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Metals in Organic Syntheses. III. Highly Regioselective Propene Hydrocarboxylation promoted by a $PdCl_2(PPh_3)_2$–PPh_3 Catalyst Precursor: *trans*-$Pd(COPr\text{-}n)Cl(PPh_3)_2$ as an Active Catalytic Species

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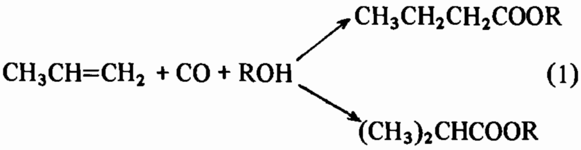
It has been recently reported that the hydrocarboxylation of propene occurs with high selectivity towards the n-butyrate ester, in the presence of a $PdCl_2(PPh_3)_2$–PPh_3 catalyst precursor (Pd/P = 4), according to the following reaction (1) [1]:



$$CH_3CH{=}CH_2 + CO + ROH \rightarrow CH_3CH_2CH_2COOR \;/\; (CH_3)_2CHCOOR$$

(1)

Most of the studies have been carried out using n-BuOH as hydrogen donor (and solvent). The high selectivity is achieved under relatively low P_{CO} at the expense of the yield. In this case the yield can be increased, while maintaining a high selectivity, by carrying out the carbonylation in the presence of molecular hydrogen; under these conditions no aldehyde has been detected in the reaction products [1] (see some results and run conditions reported below).

Here we report that by allowing the reaction solution to stand several hours at room temperature (after the carbonylation has taken place, either in the presence of molecular hydrogen or in its absence), white crystals of *trans*-$Pd(COPr\text{-}n)Cl(PPh_3)_2$, (A), can be isolated in *ca.* 70% yield. The i.r. spectrum of complex (A) shows a band of strong intensity at 1690 cm^{-1} due to $\nu(C{=}O)$ and a band of weak intensity at *ca.* 330 cm^{-1} attributable to $\nu(Pd{-}Cl)$. The ^1H n.m.r. spectrum can be poorly interpreted due to low solubility in a suitable solvent (C_6D_6). The presence of a n-Pr group has been unambiguously proved by single-crystal X-ray techniques.

The complex crystallizes in the monoclinic system, space group C_{2h}^5–$P2_1/n$ with four molecules in a unit cell; the lattice constants are a = 13.252(8), b = 23.805(10), c = 12.193(8) Å, β = 115.1(1)°, D_o = 1.40, D_c = 1.406 g cm^{-3}.

Three-dimensional diffraction data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized Mo$K\bar{\alpha}$ radiation. Data collection in the range $3 \leqslant 2\theta \leqslant 46°$ gave 4775 measurements; correction for Lorentz and polarisation effects, and for long-term intensity variation of the radiation yielded 2862 unique observed [$I \geqslant 2.5\,\sigma(I)$] reflections. Absorption correction was applied following North *et al.* [2]. The structure was solved by the heavy atom technique and refined by full-matrix least-squares to a conventional R value of 0.061.

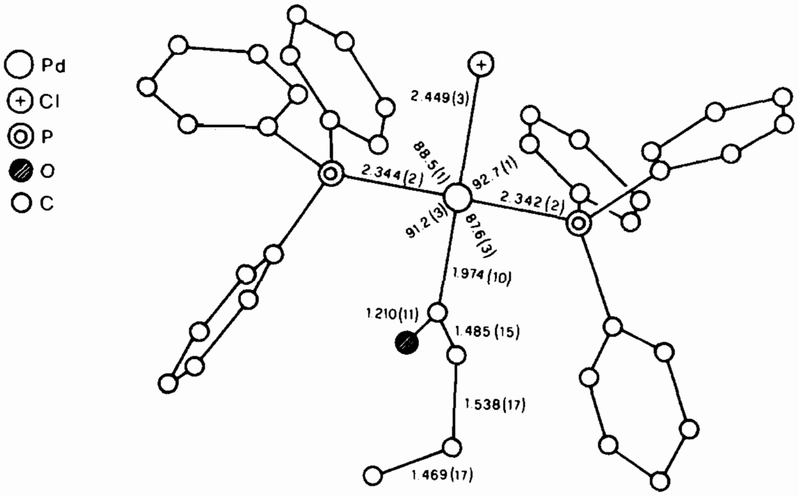


Fig. 1. Molecular structure of *trans*-$Pd(COPr\text{-}n)Cl(PPh_3)_2$. Hydrogen atoms are omitted.

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The stereochemistry of the complex is shown in Fig. 1 where the most relevant bond lengths and angles are marked.

The structure described by the cell constants and the atomic parameters consists of the packing of discrete molecules of *trans*-Pd(COPr-n)Cl(PPh$_3$)$_2$ separated by van der Waals contacts, which agree with those predicted from radii-sum rules.

The Pd atom is four-coordinated and is surrounded in an approximately planar fashion by two *trans* phosphorus atoms of the PPh$_3$ ligands, a chlorine atom and a σ-bonded carbon of (COPr-n) group.

The triphenylphosphine geometry in this compound as judged by P–C distances, C–P–C and P–C–C angles and by the dihedral angles between the phenyl ring planes is in agreement with the geometry of the triphenylphosphine ligand and its derivatives in other transition metal complexes, with the same *trans* configuration [3].

The value of 1.974(10) Å was found for the palladium–carbon distance. There appears to be a small π-interaction between these two atoms since a Pd–C(sp^2) distance of 2.05 Å would be expected from the sum of covalent radii [4].

The Pd–Cl bond length of 2.449(3) Å, determined in the present complex, is not only significantly greater than that predicted from available covalent radii (2.30 Å) [5] but is among the longest ones recorded for square planar complexes of palladium [6]. The long palladium–chlorine bond would be attributed to the 'structural' *trans* effect of the carbon σ-bonded group [4].

The two Pd–P bonds are equal within the experimental error (mean Pd–P distance 2.343(2) Å) and are typical of values in complexes of this sort [7, 8].

As for the (COPr-n) group, its dimensions fairly agree with those already found in similar compounds [5].

Complex (A) is an active catalytic species in reaction (1): for example, under $P_{CO} = P_{H_2} = 13$ atm, whether using 0.1 mmol of PdCl$_2$(PPh$_3$)$_2$ or of (A), 0.2 mmol of PPh$_3$, 25 mmol of propene, 0.1 mol of n-BuOH, at 100 °C, in 4 hours, yield and selectivity are *ca.* 50 and 80%, respectively, in both cases.

The isolation of complex (A) strongly supports a reaction mechanism occurring *via* olefin insertion into a Pd–H bond [9] rather than into a Pd–COOR bond [10].

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