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Reactions of Carbonyl Sulfide and Carbon Disulfide with Iron and Ruthenium Complexes. Synthesis and Reactivity of Dicarbonyl(η^2-carbonyl sulfide)bis(triphenylphosphine)ruthenium(0)

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The reaction of $Fe(CO)_2(PPh_3)_3$ with COS in toluene results in the formation of $Fe(CO)_3(PPh_3)_2$ and $SPPh_3$. When liquefied COS is used as the solvent, $Fe(S_2CO)(CO)_2(PPh_3)_2$ is also formed. The analogous ruthenium complex, $Ru(CO)_2(PPh_3)_3$, reacts with COS to afford $Ru(CO)_2(\eta^2\text{-COS})(PPh_3)_2$. This COS complex reacts with additional COS to give $Ru(S_2CO)(CO)_2(PPh_3)_2$ and with PPh_3 to give $Ru(CO)_3(PPh_3)_2$ and $SPPh_3$.

Introduction

The activation of heteroallenes by transition-metal complexes is a topic of much current activity.[1-3] The bonding of isocyanates,[2,4-8] ketenes,[9,10] carbodiimides,[11-13] isothiocyanates,[14,15] and carbon disulfide[2,16-20] to metal complexes has been studied. Owing to the widespread interest in incorporating CO_2 into organic substrates and the paucity of successful examples of metal-promoted CO_2 reductions that lead to this end,[1] other heteroallenes have received much attention as model systems for CO_2 activation.[9-11] In spite of its similarity to CO_2, carbonyl sulfide, COS, has received surprisingly little attention as a model for CO_2 coordination[4,21-23] and reduction.[24] Here we report on some of our investigations into the coordination chemistry of carbonyl sulfide, and the reactivity of metal–(carbonyl sulfide) complexes.

Experimental Section

All reactions were performed in freshly distilled solvents under a nitrogen atmosphere. Carbonyl sulfide was obtained from the Matheson Gas Co., East Rutherford, NJ. Carbon disulfide was distilled from P_2O_5 prior to use. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Phosphorus nuclear magnetic resonance spectra were recorded on a JEOL FX 90Q spectrometer, with broad-band ^1H decoupling. Peak positions are relative to 85% phosphoric acid, with downfield values reported as positive. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL, and Galbraith Laboratories, Inc., Knoxville, TN.

$Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$. Carbon disulfide (4 mL) was syringed into a Schlenk flask that contained 0.100 g of $Fe(CO)_2(PPh_3)_3$.[25] The solution was stirred for 30 min and then diluted with 10 mL of hexane. The orange crystals were filtered, washed with hexane, and dried under vacuum. The yield was 0.079 g (90%). The complex was identified by comparison of IR and NMR spectra with spectra of an authentic sample.[26] ^{31}P NMR ($CDCl_3$, −40 °C): δ 58.1 (s).

$Fe(CO)_3(PPh_3)_2$. A toluene solution of $Fe(CO)_2(PPh_3)_3$ (0.105 g in 10 mL) was stirred in a 20-mL vessel under 1 atm of COS for 1 h. The volume of the solution was reduced to 5 mL under vacuum, and the solution was filtered. The solids were washed twice with acetone, and the acetone solution was filtered and combined with the toluene filtrate. The solution was evaporated to dryness; the orange solids were dissolved in the minimum amount of benzene and filtered. The solution was diluted with 40 mL of methanol and cooled overnight (−30 °C). The yellow crystals that formed were separated by filtration and dried under vacuum. The yield was 0.026 g (33%). The compound was identified by comparing IR and NMR spectra with those of an authentic sample.[27] ^{31}P NMR ($CDCl_3$): δ 82.4 (s).

