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Novel Double Insertion of Carbon Disulfide into Two Ru–H Bonds of $[(dppm)_2Ru(H)_2]$ (dppm = $Ph_2PCH_2PPh_2$): Synthesis and Crystal Structure of a Methanedithiolate Complex

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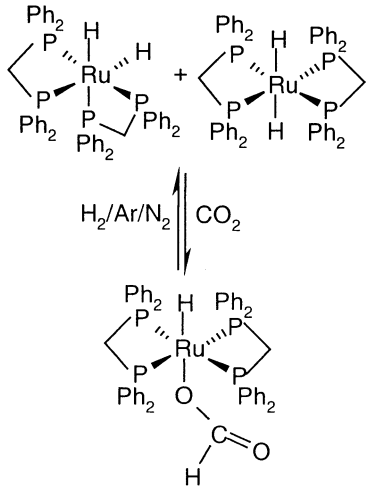
Addition of excess carbon disulfide to *cis*/*trans*-$[(dppm)_2Ru(H)_2]$ results in the methanedithiolate complex $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$ **4** via the intermediacy of *cis*-$[(dppm)_2Ru(H)(SC(S)H)]$ **2**. The X-ray crystal structure of this species has been determined.

The insertion of heterocumulenes such as CO_2, CS_2, and COS into metal−hydride and metal−carbon bonds is an important chemical reaction in functionalizing these molecules.[1−4] The focus of current research in this field is the utilization of these species as C_1 synthetic units to generate useful organic compounds.

During the course of our reactivity studies of carbon dioxide with metal hydride complexes, we found that CO_2 undergoes insertion into the M−H bond of *cis*/*trans*-$[(dppm)_2Ru(H)_2]$[5] (dppm = $Ph_2PCH_2PPh_2$) to afford the hydride formate species, *trans*-$[(dppm)_2Ru(H)(OC(O)H)]$ **1**.[6] Attempts to hydrogenate the hydride formate derivative only resulted in the recovery of the starting dihydride complex. In addition, purging solutions containing **1** with either N_2 or Ar yielded once again the dihydride complex *cis*/*trans*-$[(dppm)_2Ru(H)_2]$ via a facile deinsertion of CO_2. Upon exposure of these solutions to 1 atm of CO_2, the hydride formate complex could be regenerated, and this cycle can be repeated any number of times without appreciable decomposition of either the starting dihydride or the formate species (Scheme 1). The complex **1** represents one of few examples of metal hydrides that reversibly bind CO_2.[4] Jessop et al.[7] recently reported having observed this species using ^{31}P NMR spectroscopy in their studies on the in situ formation of ruthenium catalysts for the hydrogenation of CO_2.

Scheme 1. Insertion of CO_2 into Ru−H Bond



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In this paper, we report our preliminary results on the insertion reactions of CS_2 into Ru−H bonds in *cis*/*trans*-$[(dppm)_2Ru(H)_2]$ to afford a novel methanedithiolate complex $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$ **4**. The methanedithiolate derivative is presumably formed due to a double insertion reaction of CS_2 into two Ru−H bonds via the intermediacy of *cis*-$[(dppm)_2Ru(H)(SC(S)H)]$ **2**.

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(6) Carbon dioxide (1 atm) was purged through a C_6D_6 solution (0.7 mL) of *cis*/*trans*-$[(dppm)_2Ru(H)_2]$ for 10 min. The NMR spectroscopy evidenced the presence of *trans*-$[(dppm)_2Ru(H)(OC(O)H)]$ complex **1** along with some unreacted starting material. The starting dihydride is not completely soluble in either benzene or toluene and is unstable in chlorinated hydrocarbons. We attempted to carry out this reaction in other solvents; however, the best results were obtained in benzene. When solutions containing complex **1** were purged with H_2, N_2, or Ar, the starting dihydride complex was recovered. ^1H NMR of **1** (C_6D_6): δ −15.65 (qnt, 1H, Ru−*H*, J(H,P) = 20.0 Hz); 4.93 (m, 4H, PCH_2P, J(H,P) = 16.0 Hz); 7.03−8.63 (m, 40H, $Ph_2PCH_2PPh_2$); 8.80 (s, 1H, Ru−OC(O)*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −1.8 (s, 4P, PCH_2P). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 35.45 (s, PCH_2P); 122.68−123.81 (m, $Ph_2PCH_2PPh_2$); 167.85 (s, Ru−OC(O)H).

