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Synthesis and Characterization of Some Ruthenium–Phosphoniodithiocarboxylate Complexes

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Addition of CS_2 to $RuClH(CO)(PCy_3)_2$ affords the cation $[RuH(CO)(S_2CPCy_3)(PCy_3)_2]^+$, which has been isolated as the tetraphenylborate salt. The closely related complex $[RuCl(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]$ is formed when the zwitterion ligand S_2CPCy_3 is added to a methanol suspension of $RuCl_2(CO)(PCy_3)_2$ and $NaBPh_4$. The reaction of carbonyl sulfide with $RuClH(CO)(PCy_3)_2$ results in the formation of $RuClH(CO)_2(PCy_3)_2$.

Carbon disulfide is known to insert into metal–hydride bonds to give metal dithioformates.[1-5] Recently it has become apparent that metal–phosphoniodithiocarboxylate complexes, $M(S_2CPR_3)L_n$, may be formed from the addition of CS_2 to metal–phosphine complexes.[6-8] We report the syntheses of several ruthenium–phosphoniodithiocarboxylate complexes and one reaction in which formation of a phosphoniodithiocarboxylato ligand is favored over formation of a dithioformato ligand when a polar solvent is employed.

Results and Discussion

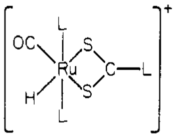
While CS_2 inserts into the RuH bond of $RuClH(CO)(PCy_3)_2$ (Cy = cyclohexyl) to afford $RuCl(S_2CH)(CO)(PCy_3)_2$,[2] we find that in a polar solvent (ethanol) a different reaction occurs. When CS_2 is added to an ethanol suspension of $RuClH(CO)(PCy_3)_2$, the yellow-orange solid dissolves and a purple solution is formed. Addition of $NaBPh_4$ to the solution precipitates $[RuH(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]$ (eq 1). The yield of the salt is low, as expected since some of the $RuClH(CO)(PCy_3)_2$ starting material must serve as a source of PCy_3.

$$RuClH(CO)(PCy_3)_2 + CS_2 \xrightarrow[NaBPh_4]{EtOH} [RuH(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4] \quad (1)$$

Coordination of CS_2 and subsequent transfer of a PCy_3 ligand to the carbon atom of CS_2 could lead to the formation of the phosphoniodithiocarboxylato ligand. Alternatively, phosphine dissociation could lead to the formation of the zwitterion adduct S_2CPR_3, which could then react with $RuClH(CO)(PCy_3)_2$ to give the insertion product. We have found that direct addition of a zwitterion adduct, S_2CPR_3 (R = Cy, Et), to $RuClH(CO)(PCy_3)_2$ results in the facile formation of the cation $[RuH(CO)(S_2CPR_3)(PCy_3)_2]^+$, which we have isolated as the tetraphenylborate salt (R = Cy, **1**; R = Et, **2**), as shown in eq 2. Although the formation of the phosphoniodithiocarboxylato ligand could be regarded as an insertion of CS_2 into a RuP bond, we believe from (2) that it is more likely that reaction 1 proceeds via disproportionation.

$$RuClH(CO)(PCy_3)_2 + S_2CPR_3 \xrightarrow[NaBPh_4]{MeOH} [RuH(CO)(S_2CPR_3)(PCy_3)_2][BPh_4] \quad (2)$$

The infrared spectra of **1** and **2** exhibit one terminal carbonyl stretching vibration and a band between 1050 and 950 cm^{-1} that we suggest is $\nu(CS)$ of the S_2CPR_3 ligand[7] (Table I). Each complex also exhibits a very weak band at $\sim$2000 cm^{-1} that may be attributed to ν(Ru–H), but the low intensity of this absorption precludes a definite assignment. The complexes exhibit several strong bands between 750 and 700 cm^{-1} that might be attributed to $\nu(CS_2)_{sym}$.[5] However, these bands are apparently not observed in other phosphoniodithiocarboxylate complexes. The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** consist of an A_2X pattern, consistent with the presence of two magnetically equivalent and one magnetically inequivalent PR_3 group. The small values of the coupling constants (see Table I) are indicative of long-range coupling.[6,7] Three isomers that should exhibit similar spectra are



