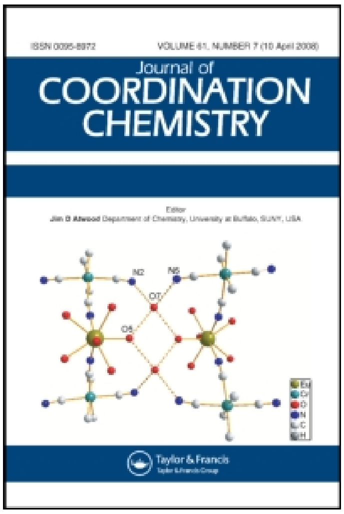

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

DI-μ-CHLORO-*BIS*[1,2-*BIS*(DIPHENYLPHOSPHINO)-ETHANEPALLADIUM(II)]: SYNTHESIS AND CRYSTAL STRUCTURE

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To cite this Article Kumar, J. Sooriya , Singh, Ajai K. , Yang, Jincai and Drake, John E.(1998) 'DI-μ-CHLORO-*BIS*[1,2-*BIS*(DIPHENYLPHOSPHINO)-ETHANEPALLADIUM(II)]: SYNTHESIS AND CRYSTAL STRUCTURE', Journal of Coordination Chemistry, 44: 3, 335 — 342

To link to this Article: DOI: 10.1080/00958979808023085

URL: http://dx.doi.org/10.1080/00958979808023085

J. Coord. Chem., 1998, Vol. 44, pp. 335–342
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Printed in Malaysia.

DI-μ-CHLORO-*BIS*[1,2-*BIS*(DIPHENYLPHOSPHINO)-ETHANEPALLADIUM(II)]: SYNTHESIS AND CRYSTAL STRUCTURE

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(Received 1 July 1997)

On reacting 1,2-*bis*(diphenylphosphino)ethanedichloropalladium(II) with equimolar amount of silver perchlorate, a binuclear complex, di-μ-chloro-*bis*[1,2-*bis*(diphenylphosphino)ethanepalladium(II)] (**1**) is formed. The crystal structure of **1** has been solved. It crystallizes with two chloroform molecules. Chloro bridges are symmetrical and normal (Pd–Cl ~ 2.414(3) Å). The immediate environment around palladium is slightly distorted square planar and the P–Pd–P angle is ~85°. IR bands at 290 and 270 cm^{-1} are observed for the chloro-bridged core of the complex.

Keywords: 1,2-*bis*(diphenylphosphino)ethane; palladium; binuclear-complex; synthesis; crystal structure

INTRODUCTION

1,2-*Bis*(diphenylphosphino)ethane (dppe) is a classical ligand. It has been used to design a variety of complexes having rich chemistry and applications, particularly in the catalytic activation of small molecules.[1–3] Appropriate tuning of steric and electronic effects in this ligand is partly responsible for such roles. The crystal structure of 1,2-*bis*(diphenylphosphinoethane)dichloropalladium(II) was first studied by Steffen and

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Palenik[4] and recently by Singh *et al.*[5] The binuclear rhodium complex $[(Ph_2PCH_2CH_2PPh_2)Rh(\mu\text{-}Cl)_2Rh(Ph_2PCH_2CH_2PPh_2)]$ has been synthesized[6] and found to give a coordinatively unsaturated centre which is useful for hydroacylation[7] of 4-pentenals and hydrogenation[8] of 2-acetamidoacrylic acid. However, a similar dppe-based framework with palladium is not known. In this system the cleavage of the chloro bridge will generate a coordinatively unsaturated palladium ion which may find catalytic applications. In this paper a facile synthesis of the binuclear palladium complex $[(Ph_2PCH_2CH_2PPh_2)Pd(\mu\text{-}Cl)_2Pd(Ph_2PCH_2CH_2PPh_2)](ClO_4)_2$ (**1**) from $[(dppe)PdCl_2]$ and its crystal structure are described.

EXPERIMENTAL

1,2-*Bis*(diphenylphosphino)ethane (dppe) and Na_2PdCl_4 were obtained from Aldrich (USA) and used as received. 1,2-*Bis*(diphenylphosphino)-ethanedichloropalladium(II) was synthesized using a literature method.[9] Elemental analyses were carried out on a Perkin-Elmer elemental analyzer (240 C). IR spectra in CsI discs were recorded in the range 200–4000 cm^{-1} on a Nicolet 5DX FT-IR spectrophotometer.

