²⁷), the hot solution was perfectly homogeneous and only traces of 3,5-(CF₃)₂C₆H₃-BIAN were obtained by workup, the reaction affording a mixture of the monoimine and 3,5-(CF₃)₂C₆H₃NHC(O)CH₃. The *pK*_a of 3,5-(CF₃)₂C₆H₃NH₂ is comprised between those of 3,5-Cl₂C₆H₃NH₂ and 4-NO₂C₆H₄NH₂, both of which afford the corresponding complex in good yields. Thus the failure to obtain the desired complex cannot be related to the poor basicity of the aniline and must be connected with its high solubility in the reaction medium. Indeed, when the reactions of the CF₃-containing anilines were repeated by adding some toluene to the reaction mixture (2 mL for 7.5 mL of AcOH); such a low amount of toluene does not prevent

Table 2. IR Data and Mp's for Ar-BIAN Ligands

R	$\nu_{\text{C=N}}$ ^a	other IR data ^a	mp (°C)
4-CN	1671, 1646	2224 (ν_{CN})	290
4-NO ₂	1674, 1654	1504, 1345 (ν_{NO_2})	>300
4-CF ₃	1665, 1645		241
3-CF ₃	1669, 1644		130
3,5-Cl ₂	1673, 1649		214
3,5-(NO ₂) ₂	1669, 1646	1638, 1616, 1539, 1533, 1361, 1343 (ν_{NO_2})	>300
3,5-(CF ₃) ₂	1675, 1652		186
3,5-Me ₂	1665, 1635		219

^a In Nujol, values in cm⁻¹.

the dissolution of ZnCl₂), the corresponding complexes all precipitated from the hot solution in good yields. The free ligands were obtained as described before without any problem.

The spectroscopic data and melting points for the ligands obtained are reported in Tables 1 and 2. The ^1H NMR spectrum of 4-CF₃C₆H₄-BIAN was identical to that reported in ref 5b. Also included in the table are the data for 3,5-(CH₃)₂C₆H₃-BIAN, which has not been reported in the literature before. This ligand was synthesized following the standard protocol (i.e., without toluene) in order to use it in the relative coordination strength studies, as detailed below.

The limit of the ZnCl₂-promoted synthesis of the Ar-BIAN ligands (*not* of the following decoordination) was reached with the very acidic 2,6-(NO₂)₂C₆H₃NH₂ (*pK*_a = -5.37²⁴) and C₆F₅NH₂ (*pK*_a = -0.36²⁸). With these amines, no condensation product could be obtained by the procedures reported above.

Comments on the Role of ZnCl₂ and the Formation of Acetanilides. Transition metal salts have long been used as promoters for the formation of imines from amines and ketones.²⁹ Although a catalytic amount is often sufficient in the case of monoimine formation, a

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stoichiometric amount is necessary to obtain diimines, the metal remaining linked to the so formed diimine, which acts as a ligand. This last promoting effect has been generally attributed to a “templating” effect or to the stabilization of the diimine by its coordination to the metal, adding a thermodynamical bias toward the condensation. However, the results obtained in this work and some other unpublished results obtained in our group when the analogous condensation employing camphorquinone in place of acenaphthenequinone was studied show that, at least in these cases, the key point is not the formation of the complex as such, but the fact that these complexes are usually less soluble in the reaction medium than the starting reagents. Precipitation of the final product thus appears to be the driving force of the double condensation. If formation of the complex were determining, then the complexes should be obtained by workup of the reaction solutions even when they do not spontaneously precipitate. However, in our experience this never happens. In all cases in which the final complex did not precipitate, it was formed in only minute amounts. This observation has important consequences for the design or modification of the synthesis of chelating diimines. Indeed a low solubility of the resulting complex with respect to the starting materials should be looked for in selecting both the metal salt and the solvent mixture. We have successfully applied this principle to the synthesis of the CF_3 -containing BIAN ligands. Indeed, toluene dissolves well the intermediate monoimine and the starting quinone, but acts as a precipitating agent toward the Ar-BIAN complexes. Although we have not independently optimized the addition of toluene to all reagent combinations, it is likely that the addition of toluene is also beneficial even in the synthesis of other Ar-BIAN ligands. It should be also noted that now that the solubility issue has been evidenced, it is no longer surprising that 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ -BIAN can be obtained from the quinone and the aniline in acetic acid even in the absence of metal salts. Indeed it is the only Ar-BIAN among those reported to be sufficiently insoluble in acetic acid to precipitate almost quantitatively from the hot solution.³⁰