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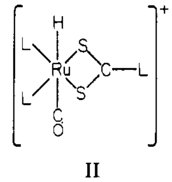
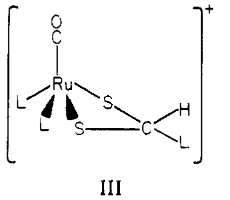


II



III

Although phosphonium–betaine ligands (isomer III) are formed when CS_2 is added to similar metal complexes,[7,9] the ^1H NMR spectra are consistent only with isomers I and II as the spectra exhibit a hydride resonance (Figure 1) that is split into a triplet by two equivalent PR_3 ligands and further split into a doublet by a more distant PR_3 group. The betaine proton of isomer III would be expected to appear further downfield[7,9] ($\delta \simeq 6$) and should couple more strongly to the

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Table I. Infrared and NMR Data of the Complexes

compd	^{1}H NMR,^{a} δ		^{31}P NMR^a	IR absn^b
	hydride	alkyl		
[RuH(CO)(S_2CPCy_3)$_2$(PCy_3)$_2$][BPh_4] (1)	−10.75 (dt, ^2J(PH) = 22.0, ^4J(PH) = 6.1)	1.88 (s) 1.48 (s) 1.24 (s)	66.3 (d) 22.8 (t, ^4J(PP) = 8.6)	1998 (vw) ν(RuH)? 1938 (vs) ν(CO) 964 (m) ν(CS) 741 (vs) 730 (vs) ν(CS_2)$_{sym}$? 703 (vs)
[RuH(CO)(S_2CPEt_3)(PCy_3)$_2$][BPh_4] (2)	−10.74 (dt, ^2J(PH) = 21.1, ^4J(PH) = 6.1)	1.82 (s) 1.50 (s) 1.18 (s)	63.9 (d) 28.7 (t, ^4J(PP) = 8.5)	2010 (vw) ν(RuH)? 1940 (vs) ν(CO) 1043 (s) ν(CS) 730 (s) ν(CS_2)$_{sym}$? 706 (s)
[RuCl(CO)(S_2CPCy_3)(PCy_3)$_2$][BPh_4] (3)		1.79 (s) 1.48 (s) 1.24 (s)	40.9 (d) 25.2 (t, ^4J(PP) = 5.7)	1953 (vs) ν(CO) 949 (m) ν(CS) 738 (vs) 728 (vs) ν(CS_2)$_{sym}$? 705 (vs)
RuClH(CO)(PCy_3)$_2$	−24.7 (t, ^2J(PH) = 18.3)		45.5 (s)	1908 (vs) ν(CO)
RuClH(CO)$_2$(PCy_3)$_2$	−5.3 (t, ^2J(PH) = 24.0)		49.9 (s)	2030 (vs) ν(CO) 1978 (m) ν(RuH) 1945 (vs) ν(CO)
$RuCl_2$(CO)(PCy_3)$_2$			34.5 (s)	1934 (vs) ν(CO)

^{a} In $CDCl_3$. J values given in Hz. ^{b} In Nujol. Phosphine bands are not tabulated.

