Note

The reaction of $CpRu(PPh_3)_2^+$ with trimethylenesulfide. Synthesis and molecular and crystal structure of $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$

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(Received November 9, 1993; revised February 2, 1994)

Abstract

The isolation and characterization of the trimethylenesulfide-coordinated complex, $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$, is reported. The structure of $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$ was determined by X-ray diffraction techniques: monoclinic space group $I2/a$, $a=23.864(10)$, $b=14.233(3)$, $c=24.385(7)$ Å, $\beta=97.10(3)°$, $Z=8$, $R=0.046$, $R_w=0.065$. The Ru is attached to two triphenylphosphine ligands, a cyclopentadienyl and the trimethylenesulfide. The Ru–S distance is 2.3459(20) Å.

Key words: Crystal structures; Ruthenium complexes; Cyclopentadienyl complexes; Sulfide complexes

Introduction

Our research into the reactions of weak sulfur donor ligands with Ru metal centers stems from the findings that RuS_2 is an excellent catalyst for the hydrodesulfurization of dibenzothiophene [1–3]. Hydrodesulfurization is an important industrial process for the removal of sulfur impurities from fossil fuel feedstocks prior to the refining process [4, 5]. Several groups have used the $CpRu(L)_x^+$ moiety ($L=PPh_3, x=2$; L = dppm, dppe, $x=1$) to coordinate sulfur-containing ligands, including persulfide [6], thiols [7–10], thiolates [11, 12], thioethers [6], thiophene [7, 13], dithiooxamide [14] and ReS_4^- [15]. Herein, we report the synthesis and crystal structure of $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$, which contains the coordinated cyclothioether, trimethylenesulfide.

Experimental

Materials and methods

Reactions were carried out under a dry nitrogen atmosphere using Schlenk techniques. $CpRu(PPh_3)_2Cl$ was prepared as described in the literature [16]. All other reagents were used as purchased without further purification. ^1H NMR spectra were obtained on a Chemagnetics A200 spectrometer using tetramethyl silane (TMS) as the reference. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN, USA.

Synthesis of $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$ (I)

A 0.2072 g (0.29 mmol) sample of $CpRu(PPh_3)_2Cl$ was dissolved in 20 ml of CH_2Cl_2 and 1 ml of trimethylenesulfide was added. In a darkened room, 0.0778 g (0.30 mmol) $AgCF_3SO_3$ was added to the solution while stirring. After 20 min, the solution was filtered through Celite. The addition of 30 ml hexanes to the filtrate gave, upon standing overnight, yellow microcrystals which were isolated by filtration. The product was washed with hexanes and dried. Yield = 0.0756 g, 29%. *Anal.* Calc. for $C_{45}H_{41}RuP_2S_2F_3O_3$: C, 59.13; H, 4.53; S, 7.02. Found: C, 58.98; H, 4.63; S, 7.21%. ^1H NMR (ppm, in $CDCl_3$): 7.26 (m, 21H), 6.95 (m, 14H), 4.79 (s, 5H), 3.27 (quartet, br, 4H), 2.74 (hextet, br, 2H).

X-ray structure analysis of $[CpRu(PPh_3)_2(C_3H_6S)]$-CF_3SO_3 (I)

Crystals were grown by the slow diffusion of hexanes into a CH_2Cl_2 solution of **I**. The crystallographic data are given in Table 1. A yellow crystal (0.28 × 0.28 × 0.36 mm) was mounted on a glass fiber with epoxy. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Cell constants were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $18.0<2\theta<20.0°$. The intensities of three standard reflections which were measured after every 60 min of X-ray exposure time drifted by 1.7%. A total of 6232 reflections (6062 unique reflections, $R_{int}=0.045$) was collected using the θ–2θ scan technique to a maximum 2θ value of 47°. The data were corrected for Lorentz and polarization effects and an analytical

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SSDI 0020-1693(94)03952-K

TABLE 1. Crystallographic data for $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$ (**I**)

