Rhodium Carbene Complexes. The Structure of $RhCl(C_2H_5OCONCS)_3(P(C_6H_5)_3)_2$ and the Synthesis and Proposed Mechanism of Formation of This and Related Complexes

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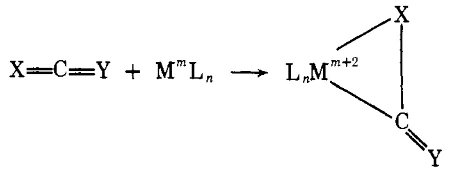
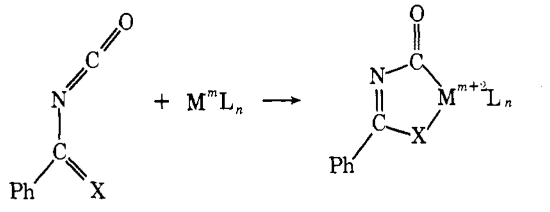
Abstract: The reaction of $RhCl(PPh_3)_3$ with benzoyl isothiocyanate, $C_6H_5CONCS = L^1$, or ethoxycarbonyl isothiocyanate, $C_2H_5OCONCS = L^2$, yields new carbene rhodium(III) complexes, $RhClL^1{}_2(PPh_3)_2$ (**1a**) or $RhClL^2{}_3(PPh_3)_2$ (**2**), respectively, which are found from three-dimensional x-ray analyses to involve planar tridentate carbene ligands formed by the condensation of two molecules of L^1 or by the condensation followed by the 1,3-shift of an ethoxycarbonyl group from three molecules of L^2. Two analogous complexes $RhCl(p\text{-}CH_3C_6H_4CONCS)_2(PPh_3)_2$ (**1b**) and $RhCl[(CH_3)_2NCONCS]_2(PPh_3)_2$ (**1c**) are prepared by the reaction of $RhCl(PPh_3)_3$ with the corresponding activated isothiocyanates, and their spectral data indicate that **1b** and **1c** have structures similar to **1a.** Cyclohexyl isocyanide is an efficient inhibitor of the condensation of activated isothiocyanates to form carbenes; rather complexes $RhClL(c\text{-}C_6H_{11}NC)(PPh_3)_2$ (**3a** for $L = L^1$ and **3b** for $L = L^2$) are formed. These involve η^2 coordination of isothiocyanate ligands at the C═S bond in a manner similar to complexes $PdL(PPh_3)_2$ (**4a–4d;** $L = C_6H_5CO\text{–}$, $p\text{-}CH_3C_6H_4CO\text{–}$, $C_2H_5OCO\text{–}$, and $(CH_3)_2NCONCS$) synthesized by the reaction of $Pd(PPh_3)_4$ with the corresponding isothiocyanates. A model complex of the possible intermediate in the condensation of three molecules of L^2, $RhClL^2{}_2(c\text{-}C_6H_{11}NC)(diphos)$ (**6**) was prepared by the reaction of "RhCl(diphos)" with L^2. The compound $RhCl(C_2H_5OCONCS)_3(PPh_3)_2\cdot(CH_3)_2CO$ crystallizes with four formula units in a triclinic cell of dimensions $a = 15.214$ (6), $b = 27.571$ (9), $c = 12.858$ (6) Å, $\alpha = 103.12$ (1), $\beta = 90.24$ (1), $\gamma = 100.04$ (1)°, $V = 5167$ Å^3. An isotropic model for the structure has been refined by full-matrix least-squares methods to an R index of 0.065 for 401 variables and 7375 observations. The two independent molecules in the unit cell differ somewhat in conformation, but are otherwise equivalent. The Rh atom is six-coordinate, being bound to trans axial phosphine groups, to an equatorial Cl ligand, and to a tridentate planar carbene ligand formed by the condensation of the ethoxycarbonyl isothiocyanate molecules. The inner coordination sphere, including the carbene ligand, bears a very close relationship to that found previously in the structure of $RhCl(C_6H_5CONCS)_2(PPh_3)_2$. On the basis structural, spectroscopic, and chemical evidence a mechanism for the formation of these rhodium carbene complexes is proposed.[2]

The nature of the coordination of various heterocumulene compounds to transition metals has been investigated in the last decade. Examples are carbon dioxide,[3-7] carbon disulfide,[8-10] carbodiimide,[11] and isothiocyanate.[8] Most commonly a three-membered metallocycle is formed via a formal oxidative addition.



The reactions of isocyanates and isothiocyanates, however, are often different from one another and are generally more complex than are those of the other heterocumulenes.[12-15] For example, phenyl isocyanate in its reaction with iron carbonyls induces a decarbonylative dimerization of two isocyanate ligands to lead to an N,N'-urea complex. We reported that the reaction of benzoyl or thiobenzoyl isocyanates with rhodium(I) and palladium(0) complexes leads to five-membered rhodia- or palladiacyclic complexes via a 1,4-addition of activated isocyanates.[16]



M^m = Rh(I) and Pd(0)
X = O or S

This paper describes first a molecular condensation of three ethoxycarbonyl isothiocyanate molecules in the presence of $RhCl(PPh_3)_3$ to yield a new carbene[17-19] complex of Rh(III). The crystal and molecular structure of this complex is described. Secondly, certain mechanistic aspects of this condensation reaction, as well as a related one involving benzoyl isothiocyanate, are investigated and described.

Experimental Section

Syntheses. All reactions were carried out under an argon atmosphere. The infrared spectra were recorded from KBr pellets with a JASCO DS-403G spectrometer. NMR spectra were measured with a JEOL C-60HL spectrometer. Elemental analyses were performed at the Microanalysis Center of Kyoto University.

Benzoyl,[20] toluoyl,[20] ethoxycarbonyl,[21-22] and N,N-dimethylcarbamoyl[23] isothiocyanates were prepared according to the reported methods. Chlorotris(triphenylphosphine)rhodium was prepared by the method of Osborn and Wilkinson.[24] Tetrakis(triphenylphosphine)palladium was prepared by the reaction of excess triphenylphosphine with tris(dibenzylideneacetone)dipalladium chloroform solvate.[25] Bis(μ-chloro)bis(1,5-cyclooctadiene)dirhodium was prepared by the method of Chatt and Venanzi.[26]

Preparation of $RhCl(PhCONCS)_2(PPh_3)_2$ (1a). To a suspension of $RhCl(PPh_3)_3$[27] (300 mg, 0.325 mmol) in a benzene (10 mL)-n-hexane (10 mL) mixed solvent was added with vigorous stirring benzoyl isothiocyanate (460 mg; 2.84 mmol). The mixture, while being refluxed for 1 h, turned gradually orange in color. A pale orange product precipitated from the reaction mixture. The stirring was continued for 14 h at room temperature. The filtration of the crude solid product gave **1a** (268 mg, 84% yield), which was recrystallized by dissolving it in dichloromethane followed by the addition of ethyl ether to yield reddish orange prisms of **1a:** mp 174.5–175.5 °C dec; IR 1617 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{52}H_{40}ClN_2O_2P_2RhS_2$: C, 63.13; H, 4.08; N, 2.83. Found: C, 63.03; H, 4.32; N, 2.89.

Preparation of $RhCl(p\text{-}ToCONCS)_2(PPh_3)_2\cdot{}^1\!/_2CH_2Cl_2$ (1b). A mixture of $RhCl(PPh_3)_3$ (300 mg, 0.325 mmol), p-ToCONCS (440 mg, 2.49 mmol), benzene (10 mL), and n-hexane (10 mL) was refluxed for 1 h and stirred for 2 h at room temperature. The resultant pale orange precipitate was filtered and recrystallized directly from dichloromethane and ethyl ether to give **1b** (255 mg; 77% yield): mp 169-173 °C dec; NMR ($CDCl_3$) τ 2.0-3.0 (m, 30), 4.77 (s, 1, CH_2Cl_2), 7.63 (s, 3, CH_3), and 7.67 (s, 3, CH_3); IR 1615, 1607 cm^{-1} (ν_{CO}). Anal Calcd for $C_{54.5}H_{45}Cl_2N_2O_2P_2RhS_2$: C, 61.76; H, 4.28; N, 2.64. Found: C, 61.58; H, 4.26; N, 2.80.

Preparation of $RhCl(Me_2NCONCS)_2(PPh_3)_2$ (1c). A mixture of $RhCl(PPh_3)_3$ (250 mg, 0.27 mmol) and N,N-dimethylcarbamoyl isothiocyanate (440 mg, 3.38 mmol) in benzene (10 mL) and n-hexane (15 mL) was refluxed for 30 min to give an orange precipitate of **1c** (216 mg; 76% yield), which was recrystallized from dichloromethane–ethyl ether: mp 175-176 °C dec; IR 1631 (ν_{CO}), 1594, and 1586 cm^{-1} (ν_{CN}); NMR ($CDCl_3$) τ 2.1-3.0 (m, 30, aromatic), 7.19 (s, 6, two CH_3), 7.22 (s, 3, CH_3), and 7.54 (s, 3, CH_3). Anal. Calcd for $C_{44}H_{42}ClN_4O_2P_2RhS_2$: C, 57.24; H, 4.58; N, 6.07. Found: C, 57.09; H, 4.60; N, 6.11.

