

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

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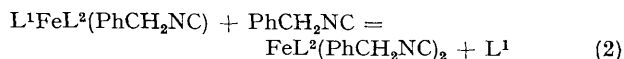
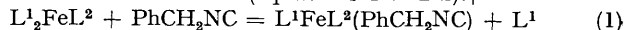
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Summary Benzyl isocyanide exerts *trans*-effects on methylimidazole dissociation from tetragonal Fe^{II} complexes of phthalocyanine, bisdimethylglyoxime, and 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclodeca-1,3,8,10-tetraene whose magnitude and direction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

AN understanding of the *trans*-effect of axial ligands coordinated 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 O₂,² CO,^{2,3} and RNC⁴ 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 methyl-

imidazole 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).[†]



L¹ = methylimidazole (meim); L² = 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)(PhCH₂NC)₂] with no evidence for the formation of the intermediate [(meim)Fe(pc)(PhCH₂NC)]. The rate of

[†] The course of the reactions is independent of the concentration of the incoming ligand and, moreover, is the same for PhCH₂NC and CO in equation (1) and for L² = pyridine and methylimidazole in equation (2).

formation of $[\text{Fe}(\text{pc})(\text{PhCH}_2\text{NC})_2]$ (λ_{max} 394 nm) is identical to the rate of disappearance of the starting complex $[(\text{meim})_2\text{Fe}(\text{pc})]$ (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 $[(\text{meim})_2\text{Fe}(\text{dmg})_2]$ in CHCl_3 proceeds in two distinct steps with rapid formation of the mixed complex $[(\text{meim})\text{Fe}(\text{dmg})_2(\text{PhCH}_2\text{NC})]$ followed by a slow reaction to give the complex $[\text{Fe}(\text{dmg})_2(\text{PhCH}_2\text{NC})_2]$ (λ_{max} 392 nm).

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

	k_1/s^{-1} ($t/^\circ\text{C}$)	
	PhCH_2NC	meim
Dimethylglyoxime system		
<i>trans</i> to meim	3.1×10^{-4} (65) ^a	6.9×10^{-4} (10) ^b
<i>trans</i> to PhCH_2NC ..	3.0×10^{-6} (65) ^a	1.99×10^{-5} (65) ^c
Phthalocyanine system ^c		
<i>trans</i> to meim	9.2×10^{-5} (30)	3.96×10^{-3} (30)
<i>trans</i> to PhCH_2NC ..	9.8×10^{-2} (20)	2.9×10^{-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 $[(\text{meim})_2\text{Fe}(\text{pc})]$, while in the glyoxime system methylimidazole is *ca.* 1000 times less labile in the mixed complex than in $[(\text{meim})_2\text{Fe}(\text{dmg})]$.

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 $[\text{Fe}(\text{pc})(\text{PhCH}_2\text{NC})_2]$ 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 $[\text{Fe}(\text{dmg})_2(\text{PhCH}_2\text{NC})_2]$ 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

‡ For the phthalocyanine system in CHCl_3 at 10 °C rates of methylimidazole dissociation are 1×10^{-3} and $1.5 \times 10^{-2} \text{ s}^{-1}$ *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.

¹ D. V. Stynes and B. R. James, *J.C.S. Chem. Comm.*, 1973, 325.

² C. J. Weschler, D. L. Anderson, and F. Basolo, *J.C.S. Chem. Comm.*, 1974, 757.

³ D. V. Stynes and B. R. James, *J. Amer. Chem. Soc.*, 1974, **96**, 2733.

⁴ D. V. Stynes, *J. Amer. Chem. Soc.*, 1974, **96**, 5942.

⁵ D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Amer. Chem. Soc.*, 1973, **95**, 5152.

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 $[(\text{meim})_2\text{Fe}(\text{tim})]^{2+}$ 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 $[\text{Fe}(\text{tim})(\text{PhCH}_2\text{NC})_2]^{2+}$ (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 $[(\text{MeCN})_2\text{Fe}(\text{tim})]^{2+}$ is fast on the n.m.r. time-scale, a solution of $[(\text{MeCN})\text{Fe}(\text{tim})(\text{PhCH}_2\text{NC})]^{2+}$ 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: $[(\text{MeCN})\text{Fe}(\text{tim})(\text{PhCH}_2)]^{2+} + \text{PhCN} = [(\text{PhCN})\text{Fe}(\text{tim})(\text{PhCH}_2\text{NC})]^{2+} + \text{MeCN}$. Similarly, methylimidazole is *ca.* 1000 times more inert in $[(\text{meim})\text{Fe}(\text{tim})(\text{PhCH}_2\text{NC})]^{2+}$ than in $[(\text{meim})_2\text{Fe}(\text{tim})]^{2+}$. Also, as in the glyoxime system, PhCH_2NC is most inert in the $[\text{Fe}(\text{tim})(\text{PhCH}_2\text{NC})_2]^{2+}$ 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.‡

We thank the National Research Council of Canada for support.

(Received, 17th September 1975; Com. 1062.)