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$CpFe(CO)_2TePh$ as a Ligand for Organometallic Dihalides $Fe(CO)_4I_2$, (*p*-Cymene)RuI_2, and $Me_5C_5RhI_2$: Synthesis and Molecular Structures[1]

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Abstract—$CpFe(CO)_2TePh$ (**I**) can substitute one carbonyl group in $Fe(CO)_4I_2$ providing $Fe(CO)_3I_2(\mu\text{-}TePh)Fe(CO)_2Cp$ (**II**) or play role of ligand to monomeric fragments [(*p*-Cymene)RuI_2] and [Cp^*RhI_2] (*p*-Cymene = (η^6-1-isopropyl-4-methylbenzene); Cp* = η^5-pentamethylcyclopentadienyl) provides the complexes (*p*-Cymene)$RuI_2(\mu\text{-}TePh)Fe(CO)_2Cp$ (**III**) and $Cp^*RhCl_2(\mu\text{-}TePh)Fe(CO)_2Cp$ (**IV**), respectively. The single-crystal X-ray diffraction of complexes **II**–**IV** (CIF files CCDC nos. 1038124 (**II**), 1038127 (**III**), 1038125 (**IV**)) revealed the shortening of M–Te bonds and the presence of intramolecular I···Te contacts.

Keywords: iron, ruthenium, rhodium, mixed-metal complexes, tellurolate ligands, X-ray diffraction, structure, organometallic compounds

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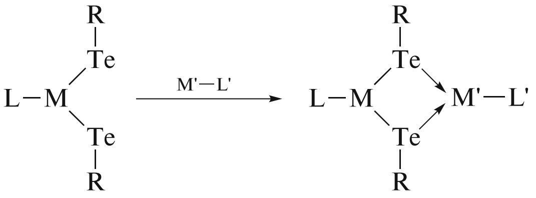
INTRODUCTION

Bis-tellurolate complexes of the transition metals are frequently used as the chelating ligands to assemble mixed-metal tellurolate-bridged complexes (Scheme 1):



Scheme 1.

Diphospino-platinum(II)-bis-tellurolates, (Dppe)-$Pt(TeR)_2$ (R = Ph or ferrocenyl (Fc)), are able to chelate $Re(CO)_3Cl$ fragment, giving tellurolate-bridged $(Dppe)Pt(\mu\text{-}TeR)_2Re(CO)_3Cl$ [1, 2]. The cyclooctadiene ligand in $(COD)MCl_2$ (M = Pd or Pt) is readily substituted by bis-tolyl-tellurolate complex [$Cp^*Ir(CO)(TeTol)_2$] allowing [$Cp^*Ir(CO)(\mu\text{-}TeTol)_2MCl_2$], stabilized only by two tellurolate bridges, similarly to the cationic mixed-metal complexes [$Cp^*Ir(CO)(\mu\text{-}TeTol)_2M'Cp^*Cl$]Cl (M = Ir, Rh) obtained in an interaction of [$Cp^*Ir(CO)(TeTol)_2$] and [$(Cp^*M'Cl)_2(\mu\text{-}Cl)_2$] [3]. Depending on the ratio of the starting reagents, an interaction of [$Cp^*Ir(CO)(TeTol)_2$] and [$(Cp^*Ru)_4(\mu_3\text{-}Cl)_4$] can give neutral [$Cp^*Ir(CO)(\mu\text{-}TeTol)_2RuCp^*Cl$] (at ratio 1 : 0.25) or dicationic [$Cp^*IrCl\{\mu\text{-}Te(\eta^6\text{-}Tol)RuCp^*\}_2RuCp^*(CO)$]$^{2+}$ (at ratio 1 : 0.75) containing the tolyl group additionally

