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Method of Establishing the Lewis Acidity of a Metal Fragment Based on the Relative Binding Strengths of Ar-BIAN Ligands (Ar-BIAN = Bis(aryl)acenaphthenequinonediimine)

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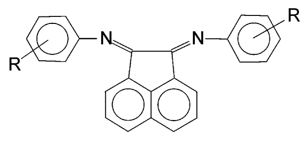
The relative coordination strengths of a series of differently substituted Ar-BIAN ligands (Ar-BIAN = bis(aryl)acenaphthenequinonediimine) to a series of palladium complexes in both the formal 0 and 2 oxidation states have been determined. In all cases a good to excellent linearity of log K_{eq} with respect to the Hammett σ constants of the substituents on the aryl fragments of the ligands was observed. The resulting ρ constant is proposed to be a good indication of the Lewis acidity of the metal fragment, a physical quantity for which experimental parameters have been determined only for a limited class of compounds. The obtained parameters allow a comparison not only of different olefin complexes among themselves but also with respect to different metal fragments such as $Pd(OAc)_2$, Pd(Me)Cl, and a π-allyl complex. The Lewis acidity of the olefin complexes is extremely variable and ranges from the less acidic (Pd(Ar-BIAN)(DMFU); DMFU = dimethyl fumarate) to two of the most acidic (Pd(Ar-BIAN)(TCNE) and Pd(Ar-BIAN)(FN); TCNE = tetracyanoethylene, FN = fumarodinitrile) complexes among those examined. A cationic π-allyl complex has the highest Lewis acidity among the complexes examined. The importance of steric effects is examined in some cases.

Introduction

Given the high importance that nitrogen ligands, especially chelating ones, have gained in homogeneous catalysis[1] and their traditional role in coordination chemistry, it is surprising that very little quantitative information exists on their relative binding strength to transition metals. A recent review on the role of nitrogen ligands in homogeneous catalysis[1a] mentions the bond dissociation energies of the adducts of some aliphatic amines with BMe_3[2] as the only quantitative data relevant to the coordination strength of nitrogen ligands, but these data are hardly of any use to predict the strength of the interaction between the usually employed ligands (most of which contain sp^2-hybridized nitrogen atoms) and a transition metal. Several papers, especially in the older literature, have been devoted to phenanthroline (Phen) and bipyridine (Bipy) complexes,[3] but all of the available data were measured in aqueous solution, where protonation of the ligand becomes important. Thus, this information cannot be transferred 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,[4] but electronic effects were not investigated.

Chart 1



Ar-BIAN
1a-l

R =	
4-OMe	**a**
4-Me	**b**
3,5-Me_2	**c**
Ph	**d**
4-Cl	**e**
3-CF_3	**f**
4-CF_3	**g**
4-CN	**h**
3,5-Cl_2	**i**
4-NO_2	**j**
3,5-$(CF_3)_2$	**k**
2,6-*i*Pr_2	**l**

Very recently,[5] we improved the synthesis of the Ar-BIAN class of ligands[6] (see Chart 1 for the ligands employed in the present study), extending it to aryl groups bearing strongly electron withdrawing substit-

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[1] (a) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497−526; *Angew. Chem.* **1994**, *106*, 517−547. (b) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159−2231. (c) Fache, F.; Dunjic, B.; Gamez, P.; Lemaire, M. *Top. Catal.* **1997**, *4*, 201−209. (d) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron Asymm.* **1998**, *9*, 1−45.

[2] (a) Brown, H. C.; Bartholomay, H., Jr.; Taylor, M. D. *J. Am. Chem. Soc.* **1944**, *66*, 435−442. (b) Brown, H. C.; Sujishi, S. *J. Am. Chem. Soc.* **1948**, *70*, 2878−2881. (c) Brown, H. C. *J. Chem. Educ.* **1959**, *36*, 424−431.

[3] (a) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135−197. (b) For a more recent reference see: Steinhouser, R. K.; Kolopajlo, L. H. *Inorg. Chem.* **1985**, *24*, 1845−1852.

[4] (a) van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 2941−2950. (b) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1981**, *51*, 241−252. (c) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1981**, *51*, 253−262. (d) For more information on the chemistry of R-DAB ligands see: van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151−239 and references therein.

[5] Gasperini, M.; Ragaini, F.; Cenini, S. *Organometallics* **2002**, *21*, 2950−2957.

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uents, and we measured the equilibrium constants for reactions 1 and 2 (DMFU = dimethyl fumarate, Tol-BIAN = 4-MeC_6H_4-BIAN).

$$\text{Pd(Tol-BIAN)(DMFU)} + \text{Ar-BIAN} \underset{20\ °\text{C}}{\overset{\text{CDCl}_3}{\rightleftharpoons}} \text{Pd(Ar-BIAN)(DMFU)} + \text{Tol-BIAN} \tag{1}$$

$$\text{Pd(3,5-Me}_2\text{C}_6\text{H}_3\text{-BIAN)(OAc)}_2 + \text{Ar-BIAN} \underset{20\ °\text{C}}{\overset{\text{CDCl}_3}{\rightleftharpoons}} \text{Pd(Ar-BIAN)(OAc)}_2 + \text{3,5-Me}_2\text{C}_6\text{H}_3\text{-BIAN} \tag{2}$$

