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Et₃P⁺- and Nitro-Substituted Pyridines and Bipyridines. Their Behavior as Ligands in Iron(II), Cobalt(II), and Ruthenium(II) Complexes

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Substituted pyridines and 2,2'-bipyridines with NO₂ and (C₂H₅)₃P⁺ groups para to the ring nitrogens have been prepared and were used as ligands in complexes with Fe(II), Ru(II), and Co(II). The pK values and reduction potentials of the free ligands were measured and the results discussed in terms of the nature of the electron-withdrawing effect of the two substituents. The information on the free ligands was then used to help interpret the metal → ligand charge-transfer data as well as the redox potentials for the complexes. The results obtained in this study were compared with previous attempts to evaluate substituent constants for the NO₂ and R₃P⁺ groups.

Introduction

Our interest in the effect of cationic substituents (and electron-withdrawing substituents as a whole) on the behavior of pyridyl ligands in complexes[1] has been further stimulated by the possibility that these substituents could be useful in adjusting the behavior of the ligands in the photochemistry of their complexes.[2-4] This paper therefore concerns the effect of the substituents on the properties of the free and complexed ligands. We have prepared some substituted pyridines and 2,2'-bipyridines with NO₂ and (C₂H₅)₃P⁺ groups para to the ring nitrogen and have investigated the pK's and reduction potentials of these ligands. We have then incorporated the ligands into complexes with Co(II), Fe(II), and Ru(II) and have investigated the electronic spectra and redox potentials of the complexes. The effects of the cationic substituent and the neutral electron-withdrawing substituent are then compared.

Experimental Section

Materials. 4-Nitropyridine was obtained by heating 4-nitropyridine *N*-oxide with a mixture of concentrated H₂SO₄ and HNO₃ at 240 °C for 20 min. The mixture was then poured into ice, neutralized with a saturated NaOH solution, and extracted with CHCl₃. The product (mp 48–49 °C) was obtained from the extract after evaporation of the solvent and crystallization from hexane. 4-Nitro-2,2'-bipyridine and 4,4'-dinitro-2,2'-bipyridine were prepared by standard literature methods.[5,6] 4-Bromopyridine was obtained by adding aqueous KOH to a chilled aqueous solution of the hydrochloride and extracting with ether. The ether was removed just before use. 4-Bromo-2,2'-bipyridine and 4,4'-dibromo-2,2'-bipyridine were prepared from the corresponding nitro compounds by standard literature methods.[5,6]

Triethyl-4-pyridylphosphonium Bromide, (P⁺py)Br. Triethylphosphine (4.0 g, 34 mmol) was added to 3.5 g of 4-bromopyridine (22.4 mmol) and the reaction mixture was left in a sealed tube under N₂ for 74 h at 85 °C. After the excess phosphine was washed out with ether, 2.8 g of a solid was obtained. It gave, on crystallization from an acetone–ether mixture, 1.8 g of the product, mp 157–158 °C. NMR (D₂O):[7] δ 8.1–8.3 (m, 2, pyridyl H$_α$), 7.3–7.5 (m, 2, pyridyl H$_β$), 2.7–2.8 (m, 6, CH₂), 1.1–1.3 (m, 9, CH₃). Anal. Calcd for C₁₁H₁₉PNBr: C, 47.84; H, 6.93. Found: C, 47.74; H, 7.08.

Triethyl-4-bipyridylphosphonium Bromide, (P⁺bpy)Br. Triethylphosphine (1.0 g, 8.5 mmol) was added to 0.35 g of 4-bromo-2,2'-bipyridine (1.5 mmol), and the reaction mixture was left in a sealed tube under N₂ for 120 h at 120 °C. After the excess phosphine was washed out with ether, 0.45 g of a white solid was obtained. Crystallization from acetone–ether yielded 0.35 g of the product, mp

179–180 °C. NMR (D₂O):[7] δ 7.5–8.9 (m, 7, bpy H), 2.5–2.8 (m, 6, CH₂), 1.0–1.3 (m, 9, CH₃). Anal. Calcd for C₁₆H₂₂N₂PBr: C, 54.40; H, 6.28. Found: C, 54.43; H, 6.39.

