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The mechanism for palladium catalyzed carbonylation of cinnamyl chloride

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Abstract

In the palladium catalyzed alkoxycarbonylation of cinnamyl chloride two mechanisms play a role. An associative mechanism was observed at low pressure, while an insertion mechanism was observed at high pressure or when an excess of ligand was used. Several putative intermediates of the catalytic alkoxycarbonylation have been synthesized and characterized, such as **5c** of which an X-ray crystal structure was obtained.

Keywords: Cinnamyl chloride; Carboxylation; Palladium catalyzed carbonylation; Acylpalladium complexes; Carbomethoxypalladium complexes

1. Introduction

The palladium catalyzed alkoxycarbonylation of allylic substrates is a powerful tool in synthetic organic chemistry to form β–γ unsaturated esters (Scheme 1) [1–6]. The reaction can be carried out under mild conditions with high atom economy and thus provides a viable alternative for traditional, stoichiometric routes.

Despite its wide applicability, relatively few mechanistic studies have been reported [6–16]. It has been suggested that the carbonylation mechanism of allylic substrates is similar to the carbonylation of benzyl moieties. In the presence of an excess of phosphine ligands (e.g. PR_3, R = alkyl group, P/Pd $\geqslant$ 2) this mechanism consists of an oxidative addition of benzyl halide to a Pd(0) species to form a $(PR_3)_2Pd(II)(\eta^3\text{-benzyl})^+X^-$ intermediate, which is in equilibrium with a $(PR_3)_2Pd(\eta^1\text{-benzyl})X$ intermediate. Treatment of such complexes with CO leads to insertion of CO in Pd-η^1-benzyl bonds [16] forming the acyl complex $(PR_3)_2Pd(C(O)benzyl)X$. In the presence of methanol the acyl group undergoes methanolysis to form the corresponding methyl ester a Pd(0) species and HX. The possible occurrence of an alternative mechanism, via formation of a Pd–CO bond, followed by association of methanol to Pd–CO rather than insertion of CO, was disproved by Milstein [12], while the insertion mechanism has been observed for cinnamyl bromide [10].

In comparison with allyl moieties, which prefer an η^3-coordination mode, benzyl moieties favor an η^1-coordination mode, especially if an excess of ligand is used, thereby enhancing insertion reactions relative to other reactions. Therefore, the mechanism of cinnamyl halide carbonylation may well be different from that of benzyl halides. We synthesized several potential intermediate complexes, starting from isolated Pd(η^3-cinnamyl)(L)(Cl) complexes bearing only one equivalent of monodentate phosphine or bidentate P–N ligand. In this

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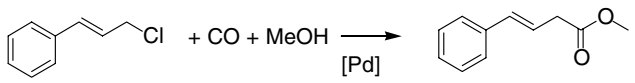


Scheme 1. Palladium catalyzed methoxycarbonylation of cinnamyl chloride.

note, we show that the alkoxycarbonylation of cinnamyl halides can proceed via both mechanisms, insertion and association and we report the first X-ray crystal structure of an intermediate of the insertion mechanism starting from an η^3-cinnamyl complex.

2. Results and discussion

2.1. Associative mechanism

We synthesized the (ligand)Pd(cinnamyl)Cl complexes **1** (see Scheme 2). As a result of the high *trans* influence of phosphorus compared to chloride combined with the steric bulk of this group, in all cases, the *syn* phenyl substituent on the allyl moiety is oriented *trans* to the phosphorus ligand [17].

Under 1 bar of CO the chloride complex **1** show slightly broadened signals in the NMR spectra, which indicates an interaction between CO and the palladium complex (233–298 K, $CDCl_3$), but no new complexes were observed. Under these conditions, the chloro complex is probably in equilibrium with [(CO)(L)Pd(η^3-cinnamyl)]$^+$[Cl$^-$] in which the cinnamyl is bonded in the highly favored η^3-fashion. Formation of a neutral LPd(CO)(Cl)(η^1-cinnamyl) complex, however, cannot be ruled out completely.

