Opposite *trans*-Effects of Benzyl Isocyanide in Heme Models

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Summary Benzyl isocyanide exerts *trans*-effects on methylimidazole dissociation from tetragonal Fe^{II} complexes of phthalocyanine, bisdimethylglyoxime, and 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclodeca-1,3,8,10-tetraene whose magnitude and direction are markedly dependent on the in-plane ligand.

AN understanding of the *trans*-effect of axial ligands co-ordinated to iron(II) porphyrins and related complexes is intimately connected with that of the 'unusual lability' of axial ligands co-ordinated to certain tetragonal complexes of normally substitution-inert Fe^{II}.[1] While there is information on the *trans*-effects of axial bases on the binding of O_2,[2] CO,[2,3] and RNC[4] in models for the heme group, there are no data on the *trans*-effect of these π-acceptor ligands on the amine ligand in the *trans*-position. We report here on a remarkable *trans*-effect of benzyl isocyanide on methylimidazole lability in several model complexes where the *trans*-effect of benzyl isocyanide depends critically on the in-plane tetradentate ligand.

Benzyl isocyanide reversibly binds to several low-spin Fe^{II} complexes giving both 1:1 and 2:1 complexes *via* a dissociative mechanism (equations 1 and 2).†

$$L^1{}_2FeL^2 + PhCH_2NC = L^1FeL^2(PhCH_2NC) + L^1 \quad (1)$$

$$L^1FeL^2(PhCH_2NC) + PhCH_2NC = FeL^2(PhCH_2NC)_2 + L^1 \quad (2)$$

L^1 = methylimidazole (meim); L^2 = phthalocyaninato (pc), bisdimethylglyoximato $(dmg)_2$, or 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclodeca-1,3,8,10-tetraene (tim).

Addition of excess of benzyl isocyanide to a solution of $[(meim)_2Fe(pc)]$ in toluene results in the formation of $[Fe(pc)(PhCH_2NC)_2]$ with no evidence for the formation of the intermediate $[(meim)Fe(pc)(PhCH_2NC)]$. The rate of

† The course of the reactions is independent of the concentration of the incoming ligand and, moreover, is the same for $PhCH_2NC$ and CO in equation (1) and for L^2 = pyridine and methylimidazole in equation (2).

formation of $[Fe(pc)(PhCH_2NC)_2]$ (λ_{max} 394 nm) is identical to the rate of disappearance of the starting complex $[(meim)_2Fe(pc)]$ (λ_{max} 425 nm), and is determined by the rate-limiting step of meim dissociation from the starting complex.

The same reaction carried out with $[(meim)_2Fe(dmg)_2]$ in $CHCl_3$ proceeds in two distinct steps with rapid formation of the mixed complex $[(meim)Fe(dmg)_2(PhCH_2NC)]$ followed by a slow reaction to give the complex $[Fe(dmg)_2(PhCH_2NC)_2]$ (λ_{max} 392 nm).

TABLE. Kinetic data for methylimidazole and benzyl isocyanide dissociation as a function of the *trans* ligand.

	k_1/s^{-1} (t/°C)	
Dimethylglyoxime system	$PhCH_2NC$	meim
trans to meim	$3{\cdot}1 \times 10^{-4}$ (65)[a]	$6{\cdot}9 \times 10^{-4}$ 10)[b]
trans to $PhCH_2NC$ ..	$3{\cdot}0 \times 10^{-6}$ (65)[a]	199×10^{-5} (65°)[c]
Phthalocyanine system[c]		
trans to meim	$9{\cdot}2 \times 10^{-5}$ (30)	$3{\cdot}96 \times 10^{-3}$ (30)
trans to $PhCH_2NC$ ..	$9{\cdot}8 \times 10^{-2}$ (20)	$2{\cdot}9 \times 10^{-2}$ (30)

[a] Methylimidazole solution. [b] $CHCl_3$ solution. [c] Toluene solution.

Kinetic data illustrating the opposite *trans*-effects in the two systems are given in the Table. In the phthalocyanine system, methylimidazole is *ca.* 10 times more labile in the mixed complex than in $[(meim)_2Fe(pc)]$, while in the glyoxime system methylimidazole is *ca.* 1000 times less labile in the mixed complex than in $[(meim)_2Fe(dmg)]$.

These *trans*-effect differences in the two systems are also observed in the rates of benzyl isocyanide dissociation. In the pc system, the benzyl isocyanide is 1000 times more labile in $[Fe(pc)(PhCH_2NC)_2]$ than in the mixed complex, consistent with the generally accepted belief that alkyl isocyanides are strong *trans*-directors. However, in the glyoxime system, benzyl isocyanide is more inert in $[Fe(dmg)_2(PhCH_2NC)_2]$ than in the mixed complex. Thus in this system the *trans*-effect order meim > $PhCH_2NC$ is maintained for both meim and $PhCH_2NC$ dissociation, while in the pc system the opposite order is observed for both meim and $PhCH_2NC$ dissociation. Clearly the construction of a *trans*-effect series analogous to that for square-planar complexes is impossible for these systems.

Effects similar to those found in the glyoxime system are observed in complexes of the macrocyclic ligand tim.[5] Reaction of $[(meim)_2Fe(tim)]^{2+}$ with benzyl isocyanide in MeCN gives an immediate colour change from red (λ_{max} 555 nm) to orange (λ_{max} 520 nm). On heating, a further reaction to give the yellow complex $[Fe(tim)(PhCH_2NC)_2]^{2+}$ (λ_{max} 490 nm) is observed. Further evidence for the greater inertness of MeCN *trans* to $PhCH_2NC$ is obtained in the n.m.r. spectrum in PhCN solution. While exchange of MeCN with $[(MeCN)_2Fe(tim)]^{2+}$ is fast on the n.m.r. time-scale, a solution of $[(MeCN)Fe(tim)(PhCH_2NC)]^{2+}$ in PhCN shows a sharp signal at δ 2·46 due to co-ordinated MeCN which slowly disappears and a new sharp signal appears at the position of free MeCN, consistent with the slow reaction: $[(MeCN)Fe(tim)(PhCH_2)]^{2+} + PhCN = [(PhCN)Fe(tim)(PhCH_2NC)]^{2+} + MeCN$. Similarly, methylimidazole is *ca.* 1000 times more inert in $[(meim)Fe(tim)(PhCH_2NC])^{2+}$ than in $[(meim)_2Fe(tim)]^{2+}$. Also, as in the glyoxime system, $PhCH_2NC$ is most inert in the $[Fe(tim)(PhCH_2NC)_2]^{2+}$ complex.

The modification of axial binding properties by the in-plane ligand in these models for the heme group may be a function of the in-plane *vs.* axial ligand bonding or the position of the iron with respect to the tetradentate ligand plane in the mixed complexes. The opposite *trans*-effects are clearly not an artifact of the solvents used. The same relative order of rate constants for the pc system is maintained if $CHCl_3$ and pure methylimidazole are used as solvents for the forward and reverse reactions respectively.‡

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‡ For the phthalocyanine system in $CHCl_3$ at 10 °C rates of methylimidazole dissociation are 1×10^{-3} and $1{\cdot}5 \times 10^{-2}$ s^{-1} *trans* to meim and $PhCH_2NC$ respectively. Rates of $PhCH_2NC$ dissociation *trans* to meim are carried out at > 1 M meim in toluene and do not change significantly in going to neat meim. Rates of dissociation *trans* to $PhCH_2NC$ are independent of the concentration of meim over the range 0·01—3·0 M.

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