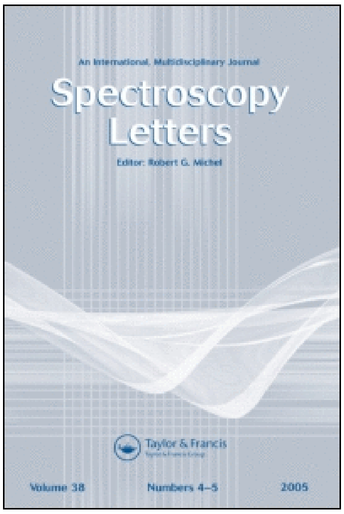

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Precious Metals - Part 2 - The Spectroscopic Characterisation and X-Ray Crystal Structure of $Pd_2(Pph_3)_3Cl_5O$

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PRECIOUS METALS - PART 2 - THE SPECTROSCOPIC CHARACTERISATION AND X-RAY CRYSTAL STRUCTURE OF $Pd_2(PPh_3)_3Cl_5O$

Key Words: Palladium, NMR, Organometallic compound.

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ABSTRACT

This work is on the synthesis and characterisation of a new phosphine stabilised palladium compound. The compound was first obtained from the rejects of cluster syntheses stored in the laboratory. Later on, it was prepared from $PdCl_2$ and triphenyl phosphine. The compound was characterised by $^{31}P\ \{^1H\}$ NMR, UV/visible spectroscopy and elemental analysis. The crystal and molecular structure of $Pd_2(PPh_3)_3Cl_5O$ was determined by X-ray analysis. The compound crystallizes in orthorhombic space group Pbca, N° 61, a = 19.009(2)Å, b= 22.283(2)Å, c=23.726(2)Å, V= 10050(20)Å^3, Z= 8 residuals $R[I>2\sigma(I)]$= 0.0457 and R(all) = 0.0636, MoKα radiation, 20 °C.

INTRODUCTION

Different kinds of waste material are generated in the industry as a consequence of hydro and/or pyrometallurgy. These residues contain up to 25% of valuable metals, as well as elements such As, Hg, Cd, Se, etc. In most cases, these residues are hazardous wastes and dangerous for the environment. The decontamination of these residues is indispensable before their recycling in the classical metallurgical plants [1].

In the last decade, considerable changes occurred in the way transition metals (Au, Pd, Pt, In, etc) are used. During the last 20 years, the synthesis and characterisation of transition metal cluster compounds has provided a stimulating challenge for inorganic chemists. A great deal of interest has been directed towards the potential catalytic applications of gold cluster compounds[2-8].

Noble metals recovery from rejects collected in the laboratory has been a frequent concern, first of all due to economic purposes and also in order to avoid possible risks to the environment when rejects of this kind are thrown directly into the ecosystem.

The rejects stored in the laboratory contain a mixture of palladium, gold, and organic solvents (diethyl ether, ethanol, n-pentane, acetone, dichlorometane).

The recovery is normally processed following Clement's method [9] or the route developed in order to obtain gold as $AuPPh_3Cl$ and palladium as $Pd(PPh_3)_2Cl_2$ [10].

In this paper a new compound, first crystallised from laboratory rejects and later obtained through the reaction between $PdCl_2$ and triphenylphosphine is presented.

This compound was characterised by $^{31}P\{^1H\}$ NMR, UV/vis spectra , elemental analysis and single crystal X-ray diffraction.

EXPERIMENTAL SECTION

Measurements

The $^{31}P\{^1H\}$ NMR spectrum of this compound in $CDCl_3$ solutions was recorded on a Brucker (DRX 500) spectrometer with H_3PO_4 as an external reference. UV-Vis absorption was realised in a U-3000 Shimadzu spectrometer. Elemental analysis was carried out at the Microanalysis Laboratory, University of São Paulo and X-ray data were measured on a Nonius CAD4 diffractometer.

Reagents

All solvents were of reagents grade and were used without further purification.

