Synthesis, molecular structures, and properties of heterometallic cobalt tetramethylcyclobutadiene complexes (C₄Me₄)Co(CO)₂TePh, (C₄Me₄)Co(CO)₂TePh[W(CO)₅], and Me₄C₄Co(µ₃-S)₂Cr₂Cp₂(µ-SC₄H₉)*

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The reaction of $Cb^*Co(CO)_2I$ (1) (Cb^* is tetramethylcyclobutadiene) with sodium phenyltelluride afforded the mononuclear complex $Cb^*Co(CO)_2TePh$ (2). The reaction of the latter with $W(CO)_5(THF)$ produced the $Cb^*Co(CO)_2TePh[W(CO)_5]$ compound (4). The reaction of 1 with the $Cp_2Cr_2(SCMe_3)_2S$ complex gave the heterometallic cluster $Cb^*Co(\mu_3-S)_2Cr_2Cp_2$ (μ -SCMe_3) (5). Complexes 2, 4, and 5 are diamagnetic. Their structures were determined by X-ray diffraction. Complex 2 contains the Co–Te bond (2.585(1) Å); complex 4, the Co–Te (2.558(8) Å) and W–Te (2.8467(6) Å) bonds. Complex 5 has the stable triangular sulfide- and *tert*-butylmercaptide-bridged core Cr_2Co (Cr–Cr and Cr–Co bond lengths are 2.626(2) and 2.673(2) Å, respectively) with Cp ligands at the chromium atoms and a Cb* ligand at the cobalt atom. Complex 5 was characterized by cyclic voltammetry. The thermolysis of complex 4 was studied.

Key words: heterometallic complexes, X-ray diffraction study, cyclopentadienyl complexes, cyclobutadiene complexes, metal carbonyls, metal chalcogenides, tungsten, cobalt, chromium, electrochemistry, thermolysis.

The extensive chemistry of chalcogenide complexes containing the stable CpFe fragment and its permethylated analog has attracted attention in view of the problem of modeling of natural FeS-containing enzymes. In particular, the chalcogen-containing complexes $CpFe(CO)_2XPh (X = S \text{ or } Se) (Fe-S, 2.282 \text{ Å}; Fe-Se,$ 2.413 Å; Fe-S-C, 113.46°; Fe-Se-C, 105.82°)^{1,2} and the heterometallic compound CpFe(CO)₂SPhW(CO)₅ (Fe-S, 2.301 Å; S-W, 2.577 Å; Fe-S-W, 106.44°)³ were reported. In addition, the heterometallic antiferromagnetic cluster $CpFe(\mu_3-S)_2Cr_2Cp_2(\mu-SBu^t)$ containing the stable Cr₂Fe core surrounded by sulfur atoms was described.⁴ It was of interest to synthesize analogs containing another metal of life, viz., cobalt, by replacing the CpFe fragment in these complexes with the isolobal stable Cb*Co fragment (Cb* is tetramethylcyclobutadiene). The

wide use of the latter fragment was covered in the review.⁵ The only cobalt complex (A) containing chalcogenide and the four-membered σ,π -bonded ring derived from tetratrifluoromethylcyclobutadiene has been structurally characterized.⁶



Results and Discussion

We used the tetramethylcyclobutadiene dicarbonyl iodide complex $Cb^*Co(CO)_2I$ (1) (see Ref. 7) as the key compound for the synthesis of heterometallic chalcogenide complexes.