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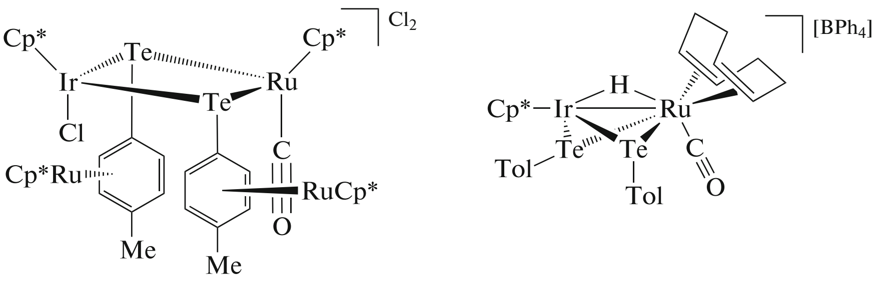
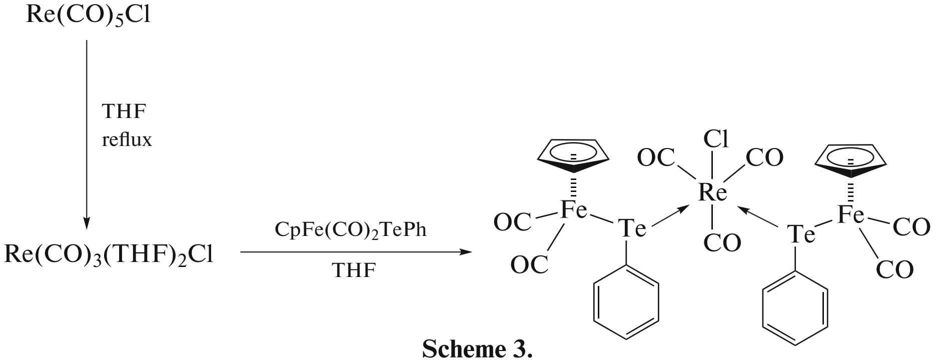
coordinated by η^6-arene type [4]. Similar CO transfer was observed in the complex $[Cp^*Ir(\mu\text{-}H)(\mu\text{-}TeTol)_2Ru(CO)(COD)][BPh_4]$ (having Ir–Ru bond 2.9038(4) Å), formed in an reaction of $[Cp^*Ir(CO)(TeTol)_2]$ and $[RuH(COD)(MeCN)_3]\text{-}[BPh_4]$ [3, 4] (Scheme 2):



Scheme 2.

Anionic complex *cis*-$[PPN][Mn(CO)_4(TePh)_2]$ can chelate cobalt ion in $Co(ClO_4)_2$ giving $(CO)_3Mn(\mu\text{-}TePh)_3Co(CO)(\mu\text{-}TePh)_2Mn(CO)_4$ [5], while the interaction of *fac*-$[Fe(CO)_3(TePh)_3]^-$ with $[Mn(CO)_3(CH_3CN)_3]^+$ produced $(CO)_3Mn(\mu\text{-}TePh)_3Fe(CO)_3$ [6].

In contrast to the vast number of chelating bis-tellurolates there are just few examples of organometallic mono-tellurolates used as monodentate ligands. For example, $Me_4C_4(CO)_2Co(TePh)$ provided $Me_4C_4(CO)_2Co(\mu\text{-}TePh)W(CO)_5$ on treatment with $W(CO)_5(THF)$ [7]. In turn, complex **I** can be easily decarbonylated thermally or photochemically to generate dimeric $[CpFe(CO)(\mu\text{-}TePh)]_2$ [8] which subsequently oxidized to give paramagnetic cation $[CpFe(CO)(\mu\text{-}TePh)]_2^+$ having one-electron Fe–Fe bond [9]. Moreover, recently we employed **I** as a monodentate tellurolate ligand to prepare homometallic cyclopentadienyl-iron-dicarbonyl complexes $[Cp_2Fe_2(CO)_2(\mu\text{-}TePh)]_2^+PF_6^-$, $\{[CpFe(CO)_2(\mu\text{-}TePh)]_2Fe(CO)Cp\}^+PF_6^-$, and mixed-metal complexes $[CpFe(CO)(PPh_3)(\mu\text{-}TePh)\text{-}Mn(CO)(NO)Cp]PF_6$ [10] or $[CpFe(CO)_2(\mu\text{-}TePh)]_2Re(CO)_3Cl$ [1] (Scheme 3):



Scheme 3.

In this paper we studied the coordination of **I** with organometallic dihalides of Fe, Ru, and Rh.

EXPERIMENTAL

All reactions and manipulations were performed using standard Schlenk techniques under an inert atmosphere of pure argon. Solvents were purified, dried and distilled under argon atmosphere prior to use. $CpFe(CO)_2TePh$ [8], $Fe(CO)_4I_2$ [11], $[(p\text{-}Cymene)RuCl_2]_2$ [12], and $[(Cp^*)RhCl_2]_2$ [13] were prepared using reported methods. Commercial reagent grade Ph_2Te_2, $Fe(CO)_5$, $[CpFe(CO)_2]_2$ were used without further purification.

