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# Metals in Organic Syntheses.
# XIII[†]. The Isolation and Molecular Structure of *trans*-[PdCl(COC$_6$H$_{13}$-n)(PPh$_3$)$_2$], an Intermediate in the Hydrocarboalcoxylation of 1-Hexene Catalyzed by the Precursor *trans*-[PdCl$_2$(PPh$_3$)$_2$]

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## Abstract

The complex *trans*-[PdCl(COC$_6$H$_{13}$-n)(PPh$_3$)$_2$] has been isolated in the course of 1-hexene hydrocarboalkoxylation catalyzed by the precursor *trans*-[PdCl$_2$(PPh$_3$)$_2$] in EtOH. The catalytic activity of the precursor and that of the acyl complex are practically the same, thus suggesting that the latter complex is an intermediate in the catalysis.

The IR spectrum of the acyl complex shows $\nu$(C=O) at 1685 cm$^{-1}$. The crystal and molecular structure of the complex was determined from three dimensional X-ray diffractometer data. The complex crystallizes in the triclinic space group $P\bar{1}$. Cell parameters were: $a$ = 17.330(8), $b$ = 11.963(7), $c$ = 10.100(7) Å, $\alpha$ = 112.4(1), $\beta$ = 97.7(1), $\gamma$ = 99.8(1)°, $Z$ = 2. Full-matrix least-squares refinement converged at $R$ = 0.067. The coordination about the metal significantly deviates from planarity towards a tetrahedral configuration. No unusual dimensions were shown.

## Introduction

The increasing interest for the hydrocarboalkoxylation of olefins catalyzed by palladium complexes is mainly due to the fact that the catalysis occurs under relatively mild conditions, and that it is efficient with a large variety of substrates, including functionalized ones [2, 3].

Recently, *trans*-[PdCl(COPr-n)(PPh$_3$)$_2$] was isolated in the course of propene hydrocarboalkoxylation catalyzed by the precursor *trans*-[PdCl$_2$(PPh$_3$)$_2$] [4, 5]. The acyl complex and the precursor present practically the same catalytic activity, thus giving direct support to a reaction pathway that involves the olefin insertion into a Pd–H bond followed by the CO addition to yield the acyl intermediate which produces the final ester upon interaction with the alkanol [4, 5].

Here we present the crystal and molecular structure of *trans*-[PdCl(COC$_6$H$_{13}$-n)(PPh$_3$)$_2$], isolated in the course of 1-hexene hydrocarboalkoxylation catalyzed in EtOH by the precursor reported above.

## Experimental

### *Materials*

Carbon monoxide, quality N37, was purchased from the S.I.O. Company. EtOH was commercial grade. 1-hexene was passed through a column of neutral Al$_2$O$_3$ and distilled before use. The catalyst precursor *trans*-[PdCl$_2$(PPh$_3$)$_2$] was prepared as described in the literature [6].

### *Synthesis of trans-[PdCl(COC$_6$H$_{13}$-n)(PPh$_3$)$_2$]*

A mixture of 70 mg of *trans*-[PdCl$_2$(PPh$_3$)$_2$] (0.10 mmol), 53 mg of PPh$_3$ (0.20 mmol), 10 mmol of 1-hexene and 10 ml of EtOH was placed in a bottle which was introduced into an autoclave. The autoclave was cooled in an ice bath, purged with carbon monoxide and then pressurized with 100 atm. of CO at room temperature. The autoclave was then placed in a thermostatted oil bath,

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[†] Part XII, see ref. [1].

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and the temperature was raised to 100 °C in *ca.* 10 min. After 4 h the autoclave was cooled in an ice bath, then after *ca.* 1 day at room temperature it was depressurized. White crystals of the complex were filtered off, washed with EtOH and dried under vacuum. Yield 70%. Found: C, 66.48; H, 5.76; Cl, 4.30. $C_{43}H_{43}ClOP_2Pd$. Calcd.: C, 66.25; H, 5.56; Cl, 4.55.

### *Collection and Reduction of X-ray Intensity Data*

Suitable crystals for X-ray analysis were separated directly from the reaction in EtOH.

Approximate unit cell dimensions were obtained from preliminary Weissenberg and precession photographs. Structure analysis defined the centro-symmetric triclinic space group $P\bar{1}$. For $Z = 2$ neither molecule has any imposed crystal symmetry. Full details of the crystal data are listed in Table I.

