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Crystal structure of (acetylferrocene oxime-κ^2C^6,N)chloro-(2-dicyclohexylphosphanyl-2′-(*N*,*N*-dimethylamino)biphenyl-κP)-palladium(II), $PdCl[(C_7H_7NO)Fe(C_5H_5)][P(C_6H_{11})_2(C_{14}H_{14}N)]$

Hong Li*,[I], Hong-Mei Li[II], Jun-Ling Si[I], Duo-Bin Mao[I] and Yu-Qing Zhang[II]

[I] Zhengzhou University of Light Industry, School of Food and Biological Engineering, Zhengzhou 450002, P. R. China
[II] Henan University of Science and Technology, Chemical Engineering and Pharmaceutics School, Luoyang 471003, P. R. China

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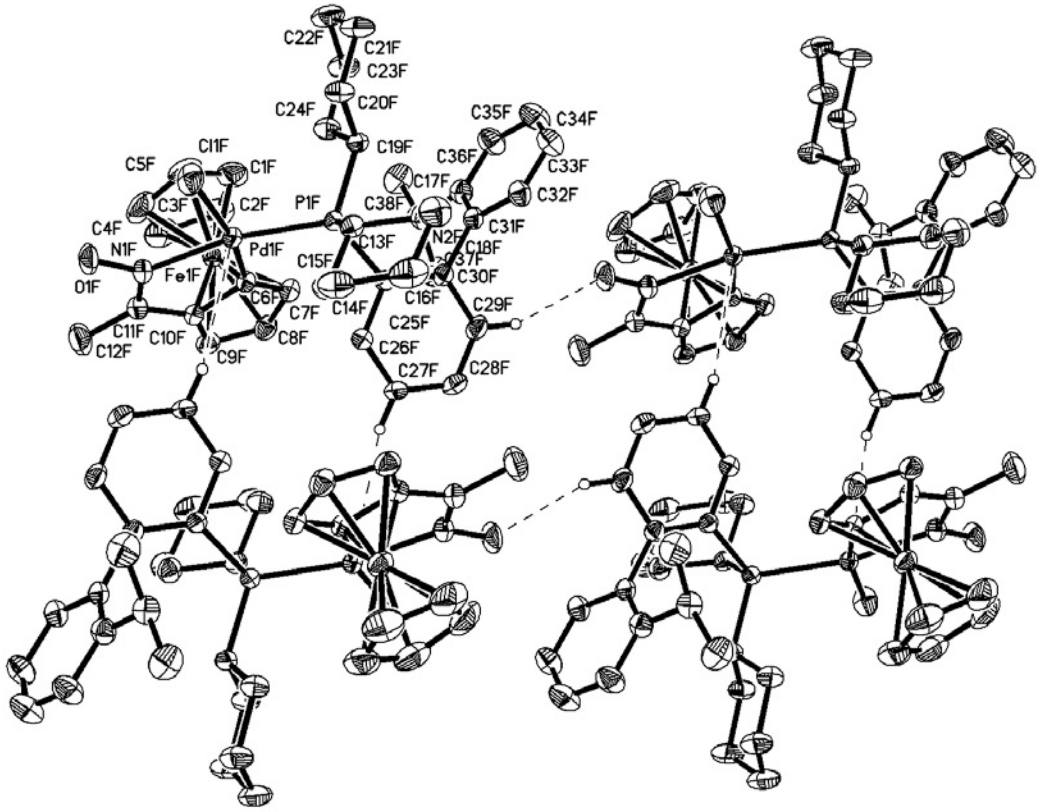

Abstract

$C_{38}H_{48}ClFeN_2OPPd$, monoclinic, $P2_1/c$ (no. 14), a = 18.378(4) Å, b = 11.744(2) Å, c = 18.808(4) Å, β = 115.89(3)°, V = 3652.1 Å^3, Z = 4, $R_{gf}(F)$ = 0.047, $wR_{ref}(F^2)$ = 0.119, T = 291 K.

Source of material

The title compound was prepared as described in literature [1], using 2-dicyclohexylphosphanyl-2′-(*N*,*N*-dimethylamino)-biphenyl instead of triphenylphosphine and recrystallized from dichloromethane/petroleum ether solution at room temperature to give the desired crystals suitable for single crystal X-ray diffraction experiment.

Experimental details

Hydrogen atom bound to oxygen was found in difference Fourier map and refined freely. The hydrogen atoms bound to C atoms were placed geometrically at idealized positions and treated as riding with d(C—H) = 0.93 - 0.96 Å, and with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C_{methyl}).

