Crystal structure of (carbonyl)(2,4-dimethylpentadienyl)[(1,2,3-η)-2,4-dimethyl-4-trimethylphosphonio-2-pentenyl]ruthenium(II), $[(CH_3)_3P(RuC_{15}H_{23}O)][BF_4]$

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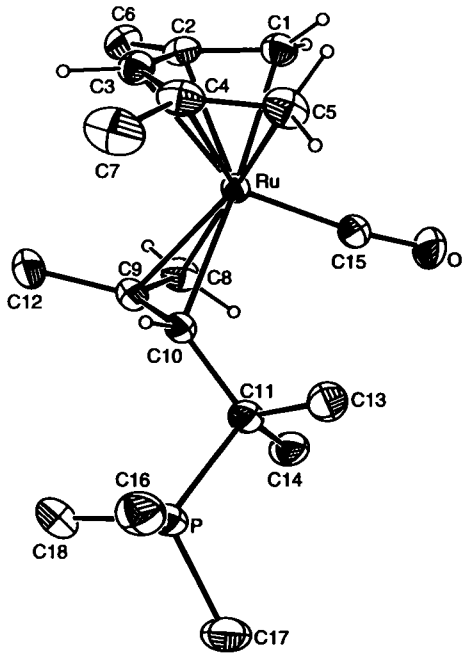

Abstract

$C_{18}H_{32}BF_4OPRu$, triclinic, $P\bar{1}$ (No. 2), $a = 7.7050(3)$ Å, $b = 8.2990(2)$ Å, $c = 19.1647(8)$ Å, $\alpha = 82.465(2)°$, $\beta = 85.703(2)°$, $\gamma = 66.432(2)°$, $V = 1113.2$ Å^3, $Z = 2$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.101$, $T = 200$ K.

Source of material

The compound was synthesized as described previously [1], and was crystallized by cooling solutions in methylene chloride/ether to 253 K.

Discussion

The structure confirms the proposed addition of trimethylphosphine to a diene ligand instead of to the metal center.

A significant residual peak near the primary ruthenium atom location was found to correspond to a second image of the complex, rotated in such a way that the carbonyl ligand was oriented essentially backwards from the primary orientation. The relative abundances of the two images were found to be about 94:6. Due to the small occupancy of the second orientation, only its ruthenium atom was included in the structure refinement.

In relation to the origin of the second ruthenium image, the low symmetry ($P\bar{1}$) would not make twinning likely, and this is further supported by the fact that the second ruthenium location is near the first. While the possibility of cocrystallization of a second product can not be entirely eliminated, spectroscopic data did not provide any indication of the presence of another carbonyl-containing species. In any event, in either case the result would be much the same, as there would be a second image or molecule present to the extent of 6%, and 6% of C, H, and even P atoms would be of minor consequence, while 6% of a Ru atom would be important.

Two orientations are adopted by the tetrafluoroborate ion, in which the F2, F3, and F4 positions of one orientation are related to their counterparts by a rotation about the B-F1 bond. The relative contributions of these orientations appear to differ slightly, at 58% vs. 42%.

Table 1. Data collection and handling.

Crystal:	yellow, prism, size 0.20 x 0.25 x 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.12 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω, 188 frames, $\Delta\varphi = 1°$; 35 frames, $\Delta\omega = 1°$
$2\theta_{max}$:	65.14°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8592, 7130
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6336
$N(param)_{refined}$:	306
Programs:	SIR97 [2], SHELXL-97 [3]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.175(5)	0.427(4)	0.478(2)	0.051
H(1B)	2*i*	0.394(5)	0.353(4)	0.485(2)	0.051
H(3)	2*i*	0.419(4)	-0.051(4)	0.612(2)	0.051
H(5A)	2*i*	0.708(5)	0.273(5)	0.616(2)	0.063
H(5B)	2*i*	0.610(5)	0.287(5)	0.536(2)	0.063
H(6A)	2*i*	0.0006	0.2451	0.5250	0.073
H(6B)	2*i*	0.0940	0.0674	0.5770	0.073
H(6C)	2*i*	0.1361	0.0653	0.4940	0.073
H(7A)	2*i*	0.6296	-0.1016	0.6945	0.112
H(7B)	2*i*	0.7325	0.0291	0.7014	0.112
H(7C)	2*i*	0.8162	-0.1185	0.6480	0.112
H(8A)	2*i*	-0.073(5)	0.362(4)	0.656(2)	0.053
H(8B)	2*i*	-0.037(5)	0.533(5)	0.678(2)	0.053
H(10)	2*i*	0.420(4)	0.211(4)	0.757(2)	0.040