Intensity data were collected on a Philips PW 1100 four-circle diffractometer. Accurate unit cell dimensions and crystal orientation matrices, together with their estimated standard errors, were obtained from least-squares refinement of the $2\vartheta$, $\omega$, $\chi$ and $\varphi$ values of 25 carefully centred high-angle reflections. Full details of the experimental conditions and data collection method used are given in Table II.

TABLE I. Crystal Data.

| | |
|---|---|
| $a$ | 17.330(8) Å |
| $b$ | 11.963(7) Å |
| $c$ | 10.100(7) Å |
| $\alpha$ | 112.4(1)° |
| $\beta$ | 97.7(1)° |
| $\gamma$ | 99.8(1)° |
| Formula wt | 779.6 |
| $\rho_{obsd}$ | 1.3 g cm$^{-3}$ |
| $\rho_{calcd}$ | 1.313 g cm$^{-3}$ |
| $Z$ | 2 |
| Unit cell volume | 1861.0 Å$^3$ |
| Space group | $P\bar{1}$ (after structure analysis) |
| Crystal dimensions | 0.3 × 0.3 × 0.5 mm |
| Absorption coeff. | 6.7 (MoKα) cm$^{-1}$ |

TABLE II. Details of Data Collection.

| | |
|---|---|
| Radiation | MoKα, $\lambda = 0.7107$ Å |
| Monochromator | graphite crystal |
| Scan method | $\vartheta-2\vartheta$ |
| Scan speed | 0.03 deg s$^{-1}$ |
| Scan width | 1.20° |
| Total background time | 20 s |
| 'Standard' reflections | (4 2 $\bar{3}$)($\bar{2}$ 2 $\bar{3}$)($\bar{4}$ 2 $\bar{2}$) every 180 min |
| $2\vartheta$ scan limit | 4–50° |
| Number of data | 6532 |
| Number of data with $I > 3\sigma(I)$ | 5177 |

### *Solution and Refinement of the Structure*

The structure was solved by conventional Patterson and Fourier syntheses. The refinement was carried out by the full-matrix least-squares using anisotropic temperature factors for all the atoms, except for C-atoms of the six phenyl rings which were assigned isotropic thermal parameters. Hydrogen atoms could not be located from Fourier difference maps but their fixed contributions were included in the refinement (idealized position with C–H = 0.95 Å). The function $\Sigma w[|F_o| - |F_c|]^2$ was minimized and unit weights were applied. Atomic scattering factors were taken from ref. 7. Allowance was made for the anomalous scattering of palladium, chlorine and phosphorus atoms, using values of $\Delta f'$ and $\Delta f''$ from ref. 8. The final conventional $R$ value for the 5177 observed reflections with $I \geqslant 3\sigma(I)$ was 0.067. Final atomic parameters are in Table III, and a selection of functions derived from them are presented in Tables IV–VI. Final atomic thermal parameters and tables of structure factors are available as supplementary material. All calculations were carried out with the SHELX-76 program for crystal structure determination [9].

### *Structure of Complex*

The stereochemical arrangement of the complex, with the atom numbering used, is shown in Fig. 1.

The structure described by the cell constants, the symmetry operations of the space group and the atomic parameters consists of the packing of discrete neutral molecules of *trans*-[$PdCl(COC_6H_{13}$-n$)(PPh_3)_2$], separated by van der Waals contacts.

The closest Pd···Pd approach is 9.39(1) Å, and all other intermolecular contacts agree with those predicted from radii-sum rules. The coordination about the metal significantly deviates from planarity towards a tetrahedral configuration (Table V). In the phosphine ligands, the corresponding bond lengths and valency angles, as well as orientations and conformations, agree well. The interbond angles at the phosphorus atoms show the usual departures from the tetrahedral value. In many compounds containing coordinated $PPh_3$ groups [10] it was found that the plane of one of the phenyl rings essentially contains the metal–phosphorus vector, another phenyl ring is twisted *ca.* 90° about its P–C bond, with respect to the first ring, while the third phenyl ring assumes an intermediate orientation. The present complex does not conform to this stereochemistry. On the phenyl groups attached to P(1), the ring C(21)–C(26) lies roughly at right angle to the plane Pd–P(1)–C(21), while the other two rings C(11)–C(16) and C(31)–C(36)

