groups (Table I), in which both the A and E bands are shifted to low frequency, as expected.[14]

Tables II and III summarize pertinent NMR spectroscopic data concerning the six metal carbonyl complexes isolated in this work. The ^{31}P chemical shifts of the complexes are very similar to those reported for diphos derivatives,[15] but the coordination shifts are the largest reported in such complexes. The cause of the large downfield shift in five-membered chelate rings has been suggested to be ring strain,[5c] but subsequent work indicates a more complex situation.[15] The especially large downfield shifts observed in the present work apparently stem from the shielding effect of an *o*-phosphino moiety in the free ligand. Generally, diphenylalkylphosphines exhibit ^{31}P NMR resonance at about −17 ppm[16] (when alkyl $\neq$ Me, Et), whereas ligands **1** and **2** absorb at −30.1 and −27.2 ppm, respectively. Thus the *o*-phosphino group is shielding by about 10–13 ppm in the *o*-phenylene system, as well as in olefinic systems.[17] Grim has shown that his group contributions to ^{31}P chemical shifts of free phosphines also hold for $(R_3P)M(CO)_5$ species. Although there are currently insufficient data in the literature to be conclusive, the coordination chemical shifts exhibited by the chelated ligands $Me_2PCH_2CH_2PMe_2$[5c] and $(neopentyl)_2PCH_2CH_2P(neopentyl)_2$[20] in $(R_2PCH_2CH_2PR_2)M(CO)_4$ indicate that group contributions derived by Grim[16] also apply in such chelated tetracarbonyls. The especially large coordination chemical shifts for **1**·$M(CO)_4$ and also **2**·$M(CO)_3$ can be accounted for if it is assumed that the shielding effect of the *o*-phosphino group becomes inoperative upon coordination, although clearly more data are needed to clarify this point.[21] Finally, it is interesting to note in the ^1H NMR spectra of the **2**·$M(CO)_3$ complexes that the largest Δ_{NMe} occurs with W, although one might expect the largest change between Cr and Mo, on the basis of the covalent radii of the three metals.

There is a paucity of information with which to compare the ^{13}C NMR data in Table III. The carbon atoms α to coordinated phosphine (C1) experience a deshielding effect of about 3 ppm, whereas the central methylene carbon atoms (C2) are shielded in all six complexes. This latter shielding appears to be approximately constant in **1** but decreases in **2** from Cr to W. In **1**·$M(CO)_4$, the carbon atoms α to nitrogen (C3) are also shielded by about double the amount that C2 atoms are shielded. Finally, coordination of the nitrogen atom in **2**·$M(CO)_3$ results in very large deshielding effects of about 10 ppm for C3 and 20 ppm for NCH_3. Indicative of substantial positive charge on nitrogen in these complexes is the observation that these shifts are similar to those obtained upon N-oxidation of a tertiary amine. For example, N-oxidation of *N*-methylpiperidine results in a downfield shift of 9.4 and 12.7 ppm for C2 and NCH_3, respectively, and upfield shifts of 5.1 and 2.6 ppm for C3 and C4,[22] respectively.

The two- and three-bond carbon–phosphorus coupling constants are reduced essentially to zero upon metal complexation with **1**, whereas C1 exhibits a triplet with a slightly larger one-bond coupling constant in the complex (Cr and Mo) than in the free ligand. With tungsten a considerably larger $^1J_{C-P}$ is observed and apparently the stringent requirements for virtual coupling[23] are not met in **1**·$W(CO)_4$, since the C1 absorption is a doublet. With the tricoordinating ligand **2**, carbon–phosphorus coupling occurs with all three carbon atoms (C1–C3), although with Cr, the coupling is so small for C3 and C2 that only peak broadening is observed. The magnitude of the coupling constant increases from Cr to W for all three carbon atoms, and as for the **1** complexes, virtual coupling does not occur with the tungsten complex.

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Registry No. **1**·$Cr(CO)_4$, 73636-55-2; **1**·$Mo(CO)_4$, 73636-56-3; **1**·$W(CO)_4$, 73636-57-4; **2**·$Cr(CO)_3$, 73636-58-5; **2**·$Mo(CO)_3$, 73636-59-6; **2**·$W(CO)_3$, 73636-60-9; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

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(14) (a) Dobson, G. R.; Taylor, R. C.; Walsh, T. D. *Inorg. Chem.* **1967**, *6*, 1929. (b) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (c) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702.

