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Crystal structure of dichlorotriethylphosphine{12-(3,4-dimethoxyphenyl)-4,5-dimethoxy-11,14-diaza-tricyclo[7.4.1.0^{2,7}]tetradeca-2(7),3,5-trien-10-one}-palladium(II) methanol solvate, $PdCl_2[P(C_2H_5)_3](C_{22}H_{26}N_2O_5) \cdot CH_3OH$

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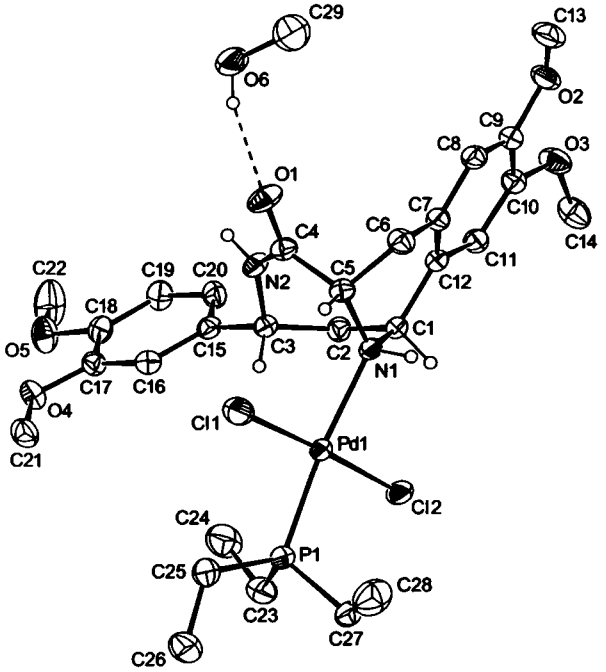

Abstract

$C_{29}H_{45}Cl_2N_2O_6PPd$, triclinic, $P\bar{1}$ (no. 2), a = 8.4763(7) Å, b = 13.135(2) Å, c = 15.418(3) Å, α = 83.99(2)°, β = 76.60(1)°, γ = 86.56(1)°, V = 1659.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.034, $wR_{obs}(F^2)$ = 0.080, T = 293 K.

Source of material

The bridged diamine 12-(3,4-dimethoxyphenyl)-4,5-dimethoxy-11,14-diaza-tricyclo[7.4.1.0^{2,7}]tetradeca-2(7),3,5-trien-10-one was obtained in few steps from a protected dipeptide, which had in turn been derived from L-dopa and DL-β-dopa [1]. 50 mg (125 μmol) of 12-(3,4-dimethoxyphenyl)-4,5-dimethoxy-11,14-diaza-tricyclo[7.4.1.0^{2,7}]tetradeca-2(7),3,5-trien-10-one a diamine incorporating a tetrahydroquinoline and an 1,4-diazepane ring [2], and 36 mg (62.5 μmol) of the chloro-bridged complex $(Et_3P)_2Pd_2Cl_2(\mu\text{-}Cl)_2$ were stirred in $CHCl_3/CH_3OH$ (1:1 *v/v*) for 12 h. The yellow solution was concentrated in vacuo and the residue overlayered with *n*-hexane. Yellow needles of the title compound were obtained.

Discussion

The crystal structure of the racemic palladium complex proves the relative configuration of the two enantiomers of the diamine ligand as (1*S*,3*S*,10*R*)/(1*R*,3*R*,10*S*). The calculated [1] conformation of the ligand is very similar to that in the title complex. The nitrogen atom of the tetrahydroisoquinoline ring [3] is coordinated to palladium, *d*(Pd—N) = 2.208(3) Å, ∠N-Pd-P = 173.68(7)°, and the phosphane ligand is situated *trans* to the N-donor. Thus, the title compound is another example in a large series of palladium and platinum complexes with *trans*-R_3P–*M*–N-donor structure, which is in perfect accordance with DFT calculations on the thermodynamic stability of such planar complexes [4]. In the crystal structure a methanol molecule is attached to the complex molecule via an hydrogen bridge to the lactam O atom.