$Fe(S_2CO)(CO)_2(PPh_3)_2$. Carbonyl sulfide (47 g) was condensed into a liquid-nitrogen-cooled pressure reactor that contained 0.69 g of $Fe(CO)_2(PPh_3)_3$. The reactor was allowed to warm to room temperature (*caution*! 12 atm), and the suspension was stirred for 16 h. The COS was distilled from the reactor, and the solids were extracted with 50 mL of toluene and filtered under nitrogen. The solids that remained were extracted with 10 mL of $CHCl_3$ and filtered. The orange filtrate was evaporated to 2 mL, and slow addition of 40 mL of hexane precipitated an orange solid that was collected by filtration, washed with hexane, and dried under vacuum. The yield was 0.086 g (15%). Anal. Calcd for $C_{39}H_{30}FeO_3P_2S_2$: C, 64.29; H, 4.15; S, 8.80; P, 8.50. Found: C, 62.92; H, 4.65; S, 9.15; P, 8.21. ^{31}P NMR ($CDCl_3$): δ 51.1 (s).

$Ru(CO)_2(PPh_3)_3$. This compound was prepared by a modification of a published procedure.[25] A suspension of $[Ru(CO)_2(N_2C_6H_4OCH_3\text{-}p)(PPh_3)_2][BF_4]$ (3.15 g) was stirred for 1.5 h in an ethanolic solution of $NaBH_4$ (2.65 g $NaBH_4$ in 135 mL absolute ethanol). The cream white product, $RuH_2(CO)_2(PPh_3)_2$, was isolated in 89% yield. The compound was refluxed with 7 equiv of PPh_3 in 200 mL of anhydrous methanol for 7 h.[28] The orange suspension was filtered, and the yellow-orange solid was washed with methanol and hexane and dried under vacuum. The overall yield was 81%. ^{31}P NMR (toluene-d_8, −48 °C): δ 49.19(s).

$Ru(CO)_2(\eta^2\text{-COS})(PPh_3)$. A suspension of $Ru(CO)_2(PPh_3)_3$ (0.307 g in 5 mL toluene) was stirred under an atmosphere of COS for 5 min. The suspension was then diluted with 10 mL of hexane and

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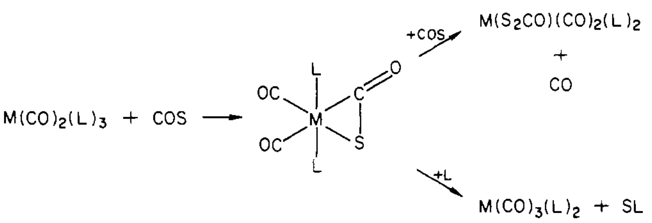
Scheme I. Synthesis and Reactions of M(COS) Complexes (M = Fe, Ru; L = PPh_3)[a]



[a] The Fe(COS) complex has not been isolated.

filtered. The cream white solid was washed with hexane and dried under vacuum. The yield was 0.240 g (99.6%). Anal. Calcd for $C_{39}H_{30}O_3P_2RuS$: C, 63.17; H, 4.05; P, 8.36; S, 4.32. Found: C, 62.88; H, 4.27; P, 8.11; S, 4.00. ^{31}P NMR (toluene-d_8, −48 °C): δ 36.32 (s).

$Ru(S_2CO)(CO)_2(PPh_3)_2$. Method A. A suspension of $Ru(CO)_2(PPh_3)_3$ (0.131 g in 5 mL of toluene) was stirred under an atmosphere of COS for 24 h. The suspension was diluted with 10 mL of hexane and filtered. The off-white solid was washed with hexane and dried under vacuum. The yield was 0.066 g (61%). The compound may be recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{39}H_{30}O_3P_2RuS_2$: C, 60.52; H, 3.91; P, 8.01; S, 8.29. Found: C, 60.46; H, 3.92; P, 7.46; S, 8.18. ^{31}P NMR ($CDCl_3$): δ 30.83 (s).

