

Synthesis and Molecular Structures of the Cobalt Complexes ($\eta^4\text{-C}_4\text{Me}_4$)Co(CO)₂SnCl₃, ($\eta^4\text{-C}_4\text{Me}_4$)Co(CO)₂(TeI₂Ph), and ($\eta^4\text{-C}_4\text{Me}_4$)Co(CO)₂(TeBrIPh) with the Shortened Co–Sn and Co–Te Bonds

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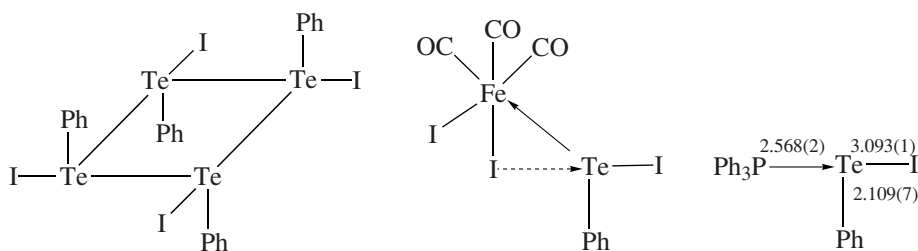
Abstract—The complex ($\eta^4\text{-C}_4\text{Me}_4$)Co(CO)₂I (**I**) reacted with excess SnCl₂ in boiling THF to give, through replacement of the iodide ligand by the fragment SnCl₃, the mononuclear complex ($\eta^4\text{-C}_4\text{Me}_4$)Co(CO)₂SnCl₃ (**II**) containing the Co–Sn bond (2.459(1) Å). In a reaction of complex **I** with phenyltellurenyl halides PhTeI and PhTeBr, an analogous insertion into the cobalt–iodine bond yielded ($\eta^4\text{-C}_4\text{Me}_4$)Co(CO)₂(TeI₂Ph) (**III**) and ($\eta^4\text{-C}_4\text{Me}_4$)Co(CO)₂(TeBrIPh) (**IV**), respectively. This type of coordination of the aryltellurenyl halide fragment to the transition metal atom was observed for the first time. X-ray diffraction analysis revealed a substantial shortening of the formally single Co–Sn and Co–Te bonds in complexes **II–IV** compared to the sum of the covalent radii of the corresponding atoms.

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Insertion reactions of the carbenoid fragment SnCl₂ into the metal–halogen and metal–metal bonds are well known. They give rise to the terminal bonds M–SnCl₃ or the bridging bonds M–SnCl₂–M, which are usually substantially shortened because of additional dative interactions [1]. On the other hand, the groups TeCl₂ possessing two more electrons behave in metal–chalcogen clusters (e.g., Re₄Q₄(TeCl₂)₄Cl₈ (Q = S, Se, and Te))

like typical monodentate Lewis bases with formally single Re–Te bonds (2.75 Å [2]).

The existence of the compound PhTeI was first reported in 1947 [3]. Its molecular structure was examined by X-ray diffraction analysis substantially later [4]. It was found that PhTeI tetramerizes into the square framework Te₄ (Te–Te 3.125(2)–3.175(2) Å, Te–I 2.799–2.830(2) Å).



The tetramer readily generates mononuclear fragments PhTeI capable of acting as Lewis bases toward iron atoms in, e.g., (CO)₃FeI₂(PhTeI) [5]. At the same time, PhTeI behaves like a Lewis acid while adding triphenylphosphine in the adduct Ph₃P(TePhI) [4] and nitrogen bases, halide anions, and thio- and selenourea

derivatives [6], also by extra coordination through the I atom at iron in the complex (CO)₃FeI₂(PhTeI). We found it interesting to introduce PhTeI into ($\eta^4\text{-Me}_4\text{C}_4$)Co(CO)₂I (**I**) by the way of replacing one carbonyl ligand at the Co atom and compare this reaction with the addition of the carbenoid SnCl₂ to complex **I**.