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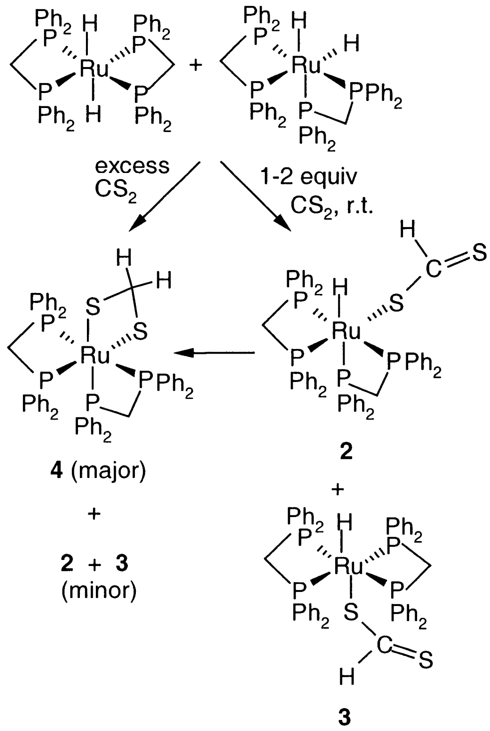
Scheme 2. Double Insertion of CS_2 into Two Ru−H Bonds



Addition of 1 or 2 equiv of CS_2 to a toluene solution of *cis*/*trans*-[(dppm)$_2$Ru(H)$_2$] and stirring for ca. 45 min at room temperature resulted in a mixture of both *cis*- and *trans*-[(dppm)$_2$Ru(H)(SC(S)H)] **2** and **3** as evidenced by NMR spectroscopy.[8] When this product mixture was crystallized from the toluene solution via slow diffusion of petroleum ether at room temperature over a period of several days, red crystals were obtained that were identified as [(dppm)$_2$Ru(η^2-S_2CH_2)] **4** by NMR.[9] Attempts to isolate the cis hydride dithioformate complex in a pure form failed, and only a mixture of the *trans*-[(dppm)$_2$Ru(H)(SC(S)H)] **3** and the methanedithiolate complexes were obtained. This indicates that the *cis*-[(dppm)$_2$Ru(H)(SC(S)H)] **2** is short-lived. However, when the reaction of the starting dihydride complex was carried out under identical conditions in the presence of excess CS_2, **4** was obtained as the major product along with small amounts of **2** and **3** (Scheme 2).[9]

The ^{1}H NMR spectrum of [(dppm)$_2$Ru(η^2-S_2CH_2)] **4** shows a broad singlet at δ 4.52 for the S_2CH_2 fragment whereas the ^{31}P NMR spectrum is composed of two apparent triplets centered at δ −7.1 and −26.5, respectively, indicating the nonplanarity of the four dppm P atoms. The presence of the methylene group was further ascertained using ^{13}C NMR spectroscopy from the singlet at δ 47.11.

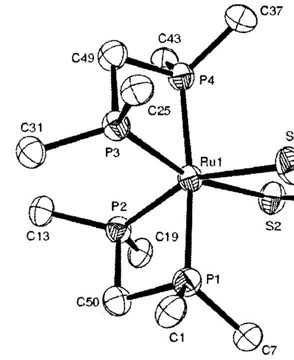


Figure 1. ORTEP view of [(dppm)$_2$Ru(η^2-S_2CH_2)] **4** at the 50% probability level. The phenyl groups on the dppm phosphorus atoms have been omitted for clarity; only one carbon of each of the phenyl groups is shown in the figure. Pertinent bond distances (Å) and angles (deg): Ru(1)−S(1) 2.4368(12), Ru(1)−S(2) 2.4245(11), C(51)−S(1) 1.824(5), C(51)−S(2) 1.812(5); S(1)−C(51)−S(2) 105.3(2), S(1)−Ru(1)−S(2) 72.96(4).

An X-ray diffraction study of [(dppm)$_2$Ru(η^2-S_2CH_2)] **4** was carried out, and the ORTEP diagram is shown in Figure 1.[10] The molecular structure can be described as a severely distorted octahedron. The methanedithiolate fragment is bound in an η^2-fashion to the metal. Two phosphorus atoms of the two separate dppm ligands and the two thiolate sulfur atoms of the methanedithiolate fragment roughly form the plane that is severely distorted. The remaining two P atoms of the two dppm moieties occupy the fifth and the sixth coordination sites of the metal. The bite angles of all three chelating ligands are remarkably similar to one another (mean 72.2°). The environment around the carbon of the S_2CH_2