Preparation of $RhCl(EtOCONCS)_3(PPh_3)_2{\cdot}Me_2CO$ (2). A benzene (20 mL) solution of $RhCl(PPh_3)_3$ (400 mg, 0.432 mmol) and ethoxycarbonyl isothiocyanate (480 mg, 3.66 mmol) was stirred for 30 min at room temperature, and was refluxed for 2 h. After the solvent and the excess ethoxycarbonyl isothiocyanate were removed under reduced pressure, n-hexane (30 mL) was added to the oily residue. Reddish-orange powder of $RhCl(EtOCONCS)_3(PPh_3)_2$ precipitated quantitatively. The crude product was dissolved in the minimal amount of acetone. Ethyl ether was added dropwise until a few microcrystals appeared. The mixture was kept in a refrigerator for 24 h to yield **2** as reddish orange prisms: mp, 115-119 °C dec; IR 1785, 1762 (ν_{CO}), and 1711 cm^{-1} (acetone); NMR ($CDCl_3$) τ 2.1-2.9 (m, 30, aromatic), 8.76 (t, 6, CH_3, J = 7.5 Hz), 5.87 (q, 4, CH_2, J = 7.5 Hz), 8.79 (t, 3, CH_3, J' = 6.8 Hz), 6.04 (q, 2, CH_2, J' = 6.8 Hz). Anal. Calcd for $C_{51}H_{51}ClN_3O_7P_2RhS_3$: C, 54.96; H, 4.61; N, 3.77. Found: C, 54.94; H, 4.69; N, 3.78.

Preparation of $RhCl(cyNC)(PhCONCS)(PPh_3)_2$ (3a). A benzene (10 mL) solution of $RhCl(PPh_3)_3$ (300 mg, 0.324 mmol) and cyclohexyl isocyanide (36.5 mg, 0.335 mmol) was stirred for 15 min at room temperature to result in a red-brown solution to which benzoyl isothiocyanate (310 mg, 1.30 mmol) was added. The reaction immediately led to a pale yellow suspension. After the mixture was stirred for 3 h at room temperature, the crude complex **3a** was filtered and then washed with ethyl ether (20 mL). The complex **3a**, isolated in 98% yield (296 mg), was unstable in solution. Therefore, the recrystallization of **3a** was achieved by dissolving it in CH_2Cl_2 to which a few drops of benzoyl isothiocyanate had been added, followed by addition of ethyl ether to give pale yellow prisms of **3a**: mp 160-162 °C dec; IR 2180 (ν_{NC}), 1668 (ν_{CO}), 1572, and 1530 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{51}H_{46}ClN_2OP_2RhS_2$: C, 65.49; H, 4.96; N, 3.00. Found: C, 65.57; H, 4.87; N, 3.03.

Preparation of $RhCl(cyNC)(EtOCONCS)(PPh_3)_2{\cdot}CH_2Cl_2$ (3b). The procedure was analogous to that of **3a** with $RhCl(PPh_3)_3$ (350 mg, 0.378 mmol), cyclohexyl isocyanide (53.2 mg, 0.488 mmol), ethoxycarbonyl isothiocyanate (355 mg, 2.71 mmol), and benzene (20 mL). The complex **3b** was isolated in 77% yield as a pale yellow powder, which was recrystallized from dichloromethane–ethyl ether–acetone (2/1/1 vol) containing a few drops of ethoxycarbonyl isothiocyanate: mp 121-123 °C dec; IR 2190 (ν_{NC}), 1700 (ν_{CO}), and 1600 cm^{-1} (ν_{CN}); NMR ($CDCl_3$) τ 2.0-3.0 (m, 30, aromatic), 4.98 (s, 2, CH_2Cl_2), 6.36 (q, 2, CH_2, J = 6.3 Hz), 8.95 (t, 3, CH_3, J = 6.3 Hz), and 11 proton multiplets around τ 9 from the cyclohexyl group. Anal. Calcd for $C_{48}H_{48}Cl_3N_2O_2P_2RhS$: C, 58.34; H, 4.90; N, 2.83. Found: C, 58.62; H, 5.16; N, 3.05.

Preparation of $Pd(PhCONCS)(PPh_3)_2$ (4a). After tetrakis(triphenylphosphine)palladium was synthesized in situ from $Pd_2dba_3{\cdot}CHCl_3$ (200 mg, 0.193 mmol), PPh_3 (400 mg, 1.53 mmol), and Et_2O (15 mL) by stirring for 1 h at room temperature, benzoyl isothiocyanate (449 mg, 2.75 mmol) was added dropwise. The reaction mixture turned to a yellow homogeneous solution from which the complex **4a** precipitated as a pale yellow powder (225 mg) in 73% yield: mp 111-116 °C dec; IR 1658 (ν_{CO}) and 1562 cm^{-1} (ν_{CN}). The NMR ($CDCl_3$) spectrum was consistent only with the presence of phenyl protons. Anal. Calcd for $C_{44}H_{35}NOP_2PdS$: C, 66.54; H, 4.44; N, 1.76. Found: C, 66.42; H, 4.43; N, 1.83.

Preparation of $Pd(p\text{-}ToCONCS)(PPh_3)_2$ (4b). This was prepared in a similar manner to **4a** with $Pd_2dba_3{\cdot}CHCl_3$ (300 mg, 0.290 mmol), PPh_3 (600 mg, 2.23 mmol), and p-toluoyl isothiocyanate (220 mg, 1.24 mmol) in benzene (20 mL) to obtain **4b** in 89% yield (424 mg) as pale yellow needles: mp 119-121 °C dec; IR 1659 (ν_{CO}) and 1551 br cm^{-1} (ν_{CN}); NMR ($CDCl_3$) τ 2.6-3.2 (m, 34, aromatic), 7.71 (s, 3, CH_3). Anal. Calcd for $C_{45}H_{37}NOP_2PdS$: C, 66.88; H, 4.62; N, 1.73. Found: C, 67.00; H, 4.49; N, 1.63.

Preparation of $Pd(EtOCONCS)(PPh_3)_2$ (4c). The conditions were similar to **4a** with $Pd_2dba_3{\cdot}CHCl_3$ (400 mg, 0.386 mmol), PPh_3 (800 mg, 3.05 mmol), and ethoxycarbonyl isothiocyanate (163 mg, 1.24 mmol) in benzene (20 mL) at room temperature. After the removal under reduced pressure of low-boiling materials, ethyl ether (20 mL) was added to precipitate **4c** (472 mg, 80% yield) as pale yellow prisms. Recrystallization was performed from $CH_2Cl_2{\cdot}Et_2O$ containing a few drops of ethoxycarbonyl isothiocyanate: mp 108-112 °C dec; IR 1700 (ν_{CO}) and 1625 cm^{-1} (ν_{CN}); NMR ($CDCl_3$) τ 2.8 (m, 30, aromatic), 6.07 (q, 2, CH_2), 8.87 (t, 3, CH_3, J = 7.0 Hz). Anal. Calcd for $C_{40}H_{35}NO_2P_2PdS$: C, 63.04; H, 4.63; N, 1.84. Found: C, 62.98; H, 4.67; N, 1.83.

When ethoxycarbonyl isothiocyanate was added in five- to sevenfold excess to the palladium(0) complex, the unexpected formation of the complex $Pd(S_2CNCOOEt)(PPh_3)_2$ occurred:[28] mp 200-202 °C dec; IR 1706 (ν_{CO}) and 1535 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{40}H_{35}NO_2P_2PdS_2$: C, 60.49; H, 4.44; N, 1.76; P, 8.07. Found: C, 60.14; H, 4.67; N, 1.97; P, 8.01.

Preparation of $Pd(Me_2NCONCS)(PPh_3)_2$ (4d). A mixture of $Pd_2dba_3{\cdot}CHCl_3$ (300 mg, 0.290 mmol) and PPh_3 (600 mg, 2.29 mmol) in benzene (20 mL) was stirred for 1 h at room temperature. To this solution, N,N-dimethylcarbamoyl isothiocyanate (187 mg, 1.44 mmol) was added to yield a yellow, homogeneous solution which was stirred for an additional 2 h. The low-boiling materials were removed under reduced pressure, and Et_2O (25 mL) was added to the residual oil to precipitate **4d** (324 mg) in 74% yield: mp 96-106 °C dec; IR 1674 (ν_{CO}), 1646, and 1616 cm^{-1} (ν_{CN}); NMR ($CDCl_3$) τ 2.85 (m, 30, aromatic), 7.13 (s, 3, CH_3), 7.81 (s, 3, CH_3). Anal. Calcd for $C_{40}H_{36}N_2OP_2PdS$: C, 63.12; H, 4.77; N, 3.68. Found: C, 63.39; H, 4.77; N, 3.84.

Preparation of $RhCl(EtOCONCS)_2(diphos)$ (5). To a benzene (4 mL) solution $[RhCL(1,5\text{-}COD)]_2$ (100 mg, 0.41 mmol), diphos (163 mg, 0.41 mmol), and ethoxycarbonyl isothiocyanate (112 mg, 0.857 mmol) were added dropwise. The mixture turned from deep yellow to a yellow-orange suspension. The reaction mixture was stirred for 15 h at room temperature. Ethyl ether (20 mL) was added to yield a deep yellow complex **5** (271 mg) in 84% yield. Recrystallization was achieved from a dichloromethane–ethyl ether mixture; mp 212-216 °C dec; IR 1770 and 1543 cm^{-1} (ν_{CO}); NMR ($CDCl_3$) τ 2.0-3.2 (m, 20, phenyl), 5.80 (q, 2, CH_2O), 5.86 (q, 2, CH_2O), 7.0-8.4 (m, 4, br, CH_2P), 8.74 (t, 6, two CH_3). Anal. Calcd for $C_{34}H_{36}ClN_2O_4P_2RhS_2$: C, 51.11; H, 4.29; N, 3.51. Found: C, 51.28; H, 4.49; N, 3.68.