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 for pellets with KBr and solutions in hexane. The starting complex **I** was prepared as described in [7].

Synthesis of $(\eta^4\text{-C}_4\text{Me}_4)\text{Co}(\text{CO})_2\text{SnCl}_3$ (II**).** A red solution of complex **I** (0.2 g, 0.57 mmol) and SnCl_2 (0.22 g, 1.14 mmol) in THF (10 ml) was refluxed for 5 h. The resulting mixture was colored yellowish green. The solvent was removed in a water aspirator vacuum and the product from the solid residue was extracted with CH_2Cl_2 (30 ml). The yellow-green extract was concentrated to 10 ml and diluted with hexane (15 ml). The solution was kept at -20°C to form yellow-green prismatic crystals suitable for X-ray diffraction analysis. The yield was 0.12 g (47% with respect to complex **I**).

IR (KBr, cm^{-1}): 2035 vs, 1990 vs, 1625 m, 1430 m, 995 m.

Synthesis of $(\eta^4\text{-C}_4\text{Me}_4)\text{Co}(\text{CO})_2\text{TeI}_2\text{Ph}$ (III**).** Iodine (0.084 g, 0.33 mmol) was added to a magnetically stirred and cooled ($+3^\circ\text{C}$, ice bath) orange solution of Ph_2Te_2 (0.136 g, 0.33 mmol) in diethyl ether (20 ml). The resulting black-red reaction mixture was stirred under cooling for an additional 20 min. Then complex **I** (0.24 g, 0.68 mmol) was added in one portion. The mixture was stirred while warming it to ambient temperature and then refluxed for 30 min. The solvent was removed in a water aspirator vacuum and the product from the solid residue was extracted with benzene (20 ml). The extract was diluted with heptane (10 ml), filtered, concentrated in a water aspirator vacuum until turbidity began, and kept at -10°C for 12 h. The resulting orange crystals were filtered off, washed with hexane, and dried *in vacuo*. The yield was 0.25 g (52%).

IR (CH_2Cl_2 , $\nu(\text{CO})$, cm^{-1}): 2040 s, 2000 s.

Single crystals were used for X-ray diffraction analysis.

Complex $(\eta^4\text{-C}_4\text{Me}_4)\text{Co}(\text{CO})_2\text{TeBrIPh}$ (IV**)** was obtained analogously. A reaction of Ph_2Te_2 (0.136 g, 0.33 mmol) with bromine (0.02 ml, 0.39 mmol) in THF (20 ml) and then with complex **I** (0.24 g, 0.68 mmol) gave yellow crystals. The yield was 0.16 g (38%).

IR (THF, cm^{-1}): 2040 s, 2000 s.

Single crystals were used for X-ray diffraction analysis.

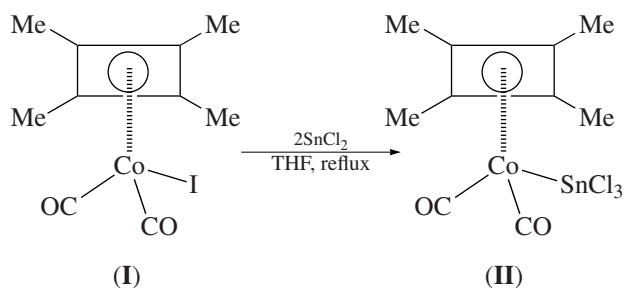
X-ray diffraction analysis. Crystallographic parameters and a summary of data collection and refinement for structures **II–IV** are given in Table 1. Structures **II–IV** were solved by the direct method and refined by the least-squares method on F^2 in the anisotropic (for H atoms, isotropic) approximation with the SHELXTL program package [8]. An analysis of the electron-density difference maps showed that two enantiomers are superimposed in the crystal. The enan-

tiomers have different positions of the Br and I atoms relative to the fragment Co–Te–C . When refining the equally probably populated positions of the halogen atoms, we imposed restrictions (DFIX) on equal Te–I and Te–Br bond lengths for two positions $\text{Br}(1)$ and $\text{Br}(1')$ and $\text{I}(1)$ and $\text{I}(1')$. The lengths of two types of Te–halogen bonds were refined via free variables. The hydrogen atoms were located geometrically.