Preparation of $Pd_2(PPh_3)_3Cl_5O$ from $PdCl_2$

0.5 g de $PdCl_2$ (28 mmol) was dissolved in 0.2 mL of hydrochloric acid in a 250 mL Erlenmeyer flask. The solution is stirred and warmed (~60 °C) until complete dissolution of $PdCl_2$. This solution is added to the emulsion of 2.3 g (8.8 mmol) of triphenyphosphine in 50 mL of EtOH. The mixture is stirred for 5 hours until complete reaction and precipitation. The precipitate formed is collected using vacuum filtration, washed with several small portions of EtOH, 30 mL of acetone is added to the precipitate that is dissolved and the solution is filtered off, the solid that was not dissolved is discarded and the filtrate is layered with 3 times the volume of Et_2OH. Slow solvent diffusion produces yellow-orange crystals. Yield: 160 mg, after recrystallization from an acetone-diethyl ether solvent mixture. The bright orange crystals are soluble in CH_2Cl_2, CH_3CN, CH_3OH, $CHCl_3$, and acetone and insoluble in saturated hydrocarbons and diethyl ether.

Anal.Calcd. for $Pd_2(PPh_3)_3Cl_5O$(Mr1191.85): C, 54.89; H, 3.72. Found:C, 54.42 ;H, 3.72. $^{31}P\{^1H\}$ NMR: singlet at δ 49.

Obtaining $Pd_2(PPh_3)_3Cl_5O$ from rejects collected in the laboratory

The laboratory reject (~5L) is filtered in order to separate the solid part from the solution.

The solution is distilled and the solvents obtained are separated following the method earlier described [10] to obtain $AuPPh_3Cl$. The solid initially obtained is burned in direct flame in order to liberate the organic material. The residue

TABLE 1

Crystallographic data for $Pd_2(PPh_3)_3Cl_5O$

Chem formula	$C_{54}H_{44}Cl_5OP_3Pd_2$
Fw	1191.85
a	19.009(2)Å
b	22.283(2)Å
c	23.726(2)Å
V	10050(20)Å^3
Z	8
Space group	Pbca (no.61)
T	20 °C
λ	1.54184 Å
ρcalc	1.575mg/m^3
μ(MoKα)	94.28 cm^{-1}
R[I>2σ (I)]	0.0457
R_w(all)	0.0636

obtained is dissolved in aqua regia. The solution is filtered and evaporated near dryness, then concentrated hydrochloric acid (three times) is added and the solution is evaporated until dryness. EtOH is added and the resulting solution is filtered through diatomaceous earth, and an emulsion of triphenylphosphine; ethanol is added and the mixture is stirred for 3 hours. A precipitate is formed and is filtered under vacuum. The precipitate is then dissolved with a small amount of acetone and filtered through diatomaceous earth. Three times this volume of Et_2O is added to the filtrate. Overnight, small crystals are formed. These crystals are dissolved in a small amount of acetone in a small flask and Et_2O is added via slow solvent diffusion, and yellow-orange crystals $Pd_2(PPH_3)_3Cl_5O$ are obtained.

X-ray determined structure

Well formed orange crystals of the formula were prepared by slow diffusion of acetone into a diethyl ether solution. A summary of crystal and refinement data is

