Crystal structure of (cyclohexanonetriphenylphosphonium) (trichlorotriphenyl)palladate(II)—benzene (1/1), [(C₆H₅)₃P(CHCH₂CO(CH₂)₃)][(C₆H₅)₃PPdCl₃] · C₆H₆

U. Casellato^I, G. Cavinato^{II}, R. Graziani^{*,II} and L. Toniolo^{III}

^I C.N.R. - ICTIMA, Corso Stati Uniti 4, I-35100 Padova, Italy

^{II} Università di Padova, Dipartimento di Chimica Inorganica, Via Loredan 4, I-35131 Padova, Italy

^{III} Università di Venezia, Dipartimento di Chimica, Calle Larga - S.Marta 2137, I-30123 Venezia, Italy

Received December 9, 1999, CCDC-No. 1267/361

Abstract

$C_{48}H_{45}Cl_3OP_2Pd$, triclinic, $P\bar{1}$ (No. 2), $a = 9.225(4)$ Å, $b = 13.734(5)$ Å, $c = 18.056(6)$ Å, $\alpha = 74.48(3)^\circ$, $\beta = 94.40(3)^\circ$, $\gamma = 98.82(3)^\circ$, $V = 2176.6$ Å³, $Z = 2$, $R(F) = 0.084$, $T = 293$ K.

Source of material

The synthesis of the complex was carried out in a stainless steel autoclave of ca. 70 ml. Catalyst, reagent and solvent were contained in a pyrex bottle placed in the autoclave. In a typical experiment, 10 ml of 2-cyclohexen-1-one, 1.5 ml of EtOH containing 2 mmol of dry HCl, 7.5 ml of dioxane together with 0.1 mmol of $\text{PdCl}_2(\text{PPh}_3)_2$ and 0.3 mmol of PPh_3 , were pressurized with 100 atm of CO at room temperature, after purging the autoclave with the same gas. The autoclave was placed for 2 h in a oil bath at 373 K, then cooled in a ice bath, and slowly depressurized. The resulting solution was filtered, and the product precipitated with ether as a yellow-orange microcrystalline powder. A crystalline product was then obtained by recrystallization from benzene. The same complex is also obtained when *trans*- $[\text{PdCl}_2(\text{PPh}_3)_2]$ is treated with 2-chloro-cyclohexanone in boiling EtOH for some hours, or by reacting phosphonium chloride with the chloro-bridge dimer $[\text{PdCl}_2(\text{PPh}_3)_2]_2$ in EtOH, as reported in [1].

Experimental details

Phenyl groups were refined as bodies (C—C 1.395 Å) and hydrogen atoms were introduced in calculated positions with fixed temperature factors.

Discussion

A quasi regular square planar configuration is realized in the $[\text{PdCl}_3(\text{PPh}_3)]^-$ anion of the ionic complex. The Pd—P bond [2.250(5) Å and 2.250(4) Å] shows double bond character. Two Pd—Cl bonds compare well themselves [2.291(5) Å and 2.282(5) Å] while the Pd—Cl bond *trans* to Pd—P is longer [2.363(5) Å], probably because of *trans* effect. The P(1)—C bonds (mean 1.83 Å) are significantly longer than the corresponding P(2)—C (phenyl) bonds (mean 1.78 Å), and the P—C(37) bond with the aliphatic ring is intermediate [1.81(1) Å]. The C=O bond of 1.24(2) Å is clearly double.

Table 1. Data collection and handling.

Crystal:	yellow-orange prism, max. dim. 0.2 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	64 cm ⁻¹
Diffractometer, scan mode:	Philips PW1100, 2 θ
2 $\theta_{\max}$:	52°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4149, 3987
Criterion for F_{obs} , $N(hkl)_{\text{gt}}$:	$F_{\text{obs}} > 4 \sigma(F_{\text{obs}})$, 3411
$N(\text{param})_{\text{refined}}$:	412
Program:	SHELX-76 [2]

