"chemical precision". Isodesmic results may exhibit slightly larger errors. However, it should be noted that the results also depend on the atomic data for Li, Be, and B. Finally, the selected heats of formation have been used to build a table of standard bond energies useful for studying the stability of the chemical species.

Acknowledgment. We thank the National Fund for Scientific Research (Belgium) for research grants in the field of supercomputing technologies.

The Chemistry of (ring)Ru^{2+} (ring = Tetramethylthiophene, *p*-Cymene)

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Described are the compounds [(ring)Ru(OTf)$_2$]$_x$, where ring = 2,3,4,5-tetramethylthiophene (TMT, **1**), and *p*-cymene (**2**). These electrophilic reagents serve as precursors to [(ring)RuL$_3$]$^{2+}$, where L$_3$ = (H$_2$O)$_3$, (NH$_3$)$_3$, and (PH$_3$)$_3$. Solutions of **1** and **2** react with carbon monoxide to give (ring)Ru(CO)(OTf)$_2$. The addition of thiophenes to CH$_2$Cl$_2$ solutions of **1** or **2** leads to the precipitation of the sandwich compounds [(ring)(SC$_4$R$_4$)Ru](OTf)$_2$, where SC$_4$R$_4$ = thiophene, 2,5-dimethylthiophene, and TMT. [(TMT)Ru(H$_2$O)$_3$](OTf)$_2$ was characterized by single-crystal X-ray crystallography, which established a piano-stool geometry with a planar TMT ligand. [(TMT)Ru(D$_2$O)$_3$](OTf)$_2$ decomposes in D$_2$O solution at 150 °C to give [(TMT)$_2$Ru]$^{2+}$, which undergoes selective deuteration at the 2,5-methyl groups. D$_2$O solutions of [(TMT)$_2$Ru]$^{2+}$ undergo photochemical loss of one TMT ligand in water to give [(TMT)Ru(D$_2$O)$_3$]$^{2+}$. Photolysis of an aqueous solution of [(TMT)(*p*-cymene)Ru]$^{2+}$ gives primarily [(TMT)Ru(H$_2$O)$_3$]$^{2+}$. A procedure is described for the reversible loading of **1** onto γ-alumina, which in turn was characterized by ^{13}C CP-MAS NMR spectroscopy.

Introduction

The chemistry of metal thiophene complexes is a topical area of research that is progressing very rapidly.[1-5] This trend is partly due to interest in a molecular level understanding of metal-catalyzed thiophene desulfurization. More fundamentally, however, little is known about the basic coordination chemistry of thiophenes. One of our recent contributions to this area centered on the synthesis of [(TMT)RuCl$_2$]$_2$, the first thiophene complex with replaceable coligands[6] (TMT is 2,3,4,5-tetramethylthiophene).

In the present contribution we describe the chemistry of [(TMT)Ru(OTf)$_2$]$_x$ (OTf = O$_2$SCF$_3$), a reagent that serves as a source of (TMT)Ru^{2+}. This reagent has permitted us to prepare a range of new thiophene complexes bearing a variety of coligands. The catalysts used commercially for fossil fuel desulfurization consist of transition-metal compounds dispersed on an oxide support, typically alumina. We therefore sought to develop the chemistry of (TMT)Ru^{2+} bound to oxygen ligands. We have investigated the corresponding chemistry of (arene)Ru^{2+} in the form of [(*p*-cymene)Ru(OTf)$_2$]$_x$ (*p*-cymene is 4-isopropyltoluene).

Results

[(TMT)RuCl$_2$]$_2$ can be prepared in 80% yield in one step from TMT and the commercially available [(*p*-cymene)RuCl$_2$]$_2$. TMT can be prepared in a two-step procedure from 2,5-dimethylthiophene, which can also be purchased in bulk. Unsuccessful attempts were made to prepare the Os and Fe analogues of [(TMT)RuCl$_2$]$_2$, in the first instance by an exchange reaction with [(*p*-cymene)OsCl$_2$]$_2$ and in the second case by the reaction of anhydrous FeCl$_2$ with refluxing TMT. The thermal exchange reaction of 2,5-dimethylthiophene and [(*p*-cymene)RuCl$_2$]$_2$ was also unsuccessful.

Synthesis and Properties of [(TMT)Ru(OTf)$_2$]$_x$. This compound was prepared by the straightforward reaction of a dichloromethane solution of [(TMT)RuCl$_2$]$_2$ with silver trifluoromethanesulfonate (AgOTf). The resulting orange solution is filtered and treated with hexane to give an orange solid. Because we were primarily interested in using this compound as a synthetic intermediate, its structure was not of specific interest. Triflate ligands can bind to one or more metals in a variety of ways,[7] and the spectral data suggest that [(TMT)Ru(OTf)$_2$]$_x$ may not have a simple structure. In CD$_2$Cl$_2$ its ^{1}H NMR spectrum consists of three pairs of methyl resonances in the ratio of 1.5:1.5:1.0:0.3:1.0:0.3. In CD$_3$NO$_2$, however, the ^{1}H NMR spectrum consisted of two singlets, indicating either a dynamic process or a single ionic species. On the basis of IR absorptions[7] in the ν_{SO} region both OTf$^-$ anions are thought to be coordinated in the solid state (Figure 1). This assignment rests on the previously noted[7]

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(1) Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1989**, *8*, 2739.

(2) Choi, M.-G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753.

(3) Cardone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.

(4) Latos-Grazynski, L.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 4065.

(5) Shaver, A.; Butler, I. S.; Gao, J. P. *Organometallics* **1989**, *8*, 2079.

(6) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 8828.

(7) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17. Frauenhoff, G. A. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1988.

