Crystal structure of bis(π-allylvalencene)dichlorodipalladium, $[PdCl(C_{15}H_{23})]_2$

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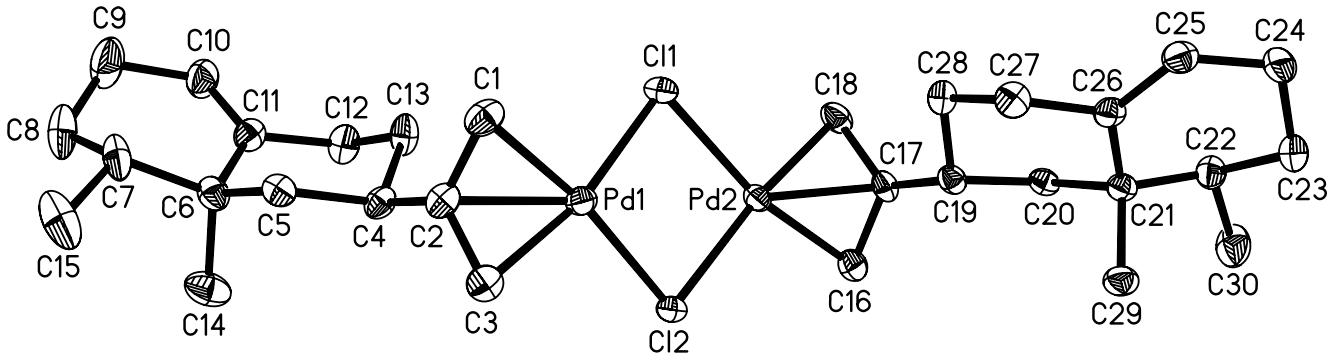
Received March 11, 2009, accepted and available on-line May 12, 2009; CCDC no. 1267/2591



Abstract

$C_{30}H_{46}Cl_2Pd_2$, monoclinic, *C*121 (no. 5), a = 22.0083(6) Å, b = 6.1827(2) Å, c = 21.5654(7) Å, β = 91.252(2)°, V = 2933.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.019, $wR_{ref}(F^2)$ = 0.039, T = 200 K.

Source of material

$PdCl_2$ (300 mg, 1.69 mmol) and LiCl (146.4 mg, 3,46 mmol) were heated in acetic acid (15 mL, 353 K) under stirring until obtaining a red homogeneous solution. Then it was cooled to 333 K. Sodium acetate (2.34 g) and valencene (344.76 mg, 1.69 mmol) were added and stirring was continued at 333 K overnight. The yellow solution was extracted with ethyl acetate (3 × 30 mL). The organic phases were washed with water, dried over Na_2SO_4 and evaporated under vacuum. Yellow pure title compound was isolated by column chromatography on silica gel using hexane/ethyl acetate (99:1, *v*/*v*) as eluent (yield 60 %).

Discussion

Catalytic oxidation of valencene ((1*R*,7*R*,8*aS*)-1,2,3,5,6,7,8,8*a*-octahydro-1,8*a*-dimethyl-7-(1-methylethenyl)naphthalene) can constitute an important transformation reaction of this cheap natural product to its corresponding oxygenated derivative, nootkatone (4-α,5-dimethyl-1,2,3,4,4α,5,6,7-octahydro-7-keto-3-isopropenylnaphthalene) which is the most important and expensive aromatic agent of the grapefruit [1,2]. The previous work we undertook on the oxidation of terpenic substrates catalyzed by palladium, allowed us to establish unambiguously the importance of the π-allyl intermediate species to control the regio- and stereoselectivity of these reactions [3,4]. As part of studies on these intermediates in monoterpenic [4] and sesquiterpenic series [5-8], we report here on the complex bis(π-allylvalencene)-dichlorodipalladium.

