of a series of cobalt-substituted proteins.

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Supplementary Material Available: Tables S1 and S2, listing anisotropic thermal parameters (2 pages); tables of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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Ruthenium(II) Solvento Complexes Containing the Tripod-like Ligands $MeC(CH_2EPh_2)_3$ (E = P or As) and Their Reactions with Carbon Monoxide. Crystal and Molecular Structure of $[Ru_2(\mu\text{-}Cl)_3(MeC(CH_2PPh_2)_3)_2][BPh_4]$

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Treatment of $[RuCl_2(DMSO)_4]$ with tripod [tripod = $MeC(CH_2EPh_2)_3$, E = P (triphos) or As (triars)] yields $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]Cl$. In the case of triars the mononuclear intermediate $[RuCl_2(DMSO)(triars)]$ can be isolated. This condenses to the corresponding trichloro-bridged complex in MeOH. The chloride ligands of $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]Cl$ can be abstracted by $AgCF_3SO_3$ in MeCN to yield $[Ru(MeCN)_3(tripod)](CF_3SO_3)_2$. When the chloride abstraction is carried out in DMSO and above 100 °C, the products are $[Ru(DMSO)_3(tripod)](CF_3SO_3)_2$, whereas if the reaction is carried out below 100 °C, the mixed-solvent complexes $[Ru(H_2O)(DMSO)_2(tripod)](CF_3SO_3)_2$ are obtained. Reaction of the DMSO complexes with carbon monoxide gives the dicarbonyl triflate complexes $[Ru(CF_3SO_3)(CO)_2(tripod)](CF_3SO_3)$. The X-ray diffraction study of a crystal of $[Ru_2(\mu\text{-}Cl)_3(tripod)_2][BPh_4]$ (orthorhombic, of space group *Pccn* and with $a = 19.991$ (8) Å, $b = 18.388$ (7) Å, $c = 25.510$ (10) Å, and $Z = 4$) is reported.

Introduction

Open sites in metal coordination spheres have long been recognized as essential features of reactive complexes. There has been a concentrated effort to synthesize and isolate complexes that either are coordinatively unsaturated and stabilized by bulky ligands[2] or possess potentially labile ligands such as phosphines,[3a] olefins,[3b] or solvent molecules.[3c] Some solvent-stabilized complexes have been shown to activate sp^3-hybridized C–H bonds.[4] Such novel reactivity has prompted a systematic search for similar compounds obtained by acidolysis of polyhydrides in suitable donor solvents.[5]

Our interest in solvento transition-metal complexes containing the facially coordinating tripod ligand [tripod = $(MeC(CH_2EPh_2)_3)$, E = P (triphos) or As (triars)] stems from preliminary studies in which it was found that $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ catalyzed a number of reactions.[6] We have, therefore, extended this chemistry to include analogous complexes of ruthenium since coordinatively unsaturated $[RuHCl(PPh_3)_3]$[7] and $[RuCl_2(PPh_3)_3]$[8] are known to be active catalysts.

Ruthenium(II) complexes containing triphos have been previously reported in the literature,[9] but they contain coordinated carbon monoxide as they were prepared by using ruthenium carbonyl complexes as starting materials. Thus, other synthetic routes were required to obtain carbonyl-free species in general and solvento complexes in particular.

Preliminary to catalytic studies, we report herein the synthesis, isolation, and spectral and reactivity studies of complexes of the type $[Ru(solvent)_3(tripod)]^{2+}$.

Results

Synthesis and Reactivity Studies. Our initial efforts were directed toward the synthesis of $[Ru(MeCN)_3(tripod)]^{2+}$ using the method outlined by Crabtree and Pearman[10] for the synthesis of the cations $[Ru(MeCN)_3L_3]^{2+}$ (L = PMe_2Ph, $PMePh_2$), i.e., halogen abstraction from $[L_3Ru(\mu\text{-}Cl)_3RuL_3]^+$ in acetonitrile. Chatt et al.[11] reported that these binuclear complexes can be obtained by refluxing $RuCl_3{\cdot}nH_2O$ ($n \sim 2$) with an excess of phosphine and with 2-methoxyethanol as a solvent. However, when triphos was used in this reaction, only moderate yields (ca. 40%) of the yellow product $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**) were obtained. The yields of **1** could be improved (ca. 60%) by reacting "ruthenium blue solutions"[12] in methanol with triphos (1 molar equiv) in 2-methoxyethanol. However, the method of choice, because of yield and ease of isolation, was the reaction of triphos with $[RuCl_2(DMSO)_4]$[13] in refluxing toluene, which gave ca. 80% yield (see eq 1). The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a singlet at δ 36.0, consistent with a face-sharing bioctahedral structure with bridging chlorides. The X-ray analysis of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2][BPh_4]$ is presented in a later section.

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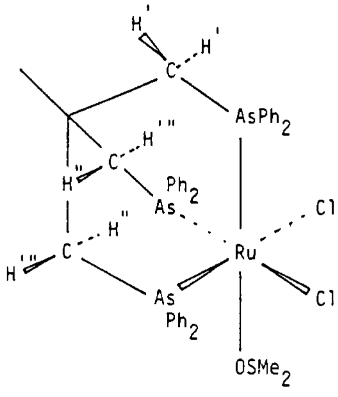
$$2[\mathrm{RuCl_2(DMSO)_4}] + 2\text{triphos} \xrightarrow{\text{toluene}} \underset{\mathbf{1}}{[\mathrm{Ru_2(\mu\text{-}Cl)_3(triphos)_2}]\mathrm{Cl}} + 8\mathrm{DMSO} \quad (1)$$

Interestingly, when triars was reacted with $[\mathrm{RuCl_2(DMSO)_4}]$ in toluene, the yellow mononuclear $[\mathrm{RuCl_2(DMSO)(triars)}]$ (**2**) precipitated in ca. 95% yield (eq 2). If one assumes an octahedral structure for **2**, one expects inequivalent methylene protons for the triars ligand, a situation that has been observed at 250 MHz in $[\mathrm{IrH_2Cl(triphos)}]$.[14] This, however, was not the case for **2**, where only one methylene singlet is observed. The equivalence of the methylene protons of the triars ligand could be caused by the formation of a fluxional five-coordinate intermediate resulting from facile DMSO dissociation. Evidence for the fluxional process is provided by the following ^{1}H NMR experiment: addition of DMSO-d_6 to a $\mathrm{CD_2Cl_2}$ solution of **2**, followed by immediate acquisition of data (ca. 5 min), showed that the peak assigned to "coordinated" DMSO had shifted upfield 0.33 ppm toward free DMSO (δ +2.55). The mode of DMSO bonding in this complex will be discussed later.

$$[\mathrm{RuCl_2(DMSO)_4}] + \text{triars} \xrightarrow{\text{toluene}} \underset{\mathbf{2}}{[\mathrm{RuCl_2(DMSO)(triars)}]} + 3\mathrm{DMSO} \quad (2)$$

Compound **2** reacted slowly at ambient temperature ($t_{1/2} > 23$ h) in $\mathrm{CH_2Cl_2}$ to form the expected binuclear complex $[\mathrm{Ru_2(\mu\text{-}Cl)_3(triars)_2}]\mathrm{Cl}$ (**3**) (eq 3). Its formation was facilitated by a hydroxylic solvent; e.g., ^{1}H NMR showed that this reaction was complete within 5 min of dissolving a sample of **2** in MeOH-d_4–$\mathrm{CD_2Cl_2}$ (1:1). Attempts to isolate $[\mathrm{RuCl_2(DMSO)(triphos)}]$ by shortening the time of the reaction shown in eq 1 to 15 min gave only lower yields of **1** and free triphos, as shown by a $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of the reaction mixture.



