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Communication

Utilization of CS_2 as a Source of C_1 Chemistry for the Generation of Methyldithioformate

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Insertion of CS_2 into the Ru–H bond of *cis*-[(dppe)$_2$Ru(H)$_2$] takes place to afford the hydride dithioformate complex *trans*-[(dppe)$_2$Ru(H)(SC(S)H)]. The hydride dithioformate complex reacts under very mild conditions with MeX (X = OTf, I) to give the hydride methyldithioformate derivative *trans*-[(dppe)$_2$Ru(H)(SC(SMe)H)][X]. Three different pathways have been found to cleave off the ester moiety from the metal complex. A method to recover the ruthenium starting material upon elimination of the methyldithioformate is presented. This is a novel case of C_1 chemistry using carbon disulfide.

The insertion of heterocumulenes such as CO_2, CS_2, and COS into metal−hydride and metal−carbon bonds of transition metal fragments and their subsequent functionalization has been receiving enormous interest due primarily to their potential as sources of C_1 chemistry for the generation of useful organic compounds.[1−3] There have been several reports on the use of carbon dioxide as a C_1 building block for the preparation of useful organic compounds by coupling with an organic substrate using homogeneous transition metal catalysts.[4] The hydrogenation of CO_2 to CO, hydrocarbons, and alcohols is a thermodynamically favorable process.[4e] The hydrogenation of CO_2 to formic acid, however, is not thermodynamically favorable. Formate esters are usually obtained via the intermediacy of formic acid. Although a number of compounds bearing CS_2 as part of the complex have been prepared and characterized,[1,5] there have been scant reports in the literature on the conversion of CS_2 into organic derivatives, e.g., alkyldithioformates, dithioacetals, etc.[6] Attempts to synthesize simple alkyldithioformates resulted in the isolation of trimers with the trithiane structure.[7] Seyferth et al.[6a,b] found that the alkyldithioformates may be prepared in situ by reacting $LiBEt_3H$ with CS_2 followed by the reaction of the dithioformate anion with an alkyl iodide. Schenk and Schwietzke[6c] reported a transition metal mediated synthesis of dithioacetals via the intermediacy of dithioformate species. The dithioic acid esters $R^1CS_2R^2$ have been prepared earlier by a Mitsunobu-type reaction of alkanedithioic acids and alcohols as reported by Kpegba and Metzner.[8]

We have been interested in studying the reactivity of heterocumulenes such as CO_2, CS_2, and COS with metal hydride complexes. We found that CO_2 undergoes insertion into the M−H bond of *cis*/*trans*-[(dppm)$_2$Ru(H)$_2$] (dppm = $Ph_2PCH_2PPh_2$) to give the hydride formate derivative *trans*-[(dppm)$_2$Ru(H)(OC(O)H)] in a reversible fashion. On the other hand, CS_2 undergoes a novel double insertion into the two Ru−H bonds of *cis*/*trans*-[(dppm)$_2$Ru(H)$_2$] to afford a methanedithiolate complex [(dppm)$_2$Ru(η^2-S_2CH_2)].[9] However, when CS_2 was reacted with *cis*-[(dppe)$_2$Ru(H)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$), the hydride dithioformate species *trans*-[(dppe)$_2$Ru(H)(SC(S)H)] **1** was obtained (eq 1). Attempts to hydrogenate the dithioformate moiety to obtain the dithioformic acid using H_2 under various conditions (1 atm, room temperature; 3 atm, 50 °C; 5 atm, 50 °C) resulted only in the recovery of the starting material.