Method B. A solution of $Ru(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$ (0.105 g in 4 mL of CH_2Cl_2) was stirred under an atmosphere of carbonyl sulfide for 14 h. Addition of 30 mL of hexane gave a yellow precipitate. The suspension was filtered and the pale-yellow solid was washed with hexane and dried under vacuum. The yield was 0.061 g (75%). The compound was identified by comparison of IR and NMR spectra with those of a sample prepared by method A.

$Ru(CO)_3(PPh_3)_2$. A solution of $Ru(CO)_2(PPh_3)_3$ (0.200 g in 20 mL of benzene) was stirred under an atmosphere of carbonyl sulfide for 0.5 h. The solution was diluted with 100 mL of methanol and cooled to 5 °C. The pale-yellow crystals that formed were collected by filtration and dried under vacuum. The yield was 0.090 g (60%). The compound was identified by comparison of IR and NMR spectra with those of an authentic sample.[29] ^{31}P NMR ($CDCl_3$): δ 55.43 (s).

$Ru(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$. This compound was prepared according to the procedure of Grundy et al.[30] A solution of CS_2 and toluene (1 mL of CS_2, 9 mL of toluene) was syringed onto 0.250 g of $Ru(CO)_2(PPh_3)_3$, and the suspension was stirred for 10 min. The yellow suspension was diluted with 30 mL of hexane and filtered, and the yellow solid was washed with hexane and dried under vacuum. The yield was 0.198 g (99%). ^{31}P NMR (C_6D_6/CH_2Cl_2): δ 36.87 (s).

Results and Discussion

Carbon disulfide reacts with $Fe(CO)_2(PPh_3)_3$ to give $Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$ and PPh_3, as shown in eq 1.

$$Fe(CO)_2(PPh_3)_3 + CS_2 \rightarrow Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2 + PPh_3 \quad (1)$$

In contrast, COS carbonylates $Fe(CO)_2(PPh_3)_3$ in toluene according to eq 2. If the reaction is performed in liquefied

$$Fe(CO)_2(PPh_3)_3 + COS \rightarrow Fe(CO)_3(PPh_3)_2 + SPPh_3 \quad (2)$$

COS, $Fe(S_2CO)(CO)_2(PPh_3)_2$ is also formed (eq 3).

$$Fe(CO)_2(PPh_3)_3 + COS(l) \rightarrow Fe(S_2CO)(CO)_2(PPh_3)_2 + Fe(CO)_3(PPh_3)_2 + SPPh_3 \quad (3)$$

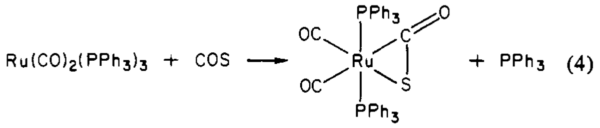
These results are consistent with the initial formation of $Fe(\eta^2\text{-}COS)(CO)_2(PPh_3)_2$ as an unstable intermediate that rapidly decomposes in toluene and reacts with COS in liquefied COS, as shown in Scheme I. We have isolated the Ru(COS) complex and have shown that it reacts with COS and PPh_3 according to Scheme I.

Table I. Infrared Data[a] for the Complexes

compd	ν(C≡O), cm^{-1}	ν(C=O/C=S), cm^{-1}	other ν, cm^{-1}
$Fe(CO)_2(PPh_3)_3$	1894 (vs)		
	1838 (vs)		
$Fe(CO)_3(PPh_3)_2$	1890 (vs, br)		
$Fe(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$	1995 (vs)	1142 (vs)	
	1925 (vs)	1155 (vs, sh)	
$Fe(S_2CO)(CO)_2(PPh_3)_2$	2022 (vs)	1688 (s, br)	838 (m)[d]
	1949 (vs)	1611 (vs)	
$Ru(CO)_2(PPh_3)_3$	1904 (vs)		
$Ru(CO)_3(PPh_3)_2$	1895 (vs, br)		
$Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$	2022 (s, sh), 2020[b]	1704 (vs)	637 (s)[c]
	2012 (vs), 1957[b]	1678 (s, sh)	
	1951 (vs)	1700[b]	
	1939 (vs, sh)		
$Ru(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$	2021 (vs, sh), 2020[b]	1126 (vs)	650 (s)[c]
	2017 (vs), 1958[b]	1128[b]	
	1951 (vs)		
	1939 (vs, sh)		
$Ru(S_2CO)(CO)_2(PPh_3)_2$	2040 (vs)	1688 (s, br)	832 (m)[d]
	1966 (vs)	1609 (vs)	

