σ- and π-Bonding Modes of Pyridine and Imidazole Type Ligands in the Transition States of Their Reactions with [Co^{III}(protoporphyrin IX dimethyl ester)(MeO)(MeOH)] in Methanol†

Smiljko Ašperger*,‡ and Biserka Cetina-Čižmek§

Research Center, Croatian Academy of Sciences and Arts, A. Kovačića 5, 10000 Zagreb, Croatia, and Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia

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The rates of replacements of MeOH by pyridine (py) and imidazole (imH) type ligands L (=4CN-py, 3CN-py, 3Cl-py, 4Cl-py, py, 4Et-py, 4Me-py, $4NH_2$-py, $4(Me)_2N$-py; $4,5(Cl)_2$-imH, $4,5(CN)_2$-imH, Bz-imH, imH, 1Et-im, 1Me-im, 2Me-imH, 2Et-imH) in [(Co^{III}P(MeO)(MeOH)] (P = protoporphyrin IX dimethyl ester) were measured by stopped-flow techniques. The methoxide ligand is firmly held while the MeOH ligand is labile and is replaced by L in a dissociative (D) mechanism. The MeO^- "orienting" ligand, an excellent electron donor, favors entry of the least basic L, not the most basic as usually observed. The plot of ln k_{obs} vs pK_a of pyridine and its derivatives exhibits a minimum rate at pK_a of about 5. The "V" diagram is explained as being due to a change in the electronic structure of the transition state, from predominantly π bonding (descending branch) to the predominantly σ bonding (ascending branch). Imidazoles show similar trends, but their rates level off for pK_a values above 7. The free energy of activation for the reaction between [Co^{III}P(MeO)] and L is more sensitive to the change in the strength of the π bond than to that of the σ bond.

Introduction

In an earlier paper[1] we studied the rates of replacements of MeOH by pyridine (py) and imidazole (imH) in (dimethyl-3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropionato)-(methanol)(methoxo)cobalt(III), [Co^{III}P(MeO)(MeOH)]. It was assumed that the transition state in the reaction with py is stabilized by σ bonding and metal to ligand π bonding, while that in the reaction with imH involves mainly σ bonding. It was recently observed[2] that the structure of [(tetramethyl-porphinato)$Fe^{III}L_2$] (L = pyridine type ligands of various σ basicities) varies in a smooth manner as the σ basicities of L's decrease, suggesting a progressive change in the electronic structure. It has also been pointed out[2] that the σ-bonding interactions between metal and the axial ligands are less important than the π-bonding interactions.

In this paper we present rates, energies, and entropies of activation (E_a, $\Delta S^{\ddagger}$) for a variety of L replacing MeOH in [Co^{III}P(MeO)(MeOH)] in methanol. The entering ligands L vary in basicity, some forming σ bonds in the reaction transition state and some forming $\sigma+\pi$ bonds of variable strengths. E_a and $\Delta S^{\ddagger}$ increase with increasing pK_a of LH^+. The plot of the logarithms of the observed rate constants vs the pK_a values of the entering pyridine ligands exhibits a minimum as the σ basicity of L is systematically increased. Imidazole ligands also show a similar trend, the only difference being that there appears to be a leveling off of the rates at high values of pK_a (above 7). It seems that increased σ donation of substituted imidazoles exhibits no observable rate acceleration probably because imidazole itself is already a good σ donor, much better than pyridine (see Table 1).

The replacements of coordinated H_2O in the cobalt(III) corrinoid aquacyanocobamide by amines, pyridines, and diazines,[3] as well as the replacements of the coordinated H_2O in the iron(III) porphyrin microperoxidase-8 by various azoles,[4] were studied recently. The authors have concluded that "group-specific factors" and basicities of entering amine ligands are the dominant factors which determine the preference of the metal for a certain class of amine ligand, the π bonding being of secondary importance. Our results suggest that, with MeO^- as the "orienting" ligand, π bonding is very important. We noticed earlier[1,5,6] that the methoxide group, a very good electron donor, strongly increases the electron density in the *trans* axial position, the [Co^{III}P(MeO)] intermediate favoring therefore the entry of the least basic amine ligand, not the most basic as usually observed. It appears that "orienting" methoxide ligand promotes metal to ligand π bonding, while electron-withdrawing orienting ligands, such as cyanide, e.g. in aquacyanocobamide,[3] favor σ bonding.

