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Phenyltellurolate-Bridged Heterometallic Complexes Combining Rhenium Tricarbonyl with (Dicarbonyl)(cyclopentadienyl)iron or Bis(diphenylphosphino)ethaneplatinum

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Abstract—A reaction of $CpFe(CO)_2TePh$ with $Re(CO)_3(THF)_2Cl$ in THF gave the heterometallic complex $[CpFe(CO)_2(\mu\text{-}TePh)]_2Re(CO)_3Cl$ (**I**). Either iron atom in complex **I** is linked to rhenium by only one Phenyltellurolate bridge. When treated with $(Dppe)Pt(TePh)_2$, complex **I** underwent transmetalation by elimination of two $CpFe(CO)_2TePh$ molecules followed by the formation of the heterometallic chelate complex $(Dppe)Pt(\mu\text{-}TePh)_2Re(CO)_3Cl$ (**II**). Complex **II** was also obtained in an independent way from $(Dppe)Pt(TePh)_2$ and $Re(CO)_3(THF)_2$. Structures **I** and **II** (**II** · MePh and **II** · $CDCl_3$) were identified by X-ray diffraction (CIF file, CCDC nos. 981467, 981468, and 981469, respectively).

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INTRODUCTION

The well-known high redox activity of rhenium sulfide complexes [1] largely depends on the introduction of heterometal-containing fragments (specifically, platinum atoms [2]), which is important for understanding of the efficiency of Pt–Re–S-containing heterogeneous catalysts for hydrocarbon reforming [3]. In principle, heterometal-containing rhenium chalcogenide clusters can be obtained from rhenium mono-, di-, and trisulfide complexes [4] as well as from dicarbonyl(cyclopentadienyl)rhenium disulfide [5, 6]. In the present work, we employed a reverse approach involving chalcogen-containing heterometal complexes. A rhenium chlorocarbonyl complex used as a source of rhenium atoms was transformed into the active form $ClRe(CO)_3(THF)_2$ by reflux in THF.

EXPERIMENTAL

All manipulations dealing with the synthesis and isolation of the complexes were carried out under argon in dehydrated solvents. The commercial complexes $[CpFe(CO)_2]_2$, $Re_2(CO)_{10}$, and Ph_2Te_2 were used as purchased; $CpFe(CO)_2TePh$ [7], $Re(CO)_5Cl$ [8], and $(Dppe)Pt(TePh)_2$ [9] were prepared as described earlier. Elemental analysis was performed on a CHNS analyzer (Carlo Erba). IR spectra were recorded on a BrukerAlpha spectrometer. X-ray diffraction was carried out on a Bruker Smart Apex CCD AXS diffractometer.

Synthesis of $[CpFe(CO)_2(\mu\text{-}TePh)]_2Re(CO)_3Cl$ (I). A clear colorless solution of $Re(CO)_5Cl$ (0.10 g, 0.28 mmol) in THF (10 mL) was refluxed while stirring it on a magnetic stirrer for 2.5 h. The solution turned yellow; the IR spectrum of the reaction mixture (THF; ν, cm^{-1}: 2030 m, 1913 s, 1893 m) provided evidence for the presence of only $Re(CO)_3(THF)_2Cl$ in solution. A dark green solution of $CpFe(CO)_2TePh$ (0.22 g, 0.56 mmol) in THF (5 mL) was gradually added to the yellow solution and stirred for 15 min. The resulting brown solution was filtered under argon, concentrated by half in vacuo, diluted with heptane (2 mL), and kept at –10°C for 24 h. The rectangular brown crystals that formed were filtered off and dried in vacuo. The crystals are suitable for X-ray diffraction. The yield of complex **I** was 0.25 g (85%).

For $C_{29}H_{20}O_7ClFe_2Te_2Re$ (M = 1069.03)

anal. calcd., %:	C, 32.58;	H, 1.88.
Found, %:	C, 33.12;	H, 1.81.