Addition of silver triflate in acetonitrile to complex **1**, resulted in complete conversion to the triflate analogue [(L)Pd(η^3-cinnamyl)(MeCN)]$^+$[$^-$OTf] (**2**) of the putative [(CO)(L)Pd(η^3-cinnamyl)]$^+$[Cl$^-$] intermediate (L = **a**, **b**). Treatment of this ionic complex **2** with ^{13}CO (1 bar, 293 K) resulted in the formation of compound **2**, containing both an η^3-cinnamyl group and a coordinated CO ligand. Addition of methoxide to complex **2a** at low temperature leads to the formation of the novel carbomethoxy complex **3a** nearly quantitatively, in which the cinnamyl group is still bonded in an η^3-fashion [18]. Warming the solution of complex **3a** to room temperature yields the methyl ester **A** and palladium metal, thereby proving that carbonylation via the associative mechanism is a feasible process for allylic species. Thus, provided that complex 1 is in equilibrium with the chloride analogue of complex **2** in the presence of CO, this mechanism is feasible for allylic chlorides.

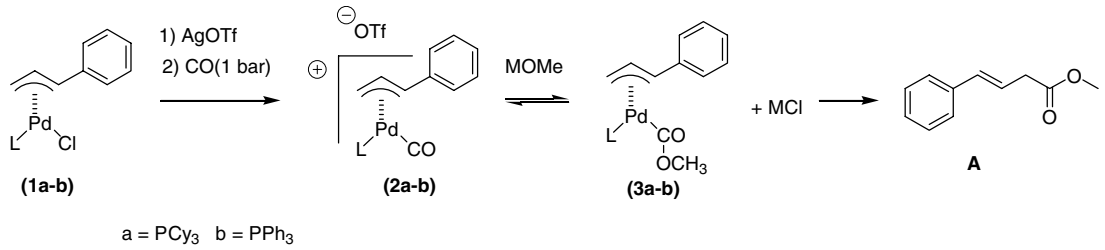
2.2. Insertion mechanism

The insertion reaction could be promoted either by adding extra ligand to complex **1** [9,10,19] or by increasing the pressure to 20 bar (δ^{13}C for Pd(acyl) is 236 ppm). In the latter case the acyl complex was formed cleanly and reversibly, presumably as the dimer [Pd(L)(acyl)(μ-Cl)]$_2$ (L = PCy_3 or PPh_3) [19]. At either higher temperature or lower pressure complex **1** was observed. The deinsertion of CO, leading to a Pd–CO complex, was not observed. Thus, without added phosphine, the chloride occupies the vacant site and stabilizes the insertion product.

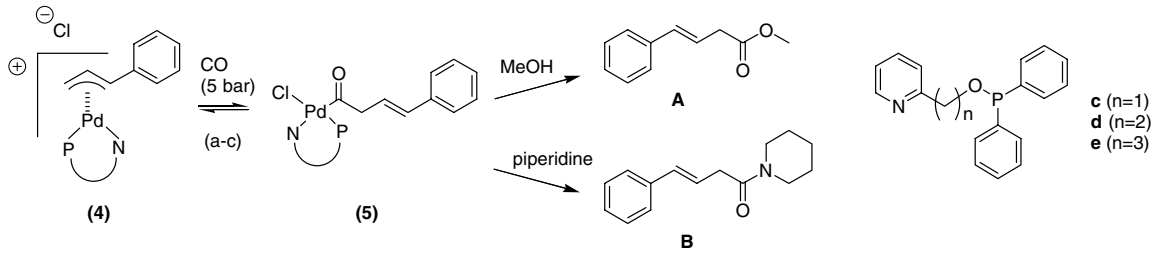
In an attempt to stabilize the acyl complexes in a different way we prepared complexes **4** bearing a hemilabile P–N ligand **c–e** (Scheme 3) [17]. Under the conditions studied, the cationic triflate complexes showed no interaction with CO (233–323 K, 1–50 bar CO, in $CDCl_3$). Using the chloride complex, at elevated CO pressure and ambient temperature, NMR spectroscopy shows the formation of the insertion product **5**. A similar influence of the counter ion has been observed before [9].

