stabilization of the transition state involving the Fe substantially out of the plane of the porphyrin ring.[3]

The trans effects in these dissociative reactions of tetragonal complexes differ in substance from the more widely investigated trans effects in square-planar complexes[10] since the energy barrier for dissociation of the ligand is independent of the nature of the entering group. The trans effect would be expected to closely parallel the trans influences in this case.

With respect to dissociation of isocyanide trans to amine ligands, the effects are similar to those observed for CO dissociation. The order of RNC lability trans to the various amines studied is pip > py > CH_3Im. The ligand exerting the largest trans effect on isocyanide dissociation is the isocyanide ligand itself. The rate of dissociation of RNC trans to RNC is a factor of 10^4 times faster than when RNC is trans to the amine ligands studied. The observed trans effect is consistent with the principle of antisymbiosis[11] and may be explained in terms of the two isocyanide ligands sharing σ and π orbitals on the metal. Attempts to detect either the $FePc(CO)_2$ or FePc(RNC)(CO) at room temperature up to 760 Torr of CO have been unsuccessful. It is well-known that strong π-acceptor ligands destabilize each other in mutually trans positions.

The kinetic data obtained in the 1-methylimidazole system allow one to evaluate the mutual trans effects of the trans ligands on each other since both CH_3Im and RNC dissociation from $FePc(RNC)(CH_3Im)$ may be measured. It is seen that the isocyanide ligand is less labile in the mixed complex while CH_3Im is more labile in the mixed complex. In the absence of steric interaction between the axial ligands and planar ligand, the iron may move out of the plane slightly in the direction of the preferred ligand. Thus we predict that in the $FePc(RNC)(CH_3Im)$ the iron may lie out of the plane toward the isocyanide ligand. Such a movement would be in the direction of the reaction coordinate for dissociation of CH_3Im but opposite to the direction of the reaction coordinate for RNC dissociation.

It is of interest that the trans effects observed in the phthalocyanine system are similar to those reported by Basolo et al.[5] for oxygen dissociation from iron porphyrin–oxygen complexes. In addition the relative labilities of the amines, piperidine, imidazole, and pyridine are similar in the two systems. These features appear to be transferable from one heme model to another and even to cobalt porphyrins.[12] The absolute features of a given heme model, i.e. how well it will bind CO or RNC and how labile these ligands will be, appear to be complicated functions of the in-plane ligand and its effect on the σ and π bonding to the axial ligands. In view of the number of factors involved in the lability of axial ligands in these systems and the large cis and trans effects observed, a large body of data will be required before a direct relationship between the structure of the macrocyclic tetradentate ligand and the lability of axial ligands coordinated to its Fe(II) complex becomes clear.

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Registry No. $FePc(RNC)_2$, 53596-02-4; $CH_3ImFePc(RNC)$, 62006-60-4; pyFePc(RNC), 62006-61-5; pipFePc(RNC), 62006-62-6; ImFePc(RNC), 62006-63-7; $(CH_3Im)_2FePc$, 55925-76-3; $(Im)_2FePc$, 16702-09-3; $(py)_2FePc$, 15650-77-8; $(pip)_2FePc$, 25232-79-5.

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Preparation, Characterization, and Reactions of the Thiocarbonyl Complexes Dicarbonyl(η^5-cyclopentadienyl)(thiocarbonyl)ruthenium(1+) and Dicarbonylbis(η^5-cyclopentadienyl)di-μ-thiocarbonyl-diruthenium

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The reaction of $CpRu(CO)_2^-$ successively with CS_2, CH_3I, and CF_3SO_3H yields the cationic thiocarbonyl complex $CpRu(CO)_2(CS)^+$. This complex reacts with N_3^- and N_2H_4 to give $CpRu(CO)_2NCS$ and with NCO^- to yield $CpRu(CO)_2CN$. With NaH, $CpRu(CO)_2(CS)^+$ is reduced to a mixture of the dimeric complexes $[CpRu(CO)(CS)]_2$ (major product) and $Cp_2Ru_2(CO)_3(CS)$. In both dimers the CS groups are in the bridging positions, and there is no evidence for nonbridged structures unlike $[CpRu(CO)_2]_2$ which exists partially in a nonbridged form. Infrared and proton NMR studies indicate that both $[CpRu(CO)(CS)]_2$ and $Cp_2Ru_2(CO)_3(CS)$ exist in cis and trans forms which interconvert too rapidly to be separated. The presence of the bridging CS groups does, however, slow the rate of isomerization. Qualitative studies indicate that this rate decreases in the order $[CpRu(CO)_2]_2 > Cp_2Ru_2(CO)_3(CS) > [CpRu(CO)(CS)]_2$. Mechanisms for these isomerizations are discussed. The preference of CS for a bridging over a terminal position in these molecules is rationalized in terms of the weakness of the $C\equiv S$ π bonds which lose little π-bond stabilization in moving from a terminal ($C\equiv S$) to a bridging ($>C=S$) position. These arguments also suggest that CO should have a lower preference for a bridging position than CS.

Introduction

One of the earliest reported[1] examples of a thiocarbonyl-containing complex was the cationic species $CpFe(CO)_2(CS)^+$, where Cp = η^5-C_5H_5. Subsequent investigation[2] revealed that the thiocarbonyl carbon is usually the preferred site of attack when $CpFe(CO)_2(CS)^+$ is exposed to nucleophiles. Recently it was found that interaction of $CpFe(CO)_2(CS)^+$ with sodium hydride generates the novel thiocarbonyl-bridged dimer

Table I. Carbonyl Stretching Frequencies (cm^{-1}) for Ru and Fe Derivatives

Complex	Solvent	M = Ru	M = Fe
$CpM(CO)_2C(S)SCH_3$	CS_2	2039 vs, 1985 vs[a]	2031 vs, 1983 vs[a]
	Hexane	2044 vs, 1991 vs	2035 vs, 1988 vs[b]
$CpM(CO)_2Cl$	C_6H_{12}	2056 vs, 2008 vs[c]	2054 vs, 2013 vs[c]
$CpM(CO)_2I$	CS_2	2047 vs, 2000 vs	2044 vs, 2000 vs[d]
$CpM(CO)_2CN$	CH_2Cl_2	2061 vs, 2014 vs[e]	2062 vs, 2016 vs[p]
$CpM(CO)_2SCN$	$CHCl_3$	2062 vs, 2013 vs[f]	2056 vs, 2013 vs[g]
	CS_2	2056 vs, 2007 vs	
$CpM(CO)_2NCS$	$CHCl_3$	2069 vs, 2023 vs[h]	2072 vs, 2035 vs[g]
	CS_2	2063 s, 2019 vs	
$CpM(CO)(CS)C(O)OCH_3$		2027 s, 1664 m[i,j]	2020 s, 1658 m[k,l]
$CpM(CO)(CS)I$	CS_2	2028 s[m]	2023 s[n]
$[CpM(CO)_2(CS)]CF_3SO_3$	CH_2Cl_2	2111 s, 2073 s[o]	2105 s, 2071 s[n,o]

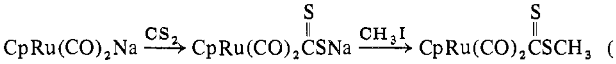
[a] ν(CS) 1031 and 1024 cm^{-1} for Ru and Fe, respectively, in CS_2. [b] Reference 6. [c] Reference 31. [d] Reference 35; in $CHCl_3$ [e] Reference 11. [f] ν(CN) 2117 and 2118 cm^{-1} for Ru and Fe, respectively. [g] Reference 9. [h] ν(CN) 2120 and 2123 cm^{-1} for Ru and Fe, respectively. [i] Hexane. [j] ν(CS) 1304 and 1316 cm^{-1} for Ru and Fe in CS_2. [k] Cyclohexane. [l] Reference 2. [m] ν(CS) 1308 (vs) and 1305 (vs) cm^{-1} for Ru and Fe. [n] Reference 36. [o] ν(CS) 1364 (s) and 1352 (s) cm^{-1} for Ru and ν(CS) 1353 (s) cm^{-1} for Fe. [p] Reference 37.