Selected bond lengths and angles in structures **II–IV** are given in Table 2. Atomic coordinates and other structural parameters of complexes **II–IV** have been deposited with the Cambridge Crystallographic Data Collection (CCDC nos. 695 353 (**II**), 693 534 (**III**), and 694 222 (**IV**); see www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

We found that a reaction of cobalt tetramethylcyclobutadiene (**I**) with excess SnCl_2 in boiling THF gives, through replacement of the iodide ligand by the fragment SnCl_3 , mononuclear complex **II** as air-stable yellowish green prisms:



The IR spectrum of complex **II** shows characteristic absorption bands due to two terminal CO groups (2035 and 1990 cm^{-1}). According to X-ray diffraction data, complex **II** (Fig. 1) is a monomer containing the Co–Sn bond ($2.4595(8)\text{ \AA}$). This bond is much shorter than the sum of the covalent radii of the Co and Sn atoms ($1.29 + 1.40 = 2.69\text{ \AA}$) [9] and is comparable with the Co–Sn distance (2.477 \AA) in the known complex $(\text{CO})_4\text{CoSnCl}_3$ [10]. The Sn–Cl bond lengths in structure **II** ($2.366(2)$ – $2.448(1)\text{ \AA}$) are on average close to the sum of the covalent radii of the Cl and Sn atoms (2.40 \AA) [11], being shorter than those in the anion SnCl_3^- (Sn–Cl 2.457 , 2.467 , and 2.488 \AA) in a tetraphenylphosphonium salt [12].

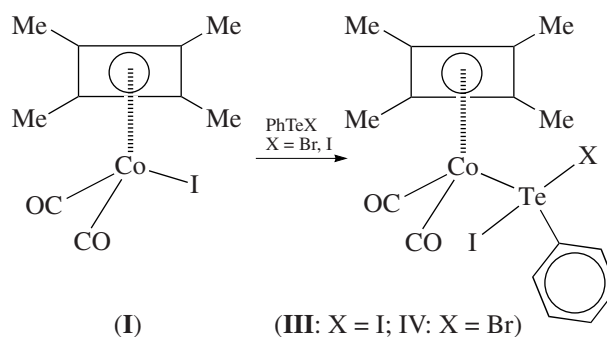
Note that a usual model of the partially multiple carbenoid bonding involving sp orbitals calls for a competition between the lone electron pair of the d electrons at the metal atom and the lone electron pair of the halide ion for the vacant orbital at bivalent carbon or tin atoms [13]. Accordingly, shortening of the M–Sn bonds should lengthen the Sn–Cl bonds, which is not the case. Apparently, additional dative M–Sn bonding involves the vacant d orbitals of tin.

Table 1. Crystallographic parameters and a summary of data collection and refinement for structures **II–IV**

