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Isothiocyanate Activation by Two Metal Centers: Examples of Bridging Isothiocyanate Coordination, Subsequent Condensation and Rearrangement Reactions, and Isocyanide Formation. Structure of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(Ph_2PCH_2PPh_2)_2]\cdot{}^1/_2C_6H_5CH_3$

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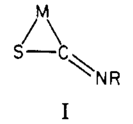
The reactions of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (DPM = $Ph_2PCH_2PPh_2$) with the isothiocyanate molecules RC(O)NCS (R = EtO, Ph) yield the complexes $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)R)(DPM)_2]$, in which the metals are bridged by the carbonyl ligand and the isothiocyanate molecule with no accompanying metal–metal bond. The carbonyl group of the isothiocyanate ligand is also coordinated to one of the Rh centers. In solution each of these species is in equilibrium with an isomeric form having a terminal carbonyl ligand and a Rh–Rh bond. $[Rh_2I_2(CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ can be prepared from $[Rh_2I_2(\mu\text{-}CO)(DPM)_2]$ but only exists as the Rh–Rh bonded isomer. $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ reacts with 1 equiv of CO to give $[Rh_2Cl_2(CO)(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ and reacts with additional CO to give $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPM)_2][Cl]$. The benzoyl isothiocyanate analogue also reacts with CO, but only the above tricarbonyl species, resulting from isothiocyanate displacement, is observed. Both isothiocyanate adducts react with MeNC to give $[Rh_2Cl_2(CNMe)(\mu\text{-}CO)(\mu\text{-}SCNC(O)R)(DPM)_2]$. The reactions of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ with PhNCS and MeNCS yield a variety of products of which the only species identified are $[Rh_2Cl_2(CO)(CNR)(DPM)_2]$ (R = Ph, Me). $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ reacts with isothiocyanates and CS_2 to yield $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(R)C(O)OEt)(DPM)_2]$ (R = Me, Ph, C(O)OEt, C(O)Ph) and $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)SC(O)OEt)(DPM)_2]$, respectively, and an X-ray structure determination of one product (R = Ph) indicates that condensation of the isothiocyanate molecules has occurred with C–N bond formation, accompanied by migration of the C(O)OEt moiety to the nitrogen atom of the PhNCS group. The unusual tridentate ligand that results can be viewed as a new isothiocyanate group, RNCS, with R = C(S)N(Ph)C(O)OEt. This group bridges the metals, bound to one via the sulfur and to the other via the carbon of the isothiocyanate group, and is additionally coordinated to one metal center by the thiocarbonyl moiety. $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]$ crystallizes with 0.5 equiv of toluene in the space group $P2_1/c$ with a = 17.964 (7) Å, b = 25.235 (10) Å, c = 15.861 (5) Å, β = 97.02 (3)°, and Z = 4. On the basis of 2112 unique observed reflections and 247 parameters varied the structure has refined to R = 0.070 and R_w = 0.095.

Introduction

In an attempt to obtain a better understanding of the possible coordination modes and the subsequent reactivites of sulfur-containing heteroallenes and related molecules in the presence of more than one metal center, we have been studying the reactions of a number of these molecules with binuclear rhodium and iridium complexes.[1-3] Interest in the chemistry of heteroallenes of the form X═C═Y (X, Y = O, NR, CR_2, S) stems in a large part from the close similarity of these molecules to carbon dioxide, a common but rather unreactive molecule. It is generally hoped that studies of heteroallene chemistry will lead to a better understanding of CO_2 activation, which may in turn lead to the utilization of CO_2 as a building block for larger organic molecules.[4] It is also anticipated that such studies will result in the increased utilization of heteroallenes in organic synthesis, several examples of which are already known.[5-7]

One group of heteroallenes, the organic isothiocyanates (S═C═NR), has been shown to undergo three general types of reactions with metal complexes. First, the molecule can bind to a metal via the carbon–sulfur double bond forming a three-centered $\overline{M\text{–}C\text{–}S}$ metallacycle.[8-15] This coordination mode (termed π or η^2 and shown below in structure I), although quite common for CS_2,[16-22] is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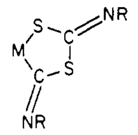
II

