ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 11, pp. 807–811. © Pleiades Publishing, Ltd., 2009.
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Phenyltellurenyl Halide Complexes of Ruthenium and Rhenium $(CO)_2RuBr_2(PhTeBr)_2$ and $(CO)_3Re(PhTeI)_3(\mu^3\text{-}I)$: Synthesis and Crystal and Molecular Structures

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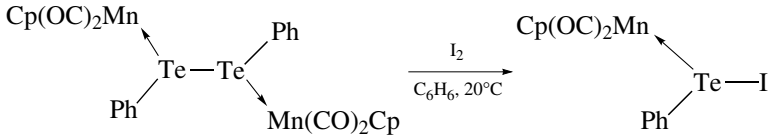
Received April 28, 2009

Abstract—Reactions of $Ru_3(CO)_{12}$ with $PhTeBr_3$ and of $Re(CO)_5Cl$ with PhTeI in benzene give the stable complexes $(CO)_2RuBr_2(PhTeBr)_2$ (**I**) and $(CO)_3Re(PhTeI)_3(\mu^3\text{-}I)$ (**II**) containing two and three ligands PhTeX (X = Br or I), respectively. The bonds between these ligands and the central metal atom are fairly shortened (on average, Ru–Te, 2.608 Å; Re–Te, 2.7554(12)–2.7634(13) Å). The Te–X bonds in the ligands PhTeBr (2.5163(5) Å) and PhTeI (2.7893(15) Å) are not lengthened appreciably. In complex **II**, the iodide anion is not coordinated by rhenium, yet being attached through weak secondary bonds to three Te atoms of the three ligands PhTeI.

DOI: 10.1134/S1070328409110037

Monomeric organyltellurium halides RTeX (X = Cl, Br, and I), in contrast to sulfur and selenium analogs, are unstable in the individual state [1, 2]. According to X-ray diffraction data, PhTeI tetramerizes to form the square core Te_4 (Te–Te 3.125(2)–3.175(2) Å) [3, 4].

Recently, we have demonstrated that the monomeric form PhTeI can be stabilized by coordination with a transition metal. For instance, a reaction of molecular iodine with $[CpMn(CO)_2]_2(\mu\text{-}Ph_2Te_2)$ (**III**) yields the complex $CpMn(CO)_2(PhTeI)$ (**IV**), in which the metal–tellurium bond is retained upon the cleavage of the Te–Te bond and the formation of the Te–I bond [5]:



In complex **IV**, the formally single Mn–Te bond (2.4267(17) Å) is shorter than that in the starting complex **III** (Mn–Te, 2.486(2) Å). Both the bonds are substantially shorter than the sum of the covalent radii of manganese and tellurium (1.39 + 1.38 = 2.77 Å) [6]. At the same time, the Te–I bond (2.868 Å) in complex **IV** is somewhat longer than the sum of the corresponding covalent radii (2.78 Å) [6]; the complex does not contain intermolecular Te···I contacts characteristic of tellurium halide derivatives.

An alternative approach to the synthesis of metal complexes with phenyltellurenyl halides involves oxidative addition of $PhTeX_3$ (X = Br or I) to iron pentacarbonyl. In the resulting complexes $(CO)_3FeX_2(PhTeX)$ (X = Br [5] or I [7]), the Fe–Te bonds are also strongly shortened (2.515 and 2.572 Å, respectively), the Te–X bonds are not lengthened, and intermolecular Te···X contacts are absent. However, the complexes contain secondary bonds between the Te atom and a halogen atom at the Fe atom (Te···Br 2.9418(13), Te···I 3.1634(5) Å).

It was interesting to trace the shortening of the formally single metal–tellurium bonds when passing from 3*d*-metal complexes (Mn and Fe) to their heavier analogs (Re and Ru), which have the same electron shell but the larger covalent radii.