Discussion

The chemistry of cyclopalladated compounds has developed into one of the most fruitful fields in organometallic chemistry [2,3]. Palladacyclic catalysts are among the most active catalysts for coupling reactions and have attracted much attention owning to their availability, facile modification, insensitivity to air or moisture and easy handling [4-6]. Among them, the cyclopalladated oxime-derived catalysts are air and water stable effective precatalysts for a wide range of useful and well-known coupling processes such as Heck and Suzuki reactions in aqueous media [7,8].

* Correspondence author (e-mail: lihong@zzuli.edu.cn)

The title compound is *trans* complexes in the solid state. The Pd atom is in a slightly distorted square-planar environment bonded to the phosphorus atom, the chloride atom, the nitrogen atom and the carbon atom of the ferrocenyl moiety. The bicyclic system formed by the palladacycle and the C_5H_3 moiety is approximately coplanar (dihedral angle is 6.4°). The bond lengths Pd—P [2.260(1) Å] and Pd—N [2.114(3) Å] in the title complex are similar to those of the related adducts [5,6]. In the crystal there are two types of intermolecular hydrogen bonds. One hydrogen bond (C–H···O = 2.611 Å) is between the oxygen atom and the adjacent C–H group of the benzene ring like in the related P(cyclohexyl)$_3$ adducts [9]. However, the chlorine atom does not participate in hydrogen bonding. The other hydrogen bond is C–H···M type (d(Pd···H) = 3.087 Å) [5,10], which contribute to the construction of the two-dimensional layers in the title crystal structure.

Table 1. Data collection and handling.

