

# Organoruthenium chalcogen complexes: synthesis of *tert*-butyl-cyclopentadienyl dicarbonyl ruthenium thio- and seleno-carboxylate complexes and crystal structure determination of $(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCO}(3\text{-NO}_2\text{-C}_6\text{H}_4)$ and $(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SeCO}(3,5\text{-(NO}_2)_2\text{-C}_6\text{H}_3)$

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## Abstract

The substituted cyclopentadienyl organoruthenium dimers  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$  (I) and  $[(1,3\text{-}^t\text{Bu-C}_5\text{H}_3)\text{Ru}(\text{CO})_2]_2$  (II) were prepared from the reaction of  $\text{Ru}_3(\text{CO})_{12}$  with *t*-butyl cyclopentadiene or 1,3-di-*t*-butylcyclopentadiene. The thermal reaction of dimer I with elemental sulfur or selenium afforded mixtures of organoruthenium polysulfides and polyselenides from which the binuclear pentasulfur and pentaselenium bridged complexes  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2(\mu\text{-S}_5)$  (III) and  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2(\mu\text{-Se}_5)$  (IV) were isolated and characterized. The organoruthenium sulfides and selenides readily react with acid chlorides  $\text{RCOCl}$  to give the S-bonded and the Se-bonded monothio- and monoseleno-carboxylate derivatives  $(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{ECOR}$  ( $\text{E} = \text{S, Se}$ ;  $\text{R} = 3\text{-NO}_2\text{-C}_6\text{H}_4$ ,  $4\text{-NO}_2\text{-C}_6\text{H}_4$ ,  $3,5\text{-(NO}_2)_2\text{-C}_6\text{H}_3$ ). The crystal structures of  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCO}(3\text{-NO}_2\text{-C}_6\text{H}_4)]$  and  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SeCO}(3,5\text{-(NO}_2)_2\text{-C}_6\text{H}_3)]$  were determined.

**Keywords:** Ruthenium; Chalcogen; Carbonyl; Cyclopentadienyl; Crystal structure

## 1. Introduction

In spite of the increasing number of reports about the organometallic complexes containing bridging sulfur and selenium groups [1–8], those containing ruthenium remain rare. It has been reported that the reaction of the dimer  $[\text{Cp}'\text{Ru}(\text{CO})_2]_2$  ( $\text{Cp}' = \text{C}_5\text{Me}_5$ ) with excess sulfur produced several polysulfide complexes upon irradiation which were characterized as  $\text{Cp}'\text{Ru}_2(\text{CO})_2\text{S}_4$ ,  $\text{Cp}'\text{Ru}_2(\text{CO})_3\text{S}_4$ ,  $\text{Cp}'_2\text{Ru}_2(\text{CO})\text{S}_4$  and  $\text{Cp}'_2\text{Ru}_2(\text{CO})_2\text{S}_6$ . The polysulfide groups in these complexes exhibit various coordination modes. Moreover, the same reaction of the dimer with excess sulfur under thermal conditions produced only  $\text{Cp}'_2\text{Ru}_2(\text{CO})_2\text{S}_6$  [9]. In our laboratory we succeeded in the isolation of the ruthenium polysulfide  $[(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2(\mu\text{-S}_5)$  [10] and the polyselenide

$(\text{C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_2\text{Se}_3$  [11] from the thermal reaction of  $(\text{C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$  with elemental sulfur and selenium respectively. We also found that such polysulfides and polyselenides react smoothly with acid chlorides to produce monothio- and monoseleno-carboxylate complexes  $[(\text{C}_5\text{H}_5)\text{M}(\text{CO})_2\text{ECOR}]$  ( $\text{M} = \text{Fe, Ru}$ ;  $\text{E} = \text{S, Se}$ ;  $\text{R} = \text{alkyl, aryl group}$ ) [10–12].

It was demonstrated that replacement of one or more of the ring hydrogens of the cyclopentadienyl ( $\text{C}_5\text{H}_5$ ) by alkyl groups produced significant changes in the reactivity, catalytic properties and other properties due to steric and electronic effects introduced by these groups [13–16].

In continuation of our efforts in this area, we report here the synthesis of the dimers  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$  and  $[(1,3\text{-}^t\text{Bu-C}_5\text{H}_3)\text{Ru}(\text{CO})_2]_2$ , the polysulfide  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2(\mu\text{-S}_5)$  and the polyselenide  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2(\mu\text{-Se}_5)$ , as well as their thio- and seleno-carboxylate derivatives.

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## 2. Experimental details

All reactions were conducted under dinitrogen by Schlenk techniques.  $\text{Ru}_3(\text{CO})_{12}$  and acid chlorides were purchased from Aldrich. *t*-Butyl-cyclopentadiene and di-*t*-butyl cyclopentadiene were prepared as previously reported [17,18]. Gray selenium powder was purchased from Fluka. Infrared (IR) spectra were recorded on a Pye–Unicam SP3-100 spectrophotometer and  $^1\text{H}$  NMR spectra on a Bruker WP80SY spectrometer with  $\text{Me}_4\text{Si}$  as internal standard. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, USA.