^1H and ^{125}Te NMR spectra were recorded on a Bruker AV 300 spectrometer with ^1H NMR spectra being referenced to residual protons present in the deuterated solvents with respect to TMS at δ = 0, and ^{125}Te NMR spectra being referenced to external Te_2Ph_2 in $CDCl_3$ (δ = 422).

Synthesis of $CpFe(CO)_2(\mu\text{-}TePh)Fe(CO)_3I_2$ (II). $CpFe(CO)_2TePh$ (90 mg, 0.25 mmol) was added to the red solution of $Fe(CO)_4I_2$ (100 mg, 0.25 mmol) in CH_2Cl_2 (10 mL). Gas evolution and color change from red to brown-yellow was observed. Reaction mixture was filtered, diluted with heptane (2.5 mL) and concentrated under reduced pressure to 1/2 and kept at −10°C for 24 h. Red-brown crystals formed were isolated, filtered, washed with heptane (2 × 5 mL) and dried in vacuo. The yield of **II** was 165 mg (85%).

For $C_{16}H_{10}O_5I_2Fe_2Te$ (M = 775.36)

anal calcd., %:	C, 24.79;	H, 2.30.
Found, %:	C, 24.89;	H, 2.44.

IR (CH_2Cl_2 ν(CO), cm^{-1}): 2080 s, 2037 s, 2014 w, 1987 w.

Synthesis of $CpFe(CO)_2(\mu\text{-}TePh)RuI_2$(*p*-Cymene) (III). [(*p*-Cymene)$RuCl_2]_2$ (74 mg, 0.121 mmol) and KI (129 mg, 0.777 mmol) were stirred in acetone (5 mL) for 45 min at ambient temperature. Orange reaction mixture turned cherry-red. The solvent was removed under reduced pressure and the solid residue was extracted with CH_2Cl_2 (2 × 5 mL). Resulting cherry-red extract was added to the green solution of 93 mg (0.242 mmol) $C_5H_5Fe(CO)_2TePh$ in CH_2Cl_2 (5 mL). Reaction mixture was stirred at for additional 2 h, filtered, concentrated to 1/3 of the initial volume, diluted with hexanes and kept overnight at −5°C to give crystalline precipitate, which was recrystallized from benzene/hexane mixture. The yield of **III** was 80.5 mg (38.2%).

For $C_{23}H_{24}O_2I_2FeRuTe$ (M = 870.74)

anal calcd., %:	C, 31.72;	H, 2.78.
Found, %:	C, 31.49;	H, 2.12.

IR (KBr; ν, cm^{-1}): 3087 v.w, 3061 v.w, 2957 w, 2923 w, 2850 w, 2008 v.s, 1965 v.s, 1571 w, 1471 m, 1433 m, 1385 w, 1115 w, 1056 w, 1017 w, 875 w, 848 w, 801 w, 735 m, 712 w, 696 w, 612 m, 572 s, 557 m, 513 w, 463 v.w, 436 v.w.

Synthesis of $CpFe(CO)_2TePhRhCl_2Cp^*$ (IV). 30 mg (0.049 mmol) of $[Cp^*RhCl_2]_2$ was added to green solution of 37 mg (0.097 mmol) $CpFe(CO)_2TePh$ in 10 mL of CH_2Cl_2. After stirring for 30 min, the deep-red solution was filtered, reduced to 1/2 of its volume and 3 mL of hexane were added. Solution was filtered from small amount of orange precipitate and stored overnight at −20°C. Red-brown crystals formed were filtered, washed with hexane, and dried in vacuo. The yield of **IV** was 47 mg (69%).

For $C_{23}H_{25}O_2Cl_2FeRhTe$ (M = 690.71)

anal calcd., %:	C, 40.00;	H, 3.65.
Found, %:	C, 40.11;	H 4.71.

IR (KBr; ν, cm^{-1}): 3098 w, 3050 w, 2983 w, 2960 w, 2920 m, 2854 w, 2022 v.s, 1976 v.s, 1572 w, 1474 m, 1451 w.br, 1434 m, 1415 w, 1384 m.br, 1359 v.w, 1181 v.w, 1157 w, 1077 v.w, 1018 m, 997 w, 850 m.br, 738 s, 693 m, 615 m, 573 s, 556 w, 536 v.w, 499 v.w, 459 m.br, 426 v.w. ^{1}H NMR (300.13 MHz; $CDCl_3$; δ, ppm): 1.51 (s., 15H, C_5Me_5), 5.25 (s., 5H, C_5H_5), 7.08–7.35, 7.98 (m., 5H, Ph). ^{125}Te NMR (94.7 MHz; $CDCl_3$; δ, ppm): 276.85 (d., $^1J_{TeRh}$ = 118.3 Hz, TePh).

