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Transition Metal Complexes with Sulfur Ligands. XIX.* Mono- and Bis-alkylation of [Ru(II)L_1L_2dttd] Complexes Controlled by the Ligands L as well as the Charge of the Resulting Compounds (dttd^{2-} = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane(−2), $L_1 = L_2 = PPh_3$; $L_1 = L_2 = PMe_3$; $L_1 = PPh_3$, $L_2 = PMe_3$)

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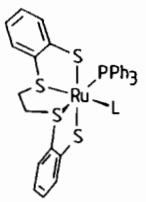
Abstract

The alkylation of the thiolato-S atoms of the dttd-ligand in [RuL_1L_2dttd] complexes was investigated ($L_1 = L_2 = PPh_3$; $L_1 = L_2 = PMe_3$; $L_1 = PPh_3$, $L_2 = PMe_3$; dttd^{2-} = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane(−2)). The substitution lability of the phosphine ligands L_1 and L_2 determines whether one or both of the thiolato-S atoms are alkylated when [RuL_1L_2dttd] is reacted with alkylhalides. [$Ru(PPh_3)_2$dttd], in which one PPh_3 is substitution labile, is doubly alkylated on reaction with CH_3I yielding [$Ru(PPh_3)I(Me_2$-dttd)]I (Me_2-dttd = 1,10-dimethyl-2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane). Reaction of the substitution inert phosphine complexes [$Ru(PMe_3)_2$dttd] and [$Ru(PPh_3)(PMe_3)$-dttd] with CH_3I yields the monoalkylated derivatives [$Ru(PMe_3)_2$(Me-dttd)]I and [$Ru(PPh_3)(PMe_3)$(Me-dttd)]I, respectively. Analogously, ethyl as well as bromine derivatives can be obtained. The cation in [$Ru(PPh_3)X(Me_2$-dttd)]X (X = I, Br) proves to be substitution inert under ordinary conditions; the anion X can be exchanged for other singly charged anions via [$Ru(PPh_3)X(Me_2$dttd)]$_2SO_4$. In concentrated H_2SO_4, [$Ru(PPh_3)Br(Me_2$-dttd)]Br could be reacted to give [$Ru(Br_2)(Me_2$dttd)]. All compounds were characterized spectroscopically as well as by elemental analyses. The structure of [$Ru(PPh_3)$-$I(Me_2$-dttd)]I was determined by X-ray structure analysis.

[$Ru(PPh_3)I(Me_2$-dttd)]I (**1**) crystallizes from CH_2Cl_2 as $1 \cdot 3CH_2Cl_2$ in the monoclinic space group $P2_1/c$ with the following unit cell dimensions: a = 20.103(0.03), b = 11.148(0.009), c = 26.985(0.03) Å; β = 130.71(0.07)°, V = 4584(3) Å^3 and Z = 4. The structure refinement stopped at R_1 = 8.86 and R_2 = 10.44% because of disorder of the CH_2Cl_2 solvate molecules. In the cation of **1** Ru is coordinated pseudo-octahedrally by I–, P– and four thioether-S atoms.

Introduction

The [$Ru(PPh_3)$dttd] fragment with the tetradentate thioether-thiolato ligand dttd^{2-} (= 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane(−2)) coordinates



numerous small nitrogen compounds such as NH_3, N_2H_4, $N_2H_3CH_3$, NO^+ and N_3^- [1]. Even the synthesis of the first diazene complex with a sulfur-coordinated metal center, [μ-N_2H_2 {$Ru(PPh_3)$dttd}$_2$], succeeded with this fragment [2]. The starting compound for these complexes is [$Ru(PPh_3)_2$dttd] [3], in which one of the PPh_3 ligands is substitution-labile and can be easily substituted at ambient temperatures. We have now observed that [$Ru(PPh_3)_2$dttd] also reacts with mineral acids yielding compounds in which supposedly the sulfur ligand is protonated reversibly; these compounds, however, could not yet be isolated in the solid state. Complexes with neutral thiol ligands RSH are rare; examples like [$CpFe(CO)_2$-(PhSH)]BF_4 or [$Ru(NH_3)_5$(RSH)]$^{2+}$ (R = H, Et) are described to be very strong acids [4, 5].

Since thiolato ligands can often be alkylated yielding thioether ligands [6], we have tried to gain

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further insight into the nucleophilicity of the dttd ligand in [Ru(dttd)] complexes by investigating their reactions with alkylhalides.