Complex **5c**, having the ligand with the shortest bridge length, was formed irreversibly, but **5d** and **5e** were found to be in equilibrium with **4d** and **4e**, respectively. As can be concluded from the P–C coupling constants, the acyl group coordinates *cis* to the phosphorus donor (^2J(P–C) = 8 Hz). This was confirmed by an X-ray crystal structure determination of complex **5c** (Fig. 1) [20].

At high temperature the η^3-cinnamyl complex **4** is the dominant species, but at low temperature the equilibrium shifts toward the acyl complex **5**. In contrast to other studies [8,19] we did not observe the reductive elimination of acid chloride.



Scheme 2. Stepwise synthesis of proposed intermediates of the associative mechanism for the palladium catalyzed carbonylation of cinnamyl chloride.



Scheme 3. Stepwise synthesis of proposed intermediates of the insertion mechanism for the palladium catalyzed carbonylation of cinnamyl chloride.

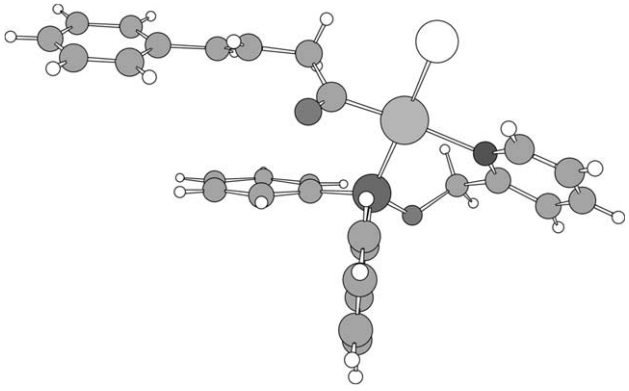


Fig. 1. Molecular structure of **5c**, determined by X-ray crystallography, showing the square planar geometry and the *cis* orientation of the acyl group and the phosphorus functionality.

The addition of methanol to the isolated complex **5c** yielded the methyl ester ($t_{1/2}$ = 4 h at 313 K). In the presence of NEt_3 the methyl ester was formed instantaneously. When NEt_3 was added without methanol, loss of CO occurred and the η^3-allyl complex **4c** was formed. Similarly, abstraction of the chloride atom by silver triflate resulted in de-insertion of CO and formation of the triflate analogue of **4c**. Treating the acyl complex **5c** with piperidine yielded the amide **B**.

In conclusion, we have shown that in the palladium catalyzed alkoxycarbonylation of cinnamyl chloride two mechanisms play a role. An associative mechanism was observed at low pressure, while an insertion mechanism was observed at high pressure or when an excess of ligand was used. Several putative intermediates of the catalytic alkoxycarbonylation have been synthesized and characterized, such as **5c** of which an X-ray crystal structure could be obtained.

3. Experimental

3.1. General procedures

^{1}H and ^{13}C NMR (300 resp. 75 MHz, TMS, $CDCl_3$), ^{31}P {1H} (121.5 MHz external 85% H_3PO_4, $CDCl_3$) were recorded on a Bruker DRX-300 spectrometer. All experiments were carried out using standard Schlenk techniques. All solvents were freshly distilled prior to use. All reactions have been performed at room temperature (292 K). High pressure NMR experiments were carried out using a sapphire tube. The complexes were isolated in quantitative yield (microcrystalline powder) and were used as such in the alkylation reaction. Elemental analyses were performed at the department of Microanalysis at the Rijksuniversiteit Groningen, The Netherlands. High Resolution Mass Spectra were recorded at the Department of Mass Spectroscopy at the university of Amsterdam, The Netherlands using FAB^+ ionization on a JEOL JMS SX/SX102A four sector mass spectrometer with 3-nitrobenzyl alcohol as a matrix. The synthesis of complexes **4** has been described in literature [17]. All other ligands and reagents have been purchased from Aldrich.