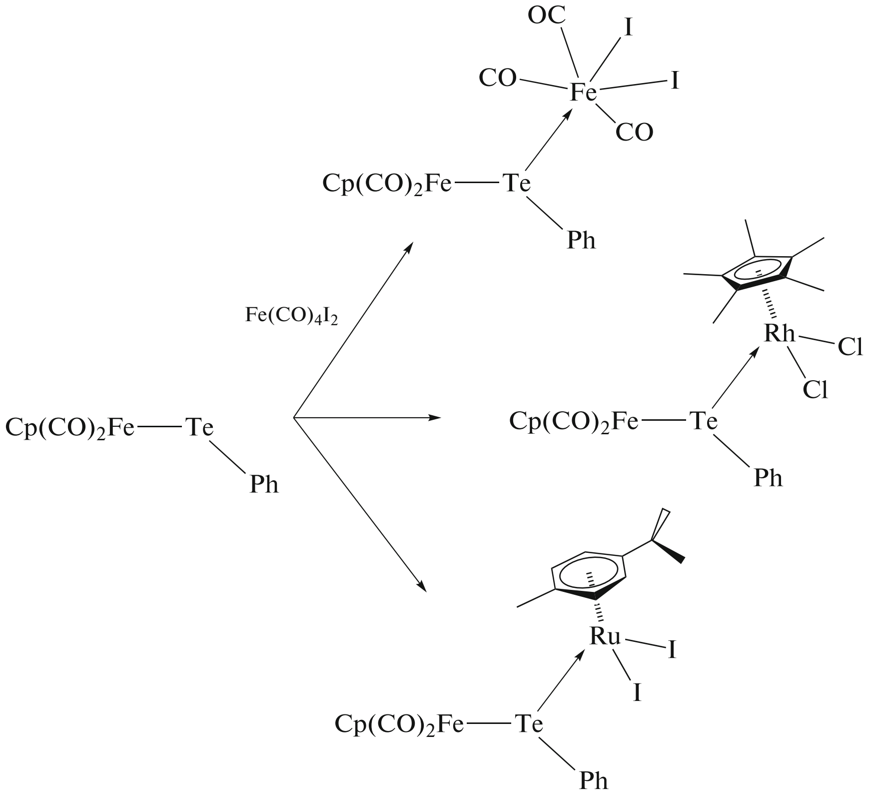
X-ray structural determination. Suitable X-ray quality crystals of **II–IV** were obtained directly during preparation (see synthetic part for details). A Bruker APEX II CCD area detector diffractometer equipped with a low-temperature attachment was used for the cell determination and intensity data collection for compounds **II–IV**. Structures **II–IV** were solved by direct methods and refined by means of least squares method for F^2 in anisotropic approximation in SHELXTL package [14]. Positions of H atoms where calculated geometrically. Appropriate empirical absorption corrections using the program SADABS. Extinction was accounted for structure **II** using $F_c^* = kF_c[1 + 0.001xF_c^2\ \lambda^3/\sin(2/q)]^{-1/4}$ with x refined to 0.0010(1). Relevant crystallographic data and structure refinement details are listed in table. Complexes **III** and **IV** were crystallized with disordered benzene and CH_2Cl_2 molecules, respectively. No reasonable model of the solvent could be obtained; therefore, the PLATON/SQUEEZE [15] program was used to generate solvent-free data sets. Atomic coordinates and other structural parameters of **II–IV** have been deposited with the Cambridge Crystallographic Data Center (CCDC nos. 1038124 (**II**), 1038127 (**III**), 1038125 (**IV**); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The treatment of **I** with $Fe(CO)_4I_2$ in CH_2Cl_2 at room temperature afforded new binuclear complex $CpFe(CO)_2(\mu\text{-}TePh)Fe(CO)_3I_2$ (**II**) as a brown crystalline material (Scheme 4):