* Correspondence author (e-mail: graziani@chim02.chim.unipd.it)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(2)	2i	−0.1050(8)	0.2464(5)	0.2232(5)	0.08
H(3)	2i	−0.3642(8)	0.2590(5)	0.2410(5)	0.08
H(4)	2i	−0.4649(8)	0.2007(5)	0.3711(5)	0.08
H(5)	2i	−0.3065(8)	0.1298(5)	0.4835(5)	0.08
H(6)	2i	−0.0473(8)	0.1172(5)	0.4657(5)	0.08
H(8)	2i	0.1739(8)	0.3429(6)	0.3866(5)	0.08
H(9)	2i	0.3093(8)	0.3867(6)	0.4997(5)	0.08
H(10)	2i	0.4382(8)	0.2581(6)	0.5933(5)	0.08
H(11)	2i	0.4316(8)	0.0858(6)	0.5738(5)	0.08
H(12)	2i	0.2961(8)	0.0421(6)	0.4607(5)	0.08
H(14)	2i	−0.0919(8)	−0.0240(5)	0.3847(4)	0.08
H(15)	2i	−0.0765(8)	−0.2073(5)	0.4027(4)	0.08
H(16)	2i	0.1533(8)	−0.2613(5)	0.3753(4)	0.08
H(17)	2i	0.3676(8)	−0.1320(5)	0.3299(4)	0.08
H(18)	2i	0.3521(8)	0.0513(5)	0.3119(4)	0.08
H(20)	2i	0.3912(8)	0.5416(6)	0.6754(5)	0.08
H(21)	2i	0.3028(8)	0.6323(6)	0.5462(5)	0.08
H(22)	2i	0.0391(8)	0.6052(6)	0.5083(5)	0.08
H(23)	2i	−0.1360(8)	0.4873(6)	0.5995(5)	0.08
H(24)	2i	−0.0475(8)	0.3966(6)	0.7288(5)	0.08
H(26)	2i	0.4371(7)	0.5547(5)	0.8730(4)	0.08
H(27)	2i	0.3895(7)	0.6863(5)	0.9352(4)	0.08
H(28)	2i	0.1344(7)	0.7034(5)	0.9576(4)	0.08

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(30)	2i	−0.0732(7)	0.5888(5)	0.9178(4)	0.08
H(32)	2i	−0.0256(7)	0.4573(5)	0.8556(4)	0.08
H(33)	2i	0.0883(7)	0.2501(5)	0.7374(4)	0.08
H(34)	2i	−0.0470(7)	0.0795(5)	0.7950(4)	0.08
H(35)	2i	−0.0862(7)	0.0240(5)	0.9350(4)	0.08
H(36)	2i	0.0098(7)	0.1392(5)	1.0174(4)	0.08
H(37)	2i	0.1450(7)	0.3097(5)	0.9598(4)	0.08
H(38A)	2i	0.483(1)	0.456(1)	0.793(1)	0.08
H(38B)	2i	0.419(1)	0.366(1)	0.699(1)	0.08
H(40A)	2i	0.384(1)	0.264(1)	0.762(1)	0.08
H(40B)	2i	0.783(1)	0.281(1)	0.828(1)	0.08
H(41A)	2i	0.641(1)	0.207(1)	0.854(1)	0.08
H(41B)	2i	0.708(1)	0.406(1)	0.876(1)	0.08
H(42A)	2i	0.690(1)	0.305(1)	0.942(1)	0.08
H(42B)	2i	0.431(1)	0.274(1)	0.908(1)	0.08
H(43)	2i	0.463(1)	0.381(1)	0.924(1)	0.08
H(44)	2i	0.504(1)	−0.0779(7)	0.2565(6)	0.08
H(45)	2i	0.306(1)	0.0056(7)	0.1763(6)	0.08
H(46)	2i	0.357(1)	0.1200(7)	0.0470(6)	0.08
H(47)	2i	0.608(1)	0.1509(7)	−0.0021(6)	0.08
H(48)	2i	0.807(1)	0.0674(7)	0.0780(6)	0.08
		0.755(1)	−0.0470(7)	0.2073(6)	0.08