The treatment of complex 1 with sodium phenyltelluride afforded the mononuclear dicarbonyl complex $Cb*Co(CO)_2TePh$ (2) as red-black crystals characterized

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^{*} Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

Scheme 1



by two CO stretching bands in the IR spectrum ($v_{CO} = 1970$ and 1900 cm⁻¹). According to the X-ray diffraction study, complex 1 contains the Co–Te single bond (2.585(1) Å) (Scheme 1, Fig. 1, Table 1). In addition, we

obtained the product of its partial decarbonylation as a black finely crystalline compound characterized by the only CO stretching band in the IR spectrum ($v_{CO} = 1960 \text{ cm}^{-1}$). According to



the elemental analysis data, this product has structure **3** analogous to many known complexes of this type, for example, to the $[(\pi-C_7H_7)Mo(CO)(\mu-TePh)]_2$ complex described in our earlier publication.⁸



Fig. 1. Molecular structure of complex 2.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compounds **2**^{*} and **4**

2		4		
Bond	d/Å	Bond	d∕Å	
Co(1)-Te(1)	2.5848(11)	Co(1)-Te(1)	2.5578(8)	
Te(1) - C(11)	2.113(7)	Te(1) - C(16)	2.132(4)	
		W(1) - 1e(1)	2.8469(6)	
Angle	ω/deg	Angle	ω/deg	
C(11)-Te(1)-Co(1) 98.15(16)		C(16)-Te(1)-W(1)	99.94(10)	
		Co(1)-Te(1)-W(1)	111.899(15)	

* For compound **2**, the bond lengths and bond angles are given for one of the two independent molecules, whose geometric parameters are virtually identical.

In turn, the reaction of complex 2 with $W(CO)_5(THF)$ produces the heterometallic compound $Cb^*Co(CO)_2TePh \cdot W(CO)_5$ (4) (Scheme 1). Complex 4 is stable in air, does not undergo decarbonylation under UV irradiation for 2 h, and crystallizes from diethyl ether, toluene, or dichloromethane as orange crystals. According to the X-ray diffraction study, complex 4 contains the Co–Te–W group with the Co–Te and W–Te single bonds (2.558(8) and 2.8467(6) Å, respectively; see Table 1).

In addition, the reaction of **1** with the $Cp_2Cr_2(SC_4H_9)_2S$ complex⁹ involves the complete decarbonylation and elimination of one *tert*-butyl group to give the heterometallic cluster $Cb^*Co(\mu_3-S)_2Cr_2(\mu-SBu^t)Cp_2$ (5) (Scheme 2).

The X-ray diffraction study showed that compound **5** contains the stable triangular core Cr_2Co (Cr-Cr, 2.630(2) Å; Cr-Co, 2.674(2) Å) (Table 2) supplemented with μ_3 -sulfide bridges and cyclopentadienyl and *tert*-butylthiolate ligands at the chromium



Fig. 2. Molecular structure of complex 4.





Table 2. Selected bond lengths (*d*) and bond angles (ω) in compound **5**^{*}

Bond	$d/{ m \AA}$	Angle	ω/deg
Co(1) - S(2)	2.150(2)	Cr(2) - Co(1) - Cr(1)) 58.82(5)
Co(1) - S(1)	2.173(2)	Co(1) - S(2) - Cr(2)	73.75(8)
Co(1)-Cr(2)	2.674(2)	Co(1) - S(2) - Cr(1)	73.88(8)
Co(1)-Cr(1)	2.681(2)	Cr(2) - S(2) - Cr(1)	69.62(8)
Cr(1) - S(1)	2.264(3)	C(19) - S(3) - Cr(2)	116.1(3)
Cr(1) - S(2)	2.306(3)	C(19) - S(3) - Cr(1)	116.2(4)
Cr(1) - S(3)	2.363(3)	Cr(2) - S(3) - Cr(1)	67.88(8)
Cr(1)-Cr(2)	2.630(2)		
Cr(2) - S(1)	2.280(3)		
Cr(2) - S(2)	2.301(3)		
Cr(2) - S(3)	2.347(3)		

* The bond lengths and bond angles are given for one of the three independent molecules, whose geometric parameters are virtually identical.