Experimental

All reactions were carried out in absolute solvents under nitrogen with the Schlenk tube technique. Spectra were run on the following instruments: Zeiss IR spectrometer IMR 16, JEOL JNM-PMX 60 NMR spectrometer, Varian MAT 212 mass-spectrometer. $[Ru(PPh_3)_2dttd]$ and $[Ru(PMe_3)_2dttd]$ were prepared according to literature methods [3].

X-ray Structure Analysis of $[Ru(PPh_3)I(Me_2\text{-}dttd)]I \cdot 3CH_2Cl_2$

A single crystal with the approximate dimensions $0.2 \times 0.1 \times 0.15$ mm was obtained from an oversaturated CH_2Cl_2 solution at 20 °C and sealed in a glass capillary without drying. A Syntex P3 diffractometer was used for the determination of the unit cell dimensions and the data collection. Data were collected using the ω-scan ($1 < 2\theta < 42°$, $\Delta\omega = 1°$, $2.6 \leq \omega \leq 29.3°$/min). The relevant diffraction data are listed in Table I.

TABLE 1. Diffraction Data of $[Ru(PPh_3)I(Me_2\text{-}dttd)]I \cdot 3CH_2Cl_2$

Space group	$P2_1/c$
Lattice constants	
a (Å)	20.103(0.03)
b (Å)	11.148(0.009)
c (Å)	26.985(0.03)
β (deg)	130.71(0.07)
V (Å^3)	4584(3)
$Z(M_r = 1210.5)$	4
D_c (g/cm^3)	1.75
μ(Mo Kα) (cm^{-1})	22.8
λ(Mo Kα-graphite monochromator) (Å)	0.71069
Temperature (K)	228
Measured independent reflections	4767
with $I \geq 4\sigma(I)$	2832
Number of parameters refined	246
Final R_1, R_2[a] (%)	8.86; 10.44

[a] $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

The structure was solved by direct methods using the SHELXTL program. The heavy atoms Ru, P, S and I were refined with anisotropic temperature factors. The H atoms of the cation were placed at calculated positions at 0.95 Å from the corresponding carbon atoms and refined as rigid groups. One of the three CH_2Cl_2 solvate molecules proved to be disordered; it was treated with constraint during the 12 final cycles of least-squares refinement. The refinement stopped at $R_1 = 8.86$ and $R_2 = 10.44\%$. Table II lists the fractional atomic coordinates of the nonhydrogen atoms of $[Ru(PPh_3)I(Me\text{-}dttd)]I$.

Syntheses and Reactions

1. $[Ru(PPh_3)I(Me_2\text{-}dttd)]I \cdot CH_2Cl_2$

1 g (1 mmol) of $[Ru(PPh_3)_2dttd]$ is suspended in 50 ml CH_2Cl_2 at room temperature. After addition of 1 ml (~16 mmol) CH_3I a red–orange solution forms within 10 min, from which the product is precipitated by addition of 100 ml of petrolether. The precipitate is redissolved in 40 ml of CH_2Cl_2. After slow addition of 60 ml of petrolether, transparent orange crystals are obtained after 24 h, which turn opaque on drying *in vacuo*. Yield: 800 mg (84%). *Anal.* Calc. for $C_{35}H_{36}Cl_2I_2PRuS_4$ (1040.7): C, 40.39; H, 3.29. Found C, 40.88; H, 3.36%.

2. $[Ru(PPh_3)Br(Me_2\text{-}dttd)]Br$

Into a suspension of 500 mg (0.5 mmol) of $[Ru(PPh_3)_2dttd]$ in 80 ml of CH_2Cl_2, CH_3Br is introduced by a gas inlet for 2 h at 30 °C; in this time the volume of the resulting yellow solution reduces to *ca.* 30 ml. Addition of 100 ml of petrolether yields a yellow precipitate, which is recrystallized from CH_2Cl_2 by careful addition of petrolether. Yield: 300 mg (70%) light yellow, needle-shaped crystals. *Anal.* Calc. for $C_{34}H_{34}Br_2PRuS_4$ (861.76): C, 47.39; H, 3.88. Found C, 48.39; H, 3.90%.

3. $[Ru(PPh_3)I(Et_2\text{-}dttd)]I \cdot CH_2Cl_2$

A suspension of 500 mg (0.5 mmol) of $[Ru(PPh_3)_2dttd]$ in 50 ml of CH_2Cl_2 is refluxed with 1.5 ml (~18 mmol) of C_2H_5I for 5 h. After filtration of the solution the complex is precipitated by addition of 100 ml of petrolether, separated and recrystallized from 30 ml CH_2Cl_2/50 ml petrolether. Yield: 260 mg (48%). *Anal.* Calc. for $C_{37}H_{40}Cl_2I_2PRuS_4$ (1068.7): C, 41.58; H, 3.77. Found C, 41.90; H, 4.01%.