2

$$2\underset{\mathbf{2}}{[\mathrm{RuCl_2(DMSO)(triars)}]} \xrightarrow[\text{slow}]{\mathrm{CH_2Cl_2}} \underset{\mathbf{3}}{[\mathrm{Ru_2(\mu\text{-}Cl)_3(triars)_2}]\mathrm{Cl}} + 2\mathrm{DMSO} \quad (3)$$

Treatment of **1** or **3** with 4.1 molar equiv of $\mathrm{AgCF_3SO_3}$ in refluxing MeCN gave, after workup, colorless crystals of $[\mathrm{Ru(MeCN)_3(tripod)}](\mathrm{CF_3SO_3})_2$ in high yields (eq 4).

$$\underset{\mathbf{1,\,3}}{[\mathrm{Ru_2(\mu\text{-}Cl)_3(tripod)_2}]\mathrm{Cl}} + 4\mathrm{AgCF_3SO_3} \xrightarrow{\mathrm{MeCN}} \underset{\mathbf{4,\,5}}{[\mathrm{Ru(MeCN)_3(tripod)}](\mathrm{CF_3SO_3})_2} + 4\mathrm{AgCl} \quad (4)$$

tripod = triphos (**1**, **4**), triars (**3**, **5**)

The ^{1}H NMR spectral data for **4** and **5** are presented in Table I and deserve some comment. While complex **5** in $\mathrm{CD_2Cl_2}$ exhibits the signals and intensity ratios expected for a facially coordinated tris(acetonitrile) complex, complex **4** does so only in $\mathrm{CD_2Cl_2}$ containing trace amounts of MeCN. Detailed studies indicate that, at least in MeOH-d_4, a facile exchange of free and coordinated acetonitrile occurs. Preliminary studies of this process in MeOH-d_4 indicate that **4** undergoes MeCN/MeCN-d_3 exchange ca. 18 times faster than **5**.[15] The bands observed in the infrared spectra of **4** and **5** are assigned to ν(CN) and are also presented in Table I.

Compound **5** could also be obtained from $[\mathrm{RuCl_2(DMSO)(triars)}]$ (**2**) by chloride abstraction with $\mathrm{AgCF_3SO_3}$ in MeCN (eq 5). In this case the reaction was complete in less than 15 min at refluxing temperature, compared with the 5 h required for the method given in eq 4.

$$\underset{\mathbf{2}}{[\mathrm{RuCl_2(DMSO)(triars)}]} + 2\mathrm{AgCF_3SO_3} \xrightarrow{\mathrm{MeCN}} \underset{\mathbf{5}}{[\mathrm{Ru(MeCN)_3(triars)}](\mathrm{CF_3SO_3})_2} + 2\mathrm{AgCl} + \mathrm{DMSO} \quad (5)$$

The chloride ligands in complexes **1** and **3** could also be abstracted by silver(I) in DMSO at elevated temperatures. However, different products were isolated depending on the reaction temperature. Thus, a solution of **1** or **3** in reagent grade DMSO when heated above 100 °C with 4.1 molar equiv of $\mathrm{AgCF_3SO_3}$ gave, after appropriate workup, good yields of orange-yellow $[\mathrm{Ru(DMSO)_3(triphos)}](\mathrm{CF_3SO_3})_2$ (**6a**) and $[\mathrm{Ru(DMSO)_3(triars)}](\mathrm{CF_3SO_3})_2$ (**6b**) (see eq 6). Their infrared spectra (ν(SO) 940 and 931 cm^{-1}, respectively) and ^{1}H NMR resonances (δ 2.59 and 2.54, respectively) suggest the presence of O-bound DMSO ligands (see Table I). O-bound DMSO ligands have ν(SO) at ca. 915 cm^{-1} and ^{1}H NMR resonances near that of free DMSO (δ 2.55), whereas S-bound DMSO ligands have ν(SO) at ca. 1100 cm^{-1} and the chemical shift values are about 1 ppm downfield from that of free DMSO.[16] However, when the reaction 6 was carried out at temperatures below 100 °C, the compounds $[\mathrm{Ru(H_2O)(DMSO)_2(triphos)}](\mathrm{CF_3SO_3})_2$ (**7a**) and $[\mathrm{Ru(H_2O)(DMSO)(triars)}](\mathrm{CF_3SO_3})_2$ (**7b**) were obtained:[17]

$$\underset{\mathbf{1,\,3}}{[\mathrm{Ru_2(\mu\text{-}Cl)_3(tripod)_2}]\mathrm{Cl}} + 4\mathrm{AgCF_3SO_3} \xrightarrow{\mathrm{DMSO}} 2\underset{\mathbf{6a,\,6b}}{[\mathrm{Ru(DMSO)_3(tripod)}](\mathrm{CF_3SO_3})_2} + 4\mathrm{AgCl} \quad (6)$$

$$\underset{\mathbf{1,\,3}}{[\mathrm{Ru_2(\mu\text{-}Cl)_3(tripod)_2}]\mathrm{Cl}} + 4\mathrm{AgCF_3SO_3} \xrightarrow{\mathrm{DMSO\ (H_2O)}} 4\mathrm{AgCl} + 2\underset{\mathbf{7a,\,7b}}{[\mathrm{Ru(H_2O)(DMSO)_2(tripod)}](\mathrm{CF_3SO_3})_2} \quad (7)$$

Their formulation is based on the following data (see Table I): (1) their infrared spectra in Nujol each show a sharp peak at 3549 and 3450 cm^{-1}, respectively, indicative of a bound O–H group; (2) the ^{1}H NMR spectra show two broad singlets at δ 4.98 (2 H) and 2.55 (12 H) for **7a** and at δ 5.68 (2 H) and 2.64 (12 H) for **7b**, assigned to bound $\mathrm{H_2O}$ (a similar chemical shift for bound $\mathrm{H_2O}$ has been reported recently[18]) and O-bound DMSO, respectively; (3) addition of $\mathrm{D_2O}$ to an NMR tube containing **7a** or **7b** in $\mathrm{CD_2Cl_2}$ followed by immediate measurement (ca. 5 min) indicates exchange between free and bound $\mathrm{H_2O}$ protons since the peak at δ 4.98 of **7a** or δ 5.68 of **7b** shifts rapidly to a broader peak at δ 3.25, i.e., toward free $\mathrm{H_2O}$ in $\mathrm{CD_2Cl_2}$. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **7a** in $\mathrm{CD_2Cl_2}$ shows only a singlet at 37.96 ppm, indicative of a symmetrical structure on the NMR time scale, which could be explained by assuming that, as postulated for compound **2**, rapid ligand dissociation occurs with formation of

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[17] Compounds **6a** and **6b** when exposed to moisture, even in the solid state, give **7a** and **7b**, respectively. This hydrolytic reaction is faster in **6a** than in **6b**.