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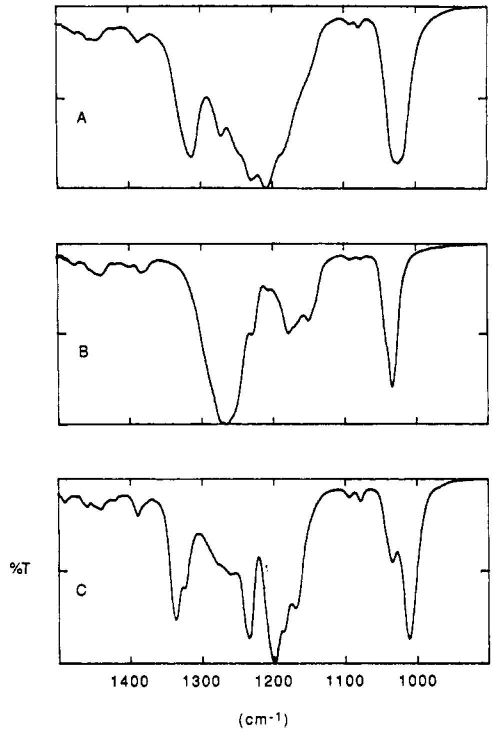

Figure 1. IR spectra in the ν_{SO} and ν_{CF} region for (a) $[(TMT)Ru(OTf)_2]_x$, (B) $[(TMT)Ru(H_2O)_3](OTf)_2$, and (C) $[(TMT)Ru(CO)(OTf)_2]$.

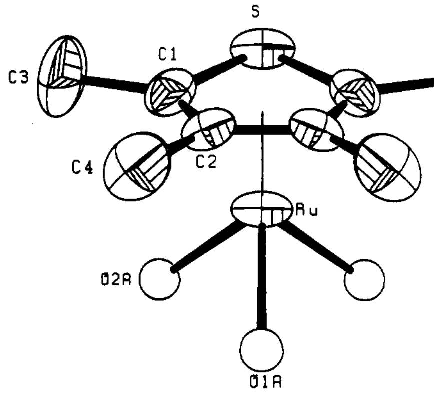

Figure 2. Structure of the cation $[(TMT)Ru(H_2O)_3]^{2+}$, with thermal ellipsoids drawn at the 35% probability level.

observations that coordinated OTf absorbs at >1300 cm^{-1}. ^{19}F NMR spectra of 1 showed three signals in $1,2-C_2D_2Cl_4$ but one signal in CD_3NO_2.[8] The corresponding $[(p\text{-cymene})Ru(OTf)_2]_x$ (2) was also prepared by the AgOTf route, and its properties closely match those of the TMT complex.

$[(ring)Ru(H_2O)_3](OTf)_2$. The triflates described above proved to be extremely reactive electrophiles. For example, THF solutions of 1 polymerized when heated at reflux. Halocarbon solutions of 1 react with atmospheric moisture to give the triaquo complex $[(TMT)Ru(H_2O)_3](OTf)_2$. This yellow, water-soluble compound was conveniently prepared simply by exposing solid samples of 1 to the atmosphere. Under these conditions we observed an increase in the weight calculated for three water molecules, concomitant with a color change from orange to yellow. Analogous behavior was observed for 2. The spectroscopic properties of $[(TMT)Ru(H_2O)_3](OTf)_2$ were in accord with the formulation. The ^{19}F NMR spectra were identical for the TMT and p-cymene derivatives. The IR spectra for the two compounds gave evidence for uncoordinated OTf^- (ν_{SO} = 1268 cm^{-1}) together with strong bands in the ν_{OH} region. The ^1H NMR spectrum of an aqueous solution of $[(TMT)Ru(H_2O)_3](OTf)_2$ showed a pair of singlets that correspond to those observed previously by us when an aqueous solution of 1 was treated with $AgBF_4$.[6]

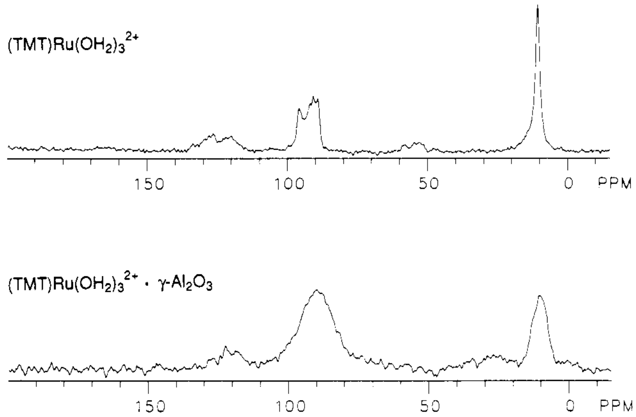

Figure 3. ^{13}C CP MAS NMR spectra of (top) solid $[(TMT)Ru(H_2O)_3](OTf)_2$ and (bottom) the same compound 5% loaded onto γ-alumina.

Table I. Selected Distances (Å) and Angles (deg) for the Cation $[(TMT)Ru(H_2O)_3]^{2+}$

Ru-O1A	2.16 (1)[a]	S-C1	1.77 (2)
Ru-O2A	2.17 (2)	C1-C2	1.42 (2)
Ru-S	2.307 (6)	C2-C2′	1.41 (2)
Ru-C1	2.08 (2)	C1-C3	1.55 (2)
Ru-C2	2.12 (2)	C2-C4	1.52 (2)
O1A-Ru-O2A	84 (1)	C1-S-C1′	89.5 (8)
O1A-Ru-S	165 (1)		

[a] Ru-O distances were constrained to a common variable.