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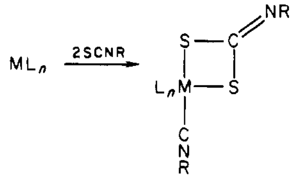
somewhat rarer for isothiocyanate molecules, and it is only recently that the first structure showing this binding mode has been reported.[15] Isothiocyanates may also undergo condensation reactions in the presence of metal complexes yielding species in which two[23-25] and in one case three[11] isothiocyanate molecules are fused and attached to the metal. Example II shows the structure of the more common condensation product involving two isothiocyanate units. This reactivity pattern, yielding structures analogous to II, is quite general among related molecules and has observed for CO_2,[26] CS_2,[1,27] allenes,[28] ketones,[29-31] imines,[29-33] and ketenes.[34] Most commonly, however, only the degradation products of isothiocyanate reactions are observed. These products commonly arise by two routes. In the presence of a sulfur-abstracting ligand, such as a phosphine, metal isocyanides and the corresponding sulfide are obtained (eq 1),[24,25,35-40] or in the presence of excess

$$ML_n \xrightarrow[X]{SCNR} L_nM\text{-}CNR + XS \qquad (1)$$



(2)

isothiocyanates a disproportionation reaction, yielding isocyanide and dithiocarbonimidato groups, can occur (eq 2).[8,13,14,25,41-46] The disproportionation reaction can readily be envisaged as proceeding via the condensed species II by C–S bond cleavage and M–S bond formation and may result in products in which the isocyanide and dithiocarbonimidato ligands remain coordinated to the same metal[8,13 14,25,41] or products in which only one remains coordinated to the metal.[13,14,25,42-46] Similar disproportionations have been reported for CO_2,[47,48] CS_2,[49] COS,[50,51] carbodiimides,[52] isocyanates,[48] and isoselenocyanates.[53]

In this paper we describe the results of our studies on the reactions of organic isothiocyanates with the binuclear rhodium complexes [$Rh_2X_2(\mu\text{-}CO)(DPM)_2$] (DPM = $Ph_2PCH_2PPh_2$; X = Cl (1), I (2)). We were interested in determining the modes of interaction of the various isothiocyanate molecules with the two metal centers and whether the presence of the second metal would result in significant differences in chemistry from that observed in related mononuclear complexes.

Experimental Section

All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen and reactions were routinely carried out under Schlenk conditions utilizing a dinitrogen atmosphere. Bis(diphenylphosphino)methane (DPM) was purchased from Strem Chemicals, hydrated rhodium trichloride from Research Organic/Inorganic Chemicals, methyl, phenyl, and ethoxycarbonyl isothiocyanates from Aldrich, and benzoyl isothiocyanate from ICN Pharmaceuticals. These and all other reagent grade chemicals were used as received. [$Rh_2Cl_2(\mu\text{-}CO)(DPM)_2$][54] (1), [$Rh_2I_2(\mu\text{-}CO)(DPM)_2$][55] (2), and CNMe[56] were prepared by the reported procedures. Infrared spectra were recorded on a Nicolet 7199 spectrometer with use of Nujol mulls on KBr plates or in solution in KBr cells. ^{1}H, $^{31}P\{^{1}H\}$, and ^{13}C-$\{^{31}P\{^{1}H\}\}$ NMR spectra were recorded on Bruker WP200, WP400 (at 161.93 MHz), and HFX-90 (at 22.6 MHz) instruments, respectively, unless otherwise noted. The phosphorus chemical shifts were measured relative to tetramethylsilane. An internal deuterium lock (usually CD_2Cl_2) was used for all samples. For all nuclei, positive shifts are downfield from the standards. Elemental analyses were performed within the department or by Canadian Microanalytical Service Ltd., Vancouver, British Columbia, Canada. Conductivity measurements were performed by using a Yellow Springs Instrument Model 31 and using approximately 1×10^{-3} M solutions in CH_2Cl_2. No conductivity was observed for any of the samples isolated in this study.