We have established the regiochemistry of the title complex using ^{1}H NMR and ^{13}C NMR sperctroscopy. The data of the isolated compound confirm the formation of the allylic protons in the exocyclic double bond. Their signals appeared as a singlet at 2.7 ppm (1H), 2.8 ppm (1H) and 3.8 ppm (2H). The corresponding ^{13}C signals appeared at 58.79 ppm and 60.13 ppm. The C10=C11 double bond still intact and gives rise to ^{1}H and ^{13}C NMR signals at 5.4 ppm and 121.07 ppm, respectively.

Its dimeric structure was confirmad by crystal structure determination. Each palladium center is coordinated by one η^3-allyl ligand. The values of allylic bonds C1—C2, C2—C3 (1.403(4), 1.411(4) Å) and C16—C17, C17—C18 (1.414(4), 1.416(4) Å), respectively, indicate a delocalized π-electron system. The metal atoms are bridged by two Cl^- ions. These four atoms form an almost planar rectangle (mean deviation from the best plane defined by Pd1/Cl1/Pd2/Cl2: 0.054 Å). The planes of allyl fragments are tilted with respect to this plane (74.7(2)° and 79.2(2)°), respectively. In general $[(allyl)PdCl]_2$ dimers consist of a planar Pd_2Cl_2 unit in the solid state, although several examples are given in which a folding angle between the both coordination planes was observed [9].

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.05 × 0.45 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.25 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20920, 5780
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5267
$N(param)_{refined}$:	307
Programs:	SHELXS-97 [10], SHELXL-97 [11], SHELXTL [12]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*c*	0.8464	–0.1303	0.3343	0.057
H(1B)	4*c*	0.8083	0.0656	0.2981	0.057
H(3A)	4*c*	0.9920	0.1062	0.3057	0.053
H(3B)	4*c*	0.9599	–0.1050	0.3392	0.053
H(4A)	4*c*	0.9394	0.3031	0.2292	0.044
H(5A)	4*c*	0.8570	0.0014	0.1717	0.046
H(5B)	4*c*	0.9293	–0.0166	0.1707	0.046
H(7A)	4*c*	0.8380	–0.0189	0.0701	0.070
H(8A)	4*c*	0.8893	0.2760	–0.0169	0.093
H(8B)	4*c*	0.8435	0.0857	–0.0364	0.093
H(9A)	4*c*	0.7984	0.4420	–0.0246	0.101
H(9B)	4*c*	0.7641	0.2472	0.0089	0.101
H(10A)	4*c*	0.7825	0.5620	0.0774	0.070
H(12A)	4*c*	0.8190	0.6350	0.1706	0.056
H(12B)	4*c*	0.8915	0.6136	0.1729	0.056
H(13A)	4*c*	0.8532	0.4831	0.2667	0.057
H(13B)	4*c*	0.8094	0.3174	0.2301	0.057
H(14A)	4*c*	0.9714	0.3992	0.1338	0.095
H(14B)	4*c*	0.9602	0.3871	0.0603	0.095
H(14C)	4*c*	0.9887	0.1845	0.0967	0.095
H(15A)	4*c*	0.9037	–0.2029	0.0053	0.135
H(15B)	4*c*	0.9279	–0.2065	0.0758	0.135
H(15C)	4*c*	0.9582	–0.0469	0.0269	0.135