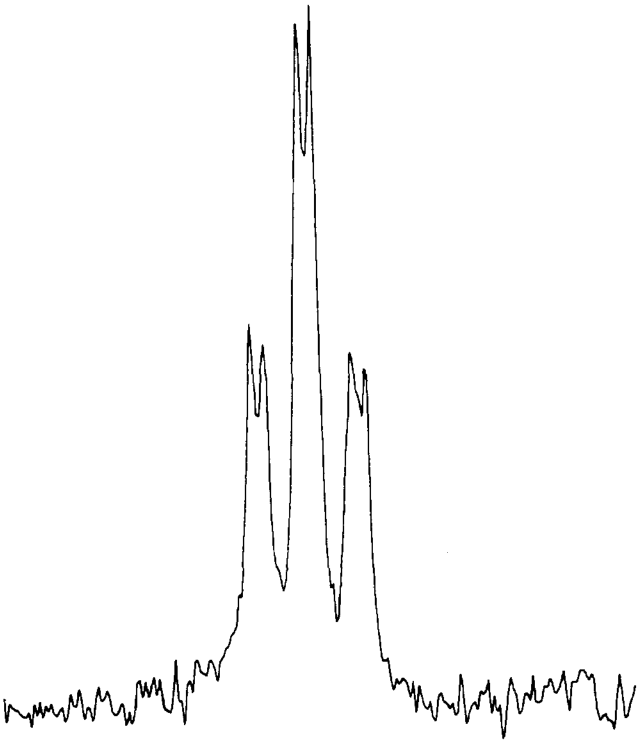

Figure 1. ^{1}H NMR spectrum of the hydride region of [RuH(CO)(S_2CPCy_3)(PCy_3)$_2$][BPh_4]. The pattern is centered at δ −10.75; the marker is 50 Hz wide.

betaine PR_3 group than to the PR_3 ligands.

The P–P coupling constant from PR_3 to S_2CPR_3 should be larger for isomer II, in which the S_2CPR_3 ligand is trans to the PR_3 ligands, than for isomer I, in which the S_2CPR_3 ligand is cis to the PR_3 ligands. For a similar complex, [RuCl(MeOH)(S_2CPEt_2Ph)(PEt_2Ph)$_2$][BPh_4], which is known to have PEt_2Ph ligands cis and trans to the S_2CPEt_2Ph ligand,[6] the coupling constants vary by a factor of 3 (^4J(cis PP) = 3.5 Hz, ^4J(trans PP) = 11.3 Hz). The values of ^4J for **1** and **2** are intermediate between these values, and we are unable to distinguish isomer I from II on the basis of the magnitude of ^4J.

An analogue of **1**, [RuCl(CO)(S_2CPCy_3)(PCy_3)$_2$][BPh_4] (**3**), may be prepared by the addition of S_2CPCy_3 to a methanol suspension of $RuCl_2$(CO)(PCy_3)$_2$ and $NaBPh_4$. The ^{31}P and ^{1}H NMR spectra of **3** are similar to the spectra of **1** and **2**, except that the hydride resonance is absent (see Table I). The analogous isomers (I, II) of **3** would have a sulfur atom or a carbonyl ligand trans to the chloro ligand, respectively, and the metal–chloride stretching frequency (ν(RuCl) = 274 cm^{-1}) is consistent with either.[2,10] Thus, we are unable to distinguish isomer I from isomer II on the basis of the metal–chlorine stretching frequency. The value of ^4J for **3** is slightly smaller than for **1** or **2** and is nearer to ^4J(cis PP) rather than ^4J(trans PP) for [RuCl(MeOH)(S_2CPEt_2Ph)(PEt_2Ph)$_2$][BPh_4].[6] Therefore, we propose that isomer I of **3** is formed. Isomer I should be favored over II for **1**, **2**, and **3** because of the sterically unfavorable cis arrangement of PCy_3 ligands in II.

Carbonyl sulfide reacts with RuClH(CO)(PCy_3)$_2$ in polar and nonpolar solvents to afford RuClH(CO)$_2$(PCy_3)$_2$. The fate of the sulfur in the reaction has not been determined, but we find no NMR spectroscopic evidence for the formation of $SPCy_3$, even if free PCy_3 is present. It is not surprising that carbonylation, rather than insertion to give [RuH(CO)($SOCPCy_3$)(PCy_3)$_2$]Cl, occurs. Unlike CS_2, COS does not form a stable zwitterion complex with PCy_3, and metal-promoted C=S bond cleavage has been shown to be more facile for COS than for CS_2.[11]

Experimental Section

$RuCl_2$(CO)(PCy_3)$_2$[2] and RuClH(CO)(PCy_3)$_2$[12] were prepared as previously described. Carbonyl sulfide was obtained from the Matheson Gas Co., East Rutherford, NJ. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. Proton and ^{31}P NMR spectra were obtained on a JEOL FX90Q spectrometer. Peak positions are relative to tetramethylsilane and 85% phosphoric acid, respectively, with downfield values reported as positive. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. All reactions were performed in air, unless otherwise noted.

