Crystal structure of chloro[1,2,3,4-(tetramethoxycarbonyl)buta-1,3-dien-1,4-diyl]-bis(triphenylphosphine)iridium(III), $[\text{Ir}\{\text{C}_4(\text{COOCH}_3)_4\}\text{Cl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$

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Abstract

$\text{C}_{48}\text{H}_{42}\text{ClIrO}_8\text{P}_2$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 21.146(3) \text{ \AA}$, $b = 11.198(2) \text{ \AA}$, $c = 18.200(4) \text{ \AA}$, $V = 4309.6 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.021$, $wR_{\text{ref}}(F^2) = 0.040$, $T = 220 \text{ K}$.

Source of material

The reaction of $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ with $(\text{MeOOC})_2\text{C}\equiv\text{C}(\text{COOMe})_2$ in acetone at 283 K resulted in the formation of the title complex $[\text{Ir}\{\text{C}_4(\text{COOMe})_4\}\text{Cl}(\text{PPh}_3)_2]$ which was previously obtained in the analogous reaction in thiophene-free benzene at 313 K – 318 K [1,2]. Crystals were obtained from methanol/chloroform solution.

Experimental details

Two carbon atoms C8 and C8A of the ester group on C2 are disordered over two positions with equal occupancies (0.50). For clarity only one position is shown in the figure. The hydrogen atoms of that methyl group were not localized and not included into the model. All other hydrogen atoms are placed in calculated positions according to the riding model.

Discussion

There are several examples of structurally characterized iridacyclopentadiene complexes [3,4]. However, five-fold coordination in mononuclear complexes is found only in one single case [5]. Here we report the second example of that type.

The title compound crystallizes as discrete molecules without any unusual intermolecular interactions. The trigonal bipyramidal co-ordination sphere of Ir is built up by two PPh_3 ligands in apical positions. The angle P1-Ir-P2 is almost linear with $177.64(3)^\circ$. Equatorial ligands are the chloro ligand and the σ -bound buta-1,3-dien-1,4-diyl ligand. The sum of angles in the equatorial plane ($\angle \text{C1-Ir-C4} = 76.4(2)^\circ$, $\angle \text{C1-Ir-Cl} = 146.8(1)^\circ$, $\angle \text{C4-Ir-Cl} = 136.8(1)^\circ$) amounts to 360.0° . The Ir–C1 and Ir–C4 bond distances are $2.015(4) \text{ \AA}$ and $2.011(4) \text{ \AA}$, respectively. Overall, there are no remarkable differences in the bond lengths and angles of the title complex compared with those in other iridacyclopentadiene complexes.

Table 1. Data collection and handling.

Crystal:	red block, size $0.12 \times 0.13 \times 0.15 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	32.89 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, φ
$2\theta_{\text{max}}$:	49.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	31004, 7588
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6604
$N(\text{param})_{\text{refined}}$:	551
Programs:	SHELXS-97 [6], SHELXL-97 [7], ORTEP-III [8]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(3)	4a	0.7338	1.1813	0.4224	0.104
H(2)	4a	0.6746	1.1950	0.3713	0.104
H(1)	4a	0.7391	1.2534	0.3488	0.104
H(4)	4a	0.8569	0.7391	0.0154	0.103
H(6)	4a	0.8097	0.6314	0.0098	0.103
H(5)	4a	0.8746	0.6156	0.0504	0.103
H(9)	4a	0.8229	0.3430	0.2147	0.112
H(8)	4a	0.8656	0.3835	0.1489	0.112
H(7)	4a	0.7922	0.4022	0.1453	0.112
H(14)	4a	0.9247	0.6003	0.5510	0.036
H(15)	4a	0.9237	0.6162	0.6793	0.043
H(16)	4a	0.8507	0.7415	0.7353	0.053
H(17)	4a	0.7819	0.8531	0.6664	0.042
H(18)	4a	0.7806	0.8339	0.5399	0.037
H(20)	4a	0.9805	0.6080	0.4151	0.047
H(21)	4a	1.0239	0.4240	0.3891	0.057

