

Effects of Peripheral TCNE–Phenyl Charge-Transfer Interactions on Ligational Energetics to a Conformationally Flexible Macrocyclic Receptor

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A previous paper describes the use of a "gated glyoxime" (Chart I) to manipulate a superstructure in the vicinity of a metal binding site, producing nonbonded repulsive effects on ligand binding.¹ Here we explore the consequences of attractive π – π interactions^{2,3} between tetracyanoethylene (TCNE) and phenyl groups positioned in a face-to-face geometry by this device.

Tetracyanoethylene and a variety of other nitriles have been previously shown to bind to $\text{Fe}(\text{DMGBF}_2)_2$ via the nitrile nitrogen as rather weak σ -donor ligands,⁴ similar to CH_3CN . We find that the binding of TCNE becomes exceptionally strong in $\text{Fe}(\text{DMGBPh}_2)_2$ complexes⁵ ($\text{DMGBPh}_2 = (\text{dimethylglyoximate})\text{-diphenylborate}$) as a result of donor–acceptor interactions (commonly known as charge-transfer interactions) with the peripheral phenyl groups.

Electronic spectra of BF_2 and BPh_2 complexes are compared in Figure 1. (Data for several nitrile complexes are collected in Table I.) A broad Fe to TCNE CT band is found in the near IR, while Fe to oxime CT bands occur at 400 nm. The red shift found in the Fe to TCNE CT band of about 1500 cm^{-1} reflects a small electronic difference between BPh_2 and BF_2 systems. Evidence of a TCNE–phenyl interaction is provided by the additional band at 500 nm in the BPh_2 system.⁶ This feature is assigned to a through-space phenyl–TCNE CT interaction. It occurs at lower energy than that reported for the benzene–TCNE CT complex (384 nm)² but has a comparable extinction coefficient and bandwidth. A coordinated TCNE would be expected to be a better acceptor than free TCNE. Both the phenyl to TCNE and the iron to TCNE CT bands appear with doubled intensity in the bis-TCNE derivative.

The C_{2v} conformation of the $\text{Fe}(\text{DMGBPh}_2)_2(\text{TCNE})\text{X}$, $\text{X} = \text{CH}_3\text{CN}$ and pyridine (PY), in which both axial phenyls are directed toward the TCNE face is inferred from the ^1H NMR spectrum.⁷ A distinct splitting of the DMG methyl resonance is found in the PY derivative, consistent with a η^1 -nitrile geometry in which the TCNE lies in the plane bisecting the glyoxime unit and sandwiched between the two axial phenyl groups. Slow rotation of the TCNE about the Fe–NC axis is enforced by the phenyl–TCNE interactions.

Thermodynamic effects of the phenyl–TCNE interaction were quantified through extensive equilibrium studies (eqs 1–4). Equilibrium constants for ligation to BPh_2 and BF_2 systems were

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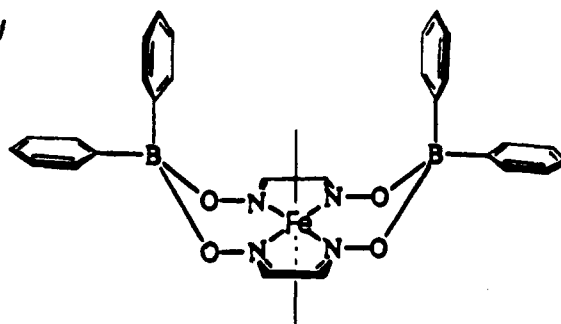
(5) $\text{Fe}(\text{DMGBPh}_2)_2(\text{PY})\text{TCNE}$. Anal. Calcd for $\text{C}_{43}\text{H}_{37}\text{N}_9\text{B}_2\text{O}_4\text{Fe}$: C, 62.88; H, 4.54; N, 15.35. Found: C, 62.13; H, 4.50; N, 15.31. ^1H NMR (CDCl_3): δ 2.63, 2.60 (s, 12 H, CH_3), 6.97, 7.68, 8.78 (PY), 7.55, 7.28 (m, Ph_{ax}), 7.2, 7.0 (Ph_{eq}). IR: ν_{NC} 2178. $\text{Fe}(\text{DMGBPh}_2)_2(\text{CH}_3\text{CN})(\text{TCNE})$. ^1H NMR (CDCl_3) δ 2.03 (s, 3H, CH_3CN), 2.75 (s, 12H, CH_3), 7.5, 7.23, 7.06, 6.93 (Ph).