IR (KBr; ν, cm^{-1}): 2021 s, 1998 s, 1970 s, 1889 s, 852 w, 735 w, 693 w, 617 w, 572 m.

TLC (silufol, toluene): brown spot, R_f 0.4.

Synthesis of $[(PPh_2CH_2CH_2PPh_2)Pt(TePh)_2Re(CO)_3Cl]$ (II). (A) A brown-yellow solution of complex **I** (0.042 g, 0.04 mmol) in toluene (5 mL) was added under argon to a clear orange solution of $(Dppe)Pt(TePh)_2$ (0.04 g, 0.04 mmol) in toluene (5 mL). The reaction mixture was stirred with a magnetic stirrer for 15 min. The resulting orange-brown solution was heated under

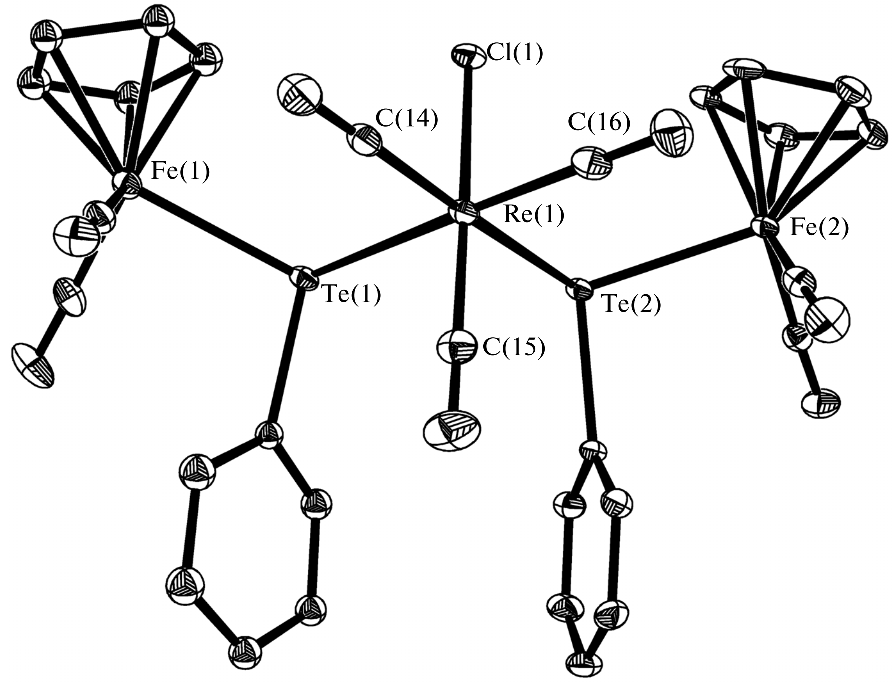

Fig. 1. Molecular structure of complex **I**. Selected bond lengths and bond angles: Re(1)–Te(1), 2.8003(4) Å; Re(1)–Te(2), 2.8165(4) Å; Re(1)–Cl(1), 2.506(1) Å; Fe(1)–Te(1), 2.5721(6) Å; Fe(2)–Te(2), 2.5717(6) Å; Te(2)–C(17), 2.133(3) and 2.136(4) Å; Cl(1)Re(1)Te(1), 84.43(3)°; Cl(1)Re(1)Te(2), 79.46(3)°; Te(1)Re(1)Te(2), 80.699(9)°; Fe(1)Te(1)Re(1), 114.13(2)°; Fe(2)Te(2)Re(1), 112.66(2)°.

reflux at 100°C for 30 min. The solution turned yellow, producing a brown precipitate. The precipitate was filtered off, and the filtrate was cooled to room temperature. The yellow prismatic crystals that formed were filtered off and dried in vacuo. The yield of complex **II** was 0.038 g (73%).