Synthesis of $[(Ph_2PCH_2CH_2PPh_2)Pd(Cl)]_2(ClO_4)_2\cdot 2CHCl_3$ (1)

1,2-*Bis*(diphenylphosphino)ethanedichloropalladium(II) (0.12 g, 0.2 mmol) was dissolved in 10 cm^3 of chloroform and mixed with a solution of $AgClO_4$ (0.04 g, 0.2 mmol) made up in 15 cm^3 of methanol under a nitrogen atmosphere. The mixture was stirred for ~2 h and the white precipitate which formed was filtered off. The filtrate was evaporated under reduced pressure and the residue recrystallized from methanol–chloroform (1 : 1). The yield of greenish yellow crystals was ~70%, M.P. 145–146°C (d). Analysis: found: C, 43.03; H, 3.48%. Calc. for $C_{54}H_{50}Cl_{10}O_8P_4Pd_2$: C, 42.68; H, 3.29%; IR: $\nu_{Pd-Cl-Pd}$: 290, 270 cm^{-1}.

X-ray Diffraction Analysis

A greenish yellow blocky crystal of $[(Ph_2PCH_2CH_2PPh_2)Pd(Cl)]_2(ClO_4)_2\cdot 2CHCl_3$ (**1**) was mounted on a glass fibre with epoxy glue. Data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated MoKα radiation using a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from 19 carefully

TABLE I Crystallographic data for $[(PPh_2CH_2CH_2PPh_2)PdCl]_2[ClO_4]_2 \cdot 2CHCl_3$ 1

Formula	$C_{54}H_{50}O_8P_4Cl_{10}Pd_2$
M	1518.21
Space group	$P\bar{1}$
a/Å	12.744(4)
b/Å	14.068(5)
c/Å	10.542(3)
α/°	109.19(3)
β/°	94.51(3)
γ/°	115.64(3)
U/Å^3	1554(1)
Z	1
D_c/g cm^{-3}	1.62
F_{000}	760.00
μ(MoKα)/mm^{-1}	1.16
2θ max/°	50
Reflections	$+h$, $\pm k$, $\pm l$,
measured	5752
observed $[F_o^2 \geq 3\sigma(F_o)^2]$, N_o	2653
R^a	0.063
R'^b	0.055
Goodness of fit,$^c S$	1.61

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$.
[c] $S = [\Sigma(|F_o| - |F_c|)/\sigma]/(N_o - N_p)$.

centred reflections in range $8.47 < 2\theta < 14.72°$, corresponded to a primitive triclinic cell whose dimensions are given in Table I together with other experimental parameters. On the basis of statistical analyses of intensity distributions and successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$.

The data were collected at a temperature of 23 ± 1°C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.20° with a take-off angle of 6.0°. Scans were made at a speed of 32.0° min^{-1} (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum 4 scans) and the counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1.

A total of 3227 unique reflections was collected. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout the data collection thus indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.88 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[10] All non-hydrogen atoms other than carbon were refined anisotropically. Hydrogen atoms were included in their idealized positions with C-H set at 0.95. The isotropic thermal parameters of all hydrogen atoms were set at 1.2 times that of the atom to which they were attached. The final cycle of full-matrix least-squares refinement[11] was based on 2653 observed reflections ($I > 3.00\sigma(I)$) and 217 variable parameters and converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors of $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.063$ and $R' = [(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2} = 0.055$.

The standard deviation of an observation of unit weight[12] was 1.61. The weighting scheme was based on counting statistics and included a factor ($p = 0.002$) to downweight the intense reflections. Plots of $\Sigma w(|F_o|-|F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.92 and $-0.72\,e\,\text{Å}^{-3}$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were included in the calculations,[14] the values for $\Delta f'$ and $\Delta f''$ being those of Creagh and McAuley.[15] All calculations were performed using the TEXASAN[16] crystallographic software package of the Molecular Structure Corporation.