Concerning the formation of the acetanilides, a further observation was made. In an attempt to further increase the yield of the synthesis of 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3$ -BIAN, the reaction time for the reaction also including toluene was increased from 45 min to 2 h. In the latter case, the initially formed precipitate completely redissolved as the reaction proceeded. After 2 h, the solution did not contain any more 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3$ -BIAN, and even the monoimine could not be detected. The only products found were acenaphthenequinone, 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3\text{NHC(O)CH}_3$, and 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3\text{NH}_2$. The water formed during the formation of the acetanilide clearly had hydrolyzed the BIAN ligand. This indicates that in a homogeneous system the acetanilide, not the BIAN ligand, is the thermodynamically favored product, although not necessarily the kinetic one. This fact

(30) It can be speculated that the solubility of the other Ar-BIAN compounds in acetic acid is largely due to the formation of hydrogen bonds between the acidic hydrogen and the imine nitrogens. Since the latter are strongly shielded in the bis-isopropyl derivative, this interaction is lacking or is very weak and the ligand precipitates. However, this explanation does not limit the validity of the concepts expressed above.

further stresses the importance of the insolubility of the BIAN–metal salt complex in order to drive the reaction in the correct direction.

Finally, a comment on the solubility of the 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3$ -BIAN ligand is worthwhile. This molecule and especially its complexes display a very different solubility in different solvents with respect to complexes derived from non-fluorinated BIAN ligands. For example, 0.05 mmol of $\text{ZnCl}_2(\text{Ph-BIAN})$ requires 2.5, 10, and 38 mL, respectively, of CH_2Cl_2 , THF, and methanol to completely dissolve. The same molar amount of the corresponding complex $\text{ZnCl}_2(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{-BIAN})$ requires 21.7, 3, and 3 mL of the same solvents to dissolve. Thus the fluorinated complex is almost 10 times less soluble in dichloromethane, but 12 times more so in methanol.

We are now exploring the use of the “solubility criterion” to synthesize other chelating diimine ligands that have eluded isolation up to now.

Relative Binding Strength of the Ligands. During our previous studies on the use of $\text{Ru}(\text{CO})_3(\text{Ar-BIAN})$ complexes to catalyze the allylic amination of olefins by nitroarenes,^{11b} we noticed that Ph-BIAN coordinates to the $\text{Ru}(\text{CO})_3$ fragment more strongly than the more basic Tol-BIAN, and indirect evidence based on chemical reactivity indicates¹² that the even more basic 4- MeOC_6H_4 -BIAN is the most weakly coordinating ligand in the series. This suggests that some of the newly reported compounds may be quite strong ligands for low-valent metal complexes. Unfortunately, several theoretical and technical problems render the $\text{Ru}(\text{CO})_3(\text{Ar-BIAN})$ system unsuitable for the determination of even relative coordination constants in an accurate and quantitative way. We thus decided to examine the relative coordinating ability of the new ligands and of others previously reported toward two palladium complexes, respectively in the 0 and 2 formal oxidation states.

As a palladium(0) series we chose the complexes $\text{Pd}(\text{L})(\text{DMFU})$ (L = bidentate chelating nitrogen ligand, DMFU = dimethylfumarate). Several complexes of the kind $\text{Pd}(\text{Ar-BIAN})(\text{olefin})$ have been reported by Elsevier and were shown to undergo both olefin and ligand exchange.³¹ However, the only system for which a quantitative measure of the ligand exchange was recorded was the $\text{Pd}(\text{Tol-BIAN})(\text{maleic anhydride}) + 2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{-BIAN}$ one. In this work, we selected DMFU as the olefin because it is the least electron-withdrawing (and thus the least perturbing for the oxidation state of the metal) among all of the ones that allowed the complex to be isolated (electron-withdrawing groups on the olefin are anyway required to this aim). The corresponding complexes with Phen (1,10-phenanthroline) and Bipy (2,2'-bipyridine) have also been reported in the literature.³² The complex $\text{Pd}(\text{Tol-BIAN})(\text{DMFU})$ has been reported to decompose in solution.³³ We noted that addition of excess DMFU (5 equiv with respect to the complex) to the solution strongly stabilizes the complex, and decomposition is only observable after several hours, a time longer than that required for our experiments.