### 2.1. Preparation of $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ (I)

Refluxing  $\text{Ru}_3(\text{CO})_{12}$  (1.0 g, 1.56 mmol) with excess *t*-butyl-cyclopentadiene (2.2 g, 18 mmole) in *n*-heptane (75 ml) for 6 h afforded a yellow solution. Air was then bubbled through this solution for 5 min to give a dark brown suspension. The solvent was removed under vacuum at 20°C and the residue was taken in  $\text{CH}_2\text{Cl}_2$  and transferred to column chromatography. An orange band was eluted with  $\text{CH}_2\text{Cl}_2$ –*n*-hexane (1:2). Evaporation of the solvent under vacuum and recrystallization from  $\text{CH}_2\text{Cl}_2$  afforded orange crystals of I.

Yield (75%); melting point (m.p.), 164–166°C. Anal. Found: C, 47.33; H, 4.83  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{Ru}_2$ . Calc.: C, 47.48; H, 4.67%. IR:  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$  1970 (vs), 1925 (s), 1745 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.31 (s, 18H); 4.82 (t, 4H); 5.30 (t, 4H) ppm.

### 2.2. Preparation of $[(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)\text{Ru}(\text{CO})_2]_2$ (II)

Refluxing  $\text{Ru}_3(\text{CO})_{12}$  (1.0 g, 1.56 mmol) with excess di-*t*-butyl-cyclopentadiene (2.5  $\text{cm}^3$ , 13 mmol) in *n*-heptane (150  $\text{cm}^3$ ) for 3 h afforded a yellow solution. Air was then bubbled through this solution for 5 min to give a dark brown suspension. The solvent was removed under vacuum at 20°C and the residue was taken in  $\text{CH}_2\text{Cl}_2$  and transferred to column chromatography. A yellow band was eluted with  $\text{CH}_2\text{Cl}_2$ –*n*-hexane (1:2). Evaporation of the solvent under vacuum and recrystallization from  $\text{CH}_2\text{Cl}_2$  afforded yellow–orange crystals of II. Yield (50%); m.p. (dec.) 160–161°C. Anal. Found: C, 54.12; H, 6.29.  $\text{C}_{30}\text{H}_{42}\text{O}_4\text{Ru}_2$ . Calc.: C, 53.89; H, 6.29%. IR:  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$  1960 (vs), 1910 (m), 1740 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.27 (s, 36H), 4.20 (t, 2H); 5.20 (d, 4H) ppm.

### 2.3. Reaction of $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ with elemental sulfur; preparation of $(\mu\text{-S}_5)[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ (III)

A benzene–toluene (1:3) (85 ml) was added to a mixture of 2 mmol of  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$  and 4 mmol of elemental sulfur  $\text{S}_8$ . The mixture was then refluxed. The reaction was monitored by IR spec-

troscopy and refluxing was continued until the reaction had gone to completion (10 h). This was identified by the disappearance of the bridging carbonyl band at 1745  $\text{cm}^{-1}$  of the starting material and the appearance of two strong terminal carbonyl bands at 2015 and 1980  $\text{cm}^{-1}$ . The solvent was removed under vacuum at 20°C and the dark green oily residue was taken in  $\text{CH}_2\text{Cl}_2$  and transferred to column chromatography.

A yellow–green band was eluted with  $\text{CH}_2\text{Cl}_2$ –*n*-hexane. TLC examination ( $\text{CH}_2\text{Cl}_2$ ) indicated that the band was a mixture of compounds which have very close  $R_f$  values. After several attempts of successive chromatography we were able to separate the major yellow fraction from which pale green crystals of the pentasulfane compound  $(\mu\text{-S}_5)[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$  (III) were obtained. Yield (30%). Anal. Found: C, 37.35; H, 3.72; S, 23.14.  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{S}_5\text{Ru}_2$ . Calc.: C, 36.87; H, 3.63; S, 22.35%. IR:  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$  2015 (s), 1980 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.19 (s, 18H); 5.30 (s, 8H) ppm.

### 2.4. Reaction of $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ with elemental selenium (gray selenium); preparation of $(\mu\text{-Se}_5)[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ (IV)

A benzene–toluene (1:3) (85 ml) was added to a mixture of 2 mmol of  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$  and 4 mmol of gray selenium. The mixture was then refluxed. The reaction was monitored by IR spectroscopy and refluxing was continued until the reaction had gone to completion (14 h). This was identified by the disappearance of the bridging carbonyl band at 1745  $\text{cm}^{-1}$  and the appearance of two strong terminal carbonyl bands at 2010 and 1975  $\text{cm}^{-1}$ . The solvent was removed under vacuum at 20°C and the residue was taken in  $\text{CH}_2\text{Cl}_2$  and transferred to column chromatography. An orange band was eluted with  $\text{CH}_2\text{Cl}_2$ –*n*-hexane (2:1). Evaporation of solvent and recrystallization from  $\text{CH}_2\text{Cl}_2$  afforded orange–red crystals of IV. Yield (25%). Anal. Found: C, 27.02; H, 2.84.  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{Se}_5\text{Ru}_2$ . Calc. C, 27.76; H, 2.73%. IR:  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 2010 (s), 1975 (vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.16 (s, 18H); 5.37 (s, 8H) ppm.

### 2.5. Reaction of $(\mu\text{-S}_5)[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ with acid chlorides $\text{RCOCl}$ and the preparation of monothiocarboxylate derivatives $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCOR}]$ (V–VII)

To a methylene chloride solution (50 ml) containing  $(\mu\text{-S}_5)[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$  (2 mmol), a solution of the acid chloride  $\text{RCOCl}$  (2.5 mmol) in 10 ml  $\text{CH}_2\text{Cl}_2$  was added slowly whilst stirring at room temperature. After 3 h the greenish color changed to yellow–orange. The solvent was removed under vacuum at 20°C and the residue was transferred to column chromatography.

