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Synthesis and X-Ray Crystal Structure of [(η^5-Tellurophene)Ru(η^5-C_5Me_5)](OTf)

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In recent years, the coordination chemistry of the group 16 heterocycle ligands of furan, thiophene, selenophene, and tellurophene opens up new research area.[1] Especially the chemistry of thiophene transition metal complexes has been extensively studied[2] as models for industrially and environmentally important hydrodesulfurization (HDS) of sulfur compounds found in crude oil. Among organic sulfur compounds, aromatic thiophene derivatives are the most difficult to desulfurize. This has led to many model studies of the reactions of thiophene and its derivatives with heterogeneous and homogenous systems. The first concern for the HDS catalysis is the binding mode of the thiophene to the catalyst. Three types of coordination modes of the group 16 heterocyclic five membered ligands are most commonly proposed: via the hetero-atom only, as an η^2-coordination involving the unsaturated carbons, or the entire π-system in an η^5-fashion. The need for developing more efficient HDS catalysts requires some novel approaches to obtaining new mechanistic information. One approach is the use of aromatic chalcogen complexes as substitutes for thiophene molecules. The other interest is to investigate the similarity and dissimilarity between the chemistry of thiophene and tellurophene transition metal complexes. Tellurium is an attractive sulfur analogue because of its NMR spectroscopic properties. ^{125}Te has a 7.03% natural abundance and a nuclear spin of 1/2.[3] The existence of the NMR-active isotope ^{125}Te makes possible to assign tellurophene bonding modes to the transition metals. The tellurophene is able to coordinate metals through the entire π system as η^5 bonding mode. In this paper, the synthesis of η^5-tellurophene coordinated Ru complex and NMR studies of this bonding mode have been reported. In addition, the first X-ray structural determined η^5-coordination mode of tellurophene has been reported.

Experimental

General Procedures. All reactions were performed under Ar atmosphere in reagent grade solvents, using standard Schlenk techniques.[4] Diethyl ether (Et_2O) was distilled from Na/benzophenone, CH_2Cl_2, and acetonitrile (CH_3CN) from CaH_2. MeOH was distilled from Mg. The solvents were stored over 4-Å molecular sieves under Ar. The ^{1}H and ^{13}C NMR spectra obtained on Bruker DPX-250 spectrometer with $CDCl_3$ as the internal lock. The ^{125}Te NMR spectrum was recorded on the Bruker BZH-300 spectrometer at room temperature and referenced to tellurophene (δ=782 ppm). Microanalysis was performed with a Perkin Elmer 240 elemental analyzer. Fast atom bombardment (FAB) spectrum was obtained with use of a VG70-VSEQ mass spectrometer.

The following compounds are prepared by literature methods: [Cp*Ru(CH_3CN)$_3$](OTf)(Cp*=C_5Me_5, OTf=O_3SCF_3),[5] Na_2Te.[6] All other compounds were purchased from commercial sources and used as received.

Synthesis of tellurophene (1). Compound **1** was prepared by a modified literature methods.[6,7] To a degassed 5 N sodium hydroxide solution (80 mL) was added Rongalite (sodium formaldehydesulfoxylate dihydrate; $HOCH_2SO_2Na\cdot 2H_2O$, 26.6 g, 0.17 mol) and tellurium (10 g, 78.4 mmol). The solution was refluxed for 2 h under Ar atmosphere. The sodium telluride as a wine-colored solution was formed. After the solution was evaporated under vacuum, the yellowish white sodium telluride was obtained. This sodium telluride is very air sensitive. To the yellowish white powder, dry degassed methanol (160 mL) was added and the mixture was stirred until the solid dissolved (system A). The butadiyne was prepared separately in a three-neck flask a gas inlet, and a condenser connected through a trap to a column (40×2.5 cm) filled with anhydrous calcium chloride and outlet needle. To a degassed solution of potassium hydroxide (5 N, 150 mL) was added 1,4-dichloro-2-butyne (25.2 g, 205 mmol) in dioxane (20 mL) (system B). Systems A and B were connected and flushed with a slow stream of dried Ar. The solution in system B was heated under reflux with vigorous stirring and the butadiyne was

bubbled into system A. The heating of system B was continued for 3 h. The gray precipitate which formed was filtered off and the resulting yellow methanol solution was diluted with water. This solution was extracted with Et_2O. The extracts were washed with saturated sodium chloride solution, dried with $MgSO_4$ and filtered. After evaporation of Et_2O and methanol under reduced pressure, the residue solution was vacuum distilled at 91-94 °C/100 mmHg to give yellow liquid tellurophene (5.4 g, 38% yield).