3.2. Numbering scheme of the cinnamyl moiety

Anti refers to a *trans* orientation to the hydrogen on the central carbon of the allylic group, whereas *syn* refers to a *cis* orientation. The numbering scheme of the carbon atoms is C{1}H_2–C{2}H–C{3}H–Ph. The numbering scheme of the hydrogen atoms is: Ha bonded to C{1}(anti), Hb bonded to C{1}(syn), Hc bonded to C{2}, Hd, bonded to C{3}.

3.3. Preparation of complexes *1*

To a yellow solution of $[(C_9H_9)$–Pd–$\mu Cl]_2$ [17] (100 mg, 193 mmol) in 20 ml of CH_2Cl_2 was added 386 mmol of ligand. After stirring for 30 min the solvent was evaporated and the complexes were obtained quantitatively as a yellow microcrystalline solids. **1a**: ^{1}H NMR ($CDCl_3$): δ 1.25 (br s, 12H, Cy-ring); 1.5 (br s, 6H, Cy-ring); 1.8 (br m, 12H, Cy-ring); 2.2 (q, 2.2, J^1 = 12 Hz, J^2 = 12 Hz, H on ipso carbon of Cy-ring); 2.65 (d, 1H, J = 11 Hz, Ha); 3.28 (d, 1H, J^1 = 6 Hz, H_b); 5.20 (dd, 1H, J^1 = 10 Hz, J^2 = 13 Hz, Hd); 5.81 (ddd, 1H, J^1 = 13 Hz, J^1 = J^2 = 10 Hz, Hc); 7.2–7.3 (m, 3H, aromatic); 7.50 (d, 2H, J = 8 Hz, ortho-aromatic H); ^{31}P NMR ($CDCl_3$): δ 45.9 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.5; 26.8; 27.3 (d, J = 11 Hz); 27.9 (d, J = 11 Hz); 30.6; 35.1 (d, J = 18 Hz); 47.3; 100.8 (d, J = 26 Hz); 110.0; 128.0; 128.3; 129.0; 129.4; 137.1. FAB-MS:

$C_{27}H_{42}PPd^+$ requires $m/z = 503.2059$, found 503.2029 (loss of Cl^-). **1b**: ^1H NMR ($CDCl_3$): δ 2.90 (d, 1H, $J = 12$ Hz, Ha); 2.95 (d, 1H, $J = 6$ Hz, Hb); 5.36 (dd, 1H, $J^1 = 10$ Hz, $J^2 = 13$ Hz, Hd); 6.01 (ddd, 1H, $J^1 = 13$ Hz, $J^2 = J^3 = 10$ Hz, Hc); ^{31}P NMR ($CDCl_3$): δ 26.4 (s); Anal. Calc. for $C_{27}H_{24}PPdCl$: C, 62.20; H, 4.64. Found: C, 61.73; H, 4.82%; FAB-MS: $C_{27}H_{24}PPd^+$ requires $m/z = 485.0650$, found 485.0669 (loss of Cl^-).