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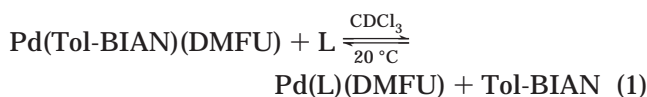
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Table 3. Relative Coordination Strength of Several Chelating Nitrogen Ligands toward Palladium(0) and -(II) Complexes

ligand	aniline pK _a	σ	K _{eq} Pd(L)(DMFU) ^a	K _{eq} Pd(L)(OAc) ₂ ^b
4-MeOC ₆ H ₄ -BIAN	5.29	-0.27	6.85	35.3
4-MeC ₆ H ₄ -BIAN	5.12	-0.17	2.56	1.70
3,5-Me ₂ C ₆ H ₃ -BIAN	4.91	-0.14		2.22
Ph-BIAN	4.58	0.00	1.00	1.00
4-ClC ₆ H ₄ -BIAN	3.98	0.23	0.85	0.10
3-CF ₃ C ₆ H ₄ -BIAN	3.20	0.43	0.21	0.011
4-CF ₃ C ₆ H ₄ -BIAN	2.75	0.54	0.38	0.0064
4-NCC ₆ H ₄ -BIAN	1.74	0.66	0.077	0.0018
3,5-Cl ₂ C ₆ H ₃ -BIAN	2.37	0.74	0.12	0.0051
4-O ₂ NC ₆ H ₄ -BIAN	1.00	0.78	0.090	0.0020
3,5-(CF ₃) ₂ C ₆ H ₃ -BIAN	1.15	0.86	0.11	0.0037
2,6-Pr ⁱ ₂ C ₆ H ₃ -BIAN	4.41		0.18	
Phen			66.4	>100
Bipy			45.1	>100
Ph-DAB			0.046	<0.001

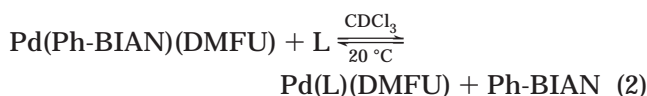
^a The K_{eq} value refers to the reaction in eq 2, at 20 °C. ^b The K_{eq} value refers to the reaction in eq 4, at 20 °C.

Competition experiments were run by reacting pre-formed Pd(Tol-BIAN)(DMFU) with an equimolar amount of a different ligand in CDCl₃ at 20 °C as in eq 1.



The evolution of the reaction was followed by ¹H NMR. With the exception of the case of 2,6-Prⁱ₂C₆H₃-BIAN, all reactions reached equilibrium in less than 20 min. Within this time frame, only the peaks attributable to the starting and final complexes and to the two free ligands were observed in the ¹H NMR spectrum, indicating that no other compound was formed. The position of the equilibrium was best evaluated by comparing the integrated intensity of the signals for the methyl groups of free and coordinated Tol-BIAN, which are well separated. To have a more interesting set of data we also included Ph-BIAN, 4-MeOC₆H₄-BIAN, 4-ClC₆H₄-BIAN, 2,6-Prⁱ₂C₆H₃-BIAN, Phen, Bipy, and Ph-DAB (Ph-DAB = diphenyldiazabutadiene) in our series. As mentioned before, the reaction with 2,6-Prⁱ₂C₆H₃-BIAN was slower than the others, likely because of steric reasons, and stabilized only after 1 h, time at which a very small, but detectable amount of an unidentified decomposition product was also present. Thus the datum for this ligand is affected by an error which is not present in the others. The data for 3,5-(NO₂)₂C₆H₃-BIAN could not be determined due to insufficient solubility of the ligand.

The data obtained have been normalized to Ph-BIAN as a reference, so that they now refer to the equilibrium in eq 2, and are reported in Table 3.