Results

The complex [Co^{III}P(MeO)(MeOH)] was prepared in methanol solution as previously described.[5] The replacements of MeOH and MeO^- ligands proceed consecutively in that order (eqs 1and 2). The differences in rates of the two replacements

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‡ Croatian Academy of Sciences and Arts.

§ University of Zagreb.

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$$[Co^{III}P(MeO)(MeOH)] + L \rightarrow [Co^{III}P(MeO)(L)] + MeOH \quad (1)$$

$$[Co^{III}P(MeO)(L)] + L \rightarrow [Co^{III}P(L)_2]^+ + MeO^- \quad (2)$$

are large enough to permit independent spectrophotometric determination of the first step at 417 nm, using stopped-flow techniques. When we previously measured[5a] the replacement rates of MeO^- by L (4CN-py < py < 4Me-py < $4NH_2$-py), at about 50 times larger concentrations of L than those in replacements of MeOH, we found that the more basic the entering ligand, the faster the replacement,[5a] in agreement with the literature (e.g. with ref 4). On the other hand, it was a great suprise when we observed that the rate of replacement of MeOH by L according to (1) shows a different kinetic behavior; i.e., the least basic amine ligand L exhibited the largest rate of entry. Since such a kinetic behavior is contrary to expectations, we felt obliged to present a large number of replacement kinetic data. Table 1 contains the rates, E_a, and $\Delta S^{\ddagger}$ for the overall replacement reactions of MeOH with various pyridines and imidazoles. The reactions follow a D [S_N1(lim)] mechanism.[5,6] The observed rate constant (k_{obs}) is given by eq 3, where k_1

$$k_{obs} = k_1k_2[L]/(k_{-1}[MeOH] + k_2[L]) \quad (3)$$

and k_{-1} are rate constants of dissociation and association of the ligand MeOH, respectively and k_2 is the rate constant of the reaction of the intermediate [$Co^{III}P(MeO)$] with L. Since the concentrations of L are small and equal (0.002 mol dm^{-3}) and the concentration of MeOH is large (MeOH is the solvent), $k_{obs} = k_1k_2[L]/k_{-1}[MeOH]$ and the equation ${k_{obs}}^{L'}/{k_{obs}}^{L''} = {k_2}^{L'}/{k_2}^{L''}$ must hold. Consequently, ${E_{a(obs)}}^{L'} - {E_{a(obs)}}^{L''} = {E_{a(k_2)}}^{L'} - {E_{a(k_2)}}^{L''}$ and ${\Delta S^{\ddagger}_{obs}}^{L'} - {\Delta S^{\ddagger}_{obs}}^{L''} = {\Delta S^{\ddagger}_{(k_2)}}^{L'} - {\Delta S^{\ddagger}_{(k_2)}}^{L''}$. It follows that E_a and $\Delta S^{\ddagger}$ in Table 1 are not absolute values, but their differences for a certain ligand L are exact, and useful for comparison. Equation 3 can be modified into eq 4, from which

$$1/k_{obs} = (k_{-1}[MeOH]/k_1k_2)(1/[L]) + 1/k_1 \quad (4)$$

the ratios k_2/k_{-1} were determined by the least-squares method, using a computer program. In Table 1 the pyridines and imidazoles are ordered according to their increased pK_a values. The dependence of $\ln(k_2/k_{-1})$ on increased pK_a values of pyridines shows a minimum at a pK_a of about 5, as depicted in Figure 1. These results represent a correction of our earlier data regarding the rates of entry of 4Me-py vs py.[5a,6] In refs 5a and 6 the overall first-order rates of entry (k_{obs}) of 4Me-py are in general smaller than those of py (at [L] = 5×10^{-4} mol dm^{-3} the rates are equal). Using the computerized stopped-flow instrumentation (see Experimental Section), we established that the rates with py, expressed as k_2/k_{-1}, are smaller than those with 4Me-py (see Figure 1). Besides, between the presentation of rates as k_{obs} of the overall process and as k_2/k_{-1}, respectively, a small difference should be expected. The latter presentation is more adequate since we are concerned with the rates of reaction of the intermediate $Co^{III}P(MeO)$ and L, i.e. with k_2 (k_{-1} being a constant, independent on the nature of L, as already mentioned).

