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Note

Preparation and structural characterization of $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ and $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$

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Abstract

The objective of the present work was to synthesize mononuclear ruthenium complex $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ (**1**) by the reaction of $Te(CH_2SiMe_3)_2$ and $[RuCl_2(CO)_3]_2$. However, the stoichiometric reaction affords a mixture of **1** and $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$ (**2**). The X-ray structures show the formation of the *cis*(Cl), *cis*(C), *trans*(Te) isomer of **1** and the *cis*(Cl), *mer*(Te) isomer of **2**. The ^{125}Te NMR spectra of the complexes are reported. The complex distribution depends on the initial molar ratio of the reactants. With an excess of $[RuCl_2(CO)_3]_2$ only **1** is formed. In addition to the stoichiometric reaction, a mixture of **1** and **2** is observed even when using an excess of $Te(CH_2SiMe_3)_2$. Complex **1** is, however, always the main product. In these cases the ^{125}Te NMR spectra of the reaction solution also indicates the presence of unreacted ligand.
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Keywords: Bis(trimethylsilylmethyl)tellane; Ruthenium complexes; X-ray diffraction; ^{125}Te NMR spectroscopy

1. Introduction

The information of the coordination chemistry of ruthenium complexes containing telluroether ligands is rather sparse (for reviews, see Refs. [1–5]). In early 1970s, the synthesis and spectroscopic characterization of mononuclear ruthenium(II) complexes in the reactions between R_2Te ($R = C_6H_5$, C_4H_9) and $RuCl_3 \cdot nH_2O$ or $[Ru(CO)_2X_2]_n$ ($X = Br$, I) producing $[RuX_2(CO)_n(TeR_2)_{4-n}]$ ($n = 1, 2$) have been described [2,6,7], and we have recently reported the preparation and crystal structure of $[RuCl_2(CO)_2(TePh_2)_2] \cdot \frac{1}{2}C_6H_6$ [8]. We have also described preliminary results of the trends in stereochemistry and bonding of the series of $[RuCl_2(CO)_2(ERR')_2]$ ($E = S$, Se, Te; $R,R' = Me$, Ph) involving different symmetric and asymmetric chalcogenoether ligands [9].

Gysling et al. [10] have discussed the preparation and structures of $[PdCl_2\{Te[(CH_2)_nSiMe_3]_2\}_2]$ ($n = 1$, 3) involving an interesting class of silylated telluroether ligands and reported the crystal structure of $[Pd(SCN)_2\{Te[(CH_2)_3SiMe_3]_2\}_2]$. As we have observed that the $Te(CH_2SiMe_3)_2$ ligand leads to interesting stereochemical features in case of palladium(II) and platinum(II) centers [11], it was decided to utilize this ligand also in exploration of coordination chemistry of ruthenium(II) complexes. In this work, we report the synthesis and structural characterization of $[RuCl_2(CO)_2\{Te(CH_2SiMe)_2\}_2]$ (**1**) and $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$ (**2**).

2. Experimental

2.1. Preparation of $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$

$Te(CH_2SiMe_3)_2$ (34.5 mg, 0.114 mmol) that was prepared according to the method of Gysling et al. [10] was dissolved in 2 ml of tetrahydrofuran (thf) and added to a suspension of 29.7 mg (0.058 mmol) of $[RuCl_2(CO)_3]_2$ in 3 ml of thf. The reaction mixture was refluxed for 5 h. The solvent was removed by evaporation, and the precipitate was dissolved in diethylether. Yellow crystals of

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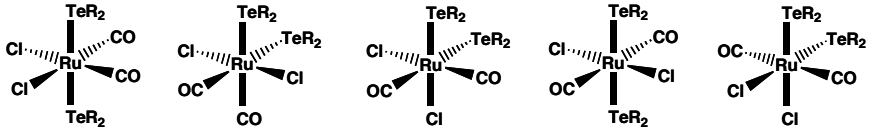
$[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ (**1**) were formed upon cooling the solution to +3 °C. Yield: (19.8 mg, 42%). Anal. Calc. for $C_{18}H_{44}Cl_2O_2RuSi_4Te_2$: C, 25.98; H, 5.33. Found: C, 26.25; H, 5.47%. ^{125}Te NMR ($CDCl_3$) δ [ppm]: 268.

