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Article

Synthesis and Reactivity of the Ruthenium(II) Dithiocarbonate Complex $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$ (dppm = Bis(diphenylphosphino)methane)

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Reaction of *cis*-$[RuCl_2(dppm)_2]$ (dppm = bis(diphenylphosphino)methane) with CS_2 and NaOH yields the first ruthenium dithiocarbonate complex, $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$. Protonation with tetrafluoroboric acid affords the xanthate complex $[Ru(\kappa^2\text{-}S_2COH)(dppm)_2]BF_4$ in a reversible manner, suggesting that this may be an intermediate in dithiocarbonate formation. $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$ reacts with methyl iodide or $[Me_3O]BF_4$ to give $[Ru(\kappa^2\text{-}S_2COMe)(dppm)_2]^+$, also obtained from the reaction of *cis*-$[RuCl_2(dppm)_2]$ with CS_2 and NaOMe. Two modifications of $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$ were examined crystallographically and the structure of $[Ru(\kappa^2\text{-}S_2COMe)(dppm)_2]BF_4$ and a new modification of *cis*-$[RuCl_2(dppm)_2]$ are also reported.

Introduction

Interest in mononuclear complexes with sulfur-containing ligands has been sustained by their relevance as models for redox-active metalloproteins.[1] Compared, for example, to dithiocarbamate complexes,[2] dithiocarbonate complexes are less well-known, although examples have been reported for a number of metals.[3−10] The most-detailed study of the reactivity of these species to date has been that of $[Rh(\kappa^2\text{-}S_2C{=}O)(triphos)]^+$ (triphos = $MeC(CH_2PPh_2)_3$) by Bianchini and co-workers, who found that this complex displays a substantial and diverse reactivity.[10]

Existing synthetic routes to dithiocarbonate complexes involve the use of xanthate,[3−8] carbon disulfide,[9] or phosphoniodithiocarboxylate[10] compounds. For example, xanthates, $[M(\kappa^2\text{-}S_2COR)_2]$ (M = Ni, Pd, Pt; R = alkyl), when treated with phosphines or phosphites (L), liberate *S*-alkyl *O*-alkyl dithiocarbonates $ROCS_2R$ to give dithiocarbonate complexes $[M(\kappa^2\text{-}S_2C{=}O)L_2]$.[6b,8] Herein, we report the synthesis and reactivity of the first ruthenium dithiocarbonate complex, $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$. This is readily accessible in one step from the reaction of *cis*-$[RuCl_2(dppm)_2]$[11] with NaOH and CS_2, a transformation proposed to involve a RuS_2COH intermediate.

Results and Discussion

Addition of *cis*-$[RuCl_2(dppm)_2]$ (**1**) to a solution of NaOH and CS_2 led cleanly to the isolation of a single new product

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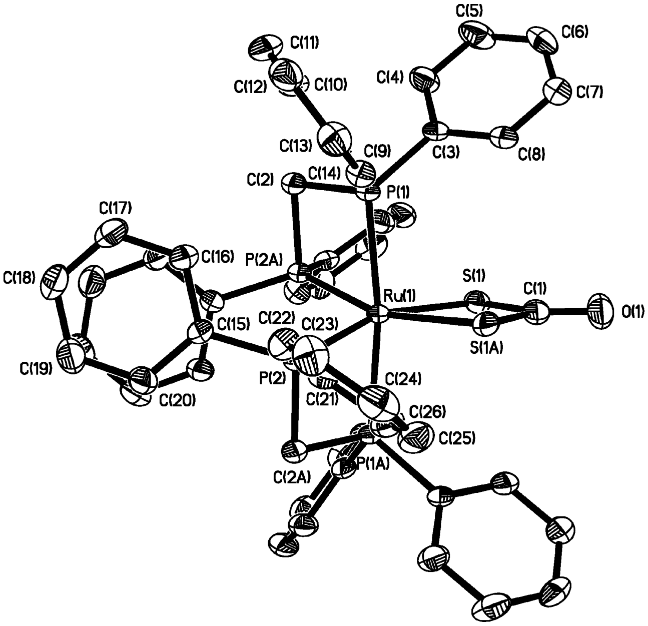
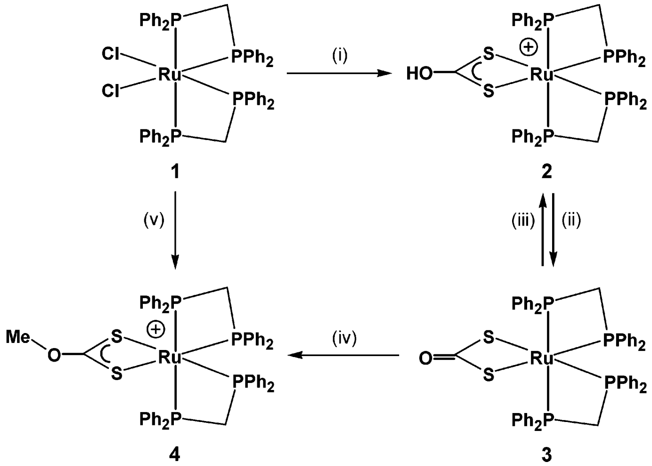