The plot of $\ln(k_2/k_{-1})$ values vs the pK_a values of the imidazoles is shown in Figure 2. Between pK_a 6.9 and 8 the rates are practically independent of the basicity of L. This is supported by a statistical treatment. The correlation coefficients r for all eight and for the first six points are almost equal, i.e. -0.95 and -0.94, respectively. On the other hand the last five points have an r value of only -0.65, while the t-test of the regression coefficient is 1.5, which is far below the theoretical value of 3.18 (for $\alpha = 0.05$). Thus $\ln(k_2/k_{-1})$ for the last five points should be considered a constant (mean 5.3). The straight lines $\ln(k_2/k_{-1}) = 5.3$ and $\ln(k_2/k_{-1}) = -0.464pK_a + 8.68$ cross at p$K_a = 7.28$.

Table 1 also shows that the entropies of activation, $\Delta S^{\ddagger}$, are most negative with entering ligands that are electron acceptors (increased "order" due to π bonding and solvent association).

Discussion

The imidazole ring is an essential component of many biological systems. Imidazole is an electron-donating ligand in both the σ and the π sense, much more electron donating than the majority of other nitrogen heterocycles.[15] On the other hand, imidazole is a considerably poorer π acceptor than pyridine.[16] There are cases where imidazole π donation is or is not important. (E.g., $[(NH_3)_5Co(5CH_3\text{-imH})]^{3+}$ is a case where π donation is not important.[17]) Co(III), a low-spin d^6 ion, has no empty π orbitals at low energy and cannot be an effective π acceptor. Unlike Co(III), low-spin Fe(III) and Ru(III) can act to accept π electron density from a donor atom.[17] In contrast to the good π donor imidazole, pyridine is a much weaker π donor, because pyridine does not have a high-energy HOMO as does imidazole.[16] The π-acceptor properties of pyridine are moderate because its LUMO is not as low in energy as, e.g., that of pyrazine, known as a good π acceptor.[18] It can be concluded that, with pyridine and imidazole entering ligands and their derivatives, we have primarily to consider ligands exhibiting σ and Co(III)→ligand π bonding. Since electron-withdrawing ligands will promote π bonding, while electron-donating ligands will favor σ bonding, the stabilization of the transition state between reaction intermediate [$Co^{III}P(MeO)$] and the entering ligand L should have its minimum at a certain pK_a of LH^+. It can be inferred from Figure 1 that Co(III)→ligand π bonding in the transition state is more important (higher rates) than ligand σ bonding. As early as 1984 we found that the [$Co^{III}P(MeO)$] intermediate favors the entry of the least basic amine ligand, not the most basic, as usually observed, which we elaborated in subsequent papers.[1,5,6]

Recently the imidazole adducts of (octaethylporphinato)-iron(III) methoxide, [Fe(OEP)(MeO)], were studied.[18] It was found that equilibrium constant K is dependent on the pK_a(LH^+) values of 2R-imH (sterically hindered imidazoles) in a way that the larger the value of K, the smaller the pK_a. It has been claimed that the formation of hydrogen bonding between the methoxide ligand and the NH moiety of 2R-imH weakened the

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Table 1. Observed Rates of Replacements of MeOH in [Co^{III}P(MeO)(MeOH)], 5×10^{-6} mol dm^{-3}, by L, 2×10^{-3} mol dm^{-3}, in Methanol (5% v/v Benzene), and Observed Energies and Entropies of Activation

