Axial Ligand Substitution in Iron(II) Phthalocyanine Adducts: Replacement of Tri-n-butyl Phosphite by Tri-n-butylphosphine

By **Dwight A. Sweigart**, Department of Chemistry, Swarthmore College, Swarthmore, Pa. 19081, U.S.A.

Iron(II) phthalocyanine, [Fe(pc)], reacts with tri-n-butyl phosphite and tri-n-butylphosphine to form low-spin bis adducts, [Fe(pc)$(PR_3)_2$]. Replacement of $P(OBu)_3$ by PBu_3 occurs rapidly and follows a strictly dissociative mechanism.

IRON(II) phthalocyanine, [Fe(pc)], has attracted considerable attention in recent years due to its similarity to iron porphyrin systems. Jones and Twigg [1-4] studied the reaction (1) of the low-spin dimethyl sulphoxide adduct, [Fe(pc)$(dmso)_2$], with imidazole (im). Replacement of the first dmso is rate determining, and the observed kinetics are second order even up to an

$$[Fe(pc)(dmso)_2] + 2im \longrightarrow [Fe(pc)(im)_2] + 2dmso \quad (1)$$

imidazole concentration of 1.45 mol dm^{-3}. These results indicate either an associative mechanism, or a dissociative mechanism in which dmso dominates the competition for the five-co-ordinate intermediate, [Fe(pc)(dmso)]. Stynes and James [5] reported that [Fe(pc)L_2] (L = a nitrogen-donor ligand) reacts with CO *via* a dissociative path to yield [Fe(CO)(pc)L]. Watkins and Balch [6] very recently reported a dissociative mechanism for exchange of nitrosotoluene in the mixed complex [Fe(pc)$(NBu^nH_2)(ONC_6H_4Me)$].

I report herein that [Fe(pc)] reacts with tri-n-butyl phosphite, $P(OBu)_3$, and tri-n-butylphosphine, PBu_3, to yield low-spin bis adducts, [Fe(pc)$(PR_3)_2$]. The kinetics of the replacement of $P(OBu)_3$ by PBu_3, reaction (2),

$$[Fe(pc)\{P(OBu)_3\}_2] + 2PBu_3 \longrightarrow [Fe(pc)(PBu_3)_2] + 2P(OBu)_3 \quad (2)$$

are reported and the mechanism shown to be strictly dissociative. The rate of dissociation of $P(OBu)_3$ from [Fe(pc)$\{P(OBu)_3\}_2$] is shown to be *ca.* 5 000 times greater than dissociation of imidazole from [Fe(pc)$(im)_2$].

EXPERIMENTAL

Iron(II) phthalocyanine was purchased from Eastman Kodak. The complexes [Fe(pc)$\{P(OBu)_3\}_2$] and [Fe(pc)$(PBu_3)_2$] were prepared by combining [Fe(pc)] (1 g) and excess of $P(OBu)_3$ or PBu_3 in benzene (400 cm^3) and stirring the suspension for 10 h. The filtered solution was then evaporated to *ca.* 20 cm^3 and 300 cm^3 of diethyl ether–ethanol (1 : 1) were added. On partial evaporation of the solvent dark crystals precipitated. Recrystallization from toluene–pentane yielded dark green (PBu_3 adduct) or bronze [$P(OBu)_3$ adduct] crystals (Found: C, 69.5; H, 7.2; N, 11.7. Calc. for [Fe(pc)$(PBu_3)_2$]: C, 69.2; H, 7.3; N, 11.5. Found: C, 62.9; H, 6.7; N, 10.8. Calc. for [Fe(pc)$\{P(OBu)_3\}_2$]: C, 62.9; H, 6.6; N, 10.5%).

Magnetic susceptibilities were measured on a standard Gouy balance. The kinetics were followed at 410 nm in toluene as solvent on a stopped-flow apparatus. The metal complex concentration was 4×10^{-5} mol dm^{-3} and PBu_3 was kept in at least a 25-fold excess, thus ensuring pseudo-first-order conditions. Rate constants were obtained from plots of ln $(A_\infty - A)$ against time which were linear over the entire reaction.