TABLE III. Fractional Atomic Positional Parameters (×$10^4$ or ×$10^3$ for C(1) to C(7)) with the e.s.d.s in Parentheses.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd | 7124(1) | 6121(1) | 9029(1) |
| Cl | 6377(2) | 6220(2) | 10926(3) |
| P(1) | 7426(1) | 4297(2) | 9025(2) |
| P(2) | 6633(1) | 7663(2) | 8550(2) |
| O | 7740(4) | 5631(6) | 6464(7) |
| C(1) | 789(1) | 616(1) | 777(1) |
| C(2) | 870(1) | 702(1) | 860(1) |
| C(3) | 936(1) | 678(2) | 777(2) |
| C(4) | 1012(1) | 780(2) | 838(2) |
| C(5) | 1010(1) | 863(2) | 760(2) |
| C(6) | 1069(2) | 955(2) | 784(3) |
| C(7) | 1064(1) | 1048(2) | 721(2) |
| Phenyl ring 1 | | | |
| C(11) | 7748(5) | 4392(8) | 10838(9) |
| C(12) | 8151(6) | 5507(10) | 11956(11) |
| C(13) | 8456(7) | 5596(11) | 13322(13) |
| C(14) | 8366(7) | 4548(10) | 13559(13) |
| C(15) | 7967(7) | 3436(12) | 12500(13) |
| C(16) | 7658(6) | 3327(10) | 11100(11) |
| Phenyl ring 2 | | | |
| C(21) | 8220(5) | 3749(7) | 8127(8) |
| C(22) | 8094(6) | 3280(8) | 6617(10) |
| C(23) | 8677(6) | 2841(10) | 5925(12) |
| C(24) | 9407(7) | 2924(10) | 6737(12) |
| C(25) | 9544(7) | 3393(10) | 8215(12) |
| C(26) | 8942(5) | 3797(8) | 8914(10) |
| Phenyl ring 3 | | | |
| C(31) | 6578(5) | 2976(8) | 8154(9) |
| C(32) | 5811(6) | 3121(10) | 8372(11) |
| C(33) | 5175(7) | 2110(11) | 7761(12) |
| C(34) | 5258(7) | 963(11) | 6954(13) |
| C(35) | 5990(6) | 798(11) | 6729(12) |
| C(36) | 6643(6) | 1793(9) | 7347(10) |
| Phenyl ring 4 | | | |
| C(41) | 7182(5) | 8395(8) | 7541(10) |
| C(42) | 7115(6) | 7752(10) | 6045(11) |
| C(43) | 7564(7) | 8296(11) | 5308(14) |
| C(44) | 8048(7) | 9440(12) | 6030(14) |
| C(45) | 8132(7) | 10071(12) | 7518(13) |
| C(46) | 7678(6) | 9580(9) | 8257(12) |
| Phenyl ring 5 | | | |
| C(51) | 5613(5) | 7020(8) | 7495(9) |
| C(52) | 5312(6) | 7241(9) | 6276(10) |
| C(53) | 4548(6) | 6682(10) | 5520(12) |
| C(54) | 4053(7) | 5947(11) | 5902(13) |
| C(55) | 4303(7) | 5721(12) | 7118(13) |
| C(56) | 5099(6) | 6259(10) | 7893(12) |
| Phenyl ring 6 | | | |
| C(61) | 6579(5) | 8977(8) | 10158(9) |
| C(62) | 6996(6) | 9212(9) | 11515(10) |
| C(63) | 6962(7) | 10198(10) | 12736(13) |
| C(64) | 6519(7) | 11001(12) | 12603(14) |
| C(65) | 6112(6) | 10824(10) | 11280(11) |
| C(66) | 6126(6) | 9806(9) | 10038(11) |

TABLE IV. Bond Lengths (Å) and Angles (°) with e.s.d.s in Parentheses.

| Distance | | Angle | |
|---|---|---|---|
| Pd–Cl | 2.430(4) | P(1)–Pd–P(2) | 167.6(1) |
| Pd–P(1) | 2.328(3) | P(1)–Pd–Cl | 89.8(2) |
| Pd–P(2) | 2.338(3) | P(1)–Pd–C(1) | 88.5(3) |
| Pd–C(1) | 1.960(10) | P(2)–Pd–C(1) | 89.9(3) |
| P(1)–C(11) | 1.795(10) | P(2)–Pd–Cl | 93.8(2) |
| P(1)–C(21) | 1.826(9) | Cl–Pd–C(1) | 170.3(3) |
| P(1)–C(31) | 1.798(8) | Pd–P(1)–C(11) | 112.9(3) |
| P(2)–C(41) | 1.835(11) | Pd–P(1)–C(21) | 118.6(4) |
| P(2)–C(51) | 1.805(8) | Pd–P(1)–C(31) | 112.9(3) |
| P(2)–C(61) | 1.805(8) | Pd–P(2)–C(41) | 117.0(4) |
| C(1)–O | 1.19(1) | Pd–P(2)–C(51) | 109.6(4) |
| C(1)–C(2) | 1.51(1) | Pd–P(2)–C(61) | 114.9(3) |
| C(2)–C(3) | 1.51(2) | C(11)–P(1)–C(21) | 102.4(5) |
| C(3)–C(4) | 1.50(2) | C(11)–P(1)–C(31) | 105.5(5) |
| C(4)–C(5) | 1.49(4) | C(21)–P(1)–C(31) | 103.5(4) |
| C(5)–C(6) | 1.30(4) | C(41)–P(2)–C(51) | 106.3(4) |
| C(6)–C(7) | 1.49(4) | C(41)–P(2)–C(61) | 103.2(5) |
| | | C(51)–P(2)–C(61) | 104.7(5) |
| | | Pd–C(1)–O | 125.5(8) |
| | | Pd–C(1)–C(2) | 113.5(6) |
| | | C(2)–C(1)–O | 121(1) |
| | | C(1)–C(2)–C(3) | 114(1) |
| | | C(2)–C(3)–C(4) | 116(1) |
| | | C(3)–C(4)–C(5) | 109(2) |
| | | C(4)–C(5)–C(6) | 123(2) |
| | | C(5)–C(6)–C(7) | 124(2) |