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12A)	2*i*	0.1006	0.0775	0.7807	0.085
H(12B)	2*i*	0.3002	–0.0005	0.7396	0.085
H(12C)	2*i*	0.1074	0.0603	0.6983	0.085
H(13A)	2*i*	0.4720	0.5666	0.7099	0.085
H(13B)	2*i*	0.6018	0.3998	0.7611	0.085
H(13C)	2*i*	0.4934	0.5878	0.7903	0.085
H(14A)	2*i*	0.1359	0.7131	0.8018	0.080
H(14B)	2*i*	0.0223	0.5961	0.7880	0.080
H(14C)	2*i*	0.1151	0.6789	0.7232	0.080

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(16A)	2*i*	0.6513	0.3057	0.8907	0.096
H(16B)	2*i*	0.6230	0.1483	0.8595	0.096
H(16C)	2*i*	0.5796	0.1742	0.9412	0.096
H(17A)	2*i*	0.2931	0.5059	0.9771	0.103
H(17B)	2*i*	0.1314	0.6271	0.9229	0.103
H(17C)	2*i*	0.3394	0.6273	0.9127	0.103
H(18A)	2*i*	0.1908	0.2266	0.9501	0.096
H(18B)	2*i*	0.2353	0.1499	0.8755	0.096
H(18C)	2*i*	0.0578	0.3315	0.8850	0.096