Preparation of $RhCl(cyNC)(EtOCONCS)_2(diphos)$ (6). To a CH_2Cl_2 (8 mL) solution of **5** (83.1 mg, 0.104 mmol) was added cyclohexyl isocyanide (29.6 mg, 0.272 mmol) to yield a yellow homogeneous solution which was stirred for 17 h at room temperature. After the low-boiling materials were removed under reduced pressure, Et_2O (10 mL) was added to give **6** as a yellow powder (86.5 mg) in 92% yield. Recrystallization of **6** was from $CH_2Cl_2{\cdot}Et_2O$: mp 165-168 °C dec; IR 2210 (ν_{NC}), 1768 (ν_{CO}), 1694 (conjugating ν_{CO}), and 1611 cm^{-1} (ν_{CN}). The measurement of an NMR spectrum of **6** was impossible because of its low solubility in suitable solvents. Anal. Calcd for $C_{41.5}H_{46}Cl_2N_3O_4P_2RhS_2$ involving $\frac{1}{2}CH_2Cl_2$ as a solvate: C, 52.43; H, 4.88; N, 4.42. Found: C, 52.37; H, 4.84; N, 4.63.

Preparation of $Pd(EtOCONCS)_2(bpy)$ (7). A benzene (20 mL) suspension of $Pd_2dba_3{\cdot}CHCl_3$ (400 mg, 0.386 mmol) and bypyridine (400 mg, 2.56 mmol) was stirred for 1 h at room temperature. Ethoxycarbonyl isothiocyanate (420 mg, 3.20 mmol) was added dropwise to the above mixture. The orange suspension turned to a reddish brown suspension after stirring 2 h at room temperature. The low-boiling material was removed under reduced pressure, and the residue was mixed with n-hexane (20 mL). The resulting oil solidified to the crude **7** as a yellow-brown powder (397 mg, 98%). It was recrystallized by dissolution in CH_2Cl_2 followed by the addition of Et_2O: mp 149-153 °C dec; IR 1771 and 1681 cm^{-1} (ν_{CO}); NMR ($CDCl_3$) ν 1.9-2.8 (m, 8, bpy), 5.60 (q, 2, CH_2), 5.73 (q, 2, CH_2), 8.60 (t, 6, two CH_3) with J = 7.0 Hz). Anal. Calcd for $C_{18}H_{18}N_4O_4PdS_2$: C, 41.19; H, 3.46; N, 10.67. Found: C, 41.22; H, 3.57; N, 10.38.

X-Ray Diffraction Study of $RhCl(EtOCONCS)_3(PPh_3)_2{\cdot}Me_2CO$ (2). The reddish-orange crystals of **2** are air stable. No symmetry, other

Table I. Positional and Thermal Parameters for the Nongroup Atoms of $RhCl(EtOCONCS)_3(PPh_3)_2 \cdot Me_2CO$

ATOM	X[a]	Y	Z	B, Å^2	ATOM	X	Y	Z	B, Å^2
RH(A)	0.201824(51)	0.114607(29)	0.133880(60)	2.50(2)	C(A1)	0.36456(72)	0.05837(41)	0.16553(84)	3.54(24)
RH(B)	0.149280(52)	-0.371287(29)	0.326059(62)	2.66(2)	C(A2)	0.26907(64)	0.22556(36)	0.22303(75)	2.71(21)
CL(A)	0.04826(17)	0.082204(98)	0.05804(21)	3.47(6)	C(A3)	0.31791(66)	0.15099(38)	0.19487(77)	2.69(22)
CL(B)	0.10495(18)	-0.36637(10)	0.51160(22)	3.98(6)	C(A4)	0.5051(11)	0.04023(57)	0.2156(14)	6.93(38)
S(A1)	0.25866(18)	0.03888(10)	0.10972(22)	3.31(6)	C(A5)	0.6530(15)	0.05909(79)	0.1858(17)	12.90(60)
S(A2)	0.16682(18)	0.19614(10)	0.17095(21)	3.29(6)	C(A6)	0.7044(15)	0.08918(83)	0.1280(17)	12.40(65)
S(A3)	0.40967(18)	0.12354(10)	0.21152(22)	3.45(6)	C(A7)	0.23292(83)	0.31098(45)	0.26746(94)	4.68(27)
S(B1)	0.16078(19)	-0.45520(11)	0.31425(22)	3.69(6)	C(A8)	0.2165(10)	0.39738(59)	0.3391(12)	8.22(39)
S(B2)	0.14479(18)	-0.28808(10)	0.31046(22)	3.30(6)	C(A9)	0.2525(16)	0.43570(91)	0.4260(19)	14.84(74)
S(B3)	0.21253(19)	-0.43464(11)	0.10077(23)	3.79(6)	C(A10)	0.38253(75)	0.29637(41)	0.30826(93)	3.74(25)
P(A1)	0.25023(18)	0.11866(10)	-0.04196(22)	3.01(6)	C(A11)	0.5288(10)	0.32807(55)	0.2620(12)	7.78(37)
P(A2)	0.15560(18)	0.09989(10)	0.30390(21)	2.80(6)	C(A12)	0.5748(12)	0.34848(66)	0.1758(14)	9.66(49)
P(B1)	-0.00540(18)	-0.39341(10)	0.26855(22)	2.92(6)	C(B1)	0.20125(69)	-0.47415(39)	0.19222(82)	3.27(23)
P(B2)	0.30097(18)	-0.34145(10)	0.39079(22)	2.96(6)	C(B2)	0.17650(67)	-0.29845(39)	0.18299(81)	3.03(22)
O(A1)	0.51749(93)	0.03185(51)	0.3007(12)	12.45(41)	C(B3)	0.18687(67)	-0.37911(38)	0.18160(80)	3.05(22)
O(A2)	0.55451(86)	0.04743(43)	0.14865(97)	9.68(32)	C(B4)	0.24887(81)	-0.54089(47)	0.0738(10)	4.69(28)
O(A3)	0.15772(57)	0.29988(30)	0.22881(65)	5.66(20)	C(B5)	0.29638(83)	-0.61705(47)	-0.0225(10)	5.70(30)
O(A4)	0.27420(53)	0.35646(31)	0.32092(62)	5.12(19)	C(B6)	0.30987(91)	-0.66671(51)	0.0020(11)	5.97(34)
O(A5)	0.40165(49)	0.29970(27)	0.39944(61)	4.36(17)	C(B7)	0.16880(87)	-0.21335(50)	0.1637(11)	5.53(31)
O(A6)	0.43159(51)	0.30801(28)	0.23219(60)	4.51(17)	C(B8)	0.1649(14)	-0.13529(79)	0.0948(16)	12.09(57)
O(B1)	0.25317(56)	-0.52556(32)	-0.00741(69)	5.76(20)	C(B9)	0.2305(25)	-0.1064(13)	0.1602(29)	24.6(14)
O(B2)	0.27105(52)	-0.58572(30)	0.07749(62)	4.99(19)	C(B10)	0.21388(88)	-0.27406(45)	0.01501(98)	4.78(28)
O(B3)	0.13467(61)	-0.19805(34)	0.24534(75)	6.76(23)	C(B11)	0.1526(11)	-0.29777(60)	-0.1638(13)	9.21(43)
O(B4)	0.19304(59)	-0.18636(35)	0.09072(71)	6.68(22)	C(B12)	0.0833(11)	-0.27556(63)	-0.2139(13)	9.19(45)
O(B5)	0.28950(63)	-0.27255(33)	-0.00929(70)	6.38(22)	O(SA1)	0.3812(17)	-0.13657(97)	0.3400(20)	22.97(93)
O(B6)	0.14264(59)	-0.28589(32)	-0.04610(71)	5.98(21)	C(SA1)	0.3469(37)	-0.0999(24)	0.4033(48)	32.4(21)
N(A1)	0.41159(67)	0.02404(37)	0.17204(77)	4.94(24)	C(SA2)	0.3880(33)	-0.0554(20)	0.3945(38)	31.6(22)
N(A2)	0.29174(54)	0.27659(31)	0.26390(63)	3.18(18)	C(SA3)	0.3125(27)	-0.1264(16)	0.4686(35)	25.6(18)
N(A3)	0.33701(53)	0.20081(30)	0.23224(62)	2.98(18)	O(SB1)	0.5200(42)	0.5048(26)	-0.1196(51)	74.5(48)
N(B1)	0.22087(60)	-0.52003(35)	0.17222(73)	4.20(21)	C(SB1)	0.4884(53)	0.4994(26)	-0.1619(48)	25.9(22)
N(B2)	0.18779(56)	-0.26140(32)	0.12669(68)	3.51(19)	C(SB2)	0.4357(25)	0.4426(16)	-0.1986(28)	21.7(14)
N(B3)	0.19375(53)	-0.34252(31)	0.12463(64)	3.14(18)	C(SB3)	0.3843(30)	0.4988(15)	-0.1918(30)	24.1(16)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

than a center of inversion, could be found on an extensive set of photographs and the crystals were assigned to the triclinic system. Unit cell dimensions obtained on a FACS-I diffractometer are a = 15.214 (6), b = 27.571 (9), c = 12.858 (6) Å, α = 103.12 (1), β = 90.24 (1), and γ = 100.04 (1)° (Delaunay reduced cell), V = 5167 Å^3, ρ_c = 1.432 g/cm^3, ρ_O = 1.35 (5) g/cm^3 (flotation in $ZnCl_2$ solution) for Z = 4, molecular weight of $C_{51}H_{51}ClN_3O_7P_2RhS_3$ = 1114.49 amu.