Formula	$C_{45}H_{41}RuP_2S_2F_3O_3$
Formula weight	914.0
Space group	*I*2/*a*
a (Å)	23.864(10)
b (Å)	14.233(3)
c (Å)	24.385(7)
α (°)	90.00
β (°)	97.10(3)
γ (°)	90.00
V (Å³)	8218.5
Z	8
D_{calc} (g/cm³)	1.48
F(000)	3655.6
μ (mm⁻¹)	0.6
Scan type	*θ*–2*θ*
Scan range	1.00 + 0.35 tan *θ*
Scan speed (°/min)	4.0–16.0
Max. 2*θ* (°)	47.0
Total reflections	6232
Unique reflections	6062
R_{int}	0.045
Reflections $I > 3\sigma(I)$	3871
Parameters	505
R	0.046
R_w	0.065
GOF	1.09
Max. Δ/σ final	0.002
Residual density	−0.48(8), 0.54(8)

TABLE 2. Final positional coordinates and equivalent thermal parameters for the non-hydrogen atoms in $[CpRu(PPh_3)_2(SC_3H_6)]CF_3SO_3$ (**I**)

Atom	*x*	*y*	*z*	B_{eq}[a]
Ru	0.573895(21)	0.45031(3)	0.154600(21)	2.918(22)
S	0.16981(14)	0.18878(23)	0.11835(13)	7.48(16)
S(1)	0.66230(7)	0.45990(12)	0.20836(7)	3.33(7)
P(1)	0.54332(7)	0.33595(11)	0.21449(7)	2.68(7)
P(2)	0.61341(7)	0.35750(12)	0.08909(7)	2.89(7)
F(1)	0.1692(7)	0.0869(15)	0.0328(6)	25.9(15)
F(2)	0.2487(5)	0.1176(15)	0.0717(7)	23.3(14)
F(3)	0.1938(10)	0.0260(10)	0.1093(10)	26.6(18)
O(1)	0.2071(4)	0.1927(10)	0.1651(5)	15.1(9)
O(2)	0.1679(6)	0.2636(7)	0.0845(5)	15.2(8)
O(3)	0.1148(4)	0.1588(10)	0.1234(5)	15.4(9)
C	0.1994(13)	0.0952(15)	0.0740(11)	15.8(17)
C(1)	0.4961(3)	0.5276(5)	0.1686(4)	4.3(4)
C(2)	0.5422(3)	0.5923(5)	0.1755(4)	4.9(4)
C(3)	0.5640(3)	0.5972(5)	0.1224(4)	4.9(4)
C(4)	0.5319(3)	0.5365(5)	0.0853(3)	4.4(3)
C(5)	0.4900(3)	0.4935(5)	0.1128(3)	4.2(3)
C(6)	0.6770(4)	0.5631(7)	0.2521(4)	6.6(5)
C(7)	0.7330(4)	0.5755(8)	0.2316(5)	7.8(6)
C(8)	0.7180(3)	0.5229(8)	0.1785(4)	6.3(5)
(C11)	0.4679(3)	0.3092(4)	0.1985(3)	3.0(3)
C(12)	0.4478(3)	0.2808(5)	0.1441(3)	3.7(3)
C(13)	0.3915(3)	0.2601(6)	0.1299(3)	4.8(4)
C(14)	0.3537(3)	0.2662(5)	0.1686(4)	4.7(4)
C(15)	0.3732(3)	0.2946(5)	0.2212(4)	4.5(4)
C(16)	0.4291(3)	0.3164(5)	0.2368(3)	3.7(3)
C(21)	0.5737(3)	0.2173(4)	0.2242(3)	3.2(3)
C(22)	0.5514(3)	0.1405(5)	0.1942(3)	3.8(3)
C(23)	0.5776(4)	0.0540(5)	0.2006(4)	5.2(4)
C(24)	0.6258(4)	0.0437(6)	0.2374(5)	6.4(5)
C(25)	0.6470(4)	0.1171(6)	0.2677(4)	5.6(4)
C(26)	0.6219(3)	0.2054(5)	0.2617(3)	4.3(3)
C(31)	0.5505(3)	0.3730(5)	0.2881(3)	3.1(3)
C(32)	0.5394(4)	0.3109(6)	0.3289(3)	4.6(4)
C(33)	0.5477(4)	0.3373(7)	0.3840(3)	5.6(5)
C(34)	0.5658(4)	0.4240(8)	0.3983(3)	6.1(5)
C(35)	0.5740(4)	0.4874(6)	0.3588(4)	5.3(4)
C(36)	0.5666(3)	0.4621(5)	0.3026(3)	3.9(3)
C(41)	0.6800(3)	0.2921(5)	0.1056(3)	3.5(3)
C(42)	0.6917(4)	0.2495(6)	0.1561(4)	5.6(4)
C(43)	0.7379(4)	0.1957(7)	0.1693(4)	5.8(4)
C(44)	0.7747(3)	0.1793(6)	0.1318(4)	5.1(4)
C(45)	0.7654(4)	0.2245(9)	0.0836(4)	8.5(6)
C(46)	0.7183(4)	0.2813(8)	0.0691(4)	7.6(6)
C(51)	0.6305(3)	0.4229(5)	0.0273(3)	3.9(3)
C(52)	0.6525(4)	0.5119(6)	0.0323(3)	5.1(4)
C(53)	0.6689(4)	0.5586(7)	−0.0124(5)	6.8(5)
C(54)	0.6648(4)	0.5162(9)	−0.0625(4)	6.8(5)
C(55)	0.6427(4)	0.4275(8)	−0.0687(3)	6.4(5)
C(56)	0.6248(3)	0.3798(6)	−0.0243(3)	4.8(4)
C(61)	0.5651(3)	0.2679(5)	0.0574(3)	3.4(3)
C(62)	0.5153(3)	0.2960(6)	0.0256(3)	4.7(4)
C(63)	0.4734(4)	0.2344(7)	0.0046(3)	5.2(4)
C(64)	0.4817(4)	0.1411(7)	0.0154(4)	6.1(5)
C(65)	0.5305(5)	0.1092(6)	0.0460(4)	6.3(5)
C(66)	0.5723(4)	0.1731(5)	0.0666(3)	4.6(4)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoids.