It is immediately clear that both Phen and Bipy are quite stronger ligands toward the Pd(DMFU) moiety than any Ar-BIAN ligands. Conversely Ph-DAB is the weakest ligand of all. Contrary to what is observed for the ruthenium complexes mentioned above, electron-donating substituents on the aryl ring of the BIAN ligands stabilize the complex with respect to electron-

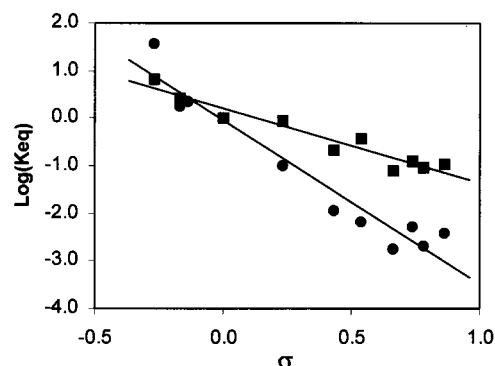


Figure 1. Plot of log(K_{eq}) for the reactions in eqs 2 (squares) and 4 (circles) as a function of the Hammett σ constants for the substituents on the aryl group of Ar-BIAN. The lines drawn correspond respectively to the functions log(K_{eq}) = -1.57σ + 0.200 (R² = 0.926) and log(K_{eq}) = -3.44σ - 0.054 (R² = 0.935).

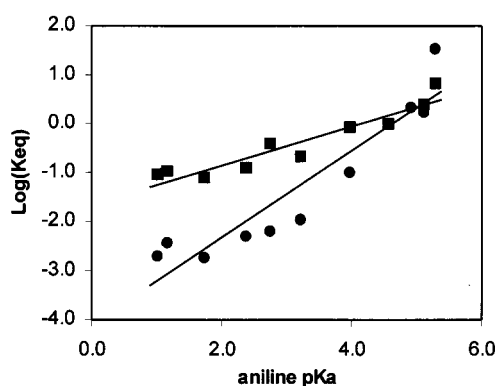


Figure 2. Plot of log(K_{eq}) for the reactions in eqs 2 (squares) and 4 (circles) as a function of the pK_a values for the substituted anilines employed in the synthesis of the corresponding Ar-BIAN. The lines drawn correspond respectively to the functions log(K_{eq}) = 0.40pK_a - 1.64 (R² = 0.893) and log(K_{eq}) = 0.88pK_a - 4.01 (R² = 0.878).

withdrawing ones, but 2,6-Prⁱ₂C₆H₃-BIAN binds more weakly than its basicity would suggest, clearly for steric reasons. The reaction between Pd(Tol-BIAN)(DMFU) and 2,6-Prⁱ₂C₆H₃-BIAN stopped at a 72:28 molar ratio between the starting and the final complex, which is in good qualitative agreement with the 65:35 value reported by Elsevier³¹ for the related reaction in which maleic anhydride was employed as the olefin and which represents the only other available data for a reaction of this kind.

Interestingly, a good correlation is found between the relative coordination constants of the Ar-BIAN ligands (with the exception of 2,6-Prⁱ₂C₆H₃-BIAN) and both the Hammett σ constants³³ of the substituents on the aryl fragment (Figure 1, R² = 0.926; additivity of the constants was supposed for the disubstituted aryls) or the pK_a of the aniline employed in the synthesis of the ligands (Figure 2, R² = 0.893). That a good agreement exists in both cases is not unexpected, because a good linear correlation exists between the pK_a values of substituted anilines and the Hammett σ constants of the substituents.³⁴ The correlation with the Hammett σ constants was not significantly improved (R² = 0.929)

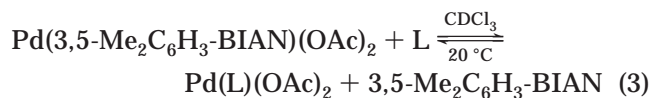
(34) Gross, K. C.; Seybold, P. G.; Peralta-Inga, Z.; Murray, J. S.; Politzer, P. *J. Org. Chem.* **2001**, *66*, 6919.

if only the 4-substituted Ar-BIAN ligands were considered, supporting additivity of the constants for this system.

To examine the sensitivity of the relative coordinating constant to the electronic influence of the substituents as a function of the oxidation state of the metal, we performed an analogous series of experiments for a typical palladium(II) complex. Palladium acetate was selected as the fixed moiety because of the sufficient solubility and stability of all of the complexes involved.³⁵ The complexes Pd(OAc)₂(L) with L = 2,6-Prⁱ₂C₆H₃-BIAN,³⁶ Phen,³⁷ and Bipy³⁷ have been previously reported in the literature.