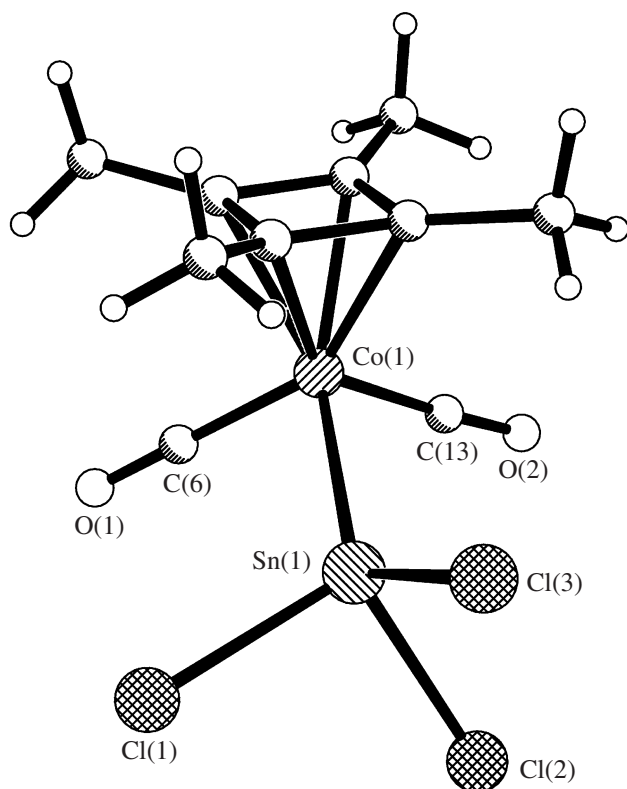
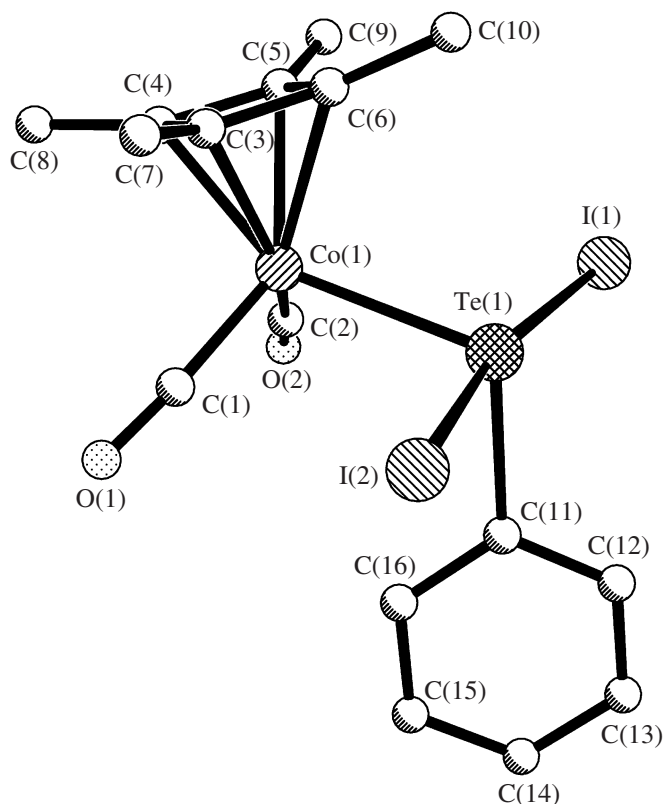
Parameter	Value		
	II	III	IV
Diffractometer	Bruker SMART 1000 CCD	Bruker APEX II CCD	Bruker APEX II CCD
Empirical formula	C ₁₀ H ₁₂ O ₂ Cl ₃ CoSn	C ₁₆ H ₁₇ O ₂ I ₂ CoTe	C ₁₆ H ₁₇ O ₂ BrICoTe
<i>M</i>	448.17	681.63	634.64
Radiation; λ , Å	MoK α ; 0.71073		
Temperature, K	120(2)	296(2)	100(2)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	
<i>a</i> , Å	7.2652(13)	15.224(2)	14.9239(11)
<i>b</i> , Å	16.211(3)	13.660(2)	13.4723(10)
<i>c</i> , Å	13.667(2)	20.039(3)	19.7016(15)
β , deg	103.321(6)	90	90
<i>V</i> , Å ³	1566.3(5)	4167.3(10)	3961.2(5)
<i>Z</i>	4	8	8
ρ_{calcd} , g cm ^{−3}	1.901	2.173	2.128
μ , mm ^{−1}	3.152	5.162	5.889
<i>F</i> (000)	864	2512	2368
θ scan range, deg	2.93–28.00	2.03–29.00	2.28–29.00
Scan mode	ω		
Number of measured reflections	10361	28590	26947
Number of independent reflections (<i>N</i> ₁)	3758 (<i>R</i> _{int} = 0.0513)	5529 (<i>R</i> _{int} = 0.0607)	5273 (<i>R</i> _{int} = 0.0603)
Number of reflections with <i>I</i> > 2 σ (<i>I</i>) (<i>N</i> ₂)	3147	3423	3841
Number of parameters refined	158	203	217
GOOF (<i>F</i> ²)	1.083	0.977	1.014
<i>R</i> ₁ for <i>N</i> ₂	0.0478	0.0353	0.0336
<i>wR</i> ₂ for <i>N</i> ₁	0.1204	0.0785	0.0803
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, <i>e</i> Å ^{−3}	1.905/−1.179	1.001/−0.542	1.560/−0.896