Preparation of Compounds. (i) [$Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2$] (3). A 500-mg sample of compound 1 (0.466 mmol) was dissolved in 4 mL of CH_2Cl_2, and ethoxycarbonyl isothiocyanate (56 μL, 0.475 mmol) was added from a syringe causing the color of the solution to change to deep red, soon after which a light brown precipitate was deposited. The reaction mixture was stirred for 10 min, whereupon 5 mL of diethyl ether

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Table I. Infrared Spectral Details

no.	compd	ν(CO), cm^{-1}	ν(^{13}CO), cm^{-1}	others, cm^{-1}
3	[Rh$_2$Cl$_2$(μ-CO)(SCNC(O)OEt)(DPM)$_2$]	1710[a]	1670[a]	
		2023, 1717[b]	1977, 1676[b]	
4	[Rh$_2$Cl$_2$(μ-CO)(SCNC(O)Ph)(DPM)$_2$]	1714[a]	1673[a]	
		2010, 1718[b]	1971, 1678[b]	
5	[Rh$_2$I$_2$(CO)(SCNC(O)OEt)(DPM)$_2$]	2001[a]		
		2001[b]		
6	[Rh$_2$Cl$_2$(CO)(μ-CO)(SCNC(O)OEt)(DPM)$_2$]	1968, 1700[a]	1912, 1665	
8	[Rh$_2$Cl$_2$(μ-CO)(CNMe)(SCNC(O)OEt)(DPM)$_2$]	1668[a]	1625[a]	2229[a,c]
		1668[b]		2216[b,c]
9	[Rh$_2$Cl$_2$(μ-CO)(CNMe)(SCNC(O)Ph)(DPM)$_2$]	1656[a]	1621[a]	2229[a,c]
		1656[b]		2220[b,c]
10	[Rh$_2$Cl$_2$(CO)(CNPh)(DPM)$_2$]	1971[a]		2165[a,c]
11	[Rh$_2$Cl$_2$(CO)(CNMe)(DPM)$_2$]	1970[a]		2169[a,c]
12	[Rh$_2$Cl$_2$(CO)(SCNC(S)N(C(O)OEt)$_2$)(DPM)$_2$]	2026[a]	1980[a]	1772,[a,d] 1711[a,d]
13	[Rh$_2$Cl$_2$(CO)(SCNC(S)N(Me)C(O)OEt)(DPM)$_2$]	2024[a]	1974[a]	1724[a,d]
14	[Rh$_2$Cl$_2$(CO)(SCNC(S)N(Ph)C(O)OEt)(DPM)$_2$]	2022[a]	1976[a]	1739[a,d]
15	[Rh$_2$Cl$_2$(CO)(SCNC(S)N(C(O)Ph)C(O)OEt)(DPM)$_2$]	2027[a]	1980[a]	1771,[a,d] 1673[a,e]
16	[Rh$_2$Cl$_2$(CO)(SCNC(S)SC(O)OEt)(DPM)$_2$]	2023[e]	1977[a]	1769

[a] KBr disk. [b] CH_2Cl_2 solution. [c] Absorption due to CNR ligand. [d] Absorption due to the unbound carbonyl of the EtO EtOC(O) group. [e] Absorption due to the unbound carbonyl of the PhC(O) group.

