

The allyl complex di- μ -chloro-bis{[(1,2,3- η)-1-(ethoxycarbonyl)-5,5-dimethyl-4-oxohexenyl]palladium(II)}

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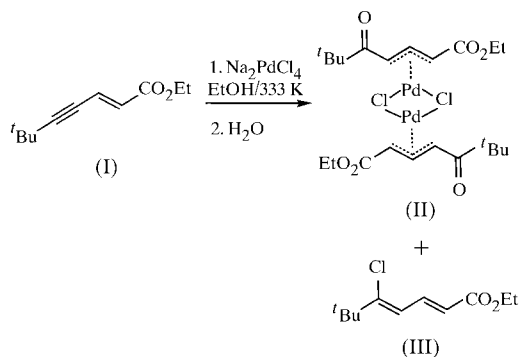
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The title compound, di- μ -chloro-bis{[(2,3,4- η)-ethyl 6,6-dimethyl-5-oxohept-2-enoato]palladium(II)}, [Pd₂Cl₂(C₁₁H₁₇O₃)₂], is a binuclear chloro-bridged palladium allyl complex that was obtained serendipitously from the reaction of ethyl 6,6-dimethyl-2-hepten-4-ynoate with Na₂PdCl₄ in water-containing alcohol. The allyl group is substituted with an ester and a *tert*-butylcarboxy group. The dimeric molecules link *via* C—H...O contacts into a two-dimensional network parallel to the *bc* plane.

Comment

The title compound (Fig. 1) belongs to the π -allylpalladium group of complexes. These complexes are important intermediates in a number of catalytic reactions such as allylic substitution (Godlesky, 1991), allylic oxidation (Bäckvall *et al.*, 1990) and 1,4-oxidations (Castaño & Bäckvall, 1995) of



conjugated dienes and in respect of the last reactions, we wanted to find out if a similar reaction is possible using enynes instead of dienes. Before employing any catalytic procedures, we tried to obtain a palladium complex of an enyne. It was thus found (see Scheme) that ethyl 6,6-dimethyl-2-hepten-4-

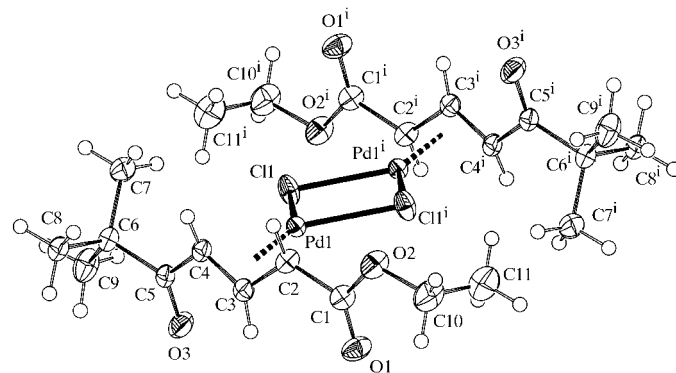


Figure 1

A view of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level [symmetry code: (i) $-x, 2 - y, 1 - z$].

ynoate, (I), reacts on heating with Na₂PdCl₄ in water-containing ethanol to give the title compound, (II), and ethyl 5-chloro-6,6-dimethyl-2,4-heptadienoate, (III), as a side product.

The molecular structure of the dimeric title complex is similar to the structure of the related di- μ -chloro-bis[η^3 -1,3-bis(pivaloyl)allylpalladium(II)] complex (Ukhin *et al.*, 1976), which was prepared *via* a completely different route. A trinuclear palladium complex with the same allyl ligand, but with bridging acetates rather than Cl, has also been reported (Ukhin *et al.*, 1981). The Pd—Cl and Pd—C distances for the current structure are well within the range reported for the two earlier structures (Ukhin *et al.*, 1976, 1981). All three refined C—H atoms of the allylic system are bent away from the Pd atom. Two C—H...O contacts (Table 2) link, in the absence of classical hydrogen bonds, the dimers into a two-dimensional network parallel to (100).

Experimental

Ethyl 6,6-dimethyl-2-hepten-4-ynoate, (I) (1.44 g, 8.0 mmol), was added to a solution of Na₂PdCl₄ (2.20 g, 6.0 mmol) in ethanol under an argon atmosphere and the mixture warmed to 333 K for 2 h. The solution, which turned bright yellow, was poured into water and extracted with toluene. The extract was washed with water, saturated aqueous NaHCO₃ solution and saturated aqueous NaCl solution, and

Table 1

Selected geometric parameters (Å, °).