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

Bond	<i>d</i> , Å	Angle	ω , deg
II			
Co(1)–C(10)	1.795(5)	Cl(1)Sn(1)Cl(3)	96.66(7)
Co(1)–C(9)	1.801(5)	Cl(1)Sn(1)Cl(2)	98.34(7)
Co(1)–Sn(1)	2.4595(8)	Cl(3)Sn(1)Cl(2)	96.31(6)
Sn(1)–Cl(1)	2.3657(16)	Cl(1)Sn(1)Co(1)	117.12(4)
Sn(1)–Cl(3)	2.4105(15)	Cl(3)Sn(1)Co(1)	124.94(4)
Sn(1)–Cl(2)	2.4484(14)	Cl(2)Sn(1)Co(1)	118.07(4)
III			
Co(1)–C(1)	1.797(5)	C(11)Te(1)Co(1)	106.48(13)
Co(1)–C(2)	1.801(6)	C(11)Te(1)I(2)	89.49(13)
Co(1)–Te(1)	2.5470(7)	C(11)Te(1)I(1)	89.11(13)
Te(1)–C(11)	2.131(5)	Co(1)Te(1)I(1)	94.08(2)
Te(1)–I(1)	2.9862(6)	Co(1)Te(1)I(2)	96.07(2)
Te(1)–I(2)	2.9503(6)	I(2)Te(1)I(1)	169.730(16)
IV			
Co(1)–C(1)	1.787(5)	C(11)Te(1)Co(1)	106.46(13)
Co(1)–C(2)	1.801(5)	C(11)Te(1)I(1)	88.81(13)
Co(1)–Te(1)	2.5321(7)	C(11)Te(1)Br(1)	88.23(15)
Te(1)–C(11)	2.126(4)	Co(1)Te(1)I(1)	95.23(7)
Te(1)–I(1)	2.979(2)	Co(1)Te(1)Br(1)	94.92(9)
Te(1)–Br(1)	2.705(3)	Br(1)Te(1)I(1)	169.85(14)
Te(1)–I(1)'	3.0237(18)	Br(1)'Te(1)I(1)'	171.38(16)
Te(1)–Br(1)'	2.728(3)		



In reactions of complex **I** with the tetrameric phenyltellurium halides $[\text{PhTeX}]_4$ ($\text{X} = \text{Br}$ and I) in ether or THF, the fragment PhTeX was inserted into the Co-I bond to give air-stable yellowish orange crystals of unusual complexes containing the ligand PhTe(I)X ($\text{X} = \text{I}$ (**III**) and Br (**IV**)) coordinated in a monodentate fashion. The IR spectra of complexes **III** and **IV** are virtually identical in the range of CO stretching vibrations (2040 and 2000 cm^{-1}). According to X-ray diffraction data, these complexes are isostructural (Table 1, Fig. 2), with close Co-Te bond lengths ($2.5470(7)$ and $2.5321(7)\text{ Å}$, respectively). These formally single bonds are substantially shorter than the sum of the covalent radii of Co and Te ($1.29 + 1.37 = 2.66\text{ Å}$), as in the previously described complex $(\eta^4\text{-Me}_4\text{C}_4)\text{Co}(\text{CO})_2\text{TePh}$ ($\text{Co-Te } 2.585(1)\text{ Å}$) [14] and its pentacarbonyltungsten