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(16A)	4*c*	0.9653	0.8520	0.5542	0.047
H(16B)	4*c*	0.9306	1.0588	0.5197	0.047
H(18A)	4*c*	0.8181	1.0378	0.5027	0.053
H(18B)	4*c*	0.7824	0.8184	0.5269	0.053
H(19A)	4*c*	0.9084	0.5881	0.6086	0.040
H(20A)	4*c*	0.8297	0.8685	0.6750	0.040
H(20B)	4*c*	0.9020	0.8954	0.6744	0.040
H(22A)	4*c*	0.8222	0.8384	0.7811	0.050
H(23A)	4*c*	0.8876	0.5174	0.8507	0.061
H(23B)	4*c*	0.8441	0.6936	0.8812	0.061
H(24A)	4*c*	0.7986	0.3365	0.8602	0.064
H(24B)	4*c*	0.7588	0.5419	0.8394	0.064
H(25A)	4*c*	0.7661	0.2667	0.7563	0.054
H(27A)	4*c*	0.7881	0.2519	0.6551	0.051
H(27B)	4*c*	0.8605	0.2598	0.6498	0.051
H(28A)	4*c*	0.8180	0.4421	0.5639	0.046
H(28B)	4*c*	0.7787	0.5940	0.6081	0.046
H(29A)	4*c*	0.9469	0.4579	0.6926	0.064
H(29B)	4*c*	0.9434	0.4386	0.7665	0.064
H(29C)	4*c*	0.9692	0.6545	0.7357	0.064
H(30A)	4*c*	0.8974	1.0011	0.8447	0.095
H(30B)	4*c*	0.9120	1.0346	0.7729	0.095
H(30C)	4*c*	0.9485	0.8572	0.8128	0.095