Herein, we report our preliminary findings on the functionalization of the dithioformate moiety of *trans*-[(dppe)$_2$Ru(H)(SC(S)H)] **1** using certain electrophilic species and the subsequent elimination of the organic group from the resulting metal derivative. Reaction of a CH_2Cl_2 solution of

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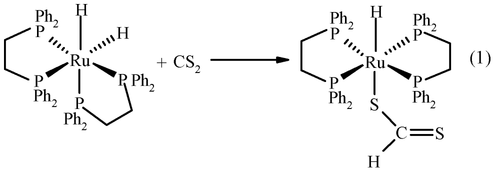

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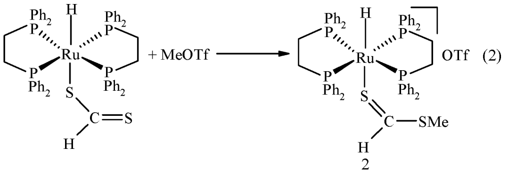
1 with 1 equiv of MeOTf resulted in an instantaneous color change from yellow to red. Upon workup and crystallization, red crystals were obtained that were identified using NMR spectroscopy as *trans*-[(dppe)$_2$Ru(H)(SC(SMe)H)][OTf] **2** (eq 2).



The ^{1}H NMR spectrum of **2** shows a quintet for the hydride ligand at δ −12.75 due to coupling with the four cis phosphorus nuclei with a $J(\mathrm{H,P_{cis}})$ of 20.0 Hz and two singlets at δ 2.48 and 8.00 for the SMe fragment and the formate hydrogen, respectively (low-field resonance found for the SCHS moiety indicates η^1-binding of the ester), whereas the ^{31}P{^{1}H} NMR spectrum is composed of only one singlet at δ 63.1, indicating the planarity of the four dppe P atoms. The ^{13}C{^{1}H} NMR spectrum shows a singlet at δ 213.48 for the RuSC moiety and another singlet at δ 17.79 for the SMe moiety. The triflate counterion appears at δ 135.76 as an unresolved broad singlet.

An X-ray diffraction study of *trans*-[(dppe)$_2$Ru(H)(SC(SMe)H)][OTf] **2** was carried out, and the ORTEP diagram of the cation is shown in Figure 1.[10] The structure consists of a distorted octahedron defined by four coplanar dppe phosphorus atoms, and the SC(SMe)H moiety, bound to the metal in an η^1-fashion, is approximately perpendicular to this plane. The trans hydride ligand that occupies the sixth coordination site on the metal was not located. The dppe bite angles P(1)−Ru(1)−P(2) and P(3)−Ru(1)−P(4) are 79.81(6)° and 83.73(6)°, respectively. The geometry around the carbon of the SCH(S) moiety is deviated slightly from an ideal sp^2 carbon atom (128.7(6)°). It is interesting to note that the two C−S distances (S(1)−C(53) and S(2)−C(53)) are respectively 1.609(8) and 1.684(9) Å, which are intermediate between C−S single and double bonds. Such intermediate distances have been reported previously by others: [(PPh$_3$)$_2$(CO)Ru(η^2-S$_2$CH)] by Gopinathan and coworkers,[11a] [(dppm)$_2$Fe(η^2-S$_2$CH)][BF$_4$] by Gao et al.,[11b] and [(CO)$_2$(PPh$_3$)$_2$Co$_2$(1,3-η^2-S$_2$CSMe)(μ-1,2-η^2-SCSMe)] by Gervasio et al.[5] This could be a result of the delocalization of electron density over the S−CH−S moiety. The third C−S distance (C(54)−S(2)) of 1.776(18) Å resembles a typical C−S single bond length of ∼1.8 Å.[12]

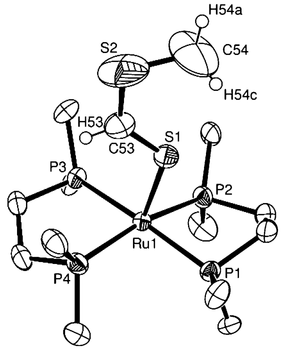


Figure 1. ORTEP view of *trans*-[(dppe)$_2$Ru(H)(SC(SMe)H)]$^+$ **2** cation at the 50% probability level. The phenyl groups on the dppe phosphorus atoms have been omitted for clarity; only one carbon of each phenyl group is shown in the figure. Pertinent bond distances (Å) and angles (deg): Ru(1)−S(1) 2.4036(18), C(53)−S(1) 1.609(8), C(53)−S(2) 1.684(9), C(54)−S(2) 1.776(18); S(1)−C(53)−S(2) 128.7(6).