3.4. Preparation of (L)Pd(η^3-cinnamyl)(MeCN)OTf (L = *a*, *b*)

To a yellow solution (20 ml) of **1** in CH_2Cl_2 (201 mg, 386 mmol) was added 101.2 mg (39.0 mmol) of anhydrous AgOTf. Upon addition, the color of the solution became light yellow and a fine white solid precipitates. 0.5 ml of MeCN was added after stirring for 3 min. Active carbon was added to remove the excess of AgOTf after stirring for 15 min. Subsequent filtration and evaporation of the solvent yielded a light yellow microcrystalline powder quantitatively. The complexes should be stored at low temperature. **a**: ^1H NMR ($CDCl_3$): δ 1.25 (br s); 1.27 (br s); 1.38 (br s) together 15H, Cy-ring; 1.7–1.9 (br m, 18H, Cy-ring); 2.02 (s, 3H, CH_3–CN); 2.90 (br d, 1H, $J = 11$ Hz, Ha); 3.53 (br d, 1H, $J = 6$ Hz, Hb); 5.59 (dd, 1H, $J^1 = 8$ Hz, $J^2 = 13$ Hz, Hd), 6.07 (ddd, 1H, $J^1 = 13$ Hz, $J^2 = J^3 = 9$ Hz, Hc); 7.4 (m, 3H, aromatic); 7.6 (d, 2H, $J = 8$ Hz, ortho-aromatic H). ^{31}P NMR ($CDCl_3$): δ 47.0 (s). **b**: ^1H NMR ($CDCl_3$): δ 1.84 (s, 3H, CH_3–CN); 3.13 (br d, 1H, $J = 9$ Hz, Ha); 3.47 (br b, 1H, Hb); 5.97 (dd, 1H, $J^1 = 13$ Hz, $J^2 = 9$ Hz, Hd); 6.30 (ddd, 1H, $J^1 = 13$ Hz, $J^2 = J^3 = 9$ Hz, Hc); 7.2–7.5 (m, 18H, aromatic); 7.71 (d, 2H, $J = 5$ Hz, ortho-aromatic H). ^{31}P NMR ($CDCl_3$): δ 27.6 (s). Anal. Calc. for $C_{30}H_{27}F_3NO_3PPdS \cdot CH_2Cl_2$: C, 48.93; H, 3.84. Found: C, 48.01; H, 3.66%.

3.5. Preparation of complexes *2*

CO was bubbled through a solution of 10 mg of (L)Pd(η^3-cinnamyl)(MeCN)OTf (L = **a**, **b**) in $CDCl_3$. The light yellow solution turned colorless within one minute (within seconds for the more basic ligands). The product could not be isolated by either evaporation of the solvent or by precipitation using pentane or hexane and was therefore characterized in situ. **2a**: ^1H NMR ($CDCl_3$): δ 1.2–1.4 (br m, 15H, Cy-ring); 1.7–2.2 (br m, 18H, Cy-ring); 3.56 (d, 1H, $J = 13$ Hz, Ha); 4.17 (d, 1H, $J = 6$ Hz, Hb); 6.3 (ddd, 1H, $J^1 = 7$ Hz, $J^2 = J^3 = 9$ Hz, Hd); 6.56 (br m, 1H, Hc); 7.4 (br m, 3H, aromatic); 7.78 (d, 2H $J = 8$ Hz, ortho-aromatic H). ^{31}P NMR ($CDCl_3$): δ 48.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 181.9. IR: 2115 cm^{-1} (C=O). **2b**: ^1H NMR ($CDCl_3$): δ 3.58 (br d, 1H, $J = 11$ Hz, Ha); 3.86 (br b, 1H, Hb); 6.44 (ddd, 1H, $J^1 = J^2 = 10$ Hz, $J^3 = 9$ Hz, Hd); 6.59 (br t, 1H, $J^1 = J^2 = 11$ Hz, Hc); 7.2–7.5 (m, 18H, aromatic); 7.80 (d, 2H, $J = 5$ Hz, ortho-aromatic H). ^{31}P NMR ($CDCl_3$): δ 25.3 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 181.4 (s). IR: 2125 cm^{-1} (C=O).

3.6. Preparation of complex *3a*

A solution of 10 mg of Pd(cinnamyl)(PCy_3)(MeCN)OTf in 0.6 ml of $CDCl_3$ was frozen at 195 K under an atmosphere of CO, after which 0.1 ml of a 1.0 M solution of NBu_4OH in methanol was added and frozen as well. Slowly, the frozen solution was heated and upon melting, the solution was mixed thoroughly. Immediately, the tube was transferred to the precooled NMR spectrometer and the product was characterized in situ. ^1H NMR ($CDCl_3$): δ 4.47 (dd, 1H, $J^1 = J^2 = 12$ Hz, Ha); 5.00 (dd, 1H, $J^1 = J^2 = 10$ Hz, Hb); 5.58 (ddd, 1H, $J^1 = 8$ Hz, $J^2 = J^3 = 13$ Hz, Hd); 5.72 (m, 1H, Hc); 7.0–7.4 (m, 5H, aromatic). ^{31}P NMR ($CDCl_3$): δ 45.1 (d, $J = 24$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 211.0 (d, $J = 23$ Hz).

