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Chalcogenate-Bridged Heterometallic Complexes Containing Tricarbonyl Rhenium Combined with Cymene Ruthenium

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Abstract—The reaction of $Re(CO)_3(THF)_2Cl$ with $(Cymen)RuCl_2$ (Cymen = *p*-methyl-*iso*-propylbenzene) in benzene gave the known heterometallic complex $(Cymen)Ru(\mu\text{-}Cl)_3Re(CO)_3$ (**I**), which was converted to the heterometallic complex $(Cymen)Ru(\mu\text{-}S\text{-}tert\text{-}Bu)_3Re(CO)_3$ (**II**) on treatment with *tert*-butylmercaptan and triethylamine. Treatment of **I** with sodium tellurophenolate in THF results in the formation of the ionic complex $[(Cymen)Ru(\mu\text{-}TePh)_3Ru(Cymen)]^+[(CO)_3Re(\mu\text{-}TePh)_3Re(CO)_3]^-$ (**III**) with homobinuclear cation and anion. The structures of **II** and **III** were determined by X-ray diffraction (CIF files CCDC nos. 1022559 (**II**) and 1022560 (**III**)).

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INTRIDUCTION

Targeted synthesis of heterometallic chalcogenide clusters is important from the standpoint of their use as precursors of mixed-metal chalcogenide nano-sized inorganic materials of a specified composition. From this standpoint, most promising are complexes that contain easily detaching organic groups (carbonyl or arene groups) at metal atoms or organic groups at chalcogen atoms. Therefore, we paid attention to three-bridged binuclear chalcogenate complexes. A known complex of this type is the ionic rhenium carbonyl complex, $Re(CO)_3(CH_3CN)_3{}^+[(CO)_3Re(\mu\text{-}S\text{-}tert\text{-}Bu)_3Re(CO)_3]^-$ containing a binuclear thiolate-bridged anion [1]. Also, cationic binuclear ruthenium complexes were reported: the thiophenolate $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}SPh)_3Ru(\eta^6\text{-}C_6H_6)]^+PF_6^-$ [2] and methylthiolate $[(Cymen)Ru(\mu\text{-}SMe)_3Ru(Cymen)]^+PF_6^-$, which unexpectedly formed on heating of $[(Cymen)Ru(\mu\text{-}MeSCH_2SMe)Cl]^+PF_6^-$ in a water–acetonitrile mixture [3]. Finally, the tellurophenolate complex $(CO)_3Mn(\mu\text{-}TePh)_3Fe(CO)_3$ has been obtained by the reaction of *fac*-$[Fe(CO)_3(TePh)_3]^-$ with $[Mn(CO)_3(CH_3CN)_3]^+$ [4].

A natural starting compound for the synthesis of heterometallic rhenium–ruthenium chalcogenate-bridged clusters is the halide-bridged complex $(Cymen)Ru(\mu\text{-}Cl)_3Re(CO)_3$ (**I**) [5], which has been prepared by the reaction of $[(Cymen)RuCl_2]_2$ and $Re(CO)_3(THF)_2Cl$ (the latter is formed upon refluxing of $Re(CO)_5Cl$ in THF).

EXPERIMENTAL

All operations involved in the synthesis and isolation of compounds were carried out under argon in dehydrated solvents. Triethylamine was distilled from sodium under argon. Commercial $[(Cymen)RuCl_2]_2$, $Re_2(CO)_{10}$, Ph_2Te_2, and *tert*-butylmercaptan were used as received. $Re(CO)_5Cl$ was prepared by a reported procedure [6]. Elemental analysis was carried out on a Carlo Erba CHNS analyzer. IR spectra were measured on a Bruker Alpha spectrometer.

Synthesis of $(Cymen)Ru(\mu\text{-}SR)_3Re(CO)_3$ ($R = C(CH_3)_3$) (II). A weighed portion of $(Cymen)Ru(\mu\text{-}Cl)_3Re(CO)_3$ (0.153 g, 0.25 mmol) was dissolved in 15 mL of CH_2Cl_2. Trietyhylamine (0.1 mL) and $HSC(CH_3)_3$ (0.08 mL) were added to the yellow-orange solution; the solution color changed to a dark mossy, black, and then to cherry-orange. After removal of the solvent, the dark precipitate was washed with 40 mL of heptane (20 mL × 2), dried in vacuum of a water-jet pump, extracted with 10 mL of CH_2Cl_2, diluted with 2.5 mL of heptane, and concentrated until crystals started to precipitate. Keeping the mother liquor at +5°C afforded yellow-orange crystals suitable for X-ray diffraction. Yield 0.137 g (71%).