Table II. Reactions of Ru(TMT)$^{2+}$ Compounds in D_2O

starting compd(s)	reacn conditions[a]	products[b]
$[(TMT)Ru(H_2O)_3]^{2+}$	hν, 4 h	NR
$[(TMT)Ru(H_2O)_3]^{2+}$	150 °C, 20 h	$[Ru(TMT\text{-}2,5\text{-}d_x)_2]^{2+}$
$[(TMT)Ru(H_2O)_3]^{2+}$, TMT-3,4-d_2	100 °C, 4 h	$[Ru(TMT)(TMT\text{-}3,4\text{-}d_2)]^{2+}$
$[(TMT)_2Ru]^{2+}$	150 °C, 20 h	$[Ru(TMT\text{-}2,5\text{-}d_x)_2]^{2+}$
$[(TMT)_2Ru]^{2+}$	hν, 8 h	$[Ru(TMT)(H_2O)_3]^{2+}$
$[(TMT)(p\text{-cymene})Ru]^{2+}$	hν, 8 h	$[Ru(TMT)(H_2O)_3]^{2+}$
TMT	150 °C, 20 h	NR

[a] Photolyses were conducted at ambient temperatures (~25 °C). [b] TMT-2,5-d_x implies partial deuteration at the 2,5-methyl group. TMT-3,4-d_2 is $SC_4\text{-}2,5\text{-}(CH_3)_2\text{-}3,4\text{-}(CDH_2)_2$. NR denotes no reaction.

Structure of $[(TMT)Ru(H_2O)_3](OTf)_2$. Crystals of $[(TMT)Ru(H_2O)_3](OTf)_2$ were grown by evaporation of a CH_2Cl_2/hexane solution of 1 in air. The crystallographic study confirms that the compound adopts a piano-stool geometry (Figure 2). The TMT ligand is planar, but a disorder in the aquo ligands and triflate precludes detailed discussion of the C–C bond distances (Table I). The cation is bisected by a crystallographically imposed mirror plane through S, Ru, and one oxygen atom of the water ligands. The Ru–O distances of 2.16 (1) and 2.17 (1) Å are slightly longer than those in $[Ru(H_2O)_6](OSO_2C_6H_4Me)_2$ (average 2.122 (16) Å)[9] but comparable to those in the

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[8] Buzinkai, J. F.; Schrock, R. R. *Inorg. Chem.* **1989**, *28*, 2837.

[9] $[Ru(H_2O)_6](OTs)_2$: Bernhard, P.; Bürgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.

related half-sandwich complex $[(C_6H_6)Ru(H_2O)_3]SO_4$ (2.151 (2) Å).[10] Compared to those in $[(TMT)_2Ru](BF_4)_2{\cdot}2CH_3NO_2$, the Ru–S and Ru–C distances of 2.307 (6) and 2.08 (2)–2.12 (2) Å are shorter by ca. 0.05 and 0.1 Å, respectively.[6] The shortening of the Ru–TMT bonds may reflect the fact that $Ru(H_2O)_3{}^{2+}$ moiety is a better π base than is $(TMT)Ru^{2+}$. As we described previously, the TMT ligand can be viewed as a tridentate diolefin–thioether ligand that tends to bind to three sites of the octahedron about the Ru center. This is borne out in the present structure, as the sulfur atom is nearly trans to O1; the O1A–Ru–S angle is 165 (1)°.

Reactions of $[(ring)Ru(OTf)_2]_x$ with Small Molecules. Both **1** and **2** react with CO to give monocarbonyl adducts. On the basis of the high-frequency ν_{SO} bands in their IR spectra, these adducts are formulated as $(ring)Ru(CO)(OTf)_2$. The *p*-cymene compound was particularly well-behaved and was obtained in analytical purity. The ν_{CO} bands for the new compounds were $>2050\ cm^{-1}$, demonstrating the weak π-basicity of the 16e $(ring)Ru(\eta^1\text{-}OTf)_2$ fragments.

In dichloromethane solution, both **1** and **2** form soluble labile adducts with H_2S. In aqueous solution, $[(TMT)Ru(H_2O)_3]^{2+}$ reacts readily with H_2S to release the TMT ligand and form a black solid. In contrast, aqueous solutions of $[(p\text{-cymene})Ru(H_2O)_3]^{2+}$ react with H_2S to give $[(p\text{-cymene})Ru]_3S_2{}^{2+}$, which we described recently.[11]

With ammonia both **1** and **2** gave yellow solids that were analyzed as $[(ring)Ru(NH_3)_3](OTf)_2$. Taube had previously described $[(C_6H_6)Os(NH_3)_3]^{2+}$.[12] The triammines are stable in water as well as nitromethane. With PH_3, a CH_2Cl_2 solution of **2** reacted to give colorless $[(p\text{-cymene})Ru(PH_3)_3](OTf)_2$, which was isolated as an analytically pure solid. The analogous reaction of **1** with PH_3 was more sluggish and, on the basis of ^1H NMR spectroscopy, gave a mixture of compounds, each of which retained coordinated TMT.

Alumina-Supported $[(TMT)Ru(H_2O)_3](OTf)_2$. We were interested in utilizing our newly synthesized TMT compounds to prepare an alumina-supported metal–thiophene complex. An aqueous solution of $[(TMT)Ru(H_2O)_3](OTf)_2$ was combined with an aqueous suspension of γ-alumina followed by rotary evaporation. The resulting free-flowing yellow solid was characterized by CP-MAS ^{13}C NMR spectroscopy.[13] We observed two signals in the range (10, 90 ppm) found for the methyl and ring carbon resonances for the unsupported triaquo complex. These data strongly suggest that $[(TMT)Ru(H_2O)_3]^{2+}$ survives treatment with alumina. Further evidence that this complex remains intact on the alumina is our finding that washing the ruthenated alumina with water liberated $[(TMT)Ru(H_2O)_3](OTf)_2$, which was identified by its ^1H NMR spectrum.

