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Carbonyl-stabilized phosphonium ylides as ligands. Equilibrium studies on the reversible formation of PdCl(η^3-allyl)(ylide) species

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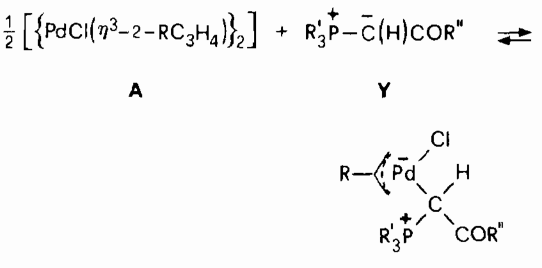
Abstract

An UV-IR study of the equilibrium between [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ and the carbonyl-stabilized phosphonium ylides R$'_3$PCHCOR$''$ in CH$_2$Cl$_2$ at 25 °C reveals that the nucleophilic ability of the ylide to bind to palladium in the Pd-C(ylide) bonded product [PdCl(η^3-2-MeC$_3$H$_4$)(R$'_3$PCHCOR$''$)] increases with increasing basicity of the ylide towards the proton with steric hindrance by phosphonium substituents playing an adverse role.

In the last two decades the coordination chemistry of ylides has attracted increasing attention owing to the peculiar electronic features and versatile chemical properties of this special type of carbanions [1].

We have recently reported on the reaction of η^3-allyl Pd(II) complexes with carbonyl-stabilized phosphonium ylides yielding Pd-C(ylide) bonded species via halide-bridge splitting and coordination of the ylide ligand to the metal through the ylide carbon atom [2] (eqn. (1)).



(1)

R=H or Me; R$'$=Ph; R$''$=Me or Ph. **B**

The monomeric complexes **B** proved stable in the solid state but easily dissociate in chlorinated solvents giving rise to an equilibrium mixture of dimer **A**, free ylide **Y** and monomer **B** [2a]. Since the coordinating ability of the ylide is likely to depend on the nucleophilicity of the ylide carbon and on the steric hindrance of the phosphonium group, we have now undertaken a quantitative study of reaction (1) hoping to assess the influence of ylide substituents on the equilibrium position.

For a preliminary study we examined the ylides with R$'$=Cy, R$''$=OMe (**Y1**), Me (**Y2**), Ph (**Y3**); R$'$=Bu^t, R$''$=Me (**Y4**); R$'$=Ph, R$''$=Me (**Y5**) reacting with [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ in CH$_2$Cl$_2$ at 25 °C. The results are described here.

The ylides **Y1**-**Y4** were prepared by a general method involving deprotonation with (Me$_3$Si)$_2$NNa in THF at 0 °C of the parent phosphonium salts HY$^+$X$^-$ (X=Cl, Br) which had been prepared by reaction of PR$'_3$ with the appropriate organic halide XCH$_2$COR$''$ in CH$_2$Cl$_2$ at r.t. **Y5** has already been described [2a].

The reaction products **B** were prepared by the general method of ref. 2. **B4** could not be isolated due to its low formation constant (*vide infra*). **B5** has already been described [2a]. Analytical and spectral data are:

B1: m.p. 159 °C dec. *Anal.* Calc. for C$_{25}$H$_{44}$ClO$_2$PPd: C, 54.65; H, 8.07. Found: C, 54.73; H, 8.18%. IR (Nujol): ν(C=O) 1671 cm^{-1}. ^{31}P{^{1}H} NMR (80 MHz, CD$_2$Cl$_2$, 233 K, a temperature low enough to shift equil. (1) far to the right): δ 35.45(s), 34.40(s) [2a].

B2: m.p. 155-157 °C dec. *Anal.* Calc. for C$_{25}$H$_{44}$ClOPPd: C, 56.29; H, 8.31. Found: C, 56.41; H, 8.67%. IR (Nujol): ν(C=O) 1628 cm^{-1}. ^{31}P{^{1}H} NMR: δ 34.16(s), 33.08(s).

B3: m.p. 103-104 °C. *Anal.* Calc. for C$_{30}$H$_{46}$ClOPPd: C, 60.51; H, 7.79. Found: C, 60.69; H, 8.12%. IR (Nujol): ν(C=O) 1605 cm^{-1}. ^{31}P{^{1}H} NMR: δ 36.18(s), 35.45(s).

