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Preliminary communication

Organometallic conformational equilibria
VII. On the planar rotation of π-allyl ligands in metal complexes

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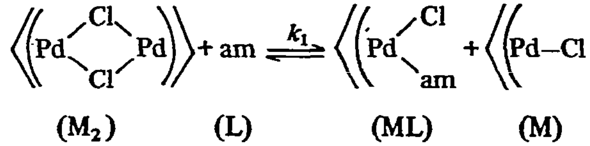
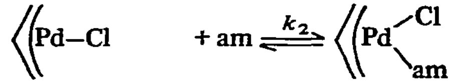
It has been demonstrated that the predominant pathway of epimerization in π-allyl(amine)palladium(II) chloride complexes involves intermolecular amine exchange[1]. In the analogous phosphine and arsine complexes Vrieze and coworkers[2,3] have proposed two mechanisms which lead to exchange an S_N2 attack upon the palladium atom to yield a five-coordinate intermediate in which the allyl group might undergo planar rotation* and an S_N1 rupture of the Pd–ligand bond. Although in several cases our data on the amine systems agree with the interpretations of Vrieze and coworkers, numerous observations, as well as "spin-saturation labelling" studies** of the reactions, warrant additional conclusions about the mechanisms which we report here.

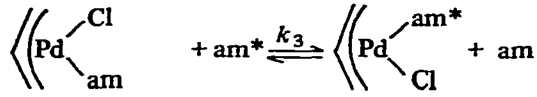
The feature common to solutions of these palladium complexes is the simultaneous occurrence of several equilibria involving free ligand, the π-allylpalladium halide dimer, and other intermediates. For example, we find the following tentative kinetic scheme (excluding reactions involving σ-bonded intermediates which are important at higher temperatures[8-10]) sufficient to explain our kinetic data.



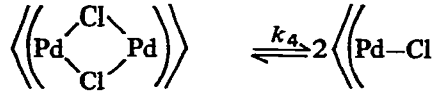
slow forward (1)



fast forward (2)



(3)



(4)

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*Planar rotation of the allylic moiety has been proposed for "five-coordinate" molybdenum complexes[4,5] Recent work has shown that these interconversions can conveniently be considered as occurring via pseudorotation of the five coordinate complex[6].

**The procedure described here is based on previous studies of "nuclear spin-depolarization transfer" and "indirect spin saturation"[7].

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These equilibria provide pathways for fairly rapid amine exchange and lead to broadening or averaging of resonances in the room temperature NMR spectra. The broadening depends upon the lifetimes of the protons in a given chemical environment and the equations above provide the following relations between lifetimes and kinetic parameters[★].

$$1/\tau(\mathrm{ML}) = (k_1 k_1/K_2)\,[\mathrm{M_2}]^{1/2} + k_2 + k_3\,[\mathrm{L}]$$

$$1/\tau(\mathrm{M_2}) = k_1\,[\mathrm{L}] + k_4$$

The interdependence of the equilibria, low precision in determining orders of reactions, and the complexity of the system make interpretations based on standard kinetic treatments dubious at best. Since our aim is to follow the pathway of the protons in the allylic moiety during the course of epimerization, we have used a more reliable alternative - "spin saturation labelling" - rather than NMR line shape studies followed by kinetic analysis. Furthermore this complimentary method allows us to investigate the possibility of epimerization by rotation of the π-allyl group in the square complex[★★].

The NMR spectrum of π-crotyl(2-picoline)palladium chloride at −56° (in $CHFCl_2$) is consistent with the presence of both *cis* and *trans* isomers. Furthermore in solutions to which π-crotyl dimer is added, resonances attributable to the dimer are observed. All of the resonances (even those of the dimer) gradually coalesce to give the averaged spectrum typical of a symmetrically substituted π-crotyl complex. These observations indicate not only a rapid *cis*–*trans* interconversion, but also a parallel equilibrium with dimer or the direct involvement of the dimer as an intermediate (this is implied by the averaging of the dimer resonances with those of the amine complex).

cis

trans

It is most convenient to follow the pathway of the exchange by observing the methyl resonances of the crotyl ligands. Hence at −56°, in the presence of excess π-crotyl palladium chloride dimer, the methyl region shows three chemically shifted doublets[★★★]: the doublet of the *cis* isomer, *C*; the doublet of the dimer, *D*; and the doublet of the *trans* isomer, *T*. If exchange is occurring faster than the spin-lattice relaxation times of these sites, then saturation of the methyl resonance in one type of complex will result in partial saturation of the resonance of the site with which it is exchanging[12,13]. In this manner one can "label" a particular site and then by observing which resonances in the remainder of the spectrum are partially saturated via the transfer of spin saturation one can determine the site(s) to which the nuclei in the irradiated site go during exchange. The degree of this transfer of saturation is related to the rate at which site exchange occurs and the value of T_1 at those sites. For example, in the absence of dimer, one may demon-