$[CpFe(CO)(CS)]_2$.[3] An interesting structural feature of $[CpFe(CO)(CS)]_2$ is the strong preference of the CS group for a bridging over a terminal position as compared to CO.

Since the chemistry of the cyclopentadienyl complexes of ruthenium often parallels that of iron, we were interested in preparing the ruthenium counterparts, $CpRu(CO)_2(CS)^+$ and $[CpRu(CO)(CS)]_2$, in order to compare the reactivities of $CpFe(CO)_2(CS)^+$ and $CpRu(CO)_2(CS)^+$ toward nucleophiles, as well as to examine the effect of the CS group in $[CpRu(CO)(CS)]_2$ on the bridged–nonbridged equilibrium which is known[4,5] to exist in solutions of $[CpRu(CO)_2]_2$.

Results and Discussion

Preparation of $CpRu(CO)_2(CS)^+$. Our approach to the synthesis of this cation was to use reactions which were successful for the preparation[6] of $CpFe(CO)_2(CS)^+$. A tetrahydrofuran (THF) solution of $CpRu(CO)_2Na$[7] when treated successively with CS_2 and CH_3I yielded the dithioester $CpRu(CO)_2C(S)SCH_3$ (eq 1). Although the ester was not isolated, the similarity of its infrared (Table I) and NMR spectra to those of $CpFe(CO)_2C(S)SCH_3$[6] as well as the expected molecular ion in its mass spectrum provided good evidence for its formation.



$$\mathrm{CpRu(CO)_2Na \xrightarrow{CS_2} CpRu(CO)_2C(=S)SNa \xrightarrow{CH_3I} CpRu(CO)_2C(=S)SCH_3} \quad (1)$$

Several routes for the cleavage of $CpRu(CO)_2C(S)SCH_3$ to $CpRu(CO)_2(CS)^+$ were examined. Exposure of $CpRu(CO)_2C(S)SCH_3$ in benzene to HCl gas followed by addition of NH_4PF_6 provided $[CpRu(CO)_2(CS)]PF_6$ in low yield with much of the dithioester remaining unchanged.[8]

Reaction of the dithioester with an acetone solution of $AgBF_4$ led to $[CpRu(CO)_2(CS)]BF_4$, but complete removal of the complex from soluble silver compounds could not be readily achieved. Trifluoromethanesulfonic acid proved to be the reagent of choice for carrying out the desired transformation. Addition of a diethyl ether solution of CF_3SO_3H to an ether solution of $CpRu(CO)_2C(S)SCH_3$ provided the desired product as the ether-insoluble $CF_3SO_3^-$ salt (eq 2).

$$\mathrm{CpRu(CO)_2C(S)SCH_3 + CF_3SO_3H \rightarrow [CpRu(CO)_2(CS)]CF_3SO_3 + CH_3SH} \quad (2)$$

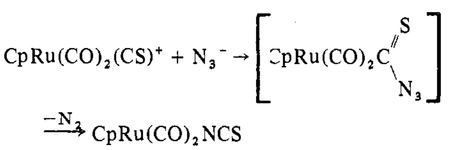
The characterization of $[CpRu(CO)_2(CS)]CF_3SO_3$ was based on analytical and spectroscopic results. Its NMR spectrum in acetone-d_6 showed a single Cp resonance at τ 3.66. The infrared spectrum in CH_2Cl_2 exhibited the expected two carbonyl absorptions at 2111 and 2073 cm^{-1} (Table I). In the thiocarbonyl region *two* bands at 1364 and 1352 cm^{-1} were observed. Only one ν(CS) absorption was expected and only one was observed for the analogous $[CpFe(CO)_2(CS)]CF_3SO_3$ (Table I). One might speculate that the occurrence of two ν(CS) bands in the Ru compound arises from a weak interaction between the $CF_3SO_3^-$ anion and the CS group.

Reactions of $CpRu(CO)_2(CS)^+$ with Nucleophiles. Previous studies of the reactions of $CpFe(CO)_2(CS)^+$ with certain nucleophiles[2] showed that attack usually took place at the thiocarbonyl carbon atom. We have investigated some of these same reactions with $CpRu(CO)_2(CS)^+$ and found similar results.

With NCO^-. When $CpRu(CO)_2(CS)^+$ was allowed to react with KNCO at room temperature, the product was identified as $CpRu(CO)_2CN$ from its infrared (Table I) and mass spectra. As for the reaction of the analogous iron complex,[2] the other product is presumed to be COS.

$$\mathrm{CpRu(CO)_2(CS)^+ + NCO^- \rightarrow CpRu(CO)_2(CN) + COS} \quad (3)$$

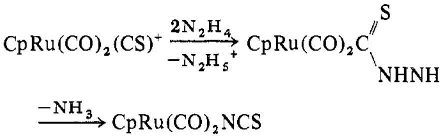
With N_3^-. The reaction of $CpRu(CO)_2(CS)^+$ with NaN_3 in acetone at room temperature yields the orange N-bound $CpRu(CO)_2NCS$ presumably[2] via a thioacyl azide intermediate (eq 4). Assignment of N-bound NCS ligand coordination is based on the observation of a C–S absorption at 829 cm^{-1} which is characteristic of N-bound thiocyanate complexes.[9] Moreover, the analogous $CpFe(CO)_2(CS)^+$ complex reacts with N_3^- to give N-bound $CpFe(CO)_2NCS$.[2]



$$\mathrm{CpRu(CO)_2(CS)^+ + N_3^- \rightarrow \left[CpRu(CO)_2C(=S)N_3\right] \xrightarrow{-N_2} CpRu(CO)_2NCS} \quad (4)$$

We have also repeated an earlier reaction[10] of $[CpRu(CO)_3]PF_6$ with KNCS to give a $CpRu(CO)_2CNS$ complex (CNS does not specify N or S bonding) which has a slightly but definitely different spectrum in the ν(CO) region (Table I) from that of the complex prepared by the above route. It appears that this latter product is either the S-bound isomer or a mixture of S- and N-bound isomers. The positions of the ν(CO) absorptions are very close to those (2061 and 2014 cm^{-1} in CH_2Cl_2) reported[11] for the S-bound isomer prepared by still another route. Thus, it tentatively appears that $CpRu(CO)_2(CS)^+$ with N_3^- and $CpRu(CO)_3^+$ with NCS^- give the N- and S-bound isomers, respectively. Further studies are required to make unequivocal assignments to the isomers and to examine conditions for their interconversion.