Synthesis of [(η^5-Tellurophene)Ru(η^5-C_5Me_5)](OTf) (2). To a solution of [Cp*Ru(CH_3CN)$_3$](OTf) (0.10 g, 0.20 mmol) in 5 mL of CH_2Cl_2 was added tellurophene (0.10 g, 0.56 mmol). The solution was stirred at room temperature for 2 h. The resulting solution was filtered through Celite. The solution was reduced to about 2 mL under vacuum, and Et_2O (10 mL) was added. The solution was kept at − 20 °C for 2 days to give yellow crystals of **2** (94 mg, 85% yield). ^{1}H NMR δ ($CDCl_3$): 6.86 (m, 2H, H2,5, $^2J_{H\text{-}Te}$=60 Hz), 6.07 (m, 2H, H3,4), 2.09 (s, 15H, Cp*). ^{13}C NMR δ ($CDCl_3$): 96.4 (Cp*), 92.2, 87.8 (C of tellurophene), 12.0 (Me of Cp*). ^{125}Te NMR δ (d^6-aceton): 107. MS (FAB, glycerol matrix): m/e 417 (M^+). Anal. Calcd for $C_{15}H_{19}O_3F_3RuSTe$: C, 31.89; H, 3.39. Found: C, 31.45; H, 3.05.

X-ray Structure Determination of 2. The crystals of complex **2** suitable for X-ray diffraction study were obtained by vapor diffusion of Et_2O into CH_2Cl_2 solution at − 20 °C. A single crystal was mounted on a fiber glass and mounted directly to the Siemens three-circle diffractometer with CCD area detector (SMART system).[8a] The crystal was centered in the beam. Preliminary orientation matrix and cell constants were determined by collection of 10 seconds and 15 frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using 0.3° ω scans at 10-seconds per frame. The raw data integrated (XY spot spread=1.6, Z spot spread=0.6) and the unit cell parameters refined (9305 reflection with I> 3σ) using SAINT.[8b] Data analysis and absorption correction were performed using Siemens XPREP and SADABS.[8c] The unit-cell parameters indicated a primitive monoclinic cell and systematic absences indicated space group Pc (no. 7). The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The 9305 reflections measured were averaged yielding 6071 unique reflections (R_{int}=0.0252). The structure was solved and refined with SHELX-97 program using direct methods[8d] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. Relevant crystal data and parameters associated with data collection for **2** are given in Table 1. Selected bond distances and angles for **2** are presented in Table 2.

Results and Discussion

Synthesis of [(η^5-Tellurophene)Ru(η^5-C_5Me_5)](OTf) (2). The reaction of [Cp*Ru(CH_3CN)$_3$](OTf) with tellurophene in CH_2Cl_2 solution results in the formation of η^5-tellurophene complex **2**, as shown in eq 1. Complex **2** is air stable in the solid state.

The ^{1}H NMR spectrum of **2** [δ 6.86 (m, H2,5, $^2J_{H\text{-}Te}$=60

Table 1. Crystal data and structure refinement for [(η^5-Tellurophene)Ru(η^5-C_5Me_5)](OTf) (2)

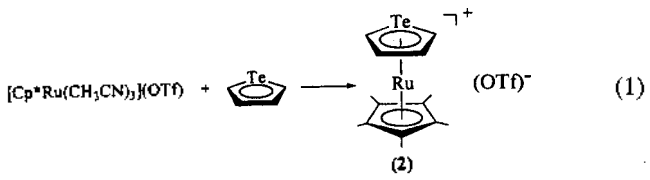
Emprical formula	$C_{15}H_{19}F_3O_3RuSTe$
Fomula weight	565.03
Temperature	293(2) K
Detector	CCD area detector
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Pc
Unit cell dimensions	a=14.88020(10) Å b=8.9496(2) Å c=14.5836(2) Å β=90.1000(10) deg
Volume	1942.12(5) Å
Z	4
Density calculated	1.932 mg/m^3
Absorption coefficient	2.424 mm^{-1}
F(000)	1088
Crystal size	0.45×0.56×0.42 mm
θ range	1.37-24.68 deg
Indexing ranges	$-17\le h\le 17$, $-6\le k\le 10$, $-16\le l\le 17$
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.025
Reflections collected/unique	8969/6071 [R_{int}=0.0252]
Data/restraint/parameters	6071/2/444
Final R indices [I>2σ (I)]	R_1=0.0339, wR_2=0.0892
R indices (all data)	R_1=0.0391, wR_2=0.0924
Largest diff. peak and hold	1.014 and −0.417 eÅ^{-3}

$wR_2=\{\Sigma[w(F_o^2-F_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$

Table 2. Selected bond distances (Å) and angles (deg) of [(η^5-Tellurophene)Ru(η^5-C_5Me_5)](OTf) (2)[a]