EXPERIMENTAL

All manipulations dealing with the synthesis and isolation of the complexes were carried out under pure argon in dehydrated solvents. IR spectra were recorded on a Specord 75IR spectrophotometer (pellets with

Table 1. Selected crystallographic parameters and the data collection statistics for structures **I** and **II**

Parameter	Value	
	I	**II**
Diffractometer	Bruker APEX II CCD	
Radiation source; λ, Å	MoK_a; 0.71073	
Temperature, K	150(2)	150(2)
Space group	*Pbcn*	$P2_1$
a, Å	12.8042(7)	9.5822(9)
b, Å	22.9592(13)	12.2920(10)
c, Å	7.1029(4)	12.8204(11)
β, deg	90	102.133(2)
V, Å^3	2088.1(2)	1476.3(2)
Z	4	2
ρ(calcd.), g/cm^3	2.819	3.131
μ, mm^{-1}	11.148	11.224
F(000)	1592	1216
θ scan range, deg	1.77–29.00	2.17–29.00
Scan mode	ω	
Number of measured reflections	21278	13119
Number of independent reflections (N_1)	2777 (R_{int} = 0.0365)	6697 (R_{int} = 0.0613)
Number of reflections with $I > 2\sigma(I)$ (N_2)	2494	4978
Number of parameters refined	105	290
GOOF (F^2)	1.087	0.965
R_1 for N_2	0.0246	0.0496
wR_2 for N_1	0.0552	0.0973
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	1.124/–0.934	1.480/–1.536

KBr). Commercial reagents $Ru_3(CO)_{12}$, $Re(CO)_5Cl$, Ph_2Te_2, and I_2 were used as purchased.

Synthesis of $(CO)_2RuBr_2(PhTeBr)_2$ (I). A mixture of $Ru_3(CO)_{12}$ (0.027 g, 0.04 mmol) and $PhTeBr_3$ (0.054 g, 0.12 mmol) in benzene (5 ml) was stirred at 80°C for 5 min. The resulting solution was colored yellowish orange. Heptane (3 ml) was added and the solution was concentrated in a water aspirator vacuum until slight turbidity appeared. The concentrated solution was transferred to a narrow tube, covered with a layer of heptane, and kept in the dark at room temperature. After five days, the long yellow needles that formed were separated, washed with hexane, and dried *in vacuo*. Among the crystals obtained, we found a few smaller yellow crystals, which were mechanically separated and examined by IR spectroscopy in hexane. The spectrum contains the absorption bands ν(CO) at 2125, 2070, and 2047 cm^{-1}. According to [8], this spectral pattern corresponds to $[(CO)_3RuBr(\mu\text{-}Br)]_2$ (in chloroform, ν(CO) = 2131, 2065, and 2059 cm^{-1}). The crystal lattice parameters determined by X-ray diffraction were identical with data for $[(CO)_3RuBr(\mu\text{-}Br)]_2$ [9]. The yield was 10 mg (19%), single crystals **I**.

For $C_{14}H_{10}Br_4O_2RuTe_2$ (M = 886.13)		
anal. calcd,(%:	C, 18.98;	H, 1.14.
Found (%):	C, 19.04;	H, 1.25.

IR (Et_2O, ν(CO), cm^{-1}): 2060 s, 2000 s.

Synthesis of $(CO)_3Re(PhTeI)_3(\mu^3\text{–}I)$ (II). Iodine (0.064 g, 0.25 mmol) was added at 0°C (ice bath) to an orange solution of Ph_2Te_2 (0.1 g, 0.25 mmol) in benzene (10 ml) stirred with a magnetic stirring bar. The black-green reaction mixture was stirred at 0°C for an additional 10 min, whereupon $Re(CO)_5Cl$ (0.18 g, 0.5 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 10 min and then at 50°C for 15 min. The black-red mixture turned dark orange. Heptane (5 ml) was added and the solution was concentrated in a water aspirator vacuum until slight turbidity appeared and kept at –10°C for 48 h. The orange crystals that formed were separated, washed with hexane, and dried *in vacuo*. The yield was 0.05 g (20% with respect to Te).

For $C_{21}H_{15}I_4O_3ReTe_3$ (M = 1391.97)		
anal. calcd, %:	C, 16.45;	H, 1.77.
Found, (%):	C, 18.12;	H, 1.09.

IR (KBr, ν(CO), cm^{-1}): 2020 s, 1930 s.

IR (CH_2Cl_2, ν(CO), cm^{-1}): 2030 s, 1950 m, 1920 m.