TABLE V. Some Mean Planes with the Distances (Å) of the Atoms to the Plane.

| | | | | |
|---|---|---|---|---|
| Plane 1: | $-0.6181X - 0.3692Y - 0.6940Z = -12.9964$ | | | |
| | Pd | −0.103(4) | Cl | −0.085(5) |
| | P(1) | 0.139(4) | C(1) | −0.436(10) |
| | P(2) | 0.135(4) | | |
| Plane 2: | $-0.9229X - 0.3846Y + 0.0152Z = -10.3291$ | | | |
| | Pd–P(1)–C(11) | | | |
| Plane 3: | $0.4708X + 0.1947Y + 0.8605Z = 12.4077$ | | | |
| | Pd–P(1)–C(21) | | | |
| Plane 4: | $0.4399X + 0.1848Y - 0.8788Z = -2.2422$ | | | |
| | Pd–P(1)–C(31) | | | |
| Plane 5: | $-0.3389X - 0.3720Y - 0.8642Z = -11.7515$ | | | |
| | Pd–P(2)–C(41) | | | |
| Plane 6: | $-0.5227X - 0.1020Y + 0.8464Z = 1.4459$ | | | |
| | Pd–P(2)–C(51) | | | |
| Plane 7: | $0.8720X + 0.4868Y + 0.0509Z = 10.7257$ | | | |
| | Pd–P(2)–C(61) | | | |

are tilted with respect to the corresponding Pd–P–C planes by 151 and 37° respectively.

For P(2), while the ring C(41)–C(46) lies approximately at right angle to the Pd–P(2)–C(41) plane, the rings C(51)–C(56) and C(61)–C(66) are tilted

TABLE VI. Some Twist, Dihedral and Torsion Angles (°).

| | | | |
|---|---|---|---|
| (a) Twist angle (°) between the phenyl ring and corresponding Pd–P–C plane | | | |
| Pd–P(1)–C(11) | and | C(11)–C(16) | 151.5(4) |
| Pd–P(1)–C(21) | and | C(21)–C(26) | 109.1(3) |
| Pd–P(1)–C(31) | and | C(31)–C(36) | 37.3(3) |
| Pd–P(2)–C(41) | and | C(41)–C(46) | 75.6(4) |
| Pd–P(2)–C(51) | and | C(51)–C(56) | 136.1(3) |
| Pd–P(2)–C(61) | and | C(61)–C(66) | 16.3(4) |
| (b) Dihedral angles (°) between the phenyl rings | | | |
| C(11)–C(16) | and | C(21)–C(26) | 97.8(4) |
| C(11)–C(16) | and | C(31)–C(36) | 82.6(4) |
| C(21)–C(26) | and | C(31)–C(36) | 119.1(3) |
| C(41)–C(46) | and | C(51)–C(56) | 130.5(4) |
| C(41)–C(46) | and | C(61)–C(66) | 103.5(3) |
| C(51)–C(56) | and | C(61)–C(66) | 85.7(3) |
| (c) Torsion angles (°) | | | |
| Pd–C(1)–C(2)–C(3) | | 162(1) | |
| C(1)–C(2)–C(3)–C(4) | | 165(1) | |
| C(2)–C(3)–C(4)–C(5) | | −95(2) | |
| C(3)–C(4)–C(5)–C(6) | | −176(2) | |
| C(4)–C(5)–C(6)–C(7) | | −172(2) | |