4. $[Ru(PPh_3)(PMe_3)(dttd)]$

To a suspension of 1 g (1 mmol) of $[Ru(PPh_3)_2dttd]$ in 50 ml of THF is added 1 ml (~13 mmol) of PMe_3. 2 h of stirring at room temperature yields a solution which contains only traces of undissolved material. Reduction of its volume to ~25 ml, filtration, addition of 70 ml of petrolether and cooling to −25 °C yields yellow needles of $[Ru(PPh_3)(PMe_3)dttd]$ as well as compact dark yellow crystals of the solvate $[Ru(PPh_3)(PMe_3)(dttd)] \cdot THF$, which can be easily separated by hand. Yield of $[Ru(PPh_3)(PMe_3)(dttd)]$: 340 mg (45%). *Anal.* Calc. for $C_{35}H_{36}P_2RuS_4$ (747.9): C, 56.21; H, 4.85. Found C, 56.27; H, 5.01%. Yield of $[Ru(PPh_3)(PMe_3)(dttd)] \cdot THF$: 200 mg (27%). *Anal.* Calc. for $C_{39}H_{44}OP_2RuS_4$ (820.1): C, 57.12; H, 5.41. Found C, 57.89; H, 5.88%.

TABLE II. Fractional Atomic Coordinates for non-Hydrogen Atoms

Atom	*x/a*	*y/b*	*z/c*	*U*	Atom	*x/a*	*y/b*	*z/c*	*U*
I2	0.5713(1)	0.1787(1)	0.22140(9)		C14	0.454(2)	−0.218(2)	0.083(1)	0.052(7)
I2	0.9742(2)	0.2095(2)	0.0819(1)		C15	0.368(2)	−0.244(2)	0.043(1)	0.058(8)
RU	0.6918(1)	−0.0004(2)	0.28342(9)		C16	0.318(2)	−0.192(2)	0.056(1)	0.053(7)
P	0.6129(5)	−0.1291(5)	0.1927(3)		C17	0.355(2)	−0.127(2)	0.112(1)	0.061(8)
S1	0.8038(5)	−0.1325(5)	0.3488(3)		C18	0.442(2)	−0.105(2)	0.150(1)	0.050(7)
S2	0.6235(5)	−0.0945(6)	0.3165(3)		C19	0.626(2)	−0.106(2)	0.133(1)	0.046(7)
S3	0.7701(5)	0.1300(5)	0.3728(3)		C20	0.654(2)	−0.182(2)	0.110(1)	0.057(7)
S4	0.7583(5)	0.0973(5)	0.2492(3)		C21	0.658(2)	−0.155(3)	0.062(2)	0.08(1)
C1	0.831(2)	0.208(2)	0.314(1)	0.050(7)	C22	0.633(2)	−0.045(3)	0.035(2)	0.09(1)
C2	0.878(2)	0.277(2)	0.305(1)	0.067(8)	C23	0.607(2)	0.036(3)	0.056(1)	0.076(9)
C3	0.933(2)	0.365(2)	0.353(1)	0.057(8)	C24	0.600(2)	0.014(2)	0.103(1)	0.060(8)
C4	0.936(2)	0.374(3)	0.402(1)	0.064(8)	C25	0.857(2)	0.036(2)	0.442(1)	0.046(7)
C5	0.886(2)	0.308(3)	0.410(1)	0.069(8)	C26	0.891(2)	−0.045(2)	0.420(1)	0.056(8)
C6	0.831(2)	0.216(2)	0.362(1)	0.041(6)	C27	0.619(2)	0.002(3)	0.367(1)	0.081(9)
C7	0.649(2)	−0.284(2)	0.221(1)	0.044(7)	C28	0.839(2)	0.006(3)	0.258(1)	0.073(9)
C8	0.603(2)	−0.350(2)	0.232(1)	0.051(7)	C29	0.702(2)	−0.201(2)	0.376(1)	0.043(6)
C9	0.630(2)	−0.466(2)	0.259(1)	0.064(8)	C30	0.775(2)	−0.224(2)	0.387(1)	0.045(7)
C10	0.709(2)	−0.498(3)	0.279(1)	0.063(8)	C31	0.832(2)	−0.310(2)	0.427(1)	0.063(8)
C11	0.757(2)	−0.432(2)	0.270(1)	0.064(8)	C32	0.815(2)	−0.376(3)	0.461(1)	0.067(8)
C12	0.730(2)	−0.321(2)	0.243(1)	0.054(7)	C33	0.739(2)	−0.351(2)	0.451(1)	0.059(8)
C13	0.494(2)	−0.141(2)	0.140(1)	0.038(6)	C34	0.681(2)	−0.269(2)	0.408(1)	0.051(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	0.060(1)	0.0240(8)	0.052(1)	0.0048(8)	0.020(1)	0.0071(9)
I2	0.101(2)	0.058(1)	0.084(2)	0.016(1)	0.054(1)	0.012(1)
RU	0.051(1)	0.0176(9)	0.037(1)	0.0000(9)	0.018(1)	0.000(1)
P	0.061(5)	0.016(3)	0.042(4)	−0.003(3)	0.026(4)	−0.002(3)
S1	0.069(5)	0.022(3)	0.050(4)	0.002(3)	0.032(4)	0.001(3)
S2	0.055(5)	0.042(4)	0.040(4)	0.001(3)	0.024(4)	−0.002(3)
S3	0.069(5)	0.023(3)	0.046(4)	−0.003(3)	0.024(4)	−0.001(3)
S4	0.065(5)	0.020(3)	0.056(4)	−0.002(3)	0.028(4)	−0.004(3)

