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Formation of a Stable Complex, $RuCl_2(S_2CPPh_3)(PPh_3)_2$, Containing an Unstable Zwitterion from the Reaction of $RuCl_2(PPh_3)_3$ with Carbon Disulfide

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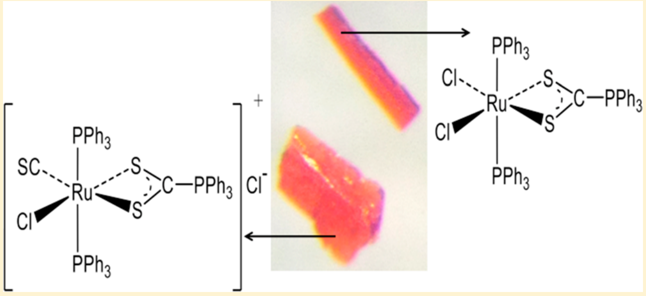
Supporting Information



ABSTRACT: New insight into the complexity of the reaction of the prominent catalyst $RuCl_2(PPh_3)_3$ with carbon disulfide has been obtained from a combination of X-ray diffraction and ^{31}P NMR studies. The red-violet compound originally formulated as a cationic π-CS_2 complex, $[RuCl(\pi\text{-}CS_2)(PPh_3)_3]Cl$, has been identified as a neutral molecule, $RuCl_2(S_2CPPh_3)(PPh_3)_2$, which contains the unstable zwitterion S_2CPPh_3. In the absence of $RuCl_2(PPh_3)_3$, there is no sign of a reaction between triphenylphosphine and carbon disulfide, although more basic trialkylphosphines form red adducts, S_2CPR_3. Despite the presence of an unstable ligand, $RuCl_2(S_2CPPh_3)(PPh_3)_2$ is remarkably stable. It survives melting at 173−174 °C intact, is stable to air, and undergoes reversible electrochemical oxidation to form a monocation. When the reaction of $RuCl_2(PPh_3)_3$ with carbon disulfide is conducted in the presence of methanol, crystals of orange $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl\cdot 2MeOH$ and yellow $RuCl_2(CS)(MeOH)(PPh_3)_2$ also form. ^{31}P NMR studies indicate that the unsymmetrical dinuclear complex $(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_2Cl$ is the initial product of the reaction of $RuCl_2(PPh_3)_3$ with carbon disulfide. A path connecting the isolated products is presented.

■ INTRODUCTION

The reaction of carbon disulfide with transition-metal complexes has been used to prepare a variety of new ligands.[1,2] Thus, carbon disulfide itself can serve as a ligand, as it does in the π complex, $Pt(\pi\text{-}CS_2)(PPh_3)_2$,[3] but it also serves as a source of the unstable carbon monosulfide ligand. It can also undergo insertion reactions to form dithiocarboxylate and dithiocarbamato ligands. Recent attention on the reactivity of carbon disulfide toward transition-metal complexes has focused on the chemical relationship between carbon dioxide and carbon disulfide and the utility of creating new catalytically active metal complexes for the conversion of carbon dioxide into polymers, fuels, and value-added chemicals.[4−9]

We became interested in the reactivity of carbon disulfide toward the active hydrogenation catalyst $RuCl_2(PPh_3)_3$ when we began to study the interaction between $RuCl_2(PPh_3)_3$ and fullerenes. $RuCl_2(PPh_3)_3$ crystallizes as a square pyramid with an agostic C−H···Ru interaction that involves one of the triphenylphosphine ligands.[10] In solution, $RuCl_2(PPh_3)_3$ is fluxional and prone to triphenylphosphine loss.[11,12] We wondered whether $RuCl_2(PPh_3)_3$ might react with C_{60} like several related molecules, e.g., $RhH(CO)(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$, to form stable coordination complexes, which might also have catalytic activity.[13−15]

Initially, we considered appropriate solvents that would allow us to react $RuCl_2(PPh_3)_3$ with C_{60} and other fullerenes. Under an inert atmosphere, $RuCl_2(PPh_3)_3$ dissolves in chloroform, acetone, benzene, and ethyl acetate to produce yellow-brown solutions that turn green upon exposure to air.[16] Of these solvents, only benzene is a suitable solvent for fullerenes. We observed that $RuCl_2(PPh_3)_3$ dissolved in carbon disulfide, a good solvent for fullerenes,[17,18] to give a red solution. However, we also became aware that $RuCl_2(PPh_3)_3$ was chemically reactive toward carbon disulfide and that there was an extensive and sometimes discombobulating literature on the topic.

Several studies of the reaction between $RuCl_2(PPh_3)_3$ and carbon disulfide have been documented and a number of ruthenium compounds isolated from that reaction. The structures proposed for these ruthenium complexes are shown in Scheme 1. Wilkinson and co-workers reported that the red solution obtained by boiling a carbon disulfide solution of $RuCl_2(PPh_3)_3$ under reflux for 5 min produced a red-violet compound (**A**) with the proposed structure $[RuCl(\pi\text{-}CS_2)(PPh_3)_3]Cl$ in 23% yield along with an orange dimeric complex, $Cl(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_2Ru(PPh_3)_2(CS)Cl$.[19] The yield of the red-violet complex could be increased to 92% when the

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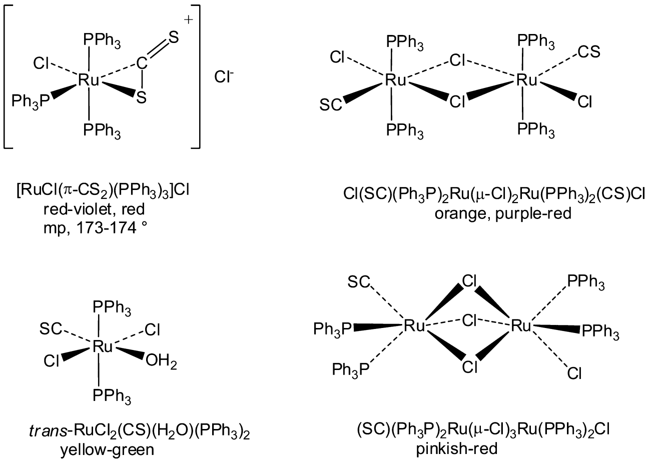
Scheme 1. Structures Assigned to the Previously Reported Products Obtained from the Reaction of $RuCl_2(PPh_3)_3$ with Carbon Disulfide



reaction was run in the presence of added triphenylphosphine in a carbon disulfide/methanol mixture. The reaction of $RuCl_2(PPh_3)_3$ with carbon disulfide was reexamined by Stephenson and co-workers, who obtained compound **A** in only 8% yield.[20,21] They also obtained the dimer $Cl(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_2Ru(PPh_3)_2(CS)Cl$ and found a third species, pinkish-red $(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_2Cl$, to be present. That third complex, $(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_2Cl$, was the only compound in Scheme 1 to be characterized by single-crystal X-ray diffraction.[22] Its $^{31}P\{^1H\}$ NMR spectrum consisted of two AB quartets, in accordance with the structure shown in Scheme 1, where two inequivalent triphenylphosphine ligands are coordinated to two different ruthenium centers.[22] Finally, Brothers and Roper obtained *trans*-$RuCl_2(CS)(H_2O)(PPh_3)_2$ by boiling a mixture of $RuCl_2(PPh_3)_3$, triphenylphosphine, and carbon disulfide in toluene for 1 week.[23] The authors did not specify the source of the coordinated water molecule.