Figure 1. Structure of [Ru(κ^2-$S_2C{=}O$)(dppm)$_2$] (**3**) (only Λ enantiomer shown). Selected bond lengths (Å) and angles (deg): P2−Ru1−P2A = 97.40(5), P2−Ru1−P1 = 102.16(3), P2A−Ru1−P1 = 71.90(3), P2A−Ru1−S1 = 96.67(4), P1A−Ru1−S1 = 93.61(3), P1−Ru1−S1 = 93.41(3). Other bond lengths are collected in Table 1.

Scheme 1[a]



[a] (i) CS_2, NaOH; (ii) NaOH or NEt_3; (iii) $HBF_4{\cdot}OEt_2$; (iv) MeI, $[Me_3O]BF_4$; (v) CS_2, NaOMe.

in 94% yield that was identified as [Ru(κ^2-$S_2C{=}O$)(dppm)$_2$] (**3**). Initial characterization was made on the basis of spectroscopic data, with key features being a resonance at 218.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum and a ν(C=O) absorption at 1568 cm^{-1} in the solid-state IR spectrum (1572 cm^{-1} in CH_2Cl_2 solution). In the FAB mass spectrum, a molecular ion was observed at m/z = 961, with the only major fragmentation ion resulting from loss of SCO. To confirm the formation of a dithiocarbonate ligand, we carried out crystallographic studies on two crystal modifications; the results of one of these (**3**$\cdot 2CH_3OH$) are shown in Figure 1.

It is plausible that dithiocarbonate **3** results from the in situ generation of Na[S_2COH] from NaOH and CS_2 in methanol. This, in turn, reacts with *cis*-[$RuCl_2$(dppm)$_2$] (**1**) to afford the xanthate complex, [Ru(κ^2-S_2COH)(dppm)$_2$]$^+$, which is deprotonated under the prevailing basic conditions. To test this hypothesis, we protonated **3** with $HBF_4{\cdot}OEt_2$ to obtain [Ru(κ^2-S_2COH)(dppm)$_2$]BF_4 (**2**) (Scheme 1). In addition to the observed chemical shift changes in the $^{31}P\{^1H\}$ NMR spectrum, no ν(C=O) absorptions were observed in the IR spectrum of the product; the presence of the BF_4^- anion was noted as a broad band centered at 1049 cm^{-1} in the solid-state infrared spectrum. A singlet at 3.83 ppm in the ^1H NMR spectrum was tentatively assigned to the xanthate proton, and the overall composition was further supported by elemental analysis. To probe the formation of **2** further, we used NMR spectroscopy to monitor the protonation of **3** with trifluoroacetic acid. This led to a clean reaction but formed only the trifluoroacetate complex, [Ru(κ^2-O_2CCF_3)(dppm)$_2$][CF_3CO_2], which has previously been reported by Robinson and co-workers.[13] It seems that although protonation does occur under these conditions, displacement of the xanthate by the coordinating anion proceeds in a faster step. The free xanthate is unstable under acidic conditions, decomposing to liberate CS_2, which was easily identified from the pungent odor upon opening the NMR tube.

It appears that no examples of this parent xanthate have been reported previously.[12] Fackler and Seidel have shown that treatment of [Pt(κ^2-$S_2C{=}O$)(PPh_2Me)$_2$] with HCl yields [$PtCl_2$(PPh_2Me)$_2$];[3b] however, the reaction with acids involving noncoordinating anions was not explored.