{[4,4'-(C₂H₅)₃P]₂bpy}Br₂, (P₂⁺bpy)Br₂. Triethylphosphine (2.0 g, 17 mmol) was added to 0.43 g of 4,4'-dibromo-2,2'-bipyridine (1.4 mmol), and the reaction mixture was left at 120 °C for 100 h in a sealed tube under N₂. Only the monophosphonium product was isolated. This product (0.40 g) was mixed with 1.0 g of triethylphosphine and heated for 5 h at 190 °C in a sealed tube. After the excess phosphine was washed out with ether, the isolated solid (0.44 g) was crystallized from ether–acetone to give 0.40 g of the product, mp 320–322 °C. NMR (D₂O): δ 8.0–9.1 (m, 6, bpy H), 2.6–3.0 (m, 12, CH₂), 1.2–1.5 (m, 18, CH₃). Anal. Calcd for C₂₂H₃₆P₂N₂Br: C, 48.02; H, 6.59. Found: C, 47.98; H, 6.66.

Preparation of the Complexes. The Co(II) complexes of 4-nitropyridine and (P⁺py)Br were prepared according to the previously reported procedure.[1] The Fe(II) and Ru(II) complexes of the substituted bipyridines were isolated as the perchlorate salts by the procedure described in the literature.[8,9]

Determination of pK_a. The pK_a values were determined spectrophotometrically. All spectra were taken on a Cary Model 15 spectrophotometer, using matched 1-cm cells. The aqueous (or aqueous alcoholic) solutions were approximately 10⁻⁵ M. The spectra were obtained in the temperature range 24–28 °C and showed no variation within the limits of this range. The values were calculated by using the formula

$$pK = pH + \log \frac{d - d_n}{d_1 - d}$$

where d_1 is the optical density for the acid form, d_n is the OD for the base form, and d is the OD at any intermediate pH. All values of d apply to the same analytical wavelength in each case. Excited-state pK_a values were estimated by using Forster cycle calculations.[10]

Cyclic Voltammetry. A Princeton Applied Research Corp. system consisting of a Model 173 potentiostat and a Model 175 universal programmer was employed in the cyclic voltammetry measurements. Millimolar solutions of Fe(II) and Ru(II) complexes (as ClO₄⁻ salts) were prepared in a 0.1 M acetonitrile solution of tetraethylammonium perchlorate. The acetonitrile was dried before use by stirring over CaH₂ and distilling over P₂O₅. The working electrode was platinum, and the auxiliary electrode was platinum gauze. The working electrode in the reduction of the free ligands was a hanging-drop electrode (Hg). All solutions were handled under nitrogen. The scan rate in all the cyclic voltammetric experiments was 100 mV/s. The reference was a saturated aqueous calomel electrode (SCE).

Results and Discussion

Ligand Preparation and Properties. The nitro compounds were synthesized by using modifications of literature methods.[5,6] The nitrobipyridine compounds were also used in the synthesis of bromo derivatives which could be treated with triethylphosphine to produce the desired phosphonium-substituted species.

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Table I. pK Values^a of the Free Ligands in Aqueous or Aqueous Alcoholic^b Solution

compd	pK_a^{c}	excited-state pK_a^{d}
py	5.17	
4-NO$_2$py	1.48	
(4-P$^+$py)Br^e	1.61	
bpy	4.27	9.2^f
4-NO$_2$bpy	3.25	5.1^g
(4-P$^+$bpy)Br^h	2.82	6.4^i
4,4'-(NO$_2$)$_2$bpy	0.06	3.9^j
(4,4'-P$^+$$_2$bpy)Br$_2$^{k}	0.03	5.6^l