(B) Toluene (5 mL) was added to $Re(CO)_5Cl$ (0.013 g, 0.036 mmol). The mixture was stirred at 50°C for 10 min until a white precipitate dissolved almost completely. Then $(Dppe)Pt(TePh)_2$ (0.036 g, 0.036 mmol) was added, and the reaction mixture was refluxed for an additional 10 min. The resulting yellow-brown clear solution was cooled to room temperature to give drops of a yellow oil that solidified upon trituration. The solution with the solidified precipitate was heated again to boiling and slowly cooled to room temperature. The yellow crystals that formed were washed with heptane (2 mL) and dried. The yield of complex **II** was 0.037 g (79%).

For $C_{41}H_{34}O_3P_2ClTe_2RePt$ (M = 1308.61)

anal. calcd., %:	C, 37.63;	H, 2.62.
Found, %:	C, 38.39;	H, 2.68.

IR (KBr; ν, cm^{-1}): 3450 brw, 3050 w, 2003 vs, 1898 vs, 1879 vs, 1572 w, 1473 w, 1435 m, 1104 m, 998 w, 881 w, 820 w, 733 w, 690 m, 632 w, 530 m, 484 w, 454 w.

X-ray diffraction study. Crystals of complex **II** as a solvate with toluene that are suitable for X-ray diffraction[1] were obtained by cooling the reaction mixture upon the synthesis. Crystals of complex **II** as a solvate with $CDCl_3$ were obtained by keeping a solution of complex II in $CDCl_3$ at –20°C. An absorption correction was applied by multiple measurements of equivalent reflections (SADABS) [10]. The structures were solved by the direct methods and refined anisotropically (for the non-hydrogen atoms but the C atoms of the disordered cyclopentadienyl and phenyl groups and the disordered THF molecules in **I** and the disordered $CDCl_3$ molecules in **II** · $CDCl_3$) by the least-squares method on F^2 (SHELXTL) [11]. The H atoms were located geometrically. Crystallographic parameters and the data collection and refinement statistics for structures **I**, **II** · MePh, and **II** · $CDCl_3$ are given in table. Selected bond lengths and bond angles are given in the captions to Figs. 1–3. The structural contribution of the disordered solvate toluene molecules in the

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[1] X-ray diffraction was carried out at the Joint Use Center of the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

Crystallographic parameters and the data collection and refinement statistics for structures **I**, **II** · MePh, and **II** · $CDCl_3$

Parameter	Value		
	I	**II** · MePh	**II** · $CDCl_3$
M	1141.10	1308.56	1427.93
Diffractometer	Bruker APEX II CCD		
Radiation (λ, Å)	MoK_α (0.71073)		
Temperature, K	150(2)		
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2_1/c$
a, Å	10.5992(11)	36.560(2)	11.0339(4)
b, Å	11.5736(12)	12.8461(7)	17.6660(7)
c, Å	14.9627(16)	21.1025(11)	23.0145(9)
α, deg	96.008(2)	90	90
β, deg	99.621(2)	114.0110(10)	102.2990(10)
γ, deg	93.120(2)	90	90
V, Å^3	1794.9(3)	9053.1(8)	4383.1(3)
Z	2	8	4
ρ_{calcd}, g/cm^3	2.111	1.920	2.164
μ, mm^{-1}	5.876	7.185	7.607
$F(000)$	1076	4864	2664
θ scan range, deg	1.95–29.00	1.22–27.51	1.47–29.00
Scan mode	ω		
Number of independent reflections (N_1)	9451 (R_{int} = 0.0282)	10390 (R_{int} = 0.0738)	11644 (R_{int} = 0.0263)
Number of reflections with $I > 2\sigma(I)$ (N_2)	7781	7202	10707
Number of parameters refined	410	442	478
GOOF (F^2)	1.035	0.857	1.123
R_1 for N_2	0.0276	0.0298	0.0239
wR_2 for N_1	0.0688	0.0579	0.0725
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.598/–2.248	1.187/–1.130	2.990/–1.636

crystal of **II** · MePh was eliminated with the SQUEEZE procedure (PLATON) [12].