An alternative reaction pathway for the formation of **3** from **1** is the initial formation of *cis*-[RuCl(OH)(dppm)$_2$], which could be followed by insertion of CS_2 into the Ru−O bond and subsequent elimination of HCl. Although relatively rare, hydroxide complexes of ruthenium such as *trans*-[RuH(OH)(dmpm)$_2$] (dmpm = bis(dimethylphosphino)methane)[14a] and [RuCl(OH)(OH_2)$_2$(PPh_3)$_2$][14b] are known, but as far as we are aware, the insertion of CS_2 into such species has not been observed.

The dithiocarbonate group in **3** was found to react with other electrophiles. Treatment with trimethyloxonium tetrafluoroborate resulted in the formation of [Ru(κ^2-S_2COMe)(dppm)$_2$]BF_4 (**4**), which was also prepared from the direct reaction of **1** with NaS_2COMe (prepared in situ from NaOMe and CS_2) and $NaBF_4$ (Scheme 1). A singlet resonance in the ^1H NMR spectrum at 3.80 ppm was assigned to the methyl group, and the overall composition was supported by a molecular ion at m/z = 977 in the FAB mass spectrum and elemental analysis. A crystallographic study was also undertaken (Figure 2).

Alkylation of **3** with methyl iodide also led to the formation of **4** (among other products), ultimately leading to displacement of the xanthate ligand by iodide to give the

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **3**, **4**, and Literature Complexes

complex	Ru−P$_{eq}$	Ru−P$_{ax}$	Ru−S	S−C	C−O	S−Ru−S	S−C−S
$[\mathrm{Ru}(\kappa^2\text{-}\mathrm{S_2C{=}O})(\mathrm{dppm})_2]$ (**3**·2CH$_3$OH)	2.3152(10)	2.3319(10)	2.4198(10)	1.764(3)	1.215(7)	72.39(5)	108.2(3)
Δ-$[\mathrm{Ru}(\kappa^2\text{-}\mathrm{S_2C{=}O})(\mathrm{dppm})_2]$ (**3**·3CHCl$_3$)	2.3140(9)	2.3308(10)	2.4011(8)	1.749(4)	1.226(4)	72.06(3)	108.21(19)
	2.3286(8)	2.3477(9)	2.4364(10)	1.764(4)			
Λ-$[\mathrm{Ru}(\kappa^2\text{-}\mathrm{S_2C{=}O})(\mathrm{dppm})_2]$ (**3**·3CHCl$_3$)	2.3138(9)	2.3280(9)	2.4157(9)	1.743(4)	1.213(5)	71.78(3)	108.4(2)
	2.3323(9)	2.3429(10)	2.4353(9)	1.765(4)			
$[\mathrm{Ru}(\kappa^2\text{-}\mathrm{S_2COMe})(\mathrm{dppm})_2]^+$ (**4**)	2.3124(6)	2.3342(6)	2.4347(6)	1.689(2)	1.320(3)	71.715(19)	115.26(13)
	2.3200(6)	2.3721(6)	2.4398(6)	1.691(2)			
$[\mathrm{Ru}(\kappa^2\text{-}\mathrm{S_2CH_2})(\mathrm{dppm})_2]$[16]	2.3171(11)	2.3079(12)	2.4245(11)	1.812(5)	-	72.96(4)	105.3(2)
	2.3181(11)	2.3571(12)	2.4368(12)	1.824(5)			
$[\mathrm{Ni}(\kappa^2\text{-}\mathrm{S_2C{=}O})(\mathrm{dippe})]$[a,6b]	-	-	-	1.759(6)	1.235(6)	79.72(6)	106.3(3)
				1.769(5)			
$[\mathrm{Pt}(\kappa^2\text{-}\mathrm{S_2C{=}O})\{\mathrm{P(OMe)Ph_2}\}_2]$[8]	-	-	-	1.765(7)	1.190(8)	75.2(1)	107.5(3)
				1.767(7)			
$[\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5Me_5})(\kappa^2\text{-}\mathrm{S_2CO^iPr})(\mathrm{PEt_3})]$[18]	-	-	2.393(2)	1.678(5)	1.315(6)	71.45(6)	113.0(3)
			2.406(2)	1.682(5)			

[a] dippe = 1,2-bis(diisopropylphosphino)ethane.

