anti- and *syn*-Isomers of a π-Allylpalladium Chloride Complex

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Summary *anti*-2-Methyl-1-t-butyl-π-allylpalladium chloride is the initial product in the reaction of 2,4,4-trimethylpent-2-ene with $PdCl_2$ in buffered acetic acid.

REACTION of olefins with palladium chloride[1] yields exclusively π-allyl complexes with the bulkiest substituent in the *syn*-position. This is because the thermodynamic stability of the complex in this configuration is higher than in the *anti*-configuration on account of the lower steric hindrance between the substituent and the metal atom. Complexes which form exceptions to this rule, *i.e.* have the bulkiest substituent in the *anti*-position, do so because the structure of the preceding intermediate enforces this configuration. In the cases known so far this is brought about either by a *cis*-configuration at the double bond of a cyclic olefin[2] or by the cisoid conformation of a substituted diene which is co-ordinated as a bidentate group to a metal.[3]

TABLE

Solvent		Temp. (°c)	Reaction time (min.)	Product distribution (% total) *Anti*- 2-Methyl-1-t-butyl-π-allyl PdCl	*Syn*- 2-Methyl-1-t-butyl-π-allyl PdCl	2-Neopentyl-π-allyl PdCl
HOAc–NaOAc[2] ..	..	85	11	>61	14	<10
HOAc–NaOAc[2] ..	..	85	210	<22	>69	<4
$HOAc–H_2O$[1] ..	..	90	10	19·5	72	8·5
$CHCl_3–Na_2CO_3$[6]	..	25	240	5	13	81

We have now found a case in which an *anti*-substituted complex forms from an olefin and $PdCl_2$, despite the bulkiness of its substituent. When 2,4,4-trimethylpent-2-ene (I) reacted with $PdCl_2$ varying amounts of *anti*- (II*a*) and *syn*-2-methyl-1-t-butyl-π-allylpalladium chloride (II*s*) together with 2-neopentyl-π-allylpalladium chloride (III) were formed depending on the reaction conditions (see Table). The complex (II*a*), m.p. 115°, was isolated after a short reaction period by repeatedly recrystallizing the crude product from methanol, and (II*s*), m.p. 162°, was obtained pure through precipitation of the crude product of several hours' reaction from a chloroform solution with pentane. The structures were assigned on the basis of n.m.r. and *X*-ray analysis.[4] The most striking feature in the n.m.r. spectra of (II*a*) and (II*s*) (see Figure 1) is the difference in chemical shift of 1·77 p.p.m. for the hydrogen geminal to the t-butyl group.

A specific conformation in the intermediate π-olefin complex must be the reason why the less stable isomeric π-allyl complex is formed. A model shows that in the situation shown in Figure 2A considerable steric hindrance will occur between the t-butyl group of the π-olefinic ligand and a chloride ligand. To ease the strain, the olefin may turn somewhat around the co-ordinate bond. This brings the methyl group *cis* to t-butyl into a position closer to, and therefore more favourable for interaction with, a chlorine ligand (Figure 2B). While we do not know the details of this reaction yet, *i.e.* whether an allylic hydrogen leaves the ligand *via* the metal atom or by direct bond-formation with a chloride ligand, we favour the latter possibility, because it will give preferential hydrogen-elimination from the *cis*-methyl group.

Prolonged heating of the reaction mixture, as well as addition of a co-ordinating compound to a solution of (II*a*), results in isomerization to (II*s*). This proves that the isomerization occurs *via* an intermediate σ,π-complex with free rotation around the carbon–metal σ-bond.[5] The kinetic parameters for the isomerization catalysed by PPh_3 were: $k_{25^\circ} = 1{\cdot}12 \times 10^{-4}$ sec.$^{-1}$, $E_A = 19$ kcal./mole (solvent = CH_2Cl_2, conc. PPh_3 = 0·023%M).

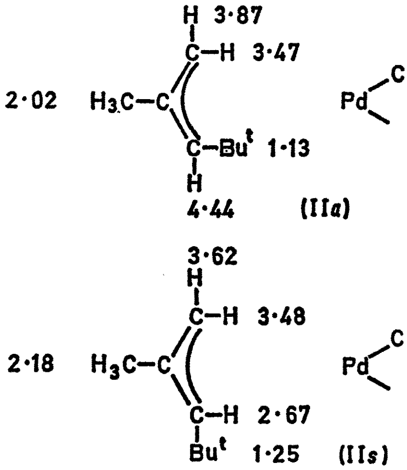

FIGURE 1

N.m.r. chemical shifts in p.p.m. downfield from Me_4Si

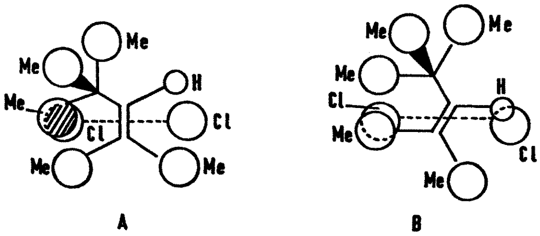

FIGURE 2

The complex (III) is formed *via* isomerization of (I) to 2,4,4-trimethylpent-1-ene (IV) *via* (II).[1] Since HCl participates in the equilibrium (I) $\rightleftarrows$ (IV) it seems reasonable that the high yield of (III) is due to a longer lifetime of HCl in the heterogeneous system $CHCl_3$–Na_2CO_3 before it reacts with the base.

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