The data obtained were normalized to Ph-BIAN as a reference by dividing the individual K_{obs} by the corresponding K_{obs} value for the reaction in which Ar = Ph, so that a set of K_{eq} values was obtained which refers to the equilibria in eqs 3 and 4.

$$\text{Pd(Ph-BIAN)(DMFU)} + \text{Ar-BIAN} \underset{20\ °\text{C}}{\overset{\text{CDCl}_3}{\rightleftharpoons}} \text{Pd(Ar-BIAN)(DMFU)} + \text{Ph-BIAN} \tag{3}$$

$$\text{Pd(Ph-BIAN)(OAc)}_2 + \text{Ar-BIAN} \underset{20\ °\text{C}}{\overset{\text{CDCl}_3}{\rightleftharpoons}} \text{Pd(Ar-BIAN)(OAc)}_2 + \text{Ph-BIAN} \tag{4}$$

Other chelating nitrogen ligands were also investigated, and it was found that phenanthroline and 2,2′-bipyridine always bind more strongly than all Ar-BIAN ligands, but Ph-DAB (Ph-DAB = phenyldiazabutadiene) is a much weaker ligand. Most interestingly, a good correlation was found for all Ar-BIAN ligands, with the exception of 2,6-*i*PrC_6H_3-BIAN, between the log K_{eq} values for the reactions in eqs 3 and 4 and either the Hammett σ constants[7] of the substituents on the Ar-BIAN ligands or the pK_a values of the anilines employed in the syntheses of the same ligands.[8] The ρ values for the two reactions, however, were very different (-1.57 and -3.44, respectively).

In the present work, we have extended the series of complexes for which the equilibrium constants have been measured, including several olefin complexes as well as both neutral and cationic palladium(II) complexes and a π-allylic system. The results allow us to discuss the binding properties of the ligands and the Lewis acidity of the metal fragment in a new quantitative light.

Results

In this work we measured the relative coordination equilibria of different Ar-BIAN ligands in three olefinic complexes, Pd(Ar-BIAN)(MA) (**2**), Pd(Ar-BIAN)(FN) (**3**), and Pd(Ar-BIAN)(TCNE) (**4**) (MA = maleic anhydride, FN = fumarodinitrile, TCNE = tetracyanoethylene), two "standard" palladium(II) complexes, Pd(Ar-BIAN)(Me)(Cl) (**5**) and [Pd(Ar-BIAN)(COD-OMe)][PF_6] (**6**) (COD-OMe = η^1:η^2-$C_8H_{12}OMe$), and one π-allylic complex, [Pd(Ar-BIAN)(η^3-$CH_2C(CH_3)CH_2$)][PF_6] (**7**). The procedure is the same as that previously employed.[5] In short, when possible, the complex bearing the Tol-BIAN ligand was prepared, a known amount was dissolved in $CDCl_3$, and a known amount of another Ar-BIAN ligand was added. The reaction was followed by ^1H NMR at 20 °C, monitoring the signals of the methyl group of free and coordinated Tol-BIAN until no further variation in the relative ratio was observed. The relative amount of the second Ar-BIAN ligand to be added is a function of its coordinating strength. The only difference with respect to the procedure reported in the previous paper is that now we prepared a stock solution in $CDCl_3$ of each complex and measured the amount of added complex by volume, rather than weighing individual amounts of complex in each NMR tube. In general, excesses up to 6 times the stoichiometric amounts were necessary for the less coordinating ligands in order to displace the equilibrium to the point that a reliable integration of the NMR signals could be obtained, and in several cases even this was not enough, so that the corresponding data could not be measured. This is especially the case for the allylic complex and for the complex with TCNE. In the case of the complex with maleic anhydride, we observed a broadening of the signals when some of the less coordinating ligands were added, leading to non-baseline separation of the signals for the free and coordinated Tol-BIAN, so that again the corresponding data could not be measured. In the case of complexes **5**, the signals of the methyl groups of free and coordinated Tol-BIAN were partly overlapped, but the corresponding signals for the 3,5-$Me_2C_6H_3$-BIAN analogue were not, allowing for the determination of the corresponding equilibrium constant. The same situation had been earlier encountered with the palladium acetate complex.[5] In the case of complex **6**, the signals of the aliphatic region of the alkyl ligand overlapped with those of both Tol-BIAN and 3,5-$Me_2C_6H_3$-BIAN and the signals of free and coordinated 4-$MeOC_6H_4$-BIAN were too close to allow a separate integration. Fortunately, the position of the methoxy protons of the COD-OMe moiety shifted enough upon exchange of coordinated 4-$MeOC_6H_4$-BIAN with other Ar-BIANs that the corresponding signals could be employed to assess the position of the equilibrium.

In order for the equilibrium data to be significant, it is essential that no other product apart from the starting and final complexes and the two free ligands is formed during the reaction. In our previous work, an unknown decomposition product had been observed when Pd(Tol-BIAN)(DMFU) was employed and it had been found that decomposition could be avoided, at least on the time scale of the equilibration experiment, by adding an excess of dimethyl fumarate to the solution. We have now identified the decomposition product as Pd(Tol-BIAN)Cl_2, clearly deriving from a reaction of the starting complex with the chloroform solvent. With the more tightly bonding olefins employed in this work, however,

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(6) (a) Compounds of the family Ar-BIAN (Ar-BIAN = bis(aryl)-acenaphthenequinonediimine) have been known for some time[6b,c] but have been brought to general attention only in recent years by Elsevier and his group.[6d] 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. For a list of applications see ref 5 and references therein. (b) Dvolaitzky, M. *C. R. Acad. Sci. Paris, Ser. C* **1969**, *268*, 1811−1813; *Chem. Abstr.* **1969**, *71*, 61566b. (c) Matei, I.; Lixandru, T. *Bul. Ist. Politeh. Iasi* **1967**, *13*, 245−255; *Chem. Abstr.* **1969**, *70*, 3623m. (d) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88−98.