3.7. Preparation of Pd(C(O)cinnamyl)(L)(Cl)

A solution of 20 mg of **1** in $CDCl_3$ was pressurized with CO to the appropriate pressure (10, 20, 50 bar). Since the product was in equilibrium with **1**, it could not be isolated and was therefore characterized in situ. **a**: ^1H NMR ($CDCl_3$): δ 1.0–2.0 (br m, 33H, Cy-rings); 3.8 (br d, 2H, $J = 5$ Hz, CH_2); 6.3 (d, 1H, $J = 18$ Hz, –CH=C<u>H</u>–Ph); 6.50 (m, 1H, –C<u>H</u>=CH–Ph); 7.0–7.6 (br m, 5H, aromatic). ^{31}P NMR ($CDCl_3$): δ 41.3 (s); ^{13}C: 236.0 (s). **b**: ^1H NMR ($CDCl_3$): δ 3.1 (br b, 2H, CH_2); 5.63 (br b, CH=C<u>H</u>–Ph); 6.08 (m, 1H, –C<u>H</u>=CH–Ph); 7.0–7.6 (br m, 5H, aromatic). ^{31}P NMR ($CDCl_3$): δ 28.6 (s); ^{13}C: 229.2 (s).

3.8. Preparation of complexes *5*

A solution of 20 mg of **4** in $CDCl_3$ was pressurized with CO to 20 bar. The pure acyl complexes **5c** and **5d** could also be obtained by preparation in an autoclave. The product was precipitated by addition of hexane (not pentane) at high pressure (20 bar). The complex was isolated in quantitative yield by removal of the solvent and slowly drying overnight (not evaporation in vacuo). **5c**: ^1H NMR ($CDCl_3$): δ 3.48 (d, 2H, $J = 6$ Hz, –C(O)–CH_2–); 5.06 (d, 2H, $J = 21$ Hz, O–CH_2); 5.88 (d, 1H, $J = 16$ Hz, –CH=C<u>H</u>–Ph); 6.20 (m, 1H, –C<u>H</u>=CH–Ph); 7.0–7.8 (br m, 18H, aromatic); 9.38 (br b, 1H, ortho-pyridine). ^{31}P NMR ($CDCl_3$): δ 119.9 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 226.5 (d, $J = 8$ Hz); FAB-MS: As a result of the loss of Cl^-, decomposition occurred in the spectrometer. M^+ could not be observed, a signal at $m/z = 544.0669$ corresponding to $C_{28}H_{27}NO_2Pd^+$, proving the existence of a Pd complex bearing two oxygen atoms (one of the ligand and one

of the carbonyl) was observed. **5d**: ^{1}H NMR ($CDCl_3$): δ 3.51 (d, 2H, $J = 7$ Hz, –C(O)–CH_2–); 3.60 (br t, 2H, $J = 5$ Hz, –CH_2–Ar); 4.11 (dt, 2H, $J = 14$ Hz, $J = 6$ Hz, O–CH_2); 6.05 (d, 1H, $J = 16$ Hz, –CH=C<u>H</u>–Ph); 6.28 (m, 1H, –C<u>H</u>=CH–Ph); 7.0–7.7 (br m, 18H, aromatic); 8.97 (d, 1H, $J = 5$ Hz, ortho-pyridine). ^{31}P NMR ($CDCl_3$): δ 107.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 38.4; 56.3; 68.0; 124.2; 126.7; 127.8; 129.0; 129.5; 130.1; 131.6; 132.8; 137.2; 152.0; 158.1; 229.6 (d, $J = 6$ Hz). **5e**: ^{1}H NMR ($CDCl_3$): δ 1.94 (br b, 2H, –CH_2–CH_2–CH_2–); 3.41 (d, 2H, $J = 7$ Hz, –C(O)–CH_2–); 3.56 (br b, 4H,, O–CH_2 + –CH_2–Ar); 6.06 (d, 1H, $J = 16$ Hz, –CH=C<u>H</u>–Ph); 6.29 (m, 1H, –C<u>H</u>=CH–Ph); 7.0–7.7 (br m, 18H, aromatic); 8.37 (d, 1H, $J = 5$ Hz, ortho-pyridine). ^{31}P NMR ($CDCl_3$): δ 118.2 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 227.5.