(6) Interaction of free TCNE with benzenes, $(\text{Ph}_2\text{B})_2\text{O}$, or any inert $\text{Fe}(\text{DMGBPh}_2)_2$ complex is far too weak and not observed at mutual concentrations below 0.01 M.

(7) Chemical shifts for the pyridine and phenyl protons resemble those in the $\text{Fe}(\text{DMGBPh}_2)_2(\text{PY})(\text{CH}_3\text{CN})$ shown to possess the sandwiched geometry¹ and in which no close phenyl–PY contacts arise. In $\text{Fe}(\text{DMGBPh}_2)_2(\text{CH}_3\text{CN})(\text{TCNE})$, the CH_3CN resonance is at δ 2.03 and thus does not experience a phenyl contact.

Chart I

C_{2v}



determined by spectrophotometric titration in dichloromethane solution. Binding constants for TCNE were typically 3–4 orders of magnitude greater than those found in the BF_2 system. Binding of TCNE to $\text{Fe}(\text{DMGBPh}_2)_2(\text{PY})_2$ was so strong ($K = 3 \times 10^4$) as to be stoichiometric at $[\text{Fe}] = 0.0001\text{ M}$ and $[\text{PY}] = 0.01\text{ M}$. At higher $[\text{PY}]$, correction for the PY –TCNE complex ($K = 12\text{ M}^{-1}$)² was required. Reaction with CO (eq 2) provided an independent and more accurate measure of the thermodynamic stability of the TCNE complex uncomplicated by PY –TCNE interactions. Kinetic data⁸ for reactions 1 and 2 reveal a TCNE ligand some 4 orders of magnitude more inert than normal ($k_{\text{TCNE}} = 6 \times 10^{-4}\text{ s}^{-1}$).

The binding of phthalonitriles, which possess LUMOs somewhat higher in energy than those of TCNE (see Table I), were also studied in reactions 1–4. While phthalonitrile (PT) is only marginally different from CH_3CN in either the BF_2 or BPh_2 system, a significant enhancement in binding of the better acceptor, 4-nitrophthalonitrile (NPT) was observed in the BPh_2 system. (For eq 1, BPh_2 , $K = 22$, $k_{\text{NPT}} = 1\text{ s}^{-1}$ (0.05 s^{-1} at 0°C); BF_2 , $K = 0.007$, k_{NPT} estimated as 20 s^{-1} .)⁹

Free energies of formation (Table II) for each complex were calculated relative to the parent $\text{Fe}(\text{CH}_3\text{CN})_2$ complexes in the BPh_2 and BF_2 systems from equilibria summarized in footnotes in Table II. The differences in free energy between the BF_2 and BPh_2 complexes, $\Delta\Delta G$, provide evidence of significant interactions between the phenyl groups and axial ligands. Large positive $\Delta\Delta G$ values reflect destabilizing effects of repulsive nonbonded interactions of pyridine with boron-linked axial phenyl groups (face-to-face). These effects correlate with the ground-state conformations deduced from the NMR. No PY –Ph contacts occur in $\text{Fe}(\text{PY})(\text{CH}_3\text{CN})$ and $\text{FePY}(\text{CO})$ which adopt the C_{2v} structure, placing the PY on the open face.¹

Negative $\Delta\Delta G$ values occur when attractive TCNE–phenyl interactions are present. A 3–5 kcal/mol enhancement is found in these cases. The magnitude of the effect is in the range expected on the basis of the enthalpy reported for TCNE–aromatic charge-transfer complexes in CH_2Cl_2 . (Example: TCNE–durene, $K = 54.2$, $\lambda = 480\text{ nm}$, $\Delta H = 5\text{ kcal/mol}$, $\Delta S = -9\text{ eu}$.)² Entropic losses are not a significant factor.¹⁰

It is interesting that the mono-TCNE complexes experience somewhat greater stabilization than the bis-TCNE complex. This suggests that the Ph–TCNE–Ph interaction in the C_{2v} conformer (the "sandwiched TCNE") is more favorable than two Ph–TCNE interactions in a C_{2h} structure. While counterintuitive, the result is expected on the basis of reported enthalpies in the hexa-

(8) Kinetic data for reaction 2 (D mechanism): $k_{\text{TCNE}} = 6 \times 10^{-4}\text{ s}^{-1}$, $k_{\text{TCNE}}/k_{\text{CO}} = 5$, and $k_{\text{CO}} = 6 \times 10^{-5}\text{ s}^{-1}$.