X-ray diffraction analysis. Crystallographic parameters and the data collection statistics for structures **I** and **II** are given in Table 1. Structures **I** and **II** were solved by the direct methods and refined by the least-squares method on F^2 in the anisotropic (for H atoms, isotropic) approximation with the SHELXTL program [10]. The positions of the H atoms were calculated geometrically. Selected bond lengths and bond angles in structures **I** and **II** are given in Table 2. Atomic coordinates and other structural parameters of complexes **I** and **II** have been deposited with the Cambridge Crystallographic Data Collection (nos. 726773 (**I**) and 712585 (**II**); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

A reaction of $Ru_3(CO)_{12}$ with $PhTeBr_3$ in hot benzene gave stable complex **I** containing two ligands PhTeBr. Apparently, a reaction intermediate is $(CO)_3RuBr_2(PhTeBr)$, a ruthenium analog of the iron

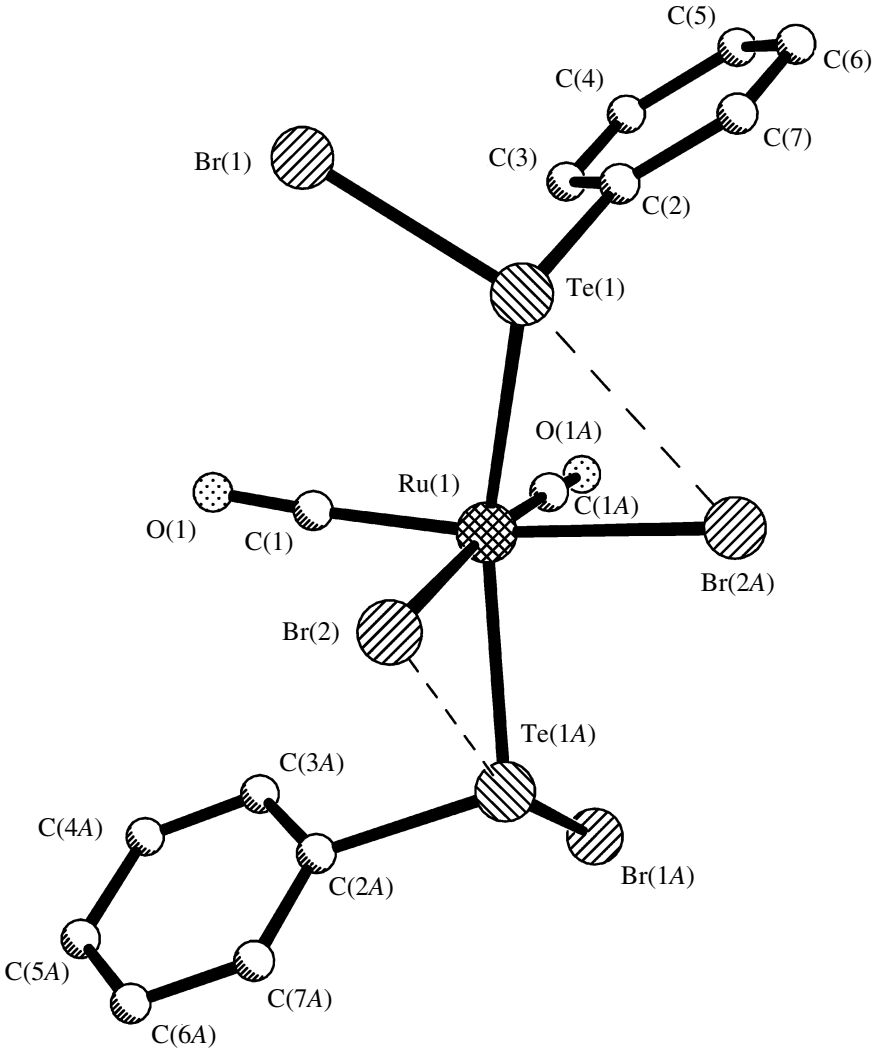
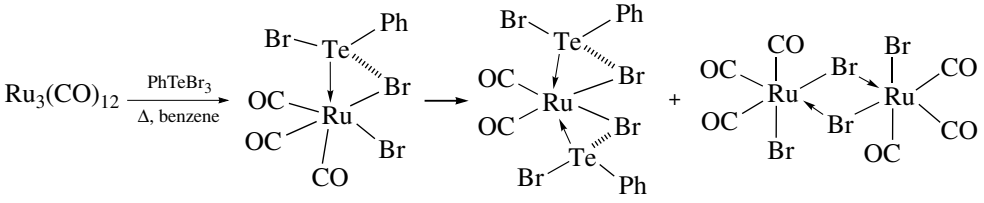


Fig. 1. Molecular structure of complex **I**.

complex $(CO)_3FeBr_2(PhTeBr)$ described in [5]. On heating, the intermediate is easily transformed into complex **I** and the known dimeric carbonylruthenium bromide $[(CO)_3RuBr(\mu\text{-}Br)]_2$, which was mechanically separated in small amounts and identified by IR spectroscopy [8] and X-ray diffraction [9].