Table II. NMR Spectral Data

compd	^{1}H, δ	^{13}C{^{31}P{^{1}H}}, δ	$^1J_{Rh-C}$, Hz	^{31}P{^{1}H}, δ	$^1J_{Rh-P}$, Hz
3	2.64 (q, 2 H), 0.70 (t, 3 H)[a,b]	199.0 (br)		12.0 (br)	
	4.14 (m, 2 H), 3.21 (m, 2 H)[c]				
4	4.14 (m, 2 H), 3.29 (m, 2 H)[c]	197.6 (br)		11.6 (br)	
5	4.20 (q, 2 H), 0.67 (t, 3 H)[b]	197.5 (d)	64.8	6.6 (m)	135.4
	4.90 (m, 2 H), 4.65 (m, 2 H)[c]			−0.6 (m)	142.5
6		228.6 (t)	45.0	8.6 (m)	126.2
		191.5 (d)	70.1	5.3 (m)	119.2
8	3.43 (q, 2 H), 0.67 (t, 2 H)[b]	232.0 (d)	23.9, 33.1	18.5 (m)	115.6
	4.55 (m, 2 H), 2.62 (m, 2 H)[c]			6.0 (m)	132.8
	3.19 (s, 3 H)[d]				
9	4.50 (m. 2 H), 2.65 (m, 2 H)[c]	234.8 (d)	22.9, 33.2	18.2 (m)	118.3
	3.17 (s, 3 H)[d]			6.0 (m)	132.3
12	4.30 (q, 2 H), 3.89 (q, 2 H), 1.33 (t, 3 H), 1.08 (t, 3 H)[b]	191.5 (d)	70.4	8.2 (m)	99.1
	4.38 (m, 2 H), 4.14 (m, 2 H)[c]			3.7 (m)	92.6
13	4.12 (q, 2 H), 1.22 (t, 3 H)[b]	191.6 (d)	69.4	9.8 (m)	107.0
	4.35 (m, 2 H), 4.20 (m, 3 H)[c]			3.3 (m)	96.0
	2.89 (s, 3 H)[e]				
14	4.06 (q, 2 H), 1.06 (t, 3 H)[b]	191.5 (d)	69.5	7.2 (m)	107.8
	4.34 (m, 2 H), 4.14 (m, 2 H)[c]			2.0 (m)	95.7
15	4.30 (q, 2 H), 0.88 (t, 3 H)[b]	191.1 (d)	73.0	7.2 (m)	99.3
	4.38 (m, 2 H), 4.12 (m, 2 H)[c]			3.3 (m)	93.0
16	4.34 (a, 2 H), 1.34 (t, 3 H)[b]	191.0 (d)	71.8	7.7 (m)	100.3
	4.40 (m, 2 H), 4.14 (m, 2 H)[c]			3.9 (m)	93.2

[a] Abbreviations used: q, quartet; t, triplet; m, multiplet; br, broad; d, doublet; dd, doublet of doublets. [b] Resonances attributable to the isothiocyanate ethyl group. [c] Resonances due to DPM methylene protons. [d] Resonances due to MeNC. [e] Resonance due to isothiocyanate methyl group.

was added to complete precipitation. The product was isolated by filtration, washed repeatedly with ether to remove traces of [Rh$_2$Cl$_2$(CO)(μ-SCNC(S)N(C(O)OEt)$_2$)(DPM)$_2$] (vide infra), and dried in vacuo. This product and all other solids described in this paper are air stable and were routinely handled in air. Spectral and physical data for all new compounds are given in Tables I and II; yield 79%. Anal. Calcd for $C_{55}H_{49}Cl_2NO_3P_4Rh_2S$: S, 54.8; H, 4.1; N, 1.2; Cl, 5.9; S, 2.7. Found: C, 54.2; H, 4.3; N, 1.2; Cl, 5.3; S, 2.9.

(ii) [Rh$_2$Cl$_2$(μ-CO)(μ-SCNC(O)Ph)(DPM)$_2$] (4). Compound **4** was prepared in a manner analogous to that of **3**, but using 500 mg of compound **1** and 65 μL of PhC(O)NCS (0.505 mmol). The tan solid isolated was washed with ether and dried in vacuo; yield 85%. Anal. Calcd for $C_{59}H_{49}Cl_2NO_2P_4Rh_2S$: C, 57.3; H, 4.0; N, 1.1; Cl, 5.7; S, 2.6. Found: C, 56.5; H, 4.0; N, 1.1; Cl, 6.0; S, 2.7.