TABLE 2

Selected bond lengths (Å) and bond angles (°) for $Pd_2(PPh_3)_3Cl_5O$

Atoms	X	Y	Z	U(eq)
Pd(1)	5317(1)	2031(1)	4249(1)	34(1)
Pd(2)	4307(1)	1616(1)	3286(1)	35(1)
P(2)	4926(1)	2157(1)	5159(1)	36(1)
P(3)	4250(1)	773(1)	2774(1)	40(1)
Cl(1)	6297(1)	1498(1)	4558(1)	40(1)
Cl(2)	4576(1)	1134(1)	4140(1)	42(1)
Cl(3)	5547(1)	1781(1)	3254(1)	40(1)
Cl(4)	4171(1)	2182(1)	2480(1)	50(1)
Cl(5)	3115(1)	1603(1)	3459(1)	53(1)
C(112)	5282(2)	2401(2)	6265(2)	47(2)
C(113)	5732(2)	2548(2)	6706(1)	56(1)
C(114)	6439(1)	2660(1)	6599(1)	57(2)
C(115)	6697(2)	2625(2)	6052(2)	52(2)
C(116)	6247(1)	2478(1)	5611(1)	44(1)
C(121)	4545(2)	1473(2)	5443(2)	45(1)
C(111)	5540(2)	2366(2)	5717(1)	39(1)
C(122)	4938(2)	947(2)	5416(2)	56(2)
C(123)	4666(3)	417(2)	5635(2)	70(2)
C(124)	4002(3)	412(2)	5879(2)	90(3)
C(125)	3609(2)	937(3)	5905(2)	107(4)
C(126)	3881(2)	1468(2)	5687(2)	71(2)
C(131)	4233(2)	2716(2)	5190(2)	44(1)
C(132)	4329(2)	3244(2)	5493(2)	62(2)
C(133)	3804(3)	3679(2)	5498(2)	83(3)
C(134)	3184(2)	3585(2)	5200(3)	89(3)
C(135)	3088(2)	3057(2)	4898(2)	75(2)
C(136)	3613(2)	2622(2)	4893(2)	58(2)
C(211)	6138(2)	3493(2)	4620(2)	53(2)
C(212)	5675(2)	3893(3)	4875(2)	80(2)
C(213)	5928(4)	4327(3)	5244(3)	122(4)
C(214)	6644(4)	4362(3)	5358(3)	128(5)
C(215)	7107(3)	3962(3)	5103(3)	108(4)
C(216)	6854(2)	3528(3)	4735(2)	72(2)
C(221)	6510(2)	2951(2)	3586(2)	48(2)
C(222)	7083(2)	2575(2)	3675(2)	61(2)
C(223)	7667(2)	2611(2)	3324(2)	75(2)

(continued)

TABLE 2. Continued

C(224)	7678(2)	3022(3)	2884(2)	82(3)
C(225)	7104(3)	3398(2)	2795(2)	92(3)
C(226)	6521(2)	3362(2)	3146(2)	72(2)
C(231)	5038(2)	3332(2)	3803(2)	47(2)
C(232)	5013(2)	3939(2)	3669(2)	64(2)
C(233)	4402(3)	4186(1)	3447(2)	77(3)
C(234)	3814(2)	3826(2)	3360(2)	73(2)
C(235)	3839(2)	3219(2)	3495(2)	59(2)
C(236)	4450(2)	2973(1)	3716(2)	48(2)
C(311)	3631(2)	708(2)	2184(2)	48(2)
C(312)	3716(3)	213(2)	1834(2)	72(2)
C(313)	3231(3)	101(2)	1408(2)	88(3)
C(314)	2661(3)	483(3)	1332(2)	76(3)
C(315)	2576(2)	978(2)	1682(2)	70(2)
C(316)	3061(2)	1091(2)	2108(2)	56(2)
C(321)	4026(2)	98(2)	3166(2)	55(2)
C(322)	3542(3)	126(2)	3604(2)	72(2)
C(323)	3322(3)	-398(3)	3896(2)	110(5)
C(324)	3585(4)	-949(2)	3695(3)	130(6)
C(325)	4069(4)	-977(2)	3257(3)	126(2)
C(236)	4290(3)	-453(2)	2992(2)	93(4)
C(331)	5102(2)	647(2)	2463(2)	56(2)
C(332)	5262(3)	923(2)	1953(2)	80(3)
C(333)	5939(4)	888(3)	1735(3)	131(7)
C(334)	6457(2)	576(3)	2027(4)	149(8)
C(335)	6298(3)	300(3)	2537(4)	141(7)
C(336)	5621(3)	336(3)	2755(2)	114(5)
O	4422(2)	2402(2)	3879(1)	31(1)

found in Table 1, Selected Frational Positional and Thermal Parameters (Å^2) in Table 2 and relevant bond distances and angles are listed in Table 3. The molecular structure is shown in Figure 1.

This compound has two palladium atoms bound to each other through two chlorine bridges, there are three PPh_3 groups attached to the palladium atoms, one oxygen atom is bonded to Pd, and the carbon atom from the phenyl group. The structural formula is $C_{54}H_{44}Cl_5OP_3Pd_2$.