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Equilibrium (1) for **Y1**, **Y2** and **Y4** could be studied by both UV–Vis and IR spectral techniques. In the UV–Vis approach, to a solution of dimer **A** were added aliquots of ylide solutions at various concentrations in the range 5×10^{-5} to 5×10^{-3} M in the dark (exposure of the solution to visible light for more than *c.* 1 h appears to promote detectable decomposition of products **B**) and the resulting spectra recorded in the 400–300 nm range. Abstract factor analysis [3] of the spectra revealed the presence of three independently absorbing species, i.e. the unreacted dimer **A**, unreacted ylide **Y** and formed monomer **B**. The equilibrium constant K_e was determined by non-linear fitting of optical density (*OD*) data to ylide concentrations according to the model

$$\mathbf{A}+2\mathbf{Y} \rightleftharpoons 2\mathbf{B}$$

$$K_e=[\mathbf{B}]^2/[\mathbf{A}][\mathbf{Y}]^2$$

$$[\mathbf{A}]=[\mathbf{A}]_0-[\mathbf{B}]/2 \qquad (2)$$

$$[\mathbf{Y}]=[\mathbf{Y}]_0-[\mathbf{B}]$$

$$OD=(\epsilon_A[\mathbf{A}]_0+\epsilon_Y[\mathbf{Y}]_0)+[\mathbf{B}](\epsilon_B-\epsilon_Y-\epsilon_A/2)$$

Values of $\log K_e$ are listed in Table 1 as the averages of determinations at five wavelengths (uncertainties quoted are averages of standard errors of estimate). The optimized parameters were $\log K_e$ and ϵ_B. During each iterative cycle of the refining procedure [4] the concentrations of all species involved were determined by solving the equilibrium and mass balance equation system at the current parameter values by means of a Newton system solver based on LU decomposition/back substitution schemes [5] (Fig. 1).

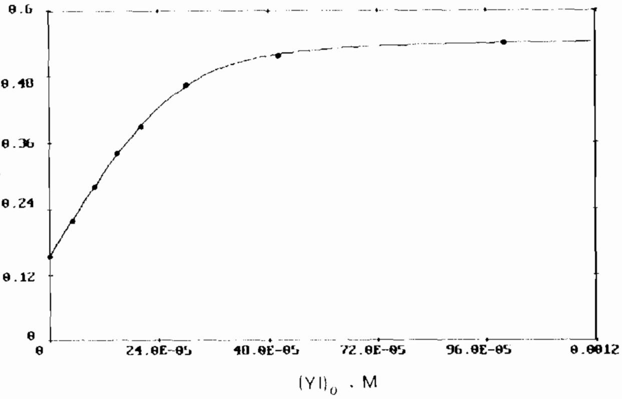


Fig. 1. Spectrophotometric titration of **A** 1×10^{-4} M with **Y1** at 320 nm.

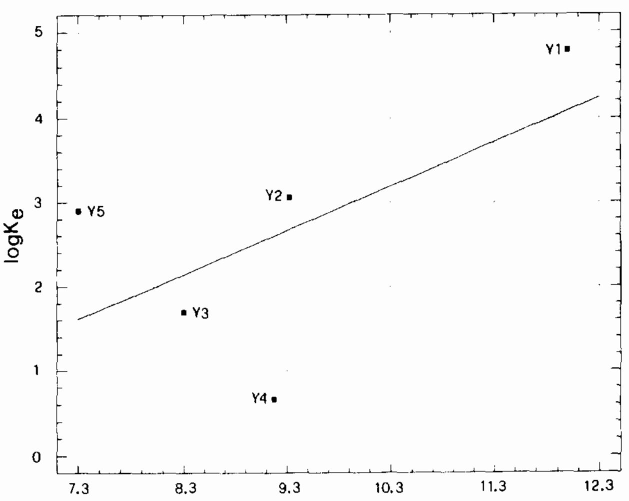


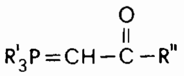
Fig. 2. Plot of $\log K_e$ vs. pK_a of the ylide for equilibrium (1). The full line is the least-squares fit to all data points.