absorption correction was applied. Neutral atom scattering factors were taken from Cromer and Waber [17]. Anomalous dispersion effects were included in F_{calc} [18]; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer [19].

The structure was solved by direct methods and refined by full-matrix least-squares. The final cycle of the full-matrix least-squares refinement was based on 3871 observed reflections ($I > 3.0\sigma(I)$) and 505 parameters and converged with $R = 0.046$, $R_w = 0.065$. The hydrogen atoms were constrained to idealized positions (C−H = 0.95 Å). Final atomic coordinates and equivalent thermal parameters for the non-hydrogen atoms are given in Table 2. Selected bond distances and angles are given in Table 3.

Results and discussion

The $CpRu(PPh_3)_2Cl$ compound can be easily dechlorinated with $AgCF_3SO_3$, leaving a vacant site for the addition of the sulfur donor ligand trimethylenesulfide. The ^1H NMR spectrum of **I** shows resonances as multiplets for the phenyl protons between 6.9 and 7.5 ppm. Two sets of peaks are assigned to the protons of the trimethylenesulfide ligand (3.27 ppm, C_α protons; 2.74 ppm, C_β protons). For reference, the signal for

TABLE 3. Selected bond distances (Å) and angles (°) for compound I

Bond distances		Bond angles	
Ru-S(1)	2.3459(20)	S(1)-Ru-P(1)	91.13(7)
Ru-P(1)	2.3616(18)	S(1)-Ru-P(2)	90.23(7)
Ru-P(2)	2.3576(19)	P(1)-Ru-P(2)	102.28(6)
Ru-C(1)	2.221(7)	Ru-S(1)-C(6)	117.9(3)
Ru-C(2)	2.238(7)	Ru-S(1)-C(8)	117.0(3)
Ru-C(3)	2.236(7)	C(6)-S(1)-C(8)	75.0(5)
Ru-C(4)	2.225(6)	S(1)-C(6)-C(7)	90.9(6)
Ru-C(5)	2.219(7)	S(1)-C(8)-C(7)	90.4(6)
S(1)-C(6)	1.823(8)	C(6)-C(7)-C(8)	95.9(7)
S(1)-C(8)	1.828(9)		
C(6)-C(7)	1.493(14)		
C(7)-C(8)	1.501(16)		