With N_2H_4. The reaction mixture of excess anhydrous hydrazine with $[CpRu(CO)_2(CS)]CF_3SO_3$ in CH_2Cl_2 solvent rapidly becomes orange. After 1 h of stirring at room temperature, an infrared spectrum of the solution showed two strong ν(CO) absorptions characteristic (Table I) of $CpRu(CO)_2NCS$. Thus, as for the iron analogue,[2] hydrazine converts the CS group to an NCS ligand (eq 5).



$$\mathrm{CpRu(CO)_2(CS)^+ \xrightarrow[-N_2H_5^+]{2N_2H_4} CpRu(CO)_2C(=S)NHNH_2 \xrightarrow{-NH_3} CpRu(CO)_2NCS} \quad (5)$$

With CH_3O^-. The reaction mixture of $CpRu(CO)_2(CS)^+$ with a suspension of excess sodium methoxide in THF became orange rapidly and gave several products of which only two were identified but could not be isolated (see eq 6). The infrared spectrum of a CS_2 solution of the reaction residue showed strong ν(CO) and ν(CS) bands at 2021 and 1304 cm^{-1}

$$\mathrm{CpRu(CO)_2(CS)^+ \xrightarrow[\text{THF}]{\mathrm{CH_3O^-}} CpRu(CO)(CS)C(O)OCH_3 + [CpRu(CO)(CS)]_2 + ?} \qquad (6)$$

which are very similar to those (Table I) of CpFe(CO)(CS)C(O)OCH$_3$.[2] We assign them to the analogous CpRu(CO)(CS)C(O)OCH$_3$. A medium-intensity band at 1655 cm^{-1} arises from ν(C═O) of the methoxycarbonyl portion of CpRu(CO)(CS)C(O)OCH$_3$. Terminal CO absorptions at 2012 and 1975 cm^{-1} and a medium band near 1125 cm^{-1} were assigned to the dimer [CpRu(CO)(CS)]$_2$ (see below).

The NMR spectrum of the reaction mixture in CS$_2$ contained singlet resonances at τ 4.67 and 6.57 for the Cp and OCH$_3$ protons of CpRu(CO)(CS)C(O)OCH$_3$. Absorptions at τ 4.79 and 4.77 were assigned to [CpRu(CO)(CS)]$_2$. Absorptions due to other products were observed in both the IR and NMR spectra but they could not be assigned unequivocally.

The generation of [CpRu(CO)(CS)]$_2$ in this reaction suggests that OCH$_3^-$ acts as a reducing agent. This was also found previously[10] in the reaction of CpRu(CO)$_3^+$ with CH$_3$O$^-$ to give some [CpRu(CO)$_2$]$_2$. In organic systems, the isopropoxide ion is known[12] to be an even better reducing agent. Therefore, CpFe(CO)$_2$(CS)$^+$ was reacted with NaOCH(CH$_3$)$_2$ in 2-propanol. This reaction rapidly gives a solution which contains all three coupling products, [CpFe(CO)$_2$]$_2$, Cp$_2$Fe$_2$(CO)$_3$(CS),[13] and [CpFe(CO)(CS)]$_2$,[3] as determined from an infrared spectrum of the reaction mixture.

With I$^-$. The [CpRu(CO)$_2$(CS)]CF$_3$SO$_3$ complex reacts slowly (18–20 h) with tetrabutylammonium iodide in refluxing CH$_2$Cl$_2$ to give CpRu(CO)$_2$I, which was also prepared by a literature method[10] and identified by its infrared spectrum. In addition, an uncharacterized residue was obtained which presumably contains polymeric CS.[14] There was no evidence for the hoped-for CpRu(CO)(CS)I. The I$^-$ replacement of CS, rather than CO, in this reaction contrasts with substitution reactions of other carbonyl–thiocarbonyl complexes, where CO replacement is common.

Preparation of [CpRu(CO)(CS)]$_2$ and Cp$_2$Ru$_2$(CO)$_3$(CS). The isolation[3] of [CpFe(CO)(CS)]$_2$ from the reaction of CpFe(CO)$_2$(CS)$^+$ with NaH suggested that the thiocarbonyl-bridged dimer [CpRu(CO)(CS)]$_2$ might also be obtained in this fashion. When CpRu(CO)$_2$(CS)$^+$ and NaH were stirred in dry THF, a color change from yellow to dark red-brown occurred. Workup and purification by chromatography on Florisil yielded two compounds (eq 7). The

$$\mathrm{CpRu(CO)_2(CS)^+ + NaH \xrightarrow{THF} [CpRu(CO)(CS)]_2 + Cp_2Ru_2(CO)_3(CS)} \qquad (7)$$

first-eluted compound was a red air-stable solid identified from spectral data and elemental analyses as [CpRu(CO)(CS)]$_2$ (yield 7–18%). The 70-eV mass spectrum exhibits a parent ion as well as a pattern characteristic of the presence of two Ru atoms. The [CpRu(CS)]$_2^+$ ion resulting from the loss of two CO groups is the base peak in the spectrum; no peaks corresponding to loss of CS instead of CO were present.

The second compound obtained from the NaH reaction, formed in *much* lower yield, was identified by spectroscopic means as having the composition Cp$_2$Ru$_2$(CO)$_3$(CS). This compound is an air-stable red-orange compound similar in appearance to [CpRu(CO)(CS)]$_2$. The difficulties in obtaining even very small samples in pure form precluded combustion analysis. The mass spectrum exhibits a parent ion for this composition and fragments corresponding to the loss of one, two, and three CO groups.

Several attempts were made to improve the yield of Cp$_2$Ru$_2$(CO)$_3$(CS). Reaction of an equimolar mixture of CpRu(CO)$_2$(CS)$^+$ and CpRu(CO)$_3^+$ with NaH did not increase the yield. The reaction of CpRu(CO)$_2$(CS)$^+$ with NaBH$_4$ produced neither of the dimeric thiocarbonyl complexes. There was no reaction between CpRu(CO)$_2^-$ and (C$_6$H$_5$O)$_2$C═S in THF at room temperature; the analogous reaction of CpFe(CO)$_2^-$ has been used successfully to prepare Cp$_2$Fe$_2$(CO)$_3$(CS).[13] With Cl$_2$C═S, CpRu(CO)$_2^-$ gave CpRu(CO)$_2$Cl as the only identifiable carbonyl-containing product. The recent preparation[15] of [CpMn(NO)(CS)]$_2$ by Zn reduction of CpMn(NO)(CS)I suggested the reaction of CpRu(CO)(CS)I (see below) and CpRu(CO)$_2$I. Refluxing the mixture with Zn dust in THF for 24 h gave no evidence for dimeric thiocarbonyl products.