TABLE 1. Formation constants for Pd–C(ylide) bonded monomers **B** from reaction (1) in CH_2Cl_2 at 25 °C

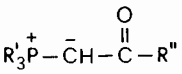
Ylide $R'_3PCHCOR''$		Code	pK_a	$\log K_e$
R′	R″			
Cy	OMe	**Y1**	12.00	4.78±0.03 (UV)
	Me	**Y2**	9.33	3.06±0.02 (UV) 3.03±0.05 (IR)
	Ph	**Y3**	8.30	1.7±0.3 (IR)
Bu^t	Me	**Y4**	9.18	0.65±0.09 (UV)
Ph	Me	**Y5**	7.30	2.91±0.03 (IR)

In the case of ylides **Y3** and **Y5** equilibrium (1) could not be studied by UV–Vis spectrophotometry due to the unfavorable values of molar extinction coefficients in eqn. (2), since the ylides happen to absorb strongly in the 400–300 nm range. In such cases we resorted to IR spectral techniques, taking advantage of the difference in ν(C=O) between free and coordinated ylide (1509 versus 1605 cm^{-1} for **Y3**; 1530 versus 1614 cm^{-1} for **Y5** in CH_2Cl_2). To a CH_2Cl_2 solution of dimer **A** were added aliquots of ylide solutions at concentrations in the range 3×10^{-3} to 5×10^{-2} M and the resulting IR spectra recorded immediately in the 1800–1450 cm^{-1} range ($[\mathbf{A}]_0=1\times10^{-2}$ M). All solutions were pre-thermostatted at 25 °C in the dark whereas the cell compartment was not. The two ν(C=O) overlapping bands were deconvoluted by fitting IR absorbance values to linear combinations of Gaussian and Lorentzian functions in the ratio $f/(1-f)$, with f being kept constant at the same best (in the least-squares sense) value for both bands [6]. The concentrations of the monomeric ylide complex **B** in eqn. (2) were evaluated from the area beneath its composite peak using the optimized band parameters from the deconvolution process. Non-linear fitting of such an area to ylide concentration gave the $\log K_e$ values listed in Table 1. These are less accurate than those obtained by UV–Vis techniques, due to the higher uncertainty in the IR cell temperature and the intrinsically less accurate peak area determination involved in the IR method. As a check on the self-consistency of the general experimental layout, the IR approach described above was also applied to determine $\log K_e$ for **Y2**. This gave a value of 3.03 ± 0.05, in fairly good agreement with that from UV–Vis measurements.

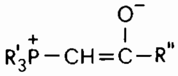
As can be seen (Fig. 2), the order of $\log K_e$ values for formation of monomers **B1–B3** in eqn. (1) appears to parallel the ylide basicity order as reflected by the reverse proton acidity trend in the pK_a values of the conjugate phosphonium acids $[R'_3PCHCOR'']Cl$, which we have determined by potentiometric titration in $MeOH/H_2O$ 1/1 vol./vol. (ionic strength 1×10^{-2} M, NaCl, at 25 °C). The higher acidity of the phenylphosphonium salt is to be attributed to the inductive withdrawal effect of the phenyl group relative to cyclohexyl, which decreases the electron density on the phosphorus atom. This in turn results in a better pπ–dπ overlap and better conjugative stabilization of the canonical form **I** in the corresponding ylide [7].


$R'_3P{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R''$

I


$R'_3\overset{+}{P}{-}\overset{-}{C}H{-}\overset{O}{\overset{\|}{C}}{-}R''$

II


$R'_3\overset{+}{P}{-}CH{=}\overset{O^-}{\overset{|}{C}}{-}R''$

III

From an alternative point of view, the more electron-donating cyclohexyl group will stabilize to a greater extent than a phenyl group the polar canonical structure **II**, thus justifying the higher basic character of the cyclohexyl–ylide ligand. On the other hand, an electron-donor substituent at the ylide carbonyl, such as OMe, will make the ylide more basic by lessening the stabilizing effect of the carbonyl through conjugation.

However, these electronic effects appear to be balanced by the steric properties of the R′ phosphonium substituent. In fact, the K_e value for **Y5** is higher than expected from the above basicity trend, probably due to the lower cone angle of PPh_3 compared to PCy_3. Steric effects appear even more important in the case of the much sterically demanding Bu^t-bearing ylide **Y4** which displays a much lower K_e even though its basicity is comparable to that of **Y2**.

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