(15) Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095.

(16) Grim, S. O.; McFarlane, W.; Davidoff, E. F. *J. Org. Chem.* **1967**, *32*, 781.

(17) Consider the following: δ_P $(Ph_2PCH{=}CH_2)$ −11.7;[16] (E-$Ph_2PCH{=}CHPPh_2$) −7.9;[18] (Z-$Ph_2PCH{=}CHPPh_2$) −23.1 ppm.[10] Thus substitution in diphenylvinylphosphine for the *E*-H by PPh_2 is deshielding (+4 ppm) whereas the corresponding replacement of the *Z*-H is *shielding* (−12 ppm).

(18) King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1971**, *93*, 4158.

(19) Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573.

(20) King, R. B.; Cloyd, J. C., Jr.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 449.

(21) Relative to chelating diphos[15] and in the absence of the shielding effect of the *o*-phosphino group, one would predict that chelated **1** should be about 4 ppm shielded, because of the difference in contribution of an ethyl (actually CH_2CH_2P) group in diphos and a propyl (actually $CH_2CH_2CH_2N$) group in **1**. In fact, relative to the corresponding diphos complexes, **1**·$M(CO)_4$ complexes are deshielded: M = Cr, 1 ppm; M = Mo, 3 ppm; M = W, 3 ppm.

(22) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 272–273.

(23) Musher, J. I.; Corey, E. J. *Tetrahedron* **1962**, *18*, 791.

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Axial Ligand Substitution Reactions of Iron(II) Phthalocyanine Adducts

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Kinetic studies of the ligand substitution reactions of six-coordinate iron(II) phthalocyanine adducts are reported: $(T)FePc(L) + X \rightarrow (T)FePc(X) + L$. The T, L, and X ligands include nitrogen and phosphorus donors. The reaction mechanism is strictly dissociative (D). The five-coordinate intermediate, (T)FePc, is extremely reactive and possesses little or no ability to discriminate between nucleophiles. Axial ligand labilities, leaving group effects, trans group effects, and discrimination ratios are discussed and compared to available information on iron porphyrins.

Introduction

Phthalocyanine complexes have been studied for many years because of their value as pigments. More recently the similarity of iron(II) phthalocyanine (FePc) and its bis adducts to iron(II) porphyrins has prompted additional investigations. Kinetic studies of ligand substitution, reaction 1, have been

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$$\text{(T)FePc(L)} + \text{X} \rightarrow \text{(T)FePc(X)} + \text{L} \qquad (1)$$

published by Jones and Twigg,[1,2] Stynes and James,[3] Watkins and Balch,[4] Sweigart,[5] and Stynes.[6] In reaction 1 T is the trans group, L the leaving group, and X the nucleophile. Typical T, L, and X ligands include imidazole (Im), *N*-methylimidazole (MeIm), pyridine (py), piperidine (pip), benzyl isocyanide (RNC), tri-*n*-butylphosphine (PBu_3), tri-*n*-butyl phosphite ($P(OBu)_3$), and carbon monoxide.

The activation enthalpies and entropies, rate retardation by excess leaving group (L),[5] and insensitivity of the rate to the nature of the nucleophile (X) clearly demonstrated that reaction 1 follows a dissociative mechanism (D), as shown in eq 2. Analogous reactions of six-coordinate iron(II) and

$$\begin{gathered}\text{(T)FePc(L)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{(T)FePc} + \text{L} \\ \text{(T)FePc} + \text{X} \xrightarrow{k_3} \text{(T)FePc(X)}\end{gathered} \qquad (2)$$

iron(III) porphyrins are also dissociatively activated (D or I_d).

Studies of the complexes of nonporphyrin nitrogen macrocycles should provide information about the factors responsible for the seemingly unique behavior found with the porphyrins. Obvious points of comparison between the phthalocyanine and porphyrin reactions include axial lability (k_1), the leaving group effect, the trans effect, and the ability of the five-coordinate intermediate to discriminate between nucleophiles (k_2/k_3). Herein we report kinetic studies of reaction 1 with a variety of T, L, and X groups. Comparisons are made to previous phthalocyanine work and, where possible, to iron porphyrin studies.