In order to cleave the organic species (the methyldithioformate) from **2**, we purged H$_2$ gas through a solution containing this compound at a steady rate for 30 min. ^{1}H NMR spectroscopy revealed the generation of methyldithioformate in small quantities and the formation of a hydride dihydrogen complex *trans*-[(dppe)$_2$Ru(H)(η^2-H$_2$)][OTf] **3**.[13] In an attempt to obtain the free ester in a quantitative yield, we reacted **2** with a slight excess of CH$_3$CN. The color of the reaction mixture turned pale yellow within a few minutes accompanied by the quantitative generation of methyldithioformate and a hydride nitrile complex *trans*-[(dppe)$_2$Ru(H)(CH$_3$CN)][OTf] **4** (Scheme 1); we reported an analogous nitrile complex with a BF$_4^-$ counterion recently.[14] The hydride nitrile complex **4** was precipitated from the reaction mixture by the addition of excess Et$_2$O, and the supernatant solution containing the free ester along with CH$_2$Cl$_2$, Et$_2$O, and CH$_3$CN was decanted carefully and subjected to distillation. The free methyldithioformate was fractionally distilled from the mixture and isolated for further characterization.

The free methyldithioformate exhibits two singlets each in the ^{1}H NMR spectrum at δ 2.68 (*Me*S) and 11.33 (*H*C(S)) and ^{13}C NMR spectrum at δ 16.00 (*Me*S) and 218.14 (H*C*(S)), respectively. The vibrational spectrum shows a medium-intensity ν(C═S) at 1110 cm^{-1} and an intense band at 304 nm in the electronic spectrum.

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(10) Crystallographic data for *trans*-[(dppe)$_2$Ru(H)(SC(SMe)H)][OTf] **2**: C$_{55}$H$_{52}$F$_3$O$_3$P$_4$RuS$_3$, fw 1139.10, monoclinic, *Cc*, $a = 12.450(6)$ Å, $b = 23.320(10)$ Å, $c = 19.433(9)$ Å, $\alpha = 90.00°$, $\beta = 106.791(7)°$, $\gamma = 90.00°$, $V = 5402(4)$ Å^3, $Z = 4$, $T = 293(2)$ K. All the hydrogen atoms were geometrically fixed and allowed to ride with the respective light atoms to which they are attached. The fluorine atoms in the counterion were shared with partial occupancy and refined isotropically. The data was corrected for absorption using the SADABS program available in the Bruker system of programs. Full-matrix least squares refinement (based on F^2, SHELX-97) of the positional and anisotropic thermal parameters for the non-hydrogen atoms converged with R1 = 0.0682 and wR2 = 0.1866 for 12328 independent reflections with $I > 2\sigma(I)$.

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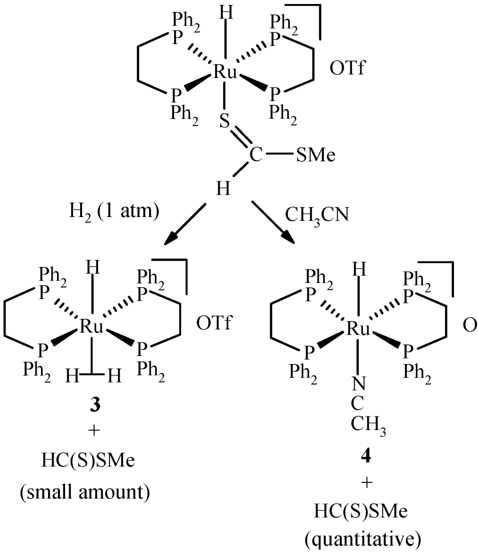
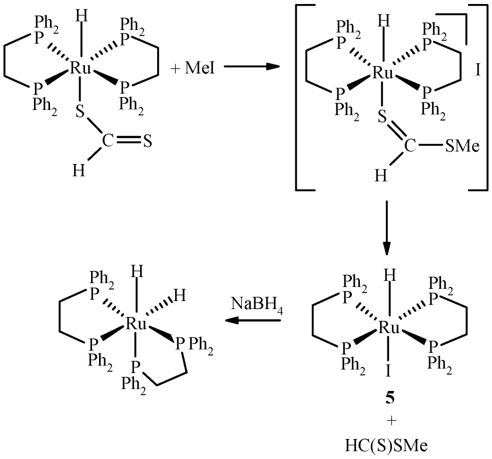
Scheme 1. Cleavage Pathways for Methyldithioformate from **2**