Aqueous Chemistry of $(TMT)Ru^{2+}$. A series of experiments were conducted to establish the stability of cationic Ru–TMT complexes toward hydrolysis (Table III). At 150 °C aqueous solutions of $[(TMT)Ru(H_2O)_3](OTf)_2$ decompose in a few hours to give $[(TMT)_2Ru]^{2+}$, as verified by NMR spectroscopy. An independent experiment showed that an aqueous solution of $[(TMT)Ru(H_2O)_3](OTf)_2$ reacts with TMT at 100 °C to give $[(TMT)_2Ru]^{2+}$. Thus, it appears that at 150 °C the triaquo complex decomposes, liberating free TMT, which is then scavenged by the remaining $[(TMT)Ru(H_2O)_3]^{2+}$. Several unsuccessful attempts were made to prepare $(TMT)Ru^{2+}$ derivatives by the reaction of TMT and $[Ru(H_2O)_6](OTs)_2$.

Table III. Microanalytical Data for New Compounds

	found		theory	
	% C	% H	% C	% H
$[(TMT)Ru(OTf)_2]_x$	22.76	2.54	22.27	2.24
$(TMT)Ru(OTf)_2(CO)$	22.32	2.12	23.28	2.13
$[(TMT)Ru(NH_3)_3](CF_3SO_3)_2$[a]	21.16	3.60	20.34	3.58
$[(TMT)Ru(H_2O)_3](CF_3SO_3)_2$	19.99	3.00	20.24	3.06
$[(p\text{-cymene})Ru(OTf)_2]_x$	26.78	2.50	27.02	2.65
$[(p\text{-cymene})Ru(H_2O)_3](CF_3SO_3)_2$	24.39	3.35	24.53	3.43
$[(p\text{-cymene})Ru(NH_3)_3](CF_3SO_3)_2$[b]	24.64	3.93	24.66	3.97
$[(p\text{-cymene})Ru(PH_3)_3](CF_3SO_3)_2$	22.84	3.75	22.68	3.65
$(p\text{-cymene})Ru(OTf)_2(CO)$	27.83	2.59	27.81	2.51
$[(TMT)(3,4\text{-}TMT\text{-}d_2)Ru](OTf)_2$	31.54	3.68	31.81	3.55
$[(TMT)(2,5\text{-}SC_4Me_2H_2)Ru](OTf)_2$	29.12	3.09	29.49	3.09
$[(TMT)(SC_4H_4)Ru](OTf)_2$	27.29	2.80	26.97	2.59
$[(TMT)(p\text{-cymene})Ru](OTf)_2$	35.75	4.05	35.66	3.89

[a] % N found (calcd): 7.04 (7.12). [b] % N found (calcd): 7.17 (7.19).

The sandwich complex $[(TMT)_2Ru]^{2+}$ is unreactive toward water at 150 °C, although we observed selective deuteration of the 2,5-methyl groups. The regiochemistry of this deuteration was established by comparisons with complexes prepared from TMT-3,4-d_2, which in turn was prepared by the $LiAlD_4$ reduction of the appropriate bis(chloromethyl)thiophene. In a control experiment we showed that no H/D exchange occurred when TMT and D_2O were heated at 150 °C for 33 h. Sauer and Angelici have shown that $[CpRu(SC_4H_{4-x}Me_x)]^+$ undergo base-catalyzed H/D exchange at both ring and 2,5-methyl carbon centers, although exchange at the methyl groups was $>10^4$ slower than for ring C–H exchange.[14]

Using TMT that was selectively deuterated at the 3,4-positions, we assigned the ^1H NMR spectra of TMT, $[(TMT)RuCl_2]_2$, $[(TMT)Ru(H_2O)_3]^{2+}$, $[(TMT)_2Ru]^{2+}$, and $[(TMT)Ru(OTf)_2]_x$. The relative chemical shifts of the 2,5- and 3,4-methyl resonances switch upon complexation, except for $[(TMT)_2Ru]^{2+}$, where the 3,4-methyl resonance is upfield of the 2,5-signal.

Synthesis of Unsymmetrical Thiophene Sandwich Compounds. The attachment of the $(arene)Ru^{2+}$ moiety to other arenes is usually accomplished with $[(arene)Ru(Me_2CO)_3]^{2+}$ or the related diacetone alcohol complexes. Such compounds are generated in situ from the chlorides.[17,18] The triflates described in this work are particularly versatile reagents for such arenation reactions because they are soluble in dichloromethane, which is even less coordinating than acetone. Typically, the addition of a slight excess of the heterocycle to a CH_2Cl_2 solution of **1** at room temperature precipitated the desired sandwich complex. This procedure was successfully applied to $[(TMT)(ring)Ru](OTf)_2$, where ring = TMT, TMT-3,4-d_2,

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[10] $[Ru(benzene)(H_2O)_3]SO_4$: Stebler-Röthlisberger, M.; Ludi, A. *Polyhedron* **1986**, *5*, 1217. Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358.

[11] Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5733.

[12] Hung, Y.; Kung, W.-J.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457.

[13] Fife, C. A.; Wasylishen, R. E. In *Solid State Chemistry: Techniques*; Cheetham, A. K., Day, P., Eds.; Clarendon: Oxford, England, 1987; p 190.

[14] Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146.

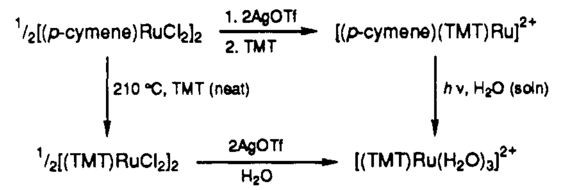
[15] Our experiments were based on the photodissociation of benzene in $[CpRu(C_6H_6)]^+$: Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

[16] Ru(arene) hydroxides: Gould, R. A.; Jones, L. L.; Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1977**, 222. Gould, R. O.; Jones, C. L.; Robertson, D. R.; Tocher, D. A.; Stephenson, T. A. *J. Organomet. Chem.* **1982**, *226*, 199. Robertson, D. R.; Stephenson, T. A. *J. Organomet. Chem.* **1976**, *116*, C29.

[17] Bennett, M. A.; Mattheson, T. W.; Robertson, G. B.; Steffen, W. L.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 32. Bennett, M. A.; Mattheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87.