[RuH(CO)(S_2CPCy_3)(PCy_3)$_2$][BPh_4] (1). Method A. Carbon disulfide (7 mL) was added to a suspension of RuClH(CO)(PCy_3)$_2$ (0.100 g in 20 mL of methanol). Sodium tetraphenylborate (0.5 g) was added to the purple solution. The solution was concentrated by

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rapid purging with N_2 while warming to ~40 °C. The purple suspension was cooled to -30 °C, and the dark red solids were collected by filtration and dried under vacuum. The crude yield was 0.076 g. The predominant product (~40% of the solid) is $[RuH(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]$, as determined by comparison of ^{31}P and ^1H NMR spectra with those of a pure sample, which was prepared by method B. Additional products, including a ruthenium hydride complex (δ -12.6 (t, J = 20.7 Hz)), were detected via NMR spectroscopy.

Method B. A suspension of $RuClH(CO)(PCy_3)_2$ (0.160 g) and S_2CPCy_3 (0.0784 g in 35 mL of absolute ethanol) was stirred for 20 min. The purple solution was filtered, and 0.30 g $NaBPh_4$ was added to the filtrate. The purple suspension was cooled to -20 °C, and the purple solid was collected by filtration, washed with ethanol, and dried under vacuum. The yield was 0.177 g (59%). Anal. Calcd for $C_{80}H_{120}BOP_3RuS_2$: C, 70.31; H, 8.85; P, 6.80; S, 4.70. Found: C, 70.57; H, 9.02: P, 6.49; S, 4.55.

$[RuH(CO)(S_2CPEt_3)(PCy_3)_2][BPh_4]$ (2). A suspension of $RuClH(CO)(PCy_3)_2$ (0.135 g) and S_2CPEt_3 (0.054 g in 20 mL of anhydrous methanol) was stirred for 5 min. Carbon disulfide (2.0 mL) was then added to the suspension, and the clear purple solution was stirred for 5 min. Addition of 0.20 g of $NaBPh_4$ gave a purple precipitate which was collected by filtration, washed with cold methanol, and dried under vacuum. The yield was 0.188 g (84%). Anal. Calcd for $C_{68}H_{102}BOP_3RuS_2$: C, 67.81; H, 8.54; P, 7.71; S, 5.32. Found: C, 67.69; H, 8.37; P, 7.45: S, 5.50.

$[RuCl(CO)(S_2CPCy_3)_2(PCy_3)_2][BPh_4]$ (3). A suspension of $RuCl_2(CO)(PCy_3)_2$ (0.080 g) and S_2CPCy_3 (0.24 g in 40 mL of deoxygenated methanol) was stirred for 0.5 h under nitrogen at 40 °C. The purple solution was cooled to 20 °C and filtered. Addition of 0.40 g of $NaBPh_4$ to the filtrate gave a red-brown solid. The solid was recrystallized three times from chloroform-methanol to give a dark red solid which analyzed as $[RuCl(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]\cdot CHCl_3$. The yield was 0.065 g (40%). Anal. Calcd for $C_{81}H_{120}BCl_4OP_3RuS_2$: C, 63.98; H, 7.95; Cl, 9.33; P, 6.11; S, 4.22. Found: C, 63.10; H, 8.07; Cl, 8.27; P, 6.59; S, 4.21.

$RuClH(CO)_2(PCy_3)_2$. Method A. Carbonyl sulfide was bubbled through a solution of $RuClH(CO)(PCy_3)_2$ (0.102 g in 10 mL of deoxygenated toluene) until the color faded from yellow to colorless. The solvent was removed under vacuum, and the white solid which remained was recrystallized from $CHCl_3$-MeOH to give the complex as white crystals. The yield was 0.069 g (60%). The complex was identified by comparison of ^1H NMR and IR spectra with those of an authentic sample.[13] The complex has previously been assigned a stereochemistry with trans PCy_3 ligands and cis CO ligands.[13] See Table I for spectral data.