RESULTS AND DISCUSSION

We have a continuing interest in designing hybrid organotellurium ligands and studying their complexation behaviour.[17–20] As a part of this programme we planned to synthesize a (Te, S_2) ligand (**L**) by a reaction given in (1), as only one (Te, S) ligand is known so far[21] and recently the *trans* influence of ArTe has been shown to be somewhat greater than that of SMe on the basis of Pt–Cl bond lengths observed in the crystal structure of $[(ArTeCH_2CH_2SMe)Cl_2Pt(II)]$.[22] The ligand **L**, an orange yellow viscous liquid, was not stable beyond a few hours and it was thus reacted with $[(dppe)Cl_2Pd]$ in the presence of $AgClO_4$ so that it could

$$\text{Te} \xrightarrow[\text{NaOH}]{\text{NaBH}_4} \text{Na}_2\text{Te} \xrightarrow{\text{ClCH}_2\text{CH}_2\text{SPh}} \text{PhSCH}_2\text{CH}_2\text{TeCH}_2\text{CH}_2\text{SPh} \qquad (1)$$

be stabilized. From this reaction mixture we isolated **1** in place of the desired complex. The complex **1** was later synthesized independently by the procedure given in the experimental section, which is very simple and may be adopted for designing binuclear complexes in general.

TABLE II Atomic coordinates and *B*(eq) values for the non-hydrogen atoms in $[(PPh_2CH_2CH_2PPh_2)PdCl]_2[ClO_4]_2 \cdot 2CHCl_3$ **1**

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Pd(1)	0.64775(8)	0.60267(8)	0.1007(1)	2.47(3)
Cl(1)	0.4609(3)	0.4837(3)	0.1407(3)	4.0(1)
Cl(2)	0.5434(5)	0.2531(4)	−0.0741(6)	10.5(3)
Cl(3)	0.6360(5)	0.1301(4)	0.0254(5)	9.7(2)
Cl(4)	0.6518(5)	0.1363(4)	−0.2408(6)	10.2(2)
Cl(5)	1.2045(4)	0.8767(4)	0.6012(5)	6.6(2)
P(1)	0.7431(3)	0.6903(3)	0.3269(3)	2.7(1)
P(2)	0.8300(3)	0.7055(3)	0.0710(3)	2.9(1)
O(1)	1.136(1)	0.931(1)	0.610(1)	10.5(6)
O(2)	1.167(1)	0.794(1)	0.466(1)	11.3(6)
O(3)	1.325(1)	0.959(1)	0.648(2)	14.9(9)
O(4)	1.181(1)	0.819(1)	0.690(1)	13.3(8)
C(1)	0.652(1)	0.725(1)	0.435(1)	3.7(3)
C(2)	0.628(1)	0.811(1)	0.432(1)	5.0(3)
C(3)	0.551(1)	0.836(1)	0.511(2)	6.5(4)
C(4)	0.506(1)	0.780(1)	0.590(2)	7.1(4)
C(5)	0.531(2)	0.694(2)	0.598(2)	9.6(6)
C(6)	0.605(1)	0.666(1)	0.517(2)	5.7(3)
C(7)	0.786(1)	0.5993(9)	0.380(1)	2.6(2)
C(8)	0.737(1)	0.485(1)	0.297(1)	3.0(2)
C(9)	0.767(1)	0.414(1)	0.343(1)	3.8(3)
C(10)	0.842(1)	0.458(1)	0.470(1)	4.1(3)
C(11)	0.898(1)	0.577(1)	0.552(1)	4.9(3)
C(12)	0.869(1)	0.647(1)	0.507(1)	4.2(3)
C(13)	0.879(1)	0.823(1)	0.355(1)	3.6(3)
C(14)	0.940(1)	0.795(1)	0.240(1)	3.6(3)
C(15)	0.824(1)	0.797(1)	−0.010(1)	3.2(2)
C(16)	0.869(1)	0.804(1)	−0.118(2)	7.6(4)
C(17)	0.864(2)	0.882(2)	−0.176(2)	9.4(5)
C(18)	0.815(1)	0.946(1)	−0.126(2)	6.2(4)
C(19)	0.780(2)	0.946(2)	−0.017(2)	10.6(6)
C(20)	0.784(2)	0.868(2)	0.044(2)	9.9(6)
C(21)	0.890(1)	0.620(1)	−0.031(1)	3.0(2)
C(22)	1.011(1)	0.667(1)	−0.022(1)	4.3(3)
C(23)	1.054(1)	0.600(1)	−0.098(1)	4.7(3)
C(24)	0.983(1)	0.491(1)	−0.187(1)	4.1(3)
C(25)	0.860(1)	0.440(1)	−0.203(1)	4.4(3)
C(26)	0.814(1)	0.505(1)	−0.123(1)	4.0(3)
C(27)	0.567(1)	0.136(1)	−0.119(2)	6.9(4)