Table 1

Analytical data, colors, melting points of the complexes  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCOR}]$  (V–VII) and  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SeCOR}]$  (VIII–IX)

| Compound                                                                     | Color  | Yield (%) | m.p. (°C) | Analysis found (calc.)% |                |                |
|------------------------------------------------------------------------------|--------|-----------|-----------|-------------------------|----------------|----------------|
|                                                                              |        |           |           | C                       | H              | N              |
| R = 3,5-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> (V)   | yellow | 70        | 114–116   | (42.77)<br>42.28        | (3.17)<br>3.00 | (5.54)<br>4.97 |
| R = 4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (VI)                    | yellow | 65        | 98–100    | (46.96)<br>46.72        | (3.70)<br>3.90 | (3.04)<br>2.97 |
| R = 3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (VII)                   | yellow | 60        | 65–67     | (46.96)<br>46.80        | (3.70)<br>3.68 | (3.04)<br>2.87 |
| R = 3,5-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> (VII) | orange | 80        | 109–110   | (39.13)<br>39.26        | (2.90)<br>2.77 | (5.07)<br>4.82 |
| R = 4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (IX)                    | orange | 75        | 104–105   | (42.60)<br>42.66        | (3.36)<br>3.46 | (2.76)<br>2.61 |
| R = 3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (X)                     | orange | 65        | 79–81     | (42.60)<br>43.14        | (3.36)<br>3.16 | (2.76)<br>2.58 |

A yellow–orange band was eluted by CH<sub>2</sub>Cl<sub>2</sub>. Evaporation of the solvent under vacuum and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–*n*-hexane mixture at –30°C produced yellow–orange crystals of the monothiocarboxylate

derivatives  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCOR}]$  (V–VII). Table 1 shows the analytical data, melting points, yields and colors of the monothiocarboxylate derivatives (V–VII). Table 2 gives the IR and <sup>1</sup>H NMR spectral data.

Table 2

IR and <sup>1</sup>H NMR spectral data for the complexes  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCOR}]$  (V–VII) and  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SeCOR}]$  (VIII–X)

| Compound                                                                      | IR (CH <sub>2</sub> Cl <sub>2</sub> )<br>(cm <sup>–1</sup> )                                        | <sup>1</sup> H NMR (CDCl <sub>3</sub> )<br>δ (ppm)                                                                                                                                                                     |
|-------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| R = 3,5-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> (V)    | 2015 vs, 1975 vs ν (CO)<br>1605 s ν (C=O)<br>1525 s, 1335 vs ν (NO <sub>2</sub> )<br>945 s ν (C–S)  | 1.28 (s, 9H, C(CH <sub>3</sub> ) <sub>3</sub> )<br>5.3–5.4 (m, 4H, C <sub>5</sub> H <sub>4</sub> )<br>9.1 (t, 1H, 4-ArH)<br>9.27 (d, 2H, 2,6-ArH)                                                                      |
| R = 4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (VI)                     | 2015 vs, 1975 ν (CO)<br>1585 ν (C=O)<br>1510 s, 1335 vs ν (NO <sub>2</sub> )<br>920 s ν (C–S)       | 1.27 (s, 9H, C(CH <sub>3</sub> ) <sub>3</sub> )<br>5.3–5.4 (m, 4H, C <sub>5</sub> H <sub>4</sub> )<br>8.2 (s, 4H, ArH)                                                                                                 |
| R = 3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (VII)                    | 2025 vs, 1980 vs ν (CO)<br>1590 s ν (C=O)<br>1515 s, 1340 vs ν (NO <sub>2</sub> )<br>940 s ν (C–S)  | 1.28 (s, 9H, C(CH <sub>3</sub> ) <sub>3</sub> )<br>5.3–5.4 (m, 4H, C <sub>5</sub> H <sub>4</sub> )<br>7.3–9.1 (m, 4H, ArH)                                                                                             |
| R = 3,5-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> (VIII) | 2005 vs, 1970 vs ν (CO)<br>1610 s ν (C=O)<br>1535 s, 1335 vs ν (NO <sub>2</sub> )<br>885 s ν (C–Se) | 1.28 (s, 9H, C(CH <sub>3</sub> ) <sub>3</sub> )<br>5.3 (t, 2H, C <sub>5</sub> H <sub>4</sub> ) <sup>a</sup><br>5.4 (t, 2H, C <sub>5</sub> H <sub>4</sub> ) <sup>a</sup><br>9.1 (t, 1H, 4-ArH)<br>9.27 (d, 2H, 2,6-ArH) |
| R = 4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (IX)                     | 2005 vs, 1970 vs ν (CO)<br>1610 s ν (C=O)<br>1535 s, 1335 vs ν (NO <sub>2</sub> )<br>885 s ν (C–Se) | 1.28 (s, 9H, C(CH <sub>3</sub> ) <sub>3</sub> )<br>5.3 (t, 2H, C <sub>5</sub> H <sub>4</sub> ) <sup>a</sup><br>5.4 (t, 2H, C <sub>5</sub> H <sub>4</sub> ) <sup>a</sup><br>8.2 (s, 4H, ArH)                            |
| R = 3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> (X)                      | 2010 vs, 1970 vs ν (CO)<br>1585 s ν (C=O)<br>1535 s, 1335 vs ν (NO <sub>2</sub> )<br>890 s ν (C–S)  | 1.28 (s, 9H, C(CH <sub>3</sub> ) <sub>3</sub> )<br>5.3 (t, 2H, C <sub>5</sub> H <sub>4</sub> ) <sup>a</sup><br>5.4 (t, 2H, C <sub>5</sub> H <sub>4</sub> ) <sup>a</sup><br>7.3–9.1 (m, 4H, ArH)                        |

<sup>a</sup> Virtual triplets.