^{a} Determined by spectrophotometry. ^{b} No real differences in pK values were observed between aqueous and 20% EtOH solutions, with the phosphonium compounds soluble in both media. ^{c} Obtained to within ±0.03 unit. ^{d} Calculated from $\Delta pK_a = 0.00209(\bar{\nu}_B - \bar{\nu}_{BH^+})$, where ΔpK is the difference between excited-state and ground-state values, $\bar{\nu}_B$ is the frequency in wavenumbers of the lowest energy $\pi \rightarrow \pi^*$ absorption maximum for the unprotonated form, and $\bar{\nu}_{BH^+}$ is the same for the protonated form. The pK values are listed to within ±0.1 unit. ^{e} Pyridine substituted with Et$_3$P$^+$. ^{f} $\bar{\nu}_B - \bar{\nu}_{BH^+} = 2300$ cm^{-1}. ^{g} $\bar{\nu}_B - \bar{\nu}_{BH^+} = 900$ cm^{-1}. ^{h} Bipyridine substituted with Et$_3$P$^+$. ^{i} $\bar{\nu}_B - \bar{\nu}_{BH^+} = 1700$ cm^{-1}. ^{j} $\bar{\nu}_B - \bar{\nu}_{BH^+} = 1800$ cm^{-1}. ^{k} Bipyridine with two Et$_3$P$^+$ substituents. ^{l} $\bar{\nu}_B - \bar{\nu}_{BH^+} = 2600$ cm^{-1}.

The pK data on the ligands is shown in Table I. The standard pK_a measurements show that the NO$_2$- and Et$_3$P$^+$-substituted bases have approximately equal base strengths, both of course diminished considerably from those of the unsubstituted compounds. (In the monosubstituted bipyridines, the values clearly show that protonation occurs on the unsubstituted ring.) Thus no real difference appears here between the effects of the NO$_2$ and the cationic Et$_3$P$^+$ substituents. In addition, excited-state pK values (Table I) were estimated by using the difference in energy between the $\pi \rightarrow \pi^*$ transition in the acid and base forms of the molecules (Forster cycle calculation).[10] No direct evaluation of these data was possible since the NO$_2$ compounds did not luminesce in water and luminescence in the other compounds is attributed to the formation of hydrates.[11] The enhancement of basicity (pK^* − pK) in the excited state of the parent bipyridine is attributable to charge migration toward the nitrogen upon excitation. Although the (pK^* − pK) values overall contain some difficulties in interpretation, one observation seems clear. The NO$_2$ group shows less basicity enhancement than Et$_3$P$^+$, or apparently less charge migration to the donor nitrogen in the excited state. It therefore exhibits here its greater π-electron-withdrawing nature. The greater basicity enhancement for the disubstituted compounds compared to that of the monosubstituted compounds could be due to a different configuration for the monoprotonated acid of the disubstituted derivative (e.g., instead of the cis or transoid structure,[12] a trans form is possible here).

The reduction potentials listed in Table II support the same suggestion about the relative effects of the substituents. Although both electron-withdrawing groups lower the potential necessary for the reduction of the π system, the NO$_2$ group shows a stronger effect in both the monosubstituted and disubstituted compounds (previous studies have shown that the first and second reductions are into the π system).[13] The reductions were observed to be irreversible, with the exception of that of the dinitro derivative. This is probably due to chemical reaction of the radical anions produced by the first reduction, and the suggestion is supported by the observed second waves, which are otherwise inconsistent with reasonable

Table II. Reduction Potentials^a (in Volts) for the Free Ligands in Acetonitrile Solutions of 0.1 M Tetraethylammonium Perchlorate (via Cyclic Voltammetry)

compd	1st wave	2nd wave
bpy	−2.21	−2.46
4-NO$_2$bpy	−1.55	−2.38
(4-P$^+$bpy)Br	−1.67	−2.22
4,4'-(NO$_2$)$_2$bpy	−0.80	−0.91
(4,4'-P$^+$$_2$bpy)Br$_2$	−1.43	−2.23

^{a} Reductions are electrochemically irreversible, except for that of the dinitro derivative.

interpretation, except for the case of the dinitro derivative. If the reaction which follows reduction is rate determining, the irreversible potentials are dependent on the rate constants for that chemical reaction, and the interpretation of the potential values should be treated with caution.