[18] Moriarity, R. M.; Gill, V. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157.

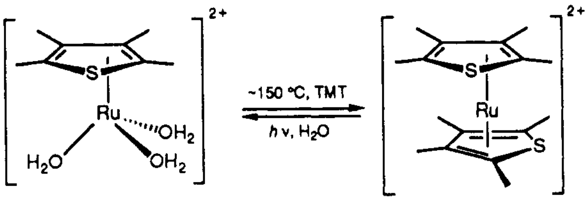
Scheme I



2,5-dimethylthiophene, and thiophene itself. The complexation of thiophene is noteworthy, since this is one of the least basic thiophenes. We had previously prepared $[(TMT)_2Ru](OTf)_2$ via the acetone method, but the CH_2Cl_2 route is superior. The procedure works well because 1 is soluble in dichloromethane but the sandwich compounds, which are strong electrolytes, are not.

The compounds $[(TMT)(TMT\text{-}3,4\text{-}d_2)Ru](OTf)_2$, $[(TMT)(2,5\text{-dimethylthiophene})Ru](OTf)_2$, and $[(TMT)(SC_4H_4)Ru](OTf)_2$ are the first examples of unsymmetrical bis(thiophene) complexes. Aqueous solutions of $[(TMT)(thiophene)Ru]^{2+}$ undergo hydrolysis in seconds at room temperature, giving $[(TMT)Ru(H_2O)_3]^{2+}$. This behavior contrasts with that for $[(TMT)_2Ru](OTf)_2$, which is stable in water up to 150 °C. Previous work has demonstrated the superior coordinating power of TMT vs that of less substituted thiophenes.[19,20]

Photochemistry of $[(TMT)(ring)Ru]^{2+}$. In contrast to its thermal stability, a D_2O solution of $[(TMT)_2Ru]^{2+}$ undergoes rapid loss of one TMT ligand upon ultraviolet photolysis (eq 1).[15] This observation has led to the development of an alternative route to $[(TMT)Ru(H_2O)_3]^{2+}$.



(1)

Dichloromethane solutions of $[(p\text{-cymene})Ru(OTf)_2]_x$ react readily with TMT to give $[(p\text{-cymene})(TMT)Ru](OTf)_2$, isolated in high yield as pale yellow crystals. Photolysis of a D_2O solution of this salt gives a ~5:1 mixture of $[(TMT)Ru(H_2O)_3]^{2+}$ and $[(p\text{-cymene})Ru(H_2O)_3]^{2+}$ (Scheme I).

Discussion

Compounds of the type $[(ring)Ru(OTf)_2]_x$ are synthetically versatile sources of $(ring)Ru^{2+}$. The triflate ligand is well-suited for this application, as it is hydrolytically more robust than BF_4^-,[22] PF_6^-,[17,22] and O_3SF^-.[7] The thermal stability of charge-neutral triflate complexes[3,22] permits solubility in solvents of low dielectric constant such as CH_2Cl_2.[23] The exceptional Lewis acidity of 1 and 2 is shown by their ability to polymerize THF and, in the case of 1, to complex thiophene. Although the project was primarily concerned with the thiophene complexes, our results suggest that compounds of the type $[(arene)Ru(OTf)_2]_x$ might find applications in the area of arene coordination chemistry.[24] Obvious extensions of this work involve $[(C_5Me_5)Ru(OTf)]_x$ and $[(C_5Me_5)Rh(OTf)_2]_x$.

The only example of a thiophene–aquo complex, $[(TMT)Ru(H_2O)_3](OTf)_2$, has been fully characterized. It exhibits the expected pseudooctahedral piano-stool structure, and it is thermally quite robust. This complex undergoes a variety of ligand substitution reactions and can be reversibly supported on γ-alumina. The supported complex is potentially interesting as a desulfurization catalyst[26] precursor, wherein the metal site is preloaded with substrate. The displacement of TMT from $[(TMT)Ru(H_2O)_3]^{2+}$ by H_2S illustrates the "poisoning" of our model catalyst site (eq 2).

$$[(C_4Me_4S)Ru(H_2O)_3]^{2+} \xrightarrow[-RuS_x]{+H_2S} C_4Me_4S \qquad (2)$$

Experimental Section

The general experimental protocols have been described.[6] NMR spectra were recorded on the following instruments: Varian XL-200-SY (^{19}F), GE QE-300 (^1H), and GE GN-300 (CP-MAS). ^{19}F NMR shifts are referenced to CF_3CO_2H. Gas chromatography was performed by use of a HP 530 instrument with split/splitless injection on a 530-μm silicone oil column. Photolyses employed an unfiltered 200-W Conrad Hannovia medium-pressure immersion lamp. Microanalyses were obtained in the School of Chemical Sciences Microanalytical Laboratory.

The following reagents were synthesized or purchased: 99.99% γ-alumina (AESAR), 2,5-dimethylthiophene (Penta Mfg., East Hannover, NJ), PH_3 (Matheson), $LiAlD_4$ (Aldrich), $[(p\text{-cymene})RuCl_2]_2$,[27] and $[(p\text{-cymene})OsCl_2]_2$.[28] TMT was purified by distillation at atmospheric pressure. Microanalytical data are presented in Table III.

$[(TMT)RuCl_2]_2$. $[(p\text{-cymene})RuCl_2]_2$ (2.003 g, 3.27 mmol) and TMT (10 mL) were loaded into a 50-mL Schlenk tube. After it was purged with nitrogen, the tube was immersed in a silicone oil bath at 210 °C for 6 h. Initially the reaction mixture was red-brown, which changes to a bright red once the reaction is complete. During the reaction we periodically (30 min) flushed the flask with nitrogen to remove any volatiles. The cooled reaction mixture was filtered, and the solids were washed with 15 mL of pentane. This filtrate was set aside for recovery of TMT. The solid was extracted into ca. 800 mL of CH_2Cl_2; this extract was concentrated to 40 mL, and hexane (10 mL) was added to complete the precipitation; yield 80% (1.626 g). ^1H NMR ($CDCl_3$): δ 1.96 (s, 2,5-Me_2, 6 H), 2.05 (s, 3,4-Me_2, 6 H).