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Table 1. Data collection and handling.

Crystal:	pale yellow block, size 0.17 × 0.23 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.10 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	47.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5576, 5180
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4431
$N(param)_{refined}$:	370
Programs:	SHELXS-86 [5], SHELXL-93 [6]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(6)	2*i*	0.0687	0.4817	0.6224	0.112
H(1)	2*i*	0.7635	0.5019	0.6538	0.040
H(2)	2*i*	0.2190	0.5654	0.7772	0.048
H(1A)	2*i*	0.7432	0.4449	0.7869	0.040
H(2A)	2*i*	0.4491	0.4483	0.8797	0.046
H(2B)	2*i*	0.5805	0.5232	0.8883	0.046
H(3)	2*i*	0.4881	0.6471	0.7908	0.042
H(5)	2*i*	0.5835	0.5803	0.5798	0.043
H(6A)	2*i*	0.4961	0.4187	0.5570	0.052
H(6B)	2*i*	0.6836	0.4191	0.5509	0.052
H(8)	2*i*	0.4893	0.2329	0.5967	0.049
H(11)	2*i*	0.6164	0.2793	0.8648	0.048
H(13A)	2*i*	0.4065	−0.0242	0.6248	0.082
H(13B)	2*i*	0.5250	0.0620	0.5764	0.082
H(13C)	2*i*	0.3403	0.0893	0.6125	0.082
H(14A)	2*i*	0.5916	0.1426	0.9598	0.075
H(14B)	2*i*	0.7524	0.1148	0.8914	0.075
H(14C)	2*i*	0.6499	0.0277	0.9520	0.075
H(16)	2*i*	0.3213	0.7837	0.8453	0.045
H(19)	2*i*	0.0468	0.5808	1.0896	0.058
H(20)	2*i*	0.2339	0.5071	0.9765	0.054
H(21A)	2*i*	0.1629	1.0270	0.8998	0.067
H(21B)	2*i*	0.1837	0.9409	0.8345	0.067

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(21C)	2*i*	0.3150	0.9514	0.8895	0.067
H(22A)	2*i*	–0.1796	0.7642	1.2174	0.116
H(22B)	2*i*	–0.0338	0.6837	1.2062	0.116
H(22C)	2*i*	–0.1796	0.6705	1.1622	0.116
H(23A)	2*i*	0.9391	0.7979	0.8579	0.073
H(23B)	2*i*	0.8880	0.9127	0.8372	0.073
H(24A)	2*i*	0.6688	0.7534	0.8881	0.100
H(24B)	2*i*	0.6167	0.8680	0.8661	0.100
H(24C)	2*i*	0.6897	0.8374	0.9500	0.100
H(25A)	2*i*	0.8292	0.9335	0.6000	0.080
H(25B)	2*i*	0.7105	0.9566	0.6903	0.080

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(26A)	2*i*	1.0258	1.0303	0.6273	0.102
H(26B)	2*i*	0.9294	1.0404	0.7260	0.102
H(26C)	2*i*	0.8641	1.0971	0.6460	0.102
H(27A)	2*i*	1.1547	0.8734	0.6833	0.063
H(27B)	2*i*	1.1497	0.7545	0.7059	0.063
H(28A)	2*i*	1.1200	0.8555	0.5413	0.108
H(28B)	2*i*	1.1135	0.7365	0.5638	0.108
H(28C)	2*i*	1.2746	0.7921	0.5581	0.108
H(29A)	2*i*	0.0732	0.3819	0.5123	0.124
H(29B)	2*i*	–0.0176	0.3068	0.5915	0.124
H(29C)	2*i*	0.1591	0.3381	0.5888	0.124