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Table I. NMR and IR Spectral Data[a]

complex	^{1}H NMR	^{31}P{^{1}H} NMR	IR (CsI), cm^{-1}
$[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**)	δ 7.40 br t (24 H), 7.18 t (12 H), 6.85 (24 H), 22.43 br s (12 H), 1.58 br quartet (6 H)	δ 36.00 s	ν(Ru–Cl–Ru) 273 br, m
$[RuCl_2(DMSO)(triars)]$ (**2**)	δ 7.54 d (12 H), 7.23 t (6 H), 7.10 t (12 H), 2.95 br s (6 H), 2.18 s (6 H), 1.34 s (3 H)		ν(SO) 1187 br, s
$[Ru_2(\mu\text{-}Cl)_3(triars)_2]Cl$ (**3**)	δ 7.34 d (24 H), 7.23 t (12 H), 6.95 t (24 H), 2.20 s (12 H), 1.53 s (6 H)		ν(RuClRu) 2653 br, m
$[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (**4**)	(CD_3CN/CD_2Cl_2) δ 7.30 m (30 H), 2.52 br s (3 H), 2.34 s (9 H), 1.71 br quartet (3 H)	δ 26.60 s	ν(CN) 2323 w, 229 w
$[Ru(MeCN)_3(triars)](CF_3SO_3)_2$ (**5**)	δ 7.40 m (12 H), 7.25 m (18 H), 2.47 s (6 H), 2.33 s (9 H), 1.53 s (3 H)		ν(CN) 2320 w, 2290 w
$[Ru(DMSO)_3(triphos)](CF_3SO_3)_2$ (**6a**)	δ 7.19 m (30 H), 2.59 br s (18 H), 2.42 m (6 H), 1.63 br quartet (3 H)	δ 37.04 s	ν(SO) 940 m
$[Ru(DMSO)_3(triars)](CF_3SO_3)_2$ (**6b**)	δ 7.37 m (18 H), 7.18 m (12 H), 2.54 br s (18 H), 2.24 s (6 H), 1.48 s (3 H)		ν(SO) 931 m
$[Ru(H_2O)(DMSO)_2(triphos)](CF_3SO_3)_2$ (**7a**)	δ 7.33 m (18 H), 7.14 m (12 H), 4.98 br s (2 H), 2.55 s (12 H), 2.39 br s (6 H), 1.60 br quartet (3 H)	δ 37.56 s	ν(OH) 3549 w ν(SO) 960 m, 945 m
$[Ru(H_2O)(DMSO)_2(triars)](CF_3SO_3)_2$ (**7b**)	δ 7.26 m (18 H), 7.12 m (12 H), 5.68 br s (2 H), 2.64 s (12 H), 2.37 s (2 H), 2.26 s (4 H), 1.60 s (3 H)		ν(OH) 3450 w ν(SO) 987 m, 948 m
$[RuCl_2(CO)(triars)]$ (**8**)	δ 7.75 m (4 H), 7.32 m (8 H), 7.20 m (12 H), 7.01 m (6 H), 2.36 s (2 H), 2.25 s (4 H), 1.50 s (3 H)		ν(CO) 1978 vs ν(RuCl) 290 w, 270 w
$[Ru(CF_3SO_3)(CO)_2(triphos)](CF_3SO_3)_2$ (**9**)	δ 7.31 m (30 H), 2.99 dd (2 H), 2.85 dd (2 H), 2.80 d (2 H), 1.98 dd (3 H)	δ 33.47 t (J_{PP} = 32 Hz, 1 P), −1.65 d (J_{PP} = 32 Hz, 2 P)	ν(CO) 2080 s, 2040 s
$[Ru(CF_3SO_3)(CO)_2(triars)](CF_3SO_3)_2$ (**10**)	δ 7.35 m (30 H), 2.84 br s (4 H), 2.77 s (2 H), 1.98 s (3 H)		ν(CO) 2075 s, 2030 s

[a] NMR data (in ppm) were taken in CD_2Cl_2 (^{1}H NMR) or CH_2Cl_2/CD_2Cl_2 (^{31}P{^{1}H} NMR), unless otherwise noted.

a fluxional five-coordinate intermediate. This is in agreement with experiment 3 above. Although the dynamic behavior can be explained by H_2O exchange, a contribution from DMSO dissociation, as found for **2**, cannot be excluded.

The solvento complexes described above reacted with CO, giving carbonyl-containing species. Thus, DMSO in compound **2** was easily replaced by CO to form $[RuCl_2(CO)(triars)]$ (**8**), analogous to $[RuCl_2(CO)(triphos)]$ reported by Siegl et al.[9] (eq 8). The

$$\underset{\mathbf{2}}{[RuCl_2(DMSO)(triars)]} + CO \xrightarrow[\text{slow}]{CH_2Cl_2} \underset{\mathbf{8}}{[RuCl_2(CO)(triars)]} + DMSO \quad (8)$$

^{1}H NMR spectrum of **8** showed that the octahedral geometry is rigid in solution since three distinct methylene signals are observed. The ν(CO) band at 1978 cm^{-1} is very strong.

Complexes **6** and **7** also reacted with carbon monoxide at ambient temperature and at 1 atm in CH_2Cl_2. In both instances the products were isolated as white powders in excellent yields and formulated as $[Ru(CF_3SO_3)(CO)_2(tripod)](CF_3SO_3)$ (eq 9a and 9b). However, while reaction 9a is complete within 5 min,

$$\underset{\mathbf{7}}{[Ru(H_2O)(DMSO)_2(triphos)](CF_3SO_3)_2} \xrightarrow[CO]{CH_2Cl_2} H_2O + 2DMSO + \underset{\mathbf{9}}{[Ru(CF_3SO_3)(CO)_2(triphos)](CF_3SO_3)} \quad (9a)$$

$$\underset{\mathbf{6}}{[Ru(DMSO)_3(triars)](CF_3SO_3)_2} \xrightarrow[CO]{CH_2Cl_2} \underset{\mathbf{10}}{[Ru(CF_3SO_3)(CO)_2(triars)](CF_3SO_3)} + 3DMSO \quad (9b)$$

reaction 9b required 30 min to go to completion. The presence and number of carbonyls and tripod ligands in **9** and **10** were established by IR and NMR spectroscopy (see Table I). Thus, in the case of compound **9** it was found that (1) there was a sixth ligand that was not labile on the NMR time scale as both the ^{31}P NMR and ^{1}H NMR spectra exhibited patterns agreeing with the proposed structure, (2) IR and ^{1}H NMR evidence excluded the possibility that this ligand could be either H_2O or DMSO, (3) aggregation to bi- or oligonuclear species with bridging CO's was ruled out as only terminal CO stretches were observed in its IR spectrum, and (4) the ^{19}F NMR spectrum (CD_2Cl_2) showed two singlets of equal intensity at δ −76.76 and −78.51 (relative to $CFCl_3$), the former being assigned to free $CF_3SO_3^-$ by comparison with the chemical shift for $AgCF_3SO_3$ in MeCN-d_3 (δ −75.50 s), where the species present in solution is probably $[Ag(MeCN)_4](CF_3SO_3)$, in which there is no direct Ag–O interaction.[19] On the basis of other examples in the literature[20] and the lack of J_{PF} coupling, the $CF_3SO_3^-$ ligand of **9** (and **10**) is probably O-bound rather than F-bound.

