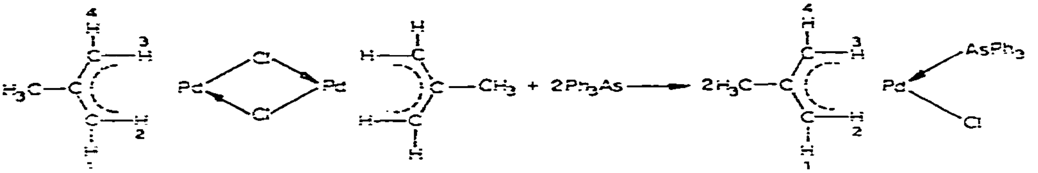
NMR kinetic studies of the reactions occurring in the system $[(\pi\text{-}C_4H_7)PdCl]_2\text{-}Ph_3As$

Recently[1] the rearrangements of the (meth)allyl groups in the systems containing $[(\pi\text{-}C_3H_4R)PdCl]_2$ and the ligand L(R = H, CH_3; L = $P(n\text{-}C_4H_9)_3$, $P(OCH_2)_3CCH_3$, Ph_3P, Ph_3As, Ph_3Sb) were extensively studied by NMR spectroscopy as a function of the type of ligand L, the ligand-to-metal ratio and the temperature. We now report more quantitative kinetic data on one of these systems *viz.* $[(\pi\text{-}C_4H_7)PdCl]_2\text{–}Ph_3As$.

Reaction of Ph_3As with the dimer $[(\pi\text{-}C_4H_7)PdCl]_2$ produces the monomer $(\pi\text{-}C_4H_7)PdCl(Ph_3As)$ according to:



The absorptions of protons 1, 2, 3 and 4 of the monomer $(\pi\text{-}C_4H_7)PdCl(Ph_3As)$ at −73° in $CDCl_3$ are magnetically non-equivalent and appear at 4.54*, 3.57, 2.78 and 3.26* ppm from TMS respectively[1]. At higher temperatures and/or at higher Ph_3As/Pd ratios the four signals begin to broaden and finally coalesce to form two peaks at 3.94 and 3.19 ppm (δ), which belong to protons (1,4) and (2,3) respectively. This interchange of protons 1 and 4 (and of 2 and 3) has been interpreted as a rotation of the π-allyl group in its own plane in a five-coordinate activated complex $(\pi\text{-}C_4H_7)PdCl(Ph_3As)_2$ (Ref. 1). A further increase of the temperature and/or the Ph_3As/Pd ratio causes a further coalescence of the signals of protons (1,4) and (2,3) to one single peak. This additional rapid interchange of protons 1 and 2 and of 3 and 4 resp. has been ascribed to the formation of a four-coordinate activated complex $(\sigma\text{-}C_4H_7)PdCl(Ph_3As)_2$ in which the allyl group is σ-bonded to the metal.

We have now studied the line widths of the monomer and the dimer (when excess dimer is present) as a function of the temperature and the Ph_3As/Pd ratio. By using standard NMR methods[2] we measured the lifetimes (τ) of the observed species and subsequently the relevant reaction constants. In Fig. 1 the changes in the spectra of the monomer and the dimer as a function of the temperature are given as an example.

In the kinetic analysis a large number of reactions were included. It was found, however, that only four relevant reactions have to be considered, *viz.*:

$$[(\pi\text{-}C_4H_7)PdCl]_2 + 2\,Ph_3As \underset{k_1}{\leftrightarrows} 2\,(\pi\text{-}C_4H_7)PdCl(Ph_3As) \qquad (1)$$

$$(\pi\text{-}C_4H_7)PdCl(Ph_3As) \underset{k_2}{\leftrightarrows} (\pi\text{-}C_4H_7)PdCl + Ph_3As \qquad (2)$$

Reaction (3) involves the rotation of the π-methallyl ligand in its own plane; proton 1 interchanges with 4, and 2 with 3.