(7) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(8) (a) Sheppard, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3072−3076. (b) Tickle, P.; Briggs, A. G.; Wilson, J. M. *J. Chem. Soc. B* **1970**, 65−71. (c) Bolton, P. D.; Hall, F. M. *J. Chem. Soc. B* **1970**, 1247−1251. (d) Kvita, V.; Sauter, H.; Rihs, G. *Helv. Chim. Acta* **1985**, *68*, 1569−1575. (e) Gross, K. C.; Seybold, P. G.; Peralta-Inga, Z.; Murray, J. S.; Politzer, P. *J. Org. Chem.* **2001**, *66*, 6919−6925.

Table 1. Relative Coordination Strengths of Ar-BIAN Ligands to Different Metal Fragments[a]

			K_{eq}					
Ar	pK_a[b]	σ[c]	Pd(Ar-BIAN)-(MA) (**2**)	Pd(Ar-BIAN)-(FN) (**3**)	Pd(Ar-BIAN)-(TCNE) (**4**)	Pd(Ar-BIAN)-(Me)(Cl) (**5**)	[Pd(Ar-BIAN)-(COD-OMe)]-[PF$_6$] (**6**)	[Pd(Ar-BIAN)(η^3-CH$_2$C(CH$_3$)CH$_2$]-[PF$_6$] (**7**)
4-MeOC$_6$H$_4$	5.29	−0.27	4.70	10.3	7.24	6.78	10.6	13.3
4-MeC$_6$H$_4$	5.12	−0.17	2.27	4.17	3.11	6.24	7.01	4.88
3,5-Me$_2$C$_6$H$_3$	4.91	−0.14			2.43	4.08	7.37	
Ph	4.58	0.00	1.00	1.00	1.00	1.00	1.00	1.00
4-ClC$_6$H$_4$	3.98	0.23	0.50	0.26		0.39	0.38	0.15
3-CF$_3$C$_6$H$_4$	3.20	0.43	0.054	0.037		0.10	0.043	
4-CF$_3$C$_6$H$_4$	2.75	0.54	0.021	0.029		0.08	0.021	
4-NCC$_6$H$_4$	1.74	0.66				0.02		
3,5-Cl$_2$C$_6$H$_3$	2.37	0.74				0.012		
3,5-(CF$_3$)$_2$C$_6$H$_3$	1.15	0.86				0.008		
2,6-^{i}Pr$_2$C$_6$H$_3$	4.41	-	0.34	0.138		0.008		0.96

[a] Data obtained at 20 °C in CDCl$_3$. [b] pK_a of the aniline employed in the synthesis of the Ar-BIAN ligand. [c] The sum of the individual σ values is reported when two substituents are present on the phenyl ring.

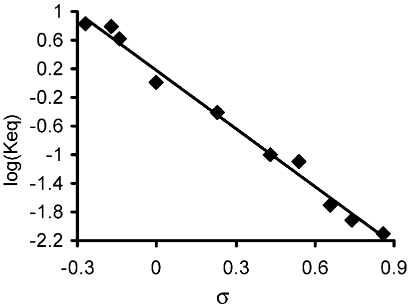

Figure 1. Plot of log K_{eq} for the exchange reaction of **5d** with Ar-BIAN as a function of the Hammett σ constants for the substituents on the aryl group of Ar-BIAN. Data are given in Tables 1 and 2.

this product was not formed on the time scale of the experiment in most cases. On the other hand, in those cases in which the exchange reaction was very slow and decomposition occurred, olefin addition could not be employed to stabilize the complexes, because this addition broadened the signals and a baseline separation for the signals of free and coordinated Tol-BIAN was no longer observed.

All the obtained data have been normalized to the equilibrium starting from the Ph-BIAN complex by dividing the observed K_{obs} value by the K_{obs} value for the reaction between the actually employed complex and Ph-BIAN. In the following, only the normalized data, K_{eq}, are reported and discussed. The results for all equilibria for which completely reliable data could be obtained are reported in Table 1. The corresponding Hammett σ value and the pK_a value of the aniline employed in the synthesis of the ligands are also shown. Where two substituents were present, the sum of the individual σ constants is reported and was employed in the following fitting. A graphical representation of the data is shown in Figure 1 and Figures S1−S5 (Supporting Information). A good to excellent (R^2 up to 0.998) linear relationship was observed between the equilibrium constant and the Hammett σ constant. A usually somewhat lower correlation also exists between the same data and the aniline pK_a value. The values for the ρ constants (hereafter referred as ρ_{BIAN}), the slope of the log K_{eq}/aniline pK_a plot, and the corresponding R^2 values are reported in Table 2. In the case of complexes **2**, **3**, **5**, and **7**, the equilibrium constant of the sterically hindered 2,6-*i*Pr$_2$C$_6$H$_3$-BIAN ligand was also measured.