For $C_{25}H_{32}O_3S_3RuRe$ ($M = 773.06$)

anal. calcd., %:	C, 33.25;	H, 2.61.
Found, %:	C, 33.89;	H, 2.73.

IR (KBr; ν, cm^{-1}): 2962 w, 2917 w, 1994 vs, 1869 vs, 1633 w.br, 1506 vw, 1469 vw, 1450 w, 1387 w, 1362 w, 1154 m, 1057 w, 1020 w, 880 vw, 849 vw, 802 vw, 633 w, 618 w, 524 m, 487 w.

Crystallographic data and structure refinement details for **I** and **II**

Parameter	Value	
	II	**III**
M	773.03	2239.22
Radiation (λ, Å)	MoK_α (0.71073)	
Measurement temperature, K	150(2)	173(2)
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	Cc
a, Å	9.6990(3)	11.569(1)
b, Å	16.6601(5)	21.337(2)
c, Å	18.0867(5)	26.334(2)
β, deg	98.930(1)	92.428(1)
V, Å^3	2887.1(2)	6495(1)
Z	4	4
ρ(calcd.), g/cm^{-3}	1.778	2.29
μ, mm^{-1}	4.953	6.860
F(000)	1528	4112
Scanning range for θ, deg	2.28–27.49	1.55–27.49
Scan mode	ω	
Number of independent reflections (N_1)	6602 (R_{int} = 0.0325)	14513 (R_{int} = 0.0235)
Number of reflections with $I > 2\sigma(I)$ (N_2)	6099	13928
Number of refined parameters	310	698
GOOF (F^2)	1.004	1.003
R_1 for N_2	0.0174	0.0214
wR_2 for N_1	0.0426	0.0485
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.145/–0.872	1.767/–0.625

Synthesis of [(Cymen)Ru(μ-TePh)$_3$Ru(Cymen)]$^+$[(CO)$_3$Re(μ-TePh)$_3$Re(CO)$_3$]$^-$ (III). A solution of NaTePh in 10 mL of MeOH prepared from Te_2Ph_2 (0.42 g, 1.04 mmol) and $NaBH_4$ (97 mg, 2.5 mmol) was added to a solution of (Cymen)Ru(μ-Cl)$_3$Re(CO)$_3$ (0.42 g, 0.69 mmol) in 10 mL of THF. The resulting claret-colored solution was stirred for 1 h and the solvent was removed. The oily residue was washed with 20 mL of heptane, reprecipitated with a CH_2Cl_2–heptane mixture, and crystallized at the CH_2Cl_2–hexane interface at +5°C. This gave yellow-orange crystals of **III** suitable for X-ray diffraction (yield 0.10 g (13%)) and a claret-colored oil that solidified upon drying.

For $C_{62}H_{58}O_6Te_6Ru_2Re_2$ (M = 2239. 27)

anal. calcd., %:	C, 38.84;	H, 5.35;	S, 12.44.
Found, %:	C, 38.59;	H, 5.19;	S, 12.41.

IR (KBr; ν, cm^{-1}): 2955w, 2923 w, 2851 w, 1999 vs, 1985 vs, 1877 vs.br, 1570 w, 1471 m, 1431 m, 1384 w, 1322 vw, 1295 vw, 1176 vw, 1015 w, 997 w, 729 ñ, 691 m, 614 w, 598 w, 509 w, 453 w.