Here we report our studies of the reaction between $RuCl_2(PPh_3)_3$ and carbon disulfide and show that compound **A** is neither a salt nor a π-CS_2 complex.

■ RESULTS AND DISCUSSION

Preparation and Structure of $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$. $RuCl_2(PPh_3)_3$ dissolves in carbon disulfide to form a red solution. Red-violet crystals precipitate from this solution over a matter of hours. The first crystals to form have been identified as $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ through single-crystal X-ray diffraction. Figure 1 shows a drawing of the complex. The two triphenylphosphine ligands are situated trans to one another, while the two chloride ligands are cis. The remaining two coordination positions are occupied by the zwitterionic S_2CPPh_3 ligand. Some bond distances for this complex are given in Table 1. The RuS_2CP portion involving the zwitterionic S_2CPPh_3 ligand is planar. Thus, the sum of the three angles about carbon is 358.84°. The structure parameters for $RuCl_2(S_2CPPh_3)(PPh_3)_2$ are similar to those of other transition-metal complexes containing zwitterionic S_2CPR_3 ligands.[24]

While solutions of $RuCl_2(PPh_3)_3$ are generally sensitive to air and turn green after exposure to the atmosphere, a solution of $RuCl_2(PPh_3)_3$ in carbon disulfide is quite stable in air, and crystals of pure $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ can be readily prepared without recourse to inert atmosphere methods. However, crystals of $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ show an unusual affinity for glass and strongly adhere to the surface of the vessel in which they are prepared. Consequently, we have found it advantageous to prepare crystals of $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ in long glass tubes up to 1 m in length. This technique has allowed us to obtain pure $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ in 20% yield based on $RuCl_2(PPh_3)_3$. However, if the reaction proceeds as shown in Scheme 2 (vide infra), the yield is 40%. Additionally, samples of $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ readily lose crystallinity upon drying, apparently because of loss of the solvate molecules. $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ is soluble in dichloromethane and is sparingly soluble in carbon disulfide, ether, benzene, toluene, and chloroform. It reacts with the polar solvents methanol and nitromethane. Crystallization of this material from a toluene/carbon disulfide mixture produces crystals of another solvate, $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$0.25CS_2$·$0.25C_7H_8$. This material has also been examined by single-crystal X-ray diffraction. The structure of the ruthenium complex is the same in both solvates. While it was more convenient to conduct the reactions described above in air, we also conducted these reactions under air-free conditions and produced the same products.

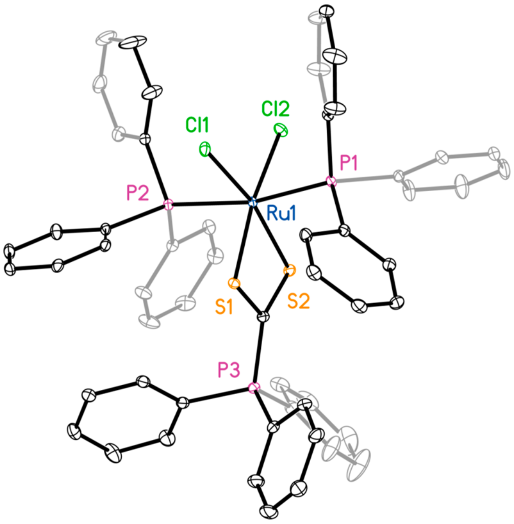


Figure 1. Molecular structure of red-violet $RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$ drawn with 50% thermal contours. The disordered phenyl group, hydrogen atoms, and solvate CS_2 are omitted for clarity.

The reactions between triphenylphosphine or $RuCl_2(PPh_3)_3$ and carbon disulfide have been monitored by ^{31}P NMR spectroscopy. When carbon disulfide is added to a solution of triphenylphosphine in dichloromethane-d_2, no shift of the ^{31}P resonance is observed either at room temperature or at temperatures as low as −80 °C. This solution is colorless. Thus, we have found no evidence for the formation of the hypothetical adduct S_2CPPh_3, although it has been known for a rather long time that the adduct S_2CPEt_3 can be isolated as a red crystalline solid.[25,26] It appears that the zwitterionic S_2CPR_3 can only be isolated when the tertiary phosphine is strongly basic.

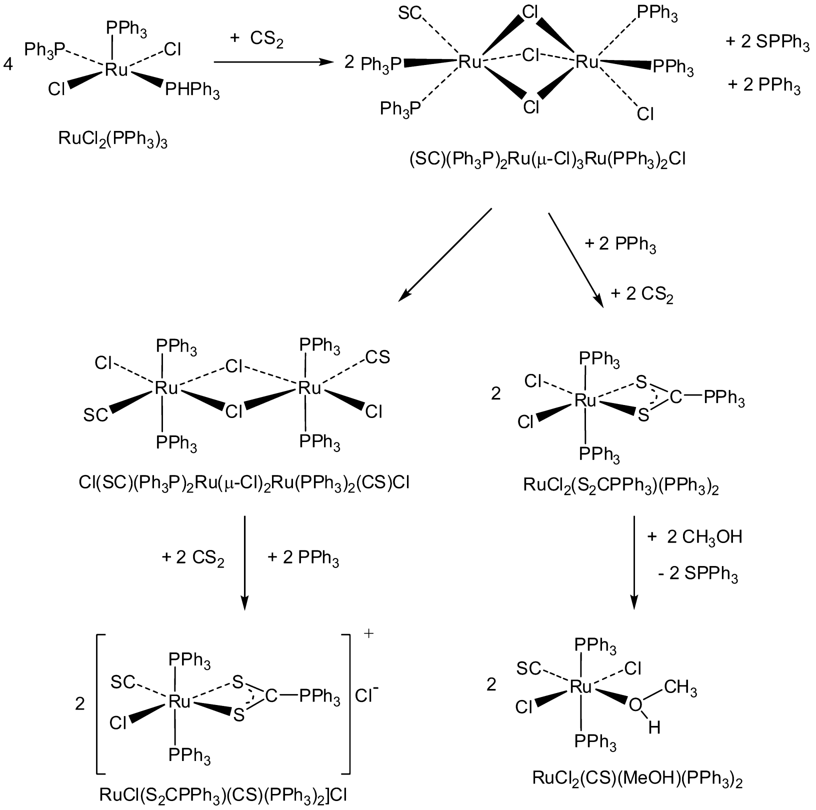
The ^{31}P NMR spectra from the reactions between $RuCl_2(PPh_3)_3$ and carbon disulfide are shown in Figure 2. Trace A shows the spectrum of $RuCl_2(PPh_3)_3$ in a dichloromethane-d_2 solution at 20 °C. At this temperature, $RuCl_2(PPh_3)_3$ is fluxional and produces a broad resonance,