	k_{obs}/s^{-1}					
L	14 °C	20 °C	25 °C	30 °C	35 °C	41 °C
			Pyridines			
4CN-py	14.2 ± 0.38	17.4 ± 0.78	20.5 ± 0.65	23.2 ± 0.72	25.3 ± 0.63	27.9 ± 0.82
3CN-py	12.9 ± 0.89	17.0 ± 1.1	18.6 ± 0.98	21.9 ± 0.81	24.8 ± 1.1	29.1 ± 1.1
3Cl-py	6.6 ± 0.91	9.0 ± 0.81	11.2 ± 0.99	13.5 ± 0.72	15.5 ± 0.63	17.1 ± 0.79
4Cl-py	7.7 ± 0.81	8.9 ± 0.95	10.9 ± 0.93	13.5 ± 0.78	17.9 ± 0.61	22.1 ± 0.86
py	2.4 ± 0.19	5.0 ± 0.5	6.4 ± 0.49	7.9 ± 0.41	9.0 ± 0.44	11.2 ± 0.70
4Et-py	2.6 ± 0.40	5.9 ± 0.90	8.1 ± 0.91	12.0 ± 0.92	14.4 ± 0.72	17.7 ± 0.67
4Me-py	3.9 ± 0.49	6.3 ± 0.42	7.8 ± 0.56	10.7 ± 0.95	14.1 ± 0.82	18.0 ± 0.84
4NH_2-py	3.8 ± 0.34	8.1 ± 0.41	11.0 ± 0.62	15.6 ± 0.42	18.5 ± 0.22	21.6 ± 0.33
4Me_2N-py	2.9 ± 0.37	6.2 ± 0.57	9.7 ± 0.6	13.4 ± 0.54	16.7 ± 0.66	19.6 ± 0.49
			Imidazoles			
4,5Cl_2-imH[a]	1.65 ± 0.02	2.13 ± 0.02	2.64 ± 0.02	3.63 ± 0.04	4.64 ± 0.03	7.21 ± 0.1
4,5$(CN)_2$-imH[a]	0.72 ± 0.01	0.97 ± 0.01	1.40 ± 0.02	1.81 ± 0.04	2.38 ± 0.05	2.97 ± 0.08
Bz-imH[a]	0.58 ± 0.01	0.75 ± 0.01	1.05 ± 0.03	1.55 ± 0.09	2.37 ± 0.11	3.27 ± 0.15
imH[a]	0.12 ± 0.005	0.17 ± 0.004	0.47 ± 0.015	0.64 ± 0.03	1.07 ± 0.09	1.58 ± 0.05
1Et-im	0.13 ± 0.006	0.29 ± 0.02	0.47 ± 0.015	0.72 ± 0.04	1.56 ± 0.04	2.25 ± 0.08
1Me-im	0.14 ± 0.007	0.28 ± 0.01	0.46 ± 0.013	0.79 ± 0.02	1.43 ± 0.04	2.42 ± 0.06
2Me-imH[a]	0.1 ± 0.005	0.26 ± 0.007	0.37 ± 0.015	0.52 ± 0.02	0.95 ± 0.06	1.53 ± 0.08
2Et-imH[a]	0.09 ± 0.003	0.16 ± 0.006	0.39 ± 0.01	0.48 ± 0.01	0.9 ± 0.035	1.38 ± 0.09

L	E_a/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	pK_a(LH$^+$)	L	E_a/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	pK_a(LH$^+$)
			Pyridines				
4CN-py	18.9 ± 1.3	−165.0 ± 4.3	1.1;[2] 1.97	4Et-py	44.8 ± 2.9	−86.0 ± 9.7	5.87[7]
3CN-py	21.8 ± 1.1	−155.6 ± 3.7	1.45;[2] 2.08	4Me-py	43.7 ± 1.6	−89.5 ± 5.2	6.02[2,7,9]
3Cl-py	26.7 ± 2.2	−144.0 ± 7.4	2.84[2]	4NH_2-py	47.1 ± 6.1	−76.2 ± 10.1	9.17[2,9]
4Cl-py	30.6 ± 2.0	−130.2 ± 6.7	3.84[7]	4Me_2N-py	52.8 ± 3.4	−58.6 ± 11.1	9.70[2]
py	40.0 ± 3.1	−104.6 ± 10	5.25;[7,9,10] 5.224				
			Imidazoles				
4,5Cl_2-imH[a]	37.6 ± 1.4	−120 ± 3	3.37[13]	1Et-im	79.9 ± 3.7	8.8 ± 6.1	7.03[13]
4,5$(CN)_2$-imH[a]	40.6 ± 1.5	−113 ± 5	3.41[13]	1Me-im	79.7 ± 1.2	8.1 ± 4.1	7.06;[1] 7.33[11]
Bz-imH[a]	50.4 ± 2.9	−83.2 ± 9.6	5.18;[10] 5.53[14]	2Me-imH[a]	74.5 ± 4.8	−11.7 ± 8.0	7.54[1]
imH[a]	75.9 ± 6.1	−6.8 ± 9.4	6.65;[11] 6.95;[9] 7.11[12]	2Et-imH[a]	78.5 ± 5.1	0.3 ± 8.5	7.87[1]

[a] pK_a value should be corrected for the presence of $2H^+$ (correction −0.3) because of the facile tautomeric proton shift between the two nitrogens; see ref 2. pK_a of MeOH is 15.5; see ref 26. Uncertainties are standard errors of the mean of five to seven runs. The underlined pK_a values are used in Figures 1 and 2.