Crystal:	red prism, size 0.19 × 0.23 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.05 cm^{-1}
Diffractometer, scan mode:	R-AXIS-IV CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12151, 6970
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6176
$N(param)_{refined}$:	411
Programs:	SHELXS-97 [11], SHELXL-97 [12]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.0674	0.5310	0.8654	0.098
H(2A)	4*e*	0.0813	0.5133	1.0071	0.104
H(3A)	4*e*	0.1271	0.3105	1.0563	0.107
H(4A)	4*e*	0.1435	0.2037	0.9449	0.108
H(5A)	4*e*	0.1062	0.3393	0.8267	0.099
H(7A)	4*e*	0.2616	0.6240	0.9506	0.050
H(8A)	4*e*	0.2786	0.5788	1.0906	0.061
H(9A)	4*e*	0.3205	0.3695	1.1216	0.060
H(12A)	4*e*	0.3452	0.0796	1.0116	0.114
H(12B)	4*e*	0.2984	0.1400	1.0536	0.114
H(12C)	4*e*	0.3913	0.1612	1.0834	0.114
H(13A)	4*e*	0.3471	0.5127	0.7046	0.047
H(14A)	4*e*	0.4879	0.5576	0.8449	0.061
H(14B)	4*e*	0.4503	0.4357	0.8198	0.061
H(15A)	4*e*	0.5563	0.4629	0.7830	0.078
H(15B)	4*e*	0.4746	0.4400	0.7082	0.078
H(16A)	4*e*	0.5381	0.5915	0.6801	0.091
H(16B)	4*e*	0.5470	0.6561	0.7566	0.091
H(17A)	4*e*	0.4384	0.7366	0.6490	0.079
H(17B)	4*e*	0.3981	0.6167	0.6216	0.079
H(18A)	4*e*	0.3316	0.7109	0.6850	0.063
H(18B)	4*e*	0.4137	0.7300	0.7603	0.063
H(19A)	4*e*	0.2088	0.6978	0.7170	0.046
H(20A)	4*e*	0.2264	0.5802	0.6248	0.062
H(20B)	4*e*	0.1872	0.4771	0.6485	0.062
H(21A)	4*e*	0.1031	0.6784	0.5735	0.083
H(21B)	4*e*	0.0899	0.5591	0.5322	0.083
H(22A)	4*e*	0.0332	0.4881	0.6116	0.086
H(22B)	4*e*	–0.0138	0.5988	0.5696	0.086
H(23A)	4*e*	0.0173	0.5999	0.7059	0.077
H(23B)	4*e*	0.0556	0.7054	0.6836	0.077
H(24A)	4*e*	0.1414	0.5058	0.7594	0.062
H(24B)	4*e*	0.1536	0.6259	0.7995	0.062
H(26A)	4*e*	0.4332	0.5564	0.9428	0.047
H(27A)	4*e*	0.5254	0.6725	1.0378	0.055
H(28A)	4*e*	0.5067	0.8679	1.0278	0.061
H(29A)	4*e*	0.3920	0.9425	0.9294	0.060
H(32A)	4*e*	0.3231	0.9187	0.7520	0.058
H(33A)	4*e*	0.2149	1.0218	0.6620	0.076
H(34A)	4*e*	0.0940	1.0236	0.6710	0.092
H(35A)	4*e*	0.0810	0.9276	0.7711	0.076
H(37A)	4*e*	0.2885	0.8670	0.9729	0.110
H(37B)	4*e*	0.2344	0.8035	1.0055	0.110
H(37C)	4*e*	0.2113	0.9267	0.9708	0.110
H(38A)	4*e*	0.0717	0.7575	0.8253	0.108
H(38B)	4*e*	0.0803	0.8598	0.8820	0.108
H(38C)	4*e*	0.1038	0.7364	0.9163	0.108
H(1E)	4*e*	0.311(4)	0.151(6)	0.837(4)	0.10(2)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4*e*	0.29972(2)	0.39309(2)	0.84725(2)	0.0374(2)	0.0293(2)	0.0381(2)	–0.0008(1)	0.0143(1)	–0.0025(1)
Fe(1)	4*e*	0.20090(3)	0.42076(5)	0.97538(4)	0.0429(3)	0.0525(4)	0.0483(3)	–0.0104(3)	0.0206(3)	–0.0015(3)
Cl(1)	4*e*	0.29656(8)	0.2858(1)	0.73692(7)	0.0946(9)	0.0457(6)	0.0599(7)	0.0016(6)	0.0408(6)	–0.0133(5)
P(1)	4*e*	0.30609(5)	0.56781(8)	0.79994(5)	0.0325(4)	0.0313(5)	0.0317(4)	–0.0009(3)	0.0118(4)	–0.0009(4)
O(1)	4*e*	0.3208(2)	0.1326(3)	0.8832(2)	0.099(3)	0.026(1)	0.068(2)	0.006(2)	0.030(2)	–0.002(2)
N(1)	4*e*	0.3145(2)	0.2397(3)	0.9110(2)	0.053(2)	0.031(2)	0.052(2)	0.001(1)	0.018(2)	–0.000(1)
N(2)	4*e*	0.1857(2)	0.8075(3)	0.8877(2)	0.054(2)	0.052(2)	0.054(2)	0.002(2)	0.031(2)	–0.002(2)
C(1)	4*e*	0.0843(3)	0.4627(6)	0.8986(4)	0.042(3)	0.101(5)	0.086(4)	–0.004(3)	0.014(3)	0.011(4)
C(2)	4*e*	0.0919(3)	0.4526(7)	0.9770(4)	0.055(3)	0.121(6)	0.095(4)	–0.009(3)	0.043(3)	–0.014(4)
C(3)	4*e*	0.1174(3)	0.3415(7)	1.0045(4)	0.067(3)	0.125(6)	0.084(4)	–0.035(4)	0.041(3)	0.008(4)
C(4)	4*e*	0.1262(3)	0.2831(6)	0.9428(5)	0.062(3)	0.074(4)	0.127(6)	–0.034(3)	0.034(4)	–0.014(4)