Method B. Carbonyl sulfide (~10 g) was condensed into a liquid-nitrogen-cooled pressure reactor which contained 0.054 g of $RuClH(CO)(PCy_3)_2$, 0.10 g of PCy_3, and 8 mL of deoxygenated methanol. The vessel was allowed to warm to room temperature (*Caution*! 12 atm). The metal complex dissolved to give an orange solution which faded to colorless and precipitated a white solid. The carbonyl sulfide was distilled off, and the white solid was collected by filtration and dried under vacuum. The complex was identified by comparison of ^1H NMR and IR spectra with those of an authentic sample.

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Registry No. 1, 80697-67-2; 2, 80697-69-4; 3, 80697-71-8; $RuClH(CO)(PCy_3)_2$, 40935-25-9; $RuClH(CO)_2(PCy_3)_2$, 55100-76-0; $RuCl_2(CO)(PCy_3)_2$, 52524-94-4; CS_2, 75-15-0.

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Stabilization of RN=NN=PR$_3$. Preparation and Structural Characterization of Stable Tetraarylphosphazide Complexes Containing Molybdenum and Tungsten

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The reaction of aromatic azides ($R'N_3$) with $MBr_2(CO)_3(PPh_3)_2$ (M = Mo, W; Ph = C_6H_5; tol = p-$CH_3C_6H_4$) in dry methylene chloride at 20 °C affords $MBr_2(CO)_3(R'N_3PPh_3)$, N_2, and $R'N{=}PPh_3$ (R' = Ph, tol). The phosphazide complexes exhibit remarkable stability with respect to N_2 loss. In contrast to the Mo(II) and W(II) complexes, $ReCl_3(CH_3CN)(PPh_3)_2$ and $ReCl_3(PPh_2Me)_3$ yield $ReCl_4(PR_3)_2$ upon treatment with the same aryl azides. Triclinic needles of $WBr_2(CO)_3(tolN_3PPh_3)$ were grown from chloroform-ether and crystallized in space group C_i^1-$P\bar{1}$ with Z = 2, a = 13.715 (6) Å, b = 9.904 (5) Å, c = 10.397 (5) Å, α = 100.98 (2)°, β = 83.11 (2)°, and γ = 85.80 (1)°. An X-ray diffraction study at -145 (5) °C showed the complex to be monomeric and seven-coordinate. The tolyl azide had inserted into the W-P bond, forming a phosphazide ligand ($tolN_3PPh_3$) which is bound to W in a chelating fashion through the α and γ nitrogen atoms; the N_3W metallacycle is nearly planar. Salient metrical parameters of the structure include the following: W-N(1) = 2.163 (4) Å, W-N(3) = 2.220 (5) Å, N(1)-N(2) = 1.279 (6) Å, N(2)-N(3) = 1.364 (6) Å, N(3)-P = 1.672 (5) Å, N(1)-C(41) = 1.423 (7) Å; N(1)-W-N(3) = 56.7 (2)°, W-N(1)-N(2) = 102.4 (3)°, W-N(3)-N(2) = 96.8 (3)°, N(1)-N(2)-N(3) = 103.8 (4)°. The full-matrix, least-squares refinement converged to $R(F)$ = 0.028 and $R_w(F)$ = 0.037 for 4066 unique data with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The reaction of tertiary phosphines with organic azides is known to proceed via a reactive intermediate, $R'NNNPR_3$, which decomposes in a bimolecular process to dinitrogen and the corresponding phosphoranimine[1] (eq 1 and 2). These

$$R'N_3 + PR_3 \xrightarrow[\text{temp}]{\text{low}} R'N{=}NN{=}PR_3 \qquad (1)$$

$$2R'N_3PR_3 \xrightarrow[\text{temp}]{\text{room}} 2R'N{=}PR_3 + 2N_2 \qquad (2)$$

intermediates, which were originally named "phosphazides" by Staudinger,[2] are only rarely stable under ambient conditions; when R = R' = C_6H_5, the phosphazide decomposes rapidly at temperatures above -20 °C. Certain phosphazides

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