2.2. Isolation of $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$

When the reaction was carried out using 120.6 mg (0.399 mmol) of $Te(CH_2SiMe_3)_2$ and 50.5 mg (0.0986 mmol) of $[RuCl_2(CO)_3]_2$, a mixture of yellow and orange crystals was obtained. Orange crystals of $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$ (**2**) could be manually separated for X-ray structure determination from the yellow crystals of **1**. ^{125}Te NMR (reaction mixture) ($CDCl_3$) δ [ppm]: 268 (**1**); 278 and 322 (intensity ratio 2:1) (**2**).



2.3. NMR spectroscopy

^{125}Te NMR spectra were recorded on a Brucker DPX400 spectrometer operating at 126.28 MHz. The spectral width was 126.58 kHz, the pulse width 10.00 μs, and the pulse delay 1.60 s. ^{125}Te accumulations contained ca. 60 000 transients. A solution of Ph_2Te_2 in $CDCl_3$ was used as an external standard. The spectra were recorded in $CDCl_3$ that served as internal ^{2}H lock. Chemical shifts (ppm) are reported relative to neat Me_2Te [$\delta(Me_2Te) = \delta(Ph_2Te_2) + 422$] [12].

2.4. X-ray crystallography

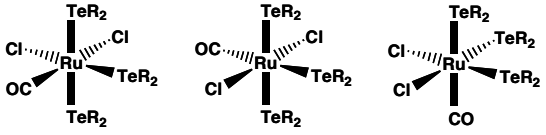
Diffraction data of **1** and **2** were collected on a Nonius Kappa-CCD diffractometer at 120 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å; 55 kV, 25 mA). Crystal data and the details of structure determinations are given in Table 1. Structures were solved by direct methods using SIR-92 [13] and refined using SHELXL-97 [14]. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in CH_3 groups (C–H = 0.98 Å) and in CH_2 groups (C–H = 0.99 Å). The scattering factors for the neutral atoms were those incorporated with the programs.

3. Results and discussion

The reaction of $Te(CH_2SiMe_3)_2$ and an excess of $[RuCl_2(CO)_3]_2$ affords $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ (**1**) in a moderate isolated yield. The ^{125}Te NMR spectrum indicates that **1** was the only tellurium-containing species in the reaction solution. A possible reaction intermediate $[RuCl_2(CO)_3\{Te(CH_2SiMe_3)_2\}]$ that has been observed and isolated in a related reaction involving the MeSePh ligand [9] could not be detected in the present reaction. The presence of only one ^{125}Te resonance at 268 ppm implies the presence of only chemically equivalent tellurium atoms. The analogous $[RuCl_2(CO)_2(TePh_2)_2]$ also exhibits one resonance in the ^{125}Te NMR spectrum at 704 ppm [8]. There are five possible structural isomers for the complex **1**.

The X-ray structure of **1** verifies the formation of the *cis*(Cl), *cis*(C), *trans*(Te) isomer. The same isomer was detected for $[RuCl_2(CO)_2(TePh_2)_2]$ in the reaction of $TePh_2$ with $[RuCl_2(CO)_3]_2$ [8] and was also shown by DFT calculations to be the most stable isomer across the whole series of chalcogenoether ligands [9]. This isomer was also suggested by John [7] to be the main isomer of $[RuCl_2(CO)_2(TeR_2)_2]$ on the basis of the intensity and number of CO stretching frequencies.

When the relative molar amount of $Te(CH_2SiMe_3)_2$ is increased to the nominal stoichiometric ratio for the production of $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ (**1**), a mixture of **1** and $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$ (**2**) is observed. There are three possible isomers for **2**.



The X-ray structure of **2** showed that the complex is a *cis*(Cl), *mer*(Te) isomer. Two ^{125}Te resonances at 278 and 322 ppm (intensity ratio of 2:1) have been observed for **2** and are consistent for the *cis*(Cl) *mer*(TeR_2) isomer of the complex.[1] The more intensive resonance corresponds to the two tellurium atoms in mutual *trans*-positions to each other and that with lower intensity corresponds to the third tellurium in the same plane as the carbonyl and chlorido ligands. Based on the relative intensities of ^{125}Te resonances of **1** and **2**, we estimate that the nominally stoichiometric reaction for **1** yielded *ca.* 80% of **1**

[1] All three possible isomers of **2**, however, are expected to show two ^{125}Te resonances with an intensity ratio of 2:1.