(iii) [Rh$_2$I$_2$(CO)(μ-SCNC(O)OEt)(DPM)$_2$] (5). Compound **2** (100 mg, 0.080 mmol) was dissolved in 2 mL of CH_2Cl_2. Addition of 9.5 μL of EtOC(O)NCS (0.081 mmol) caused a change in color of the reaction mixture to red-purple, from which a precipitate was isolated by addition of 10 mL of hexane. The red-purple solid was filtered, washed with hexane, and dried in vacuo.

(iv) [Rh$_2$Cl$_2$(CNMe)(μ-CO)(μ-SCNC(O)OEt)(DPM)$_2$] (8). A 100-mg sample of compound **3** (0.083 mmol) was suspended in 3 mL of CH_2Cl_2, and 4.4 μL of MeNC (0.08 mmol) was added by syringe. The solid dissolved giving a red solution. Addition of 10 mL of diethyl ether precipitated a yellow solid that was filtered, washed with ether, and dried in vacuo; yield 85%. Anal. Calcd for $C_{57}H_{52}Cl_2N_2O_3P_4Rh_2S$: C, 55.0; H, 4.2; N, 2.2. Found: C, 54.8; H, 4.4; N, 2.5.

(v) [Rh$_2$Cl$_2$(CNMe)(μ-CO)(μ-SCNC(O)Ph)(DPM)$_2$] (9). Compound **9**, as a yellow solid, was obtained as described for compound **8** except using 100 mg (0.081 mmol) of compound **4** and 4.4 μL of MeNC (0.08 mmol); yield 80%. Anal. Calcd for $C_{61}H_{52}Cl_2N_2O_2P_4Rh_2S$: C, 57.3; H, 4.1; N, 2.2. Found: C, 56.6; H, 4.1; N, 2.3.

(vi) [Rh$_2$Cl$_2$(CO)(CNPh)(DPM)$_2$] (10). Compound **1** (100 mg, 0.093 mmol) was dissolved in 5 mL of CH_2Cl_2, PhNCS (12.6 μL, 0.105 mmol) was added via syringe, and the resulting red solution was stirred for ca. 2 h. After the mixture was left standing for 24 h, a solid began to precipitate, which, after standing for several days, was collected by filtration and washed with ether. The yield of yellow solid was only ca. 20%.

(vii) [$Rh_2Cl_2(CO)(\mu$-SCNC(S)N(C(O)OEt)$_2$)(DPM)$_2$] (12). Method a. Compound 1 (100 mg, 0.093 mmol) was dissolved in 3 mL of CH_2Cl_2, and EtOC(O)NCS (50 μL, 0.415 mmol) was added by syringe. The color of the solution changed to orange immediately. Addition of 10 mL of hexane precipitated a yellow-orange solid which was isolated by filtration, washed with hexane, and dried in vacuo.

Method b. Compound 3 (100 mg, 0.083 mmol) was suspended in 3 mL of CH_2Cl_2, and EtOC(O)NCS (10 μL, 0.085 mmol) was added by syringe. The solid dissolved within a minute, yielding a clear orange solution. Addition of hexane precipitated compound 12 which was isolated as described above; yield 72%. Anal. Calcd for $C_{59}H_{54}Cl_2N_2O_5P_4Rh_2S_2$: C, 53.0; H, 4.1; N, 2.1; S, 5.3. Found: C, 52.1; H, 4.4; N, 1.9, S, 5.0.

(viii) [$Rh_2Cl_2(CO)(\mu$-SCNC(S)N(Me)C(O)OEt)(DPM)$_2$] (13). To a suspension of 3 (100 mg, 0.083 mmol) in 3 mL of CH_2Cl_2 was added MeNCS (0.3 mL, 4.4 mmol). The solid dissolved giving an orange solution, from which a solid was precipitated by addition of 100 mL of hexane. Yellow-orange samples of 13 were isolated by filtration, washed with hexane, and dried in vacuo; yield 75%. Anal. Calcd for $C_{57}H_{52}Cl_2N_2O_3P_4Rh_2S_2$: C, 53.6; H, 4.1; N, 2.2. Found: C, 53.2; H, 4.1; N, 2.5.