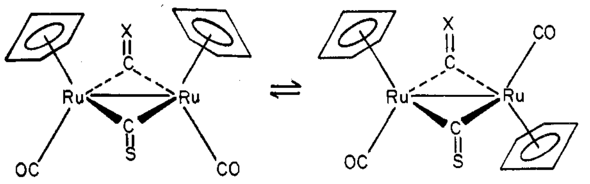
Table II. Carbonyl Stretching Frequencies (cm^{-1}) for [CpRu(CO)(CS)]$_2$ and Cp$_2$Ru$_2$(CO)$_3$(CS) in Various Solvents at Room Temperature

Solvent	ν(CO)^a		
	[CpRu(CO)(CS)]$_2$		
Hexane	2019 (10)	1981 (10.8)	
CS$_2$	2012 (10)	1976 (7.9)	
CHCl$_3$	2017 (10)	1980 (6.5)	
CH$_2$Cl$_2$	2010 (10)	1975 (5.2)	
CH$_3$CN	2005 (10)	1969 (3.4)	
	Cp$_2$Ru$_2$(CO)$_3$(CS)		
CS$_2$	2008 (10)	1969 (11.4)	1813 (5.5)
CH$_2$Cl$_2$	2006 (10)	1969 (5.9)	1806 (3.4)
CH$_3$CN	2000 (10)	1963 (2.9)	1806 (3.2)

^{a} Intensities (in absorbance units) relative to the high-frequency absorption are given in parentheses.

Spectral Properties of [CpRu(CO)(CS)]$_2$ and Cp$_2$Ru$_2$(CO)$_3$(CS). Infrared Spectra. Infrared absorptions in the ν(CO) region for [CpRu(CO)(CS)]$_2$ and Cp$_2$Ru$_2$(CO)$_3$(CS) in different solvents are given in Table II. For [CpRu(CO)(CS)]$_2$, two terminal ν(CO) absorptions are observed; there is no evidence for bridging CO groups. In the ν(CS) region only bridging ν(CS) frequencies are observed. Thus, in [CpRu(CO)(CS)]$_2$, as in its Fe analogue,[3] the CS groups take up the bridging positions. There is no evidence for terminal ν(CS) frequencies which eliminates the presence of a nonbridged structure such as occurs in [CpRu(CO)$_2$]$_2$.[4,5,19] The spectra of Cp$_2$Ru$_2$(CO)$_3$(CS) (Table II) show two ν(CO) bands for terminal CO groups and one for a bridging CO group. In the ν(CS) region there is evidence for only a bridging CS group. Thus, as in [CpRu(CO)(CS)]$_2$, the CS group has forced the molecule into bridging structures with the CS in the bridging position. There is no evidence for a nonbridged isomer.

The solvent dependence (Table II) of the ν(CO) band intensities of [CpRu(CO)(CS)]$_2$ and Cp$_2$Ru$_2$(CO)$_3$(CS) suggests that they exist as mixtures of the cis and trans isomers (eq 8). Since the cis and trans isomers of the analogous [CpFe(CO)(CS)]$_2$ were sufficiently nonfluxional that they could be isolated and the cis isomer characterized by an x-ray investigation,[3] ν(CO) assignments were readily made to absorptions in spectra of the isomers of [CpFe(CO)(CS)]$_2$. These assignments are given in Table III. By analogy, ν(CO) assignments were made to the cis and trans isomers of both



(8)

cis trans

X = O or S

Table III. ν(CO) and ν(CS) Data (cm^{-1}) for Binuclear Ru and Fe Compounds in CS_2 at Room Temperature

Compd	M = Ru	M = Fe
cis-$[CpM(CO)_2]_2$	2004, 1960, 1785^a	2001, 1957, 1785^b
trans-$[CpM(CO)_2]_2$	1960, 1785^a	1957, 1785^b
cis-$Cp_2M_2(CO)_3(CS)$	2008, 1969, 1813 1125	2006, 1969, 1811^c 1134
trans-$Cp_2M_2(CO)_3(CS)$	1969, 1813 1125	1969, 1811^c 1134
cis-$[CpM(CO)(CS)]_2$	2012, 1976, 1118	2011 vs, 1982 m, 1124 s^d
trans-$[CpM(CO)(CS)]_2$	1976, 1128	1979 vs, 1131 s^d

[a] Reference 5. [b] Reference 16. [c] Reference 13. [d] Reference 3.

$[CpRu(CO)(CS)]_2$ and $Cp_2Ru_2(CO)_3(CS)$; these are given in Table III. Also given in Table III are assignments made by Manning to isomers of the analogous $[CpFe(CO)_2]_2$[16] and $[CpRu(CO)_2]_2$[5] complexes, as well as assignments to the recently synthesized $Cp_2Fe_2(CO)_3(CS)$.[13] In all of these compounds the cis isomer shows two terminal ν(CO) absorptions, while the trans isomer exhibits only one: cis, 2000–2012 (vs), 1957–1982 (m) cm^{-1}; trans, 1957–1979 (vs) cm^{-1}. For those derivatives with bridging CO groups, the ν(CO) band occurs at 1785–1813 (m) cm^{-1}. Those with bridging CS groups exhibit a ν(CS) band at 1118–1134 (s) cm^{-1}.

In both the Fe and Ru series of $Cp_2M_2(CO)_x(CS)_{4-x}$ complexes, where $x = 2$–4, the ν(CO) frequencies for both the terminal and bridging CO groups increase (Table III) with increasing numbers of CS groups in the molecule. This is a trend which suggests that bridging CS, like terminal CS groups,[17,18] are more electron withdrawing than their CO analogues.

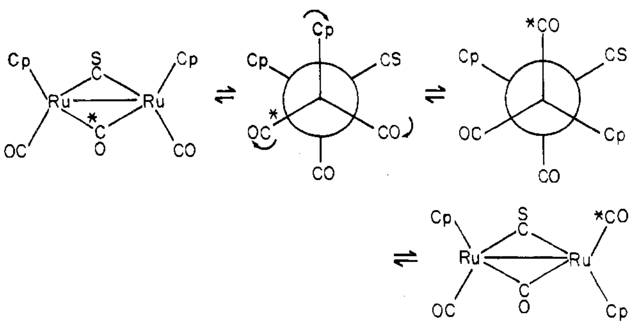
It should be noted that when a sample of $[CpRu(CO)(CS)]_2$ or $Cp_2Ru_2(CO)_3(CS)$ is dissolved in a solvent, the relative intensities of the ν(CO) bands reported in Table II are established immediately, and there is no change in intensities with time. This means that the cis–trans equilibrium (eq 8) is established very rapidly and the interconversion of isomers must be very fast.