For this second system, Tol-BIAN could not be employed as a standard ligand, because the signals for the methyl protons of free and coordinated Tol-BIAN are almost degenerate. To solve this problem, the previously unreported 3,5-Me₂C₆H₃-BIAN ligand and its palladium acetate complex were synthesized following standard procedures (see Experimental Part). In this case, the signals of the methyl groups shifted enough upon coordination of the ligand that a good separation was observed. Only one signal for the four methyl groups was observed for either the free or the coordinated ligand. No other notable feature is present in the ¹H NMR spectra of Pd(OAc)₂(Tol-BIAN) and Pd(OAc)₂(3,5-Me₂C₆H₃-BIAN) except for a strong shift to high fields of the signals of the acetate protons. This shift has been earlier observed in the related complex with 2,6-Prⁱ₂C₆H₃-BIAN and explained with the position of the acetate groups, placed over the plane (in the shield cone) of the aryl groups of the BIAN ligand.³⁶ The latter are almost perpendicular to the acenaphthene plane. The effect is observed during the exchange reactions even for all other Ar-BIAN complexes, but not for the Phen and Bipy ones, which give signals in the expected range.

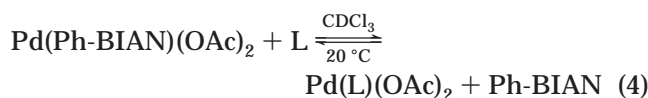
The reaction in eq 3 was found to be slower than that in eq 1, and the onset of the equilibrium took 3–4 h at 20 °C. Moreover, the equilibrium was found to be much more sensitive to electronic factors than the one involving the Pd(0) complex, and in the case of the weakest ligands it was necessary to add a 4-fold molar excess of ligand in order to obtain an amount of final complex that could be reliably quantified.



On the other hand, in this series an equimolar amount of Phen or Bipy with respect to the starting complex gave an essentially quantitative substitution, so that only a lower limit can be estimated for their relative coordination constants. At the opposite side, Ph-DAB did not displace 3,5-Me₂C₆H₃-BIAN from palladium(II) at a measurable extent (at least under the time frame examined), even when it was present in a 4-fold molar excess. 2,6-Prⁱ₂C₆H₃-BIAN did not give any detectable reaction even after 3 days. It is unlikely that the

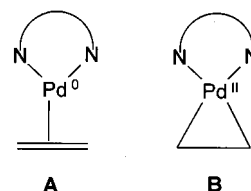
thermodynamic equilibrium constant is so small in this case. It is more likely that the failure to observe the new complex is due to an extremely slow reaction. Such a behavior strongly points to an associative mechanism for this substitution. In all cases, only signals attributable to the starting and final complexes and to the two free ligands were observed in the time frame examined, as also confirmed by comparison of the observed signal with those reported in the literature for the previously reported compounds. Moreover, only two signals (for the starting and final complex) were observed for the methyl protons of the acetate groups. Independent measurement of the relative coordination constants based on the ratio between the integrated intensities of these acetate signals gave values within ±4% of those calculated from the ligand methyl signals, further supporting the assumption that no other species is present during the reaction.³⁸

Again, data have been normalized to Ph-BIAN as a reference, and the results reported in Table 3 refer to the equilibrium in eq 4.



Even for this system, a good correlation exists between the K_{eq} value and the Hammett σ constants for the substituents (Figure 1, $R^2 = 0.935$). As for the Pd(0) series, the correlation with the $\text{p}K_{\text{a}}$ values of the substituted anilines is a bit worse (Figure 2, $R^2 = 0.878$), but still fair. It should be noted that the points that deviate more are those at the extremes of the series and are the ones for which a small amount of either free ligand or coordinated ligand is present. Under these conditions, even a small imprecision in the determination of the absolute integral of the minor signal results in a much larger relative error in the K_{eq} value.

The comparison of the data for the two series in Figure 1 immediately reveals that the second line has a much larger slope. The values for the ρ constant for the Pd(L)(DMFU) and Pd(L)(OAc)₂ series are respectively –1.57 and –3.44, indicating that more electron-rich ligands bind more strongly in both series, but the effect is much larger (about 75 times) in the Pd(II) series. The observed effect is relevant to the question of the effective oxidation state of palladium in the Pd(L)(olefin) complexes. In general, two limiting structures are possible for a metal–olefin complex in which the olefin bears electron-withdrawing substituents, A and B. The first neglects back-donation and considers the metal in the zero oxidation state, whereas the second implies a complete (formal) donation of two electrons to the olefin, with the formation of a metal-lacyclopropane with the metal in the +2 oxidation state.