Table 1. Selected Bond Distances and Angles for Ruthenium Complexes

	$RuCl_2(S_2CPPh_3)(PPh_3)_2\cdot CS_2$	$[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl\cdot 2MeOH$	$[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6)\cdot 1.35CH_2Cl_2$	$RuCl_2(CS)(MeOH)(PPh_3)_2$
Distances, Å				
Ru1−Cl1	2.4751(8)	2.4199(5)	2.4058(6)	2.3827(3)
Ru1−Cl2	2.4670(9)			2.3858(5)
Ru1−P1	2.3727(9)	2.4179(5)	2.4031(6)	2.3984(6)
Ru1−P2	2.4012(9)	2.4016(4)	2.4047(6)	2.3941(6)
Ru1−S1	2.3038(8)	2.3234(4)	2.3227(6)	
Ru1−S2	2.3139(8)	2.5322(5)	2.5389(6)	
S1−C55	1.691(3)	1.6692(13)	1.667(2)	
S2−C55	1.689(3)	1.6819(13)	1.684(2)	
P3−C55	1.792(3)	1.8087(13)	1.811(2)	
Ru1−C56		1.8162(13)	1.816(2)	
C56−S3		1.5651(14)	1.559(2)	
Ru1−C37				1.769(2)
C37−S1				1.573(2)
Ru1−O1				2.2503(15)
Angles, deg				
Cl1−Ru1−Cl2	101.69(3)			163.908(19)
Cl1−Ru1−P1	84.12(3)	84.507(12)	86.466(19)	92.949(18)
Cl1−Ru1−P2	89.05(3)	87.674(12)	85.515(19)	91.589(18)
Cl2−Ru1−P1	85.93(3)			87.706(18)
Cl2−Ru1−P2	87.21(3)			87.337(18)
P1−Ru1−P2	169.14(2)	171.986(12)	171.88(2)	174.977(19)
P1−Ru1−S1	96.71(3)	91.278(12)	95.761(19)	
P1−Ru1−S2	98.15(3)	91.661(13)	89.867(19)	
P2−Ru1−S1	91.94(3)	96.704(13)	92.31(2)	
P2−Ru1−S2	90.64(3)	90.226(13)	91.92(2)	
S1−Ru1−S2	73.01(3)	71.307(12)	70.90(2)	
S1−Ru1−Cl1	91.92(3)	162.610(12)	164.44(2)	
S1−Ru1−Cl2	166.34(3)			
S2−Ru1−Cl1	164.91(3)	91.912(12)	93.75(2)	
S2−Ru1−Cl2	93.36(3)			
S1−C55−S2	108.74(16)	115.58(5)	114.97(13)	
S1−C55−P3	123.80(16)	121.87(8)	120.79(14)	
S2−C55−P3	126.30(16)	122.55(7)	124.25(14)	
C56−Ru1−Cl1		105.95(4)	105.49(7)	
C56−Ru1−S1		91.03(4)	89.93(7)	
C56−Ru1−S2		162.01(4)	160.73(7)	
C56−Ru1−P1		92.14(4)	90.27(7)	
C56−Ru1−P2		88.44(4)	90.65(7)	
S3−C56−Ru1		173.69(9)	172.86(15)	
O1−Ru1−Cl1				79.37(4)
O1−Ru1−Cl2				84.60(4)
O1−Ru1−P1				87.75(4)
O1−Ru1−P2				90.98(4)
O1−Ru1−C37				173.38(8)
Cl1−Ru1−C37				94.51(7)
Cl2−Ru1−C37				101.57(7)
P1−Ru1−C37				90.06(7)
P2−Ru1−C37				91.72(7)
S1−C37−Ru1				175.96(14)

labeled a.[27,28] As others have noted,[27,28] triphenylphosphine dissociates from this complex to produce resonance b and some dimeric ruthenium complexes, which are the cause of the other resonances in the 53−37 ppm range. Immediately after the addition of carbon disulfide, the spectrum shown in trace B was produced. The resonances of $RuCl_2(PPh_3)_3$ and triphenylphosphine have vanished, while a set of new resonances labeled c, which are due to the previously characterized dinuclear complex $(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_2Cl$,[29] have appeared along with the singlet (d), which is due to triphenylphosphine sulfide. The spectrum shown in trace C was obtained 2 h after the addition of carbon disulfide. Two new resonances, labeled e, appeared. These resonances are due to the accumulation of $RuCl_2(S_2CPPh_3)(PPh_3)_2$. Shortly after this time, crystals of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ began to form on the walls of the NMR sample tube. Trace D shows the spectrum obtained by dissolving crystals of $RuCl_2(S_2CPPh_3)(PPh_3)_2\cdot CS_2$ in dichloro-