Data were collected in the manner previously described.[29] Ni-filtered Cu Kα radiation was used. Details of data collection include: aperture 5 mm by 5 mm 32 cm from crystal; scan rate 2° in 2θ/min from 0.9° below Kα_1 peak to 0.9° above Kα_2 peak; background counting times of 10 s at each end of the scan range; data collected out to 94° in 2θ; 9875 reflections examined, of which 2056 have $F_o^2 < 3\sigma(F_o^2)$ and 7375 unique reflections have $F_o^2 \geq 3\sigma(F_o^2)$; the crystal had approximate dimensions 0.28 × 0.16 × 0.12 mm, with well-developed faces of the forms $\{01\bar{1}\}$, $\{010\}$, and $\{100\}$, calculated volume 0.00571 mm^3, range of transmission factors 0.407–0.555 based on μ(Cu Kα) = 53.56 cm^{-1}.

Computer programs, sources of atomic scattering factors, and other procedures have been described previously.[30] A value of p of 0.03 was used in the estimation of standard deviations.[28] The centrosymmetric space group C_i^1-$P\bar{1}$ was assumed. Even so, this implies the presence of two formula units per asymmetric unit and necessitates the location of 64 individual atoms and 12 rigid phenyl groups. That the cell is indeed triclinic was established by extensive photography, through a cell reduction, by the fact that the two independent molecules in the unit cell differ somewhat in their conformations. From an origin-removed, sharpened Patterson function the Rh, Cl, and P atoms were located. Through the usual procedure of interspersed Fourier and full-matrix least-squares refinements the other nonhydrogen atoms in the cell were located. Considerable difficulty was experienced with the acetone molecules of solvation. While one such molecule is reasonably well defined, the other is not. The assignment of two acetone molecules in the asymmetric unit is based on analytical data. Neither those data nor the present structural results precludes the possibility that one of the supposed acetone molecules might be a diethyl ether molecule. (The crystals used in this study were recrystallized from an acetone-diethyl ether mixture.)

The final refinement model for this structure involves 401 variables and 7375 observations and takes account of only isotropic thermal motion. Anisotropic refinement would have involved considerable extra expense with little gain of chemical import. This is particularly true in view of problems in the location of the solvent molecules and certain terminal portions of the Rh-containing molecules. Nevertheless, agreement between the chemically interesting portions of the two independent molecules is very satisfactory. In the final refinement the 16 hydrogen atoms of the methine carbon atoms and the 60 hydrogen atoms of the phenyl rings were included as fixed contributions, based on a C–H distance of 0.95 Å. No attempt was made to include the hydrogen atoms of the solvent molecules. This final, full-matrix refinement converged to values of R and R_w (on F) of 0.065 and 0.079, respectively, and to an error in an observation of unit weight of 3.12 e. In a final difference Fourier map the maximum electron density was 1.08 e/Å^3. The top 20 peaks, down to 0.5 e/Å^3, were associated with the heavy atoms, and not with the solvent molecules. But the absence of high density and the low R index are further justifications for termination of the refinement at the isotropic stage. Examination of $\sum w(|F_o| - |F_c|)^2$ (the function minimized in the refinement) vs. $|F_o|$, setting angles, and Miller indices indicates a trend toward slightly poorer agreement at low values of 2θ. This probably results from the difficulties with the characterization of the solvent molecules. Of the 2057 reflections having $F_o^2 < 3\sigma(F_o^2)$ and omitted from the refinement, 80 have $Q > 3\sigma(F_o^2)$ and of these seven have $Q > 7\sigma(F_o^2)$, where $Q = |F_o^2 - F_c^2|$.

Tables I and II present the parameters and associated errors for the group and nongroup atoms. Table III provides information on the idealized positions of the H atoms. Values of $10|F_o|$ and $10|F_c|$ (in electrons) for the observations used in the calculations are presented in Table IV.[31]

Results and Discussion

Syntheses and Spectroscopic Characterization of New Tridentate Carbene Complexes of Rh(III). When an excess of PhCONCS was added to $RhCl(PPh_3)_3$ orange-red crystals of $RhCl(PhCONCS)_2(PPh_3)_2$, **1a**, were isolated in 84% yield. An x-ray structural determination[2a,19] indicates unequivocally

Table II. Derived Parameters for the Rigid Group Atoms of $RhCl(EtOCONCS)_3(PPh_3)_2 \cdot Me_2CO$

ATOM	X	Y	Z	B, Å^2	ATOM	X	Y	Z	B, Å^2
01C1	0.37135(34)	0.13222(26)	-0.04281(57)	2.89(22)	07C1	-0.02205(48)	-0.38768(27)	0.13116(42)	3.14(23)
01C2	0.41899(48)	0.09289(19)	-0.07349(57)	4.33(26)	07C2	-0.04563(50)	-0.34367(2[illegible])	0.11273(50)	3.96(25)
01C3	0.51195(48)	0.10287(26)	-0.06460(63)	5.42(30)	07C3	-0.05635(52)	-0.33846(23)	0.00849(61)	5.06(29)
01C4	0.55727(34)	0.15218(31)	-0.02503(67)	5.74(32)	07C4	-0.04349(53)	-0.37726(30)	-0.07734(44)	4.88(29)
01C5	0.50963(46)	0.19151(22)	0.00565(61)	4.92(29)	07C5	-0.01991(51)	-0.42127(24)	-0.05891(47)	4.38(26)
01C6	0.41667(46)	0.18153(22)	-0.00324(57)	3.71(24)	07C6	-0.00919(48)	-0.42648(21)	0.04534(57)	3.93(25)
02C1	0.21780(46)	0.06114(21)	-0.14783(48)	3.01(23)	08C1	-0.06249(44)	-0.45696(20)	0.27389(56)	2.89(22)
02C2	0.16181(45)	0.01846(26)	-0.12988(42)	3.03(22)	08C2	-0.04888(44)	-0.47258(25)	0.36743(47)	3.94(25)
02C3	0.13675(45)	-0.02388(21)	-0.21359(58)	3.84(25)	08C3	-0.09205(52)	-0.51985(28)	0.37860(48)	4.95(28)
02C4	0.16748(52)	-0.02355(24)	-0.31524(48)	4.89(29)	08C4	-0.14883(49)	-0.55149(21)	0.29625(63)	4.92(27)
02C5	0.22367(52)	0.01912(30)	-0.33319(43)	5.26(30)	08C5	-0.16243(46)	-0.53587(25)	0.20271(52)	4.89(29)
02C6	0.24873(45)	0.06147(23)	-0.24949(59)	4.41(27)	08C6	-0.11926(49)	-0.48861(27)	0.19153(44)	3.85(25)
03C1	0.21483(46)	0.16633(25)	-0.10380(53)	3.17(23)	09C1	-0.08299(43)	-0.35508(25)	0.34209(53)	3.18(23)
03C2	0.12660(42)	0.17358(26)	-0.09519(52)	3.77(24)	09C2	-0.05692(35)	-0.31410(26)	0.42852(55)	3.46(23)
03C3	0.09396(37)	0.20363(29)	-0.15433(63)	4.94(29)	09C3	-0.12067(51)	-0.28840(23)	0.48187(49)	4.58(27)
03C4	0.14955(53)	0.22643(27)	-0.22208(59)	5.37(30)	09C4	-0.21050(45)	-0.30369(29)	0.44881(60)	4.85(29)
03C5	0.23778(49)	0.21918(28)	-0.23069(55)	5.49(30)	09C5	-0.23657(35)	-0.34467(30)	0.36238(63)	5.80(31)
03C6	0.27043(35)	0.18913(28)	-0.17155(59)	4.27(26)	09C6	-0.17281(49)	-0.37037(23)	0.30902(50)	4.67(28)
04C1	0.07078(38)	0.13428(25)	0.37245(51)	2.77(22)	10C1	0.32569(48)	-0.28535(22)	0.50212(47)	2.81(22)
04C2	0.06520(41)	0.14301(27)	0.48302(49)	3.63(24)	10C2	0.41559(41)	-0.26756(28)	0.53257(58)	4.42(27)
04C3	-0.00433(48)	0.16482(28)	0.53244(38)	4.49(27)	10C3	0.44021(39)	-0.22608(29)	0.61828(63)	5.58(30)
04C4	-0.06827(41)	0.17789(27)	0.47129(56)	4.55(27)	10C4	0.37494(57)	-0.20239(25)	0.67353(53)	5.65(32)
04C5	-0.06268(41)	0.16916(28)	0.36073(54)	4.40(26)	10C5	0.28505(50)	-0.22017(29)	0.64308(59)	5.87(32)
04C6	0.00684(46)	0.14735(26)	0.31131(38)	3.57(24)	10C6	0.26042(35)	-0.26165(28)	0.55738(60)	4.14(26)
05C1	0.25008(40)	0.11740(27)	0.40044(55)	3.33(24)	11C1	0.35764(47)	-0.38523(25)	0.44312(55)	3.30(23)
05C2	0.29988(51)	0.08181(20)	0.41731(59)	4.32(26)	11C2	0.30908(37)	-0.41269(28)	0.50904(59)	4.04(26)
05C3	0.37640(49)	0.09707(28)	0.48466(65)	5.41(29)	11C3	0.34938(52)	-0.44426(27)	0.55685(57)	5.31(29)
05C4	0.40312(44)	0.14794(32)	0.53513(61)	6.12(33)	11C4	0.43825(54)	-0.44838(28)	0.53874(64)	6.05(32)
05C5	0.35333(53)	0.18353(21)	0.51825(62)	5.76(32)	11C5	0.48681(38)	-0.42092(32)	0.47283(67)	6.05(32)
05C6	0.27680(49)	0.16827(24)	0.45090(62)	4.00(26)	11C6	0.44650(46)	-0.38934(27)	0.42502(56)	4.59(27)
06C1	0.10715(44)	0.03411(19)	0.30672(53)	2.90(22)	12C1	0.37225(44)	-0.32136(26)	0.28946(50)	3.20(23)
06C2	0.06940(46)	-0.00017(24)	0.21396(40)	2.98(22)	12C2	0.40777(50)	-0.35696(20)	0.21477(59)	3.96(25)
06C3	0.02855(44)	-0.04890(22)	0.21827(44)	3.21(23)	12C3	0.46185(52)	-0.34168(27)	0.13679(54)	5.12(30)
06C4	0.02546(47)	-0.06336(19)	0.31534(57)	4.43(27)	12C4	0.48041(50)	-0.29079(31)	0.13349(56)	5.86(32)
06C5	0.06321(50)	-0.02908(26)	0.40811(43)	4.39(26)	12C5	0.44489(53)	-0.25519(21)	0.20818(64)	5.35(29)
06C6	0.10406(46)	0.01965(24)	0.40380(42)	3.91(25)	12C6	0.39081(49)	-0.27047(23)	0.28616(53)	4.03(25)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
R01	0.46431(34)	0.14220(19)	-0.03392(37)	0.0155(44)	-2.7676(45)	-3.1046(49)
R02	0.19274(30)	0.01879(18)	-0.23154(38)	-0.7840(58)	2.4399(40)	1.8171(58)
R03	0.18219(34)	0.19638(17)	-0.16294(36)	-1.4458(48)	2.6892(44)	0.6110(50)
R04	0.00126(30)	0.15609(16)	0.42187(38)	0.8446(89)	2.0763(38)	-1.4184(88)
R05	0.32660(34)	0.13267(20)	0.46778(40)	0.1461(46)	-2.9597(45)	-2.5255(49)
R06	0.06630(28)	-0.01463(17)	0.31103(36)	-1.761(17)	-1.7916(42)	-2.870(17)
R07	-0.03277(29)	-0.38247(18)	0.02691(40)	-2.8968(49)	2.7731(40)	1.5997(49)
R08	-0.10566(31)	-0.50423(18)	0.28507(38)	1.3304(91)	2.0371(46)	-0.2742(92)
R09	-0.14674(34)	-0.32938(18)	0.39545(38)	2.0473(53)	2.5136(44)	-2.4577(55)
R10	0.35032(36)	-0.24387(18)	0.58783(39)	1.3579(47)	-2.9680(45)	-2.2620(46)
R11	0.39794(35)	-0.41680(18)	0.49093(38)	-1.3211(50)	2.6465(47)	-2.6565(52)
R12	0.42633(32)	-0.30607(20)	0.21148(39)	0.1138(48)	-2.7568(43)	2.2381(50)