Reaction (4) involves the formation of the σ-allyl form; proton 1 interchanges with 2, and 3 with 4.

$$(\pi\text{-}C_4H_7)PdCl(Ph_3As) + Ph_3As^* \underset{k_3}{\rightleftarrows} (\pi\text{-}C_4H_7)PdCl(Ph_4As^*) + Ph_3As \quad (3)$$

$$(\pi\text{-}C_4H_7)PdCl(Ph_3As) + Ph_3As^* \underset{k_4}{\rightleftarrows} (\pi\text{-}C_4H_7)PdCl(Ph_3As^*) + Ph_3As \quad (4)^{**}$$

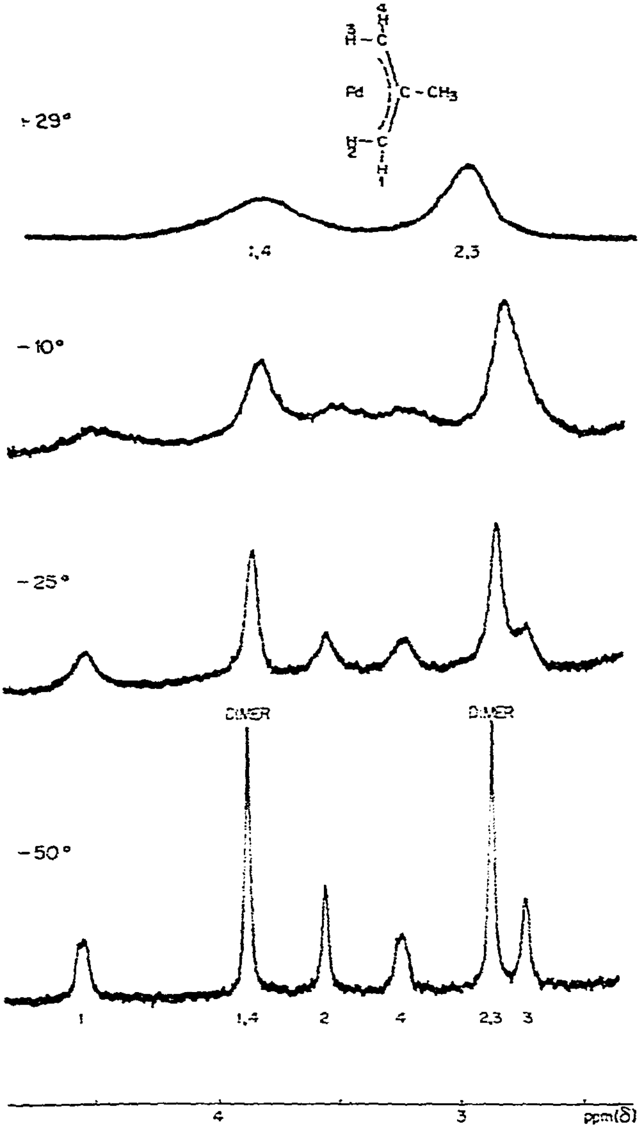


Fig. 1. The dependence of the linewidths of the signals of protons 1, 2, 3 and 4 of the monomer and the dimer at 100 Mc (equations II and III). The concentrations of the monomer and the dimer in $CDCl_3$ are 0.15 and 0.075 mole/l resp.

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[*] The signals of protons 1 and 4 are broader than those of 2 and 3, due to long-range coupling between these protons, as was shown by double resonance. For reasons not yet understood the long-range coupling disappears at higher Ph_3As to Pd ratios. Therefore we have calculated our kinetic parameters, where necessary, on the line widths of protons 2 and 3.

[**] It should be noted, that, by writing the equations (1) to (4) as shown above, we assume that no intermediates occur. This of course an arbitrary assumption, since we cannot yet determine, if intermediates are present or not.