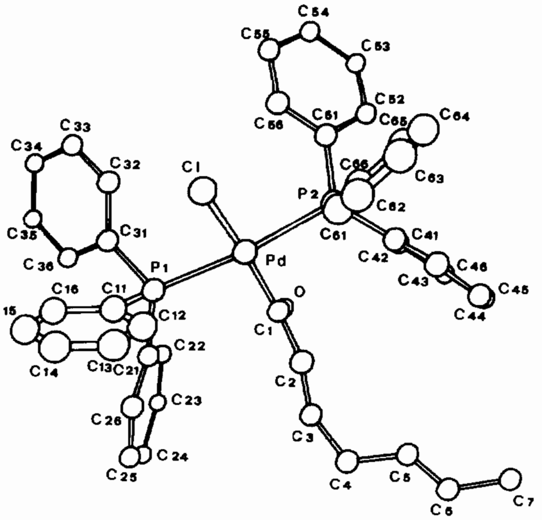

Fig. 1. Molecular structure of *trans*-[PdCl(COC$_6$H$_{13}$-n)-(PPh$_3$)$_2$].

with respect to the corresponding Pd–P–C planes by 136 and 16° respectively.

The two Pd–P bonds, 2.328(3) and 2.338(3) Å, do not differ significantly (mean Pd–P distance 2.333(3) Å) and are typical of values in similar complexes [11, 12]. Nevertheless it is significant that the Pd–P bond length does not reach the sum of the simple bond covalent radii, 2.41 Å (1.31 Å is the covalent radius of Pd$^{2+}$ in its planar derivatives; 1.10 Å is the covalent radius of phosphorus [13]). This shortening has been used as evidence for a Pd–P double bond, *i.e.*, $d_\pi - d_\pi$ bonding from the non-bonding d orbitals on metal to the empty phosphorus d orbitals [14]. The present results support this hypothesis.

The Pd–Cl distance of 2.430(4) Å is not only significantly longer than that predicted from available covalent radii (2.30 Å) [13], but is among the longest ones recorded for palladium complexes [15]. The long palladium–chlorine bond would be attributed to the 'structural' *trans*-effect of the carbon σ-bonded group [16] and is a consequence of the short and strong Pd–C(acyl) bond 1.96(1) Å. In addition it seems that this short Pd–C(acyl) bond noted in the present study possesses partial double-bond character, arising from 'back donation' of d electrons from the metal into the empty π-antibonding orbital of the acyl group. Within the acyl ligand an approximately T T G T T conformation (T, *trans*; G, *gauche*) of the carbon atoms chain is observed (Table VI) with mean $C_{sp^3}$–$C_{sp^3}$ bond distance of 1.46(4) Å which is significantly shorter than that predicted from available covalent radii (1.54 Å) [13]. This difference may be attributed to the error introduced by the large thermal motions of these carbon atoms.

Finally, in Table VII the relevant dimensions of *trans*-[PdCl(COHex)(PPh$_3$)$_2$] are compared with those observed in the crystal and molecular structures of other Pd$^{II}$ and Pt$^{II}$ complexes determined in our laboratory.

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TABLE VII.

| | This work | $[PdCl(COPr)(PPh_3)_2]$ Ref. 4 | $[PtCl(COPr)(PPh_3)_2]$ Ref. 5 | $[PtCl(COHex)(PPh_3)_2]$ Ref. 17 |
|---|---|---|---|---|
| M–Cl | 2.430(4) | 2.446(1) | 2.450(4) | 2.431(3) |
| M–$P_1$ | 2.328(3) | 2.340(1) | 2.314(4) | 2.302(3) |
| M–$P_2$ | 2.338(3) | 2.342(1) | 2.320(4) | 2.301(3) |
| M–C(acyl) | 1.96(1) | 1.996(6) | 2.00(2) | 2.02(1) |
| $P_1$–M–$P_2$ | 167.6(1) | 176.5(1) | 176.3(2) | 176.0(1) |
| $P_1$–M–Cl | 89.8(2) | 92.7(1) | 91.6(1) | 88.9(1) |
| $P_1$–M–C(acyl) | 88.5(3) | 87.7(2) | 88.2(4) | 93.0(3) |
| $P_2$–M–C(acyl) | 89.9(3) | 91.0(2) | 93.0(4) | 90.8(3) |
| $P_2$–M–Cl | 93.8(2) | 88.5(2) | 87.3(1) | 87.2(1) |
| Cl–M–C(acyl) | 170.3(3) | 178.8(2) | 179.5(4) | 177.3(3) |

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