The relative amounts of the cis and trans forms change with the polarity of the solvent (Table II), the cis form increasing in concentration with increasing solvent polarity. This trend was previously observed for $[CpFe(CO)_2]_2$[16] and $[CpRu(CO)_2]_2$.[5]

Proton NMR Spectra and Mechanisms of Cis–Trans Isomerization. Proton NMR spectra[3] of the isolated isomers of $[CpFe(CO)(CS)]_2$ in CS_2 solution at room temperature each showed a single Cp resonance: at τ 5.22 for the cis isomer and τ 5.32 for the trans. The spectrum of $[CpRu(CO)(CS)]_2$ under the same conditions shows two singlets at τ 4.78 and 4.80 corresponding to the two isomers of the complex present in solution. The relative intensity of the τ 4.78:τ 4.80 absorptions is approximately 3:2. Thus, the cis $\rightleftarrows$ trans interconversion is slow (i.e., both isomers are observed) on the NMR time scale, yet the infrared studies (see above) indicated that it must be complete within seconds at room temperature. This interconversion is, therefore, slower than that of $[CpRu(CO)_2]_2$.[4,19]

The proton NMR spectrum of $Cp_2Ru_2(CO)_3(CS)$ in CS_2 solution at ambient temperature shows only one cyclopentadienyl resonance (τ 4.84) despite the infrared results (see above) which indicated the presence of both cis and trans isomers under these conditions. The NMR singlet indicates that the cis and trans isomers are rapidly interconverting on the NMR time scale. When the solution is cooled, the singlet broadens reaching a coalescence temperature at −48 °C. Below this temperature the band splits into two distinct resonances at τ 4.83 and 4.85. The relative intensity of the τ 4.83:τ 4.85 peaks measured at −50 °C is approximately 2:1. This ratio decreases to about 1:1 at approximately −110 °C. The proton NMR studies indicate that the rate of cis $\rightleftarrows$ trans isomerization decreases in the order $[CpRu(CO)_2]_2 > Cp_2Ru_2(CO)_3(CS) > [CpRu(CO)(CS)]_2$. The bridging CS groups, therefore, markedly decrease the rate of isomerization.

Scheme I



The mechanism of cis–trans isomerization for $[CpFe(CO)_2]_2$ is now well understood.[19,20] The proposed Adams–Cotton mechanism also accounts for the limited data available for the cis–trans isomerization of $Cp_2Ru_2(CO)_3(CS)$ as shown in Scheme I. The general features of the mechanism involve (1) simultaneous opening of the CS and *CO bridges, (2) rotation by 120° around the Ru–Ru bond, and (3) closure of the trans CS and CO (formerly a terminal CO) to yield the trans isomer. The slower rate of isomerization of $Cp_2Ru_2(CO)_3(CS)$ as compared to that for $[CpRu(CO)_2]_2$ could be related to the preference of CS for a bridging rather than a terminal position thus requiring a higher activation energy for the bridge-opening steps. Also rotation in the nonbridged forms may be sterically or electronically[4] less favorable.

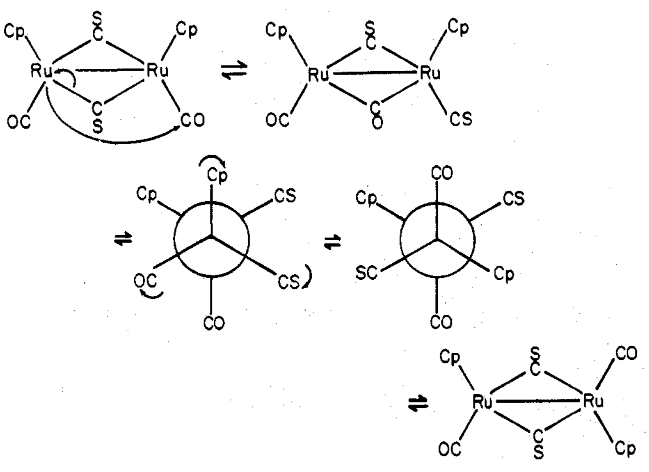
The cis–trans isomerization (eq 8) of $[CpRu(CO)(CS)]_2$, however, cannot take place by the Adams-Cotton mechanism. This can be seen in Scheme I by mentally replacing the bridging *CO by CS. In the cis to trans isomerization, one of the bridging CS groups is required to move into a terminal position. Since no terminal CS groups are observed even when the cis:trans ratio is changed by changing the solvent, this mechanism is eliminated.

One mechanism that could account for the isomerization involves simple dissociation of a terminal CO group yielding an unsaturated intermediate which could readd CO to give either the cis or trans isomer. This mechanism requires that the terminal CO groups exchange with free ^{13}CO in solution. However, when a cis–trans mixture of $[CpRu(CO)(CS)]_2$ was stirred in CS_2 solution under an atmosphere of ^{13}CO at room temperature for 3 days (isomerization proceeds within seconds under these conditions), there was no infrared evidence for exchange, thus eliminating this mechanism also.

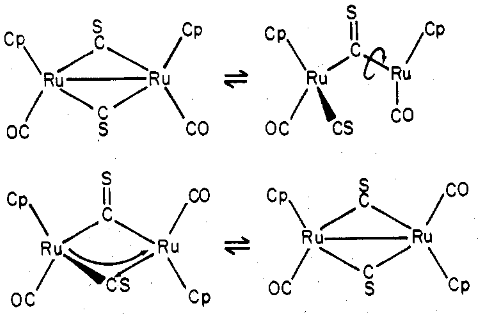
Recently it has been suggested[21] that $Cp_2Rh_2(CO)_3$, with one bridging and two terminal CO's, exchanges bridging and terminal CO groups by direct exchange of CO sites. As applied to $[CpRu(CO)(CS)]_2$, this interchange would proceed as shown in the first step of Scheme II. Subsequent steps to the trans isomer then simply involve the normal processes of the Adams–Cotton mechanism.

Another possible mechanism could involve cleavage of the Ru–Ru and one bridging CS bond to give an intermediate with planar coordination at the three-coordinate Ru on the right in Scheme III. Rotation around the bond to the bridging CS followed by closure will give the trans isomer. All presently available experimental evidence is consistent with the mechanisms given in both Schemes II and III and does not distinguish between them.

Scheme II



Scheme III



Reactions of $[CpRu(CO)(CS)]_2$ with Halogens. The carbonyl dimer $[CpRu(CO)_2]_2$ has been shown to react readily with Cl_2, Br_2, and I_2 in CH_2Cl_2 solution at room temperature to provide the halide complexes $CpRu(CO)_2X$ in high yield.[11] When $[CpRu(CO)(CS)]_2$ (7 μmol) was stirred with 27.6 mmol of I_2 in 10 mL of CH_2Cl_2 at room temperature, the red solution immediately turned red-brown. After 20 min, the solution was evaporated to dryness leaving a dark red-black product mixture. The presence of CpRu(CO)(CS)I in this mixture was supported by the mass spectrum which showed *m/e* peaks for $CpRu(CO)(CS)I^+$, $CpRu(CS)I^+$, and $CpRu(CS)^+$. Infrared bands at 2028 (vs) and 1308 (vs) cm^{-1} observed for a CS_2 solution of the mixture were assigned to the $\nu(CO)$ and $\nu(CS)$ absorptions, respectively. A resonance at τ 4.57 in the ^1H NMR spectrum of a CS_2 solution of the mixture was assigned to the Cp protons of this compound.