C(5)	4*e*	0.1060(3)	0.3579(6)	0.8775(4)	0.058(3)	0.111(5)	0.070(3)	–0.035(3)	0.021(3)	–0.015(3)
C(6)	4*e*	0.2954(2)	0.4503(3)	0.9450(2)	0.036(2)	0.033(2)	0.043(2)	–0.005(2)	0.015(2)	0.001(2)
C(7)	4*e*	0.2781(2)	0.5505(3)	0.9775(2)	0.049(2)	0.037(2)	0.043(2)	–0.006(2)	0.025(2)	–0.004(2)
C(8)	4*e*	0.2872(3)	0.5251(4)	1.0551(2)	0.061(3)	0.049(2)	0.046(2)	–0.011(2)	0.027(2)	–0.009(2)
C(9)	4*e*	0.3096(3)	0.4094(4)	1.0722(2)	0.053(2)	0.057(3)	0.037(2)	–0.014(2)	0.015(2)	–0.001(2)
C(10)	4*e*	0.3137(2)	0.3619(3)	1.0039(2)	0.041(2)	0.037(2)	0.043(2)	–0.006(2)	0.012(2)	0.004(2)
C(11)	4*e*	0.3232(2)	0.2462(3)	0.9823(2)	0.048(2)	0.040(2)	0.048(2)	–0.004(2)	0.017(2)	0.006(2)
C(12)	4*e*	0.3411(4)	0.1480(4)	1.0376(3)	0.102(4)	0.050(3)	0.075(3)	0.003(3)	0.037(3)	0.019(3)
C(13)	4*e*	0.3738(2)	0.5627(3)	0.7505(2)	0.037(2)	0.043(2)	0.039(2)	–0.002(2)	0.017(2)	–0.003(2)
C(14)	4*e*	0.4571(2)	0.5091(4)	0.7999(2)	0.043(2)	0.063(3)	0.045(2)	0.006(2)	0.019(2)	0.000(2)
C(15)	4*e*	0.5031(3)	0.4940(5)	0.7502(3)	0.042(2)	0.093(4)	0.061(3)	0.009(2)	0.024(2)	–0.008(3)
C(16)	4*e*	0.5124(3)	0.6055(5)	0.7147(3)	0.051(3)	0.120(5)	0.066(3)	–0.015(3)	0.035(2)	–0.008(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(17)	4*e*	0.4301(3)	0.6628(5)	0.6675(3)	0.068(3)	0.087(4)	0.051(3)	–0.008(3)	0.035(2)	0.006(3)
C(18)	4*e*	0.3843(3)	0.6781(4)	0.7171(3)	0.054(2)	0.053(3)	0.052(2)	–0.006(2)	0.025(2)	0.002(2)
C(19)	4*e*	0.2072(2)	0.6151(3)	0.7230(2)	0.034(2)	0.039(2)	0.036(2)	–0.001(2)	0.008(1)	–0.003(2)
C(20)	4*e*	0.1863(2)	0.5593(4)	0.6429(2)	0.046(2)	0.068(3)	0.034(2)	0.000(2)	0.011(2)	–0.005(2)
C(21)	4*e*	0.1026(3)	0.5970(5)	0.5820(3)	0.054(3)	0.094(4)	0.038(2)	0.005(3)	0.001(2)	–0.010(2)
C(22)	4*e*	0.0378(3)	0.5700(5)	0.6083(3)	0.040(2)	0.084(4)	0.068(3)	0.003(2)	0.001(2)	–0.018(3)
C(23)	4*e*	0.0576(3)	0.6231(5)	0.6885(3)	0.039(2)	0.082(4)	0.062(3)	0.007(2)	0.013(2)	–0.008(2)
C(24)	4*e*	0.1414(2)	0.5871(4)	0.7501(3)	0.040(2)	0.062(3)	0.048(2)	0.005(2)	0.015(2)	0.001(2)
C(25)	4*e*	0.3554(2)	0.6776(3)	0.8764(2)	0.034(2)	0.035(2)	0.033(2)	–0.003(1)	0.014(1)	–0.001(1)
C(26)	4*e*	0.4245(2)	0.6346(3)	0.9393(2)	0.037(2)	0.037(2)	0.039(2)	0.001(2)	0.013(2)	0.001(2)
C(27)	4*e*	0.4803(2)	0.7038(4)	0.9964(2)	0.034(2)	0.052(2)	0.039(2)	–0.005(2)	0.005(2)	0.001(2)
C(28)	4*e*	0.4683(2)	0.8198(4)	0.9912(2)	0.046(2)	0.052(2)	0.046(2)	–0.012(2)	0.012(2)	–0.013(2)
C(29)	4*e*	0.3996(2)	0.8641(4)	0.9318(3)	0.052(2)	0.034(2)	0.060(3)	–0.007(2)	0.021(2)	–0.012(2)
C(30)	4*e*	0.3403(2)	0.7952(3)	0.8745(2)	0.038(2)	0.034(2)	0.041(2)	–0.002(2)	0.017(2)	–0.004(2)
C(31)	4*e*	0.2673(2)	0.8576(3)	0.8167(2)	0.042(2)	0.031(2)	0.046(2)	0.002(2)	0.016(2)	–0.001(2)
C(32)	4*e*	0.2744(3)	0.9194(3)	0.7560(2)	0.058(2)	0.043(2)	0.049(2)	0.004(2)	0.027(2)	0.002(2)
C(33)	4*e*	0.2096(3)	0.9814(4)	0.7021(3)	0.071(3)	0.064(3)	0.057(3)	0.012(2)	0.029(2)	0.016(2)
C(34)	4*e*	0.1378(3)	0.9832(5)	0.7079(3)	0.066(3)	0.084(4)	0.072(3)	0.026(3)	0.023(3)	0.023(3)
C(35)	4*e*	0.1301(3)	0.9254(4)	0.7681(3)	0.051(3)	0.071(3)	0.071(3)	0.018(2)	0.029(2)	0.016(3)
C(36)	4*e*	0.1937(2)	0.8643(4)	0.8241(3)	0.049(2)	0.042(2)	0.052(2)	0.005(2)	0.024(2)	–0.002(2)
C(37)	4*e*	0.2341(3)	0.8552(5)	0.9659(3)	0.087(4)	0.079(4)	0.065(3)	–0.006(3)	0.043(3)	–0.010(3)
C(38)	4*e*	0.1034(3)	0.7887(5)	0.8769(3)	0.067(3)	0.081(4)	0.087(4)	–0.008(3)	0.050(3)	–0.009(3)

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