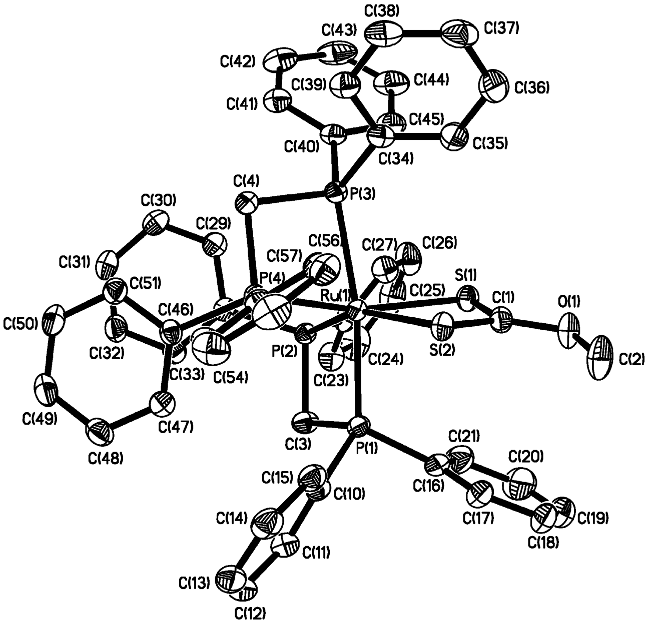

Figure 2. Structure of $[\mathrm{Ru}(\kappa^2\text{-}\mathrm{S_2COMe})(\mathrm{dppm})_2]\mathrm{BF_4}$ (**4**) (only Δ enantiomer shown). Selected bond lengths (Å) and angles (deg): O1−C2 = 1.447(3), P2−Ru1−P4 = 95.58(2), P2−Ru1−P1 = 71.74(2), P4−Ru1−P1 = 101.55(2), P2−Ru1−P3 = 102.64(2), P4−Ru1−P3 = 71.411(19), P2−Ru1−S1 = 96.31(2), P1−Ru1−S1 = 91.87(2), P3−Ru1−S1 = 95.98(2), P4−Ru1−S2 = 100.49(2), P1−Ru1−S2 = 87.72(2), P3−Ru1−S2 = 99.19(2), C1−S1−Ru1 = 86.28(8), C1−O1−C2 = 118.3(2), O1−C1−S2 = 126.01(18), O1−C1−S1 = 118.72(17). Other bond lengths are collected in Table 1.

known compound *cis*-$[\mathrm{RuI_2}(\mathrm{dppm})_2]$.[15] The dithiocarbonate ligand is lost in a similar manner in the reaction of $[\mathrm{Ni}(\kappa^2\text{-}\mathrm{S_2C{=}O})(\mathrm{dppe})]$ with methyl iodide to yield $[\mathrm{NiI_2}(\mathrm{dppe})]$.[6a]

Previous routes to dithiocarbonate complexes have frequently involved the reactions of xanthate complexes with bases such as phosphines.[3−8] However, treatment of **4** with NaOH in water and tetrahydrofuran (1:2) gave no reaction, suggesting that **4** is not an intermediate in the observed reaction between **1** and NaOH and CS$_2$ in methanol. Compound **4** also showed no reaction under acidic conditions (excess trifluoroacetic acid).

Crystallographic Studies

During the course of this work, crystal structures were determined for two crystal modifications of **3** (**3**·2CH$_3$OH and **3**·3CHCl$_3$), **4**·CH$_3$OH, and **1**·PrOH, the results of which are summarized in Figures 1 and 2 and Table 1. Figures depicting the other structures are included in the Supporting Information, along with a brief discussion of the structure of **1**·PrOH.

In **3**·3CHCl$_3$ there are two independent molecules in the asymmetric unit (Δ and Λ enantiomers), whereas **3**·2CH$_3$OH contains a single dithiocarbonate complex. Gross structural features of all three are similar, each containing a distorted octahedral geometry with cis-interligand angles ranging between 71.90(3) and 102.16(3)°. In **3**·2CH$_3$OH, the dithiocarbonate is symmetrically bound to ruthenium, whereas the same feature in both molecules in **3**·3CHCl$_3$ shows a slight asymmetry. The Ru−S bond lengths vary between 2.4364(10) and 2.4011(8) Å, with both extremes being observed in the Δ isomer in **3**·3CHCl$_3$; C−S (1.765(4)−1.743(4) Å) and C−O (1.226(4)−1.213(5) Å) bonds vary within much smaller ranges. These bond lengths are comparable to those found in $[\mathrm{Ni}(\kappa^2\text{-}\mathrm{S_2C{=}O})(\mathrm{dippe})]$ (dippe = 1,2-bis(diisopropylphosphino)ethane)[6b] and $[\mathrm{Pt}(\kappa^2\text{-}\mathrm{S_2C{=}O})\{\mathrm{P(OMe)Ph_2}\}_2]$;[8] however, the ligand bite angles in **3** (S−Ru−S = 72.39(5)−1.78(3)°) are significantly smaller than those found in related nickel or platinum complexes (Table 1). These observations indicate that the $\mathrm{RuS_2C{=}O}$ unit is softly bound to the ruthenium center, allowing for significant distortions depending on the structure modification.