RESULTS

The [Fe(pc)$(PBu_3)_2$] complex is bright green in toluene and [Fe(pc)$\{P(OBu)_3\}_2$] is blue-green. Absorptions in the visible spectrum are as follows [λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})]: [Fe(pc)$(PBu_3)_2$] 670 (120), 641 (33), 607 (27), 472 (9), 405 (34), and 371 (40); [Fe(pc)$\{P(OBu)_3\}_2$] 662 (90), 602 (28), 437 (12), and 376 (32). Addition of $P(OBu)_3$ to a toluene solution of [Fe(pc)$\{P(OBu)_3\}_2$] caused a very slight ($\leqslant 5\%$) increase in intensity of the absorption maxima, showing that the extent of dissociation of [Fe(pc)$\{P(OBu)_3\}_2$] to [Fe(pc)$\{P(OBu)_3\}$] occurring in the absence of excess of $P(OBu)_3$ must be very small, and accordingly not of kinetic significance. Analysis of the kinetic data, discussed below, confirms this. However, spectral results in other solvents, such as chloroform, suggest that dissociation to [Fe(pc)$\{P(OBu)_3\}$] or [Fe(pc)$\{P(OBu)_3\}$(solvent)] may be significant at low concentrations. Both the PBu_3 and $P(OBu)_3$ adducts are diamagnetic as solids (Gouy method).

The kinetic results for reaction (2) are given in the Table.

Rate data for reaction (2) *

T	$10^3[P(OBu)_3]$	$10^3[PBu_3]$	k_{obs}
K	mol dm^{-3}		s^{-1}
299	0	2.4	18.7
	0	6.0	18.7
289.2	0	1.1	5.78
	0	2.4	5.83
	0	6.0	5.73
281	0	1.1	2.10
	0	2.4	1.98
	0	6.0	2.04
273	0	1.0	0.620
	5.1	1.0	0.183
	5.1	2.2	0.295
	0	3.7	0.640
	5.1	3.7	0.391
	0	8.0	0.630
	5.1	8.0	0.506

* Toluene solvent; [Fe(pc)$\{P(OBu)_3\}_2$] concentration was 4×10^{-5} mol dm^{-3}.

With no excess of $P(OBu)_3$ present the rate was independent of the nucleophile concentration, equation (3), and therefore

$$\text{Rate} = k_1[Fe(pc)\{P(OBu)_3\}_2] \quad (3)$$

the observed pseudo-first-order rate constant is simply k_1. Excess of $P(OBu)_3$ caused a marked retardation in the rate (Figure).

---

[1] J. G. Jones and M. V. Twigg, *Inorg. Chem.*, 1969, **8**, 2120.

[2] H. P. Bennett, J. G. Jones, and M. V. Twigg, *Inorg. Chim. Acta*, 1970, **4**, 180.

[3] J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 103.

[4] J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1975, **12**, L15.

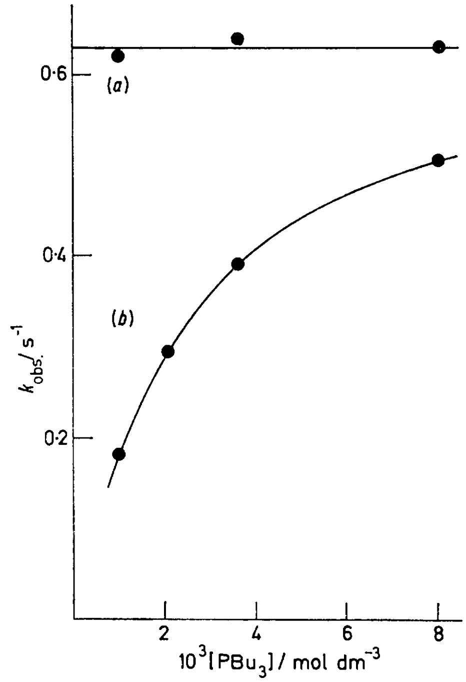
[5] D. V. Stynes and B. R. James, *J. Amer. Chem. Soc.*, 1974, **96**, 2733.

[6] J. J. Watkins and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2720.

DISCUSSION

The analytical data clearly show that PBu_3 and $P(OBu)_3$ react with [Fe(pc)] to yield bis adducts. The adducts are low spin as are the well known [7] analogues containing pyridine, quinoline, imidazole, dmso, *etc.* as the axial groups. While this work was in progress Watkins and Balch [6] reported the preparation of the bis adduct with $P(OEt)_3$.