$[(TMT)Ru(OTf)_2]_x$. A Schlenk flask was loaded with $[(TMT)RuCl_2]_2$ (1.00 g, 1.60 mmol), AgOTf (1.66 g, 6.47 mmol), and CH_2Cl_2 (25 mL). The reaction mixture was stirred vigorously for 3 h. The slurry was filtered, concentrated, and diluted with hexane to complete the precipitation of the product; yield 80% (1.40 g, 2.60 mmol). ^1H NMR (CD_3NO_2): δ 2.08 (s, 2,5-Me_2, 6 H), 2.18 (s, 3,4-Me_2, 6 H). ^{19}F NMR (CD_3NO_2): δ -1.904. IR (KBr): ν_{SO} = 1315 cm^{1-}, ν_{CF} = 1232 cm^{-1}. $[(p\text{-cymene})Ru(OTf)_2]_x$ was prepared analogously.

TMT-*β,β'*-d_2. Solid $LiAlD_4$ (2 g, 0.05 mmol) was loaded into a 100-mL Schlenk flask equipped with an additional funnel and magnetic stirbar. THF (20 mL) was added. 3,4-Bis(chloromethyl)-2,5-dimethylthiophene (9.0 g, 0.043 mmol) dissolved in 20 mL of THF was transferred to the addition funnel. The reaction flask was cooled to 0 °C, and the thiophene solution was added dropwise to the suspension. After the addition was complete, the mixture was stirred a further 0.5 h and then heated to

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reflux for 12 h. The cooled reaction mixture was hydrolyzed and filtered through Celite, the residue being washed liberally with Et_2O. The yellow filtrate was concentrated and purified by low-temperature fractionation on a high-vacuum line; yield 64% (3.89 g). Anal. Calcd (found) for $C_8H_{10}D_2S$: C, 67.54 (67.24); H + D, 8.62 (8.61). ^1H NMR ($CDCl_3$): δ 2.01 (1:1:1 t, 3,4-Me_2, 4 H), 2.32 (s, 2,5-Me_2, 6 H).

(TMT)Ru(CO)(OTf)$_2$. A solution of $[(TMT)Ru(OTf)_2]_x$ (150 mg, 0.278 mmol) in 15 mL of CH_2Cl_2 was purged with a stream of CO. The reaction solution was stirred for 2 h. The yellow precipitate was filtered, washed with Et_2O, and dried in vacuo; yield 76% (120 mg). ^1H NMR (CD_3NO_2): δ 2.14 (s, 6 H), 2.34 (s, 6 H). IR: $\nu_{CO} = 2054$ cm^{-1}. A similar procedure was used to prepare (*p*-cymene)Ru(CO)(OTf)$_2$ (50% yield). ^1H NMR (CD_3NO_2): δ 2.14 (s, 6 H), 2.34 (s, 6 H). IR (KBr): $\nu_{CO} = 2054$ cm^{-1}, $\nu_{SO} = 1333$, 1318 cm^{-1}.

[(*p*-cymene)Ru(PH$_3$)$_3$](OTf)$_2$. A stirred solution of [(*p*-cymene)Ru(OTf)$_2$]$_x$ (200 mg, 0.375 mmol) in CH_2Cl_2 (20 mL) was purged with gaseous PH_3. The reaction solution changed color from red-orange to pale yellow. After 20 min the slurry was filtered, giving a pale yellow precipitate and a virtually colorless filtrate. After it was washed with CH_2Cl_2, the product was obtained in a yield of 74% (0.175 g). ^1H NMR (CD_3NO_2): δ 1.31 (d, 6 H), 2.46 (s, 3 H), 2.97 (m, 1 H), 4.57 (d, 3 H), 6.47 (d, 2 H), 6.63 (d, 2 H). IR (KBr): $\nu_{SO} = 1262$ cm^{-1}, $\nu_{PH} = 2394$ cm^{-1}.

[(ring)Ru(H$_2$O)$_3$](OTf)$_2$. A sample of $[(ring)Ru(OTf)_2]_x$ was exposed to the atmosphere (ca. 0.5 h) until it had gained the calculated amount of weight. During this transformation the color changed from orange to yellow. Data for $[(TMT)Ru(H_2O)_3](OTf)_2$ are as follows. ^1H NMR (D_2O): δ 1.86 (s, 2,5-Me_2, 6 H), 1.93 (s, 3,4-Me_2, 6 H). ^{19}F NMR (D_2O): δ −2.606. IR (KBr): $\nu_{SO} = 1268$ cm^{-1}. UV-vis (H_2O); λ (ϵ)): 442 sh (310), 372 (792), 302 nm (536). Data for [(*p*-cymene)Ru(H$_2$O)$_3$](OTf)$_2$ are as follows. ^1H NMR (D_2O): δ 1.20 (d, 6 H), 2.11 (s, 3 H), 2.75 (m, 1 H), 5.60 (d, 2 H), 5.84 (d, 2 H). ^{19}F NMR (D_2O): δ −2.606. UV-vis (H_2O); λ (ϵ)): 402 (568), 310 (888), 284 nm (991).

[(TMT)Ru(NH$_3$)$_3$](OTf)$_2$. A solution of $[(TMT)Ru(OTf)_2]_x$ (165 mg, 0.306 mmol) in CH_2Cl_2 was treated with a slight excess of gaseous NH_3. After several minutes the solution turned pale yellow and a yellow precipitate formed. The precipitate was purified by dissolution in nitromethane, filtration, and dilution of the filtrate with Et_2O. The yield was 83% (0.15 g). ^1H NMR (CD_3NO_2): 2.08 (s, 6 H), 2.12 (s, 6 H), 3.09 (s, br, 9 H). IR (KBr): ν_{NH} 3277 cm^{-1} (br), $\nu_{SO} = 1264$ cm^{-1}.