[a] x_c, y_c, and z_c are the fractional coordinates of the origin of the rigid group. [b] The rigid group orientation angles delta, epsilon, and eta (radians) have been defined previously: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

that **1a** contains a planar, tridentate carbene ligand formed by the condensation of two isothiocyanate molecules via a carbon-sulfur bond as depicted in Scheme I. The infrared spectrum of **1a** is consistent with this unexpected structure, since the ν(C=O) band appears at 1617 cm^{-1}, which is lower than that of the common acid amides, and the ν(C=N) band falls below 1500 cm^{-1}. The structural and spectroscopic results suggest extensive electron delocalization within the nearly planar carbene ligand connected to the $RhCl(PPh_3)_2$ moiety.

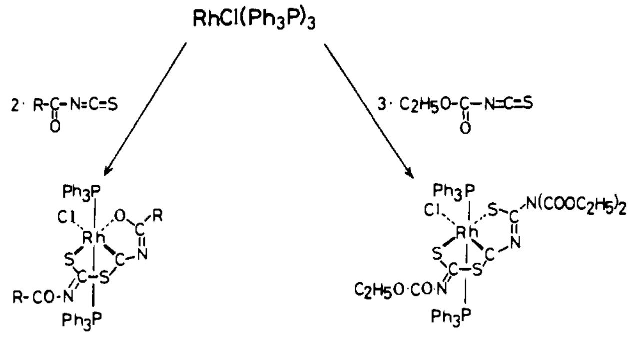
Analogous tridentate carbene rhodium complexes $RhCl(p\text{-}MeC_6H_4CONCS)_2(PPh_3)_2$ (**1b**) and $RhCl(Me_2NCONCS)_2(PPh_3)_2$ (**1c**) are similarly prepared in 77 and 76% yields, respectively, by reacting $RhCl(PPh_3)_3$ with the corresponding activated isothiocyanates. The infrared spectrum of **1b** shows ν(C=O) bands at 1615 and 1607 cm^{-1} and its NMR spectrum indicates two nonequivalent aroyl methyl protons at τ 7.63 and 7.67, consistent with a structure for **1b** analogous to **1a**. The infrared spectrum of **1c** shows a ν(C=O) band at 1631 cm^{-1} and two broad ν(C=N) bands at 1594 and 1586 cm^{-1}. This suggests that the carbonyl function of the *N,N*-dimethylcarbamoyl group delocalizes electrons in the carbene ligand to a lesser extent than in **1a** or **1b**. Moreover, the NMR spectrum of the $N\text{-}CH_3$ proton signals appears as a set of two singlets at τ 7.22 and 7.54 (each 3 H), suggestive of restricted rotation around the $C=N^+(CH_3)_2$ portion of the molecule, as well as a sharp singlet at τ 7.19 (6 H) of the freely rotating dimethylamino group (connected directly to the ligand plane).

The reaction of $RhCl(PPh_3)_3$ with an excess of EtOCONCS, however, is different in that it yields a compound of surprising composition $RhCl(EtOCONCS)_3(PPh_3)_2$ (**2**) in

Table III. Idealized Positions of the Hydrogen Atoms

Atom	x	y	z	Atom	x	y	z
H1C(A5)	0.676	0.026	0.182	H105C6	0.244	0.193	0.439
H2C(A5)	0.661	0.074	0.265	H106C2	0.071	0.010	0.148
H1C(A8)	0.155	0.383	0.354	H106C3	0.002	−0.072	0.155
H2C(A8)	0.211	0.409	0.275	H106C4	−0.003	−0.097	0.318
H1C(A1)	0.557	0.302	0.280	H106C5	0.061	−0.039	0.474
H2C(A1)	0.534	0.355	0.329	H106C6	0.130	0.043	0.467
H1C(B5)	0.350	−0.600	−0.050	H107C2	−0.055	−0.317	0.171
H2C(B5)	0.251	−0.623	−0.081	H107C3	−0.073	−0.308	−0.004
H1C(B8)	0.105	−0.134	0.126	H107C4	−0.051	−0.374	−0.149
H2C(B8)	0.159	−0.128	0.026	H107C5	−0.011	−0.448	−0.118
H1C(B1)	0.147	−0.335	−0.193	H107C6	0.007	−0.456	0.058
H2C(B1)	0.214	−0.285	−0.182	H108C2	−0.011	−0.451	0.424
H101C2	0.389	0.059	−0.101	H108C3	−0.083	−0.531	0.443
H101C3	0.545	0.076	−0.084	H108C4	−0.178	−0.584	0.304
H101C4	0.622	0.159	−0.017	H108C5	−0.201	−0.558	0.146
H101C5	0.542	0.225	0.034	H108C6	−0.128	−0.478	0.128
H101C6	0.385	0.208	0.017	H109C2	0.004	−0.304	0.451
H102C2	0.140	0.018	−0.061	H109C3	−0.103	−0.261	0.541
H102C3	0.098	−0.053	−0.202	H109C4	−0.254	−0.286	0.486
H102C4	0.151	−0.053	−0.372	H109C5	−0.298	−0.355	0.340
H102C5	0.246	0.019	−0.403	H109C6	−0.191	−0.398	0.249
H102C6	0.287	0.090	−0.262	H110C2	0.460	−0.283	0.494
H103C2	0.088	0.158	−0.050	H110C3	0.501	−0.214	0.638
H103C3	0.034	0.209	−0.148	H110C4	0.392	−0.174	0.731
H103C4	0.128	0.248	−0.261	H110C5	0.240	−0.204	0.680
H103C5	0.276	0.235	−0.276	H110C6	0.199	−0.274	0.536
H103C6	0.330	0.184	−0.178	H111C2	0.248	−0.410	0.521
H104C2	0.109	0.134	0.524	H111C3	0.316	−0.463	0.601
H104C3	−0.009	0.171	0.607	H111C4	0.466	−0.470	0.571
H104C4	−0.117	0.192	0.504	H111C5	0.548	−0.424	0.460
H104C5	−0.107	0.178	0.319	H111C6	0.480	−0.371	0.380
H104C6	0.011	0.142	0.235	H112C2	0.395	−0.392	0.217
H105C2	0.282	0.047	0.383	H112C3	0.485	−0.366	0.085
H105C3	0.410	0.073	0.498	H112C4	0.517	−0.280	0.080
H105C4	0.455	0.158	0.582	H112C5	0.458	−0.220	0.207
H105C5	0.372	0.219	0.553	H112C6	0.368	−0.246	0.338

Scheme I



1a: $R=C_6H_5$ (82%)
1b: $R=p\text{-}CH_3\text{-}C_6H_4$ (77%)
1c: $R=(CH_3)_2N$ (76%)

2 (90%)

which three molecules of the isothiocyanate are involved. Two kinds of ethoxycarbonyl proton signals occur in 2:1 intensity ratio at τ 8.76 t, 5.87 q (J = 7.5 Hz), and τ 8.79 t, 6.04 q (J' = 6.8 Hz) in the NMR spectrum of **2.** The infrared spectrum of **2** shows the corresponding ν(C=O) bands at 1785 and 1765 cm^{-1}. These spectroscopic observations clearly indicated that two of the three ethoxy carbonyl groups are different from the other. The presence of one molecule of acetone solvate is supported by the NMR (τ 7.95, s, 6 H) and the infrared spectra ($\nu_{C=O}$ 1711 cm^{-1}). The spectroscopic data did not suggest an unambiguous formulation of **2** which involves a ligand formed from the unusual molecular condensation of three EtOCONCS molecules. Consequently, an x-ray diffraction study of **2** was undertaken and is described in the following section.