Scheme 2. Reaction of **1** with MeI and the Recovery of *cis*-[(dppe)$_2$Ru(H)$_2$]



In an effort to recycle the ruthenium, we examined the reactivity of **1** with other electrophiles; **1** reacts with 5 equiv of MeI in a facile manner to provide free methyldithioformate and *trans*-[(dppe)$_2$Ru(H)I] **5** through the intermediacy of *trans*-[(dppe)$_2$Ru(H)(SC(SMe)H)][I] that was observed NMR spectroscopically (Scheme 2). We are currently studying the kinetics of this reaction, the results of which will be published shortly. The complex **5** provides a route to recover the starting dihydride *cis*-[(dppe)$_2$Ru(H)$_2$]: when **5** was reacted with excess NaBH$_4$ in a THF−methanol solution, the dihydride was obtained in a yield of 48.2%; for comparison with the reaction of **2** with hydrogen (Scheme 1), we carried out this reaction under an atmosphere of H$_2$ and found that the yield of the product obtained was unaffected. This reaction pathway indicates that by employing a good coordinating ligand as the counterion in **2** it would be possible to obtain a precursor from which the ruthenium dihydride complex *cis*-[(dppe)$_2$Ru(H)$_2$] could be recovered.

In another attempt to recover the ruthenium dihydride complex *cis*-[(dppe)$_2$Ru(H)$_2$], we reacted **2** with NaBH$_4$ in a mixture of THF−MeOH solvents and upon workup obtained *cis*-[(dppe)$_2$Ru(H)$_2$] complex in 68% yield. The other products of the reaction have not been separated and identified; we assume that the free ester under the reaction conditions would have undergone reduction to a thiol. Efforts are in progress to isolate the sulfur-containing products and identify them.

The present results represent an important case of functionalization and the subsequent elimination of an organic compound from a transition metal center using CS$_2$. Schenk and Schwietzke functionalized the CS$_2$ bound to a tungsten center by the use of a nucleophile LiBEt$_3$H to generate the dithioformate species.[6c] In our case, we bring about the insertion of CS$_2$ into a M−H bond to give the dithioformate. In this respect our approach differs from that of Schenk and Schwietzke.[15] While there are other examples of similar activation sequences reported in the literature,[1] our work is unprecedented with regard to the elimination of the organic moiety and the subsequent regeneration of the starting dihydride complex. In addition, each one of the products in the sequence of reactions to afford the methyldithioformate presented here is obtained in fairly high yields, making the process look quite attractive. Methyldithioformate has been found to be quite a reactive species; it reacts rapidly with certain dienes to give Diels−Alder adducts, consequently finding use in organic synthesis.[7b,16] It should be possible to use the present route to obtain other alkyl/aryl dithioesters as well from the hydride dithioformate complex using appropriate electrophiles. Consequently, the study of the chemistry of such esters bound to transition metal fragments could become accessible. These investigations are in progress in our laboratories.

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Supporting Information Available: Synthesis and characterization details for the compounds, stack plots of the NMR spectra of the reactions of **2** with H$_2$ and CH$_3$CN and of **1** with MeI, and IR and electronic spectra of methyldithioformate. X-ray crystallographic data for *trans*-[(dppe)$_2$Ru(H)(SC(SMe)H)][OTf] **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The alkyl dithioformate species was found to bind in an η^2-fashion in the tungsten complex [(dppe)W(η^2-SCHSR)(CO)$_2$];[6c] in our complex, the methyldithioformate is bound to ruthenium in an η^1-manner.

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