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Pd	2i	0.2170(1)	0.2493(1)	0.2158(1)	0.0418(6)	0.0499(6)	0.0680(8)	0.0010(5)	0.0262(6)	−0.0117(6)
Cl(1)	2i	0.0653(5)	0.1324(3)	0.1657(3)	0.079(2)	0.062(2)	0.063(2)	0.001(2)	0.019(2)	−0.023(1)
Cl(2)	2i	0.3625(5)	0.3689(4)	0.2649(3)	0.082(2)	0.083(2)	0.084(2)	−0.038(2)	0.025(2)	−0.023(2)
Cl(3)	2i	0.3070(4)	0.3308(4)	0.0922(3)	0.050(2)	0.098(2)	0.072(2)	0.001(2)	0.030(2)	−0.007(2)
P(1)	2i	0.1286(4)	0.1632(3)	0.3314(3)	0.043(2)	0.046(2)	0.060(2)	0.002(1)	0.019(1)	−0.016(1)
P(2)	2i	0.2342(4)	0.4106(3)	0.8072(3)	0.041(2)	0.049(2)	0.063(2)	−0.001(1)	0.020(1)	−0.018(1)
O(1)	2i	0.6703(4)	0.3338(3)	0.6953(3)	0.089(2)	0.136(2)	0.156(2)	0.023(1)	0.045(1)	−0.058(1)
C(1)	2i	−0.0596(8)	0.1810(5)	0.3433(5)	0.053(2)	0.046(2)	0.070(2)	0.000(2)	0.024(2)	−0.021(2)
C(2)	2i	−0.1489(8)	0.2210(5)	0.2800(5)	0.053(2)	0.062(2)	0.064(2)	0.005(2)	0.023(2)	0.000(2)
C(3)	2i	−0.2950(8)	0.2281(5)	0.2900(5)	0.067(2)	0.062(2)	0.081(2)	0.010(2)	0.030(2)	−0.001(2)
C(4)	2i	−0.3518(8)	0.1952(5)	0.3634(5)	0.062(2)	0.064(2)	0.095(2)	0.004(2)	0.032(2)	−0.019(2)
C(5)	2i	−0.2625(8)	0.1552(5)	0.4267(5)	0.076(2)	0.074(2)	0.091(2)	0.013(2)	0.040(2)	−0.024(2)
C(6)	2i	−0.1164(8)	0.1481(5)	0.4167(5)	0.075(2)	0.067(2)	0.065(2)	0.015(2)	0.038(2)	−0.004(2)
C(7)	2i	0.2264(8)	0.1897(6)	0.4165(5)	0.063(2)	0.057(2)	0.057(2)	0.021(2)	0.028(2)	−0.007(2)
C(8)	2i	0.2301(8)	0.2868(6)	0.4275(5)	0.049(2)	0.067(2)	0.076(2)	−0.021(2)	0.018(2)	−0.038(2)
C(9)	2i	0.3065(8)	0.3115(6)	0.4912(5)	0.103(2)	0.090(2)	0.104(2)	0.014(2)	0.014(2)	−0.048(2)
C(10)	2i	0.3791(8)	0.2390(6)	0.5440(5)	0.099(2)	0.128(2)	0.095(2)	−0.012(2)	0.032(2)	−0.047(2)
C(11)	2i	0.3754(8)	0.1419(6)	0.5330(5)	0.061(2)	0.099(2)	0.083(2)	0.015(2)	0.001(2)	−0.034(2)
C(12)	2i	0.2990(8)	0.1172(6)	0.4692(5)	0.058(2)	0.076(2)	0.070(2)	0.003(2)	0.008(2)	−0.015(2)
C(13)	2i	0.1291(8)	0.0253(5)	0.3471(4)	0.066(2)	0.044(2)	0.065(2)	0.014(2)	0.024(2)	−0.017(2)
C(14)	2i	0.0083(8)	−0.0476(5)	0.3727(4)	0.084(2)	0.057(2)	0.065(2)	0.002(2)	0.029(2)	−0.014(2)
C(15)	2i	0.0170(8)	−0.1509(5)	0.3829(4)	0.081(2)	0.058(2)	0.074(2)	−0.012(2)	0.029(2)	−0.023(2)
C(16)	2i	0.1465(8)	−0.1813(5)	0.3674(4)	0.109(2)	0.054(2)	0.065(2)	0.020(2)	0.013(2)	−0.016(2)
C(17)	2i	0.2673(8)	−0.1084(5)	0.3418(4)	0.079(2)	0.072(2)	0.082(2)	0.030(2)	0.013(2)	−0.021(2)
C(18)	2i	0.2586(8)	−0.0051(5)	0.3317(4)	0.050(2)	0.054(2)	0.086(2)	0.014(2)	0.016(2)	−0.018(2)
C(19)	2i	0.1775(8)	0.4633(6)	0.7103(5)	0.041(2)	0.067(2)	0.065(2)	−0.019(2)	0.025(2)	−0.018(2)
C(20)	2i	0.2762(8)	0.5297(6)	0.6589(5)	0.079(2)	0.071(2)	0.065(2)	−0.006(2)	0.019(2)	−0.018(2)
C(21)	2i	0.2263(8)	0.5809(6)	0.5861(5)	0.100(2)	0.071(2)	0.070(2)	−0.022(2)	0.024(2)	−0.005(2)
C(22)	2i	0.0777(8)	0.5656(6)	0.5647(5)	0.133(2)	0.078(2)	0.061(2)	−0.008(2)	0.007(2)	−0.012(2)
C(23)	2i	−0.0210(8)	0.4991(6)	0.6161(5)	0.096(2)	0.098(2)	0.082(2)	0.032(2)	0.001(2)	−0.020(2)