(ix) [$Rh_2Cl_2(CO)(\mu$-SCNC(S)XC(O)OEt)(DPM)$_2$] (X = NPh (14), NC(O)Ph (15), S (16)). Orange samples of compounds 14, 15, and 16 were prepared as described for 13 but reacting compound 3 (100 mg, 0.083 mmol) with 0.2 mL of PhNCS (1.67 mmol), PhC(O)NCS (1.49 mmol), or CS_2 (3.3 mmol), respectively. Yields: 14, 85%; 15, 82%; 16, 90%. Anal. Calcd for $C_{62}H_{54}Cl_2N_2O_3P_4Rh_2S_2$ (14): C, 55.6; H, 4.1; N, 2.1; S, 4.8. Found: C, 55.9; H, 4.3; N, 2.1; S, 5.1. Calcd for $C_{63}H_{54}Cl_2N_2O_4P_4Rh_2S_2$ (15): C, 55.3; H, 4.0; N, 2.0; Cl, 5.2; S, 4.7. Found: C, 54.7; H, 4.3; N, 1.9; Cl, 5.3; S, 4.8. Calcd for $C_{56}H_{49}Cl_2NO_3P_4Rh_2S_3$ (16): C, 52.5; H, 3.9; N, 1.1; S, 7.5. Found: C, 52.2; H, 4.1; N, 1.2; S, 6.9.

Reaction of 3 with CO. Compound 3 (100 mg, 0.083 mmol) was suspended in 2 mL of CH_2Cl_2 in a three-necked, 50-mL round-botton flask, and the dinitrogen atmosphere was replaced by CO. After the mixture was stirred for 5 min, the solids had dissolved, yielding a yellow solution. Addition of 10 mL of diethyl ether resulted in the precipitation of a yellow solid which appeared from its infrared and ^{1}H and $^{31}P\{^1H\}$ NMR spectra to be a mixture of [$Rh_2Cl_2(CO)(\mu$-CO)(μ-SCNC(O)OEt)(DPM)$_2$] (6) and [$Rh_2(CO)_2(\mu$-Cl)(μ-CO)(DPM)$_2$][Cl][57] (7).

Reaction of 4 with CO. Reacting compound 4 with CO in the manner described for compound 3 yielded only 7. Monitoring the reaction at intermediate times showed the presence of compounds 4 and 7 but showed no indication of a compound analogous to 6.

Attempted Reactions of 3 with MeNCO, PhNCO, Allene, and CO_2. Compound 3 (50 mg, 0.042 mmol) was suspended in 5 mL of CH_2Cl_2. The reagents were added by syringe for the liquids, MeNCO (0.5 mL, 8.1 mmol), and PhNCO (0.5 mL, 4.6 mmol) or by replacing the N_2 atmosphere in the 50-mL flask by either allene or CO_2. No reaction was observed after 24 h in any of the reactions, and compound 3 was recovered quantitatively.

Preparation of ^{13}CO-Labeled Samples. ^{13}CO-labeled samples of compounds 3–16 were prepared exactly as described previously but utilizing ^{13}CO-labeled compounds 1 and 2 and a ^{13}CO atmosphere for compound 6.

X-ray Data Collection. Orange crystals of [$Rh_2Cl_2(CO)(\mu$-SCNC(S)N(Ph)C(O)OEt)(DPM)$_2$]$\cdot 0.5C_7H_8$ (14) were grown from a saturated toluene solution of the complex. Although these crystals were small and diffracted rather poorly, we were unable to obtain better ones, so X-ray data collection was carried out on one of the more suitable crystals that was mounted on a glass fiber with epoxy resin. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 16 reflections in the range $4.0° \leq 2\theta \leq 17.0°$, which were accurately centered or an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The $2/m$ diffraction symmetry and the systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) were consistent with the space group $P2_1/c$.