5a. [Ru(PPh$_3$)(PMe$_3$)(Me-dttd)]I

A solution of 300 mg (0.4 mmol) of [Ru(PPh$_3$)-(PMe$_3$)dttd] and 0.5 ml (~8 mmol) of CH_3I in 30 ml of CH_2Cl_2 is stirred for 1 h at 30 °C and evaporated to dryness. The residue is dissolved in 20 ml of CH_2Cl_2 and the solution is filtered. After slow addition of 50 ml of petrolether, 310 mg (87%) of yellow crystals are obtained after 1 day at 20 °C. *Anal.* Calc. for $C_{36}H_{39}IPRuS_4$ (889.9): C, 48.59; H, 4.42. Found: C, 49.60; H, 4.06%.

5b. [Ru(PMe$_3$)$_2$(Me-dttd)]I

Exactly the same procedure with 300 mg (0.55 mmol) of [Ru(PMe$_3$)$_2$dttd] and 0.5 ml (~8 mmol) of CH_3I yields 320 mg of [Ru(PMe$_3$)$_2$Me-dttd]I (85%) as fine yellow crystals. *Anal.* Calc. for $C_{21}H_{33}IP_2RuS_4$ (703.7): C, 35.85; H, 4.73. Found: C, 36.10; H, 5.11%.

6. [Ru(PPh$_3$)I(Me$_2$-dttd)](N$_3$); exchange of the mono anions via the sulfates

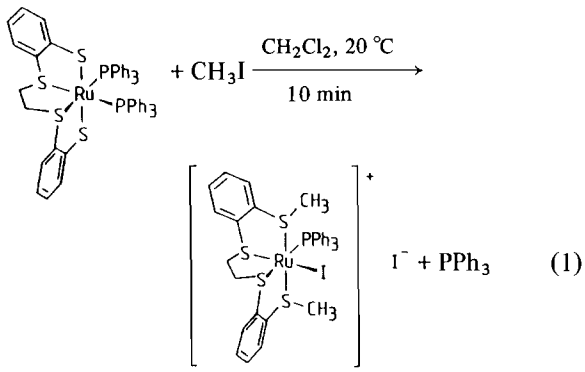
To 450 mg (0.4 mmol) of [Ru(PPh$_3$)I(Me$_2$-dttd)]-I·CH_2Cl_2 in 20 ml of MeOH are added a few drops of H_2O and *ca.* 500 mg of Ag_2SO_4. After warming to 40 °C, an orange solution forms above the white solid silver salts at the bottom of the Schlenk tube. The solution is filtered, and to the filtrate is rapidly added a solution of 1 g NaN_3 (or the desired alkali-X-salts) in 50 ml of MeOH/H_2O (1:1). The mixture turns turbid by precipitation of the complex salt. After addition of another 30 ml of H_2O the complex salt is extracted with 4 X 15 ml of CH_2Cl_2, the combined extracts are washed with H_2O, dried over Na_2SO_4 and filtered. The filtrate is reduced to 10 ml. After addition of 50 ml of petrolether 220 mg of [Ru(PPh$_3$)I-(Me$_2$-dttd)]N_3·CH_2Cl_2 (54%) crystallize within 24 h at room temperature. *Anal.* Calc. for $C_{35}Cl_2H_{36}IN_3PRuS_4$ (955.8): C, 43.98; H, 3.80; N, 4.40. Found: C, 44.58; H, 3.80; N, 4.40%.