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\times 10^3$ ) with esds in parentheses for compound (VII)

|       | x         | y         | z         | U(eq) |
|-------|-----------|-----------|-----------|-------|
| Ru(1) | 3942.9(2) | 3860.9(1) | 1722.3(1) | 18(1) |
| S(1)  | 4494(1)   | 4123(1)   | 3626(1)   | 25(1) |
| O(1)  | 6695(3)   | 2771(1)   | 2053(2)   | 49(1) |
| O(2)  | 6932(2)   | 4776(1)   | 1179(1)   | 35(1) |
| O(3)  | 8078(2)   | 3978(1)   | 3367(1)   | 35(1) |
| O(4)  | 6855(3)   | 4053(1)   | 8934(1)   | 48(1) |
| O(5)  | 4423(3)   | 3930(1)   | 7713(2)   | 45(1) |
| N(1)  | 6118(3)   | 4032(1)   | 7980(2)   | 32(1) |
| C(1)  | 5689(3)   | 3189(1)   | 1953(2)   | 29(1) |
| C(2)  | 5876(3)   | 4416(1)   | 1415(2)   | 25(1) |
| C(3)  | 6932(3)   | 4071(1)   | 4005(2)   | 23(1) |
| C(4)  | 6494(3)   | 4074(1)   | 6028(2)   | 24(1) |
| C(5)  | 7312(3)   | 4132(1)   | 7109(2)   | 26(1) |
| C(6)  | 9194(4)   | 4285(1)   | 7400(2)   | 30(1) |
| C(7)  | 10305(3)  | 4377(1)   | 6576(2)   | 32(1) |
| C(8)  | 9546(3)   | 4305(1)   | 5487(2)   | 26(1) |
| C(9)  | 7640(3)   | 4157(1)   | 5204(2)   | 23(1) |
| C(10) | 1601(3)   | 4410(1)   | 785(2)    | 24(1) |
| C(11) | 2152(3)   | 3910(1)   | 106(2)    | 22(1) |
| C(12) | 1737(3)   | 3327(1)   | 590(2)    | 23(1) |
| C(13) | 1005(3)   | 3470(1)   | 1593(2)   | 25(1) |
| C(14) | 906(3)    | 4134(1)   | 1691(2)   | 25(1) |
| C(15) | 1816(4)   | 2686(1)   | 66(2)     | 31(1) |
| C(16) | 2039(5)   | 2163(1)   | 924(3)    | 47(1) |
| C(17) | –94(5)    | 2600(2)   | –658(3)   | 51(1) |
| C(18) | 3411(5)   | 2644(1)   | –643(3)   | 46(1) |

Table 4

Selected bond distances (angströms) and bond angles (deg) for  $[(^i\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCO}(3\text{-(NO}_2\text{-C}_6\text{H}_4))$  (VII)

|              |          |                        |           |
|--------------|----------|------------------------|-----------|
| Ru(1)–S(1)   | 2.388(1) | C(1)–Ru(1)–C(2)        | 91.2(1)   |
| Ru(1)–C(10)  | 2.230(2) | C(1)–Ru(1)–S(1)        | 90.51(8)  |
| Ru(1)–C(11)  | 2.219(2) | C(1)–Ru(1)–C(100)      | 128.2     |
| Ru(1)–C(12)  | 2.265(2) | C(2)–Ru(1)–C(100)      | 124.3     |
| Ru(1)–C(13)  | 2.239(2) | C(2)–Ru(1)–S(1)        | 91.10(7)  |
| Ru(1)–C(14)  | 2.235(2) | C(3)–S(1)–Ru(1)        | 106.11(8) |
| Ru(1)–C(1)   | 1.891(2) | S(1)–C(3)–C(9)         | 116.6(2)  |
| Ru(1)–C(2)   | 1.890(2) | O(3)–C(3)–S(1)         | 124.5(2)  |
| S(1)–C(3)    | 1.742(2) | O(3)–C(3)–C(9)         | 118.9(2)  |
| C(1)–O(1)    | 1.139(3) | C(100)–Ru(1)–S(1)–C(3) | 179.6     |
| C(2)–O(2)    | 1.137(3) |                        |           |
| C(3)–O(3)    | 1.220(3) |                        |           |
| C(3)–O(9)    | 1.505(3) |                        |           |
| C(4)–C(5)    | 1.385(3) |                        |           |
| C(4)–C(9)    | 1.393(3) |                        |           |
| C(5)–C(6)    | 1.381(3) |                        |           |
| C(6)–C(7)    | 1.378(4) |                        |           |
| C(7)–C(8)    | 1.386(3) |                        |           |
| C(8)–C(9)    | 1.393(3) |                        |           |
| C(10)–C(14)  | 1.406(3) |                        |           |
| C(10)–C(11)  | 1.439(3) |                        |           |
| C(11)–C(12)  | 1.424(3) |                        |           |
| C(12)–C(13)  | 1.433(3) |                        |           |
| C(13)–C(14)  | 1.422(3) |                        |           |
| C(12)–C(15)  | 1.513(3) |                        |           |
| C(15)–C(16)  | 1.527(4) |                        |           |
| C(15)–C(17)  | 1.536(4) |                        |           |
| C(15)–C(18)  | 1.522(4) |                        |           |
| C(5)–N(1)    | 1.468(3) |                        |           |
| N(1)–O(4)    | 1.221(3) |                        |           |
| N(1)–O(5)    | 1.228(3) |                        |           |
| Ru(1)–C(100) | 1.881    |                        |           |