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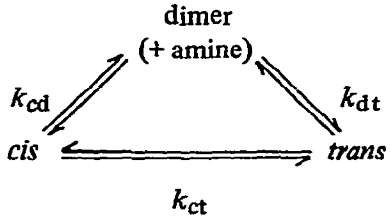
[★] For a summary of the standard kinetic analysis see ref. 11.

[★★] It is interesting to note that in the square planar complex bis-π-allylpalladium no evidence of planar rotation has been observed[12].

[★★★] Resonances were observed at τ 8.92 (*C*), τ 8.48 (*T*), and τ 8.64 (*D*), each with a splitting of 6 Hz. Each of these resonances is attributed to π-crotyl complexes with the methyl group *syn* to the central proton. In addition in all solutions prepared from the crystalline complex a doublet (6 Hz) of very low intensity (<6%) was observed at τ 8.77. By analogy to π-1,2,3-$(CH_3)_3C_3H_2PdLCl$ systems[9] we tentatively assign this doublet to the methyl resonance of *cis*-[*anti*-π-crotyl] aminepalladium chloride.

strate that the *cis* and *trans* isomers interconvert at low temperatures by irradiating the frequency of the *cis* methyl resonance with sufficient power to cause complete saturation, while also observing the *trans* resonance. Under circumstances such that the T_1 is long compared to the half-time of interconversion, $\tau < T_1$, one notices a decrease in intensity of the *trans* doublet.

In a system containing sufficient dimer to observe saturation effects readily, one may determine the prevalent path in equilibria proceeding via several paths.



At low temperature, irradiation at the *cis* methyl resonance causes a high degree of saturation in the dimer resonance and a smaller degree of saturation in the *trans* doublet[★]. Analogous results are noted when the *trans* methyl doublet is irradiated. Irradiation at the midpoint of the dimer doublet produces effectively equal collapse of both the *cis* and *trans* resonances. Therefore we may conclude that in systems where $[\mathrm{Pd}]/[\mathrm{L}] > 1/k_{cd} \sim k_{dt} \gg k_{ct}$; $k_{cd} \gg k_{ct}$; and $k_{td} \gg k_{tc}$. This implies that the predominant pathway of epimerization involves the intermediacy of the dimer (or of a species which is rapidly converted to the dimer). Thus under these conditions, a given *cis* complex is most likely to be converted first to the dimer, and then subsequently to the *trans* complex rather than proceeding directly from *cis* to *trans*.

For both the $[\mathrm{Pd}]/[\mathrm{L}] > 1$ and $[\mathrm{Pd}]/[\mathrm{L}] < 1$ systems we find that $1/\tau(\mathrm{ML})$ is a function of dimer and amine concentrations; whereas for $[\mathrm{Pd}]/[\mathrm{L}] \simeq 1$, $1/\tau(\mathrm{ML})$ is effectively independent of [ML] until [ML] > 0.5 molar. Such observations are consistent with predominance of the S_N2 mechanism in the former cases and of the S_N1 mechanism in the latter (see eq.1 through 4)[★★]. This point is further supported by our previous studies on allyl complexes, which show that the process which corresponds to *cis–trans* isomerism in the crotyl complexes occurs with amine exchange. Hence these results lend further support to our conclusion that planar rotation mechanisms play a minor role, if any, in the epimerization or isomerization reactions of these formally "four-coordinate" square planar complexes. While our data do not permit us to conclude the nature of the rearrangement which takes place in the five-coordinate intermediate expected in the S_N2 reaction[3], we feel that it is convenient to consider the rearrangement as a pseudo-rotation. Hence, a "planar rotation" could occur if the metal were in a formally five-coordinate, seven-coordinate, or other stereochemically nonrigid structure.

[★] At −56° when [*trans*] = 2 [dimer], which gives equal numbers of T and D sites, one observes 15% saturation of T and 29% saturation of D upon 100% saturation of C.

[★★] For the 2-picoline ligand the activation energy associated with epimerization in the $[\mathrm{Pd}]/[\mathrm{L}] \simeq 1$ solution is estimated as 13.3 kcal·mole^{-1}. We have noted a direct dependence of activation energy on base strength, E_a increasing in the series: pyridine, 2-picoline, 2,6-lutidine.

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