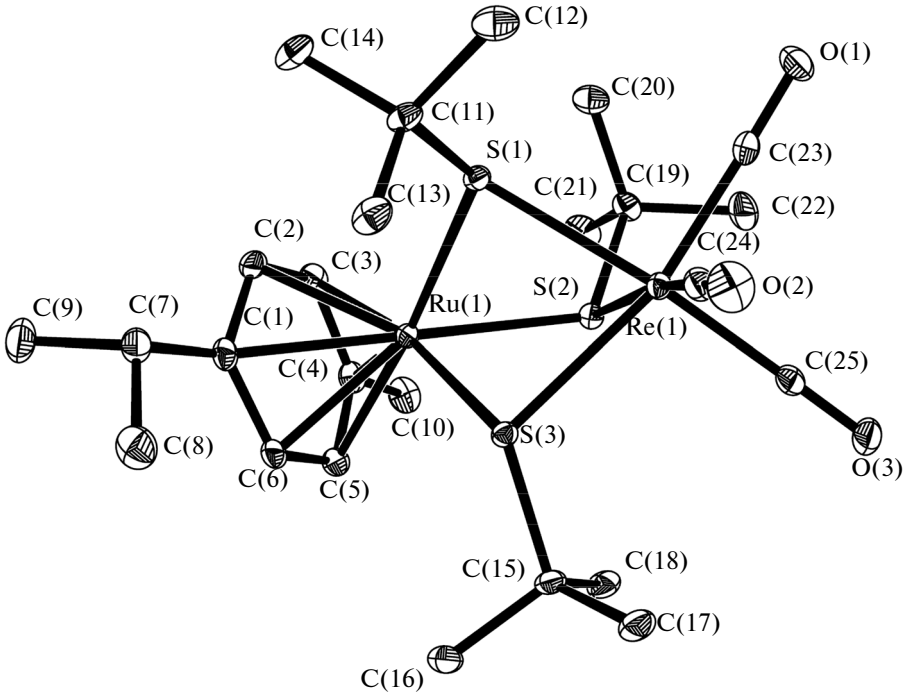
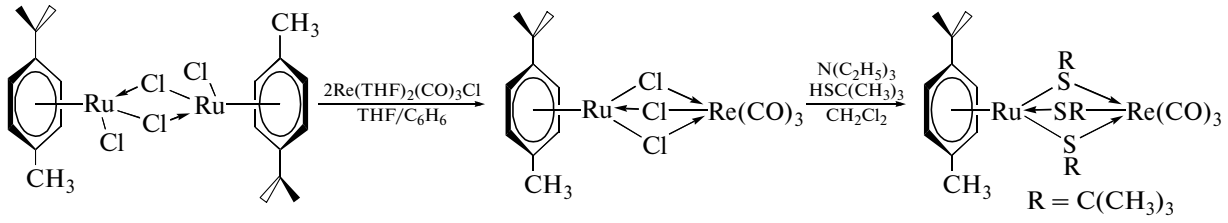


Fig. 1. Molecular structure of (Cymen)Ru(μ-$SCMe_3$)$_3$Re(CO)$_3$ (**II**). Selected bond lengths and angles: Re(1)–S(5), 2.4964(5); Re(1)–S(3), 2.4974(6); Re(1)–S(4), 2.5031(6); Ru(1)–S(5), 2.4132(6); Ru(1)–S(3), 2.4322 (6); Ru(1)–S(4), 2.4405(6) Å; Ru(1)S(3)Re(2), 88.64(2)°; Ru(1)S(4)Re(2), 88.33(2)°; Ru(1)S(5)Re(2), 89.10(2)°.

X-ray diffraction analysis was performed on a Bruker Smart APEX II CCD AXS diffractometer. The crystallographic data and structure refinement parameters for **II** and **III** are summarized in the table. The absorption corrections were applied by the multiple measurement of equivalent reflections (SADABS) [7]. The structures were solved by the direct method and refined by least squares relative to F^2 in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [8]. The coordinates of disordered atoms of the phenyl and isopropyl groups in structure **III** were refined in the isotropic approximation with similar geometry restraint (SAME instruction in SHELXTL). The positions of H atoms were calculated geometrically. Selected bond lengths and angles are given in the captions to Figs. 1 and 2. Atom coordinates and other parameters of structures **II** and **III** are deposited with the Cambridge Crystallographic Data Centre (nos. 1022559 and 1022560, respectively, http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The complex (Cymen)Ru(μ-Cl)$_3$Re(CO)$_3$ (**I**) containing no Ru–Re bond [5] undergoes complete replacement of chlorine atoms by thiolate bridges when treated with *tert*-butylmercaptan and triethylamine in CH_2Cl_2, being thus converted to yellow-orange crystals of complex **II**:



The IR spectrum of **II** exhibits two CO stretching bands at 1994 and 1869 cm^{-1}. According to X-ray diffraction data (Fig. 1), the Ru–S (average 2.428 Å) and Re–S (average 2.499 Å) bonds in **II** are much shorter than the sum of covalent radii ($r_{Re} + r_S = 2.56$, $r_{Ru} + r_S = 2.51$ Å) [9], probably, due to the dative interactions of the lone electron pairs (LEP) of metal atoms with the vacant *d*-orbitals of sulfur. There is no binding