C(100), center of cyclopentadienyl ring

## 2.6. Reaction of $(\mu\text{-Se}_5)[(\text{'Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ with acid chlorides $\text{RCOCl}$ and the preparation of monoselenocarboxylate derivatives $[(\text{'Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{-SeCOR}]$ (VIII–X)

To a methylene chloride solution (50 ml) containing  $(\mu\text{-Se}_5)[(\text{'Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$  (2 mmol), a solution of the acid chloride  $\text{RCOCl}$  (2.5 ml) in 10 ml  $\text{CH}_2\text{Cl}_2$  was added slowly whilst stirring at room temperature. After 30 min the color changed from orange red to yellow–orange. The solvent was then removed under vacuum at  $20^\circ\text{C}$  and the residue was transferred to column chromatography. An orange band was eluted with  $\text{CH}_2\text{Cl}_2$ . Evaporation of the solvent under vacuum and recrystallization from  $\text{CH}_2\text{Cl}_2$ –*n*-hexane mixture at  $-30^\circ\text{C}$  produced orange crystals of the monoselenocarboxylate derivatives  $[(\text{'Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SeCOR}]$  (VIII–X). Table 1 shows the analytical data, melting points, yields and colors of compounds (VIII–X). Table 2 gives the IR and  $^1\text{H}$  NMR spectral data.

## 2.7. Crystal structure analysis for $[(\text{'Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCO}(3\text{-NO}_2\text{-C}_6\text{H}_4)]$ (VII)

Suitable crystals were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ . Crystal data were as follows:  $\text{C}_{18}\text{H}_{17}\text{NO}_5\text{SRu}$ , molecular mass, 460.5; monoclinic; space group  $P2_1/c$  with  $a = 712.2$  (3),  $b = 2128.4$  (9),

$c = 1229.5$  (5) pm and  $\beta = 97.52$  (3) $^\circ$ ;  $V = 1847.7 \times 10^6$  pm $^3$ ;  $d_{\text{calc.}} = 1.655$  g cm $^{-3}$ ;  $Z = 4$ ;  $\mu = 0.99$  mm $^{-1}$ ,  $F(000) = 928$ . The cell constants and reflections were measured at a temperature of 200 K on a Siemens (Nikolet Syntex) R3m/V diffractometer with a graphite monochromator,  $\lambda(\text{Mo K}\alpha) = 71.073$  pm. An  $\omega$  scan with a variable scan speed  $5.0\text{--}29.3^\circ$  min $^{-1}$ ,  $\Delta\omega = 0.60^\circ$  and a scan range  $3.9^\circ \leq 2\theta \leq 52.1^\circ$ . There were 3633 independent reflections with 3263 significant ( $I \geq 2\sigma$ ). The structure was solved by use of the program SHELXTL PLUS [19] by direct methods and refined by use of the program SHELXL93 [20]. Hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The refinement converged at  $R_1 = 0.023$  (for 3263 significant reflection) and  $wR_1 = 0.060$  (for all reflection). Atomic coordinates are given in Table 3 and selected bond distances and bond angles in Table 4 [21]. Tables of thermal parameters and hydrogen atom coordinates and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

## 2.8. Crystal structure analysis for $[(\text{'Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCO}(3,5\text{-(NO}_2)_2\text{-C}_6\text{H}_3)]$ (VIII)

Suitable crystals were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ . Crystal data were as follows:

Table 5  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\times 10^3$ ) with esds in parentheses for compound (VIII)