Intensity data were collected at 22 °C on a CAD4 diffractometer in the bisecting mode employing the ω–2θ scan technique. Backgrounds were scanned for 25% of the peak width on either end of the peak scan. The intensities of two standard reflections were measured every 1 h of exposure to assess possible crystal decomposition or movement. No significant variation in these standards was noted so no correction was applied to the data. A total of 10 082 unique reflections were measured and processed in the usual manner using a value of 0.04 for p.[58] Of these only 2112 were considered to be observed and were used in subsequent calculations. See Table III for pertinent crystal data and details of intensity collection.

Table III. Summary of Crystal Data and Details of Intensity Collection

compd	[$Rh_2Cl_2(CO)(\mu$-SCNC(S)N(Ph)C(O)OEt)(DPM)$_2$]$\cdot 0.5C_7H_8$
fw	1385.93
space group	$P2_1/c$ (No. 14)
a, Å	17.964 (7)
b, Å	25.235 (10)
c, Å	15.861 (5)
β, deg	97.02 (3)
ρ(calcd), g/m^3	1.29
V, Å^3	7136
radiatn	Mo Kα, $\overline{\lambda} = 0.709\,260$
detector aperture, mm	$(2.00 + 0.500 \tan \theta) \times 4$
2θ limits, deg	$0.1 \leq 2\theta \leq 45.0$
scan type	$\omega/2\theta$
scan width, deg	$0.75 + 0.35 \tan \theta$ in ω
scan speed, deg min^{-1}	2.63-20.12 in 2θ
bkgd	25% on low- and high-angle sides
rflctns measd	$\pm h, +k, +l$, 10 082
abs coeff μ, cm^{-1}	7.168
cryst dimens, mm	0.05 × 0.10 × 0.11
range in abs corr factors	0.918-0.969
final no. parameters varied	247
error in observn of unit wt	2.04
R	0.070
R_w	0.095

Structure Solution and Refinement. The structure was solved in the space group $P2_1/c$ by using a sharpened Patterson synthesis to locate the two independent rhodium atoms. Subsequent refinements and difference Fourier calculations led to the location of all the remaining non-hydrogen atoms. Atomic scattering factors for hydrogen[59] and other atoms[60] were obtained from the usual sources. Anomalous dispersion[61] terms for Rh, Cl, S, and P were included in F_c. The carbon atoms of all phenyl groups were refined as rigid groups having D_{6h} symmetry and C–C distances of 1.392 Å; the isotropic thermal parameter for each of these carbon atoms was refined. All phenyl hydrogen atoms as well as the DPM and ethyl methylene hydrogen atoms were included in their idealized locations (utilizing C–H distances of 0.95 Å) and were not refined. These atoms were assigned thermal parameters of 1 Å^2 greater than the B (or equivalent isotropic B) of their attached carbon atom. Absorption corrections were applied to the data by using Gaussian integration.[62]

The large thermal parameters of the carbon atoms of the ethyl group suggested a possible disorder of these atoms so they were

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[62] In addition to local programs, the following were used: FASTFO, an adapted version of FORDAP by R. J. Dellaca; BUCILS, least-squares program adapted from the Northwestern program NUCLS; ORFFE, for calculating bond lengths and angles and associated standard deviations by W. Busing and H. A. Levy; ORTEP, plotting program by C. K. Johnson; AGNOST, absorption and extinction program from Northwestern University.

