Crystal structure of (*E*)-2-ruthenocenylethenylcobaltocenium hexafluorophosphate, $[(C_5H_5)Ru(C_{12}H_{10})Co(C_5H_5)][PF_6]$

G. Laus, C. E. Strasser, K. Wurst and H. Schottenberger*

University of Innsbruck, Faculty of Chemistry and Pharmacy, Innrain 52a, 6020 Innsbruck, Austria

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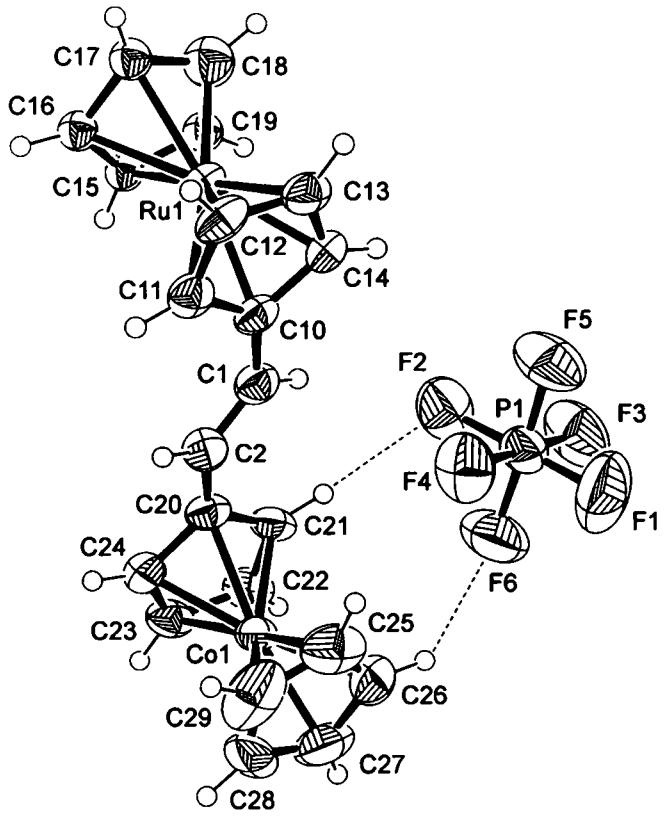

Abstract

$C_{22}H_{20}CoF_6PRu$, monoclinic, $P12_1/c1$ (no. 14), a = 9.9053(2) Å, b = 11.4730(3) Å, c = 18.5156(5) Å, β = 94.940(2)°, V = 2096.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.094, T = 233 K.

Source of material

Recently, heteronuclear bimetallocene-based cationic donor-acceptor conjugates have been found to exhibit irregular solvatochromism [1]. Molecules of this type containing a ruthenocene unit are particularly difficult to crystallize. Only the crystal structures of the 1,1′-dicobaltocenylruthenocene dication (CARN 130638-54-9) [2] and neutral (*E*)-2-(10-formylruthenocenyl)ethenyl-10,2,20,3,30,4,40,5-octamethylferrocene (CARN 848047-30-3) [3] have been described so far. The title compound (CARN 872088-21-6) was prepared by Knoevenagel condensation of methylcobaltocenium hexafluorophosphate and ruthenocenecarbaldehyde. Suitable crystals were now obtained by very slow evaporation of a solution in acetonitrile.

* Correspondence author (e-mail: herwig.schottenberger@uibk.ac.at)

Experimental details

The unsubstituted Cp ring of the ruthenocene part exhibits a positional disorder with a 2:1 occupancy. Disordered carbon atoms were refined only isotropically.

Discussion

Bond lengths in the conjugated bridge are 1.301 Å (C1—C2), 1.465 Å (C1—C10), and 1.463 Å (C2—C20), indicating a regular ethene structure. The pertinent angles C10–C1–C2 and C1–C2–C20 are 125.7° and 123.9°, respectively. The C1=C2 double bond is rotated out of the adjacent Cp plane of the ruthenocene (ruc) by 12.2°, of the cobaltocene (coc) by 13.3°. The planes of the bridged Cp rings of ruc and coc are nearly parallel (interplanar angle 1.5°), and the Cp rings of the individual metallocene systems are slightly twisted (approximately 20°). Co—centroid distances are 1.64 Å (to the substituted Cp ring) and 1.63 (to the unsubstituted Cp ring), whereas Ru—centroid distances are 1.81 Å (substituted) and 1.82 Å (unsubstituted). Short C(coc)H···F contacts are observed between H21 and F2 with a distance *d* of 2.38 Å (d(C21···F2) = 3.315 Å, ∠C21–H21···F2 = 173.9°) and between H26 and F6 with a distance of 2.53 Å (3.336 Å, 143.8°). The anion also forms weak hydrogen bridges with C(coc)H at 1–x,½+y,½–z, where H24′···F4 distance is 2.53 Å (3.310 Å, 140.6°) and H29′···F5 distance is 2.58 Å (3.492 Å, 165.2°), and with C(ruc)H at 1–x,1–y,2–z with a H13″···F3 distance of 2.49 Å (3.352 Å, 151.8°).