TABLE 3

Selected bond lengths [Å] and angles [deg]

Pd(1)–O	2.085(3)
Pd(1)–P(2)	2.284(2)
Pd(1)–P(1)	2.2994(14)
Pd(1)–Cl(1)	2.3279(14)
Pd(1)–Cl(2)	2.4590(14)
Pd(1)–Cl(3)	2.4663(14)
Pd(1)–Pd(2)	3.1251(6)
Pd(2)–P(3)	2.240(2)
Pd(2)–O	2.257(3)
Pd(2)–Cl(5)	2.303(2)
Pd(2)–Cl(4)	2.307(2)
Pd(2)–Cl(2)	2.3497(14)
Pd(2)–Cl(3)	2.3856(14)
O–Pd(1)–P(2)	84.51(10)
O–Pd(1)–P(1)	94.76(10)
P(2)–Pd(1)–P(1)	99.39(5)
O–Pd(1)–Cl(1)	170.93(10)
P(2)–Pd(1)–Cl(1)	100. 92(6)
P(1)–Pd(1)–Cl(1)	91.53(5)
O–Pd(1)–Cl(2)	79.03(10)
P(2)–Pd(1)–Cl(2)	161.35(5)
P(1)–Pd(1)–Cl(2)	90.71(5)
Cl(1)–Pd(1)–Cl(2)	94.39(5)
O–Pd(1)–Cl(3)	80.21(10)
P(2)–Pd(1)–Cl(3)	89.22(5)
P(1)–Pd(1)–Cl(3)	169.63(5)
Cl(1)–Pd(1)–Cl(3)	92.52(5)
Cl(2)–Pd(1)–Cl(3)	79.46(5)
O–Pd(1)–Pd(2)	46.20(9)
P(2)–Pd(1)–Pd(2)	113.66(4)
P(1)–Pd(1)–Pd(2)	121.58(4)
Cl(1)–Pd(1)–Cl(3)	92.52(5)

(continued)

TABLE 3. Continued

Cl(1)–Pd(1)–Pd(2)	124.74(4)
Cl(2)–Pd(1)–Pd(2)	47.96(3)
Cl(3)–Pd(1)–Pd(2)	48.78(3)
P(3)–Pd(2)–O	173.50(9)
P(3)–Pd(2)–Cl(5)	92.20(6)
O–Pd(2)–Cl(5)	89.66(9)
P(3)–Pd(2)–Cl(4)	90.19(6)
O–Pd(2)–Cl(4)	95.95(10)
Cl(5)–Pd(2)–Cl(4)	92.56(6)
P(3)–Pd(2)–Cl(2)	95.49(5)
O–Pd(2)–Cl(2)	78.18(9)
Cl(5)–Pd(2)–Cl(2)	93.08(6)
Cl(4)–Pd(2)–Cl(2)	171.82(6)
P(3)–Pd(2)–Cl(3)	99.21(5)
O–Pd(2)–Cl(3)	78.73(9)
Cl(5)–Pd(2)–Cl(3)	168.31(6)
Cl(4)–Pd(2)–Cl(3)	89.97(6)
Cl(2)–Pd(2)–Cl(3)	83.34(5)
P(3)–Pd(2)–Pd(1)	132.45(4)
O–Pd(2)–Pd(1)	41.81(8)
Cl(5)–Pd(2)–Pd(1)	118.53(5)
Cl(4)–Pd(2)–Pd(1)	120.90(4)
Cl(2)–Pd(2)–Pd(1)	51.01(4)
Cl(3)–Pd(2)–Pd(1)	51.04(3)
Pd(2)–Cl(2)–Pd(1)	81.03(3)
Pd(2)–Cl(3)–Pd(1)	80.18(4)
C(236)–O–Pd(1)	117.9 (3)
C(236)–O–Pd(2)	124.4 (3)
Pd(1)–O–Pd(2)	92.00(13)