Scheme 2. Reaction Paths for the Transformations Reported in This Paper



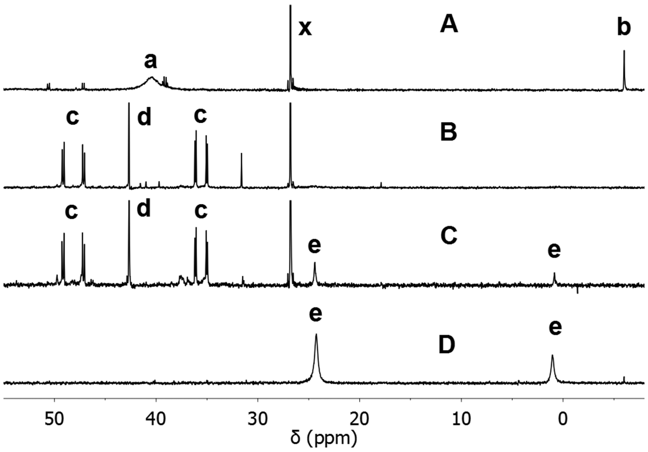


Figure 2. $^{31}P\{^1H\}$ NMR spectra at 20 °C of the reaction between a dichloromethane-d_2 solution of $RuCl_2(PPh_3)_3$ and carbon disulfide. Trace A shows the spectrum before the addition of carbon disulfide. The peak labeled a arises from $RuCl_2(PPh_3)_3$, peak b comes from triphenylphosphine, and peak x is due to triphenylphosphine oxide added as a reference. Trace B shows the spectrum after the addition of carbon disulfide. The two AB doublets labeled c are due to $(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_2Cl$, and the singlet d comes from triphenylphosphine sulfide. Trace C shows the same sample after 2 h. The resonances labeled e are due to the formation of $RuCl_2(S_2CPPh_3)(PPh_3)_2$. Trace D shows the spectrum of crystals of $RuCl_2(S_2CPPh_3)(PPh_3)_2{\cdot}CS_2$ dissolved in dichloromethane-d_2.

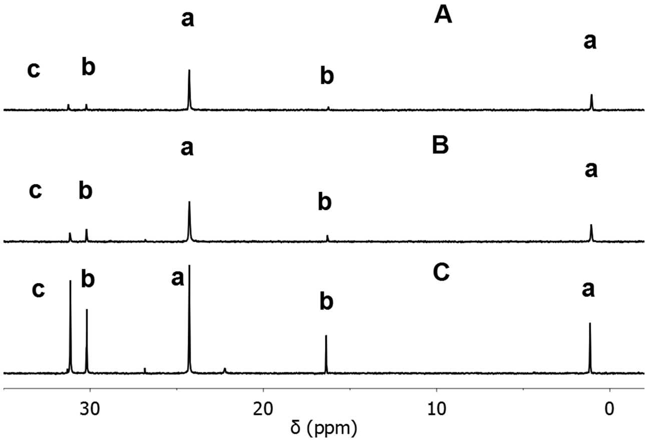


Figure 3. $^{31}P\{^1H\}$ NMR spectra at 20 °C dichloromethane-d_2 solutions of the products that precipitate from the reaction of $RuCl_2(PPh_3)_3$ and triphenylphosphine with carbon disulfide. Traces A–C are acquired from the material that precipitates after 1, 2, and 3 days, respectively. The peaks labeled a arise from $RuCl_2(S_2CPPh_3)(PPh_3)_2$, peaks labeled b arise from $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$, while resonances labeled c are presumed to arise from the dimer $(SC)Cl(Ph_3P)_2Ru(\mu\text{-}Cl)_2Ru(PPh_3)_2Cl(CS)$.

methane-d_2. Two resonances in a 2:1 intensity ratio appear as expected for this complex.

We have also examined the material that precipitates from a carbon disulfide solution containing $RuCl_2(PPh_3)_3$ and triphenylphosphine. Figure 3 shows $^{31}P\{^1H\}$ NMR spectra of dichloromethane-d_2 solutions of the products that precipitate after 1, 2, and 3 days. Initially, the precipitate is largely $RuCl_2(S_2CPPh_3)(PPh_3)_2{\cdot}CS_2$ (resonances labeled a), but over time, the salt $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$ (resonances labeled b) is produced as well along with what we presume is the dimer $(SC)Cl(Ph_3P)_2Ru(\mu\text{-}Cl)_2Ru(PPh_3)_2Cl(CS)$ (resonance labeled c). The reported chemical shift for this complex in chloroform-d is 31.3 ppm. We were not able to obtain this material in crystalline form suitable for X-ray diffraction.

$RuCl_2(S_2CPPh_3)(PPh_3)_2$ is a remarkably stable molecule, particularly when one considers the fact that the free ligand, S_2CPPh_3, cannot be detected in solutions of triphenylphosphine in carbon disulfide. No new resonances appeared in the ^{31}P NMR spectrum after a solution of $RuCl_2(S_2CPPh_3)(PPh_3)_2 \cdot CS_2$ in dichloromethane-d_2 had been stored for 3 days. A crystalline sample of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ melted sharply at 173−174 °C: after cooling and reheating again, it melted sharply at the same temperature. Thus, the complex is quite thermally stable. The cyclic voltammogram shown in Figure 4 reveals that $RuCl_2(S_2CPPh_3)(PPh_3)_2$ undergoes a reversible oxidation to form the cation $[RuCl_2(S_2CPPh_3)(PPh_3)_2]^+$, which we presume is a ruthenium(III) complex. Only irreversible processes were seen upon attempted reduction of $RuCl_2(S_2CPPh_3)(PPh_3)_2$. However, the electrochemistry of the cation $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]^+$ reveals a reversible reduction, but no oxidation to form the corresponding ruthenium(III) compound. The inability to observe oxidation of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]^+$ to the ruthenium(III) state is probably due to the ability of the thiocarbonyl group to stabilize the ruthenium(II) state and the cationic nature of this complex.