7. [Ru(Br)$_2$(Me$_2$-dttd)]

200 mg (0.23 mmol) of [Ru(PPh$_3$)Br(Me$_2$-dttd)]-Br are dissolved in 5 ml of concentrated H_2SO_4, and under slight evolution of Br_2 a green solution forms. This solution is added dropwise to 50 ml of H_2O/MeOH (1:1) forming a yellow solution, to which 1 g of NH_4Br in 50 ml of H_2O are added rapidly. On standing for 24 h fine light yellow crystals precipitate, which are separated and washed with MeOH and CH_2Cl_2. Yield: 100 mg (73%). *Anal.* Calc. for $C_{16}H_{18}Br_2RuS_4$ (599.5): C, 32.06; H, 3.03. Found: C, 32.80; H, 3.23%.

Results and Discussion

Treating the yellow suspension of [Ru(PPh$_3$)$_2$dttd] in CH_2Cl_2 with CH_3I (eqn. (1))



(1)

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yields rapidly an orange red solution, from which **1** precipitates on addition of petrolether. The alkylation of both thiolato-S atoms is accompanied by the substitution of one PPh_3 ligand by iodide. The same reaction occurs if only one equivalent of CH_3I is applied; in this case, however, 50% of the educt are regained unreacted.

Complex **1** could not be unambiguously characterized by spectroscopic methods. As expected, the KBr-IR spectra of **1** and [Ru(PPh$_3$)$_2$dttd] show only minor differences; the intensity of the band at 1570 cm^{-1}, which is characteristic for the dttd ligand, decreased clearly and indicated a reaction of the sulfur ligand. In the FD mass spectrum no molecular ion could be observed at *m/e* = 956; peaks at *m/e* = 829, 814 and 799 are compatible with the fragment ions $[M-I]^+$, $[M-I-CH_3]^+$ and $[M-I-2CH_3]^+$, respectively. The ^1H NMR spectrum showed two singlets at 2.3 and 3.15 ppm, besides the typical resonances of the PPh_3 as well as the dttd ligand. Because the CH_3 signals and the AA'BB' pattern of the C_2H_4 bridge in the dttd entity overlapped, the reaction according to eqn. (1) was carried out with CD_3I. The ^1H NMR spectrum of the CD_3 product showed clearly that two methyl groups had been introduced into the starting complex; however, it was not possible to decide whether only the thiolato-S atoms had been alkylated or whether the alkylation of one thiolato-S atom had eventually been accompanied by the formation of a Ru–CH_3 entity. This latter possibility had to be considered especially because of the large chemical shift difference of the two CH_3 signals. To decide this question an X-ray structure determination was carried out.

The crystal lattice of [Ru(PPh$_3$)I(Me$_2$-dttd)]I·$3CH_2Cl_2$ consists of discrete $[Ru(PPh_3)I(Me_2\text{-dttd})]^+$-cations, I-anions and disordered CH_2Cl_2 solvate molecules. Figure 1 shows the molecular structure of the $[Ru(PPh_3)I(Me_2\text{-dttd})]^+$-cation; in Table III relevant bond distances and angles are listed. The Ru center is coordinated pseudo-octahedrally by iodine, phosphorus and four sulfur atoms. Figure 1 shows clearly that in reaction (1) both thiolato-S atoms of