On the basis of the spectroscopic features of Pd(Ar-BIAN)(olefin) complexes, it was suggested that reso-

(35) Several of the PdCl₂(L) complexes, on the other hand, were not completely soluble under the reaction conditions.

(36) van Asselt, R.; Elsevier, C. J.; Amatore, C.; Jutand, A. *Organometallics* **1997**, *16*, 317.

(37) Milani, B.; Alessio, E.; Mestroni, G.; Sommazzi, A.; Garbassi, F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1994**, 1903.

nance structure **B** may be more important than structure **A** in describing the bonding in these complexes.³¹ Similar arguments had been earlier applied to the related Pd(R-DAB)(olefin) complexes.²³ In general, the problem highlighted is an old one and dates back to the first olefin complexes of metals in a low oxidation state.³⁹ Our data indicates that, whichever description is given, there is large difference in the electrophilicity of a Pd(olefin) moiety with respect to that of a "true" palladium(II) compound. Although a larger set of data for more series of compounds would be required in order to check if they all divide in two well-separated groups, to the best of our knowledge, this is the first time that equilibrium constant data are used to shed light on this problem.

The fact that strongly donating compounds are better ligands than weakly donating ones *with the same geometrical features* should not be considered to imply that Phen and Bipy are more basic than all Ar-BIAN ligands. The different angle between the lone pairs on the nitrogen atoms of these last two compounds with respect to that in Ar-BIAN ligands surely plays a role in determining the stability of the corresponding complexes. Anyway, the much larger stability of Phen and Bipy palladium complexes with respect to Ar-BIAN ones is a new and unexpected fact that will have to be considered in the study of those catalytic systems in which both kinds of ligands can be employed

Experimental Part

General Procedures. The syntheses of the ligands were generally performed under a dinitrogen atmosphere, but can also be performed in the air without problems. The decoordination reactions were always performed in the air. All organic reagents were commercial products and were used as received. Dry ZnCl₂ was stored in an oven at 120 °C and quickly weighed in the air just before use. NMR spectra were recorded on a Bruker AC 300 FT (300 MHz) at RT. IR spectra were recorded on a FTS-7 Bio Rad FT-IR spectrometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. All ligands gave an observable M⁺ peak in the EI mass spectrum. Except for the spectrum of crude 3,5-Cl₂C₆H₃-BIAN, the peak corresponding to the mass of the monoimine was never detected. No absorption was observed in the region 1700–1750 cm⁻¹ of the IR spectra of the ligands, again with the exception of that of crude 3,5-Cl₂C₆H₃-BIAN. Monoimines, on the other hand, always have an absorption in this region, and the lack of such an absorption is the most sensitive test for their absence. Pd(Tol-BIAN)(DMFU) was prepared as reported in the literature.³¹

Synthesis of ZnCl₂(Ar-BIAN) Complexes. The intermediate ZnCl₂(Ar-BIAN) complexes were prepared similarly to what is reported in the literature.^{1–3} In a flask equipped with a side port and a reflux condenser, acenaphthenequinone (500 mg, 2.74 mmol) and dry ZnCl₂ (1.0 g, 7.34 mmol) were suspended in glacial acetic acid (7.5 mL). In the case of the CF₃-containing anilines, toluene (2 mL) was also added. The flask was heated to about 50–60 °C, and the aniline (6.3 mmol)

was then added. The solution was reflux heated for 45 min and then filtered on a Buckner while hot. It is important not to exceed this reaction time (vide supra). The solids obtained in the synthesis of the derivatives with the 4-nitro, 4-cyano, 3,5-dinitro, and 3,5-dichloro were then suspended in hot acetic acid (5 mL) for 15 min and filtered again. The solid was washed on the filter with diethyl ether to help remove the acetic acid and dried in vacuo. Care must be taken to eliminate any residue of the acetic acid employed as solvent in the synthesis, as this has a strongly negative effect on the effectiveness of the separation in the following step. In the case of the CF₃-containing products, the purification with acetic acid was not performed, but the residue was washed with diethyl ether.