The binuclear complex **1** is soluble in methanol, ethanol, DMF and DMSO. Crystals were grown containing two molecules of chloroform. The final coordinates of the non-hydrogen atoms are given in Table II, important bond distances and angles in Table III and an ORTEP diagram is shown in Figure 1. Additional material comprising H-atom coordinates, thermal parameters and observed and calculated structure factors are available from the authors upon request.

TABLE III Bondlengths (Å) and angles (°) for $[(PPh_2CH_2CH_2PPh_2)PdCl]_2[ClO_4]_2 \cdot 2CHCl_3$ **1**[a]

Pd(1)-Cl(1)	2.414(3)	Pd(1)-Cl(1)′	2.413(3)
Pd(1)-P(1)	2.236(3)	Pd(1)-P(2)	2.256(3)
P(1)-C(13)	1.82(1)	P(2)-C(14)	1.83(1)
P(1)-C(1)	1.80(1)	P(2)-C(15)	1.78(1)
P(1)-C(7)	1.81(1)	P(2)-C(21)	1.80(1)
C(1)-C(6) ring	1.39(4) av.	C(15)-C(20) ring	1.35(7) av.
C(7)-C(12) ring	1.38(2) av.	C(21)-C(26) ring	1.37(2) av.
C(13)-C(14)	1.52(2)	Cl(2)-C(27)	1.73(2)
Cl(2)-C(28)	1.74(2)	Cl(2)-C(29)	1.74(2)
Cl(5)-O(1)	1.37(1)	Cl(5)-O(2)	1.39(1)
Cl(5)-O(3)	1.38(1)	Cl(5)-O(4)	1.40(1)
Cl(1)-Pd(1)-P(1)	92.7(1)	Cl(1)-Pd(1)-P(2)	174.6(1)
Cl(1)′-Pd(1)-P(2)	96.0(1)	Cl(1)′-Pd(1)-P(1)	176.3(1)
P(1)-Pd(1)-P(2)	84.9(1)	Cl(1)-Pd(1)-Cl(1)′	86.7(1)
Pd(1)-Cl(1)-Pd(1)′	93.3(1)	Pd(1)-P(2)-C(14)	109.5(4)
Pd(1)-P(1)-C(13)	108.1(4)	Pd(1)-P(2)-C(15)	110.5(4)
Pd(1)-P(1)-C(1)	112.5(4)	Pd(1)-P(2)-C(21)	114.7(4)
Pd(1)-P(1)-C(7)	110.6(4)	P(2)-C(14)-C(13)	110.6(8)
P(1)-C(13)-C(14)	108.0(5)	C(14)-P(2)-C(15)	108.6(5)
C(13)-P(1)-C(1)	108.9(5)	C(14)-P(2)-C(21)	105.5(5)
C(13)-P(1)-C(7)	108.7(5)	C(15)-P(2)-C(21)	107.8(5)
C(1)-P(1)-C(7)	108.2(5)	P(2)-C(15)-C(16)	124(1)
P(1)-C(1)-C(2)	118(1)	P(2)-C(15)-C(20)	120(1)
P(1)-C(1)-C(6)	121(1)	P(2)-C(21)-C(22)	120.4(9)
P(1)-C(7)-C(8)	120.7(9)	P(2)-C(21)-C(26)	121.0(9)
P(1)-C(7)-C(12)	119.3(9)	C(16)-C(15)-C(20) ring	120(3) av.
C(2)-C(1)-C(6) ring	120(2) av.	C(22)-C(21)-C(26) ring	120(2) av.
C(8)-C(7)-C(12) ring	120.0(5) av.	O(1)-Cl(5)-O(3)	109.2(9)
O(1)-Cl(5)-O(2)	108.1(8)	O(2)-Cl(5)-O(3)	116(1)
O(1)-Cl(5)-O(4)	109(1)	O(3)-Cl(5)-O(4)	107.3(9)
O(2)-Cl(5)-O(4)	107.6(9)	Cl(2)-C(27)-Cl(4)	110.7(9)
Cl(2)-C(27)-Cl(3)	111.8(9)	Cl(3)-C(27)-Cl(4)	110.0(9)

[a] Symmetry equivalent position $(1-x, 1-y, -z)$ denoted by primes.