Experimental Section

Ferrous phthalocyanine, FePc, was purchased from Eastman Kodak. The six-coordinate adducts $FePcL_2$ (L = PBu_3, $P(OBu)_3$, Im, pip, py) were synthesized by published methods.[5,7] The ligands were purchased from standard sources and distilled or recrystallized prior to use.

The kinetics of reaction 1 were followed on a Durrum stopped-flow apparatus or a Perkin-Elmer 323 spectrophotometer. Purified and dried acetone was used as the solvent. Most reactions were studied at 21 °C. Pseudo-first-order conditions were used for all reactions with the nucleophile and leaving group concentrations being at least 10 times the total metal complex concentration, which was approximately 5×10^{-5} M. The rate data were fit to eq 4 by using a relative-deviation least-squares program.

Mixed-ligand complexes, FePcLL′, were generated in situ as described below. Optical spectra of the $FePcL_2$ and FePcLL′ complexes were recorded on a Perkin-Elmer 323 spectrophotometer. The spectra of the mixed-ligand adducts in general differed significantly from the spectra of $FePcL_2$ and $FePcL'_2$, and this made possible kinetic studies using FePcLL′ as the reactant.

Results

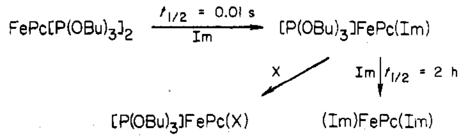
The results are given in Table I. For every reaction studied the data fit the expected rate law, eq 3; k_1 and k_2/k_3 were

$$k_{\text{obsd}} = \frac{k_1 k_3[\text{X}]}{k_2[\text{L}] + k_3[\text{X}]} \qquad (3)$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \left(\frac{1}{k_1}\right)\left(\frac{k_2}{k_3}\right)\left(\frac{[\text{L}]}{[\text{X}]}\right) \qquad (4)$$

extracted by linear least-squares fitting to eq 4 by plotting $1/k_{\text{obsd}}$ vs. $1/[\text{X}]$ at a fixed value of [L]. Mass-law rate retardation was observed for each reaction except at very small values of [L]. At high nucleophile concentrations the reactions reached a limiting rate (k_1).

Scheme I



The mixed-ligand complexes $[P(OBu)_3]$FePc(L) (L = Im, MeIm, pip, py) were generated in situ by adding the ligand L to $FePc[P(OBu)_3]_2$. The mixed complex formed rapidly as shown in Scheme I. Replacement of the second $P(OBu)_3$ either is very slow or does not occur for thermodynamic reasons, and so it was possible to measure reaction rates by using the mixed complexes as reactants and a third ligand (X) as the nucleophile.

For reaction 5 we previously reported[5] that the displacement

$$FePc[P(OBu)_3]_2 + 2PBu_3 \rightarrow FePc(PBu_3)_2 + 2P(OBu)_3 \qquad (5)$$

of the first $P(OBu)_3$ group was rate determining. The limiting rate constant for reaction 5 is 21 s^{-1} but is 50 s^{-1} for Im or MeIm as the nucleophile. Since the data are very consistent with a dissociative mechanism, and in particular show the limiting rate constant to be nucleophile independent for cases where the leaving group is known with certainty, we are forced to conclude that the second $P(OBu)_3$ displacement is rate determining in reaction 5. Therefore, the appropriate entry in Table I lists PBu_3 as the trans group and $P(OBu)_3$ as the leaving group.

It was possible to separate reaction 6 into two steps by

$$FePc(py)_2 + 2pip \rightarrow FePc(pip)_2 + 2py \qquad (6)$$

varying the wavelength at which the reaction was followed. At 426 nm a single step was seen, while at 635 nm there was an absorbance increase followed by an absorbance decrease. The step at 426 nm gave the same rate constant as the slower step at 635 nm and clearly corresponds to the reaction of the mixed complex (pip)FePc(py). The rate constant for the first pyridine loss was calculated from the initial absorbance increase at 635 nm as well as from the time of maximum absorbance.[8] The limiting rate constant obtained (0.9 s^{-1}) agrees tolerably well with that found for the reaction of $FePc(py)_2$ with PBu_3, for which the first step is definitely rate determining.