(9) Data for phthalonitrile (eq 1): for BPh_2 , $K = 3$; for BF_2 , $K = 0.007$. Assuming $k_{\text{PT}}/k_{\text{PY}} = 2$, we calculate $k_{\text{PT}} = 5$ and 20 s^{-1} respectively.

(10) In multisite binding of a substrate to a preorganized host, enthalpic contributions for each interaction are additive while entropic losses are largely factored out by use of the BF_2 reference.

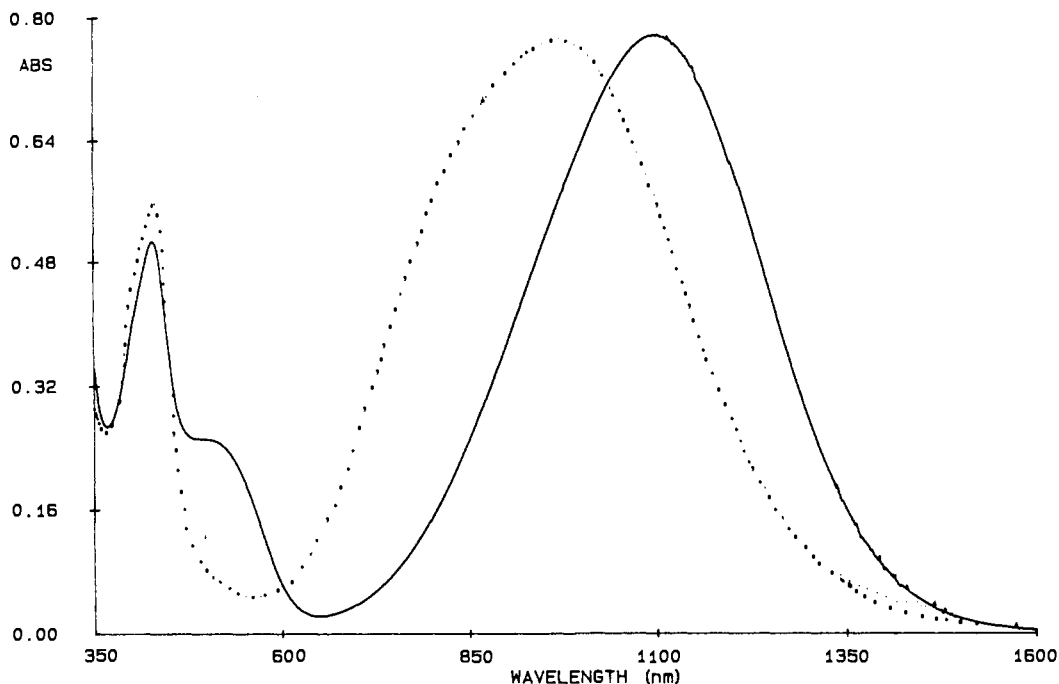
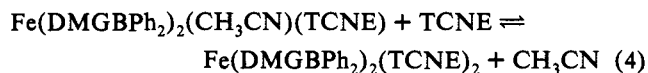
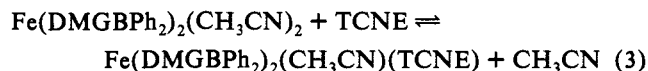
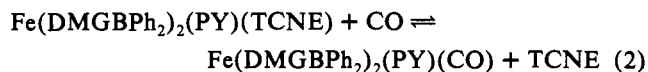
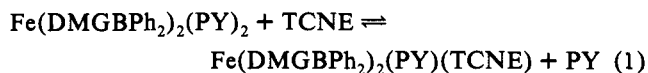


Figure 1. Visible spectra. Solid line: $\text{Fe}(\text{DMGBPh}_2)_2(\text{PY})(\text{TCNE})$. Dotted line: $\text{Fe}(\text{DMGBF}_2)_2(\text{PY})(\text{TCNE})$.