From the above evidence it is assumed that although the NO$_2$ and Et$_3$P$^+$ substituents may affect the σ-donor ligancy of the pyridyl systems in a nearly equivalent manner, phenomena which directly involve the ring π system of the complexes formed with these ligands will show a greater effect by the NO$_2$ group.

Properties of the Complexes. The NO$_2$- and Et$_3$P$^+$-substituted bipyridines showed similar complexing tendencies. The tris complexes were readily obtained from the monosubstituted ligands, by using the same method employed for the corresponding unsubstituted bipyridine complexes.[8,9] Repeated attempts to complex Ru(II) with either of the disubstituted ligands produced only the bis complexes. The tris complex of Fe(II) with the disubstituted Et$_3$P$^+$ ligand was formed, but the dinitro ligand failed to yield a definable complex. The Co(II) complexes formed were of the CoBr$_3$L type. The complexes obtained are listed, with their analyses, in Table III.

Table IV gives the energies of the common metal → ligand charge-transfer transitions. The lowest energy or most familiar transition occurs around 20 000 cm^{-1} and is assigned to $\pi^*(1) \leftarrow t_2$.[14] It is characterized by log ϵ values in the range of 3.7–4.0 for the (bpy)$_3$Fe^{II} complexes and 4.0–4.3 for the (bpy)$_3$Ru^{II} complexes.[14] Moreover the high-energy shoulder which is observed for the unsubstituted bipyridyl complexes[14] is present in the other tris(bipyridyl) spectra as well, though barely discernible in some cases. The transition energies in the tris(bipyridyl) spectra show little effect of changing solvent, while the spectra of the bis(bipyridyl)ruthenium(II) complexes show a substantial solvent shift, in agreement with previous observations.[14,15] The tris complexes of Ru(II) show larger transition energies than the corresponding Fe(II) complexes, which is accounted for by the lower energy of the Ru(II) t$_2$ orbitals, presumably due to more substantial metal–ligand π interaction[14a,16] (vide infra).

A second, less familiar transition is observed in the 27 000-cm^{-1} region of the spectra of some Fe(II) complexes (some structure is discernible here in the other Fe(II) spectra, but at a much lower intensity). The inconsistency in appearance of this band, plus the inability to observe it in the tris(bipyridyl)ruthenium spectra, makes the origin of the transition ambiguous, but it has been assigned to a charge transfer from the metal t$_2$ orbital into the second ring π^* orbital.[14] The bis complexes show both bands clearly,[15] and

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Table III. List of Complexes and Their Elemental Analyses

	% C		% H		% Cl	
complex	calcd	found	calcd	found	calcd	found
$Et_4N^+[Co(NO_2py)Br_3]$	28.23	28.05	4.34	4.38		
$[Co(P^+py)Br_3]$	26.69	26.52	3.84	3.65		
$[Fe(NO_2bpy)_3](ClO_4)_2\cdot3H_2O$	39.49	39.29	2.96	2.64		
$[Fe(P^+bpy)_3]ClO_4)_5\cdot4H_2O$	39.89	39.71	5.12	4.84		
$[Fe(P^+_2bpy)_3](ClO_4)_8\cdot2H_2O$	38.50	38.58	5.44	5.88	13.80	13.94
$[Ru(NO_2bpy)_3](ClO_4)_2$	39.87	39.75	2.32	2.72	7.85	8.35
$[Ru(P^+bpy)_3](ClO_4)_5\cdot5H_2O$	38.22	38.04	5.04	4.78	11.75	11.25
$[Ru[(NO_2)_2bpy]_2Cl_2\cdot H_2O^a$	35.19	35.02	2.05	2.07	10.41	10.61
$[Ru(P^+_2bpy)_2Cl_2](ClO_4)_4\cdot5H_2O$	36.66	36.32	5.69	5.12	14.79	14.66

a Bis(4,4'-dinitrobipyridine)dichlororuthenium complex.