Te-Ru	2.6340(8)
C(2)-Ru	2.226(9)
C(3)-Ru	2.202(8)
C(4)-Ru	2.210(7)
C(5)-Ru	2.229(9)
C(11)-Ru	2.188(8)
C(12)-Ru	2.186(8)
C(13)-Ru	2.183(7)
C(14)-Ru	2.175(8)
C(15)-Ru	2.180(8)
C(2)-Te	2.090(10)
C(5)-Te	2.094(9)
C(2)-C(3)	1.398(12)
C(3)-C(4)	1.443(12)
C(4)-C(5)	1.406(12)
Te-C(2)-C(3)	112.7(7)
C(2)-C(3)-C(4)	117.0(8)
C(3)-C(4)-C(5)	116.4(8)
C(4)-C(5)-Te	112.7(7)
C(5)-Te-C(2)	80.5(4)
C(11)-C(12)-C(13)	108.1(7)
C(12)-C(13)-C(14)	108.5(7)
C(13)-C(14)-C(15)	108.3(7)
C(14)-C(15)-C(11)	108.3(7)
C(15)-C(11)-C(12)	106.9(7)

[a] Bond distances and angles are averaged by two crystallographically independent of molecules.



(1)

Hz); 6.07 (m, H3,4)] was assigned by comparison with spectra for the analogous thiophene[9] and selenophene[10] complexes, as well as by observation of ^{125}Te satellite peaks. The ^{125}Te satellite peaks are also used to definitively assign the resonances for protons H2 and H5. Coupling of protons in the 2,5-position to the ^{125}Te (7.03% natural abundance) nucleus is observed in the satellite peaks, which give a two bond coupling constant of $^2J_{H\text{-}Te}$=60 Hz. This coupling constant is smaller than that of free tellurophene ($^2J_{H\text{-}Te}$=102 Hz).[11] The ^{1}H NMR resonances of H2, H5 (δ 6.86) in **2** are 2.1 ppm upfield, while the chemical shifts for H3 and H4 (δ 6.07) show 1.8 ppm upfield of those for free tellurophene (δ 8.90, 7.82). In the ^{13}C NMR spectrum of **2**, the chemical shifts at 92.9 and 87.8 ppm lie considerably upfield (40-50 ppm) of those in free tellurophene (δ 138, 127 ppm in $CDCl_3$). These upfield shifts in ^{1}H and ^{13}C NMR spectra are commonly observed when arene[12] and thiophene[13] ligands are π-bound in complexes. The ^{1}H and ^{13}C NMR spectra support η^5-coordination mode of tellurophene. The η^5-tellurophene bonding mode was also confirmed by X-ray crystallographic determination (Figure 1).

^{125}Te NMR spectrum of 2. One goal of the studies described in this paper is to determine the usefulness of ^{125}Te NMR spectroscopy for establishing the η^5-coordination mode of tellurophene binding in transition metal complexes. The ^{125}Te nucleus has a natural abundance of 7.03% and a relative receptivity that is 12.6 times larger than ^{13}C.[3] Therefore the ^{125}Te NMR spectrum of **2** could be obtained without difficulties The ^{125}Te NMR chemical shift of **2** shows at 107 ppm which is further upfield (675 ppm) than that of free tellurophene (782 ppm).[11] Such upfield shift in ^{125}Te NMR is indicative to η^5-coordination of tellurophene to the ruthenium metal.

X-ray Structure of 2. Complex **2** was characterized by X-ray crystallography and crystallizes in the monoclinic space group Pc with Z=4, which requires that there be two independent molecules within the asymmetric unit. The ORTEP drawing of [(η^5-Tellurophene)Ru(η^5-C_5Me_5)](OTf) (**2**) is given in Figure 1. It clearly shows that the tellurophene ring in **2** bound to ruthenium through the tellurium and the four carbons as η^5-coordination mode. In contrast to the free tellurophene[14] and 2,2'-bitellurophene[15] are planar structure, the tellurophene ring in **2** is slightly bent. The tellurium atom is out of the plane of the ring carbon atoms [C 2, C3, C4, and C5] by 0.213(3) Å. The dihedral angle between the plane of the ring carbons [C2, C3, C4, and C5] and the C2-Te-C5 plane is 7.9(5)°. This angle is larger by 3(1)° and 3.4(6)° than the corresponding angle in the η^5-thiophene complexes of [(η^5-Me_4T)$_2$Ru]$^{+}$[2,16] and (η^5-2,5Me_2T)Cr(CO)$_3$[17], respectively. The average Te-Ru bond distance [2.634(1) Å] of two crystallo-graphically independent two molecules in **2** is very similar that in (MeC_5H_4)$_4$Ru$_4$Te$_4$ [2.62 Å][18] and 0.1 A shorter than that in Ru$_4$(CO)$_{10}$(μ-CO)(μ$_4$-Te)$_2$ [2.734(1) Å].[19] The C-Te bond distances [2.057(10), 2.067(9), 2.118(9), 2.133(10) Å] of the tellurophene ring in **2** are slightly larger than the corresponding C-Te bond distance [2.055(6) Å][11,14] in uncoordinated free tellurophene.