[a] In Nujol mull unless otherwise noted. [b] In CH_2Cl_2. [c] $\nu(\overline{MCS})$. [d] π deformation.

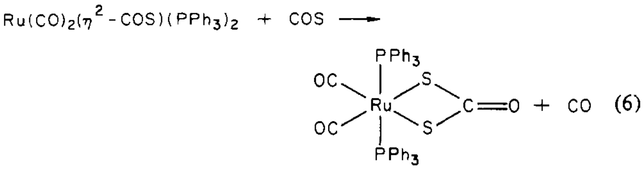
When a toluene solution of $Ru(CO)_2(PPh_3)_3$ is exposed to an atmosphere of COS, $Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ is deposited as a cream white microcrystalline solid (eq 4). The complex



exhibits IR absorptions characteristic of the η^2 coordination of COS through the C=S bond[4] ν(C=O) = 1701 (vs), 1678 (sh) cm^{-1}, $\nu(\overline{RuCS})$ = 638 (m) cm^{-1}). The presence of two terminal carbonyl stretching vibrations in the infrared spectrum[31] (see Table I), along with the singlet observed in the ^{31}P NMR spectrum, is consistent only with the isomer depicted in eq 4. The complex is stable in the solid state when stored under an atmosphere of nitrogen but is unstable in solution, decomposing to give $Ru(CO)_3(PPh_3)_2$, $SPPh_3$, and some unidentified products. The decomposition of $Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ in the presence of 1 equiv of PPh_3 was followed by ^{31}P NMR spectroscopy. After 15 min the only species detected were $Ru(CO)_3(PPh_3)_2$ and $SPPh_3$ (eq 5).

$$Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2 + PPh_3 \rightarrow Ru(CO)_3(PPh_3)_2 + SPPh_3 \quad (5)$$

Carbonyl sulfide reacts with $Ru(CO)_2(\eta^2\text{-}COS)(PPh_3)_2$ to afford $Ru(S_2CO)(CO)_2(PPh_3)_2$, as shown in eq 6. The



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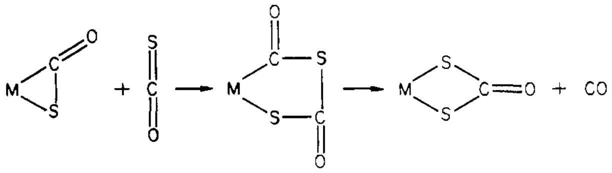
Scheme II. Possible Pathway to Reductive Disproportionation of COS



complex exhibits IR absorption characteristics of a bidentate dithiocarbonate ligand, S_2CO^{2-}, coordinated through the sulfur atoms[32,33] (see Table I). The IR and NMR spectra are consistent with the presence of cis-carbonyl and trans-phosphine ligands.

Equations 4 and 6 represent a two-electron oxidation of ruthenium and disproportionation of two molecules of COS to give the dithiocarbonate anion and carbon monoxide (eq 7). It was recently reported by Pasquali et al.[24] that vanadocene promotes this two-electron disproportionation of COS.