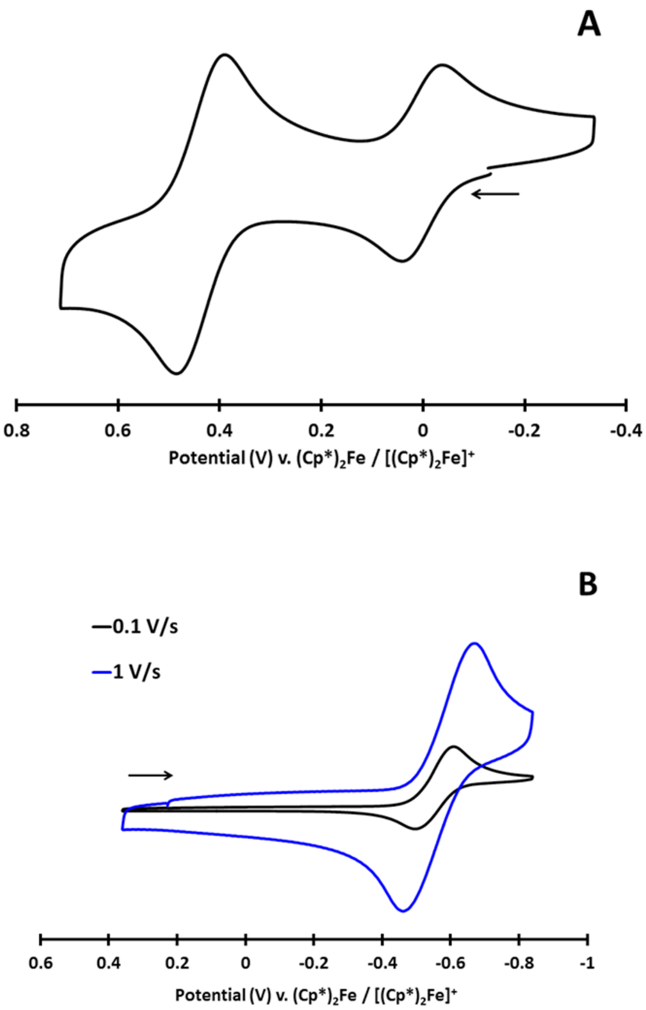


Figure 4. Cyclic voltammetry of (A) $RuCl_2(S_2CPPh_3)(PPh_3)_2 \cdot CS_2$ with decamethylferrocene present as an internal standard and (B) $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl \cdot 2MeOH$ in a dichloromethane solution with 0.10 M Bu_4NPF_6 as the supporting electrolyte at a glassy carbon electrode. Potentials are referenced to the decamethylferrocene/decamethylferrocinium couple.

Formation of the Cation $RuCl(S_2CPPh_3)(CS)(PPh_3)_2]^+$. The cation $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]^+$ was obtained by reacting $RuCl_2(PPh_3)_3$ with carbon disulfide in the presence of triphenylphosphine and methanol. This was a heterogeneous reaction, with the two solvents forming two layers. After removal of carbon disulfide through evaporation under vacuum, a mixture of four different types of crystals was produced. These crystals were manually separated to yield orange blocks of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl \cdot 2MeOH$ along with colorless blocks of triphenylphosphine, red-violet needles of $RuCl_2(S_2CPPh_3)(PPh_3)_2$, and yellow blocks of $RuCl_2(CS)(MeOH)(PPh_3)_2$. The identity of each crystal type was determined by single-crystal X-ray diffraction.

The structure of orange $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl \cdot 2MeOH$ is shown in Figure 5. It contains two triphenylphosphine ligands in trans positions, a chelating S_2CPPh_3 ligand, and a chloride and a carbon monosulfide ligand in cis positions. While the RuS_2CP portion of this cation is planar, as it is in $RuCl_2(S_2CPPh_3)(PPh_3)_2$, the two Ru−S bond distances are decidedly different [Ru1−S1, 2.3234(4) Å; Ru1−S2, 2.5322(5) Å], with the longer Ru−S distance occurring with the sulfur atom that is positioned trans to the carbon monosulfide ligand, which, as expected, exerts a strong structural trans effect.

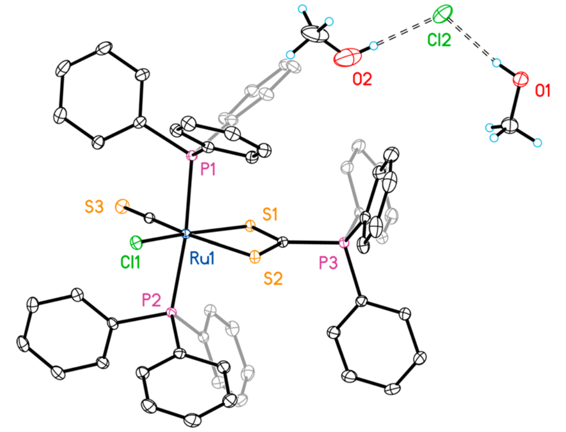


Figure 5. Asymmetric unit of orange $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl \cdot 2MeOH$ drawn with 50% thermal contours showing hydrogen bonding to the chloride anion. Most hydrogen positions and the disorder in one of the two methanol sites were omitted for clarity.

We found that we could selectively precipitate the orange salt $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6) \cdot 1.35CH_2Cl_2$ by treating a dichloromethane solution of the mixture of products from the reaction of $RuCl_2(PPh_3)_3$ with carbon disulfide and triphenylphosphine with ammonium hexafluorophosphate. Orange crystals of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6) \cdot 1.35CH_2Cl_2$ were examined by X-ray diffraction. As seen in the data in Table 1, the cation in this salt has dimensions that are nearly identical with those found in the chloride salt, $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl \cdot 2MeOH$.

The $^{31}P\{^1H\}$ NMR spectrum of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl \cdot 2MeOH$ in a dichloromethane-d_2 solution shows two resonances: a triplet ($J_{P,P}$ = 4 Hz) at 16.4 ppm due to the S_2CPPh_3 ligand and a doublet ($J_{P,P}$ = 4 Hz) at 30.15 ppm assigned to the two equivalent triphenylphosphine ligands with an intensity ratio of 1:2. A dichloromethane-d_2 solution of

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$[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6)\cdot 1.35CH_2Cl_2$ produces a similar spectrum but has added resonances from the anion.

The absorption spectra obtained from $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl\cdot 2MeOH$ and $RuCl_2(S_2CPPh_3)(PPh_3)_2\cdot CS_2$ are shown in Figure 6. For the most part, these spectra are similar. However, the spectrum of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ shows low-energy features at 805 nm with a shoulder at 1050 nm, but similar features are absent from the spectrum of the cation. These visible absorptions are likely associated with the RuS_2C unit because the related free ligand S_2CPEt_3 is itself red. Crystals of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl\cdot 2MeOH$ and $RuCl_2(S_2CPPh_3)(PPh_3)_2\cdot CS_2$ are not luminescent at room temperature or at 77 K.