The immediate environment about palladium in **1** is a slightly distorted square plane. Pd–P bond distances are of the same order as reported for $[(dppe)PdCl_2]$ (2.226–2.233 Å)[4–5] and other complexes containing dppe as a ligand.[23] The P–Pd–P bond angle in the present complex is also close to that of monomeric $[(dppe)PdCl_2]$ (85.82°).[4] Pd–Cl bridges are symmetrical and bondlengths lie within the range (2.33–2.53 Å)[24–27] known for various unstrained Pd–Cl bridges. In strained bridges Pd–Cl bond lengths up to 2.94 Å are known.[27] Bond angles/lengths of the phenyl rings are normal. Two chloroform molecules are present in the lattice of **1** and have no significant interaction with the complex molecule. The $Pd(\mu\text{-}Cl)_2Pd$ system gives bands in the IR spectrum at 290 and 270 cm^{-1} as reported earlier.[28]

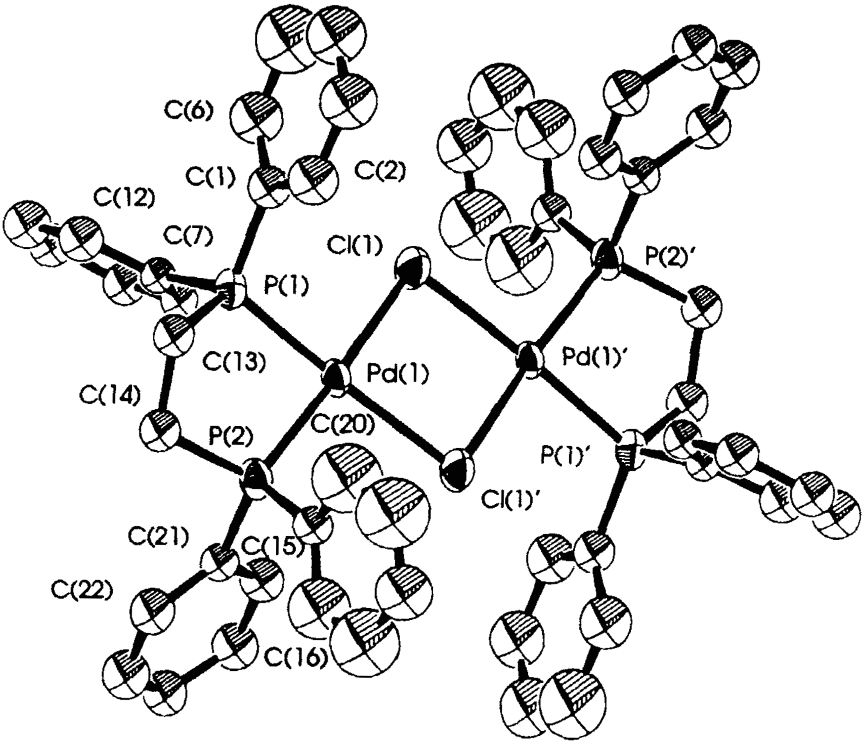

FIGURE 1 ORTEP plot of the molecule $[(Ph_2PCH_2CH_2PPh_2)PdCl]_2(ClO_4)_2\cdot 2CHCl_3$ (**1**). Atoms are drawn with 30% probability ellipsoids and hydrogen atoms are omitted for clarity.

Acknowledgements

The authors (AKS and JSK) thank the Department of Science and Technology (India) for financial support.

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[11] Least-squares: Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ where $w=4F_o^2(F_o^2)$, $\sigma 2(F_o^2)=[S^2(C+R^2B)+(pF_o^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, Lp = Lorenz polarization factor, and $p=p$ factor.

[12] Standard deviation of an observation of unit weight: $[\Sigma w(|\mathrm{F}_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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