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*c*	0.8474(1)	0.0183(5)	0.3173(1)	0.050(2)	0.043(2)	0.050(2)	–0.013(1)	–0.009(1)	0.009(1)
C(2)	4*c*	0.9004(1)	0.0791(4)	0.2867(1)	0.045(2)	0.030(1)	0.042(2)	–0.003(1)	–0.006(1)	0.002(1)
C(3)	4*c*	0.9543(1)	0.0420(5)	0.3218(1)	0.047(2)	0.040(2)	0.045(2)	0.003(1)	–0.002(1)	0.005(1)
C(4)	4*c*	0.8998(1)	0.2239(4)	0.2297(1)	0.041(1)	0.032(2)	0.038(1)	–0.008(1)	–0.006(1)	0.002(1)
C(5)	4*c*	0.8950(1)	0.0869(4)	0.1705(1)	0.039(2)	0.031(1)	0.045(2)	–0.001(1)	0.006(1)	0.001(1)
C(6)	4*c*	0.8954(1)	0.2141(4)	0.1092(1)	0.046(1)	0.040(2)	0.041(1)	–0.003(1)	0.010(1)	0.000(1)
C(7)	4*c*	0.8750(2)	0.0581(6)	0.0555(2)	0.082(3)	0.054(2)	0.039(2)	–0.004(2)	0.016(2)	–0.014(2)
C(8)	4*c*	0.8547(2)	0.1879(7)	–0.0027(1)	0.121(3)	0.080(2)	0.033(2)	–0.001(3)	0.003(2)	–0.011(2)
C(9)	4*c*	0.8020(2)	0.3335(7)	0.0091(2)	0.108(3)	0.100(3)	0.044(2)	0.009(3)	–0.018(2)	–0.009(2)
C(10)	4*c*	0.8094(2)	0.4456(6)	0.0694(1)	0.061(2)	0.072(2)	0.041(2)	0.009(2)	–0.007(2)	–0.002(2)
C(11)	4*c*	0.8505(1)	0.3974(5)	0.1134(2)	0.045(2)	0.043(2)	0.037(2)	–0.005(1)	–0.002(1)	0.006(1)
C(12)	4*c*	0.8531(2)	0.5304(4)	0.1714(1)	0.064(2)	0.034(1)	0.042(2)	0.008(1)	–0.006(1)	–0.000(1)
C(13)	4*c*	0.8493(2)	0.3909(4)	0.2293(1)	0.069(2)	0.038(2)	0.034(2)	0.007(1)	–0.002(1)	–0.005(1)
C(14)	4*c*	0.9598(1)	0.3045(6)	0.0990(2)	0.048(2)	0.068(2)	0.074(2)	0.001(2)	0.015(2)	0.024(2)
C(15)	4*c*	0.9201(2)	–0.1146(7)	0.0395(2)	0.122(4)	0.075(3)	0.076(3)	0.011(2)	0.044(3)	–0.011(2)
C(16)	4*c*	0.9281(1)	0.9055(5)	0.5326(1)	0.044(2)	0.038(2)	0.038(2)	0.003(1)	0.006(1)	0.003(1)
C(17)	4*c*	0.8720(1)	0.8360(4)	0.5564(1)	0.040(2)	0.036(1)	0.031(1)	0.006(1)	0.008(1)	–0.000(1)
C(18)	4*c*	0.8218(1)	0.8858(5)	0.5167(1)	0.039(2)	0.051(2)	0.043(2)	0.015(1)	0.011(1)	0.009(1)
C(19)	4*c*	0.8700(1)	0.6741(5)	0.6094(1)	0.033(1)	0.034(1)	0.033(1)	0.007(1)	0.005(1)	0.003(1)
C(20)	4*c*	0.8685(1)	0.7884(4)	0.6722(1)	0.030(1)	0.031(1)	0.039(1)	–0.001(1)	0.006(1)	0.004(1)
C(21)	4*c*	0.8748(1)	0.6333(4)	0.7284(1)	0.029(1)	0.033(1)	0.036(1)	0.002(1)	0.002(1)	0.007(1)
C(22)	4*c*	0.8612(1)	0.7587(5)	0.7888(1)	0.044(1)	0.047(2)	0.035(1)	0.003(1)	0.001(1)	0.002(1)
C(23)	4*c*	0.8509(1)	0.6070(5)	0.8434(1)	0.052(2)	0.069(2)	0.033(2)	–0.002(2)	0.002(1)	0.007(1)
C(24)	4*c*	0.7966(1)	0.4608(6)	0.8313(1)	0.045(2)	0.073(2)	0.042(2)	–0.004(2)	0.006(1)	0.018(2)
C(25)	4*c*	0.7943(1)	0.3786(5)	0.7659(1)	0.038(2)	0.049(2)	0.048(2)	–0.007(1)	–0.004(1)	0.017(1)
C(26)	4*c*	0.8288(1)	0.4499(4)	0.7201(1)	0.032(1)	0.034(1)	0.038(1)	0.003(1)	–0.003(1)	0.010(1)
C(27)	4*c*	0.8239(1)	0.3490(4)	0.6567(1)	0.048(2)	0.034(1)	0.047(2)	–0.004(1)	0.001(1)	0.005(1)
C(28)	4*c*	0.8177(1)	0.5158(4)	0.6047(1)	0.045(2)	0.038(2)	0.032(1)	0.001(1)	0.000(1)	–0.001(1)
C(29)	4*c*	0.9395(1)	0.5373(5)	0.7310(1)	0.032(2)	0.049(2)	0.048(2)	0.006(1)	–0.000(1)	0.010(1)
C(30)	4*c*	0.9091(2)	0.9281(6)	0.8064(2)	0.080(2)	0.061(2)	0.049(2)	–0.022(2)	0.001(2)	–0.011(2)
Cl(1)	4*c*	0.81499(3)	0.4693(1)	0.40834(3)	0.0270(3)	0.0710(5)	0.0454(4)	–0.0048(3)	0.0041(3)	0.0003(4)
Cl(2)	4*c*	0.96541(3)	0.4888(1)	0.42232(3)	0.0260(3)	0.0649(5)	0.0421(4)	–0.0026(3)	0.0028(3)	–0.0140(3)
Pd(1)	4*c*	0.896198(8)	0.25106(3)	0.369789(9)	0.0309(1)	0.0473(1)	0.0338(1)	–0.00519(9)	–0.00157(8)	0.00527(9)
Pd(2)	4*c*	0.884367(8)	0.68953(3)	0.469578(9)	0.02845(9)	0.0505(1)	0.0298(1)	0.00386(9)	0.00518(7)	0.00507(9)

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