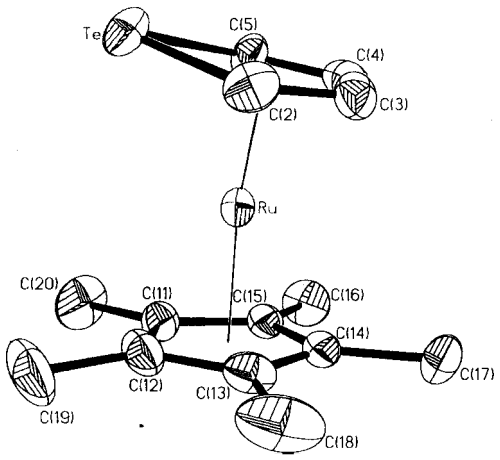


Figure 1. ORTEP drawing the cation in [(η^5-Tellurophene)Ru(η^5-C_5Me_5)] (OTf) (2). (30% probability ellipsoids).

Summary

The synthesis of new η^5-tellurophene ruthenium complex has been undertaken so that a comparison of ^{1}H and ^{13}C NMR spectroscopic data could be made with the known analogous η^5-thiophene complexes. ^{125}Te NMR spectroscopy may be a useful probe for detecting η^5-tellurophene coordination mode in transition metal complexes. In the X-ray structure of [(η^5-Tellurophene)Ru(η^5-C_5Me_5)](OTf) the tellurophene ring is slightly bent with the tellurium atom out of the plane of the ring carbon atoms. The Te-C bond distances of the tellurophene are slightly elongated upon the η^5-coordination to the ruthenium metal.

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Supporting Information Available. ORETP drawings, full tables of crystal data, atomic coordinates, bond distances, bond angles, and anisotropic thermal displacement parameters (21 pages); listings of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Preparation of *gem*-Difluorinated β-Phenylthio Substituted Allylic Bromides and Their Reactions

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The introduction of difluoromethylene (CF_2) unit into organic molecules has recently been received much attention because of inhancement of biological properties of pharmaceuticals and agrochemicals.[1,2] A variety of biologically interesting compounds that contain the difluoromethylene group, such as the antitumor nucleoside Gemcitabine[3] and α,α-difluoroalkylphosphonate-based mimics,[4] have been discovered in recent work. Although there have been various methods for the introduction of difluoromethylene functionality, the synthetic methods which the difluoromethylene phosphonate group is directly attached to an vinyl carbon atom have been quite limited.[5-8] *gem*-Difluoroallylation is one of valuable methods for the construction of difluoromethylene frameworks because of a wide range of functional group transformations of alkene group. The most potential reagent for *gem*-difluoroallylation is *gem*-difluoroallylic bromide. The synthetic method for the 3-bromo-3,3-difluoropropene as a *gem*-difluoroallylic bromide has been well known.[9] However, we are interested in the preparation of *gem*-difluorinated β-phenylthio substituted allylic bromides because the presence of phenylthio group at the vinyl carbon could provide more versatility for the functional group transformation than in the case of the presence of alkene group only. Unfortunately, there has been no methodology for the preparation of *gem*-difluorinated β-phenylthio substituted allylic bromides. In this paper, we wish to describe a new synthetic method for the preparation of *gem*-difluorinated β-phenylthio substituted allylic bromides and their reactions.

Perfluorinated dithioketals which we have developed[10] are promising reagents to approach *gem*-difluorinated β-phenylthio substituted allylic bromides. Thus, the starting materials, 1,1,1-trifluoro-2,2-bis(phenylthio)propane (**1a**) and 1,1,1-trifluoro-2,2-bis(phenylthio)butane (**1b**), were prepared in 82% and 79% isolated yields, respectively, from the reaction of 1,1,1-trifluoro-2-propanone and 1,1,1-trifluoro-2-butanone with thiophenol in the presence of $AlCl_3$ at − 78 °C for 20 hours. The treatment of **1a** and **1b** with a mixture of 2 equiv. of $TiCl_4$ and 3 equiv. of $LiAlH_4$ in THF at reflux temperature for 3 hours resulted in the formation of 1,1-difluoro-2-