|       | <i>x</i>  | <i>y</i>  | <i>z</i>  | <i>U</i> (eq) |
|-------|-----------|-----------|-----------|---------------|
| Ru(1) | 4994.1(1) | 5450.5(5) | 6180.5(2) | 26(1)         |
| Se(1) | 6012(1)   | 4770(1)   | 5368(1)   | 32(1)         |
| O(1)  | 4864(1)   | 7934(5)   | 5231(2)   | 48(1)         |
| O(2)  | 5312(2)   | 8768(5)   | 6746(2)   | 57(1)         |
| O(3)  | 6287(1)   | 5981(5)   | 6297(2)   | 46(1)         |
| O(4)  | 8729(1)   | 3655(6)   | 3405(2)   | 60(1)         |
| O(5)  | 7907(2)   | 3968(7)   | 3444(2)   | 67(1)         |
| O(6)  | 8945(2)   | 5400(5)   | 5235(2)   | 56(1)         |
| O(7)  | 8198(2)   | 6376(7)   | 6084(2)   | 64(1)         |
| N(1)  | 8221(2)   | 4015(6)   | 3686(2)   | 41(1)         |
| N(2)  | 8431(2)   | 5736(6)   | 5546(2)   | 42(1)         |
| C(1)  | 4927(2)   | 7034(7)   | 5581(2)   | 32(1)         |
| C(2)  | 5227(2)   | 7502(7)   | 6510(2)   | 38(1)         |
| C(3)  | 6472(2)   | 5413(6)   | 5755(2)   | 29(1)         |
| C(4)  | 7373(2)   | 4732(6)   | 4699(2)   | 28(1)         |
| C(5)  | 7960(2)   | 4546(6)   | 4359(2)   | 29(1)         |
| C(6)  | 8322(2)   | 4830(6)   | 4619(2)   | 34(1)         |
| C(7)  | 8063(2)   | 5334(6)   | 5248(2)   | 33(1)         |
| C(8)  | 7473(2)   | 5525(6)   | 5611(2)   | 29(1)         |
| C(9)  | 7119(2)   | 5204(6)   | 5337(2)   | 29(1)         |
| C(10) | 4765(2)   | 2388(7)   | 6280(2)   | 35(1)         |
| C(11) | 4311(2)   | 3398(7)   | 6274(2)   | 35(1)         |
| C(12) | 4072(2)   | 4668(6)   | 6808(2)   | 33(1)         |
| C(13) | 4390(2)   | 4354(7)   | 7137(2)   | 34(1)         |
| C(14) | 4816(2)   | 2961(7)   | 6819(2)   | 38(1)         |
| C(15) | 3536(2)   | 5888(7)   | 7024(2)   | 38(1)         |
| C(16) | 3031(3)   | 4694(11)  | 7497(4)   | 67(2)         |
| C(17) | 3582(3)   | 7676(10)  | 7349(3)   | 61(2)         |
| C(18) | 3431(2)   | 6422(11)  | 6469(3)   | 55(2)         |

$C_{18}H_{16}N_2O_7SeRu$ ; molecular mass 552.4; monoclinic; space group  $C2/c$  with  $a = 2633$  (1),  $b = 708.8$  (3),  $c = 2395$  (1) pm and  $\beta = 61.63$  (3) $^\circ$ ;  $V = 3932.3 \times 10^6$  pm $^3$ ;  $d_{calc.} = 1.866$  g cm $^{-3}$ ;  $Z = 8$ ;  $\mu = 2.69$  mm $^{-1}$ ,  $F(000) = 2176.0$ . The cell constants and reflections were measured at a temperature of 200 K on a Siemens (Nikolet Syntex) R3m/V diffractometer with a graphite monochromator,  $\lambda(Mo K\alpha) = 71.073$  pm. An  $\omega$  scan with a variable scan speed  $5.0^\circ$ – $29.3^\circ$  min $^{-1}$ ,  $\Delta\omega = 0.60^\circ$  and a scan range  $3.8^\circ \leq 2\theta \leq 48.1^\circ$ . There were 3067 independent reflections with 2561 significant ( $I \geq 2\sigma$ ). The structure was solved by use of the program SHELXTL PLUS [19] by direct methods and refined by use of program SHELXL 93 [20]. Hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The refinement converged at  $R_1 = 0.032$  (for 2561 significant reflections),  $wR_2 = 0.093$  (for all reflections). Atomic coordinates are given in Table 5 and selected bond distances and bond angles in Table 6 [21]. Tables of thermal parameters and H-atom coordinates and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

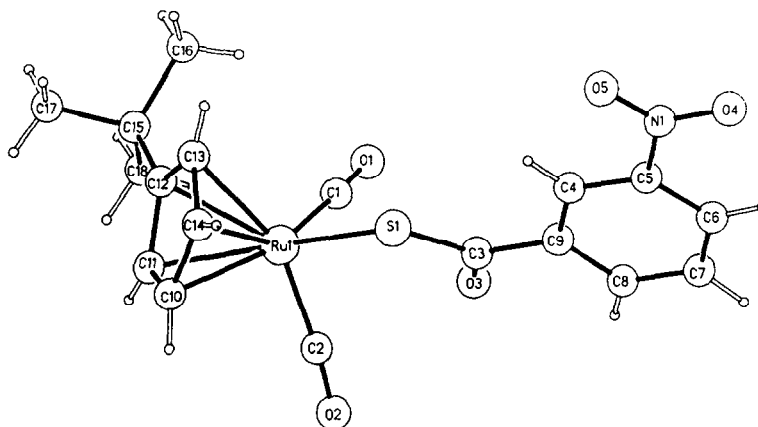
### 3. Discussion

The reaction of  $Ru_3(CO)_{12}$  with *t*-butyl-cyclopentadiene and with 1,3-di-*t*-butyl-cyclopentadiene in boiling *n*-heptane produced the substituted cyclopentadienyl organoruthenium dimers  $[(^tBu-C_5H_4)Ru(CO)_2]_2$  (I) and  $[(1,3-^tBu_2-C_5H_3)Ru(CO)_2]_2$  (II) respectively. These new dimers were characterized by elemental analysis,  $^1H$  NMR and IR spectroscopy. The presence of *t*-butyl substituents on the cyclopentadienyl ring of the ruthenium dimers I and II leads to remarkable variation in the properties, reactivity and structure relative to the unsubstituted analogue. From the refluxing time needed for the formation of the dimer, it was observed that the rate of formation is enhanced by substitution  $[(C_5H_5)Ru(CO)_2]_2$  8 h,  $[(^tBu-C_5H_4)Ru(CO)_2]_2$  6 h,  $[(1,3-^tBu_2-C_5H_3)Ru(CO)_2]_2$  4 h. This was attributed to the increase in the basicity of the ring due to the presence of electron donating *t*-butyl groups [12]. The  $^1H$  NMR spectrum of I shows a singlet at  $\delta$  1.31 ppm (18H) for the *t*-butyl groups and two triplets at  $\delta$  4.82 ppm (4H) and  $\delta$  5.30 ppm (4H) for the ring protons, similar to that observed in the iron analogue