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}
Pd(1)	2*i*	0.76819(3)	0.68125(2)	0.70068(2)	0.0303(2)	0.0339(2)	0.0454(2)	–0.0006(1)	–0.0137(1)	–0.0020(1)
Cl(1)	2*i*	0.6165(2)	0.76946(8)	0.60952(9)	0.0807(8)	0.0445(6)	0.0944(8)	–0.0008(5)	–0.0582(7)	0.0031(5)
Cl(2)	2*i*	0.9184(1)	0.60066(7)	0.79671(7)	0.0405(5)	0.0449(5)	0.0621(6)	–0.0038(4)	–0.0254(4)	0.0036(4)
P(1)	2*i*	0.8892(1)	0.82293(7)	0.71577(7)	0.0352(5)	0.0372(5)	0.0590(6)	–0.0033(4)	–0.0150(4)	–0.0029(4)
O(1)	2*i*	0.2805(3)	0.5330(3)	0.6258(2)	0.040(2)	0.101(2)	0.046(2)	–0.006(2)	–0.019(1)	–0.016(2)
O(2)	2*i*	0.4623(3)	0.0649(2)	0.7066(2)	0.067(2)	0.038(2)	0.067(2)	–0.011(1)	–0.021(2)	–0.013(1)
O(3)	2*i*	0.5555(4)	0.0878(2)	0.8528(2)	0.081(2)	0.039(2)	0.069(2)	–0.016(1)	–0.036(2)	0.007(1)
O(4)	2*i*	0.1151(3)	0.8899(2)	0.9613(2)	0.061(2)	0.036(1)	0.053(2)	0.003(1)	–0.007(1)	–0.007(1)
O(5)	2*i*	–0.0331(4)	0.7773(2)	1.0987(2)	0.063(2)	0.060(2)	0.050(2)	0.013(1)	0.010(1)	–0.008(1)
O(6)	2*i*	–0.0047(4)	0.4436(3)	0.6230(3)	0.042(2)	0.106(3)	0.142(3)	0.003(2)	–0.013(2)	–0.075(3)
N(1)	2*i*	0.6737(3)	0.5320(2)	0.6874(2)	0.026(1)	0.037(2)	0.037(2)	–0.001(1)	–0.007(1)	–0.006(1)
N(2)	2*i*	0.3225(3)	0.5662(2)	0.7572(2)	0.029(2)	0.055(2)	0.038(2)	0.002(1)	–0.012(1)	–0.008(1)
C(1)	2*i*	0.6402(4)	0.4572(2)	0.7682(2)	0.030(2)	0.034(2)	0.040(2)	0.001(1)	–0.013(1)	–0.004(1)
C(2)	2*i*	0.5197(4)	0.5020(3)	0.8475(2)	0.039(2)	0.039(2)	0.039(2)	0.003(2)	–0.014(2)	–0.007(2)
C(3)	2*i*	0.4151(4)	0.5927(3)	0.8211(2)	0.032(2)	0.037(2)	0.038(2)	–0.002(1)	–0.010(2)	–0.004(2)
C(4)	2*i*	0.3756(4)	0.5435(3)	0.6731(2)	0.037(2)	0.043(2)	0.038(2)	–0.006(2)	–0.014(2)	–0.001(2)
C(5)	2*i*	0.5557(4)	0.5274(3)	0.6300(2)	0.038(2)	0.040(2)	0.032(2)	–0.003(2)	–0.012(2)	–0.002(1)
C(6)	2*i*	0.5775(5)	0.4242(3)	0.5911(2)	0.050(2)	0.044(2)	0.038(2)	–0.002(2)	–0.013(2)	–0.008(2)
C(7)	2*i*	0.5615(4)	0.3381(3)	0.6652(2)	0.035(2)	0.037(2)	0.039(2)	–0.001(2)	–0.009(2)	–0.009(2)
C(8)	2*i*	0.5157(4)	0.2419(3)	0.6506(2)	0.039(2)	0.047(2)	0.042(2)	–0.002(2)	–0.011(2)	–0.015(2)