[(*p*-cymene)Ru(NH$_3$)$_3$](OTf)$_2$. A solution of [(*p*-cymene)Ru(OTf)$_2$]$_x$ (80 mg, 0.15 mmol) in 10 mL of CH_2Cl_2 was purged with NH_3 for 20 min. The solution turned yellow immediately, and a precipitate formed. The solution was filtered and the residue washed with Et_2O and dried in vacuo. The product was obtained in 58% yield (88 mg). ^1H NMR (CD_3NO_2): δ 1.31 (d, 6 H), 2.28 (s, 3 H), 2.90 (m, 1 H), 3.15 (s, 9 H), 5.63 (d, 2 H), 5.88 (d, 2 H). IR (KBr): $\nu_{SO} = 1262$ cm^{-1}, $\nu_{PH} = 2394$ cm^{-1}.

Reaction of [(TMT)Ru(H$_2$O)$_3$]$^{2+}$ with H$_2$S. A stirred solution (yellow) of 1 (15 mg) in 2 mL of H_2O was treated with gaseous H_2S. After several minutes the solution had decolorized concomitant with the formation of a black precipitate. The solution was extracted with CH_2Cl_2, and this extract was assayed for TMT by gas chromatography.

Reactions of (TMT)Ru^{2+} Compounds in D$_2$O. Approximately 8 mg of the starting compound was dissolved in ca. 0.3 mL of D_2O. The solution was syringed into a 4-mm tube (quartz or Pyrex) equipped with a vacuum adaptor. The tube was flame-sealed under vacuum. After they were warmed to ambient temperature, the tubes were treated under the reaction conditions listed in Table III; the progress of the reactions was monitored by ^1H NMR spectroscopy.

[(TMT)(DMT)Ru](OTf)$_2$ and Related Compounds. In a typical synthesis 2,5-dimethylthiophene (DMT) (300 μL) was added to a stirred solution of $[(TMT)Ru(OTf)_2]_x$ (0.115 g, 0.213 mmol) in CH_2Cl_2 (10 mL). After several minutes (at room temperature), a pale yellow precipitate appeared. The slurry was stirred overnight, after which the solid was filtered, washed with Et_2O, and dried in vacuo; yield 70% (0.095 g). ^1H NMR (D_2O): δ 2.22 (s, 6 H), 2.35 (s, 6 H), 2.38 (s, 6 H), 6.53 (s, 2 H). A related procedure was used for the synthesis of the following other sandwich compounds: $[(TMT)(SC_4H_4)Ru](OTf)_2$ (yield 35%); [(TMT)(TMT-3,4-*d*$_2$)Ru](OTf)$_2$ (yield 70%), ^1H NMR (D_2O) δ 2.04 (s, 3,4-Me_2, 10 H), 2.25 (s, 12 H); [(*p*-cymene)(DMT)Ru](OTf)$_2$ (yield 75%), ^1H NMR (D_2O) δ 1.19 (s, 6 H) 2.30 (s, 3 H), 2.33 (s, 6 H), 2.77 (m, 1 H), 6.70 (s, 4 H), 6.81 (s, 2 H).

Table IV. Crystal and Experimental Data for [(TMT)Ru(H$_2$O)$_3$](OTf)$_2$

formula	$(RuSO_3C_8H_{18})(SF_3O_3C)_2$
cryst syst	orthorhombic
space group	*Pnma*
a, Å	13.364 (4)
b, Å	19.575 (3)
c, Å	8.292 (2)
V, Å^3	2169 (2)
Z	4
density (calc), g/cm^3	1.817
color, habit	orange-yellow, columnar
dimens, mm	0.1 × 0.2 × 0.4
diffractometer	Enraf-Nonius CAD4
μ, cm^{-1}	10.71
transmissn factor range	0.896–0.797 (numerical)
2θ limit, deg	2.0–48.0 ($-h,+k,+l$), 2.0–8.0 ($\pm h,k,l$)
no. of intensities (unique, R_i)	2097 (1756, 0.013)
no. of intensities $>2.58\sigma(I)$	859
R	0.071
R_w (for $w = 1/\sigma^2(F_o) + pF_o^2$)	0.087 ($p = 0.02$)
max density in ΔF map, e/Å^3	0.69

[(*p*-cymene)(TMT)Ru](OTf)$_2$. The triflate [(*p*-cymene)Ru(OTf)$_2$]$_x$ was synthesized in situ by the reaction of [(*p*-cymene)RuCl$_2$]$_2$ (0.500 g, 0.816 mmol) and AgOTf (0.849 g, 3.30 mmol) in 20 mL of CH_2Cl_2. After the red solution was filtered, 200 μL of TMT was added and the solution was stirred for 2 h. The solvent was removed, and a yellow oily mateial remained. The yellow oil was triturated with 30 mL of Et_2O, the mixture was filtered, and the residue was dried in vacuo. The resulting pale yellow solid was characterized as [(*p*-cymene)(TMT)Ru](OTf)$_2$, generated in 82% yield (898 mg). ^1H NMR (D_2O): δ 1,21 (d, 6 H), 2.22 (s, 3 H), 2.26 (s, 6 H), 2.29 (s, 6 H), 2.79 (m, 1 H), 6.48 (d, 2 H), 6.63 (d, 2 H).

γ-Al$_2$O$_3$-Supported [(TMT)Ru(H$_2$O)$_3$](OTf)$_2$. An aqueous solution of $[(TMT)Ru(H_2O)_3](OTf)_2$ (100 mg) in 10 mL of water was treated with 1 g of γ-alumina, and the solution was rotary-evaporated to dryness, giving a pale yellow, free-flowing solid. When this solid was washed with H_2O, a yellow solution was obtained, which was shown by UV-vis spectroscopy to be identical with $[(TMT)Ru(H_2O)_3]^{2+}$.

