

### Reversible Phosphine Binding to Palladium Arylazo-oximates: Correlation of Equilibrium Constants with Cone Angles

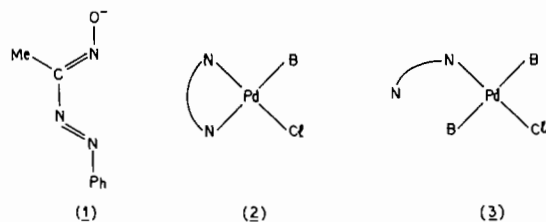
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#### Introduction

Reactivity patterns of pyramidal phosphorus ligands are often controlled by steric properties of such ligands [1]. Herein we report the systematics of equilibrium data with special reference to the case where a phosphine ligand (B) is in active competition with one end of a palladium-bound bidentate arylazo-oximate ligand (1). The concerned species are (2) and (3).



#### Experimental

The various phosphines were obtained from Strem Chemical Inc. (U.S.A.) and Eastman Organic Chemicals (U.S.A.). For the present work, (2) was first generated in solution by adding the phosphine ligands to  $\text{Pd}_2\text{Cl}_2\text{L}_2$  in (2:1) ratio [2]. The equilibrium (1) (*vide infra*) was then brought about by adding various concentrations of B. The equilibrium constant was calculated from the spectra data using the relations  $K = a/(a_0 - a)(b - a)$  and  $A/\epsilon = (a_0 - a)$ , where  $a_0$  is the total concentration of palladium species,  $b_0$  is the concentration of B added to (2),  $a$  is the equilibrium concentration of (3),  $A$  is the absorbance (1 cm path length) of the equilibrium mixture at 550 nm and  $\epsilon$  is the extinction coefficient of (2) at the same wavelength. Even though the band peak for (2) is at 520 nm, the point of observation was at 550 nm to avoid intensity contribution from a strong 430 nm band. Data for two cases are collected in Table I.

TABLE I. Selected Equilibrium Data<sup>a</sup> for the Reaction (1) in Benzene at 298 K.

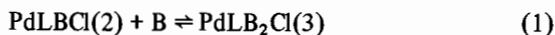
	$10^4 b_0$	$10^4 A/\epsilon$	$10^{-4} K$
	1.00	0.67	0.73
B = P( <i>p</i> -tolyl) <sub>3</sub>	2.00	0.49	0.70
a = $1.00 \times 10^{-4}$	3.00	0.37	0.71
$\epsilon = 4900$	4.00	0.30	0.71
	1.94	0.73	6.93
B = PMePh <sub>2</sub>	2.13	0.638	6.57
a = $2.36 \times 10^{-4}$	2.32	0.544	6.52
$\epsilon = 4775$	2.52	0.450	6.81

<sup>a</sup>All symbols have the same meaning as in text.

Electronic spectra were measured on a Cary 17D recording spectrophotometer. PMR spectra were recorded on Varian T60A or EM-390 spectrometer using  $\text{CDCl}_3$  as solvent and TMS as the internal standard.

#### Results and Discussion

Complexes (2) and (3) where B = triarylphosphine were reported earlier [2]. Herein the cases of PMePh<sub>2</sub>, PMe<sub>2</sub>Ph and Pcy<sub>3</sub> (cy = cyclohexyl) are also considered. An allowed MLCT electronic transition at 520 nm is uniformly characteristic of (2) [(3) is transparent in this region]. When B is added to a solution of (2), the 520 nm band progressively loses intensity. Variable concentration spectra display a well defined isosbestic point. Results are in agreement with the presence of the equilibrium (1).



Equilibrium constant data are collected in Table II. The effect of the addition of PPh<sub>3</sub> on the PMR spectra of (2) (B = PPh<sub>3</sub>) and its bromo-analogue were studied in  $\text{CDCl}_3$  (Table III). The methyl signal first broadened and then sharpened again. After the (2): B ratio crossed 1:1 no further changes occurred. In the relatively concentrated (~0.1 M) solution used for PMR measurements, all B added is consumed since  $K$  is large) till (2): B ratio reaches the value 1:1. At this stage all the palladium(II) is present as (3). At lower proportion of B, (2) and (3) coexist and interconvert producing a broad average signal. The shift of  $\delta$  Me in going from (2) to (3) is due to aromatic ring currents [2].

A measure of the steric demand of B is its cone angle,  $\theta$  [1, 3]. In case of predominant steric control of a reaction of the type (R = reactant, P = product),

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TABLE II. Equilibrium Constants (K) for the Reaction (1) at 298 K in Benzene.