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(22)	4a	0.9593	0.2611	0.3719	0.062
H(23)	4a	0.8514	0.2793	0.3836	0.058
H(24)	4a	0.8068	0.4649	0.4084	0.044
H(26)	4a	0.9078	0.9181	0.4930	0.048
H(27)	4a	0.9820	1.0567	0.4559	0.060
H(28)	4a	1.0306	1.0404	0.3424	0.064
H(29)	4a	1.0077	0.8793	0.2678	0.054
H(30)	4a	0.9347	0.7376	0.3048	0.041
H(32)	4a	0.5662	0.9319	0.2667	0.054
H(33)	4a	0.5145	1.0936	0.3198	0.079
H(34)	4a	0.5269	1.1363	0.4417	0.086
H(35)	4a	0.5959	1.0257	0.5114	0.092

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(36)	4a	0.6467	0.8630	0.4622	0.063
H(38)	4a	0.5178	0.7297	0.3462	0.047
H(39)	4a	0.4456	0.5788	0.3672	0.057
H(40)	4a	0.4786	0.3821	0.3758	0.047
H(41)	4a	0.5838	0.3375	0.3630	0.047
H(42)	4a	0.6577	0.4871	0.3423	0.041
H(44)	4a	0.6815	0.9337	0.2192	0.039
H(45)	4a	0.6856	0.9514	0.0929	0.043
H(46)	4a	0.6568	0.7942	0.0195	0.052
H(47)	4a	0.6239	0.6171	0.0713	0.059
H(48)	4a	0.6221	0.5946	0.1979	0.045