Table 1. Data collection and handling.

Crystal:	orange plate, size 0.02 × 0.08 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.48 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11972, 3288
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2702
$N(param)_{refined}$:	275
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	4*e*		0.4600	0.2043	0.8803	0.058
H(2)	4*e*		0.5813	0.0751	0.7797	0.062
H(11)	4*e*		0.8141	0.1019	0.8426	0.057
H(12)	4*e*		0.9935	0.2188	0.9151	0.061
H(13)	4*e*		0.8783	0.3695	0.9850	0.063
H(14)	4*e*		0.6268	0.3472	0.9582	0.056
H(21)	4*e*		0.2361	0.1865	0.8210	0.055
H(22)	4*e*		0.0461	0.0766	0.7520	0.064

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(23)	4e		0.1507	–0.0814	0.6798	0.063
H(24)	4e		0.4017	–0.0693	0.7052	0.061
H(25)	4e		0.4190	0.3200	0.6784	0.093
H(26)	4e		0.1743	0.3492	0.6744	0.086
H(27)	4e		0.0603	0.2088	0.5900	0.097
H(28)	4e		0.2341	0.0864	0.5393	0.114
H(29)	4e		0.4641	0.1539	0.5957	0.117
C(15)	4e	0.67	0.683(1)	–0.0158(7)	1.0305(4)	0.036(2)
H(15)	4e	0.67	0.6172	–0.0611	1.0041	0.043
C(16)	4e	0.67	0.823(1)	–0.0332(8)	1.0316(5)	0.039(2)
H(16)	4e	0.67	0.8656	–0.0915	1.0063	0.046
C(17)	4e	0.67	0.889(1)	0.053(1)	1.0780(6)	0.042(4)
H(17)	4e	0.67	0.9828	0.0616	1.0892	0.050
C(18)	4e	0.67	0.786(2)	0.123(1)	1.1036(6)	0.064(3)

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(18)	4e	0.67	0.7993	0.1873	1.1346	0.077
C(19)	4e	0.67	0.6566(9)	0.079(1)	1.0744(5)	0.041(2)
H(19)	4e	0.67	0.5709	0.1083	1.0831	0.049
C(16A)	4e	0.33	0.883(2)	0.027(2)	1.064(1)	0.037(7)
H(16A)	4e	0.33	0.9730	0.0049	1.0592	0.045
C(15A)	4e	0.33	0.771(3)	–0.029(2)	1.035(1)	0.072(8)
H(15A)	4e	0.33	0.7710	–0.0963	1.0067	0.086
C(18A)	4e	0.33	0.702(2)	0.128(1)	1.0984(9)	0.039(4)
H(18A)	4e	0.33	0.6477	0.1832	1.1191	0.046
C(17A)	4e	0.33	0.840(2)	0.125(1)	1.1049(8)	0.027(4)
H(17A)	4e	0.33	0.8968	0.1780	1.1314	0.033
C(19A)	4e	0.33	0.655(2)	0.031(2)	1.054(1)	0.049(5)
H(19A)	4e	0.33	0.5647	0.0104	1.0409	0.059