Description of the Structure of RhCl(EtOCONCS)$_3$(PPh$_3$)$_2$ (2). The structure of RhCl(EtOCONCS)$_3$(PPh$_3$)$_2$·Me$_2$CO consists of well-separated molecules. The disposition of the four Rh-containing molecules and four acetone molecules in the unit cell is shown in Figure 1. Figure 2 displays a projection of the two Rh-containing molecules onto the ligand plane. Other than the obvious conformational differences between the two independent molecules in the cell (molecules A and B) there are no substantial differences between them, especially within the inner coordination sphere where problems of high thermal motion do not exist.

In each molecule the Rh atom is approximately octahedrally coordinated. The six coordination sites are occupied by the chloro ligand, by trans phosphine ligands, and by a tridentate ligand. It is clear from the figures that this tridentate ligand in a formal sense is formed by the condensation and rearrangement of three molecules of EtOCONCS. The two fused, five-membered metallocycle arrangement is completely analogous to that found in RhCl(PhCONCS)$_2$(PPh$_3$)$_2$(**1a**),[19] with the exception that an O atom has been replaced by an S atom with ensuing geometrical changes. Again in analogy with the previous structure **1a** the molecule **2** may be considered a carbene[18,19] complex of Rh(III). Some comparisons of geometrical parameters within the inner coordination sphere of **1a** and **2** are made in Table V. Bond distances and angles in **2** are tabulated in Table VI. The planar nature of the carbene ligand in **2** may be deduced from the least-squares planes of

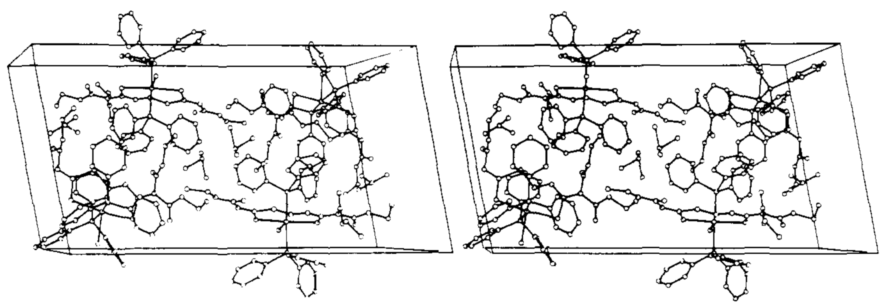


Figure 1. A stereoscopic view of the unit cell of $RhCl(EtOCONCS)_3(PPh_3)_2 \cdot Me_2CO$. All atoms are drawn at the 50% probability level for an isotropic B of 1 Å^2. Hydrogen atoms are not shown. In this view the y axis is from left to right, the x axis from bottom to top, and the z axis goes approximately into the paper.

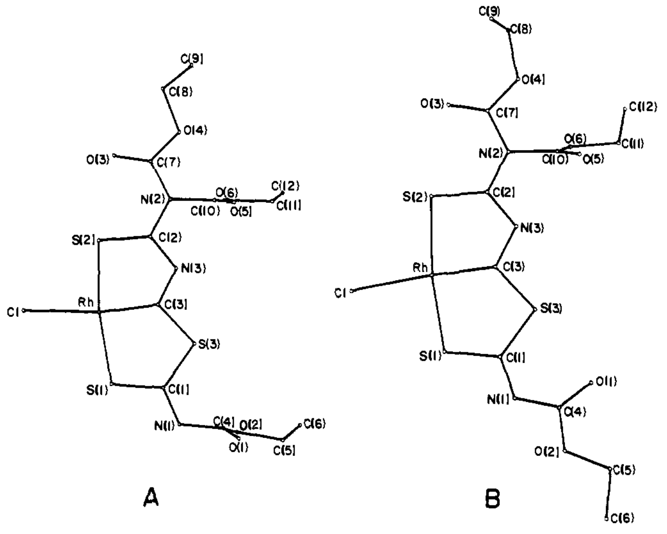


Figure 2. The equatorial planes of the independent molecules A and B showing the labeling scheme as well as the obvious conformational differences. The phosphine groups above and below each Rh atom are not shown.

Table VII. The discussion and comparisons of the structure of **1a** have been presented;[19] the close similarity of the chemically interesting tridentate ligand system in **2** does not therefore demand a similar detailed discussion.

The structure of **2** is consistent with the spectral information discussed above. The presence of two equivalent ethoxycarbonyl groups requires an ethoxycarbonyl group migration during the condensation process. Although many carbene-transition metal complexes have been reported[17,18] from various precursors, the formation of such tridentate and planar carbene ligands in **1** and **2** from the formal oxidative addition of the condensed heterocumulene linkage is an amazing one. We now examine some aspects of the mode of formation of these ligands.

The Primary Step in the Condensation of Activated Isothiocyanates. The Formation of η^2-Isothiocyanate Rhodium(III) and Palladium(II) Complexes. In order to elucidate a plausible mechanism for the formation of the tridentate carbene rhodium(III) complexes **1** and **2** from the condensation of two or three activated isothiocyanate molecules, several reactions summarized in Scheme II were carried out.

When cyNC is present in the reaction of $RhCl(PPh_3)_3$ with PhCONCS or EtOCONCS, formation of the tridentate carbene complexes is completely inhibited. The elemental analyses of the pale yellow powders isolated in both cases suggest the composition $RhCl(RCONCS)(cyNC)(PPh_3)_2$, **3a** for R = C_6H_5, **3b** for R = C_2H_5O. Complexes **3a** and **3b** are unstable in solution and decompose by dissociation of the isothiocyanate

Table V. Comparison of Distances (Å) and Angles (deg) in the Inner Coordination Spheres of $RhCl(PhCONCS)_2(PPh_3)_2$ (**1a**) and $RhCl(EtOCONCS)_3(PPh_3)_2$ (**2**)

	1a	2
Rh-Cl	2.455 (2)	2.463 (3)[a]
Rh-P	2.379 (4)	2.396 (5)
Rh-S(1)[b]	2.287 (2)	2.334 (23)
S(1)-C(1)	1.739 (7)	1.700 (11)
C(1)-S(3)	1.771 (7)	1.768 (11)
S(3)-C(3)	1.737 (7)	1.743 (10)
C(3)-Rh	1.930 (6)	1.930 (11)
C(3)-N(3)	1.326 (8)	1.347 (27)
N(3)-C(2)	1.385 (8)	1.349 (11)
C(2)-(S, O(2))	1.238 (8)	1.685 (10)
(S, O(2))-Rh	2.098 (4)	2.353 (11)
Rh-S(1)-C(1)	104.0 (2)	103.9 (7)
S(1)-C(1)-S(3)	120.9 (4)	121.0 (6)
C(1)-S(3)-C(3)	99.6 (3)	101.0 (8)
S(3)-C(3)-Rh	126.7 (4)	125.5 (6)
S(3)-C(3)-N(3)	114.2 (5)	110.1 (8)
C(3)-N(3)-C(2)	110.4 (6)	113.8 (18)
N(3)-C(2)-(S, O(2))	122.9 (6)	124.6 (16)
C(2)-(S, O(2))-Rh	109.9 (4)	94.6 (7)

[a] The standard deviation in parentheses is the larger of that estimated from agreement between the results for molecules A and B or from individual results from the inverse matrix and is for a single observation rather than for the mean. [b] The labeling scheme for compound **1a** has been redefined to correspond to that used for compound **2** in the present paper.

Scheme II

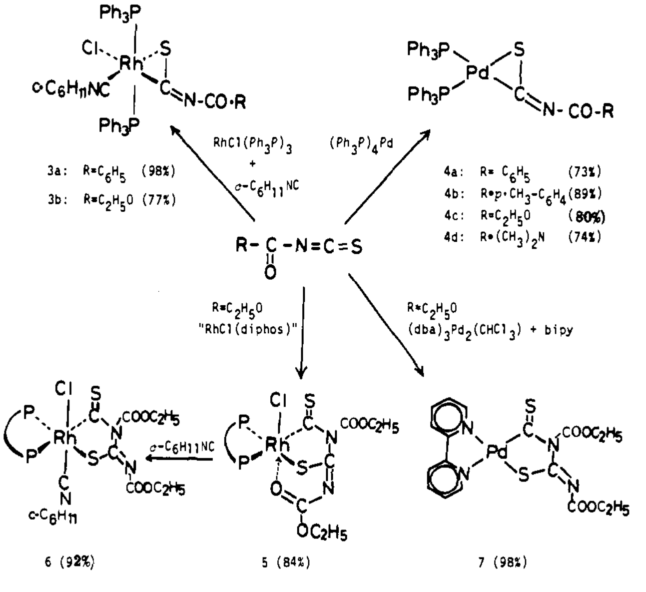


Table VI. Bond Distances (Å) and Angles (deg) in RhCl(EtOCONCS)$_3$(PPh$_3$)$_2$·Me$_2$CO[a]