Decoordination of the Ligands. The complex (10 mmol) was suspended in CH₂Cl₂ (200 mL) in a separating funnel, and a solution of sodium or potassium oxalate (30 mmol) in water (20 mL) was added. After shaking for 5 min a white precipitate of Zn(C₂O₄) was present, suspended in the aqueous phase. The phases were separated and the organic layer was washed with water (2 × 20 mL), dried with Na₂SO₄, filtered, and evaporated to dryness, affording the analytically pure ligands in almost quantitative yields (with respect to the intermediate complex). A larger excess of oxalate can also be used, in which case Zn(C₂O₄) is partly solubilized in the aqueous phase as [Zn(C₂O₄)₂]²⁻, but the efficiency of the decoordination of the Ar-BIAN ligand is not altered. In the case of ZnCl₂(3,5-(NO₂)₂-BIAN), the biphasic suspension was irradiated with ultrasound in an ultrasonic bath for 30 min before shaking it, to disaggregate the very insoluble particles of the complex, which also enclose some coprecipitated ZnCl₂. In this case the ligand was only sparingly soluble in CH₂Cl₂ and was recovered by filtration. To this aim, it was essential to use a large excess of oxalate (a saturated solution) during the decoordination procedure, so that all of the zinc remained in solution and was not collected together with the free ligand. Only in the case of 3,5-Cl₂C₆H₃-BIAN was the crude ligand purified by flash chromatography (silica, toluene/hexane, 4:1).

Total yields (after decoordination) and the elemental analyses are given in the following for the individual ligands.

4-NO₂C₆H₄-BIAN: 85%. Anal. Calcd for C₂₄H₁₄N₄O₄: C, 68.2; H, 3.3; N, 13.3. Found: C, 68.0; H, 3.6; N, 13.0.

4-NCC₆H₄-BIAN·H₂O: 70%. Anal. Calcd for C₂₆H₁₆N₄O: C, 78.0; H, 4.0; N, 14.0. Found: C, 78.1; H, 4.2; N, 13.8.

4-CF₃C₆H₄-BIAN: 73%. Anal. Calcd for C₂₆H₁₄N₂F₆: C, 66.7; H, 3.0; N, 6.0. Found: C, 66.5; H, 3.1; N, 5.8.

3-CF₃C₆H₄-BIAN: 85%. Anal. Calcd for C₂₆H₁₄N₂F₆: C, 66.7; H, 3.0; N, 6.0. Found: C, 66.5; H, 3.0; N, 5.9.

3,5-(NO₂)₂C₆H₃-BIAN·2H₂O: 70%. Anal. Calcd for C₂₄H₁₆N₆O₁₀: C, 52.6; H, 3.0; N, 15.3. Found: C, 52.4; H, 2.7; N, 15.0.

3,5-Cl₂C₆H₃-BIAN: 85% (crude product; 70% after chromatographic purification on silica, eluent toluene/hexane, 4:1). Anal. Calcd for C₂₄H₁₂N₂Cl₄: C, 61.3; H, 2.6; N, 6.0. Found: C, 61.1; H, 2.5; N, 5.8.

3,5-(CF₃)₂C₆H₃-BIAN: 65%. Anal. Calcd for C₂₈H₁₂N₂F₁₂: C, 55.6; H, 2.0; N, 4.6. Found: C, 55.7; H, 2.3; N, 4.3.

3,5-Me₂C₆H₃-BIAN: 98%. Anal. Calcd for C₂₈H₂₄N₂: C, 86.6; H, 6.2; N, 7.2. Found: C, 86.3; H, 6.4; N, 7.6.

Synthesis of Pd(OAc)₂(Ar-BIAN) (Ar = 4-tolyl, 3,5-Me₂C₆H₃). The synthesis of these complexes was performed by the procedure reported in ref 36. The proton numbering for the NMR data is the same as in Table 1.

Ar = 4-tolyl. Yield: 74.3%. ¹H NMR (CDCl₃, 298 K) δ, ppm: 7.18 (d, *J* = 7.3 Hz, 2H, H₁), 7.53 (pst, 2H, H₂), 8.12 (d, *J* = 8.3 Hz, 2H, H₃), 7.33 (d, 8.1 Hz, 4H, H_{4,8}), 7.54 (d, *J* = 8.1 Hz, 4H, H_{5,7}), 2.46 (s, 6H, CH₃Ar), 1.59 (s, 6H, CH₃C(O)O). Anal. Calcd for C₃₀H₂₆N₂O₄Pd: C, 61.7; H, 4.4; N, 4.8. Found: C, 61.4; H, 4.2; N, 4.5.