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}
Ru(1)	4e	0.77338(4)	0.14306(3)	0.98871(2)	0.0345(2)	0.0407(2)	0.0396(2)	0.0011(2)	0.0000(2)	0.0098(2)
Co(1)	4e	0.26419(7)	0.13066(6)	0.68202(3)	0.0448(4)	0.0436(4)	0.0325(4)	–0.0026(3)	–0.0019(3)	0.0006(3)
C(1)	4e	0.5344(5)	0.1742(5)	0.8580(3)	0.052(3)	0.047(3)	0.044(3)	0.001(2)	0.000(2)	0.008(3)
C(2)	4e	0.5080(5)	0.1049(5)	0.8030(3)	0.057(3)	0.051(3)	0.047(3)	0.002(3)	0.004(3)	0.002(3)
C(10)	4e	0.6698(5)	0.2094(4)	0.8883(3)	0.043(3)	0.042(3)	0.042(3)	–0.001(2)	–0.004(2)	0.013(2)
C(11)	4e	0.7987(5)	0.1643(5)	0.8738(3)	0.056(3)	0.048(3)	0.040(3)	0.002(3)	0.007(2)	0.011(2)
C(12)	4e	0.8994(5)	0.2299(5)	0.9145(3)	0.039(3)	0.057(3)	0.057(3)	–0.001(3)	0.001(2)	0.026(3)
C(13)	4e	0.8349(6)	0.3140(5)	0.9537(3)	0.060(4)	0.041(3)	0.052(3)	–0.011(3)	–0.013(3)	0.011(3)
C(14)	4e	0.6936(5)	0.3018(4)	0.9385(3)	0.054(3)	0.040(3)	0.044(3)	0.008(2)	–0.003(2)	0.007(2)
C(20)	4e	0.3710(5)	0.0707(5)	0.7752(3)	0.048(3)	0.049(3)	0.036(3)	–0.004(2)	–0.003(2)	0.008(2)
C(21)	4e	0.2461(5)	0.1224(5)	0.7903(3)	0.059(3)	0.050(3)	0.029(3)	–0.010(3)	–0.001(2)	0.000(2)
C(22)	4e	0.1392(5)	0.0612(5)	0.7512(3)	0.047(3)	0.067(4)	0.046(3)	–0.014(3)	0.008(3)	0.002(3)
C(23)	4e	0.1979(6)	–0.0275(5)	0.7109(3)	0.065(4)	0.048(3)	0.043(3)	–0.018(3)	–0.006(3)	0.000(3)
C(24)	4e	0.3385(6)	–0.0207(5)	0.7254(3)	0.063(4)	0.043(3)	0.046(3)	0.003(3)	–0.002(3)	0.004(3)
C(25)	4e	0.3533(8)	0.2765(7)	0.6503(4)	0.091(5)	0.078(5)	0.061(4)	–0.031(4)	0.000(4)	0.022(4)
C(26)	4e	0.2179(8)	0.2927(5)	0.6478(3)	0.106(6)	0.051(4)	0.058(4)	0.012(4)	0.006(4)	0.011(3)
C(27)	4e	0.1544(8)	0.2149(7)	0.6011(4)	0.091(5)	0.078(5)	0.068(5)	–0.008(4)	–0.033(4)	0.021(4)
C(28)	4e	0.250(1)	0.1471(6)	0.5731(3)	0.20(1)	0.056(4)	0.028(3)	0.002(6)	0.011(5)	0.003(3)
C(29)	4e	0.3791(9)	0.1847(8)	0.6043(5)	0.101(6)	0.108(7)	0.092(6)	0.029(5)	0.055(5)	0.054(5)
P(1)	4e	0.2307(2)	0.4683(2)	0.86042(9)	0.065(1)	0.066(1)	0.059(1)	0.0068(8)	0.0076(8)	–0.0098(8)
F(1)	4e	0.2222(6)	0.5852(4)	0.8193(3)	0.220(6)	0.087(3)	0.130(4)	0.049(4)	0.056(4)	0.039(3)
F(2)	4e	0.2361(5)	0.3475(3)	0.9020(2)	0.134(4)	0.075(3)	0.086(3)	–0.011(2)	0.030(3)	0.004(2)
F(3)	4e	0.1095(4)	0.5067(4)	0.9039(3)	0.089(3)	0.137(4)	0.121(4)	0.015(3)	0.030(3)	–0.053(3)
F(4)	4e	0.3498(4)	0.4240(4)	0.8166(2)	0.090(3)	0.097(3)	0.102(3)	0.010(2)	0.048(2)	–0.001(2)
F(5)	4e	0.3326(4)	0.5194(4)	0.9206(3)	0.092(3)	0.125(4)	0.114(4)	–0.032(3)	–0.012(3)	–0.040(3)
F(6)	4e	0.1274(5)	0.4109(5)	0.8010(3)	0.106(3)	0.167(5)	0.108(4)	0.048(3)	–0.038(3)	–0.068(3)

References

1. Laus, G.; Strasser, C. E.; Holzer, M.; Wurst, K.; Pürstinger, G.; Ongania, K.-H.; Rauch, M.; Bonn, G.; Schottenberger, H.: The (*E*)-2-ferrocenylethenylcobaltocenium cation. A missing link in heteronuclear bimetallocene-based donor-acceptor conjugate chemistry exhibiting irregular solvatochromism. Organometallics **24** (2005) 6085-6093.
2. Jaitner, P.; Schottenberger, H.; Gamper, S.; Obendorf, D.: Termetallocenes. J. Organomet. Chem. **475** (1994) 113-120.
3. Obendorf, D.; Schottenberger, H.; Wurst, K.; Schuler, N.; Laus, G.: Synthesis and electrochemistry of novel heteronuclear Fe—Ru bi- and quatermetallocenes, conjugatively connected by ethene and thiophene bridges. J. Organomet. Chem. **690** (2005) 811-817.
4. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.