Distance	Molecule A	Molecule B	Distance	Molecule A	Molecule B
Rh-Cl	2.463 (3)	2.462 (3)	C(1)-N(1)	1.299 (13)	1.319 (12)
Rh-P(1)	2.401 (3)	2.395 (3)	N(1)-C(4)	1.482 (17)	1.369 (14)
Rh-P(2)	2.399 (3)	2.389 (3)	C(4)-O(1)	1.190 (17)	1.210 (13)
Rh-S(1)	2.354 (3)	2.321 (3)	C(4)-O(2)	1.173 (16)	1.348 (13)
Rh-S(2)	2.345 (3	2.360 (3)	O(2)-C(5)	1.528 (22)	1.471 (13)
Rh-C(3)	1.938 (10)	1.922 (10)	C(5)-C(6)	1.382 (25)	1.520 (17)
P(1)-Cl(R01,R07)	1.816 (6)	1.829 (7)	C(2)-N(2)	1.367 (11)	1.369 (12)
P(1)-Cl(R02,R08)	1.831 (6)	1.831 (6)	N(2)-C(10)	1.456 (13)	1.472 (14)
P(1)-Cl(R03,R09)	1.835 (8)	1.842 (7)	C(10)-O(5)	1.186 (11)	1.190 (13)
P(2)-Cl(R04,R10)	1.820 (7)	1.836 (6)	C(10)-O(6)	1.297 (12)	1.285 (13)
P(2)-Cl(R05,R11)	1.843 (6)	1.838 (9)	O(6)-C(11)	1.502 (15)	1.488 (17)
P(2)-Cl(R06,R12)	1.843 (7)	1.819 (7)	C(11)-C(12)	1.479 (20)	1.517 (21)
S(1)-C(1)	1.707 (11)	1.692 (11)	N(2)-C(7)	1.406 (13)	1.383 (14)
S(3)-C(1)	1.770 (11)	1.766 (11)	C(7)-O(3)	1.206 (12)	1.196 (14)
S(3)-C(3)	1.734 (10)	1.751 (10)	C(7)-O(4)	1.330 (13)	1.339 (14)
S(2)-C(2)	1.683 (10)	1.686 (11)	O(4)-C(8)	1.525 (16)	1.531 (20)
C(3)-N(3)	1.328 (11)	1.366 (12)	C(8)-C(9)	1.386 (24)	1.323 (36)
C(2)-N(3)	1.353 (11)	1.344 (12)			

Angle	Molecule A	Molecule B	Angle	Molecule A	Molecule B
Cl-Rh-P(1)	89.11 (10)	89.04 (10)	O(2)-C(5)-C(6)	112.0 (18)	106.7 (10)
Cl-Rh-P(2)	90.28 (10)	89.11 (10)	S(3)-C(3)-N(3)	110.7 (7)	109.5 (7)
Cl-Rh-S(1)	100.86 (10)	88.15 (10)	N(3)-C(2)-N(2)	112.7 (8)	111.9 (9)
Cl-Rh-S(2)	88.01 (9)	100.77 (10)	S(2)-C(2)-N(2)	123.9 (8)	122.4 (8)
Cl-Rh-C(3)	170.6 (3)	176.2 (3)	C(2)-N(2)-C(7)	124.4 (9)	124.7 (10)
P(1)-Rh-P(2)	172.97 (10)	174.62 (10)	N(2)-C(7)-O(3)	124.5 (11)	126.8 (13)
P(1)-Rh-S(1)	86.94 (10)	92.36 (10)	N(2)-C(7)-O(4)	108.4 (10)	108.4 (11)
P(1)-Rh-S(2)	93.68 (10)	87.98 (10)	O(3)-C(7)-O(4)	127.0 (11)	124.8 (13)
P(1)-Rh-C(3)	90.2 (3)	92.2 (3)	C(7)-O(4)-C(8)	114.8 (10)	122.3 (12)
P(2)-Rh-S(1)	86.30 (10)	92.63 (10)	O(4)-C(8)-C(9)	109.0 (15)	97.9 (22)
P(2)-Rh-S(2)	93.29 (10)	87.40 (10)	C(7)-N(2)-C(10)	118.0 (9)	116.3 (10)
P(2)-Rh-C(3)	91.6 (3)	89.9 (3)	C(2)-N(2)-C(10)	117.6 (8)	118.7 (9)
S(1)-Rh-S(2)	171.12 (10)	171.09 (00)	N(2)-C(10)-O(5)	121.7 (10)	123.0 (12)
S(1)-Rh-C(3)	88.5 (3)	88.2 (3)	N(2)-C(10)-O(6)	108.0 (9)	108.3 (11)
S(2)-Rh-C(3)	82.7 (3)	82.9 (3)	O(5)-C(10)-O(6)	130.4 (11)	128.7 (12)
Rh-S(1)-C(1)	103.4 (4)	104.4 (4)	C(10)-O(6)-C(11)	115.9 (9)	118.1 (11)
S(1)-C(1)-S(3)	121.0 (6)	120.9 (6)	O(6)-C(11)-C(12)	111.2 (12)	107.9 (13)
C(1)-S(3)-C(3)	101.5 (5)	100.4 (5)			
S(3)-C(3)-Rh	125.3 (6)	125.6 (6)			
C(3)-N(3)-C(2)	115.0 (8)	112.5 (9)			
N(3)-C(2)-S(2)	123.4 (7)	125.7 (8)	Torsion Angle		
C(2)-S(2)-Rh	95.1 (3)	94.1 (4)			
Rh-C(3)-N(3)	123.9 (7)	124.8 (7)	C(2)-N(2)-C(7)-O(3)	−5 (2)	−5(2)
S(1)-C(1)-N(1)	118.1 (9)	114.7 (8)	N(2)-C(7)-O(4)-C(8)	−176 (1)	168 (1)
S(3)-C(1)-N(1)	120.9 (9)	124.4 (8)	C(7)-O(4)-C(8)-C(9)	157 (1)	86 (2)
C(1)-N(1)-C(4)	118.9 (11)	120.2 (10)	C(2)-N(2)-C(10)-O(5)	−89 (1)	−86 (1)
N(1)-C(4)-O(1)	114.5 (16)	130.2 (12)	N(2)-C(10)-O(6)-C(11)	−179 (1)	177 (1)
N(1)-C(4)-O(2)	111.4 (15)	108.1 (10)	C(10)-O(6)-C(11)-C(12)	−170 (1)	−141 (1)
O(1)-C(4)-O(2)	131.2 (18)	121.7 (12)	C(1)-N(1)-C(4)-O(1)	110 (2)	−6 (2)
C(4)-O(2)-C(5)	114.1 (15)	117.7 (9)	N(1)-C(4)-O(2)-C(5)	−174 (1)	175 (1)
			C(4)-O(2)-C(5)-C(6)	−152 (2)	−175 (1)

Distance	Solvent 1	Solvent 2	Angle	Solvent 1	Solvent 2
C(S1)-O(S1)	1.33 (6)	0.70 (12)	O(S1)-C(S1)-C(S2)	111 (6)	117 (11)
C(S1)-C(S2)	1.31 (6)	1.59 (7)	O(S1)-C(S1)-C(S3)	96 (5)	70 (4)
C(S1)-C(S3)	1.29 (6)	1.63 (7)	C(S2)-C(S1)-C(S3)	145 (7)	144 (11)

[a] Some of the peripheral atoms, in particular atoms O(1), O(2), C(5), C(6), C(9), and C(12) of molecule A and C(8) and C(9) of molecule B, as well as all atoms of the solvent molecules, have high thermal parameters, and distances and angles involving these atoms are not representative.

ligands. The infrared spectrum of **3a** shows a ν(C=O) band at 1668 cm^{-1} as well as a ν(C=N) band at 1530 cm^{-1}. The corresponding absorptions are observed at 1700 and 1600 cm^{-1} for **3b**. The appearance of these two bands in the infrared spectra is consistent with a structure involving an η^2-coordination of the isothiocyanate (Scheme II).[8] An alternative structure involving a five-membered metallocyclic skeleton similar to that found in benzoyl and thiobenzoyl isothiocyanate complexes[16] is unlikely, since no ν(C=O) band is expected for that structure. Complexes related to **3a** and **3b** are prepared by treating activated isothiocyanates with Pd(PPh$_3$)$_4$. The expected[32] bis(triphenylphosphine)(η^2-isothiocyanate)-palladium complexes, **4a–4d**, are prepared without difficulty, and they readily dissociate in solution in a manner similar to **3a**, **3b**, and to the other isothiocyanate complexes reported earlier.[8] The ν(C=O) band of **4a** at 1658 cm^{-1} and **4c** at 1700

Table VII. Least-Squares Planes

Atom	Molecule 1	Molecule 2
Deviations of Atoms from Planes, Å		
Rh	−0.002 (1)	−0.003 (1)
Cl	0.020 (3)	0.019 (3)
S(1)	−0.012 (3)	−0.012 (3)
S(2)	−0.012 (3)	0.009 (3)
S(3)	0.020 (3)	0.014 (3)
N(3)	0.015 (8)	−0.026 (8)
C(1)	−0.090 (11)	0.108 (10)
C(2)	0.012 (9)	0.000 (10)
C(3)	0.024 (10)	0.016 (10)