Atomic coordinates and other parameters of structures **I**, **II** · MePh, and **II** · $CDCl_3$ have been deposited with the Cambridge Crystallographic Data Collection (nos. 981467, 981468, and 981469, respectively; http://www.ccdc.cam.ac.uk/data_request/cif).

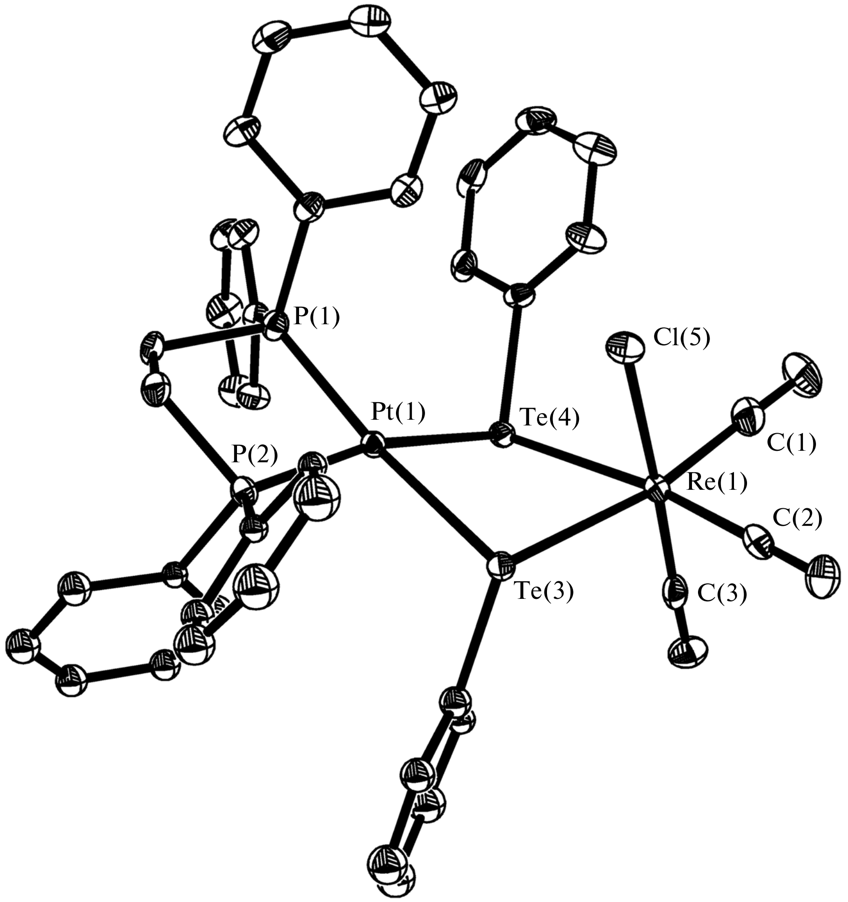
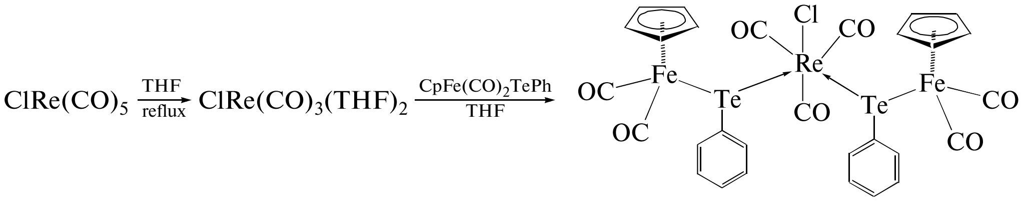


Fig. 2. Molecular structure of complex **II** in solvate **II** · MePh. Selected bond lengths and bond angles: Pt(1)–P(2), 2.259(1) Å; Pt(1)–P(1), 2.269(1) Å; Pt(1)–Te(4), 2.6330(4) Å; Pt(1)–Te(3), 2.6450(4) Å; Re(1)–Cl(5), 2.510(2) Å; Re(1)–Te(3), 2.7847(4) Å; Re(1)–Te(4), 2.7910(4) Å; P(2)Pt(1)P(1), 85.13(5)°; Te(4)Pt(1)Te(3), 83.62(1)°; Cl(5)Re(1)Te(3), 78.97(3)°; Cl(5)Re(1)Te(4), 89.93(3)°; Te(3)Re(1)Te(4), 78.26(1)°.