The closest structural analogue to **3** is the isoelectronic complex $[\mathrm{Ru}(\kappa^2\text{-}\mathrm{S_2CH_2})(\mathrm{dppm})_2]$ reported recently by Jagirdar and co-workers.[16] The Ru−S lengths in the methanedithiolate compound are at the longer end of those seen in **3**, whereas the C−S bond distances are appreciably greater than those found in **3**. This may be due to the partial double-bond character resulting from the resonance forms shown in Chart 1. In **3**, the C−O distance shows double-bond character, which it has in common with all reported dithiocarbonate complexes,[3−10] and the bond length compares well with the average of 1.210 Å found in ketones.[17]

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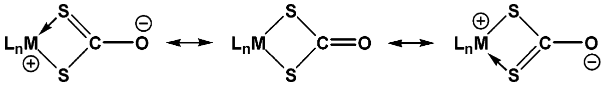
Chart 1. Resonance Forms for the Dithiocarbonate Ligand



The Ru−S bond lengths in $[Ru(\kappa^2\text{-}S_2COMe)(dppm)_2]BF_4$ (**4**) are slightly longer than those found in **3**, whereas the C−S distances are considerably shorter, reflecting the partial double-bond character present. The C−O bond length is relatively short, although the multiple-bond character is not as pronounced as that in **3**. The S−C−S angle of the xanthate ligand in **4** is substantially larger than that found in **3**, whereas the S−Ru−S bite angle is only marginally smaller than the corresponding feature in **3**. Apart from this slightly larger S−Ru−S angle, the structural features of the methyl xanthate ligand are similar to those found for the isopropyl xanthate moiety in $[Ru(\eta^5\text{-}C_5Me_5)(\kappa^2\text{-}S_2CO^iPr)(PEt_3)]$[18] (Table 1).

Conclusions

The first dithiocarbonate compound of ruthenium, $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$ (**3**), has been prepared from the reaction of carbon disulfide and hydroxide in methanol with *cis*-$[RuCl_2(dppm)_2]$ (**1**). The reactivity of **3** centers on the oxygen of the dithiocarbonate ligand, which can be alkylated or protonated to yield either alkyl or parent xanthate products, respectively. The latter is a plausible intermediate in the formation of **3** and is the first such example of this ligand to be reported, to the best of our knowledge.

Experimental Section

General Procedures. All manipulations were carried out under aerobic conditions using commercially available solvents and reagents as received. Infrared and NMR spectroscopy were carried out at 25 °C using Shimadzu FTIR 8700 (KBr plates with Nujol) and Bruker AMX-300 (^1H, 299.87 MHz; ^{31}P, 121.39 MHz) or AMX-400 (^1H, 400.14 MHz; ^{31}P, 161.97 MHz) spectrometers, respectively. Infrared spectroscopic features due to the bis(diphenylphosphino)methane ligands have been omitted to aid clarity. FAB-MS spectra (nitrobenzyl alcohol matrixes) were measured using a VG 70-SB magnetic sector mass spectrometer. Elemental microanalyses were performed at UCL. Solvates were determined by ^1H NMR spectroscopy. *cis*-$[RuCl_2(dppm)_2]$ (**1**) was prepared according to a published procedure.[11]