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	2*i*	0.9397(8)	0.31085(2)	0.32919(2)	0.624784(9)	0.02927(9)	0.02791(9)	0.02699(9)	–0.01145(6)	–0.00100(6)	–0.00151(6)
Ru'	2*i*	0.0603	0.2750(4)	0.2125(4)	0.6434(1)	0.029(1)	0.028(1)	0.025(1)	–0.0109(9)	–0.0029(9)	–0.0037(9)
P	2*i*		0.3346(1)	0.3778(1)	0.87432(3)	0.0634(4)	0.0480(4)	0.0289(3)	–0.0185(3)	–0.0048(3)	–0.0039(3)
F(1)	2*i*		0.7289(4)	–0.4178(3)	0.8865(2)	0.117(2)	0.059(1)	0.111(2)	–0.023(1)	–0.032(2)	–0.006(1)
F(2)	2*i*	0.58(2)	0.636(2)	–0.160(2)	0.8262(4)	0.160(9)	0.104(5)	0.040(2)	–0.032(6)	–0.021(4)	0.022(3)
F(3)	2*i*	0.58	0.510(1)	–0.198(2)	0.9289(7)	0.098(5)	0.170(8)	0.154(9)	–0.059(5)	0.069(5)	–0.039(6)
F(4)	2*i*	0.58	0.801(1)	–0.215(1)	0.9200(4)	0.102(5)	0.101(4)	0.097(4)	–0.044(3)	–0.043(4)	–0.013(3)
F(2')	2*i*	0.42	0.529(3)	–0.141(2)	0.8408(9)	0.20(2)	0.063(4)	0.11(1)	0.001(7)	–0.11(1)	0.000(5)
F(3')	2*i*	0.42	0.564(3)	–0.181(2)	0.9484(5)	0.27(2)	0.078(5)	0.045(4)	–0.019(7)	0.037(6)	0.000(3)
F(4')	2*i*	0.42	0.799(2)	–0.172(2)	0.878(2)	0.081(6)	0.087(7)	0.32(3)	–0.031(5)	0.07(1)	–0.09(1)
O	2*i*		0.2412(4)	0.7141(3)	0.5934(1)	0.105(2)	0.042(1)	0.051(1)	–0.036(1)	–0.008(1)	0.0064(9)
B	2*i*		0.6651(6)	–0.2398(5)	0.8895(2)	0.073(2)	0.060(2)	0.039(2)	–0.024(2)	–0.006(2)	–0.002(1)
C(1)	2*i*		0.2848(4)	0.3396(4)	0.5070(1)	0.046(1)	0.045(1)	0.036(1)	–0.016(1)	–0.002(1)	–0.005(1)
C(2)	2*i*		0.2816(3)	0.1795(3)	0.5410(1)	0.041(1)	0.038(1)	0.034(1)	–0.0086(9)	–0.0024(9)	–0.0118(9)
C(3)	2*i*		0.4286(4)	0.0609(3)	0.5869(1)	0.042(1)	0.035(1)	0.042(1)	–0.0058(9)	0.000(1)	–0.0061(9)
C(4)	2*i*		0.5797(4)	0.0924(4)	0.6116(2)	0.032(1)	0.059(2)	0.045(1)	–0.004(1)	0.0009(9)	–0.012(1)
C(5)	2*i*		0.6117(4)	0.2488(5)	0.5889(2)	0.037(1)	0.072(2)	0.050(2)	–0.024(1)	0.002(1)	–0.009(1)
C(6)	2*i*		0.1135(4)	0.1355(4)	0.5336(2)	0.050(1)	0.048(1)	0.052(2)	–0.020(1)	–0.003(1)	–0.014(1)
C(7)	2*i*		0.6999(5)	–0.0357(5)	0.6688(2)	0.050(2)	0.081(2)	0.058(2)	0.010(2)	–0.014(1)	–0.000(2)
C(8)	2*i*		0.0226(4)	0.3967(4)	0.6753(1)	0.035(1)	0.053(1)	0.044(1)	–0.017(1)	0.0022(9)	–0.009(1)
C(9)	2*i*		0.1656(4)	0.2711(3)	0.7195(1)	0.044(1)	0.043(1)	0.034(1)	–0.020(1)	0.0035(9)	–0.0025(9)
C(10)	2*i*		0.3214(3)	0.3077(3)	0.7406(1)	0.038(1)	0.0314(9)	0.0279(9)	–0.0122(8)	–0.0009(8)	–0.0010(8)
C(11)	2*i*		0.3135(4)	0.4606(3)	0.7795(1)	0.054(1)	0.038(1)	0.031(1)	–0.016(1)	–0.0056(9)	–0.0021(9)
C(12)	2*i*		0.1687(5)	0.0856(4)	0.7360(2)	0.079(2)	0.056(2)	0.046(2)	–0.042(2)	0.003(1)	0.002(1)
C(13)	2*i*		0.4859(5)	0.5080(5)	0.7583(2)	0.075(2)	0.068(2)	0.043(1)	–0.044(2)	–0.009(1)	–0.006(1)
C(14)	2*i*		0.1302(5)	0.6271(4)	0.7725(2)	0.071(2)	0.038(1)	0.041(1)	–0.010(1)	–0.009(1)	–0.005(1)
C(15)	2*i*		0.2630(4)	0.5692(3)	0.6098(1)	0.054(1)	0.038(1)	0.033(1)	–0.018(1)	–0.002(1)	0.0000(9)
C(16)	2*i*		0.5741(5)	0.2355(5)	0.8936(2)	0.072(2)	0.063(2)	0.050(2)	–0.017(2)	–0.017(2)	–0.002(1)
C(17)	2*i*		0.2670(6)	0.5544(5)	0.9277(2)	0.095(3)	0.062(2)	0.040(1)	–0.017(2)	–0.006(2)	–0.014(1)
C(18)	2*i*		0.1881(5)	0.2580(5)	0.8990(2)	0.080(2)	0.072(2)	0.039(1)	–0.033(2)	0.001(1)	0.005(1)

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