Discussion

The results indicate that reaction 1 proceeds by a strictly dissociative mechanism. A number of kinetic studies of iron porphyrin substitution reactions have been reported and it is now possible to make some comparisons with the phthalocyanine reactions described herein.

Table I shows that the axial ligand lability as measured by k_1 spans a large range (about 10^6). Table II shows a comparison with some iron(II) porphyrin data, and it can be seen that the porphyrins are much more labile. Related to this increased lability is the greatly different discriminating ability of the five-coordinate intermediates in the porphyrin and phthalocyanine reactions. Considering first the phthalocyanines, Table I shows that the discrimination ratio (k_2/k_3) is near unity for all of the reactions. In contrast Jones and Twigg[2] recently suggested that k_2/k_3 can be as large as 10^3–10^4 and correlates, at least qualitatively, with the overall equi-

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(1) Jones, J. G.; Twigg, M. V. *Inorg. Chem.* **1969**, *8*, 2120; *Inorg. Chim. Acta* **1974**, *10*, 103; **1975**, *12*, L15.

(2) Jones, J. G.; Twigg, M. V. *J. Chem. Soc. Dalton Trans.* **1978**, 1709.

(3) Stynes, D. V.; James, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 2733.

(4) Watkins, J. J.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2720.

(5) Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1476.

(6) Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 1170.

(7) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 28. Taube, R. *Pure Appl. Chem.* **1974**, *38*, 427.

(8) Pearson, R. G.; Sweigart, D. A. *Inorg. Chem.* **1970**, *9*, 1167.

Table I. Kinetic Data[a] for the Reaction (T)FePc(L) + X → (T)FePc(X) + L

trans group (T)	leaving group (L)	[L]/M	nucleophile (X)	[X]/M	k_1/s^{-1}	k_2/k_3
$P(OBu)_3$	$P(OBu)_3$	0.0015	Im	0.0050–0.104	52	
$P(OBu)_3$	$P(OBu)_3$	0.0097	Im	0.0050–0.104	47 ± 4	1.2 ± 0.2
$P(OBu)_3$	$P(OBu)_3$	0.0502	Im	0.020–0.22	48 ± 4	1.2 ± 0.2
$P(OBu)_3$	$P(OBu)_3$	0.050	MeIm	0.0050–0.50	54 ± 5	0.44 ± 0.2
$P(OBu)_3$	$P(OBu)_3$	0.10	MeIm	0.020–0.50	70 ± 5[b]	0.50 ± 0.2
$P(OBu)_3$	Im	0.0050	PBu_3	0.0028–0.054	2.2 ± 0.15	1.4 ± 0.2
$P(OBu)_3$	MeIm	0.010	PBu_3	0.0050–0.050	2.3 ± 0.25	0.82 ± 0.25
$P(OBu)_3$	pip	0.0092	PBu_3	0.0026–0.055	15 ± 2.5	1.7 ± 0.6
$P(OBu)_3$	py	0.050	PBu_3	0.010–0.10	30 ± 4	0.67 ± 0.2
PBu_3	$P(OBu)_3$	0.0075	PBu_3	0.0017–0.014	21 ± 2.5	0.69 ± 0.15
pip	pip	0.050	PBu_3	0.010–0.10	0.60 ± 0.16	0.74 ± 0.23
pip	pip	0.050	Im	0.0050–0.25	0.70 ± 0.10	0.93 ± 0.3
pip	py	0.041	pip	0.050–0.50	0.45 ± 0.10	1.3 ± 0.3
py	py	0.041	pip	0.050–0.50	0.90 ± 0.15	1.6 ± 0.4
py	py	0.050	PBu_3	0.0050–0.10	0.75 ± 0.15	1.5 ± 0.4
Im	py	0.050	Im	0.010–0.25	0.075 ± 0.01	0.70 ± 0.2
Im	Im	0.0050	PBu_3	0.0050–0.027	0.0018 ± 0.0004	0.92 ± 0.2
Im	$P(OBu)_3$	0.001	Im	0.10	0.00010	

[a] Solvent acetone, 21 °C; errors are at least one standard deviation. [b] Temperature is 23 °C.