$[Ru(\kappa^2\text{-}S_2COH)(dppm)_2]BF_4$ (2). A diethyl ether (10 mL) suspension of $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$ (**3**) (33 mg, 0.034 mmol) was treated with tetraflouroboric acid diethyl ether complex (3 drops, excess), and the reaction mixture was stirred for 5 min. The precipitate was broken up by sonication in an ultrasound bath and then filtered and washed with diethyl ether (10 mL) and hexane (10 mL). Yield: 32 mg (90%). IR (KBr/Nujol): 1339, 1312, 1236, 1049 (ν(BF)), 885 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ −4.4, −16.7 (t × 2, J_{PP} = 35.7 Hz, dppm). ^1H NMR ($CDCl_3$): δ 3.83 (s, 1H, OH), 4.64, 5.03 (m × 2, 2 × 2H, PCH_2P), 6.54, 7.00, 7.06, 7.30, 7.64 (m × 5, PC_6H_5, 40H). FAB-MS *m*/*z* (abundance): 979 (38) $[M + H_2O]^+$. Anal. Calcd for $C_{51}H_{45}BF_4OP_4RuS_2$: C, 58.4; H, 4.3. Found: C, 58.7; H, 4.5.

$[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]$ (3). (a) NaOH (32 mg, 0.800 mmol) was dissolved in methanol (10 mL), and carbon disulfide (61 mg, 0.801 mmol) was added. The reaction mixture was stirred for 10 min. *cis*-$[RuCl_2(dppm)_2]$ (**1**) (150 mg, 0.159 mmol) was dissolved in dichloromethane (10 mL) and added to the mixture. The solution was stirred for 2 h. All solvent was removed under reduced pressure; the residue was taken up in a minimum quantity of dichloromethane and filtered through diatomaceous earth. Ethanol (20 mL) was added, and the solvent volume was concentrated under reduced pressure until precipitation was complete. The pale green product was filtered and washed with ethanol (10 mL) and hexane (10 mL). Yield: 144 mg (94%). (b) Complex **2** (30 mg, 0.029 mmol) was dissolved in dichloromethane (10 mL) and treated with triethylamine (4 drops, excess) and the reaction mixture was stirred for 20 min. Ethanol (20 mL) was added, and the solvent volume was concentrated under reduced pressure until precipitation was complete. The pale green product was filtered and washed with ethanol (10 mL) and hexane (10 mL). Yield: 23 mg (82%). IR (CH_2Cl_2): 1605, 1572 (ν(C=O)). IR (KBr/Nujol): 1685, 1568 (ν(C=O)), 1312, 1238, 972, 849 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ −4.3, −19.5 (t × 2, J_{PP} = 32.6 Hz, dppm). ^1H NMR ($CDCl_3$): 4.26, 4.72 (m × 2, 2 × 2H, PCH_2P), 6.40, 6.85, 7.17, 7.26, 7.49, 7.24 (m × 6, 40H, PC_6H_5). ^{13}C NMR (CD_2Cl_2): δ 45.7 (m, CH_2), 129.6−134.2 (C_6H_5), 218.6 (s, CO). FAB-MS *m*/*z* (abundance): 961 (53) $[M]^+$, 902 (100) $[M - SCO]^+$. Anal. Calcd for $C_{51}H_{44}OP_4RuS_2{\cdot}2CH_2Cl_2$: C, 56.2; H, 4.3. Found: C, 56.2; H, 4.4%.

$[Ru(\kappa^2\text{-}S_2COMe)(dppm)_2]BF_4$ (4). (a) NaOMe (17 mg, 0.325 mmol) was dissolved in methanol (10 mL), and carbon disulfide (25 mg, 0.328 mmol) was added. The reaction mixture was stirred for 20 min. *cis*-$[RuCl_2(dppm)_2]$ (**1**) (100 mg, 0.106 mmol) was dissolved in dichloromethane (10 mL) and added to give a colorless precipitate. The solution was treated with an aqueous solution (0.5 mL) of $NaBF_4$ (24 mg, 0.219 mmol), and the reaction mixture was stirred for 1 h. All solvent was removed under reduced pressure; the residue was taken up in a minimum quantity of dichloromethane and filtered through diatomaceous earth. Methanol (20 mL) was added, and the solvent volume was concentrated under reduced pressure until precipitation was complete. The colorless product was filtered and washed with ethanol (10 mL) and hexane (10 mL). Yield: 81 mg (72%). (b) Complex **3** (30 mg, 0.031 mmol) was dissolved in dichloromethane (10 mL) and treated with trimethyloxonium tetrafluoroborate (4 drops, excess); the reaction mixture was stirred for 30 min. Ethanol (20 mL) was added, and the solvent volume was concentrated under reduced pressure until precipitation was complete. The product was filtered and washed with ethanol (10 mL) and hexane (10 mL). Yield: 19 mg (58%). IR (KBr/Nujol): 1335, 1312, 1248, 1057 (ν(BF)), 957 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ −2.1, −14.5 (t × 2, J_{PP} = 35.8 Hz, dppm). ^1H NMR ($CDCl_3$): δ 3.80 (s, 3H, OCH_3), 4.45, 4.90 (m × 2, 2 × 2H, PCH_2P), 6.42, 6.95, 7.05, 7.23, 7.36, 7.57 (m × 6, 40H, PC_6H_5). FAB-MS *m*/*z* (abundance): 977 (100) $[M]^+$. Anal. Calcd for $C_{52}H_{47}BF_4OP_4RuS_2$: C, 58.7; H, 4.5. Found: C, 58.5; H, 4.4.