For reaction (2) all the absorbance change between reactant and product was observed during the kinetic runs. This strongly suggests that replacement of the first $P(OBu)_3$ ligand is rate determining, analogous to the results of Jones and Twigg [1-4] for reaction (1). The enhanced lability of $P(OBu)_3$ in $[Fe(pc)(PBu_3)\{P(OBu)_3\}]$ relative to $[Fe(pc)\{P(OBu)_3\}_2]$ is to be expected from the greater base strength, towards a soft centre, of PBu_3. In other words, PBu_3 exerts a greater *trans* effect [8] than $P(OBu)_3$.



Results for reaction (2) at 0 °C with excess of $P(OBu)_3$. Concentrations are (*a*) 0, (*b*) 0.0051 mol dm^{-3}

The rate data in the Table suggest the simple dissociative mechanism (4)—(6) for reaction (2). With no excess of $P(OBu)_3$, *i.e.* L, equation (7) reduces to $k_{obs.} = k_1$. Excess of $P(OBu)_3$ causes a rate retardation in quantitative agreement with equation (7). Thus a plot of $k_{obs.}$ against $[X]^{-1}$ for the data at 273 K in the

$$[Fe(pc)L_2] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(pc)L] + L \qquad (4)$$

$$[Fe(pc)L] + X \xrightarrow{k_3} [Fe(pc)LX] \qquad (5)$$

$$[Fe(pc)LX] + X \xrightarrow{\text{fast}} [Fe(pc)X_2] + L \qquad (6)$$

$$k_{obs.} = \frac{k_1k_3[X]}{k_2[L] + k_3[X]} \qquad (7)$$

Table with excess of $P(OBu)_3$ (5.1×10^{-3} mol dm^{-3}) was linear yielding (from the intercept) $k_1 = 0.65$ s^{-1} in agreement with the directly observed value of 0.63 s^{-1}. The gradient of the plot yielded $k_2/k_3 = 0.50$. An Arrhenius plot of the k_1 values in the Table yields $\Delta H^‡ = 20.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^‡ = 16.2 \pm 0.4$ cal K^{-1} mol^{-1}.* Both these values are reasonable for a dissociative step, and it seems that reaction (2) follows a strictly dissociative path.

Stynes and James [5] reported a value of 0.0026 s^{-1} for the dissociation of imidazole from $[Fe(pc)(im)_2]$ in toluene at 23 °C. The extrapolated value of k_1 at 23 °C for $[Fe(pc)\{P(OBu)_3\}_2]$ is *ca.* 13 s^{-1}, an increase of 5 000. One expects $P(OBu)_3$ to exert a greater *trans* effect than imidazole and so a rate increase is not surprising. That the rate increase is not due simply to a greater binding constant for imidazole is shown by the following preliminary observations. Addition of imidazole to a toluene solution of $[Fe(pc)\{P(OBu)_3\}_2]$ causes a rapid colour change from blue-green to blue. The visible spectrum shows that the product is not $[Fe(pc)(im)_2]$ (which is green). The addition of excess of $P(OBu)_3$ rapidly converts the blue complex back into $[Fe(pc)\{P(OBu)_3\}_2]$, while addition of PBu_3 rapidly yields $[Fe(pc)(PBu_3)_2]$. It was found that excess of $P(OBu)_3$ and PBu_3 slowly converted $[Fe(pc)(im)_2]$ to the respective phosphite and phosphine adducts. A tentative explanation is that the blue complex is $[Fe(pc)(im)\{P(OBu)_3\}]$ which reacts rapidly with PBu_3 due to the *trans* effect of $P(OBu)_3$ [equations (8) and (9)].

$$[Fe(pc)(im)_2] + 2PBu_3 \xrightarrow{\text{slow}} [Fe(pc)(PBu_3)_2] \qquad (8)$$

$$[Fe(pc)(im)\{P(OBu)_3\}] + 2PBu_3 \xrightarrow{\text{fast}} [Fe(pc)(PBu_3)_2] \qquad (9)$$

I thank the Research Corporation for support.

[6/111 *Received, 19th January,* 1976]

---

* 1 cal = 4.184 J.

[7] A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1968, **7**, 59.

[8] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., Wiley, London, 1967.