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π-COMPLEXES OF $PdCl_2$ WITH 1,3-BUTADIENE AND 1,3-CYCLOOCTADIENE

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Although the formation of π-complexes between olefins, and non-conjugated diolefins, and $PdCl_2$ has been known for several years (1), complexes in which palladium is bound to a conjugated diolefinic ligand have not yet been described.

Complexes of this type with 1,3-butadiene were prepared by us by ligand exchange, with a careful control of the reaction temperature. By operating at a temperature between -80° and-20°C, preferably at-40°C, it was possible to obtain the quantitative ligand exchange between liquid 1,3-butadiene and $\pi(PdCl_2\cdot n\text{-pentene})_2$, according to the equation:

$$2C_4H_6+(PdCl_2\cdot C_5H_{10})_2 \xrightarrow[-40°C]{C_4H_6} 2C_5H_{10}+(PdCl_2\cdot C_4H_6)_2$$

The preparation of a series of π-complexes between $PdCl_2$ and α-olefins has been described by us in another paper (2).

An identical reaction was obtained with 1,3-cyclooctadiene at +20°C.

Identical qualitative results were obtained by employing ligand exchange on the π complex of $PdCl_2$-benzonitrile, and even more simply, by letting palladium chloride to react slowly in the liquid diolefins at the temperatures reported above. In this case, however, quantitative yields were not obtained since not all the $PdCl_2$ employed reacted.

No alteration or isomerization of the diolefin in excess occurred during these preparations. The complex from 1,3-butadiene and that obtained from 1,3-cyclooctadiene precipitated as brown-coloured crystals from the liquid diolefin; then they separate after filtration and repeated washings with anhydrous n-pentane at -40°C for the butadiene complex and at room temperature for the cyclooctadiene complex. Both complexes can be purified by repeated dissolution in benzene or toluene and reprecipitation in petroleum ether at 20°C and -40°C respectively.

The complex $(PdCl_2 \cdot C_4H_6)_2$, which is slightly soluble in hydrocarbons at low temperature, is unstable above -20°C. At room temperature it changes nearly quantitatively (96%) into the corresponding π-allylic complex $(PdCl \cdot C_4H_6Cl)_2$, which is just the product usually obtained by the reaction between 1,3-butadiene and $(PdCl_2 \cdot C_6H_5\text{-}CN)_2$ when the temperature was not controlled(3).

The instability of the compound made it impossible to carry out elemental analysis and to determine its molecular weight. However, its formula is sure, since the above transformation into the isomer allyl compound takes place practically without weight loss.

The π-complex with 1,3-cyclooctadiene, on the contrary, is stable up to the melting temperature (110°C) and is well soluble in hydrocarbons.

The elemental analysis and the determination of molecular weight by cryoscopy in benzene are in good agreement with the formula and molecular size attributed to the new compound:

Analysis: for $(PdCl_2 \cdot C_8H_{12})_n$ Calc. C=33·7; H=4·22; Cl=24·8.
Found C=34·04; H=4·36; Cl=25·11.

Cryoscopy in benzene (2·8% p.p.):
for $(PdCl_2 \cdot C_8H_{12})_2$ Calc. = 570
Found = 550.

The π nature of the bond between diolefin and palladium in the two complexes described was evidenced by characteristic reactions of the π complexes and further confirmed by physical-chemical studies. In both cases, by reaction with tallium acetylacetonate (4,5), palladium diacetylacetonate is obtained (dec.p. 205°-210°C, IR and NMR spectra identical with that of a sample), and the initially present diolefin is recovered, pure by gas-chromatographic analysis.

Furthermore, in both cases, the diolefin molecule is quantitatively replaced by the reaction with 1,5-cyclooctadiene, which, as shown by us, is of general use to remove a monoolefin, π-coordinated to $PdCl_2$, without altering its configuration (2). It is thus obtained the yellow complex ($PdCl_2$·1,5-cyclooctadiene) with dec.p. 200°-220°C (6).

The I.R. spectra in Nujol reported in the spectral region 1400 ÷ 1800 cm^{-1} in figs.1 and 2 reveal the presence of the absorption band relating to the unperturbed C=C (1660 cm^{-1}) and of that around 1500 cm^{-1} concerning a transition metal coordinated double bond (7).