Table 2. Values of ρ_{BIAN} and of the Angular Coefficient of the Correlation log K_{eq} vs Aniline pK_a Values for Different Metal Fragments[a]

metal fragment	ρ_{BIAN}	$R^2(\sigma)$	slope of log K_{eq} vs aniline pK_a	R^2(aniline pK_a)
Pd(DMFU)[b]	−1.57	0.926	0.40	0.893
Pd(Me)(Cl)	−2.71	0.989	0.744	0.955
Pd(MA)	−2.77	0.961	0.888	0.983
Pd(FN)	−3.21	0.992	1.01	0.979
Pd(TCNE)	−3.16	0.992	1.13	0.956
Pd(OAc)$_2$[b]	−3.44	0.935	0.88	0.878
Pd(COD-OMe)$^+$	−3.47	0.983	1.11	0.980
Pd(η^3-CH$_2$C(CH)$_3$CH$_2$)$^+$	−3.88	0.998	1.43	0.991

[a] Data obtained at 20 °C in CDCl$_3$. [b] Data from ref 5.

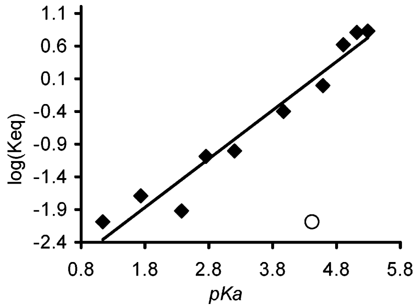

Figure 2. Plot of log K_{eq} for the exchange reaction of **5d** with Ar-BIAN as a function of the pK_a of the aniline employed in the synthesis of Ar-BIAN. Data are given in Tables 1 and 2. The open circle corresponds to the data for 2,6-*i*Pr$_2$C$_6$H$_3$-BIAN and was not included in the fitting.

Obviously, the corresponding data cannot be analyzed in terms of the Hammett σ constants, which do not exist for ortho substituents, but a comparison within the log K_{eq} vs aniline pK_a correlation is possible. Figures 2 and 3 and Figures S6−S9 (Supporting Information) show the fitting obtained, excluding the point for 2,6-*i*Pr$_2$C$_6$H$_3$-BIAN, but the corresponding data are also shown with a different marker to allow a comparison.

Discussion

The first observation which emerges from the data is that the existence of a linear relationship between the relative binding strength of Ar-BIAN ligands and either the Hammett σ constant or, to a lower extent, the aniline pK_a is a general and up to now unrecognized phenomenon. No exception was found. The second

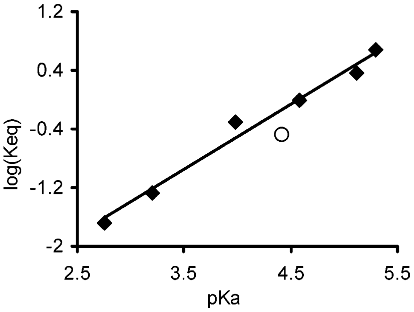

Figure 3. Plot of log K_{eq} for the exchange reaction of **2d** with Ar-BIAN as a function of the pK_a of the aniline employed in the synthesis of Ar-BIAN. Data are given in Tables 1 and 2. The open circle corresponds to the data for 2,6-iPr$_2$C$_6$H$_3$-BIAN and was not included in the fitting.

observation is that, although more basic ligands coordinate more strongly in all cases, the slope of the line describing the correlation is highly variable. It is immediately evident that the metal fragments which are intuitively more electron poor have more negative values of ρ_{BIAN}. Although this may have been qualitatively foreseen, no experimental quantitative data have ever been reported in the literature supporting this observation. Most importantly, the fact that ρ_{BIAN} can be considered as a measure of the Lewis acidity of the metal fragment allows for the first time a direct comparison of metal fragments bearing completely different ligands and having different oxidation states. In the literature, very little experimental quantitative information exists on the Lewis acidity of transition-metal complexes. One approach is based on the measurement of the acidity of a coordinated water molecule.[9] However, stable water complexes (which also need to be water soluble) of the typical metal complexes which are commonly employed as catalysts are very rare, and the method is of limited application. An electrophilicity scale has been determined from kinetic data for the nucleophilic attack of different nucleophiles on metal π-complexes.[10] However, what is measured in these systems is the electrophilicity of the whole complex, and it is not obvious how the same metal fragment would behave when coordinated to a ligand very different from a polyolefin or arene. Note that, according to IUPAC, Lewis acidity is defined as a thermodynamic phenomenon, whereas electrophilicity is a kinetic one; thus, this last approach gives in any case different, at least from a quantitative point of view, information with respect to that here discussed. A spectroscopic series has been reported, based on the fluorescence maxima of 10-methylacridone−metal ion complexes.[11] However, this series concerns strong Lewis acids and the only transition-metal compounds included are metal chlorates or triflates. This approach is unlikely to be successful for the type of compounds discussed in the present paper. On the other hand, we recognize that our approach would not be suitable for most of the Lewis acids to which the fluorescence method can be applied, since complexes with different numbers of ligands would surely be formed. An experimental Lewis acidity scale that may allow a comparison between different transition-metal fragments independent of the oxidation state and the other ligands is thus still missing.[11] The ρ_{BIAN} scale allows for the first time such a comparison. It should also be noted that, although in the present paper we only measured constants for palladium complexes, there is no reason for which a comparison between the ρ_{BIAN} constants even of complexes of different metals should not be performed, making its use much more general. The only limitation is represented by the fact that the metal fragment to be examined must have two vacant cis coordination sites. However, considering that bidentate ligands are those most commonly employed in homogeneous catalysis and that most metal-based reactions require the availability of such two vacant cis positions, it emerges that the large majority of the most interesting cases will fulfill the requirement to be analyzed by this method.