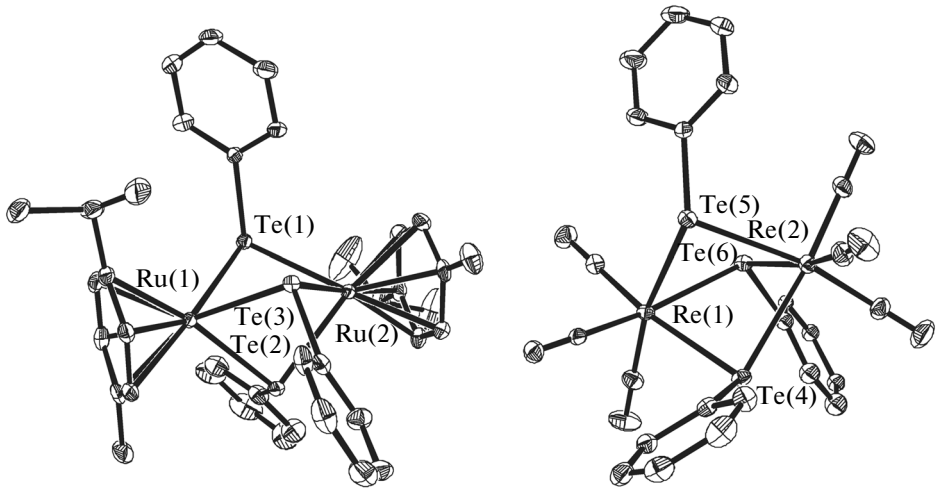


Fig. 2. Molecular structure of $[(Cymen)Ru(\mu\text{-}TePh)_3Ru(Cymen)]^+[(CO)_3Re(\mu\text{-}TePh)_3Re(CO)_3]^-$ (**III**). Bond lengths: Re(1)–Te(4), 2.7822(5); Re(1)–Te(6), 2.7918(4); Re(1)–Te(5), 2.8007(4); Re(2)–Te(5), 2.7878(4); Re(2)–Te(4), 2.7908(4); Re(2)–Te(6), 2.8090(4); Ru(1)–Te(2), 2.6409(5); Ru(1)–Te(1), 2.6712(5); Ru(1)–Te(3), 2.6714(5), Ru(2)–Te(3) 2.6510(5); Ru(2)–Te(1), 2.6609(5); Ru(2)–Te(2), 2.6665(5) Å.

between rhenium and ruthenium, as in the above-mentioned dirhenium anionic complex $[(CO)_3Re(S\text{-}tert\text{-}Bu)_3Re(CO)_3]^-$ in which the Re···Re distances are 3.487 Å , while the Re–S bond length is 2.509–2.525 Å [1]. Similarly, in the cationic binuclear ruthenium complex $[(\eta^6\text{-}C_6H_6)Ru(SPh)_3Ru(\eta^6\text{-}C_6H_6)]^+$, the Ru···Ru distance is 3.358 Å , while the Ru–S bond length is 2.376–2.424 Å [2].

On the other hand, an attempt to prepare a tellurophenyl analog of the heterometallic complex **II** by the reaction of **I** with sodium phenyltelluride in methanol unexpectedly resulted in the ionic complex consisting of the diruthenium cation $[(Cymen)Ru(\mu\text{-}TePh)_3Ru(Cymen)]^+$ and the dirhenium anion $[(CO)_3Re(\mu\text{-}TePh)_3Re(CO)_3]^-$ each containing three tellurophenyl bridges. Complex **III** was isolated as yellow-orange crystals; the IR spectrum of the complex contained three CO stretching bands at 1999, 1985, and 1877 cm^{-1}. According to X-ray diffraction data (table, Fig. 2), there are no bonds between ruthenium and rhenium atoms in **III**, while the Ru–Te bonds in the cation (average 2.660 Å) and the Re–Te bonds in the anion (average 2.794 Å) are substantially shortened with respect to the sum of the covalent radii ($r_{Re} + r_{Te} = 2.89$ Å, $r_{Ru} + r_{Te} = 2.84$ Å) [9], apparently, due to dative interactions between the LEP of metal atoms and the vacant *d*-orbitals of tellurium.

The different reaction routes of **I** with *tert*-butylmercaptan and sodium phenyl telluride may be dictated by the difference between the polarity of solvents, namely, dichloromethane in the former reaction and methanol in the latter reaction. Perhaps, complex **I** dissociates in methanol, and after that, reactions of the resulting complexes $(Cymen)RuCl_2(MeOH)$ and $Re(CO)_3Cl(MeOH)_2$ with PhTeNa give rise to the binuclear ruthenium cation and the rhenium anion.

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