Table II. Axial Labilities of Iron Phthalocyanines and Iron Porphyrins: $(T)Fe(N_4)(L) \rightarrow (T)Fe(N_4) + L$

substrate	k_1/s^{-1}	solvent
(py)FePc(py)[a]	0.8	acetone, 21 °C
(py)Fe(TPP)(py)[b]	12000	toluene, 25 °C
(py)Fe(PPIXDME)(py)[c]	1000	$CDCl_3$, 0 °C
(Im)FePc(Im)[a]	0.002	acetone, 21 °C
(Im)Fe(TPP)(Im)[b]	1700	toluene, 25 °C
(Im)Fe(DeuDME)(Im)[d]	>1500	benzene, 25 °C

[a] This work. [b] Lavalette, D.; Tetreau, C.; Momenteau, M. *J. Am. Chem. Soc.* 1979, *101*, 5395. TPP is tetraphenylporphyrin; the trans base (py or Im) is covalently attached to the porphyrin macrocycle. [c] von Goldammer E.; Zorn, H. *Biophys. Chem.* 1975, *3*, 249. PPIXDME is protoporphyrin dimethyl ester. [d] White, D. K.; Cannon, J. B.; Traylor, T. G. *J. Am. Chem. Soc.* 1979, *101*, 2443. DeuDME is deuterioporphyrin dimethyl ester.

Table III. Discrimination Ratios for Reaction 1[a]

T	L	X	k_2/k_3	K_{eq}
Im	Im	CO	4.2	0.03
pip	pip	CO	3.3	0.85
py	py	CO	3.4	2.7
RNC	RNC	MeIm	2.9	6.2
MeIm	MeIm	RNC	11	400
py	py	RNC	2.3	3200
pip	pip	RNC	1.0	3200

[a] Data from: Stynes, D. V.; James, B. R. *J. Am. Chem. Soc.* 1974, *96*, 2733; Stynes, D. V. *Inorg. Chem.* 1977, *16*, 1170. The solvent was toluene at 23 °C; RNC is benzyl isocyanide.

Table IV. Discrimination Ratios for the Reaction of the Five-Coordinate Iron Porphyrin Fe(Por)(T) with Nucleophiles L and X

substrate	L	X	k_X/k_L	conditions
Fe(PPIX)(CN)	OH^-	CN^-	0.0002	detergent, pH 10[a]
Fe(TPP)pip	O_2	pip	0.3	CH_2Cl_2, −79 °C[b]
Fe(TPP)pip	CO	pip	10	CH_2Cl_2, −79 °C[b]
Fe(TPP)pip	CO	pip	0.002 ?	toluene, 23 °C[c]
Fe(DeuDME)Im	CO	Im	>8	benzene, 25 °C[d]
Fe(TPP-Im)	CO	Im	40	toluene, 25 °C[e]
Fe(TPP-Im)	CO	py	100	toluene, 25 °C[e]

[a] Simplicio, J. *Biochemistry* 1972, *11*, 2529. [b] Weschler, C. J.; Anderson, D. L.; Basolo, F. *J. Am. Chem. Soc.* 1975, *97*, 6707. [c] Stynes, D. V.; James, B. R.; *J. Chem. Soc., Chem. Commun.* 1973, 325. The k_X/k_L value is probably in error.[e,d] [d] White, D. K.; Cannon, J. B.; Traylor, T. G. *J. Am. Chem. Soc.* 1979, *101*, 2443. [e] Lavalette, D.; Tetreau, C.; Momenteau, M. *Ibid.* 1979, *101*, 5395. The Im base is covalently attached to the TPP macrocycle.

librium constant for reaction 1. We did not measure equilibrium constants for the reactions reported in this study, but it can be deduced from the experimental conditions that many of the K_{eq}'s must be large. In Table III discrimination ratios for reactions studied by Stynes and James[3] and Stynes[6] are listed along with the equilibrium constants. It is clear that no correlation with K_{eq} exists. It should be noted that the ratios in Table III were not directly measured via a mass-law retardation effect but were calculated from known dissociation rate constants and K_{eq} values. For this reason the error limits are necessarily quite large, and it is by no means certain that the deviations from unity are significant. Considering the results in Tables I and III, we are hesitant to accept the claim by Jones and Twigg[2] that the discrimination ratio can be as large as 10^3–10^4. Instead we suggest that the ratio will always be near unity, implying that the five-coordinate intermediate, (T)FePc, is not discriminating and is, therefore, a very reactive species.