A few comments on this more generalized use of ρ_{BIAN} are worth making.

The determination of ρ_{BIAN} requires the determination of a series of equilibrium constants, rather than a single measure. However, once the parent compound is synthesized, all equilibrium constants can be determined almost in parallel, typically in a few hours of NMR time.

Different metal complexes will be differently sensitive to steric hindrance. However, the use of a series of ligands having very similar, if not identical, steric requirements will elide the steric factor, so that a purely electronic effect is observed.

It may be suggested that a monodentate ligand may be of more general use than a bidentate one. However, there are few complexes in which a clean substitution of only one monodentate nitrogen ligand is likely to be observed, whereas clean substitution of a chelating ligand is probably much more frequent.

Other ligands may be employed in place of Ar-BIANs. However, Ar-BIAN ligands have some advantages that should be considered. First, although not commercially available (at least at the moment), they are very easily synthesized[5] in multigram amounts in a short time from inexpensive materials. Moreover, they are obtained in high purity without the use of column chromatography. As a comparison, a few substituted bipyridines and phenanthrolines are commercially available, but they would be completely insufficient for the determination of a meaningful series of equilibria and the synthesis of the missing ligands is much more experimentally demanding than that of Ar-BIANs.[12] With respect to other chelating Schiff bases, Ar-BIAN ligands are also chemically robust.

Coming back to the data collected in the present work, they can be employed to give an experimental answer, or at least a different contribution, to a longstanding question.

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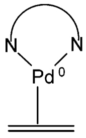
[9] For some examples see: (a) Dadci, L.; Elias, H.; Frey, U.; Hörnig, A.; Koelle, U.; Merbach, A. E.; Paulus, H.; Schneider, J. S. *Inorg. Chem.* **1995**, *34*, 306−315. (b) Hofmann, A.; Jaganyi, D.; Munro, O. Q.; Liehr, G.; van Eldik, R. *Inorg. Chem.* **2003**, *42*, 1688−1700. (c) Minsker, K. S.; Ivanova, S. R.; Babkin, V. A. *Dokl. Akad. Nauk* **1995**, *343*, 646−650; *Chem. Abstr.* **1997**, *127*, 56353.

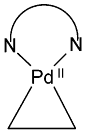
[10] (a) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525−543 and references therein. (b) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957; *Angew. Chem.* **1994**, *106*, 990−1010.

[11] (a) Another Lewis acid scale reported by the same authors and based on EPR data suffers from the same limitations as that based on fluorescence data but also requires a sophisticated apparatus and is of more limited application.[11c,d] (b) Fukuzumi, S.; Ohkubo, K. *J. Am. Chem. Soc.* **2002**, *124*, 10270−10271. (c) Ohkubo, K.; Menon, S. C.; Orita, A.; Otera, J.; Fukuzumi, S. *J. Org. Chem.* **2003**, *68*, 4720−4726. (d) Fukuzumi, S.; Ohkubo, K. *Chem. Eur. J.* **2000**, *6*, 4532−4535.

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 metallacyclopropane with the metal in the +2 oxidation state.



A



B

On the basis of the spectroscopic features of Pd(Ar-BIAN)(olefin) complexes, it was suggested that resonance structure **B** may be more important than structure **A** in describing the bonding in these complexes.[13] Similar arguments had been earlier applied to the related Pd(R-DAB)(olefin) complexes.[4] In general, the problem highlighted is an old one and dates back to the first olefin complexes of metals in a low oxidation state.[14] In our earlier paper,[5] we could only compare the data for Pd(Ar-BIAN)(DMFU) and Pd(Ar-BIAN)(OAc)$_2$ and noted that a large difference existed between the two. A more general conclusion was demanded for the moment at which data on a more extensive set of compounds would be available. Now that these data are available, we can conclude the following. The Lewis acidity of the olefin complexes is extremely variable and range from the less acidic (Pd(Ar-BIAN)(DMFU)) to two of the most acidic complexes (Pd(Ar-BIAN)(TCNE) and Pd(Ar-BIAN)(FN)) among those examined. This is even more impressive when we consider that complexes of the type here examined with olefins bearing no electron-withdrawing group are not stable enough to be isolated but are surely formed in solution during the catalytic reactions which involve them: for example, hydrogenation.[15] The ρ_{BIAN} values for the TCNE and FN series are very close, with that for the FN complexes being surprisingly more negative than that for the TCNE series. One would expect the contrary to occur. However, the values are close and the reverse order is observed when the slopes of the log K_{eq} vs aniline pK_a plots for the two series are compared. The only conclusion that can be drawn from these values is that there appears to be a limiting value to the amount of charge that palladium can transfer to the olefin in such complexes and increasing the electron-withdrawing power of the olefin over a certain limit is ineffective in further polarizing the metal. To the best of our knowledge, such an "electronic saturation" effect is unprecedented and some caution should be taken in generalizing it until more data are available.

