Crystal structure of diiodo[(+)-1,2-bis((2*S*,5*S*)-2,5-dimethylphospholano)benzene-*P,P'*]nickel, $C_{18}H_{28}I_2NiP_2$

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Table 1. Data collection and handling.

Crystal:	dark violet needle, size 0.10 x 0.12 x 0.80 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	37.06 cm ⁻¹
Diffractometer, scan mode:	Enraf Nonius CAD4, ω
$2\theta_{\max}$:	50.1°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	2294, 2071
Criterion for I_{obs} , $N(hkl)_{\text{gi}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1705
$N(\text{param})_{\text{refined}}$:	208
Programs:	XCAD4 [2], SHELXL-97 [3], DIFABS [4], ZORTEP [5]

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(1)	4a	0.2322	-0.1755	0.0495	0.040
H(2A)	4a	0.1641	-0.0907	-0.0522	0.072
H(2B)	4a	0.2520	0.0263	-0.0452	0.072
H(3A)	4a	0.3446	-0.1037	-0.1252	0.063
H(3B)	4a	0.3279	-0.2182	-0.0733	0.063
H(4)	4a	0.4843	-0.0142	-0.0534	0.045
H(5A)	4a	0.5697	-0.2579	-0.0450	0.081
H(5B)	4a	0.6507	-0.1366	-0.0406	0.081
H(5C)	4a	0.5865	-0.1737	-0.1134	0.081
H(6A)	4a	0.2261	0.0719	0.0923	0.089
H(6B)	4a	0.2003	-0.0444	0.1412	0.089
H(6C)	4a	0.1071	-0.0097	0.0793	0.089
H(7)	4a	0.5234	-0.0442	0.2956	0.039
H(8A)	4a	0.6335	-0.1638	0.3710	0.046
H(8B)	4a	0.6343	-0.2776	0.3175	0.046
H(9A)	4a	0.8232	-0.1858	0.3075	0.050
H(9B)	4a	0.7626	-0.0533	0.2992	0.050
H(10)	4a	0.7598	-0.2478	0.1991	0.042
H(11A)	4a	0.8375	-0.0053	0.1747	0.072
H(11B)	4a	0.8223	-0.1050	0.1136	0.072
H(11C)	4a	0.9215	-0.1248	0.1746	0.072
H(12A)	4a	0.4143	-0.2779	0.2849	0.060
H(12B)	4a	0.3479	-0.1554	0.2596	0.060
H(12C)	4a	0.3815	-0.1739	0.3411	0.060
H(14)	4a	0.3658	-0.3531	0.0103	0.037
H(15)	4a	0.4018	-0.5467	0.0579	0.041
H(16)	4a	0.5275	-0.5665	0.1565	0.038
H(17)	4a	0.6038	-0.3943	0.2133	0.035

Abstract

$C_{18}H_{28}I_2NiP_2$, tetragonal, $P4_1$ (No. 76), $a = 10.957(3)$ Å, $c = 18.948(5)$ Å, $V = 2274.8$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.039$, $R_w(F^2) = 0.074$, $T = 193$ K.

Source of material

A solution of [(+)-1,2-bis((2*S*,5*S*)-2,5-dimethylphospholano)benzene][(S,S)-Me-Duphos] (1.5 g, 4.9 mmol) in dry dichloromethane (5 ml) was added to a stirred solution of $NiI_2 \cdot 6H_2O$ (4.12 g, 9.8 mmol) in dry ethanol (70 ml). After stirring for 10 min the precipitate was filtered off, washed with cold ether and dried under reduced pressure to give $C_{18}H_{28}I_2NiP_2$ (2.5 g, 82 %) as dark violet crystals.

Discussion

$C_{18}H_{28}I_2NiP_2$ is used as highly selective catalyst in the asymmetric double-bond isomerization of 2-*tert*-butyl-4,7-dihydro-1,3-dioxepin. The nickel atom is coordinated by a square plane formed of two iodine and two phosphorus atoms like in the isostructural chlorine compound [1].