**Fig. 1.** Molecular structure **II**.**Fig. 2.** Molecular structure **III**.

adduct ($\eta^4\text{-Me}_4\text{C}_4$)Co(CO)₂TePh[W(CO)₅] [14] (Co–Te 2.558(8) Å) [14]. The shortening is probably due to the same scheme of an additional dative interaction involving the lone electron pair of cobalt. The latter can also be responsible for the longer Te–I bonds in complex **III** (2.9503(6) Å) and the longer Te–Br bonds in complex **IV** (2.705(3) Å) than the sum of the covalent radii of these atoms (2.70 and 2.50 Å). The presence of the lone electron pair at tellurium is also important, which makes the fragment X–Te–I nearly linear (the angle XTeI is $\sim 170^\circ$).

Unlike the complex (CO)₃FeI₂(PhTeI), structures **III** and **IV** contain no bridge M–X–Te (apparently, the X atom first should replace one CO group at the cobalt atom). In addition, the heterohalide environment of the Te atom in complex **IV** shows equiprobable disorders of the Br and I atoms over two positions (Table 2); the specific intermolecular interactions Te \cdots I and Te \cdots Br characteristic of tellurium halides are not detected.

In conclusion, it should be emphasized that the insertion of SnCl₂ and PhTeX (X = I or Br) into the Co–I bond unexpectedly yields structurally similar products, although the Te atom has an extra electron pair. Apparently, this is because the vacant *d* orbitals of tin and tellurium participate in a dative interaction.

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REFERENCES

1. Holt, M.S., Wilson, W.L., and Nelson, J.H., *Chem. Rev.*, 1989, vol. 89, p. 11.
2. Efremova, O.A., Mironov, Yu.V., and Fedorov, V.E., *Eur. J. Inorg. Chem.*, 2006, p. 2533.
3. Schulz, P. and Klar, G., *Z. Naturforsch., B: Chem. Sci.*, 1975, vol. 30, p. 40.
4. Boyle, P.D., Cross, W.I., Godfrey, S.M., et al., *Angew. Chem., Int. Ed. Engl.*, 2000, vol. 39, p. 1796.
5. Torubaev, Yu.V., Pasynskii, A.A., and Matur, P., *Koord. Khim.*, 2008, vol. 34, no. 11, p. 807.
6. Sadekov, I.D. and Minkin, V.I., *Zh. Org. Khim.*, 1999, vol. 35, no. 7, p. 981.
7. Butovskii, M.V., Englert, U., Fil'chikov, A.A., et al., *Eur. J. Inorg. Chem.*, 2002, p. 2656.
8. Sheldrick, G.M., *SHELXTL-97. Version 5.50*, Madison (WI, USA): Bruker AXS Inc., 1997.
9. Biryukov, B.P. and Struchkov, Yu.T., *Usp. Khim.*, 1970, vol. 39, p. 1672.
10. Klufers, P., *Z. Naturforsch. B, B: Chem. Sci.*, 1991, vol. 46, p. 187.
11. Cordero, B., Gomez, V., Platero-Prats, A.E., et al., *Dalton Trans.*, 2008, p. 2832.
12. Muller, U., Mronga, N., Schumacher, C., et al., *Z. Naturforsch., A: Phys. Sci.*, vol. 37, p. 1122.
13. Nefedov, O.M., Ioffe, A.I., and Menchikov, L.G., *Khimiya karbenov* (The Chemistry of Carbenes), Moscow: Khimiya, 1990.
14. Pasynskii, A.A., Skabitskii, I.V., Shapovalov, S.S., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2007, no. 9, p. 1669.