Overall, the traditional qualitative picture that palladium complexes of olefins with strongly electron-withdrawing substituents such as TCNE should be considered as palladium(II) complexes is confirmed, but a warning may be raised against extending this assumption too far, as the Lewis acidity of the dimethyl fumarate complex is much lower than that of typical palladium(II) complexes.

The trends in the "classical" palladium(II) complexes are not surprising. The strongly donating methyl group dominates when the Pd(Cl)(Me) and Pd(OAc)$_2$ moieties are compared, despite the fact that the chloride ligand is expected to donate to a lesser extent than an acetate group. If the chloride is replaced by a neutral olefin ligand, as in **6**, and a cationic complex is generated, then the Lewis acidity of the metal fragment increases markedly, which was also expected.

The value observed for the π-allylic complex is also interesting. The standard rules for attributing oxidation states result in a negatively charged allylic fragment, bound to a palladium(II) moiety. However, the well-known fact that allylic ligands can be attacked easily by nucleophiles supports an alternative description, in which a cationic allyl fragment is bound to a palladium(0) moiety. The observed ρ_{BIAN} value is the most negative of all and clearly shows that the traditional "formal" rules are quite adequate even in this case. It is worth making a comparison between these allyl complexes **7** and the COD-OMe complexes **6**. Both are cationic complexes, and if we consider the limiting resonance structure for **7**, the metal coordinates in both cases to an η^1-alkyl and an η^2-olefin group. However, the ρ_{BIAN} values differ and indicate that an allyl moiety withdraws more charge from palladium than two separate alkyl and olefin groups.

For some of the series, the value of the equilibrium constant for the sterically hindered 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$-BIAN ligand could also be determined. We have previously reported[5] that, in the Pd(DMFU) series, the corresponding point in the K_{eq} vs aniline pK_a was clearly below the line individuated by the other points, indicating that this ligand coordinates less strongly in this system than would be expected on the basis of its basicity, clearly for steric reasons. The corresponding constant for the Pd(OAc)$_2$ moiety could not even be determined, because the exchange reaction was too slow, apparently again for steric reasons. Exchange was attempted with this ligand even for the systems reported in this study. As was expected, in some cases the reaction did not reach completion before decomposition begun to be observed. However, in four cases a clean reaction was observed. In two of these, the Pd(FN) and Pd(Cl)(Me) series, the point for 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_4$-BIAN falls quite below the line individuated by the other ligands (Figure S6 (Supporting Information) and Figure 2), evidencing again the onset of steric effects. However, in the other two cases (namely the complexes with maleic anhydride and the allylic complex, **2** and **7**, respectively, Figure 3 and Figure S9 (Supporting Information)) the point corresponding to 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_4$-BIAN nicely fit the general

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(12) Moreover, it is expected that the sensitivity of the equilibrium constant to a substituent on the ring of a pyridine ring should be much higher than that observed for the Ar-BIAN ligands, in which the aryl group lies more or less perpendicularly to the −N=CC=N− moiety. Since the sensitivity displayed by Ar-BIAN ligands is already such that in several cases the coordinating strength of the more electron-poor ligands could not be determined, the measurement of accurate equilibrium constants with different phenanthrolines or bipyridines would probably be confined to a limited range of substituents having σ constants close to each other. This would strongly affect the reliability of the correlation in a negative way.

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correlation (in the case of **7** it is even slightly above the line, but the distance is within the general uncertainty). This indicates that steric effects are not always important, even with an apparently very sterically hindered ligand. It can be noted that the series for which the steric effect is small are the only ones in which the constant ligand in the series binds asymmetrically with respect to the coordination plane. This should permit some torsion of the aryl groups of the Ar-BIAN ligand, which minimizes steric repulsion. Such a torsion effect can indeed be observed when the previously reported X-ray crystal structures of **2l**[6d] and **5l** are compared.[13] The fact that the allylic complex is the one for which the least steric effect is observed may appear surprising, given the importance asymmetric addition reactions have on this kind of complex and the traditional role steric effects have on these reactions. However, we note that the complex chosen has unusually small terminal groups on both ends of the allyl moiety (actually, no asymmetric synthesis would be possible on this allyl group) and steric effects are likely to become important even in this series if the terminal CH_2 groups are substituted with more bulky substituents.

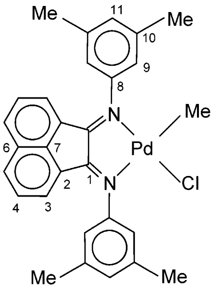
Conclusions

In this work we have measured the relative coordination ability of different Ar-BIAN ligands toward several palladium complexes, chosen so as to represent all the commonly encountered ones. A linear correlation between the relative coordination strength and either the Hammett σ constant of the substituents on the ligands or the pK_a of the aniline employed in their synthesis was always found, but the slope of the plots is highly variable. This allowed us to define a new experimental parameter, ρ_{BIAN}, which is a measure of the Lewis acidity of the metal fragment investigated. Until now, an experimental measure of this kind was limited to few classes of compounds and only calculations could be used in a general way. However, the charge distribution generated by calculations strongly relies on the method and the parameters employed in the calculation itself, so that a comparison between calculations reported in different papers is seldom possible. Finally, it is worth mentioning that the method here described only employs apparatus that is available in any research laboratory. No sophisticated technique is needed, so that anybody can measure the parameter for any compound he/she is interested in. The next step will be trying to correlate the ρ_{BIAN} values to other physical or chemical properties, especially to catalytic activity, a field where the Lewis acidity of the metal is well-known to play an important role.