RESULTS AND DISCUSSION

We found that $CpFe(CO)_2TePh$ reacts with $Re(CO)_3(THF)_2Cl$ (prepared from $Re(CO)_5Cl$ in boiling THF) to give a new heterometallic complex **I**.



The IR spectrum of complex **I** in toluene contains absorption bands due to the stretching vibrations of the CO groups coordinated to the rhenium atom (ν: 2005, 1913, and 1894 cm^{-1}) and the iron atoms (ν: 2030, 2022; and 1981 cm^{-1}).

According to X-ray diffraction data (Fig. 1, table), complex **I** shows a *fac*-conformation of the CO groups, which is typical of disubstituted rhenium carbonyl halides. The Fe–Te bonds (2.5715(7)Å) are somewhat shorter than those in the starting complex $CpFe(CO)_2TePh$ (2.617 Å) and than the sum of the covalent radii of Fe and Te (2.70 Å) [13]. The Re–Te bonds (2.8165(3) and 2.8003(4) Å) are also shorter than the sum of the corresponding covalent radii ($R_{Re} + R_{Te} = 1.51 + 1.38 = 2.89$ Å) [13], yet being longer than those in $Re(CO)_3(\mu\text{-TeIPh})_3(\mu_3\text{-I})$ (2.7554(12) Å) [14]. Note that the shortening of the M–Te bonds results in no lengthening of the Te–C

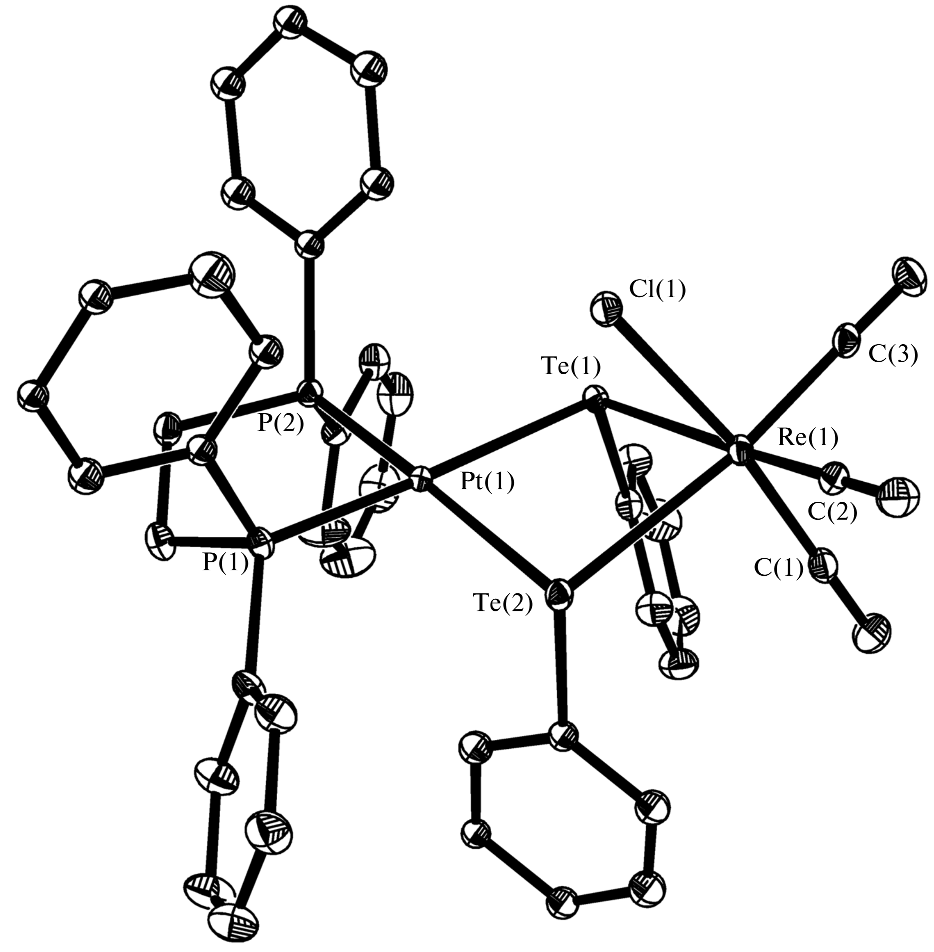
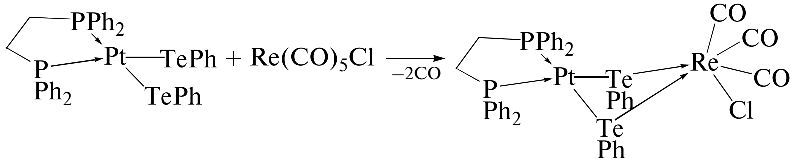