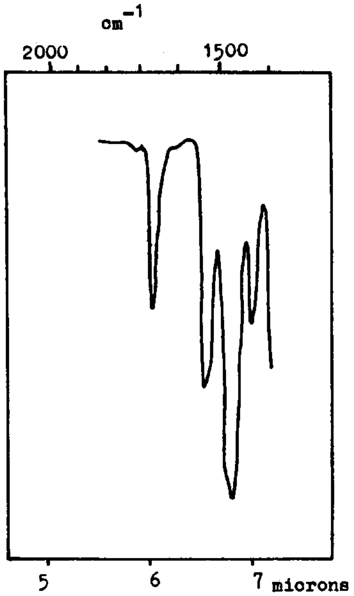


Fig.1 - IR spectrum in Nujol of: π-$(C_8H_{12}.PdCl_2)_2$

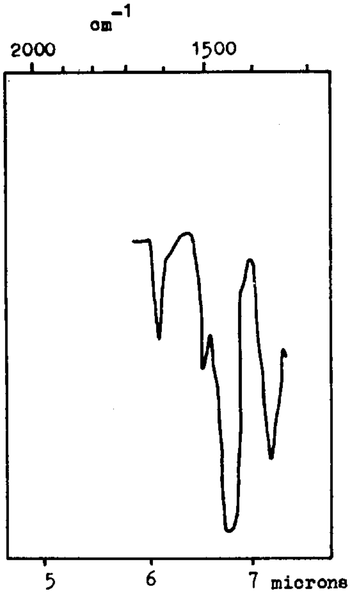


Fig.2 - IR spectrum in Nujol at -40°C of: π-$(C_4H_6.PdCl_2)_2$

Hence, we must conclude that, in the two compounds, only one of the two double bonds is engaged in the coordination and the other one is free: the ligand is monodentate.

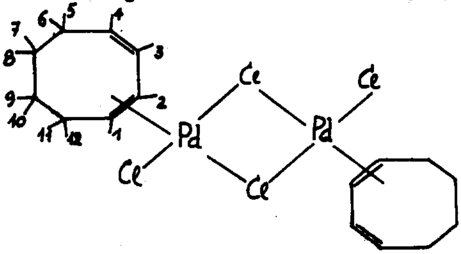
The NMR analysis, performed at 100 Mc/sec, on a Varian HA 100 spectrometer equipped with a HP frequentiometer mod.5512 A, on the π complex ($PdCl_2$·1,3-cyclooctadiene) on saturated solutions in $CDCl_3$, gave the following results:

$\tau_{1,2}$ = 620 ± 5 cps, area 2; $\tau_{3,4}$ = 600 ± 5 cps, area 2;

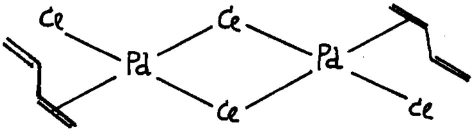
$\tau_{5,6}$ = $\tau_{11,12}$ = 204 ± 5 cps, area 4 (broad band);

$\tau_{7,8}$ = $\tau_{9,10}$ = 143 ± 5 cps, area 4; from TMS (tetramethylsylane).

The reference TMS is extrapolated by the real shifts as regards $CHCl_3$, since TMS decomposes the solute. The four unsaturated -CH= bonds have been resolved into two groups of equivalent area: this fully proves the result given by I.R. examination. Therefore the following formula can be attributed to the complex



The NMR analysis of the complex with 1,3-butadiene had to be performed at -40°C, that is under conditions of scarce solubility of the compound. Consequently, in this case, the resolution of the peaks of the unsaturated -CH= bonds was not obtained, but only a qualitative proof of their existence has been given. However, the chemical behaviour of this complex and the close analogy between the I.R. spectra of the two compounds described, does not leave any doubt that only the dimeric structure:



is to be assumed.

Research in progress in our laboratory (8) have demonstrated that also trans-1,3-pentadiene and cis-trans-2,4-hexadiene give, under suitable conditions, π-complexes of the same type. Thanks to their higher stability, it was possible to determine their molecular weight, which is in agreement with the dimeric formula.

References

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