Addition of an excess of MeCN to $[Ru(H_2O)(DMSO)_2(triphos)](CF_3SO_3)_2$ in CH_2Cl_2 gave a quantitative yield of $[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$, as shown by the ^{31}P NMR spectrum of the solution.

The addition of 1 equiv of chloride to **9** resulted in rapid formation of the previously reported monochloride cation **11** (eq 10),[9] which reacted further with a second equiv of chloride to yield the dichloro complex **12** (eq 11).

$$\underset{\mathbf{9}}{[Ru(CF_3SO_3)(CO)_2(triphos)](CF_3SO_3)} + NEt_4Cl \xrightarrow{CH_2Cl_2} NEt_4CF_3SO_3 + \underset{\mathbf{11}}{[RuCl(CO)_2(triphos)](CF_3SO_3)} \quad (10)$$

$$\underset{\mathbf{9}}{[Ru(CF_3SO_3)(CO)_2(triphos)](CF_3SO_3)} + 2NEt_4Cl \xrightarrow{CH_2Cl_2} 2NEt_4CF_3SO_3 + \underset{\mathbf{12}}{[RuCl_2(CO)(triphos)]} + CO \quad (11)$$

$[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (**4**) reacted readily with CO in CH_2Cl_2, forming three different species that were detected by ^{31}P{^{1}H} NMR spectra, all of them giving patterns agreeing with an A_2X spin system. Their relative amounts depended on the reaction conditions. One of the products is compound **9**, while the other two are likely to be mixed carbonyl–acetonitrile species, in agreement with the observation that MeCN is a better donor than DMSO.[21] Given the complexity of this reaction, it was not

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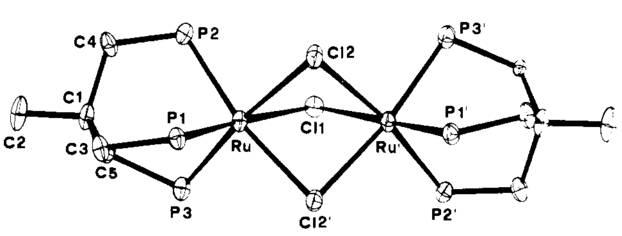

Figure 1. Inner coordination sphere of the complex cation $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]^+$. The ellipsoids represent 30% probability.

Table II. Selected Bond Lengths (Å) and Angles (deg)

Ru–Cl(1)	2.488 (3)	P(2)–C(18)	1.877 (13)
Ru–Cl(2)	2.500 (3)	P(2)–C(24)	1.840 (13)
Ru–Cl(2)′	2.494 (3)	P(3)–C(5)	1.859 (11)
Ru–P(1)	2.296 (3)	P(3)–C(30)	1.865 (13)
Ru–P(2)	2.308 (3)	P(3)–C(36)	1.852 (14)
Ru–P(3)	2.310 (3)	C(1)–C(2)	1.570 (17)
P(1)–C(3)	1.876 (13)	C(1)–C(3)	1.564 (18)
P(1)–C(6)	1.856 (14)	C(1)–C(4)	1.584 (18)
P(1)–C(12)	1.858 (14)	C(1)–C(5)	1.505 (17)
P(2)–C(4)	1.824 (13)		

Cl(1)–Ru–Cl(2)	78.0 (1)	P(1)–Ru–P(3)	85.5 (1)
Cl(1)–Ru–P(1)	175.2 (1)	P(2)–Ru–P(3)	90.8 (1)
Cl(1)–Ru–P(2)	95.7 (1)	Ru–P(1)–C(3)	113.1 (4)
Cl(1)–Ru–P(3)	96.7 (1)	Ru–P(1)–C(6)	115.7 (4)
Cl(2)–Ru–Cl(2)′	75.5 (1)	Ru–P(1)–C(12)	121.1 (4)
Cl(2)–Ru–P(1)	99.3 (1)	Ru–P(2)–C(4)	112.3 (4)
Cl(2)–Ru–P(2)	95.8 (1)	Ru–P(2)–C(18)	119.1 (4)
Cl(2)–Ru–P(3)	171.9 (1)	Ru–P(2)–C(24)	118.4 (4)
Cl(2)′–Ru–P(1)	97.3 (1)	Ru–P(3)–C(5)	110.9 (4)
Cl(2)′–Ru–P(2)	170.1 (1)	Ru–P(3)–C(30)	119.0 (4)
Cl(2)′–Ru–P(3)	97.5 (1)	Ru–P(3)–C(36)	120.2 (4)
P(1)–Ru–P(2)	88.6 (1)		

thought worthwhile investigating it further. However, it is noteworthy that the acetonitrile compound gives a complex mixture of products while its DMSO analogue, **7**, as mentioned earlier, gives only one product.

Description of the Structure of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2][BPh_4]$. The crystal structure consists of discrete $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]^+$ cations and $[BPh_4]^-$ anions with no short contacts among atoms of different ions.

The inner coordination sphere of the cation is shown in Figure 1, and a perspective view of all the heavy atoms of the cation is available as supplementary Figure S1. Relevant bond lengths and angles are listed in Table II.

Each ruthenium atom is coordinated by the three P atoms of the triphos ligand and by three bridging Cl atoms. The two P_3Ru units are exactly eclipsed, while the bridging chlorine atoms are staggered with respect to the six P atoms.

The geometry of the whole coordination polyhedron, which possesses an approximate C_{3v} symmetry, is cofacial bioctahedral. A binary axis runs through a C(1) atom such that only half of the cation is symmetry independent.

Bond lengths and angles in the $[Ru_2(\mu\text{-}Cl)_3P_6]^+$ unit are very similar to those observed in related compounds, particularly in $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]^+$[22] and $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]^+$[23] (Table III).

The Ru–Ru distance (3.455 (1) Å) is comparable with those found in the diethyl- and dimethylphenylphosphine complexes (3.443 (4) and 3.39 (1) Å, respectively). These distances are longer than those generally attributed to two-electron Ru–Ru bonds and are considered an indication of a repulsive, more than an attractive, Ru–Ru interaction.[27-29] Thus the Ru–Cl–Ru bond angles, which are equivalent and average to a value of 87.8°, are larger than those calculated for the ideal cofacial bioctahedral geometry, i.e., 75.0°. Accordingly, the Cl–Ru–Cl angles, which average 77.2°, are smaller than the ideal value of 90°. The same degree of distortion, which indicates elongation relative to an ideal cofacial bioctahedral geometry, is observed in $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]^+$ and $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]^+$. Also in these binuclear species, the ruthenium atoms are further apart than they would be in a regular face-sharing bioctahedron.

Dimensions in the triphos ligand are normal with small deviations from the ideal geometry, as generally found in other triphos complexes.[30-33] The angles at the phosphorus atoms show the usual distortions, their average values being Ru–P–C(aryl) = 118.9°, Ru–P–C(alkyl) = 111.8°, C(alkyl)–P–C(aryl) = 103.0°, and C(aryl)–P–C(aryl) = 98.5°.

The tetraphenylborate anion has a crystallographically required 2-fold axis passing through the boron atom so that only half of it is symmetry independent. It presents the usual deviations from the ideal geometry.[34-36] The B–C bond lengths are comparable and average to 1.64 Å. The C–B–C bond angles average 109.5°.