Reaction (3) was measured between —80° and —40° with a slight excess of free arsine. At higher temperatures and/or higher Ph_3As/Pd ratio the formation of the σ-allyl form begins to take place [reaction (4)], whereas with too small an excess of free arsine the dissociation reaction [reaction (2)] becomes important. Reaction (4) was measured at such conditions that reaction (3) is too fast to be followed by NMR.

Using the symbols M_2, ML and L for the dimer, monomer and arsine, we can write down the following rate equations

$$1/\tau\,(\mathrm{ML}) = k_2 + (k_3 + k_4)\,[\mathrm{L}] + k_{-1}\,[\mathrm{ML}], \qquad \text{(I)}$$

which, when excess dimer is used, can be written as

$$1/\tau\,(\mathrm{ML}) = k_2 + (k_3 + k_4)\,\sqrt{K_2\,[\mathrm{ML}]} + k_{-1}\,[\mathrm{ML}] \qquad \text{(II)}$$

since

$$K_2 = [\mathrm{M}]\cdot[\mathrm{L}]/[\mathrm{ML}] = [\mathrm{L}]^2/[\mathrm{ML}]^{*}$$

$$1/\tau\,(\mathrm{M_2}) = k_1\,[\mathrm{L}]^2 = k_1\cdot K_2\,[\mathrm{ML}] \qquad \text{(III)}$$

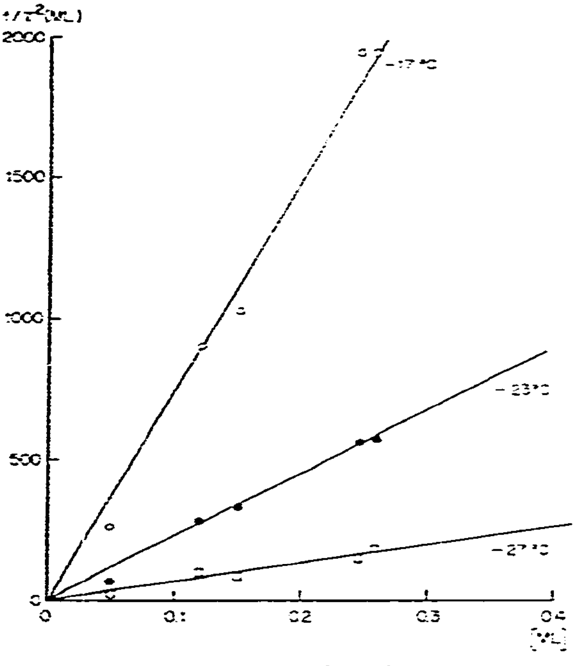

Fig. 2. The dependence of $1/\tau^2$ (ML) on [ML] for reaction 3 (equation II), when excess dimer is present, at —17, —23 and —27°. Reaction 3 is first order in the ligand L concentration.

Fig. 2 gives an example of plots which describe the dependence of $1/\tau$(ML) (for reaction (3) with excess dimer present) on [L] (which is proportional to $\sqrt{\mathrm{ML}}$) at several temperatures. From the rate plots and formulae (I), (II) and (III) the following data were obtained:

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[*] It is assumed that L ≅ M, which is a good approximation since reaction (1) lies on the far right.

$$k_1 = 1.05 \times 10^{11}\,e^{-200/RT}\ \text{mole}^{-2}\,l^2\,\text{sec}^{-1}$$

$$k_3 = 5.45 \times 10^{11}\,e^{-6400/RT}\ \text{mole}^{-1}\,l^{+1}\,\text{sec}^{-1}$$

$$k_4 = 1.43 \times 10^{7}\,e^{-7100/RT}\ \text{mole}^{-1}\,l^{+1}\,\text{sec}^{-1}$$

$$K_2 = 1.24 \times 10^{2}\,e^{-12500/RT}\ \text{mole}\ l^{-1}$$

(k_{-1} and k_2 are negligible compared with the other constants).