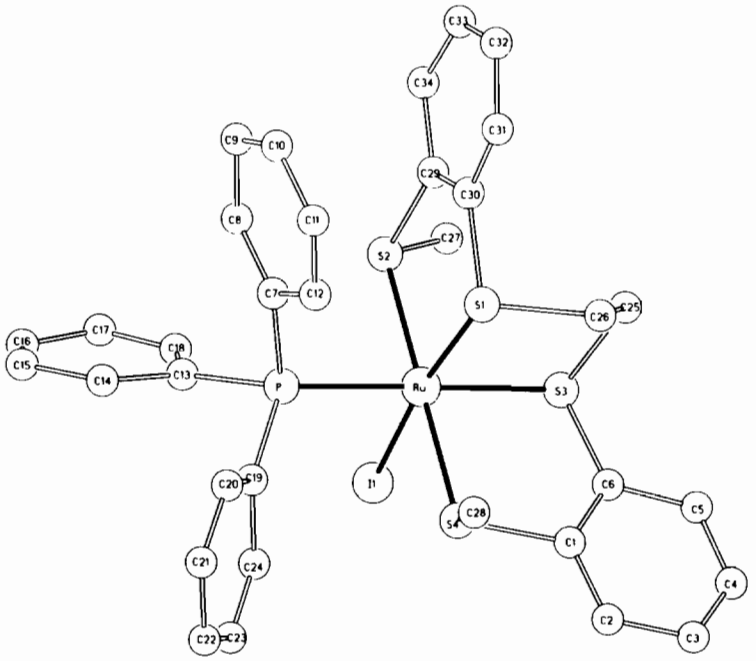


Fig. 1. Molecular structure of the [Ru(PPh$_3$)I(Me$_2$-dttd)]$^+$-cation.

TABLE III. Selected Bond Distances (Å) and Angles (deg) for [Ru(PPh$_3$)I(Me$_2$-dttd)]$^+$

Ru–S1	2.274(0.007)	S1–Ru–S2	86.8(0.3)
Ru–S2	2.319(0.011)	S1–Ru–S3	86.7(0.2)
Ru–S3	2.335(0.007)	S1–Ru–S4	94.4(0.3)
Ru–S4	2.332(0.012)	S3–Ru–S4	86.7(0.3)
Ru–P	2.344(0.007)	I–Ru–S1	171.4(0.2)
Ru–I	2.714(0.004)	I–Ru–S2	93.2(0.2)
S1–C30	1.791(0.037)	I–Ru–S3	84.7(0.2)
S2–C29	1.780(0.021)	I–Ru–S4	85.6(0.2)
S3–C6	1.713(0.035)	I–Ru–P	94.7(0.2)
S4–C1	1.837(0.023)	P–Ru–S3	179.1(0.3)
S1–C26	1.815(0.022)		
S2–C27	1.779(0.044)		
S3–C25	1.836(0.021)		
S4–C28	1.807(0.041)		
C26–C25	1.482(0.052)		

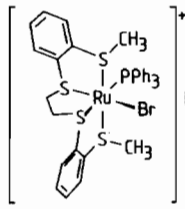
[Ru(PPh$_3$)$_2$dttd] have been alkylated and an Ru–CH$_3$ entity does not form. One of the S-methyl groups is pointing toward the other one and away from the PPh$_3$ ligand, causing the magnetic nonequivalence of the CH$_3$ groups in the ^{1}H NMR spectrum. Their non-coalescence up to 140 °C indicates no inversion at sulfur as is often observed in thioether ligands [7].

Bond distances and angles (Table III) show values in the usual range as observed in other Ru(II) complexes with tetradentate sulfur ligands. The mean Ru–S distance in [Ru(PPh$_3$)I(Me$_2$-dttd)]$^+$ (2.345 Å) is only marginally shorter than in [μ-N$_2$H$_2$\{Ru(PPh$_3$)-dttd\}$_2$] (2.343 Å), in which the sulfur ligand has thioether as well as (larger) thiolate-S donor atoms. Deviations of the angles from 90° and 180°, respectively, are certainly due to the steric requirements imposed by the tetradenticity of the Me$_2$-dttd ligand.

Further Reactions

Alkylation of the dttd ligand in [Ru(PPh$_3$)$_2$dttd] occurs also with CH$_3$Br as well as C$_2$H$_5$I, but the

$$[Ru(PPh_3)_2dttd] + 2CH_3Br \xrightarrow[2\ h]{CH_2Cl_2,\ 30\ °C}$$



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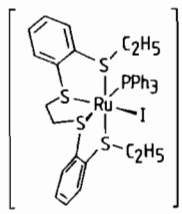
$$[Ru(PPh_3)_2dttd] + 2C_2H_5I \xrightarrow[5\ h]{CH_2Cl_2,\ 40\ °C}$$



(3)

3

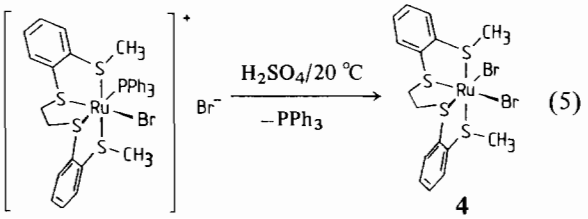
reaction rates decrease. No reaction was observed with CH_3Cl or C_2H_5Br. **2** crystallizes into light yellow needles and is less soluble than **1**. **3** is isolated in very soluble orange microcrystals. Spectroscopic data are listed in Table IV. **1**, **2** as well as **3** proved to be very stable compounds whose cations are largely substitution inert. The complexes decompose slowly only above 150 °C, and substitution reactions with CO, N_2, N_2H_4 or H_2O could not be observed even under drastic conditions. The halide anions, however, are easily exchanged for other singly charged anions via the reaction with Ag_2SO_4 according to eqn. (4).