Pd1—Cl1	2.3836 (11)	O1—C1	1.202 (2)
Pd1—C2	2.109 (2)	O2—C1	1.330 (2)
Pd1—C3	2.0913 (18)	O2—C10	1.450 (2)
Pd1—C4	2.138 (2)	O3—C5	1.208 (2)
Pd1—Cl1 ⁱ	2.3811 (11)		
Cl1—Pd1—Cl1 ⁱ	88.91 (3)	O2—C1—C2	110.19 (16)
Pd1—Cl1—Pd1 ⁱ	91.09 (3)	O3—C5—C4	119.46 (15)
Cl1—O2—C10	116.07 (15)	O3—C5—C6	122.83 (16)
O1—C1—O2	125.06 (18)	O2—C10—C11	111.07 (18)
O1—C1—C2	124.74 (16)		

Symmetry code: (i) $-x, 2 - y, 1 - z$.

dried with anhydrous MgSO₄. After filtration and removal of the solvent, the crude yellow oil was subjected to column chromatography on SiO₂, eluting with cyclohexane/diethyl ether (20:1). The by-product eluted first and yielded 273 mg (21%) of ethyl 5-chloro-6,6-dimethyl-2,4-heptadienoate, (III). Subsequent elution with diethyl ether/CH₂Cl₂ (2:1) gave a purified yellow oil. Addition of pentane to this oil induced crystallization to give 1.15 g (56%) of the π -allylpalladium complex (II).

Crystal data

[Pd ₂ Cl ₂ (C ₁₁ H ₁₇ O ₃) ₂]	Z = 1
<i>M_r</i> = 678.23	<i>D_x</i> = 1.734 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 6.6157 (11) Å	Cell parameters from 25 reflections
<i>b</i> = 9.654 (4) Å	θ = 9.6–14.0°
<i>c</i> = 10.748 (4) Å	μ = 1.623 mm ⁻¹
α = 101.96 (3)°	<i>T</i> = 150 K
β = 90.13 (3)°	Plate, orange
γ = 104.29 (3)°	0.50 × 0.42 × 0.13 mm
<i>V</i> = 649.7 (4) Å ³	

Data collection

CAD-4T diffractometer	<i>R</i> _{int} = 0.034
ω scans	θ _{max} = 27.5°
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	<i>h</i> = -8 → 8
<i>T</i> _{min} = 0.549, <i>T</i> _{max} = 0.805	<i>k</i> = -12 → 12
6309 measured reflections	<i>l</i> = -13 → 13
2994 independent reflections	3 standard reflections
2903 reflections with <i>I</i> > 2 σ (<i>I</i>)	frequency: 60 min
	intensity decay: 3%

Refinement

Refinement on <i>F</i> ²	H atoms: see below
<i>R</i> (<i>F</i>) = 0.018	$w = 1/[\sigma^2(F_o^2) + (0.0134P)^2 + 0.2250P]$
<i>wR</i> (<i>F</i> ²) = 0.044	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.119	$(\Delta/\sigma)_{\max} < 0.002$
2994 reflections	$\Delta\rho_{\max} = 0.45 \text{ e } \text{Å}^{-3}$
161 parameters	$\Delta\rho_{\min} = -0.68 \text{ e } \text{Å}^{-3}$

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8—H8B...O1 ⁱ	0.98	2.56	3.392 (3)	143
C9—H9C...O2 ⁱⁱ	0.98	2.50	3.394 (3)	152

Symmetry codes: (i) $-x, 2 - y, -z$; (ii) $x, y - 1, z$.

The allylic H atoms were located from a difference map and their positions refined with individual isotropic displacement parameters. Their C—H distances range from 0.91 (2) to 0.96 (3) Å. No additional symmetry was found with *PLATON/LEPAGE* (Spek, 2000), nor any solvent-accessible voids with *PLATON/SOLV* (Spek, 2000). All other H atoms were treated as riding on and with isotropic displacement parameters related to their carrier atoms. The methyl moieties were refined as rigid rotators.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1012). Services for accessing these data are described at the back of the journal.

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