Crystal structure of dichloro(3-methylthio-2-methylpropyl)diphenylphosphine-palladium(II) — dichloromethane (1:1), $\text{Pd}(\text{C}_{17}\text{H}_{21}\text{PS})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$

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Abstract

$\text{C}_{18}\text{H}_{23}\text{Cl}_4\text{PPdS}$, monoclinic, $P12_1/n1$ (No. 14), $a = 11.8279(1) \text{ \AA}$, $b = 14.6142(2) \text{ \AA}$, $c = 12.4063(1) \text{ \AA}$, $\beta = 93.876(1)^\circ$, $V = 2139.6 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.021$, $wR_{\text{ref}}(F^2) = 0.049$, $T = 120 \text{ K}$.

Source of material

Dichloro[3-methylthio-2-methylpropyl]diphenylphosphine-palladium(II) dichloromethane, $\text{C}_{18}\text{H}_{23}\text{Cl}_4\text{PPdS}$ was prepared by adding a sample of the ligand (1.5 mmol) to a filtered solution of $[\text{PdCl}_2(\text{PhCN})_2]$ (0.59 g, 1.5 mmol) in benzene (50 ml). The mixture was stirred at room temperature for 2 h. During that time, solution changed its color from red-brown to bright yellow, and a yellow precipitate was formed. Solvent was removed under reduced pressure till a volume of about 25 ml. The yellow precipitate was collected and dried under vacuum at 323 K (yield 88%, mp 519 K, dec.). Recrystallization was made from dichloromethane/diethylether.

Discussion

In the last two decades many Pd(II)-based catalysts were successfully utilized in the synthesis of alternating aliphatic polyketones [1–3]. The mechanism for the copolymer chain growth involves migratory CO insertion into Pd-alkyl bond of the growing polymer chain, followed by migratory alkene insertion into the resulting Pd-acyl bond [4]. These steps depend on the relative stability of the complex and complex intermediates, which are directly affected by the donor/acceptor ability of the coordinating ligands. Recently, some palladium(II) complexes with phosphorus-sulfur mixed-donor bidentate ligands have shown catalytic activity towards cyclic olefin polymerization [5]. We have synthesized a new palladium(II) complex containing a phosphorus-sulfur mixed donor ligand with a propylene backbone, $[\text{PdCl}_2(\text{C}_{17}\text{H}_{21}\text{PS})] \cdot \text{CH}_2\text{Cl}_2$, that enhances its ability to form five coordinated species as compared with similar ligands having ethylene backbone [5]. The complex is a non-electrolyte as shown by its molar conductivity in nitromethane ($M = 4.6 \text{ S cm}^2 \text{ mol}^{-1}$). The palladium atom is at the center of an approximately square-planar arrangement formed by two chlorine, phosphorus and sulfur atoms forming a 6-membered chelate ring. The metal-chlorine distances of 2.3926(5) Å for Pd—Cl1 and 2.3148(5) Å for Pd—Cl2 are in harmony with the greater trans influence of P versus S atom. This is consistent with previous observations on the relationship between the length of Pd—Cl bonds and the trans influence of P and S atoms [5].

Table 1. Data collection and handling.

Crystal:	yellow, irregular fragment, size $0.30 \times 0.30 \times 0.30 \text{ mm}$
Wavelength:	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	15.40 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ
$2\theta_{\text{max}}$:	51.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	32534, 4197
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3905
$N(\text{param})_{\text{refined}}$:	228
Programs:	SHELX-97 [6], ORTEP3 [7]

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	4e	0.9078	0.3600	0.2470	0.017
H(1B)	4e	0.8221	0.2764	0.2313	0.017
H(2)	4e	0.6741	0.3690	0.2940	0.017
H(3A)	4e	0.7047	0.5312	0.2993	0.018
H(3B)	4e	0.8369	0.5143	0.2917	0.018
H(4A)	4e	0.7834	0.4449	0.1140	0.033
H(4B)	4e	0.6518	0.4570	0.1332	0.033
H(4C)	4e	0.7006	0.3583	0.1055	0.033
H(5A)	4e	0.5926	0.4739	0.4712	0.032
H(5B)	4e	0.6546	0.4414	0.5833	0.032
H(5C)	4e	0.6532	0.3760	0.4798	0.032
H(6A)	4e	0.2732	0.3111	0.4789	0.033

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(6B)	4e	0.3570	0.2273	0.4603	0.033
H(12)	4e	1.1024	0.3062	0.3187	0.022
H(13)	4e	1.2386	0.2044	0.2636	0.025
H(14)	4e	1.2221	0.0479	0.2953	0.025
H(15)	4e	1.0657	−0.0078	0.3803	0.027
H(16)	4e	0.9255	0.0928	0.4314	0.022
H(22)	4e	0.8402	0.2094	0.6131	0.017
H(23)	4e	0.7005	0.1134	0.6752	0.022
H(24)	4e	0.5484	0.0664	0.5577	0.025
H(25)	4e	0.5388	0.1111	0.3770	0.024
H(26)	4e	0.6803	0.2044	0.3126	0.020