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(8) To a C_6D_6 solution (0.7 mL) of *cis*/*trans*-[(dppm)$_2$Ru(H)$_2$] (0.015 g, 0.017 mmol) under an N_2 atmosphere in an NMR tube was added 2 equiv of CS_2 (2 μL, 0.034 mmol), and the mixture was shaken well. The color of the solution changed from greenish yellow to deep orange within a few minutes. If this solution is left for several hours at room temperature, a yellow insoluble solid separates out. The orange solution was identified as consisting of a mixture of *cis*- and *trans*-[(dppm)$_2$Ru(H)(SC(S)H)] complexes (**2** and **3**) using NMR spectroscopy. The composition of the yellow solid could not be ascertained. ^{1}H NMR of **2** (C_6D_6): δ −10.85 (unres d q, 1H, Ru−*H*, J(H,P$_{\text{trans}}$) = 18.4 Hz); 4.59, 4.92 (br s, 4H, PC*H*$_2$P); 6.75−8.81 (m, 40H, *Ph*$_2$PCH$_2$P*Ph*$_2$); 11.65 (s, 1H, Ru−SC(S)*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ −14.2 (t, J(P,P) = 35.0 Hz); −8.3 (t). ^{1}H NMR of **3** (C_6D_6): δ −9.49 (qnt, 1H, Ru−*H*, J(H,P) = 22.7 Hz); 5.20 (br s, 4H, PC*H*$_2$P); 6.75−8.81 (m, 40H, *Ph*$_2$PCH$_2$P*Ph*$_2$); 10.99 (s, 1H, Ru−SC(S)*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 0.5 (s, *P*CH$_2$*P*). Attempts to isolate **2** and **3** from a preparative scale experiment only yielded a mixture of **3** (minor) and **4**.

(9) To a toluene solution (10 mL) of *cis*/*trans*-[(dppm)$_2$Ru(H)$_2$] (0.100 g, 0.11 mmol) under an N_2 atmosphere was added 5 equiv of CS_2 (33.0 μL, 0.55 mmol), and the solution was stirred for $^1/_2$ h. The greenish yellow solution turned dark orange accompanied by the formation of an insoluble yellow solid. Upon workup of the reaction mixture followed by crystallization from toluene−petroleum ether, dark red crystals of [(dppm)$_2$Ru(η^2-S_2CH_2)] complex **4** were obtained in a yield of 37% (0.040 g). ^{1}H NMR of **4** (C_6D_6): δ 4.52 (br s, 2H, SC*H*$_2$S); 4.41, 4.75 (br m, 4H, PC*H*$_2$P); 6.46−8.10 (m, 40H, *Ph*$_2$PCH$_2$P*Ph*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ −7.1 (apparent t, *P*CH$_2$*P*, J(P,P) = 27.0 Hz); −26.5 (t). ^{13}C{^{1}H} NMR (C_6D_6): δ 47.11 (s, S*C*H$_2$S); 46.53 (m, P*C*H$_2$P); 125.34−133.32 (m, *Ph*$_2$PCH$_2$P*Ph*$_2$). Anal. Calcd for $C_{51}H_{46}P_4RuS_2$: C, 64.61; H, 4.89. Found: C, 64.11; H, 5.15 (X-ray crystallography shows a toluene molecule in the lattice outside the core; however, analytical data does not indicate the presence of solvent; the sample was dried under vacuum for ca. 4 h before analysis was carried out, which could have resulted in the loss of the solvent).

(10) (a) Crystallographic data for [(dppm)$_2$Ru(η^2-S_2CH_2)] **4**: $C_{58}H_{54}P_4RuS_2$, fw 1040.08, triclinic, $P\bar{1}$, a = 13.7210(9) Å, b = 14.2316 (9) Å, c = 14.9978(10) Å, α = 85.2780(10)°, β = 78.8770(10)°, γ = 61.7960(10)°, V = 2532.3(3) Å^3, Z = 2, T = 293(2) K. All the hydrogen atoms were geometrically fixed and allowed to ride with the respective light atoms to which they are attached. The data was corrected for absorption using the program SADABS available in the Bruker system of programs. Full-matrix least squares refinement (based on F^2, SHELXL-97) of the positional and anisotropic thermal parameters for the non-hydrogen atoms converged with R1 = 0.0602 and wR2 = 0.1069 for 10158 independent reflections with $I > 2\sigma(I)$. (b) A solvent molecule toluene in the lattice outside the core was located from the difference map. It showed high positional and thermal disorder. It was not subjected to accurate least squares refinement, and near convergence the refinement was stopped while the core was refined to a final convergence.

group is nearly tetrahedral (105.3(2)°). The Ru−P bond distances vary between 2.3079(12) and 2.3571(12) Å. The C−S bond lengths were found to be nearly the same, 1.812(5) and 1.824(5) Å, respectively. These distances resemble a C−S single bond (typically ∼1.8 Å).[11]