atoms and a tetramethylcyclobutadiene ligand at the cobalt atom.*

Unlike the antiferromagnetic complexes $Cp_2Cr_2(SC_4H_9)_2S$ (see Ref. 9) and $Cp_2Cr_2(\mu$ -SCMe₃)(μ -S)₂Co(CO)₂ (see Ref. 11) studied earlier, complex **5** is diamagnetic, which can be due to the electron-donating properties of the Cb* ligand. Actually, the cyclic voltammogram of $Cp_2Cr_2(\mu$ -SCMe₃)(μ -S)₂Co(CO)₂ showed an irreversible one-electron oxidation wave at +0.39 V, whereas the cyclic voltammogram of complex **5** containing Cb* ligands instead of two electron-withdraw-



Fig. 3. Molecular structure of complex 5.

ing carbonyl groups had a reversible one-electron oxidation wave at -0.11 V (along with an irreversible twoelectron oxidation wave at +1.09 V). The sandwich complex CpCoCb*, in which the dichromium disulfide fragment of cluster **5** is formally replaced by the isoelectronic Cp ligand, is characterized by a reversible one-electron oxidation waves at +0.26 V and two irreversible one-electron oxidation waves at +0.66 and +0.99 V, *i.e.*, the Cp fragment is more electron-withdrawing with respect to the Cb*Co group than the cluster ligand $[Cp_2Cr_2(\mu SC_4H_9)(\mu_3-S)_2].$

A study of the thermolysis of heterometallic complex **4** under argon showed that the Cb* ligand, like the cyclopentadienyl ligand, is eliminated in the last step and that carbides and oxides are absent among the pyrolysis products, in spite of the fact that the formation of these compounds is typical¹² of the thermolysis of carbonylchalcogenides at M : X > 1.

^{*} The presence of three structurally similar independent molecules is associated with a pseudosymmetry, which is not a unique feature of this structure (see Ref. 10).

The loss of the first two carbonyl groups is accompanied by the endothermic effect. A further rise of the temperature leads to the loss of the other CO groups, the process being highly exothermic. Then the Ph group is eliminated with a weak endothermic effect, and only the final exothermic step of thermolysis leads to the elimination of the Cb* ring. Presumably, the exothermic processes of the ligand removal is accompanied by the formation of new M—Te and M—M bonds.

Therefore, the Cb*Co fragment not only forms stable bonds with chalcogens but also can form heterometallic chalcogenides by binding other metal atoms through the chalcogen atom (for example, by binding tungsten through tellurium) or by supplementing this binding with direct metal—metal bonds, as in the case of the addition of sulfur and chromium atoms of the cluster fragment $[Cp_2Cr_2(\mu-SC_4H_9)(\mu_3-S)_2].$

Experimental

All operations associated with the synthesis and isolation of the complexes were carried out under pure argon and in anhydrous solvents. The Cb*Co(CO)₂I (see Ref. 7) and Cp₂Cr₂(μ -SC₄H₉)₂(μ -S) (see Ref. 9) complexes were synthesized according to procedures described earlier. The elemental analysis was performed on a Carlo Erba CHNS analyzer.

The IR spectra were recorded on a Specord 75 IR spectrophotometer in KBr pellets.

X-ray diffraction study. The crystallographic data and the X-ray diffraction data collection and refinement statistics for compounds 2, 4, and 5 are given in Table 3. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic and isotropic thermal parameters (H atoms were refined using a riding model). Semiempirical absorption corrections were applied based on equivalent reflections (SADABS). All calculations were carried out with the use of the SHELXTL program package.¹³ The principal geometric parameters for compounds 2, 4, and 5 are given in Tables 1 and 2. The complete tables of the atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters were deposited with the Cambridge Structural Database.

Cyclic voltammograms (CV) of the complexes were recorded on a PAR 273 (Princeton Applied Research) potentiostat/galvanostat using the standard software. The measurements were carried out in a temperature-controlled three-electrode electrochemical cell under special-purity argon. A SU-2000 disk glassy-carbon electrode (0.0058 cm²) pressed into Teflon was used as the working electrode, and a platinum plate with a surface area of 1 cm² served as the auxiliary electrode. The potentials were measured relative to the silver reference electrode in the same solution and are given relative to the Fc/Fc⁺ pair.