Crystallografic data and structure refinement details for compounds **II–IV**

Parameter	Value		
	II	**III** · C_6H_6	**IV** · $2CH_2Cl_2$
Fw	860.27	948.74	860.54
Temperature, K	150(2)	150(2)	298(2)
Radiation (λ, Å)	MoK_α (0.71073)		
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2/c$	$P2_1/c$
a , Å	9.9777(4)	11.0670(3)	11.0785(4)
b, Å	10.5147(4)	14.7303(5)	10.4103(4)
c, Å	12.9876(5)	19.2754(6)	27.651(1)
α, deg	69.411(1)	90	90
β, deg	73.202(1)	106.16(1)	99.773(1)
γ, deg	88.128(1)	90	90
V, $Å^3$	1217.48(8)	3018.12(16)	3142.7(2)
Z	2	4	4
ρ_{calcd}, g cm^{-3}	2.347	1.916	1.819
Absorption coefficient, mm^{-1}	5.145	3.989	2.428
F(000)	796	1624	1680
θ Range, deg	2.08–29.00	2.20–26.44	2.09–29.00
Reflection collected	13524	22347	27753
Independent reflections	6449	6210	8361
Reflections with $I > 2\sigma(I)$	5932	5789	7611
Restraints/parametets	0/263	26/263	0/330
GOOF (F^2)	1.050	1.079	1.011
R indexes ($I > 2\sigma(I)$)	$R_1 = 2.37$, $wR_2 = 5.79$	$R_1 = 3.83$, $wR_2 = 8.79$	$R_1 = 2.40$, $wR_2 = 5.62$
R indexes (all data)	$R_1 = 2.66$, $wR_2 = 5.93$	$R_1 = 4.14$, $wR_2 = 8.93$	$R_1 = 2.77$, $wR_2 = 5.82$
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	1.625/–1.582	2.849/–2.131	1.525/–0.941



Scheme 4.

In agreement with the decrease of electron density on the Fe atom of $Fe(CO)_3I_2$ fragment and its withdrawal from $CpFe(CO)_2TePh$ fragment, the CO vibration bands of $CpFe(CO)_2$ in the IR spectrum of **II** are shifted to the high-frequencies (2014, 1987 cm^{-1}) as compared to the starting **I** (2005, 1968 cm^{-1}). At the same time CO bands of $Fe(CO)_3I_2$ fragment in **II** (2080, 2037 cm^{-1}) are shifted to the lower frequencies area as compared to $Fe(CO)_4I_2$ (2137, 2090, 2072 cm^{-1}).

In the solid state of **II** (table, Fig. 1) the Fe(1)–Te(1) distance (2.5690(4) Å) is shorter as compared to 2.617 Å in the starting **I** and for the sum of Fe and Te covalent radii ($r_{Te} + r_{Fe} = 1.39 + 1.32 = 2.71$ Å) [16]). Similar pattern is observed for Fe(2)–Te(1) distance (2.6117(4) Å). This shortening can be rationalized in terms of back donation of *d*-electrons from the filled orbitals of Fe atom to the Te-centered LUMO of the ligand [17], being more pronounced in the case of electron-rich $CpFe(CO)_2$ fragment.

Interaction of **I** and dimeric $[(p\text{-Cymene})RuI)_2(\mu\text{-}I)_2]$ afforded mixed-metal complex **III** as the dark cherry-red crystals. In the solid state its molecule has shortened Fe–Te (2.5661(9) Å) and Ru–Te (2.6783(6) Å) bonds (Scheme 4, table, Fig. 2).

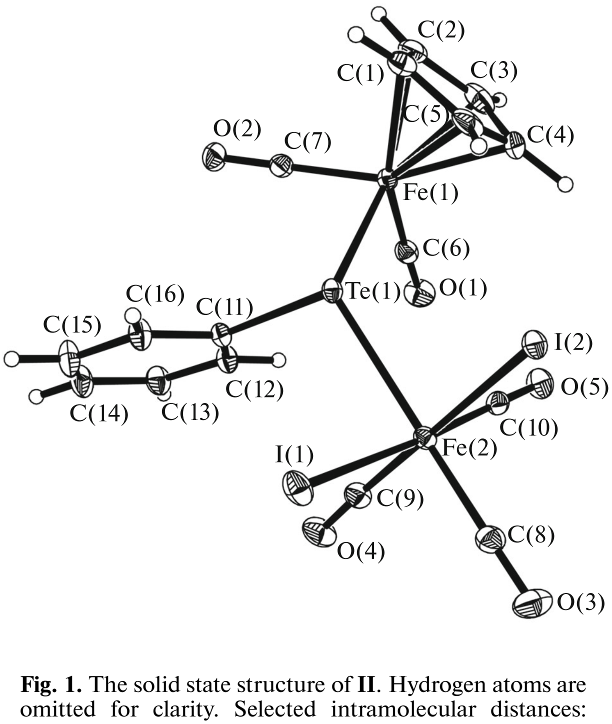


Fig. 1. The solid state structure of **II**. Hydrogen atoms are omitted for clarity. Selected intramolecular distances: Fe(1)–Te(1) 2.5690(4), Te(1)–Fe(5) 2.6117(4), Fe(5)–I(1) 2.6482(4), Fe(5)–I(2) 2.6527(5), Te(1)–C(11) 2.130(3) Å.