Another component of the mixture was $CpRu(CO)_2I$. Its presence was supported by peaks for $CpRu(CO)_2I^+$, $CpRu(CO)I^+$, and $CpRuI^+$ in the mass spectrum. Also, infrared absorptions at 2046 (s) and 1999 (s) cm^{-1} were identical with those of an authentic sample of $CpRu(CO)_2I$.[10] A resonance for the Cp protons of $CpRu(CO)_2I$ was observed at τ 4.61 in the ^1H NMR spectrum of the mixture.

Although two compounds were identified in the reaction mixture as summarized in eq 9, additional $\nu(CS)$ bands (at

$$[CpRu(CO)(CS)]_2 + I_2 \rightarrow CpRu(CO)(CS)I + CpRu(CO)_2I + ? \qquad (9)$$

1352 (m) and 1267 (s) cm^{-1}) in the infrared spectrum and an unassigned proton resonance (at τ 4.54) indicated the presence of at least one more complex, which was not characterized.

Conclusions

In $[CpRu(CO)(CS)]_2$ and $Cp_2Ru_2(CO)_3(CS)$, where the CS ligand could, in principle, occupy either a bridging or terminal position, the CS group always chooses the bridging site. The strong tendency of CS to occupy a bridging position is presumably also the reason that $[CpRu(CO)(CS)]_2$ and $Cp_2Ru_2(CO)_3(CS)$ exist in the bridging forms only, whereas $[CpRu(CO)_2]_2$ exists partially in the nonbridged form.[4,5] The existence of $[CpFe(CO)(CS)]_2$[3] and $[CpMn(NO)(CS)]_2$[15] in only the CS-bridged forms also supports a CS site preference for a bridging position.

A logical reason for this preference is the low stability (i.e., high energy) of the 2p–3p π bonds between the C and S.[17,22] Therefore, the migration of CS from a terminal (C≡S) to a bridging (>C=S) position results in the loss of little C—S π-bond stabilization. The stabilization gained by forming a bond to another metal apparently more than compensates for the loss in C≡S π bonding.

This poor C—S π bonding also is frequently cited as the reason for the high reactivity of thioketones (>C=S) in organic systems.[23] It also contributes to the very low bond energy of C≡S (166 kcal/mol)[24] as compared to that of its oxygen analogue, C≡O (256 kcal/mol).[25] The greater strength of π bonds between C and O means that CO should have a lesser tendency than CS to prefer a bridging position.

The weakness of the C≡S bond also probably accounts for the conversion of C≡S to C≡N—R in the reaction[26]

$$W(CO)_5(C{\equiv}S) + H_2NR \rightarrow W(CO)_5(C{\equiv}N{-}R) + H_2S \qquad (10)$$

In this case, the higher strength of the C≡N bond in the isocyanide (~212 kcal/mol, which is approximately the same for nitriles and isocyanides[27]) strongly favors the reaction. There are several other reactions[1,26,28] of the CS ligand with nucleophiles which result in the conversion of CS into products with less CS π bonding. The occurrence of these reactions may be understood, at least in part, in terms of the weakness of the CS π bonds.

Experimental Section

Methods and Materials. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., or Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Peak positions were determined with an expanded-scale recorder, calibrated in the carbonyl region with gaseous CO and DCl and in the thiocarbonyl region with polystyrene. Values are believed accurate within ±3 cm^{-1}. NMR spectra were recorded with a Varian A-60 or HA-100 instrument. Mass spectra were obtained with an AEI MS 902 spectrometer with exact masses based on ^{102}Ru unless specified otherwise.

All reactions were run under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was distilled from $LiAlH_4$. All other solvents and reagents were used as obtained from commercial sources with drying effected by storage over Linde 4-A molecular sieves in some cases. $RuCl_3 \cdot xH_2O$ was provided by Matthey Bishop, Inc. Thallium cyclopentadienide was prepared by a published procedure[29] or purchased from Alfa Products, Danvers, Mass. Before use, NaH was freed of mineral oil by washing with benzene and hexane.

Preparation of $[CpRu(CO)_2]_2$ and $CpRu(CO)_2Cl$. $[Ru(CO)_3Cl_2]_2$ was prepared by the method of Cleare and Griffith.[30] The reaction of $[Ru(CO)_3Cl_2]_2$ (from ~2 g of $RuCl_3 \cdot xH_2O$) with thallium cyclopentadienide was carried out by refluxing with 75 mL of dry THF for 20 h. After cooling, the solution was filtered through Celite, and the flask and frit were washed with THF. After solvent evaporation, the residue was extracted with benzene until the extracts were faintly colored. The benzene extracts were filtered and evaporated to give a red-orange mixture of $[CpRu(CO)_2]_2$[7] and $CpRu(CO)_2Cl$,[31] whose ratio (determined by infrared analysis) varied depending on the quantity of TlCp employed. Use of 1.5 mol of TlCp/mol of Ru gave a product which was largely $[CpRu(CO)_2]_2$. These mixtures of $[CpRu(CO)_2]_2$ and $CpRu(CO)_2Cl$ were employed directly in the preparation of $CpRu(CO)_2Na$.

Preparation of $[CpRu(CO)_2(CS)]CF_3SO_3$. Solutions of $CpRu(CO)_2Na$ (often contaminated with $[CpRu(CO)_2]_2Hg$[31]) in THF were prepared by Na/Hg (1.5 g of Na in 20 mL of Hg) reduction of $CpRu(CO)_2Cl$ (2.55 g, 10 mmol) or a mixture of $CpRu(CO)_2Cl$ and $[CpRu(CO)_2]_2$ in a 100-mL three-neck flask with a stopcock attached to the bottom. This reaction was carried out with vigorous stirring for 45 min at room temperature. (The extent of reaction was monitored by adding small aliquots of the reaction mixture to CH_3I, evaporating the solvents, and examining hexane extracts in the ν(CO) region. The intensity of the 2023 (s) and 1965 (s) cm^{-1} bands of $CpRu(CO)_2CH_3$[32] indicated the amount of $CpRu(CO)_2^-$ formed in the reduction. Attempted reductions using C_8K[33] or $NaK_{2.8}$[34] gave little evidence for the formation of $CpRu(CO)_2^-$.)

The excess amalgam was drained through the bottom stopcock. (In reductions of $CpRu(CO)_2Cl$, the excess Na/Hg was in the form of a sand which was very difficult to remove from the reaction vessel. However, subsequent additions of CS_2 and CH_3I may be carried out in the presence of the Na/Hg if contact is kept to a minimum.) Two milliliters (29 mmol) of dry CS_2 was added. After 20–30 s of stirring, CH_3I (0.8 mL, 12.5 mmol) was added and the stirring was continued for 5 min more. (Use of too large an excess of CH_3I gives large amounts of $CpRu(CO)_2I$.)