Parameter	2	4	5
Molecular formula	C ₁₆ H ₁₇ CoO ₂ Te	C ₂₁ H ₁₇ CoO ₇ TeW	C ₂₂ H ₃₁ CoCr ₂ S ₃
Molecular weight	427.83	751.73	554.58
Diffractometer	Bruker Smart CCD	Bruker Smart CCD	Bruker Smart CCD
T/K	120	120	120(2)
Space group	$P\overline{1}$	P2(1)/n	P2(1)/n
a/Å	8.3940(17)	9.796(2)	14.207(3)
b/Å	13.634(3)	16.717(4)	34.661(7)
c/Å	15.634(3)	14.852(4)	15.144(3)
α/deg	95.57(3)	90	90
β/deg	104.55(3)	105.434(8)	112.546(7
γ/deg	97.68(3)	90	90
$V/Å^3$	1700.3(6)	2344.4(10)	6887(3)
Z	4	4	12
<i>F</i> (000)	832	1408	3432
$\rho_{calc}/g m^{-3}$	1.671	2.130	1.604
Radiation, λ (Mo-K α)/Å	0.71073	0.71073	0.71073
Linear absorption, μ/mm^{-1}	2.689	6.867	1.923
Scanning mode	ω	ω	ω
Scan range/deg	1.52-26.97	2.48-29.00	1.17-26.00
Number of measured reflections	8019	13140	48156
Number of independent reflections	7399	6020	13509
R _{int}	0.0214	0.0238	0.1094
Number of reflections with $[I > 2\sigma(I)]$	4951	5478	7351
Number of parameters	369	281	757
R_1	0.0521	0.0284	0.0764
wR_2	0.1445	0.0628	0.1535
GOOF	0.963	1.026	1.012
$\rho_{\text{max}}/\rho_{\text{min}}/e$ Å ⁻³	1.575/-1.280	1.759/-2.113	1.131/-0.661

 Table 3. Crystallographic data for complexes 2, 4, and 5

The measurements were performed in dichloromethane using $0.2 M \operatorname{Bu}_4 \operatorname{NPF}_6$ as the supporting electrolyte.

Differential scanning calorimetry (DSC) and thermogravimetry (TG) were carried out on DSC-20 and TG-50 units of a Mettler TA-3000 thermoanalyzer. The experiments were performed under an inert atmosphere (dry argon) at a constant heating rate of 5 deg min⁻¹. The weight loss during heating was monitored directly on the TG-50 unit; the accuracy of the weighing was $\pm 2 \cdot 10^{-3}$ mg. The temperatures of anomalous points in the thermograms were determined with an accuracy of $\pm 0.5^{\circ}$.

Synthesis of cobalt π -tetramethylcyclobutadienedicarbonylphenyltelluride, Cb*Co(CO)₂TePh (2), and the dimer of cobalt π -tetramethylcyclobutadienecarbonyl- μ -phenyltelluride, [Cb*Co(CO)TePh]₂ (3). A colorless PhTeNa solution, which was prepared by the reaction of Na (0.33 g, 14.28 mmol) with Ph₂Te₂ (0.29 g, 0.71 mmol) in THF (20 mL) at room temperature for 2 h, was filtered and added to a red solution of compound 1 (0.50 g, 1.43 mmol) in THF (20 mL). The solution turned dark-brown ($v_{CO} = 1970$ and 1900 cm⁻¹). The TLC pattern (Silufol, benzene) showed a red spot with $R_{\rm f} = 0.5$, which gradually turned colorless. The solvent was removed in vacuo (20 Torr), and the residue was extracted with petroleum ether (60 mL) at 30-70 °C. The brown solution was concentrated in vacuo to 10 mL. After storage at -18 °C for 1 day, a black precipitate of 3 was obtained. The precipitate was separated by filtration, washed with cold pentane, and dried in vacuo. IR (v_{CO}, CH₂Cl₂): 1960 cm⁻¹. Found (wt.%): C, 45.14; H, 3.14. C₁₅H₁₇OCo. Calculated (wt.%): C, 45.06; H, 4.29.