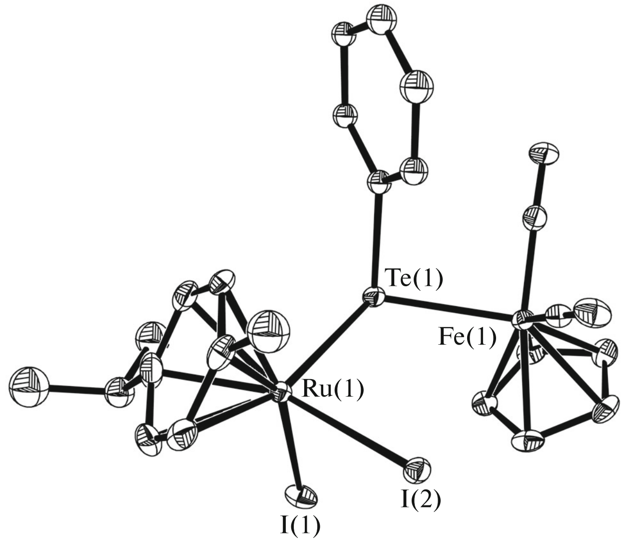


Fig. 2. The solid state structure of **III**. Hydrogen atoms are omitted for clarity. Selected intramolecular distances and bond angles: Te(1)–Fe(1) 2.5661(9), Te(1)–Ru(1) 2.6783(6), I(1)–Ru(1) 2.7423(6), I(2)–Ru(1) 2.7174(6) Å and Te(1)Ru(1)I(2) 94.12(2)°, Te(1)Ru(1)I(1) 84.27(2)°, I(2)Ru(4)I(1) 88.39(2)°, Fe(1)Te(1)Ru(1) 121.46(2)°.

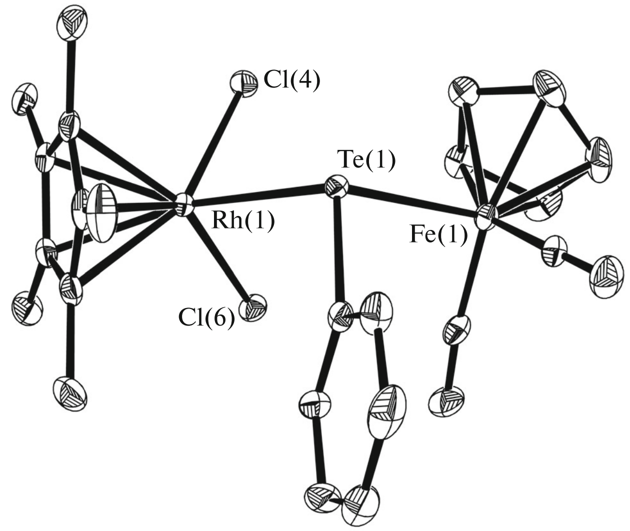


Fig. 3. The solid state structure of **IV**. Hydrogen atoms are omitted for clarity. Selected intramolecular distances and bond angles: Te(1)–Fe(1) 2.5692(3); Te(1)–Rh(1) 2.6393(2); Te(1)–C(8) 2.119(2); Rh(1)–Cl(6) 2.3982(6); Rh(1)–Cl(4) 2.4269(6) Å and C(8)Te(1)Fe(1) 97.46(6)°, C(8)Te(1)Rh(1) 103.85(6)°, Fe(1)Te(1)Rh(1) 117.091(9)°.

The reaction of **I** with dimeric $[RhCl_2Cp^*]_2$ afforded brown crystalline mixed-metal complex **IV** which is isoelectronic analog of **III** and shows similarity of the core geometry (table, Fig. 3) which is even more pronounced, taking into account the nearness of Ru and Rh covalent radii (1.46 and 1.42 Å, respectively [16]).

It could be resumed that $CpFe(CO)_2TePh$ can play the role of ligand for iron-tricarbonyl-diiodide or for monomeric (*p*-Cymene)RuI_2 and Cp^*RhI_2. In all new complexes the presence of intramolecular M–I → Te contacts takes place and the strong shortening of M–Te bonds due to additive dative M → L interaction.

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