Table IV shows that five-coordinate porphyrin complexes, in contrast to the phthalocyanines, display considerable discriminating ability. That five-coordinate iron porphyrins are more stable, and hence selective, is to be expected since five-coordination is the favored geometry in deoxyhemoglobin and deoxymyoglobin and in the sterically hindered Fe(TPP)(2-MeIm) complex. In other words, five-coordinate iron porphyrins are reasonably stable species whereas five-coordinate iron phthalocyanines are not. Stynes and James[3] suggest that the relative ease of spin-state conversion from low spin in (T)Fe(Por)(L) to high spin in (T)Fe(Por), accompanied by a displacement of the metal from the mean porphyrin plane, is not feasible with the phthalocyanines because of the large ligand field caused by the smaller Pc core hole size.

The facile spin-state change and out-of-plane metal movement possessed by the porphyrins give them the dynamic and thermodynamic flexibility required by biological systems and account for their greater lability and selectivity as compared to the phthalocyanine complexes.

Table V gives the leaving group series for reaction 1. The reversal in the order of $P(OBu)_3$ and Im as the trans group is changed is striking. As the trans group changes from Im

Table V. Leaving Group Series for Reaction 1[a]

trans group	leaving group (L)						
Im	py	>	Im	>	$P(OBu)_3$		
	80		(1)		0.11		
	750		9		(1)		
$P(OBu)_3$	py	⩾	$P(OBu)_3$	>	pip	>	Im ≈ MeIm
	14		11		7		(1)
	1.2		(1)		0.6		0.08

[a] The solvent was acetone at 21 °C; the numbers are relative reactivities.

Table VI. Trans-Effect Series for Reaction 1[a]

leaving group	trans group (T)						
Im	$P(OBu)_3$	>	Im				
	2400		1				
$P(OBu)_3$	$P(OBu)_3$	⩾	PBu_3	>	Im		
	250 000		210 000		1		
MeIm	$P(OBu)_3$	>	RNC[b]	>	MeIm		
	3500		16		1		
RNC[b]	RNC	>	pip	>	py	>	MeIm
	5000		4		2		1
py	$P(OBu)_3$	>	pip	⩾	py	>	Im
	400		6		5		1

[a] The solvent was acetone at 21 °C except as noted; numbers are relative reactivities. [b] The solvent was toluene at 23 °C; data from: Stynes, D. V., *Inorg. Chem.* 1977, *16*, 1170.

to $P(OBu)_3$, the lability of $P(OBu)_3$ relative to Im increases by a factor of 100. Imidazole is primarily a σ donor with some π-donor properties, whereas $P(OBu)_3$ is both a good σ donor and π acceptor. This means that synergic π bonding occurs in the mixed complex, with the result that $P(OBu)_3$ is extremely inert trans to Im. Trans to $P(OBu)_3$, both Im and $P(OBu)_3$ are labilized (trans effect), but $P(OBu)_3$ becomes more labile because of the loss of the synergic π bonding and the necessity for the $P(OBu)_3$ ligand to compete for π-electron density with the trans $P(OBu)_3$ group.

The trans-effect series is summarized in Table VI. The π-acceptor ligands $P(OBu)_3$ and RNC are high in the series, in agreement with the well-known trans effect found in Pt(II) complexes. $P(OBu)_3$ is the best trans activator yet reported. Both $P(OBu)_3$ and RNC are much less effective, relative to imidazole, when trans to the π-donor Im ligand. As described above, the reason for this is the synergic π bonding present in, e.g., $[P(OBu)_3]FePc(Im)$ that is lost upon dissociation of the Im group. Unfortunately, very little is known about the trans effect in iron porphyrins. Basolo et al.[9] found the order py ≥ pip ≥ MeIm for reaction 7. This agrees with the

$$Fe(TPP)(L)(O_2) + L \rightarrow Fe(TPP)L_2 + O_2 \qquad (7)$$

phthalocyanine series in that MeIm is the poorest trans activator. However, the position of a good π acceptor in this series is unknown. As shown above, the synthesis of mixed-ligand complexes, $[P(OBu)_3]FePc(L)$, was possible because $P(OBu)_3$ is high in the trans-effect series, and this in turn allowed the necessary reactions to be studied to establish the fairly extensive trans-effect series given in Table VI. Similar experiments are in progress with iron porphyrins.