Ar = 3,5-Me₂C₆H₃. Yield: 78.4%. ¹H NMR (CDCl₃, 298 K) δ, ppm: 7.18 (d, *J* = 7.4 Hz, 2H, H₁), 7.53 (pst, 2H, H₂), 8.11 (d, *J* = 8.3 Hz, 2H, H₃), 7.18 (s, 4H, H_{4,8}), 7.13 (s, 2H, H₆),

(38) The largest deviations are observed at the extremes of the series, in accord with the following about the experimental error. Although the values calculated by integrating the acetate signals are slightly different from the ones calculated from the arylmethyl groups, the relative coordination strength order is unchanged, as is the ρ value (–3.48). The ratio determined from the arylmethyl groups is deemed to be more reliable because the corresponding signals are 2 times more intense and thus more precisely integrated.

(39) Malatesta, L.; Cenini, S. *Zerovalent Compounds of Metals*; Academic Press: London, 1974.

2.42 (s, 12H, CH_3Ar), 1.60 (s, 6H, $CH_3C(O)O$). Anal. Calcd for $C_{32}H_{30}N_2O_4Pd$: C, 62.7; H, 4.9; N, 4.6. Found: C, 62.8; H, 5.1; N, 4.9.

Exchange Experiments. All NMR spectra were recorded under a N_2 atmosphere. $CDCl_3$ was purified by passing it through a basic alumina column, drying with activated molecular sieves, and degassing by three freeze–pump–thaw cycles, followed by storage under a N_2 atmosphere. The purification over basic alumina is essential in order to eliminate traces of HCl that are present in commercial $CDCl_3$ and that may react with the ligands, altering the equilibrium position. A delay of 10 s was always used during collection of 1H NMR spectra.

Pd(L)(DMFU) Series. Pd(Tol-BIAN)(DMFU) (5.0 mg, 8.18×10^{-3} mmol) and DMFU (5.9 mg, 4.09 mmol) were weighed in a NMR tube and dissolved in $CDCl_3$ (0.6 mL). In some cases, hexamethylbenzene (3.5 mg, 2.15×10^{-2} mmol) was also added as internal standard. A spectrum was recorded, after which the second ligand (8.18×10^{-3} mmol) was added. A spectrum was recorded immediately and then every 10 minutes at 20 °C, until two consecutive spectra did not show any further modification. In all cases in which hexamethylbenzene was present as an internal standard, the sum of the integrated intensities of the peaks due to the methyl groups of coordinated ($\delta = 2.50$ ppm) and free ($\delta = 2.46$ ppm) Tol-BIAN was constant. The value of the ratio between the integrated intensities of these two signals allows the calculation of the molar amounts of Pd(Tol-BIAN)(DMFU) and Tol-BIAN present at equilibrium. The latter is equal to the molar amount

of Pd(L)(DMFU) formed. The amount of free L remained is obtained by the difference with the initially added one. It should be noted that the amount of reagents weighed in each experiment may differ slightly from the molar amount stated above, and calculations were performed on the actually added amounts. The equilibrium constant for the reaction in eq 1 is calculated from the ratio (eq 5):

$$K_{eq}(\text{Tol-BIAN}) = \frac{[\text{Pd(L)(DMFU)}] [\text{Tol-BIAN}]}{[\text{Pd(Tol-BIAN)(DMFU)}] [\text{L}]} \quad (5)$$

where molar amounts can be employed instead of concentrations. The equilibrium constants for the reaction in eq 2 were calculated by dividing the corresponding values relative to Tol-BIAN by the value calculated from eq 5 for Ph-BIAN (0.39).

Pd(L)(OAc)₂ Series. The reactions were performed as detailed above (Pd(OAc)₂(3,5-Me₂C₆H₃-BIAN): 5.0 mg, 8.16×10^{-3} mmol), but hexamethylbenzene was omitted and 1 mL of $CDCl_3$ had to be employed in order to dissolve the reagents completely. The amount of ligand used was 8.16×10^{-3} mmol, except for 4-NO₂C₆H₄-BIAN, 3,5-(CF₃)₂C₆H₃-BIAN, 3,5-Cl₂C₆H₃-BIAN, 4-NCC₆H₄-BIAN, 2,6-Prⁱ₂C₆H₃-BIAN, and Ph-DAB, for which it was 3.26×10^{-2} mmol.

Acknowledgment. We thank MURST (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale) for financial support.

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