Experimental Section

General Procedures. The synthesis of the ligands was carried out as previously reported.[5] NMR spectra were recorded under N_2 on a Bruker AC 300 FT, operating at 300 MHz for ^{1}H, at 75 MHz for ^{13}C, and at 121 MHz for ^{31}P, at 20 °C. The ^{1}H NMR and ^{13}C NMR signals of the compounds described in the following have been attributed by HSQC techniques and by comparison with the spectra of previously reported members of the same series of compounds. $CDCl_3$ 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 an 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 the collection of ^{1}H NMR spectra of the equilibrating mixtures. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. Pd(Tol-BIAN)(MA) (**2b**), Pd(Tol-BIAN)(FN) (**3b**), and Pd(Tol-BIAN)(TCNE) (**4b**) were prepared as reported in the literature.[13]

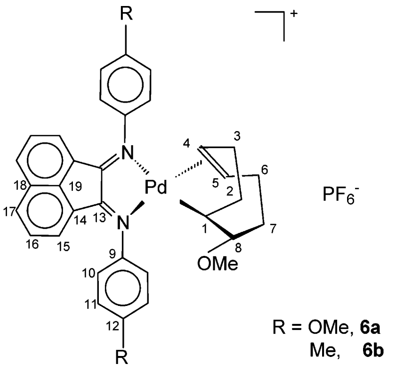
Pd(3,5-Me$_2$C$_6$H$_4$-BIAN)(Me)(Cl) (5c). This complex was prepared by the method reported for **5a** and **5l**.[16]



5c

Yield: 85.0%. Anal. Calcd for $C_{29}H_{27}N_2PdCl$: C, 63.86; H, 4.99; N, 5.14. Found: C, 63.79; H, 5.15; N, 5.10. ^{1}H NMR ($CDCl_3$, δ): 8.07 (d, J = 8.6 Hz, 1H, H5), 8.04 (d, J = 8.6 Hz, 1H, H5A), 7.50 (pst, 1H, H4), 7.46 (pst, 1H, H4A), 7.19 (d, J = 7.3 Hz, 1H, H3), 7.10 (s, 1H, H11), 7.04 (s, 1H, H11A), 6.97 (s, 2H, H9), 6.83 (s, 2H, H9A), 6.64 (d, J = 7.3 Hz, 1H, H3A), 2.44 (s, 6H, CH_3), 2.41(s, 6H, CH_3), 0.94 (s, 3H, CH_3−Pd). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 146.9, 146.1, 140.2, 139.2, 131.4, 131.1, 130.7, 129.5, 129.0, 126.9, 126.5, 125.4, 125.3, 119.2, 119.1, 21.8, 4.1.

[Pd(COD-OMe)(*p*-MeOC$_6$H$_4$-BIAN)](PF$_6$) (6a) and [Pd(COD-OMe)(Tol-BIAN)](PF$_6$) (6b). They were prepared by the method reported for **6l**.[17]



6a. Yield: 73.4%. Anal. Calcd for $C_{35}H_{35}N_2O_3PdPF_6$: C, 53.68; H, 4.51; N, 3.58. Found: C, 53.62; H, 4.51; N, 3.57. ^{1}H NMR ($CDCl_3$, δ): 8.05 (d, J = 8.3 Hz, 2H, H17), 7.48 (pst, 2H, H16), 7.39 (d br, 4H, H10), 7.11 (d, J = 8.9 Hz, 4H, H11), 6.85 (d, J = 7.3 Hz, 2H, H15), 5.73 (m, 1H, H4), 5.23 (m, 1H, H5), 3.92 (s, 6H, OCH_3), 3.47 (m, 1H, H8), 2.86 (br, 1H, H6), 2.73 (s, 3H, COD-OCH_3), 2.54 (br, 2H, H6A, H1), 2.27 (m, 3H, H2, H3, H3A), 1.95 (m, 2H, H7, H7A), 1.47 (m, 1H, H2A). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 159.5, 138.9, 132.2, 131.6, 128.9, 126.2, 122.4, 115.9, 109.1, 108.5, 81.3, 56.2, 56.1, 33.5, 31.7, 28.4, 26.7.

6b. Yield: 70.5%. Anal. Calcd for $C_{35}H_{35}N_2OPdPF_6$: C, 55.97; H, 4.70; N, 3.73. Found: C, 55.95; H, 4.81; N, 3.48. ^{1}H NMR ($CDCl_3$, δ): 8.04 (d, J = 8.3 Hz, 2H, H17), 7.46 (pst, 2H,

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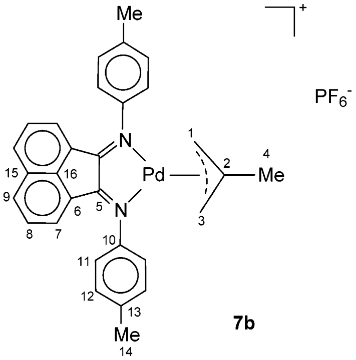
H16), 7.43 (d, $J = 8.3$ Hz, 2H, H15), 7.34 (br, 4H, H10), 6.79 (d, $J = 7.2$ Hz, 4H, H11), 5.72 (m, 1H, H4), 5.24 (m, 1H, H5), 3.47 (m, 1H, H8), 2.87 (m, 1H, H6), 2.68 (s, 3H, COD-OCH$_3$), 2.57 (m, 1H, H1), 2.52 (br, 1H, H6A), 2.49 (s, 6H, CH$_3$), 2.27 (br, 3H, H2, H3, H3A), 1.95 (m, 2H, H7, H7A), 1.46 (m, 1H, H2A).