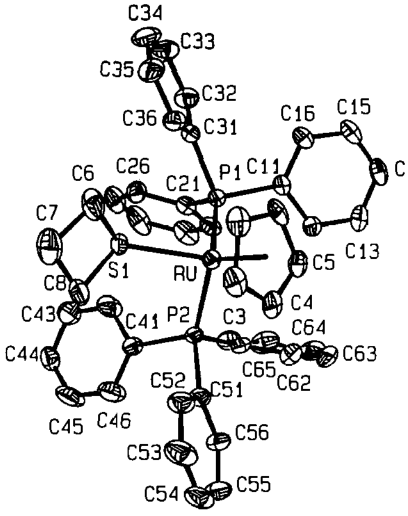

Fig. 1. ORTEP plot (30% probability ellipsoids) of $[CpRu(PPh_3)_2(C_3H_6S)]CF_3SO_3$ showing cation atom labeling scheme. The hydrogen atoms are omitted for clarity.

the C_α protons is observed at 3.23 ppm and the C_β protons signal is observed at 3.00 ppm in neat trimethylenesulfide (Sadtler NMR Index No. 19046 M).

The Ru in I is in a pseudooctahedral geometry formed by the Cp ligand (occupying three sites), the two P atoms of the PPh_3 ligands and the S of the trimethylenesulfide (Fig. 1). The Ru–S(1) distance of 2.3459(20) Å in I is slightly shorter than the Ru–S distance of 2.377(2) Å in $[CpRu(PPh_3)_2(n\text{-}C_3H_7SH)]BF_4$ [7], 2.369(2) Å in $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)]BF_4$ [9] and 2.375(2) Å in $[CpRu(PPh_3)_2(i\text{-}C_4H_9SH)]BF_4$ and is considerably shorter than the Ru–S distance of 2.396(2) Å in $[CpRu(PPh_3)_2(t\text{-}C_4H_9SH)]BF_4$ [10]. The Ru–S distance in $[CpRu(dppm)(t\text{-}C_4H_9SH)]PF_6$ is 2.371(2) Å [8]. The Ru–S distance in I is not quite as short as the comparable distance in the $[CpRu(dppe)(HC(S)C_6H_5)]PF_6$ complex (Ru–S distance is 2.314(1) Å) [20]. As expected, the Ru–S distance shows some dependency to steric constraints about the Ru center. This is supported by angular data for these compounds. The smaller C–S–C angle in trimethylenesulfide allows for a closer contact to the Ru atom than the larger t-butylthiol ligand.

The angles about the S atom in I are 117.9(3)° for Ru–S(1)–C(6), 117.0(3)° for Ru–S(1)–C(8) and 75.0(5)° for C(6)–S(1)–C(8). In the phenethyl mercaptan complex, $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)]BF_4$, the angles involving the sulfur atom are 114.9° for Ru–S–H(S), 95.7° for C(43)–S–H(S) and 110.1(3)° for Ru–S–C(43) [9]. For the $[CpRu(PPh_3)_2(t\text{-}C_4H_9SH)]BF_4$ complex, the angles are 125.7(3), 111.7(1) and 91.9(3)° for the C–S–Ru, Ru–S–H and C–S–H angles, respectively [10]. The C–S–H angle is 99(3)° and the Ru–S–H angle is 97(3)° in $[CpRu(PPh_3)_2(n\text{-}C_3H_7SH)]BF_4$ [7].

The trimethylenesulfide ligand is not planar with torsion angles of −19.2(5)° for C(8)–S(1)–C(6)–C(7) and 19.2(5)° for C(6)–S(1)–C(8)–C(7). For calculating the least-squares planes, the ring was divided into two three-membered rings C(6)–S(1)–C(8) and C(6)–C(7)–C(8). C(7) lies 0.492(17) Å out of the C(6)–S(1)–C(8) plane. S(1) is 0.710(23) Å above the plane C(6)–C(7)–C(8). The dihedral angle between these two planes is 29.4°.

The C(6)–S(1) and C(8)–S(1) distances of 1.823(8) and 1.828(9) Å, respectively, are typical C–S single bond distances. The angles about the trimethylene sulfide ring range from 75.0(5) (C–S–C) to 95.9° (C–C–C). Despite the ring strain, attempts to hydrogenate the C–S bond by refluxing a CH_2Cl_2 solution of I under an H_2 atmosphere for 18 h showed no signs of hydrogenation. Further studies on the reactivity of I are currently underway.

Supplemental material

A listing of general temperature factor expressions (*U*), hydrogen atom parameters, bond distances and angles (5 pages) and tables of calculated and observed structure factors (33 pages) are available from the authors upon request.

Acknowledgements

Funding was provided by the A.S.U. Faculty Research Committee and Competitive Applied Research Grant.

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