Table IV. Charge-Transfer Absorption Bands of the Complexes*a*

	ν_{max}, cm^{-1} ($10^{-3}\epsilon$)			
complex	H$_2$O		CH$_3$CN	
$[Fe(bpy)_3](ClO_4)_2$	19 120 (9.0)	28 571 (8.0)	19 267 (9.0)	28 571 (8.2)
$[Fe(NO_2bpy)_3](ClO_4)_2$	17 605		17 762 (9.4)	
$[Fe(P^+bpy)_3](ClO_4)_5$	18 484 (10.5)		18 518 (8.0)	
$[Fe(P^+_2bpy)_3](ClO_4)_8$	18 450 (7.0)	26 316 (6.5)	18 382 (5.5)	26 316 (6.2)
$[Ru(bpy)_3](ClO_4)_2$	22 321 (13.2)		22 272 (12.1)	
$[Ru(NO_2bpy)_3](ClO_4)_2$	20 576 (15.0)		20 661 (16.4)	
$[Ru(P^+bpy)_3](ClO_4)_5$	21 459 (18.2)		21 505 (18.0)	
$[Ru(bpy)_2Cl_2]$	20 492 (3.1)	29 439 (2.9)	18 116 (5.8)	26 666 (6.4)
$Ru[(NO_2)_2bpy]_2Cl_2$ *b*	17 452 (5.3)	21 978 (4.8)	16 234 (7.6)	20 618 (6.4)
$[Ru(P^+_2bpy)_2Cl_2](ClO_4)_4$	18 182 (15.5)	25 125 (14.7)	16 806 (17.1)	23 529 (14.6)
$Et_4N^+[Co(NO_2py)Br_3]$ *c*		26 315		
$[Co(P^+py)Br_3]$ *c*		28 653		

a Measured with a Cary Model 14 spectrophotometer. *b* Bis(4,4'-dinitrobipyridine)dichlororuthenium complex. *c* Measured on Nujol mulls spread on filter paper.

this observation was useful in the present work as evidence for the formulation of these complexes as bis(bipyridyls).

Most importantly, the effect of the various substituents is noted. In the tris complexes of both metals, the NO$_2$ substituent shows twice the effect of the Et$_3$P$^+$ in lowering the energy of the charge transfer, despite the positive charge on the latter. (This effect is smaller in the bis complex.) Thus the NO$_2$ exhibits the greater withdrawing effect on the ring π system, resulting in a lowering of the π^* orbital energy beyond that shown by Et$_3$P$^+$.

As noted in the previous study on the [CoBr$_3$L] system,[1] the Et$_3$P$^+$-substituted pyridine complex showed an absorption at 28 650 cm^{-1}, which was assigned as before to a metal → pyridine charge-transfer transition. This band was missing in Et$_4$N$^+$[Co(C$_5$H$_5$N)Br$_3$]$^-$ and was assumed to be obscured by the Br → Co transitions at 34 000–37 000 cm^{-1}. In the present work, the NO$_2$-substituted pyridine complex clearly showed this transition, at 26 315 cm^{-1}. Thus in this pyridyl ring system, the NO$_2$ group again is more effective in lowering the metal–ligand charge-transfer (MLCT) energy.