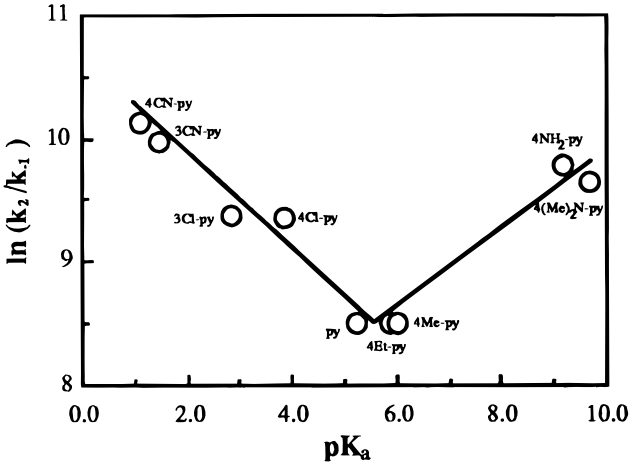

Figure 1. Dependence of ln(k_2/k_{-1}) in replacements of MeOH of [Co^{III}P(MeO)(MeOH)] (5×10^{-6} mol dm^{-3}) by various pyridine type ligands (2×10^{-3} mol dm^{-3}) on their pK_a values, in methanol (5% v/v benzene), at 25 °C. The descending branch is inferred to correspond to the decrease in metal→ligand π bonding and the ascending branch to the increase of σ bonding.

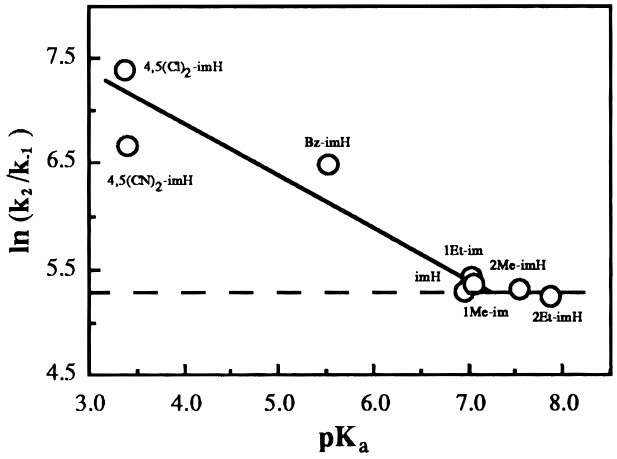

Figure 2. Plot of ln(k_2/k_{-1}) in replacements of MeOH of [Co^{III}P(MeO)(MeOH)] by imidazole type ligands vs their pK_a values. Reaction conditions were as for Figure 1.

Fe−OMe bonding. On the other hand, the authors observed that the equilibrium reaction of [Fe(OEP)(MeO)] with unhindered imidazoles proceeded to form the six-coordinated ferric low-spin complexes; the correlation of the equilibrium constant to pK_a values displayed the opposite trend; i.e., the larger the K, the larger the pK_a. We also observed steric hindrance with 4,5$(CN)_2$-imH (slower rate of entry than expected; see Figure 2), but the general trend with sterically hindered and unhindered imidazole adducts remained the same: the smaller the pK_a value, the higher the rate. Recently the equilibrium constants K for the substitution of coordinated H_2O in the iron(III) porphyrin microperoxidase-8 by various azoles have been determined[4] in 20% aqueous MeOH and a linear relationship between log K and pK_a(LH$^+$) was found. The authors have pointed out that important factors which determine the preference of iron(III) porphyrins for imidazole (as histidine) over pyridine and amines are group-specific factors > basicity > π bonding. The equilibrium constant K for the substitution of coordinated H_2O