Discussion

As pointed out in the previous section, a high-yield synthesis of a well-characterized, tripod-containing complex starting from $RuCl_3 \cdot nH_2O$ was not possible by direct methods. This is perhaps not surprising since the method of Chatt et al.[11] requires the use of excess phosphine in order to ensure complete reduction of the Ru(III) starting material. Obviously, the use of triphos as a reductant would result in low yields because of partial oxidation of the terdentate ligand. Moreover, the exact actual composition of "$RuCl_3 \cdot nH_2O$" may vary from batch to batch and the oxidation state is not well determined.[37a]

The reason for the relatively low yield from the "ruthenium blue solution" is not clear but may be related to the report[12] that these solutions contain mainly the cluster species $[Ru_5Cl_{12}]^{2-}$, which may give rise to phosphine-containing polymetallic species of variable compositions.

We find that replacement of DMSO from easily accessible $[RuCl_2(DMSO)_4]$ provides a smooth, high-yield synthetic method for the preparation of tripod-containing ruthenium species.

A recent report[38] has shown the general applicability of this synthetic methodology to two other potentially terdentate ligands, i.e., $PhCH_2N(CH_2CH_2CH_2EPh_2)_2$ [E = P (DPBA) or As (DABA)]. For example, the reaction of $[RuCl_2(DMSO)_4]$ with DABA in acetone gave *trans*-$[RuCl_2(DMSO)(DABA)]$, in which the DABA ligand coordinates meridionally, the chlorides being trans to one another.

The easy formation of binuclear **3** from **2** is likely to be associated with the lability of the DMSO ligand in **2** mentioned earlier, and a possible pathway is shown in eq 12 and 13. The failure

$$\underset{\mathbf{2}}{[RuCl_2(DMSO)(triars)]} \rightarrow \text{“}RuCl_2(triars)\text{”} + DMSO \qquad (12)$$

$$\text{“}RuCl_2(triars)\text{”} + \mathbf{2} \rightarrow \underset{\mathbf{3}}{[Ru_2(\mu\text{-}Cl)_3(triars)_2]Cl} + DMSO \qquad (13)$$

to detect $[RuCl_2(DMSO)(triphos)]$ as an intermediate in the preparation of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**) by the reaction de-

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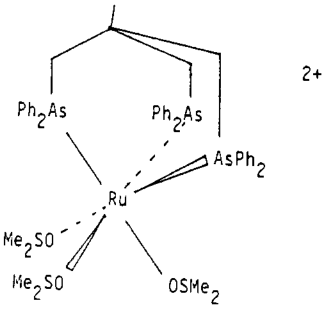
Table III. Relevant Distances (Å) and Angles (deg) in Related $Ru_2(\mu\text{-}Cl)_3$ Complexes[a]

compd	Ru···Ru	Ru-Cl*	Ru-P*	P-Ru-P*	Ru-Cl-Ru*	Cl-Ru-Cl*	ref
$[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]^+$	3.39	2.49	2.29	96	86	79	23
$[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]^+$	3.443 (4)	2.48	2.32	96.9	87.7	76.9	22
$[Ru_2(\mu\text{-}Cl)_3(triphos)_2]^+$	3.455 (1)	2.49	2.31	88.3	87.8	77.2	this work
$[Ru_2(\mu\text{-}Cl)_3Cl(CS)(PPh_3)_4]$	3.35 (2)	2.50	2.31	101.2	84.5	79.7	24
$[Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5]$	3.367 (2)	2.49	2.29	98.3	85.2	79.3	25
$[Ru_2(\mu\text{-}Cl)_3Cl_2(P\text{-}n\text{-}Bu_3)_4]$	3.115	2.14	2.33	102.3	79.4	83.5	26

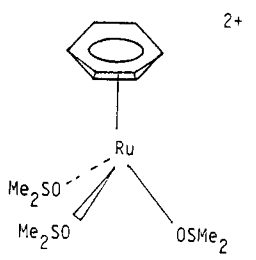
[a] Asterisk indicates an average value.

scribed in eq 1 could be due to the stronger trans effect of a phosphine donor relative to an arsine donor[39] speeding up the equivalent of reactions 12 and 13.

The complexes $[RuS_3(tripod)]^{2+}$ (S = DMSO, CH_3CN) are not the only tris(phosphine) solvent complexes of the group 8 metals known. The pertinent work of Crabtree and Pearman has been mentioned in the previous section.[10] At least two other examples can be found in the literature of the synthesis of ruthenium or osmium tris(phosphine) tris(solvento) complexes by acidolysis of hydride precursors in the appropriate solvents.[40] A direct analogue of **6**, **13**, was recently prepared by Stebler-Röthlisberger and Ludi.[37b]

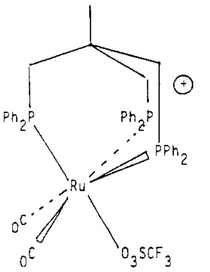


6

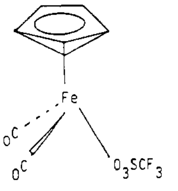


13

Equation 9 shows that the solvento ligands of **6** and **7** can easily be replaced by the strong π-acid, carbon monoxide, with concomitant ligation of one triflate anion. Although triflate, $CF_3CO_3^-$, is not considered to be as weakly coordinating as PF_6^- or BF_4^- (there are several examples in the literature of metal-bound triflate[20]), it is surprising that it coordinates in preference to DMSO or H_2O. However, this can be explained with reference to the coligand CO. The π-acidity of this ligand increases the fractional positive charge on the d^6 Ru(II) center, a situation that can be partially relieved by direct coordination of the anionic triflate. A report by Humphrey et al.[20] concerning the crystal structure of $[Fe(CF_3SO_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ (**14**) is particulary relevant in light of its isolobality with **9**.



9



14

The triflate ligands of **9** can be readily replaced by chloride to form the known complex **11**.[9] In the presence of excess chloride, compound **11** reacts further to form the monocarbonyl species (eq 11). In light of these results, it was surprising to find that treatment of **9** with a strong hydride source, $LiHBEt_3$, in THF did not give the previously reported $[RuH(CO)_2(triphos)]^+$,[41] but rather a complex showing three inequivalent phosphorus nuclei.[42] Although its thermal instability precluded its further characterization, the complex must contain a ligand environment that renders the ruthenium atom chiral, as reported by Hommeltoft and Baird[42] for some related compounds.

Finally, a comment should be made about the mode of bonding of DMSO in complexes **2**, **6**, and **7**. Compounds **6** and **7** on the basis of IR and ^1H NMR data, are clear-cut cases of O-bound DMSO complexes, while for **2**, on the same basis, a case can be made for an S-bound complex.

The reasons for the prevalence of O-bound DMSO in **2**, **6**, and **7** are likely to be both electronic and steric. First of all, ruthenium exhibits a more pronounced affinity for oxygen ligands than other noble metals. Second, an S-bound ligand would presumably compete electronically with the tripod ligands since both are known to be weak π-acceptors. Finally, in the case of **6** it seems likely that a facial array of O-bound DMSO ligands would be favored since this would relieve steric crowding around the metal.