Table 1
Details of the single-crystal X-ray structure determination of **1** and **2** · $\frac{1}{2}Et_2O$

	1	**2** · $\frac{1}{2}Et_2O$
Empirical formula	$C_{18}H_{44}Cl_2O_2RuSi_4Te_2$	$C_{27}H_{71}Cl_2O_{1.50}RuSi_6Te_3$
Relative molecular mass	832.06	1135.18
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/n$
a (Å)	26.423(5)	14.514(3)
b (Å)	10.182(2)	16.003(3)
c (Å)	12.770(3)	21.321(4)
β (°)		90.76(3)
V (Å^3)	3436(1)	4952(2)
Z	4	4
$F(000)$	1624	2252
D_{calc} (g cm^{-3})	1.609	1.533
μ (Mo Kα) (mm^{-1})	2.428	2.322
Crystal size (mm)	0.40 × 0.10 × 0.10	0.20 × 0.10 × 0.05
θ Range (°)	2.99–26.00	3.05–26.00
Number of reflections collected	24921	40467
Number of unique reflections	6257	9660
Number of observed reflections[a]	5879	7999
Number of parameters/ restrains	275/0	386/4
R_{int}	0.0744	0.1178
R_1[b]	0.0361	0.0578
wR_2[c]	0.0902	0.1481
R_1 (all data)[b]	0.0401	0.0701
wR_2 (all data)[c]	0.0983	0.1582
Goodness-of-fit	1.038	1.049
Maximum and minimum heights in final difference Fourier synthesis (e Å^{-3})	0.906, −0.845	2.204, −2.032

[a] $I \leqslant 2\sigma(I)$.
[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

and 20% of **2**. It is interesting to note that the analogous reaction of $TePh_2$ and $[RuCl_2(CO)_3]_2$ with stoichiometric molar amounts produced only the *cis*(Cl), *cis*(C), *trans*(Te) isomer of $[RuCl_2(CO)_2(TePh_2)_2]$ with some unreacted $TePh_2$ [8]. It was reported by Hieber and John [6] that the reaction of $TePh_2$ with $RuCl_3$ in a molar ratio of 4:1 gave 25% the bis($TePh_2$) complex and 40 % of the tris($TePh_2$) complex.

Even a prolonged reflux upon using an excess of $Te(CH_2SiMe_3)_2$ in the reaction afforded a mixture of **1** and **2** with the complex **1** formed as the main product. In this case, however, the resonance due to free telluroether (26 ppm) was also present in the ^{125}Te NMR spectrum of the reaction solution.

The molecular structures of $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ (**1**) and $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3] \cdot \frac{1}{2}Et_2O$ (**2** · $\frac{1}{2}Et_2O$) indicating the numbering of the atoms are shown in Fig. 1. Both lattices are composed of discrete complexes. The lattice of **2** further contains a solvent diethyl ether molecule that is disordered in two symmetry-related orientations (occupation factor 0.5). The coordination polyhedron around ruthenium in both complexes is a slightly distorted octahedron (see Table 2). In complex **1** the Te(1)–Ru(1)–Te(2) angle is 163.80(3)° with the telluroether ligands inclined towards chlorido ligands and away from the carbonyl ligands. The same, though smaller effect is seen in complex **2** that shows the Te(1)–Ru(1)–Te(2) angle of 167.76(3)°.

The Ru–Te lengths are 2.6441(8) and 2.6442(8) Å in complex **1** and range from 2.6038(9) to 2.6493(9) Å in **2** (see Table 2). The two Ru–Te bonds in **2** that are *trans* to each other [Ru(1)–Te(1) and Ru(1)–Te(2)] are of comparable length to those in **1** and $[RuCl_2(CO)_2(TePh_2)_2]$ {2.6477(5) and 2.6637(5) Å [8]} that also exhibit mutual *trans*-orientations (see Fig. 2). By contrast, Ru(1)–Te(3)