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

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	4a		0.7805(2)	0.8834(3)	0.3311(2)	0.021(2)	0.026(2)	0.034(2)	-0.001(2)	-0.006(2)	0.001(2)
C(2)	4a		0.8114(2)	0.8859(4)	0.2656(2)	0.023(2)	0.034(2)	0.034(2)	0.001(2)	-0.004(2)	0.005(2)
C(3)	4a		0.8173(2)	0.7656(4)	0.2328(2)	0.021(2)	0.038(2)	0.027(2)	-0.001(2)	-0.001(2)	0.005(2)
C(4)	4a		0.7918(2)	0.6803(3)	0.2771(2)	0.018(2)	0.029(2)	0.028(2)	-0.002(2)	-0.004(2)	0.006(2)
C(5)	4a		0.7662(2)	0.9933(3)	0.3743(4)	0.036(3)	0.025(2)	0.048(2)	-0.004(1)	-0.008(3)	-0.003(2)
C(6)	4a		0.7197(3)	1.1860(4)	0.3723(4)	0.083(3)	0.039(2)	0.087(4)	0.017(2)	-0.022(4)	-0.011(3)
C(7)	4a		0.8378(3)	0.9921(4)	0.2296(4)	0.039(3)	0.044(3)	0.081(5)	-0.003(2)	-0.008(3)	0.037(3)
C(8A)	4a	0.50(1)	0.9085(5)	1.1471(8)	0.2229(6)	0.074(8)	0.036(6)	0.069(8)	-0.027(5)	0.025(6)	0.002(5)
C(8)	4a	0.50	0.8679(8)	1.1114(8)	0.1328(7)	0.18(2)	0.035(6)	0.08(1)	0.031(7)	0.10(1)	0.040(6)
C(9)	4a		0.8503(2)	0.7428(4)	0.1616(2)	0.035(2)	0.038(3)	0.029(2)	-0.002(2)	0.006(2)	0.008(2)
C(10)	4a		0.8406(3)	0.6700(6)	0.0403(3)	0.095(4)	0.079(4)	0.031(3)	-0.003(4)	0.014(3)	-0.005(3)
C(11)	4a		0.7879(2)	0.5517(4)	0.2544(2)	0.030(2)	0.033(2)	0.022(2)	0.001(2)	-0.000(2)	-0.003(2)
C(12)	4a		0.8285(3)	0.4020(5)	0.1770(4)	0.083(4)	0.048(3)	0.093(5)	-0.014(3)	0.039(4)	-0.034(3)
C(13)	4a		0.8526(2)	0.7154(3)	0.5325(2)	0.029(2)	0.020(2)	0.028(2)	-0.003(2)	0.000(2)	0.001(2)
C(14)	4a		0.8957(2)	0.6501(3)	0.5741(2)	0.028(2)	0.029(2)	0.033(2)	-0.004(2)	-0.002(2)	0.002(2)
C(15)	4a		0.8952(2)	0.6598(4)	0.6510(2)	0.037(2)	0.038(3)	0.032(2)	-0.004(2)	-0.007(2)	0.010(2)
C(16)	4a		0.8516(2)	0.7355(4)	0.6843(2)	0.055(3)	0.052(3)	0.026(2)	-0.019(3)	-0.002(2)	-0.001(2)
C(17)	4a		0.8100(2)	0.8012(4)	0.6433(2)	0.041(2)	0.035(2)	0.029(2)	0.001(2)	0.006(2)	-0.005(2)
C(18)	4a		0.8096(2)	0.7906(3)	0.5675(2)	0.034(2)	0.028(2)	0.031(2)	-0.002(2)	-0.001(2)	-0.003(2)
C(19)	4a		0.8896(2)	0.5579(4)	0.4125(2)	0.038(2)	0.027(2)	0.022(2)	0.005(2)	-0.003(2)	-0.003(2)
C(20)	4a		0.9540(2)	0.5427(4)	0.4079(3)	0.039(3)	0.040(3)	0.040(3)	0.007(2)	-0.006(2)	-0.011(2)
C(21)	4a		0.9803(2)	0.4323(5)	0.3927(3)	0.051(3)	0.050(3)	0.041(3)	0.026(3)	-0.004(2)	-0.008(2)
C(22)	4a		0.9417(2)	0.3351(4)	0.3829(3)	0.074(3)	0.041(3)	0.041(3)	0.025(3)	0.007(3)	-0.001(2)
C(23)	4a		0.8772(3)	0.3460(4)	0.3892(2)	0.082(3)	0.030(2)	0.034(3)	-0.005(2)	0.000(2)	-0.001(2)
C(24)	4a		0.8504(2)	0.4573(4)	0.4041(2)	0.044(3)	0.034(2)	0.032(2)	0.003(2)	0.002(2)	0.002(2)
C(25)	4a		0.9140(2)	0.8130(3)	0.4029(2)	0.020(2)	0.034(2)	0.030(2)	0.001(2)	-0.002(2)	0.004(2)
C(26)	4a		0.9280(2)	0.9096(4)	0.4479(3)	0.042(3)	0.038(3)	0.041(3)	-0.007(2)	0.003(2)	0.003(2)
C(27)	4a		0.9721(3)	0.9929(4)	0.4253(3)	0.051(4)	0.047(3)	0.052(4)	-0.019(2)	0.008(3)	-0.005(2)
C(28)	4a		1.0016(3)	0.9830(4)	0.3576(3)	0.043(3)	0.049(3)	0.069(5)	-0.019(2)	0.005(3)	0.011(3)
C(29)	4a		0.9877(2)	0.8871(4)	0.3131(3)	0.032(2)	0.060(3)	0.044(3)	-0.001(2)	0.008(2)	0.003(2)
C(30)	4a		0.9440(2)	0.8021(4)	0.3352(2)	0.024(2)	0.048(3)	0.031(2)	-0.002(2)	-0.004(2)	-0.000(2)