Experimental Section

All operations were performed under an argon atmosphere. Unless otherwise state, solvents were dried and deoxygenated prior to use. Elemental analyses were performed by the Microanalytical Laboratory of the Swiss Federal Institute of Technology (ETH). Infrared spectra were recorded on a Beckman Model 4250 spectrophotometer with CsI disks. The ^{31}P NMR spectra were recorded on a Bruker HX 90 spectrometer operating at 36.43 MHz in 10-mm sample tubes. A positive sign of chemical shift denotes a resonance to low field of the reference (external H_3PO_4). The ^1H NMR spectra were recorded on a Bruker WM 250 spectrometer. The ^{19}F NMR spectra were recorded on a Bruker HX-90 spectrometer operating at 84.66 MHz in 5-mm tubes. A positive sign of chemical shift indicates a signal downfield of the standard (external $CFCl_3$). Triphos and triars were prepared according to published procedures[43] as was $[RuCl_2(DMSO)_4]$.[13]

$[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (1). A warm toluene (5 mL) solution of triphos (0.61 g, 0.98 mmol) was added to a pale yellow toluene (20 mL) slurry of $[RuCl_2(DMSO)_4]$ (0.48 g, 0.98 mmol) that had been heated to +80 °C for 10 min. The slurry, which immediately turned orange, was heated overnight to ca. +90 °C. After cooling, the yellow powder was filtered off, washed with toluene (5 mL) and diethyl ether (5 mL), and dried. Yield: 0.62 g (0.39 mmol), 80%. A satisfactory elemental analysis was obtained for $[Ru_2(\mu\text{-}Cl)_3(triphos)_2][BPh_4]$, which was obtained from **1** by anion exchange with $Na[BPh_4]$ in MeOH. Anal. Calcd for $C_{106}H_{98}BCl_3P_6Ru_2$: C, 67.82; H, 5.27; Cl 5.67. Found: C, 67.57; H, 5.19; Cl, 5.72.

$[RuCl_2(DMSO)(triars)]$ (2). Compound **2** was synthesized by following the procedure for **1**. In a typical synthesis, $[RuCl_2(DMSO)_4]$ (1.00 g, 2.1 mmol) and triars (1.56 g, 2.10 mmol) gave an orange-yellow powder, which was filtered off, washed with toluene (5 mL) and diethyl ether (5 mL), and dried. Yield: 2.00 g (1.99 mmol), 96%. Anal. Calcd for $C_{43}H_{45}As_3Cl_3Cl_2ORuS$: C, 51.30; H, 4.51; Cl, 7.04. Found: C, 51.41; H, 4.53; Cl, 7.21.

$[Ru_2(\mu\text{-}Cl)_3(triars)_2]Cl$ (3). Method a. "Palladium black" (0.1 g) was added to "$RuCl_3\cdot xH_2O$" (1.00 g, 3.90 mmol), and the mixture was dissolved in MeOH (20 mL). Hydrogen gas was bubbled through the stirred dark brown-red suspension until a blue solution resulted (ca. 30 min). Palladium metal was removed by filtration, and 1 molar equiv of triars (2.95 g, 3.90 mmol) was added to the filtrate. The slurry, on refluxing overnight, gave a brown precipitate that was collected by filtration, suspended in 2-methoxyethanol (20 mL), and refluxed for 30

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(42) δ_1 = 51.4 (dd, J_1 = 45 Hz, J_2 = 3 Hz); δ_2 = 11.1 (dd, J_3 = 32 Hz, J_2 = 3 Hz); δ_3 = 4.2 (dd, J_1 = 45 Hz, J_3 = 32 Hz).

(43) Hewerson, W.; Watson, J. *J. Chem. Soc.* **1962**, 1940.

Table IV. Crystallographic Data for $[Ru_2(\mu\text{-}Cl)_3(triphos)_2][BPh_4]$

formula	$C_{106}H_{98}BCl_3P_6Ru$
mol wt	1877.10
cryst class	orthorhombic
space group	*Pccn*
unit cell params	
a, Å	19.991 (8)
b, Å	18.388 (7)
c, Å	25.510 (10)
V, Å^3	9377
ρ_{calcd}, g cm^{-3}	1.330
Z	4
cryst size, mm	0.12 × 0.14 × 0.37
diffractometer	Nicolet R3
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
abs coeff, cm^{-1}	5.5
norml T_{min}	1.45
data collcn technique	ω-scan
scan range, deg	$3 \geqslant 2\theta \geqslant 50$
ω-scan width, deg	0.8
scan speed	variable according to intens
bkgd time	half of scan time
intens control stds	3 measd every 100 reflcns
no. of total reflcns measd	12720
no. of unique reflcns measd	10300
no. of reflcns with $I > 3\sigma(I)$	3200
final $R(F) = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.057
final $R_w(F) = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum(F_o)^2]^{1/2}$	0.069

min. The resulting cloudy orange solution was filtered through Celite, and the methoxyethanol was stripped. Addition of a minimum of ethanol (ca. 5 mL) to the solid residue and storage of the solution at −20 °C gave an orange-yellow solid, which was filtered off and dried. Yield: 1.83 g (0.99 mmol), 51%. Anal. Calcd for $C_{82}H_{78}As_3Cl_4Ru_2$: C, 53.03; H, 4.24; Cl, 7.64. Found: C, 51.87; H, 4.01; Cl, 7.70.

Method b. A sample of $[RuCl_2(DMSO)(triars)]$ (**2**) was dissolved in a 1:1 MeOD-d_4–CD_2Cl_2 solution. Quantitative formation of the binuclear complex **3**, with liberation of 2 equiv of DMSO (^1H NMR), occurred within 5 min at room temperature.

$[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (4). $AgCF_3SO_3$ (0.14 g, 0.54 mmol) was added to a MeCN solution (10 mL) of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**) (0.21 g, 0.13 mmol) with formation of AgCl. The resulting yellow slurry was refluxed for 3–4 h. More AgCl precipitated, and the solution became paler. The slurry was then allowed to cool, and AgCl was removed by filtration through Celite. The solvent was reduced to half of the original volume, and toluene (ca. 15 mL) was added, with stirring, until a colorless solid precipitated. The solid was filtered off, washed with toluene (5 mL) and diethyl ether (5 mL), and dried. Yield: 0.14 g (0.12 mmol), 92%. Anal. Calcd for: $C_{49}H_{48}F_6N_3O_6P_3RuS_2$: C, 51.30; H, 4.23; N, 3.66. Found: C, 51.37; H, 4.31; N, 3.31.

$[Ru(MeCN)_3(triars)](CF_3SO_3)_2$ (5). Method a. Solid $AgCF_3SO_3$ (0.57 g, 2.2 mmol) was added to a yellow MeCN (30 mL) solution of $[Ru_2(\mu\text{-}Cl)_3(triars)_2]Cl$ (**3**) (0.98 g, 0.53 mmol), and the mixture was heated to reflux for 5 h. After cooling, the AgCl precipitate was filtered from the pale yellow solution through Celite. The volume of the filtrate was reduced by half, and toluene (ca. 30 mL) was added with vigorous stirring until a crystalline precipitate formed. This was filtered off, washed with toluene (5 mL) and diethyl ether (5 mL), and dried. Yield: 1.08 g (0.85 mmol), 80%. Anal. Calcd for $C_{49}H_{48}As_3F_6N_3O_6RuS_2$: C, 46.01; H, 3.79; N, 3.28. Found: C, 46.24; H, 3.82; N, 3.22.