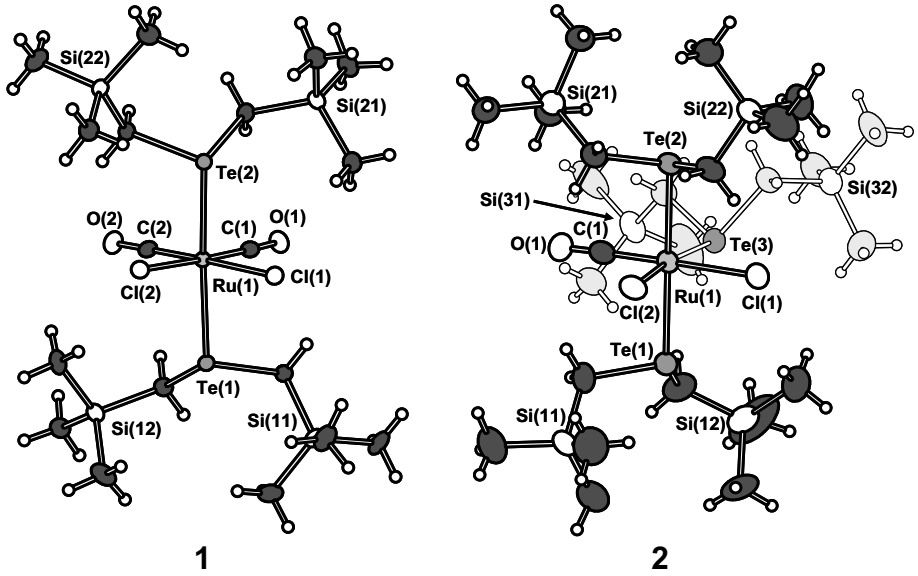


Fig. 1. The molecular structures of $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ (**1**) and $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$ (**2**) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50 % probability. The disordered solvent molecule in the lattice of **2** · $\frac{1}{2}Et_2O$ is not displayed for clarity.

Table 2
Selected bond lengths (Å) and angles (°) of complexes **1** and **2**

	1	2
Ru(1)–Te(1)	2.6441(8)	2.6419(9)
Ru(1)–Te(2)	2.6442(8)	2.6493(9)
Ru(1)–Te(3)		2.6038(9)
Ru(1)–Cl(1)	2.436(2)	2.476(2)
Ru(1)–Cl(2)	2.438(2)	2.436(2)
Ru(1)–C(1)	1.862(8)	1.827(8)
Ru(1)–C(2)	1.850(8)	
Te(1)–Ru(1)–Te(2)	163.80(3)	167.76(3)
Te(1)–Ru(1)–Te(3)		97.43(3)
Te(2)–Ru(1)–Te(3)		93.44(3)
Te(1)–Ru(1)–Cl(1)	81.54(5)	84.27(5)
Te(1)–Ru(1)–Cl(2)	88.45(4)	78.94(5)
Te(1)–Ru(1)–C(1)	93.3(2)	94.4(2)
Te(1)–Ru(1)–C(2)	96.8(2)	
Te(2)–Ru(1)–Cl(1)	85.93(5)	91.45(5)
Te(2)–Ru(1)–Cl(2)	81.26(4)	89.66(5)
Te(2)–Ru(1)–C(1)	97.2(2)	90.3(2)
Te(2)–Ru(1)–C(2)	95.6(2)	
Te(3)–Ru(1)–Cl(1)		83.22(5)
Te(3)–Ru(1)–Cl(2)		173.11(5)
Te(3)–Ru(1)–C(1)		95.1(2)
Cl(1)–Ru(1)–Cl(2)	89.79(6)	90.56(7)
Cl(1)–Ru(1)–C(1)	91.1(2)	177.7(2)
Cl(1)–Ru(1)–C(2)	178.3(2)	
Cl(2)–Ru(1)–C(1)	178.2(2)	
Cl(2)–Ru(1)–C(2)	89.8(2)	
C(1)–Ru(1)–C(2)	89.4(3)	

in **2.** [2.6039(9) Å] that lies in *trans*-position to Ru(1)–Cl(2) is significantly shorter. The trend in the ^{125}Te chemical shifts are consistent with the structural observations for **2**. The more intensive resonance at 268 ppm assigned to the two tellurium nuclei *trans* to each other is more shielded than the less intensive ^{125}Te resonance at 322 ppm that is assigned to the third tellurium lying in *trans* position to the chlorido ligand. This implies that this last tellurium atom is a stronger donor and binds more strongly to ruthenium than the two former atoms.

The Ru–Cl lengths 2.436(2) and 2.438(2) Å in **1** are similar to those in $[RuCl_2(CO)_2(TePh_2)_2]$ {2.437(2) and 2.443(1) Å [8]}. While Ru(1)–Cl(1) in **2** is significantly longer [2.476(2) Å], Ru(1)–Cl(2) [2.436(2) Å] is of comparable length to those in **1** and $[RuCl_2(CO)_2(TePh_2)_2]$. The Ru–C lengths of 1.850(8) and 1.862(8) Å in **1** are of similar length to those in $[RuCl_2(CO)_2(TePh_2)_2]$ {1.870(6) and 1.854(6) Å [8]}, but that in **2** is shorter [1.822(8) Å].