Table 6  
Selected bond distances (angstroms) and bond angles (deg) for  $[(^tBu-C_5H_4)Ru(CO)_2SeCO(3,5-(NO_2)_2-C_6H_3)]$  (VIII)

|              |          |                         |          |
|--------------|----------|-------------------------|----------|
| Ru(1)–Se(1)  | 2.498(1) | C(1)–Ru(1)–C(2)         | 91.5(2)  |
| Ru(1)–C(10)  | 2.235(5) | C(1)–Ru(1)–Se(1)        | 88.6(1)  |
| Ru(1)–C(11)  | 2.240(5) | C(1)–Ru(1)–C(100)       | 125.8    |
| Ru(1)–C(12)  | 2.234(4) | C(2)–Ru(1)–C(100)       | 125.6    |
| Ru(1)–C(13)  | 2.218(5) | C(2)–Ru(1)–Se(1)        | 91.9(1)  |
| Ru(1)–C(14)  | 2.234(5) | C(3)–Se(1)–Ru(1)        | 105.7(1) |
| Ru(1)–C(1)   | 1.895(5) | Se(1)–C(3)–C(9)         | 115.6(3) |
| Ru(1)–C(2)   | 1.890(5) | O(3)–C(3)–C(9)          | 119.2(4) |
| Se(1)–C(3)   | 1.897(4) | O(3)–C(3)–Se(1)         | 125.2(3) |
| C(1)–O(1)    | 1.127(5) | C(100)–Ru(1)–Se(1)–C(3) | 102.6    |
| C(2)–O(2)    | 1.138(6) |                         |          |
| C(3)–O(3)    | 1.218(5) |                         |          |
| C(3)–O(3)    | 1.218(5) |                         |          |
| C(3)–C(9)    | 1.519(6) |                         |          |
| C(4)–C(5)    | 1.369(6) |                         |          |
| C(4)–C(9)    | 1.387(6) |                         |          |
| C(5)–C(6)    | 1.377(7) |                         |          |
| C(6)–C(7)    | 1.374(7) |                         |          |
| C(7)–C(8)    | 1.381(6) |                         |          |
| C(8)–C(9)    | 1.387(6) |                         |          |
| C(10)–C(11)  | 1.399(7) |                         |          |
| C(11)–C(12)  | 1.442(7) |                         |          |
| C(10)–C(14)  | 1.420(7) |                         |          |
| C(12)–C(13)  | 1.413(7) |                         |          |
| C(13)–C(14)  | 1.415(7) |                         |          |
| C(12)–C(15)  | 1.520(6) |                         |          |
| C(15)–C(16)  | 1.528(8) |                         |          |
| C(15)–C(17)  | 1.522(8) |                         |          |
| C(15)–C(18)  | 1.529(7) |                         |          |
| C(5)–N(1)    | 1.469(6) |                         |          |
| C(7)–N(2)    | 1.478(6) |                         |          |
| N(1)–O(4)    | 1.204(5) |                         |          |
| N(2)–O(6)    | 1.218(5) |                         |          |
| Ru(1)–C(100) | 1.878    |                         |          |

C(100), center of cyclopentadienyl ring

Fig. 1. Molecular structure of  $(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCO}(3\text{-NO}_2\text{-C}_6\text{H}_4)$ .

[12]. However, the  $^1\text{H}$  NMR of dimer II shows a remarkable difference from that observed in the iron analogue [12]. Compound II exhibits a singlet at  $\delta$  1.27 ppm (36H) for the *t*-butyl groups, a triplet at  $\delta$  4.20 ppm (2H) for H(2) and a doublet at  $\delta$  5.20 (4H) for H(4,5) of the ring protons.

In contrast, the iron analogue  $[(1,3\text{-}^t\text{Bu}_2\text{-C}_5\text{H}_3)\text{-Fe}(\text{CO})_2]_2$  [12] exhibits a singlet at  $\delta$  1.39 ppm (36H) for the *t*-butyl groups, a doublet at  $\delta$  3.85 ppm (4H) for H(4,5) and a triplet at  $\delta$  5.07 (2H) for H(2) of the ring protons. It was suggested [12] that the ring protons that are shifted down field are those that fall within the shielding cone of the bridging carbonyl group. In the iron dimer the ring protons (4,5) fall within the shielding cone of the bridging carbonyl as confirmed by X-ray molecular structure [21]. Thus, on the basis of the above discussion, the cyclopentadienyl ring in compound II must be situated in such a way that H(2)  $\delta$  (4.20 ppm) rather than H(4,5)  $\delta$  (5.20 ppm) falls within the shielding cone of the bridging carbonyl group.

The pentasulfide  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2(\mu\text{-S}_5)$  (III) and the pentaselenide  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2(\mu\text{-Se}_5)$  (IV) were characterized on the basis of elemental analysis, IR and  $^1\text{H}$  NMR spectroscopy. The IR spectroscopy of compounds III and IV shows two terminal carbonyl stretching bands at 2015, 1980  $\text{cm}^{-1}$  and 2010, 1975

$\text{cm}^{-1}$  respectively. These values are similar to those obtained for the pentasulfide  $[(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2(\mu\text{-S}_5)$  previously reported [10].