Method b. Solid $AgCF_3SO_3$ (0.29 g, 1.1 mmol) was added to a slurry of $[RuCl_2(DMSO)(triars)]$ (**2**) (0.56 g, 0.56 mmol) in MeCN (20 mL) and the mixture refluxed for 15 min. The slurry was worked up as in method a. Yield: 0.58 g (0.45 mmol), 81%.

$[Ru(DMSO)_3(triars)](CF_3SO_3)_2$ (6b). Solid $AgCF_3SO_3$ (0.085 g, 0.33 mmol) was added to a warm reagent grade DMSO solution (20 mL) of $[Ru_2(\mu\text{-}Cl)_3(triars)_2]Cl$ (0.15 g, 0.081 mmol), and the mixture was heated to 110 °C for 2 h. The precipitated AgCl was removed by filtration through Celite, and the solvent was removed from the orange filtrate in vacuo with heating. A minimum amount of CH_2Cl_2 (ca. 5 mL) was added to the resulting oil. An orange powder was precipitated from the solution by addition of toluene (ca. 20 mL) to the stirred solution. The solid was filtered, washed with toluene and with diethyl ether, and dried. Yield: 0.16 g (0.11 mmol), 69%. Anal. Calcd for $C_{49}H_{57}As_3F_6O_9RuS_5\cdot{}^1/_3C_7H_8$: C, 43.39; H, 4.24. Found: C, 43.24; H, 4.20. The presence of toluene in the above ratio was confirmed by ^1H NMR spectroscopy. $[Ru(DMSO)_3(triphos)](CF_3SO_3)_2$ (**6a**) was prepared as described for **6b**.

Table V. Final Positional Parameters of the Non-Hydrogen Atoms (×10^4)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cl(1)	2500	2500	−2 (1)
Ru(1)	16480 (4)	2339 (1)	6998 (4)
P(1)	935 (1)	2171 (2)	1395 (1)
P(2)	867 (1)	3112 (2)	334 (1)
P(3)	1119 (2)	1345 (2)	334 (1)
Cl(2)	2371 (1)	3319 (2)	1074 (1)
C(1)	−111 (5)	2033 (7)	615 (5)
C(4)	13 (6)	2873 (7)	519 (5)
C(3)	86 (6)	1840 (8)	1192 (5)
C(2)	−888 (6)	191 (1)	580 (6)
C(5)	223 (5)	1557 (6)	213 (5)
C(6)	1216 (7)	1509 (7)	1898 (5)
C(7)	907 (8)	859 (8)	2017 (6)
C(8)	120 (1)	36 (1)	2371 (7)
C(9)	1801 (8)	53 (1)	2606 (6)
C(10)	2108 (7)	119 (1)	2498 (6)
C(11)	1825 (7)	1672 (9)	2149 (5)
C(12)	713 (6)	2936 (7)	1838 (5)
C(13)	1006 (8)	3619 (9)	1784 (6)
C(14)	83 (1)	4186 (9)	2149 (8)
C(15)	402 (9)	404 (1)	1556 (7)
C(16)	11 (1)	336 (1)	2584 (6)
C(17)	260 (8)	2814 (9)	2242 (5)
C(18)	915 (6)	4111 (7)	483 (5)
C(19)	356 (7)	4497 (7)	634 (7)
C(20)	394 (9)	5236 (9)	718 (9)
C(21)	989 (9)	5596 (9)	668 (9)
C(22)	1552 (9)	5221 (9)	514 (6)
C(23)	1519 (7)	4466 (8)	414 (6)
C(24)	835 (6)	3193 (7)	−384 (5)
C(25)	286 (7)	2955 (8)	−698 (6)
C(26)	315 (9)	3000 (9)	−1244 (6)
C(27)	86 (1)	327 (1)	−1488 (6)
C(28)	1397 (9)	352 (1)	−1195 (6)
C(29)	1397 (7)	3465 (8)	−656 (6)
C(30)	1097 (6)	473 (6)	706 (6)
C(31)	506 (8)	51 (8)	757 (6)
C(32)	529 (8)	−616 (9)	1007 (7)
C(33)	1118 (9)	−88 (1)	1209 (8)
C(34)	169 (1)	−481 (8)	1174 (7)
C(35)	1668 (8)	187 (8)	915 (6)
C(36)	1368 (6)	1014 (7)	−323 (5)
C(37)	1455 (8)	1501 (7)	−730 (7)
C(38)	1571 (9)	1264 (9)	−1242 (6)
C(39)	165 (1)	56 (1)	−1348 (6)
C(40)	161 (1)	5 (1)	−942 (8)
C(41)	147 (1)	270 (9)	−433 (7)
C(42)	2090 (7)	689 (1)	−1544 (6)
C(43)	151 (1)	655 (1)	−1705 (7)
C(44)	119 (1)	600 (1)	−143 (1)
C(45)	144 (1)	577 (1)	−95 (1)
C(46)	198 (1)	611 (2)	−77 (1)
C(47)	2299 (8)	664 (2)	−1048 (9)
C(48)	1971 (6)	7952 (8)	−2257 (6)
C(49)	158 (1)	851 (1)	−2072 (8)
C(50)	110 (1)	891 (1)	−2364 (9)
C(51)	99 (1)	871 (1)	−286 (1)
C(52)	128 (1)	808 (2)	−303 (1)
C(53)	177 (1)	772 (1)	−2753 (9)
B(1)	2500	7500	−1900 (9)

$[Ru(H_2O)(DMSO)_2(triphos)](CF_3SO_3)_2$ (7a). A warm DMSO solution (5 mL) of $AgCF_3SO_3$ (0.66 g, 2.6 mmol) was added to a warm DMSO solution (15 mL) of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (1.0 g, 0.63 mmol). The resulting slurry was heated to +80 °C for 3 h and cooled; the precipitated AgCl was filtered, and the solvent was stripped from the filtrate with heating. The yellow solid was dissolved in CH_2Cl_2 (ca. 7 mL), and the cloudy solution was filtered. A yellow solid was precipitated by addition of toluene (5 mL) and ether (2 mL) to the solution. This solid was washed with toluene (5 mL) and diethyl ether (5 mL) and dried. Yield: 1.14 g (0.95 mmol), 76%. Anal. Calcd for $C_{47}H_{53}F_6O_9P_3RuS_4$: C, 47.11; H, 4.47. Found: C, 47.04; H, 4.46. $[Ru(H_2O)(DMSO)_2(triars)](CF_3SO_3)_2$ (**7b**) was prepared as described for **7a**.

$[RuCl_2(CO)(triars)]$ (8). A CH_2Cl_2 solution (5 mL) of **2** (0.050 g, 0.049 mmol) was freeze–thaw–degassed three times and placed under an atmosphere of CO. The orange solution, which immediately became yellow, was stirred for 2 h. Hexane (ca. 15 mL) was then added until a lemon yellow solid precipitated. This was filtered off, washed with hexane (2 × 5 mL), and dried. Yield: 0.040 g (0.041 mmol), 81%. Anal. Calcd for $C_{42}H_{39}As_3ClORu\cdot{}^1/_5CH_2Cl_2$: C, 52.06; H, 4.09; Cl, 8.74. Found: C, 51.73; H, 4.08; Cl, 9.11. The presence of CH_2Cl_2 in the indicated ratio was confirmed by ^1H NMR in $CDCl_3$.