CP-MAS ^{13}C NMR Spectroscopy. CP-MAS ^{13}C NMR spectra were recorded on 300-mg samples with a General Electric GN-300WB spectrometer. The spectra were recorded by the cross polarization magic angle spinning technique with bilevel decoupling. The samples were loaded into Kel-F rotors, and the spectra were obtained at ambient temperature. The ^{13}C spectra of $[(TMT)Ru(H_2O)_3](OTf)_2$ were collected with a contact time of 3 ms and a scan delay of 10 s, while the spectrum of $[(TMT)Ru(H_2O)_3](OTf)_2 \cdot \gamma\text{-}Al_2O_3$ was recorded with a contact time of 2 ms and a scan delay of 2 s.

Crystal Structure Determination. Crystals of $[(TMT)Ru(H_2O)_3](O_3SCF_3)_2$ were obtained by slow evaporation of a CH_2Cl_2/hexane solution in air. The structure was solved by direct methods (SHELX-86).[29] The correct ruthenium atom position was deduced from an E map. Subsequent least-squares–difference Fourier calculations revealed atomic positions for the remaining non-hydrogen atoms, including the disordered water ligands and CF_3 groups. The water ligands around the Ru were severely disordered. Mirror symmetry was imposed on set A, and set B was disordered about the mirror. Owing to high correlation coefficients, Ru–O bond lengths were constrained to a common variable. Hydrogen atoms were not included in structure factor calculations. In the final cycle of least squares, disordered oxygen

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Table V. Selected Positional Parameters for the Cation in $[(TMT)Ru(H_2O)_3](OTf)_2$

	x/a	y/b	z/c
Ru	0.5623 (1)	−0.25	0.4577 (2)
O1A	0.7227 (7)	−0.25	0.421 (6)
O2A	0.597 (3)	−0.176 (1)	0.645 (3)
O1B	0.7195 (6)	−0.233 (1)	0.411 (3)
O2B	0.600 (2)	−0.210 (1)	0.692 (1)
O3B	0.593 (2)	−0.3437 (7)	0.589 (2)
S	0.3911 (4)	−0.25	0.4233 (8)
C1	0.466 (1)	−0.1863 (9)	0.331 (2)
C2	0.5361 (10)	−0.2140 (7)	0.221 (2)
C3	0.440 (2)	−0.1102 (9)	0.364 (3)
C4	0.602 (1)	−0.169 (1)	0.117 (2)

atoms and the CF_3 groups were refined with common isotropic thermal parameters and anisotropic thermal coefficients were refined for the remaining non-hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the final cycle. The highest peaks in the final difference Fourier map were in the vicinity of the disordered fluorine atoms. A final analysis of variance between observed and calculated structure factors showed an inverse dependence on sin θ. Details of the crystallography are presented in Table IV. Selected atomic coordinates are given in Table V.

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Supplementary Material Available: Tables of bond distances and angles, positional parameters, and thermal parameters (5 pages); a table of structure factors (6 pages). Ordering information is given on any current masthead page.

Mechanistic Studies of the Reductive Coupling of Carbon Monoxide in Seven-Coordinate Niobium(I) and Tantalum(I) Dicarbonyl Complexes

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The mechanism by which the two carbonyl ligands in the seven-coordinate complexes $[M(CO)_2(dmpe)_2Cl]$ [M = Ta, Nb; dmpe = 1,2-bis(dimethylphosphino)ethane] are reductively coupled has been elucidated. The first step involves two-electron reduction to afford the $[M(CO)_2(dmpe)_2]^-$ anion, the tantalum analogue of which was structurally characterized as the tetra-*n*-hexylammonium salt. The geometry of this anion is distorted octahedral with *cis*-carbonyl ligands. Reaction of the anion with 1 equiv of trialkylsilyl chloride yields the siloxycarbyne species $[M(\equiv COSiR_3)(CO)(dmpe)_2]$ (M = Ta or Nb), formed by electrophilic attack of the silyl halide on the carbonyl oxygen atom. The tantalum triisopropylsiloxycarbyne complex, the X-ray structural analysis of which is described, reacts with 1 equiv of trimethylsilyl chloride to afford the asymmetric acetylene complex, $[Ta\{Me_3SiOC{\equiv}COSi(i\text{-}Pr)_3\}(dmpe)_2Cl]$, which was also structurally characterized. The transition state between the carbyne and coupled products may be an η^2-ketenyl of the type $[Ta\{\eta^2\text{-}(O)\text{-}CCOSiR_3\}(dmpe)_2X]^-$ (X = halide). Such an assignment is supported by a series of experiments involving addition of different silyl halide reagents (Me_3SiX; X = Cl, I, OTf) to $(n\text{-}C_6H_{13})_4N[Ta(CO)_2(dmpe)_2]$. The generality of the reaction mechanism is discussed.

Introduction

Reaction chemistry that yields useful organic substrates starting from abundant C_1 precursors such as carbon monoxide has great potential value. Reduction of CO by alkali metals[1] or electrochemically[2] affords $M_2(C_2O_2)$ and higher oligomers from which a variety of organic products has been isolated.[1-3] The reductive coupling of CO has also been accomplished by using soluble transition, lanthanide, and actinide metal complexes.[4] As shown schematically in eqs 1 and 2, nearly all of these reactions are believed to proceed via the intra- or intermolecular coupling of oxocarbenes, with the carbonyl oxygen atoms ultimately bonded to the metal center(s).[5] Recently, however, theoretical calculations and experimental studies of the reaction of CO with $[Cp^*{}_2Hf(H)(CH_2CHMe_2)]$[6] have

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