in the cobalt(III) corrinoid aquacyanocobinamide (vitamin B_{12}) by various amines and six-membered heterocycles in aqueous solution determined by the same authors[3] has a special relevance to our work. In their experiments the CN^- ligand is very firmly held and can be considered as inert (at least in the dark), while the H_2O ligand is kinetically very labile. Their reaction took place in aqueous solution and is dissociative in nature (I_d type[19]). Analogously, in our [Co^{III}P(MeO)(MeOH)] replacements, methoxide is firmly held while the MeOH ligand is kinetically labile. The solvent is methanol, and the mechanism is also dissociative (D type[6]). Of course, the chelate is different and, what we consider most important, the orienting ligand *trans* to the leaving ligand is different: in our case this is methoxide, an excellent electron donor, while in the mentioned vitamin B_{12} replacements the orienting ligand is cyanide, which can function as an electron-withdrawing ligand (Hammet's σ_m and σ_p are 0.56 and 0.66, respectively). The data in Table 1 also show the importance of group factors: the replacement rates of pyridine derivatives are larger than those of imidazole derivatives. (Just the reverse observation was made by the previously mentioned authors[4] in the replacements of coordinated H_2O in the iron(III) porphyrin microperoxidase-8.) Furthermore, the replacements in vitamin B_{12} show the linear free energy relationship $\log K = a(pK_a) + b$, while in our replacements, generally speaking, the dominant trend is the smaller the pK_a, the larger the k_{obs}. We believe that, besides all mentioned factors which direct metal→ligand bonding such as the α effect, group-specific factors, basicity of L, and π bonding,[3,4] there can be a dominant influence of the orienting ligand *trans* to the leaving ligand. This appears to be the case with our methoxo complex.

One might try to find an alternative explanation for the kinetic data presented in this paper in the supposition that the kinetics we followed are in fact related to the $\pi-\pi$ interactions between the porphyrin ring and the entering ligands, e.g. pyridines. The idea of $\pi-\pi$ interactions in porphyrin systems was first put forward by Mohr and Scheler.[20] They observed that in alkaline aqueous solution (pH >10) protohemin forms a green pyridine complex containing two ligands per hemin dimer. They also found that similar hemin complexes are formed by *N*-alkylpyridinium halides, the absorption spectra being nearly identical to those of the corresponding pyridine complexes, although there is no possibility of interaction with the positively charged hemin iron. Moreover, pyridinium cations have a higher affinity for hemin than the neutral pyridines. This behavior they attributed to electrostatic attractions between the propionylic groups of porphyrin and the positively charged pyridinium salts. They also found that the substitution of pyridine in position 4 by a cyano group increased the affinity for hemin. Marques, Byfield, and Pratt[21] studied the coordination of ammonia, aniline, and pyridine by the iron(III) porphyrin microperoxidase-8 (MP-8) and found that all these ligands bind through coordination to the metal, replacing coordinated H_2O, and not through $\pi-\pi$ interactions with the porphyrin ring. They found obvious similarities in the spectra among all three entering ligands, which supported the conclusion. On the other hand, the adduct of MP-8 at pH 12 with 1-methylpyridinium (which cannot act as a ligand) showed a totally different spectrum, suggesting the formation of a $\pi-\pi$ adduct at this high pH. From this literature survey[21−25] it can be concluded that the $\pi-\pi$ adduct formation as an alternative explanation of our kinetic results has no support indeed. The original observation by Mohr and Scheler[20] relates only to the alkaline aqueous solution (pH >10) of protohemin. As already mentioned, they attributed the $\pi-\pi$ interaction to electrostatic attraction between the propionylic groups of the porphyrin and the positively charged pyridinium ion. In our case, the propionylic groups are blocked in the form of dimethyl esters.

Furthemore the formation of the $\pi-\pi$ adduct should be an associative process, while we clearly measured the kinetics of reactions 1 and 2. Reaction 1 is a dissociative process of the D [S_N1(lim)] type: the pyridine type ligands (4CN-py, py, 4Me-py) gave ideal limiting rates ($k_{obs} = 57.8\ s^{-1}$ at 25 °C).[1,5a] $\pi-\pi$ adduct formation could not produce such kinetics.