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Pd	4e	0.92427(1)	0.393988(9)	0.53822(1)	0.01100(8)	0.01007(8)	0.01057(8)	−0.00006(5)	−0.00004(5)	−0.00131(5)
Cl(1)	4e	0.93086(4)	0.49546(3)	0.68985(4)	0.0164(2)	0.0179(2)	0.0160(2)	−0.0011(2)	0.0015(2)	−0.0070(2)
Cl(2)	4e	1.06395(4)	0.30000(3)	0.61723(4)	0.0218(2)	0.0186(2)	0.0173(2)	0.0057(2)	−0.0078(2)	−0.0020(2)
Cl(3)	4e	0.43760(5)	0.32658(4)	0.58631(4)	0.0270(3)	0.0336(3)	0.0225(3)	−0.0044(2)	0.0010(2)	0.0083(2)
Cl(4)	4e	0.39897(5)	0.34913(5)	0.35277(5)	0.0397(3)	0.0444(4)	0.0216(3)	−0.0100(3)	−0.0017(2)	0.0030(2)
P(1)	4e	0.88710(4)	0.28840(3)	0.41114(4)	0.0121(2)	0.0092(2)	0.0095(2)	0.0003(2)	−0.0002(2)	0.0001(2)
S(1)	4e	0.78754(4)	0.49073(3)	0.46650(4)	0.0142(2)	0.0137(2)	0.0166(2)	0.0030(2)	0.0014(2)	−0.0002(2)
C(1)	4e	0.8417(2)	0.3303(1)	0.2771(2)	0.0153(9)	0.0147(9)	0.0123(9)	0.0006(7)	0.0015(7)	0.0009(7)
C(2)	4e	0.7423(2)	0.3973(1)	0.2641(2)	0.0129(9)	0.0133(9)	0.017(1)	0.0000(7)	−0.0011(7)	0.0024(7)
C(3)	4e	0.7676(2)	0.4889(1)	0.3207(2)	0.0149(9)	0.0148(9)	0.016(1)	0.0024(7)	0.0000(7)	0.0031(7)
C(4)	4e	0.7173(2)	0.4161(1)	0.1433(2)	0.028(1)	0.017(1)	0.020(1)	−0.0011(8)	−0.0062(9)	0.0032(8)
C(5)	4e	0.6571(2)	0.4397(2)	0.5046(2)	0.015(1)	0.025(1)	0.025(1)	0.0020(8)	0.0067(8)	0.0021(8)
C(6)	4e	0.3531(2)	0.2945(2)	0.4697(2)	0.028(1)	0.026(1)	0.028(1)	−0.0043(9)	0.0025(9)	0.0000(9)
C(11)	4e	0.9993(2)	0.2095(1)	0.3799(1)	0.0136(9)	0.0134(9)	0.0099(9)	0.0020(7)	−0.0014(7)	−0.0009(7)
C(12)	4e	1.0939(2)	0.2424(1)	0.3305(2)	0.018(1)	0.014(1)	0.023(1)	−0.0004(8)	0.0029(8)	0.0016(8)
C(13)	4e	1.1752(2)	0.1818(2)	0.2985(2)	0.016(1)	0.024(1)	0.023(1)	0.0012(8)	0.0050(8)	0.0012(8)
C(14)	4e	1.1655(2)	0.0888(1)	0.3169(2)	0.020(1)	0.022(1)	0.020(1)	0.0079(8)	0.0029(8)	−0.0012(8)
C(15)	4e	1.0726(2)	0.0559(1)	0.3670(2)	0.027(1)	0.013(1)	0.028(1)	0.0044(8)	0.0063(9)	0.0007(8)
C(16)	4e	0.9895(2)	0.1158(1)	0.3979(2)	0.019(1)	0.015(1)	0.021(1)	0.0015(8)	0.0048(8)	0.0012(8)
C(21)	4e	0.7743(2)	0.2165(1)	0.4567(2)	0.0130(9)	0.0083(9)	0.0143(9)	0.0004(7)	0.0020(7)	−0.0013(7)
C(22)	4e	0.7795(2)	0.1892(1)	0.5648(2)	0.0155(9)	0.0136(9)	0.0138(9)	0.0008(7)	0.0006(7)	−0.0011(7)
C(23)	4e	0.6961(2)	0.1327(1)	0.6019(2)	0.024(1)	0.016(1)	0.015(1)	0.0003(8)	0.0060(8)	0.0010(7)
C(24)	4e	0.6060(2)	0.1042(1)	0.5319(2)	0.020(1)	0.014(1)	0.028(1)	−0.0049(8)	0.0085(9)	−0.0010(8)
C(25)	4e	0.6002(2)	0.1309(1)	0.4246(2)	0.017(1)	0.019(1)	0.025(1)	−0.0031(8)	−0.0016(8)	−0.0043(8)
C(26)	4e	0.6841(2)	0.1866(1)	0.3864(2)	0.019(1)	0.0139(9)	0.016(1)	0.0002(8)	−0.0013(8)	−0.0004(7)

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