$$2[Ru(PPh_3)X(R_2\text{-dttd})]X + Ag_2SO_4 \xrightarrow[-AgX]{MeOH/H_2O/20\,^\circ C} [Ru(PPh_3)X(R_2dttd)]_2SO_4$$

$$[Ru(PPh_3)X(R_2dttd)]_2SO_4 + 2MY \xrightarrow[-M_2SO_4]{MeOH/H_2O/20\,^\circ C} 2[Ru(PPh_3)X(R_2\text{-dttd})]Y \quad (4)$$

(R = CH_3, C_2H_5, X = Br, I, M = Na, K, Y = halides, N_3^-, PF_6^-, MnO_4^-)

This reaction sequence is possible because of the remarkably different solubility of the salts with SO_4^{2-} anions and singly charged anions X^-, respectively. The sulfates are very soluble in $MeOH/H_2O$ mixtures and practically insoluble in CH_2Cl_2, in contrast, the X^- salts are easily soluble in CH_2Cl_2 and only poorly soluble in MeOH or H_2O. Hence, it is possible to synthesize almost any X^- salt by adding alkali salts to the $MeOH/H_2O$ solution of $[Ru(PPh_3)X(R_2\text{-dttd})]_2SO_4$. Substitution of the metal bound halides in $[Ru(PPh_3)X(R_2\text{-dttd})]^+$ could not be achieved. Only in the mass spectra of $[Ru(PPh_3)I(Me_2\text{-dttd})]Y$ (Y = Cl, Br, N_3) were fragment ions observed which indicated an exchange of ionic and ligating halides and pseudohalides (cf. Table IV). The stability of the $[Ru(Me_2\text{-dttd})]$ fragment is also seen during the dissolution of $[Ru(PPh_3)Br(Me_2\text{-dttd})]Br$ in concentrated H_2SO_4. In this case, however, the PPh_3 ligand can be substituted as shown by eqn. (5).

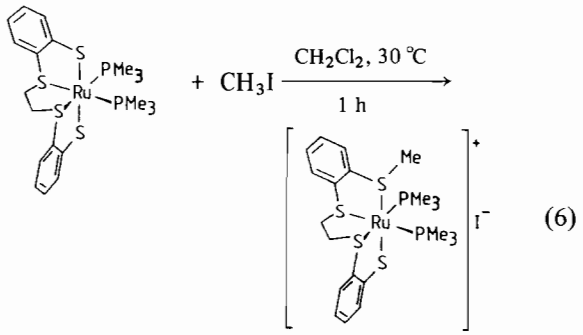


(5)

4

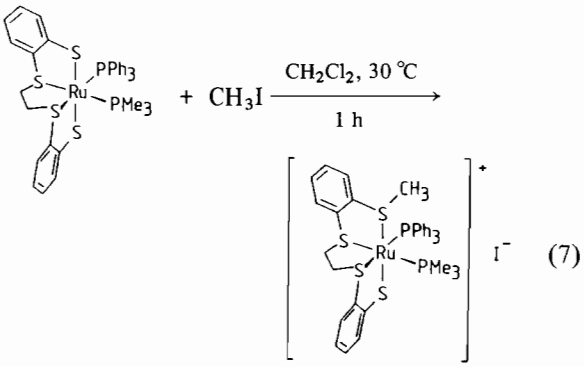
Careful dilution of the H_2SO_4 solution by adding $MeOH/H_2O$ and NH_4Br simultaneously yields a light yellow, microcrystalline precipitate of **4**, which is insoluble in common solvents and could only be characterized by elemental analysis, IR- and mass-spectra.

In contrast to the behaviour of $[Ru(PPh_3)_2dttd]$, the phosphine ligands in $[Ru(PMe_3)_2dttd]$ and $[Ru(PPh_3)(PMe_3)dttd]$ are practically substitution inert; reaction of these complexes with CH_3I yields the monoalkylated products **5** and **6**, respectively.