The mother liquor was concentrated *in vacuo* at room temperature to 1/10 of the initial volume. After storage at -18 °C for 1 day, red-black crystals of **2** precipitated. The crystals were filtered off, washed with cold petroleum ether (2 mL), and dried in air over a short period of time. IR (v_{CO}, CH₂Cl₂): 1970, 1900 cm⁻¹. Since the storage of crystals of **2** *in vacuo* and grinding of the crystals with KBr led to their rapid transformation into black product **3**, the elemental composition of **2** was not determined. The total yield of **2** and **3** was 0.12 g (20%). Single crystals of **2** were studied by X-ray diffraction.

Synthesis of π -tetramethylcyclobutadienedicarbonylcobalt- μ -phenyltelluride tungstenpentacarbonyl, Cb*(CO)₂Co- μ -TePhW(CO)₅ (4). A solution of W(CO)₅(THF), which was prepared by the UV irradiation of a solution of $W(CO)_6$ (0.25 g, 0.7 mmol) in THF (20 mL) for 40 min with argon bubbling, was added to a red-brown solution of 2, which was prepared from 1 (0.25 g, 0.7 mmol) and 0.7 mM sodium phenvltelluride (the latter was prepared by the reduction of Ph_2Te_2 (0.7 mmol) with a tenfold excess of sodium in THF (20 mL)). The reaction mixture was stirred for 20 min and then concentrated to dryness. The residue was extracted with petroleum ether, diethyl ether, or dichloromethane. After removal of the solvent, the same substance was obtained. The latter crystallized as orange rhombic prisms and was characterized by X-ray diffraction. The yield was 0.11 g (0.15 mmol, 22%). IR (v/cm^{-1}): 2060 s, 2030 s, 2000 s, 1930 s, 1430 s, 1020 s, 740 s, 690 m, 600 s, 590 s, 520 s. Found (wt.%): C, 33.2; CO, 26.6;*; Ph, 9.1;* Me₄C₄, 14.2.* C₂₁H₁₇O₇TeCoW. Calculated (wt.%): C, 33.5; CO, 26.0; Ph, 10.2; Me₄C₄, 14.3.

Synthesis of dichromium π -tetramethylcyclobutadienecobaltbis(π -cyclopentadienyl)-bis(μ ³-sulfide)-(μ -tert-butylthiolate), Crystals suitable for X-ray diffraction were grown by crystallization at the CH_2Cl_2 —hexane interface.

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[[]Cr–Cr][Cr–Co],(Cp₂Cr₂(\mu-SC₄H₉)(\mu³-S)₂CoCb* (5). A darkviolet solution of Cp₂Cr₂(\mu-SC₄H₉)₂(\mu-S) (0.38 g, 0.85 mmol) and 1 (0.3 g, 0.85 mmol) in benzene (35 mL) was refluxed for 2.5 h. The resulting dark-brown solution was concentrated *in vacuo* to 10 mL. Small needle-like crystals that precipitated after storage of the solution at 5 °C for 2 days were separated by decantation, washed with petroleum ether (10 mL), and dried *in vacuo*. The yield was 0.23 g (49%). IR (KBr), v/cm⁻¹: 2920 m br, 2870 m br, 1430 m br, 1355 m, 1225 w, 1150 m, 1100 w, 1005 s, 780 v.s. Found (wt.%): C, 47.6; H, 5.6; S, 16.5. C₂₂H₃₁S₃Cr₂Co. Calculated (wt.%): C, 47.65; H, 5.63; S, 17.34.

^{*} Determined by the DSC method.