C(9)	2*i*	0.5092(4)	0.1611(3)	0.7146(3)	0.038(2)	0.036(2)	0.056(2)	–0.002(2)	–0.012(2)	–0.011(2)
C(10)	2*i*	0.5523(4)	0.1743(3)	0.7948(2)	0.042(2)	0.037(2)	0.049(2)	–0.004(2)	–0.012(2)	–0.001(2)
C(11)	2*i*	0.5915(4)	0.2701(3)	0.8105(2)	0.041(2)	0.040(2)	0.041(2)	–0.001(2)	–0.015(2)	–0.004(2)
C(12)	2*i*	0.5946(4)	0.3535(3)	0.7460(2)	0.028(2)	0.035(2)	0.040(2)	–0.001(1)	–0.007(1)	–0.005(2)
C(13)	2*i*	0.4310(6)	0.0465(3)	0.6233(3)	0.084(3)	0.050(3)	0.086(3)	–0.012(2)	–0.040(3)	–0.020(2)
C(14)	2*i*	0.6445(6)	0.0937(3)	0.9194(3)	0.096(4)	0.044(2)	0.052(2)	–0.007(2)	–0.027(2)	0.003(2)
C(15)	2*i*	0.2964(4)	0.6368(3)	0.8992(2)	0.032(2)	0.041(2)	0.037(2)	–0.001(1)	–0.012(2)	–0.005(2)
C(16)	2*i*	0.2657(4)	0.7427(3)	0.8944(2)	0.040(2)	0.041(2)	0.032(2)	–0.005(2)	–0.009(2)	–0.002(2)
C(17)	2*i*	0.1551(4)	0.7876(3)	0.9607(2)	0.042(2)	0.037(2)	0.041(2)	0.001(2)	–0.013(2)	–0.009(2)
C(18)	2*i*	0.0726(4)	0.7256(3)	1.0354(2)	0.038(2)	0.049(2)	0.039(2)	0.004(2)	–0.005(2)	–0.005(2)
C(19)	2*i*	0.1019(5)	0.6219(3)	1.0405(3)	0.046(2)	0.045(2)	0.045(2)	0.000(2)	–0.001(2)	0.006(2)
C(20)	2*i*	0.2144(4)	0.5777(3)	0.9723(2)	0.047(2)	0.034(2)	0.052(2)	0.004(2)	–0.012(2)	–0.001(2)
C(21)	2*i*	0.2012(5)	0.9578(3)	0.8905(3)	0.066(3)	0.038(2)	0.063(3)	–0.002(2)	–0.018(2)	0.001(2)
C(22)	2*i*	–0.1129(7)	0.7193(4)	1.1774(3)	0.089(4)	0.099(4)	0.068(3)	0.029(3)	0.033(3)	0.009(3)
C(23)	2*i*	0.8621(5)	0.8427(3)	0.8330(3)	0.059(3)	0.054(3)	0.072(3)	–0.007(2)	–0.015(2)	–0.019(2)
C(24)	2*i*	0.6941(6)	0.8235(4)	0.8894(4)	0.076(3)	0.079(4)	0.087(4)	–0.013(3)	0.010(3)	–0.030(3)
C(25)	2*i*	0.8234(6)	0.9425(3)	0.6623(4)	0.060(3)	0.041(2)	0.106(4)	0.001(2)	–0.037(3)	0.007(2)
C(26)	2*i*	0.9196(7)	1.0363(3)	0.6657(4)	0.085(4)	0.046(3)	0.130(5)	–0.011(2)	–0.040(3)	0.008(3)
C(27)	2*i*	1.1067(4)	0.8120(3)	0.6726(3)	0.036(2)	0.046(2)	0.075(3)	–0.005(2)	–0.013(2)	0.001(2)
C(28)	2*i*	1.1583(6)	0.7978(5)	0.5753(4)	0.066(3)	0.119(5)	0.082(4)	–0.006(3)	–0.004(3)	–0.020(3)
C(29)	2*i*	0.0572(7)	0.3614(5)	0.5753(4)	0.082(4)	0.117(5)	0.119(5)	0.007(4)	–0.020(4)	–0.060(4)

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