Gopinathan et al.[12] reported the structural aspects of the $[(PPh_3)_2(CO)(Cl)Ru(\eta^2\text{-}S_2CH)]$ complex. They suggested delocalization of electron density over the S−CH−S moiety resulting in a C−S bond length of 1.67(1) Å, intermediate between C−S single and double bonds. In addition, the carbon of the dithioformate fragment was found to be a strained sp^2 carbon atom (115.0°). Gao and co-workers[13] reported an iron dithioformate complex $[(dppm)_2Fe(\eta^2\text{-}S_2CH)][BF_4]$; the C−S bond lengths in this complex were once again found to be intermediate between a single- and a double-bond distance. The SCS bond angle in this case was also strained (113.3(6)°). In addition to these two compounds that are closely related to our system, there are other complexes obtained due to monoinsertion of CS_2 into M−H bonds.[14,15]

The initial reaction in the reduction of CS_2 to methanedithiolate is a typical insertion of an unsaturated substrate into M−H bonds; however, further work will be necessary to learn more about the mechanism of the formation of **4**. Although prior to this work few instances of reduction of CS_2 to methanedithiolate have been observed, only one compound has been structurally characterized. Jia and Meek[16] reported having observed a species of the type $[(Cyttp)Ru(S_2CH_2)]$; Chaudret and co-workers[17] obtained $[(PCy_3)_2Ru(H_2)(S_2CH_2)]$ from $[(PCy_3)_2Ru(H)_2(H_2)_2]$ and CS_2; Esteruelas et al.[18] prepared an osmium derivative $[(P^iPr_3)_2Os(H)(CO)(S_2CH_2)][BF_4]$ by reacting $[(P^iPr_3)_2Os(\eta^2\text{-}H_2)(CO)(S_2CH)]$ with $HBF_4{\cdot}Et_2O$; Jones and Selmeczy[19] reported $[Cp^*Rh(PMe_3)(\eta^2\text{-}S_2CH_2)]$ complex obtained from $[Cp^*Rh(PMe_3)H_2]$ and CS_2, and Okuda[20] reported $[Cp_2Mo(\eta^2\text{-}S_2CH_2)]$ formed from molybdocene dihydride and CS_2. The structure of only the rhodium derivative is known. In the rhodium complex, the SCS angle and the C−S distances were found to be 104.82° and 1.832 and 1.821 Å, respectively.

We attempted to explore the scope and utility of this reaction: CS_2 undergoes insertion into the Ru−H bond of *cis*-$[(dppe)_2Ru(H)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to afford the *trans*-$[(dppe)_2Ru(H)(SC(S)H)]$ **5** complex;[21] this compound under thermal conditions in toluene solvent gives the methane dithiolate derivative $[(dppe)_2Ru(\eta^2\text{-}S_2CH_2)]$ **6**.[22] Detailed studies of these and other reactions and their mechanisms are in progress in our laboratories.

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Supporting Information Available: X-ray crystallographic data for $[(dppm)_2Ru(\eta^2\text{-}S_2CH_2)]$ **4** in CIF format. The stack plots of the NMR spectra of the reactions of $[(dppm)_2RuH_2]$ with CO_2 and CS_2 in C_6D_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) To a toluene solution (15 mL) of *cis*-$[(dppe)_2RuH_2]$ (0.100 g, 0.11 mmol) under an N_2 atmosphere was added excess CS_2 (1 mL, 0.016 mol), and the solution was stirred for ca. 10 h. A yellow solid of *trans*-$[(dppe)_2Ru(H)(SC(S)H)]$ **5** precipitated out during this time. The volume of the solution was reduced to 3 mL, and excess Et_2O was added to cause complete precipitation, after which the solid was filtered off and dried in vacuo. Quantitative yield. ^1H NMR ($CDCl_3$): δ −13.88 (qnt, 1H, Ru−*H*, *J*(H,P) = 20.0 Hz); 2.16 and 2.71 (br s, 8 H, PCH_2CH_2P); 6.83−7.38 (m, 40 H, $Ph_2PCH_2CH_2PPh_2$); 9.69 (s, 1 H, Ru−SC(S)*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.9 (s, 4P, PCH_2CH_2P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 33.24 (PCH_2CH_2P); 127.36−138.95 ($Ph_2PCH_2CH_2PPh_2$); 244.69 (s, Ru−S*C*(S)H). Anal. Calcd for $C_{53}H_{50}P_4RuS_2$: C, 66.39; H, 5.32. Found: C, 66.10; H, 5.42.

(22) Characterization data for $[(dppe)_2Ru(\eta^2\text{-}S_2CH_2)]$ **6**: ^1H NMR ($CDCl_3$): δ 1.90 (s, 2H, SCH_2S); 2.05, 1.89 (br m, 8H, PCH_2CH_2P); 6.68−8.25 (m, 40H, $Ph_2PCH_2CH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.8 (apparent t, PCH_2CH_2P, *J*(P,P) = 18.4 Hz); 57.0 (t).