What is known at this time suggests that metalloporphyrins and metallophthalocyanines may have similar trans-effect series, but ones that differ drastically from those of other macrocycles. Although imidazole is trans deactivating in FePc and Fe(Por) complexes, it is apparently trans activating in Fe(TIM), $Fe(DMG)_2$, and Fe(TAAB) complexes.[10] These differences must be related to the ability of the metal and the macrocycle to transmit π-electron density. Since the imidazole ligand trans to dioxygen in HbO_2 and MbO_2 must influence the dynamics and thermodynamics of oxygenation, it is important that an extended trans-effect series for metalloporphyrins be determined and that the position of imidazole in this series be understood.

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Registry No. $(P(OBu)_3)FePc(P(OBu)_3)$, 61005-31-0; $(P(OBu)_3)FePc(Im)$, 73612-14-3; $(P(OBu)_3)FePc(MeIm)$, 73612-15-4; $(P(OBu)_3)FePc(pip)$, 73612-16-5; $(P(OBu)_3)FePc(py)$, 73612-17-6; $(PBu_3)FePc(P(OBu)_3)$, 73612-18-7; (pip)FePc(pip), 21194-13-8; (pip)FePc(py), 73612-19-8; (py)FePc(py), 20219-84-5; (Im)FePc(py), 73612-20-1; (Im)FePc(Im), 20219-85-6; (MeIm)FePc(MeIm), 55925-76-3; Im, 288-32-4; MeIm, 616-47-7; PBu_3, 102-85-2; pip, 110-89-4.

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(9) Weschler, C. J.; Anderson, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1975**, *97*, 6707.

(10) Pang, I. W.; Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 2192. Baldwin, D. A.; Pfeiffer, R. M.; Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 5152. Pang, I. W.; Singh, K.; Stynes, D. V. *J. Chem. Soc., Chem. Commun.* **1976**, 132. Pang, I. W.; Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 590.

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Preparation and Stereochemistry of Bis(carboxylato)bis(tertiary phosphine)bis(disilylamido)dimolybdenum(II) Complexes

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Tetrakis(acetato)dimolybdenum, $Mo_2(O_2CMe)_4$, reacts with the lithium silylamides $LiN(SiMe_3)_2$, $LiN(SiMe_2H)_2$, or $LiN(SiMe_3)(Me)$ in the presence of tertiary phosphines (PMe_3, PMe_2Ph, or PEt_3) to give complexes of the type $Mo_2(O_2CMe)_2(NR_2)_2(PR_3)_2$. The stereochemistry of the red, pentane-soluble complexes has been determined by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ nuclear magnetic resonance and infrared spectroscopy. When the silylamide is $N(SiMe_2H)_2$, the phosphines and silylamide groups are oriented trans relative to the metal–metal bond. In contrast, when the silylamide is $N(SiMe_3)_2$ or $N(SiMe_3)(Me)$, the phosphine and silylamide groups are trans to each other on the same molybdenum atom. Tetrakis(pivalato)dimolybdenum, $Mo_2(O_2CCMe_3)_4$, behaves similarly with one exception; i.e., the $N(SiMe_3)_2$ complexes are of the type $Mo_2(O_2CCMe_3)_3[N(SiMe_3)_2](PR_3)$. The stereochemistry of these complexes is independent of the carboxylate or phosphine group but dependent upon the nature of the silylamide. This effect is ascribed to a trans influence.

Compounds of the general type $Mo_2(O_2CR)_2(R')_2(PR''_3)_2$, where R, R′, and R″ are uninegative groups, are of some interest since a number of geometrical isomers are possible. Only a few complexes of this general type have been de-

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