Previous workers have measured substituent effects on MLCT energies in systems such as Ru^{II}(NH$_3$)$_5$L[17] and Fe^{II}(CN)$_5$L,[18] where the ligands L were various cationic pyridine and pyrazine systems (i.e., the pyrazinium ion, pyH$^+$, the N-methylpyrazinium ion, and the 4-pyridylpyridinium ion). The lowering in MLCT energy for these complexes from the MLCT energy for the complexes of the corresponding unsubstituted ligands appears to be somewhat greater than the shifts found in the present study. This may be attributable to the pentaammine and pentacyano moieties, wherein a greater amount of charge is donated to the central metal, raising the metal donor orbital energy and making the MLCT energy more susceptible to changes at the acceptor pyridyl ligand. A recent measurement of the MLCT energy for the

Table V. Oxidation Potentials via Cyclic Voltammetry for the Complexes in Acetonitrile Solutions of 0.1 M Tetraethylammonium Perchlorate

complex	$E_{1/2}$,*a* V	ΔE_p,*b* mV
$[Fe(bpy)_3](ClO_4)_2$	1.06	60
$[Fe(NO_2bpy)_3](ClO_4)_2$	1.33	70
$[Fe(P^+bpy)_3](ClO_4)_5$	1.31	100
$[Fe(P^+_2bpy)_3](ClO_4)_8$	1.52	80
$[Ru(bpy)_3](ClO_4)_2$	1.29	70
$[Ru(NO_2bpy)_3](ClO_4)_2$	1.54	80
$[Ru(P^+bpy)_3](ClO_4)_5$	1.52	60
$[Ru(bpy)_2Cl_2]$	0.35	70
$Ru[(NO_2)_2bpy]_2Cl_2$ *c*	0.85	70
$[Ru(P^+_2bpy)_2Cl_2](ClO_4)_4$	0.75	120

a Values (vs. SCE) were obtained by taking the average of the anodic and cathodic peak potentials; ±0.01 V. *b* Separation between anodic and cathodic waves. *c* Bis(4,4'-dinitrobipyridine)-dichlororuthenium complex.

Ru(py)$_6^{2+}$ ion (29 300 cm^{-1})[19] allows a comparison with the lower value[20] of 24 500 cm^{-1} for Ru(NH$_3$)$_5$py^{2+}, indicating the raised donor orbital energy in the latter complex.

The effect of ligand substituents and varying central metal on the MLCT energies is further explained by considering the redox energies of the complexes (Tables V and VI). Previous studies have clearly shown that oxidation of these complexes takes place at the metal, while the two lowest energy reductions take place into π^* orbitals largely centered on the rings.[13,21] Our results are entirely consistent with this. The reduction potentials listed are substituent dependent but independent of whether the central ion is Fe(II) or Ru(II). Most importantly, the order of the first-wave reduction potentials parallels the order of the charge-transfer energies for the complexes of a

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Table VI. Reduction Potentials via Cyclic Voltammetry for the Complexes in Acetonitrile Solutions of 0.1 M Tetraethylammonium Perchlorate

complex	1st wave		2nd wave		3rd wave	
	$E_{1/2}{}^a$	$\Delta E_p{}^b$	$E_{1/2}{}^a$	$\Delta E_p{}^b$	$E_{1/2}{}^a$	$\Delta E_p{}^b$
$[Fe(bpy)_3](ClO_4)_2$	−1.40	65	−1.59	60	−1.89	80
$[Fe(NO_2bpy)_3](ClO_4)_2$	−0.64^c		−0.93^c			
$[Fe(P^+bpy)_3](ClO_4)_5$	−0.96	80	−1.07	65	−1.25	65
$[Fe(P^+{}_2bpy)_3](ClO_4)_8$	−0.74	70	−0.84	70	−0.98	60
$[Ru(bpy)_3](ClO_4)_2$	−1.40	70	−1.58	60	−1.83	70
$[Ru(NO_2bpy)_3](ClO_4)_2$	−0.63^c		−1.33^c			
$[Ru(P^+bpy)_3](ClO_4)_5$	−0.96	70	−1.07	70	−1.27	60

^{a} Values (in V vs. SCE) were obtained by taking the average of the anodic and cathodic peak potentials; ±0.01 V. ^{b} Separation, in mV, between the anodic and cathodic waves. ^{c} Reductions are electrochemically irreversible. A desorption spike was observed in the first anodic wave.