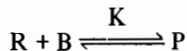
B	$\theta^a$	$10^{-2}K$
PMe <sub>2</sub> Ph	122	2310 ± 50
PMePh <sub>2</sub>	136	670 ± 20
PPh <sub>3</sub>	145	28 ± 2
P( <i>p</i> -tolyl) <sub>3</sub>	145	70 ± 2
Pcy <sub>3</sub>	170	[0.5] <sup>b</sup>
P( <i>o</i> -tolyl) <sub>3</sub>	194	[0.006] <sup>b</sup>

<sup>a</sup>From ref. 1. <sup>b</sup>Extrapolated values from linear  $\ln K-\theta$  plot of Fig. 1, values too small to allow experimental determination.

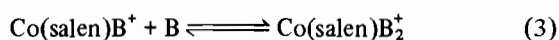
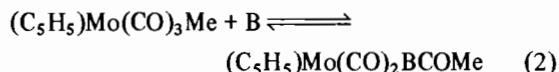
TABLE III. Methyl Proton Chemical Shifts in CDCl<sub>3</sub>.

[(2)]:[PPh <sub>3</sub> ]	$\omega(\text{Hz})^a$	$\delta_{\text{Me}}(\text{ppm})$	
		X = Cl	X = Br
1:0.00	3.0	2.03	2.13
1:0.25	7.8	1.92	1.90
1:0.50	7.6	1.37	1.40
1:0.75	4.2	1.03	1.07
1:1.00	2.5	0.87	0.87

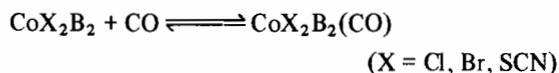
<sup>a</sup>Full width at half height at 90 MHz.



the equilibrium constant K usually decreases with increase in cone angle of B. We have considered the possibility that there may be an approximate linear correlation of free energy change or simply  $\ln K$  with  $\theta$ . Some literature data [4, 5] were analysed and indeed such a relationship was found applicable (Fig. 1) for reactions such as:



We also record that the  $\ln K-\theta$  linear relation applies even in case [6] where metal bound B controls the insertion and elimination of other molecules *e.g.*,



equilibrium (1) fits reasonably well into the linear  $\ln K-\theta$  pattern (Fig. 1) for B = PPh<sub>3</sub>, PMePh<sub>2</sub>, PMe<sub>2</sub>Ph. The trend of this equilibrium with these phosphines is therefore set by phosphine bulkiness. Pcy<sub>3</sub> and P(*o*-tolyl)<sub>3</sub> are too bulky to react (K ~ 0; Table II).

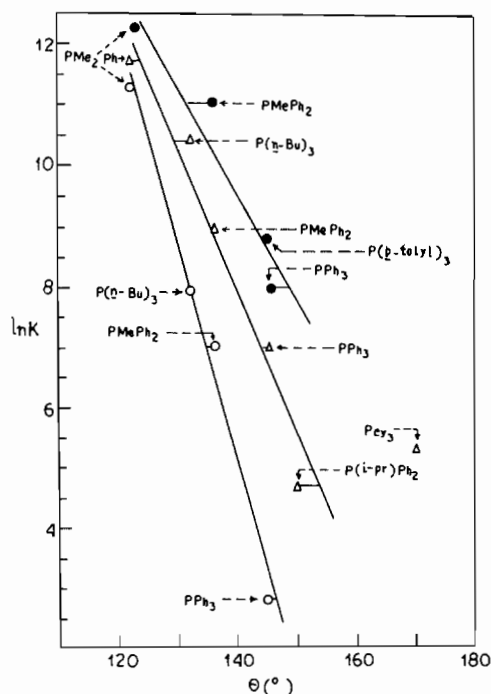


Fig. 1. Plots of  $\ln K$  versus  $\theta$ : (●), equilibrium (1); (Δ), equilibrium (2); (○), equilibrium (3). The lines are least square fitted. The ill-behaved Pcy<sub>3</sub> point in (2) was not included in fitting.

For PPh<sub>3</sub> and P(*p*-tolyl)<sub>3</sub>,  $\theta$  is invariant but  $K[\text{PPh}_3] < K[\text{P}(\textit{p}\text{-tolyl})_3]$  (Table II). However the difference of the two K values is not large enough to make P(*p*-tolyl)<sub>3</sub> deviate significantly from the linear  $\ln K-\theta$  plot (Fig. 1). It is proposed that the relatively small but significant differences in the K values for the two ligands arise from the electron releasing character of the methyl substituent.

#### Acknowledgements

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#### References

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