X-ray Crystallography. Crystals of $\mathbf{1}{\cdot}PrOH$ were grown by slow diffusion of ethanol into a dichloromethane solution of the complex (containing small amounts of propanol), whereas crystals of $\mathbf{3}{\cdot}2CH_3OH$ were obtained from slow diffusion of methanol into a dichloromethane solution of the complex. Slow evaporation of a concentrated chloroform solution of **3** led to crystals of $\mathbf{3}{\cdot}3CHCl_3$ being obtained. Although crystals of $\mathbf{4}{\cdot}CH_3OH$ were obtained by layering a chloroform solution of the complex with hexane, a molecule of methanol was retained. Single crystals were mounted

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Table 2. Crystal Data for Compounds **3** (Two Modifications) and **4**

	3·$2CH_3OH$	**3**·$3CHCl_3$	**4**·CH_3OH
chemical formula	$C_{52}H_{44}O_3P_4RuS_2$	$C_{54}H_{47}Cl_9OP_4RuS_2$	$C_{53}H_{51}BF_4O_2P_4RuS_2$
fw	1017.95	1320.04	1095.82
cryst syst	monoclinic	monoclinic	monoclinic
cryst color	yellow	yellow	yellow
cryst size (mm^3)	0.15 × 0.08 × 0.08	0.28 × 0.28 × 0.20	0.64 × 0.64 × 0.42
space group	$C2/c$	$P2/1$	$C2/c$
a (Å)	16.834(4)	14.8972(17)	35.754(2)
b (Å)	15.592(4)	18.274(2)	11.8150(7)
c (Å)	17.693(4)	21.145(2)	24.7544(14)
α (deg)	90	90	90
β (deg)	95.004(4)	91.065(2)	109.9030(10)
γ (deg)	90	90	90
V ($Å^3$)	4626(2)	5755.4(11)	9832.5(10)
Z	4	4	8
D_{calcd} (g/cm^3)	1.462	1.523	1.481
T (K)	150(2)	150(2)	150(2)
μ(Mo Kα) (mm^{-1})	0.612	0.912	0.591
F(000)	2120	2672	4496
no. of reflns collected	19290	50105	42408
no. of unique reflns (R_{int})	5530 (0.0813)	26107 (0.0188)	11725 (0.0186)
R1 ($I > 2\sigma(I)$)	0.0713	0.0369	0.0382
wR′2 (all data)	0.1924	0.1002	0.1069

on glass fibers, and all geometric and intensity data were taken from these samples on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction and integration were carried out with SAINT+ and absorption corrections were applied using the SADABS program. The structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their thermal parameters were linked to those of the atoms to which they were attached (riding model). Structure solution and refinement used the SHELXTL PLUS version 6.10 program package.[19] Selected crystal data are given in Table 2 (see the Supporting Information for crystal data for **1**·PrOH).

Crystallographic data for the structure of complexes **1**·PrOH, **3**·$2CH_3OH$, **3**·$3CHCl_3$, and **4**·CH_3OH have been deposited with the Cambridge Crystallographic Data Centre as CCDC 278731, CCDC 278732, CCDC 278733, and CCDC 283230, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44 (1223) 336-033. E-mail for inquiry: fileserv@ccdc.cam.ac.uk.)

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Supporting Information Available: Crystal data and structural discussion for **1**·PrOH and figures depicting the crystal structures of **1**·PrOH and **3**·$3CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] *SHELXTL*, version 6.10; Bruker AXS: Madison, WI, 2000.