Fig. 3. Molecular structure of complex **II** · $CDCl_3$. Selected bond lengths and bond angles: Pt(1)–P(2), 2.260(1) Å; Pt(1)–P(1), 2.261(1) Å; Pt(1)–Te(2), 2.6479(3) Å; Pt(1)–Te(1), 2.6617(3) Å; Re(1)–Cl(1), 2.522(1) Å; Re(1)–Te(1), 2.7946(3) Å; Re(1)–Te(2), 2.8020(3) Å; P(2)Pt(1)P(1), 85.96(4)°; Te(2)Pt(1)Te(1), 87.847(9)°; Cl(1)Re(1)Te(1), 79.02(2)°; Cl(1)Re(1)Te(2), 78.07(2)°.

bonds: their lengths are close to the sum of the covalent radii of Te and C (2.12 Å [13]); i.e., the additional M ⟶ Te dative interaction involves the vacant *d* orbitals of Te.

Attempted synthesis of a chalcogen-bridged chelate heterocycle by a reaction between (Dppe)Pt$(TePh)_2$ and complex **I**, during which one CO group at either iron atom should be replaced by a benzenetellurolate bridge, gave chelate complex **II**: two $CpFe(CO)_2TePh$ molecules were replaced by a molecule of the Pt complex (transmetalation of **I**). The yield of complex **II** was 73%, yellow prisms. The same complex was obtained in 78% yield by an independent synthesis from (Dppe)Pt$(TePh)_2$ and $Re(CO)_5Cl$ in boiling toluene. The crystals of **II** suitable for X-ray diffraction were obtained by its crystallization from hot toluene (solvate **II** · MePh) or grown from deuterated chloroform (solvate **II** · $CDCl_3$).



According to the X-ray diffraction data (Figs. 2, 3; table), heterobinuclear complex **II** contains two bridging TePh groups between the platinum and rhenium atoms. The Pt–Te (2.6329(4) and 2.6451(4) Å) and Re–Te bonds (2.7848(4) and 2.7909(4) Å) are shorter than the sum of the covalent radii of the corresponding atoms ($R_{Pt} + R_{Te} = 2.74$ Å; $R_{Re} + R_{Te} = 2.89$ Å) [13]. The IR spectrum of complex **II** shows three bands due to the stretching vibrations of three CO groups sharing a common face (2003 vs, 1898 vs, 1879 vs), which are not very different from those found in complex **I**.

To sum up, we demonstrated that carbonyl complexes of iron and rhenium can firmly be held together by Phenyltellurolate bridges to form a Fe(TePh)Re(TePh)Fe chain with shortened M–Te bonds. However, treatment of complex **I** with the chelating complex (Dppe)Pt$(TePh)_2$ produces, via transmetalation, the chelate ring Pt$(TePh)_2$Re.

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