Plane Equations

Plane 1: $4.369x + 7.324y - 12.259z = 0.082$

Plane 2: $13.973x + 15.351y + 3.419z = 2.634$

Interplanar Angle

Plane 1/Plane 2 87.9°

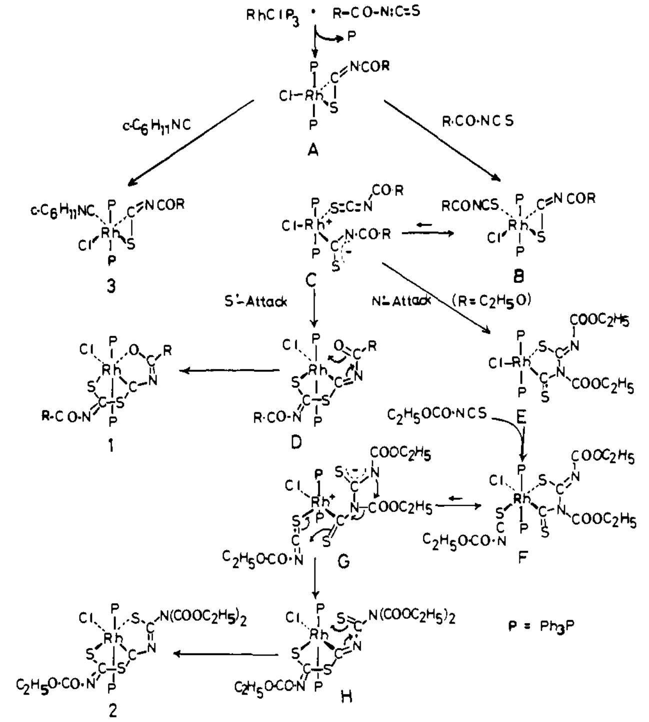
cm^{-1} corresponds well with the related rhodium cyclohexylisocyanide complexes, **3a** (1668 cm^{-1}) and **3b** (1700 cm^{-1}), which involve the presumed η^2-coordination of the isothiocyanate. The palladium complexes **4b** and **4d** show comparable ν(CO) and ν(CN) bands, and hence all four probably have the structure shown (Scheme II).

The structural similarity of **3a** and **3b** to the corresponding palladium complexes **4a** and **4c** suggests that the primary step in the condensation reaction of phenyl- or ethoxycarbonyl isothiocyanate molecules to lead to the tridentate carbene complexes of Rh(III), **1a**, and **2**, is the η^2-coordination of these acceptors to the rhodium metal via their C=S bonds. The subsequent step is expected to be the σ-coordination of a second isothiocyanate molecule to the sixth coordination site, occupied by cyclohexyl isocyanide in the model complexes **3a** and **3b**. The x-ray structure of **1a**[2a,19] indicates that carbon–sulfur bond formation occurs between the sulfur atom of the initially coordinated benzoyl isothiocyanate molecule and the most electrophilic central carbon atom of the second one. Thus the initial step in the formation of a tridentate carbene complex $RhCl(PhCONCS)_2(PPh_3)_2$ (**1a**) plausibly involves the η^2-coordination of the first isothiocyanate molecule.

A Model Complex of the Intermediate Involving Two Molecules of EtOCONCS. The formation of $RhCl(EtOCONCS)_3(PPh_3)_2$ (**2**) is more complex than that of **1**, because (1) an unusual condensation of the three molecules of isothiocyanate occurs around the rhodium atom resulting in a carbene ligand and (2) a 1,3-shift of one of the ethoxycarbonyl groups is necessary to generate the final structure of **2**. The results above suggest that η^2-coordination of the first isothiocyanate molecule followed by the σ-coordination of the second molecule is the most plausible pathway to **1**. The next step involves for **1** carbon–sulfur bond formation, while for **2** it involves carbon–nitrogen bond formation. It was therefore necessary to devise a model reaction in order to understand the structure of the highly reactive intermediate complex involving two molecules of ethoxycarbonyl isothiocyanate, and to decide when migration of the ethoxycarbonyl group occurs. Since the structure of **2** involves trans axial phosphine ligands and the tridentate equatorial carbene ligand, we thought it likely that if the phosphine ligands were constrained to a cis geometry the tridentate planar carbene ligand could not form, but rather we might isolate a complex containing two EtOCONCS groups. Thus a reaction of "RhCl(diphos)", prepared in situ from $[RhCl(1,5\text{-}COD)]_2$ and 1,2-bis(diphenylphosphino)ethane, with EtOCONCS was carried out. The deep yellow product isolated from the reaction has the composition $RhCl(EtOCONCS)_2(diphos)$ (**5**). The ν(C=O) bands appear at 1770 and 1543 cm^{-1}. The 1543-cm^{-1} band is indicative of intramolecular coordination of one of the carbonyl oxygen atoms to the sixth coordination site of the rhodium atom. The NMR spectrum of **5** indicates two ethyl methylene quartets at τ 5.80 and 5.86. When **5** is reacted with cyclohexyl isocyanide in order to cleave intramolecular coordination $RhCl(EtOCONCS)_2(cyCN)(diphos)$ (**6**) is obtained in 92% yield as a sparingly soluble yellow powder. The infrared spectrum of **6** shows ν(C=O) bands at 1768 and 1694 cm^{-1}, indicative of the presence of one nonconjugating carbonyl and one conjugating carbonyl group. The most reasonable formulation of **6** is, therefore, the five-membered rhodiacyclic structure depicted in Scheme II. It arises simply by carbon–nitrogen and rhodium–sulfur bond formation involving two EtOCONCS molecules. In order to obtain further substantiation of the proposed structure of **6**, an analogous palladium complex $Pd(EtOCONCS)_2(bpy)$ (**7**) was prepared from $Pd_2dba_3 \cdot CHCl_3$,[25] bpy, and EtOCONCS in 98% yield. The two carbonyl bands in the infrared spectrum of **7** at 1771 and 1681 cm^{-1} are extremely close to these absorptions in the corresponding rhodium complex **6**. From these experiments it is plausible to assume that the condensation of three molecules of EtOCONCS to form the tridentate carbene ligand of **2** proceeds via an intermediate involving a five-membered rhodiacyclic structure shown in Scheme II for **5** and **6**. Further reaction will occur if the Rh atom is five-coordinate and coordinately unsaturated, thus providing a site for the attachment of the third EtOCONCS molecule. Note that the model complex **6** does not involve a 1,3-shift of the EtOCONCS group; we assume that this shift will occur at the final stage of the reaction with concurrent carbenoid formation.

A Plausible Mechanism for Carbenoid Formation. Based on the crystallographic, spectroscopic, and chemical evidence cited above what we believe is a plausible mechanism for the formation of the rhodium carbene complexes **1** and **2** is presented here in Scheme III.

Scheme III



The first step in the reaction is the formation of the five-coordinate complex A, involving an η^2-coordination of the C=S bond of an isothiocyanate ligand, to which a second isothiocyanate molecule coordinates to complete the stable six coordination around the rhodium(III) atom (complex B). A complex similar to B has been proposed by Baird, Hartwell, and Wilkinson[8] on the basis of infrared spectroscopic results. The cyclohexyl isocyanide (η^2-isothiocyanate)rhodium complexes **3a** and **3b** and the bis(triphenylphosphine)(η^2-isothiocyanate)palladium complexes **4a**–**4d** readily dissociate the coordinating isothiocyanate ligands as discussed earlier. Thus, the intermediate zwitterion C is a reasonable formulation, in which the S terminus of the η^2-ligand has dissociated from the metal as a result of the trans influence of the σ-bonded isothiocyanate. The anionic part of C is stabilized by the electron delocalization within the S–C–N–C–O– entity, and it behaves as an ambidentate anion to the nucleophilic attack of the coordinating isothiocyanate, whose electrophilicity is increased by coordination to the cationic rhodium atom. When the sulfur atom of the anionic part in C attacks the central carbon atom of the second isothiocyanate ligand a five-coordinate imidoyl intermediate (D) is produced, which undergoes an electron reorganization to form the tridentate carbene skeleton of **1**, completing the stable six-coordination about Rh(III). On the other hand, the anionic part of C cannot delocalize extensively when R is an ethoxy group, because the carbonyl group is strongly conjugated with the lone-pair electrons on the ethoxy group. As a result, the electron density on the nitrogen terminus becomes high and a carbon–nitrogen bond is formed with the second isothiocyanate ligand to give a five-membered coordinatively unsaturated rhodiacyclic intermediate, E. A model complex of E was isolated above by controlling the stereochemistry (**5**, **6**). The sixth coordination site of the intermediate E then accepts the third EtOCONCS molecule to give F. In a manner similar to the B → C pathway, another zwitterion intermediate G is formed by dissociation of the S terminus. The most nucleophilic N atom of G becomes the trigger for the 1,3-shift of the ethoxycarbonyl group and concurrent S–C bond formation to give the imidoyl intermediate H. As in the D → **1** pathway, the drive toward stable six-coordination about Rh(III) leads from H to the desired complex **2**. Based on molecular models it would appear that in intermediate F the distance between the attacking N atom and the rearranging ethoxycarbonyl group is too great to bring about the 1,3-shift. Hence we believe that breaking of the Rh–S bond prior to rearrangement is necessary.

Acknowledgments. This work was supported at Nagoya University by the Ministry of Education of Japan (Grant No. 011006) and at Northwestern University by the U.S. National Science Foundation (Grant No. CHE76-10335).

Supplementary Material Available: Table IV, a listing of structure amplitudes (50 pages). Ordering information is given on any current masthead page.

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(27) Abbreviations: Ph = phenyl, To = tolyl, Me = methyl, Et = ethyl, cy = cyclohexyl, diphos = 1,2-bis(diphenylphosphino)ethane, bpy = bipyridine, dba = dibenzylidene acetone, 1,5-COD = 1,5-cyclooctadiene.
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(31) Supplementary material.
(32) When a large excess of EtOCONCS is reacted with $Pd(PPh_3)_4$ a dithiocarbimate complex, $Pd(S_2C = NCOOEt)(PPh_3)_2$, is isolated.[28]