[CH$_2$=C(CH$_3$)CH$_2$OP(NMe$_2$)$_3$][PF$_6$] (8). This product was prepared by reaction of 2-methyl-2-propen-1-ol, CCl$_4$, and tris(dimethylamino)phosphine following the procedure reported for related compounds.[18] Anal. Calcd for $C_{10}H_{25}N_3OP_2F_6$: C, 31.67; H, 6.64; N, 11.08. Found: C, 31.33; H, 6.44; N, 10.80. ^{1}H NMR (CDCl$_3$, δ): 5.1 (d, $J_{H-P} = 14.4$ Hz, 2H, CH$_2$), 4.59 (d, $J_{H-P} = 7.1$ Hz, 2H, CH$_2$O), 2.83 (d, $J_{H-P} = 10.1$ Hz, 18H, N(CH$_3$)$_2$), 1.83 (s, 3H, CH$_3$). ^{31}P NMR (CDCl$_3$, 298 K): δ 37.1 (s, P(NMe$_2$)$_3$), −143.7 (sept., $J_{P-F} = 712$ Hz, PF$_6^-$).

[Pd(Tol-BIAN)(η^3-CH$_2$C(CH$_3$)CH$_2$)][PF$_6$] (7b). This compound was prepared by the method reported for **7l**.[19] The required **8** was prepared as described above.



7b

Yield 50.1%. Anal. Calcd for $C_{30}H_{27}N_2F_6PPd$: C, 54.03; H, 4.08; N, 4.20. Found: C, 54.44; H, 4.28; N, 3.81. ^{1}H NMR (CDCl$_3$, δ): 8.10 (d, $J = 8.3$ Hz, 2H, H9), 7.53 (pst, 2H, H8), 7.41 (m, 8H, H11, H12), 7.18 (d, $J = 7.3$ Hz, 2H, H7), 3.42 (s, 2H, H1$_{syn}$, H3$_{syn}$), 3.30 (s, 2H, H1$_{anti}$, H3$_{anti}$), 2.52 (s, 6H, CH$_3$), 2.16 (s, 3H, (CH$_2$)$_2$CCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 146.6, 138.8, 136.4, 132.3, 131.7, 131.0, 128.9, 126.0, 120.9, 64.0, 23.9, 21.7.

Table 3

Pd(Ar-BIAN)(L)	amt of complex (10^{-3} mmol)	^{1}H NMR of ligand (ppm) coord	free
Pd(Tol-BIAN)(MA) (**2b**)	5.859	2.50	2.46
Pd(Tol-BIAN)(FN) (**3b**)	5.325	2.50	2.46
Pd (Tol-BIAN) (TCNE) (**4b**)	4.072	2.53	2.46
[Pd (Tol-BIAN)(η^3-C$_4$H$_7$)][PF$_6$] (**7b**)	3.529	2.51	2.46
Pd(3,5-(CH$_3$)$_2$C$_6$H$_3$-BIAN)-(CH$_3$)(Cl) (**5c**)	4.523	2.41, 2.44	2.38

Exchange Experiments. A solution of a known amount of Pd(L)(Ar-BIAN) in 0.6 mL of CDCl$_3$ was introduced in an NMR tube. A spectrum was recorded, after which the second ligand (1 equiv with respect to the complex for ligands having electron-donating substituents on the aryl ring and 2−6 equiv for ligands having electron-withdrawing substituents) was added to the NMR tube. A spectrum was recorded immediately and then every 15 min at 20 °C, until two consecutive spectra did not show any further variation. The value of the ratio between the integrated intensities of the peaks due to the methyl groups of coordinated and free ligand allows further calculations to obtain the equilibrium constant. The mathematical procedure was illustrated in a previous publication.[5] The identity and amounts of complexes **2**−**5** and **7** employed and the position of the signals for the free and coordinated ligands used for the integration are reported in Table 3.

In the case of complexes **6**, compound **6a** (3.793×10^{-3} mmol) was employed as a starting material and the signal for the methyl group on the COD-OMe moiety was used for the quantification of the starting and exchanged complexes. The following values were observed for the aforementioned signals: **6a**, 2.73 ppm; **6b**, 2.68 ppm; **6c**, 2.71 ppm; **6d**, 2.63 ppm; **6e**, 2.79 ppm; **6f**, 2.63 ppm; **6g**, 2.64 ppm.

Acknowledgment. We thank Dr. A. Caselli for help in discussing NMR spectra and the MIUR (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale) for financial support.

Supporting Information Available: Plots of log K_{eq} vs Hammett σ values and of log K_{eq} vs pK_a values of the aniline employed in the synthesis of the Ar-BIAN ligands for the reactions in eqs 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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