[Ru(CF$_3$SO$_3$)(CO)$_2$(triphos)](CF$_3$SO$_3$) (9). A yellow CH_2Cl_2 solution (5 mL) of $[Ru(H_2O)(DMSO)_2(triphos)](CF_3SO_3)_2$ (0.050 g, 0.042 mmol) was freeze–thaw–degassed three times and then stirred under an atmosphere of CO. The solution, which became colorless within 5 min, was stirred for an additional 10 min to ensure complete reaction. Addition of diethyl ether (ca. 10 mL) with vigorous stirring gave a colorless solid, which was filtered, washed with diethyl ether, and dried. Yield: 0.041 g, (0.038 mmol), 90%. Anal. Calcd for $C_{45}H_{39}F_6O_8P_3RuS_2$: C, 50.04; H, 3.65. Found: C, 49.70; H, 3.57.

[Ru(CF$_3$SO$_3$)(CO)$_2$(triars)](CF$_3$SO$_3$) (10). Complex **10** was prepared analogously to **9**, i.e., by keeping $[Ru(DMSO)_3(triars)](CF_3SO_3)_2$ (0.026 g, 0.020 mmol) under 1 atm of CO, in CH_2Cl_2 for 3 h. Yield: 0.021 g (0.017 mmol), 87%. Anal. Calcd for $C_{45}H_{39}As_3F_6O_8RuS_2$: C, 44.60; H, 3.25. Found: C, 44.29; H, 3.33.

[RuCl(CO)$_2$(triphos)](CF$_3$SO$_3$) (11). Addition of 1 equiv of $NEt_4Cl\cdot 2H_2O$ to a colorless CH_2Cl_2 solution of $[Ru(CF_3SO_3)(CO)_2(triphos)](CF_3SO_3)$ gave a pale yellow solution, from which the solvent was removed in vacuo after 30 min of stirring. A white powder was isolated from an acetone solution of the residual as described by Siegl et al.[9] IR (CsI), cm^{-1}: ν(CO) 2079 s. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 26.24 t (J = 32 Hz, 1 P), −2.28 d (J = 32 Hz, 2 P).

[RuCl$_2$(CO)(triphos)] (12). Addition of 2 equiv of $NEt_4Cl\cdot 2H_2O$ to a colorless CH_2Cl_2 solution of $[Ru(CF_3SO_3)(CO)_2(triphos)](CF_3SO_3)$ gave a yellow precipitate, which was isolated from the cooled solution as described by Siegl et al.[9] IR (CsI), cm^{-1}: ν(CO) 2008 s; ν(Cl) 291 w, 275 w, sh. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ +27.80 d (J = 41 Hz, 2 P), −7.83 t (J = 41 Hz, 1 P).

Collection and Reduction of X-ray Intensity Data. The X-ray analysis was undertaken on yellow crystals grown by slow evaporation of a solution of the complex in CH_2Cl_2–MeOH. They are orthorhombic and belong to the space group *Pccn*, as apparent from systematic absences ($h0l$ for $l = 2n$, $0kl$ for $l = 2n$, and $hk0$ for $h + k = 2n$). A prismatic crystal of 0.12 × 0.14 × 0.37 mm approximate dimensions was selected for the collection of the intensities on a Nicolet R3 computer-controlled diffractometer using Mo Kα (λ = 0.71069 Å) graphite-monochromatized radiation. Cell dimensions, determined by least-squares refinement of the setting angles of 15 carefully centered reflections, are a = 19.991 (8) Å, b = 18.388 (7) Å, c = 25.510 (10) Å, and V = 9377 Å^3. The calculated density is 1.330 g cm^{-3} for Z = 4. The data collection was made by an ω-scan mode with scan range 0.8° and variable scan speed according to the intensities. The background counts were measured for half of the scan time with an offset of 1°.

Three standard reflections were measured every 100 reflections. Their intensities remained constant during the whole data collection. The intensities were processed as already described[44] by using an ignorance factor of p = 0.009 and correcting for shape anisotropy (μ(Mo Kα) = 5.5 cm^{-1}). From a total of 12 720 reflections collected ($3° \geq 2\theta \geq 50°$), a unique set of 3200, having $I \geq 3\sigma(I)$, were considered as observed and used in subsequent calculations. The crystallographic and data collection parameters are summarized in Table IV.

Solution and Refinement of the Structure. The structure was solved by the usual combination of Patterson and Fourier methods. The isotropic refinement converged at R = 0.081. Afterward, the hydrogen contributions were taken into account, and all the non-hydrogen atoms were allowed to vibrate anisotropically. The refinement converged at R = 0.057 and R_w = 0.069. A final electron density map did not reveal any residual peaks. The refinement was carried out with a full matrix, and the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o)^2$. Scattering factors and anomalous dispersion terms were taken from ref 45. The calculations were carried out on the Data General Eclipse MV8000II computer using local programs. Final positional parameters of the non-hydrogen atoms are listed in Table V. Anisotropic thermal parameters and a listing of observed and calculated structure factors are available as supplementary material.

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Registry No. **1**, 103500-17-0; **2**, 112220-32-3; **3**, 112220-33-4; **4**, 103500-16-9; **5**, 109124-78-9; **6a**, 112220-35-6; **6b**, 112220-37-8; **7a**, 112220-39-0; **7b**, 112220-41-4; **8**, 112220-42-5; **9**, 112220-44-7; **10**, 112220-46-9; **11**, 112220-47-0; **14**, 37843-35-9; $[Ru_2(\mu\text{-}Cl)_3(triphos)_2][BPh_4]$, 112220-49-2; $[RuCl_2(DMSO)_4]$, 59091-96-2.

Supplementary Material Available: Figure S1, showing a perspective view of all the heavy atoms of the cationic complex, and Table S1, containing anisotropic thermal parameters (3 pages); Table S2, listing observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Crystal Structure Determination of Dipotassium Dihydroxotrioxoruthenate(VI): Configuration of the Ruthenate Ion and Its Electronic Properties

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A crystal structure determination has been performed on the compound formerly called dipotassium ruthenate hydrate. This determination revealed a five-coordinate ruthenium, with three equatorial oxygens and two apical hydroxyl ions in a trigonal-bipyramidal arrangement, with symmetry approximately D_{3h}. The dimensions of the orthorhombic unit cell are a = 8.012 (2) Å, b = 10.588 (8) Å, and c = 6.687 (3) Å, in space group $P2_12_12_1$ and with Z = 4. It is shown that this structure is related to that of $BaRuO_3(OH)_2$. Molecular orbital energy levels have been calculated in the arrangement found according to the modified Wolfsberg–Helmholz method. The results of this calculation have been used to interpret the ligand field spectrum of the $RuO_3(OH)_2^{2-}$ ion and are in agreement with the magnetic susceptibility data from which followed that g = 1.93 and S = 1. It is shown that the previous lack of resemblance between calculated and measured spectra of $RuO_3(OH)_2^{2-}$ is mainly due to the erroneous assumption of tetrahedral coordination of the ruthenium ion.

Introduction

Until about 10 years ago, ruthenate was generally believed to occur only as tetraoxo anions, as reflected in the description of its chemistry[1] in the interpretation of ligand field spectra[2-6] and vibrational spectra.[7,8] However, in 1976 it was shown[9] that in $BaRuO_4\cdot H_2O$ the Ru(VI) ion is coordinated by five oxygens, in

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