Table 3. Atomic coordinates and displacement parameters (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
I(2)	4a	0.62331(9)	0.16663(7)	0.21014(4)	0.0691(6)	0.0243(4)	0.0328(4)	−0.0109(4)	−0.0102(5)	−0.0007(4)
I(1)	4a	0.46472(9)	0.19249(7)	0.04131(5)	0.0659(6)	0.0191(4)	0.0464(5)	−0.0002(4)	−0.0193(5)	0.0043(4)
Ni	4a	0.5257(1)	0.0232(1)	0.12332(8)	0.0335(9)	0.0167(7)	0.0262(7)	−0.0012(6)	−0.0015(6)	−0.0005(6)
P(2)	4a	0.5824(3)	−0.1291(3)	0.1866(2)	0.029(2)	0.022(2)	0.025(1)	−0.005(1)	0.001(1)	0.002(1)
P(1)	4a	0.4315(3)	−0.1021(2)	0.0552(2)	0.032(2)	0.017(1)	0.025(2)	0.001(1)	−0.001(1)	0.001(1)
C(1)	4a	0.264(1)	−0.091(1)	0.0425(7)	0.024(6)	0.027(6)	0.048(7)	−0.002(5)	−0.001(6)	0.007(6)
C(2)	4a	0.246(1)	−0.063(1)	−0.0365(9)	0.07(1)	0.048(9)	0.06(1)	−0.003(8)	−0.034(9)	−0.004(9)
C(3)	4a	0.344(2)	−0.129(1)	−0.0751(7)	0.09(1)	0.034(8)	0.035(7)	−0.022(8)	−0.013(8)	−0.004(6)
C(4)	4a	0.466(1)	−0.101(1)	−0.0411(6)	0.062(8)	0.026(6)	0.024(6)	0.004(6)	0.006(7)	−0.003(6)
C(5)	4a	0.578(1)	−0.174(1)	−0.0619(7)	0.08(1)	0.048(9)	0.037(8)	0.010(8)	0.027(7)	−0.001(7)
C(6)	4a	0.193(1)	−0.011(1)	0.0933(8)	0.040(8)	0.06(1)	0.08(1)	0.013(8)	0.003(8)	−0.007(9)
C(7)	4a	0.530(1)	−0.131(1)	0.2800(5)	0.062(8)	0.021(6)	0.016(6)	0.005(6)	0.006(6)	−0.004(5)
C(8)	4a	0.637(1)	−0.188(1)	0.3206(6)	0.047(8)	0.040(7)	0.027(6)	−0.010(6)	−0.002(6)	0.006(6)
C(9)	4a	0.752(1)	−0.141(1)	0.2881(7)	0.048(8)	0.037(7)	0.040(7)	0.010(6)	−0.016(7)	−0.003(6)
C(10)	4a	0.746(1)	−0.159(1)	0.2077(7)	0.027(6)	0.039(7)	0.038(6)	−0.003(6)	−0.001(6)	0.006(6)
C(11)	4a	0.840(1)	−0.093(1)	0.1638(8)	0.034(8)	0.042(8)	0.07(1)	−0.008(6)	0.012(7)	−0.010(7)
C(12)	4a	0.408(1)	−0.190(1)	0.2925(7)	0.031(6)	0.043(7)	0.045(7)	−0.002(6)	0.016(7)	0.003(7)
C(13)	4a	0.458(1)	−0.257(1)	0.0863(6)	0.030(6)	0.018(6)	0.031(6)	−0.006(5)	0.007(5)	0.004(5)
C(14)	4a	0.413(1)	−0.361(1)	0.0523(7)	0.034(7)	0.025(6)	0.034(6)	0.000(5)	0.005(6)	−0.014(6)
C(15)	4a	0.436(1)	−0.476(1)	0.0796(7)	0.024(7)	0.032(7)	0.046(8)	0.000(5)	−0.002(6)	−0.007(6)
C(16)	4a	0.509(1)	−0.488(1)	0.1388(6)	0.039(7)	0.015(6)	0.041(7)	−0.003(5)	0.019(6)	−0.001(5)
C(17)	4a	0.554(1)	−0.386(1)	0.1725(6)	0.026(6)	0.030(7)	0.030(6)	0.009(5)	−0.013(5)	0.007(5)
C(18)	4a	0.528(1)	−0.270(1)	0.1464(6)	0.030(6)	0.023(6)	0.030(6)	0.000(5)	−0.001(5)	−0.002(5)

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