$$(L)_nRu^0 + 2COS \rightarrow (L)_nRu^{II}(S_2CO) + CO \quad (7)$$

They propose that a C=O bound carbonyl sulfide complex is formed and nucleophilic attack by the exocyclic sulfur atom upon the electrophilic carbon atom of another molecule of COS leads to formation of the products, a metal dithiocarbonate and a metal carbonyl. For a C=S bound carbonyl sulfide, nucleophilic attack by the exocyclic oxygen atom would lead to formation of a metal *mono*thiocarbonate and a metal–*thio*carbonyl. Our results indicate that C=S bound carbonyl sulfide ligands react with COS to give dithiocarbonates.[34] These products could arise from an electrophilic attack on the endocyclic sulfur atom by another COS molecule, followed by elimination of CO, as shown in Scheme II. A similar mechanism has been proposed for the disproportionation of isothiocyanates,[35] and head-to-tail dimers have been proposed as intermediates in other heteroallene disproportionations.[36] Head-to-tail heteroallene dimers have been isolated[10,18-20] and characterized, but in these instances the dimers are stable and do not disproportionate.[37] An alternative mechanism for a metal-promoted reductive disproportionation of COS involves cleavage of the coordinated C=S bond to afford a metal sulfide, which then reacts with an additional molecule of COS to yield a dithiocarbonate.[38] The instability of $Ru(CO)_2(\eta^2\text{-COS})(PPh_3)_2$ has precluded our attempts to distinguish these two possible mechanisms of reaction 6.

Equations 4–6 are summarized in Scheme I. We have isolated the Ru(COS) intermediate and demonstrated that it does react subsequently with PPh_3 and COS according to Scheme I. It must be emphasized that we were able to isolate $Ru(CO)_2(\eta^2\text{-COS})(PPh_3)_2$ because reaction 4 proceeds rapidly and $Ru(CO)_2(\eta^2\text{-COS})(PPh_3)_2$ precipitates before reaction 5 becomes significant. The iron complex, $Fe(CO)_2(PPh_3)_3$, reacts more slowly with COS, and the proposed intermediate, $Fe(CO)_2(\eta^2\text{-COS})(PPh_3)_2$, apparently decomposes before precipitation occurs.

The carbon disulfide analogues of $Ru(CO)_2(\eta^2\text{-COS})(PPh_3)_2$ and $Fe(CO)_2(\eta^2\text{-COS})(PPh_3)_2$ have been prepared[26,30] and are much more stable than the COS complexes. Since vigorous conditions are often required, sulfur abstraction from a metal–(η^2-CS_2) complex[39] is not a general method for the preparation of metal thiocarbonyls. In contrast, sulfur elimination from metal–(η^2-COS) complexes is much more facile. Metal complexes that form stable CS_2 adducts often react with COS to give a carbonylation product.[4,20,22]

The bond energy of the C=S bond in COS is 72 kcal/mol whereas it is 107 kcal/mol in CS_2.[40] The weakening of the C=S bond of COS upon complexation to a metal complex is apparently sufficient to promote sulfur elimination. The stronger C=S bond of CS_2 is less susceptible to metal-promoted cleavage, but the presence of a suitable sulfur acceptor (e.g., PPh_3) can facilitate sulfur elimination.[39]

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Registry No. $Fe(CO)_2(\eta^2\text{-}CS_2)(PPH_3)_2$, 64424-68-6; $Fe(CO)_3(PPh_3)_2$, 21255-52-7; $Fe(S_2CO)(CO)_2(PPh_3)_2$, 81011-75-8; $Ru(CO)_2(PPh_3)_3$, 35880-54-7; $Ru(CO)_2(\eta^2\text{-COS})(PPh_3)_2$, 81027-57-8; $Ru(S_2CO)(CO)_2(PPh_3)_2$, 81011-76-9; $Ru(CO)_2(\eta^2\text{-}CS_2)(PPh_3)_2$, 81011-77-0; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $Fe(CO)_2(PPh_3)_3$, 15739-18-1; $[Ru(CO)_2(N_2C_6H_4OCH_3\text{-}p)(PPh_3)_2][BF_4]$, 54733-55-0; $RuHz(CO)_2(PPh_3)_2$, 21029-29-8; COS, 463-58-1.

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