Table I. Visible Spectral Data^a (λ_{max} , nm)

	MO _x CT		MA _x CT		Ph CT BPh ₂
	BPh ₂	BF ₂	BPh ₂	BF ₂	
$\text{Fe}(\text{PY})_2$	526	521	380	367	
$\text{Fe}(\text{PY})(\text{TCNE})^c$	430	430	1100	970	504
$\text{Fe}(\text{CH}_3\text{CN})(\text{TCNE})$	400	401	1055	970	508
$\text{Fe}(\text{TCNE})_2$	383	388	1092	922	513
$\text{Fe}(\text{PY})(\text{NPT})$	470	460	625	560	
$\text{Fe}(\text{PY})(\text{PT})$	470	460	<i>b</i>	<i>b</i>	
$\text{Fe}(\text{CH}_3\text{CN})_2$	453	444			
$\text{Fe}(\text{CH}_3\text{CN})(\text{PY})$	490	488	354		

^a MO_x CT, metal to oxime CT band. MA_x CT, metal to axial ligand (PY, TCNE, NPT, PT) CT band. Ph CT is the intramolecular phenyl to TCNE CT band. ^b MA_x CT position overlaps MO_x CT band. ^c $\epsilon = 5200, 2600, \text{ and } 8000 \text{ cm}^{-1} \text{ M}^{-1}$ at 430, 504, and 1100 nm, respectively.



methylbenzene–TCNE system.¹¹ Data for the other nitriles show that the CT stabilization drops off in the expected order $\text{TCNE} > \text{NPT} > \text{PT} > \text{CH}_3\text{CN}$.

As a receptor, this device incorporates many advantages over conventional organic hosts.¹² The metal–ligand interaction provides a level of control very difficult to achieve in organic

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Table II. Free Energies of Ligation (kcal/mol) to $\text{Fe}(\text{DMGX})_2(\text{CH}_3\text{CN})_2$ Complexes at 25 °C in CH_2Cl_2

	X		$\Delta\Delta G$
	BF ₂ ^c	BPh ₂ ^d	
$\text{Fe}(\text{CH}_3\text{CN})_2$	0.0	0.0	0.0
$\text{Fe}(\text{CH}_3\text{CN})\text{PY}$	-5.8	-5.6	0.2
$\text{Fe}(\text{PY})_2$	-9.1	-6.4	2.7
$\text{Fe}(\text{CH}_3\text{CN})\text{TCNE}$	-1.6	-5.3	-3.7
$\text{Fe}(\text{PY})\text{CO}$	-12.6	-12.9	-0.3
$\text{Fe}(\text{PY})\text{TCNE}$	-7.9	-12.5	-4.6
$\text{Fe}(\text{TCNE})_2$	-2.7	-5.0	-2.3
$\text{Fe}(\text{PY})\text{NPT}^a$	-6.1	-8.2	-2.1
$\text{Fe}(\text{PY})\text{PT}^b$	-6.1	-7.0	-0.8

^a NPT = 4-nitrophthalonitrile. ^b PT = phthalonitrile. ^c Equilibrium constants, BF₂ system. Binding to $\text{Fe}(\text{CH}_3\text{CN})_2$: PY, $K_1 = 1.8 \times 10^4$, $K_2 = 250$; TCNE, $K_1 = 15 \pm 5$, $K_2 = 6 \pm 3$. Binding to $\text{Fe}(\text{PY})_2$: TCNE, $K_1 = 0.14$; CO, $K_1 = 4 \times 10^2$. ^d Equilibrium constants, BPh₂ system. Binding to $\text{Fe}(\text{CH}_3\text{CN})_2$: PY, $K_1 = 1.2 \times 10^4$, $K_2 = 4.0$; TCNE, $K_1 = 8000$, $K_2 = 0.55$. Binding to $\text{Fe}(\text{PY})_2$: TCNE, $K_1 = 3 \times 10^4$; CO, $K_1 = 5 \times 10^4$; NPT, $K_1 = 22$; PT, $K_1 = 3$. For $\text{Fe}(\text{PY})(\text{TCNE}) + \text{CO} = \text{Fe}(\text{PY})(\text{CO}) + \text{TCNE}$: $K = 1.6$. The CO solubility in CH_2Cl_2 is taken as 0.008 M at 1 atm total pressure. Estimated error in K is <20% except as noted.

receptors. By grafting weak interactions onto much stronger ligational energies, binding is assured even in the absence of peripheral assistance. Off-setting entropy losses, which generally prohibit the experimental observation of interactions weaker than a few kcal/mol, are eliminated. The flexibility of these systems allows considerable geometry optimization by the interacting fragments and avoids "entry barriers" which may be encountered in more rigid hosts.¹³

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