C(24)	2i	0.0289(8)	0.4480(6)	0.6889(5)	0.079(2)	0.067(2)	0.062(2)	−0.005(2)	0.019(2)	−0.005(2)
C(25)	2i	0.2088(7)	0.4976(5)	0.8603(4)	0.044(2)	0.043(2)	0.068(2)	−0.006(2)	0.019(2)	−0.018(2)
C(26)	2i	0.3258(7)	0.5622(5)	0.8828(4)	0.066(2)	0.056(2)	0.058(2)	0.006(2)	0.019(2)	−0.015(2)
C(27)	2i	0.2990(7)	0.6363(5)	0.9178(4)	0.084(2)	0.066(2)	0.074(2)	−0.005(2)	0.013(2)	−0.044(2)
C(28)	2i	0.1551(7)	0.6460(5)	0.9305(4)	0.098(2)	0.059(2)	0.074(2)	0.035(2)	0.031(2)	−0.012(2)
C(29)	2i	0.0382(7)	0.5814(5)	0.9081(4)	0.068(2)	0.067(2)	0.092(2)	0.022(2)	0.032(2)	−0.030(2)
C(30)	2i	0.0650(7)	0.5072(5)	0.8730(4)	0.059(2)	0.070(2)	0.078(2)	0.005(2)	0.026(2)	−0.019(2)
C(31)	2i	0.1253(7)	0.2908(5)	0.8450(4)	0.039(2)	0.046(2)	0.056(2)	0.008(2)	0.008(2)	−0.008(2)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(32)	2i	0.0712(7)	0.2259(5)	0.7985(4)	0.038(2)	0.056(2)	0.073(2)	0.001(2)	0.016(2)	−0.021(2)
C(33)	2i	−0.0051(7)	0.1297(5)	0.8310(4)	0.076(2)	0.041(2)	0.074(2)	0.012(2)	0.018(2)	−0.012(2)
C(34)	2i	−0.0272(7)	0.0985(5)	0.9099(4)	0.074(2)	0.052(2)	0.067(2)	0.006(2)	0.013(2)	−0.001(2)
C(35)	2i	0.0269(7)	0.1634(5)	0.9563(4)	0.068(2)	0.057(2)	0.062(2)	−0.001(2)	0.022(2)	0.007(2)
C(36)	2i	0.1031(7)	0.2595(5)	0.9239(4)	0.076(2)	0.048(2)	0.050(2)	0.001(2)	0.015(2)	−0.016(2)
C(37)	2i	0.425(1)	0.390(1)	0.810(1)	0.036(2)	0.066(2)	0.064(2)	0.002(2)	0.016(2)	−0.019(2)
C(38)	2i	0.445(1)	0.329(1)	0.750(1)	0.053(2)	0.081(2)	0.115(2)	0.001(2)	0.033(2)	−0.060(2)
C(39)	2i	0.608(1)	0.316(1)	0.757(1)	0.094(2)	0.087(2)	0.113(2)	−0.001(2)	0.066(2)	−0.047(2)
C(40)	2i	0.680(1)	0.277(1)	0.834(1)	0.058(2)	0.115(2)	0.090(2)	0.033(2)	0.016(2)	−0.018(2)
C(41)	2i	0.656(1)	0.338(1)	0.891(1)	0.090(2)	0.134(2)	0.116(2)	0.053(2)	0.023(2)	−0.028(2)
C(42)	2i	0.482(1)	0.342(1)	0.890(1)	0.037(2)	0.106(2)	0.078(2)	0.017(2)	0.014(2)	−0.009(2)
C(43)	2i	0.527(1)	−0.0280(7)	0.2001(6)	0.049(2)	0.108(2)	0.062(2)	0.014(2)	0.024(2)	0.008(2)
C(44)	2i	0.415(1)	0.0191(7)	0.1549(6)	0.125(2)	0.150(2)	0.149(2)	0.004(2)	0.074(2)	0.001(2)
C(45)	2i	0.444(1)	0.0836(7)	0.0820(6)	0.085(2)	0.168(2)	0.138(2)	0.054(2)	−0.001(2)	0.015(2)
C(46)	2i	0.585(1)	0.1010(7)	0.0543(6)	0.084(2)	0.086(2)	0.071(2)	−0.011(2)	0.038(2)	−0.013(2)
C(47)	2i	0.697(1)	0.0539(7)	0.0995(6)	0.103(2)	0.160(2)	0.155(2)	−0.044(2)	0.071(2)	−0.024(2)
C(48)	2i	0.668(1)	−0.0106(7)	0.1724(6)	0.077(2)	0.171(2)	0.211(2)	0.039(2)	0.028(2)	0.024(2)

References

1. Bardi, R.; Piazzesi, A. M.; Del Pra, A.; Cavinato, G.; Toniolo, L.: Reactivity of functionalized Halo-derivates with Transitionmetal Complexes - Synthesis and X-ray Diffraction Study of [Ph₃P(CH₂CH₂COCH₃)]⁺ [PdCl₃(PPh₃)][−] obtained by Reaction of *trans*-[PdCl₂(PPh₃)₂] with CH₃COCH₂CH₂Cl. *Inorg. Chim. Acta* **75** (1983) 15-19.
2. Sheldrick, G. M.: SHELX-76, Program for Crystal Structures Determination. Cambridge 1976.