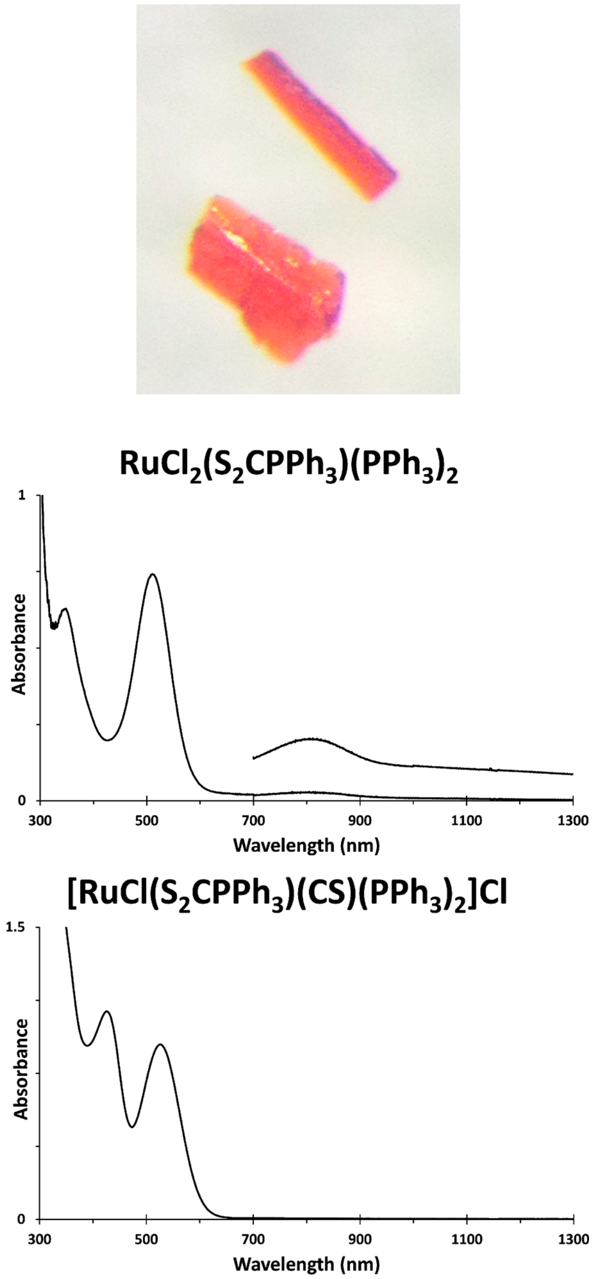

Figure 6. Top: Photographs of a red-violet needle of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ (upper) and an orange block of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl\cdot 2MeOH$ (lower). Bottom: UV/vis absorption spectra of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ and $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$ in a dichloromethane solution.

Preparation and Identification of $RuCl_2(CS)(MeOH)(PPh_3)_2$. Yellow blocks of $RuCl_2(CS)(MeOH)(PPh_3)_2$ formed in small amounts in the reaction of $RuCl_2(PPh_3)_3$ with carbon disulfide, triphenylphosphine, and methanol. Additionally, we have found that $RuCl_2(CS)(MeOH)(PPh_3)_2$ is formed, along with triphenylphosphine sulfide, by sonication of a sample of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ in methanol. The $^{31}P\{^1H\}$ NMR spectrum of the isolated complex in a dichloromethane-d_2 solution shows a simple singlet at 31.1 ppm. The IR spectrum shows a characteristic $\nu(CS)$ at 1280 cm^{-1}. The crystallographically obtained structure of the complex is shown in Figure 7. The complex is six-coordinate with trans triphenylphosphine ligands, cis chloride ligands, a carbon monosulfide ligand, and a coordinated methanol ligand. While this appears to be a rather ordinary six-coordinate ruthenium(II) complex, the Cl1−Ru−Cl2 angle [163.908(19)°] is somewhat bent so that both chloride ions are drawn toward the methanol ligand. The mode of preparation of this complex suggests that the carbon monosulfide ligand is obtained from the S_2CPPh_3 ligand in its precursor, $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]^+$. $RuCl_2(CS)(MeOH)(PPh_3)_2$ has been obtained previously through another route.[21] Note that $RuCl_2(CS)(MeOH)(PPh_3)_2$ is similar to the product $RuCl_2(CS)(OH_2)(PPh_3)_2$ that Brothers and Roper produced from $RuCl_2(PPh_3)_3$ via a rather lengthy reaction.[23]

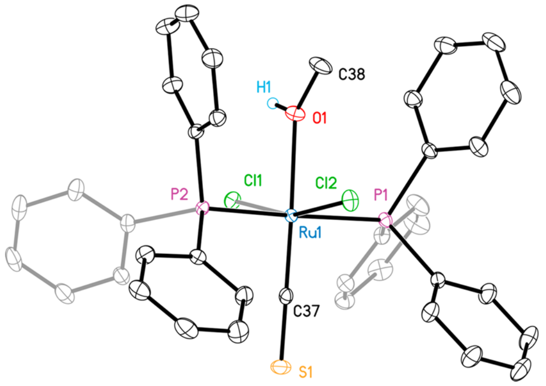

Figure 7. Structure of yellow $RuCl_2(CS)(MeOH)(PPh_3)_2$ drawn with 50% thermal contours.

■ CONCLUSIONS

The reaction between $RuCl_2(PPh_3)_3$ and carbon disulfide is complex, with several different compounds emerging at different time intervals. Scheme 2 summarizes the products that have been obtained from the reactions of $RuCl_2(PPh_3)_3$ and carbon disulfide and shows the reaction paths that connect them. All compounds shown have been identified by ^{31}P NMR spectroscopy and by single-crystal X-ray diffraction with the exception of $Cl(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_2Ru(PPh_3)_2(CS)Cl$, whose crystal structure has not been obtained despite our efforts and those of others. The initial formation of the unsymmetrical dinuclear complex $(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_2Cl$, as demonstrated by the data in Figure 2, contributes to the complexity of the situation because two different ruthenium coordination environments are produced by its creation. Fragmentation of this dimer can yield the hypothetical fragments "$(SC)(Ph_3P)_2RuCl_2$" and "$Ru(PPh_3)_2Cl_2$". The latter can react with carbon disulfide and triphenylphosphine to form $RuCl_2(S_2CPPh_3)(PPh_3)_2$, which initially precipitates from solution. As shown in Scheme 2, the "$(SC)(Ph_3P)_2RuCl_2$" fragment can dimerize to form $Cl(SC)(Ph_3P)_2Ru(\mu\text{-}Cl)_2Ru(PPh_3)_2(CS)Cl$, which can subsequently react with carbon disulfide and triphenylphosphine to form $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$. The ruthenium complexes shown in Scheme 2 all involve ruthenium(II). The formation of triphenylphosphine sulfide is always accompanied by the formation of a coordinated CS ligand according to the reaction:

$$CS_2 + PPh_3 \rightarrow CS\ (\text{as a ligand}) + SPPh_3$$

The red-violet compound (**A**), which had been proposed to be the π-carbon disulfide adduct $[RuCl(\pi\text{-}CS_2)(PPh_3)_3]Cl$, has now been correctly identified as $RuCl_2(S_2CPPh_3)(PPh_3)_2$, a remarkably stable complex that contains the otherwise unstable zwitterionic S_2CPPh_3 ligand. Note that the melting point reported for **A** (173−174 °C) is identical with that obtained by us for $RuCl_2(S_2CPPh_3)(PPh_3)_2$. The misidentification of **A** as a salt may have resulted from coprecipitation of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$ with $RuCl_2(S_2CPPh_3)(PPh_3)_2$ because both are formed in the reaction of $RuCl_2(PPh_3)_3$ with carbon disulfide. Additionally, both have similar colors, as shown in Figure 6, and similar melting points. Previous workers have not recognized the presence of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$ in the $RuCl_2(PPh_3)_3$/carbon disulfide reaction. Although there are several studies of coordination complexes of the zwitterionic S_2CPR_3 ligands, where the R substituents are aliphatic groups and the free ligand can itself be isolated,[2] there are few reports of complexes containing the unstable S_2CPPh_3 ligand and no reports of the chemical behavior of these compounds. Thus, the reaction of carbon disulfide with $IrCl(CO)(PPh_3)_2$ and triphenylphosphine has been shown by X-ray diffraction studies to produce the cation $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]^+$, which was originally formulated as the π-CS_2 complex $[Ir(\pi\text{-}CS_2)(CO)(PPh_3)_2]^+$.[30,31] By analogy, Clark et al. suggested that $[RuCl(\pi\text{-}CS_2)(PPh_3)_3]Cl$ might be better formulated as $RuCl_2(S_2CPPh_3)(PPh_3)_2$, but they did not investigate the matter any further. The reaction of the radical cation $[Fe(CO)_3(PPh_3)_2](PF_6)$ with carbon disulfide was reported to yield a mixture of $[Fe(S_2CPPh_3)(CO)_2(PPh_3)_2](PF_6)_2$ and $Fe(CO)_3(PPh_3)_2$.[32,33] $[Fe(S_2CPPh_3)(CO)_2(PPh_3)_2](PF_6)_2$ was not characterized crystallographically.

EXPERIMENTAL SECTION

Materials. $RuCl_2(PPh_3)_3$ was prepared according to a reported method.[16] Carbon disulfide, triphenylphosphine, and methanol were purchased commercially and used as received.

$RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$. A sample of $RuCl_2(PPh_3)_3$ (199 mg, 0.21 mmol) was dissolved in 8 mL of CS_2, forming a dark-red solution within 2 min. This solution was filtered into a 5-mm-diameter open glass tube, approximately 1 m in length, and capped with a rubber septum. Red-violet needles formed within 1 h. The red-violet needles were collected after 24 h (yield: 43 mg, 20%). Mp: 173−174 °C. $^{31}P\{^1H\}$ NMR (dichloromethane-d_2 at 298 K): δ 24.26 (s), 1.03 (s). FTIR (cm^{-1}): 3050, 2924, 2855, 1584, 1519, 1479, 1432, 1184, 1102, 1090, 1070, 1028, 988, 951, 739, 716, 684, 563, 508. UV/vis [dichloromethane; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 348 (2100), 510 (2400), 805 (95).

Reaction of $RuCl_2(PPh_3)_3$ and Triphenylphosphine in Methanol/Carbon Disulfide. A sample of 310 mg (0.33 mmol) of $RuCl_2(PPh_3)_3$ and 510 g (1.9 mmol) of triphenylphosphine was placed in a 100 mL flask equipped with a stir bar. This flask was vacuum-pumped and nitrogen-backfilled five times. In a separate flask, carbon disulfide (10 mL) and methanol (10 mL) were purged with nitrogen for 15 min. During the purge, methanol and carbon disulfide formed two layers, which were mixed using a stir bar. This solvent mixture was transferred by a cannula into the primary flask, forming a red-violet two-phase solution. The mixture was evaporated under vacuum, with

Table 2. Crystal Data for the Ruthenium Complexes

	$RuCl_2(S_2CPPh_3)(PPh_3)_2$·$CS_2$	$[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$·2MeOH
chemical formula	$C_{56}H_{45}Cl_2P_3RuS_4$	$C_{58}H_{53}Cl_2O_2P_3RuS_3$
fw	1111.04	1143.06
radiation source, λ (Å)	0.7749	0.71073
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
T (K)	100(2)	90(2)
a (Å)	12.855(3)	12.8823(17)
b (Å)	13.242(3)	12.8979(16)
c (Å)	17.825(4)	16.549(2)
α (deg)	72.625(4)	82.295(4)
β (deg)	68.880(3)	72.142(4)
γ (deg)	61.107(3)	87.187(4)
V (Å^3)	2449.2(10)	2593.5(6)
Z	2	2
d_{calc} (g cm^{-3})	1.507	1.464
μ (mm^{-1})	0.923	0.662
$F(000)$	1136	1176
cryst size (mm^3)	0.25 × 0.10 × 0.08	0.21 × 0.16 × 0.13
reflns collected	79995	46032
data/param/restraints	18182/621/0	17221/641/0
R(int)	0.0520	0.0257
R1 [$I > 2\sigma(I)$][a]	0.0426	0.0273
wR2 (all data)[a]	0.1030	0.0639
largest difference peak and hole (e Å^{-3})	1.336 and −2.566	0.676 and −0.611

	$[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6)$·$1.35CH_2Cl_2$	$RuCl_2(CS)(MeOH)(PPh_3)_2$
chemical formula	$C_{57.10}H_{47.20}Cl_{3.20}F_6P_4RuS_3$	$C_{38}H_{34}Cl_2OP_2RuS$
fw	1281.92	772.62
radiation source, λ (Å)	0.71073	0.7749
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
T (K)	90(2)	100(2)
a (Å)	14.4932(11)	12.5945(7)
b (Å)	23.7721(17)	16.5294(9)
c (Å)	16.6197(12)	16.4597(9)
α (deg)	90	90
β (deg)	102.8060(17)	102.182(3)
γ (deg)	90	90
V (Å^3)	5583.6(7)	3349.4(3)
Z	4	4
d_{calc} (g cm^{-3})	1.525	1.532
μ (mm^{-1})	0.719	1.021
$F(000)$	2601	1576
cryst size (mm^3)	0.26 × 0.16 × 0.13	0.05 × 0.05 × 0.05
reflns collected	94222	42744
data/param/restraints	18591/701/22	6194/411/0
R(int)	0.0334	0.0626
R1 [$I > 2\sigma(I)$][a]	0.0455	0.0246
wR2 (all data)[a]	0.1196	0.0599
largest difference peak and hole (e Å^{-3})	2.452 and −1.323	0.339 and −0.445

[a] For data with $I > 2\sigma(I)$, $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] For all data, $wR2 = \{\sum[w(F_o - F_c)^2]/\sum[w(F_o^{\,2})^2]\}^{1/2}$.

preferential loss of carbon disulfide. By the time most of the carbon disulfide was removed, crystals formed. The crystals were extracted and examined microscopically. The precipitate was determined to contain four different types of crystals: colorless blocks of PPh_3, orange blocks of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl{\cdot}2MeOH$, red-violet needles of $RuCl_2(S_2CPPh_3)(PPh_3)_2$, and yellow blocks of $RuCl_2(CS)(MeOH)(PPh_3)_2$. These crystals were manually separated to produce separate samples of each compound.