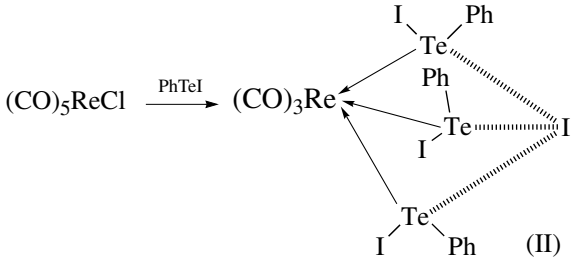
The IR spectrum of complex **I** isolated as long yellow needles shows two intense absorption bands at 2060 and 2000 cm^{-1} (CO stretches). According to X-ray diffraction data (Fig. 1), the ligands PhTeBr in structure **I** are *trans* to each other. The Te–Ru bonds (2.6103(2) Å) are substantially shorter than the sum of the covalent radii of the Ru and Te atoms (2.84 Å) [6], while the Te–Br bonds (2.5163(5) Å) in the ligand PhTeBr are not lengthened, being even slightly shorter than the sum of the covalent radii of the Te and Br atoms (2.58 Å) [6]. Either Br atom that is attached to ruthenium in the *cis*-position (Ru(1)–Br(2), 2.5735(4) Å) is also coordinated by one Te atom (Te(1)–Br(2*A*) 3.0701(5) Å; the angle Br(1)Te(1)Br(2*A*) is 162.297(1) Å). Thus, the coordina-

Table 2. Selected bond lengths and bond angles in structures **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I		Re(1)–C(3)	1.92(2)
Ru(1)–Te(1)	2.6103(2)	Re(1)–Te(1)	2.7634(13)
Ru(1)–Br(2)	2.5735(4)	Te(1)–I(1)	2.7731(16)
Ru(1)–C(1)	1.880(4)	Te(2)–I(2)	2.7893(15)
Te(1)–C(2)	2.106(3)	Te(3)–I(3)	2.7767(17)
Te(1)–Br(1)	2.5163(5)	Te(1)–I(4)	3.2927(2)
Te(1)–Br(2*A*)	3.0702(1)	Te(2)–I(4)	3.2599(2)
II		Te(3)–I(4)	3.2779(2)
Re(1)–Te(2)	2.7554(12)	Te(1)–C(4)	2.114(16)
Re(1)–Te(3)	2.7606(12)	Te(2)–C(10)	2.120(16)
Re(1)–C(1)	1.926(17)	Te(3)–C(16)	2.158(16)
Re(1)–C(2)	1.908(17)		
Angle	**ω, deg**	**Angle**	**ω, deg**
I		C(4)Te(1)I(1)	95.1(5)
C(2)Te(1)Br(1)	92.90(9)	Re(1)Te(1)I(1)	98.26(5)
C(2)Te(1)Ru(1)	105.48(9)	I(3)Te(3)I(4)	178.99(5)
Br(1)Te(1)Ru(1)	109.168(15)	I(1)Te(1)I(4)	174.41(5)
Br(2)Ru(1)Te(1)	88.055(12)	I(2)Te(2)I(4)	176.69(5)
Br(2*A*)Ru(1)Te(1)	72.632(12)	Te(3)I(4)Te(1)	70.10(5)
Br(1)Te(1)Br(2*A*)	162.297(1)	Te(1)I(4)Te(2)	72.07(5)
II		Te(2)I(4)Te(3)	72.48(5)
C(4)Te(1)Re(1)	107.5(4)		

tion polyhedron of each Te atom is a trigonal bipyramid (typical of tellurium) with a stereochemically active lone electron pair as one of the vertices.

A reaction of equimolar amounts of $Re(CO)_5Cl$ with PhTeI in benzene gave orange crystals of a new stable complex **II**. According to X-ray diffraction data (Fig. 2), the coordination polyhedron of the Re atom in complex **II** is an octahedron (facial isomer) with three CO ligands and three ligands PhTeI. The Re–Te bonds (2.7554(12)–2.7634(13) Å) are appreciably shorter than the sum of the covalent radii of rhenium and tellurium (1.51 + 1.38 = 2.89 Å) [6].