The dark red solution was filtered through Celite, and the flask and frit were washed with THF. The THF solution was evaporated to a dark viscous oil which was extracted with benzene until the extracts were a faint yellow. The benzene portions were filtered through Celite, combined, and evaporated. The resulting residue was extracted in a similar fashion with diethyl ether. After filtration, the ether solution was concentrated to ca. 50 mL. At this stage the solution contains impure dithioester, $CpRu(CO)_2C(S)SCH_3$. Generally this solution would be converted to $[CpRu(CO)_2(CS)]CF_3SO_3$ as described in the next section; however, in one preparation, the dithioester was partially purified by chromatography on Florisil using 9:1 (v/v) C_6H_6/CH_2Cl_2 as the eluent. Reasonably pure material could be obtained from the later fractions. ^{1}H NMR (CS_2): τ 4.69 (s, C_5H_5) and τ 7.50 (s, CH_3). Mass spectrum (70 eV): $CpRu(CO)_2C(S)SCH_3^+$, $CpRu(CO)C(S)SCH_3^+$, $CpRu(CS)SCH_3^+$, $CpRuC(S)S^+$, and $CpRu(CS)^+$. Mol wt: calcd for $C_9H_8O_2S_2Ru$, 313.9003; found, 313.9004.

$[CpRu(CO)_2(CS)]CF_3SO_3$. To the ether solution (above) of $CpRu(CO)_2C(S)SCH_3$ was added dropwise (under N_2) a solution of 1.2 mL of CF_3SO_3H (Aldrich) in 25 mL of ether with good stirring. After 30 min, the product was collected by filtration and washed with ether. Recrystallization from acetone/ether provided the tan compound (0.995 g) in 24% overall yield, based on $CpRu(CO)_2Cl$. IR (CH_2Cl_2): 2111 (s), 2073 (s), 1364 (s), and 1352 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 3.66 (s, C_5H_5). Anal. Calcd for $C_9H_5O_5F_3S_2Ru$: C, 26.03; H, 1.21; S, 15.44. Found: C, 26.19; H, 1.28; S, 15.40.

$CpRu(CO)_2CN$. A dry Schlenk tube was charged with $[CpRu(CO)_2(CS)]CF_3SO_3$ (92 mg, 0.22 mmol) and KNCO (179 mg, 2.2 mmol). Dry acetone (20 mL) was added, and the solution was stirred for 90 min at room temperature. After the solvent was evaporated off under reduced pressure, the residue was dissolved in a small volume of CH_2Cl_2, the solution was filtered, and hexane was added to give a cloudy solution. Cooling to −20 °C gave a brown product (35 mg, 64%) which was washed with hexane. Its infrared spectrum in CH_2Cl_2 solution (2129 (w), 2064 (vs), and 2016 (vs) cm^{-1}) was the same within experimental error as that reported[11] for $CpRu(CO)_2CN$ prepared by a different method. Mass spectrum (70 eV): $CpRu(CO)_2(CN)^+$, $CpRu(CO)(CN)^+$, and $CpRu(CN)^+$ (base peak). Mol wt: calcd for $C_8H_5NO_2Ru$, 248.9357; found, 248.9369.

Reaction of $[CpRu(CO)_2(CS)]CF_3SO_3$ with NaN_3. A (44 mg, 0.10 mmol) sample of $[CpRu(CO)_2(CS)]CF_3SO_3$ was stirred at room temperature with NaN_3 (80 mg, 1.23 mmol) in 15 mL of acetone and 0.5 mL of H_2O for 20 min. After evaporation to dryness, the product was extracted with $CHCl_3$. The $CHCl_3$ solution was filtered and concentrated to a small volume. Addition of hexane and cooling to −20 °C gave 20 mg (71%) of the orange-brown solid product, $CpRu(CO)_2NCS$. IR ($CHCl_3$): 2120 (m), 2069 (vs), and 2023 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): τ 4.51 for C_5H_5. Mass spectrum (70 eV): $CpRu(CO)_2(NCS)^+$, $CpRu(CO)(NCS)^+$, $CpRu(NCS)^+$, $CpRuN^+$ (weak). Mol wt: calcd for $C_8H_5NO_2SRu$, 280.9078; found, 280.9102. Anal Calcd for $C_8H_5NO_2SRu$: C, 34.28; H, 1.79. Found: C, 33.86; H, 2.25.

Reaction of $[CpRu(CO)_3]PF_6$ with KNCS. Similar to a previous procedure,[10] samples of $[CpRu(CO)_3]PF_6$[10] (202 mg, 0.5 mmol) and KNCS (818 mg, 8.4 mmol) were stirred with 20 mL of acetone and 1 mL of H_2O. The solution which immediately turned yellow was evaporated to dryness after 16 h. After extraction of the residue with $CHCl_3$, the extract was filtered and concentrated to a small volume. Addition of hexane and cooling to −20 °C provided a sticky orange solid, $CpRu(CO)_2SCN$. IR ($CHCl_3$): 2117 (m), 2062 (vs), and 2013 (vs) cm^{-1}; literature values for the compound prepared by this procedure are 2123 (m), 2053 (vs), and 2008 (vs) cm^{-1} in methylcyclohexane solvent;[10] for $CpRu(CO)_2SCN$ prepared by another route,[11] the values are 2118, 2061, and 2012 cm^{-1} in CH_2Cl_2. ^{1}H NMR ($CHCl_3$): τ 4.42 for C_5H_5; this compares with τ 4.50 reported previously for $CpRu(CO)_2SCN$.[11]

Preparation of $[CpRu(CO)(CS)]_2$ and $Cp_2Ru_2(CO)_3(CS)$. In a Schlenk tube were placed 79 mg (0.19 mmol) of $[CpRu(CO)_2(CS)]CF_3SO_3$, a 10–15 molar excess of NaH, and finally 12 mL of dry THF. Gas evolution was immediate and the color rapidly changed to a dark red-brown. After 15 min of stirring, the solution was filtered, and the flask and frit were washed with a little THF. Following evaporation of the solvent, the product mixture was extracted with several small (1–2 mL) portions of benzene. The benzene extracts were placed on a 1 × 30 cm Florisil/hexane column. Elution with benzene brought down a broad red band which was collected and evaporated to yield 8 mg, 18% of $[CpRu(CO)(CS)]_2$. Further purification may be effected by dissolving in a minimum volume of CS_2, adding a large volume (>20-fold) of hexane, and cooling at −20 °C for several days. IR (CS_2): 2012 (s), 1976 (s), 1128 (s), and 1118 (sh) cm^{-1}. ^{1}H NMR (CS_2): τ 4.78 and 4.80 of approximate ratio 3:2. Mass spectrum (70 eV): prominent ions $Cp_2Ru_2(CO)_2(CS)_2^+$, $Cp_2Ru_2(CO)(CS)_2^+$, $Cp_2Ru_2(CS)_2^+$, $Cp_2Ru_2(CS)^+$, $CpRu_2(CS)^+$, and Cp_2Ru^+. Mol wt: calcd for $C_{14}H_{10}O_2S_2Ru_2$, 477.8196; found, 477.8223. Anal. Calcd for $C_{14}H_{10}O_2S_2Ru_2$: C, 35.28; H, 2.11; S, 13.45. Found: C, 35.02; H, 1.89; S, 13.33.