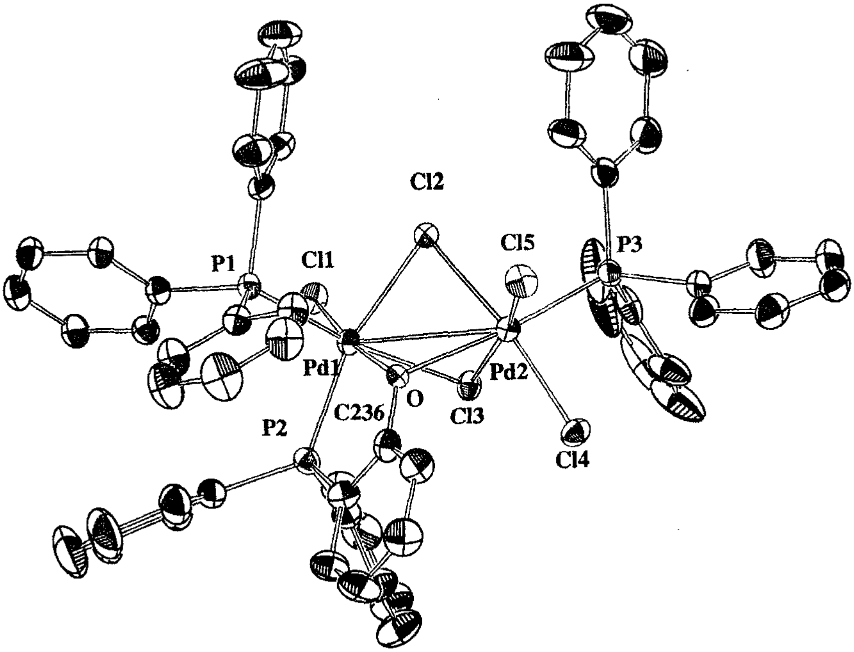

FIG.1. Molecular structure for $Pd_2(PPh_3)_3Cl_5O$.

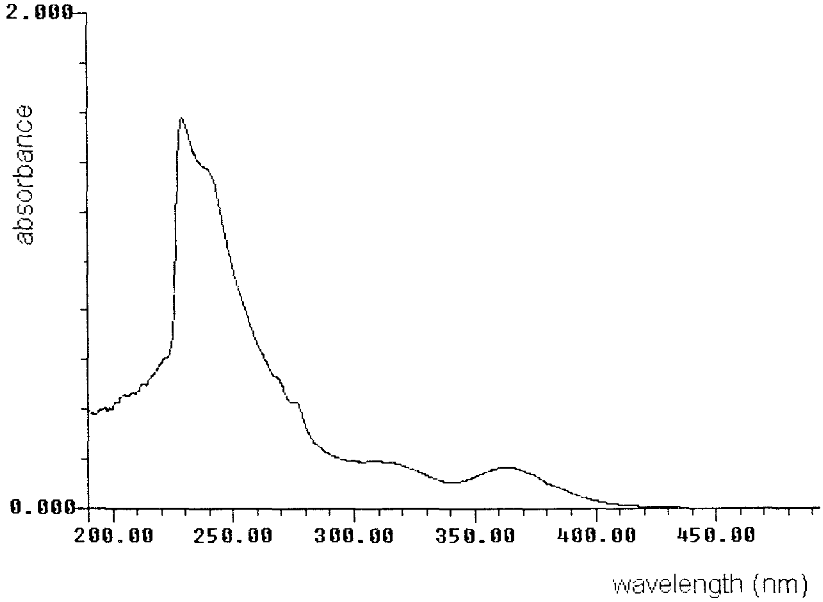

FIG. 2. UV/visible absorption Spectrum of $Pd_2(PPh_3)_3Cl_5O$.

RESULTS AND DISCUSSION

The $^{31}P\{^{1}H\}$ NMR spectrum in d-chloroform showed one peak at δ 50.2 as a result of the fluxional behaviour of different sites at room temperature.

The UV/visible absorption spectrum is shown in Figure 2. The spectrum of the compound showed a broad absorption band due to the presence of aromatic groups in the triphenylphosphine ligand and several shoulders.

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