given metal. Thus, while both electron-withdrawing substituents lower the potential for reduction of the rings (lower the energy of the LUMO), the nearly doubled effect of the NO_2 group is observed. On the other hand, while both substituents raise the potential necessary for oxidation because of their electron-withdrawing effect on the metal, there is no difference between the two substituents. This relates to the comparable pK's of the bipyridine bases containing the two substituents. The nature of the central metal does affect the oxidation potential however, since the differing metal → ligand π-bonding tendencies result in the lowering of the energy of the Ru(II) filled d orbitals more than the energy of the Fe(II) orbitals, and if oxidation takes place at the metal, then this serves to raise the potential necessary for oxidation of the Ru(II). Note that the bis complexes have substantially lower oxidation potentials, showing the effect of reducing the positive charge on the metal by replacing a neutral bipyridyl ligand with Cl⁻. (Although direct comparisons of the charge-transfer energies for bis- and tris(bipyridyl) complexes are difficult, the former seem to have generally lower MLCT energy values as a consequence of the reduced positive charge on the metal.)

Conclusions

The total picture presented in this work is quite self-consistent and provides an insight into the effect of cationic substituents that has been puzzling us for some time.[1] The cationic phosphonium substituent reduces the ligancy of the pyridyl bases, but not to any greater extent than electron-withdrawing neutral substituents. Therefore it shows no greater influence on those characteristics of the complex which depend on the ligancy of the base. On the other hand, the neutral NO_2 substituent, which exerts a greater withdrawing effect on the ring π system, lowers the LUMO of the complexes more than R_3P^+ and therefore has a greater influence on those properties which depend on the energy of the LUMO.

Eaborn has suggested[22] that the difference between the electron-withdrawing effect of the two substituents on an attached aryl system becomes more exaggerated in favor of NO_2 as the availability of negative charge to the aryl system is increased. For example, in the acid desilylation of p-$XC_6H_4SiMe_3$, the Me_3P^+ substituent is more deactivating than NO_2 (more electron withdrawing), while in the cleavage of p-$XC_6H_4CH_2SiMe_3$ with base, the NO_2 group shows a substantially greater effect. The latter reaction involves the formation of the benzyl carbanion, p-$XC_6H_4CH_2^-$, which can be stabilized to a greater extent by the NO_2 substituent. In the MLCT and reduction potential measurements obtained in the present study, negative charge is introduced directly into the ring, perhaps providing a situation with an even greater π-electron availability than is found in the usual experiments on substituent effects.

A real comparison of substituent σ values is difficult to obtain in this case because of the differing reaction conditions used in their measurement, and different values are often quoted from different sources. From ^{19}F NMR measurements on substitued fluorobenzenes in dimethyl sulfoxide,[23] σ_I (inductive) constants were obtained as 0.43 and 0.53 for Me_3P^+ and NO_2, respectively. Values of σ_R (conjugative) were obtained as 0.20 and 0.24 for Me_3P^+ and NO_2, respectively. Summing these values yields σ_P constants of 0.63 and 0.77 for the two substituents. From measurements of the ionization constants of substituted phenols or anilines, values of σ^- (substituent constant in the presence of enhanced electron availability) were obtained[24] as 1.02 (phenol) or 0.95 (dimethylaniline) for the Me_3P^+ substituent and 1.27 for NO_2. Thus, the small difference in σ_P values between the two substituents (0.14) is increased to 0.28 (average) when σ^- is used as the criterion for electron-withdrawing behavior. It is therefore suggested that this difference is even further exaggerated when the MLCT energies and reduction potentials presented in this paper are considered.

The use of ligands with substituents remote from the coordination site allows one to examine a series of complexes displaying variations in ligand properties, yet with the same stereochemical environment at the coordination site. Such perturbations of ligand properties not only may lead to systematic variations of metal–ligand bonding in the ground state but in some cases may also be used to tune excited-state energies.[25]

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