The spectrum of [Co^{III}P(MeO)(MeOH)] has a Soret peak at 417 nm and α and β peaks at 565 and 532 nm. All spectral changes due to replacements (eqs 1 and 2) are similar. There are slight changes in the α and β peaks and a bathochromic shift of a Soret peak of about 4−10 nm, depending on ligand nature.

Because of all the reasons quoted, we must reject the idea of $\pi-\pi$ adduct formation.

Regarding the basicity of the methoxide orienting ligand, we already stressed that alkoxides are excellent electron donors. We observed the following sequence: methoxide < isopropoxide < *sec*-butoxide. One should bear in mind that our replacements were performed in absolute methanol. As pure liquids, methanol, ethanol, and other simple alcohols are weaker acids than when dissolved in aqueous solution. The pK_a for methanol as a pure liquid is approximately 17 ($K_{MeOH} = [CH_3OH_2^+][CH_3O^-] = 1.2 \times 10^{-17}\ M^2$). Thus, methoxide in methanol is a stronger base than is hydroxide in water[26] and obviously an excellent electron donor much better than hydroxide in aqueous solution. The much smaller K_{MeOH}, as compared with K_w, comes in large part from the lower dielectric constant of methanol (32.6:78.5). Greater energy is required to separate methoxide from its proton (or from the positive metal center) in methanol than for analogous separation of hydroxide in aqueous solution.[26]

Tobe and co-workers studied the influence of L on the rate of acid hydrolysis of $Co^{III}(en)_2LCl^+$ yielding $Co^{III}(en)_2LH_2O^{2+}$. They arranged the groups L in order of decreasing tendency to donate electrons to cobalt and increasing tendency to accept electrons.[27] The hydroxide ion is considered the strongest electron donor among 21 ligands listed. The electron-donating ability of CN^- is placed much below that of OH^-. On the other hand, there are reports[23,24] that CN^- is a better donor than OH^-. Besides, it is difficult to discern the modes of bonding of ligands which can σ-bond and ligand to metal and metal to ligand π-bond.

Experimental Section

Materials. Methanol was Merck AR grade (99.8%). Pyridine, py (Merck AR grade), was kept under KOH and freshly distilled before use; 3Cl-py, 4Me-py, and 4Et-py (Fluka, >97%) were also freshly

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distilled before use; 4CN-py, 3CN-py, and 4Cl-py·HCl (Fluka, >97%) and $4NH_2$-py and $4(Me)_2N$-py (Merck, >98%) were recrystallized from EtOH before use. Imidazole, imH (Fluka, AR grade), and 2Me-imH, 2Et-imH, and $4,5(CN)_2$-imH, $4,5(Cl)_2$-imH (Aldrich, >98%) were purified by sublimation, dried *in vacuo*, and placed in sealed containers. Bz-imH (Aldrich, >98%) was recrystallized from hot water, dried *in vacuo*, and placed in a sealed container. 1Me-im (Aldrich, >98%) and 1Et-im (Chamalog, purum) were distilled before use.

Spectrophotometry. Absorption spectra were recorded on a Pye Unicam SP-8-100 UV/vis spectrophotometer.

Kinetics. A Durum D-110 stopped-flow spectrophotometer, equipped with a thermostated cell compartment, was used for kinetic measurements. All computations were done on a Compaq Deskpro 386s computer with OLIS software.

The stock solution of $[Co^{II}P]$ in benzene was 10^{-4} mol dm^{-3}. $[Co^{III}P(MeO)(MeOH)]$ is formed in methanolic solution (dilution 1:10) after 2 days in the presence of O_2. The methanolic solutions of $[Co^{III}P(MeO)(MeOH)]$ can be also prepared from $[Co^{III}P(Cl)]$. Immediately on dissolution, chloride is released and the complex equilibrates to $[Co^{III}P(MeOH)_2]$ and $[Co^{III}P(MeO)(MeOH)]$. The methoxo−methanol complex widely predominates. The spectra of the methoxo−methanol complex produced both ways are identical. The solutions of pyridine and imidazole adducts were prepared in methanol. The ionic strength of all reaction solutions was the same (5×10^{-2} mol dm^{-3}) and was achieved by addition of $LiClO_4$.

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