(II)

Such a shortening is usually attributed to an additional dative interaction of the lone electron pair at a metal atom with the antibonding Te–X orbitals of the ligand. However, as in complex **I**, the Te–I bond (2.7893(15) Å (II)) in the ligand PhTeI is not lengthened; i.e., the shortening of the Ru–Te and Re–Te bonds is probably due to dative interactions involving the vacant *d* orbitals of tellurium. Note that the iodide anion is not coordinated by the Re atom (Re(1)···I(4) 4.067(1) Å) but is simultaneously attached to three Te atoms through weak secondary bonds (on average, Te···I 3.28 Å; the angle TeITe is 70.10(5)°–72.48(5)°). Secondary bonding is typical of tellurenyl halides [11] and their metal complexes [7]; however, triple coordination of an iodide anion was found earlier only in molybdenum–tellurium iodide clusters with the core $Mo_3(\mu^3\text{-}Te)_7(\mu^3\text{-}I)$ [12] and in the telluronium salts $[(Ph_3Te)_4(\mu^3\text{-}I)_2(MesTeI_2)_2]$ [13] and $[o\text{-}C_6H_4(CH_2TeMe_2)_2(\mu^3\text{-}I)_4]$ [14]. The angles I–Te···I in complexes **II** are nearly flat (I(3)Te(3)I(4), 178.99(5)°). Thus, complex **II** can be described as an ionic complex composed of the cation $[(CO)_3Re(PhTeI)_3]$ and the iodide anion chelated by the metal tris(phenyltellurenyl iodide) fragment (Fig. 2).

In conclusion, note that the crystals of complexes **I** and **II** do not show specific intermolecular interactions Te···I or Te···Br characteristic of tellurium halides.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 09-03-00961), the Division of the Chemistry and Materials Sciences of the Russian Academy of Sciences (grant OKh 1.3), and the

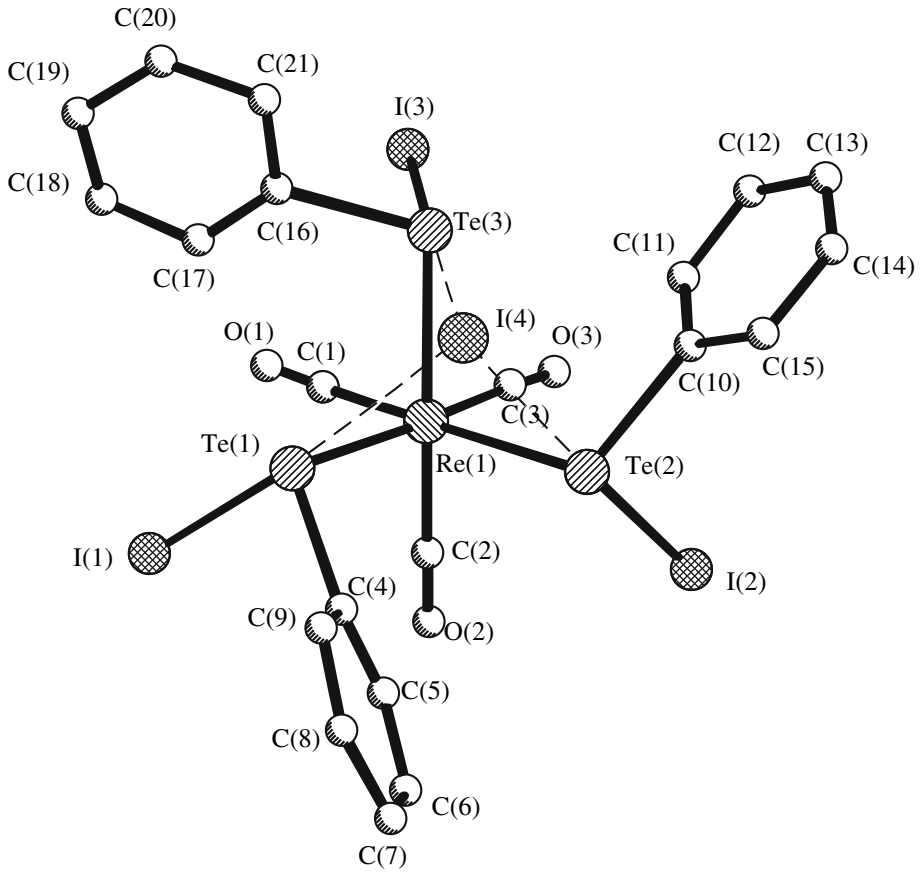


Fig. 2. Molecular structure of complex **II**.

Presidium of the Russian Academy of Sciences (grant 8P22).

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