The relative Ru–Cl bond lengths in **1**, **2**, and $[RuCl_2(CO)_2(TePh_2)_2]$ [8] appear to be dependent on the identity of *cis*-ligands rather than on that of *trans*-ligands (see Fig. 2). Both Ru–Cl bonds in **1** and $[RuCl_2(CO)_2(TePh_2)_2]$ show *cis*-relations to two Te-donors, one Cl donor, and one carbonyl carbon donor. Ru(1)–Cl(2) in **2** shows exactly the same number and orientation of *cis*-neighbours and therefore also a length that agrees well with the Ru–Cl bond lengths in **1** and $[RuCl_2(CO)_2(TePh_2)_2]$ [8]. As shown in Fig. 1, Ru(1)–Cl(1) has three Te-donors and one Cl donor as *cis*-neighbours. This bond is significantly longer.

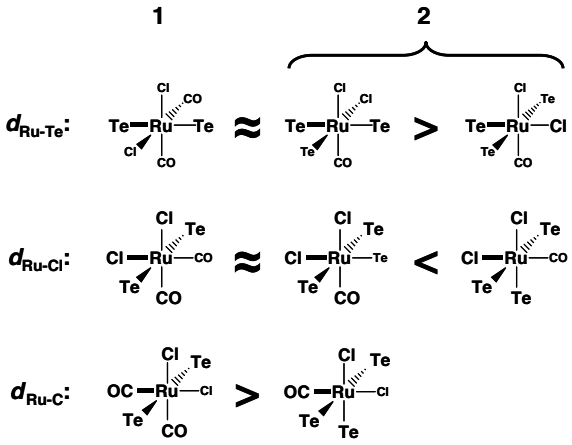


Fig. 2. The dependence of the lengths of the Ru–Te, Ru–Cl, and Ru–C bonds (marked in bold) on the identity of *cis*- and *trans*-donor atoms.

The identity of *cis*-ligands also seems to influence the Ru–C bonds, since all carbonyl carbon atoms in **1**, **2**, and $[RuCl_2(CO)_2(TePh_2)_2]$ lie *trans* to a chloride ligand. The two Ru–C bonds in **1** and $[RuCl_2(CO)_2(TePh_2)_2]$ [8] show one C donor, one Cl donor and two Te-donors in relative *cis*-positions. All four Ru–C bonds in question are approximately equally long. The Ru–C bond in **2** has three Te donors and one Cl donor in *cis*-positions and is significantly shorter than the bonds in **1** and $[RuCl_2(CO)_2(TePh_2)_2]$ [8].

4. Conclusions

The *cis*(Cl), *cis*(C), *trans*(Te) isomer of $[RuCl_2(CO)_2\{Te(CH_2SiMe_3)_2\}_2]$ (**1**) can be produced in a moderate yield by the reaction of $[RuCl_2(CO)_3]_2$ and $Te(CH_2SiMe_3)_2$. The reaction affords pure **1** only, when it is carried out with an excess of $[RuCl_2(CO)_3]_2$. With stoichiometric amounts of the starting materials or by using an excess of $Te(CH_2SiMe_3)_2$, a mixture containing **1** and the *cis*(Cl), *mer*(TeR_2) isomer of $[RuCl_2(CO)\{Te(CH_2SiMe_3)_2\}_3]$ (**2**) is formed. In each case, **1** was the main product and **2** a side product. When using a large excess of $Te(CH_2SiMe_3)_2$, unreacted ligand was also present in the reaction mixture. We note that while the corresponding reaction of $[RuCl_2(CO)_3]_2$ and $TePh_2$ only afforded the *cis*(Cl), *cis*(CO), *trans*(Te) isomer of $[RuCl_2(CO)_2(TePh_2)_2]$ with no indication of the tris($TePh_2$) complex [8], the reaction of $TePh_2$ with $RuCl_3$ in a molar ratio four-to-one yielded 25% the bis($TePh_2$) complex and 40 % of the tris($TePh_2$) complex [2]. The factors affecting the complex formation using a number of chalcogenoethers are currently under investigation.

5. Supplementary material

CCDC 663418 and 663419 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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