$[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl{\cdot}2MeOH$. $RuCl_2(PPh_3)_3$ (203 mg, 0.21 mmol) and PPh_3 (116 mg, 0.44 mmol) were dissolved in 8 mL of carbon disulfide to form a deep-red solution. A 0.5 mL portion of methanol was added, and the mixture turned violet. This mixture was filtered into four 5-mm-diameter open tubes of ca. 20 cm length. The resulting tubes then showed two distinct layers: the lower layer was a deep-red solution (CS_2), and the top layer was black and viscous. The tubes were inverted several times to allow mixing and were allowed to stand for 1 week. Orange blocks up to 5 mm on a side formed, and these crystals were collected from all four tubes (yield: 88 mg, 39%). Mp: 175 °C. $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 298 K): δ 30.15 (d, $J_{P,P}$ = 4 Hz), 16.45 (t, $J_{P,P}$ = 4 Hz) with integration 2:1. FTIR (cm^{-1}): 3181 (ν_{OH}), 3047, 1617, 1581, 1479, 1433, 1263 (ν_{CS}), 1186, 1163, 1108, 1088, 1025, 995, 971, 849, 747, 727, 693, 558, 511.

$[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6){\cdot}1.35CH_2Cl_2$. A mixture of $RuCl_2(S_2CPPh_3)(PPh_3)_2$, $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl$, and $RuCl_2(CS)(MeOH)(PPh_3)_2$ (11.5 mg) prepared as described above was dissolved in 2 mL of dichloromethane to form a dark-red solution. Ammonium hexafluorophosphate (25 mg, 150 μmol) was dissolved in 4 mL of methanol, and the resulting solution was added to the dichloromethane solution. Red-orange blocks suitable for X-ray diffraction formed from the resulting dark-red solution within 1 day (yield: 1 mg). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 298 K): δ 30.23 (d, $J_{P,P}$ = 4 Hz), 16.42 (t, $J_{P,P}$ = 4 Hz) [phosphorus from $(PF_6)^-$ at −144.9 with $J_{P,F}$ = 710 Hz]. FTIR (cm^{-1}): 3320 (ν_{OH}), 3050, 1586, 1480, 1433, 1271 (ν_{CS}), 1186, 1108, 1092, 1028, 998, 971, 823, 742, 692, 623, 611, 556, 513, 503. UV/vis [dichloromethane; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 427 (1400), 527 (1100).

$RuCl_2(CS)(MeOH)(PPh_3)_2$. Crystals suitable for X-ray diffraction were obtained by dissolving $RuCl_2(S_2CPPh_3)(PPh_3)_2{\cdot}CS_2$ in methanol under air or anaerobic conditions and allowing the purple solution to stand. Yellow blocks formed amidst a purple solution. Alternatively, sonication of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ (35 mg, 34 μmol) in methanol (20 mL) resulted in the formation of 6 mg (23%) of a yellow precipitate of $RuCl_2(CS)(MeOH)(PPh_3)_2$ within a murky purple solution. Mp: 182−184 °C. $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 298 K): δ 31.1 (s). FTIR (cm^{-1}): 3560 (ν_{OH}), 3051, 2950, 1574, 1509, 1479, 1433, 1280 (ν_{CS}), 1183, 1158, 1088, 1028, 995, 846, 740, 687, 513, 501.

Physical Measurements. IR spectra were recorded on a Bruker Alpha FTIR spectrometer. NMR data were collected on a Bruker Avance DRX 500 MHz spectrometer. UV/vis absorption spectra were collected on a Shimadzu UV-3600 spectrophotometer. All cyclic voltammograms were collected under an inert dinitrogen (Praxair, 99.999%) atmosphere in a dichloromethane solution with a 0.10 M (n-Bu_4N)(PF_6) supporting electrolyte that had been stored on 3 Å molecular sieves for a minimum of 48 h before use. Scans were performed using a glassy carbon working electrode, a silver wire pseudo reference electrode, and a platinum wire counter electrode. The silver wire pseudo reference electrode was referenced against an internal decamethylferrocene (Fc*) standard. Under these experimental conditions, the $Fc^{*0/+1}$ couple has $E^{0\prime}$ = −0.59 V versus $Fc^{0/1+}$.

Single-Crystal X-ray Crystallography and Data Collection. Crystals of $RuCl_2(S_2CPPh_3)(PPh_3)_2$ (red-violet needles) and $RuCl_2(CS)(MeOH)(PPh_3)_2$ (yellow blocks) were mounted in the 100 K nitrogen cold stream provided by an Oxford Cryostream low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a Photon 100 CMOS detector. Data were collected with the use of synchrotron radiation (λ = 0.77490 Å) at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley Laboratory. Crystals of $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl{\cdot}2MeOH$ (orange blocks) and $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6){\cdot}1.35CH_2Cl_2$ (orange blocks) were selected for data collection on a Bruker D8 DUO diffractometer employing Mo Kα radiation (λ = 0.71073 Å) and a Cryo Industries low-temperature apparatus. All data sets were reduced with the use of Bruker *SAINT*,[34] and a multiscan absorption correction was applied with the use of *SADABS*.[34] Structure solution and refinement were conducted with *SHELXS-2008*[35] and *SHELXL-2014*,[36] respectively. Crystallographic data are reported in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for $RuCl_2(S_2CPPh_3)(PPh_3)_2{\cdot}CS_2$, $RuCl_2(S_2CPPh_3)(PPh_3)_2{\cdot}0.25CS_2{\cdot}0.25C_7H_8$, $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2]Cl{\cdot}2MeOH$, $[RuCl(S_2CPPh_3)(CS)(PPh_3)_2](PF_6){\cdot}1.35CH_2Cl_2$, and $RuCl_2(CS)(MeOH)(PPh_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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