The  $^1\text{H}$  NMR spectra of compounds III and IV respectively show singlets at  $\delta$  (1.19 ppm, 18H), (1.16 ppm, 18H) for the *t*-butyl groups and singlets at  $\delta$  (5.30 ppm, 8H), (5.37 ppm, 8H) for the ring protons. Although the four ring protons of  $(^t\text{Bu-C}_5\text{H}_4)$  constitute an AA'BB' system, their splitting pattern seems to be markedly affected by the structural and electronic environment around the metal center. It has been found that the ring protons of this system appear as a symmetrical multiplet in  $(^t\text{Bu-C}_5\text{H}_4)_2\text{TiCl}_2$  [16], as an unsymmetrical multiplet in  $(^t\text{Bu-C}_5\text{H}_4)_2\text{Ti}(\text{Cl})(\text{NCS})$  [16] as a singlet in  $(^t\text{Bu-C}_5\text{H}_4)_2\text{Ti}(\text{NCS})_2$  [16,22] as two virtual triplets in  $(\text{Me}_3\text{Si-C}_5\text{H}_4)\text{TiCl}_2$  [16,22] and as four multiplets in  $(^t\text{Bu-C}_5\text{H}_4)\text{Fe}(\text{CO})(\text{PPh}_3)\text{SCOR}$  [23]. In view of the above discussion, the  $^1\text{H}$  NMR data of compounds III and IV in which the Cp-ring protons appear as a singlet could be possible.

The organoruthenium sulfide (III) and selenide (IV), as well as their parent mixtures, react readily at room temperature with acid chlorides  $\text{RCOCl}$  ( $\text{R} = 3\text{-NO}_2\text{-C}_6\text{H}_4$ ,  $4\text{-NO}_2\text{-C}_6\text{H}_4$ ,  $3,5\text{-(NO}_2)_2\text{-C}_6\text{H}_3$ ) to produce the monothio- and the monoseleno-carboxylate derivatives  $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{ECOR}]$  ( $\text{E} = \text{S, Se}$ ) (V–X).

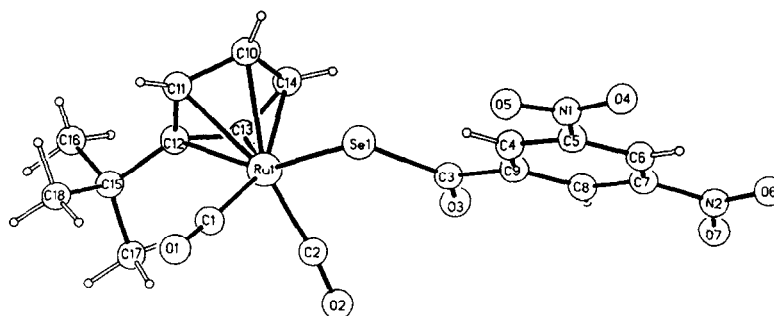
Fig. 2. Molecular structure of  $(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SeCO}(3,5\text{-(NO}_2)_2\text{-C}_6\text{H}_3)$ .

Table 1 presents their colors, yields, melting points and their elemental analyses. The reactivity of organoruthenium sulfides and selenides toward acid chlorides as electrophiles has been attributed to the presence of sulfur and selenium atoms which are considered as the nucleophilic centers in the bridged organoruthenium complexes [24–26].

### 3.1. Molecular structures of $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SCO}(3\text{-NO}_2\text{-C}_6\text{H}_4)]$ (VII) and $[(^t\text{Bu-C}_5\text{H}_4)\text{Ru}(\text{CO})_2\text{SeCO}(3,5\text{-(NO}_2)_2\text{-C}_6\text{H}_3)]$ (VIII)

The molecular structures of compounds VII and VIII are shown in Figs. 1 and 2. Bond distances, selected bond angles and torsional angles are shown in Tables 4 and 6. Compound VII possesses a Ru–S bond distance of 2.388(1) Å which is in the normal range of single Ru–S bond distance [12] and Ru–S–C<sub>3</sub> angle of 106.11(8)° with almost Sp<sup>3</sup> hybridization of the sulfur atom.

In compound VIII, the Ru–Se bond distance is 2.498(1) Å, which is in the normal range of single Ru–Se bond distance [27]. The selenium atom also exhibits an Sp<sup>3</sup> hybridization, as concluded from the C<sub>3</sub>–Se–Ru bond angle of 105.7°(1). In both compounds, the angles at Ru, between S (or Se) and the carbonyls, are around 90°; this is similar to those observed for  $[(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{SCO}(2\text{-NO}_2\text{-C}_6\text{H}_4)]$  [12].

The position of the cyclopentadienyl ring relative to the S–C and Se–C bonds seems to be dependent on the *t*-butyl substituent on the Cp ring, as well as on the chalcogen atom. The trans relationship between the Ru–Cp and the C–S bond (C100–Ru–S–C<sub>3</sub> = –179.6°) contrasts with the corresponding cis relationship observed for the unsubstituted cyclopentadienyl ruthenium analogue  $[(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{SCO}(2\text{-NO}_2\text{-C}_6\text{H}_4)]$  [12]. Moreover, the relationship between the Ru–Cp and the C–Se bond in compound VIII is neither cis nor trans, but half way between them (C100–Ru–Se–C<sub>3</sub> = –102.6°).

### Acknowledgment

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