The frequency factors of reactions (1) and (3) are high and very similar, which is in agreement with the mechanism proposed earlier for the reaction of Ph_3As with the monomer and the dimer[1]. This mechanism involves an attack of the ligand molecule along the negative X-axis on the monomer, which is sterically the most favourable reaction path (an idealized structure of the five-coordinate form is shown in Fig. 3). The activation energies of reactions (3) and (4) are not much different, but the frequency factor of the latter is much lower. Apparently the reaction path for reaction (4) is different from that of reaction (3). We suggest that here the attack of the free arsine ligand along the positive X-axis is a possible mechanism.

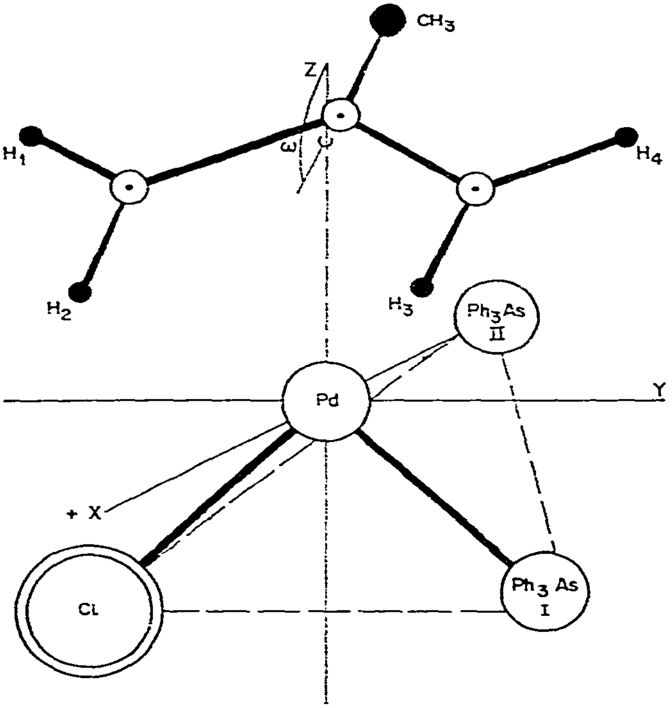

Fig. 3. The idealized structure of the pseudo-trigonal five-coordinate form $(\pi\text{-}C_4H_7)PdCl(Ph_3As)_2$ in reaction (3).

From a number of notes[1-5] published recently on the so-called "dynamic" allyl group [which is defined by its NMR spectrum with collapsed signals of protons 1, 2, 3 and 4; in our case reaction (4)], it appears that some confusion still exists about the nature of the "dynamic" form. In view of this we would like to stress once more what we have clearly pointed out in previous publications[1,11], *viz.* that essentially only two different forms of the allyl group exist; a σ-bonded form, in which only one carbon atom is taking part in the bonding with the metal atom, and a π-bonded one, where all three carbon atoms are involved. The NMR spectrum of the "dynamic" form is a consequence of a rapid equilibrium between the two forms, as has also been suggested by other authors[6-10].

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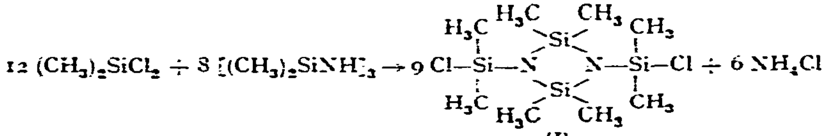
Functionally substituted cyclodisilazane derivatives

Wannagat recently observed that a four-membered ring compound, N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, was obtained in a surprisingly high yield during attempts to produce dichlorotrisilazanes by equilibrating dichlorodimethylsilane and cyclotrisilazanes or cyclotetrasilazanes[1]. In studies of the same equilibration in this laboratory, N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (I) has been obtained in a mean yield of 54% when dichlorodimethylsilane and hexamethylcyclotrisilazane were equilibrated for 48 h at 175°.



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