Further elution with benzene provided $Cp_2Ru_2(CO)_3(CS)$ containing a small amount of $[CpRu(CO)(CS)]_2$. IR (CS_2): 2008 (s), 1969 (s), 1813 (m), and 1125 (m) cm^{-1}. ^{1}H NMR (CS_2): τ 4.84 (singlet). Mass spectrum (70 eV): observed ions $Cp_2Ru_2(CO)_3(CS)^+$, $Cp_2Ru_2(CO)_2(CS)^+$, $Cp_2Ru_2(CO)(CS)^+$, and $Cp_2Ru_2(CS)^+$. Mol wt: calcd for $C_{14}H_{10}O_3SRu_2$ as ^{99}Ru, 455.8473; found, 455.8418.

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Registry No. $CpRu(CO)_2C(S)SCH_3$, 61930-80-1; $CpRu(CO)_2I$, 31781-83-6; $CpRu(CO)_2SCN$, 31741-74-9; $CpRu(CO)_2NCS$, 31741-75-0; $CpRu(CO)(CS)C(O)OCH_3$, 61930-81-2; $CpRu(CO)(CS)I$, 61930-82-3; $[CpRu(CO)_2(CS)]CF_3SO_3$, 61930-84-5; *cis*-$Cp_2Ru_2(CO)_3(CS)$, 61930-77-6; *trans*-$Cp_2Ru(CO)_3(CS)$, 61930-76-5; *cis*-$[CpRu(CO)(CS)]_2$, 61930-78-7; *trans*-$[CpRu(CO)(CS)]_2$, 61989-65-9; $[CpRu(CO)_2]_2$, 12132-87-5; $CpRu(CO)_2Cl$, 32611-12-4; $[Ru(CO)_3Cl_2]_2$, 22594-69-0; $CpRu(CO)_2Na$, 61930-79-8; $CpRu(CO)_2CN$, 36180-35-5; NaN_3, 26628-22-8; $[CpRu(CO)_3]PF_6$, 31741-71-6.

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Porphyrins and Large Metal Ions. Crystal and Molecular Structure of 2,3,7,8,12,13,17,18-Octaethylporphinatochlorothallium(III)

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The structure of 2,3,7,8,12,13,17,18-octaethylporphinatochlorothallium(III), $C_{36}H_{44}N_4TlCl$, has been determined from three-dimensional diffractometer data. A total of 8776 independent reflections were measured. The compound crystallizes in the triclinic space group $P\bar{1}$ with a unit cell of $a = 14.063$ (3) Å, $b = 14.983$ (6) Å, $c = 10.202$ (5) Å, $\alpha = 99.05$ (4)°, $\beta = 104.07$ (2)°, $\gamma = 66.92$ (3)°. There are two molecules in the unit cell. The structure was solved by heavy-atom methods and refined by least-squares techniques to a final conventional R index of 0.053 for the 5553 reflections having $I \geq 2\sigma_I$. Molecules of solvation included in the solid state consist of one dichloromethane molecule and one water molecule per formula unit. The metalloporphyrin is a square-pyramidal complex with a chlorine atom as the axial ligand. The average Tl–N bond length is 2.212 (6) Å, while the Tl–Cl distance is 2.449 (3) Å. The metal ion is located 0.69 Å out of the mean plane of the four pyrrole nitrogen atoms. The porphinato core is highly expanded with an average radius of 2.10 Å. The macrocycle shows some deviation from planarity, exhibiting a net doming toward the metal ion.

Introduction

In recent years thallium salts have become increasingly more important as reagents in organic syntheses.[1,2] Thallic salts are powerful but selective oxidizing agents due to the ease of reduction from the +3 to the +1 oxidation state. Several reactions between porphyrins and thallic salts have been reported; for example, treatment of 2,3,7,8,12,13,17,18-octaethylporphine (H_2(OEP)) with thallium(III) trifluoroacetate (TTFA) gave[3,4] a metalloporphyrin characterized as in Figure 1. In the absence of trifluoroacetic acid the thallium(III) porphyrin was stable toward oxidation by excess TTFA,[4] presumably owing to the high oxidation potential ($E^1{}_{1/2} = 1.00$ V vs. SCE)[5] of the macrocycle containing a thallium ion. However, addition of acid[3,6] or treatment of zinc(II) porphyrins ($E^1{}_{1/2} = 0.63$ V) with TTFA[7] causes formation of oxophlorins, dioxoporphodimethenes, and other meso (methine) oxygenated macrocycles. On the other hand, porphyrins protected from methine oxidation by formation by their thallium(III) complexes are susceptible to efficient modification of labile side chains[8,9] using thallium reagents.

In addition to its role as a reagent, thallium presents interesting steric properties because of its size. Here we report the steric arrangement obtained when a large metal ion is complexed with the porphyrin moiety. The radius of the porphinato core has been found to contract to 1.93 Å to accommodate a small ion like Ni(II)[10] or expand to ~2.09 Å to accommodate a large ion like Sn(IV).[11,12] The complexation of a very large metal like Tl(III) might be expected to have a significant effect on the geometry of the porphyrin, as well as on its chemical reactivity. The original formulation (Figure 1) suggested a six-coordinate complex, though it was stressed that there was no evidence for coordination of the water molecule to the metal atom.[4] We wished to determine whether or not the porphyrin core would be able to expand enough to form a six-coordinate complex or whether the metal ion would lie significantly out of the plane of the macrocycle, as is found for high-spin iron(II) metalloporphyrins.[13] The latter possibility would probably result in a five-coordinate complex. There have been very few x-ray structure determinations reported for thallium complexes;[14-16] relatively little is known about their stereochemistry. For these reasons a study of thallium(III) octaethylporphyrin was begun.

Table I. Crystal Data for $(C_{36}H_{44}N_4)TlCl\cdot CH_2Cl_2\cdot H_2O$[a]

$a = 14.063$ (3) Å
$b = 14.983$ (6) Å
$c = 10.202$ (5) Å
$\alpha = 99.05$ (4)°
$\beta = 104.07$ (2)°
$\gamma = 66.92$ (3)°
$V = 1913.4$ Å^3

Fw 875.6
$Z = 2$
$d_{calcd} = 1.52$ g/cm^3
$\mu = 44.87$ cm^{-1} (Mo Kα radiation)
Systematic absences: none
Space group $P\bar{1}$

[a] Estimated standard deviation of least significant figures shown in parentheses.

Experimental Section

Crystals of the title compound almost always proved to be twinned. However, the nature of the twinning was such that it was possible to distinguish the members of the twins by morphology. A large crystal was grown slowly over a period of several months from a mixture of dichloromethane, methanol, and dioxane. Due to the apparent formation of hydrogen chloride in this mixture, the hydroxide ligand originally present was replaced by chloride; similar substitutions with cyanide and iodide have also been reported.[4] It was possible to cleave the crystal and separate the twins. The reflections measured during the data collection were unquestionably single peaks, indicating a clean separation of the twins. The fragment used for intensity measurements was a reddish plate. Except for the {010} planes, which are the prominent faces of the plate, the crystal faces were not well defined. However the other faces were approximated by the following indices (number following indices is the distance in millimeters from an arbitrary point inside the crystal): $(\bar{1}\bar{1}0)$ (0.205), (110) (0.198), $(3\bar{2}0)$ (0.158), $(\bar{3}20)$ (0.164), (001) (0.262), $(00\bar{1})$ (0.285), and $(\bar{2}\bar{1}1)$ (0.219).

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