C(31)	4a		0.6116(2)	0.8790(3)	0.3581(2)	0.026(2)	0.026(2)	0.042(3)	-0.002(2)	0.010(2)	-0.007(2)
C(32)	4a		0.5722(2)	0.9490(4)	0.3162(3)	0.035(3)	0.037(3)	0.062(3)	0.006(2)	0.006(2)	-0.004(2)
C(33)	4a		0.5410(3)	1.0464(5)	0.3484(4)	0.045(3)	0.030(3)	0.122(6)	0.011(2)	0.015(3)	0.002(3)
C(34)	4a		0.5489(3)	1.0729(5)	0.4207(4)	0.067(4)	0.040(3)	0.108(6)	0.001(3)	0.047(4)	-0.028(4)
C(35)	4a		0.5893(4)	1.0057(5)	0.4625(4)	0.092(5)	0.067(5)	0.071(5)	-0.006(3)	0.034(4)	-0.032(3)
C(36)	4a		0.6201(3)	0.9089(4)	0.4329(3)	0.063(3)	0.051(3)	0.045(3)	-0.003(3)	0.016(3)	-0.015(2)
C(37)	4a		0.5952(2)	0.6255(3)	0.3415(2)	0.027(2)	0.026(2)	0.023(2)	-0.006(2)	-0.002(2)	-0.001(2)
C(38)	4a		0.5316(2)	0.6510(4)	0.3494(3)	0.026(2)	0.034(2)	0.058(3)	-0.000(2)	0.004(2)	0.008(2)
C(39)	4a		0.4883(2)	0.5604(4)	0.3621(3)	0.024(2)	0.047(3)	0.070(4)	0.001(2)	0.005(2)	0.003(3)
C(40)	4a		0.5079(2)	0.4426(4)	0.3673(3)	0.037(2)	0.040(3)	0.041(3)	-0.013(2)	0.002(2)	0.002(2)
C(41)	4a		0.5705(2)	0.4164(4)	0.3597(2)	0.044(2)	0.028(2)	0.046(3)	-0.005(2)	0.005(2)	0.003(2)
C(42)	4a		0.6151(2)	0.5062(3)	0.3470(3)	0.022(2)	0.034(3)	0.046(3)	-0.005(2)	0.005(2)	0.001(2)
C(43)	4a		0.6511(2)	0.7626(4)	0.2227(2)	0.023(2)	0.025(2)	0.032(2)	0.000(2)	-0.004(2)	-0.001(2)
C(44)	4a		0.6702(2)	0.8691(4)	0.1899(2)	0.033(2)	0.029(2)	0.036(2)	-0.002(2)	-0.008(2)	0.004(2)
C(45)	4a		0.6724(2)	0.8800(3)	0.1141(2)	0.043(2)	0.028(2)	0.037(3)	-0.004(2)	0.000(2)	0.008(2)
C(46)	4a		0.6553(2)	0.7863(4)	0.0703(2)	0.056(3)	0.050(3)	0.025(2)	-0.008(3)	0.002(2)	0.010(2)
C(47)	4a		0.6360(3)	0.6803(4)	0.1014(2)	0.073(3)	0.048(3)	0.026(2)	-0.014(3)	0.001(2)	-0.007(2)
C(48)	4a		0.6343(2)	0.6670(4)	0.1773(2)	0.051(3)	0.028(2)	0.035(2)	-0.013(2)	0.004(2)	-0.004(2)
O(1)	4a		0.7752(2)	1.0030(2)	0.4392(2)	0.107(4)	0.041(2)	0.031(2)	0.016(2)	-0.007(2)	-0.002(1)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(2)	4a		0.7376(2)	1.0761(2)	0.3333(2)	0.083(3)	0.025(1)	0.056(2)	0.019(2)	-0.032(2)	-0.004(1)
O(3)	4a		0.8622(2)	1.0726(4)	0.2671(2)	0.120(4)	0.092(3)	0.061(3)	-0.072(3)	-0.026(3)	0.033(2)
O(4)	4a		0.8380(3)	0.9966(3)	0.1591(2)	0.121(4)	0.048(2)	0.045(2)	-0.012(2)	0.011(3)	0.018(2)
O(5)	4a		0.9065(1)	0.7541(3)	0.1530(2)	0.043(2)	0.061(2)	0.049(2)	-0.011(2)	0.019(1)	-0.009(2)
O(6)	4a		0.8111(1)	0.7064(3)	0.1091(2)	0.053(2)	0.071(2)	0.029(2)	-0.000(2)	-0.004(1)	-0.003(2)
O(7)	4a		0.7467(2)	0.4837(2)	0.2731(2)	0.043(2)	0.040(1)	0.062(2)	-0.014(2)	0.018(2)	-0.011(1)
O(8)	4a		0.8357(2)	0.5194(3)	0.2106(2)	0.042(2)	0.033(2)	0.052(2)	-0.005(1)	0.018(2)	-0.015(1)
P(1)	4a		0.85349(4)	0.70412(8)	0.43100(5)	0.0234(4)	0.0242(6)	0.0243(5)	0.0015(4)	-0.0016(4)	0.0002(4)
P(2)	4a		0.65224(4)	0.74551(8)	0.32268(5)	0.0206(4)	0.0237(6)	0.0261(5)	-0.0019(4)	0.0016(4)	-0.0011(4)
Cl	4a		0.70776(6)	0.6249(1)	0.47583(6)	0.0468(7)	0.091(1)	0.0357(6)	-0.0316(7)	-0.0073(6)	0.0283(6)
Ir	4a		0.753669(7)	0.72575(1)	0.374405(7)	0.02115(6)	0.02164(5)	0.02123(5)	-0.00184(7)	0.00020(8)	0.00180(6)

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