(6)

5



(7)

6

When petrolether is slowly added to the reaction solutions, compounds **5** and **6** precipitate as yellow crystals Analogously to the reaction (4), the halide anions can be exchanged according to eqn. (8):

$$[Ru(PMe_3)L(Me\text{-dttd})]I \xrightarrow[MeOH/H_2O,\ 20\,^\circ C]{I + Ag_2SO_4,\ 2 + MY} [Ru(PMe_3)L(Me\text{-dttd})]Y \quad (8)$$

(L = PMe_3, PPh_3; MY = alkali salt with the new anion Y)

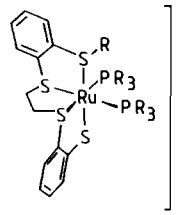
Further alkylation of **5** and **6**, even with a large excess of CH_3I, could not be achieved. Evidently the nature of the phosphine ligands in $[Ru(PR_3)_2dttd]$ determines whether only one or both thiolate-S atoms of the dttd ligand are alkylated. It is reasonable

TABLE IV. Selected Data of the Complexes

	^{1}H NMR (ppm, in CD_2Cl_2)[a]		FD-MS (*m/e*), ^{102}Ru
[Ru(PPh$_3$)I(Me$_2$-dttd)]I (1)	2.2, 3.35 m	C_2H_4 (4)	829 $[M-I]^+$
			814 $[M-I, -CH_3]^+$
	2.3s	CH_3 (3)	799 $[M-I, -2CH_3]^+$
	3.15s	CH_3 (3)	
	7.3m	C_6H_5, C_6H_4 (23)	
[Ru(PPh$_3$)Br(Me$_2$-dttd)]Br (2)	2.2, 3.3 m	C_2H_4 (4)	767 $[M-Br, -CH_3]^+$
			752 $[M-Br, -2CH_3]^+$
	2.3s	CH_3 (3)	
	3.15s	CH_3 (3)	
	7.3m	C_6H_5, C_6H_4 (23)	
[Ru(PPh$_3$)I(Et$_2$-dttd)]I (3)	1.0t	CH_3 (3)	954 $[M-Et]^+$
	1.95t	CH_3 (3)	856 $[M-I]^+$
	2.75q	CH_2-Me (2)	828 $[M-I, -Et]^+$
	3.6q	CH_2-Me (2)	799 $[M-I, -2Et]^+$
	2.2–4.0m	C_2H_4 (4)	
	7.3m	C_6H_5, C_6H_4 (23)	
[Ru(PPh$_3$)I(Me$_2$-dttd)]N$_3$	2.2, 3.35 m	C_2H_4 (4)	829 $[M-N_3]^+$
			814 $[M-N_3, -CH_3]^+$
	2.3s	CH_3 (3)	729 $[M-I, -CH_3]^+$
	3.15s	CH_3 (3)	714 $[M-I, -2CH_3]^+$
	7.3m	C_6H_5, C_6H_4 (23)	
[Ru(PMe$_3$)$_2$(Me-dttd)]I (5)	1.7d	PMe_3 (18)	704 $[M]^+$
	1.5–3.9m	C_2H_4 (4)	577 $[M-I]^+$
	3.05s	CH_3 (3)	562 $[M-I, -CH_3]^+$
	7.7m	C_6H_4 (8)	
[Ru(PPh$_3$)(PMe$_3$)(Me-dttd)]I (6)	1.3d	PMe_3 (9)	875 $[M-CH_3]^+$
	1.2–3.7m	C_2H_4 (4)	763 $[M-I]^+$
	2.55s	CH_3 (3)	748 $[M-I, -CH_3]^+$
	7.4m	C_6H_5, C_6H_4 (23)	
[Ru(Br)$_2$(Me$_2$-dttd)] (4)		[b]	600 M^+
			490 $[M-Br, -2CH_3]^+$

[a] Values in brackets: relative intensities; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [b] No 60 MHz ^{1}H NMR spectrum available.

to assume that the substitution lability and inertness of the phosphine ligands are responsible for the different alkylation behaviour of the complexes. The first step of alkylation leads to a positively charged complex:

$$[Ru(PR_3)_2dttd + RX \longrightarrow \left[\text{  }\right]^+ X^- \quad (9)$$

If this positive charge can be neutralized by substituting one PR_3 ligand by the X^- anion (and provided that X^- is sufficiently nucleophilic), alkylation of the second thiolate-S atom can take place. Thus, in the end, the complex charge resulting from alkylation determines the mono- or bis-alkylation of the dttd-ligand. Table IV lists selected ^{1}H NMR and mass spectroscopic data for the complexes.

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