3.9. Characterization of *A* and *B*

A: ^{1}H NMR ($CDCl_3$): δ 3.22 (d, 2H, $J = 7$ Hz, CH_2); 3.68 (s, 3H, CH_3); 6.25 (m, 1H, –C<u>H</u>=CH–Ph); 6.45 (d, 1H, 16 Hz, –CH=C<u>H</u>–Ph); 7.0–7.8 (m, 5H, aromatic). **B**: ^{1}H NMR ($CDCl_3$): δ 1.6 (m, 6H, N–(CH_2–C<u>H</u>$_2$)$_2$–C<u>H</u>$_2$); 3.10 (d, 2H, $J = 7$ Hz, =CH–C<u>H</u>$_2$–C(O)–); 6.31 (m, 1H, Ph–CH=C<u>H</u>–CH_2–C(O)–); 6.48 (d, 1H, $J = 16$ Hz, Ph–C<u>H</u>=CH–CH_2–C(O)–); 7.2–7.9 (m, 5H, aromatic H).

3.10. Crystal structure determination of *5c*

$C_{28}H_{25}ClNO_2PPd$, $M_w = 580.3$, triclinic, $P\bar{1}$, $a = 9.125(1)$ Å, $b = 11.172(2)$ Å, $c = 13.127(4)$ Å, $\alpha = 79.68(2)°$, $\beta = 74.13(1)°$, $\gamma = 83.96(1)°$, $V = 1264.2(5)$ Å^3, $Z = 2$, Dx = 1.52 g cm^{-3}, λ (Cu Kα) = 1.5418 Å, λ (Cu Kα) = 76.94 cm^{-1}, F (0 0 0) = 588, room temperature, Final $R = 0.069$ for 5201 reflections.

A crystal with dimensions $0.35 \times 0.45 \times 0.50$ mm approximately was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation and ω–2θ scan. A total of 5201 unique reflections was measured within the range $-10 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 16$. Of these, 5040 were above the significance level of $4\sigma(F_{obs})$ and were treated as observed. The range of $(\sin\theta)/\lambda$ was 0.040–0.630 Å ($3.5 \leqslant \theta \leqslant 76.1°$). Two reference reflections ([2 2 1], [1 0 2]) were measured hourly and showed 5% decrease during the 83 h collecting time, which was corrected for. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $40.04 \leqslant \theta \leqslant 41.92°$. Corrections for Lorentz and polarisation effects were applied. Absorption correction was performed with the program PLATON [21] following the method of North et al. [22] using Ψ-scans of five reflections, with coefficients in the range 0.669–0.981. The structure was solved by the PATTY option of the DIRDIF99 program system [23].

The hydrogen atoms were calculated and a riding model was used during refinement. Full-matrix least-squares refinement on F^2, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, converged to $R_1 = 0.069$, $wR_2 = 0.075$, $(\Delta/\sigma)_{max} = 0.03$, $S = 1.5$. A weighting scheme $w = [7000 + 0.01\sigma(F_{obs})^2 + 0.01/(\sigma(F_{obs}))]^{-1}$ was used. The secondary isotropic extinction coefficient [21,22,24–26] refined to $G = 1181(30)$. A final difference Fourier map revealed a residual electron density between -1.56 and 2.04 e Å^{-3} in the vicinity of the Pd. Scattering factors were taken from Cromer and Mann [27], International Tables for X-ray Crystallography [28]. The anomalous scattering of Pd, P and Cl was taken into account [29]. All calculations were performed with XTAL3.7 [30] unless stated otherwise.

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