Table IV. Positional Parameters (×10^4) and Isotropic Thermal Parameters for the Nongroup Atoms

atom	x^a	y	z	B,^{b} Å^2	atom	x	y	z	B, Å^2
Rh(1)	2055 (2)	−1414 (1)	1811 (2)	2.64^b	Rh(2)	2551 (2)	−689 (1)	665 (2)	2.91^b
Cl(1)	3121 (5)	−2020 (4)	1729 (6)	3.56^b	Cl(2)	2644 (6)	157 (4)	−204 (6)	4.44^b
S(1)	1391 (6)	−396 (4)	1071 (6)	3.15^b	S(2)	1318 (5)	−1822 (4)	2733 (6)	2.90^b
P(1)	2797 (6)	−1042 (4)	2986 (6)	2.9 (3)	P(2)	3279 (6)	−249 (4)	1755 (7)	3.5 (3)
P(3)	1353 (6)	−1891 (4)	743 (6)	2.8 (2)	P(4)	1986 (6)	−1139 (4)	−527 (7)	3.2 (3)
O(1)	3910 (14)	−1320 (10)	406 (15)	4.0 (6)	O(2)	−33 (15)	−2308 (11)	3146 (16)	4.9 (7)
O(3)	−904 (17)	−1832 (12)	3651 (19)	6.8 (8)	N(1)	641 (15)	−935 (11)	2103 (17)	2.7 (7)
N(2)	−33 (16)	−1435 (13)	2989 (17)	3.6 (7)	C(1)	3431 (21)	−1062 (15)	521 (23)	3.4 (9)
C(2)	3566 (19)	−715 (14)	2602 (21)	3.4 (9)	C(3)	1779 (19)	−1815 (14)	−272 (22)	3.5 (9)
C(4)	1273 (18)	−892 (12)	1713 (20)	1.8 (8)	C(5)	612 (16)	−1358 (13)	2568 (19)	1.4 (7)
C(6)	−305 (27)	−1910 (21)	3307 (29)	6.1 (12)	C(7)	−1254 (32)	−2363 (21)	3875 (49)	14.7^b
C(8)	−1836 (40)	−2145 (33)	4299 (71)	26.8^b					

^{a} Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. ^{b} The value quoted for atoms refined anisotropically is the equivalent B.

removed from the refinement and structure factor calculations. However, a subsequent difference Fourier map confirmed their positions and showed that the electron density associated with them was rather smeared out. These atoms were reinserted and refined as previously, resulting in large thermal parameters for these groups. It is probable that the ethyl groups are disordered over a number of closely spaced positions rather than over a few clearly defined positions.

The toluene molecule of solvation was found to be severely disordered about the 2(*d*) inversion centers. Although the electron density was clearly attributable to a planar group of approximately D_{6h} symmetry, the peak maxima corresponding to the individual carbon positions of the aryl ring were not clearly resolved; instead an almost continuous disk of electron density was observed. Similarly, no distinct positions were apparent for the toluene methyl group. Initially the toluene aryl group was input as a rigid group (in which only the three unique positions were defined) fixed at the inversion center, with an orientation corresponding to the "best" carbon positions from the Fourier map. The occupancy factor of this group was varied but indicated that a full molecule occupied this special position so the occupancy was set at 1.0 in subsequent cycles. A difference Fourier map at this point did not establish the positions of the toluene methyl group so its position was idealized such that it was 6-fold disordered around the ring. Neither the positions nor the thermal parameters of these carbons were refined, instead their *B*'s were set at 1.0 Å^2 greater than those of their attached aryl carbon atom. Another area of electron density was located in a position isolated from the complex and the solvent molecules; however, this could not be adequately described as a solvent molecule so was left unaccounted for in the final refinements.

The final model, in space group $P2_1/c$, refined to $R = 0.070$ and $R_w = 0.095$ based on 247 parameters varied and 2112 unique observations. No doubt the very badly behaved toluene molecule of crystallization and the unaccounted for electron density together account for the rather high *R* values. Because of the small, weakly diffracting crystal only a small (ca. 21%) percentage of reflections collected were observed so only Rh(1), Rh(2), Cl(1), Cl(2), S(1), S(2), C(7), and C(8) were refined anisotropically in order to achieve a reasonable data/parameter ratio. On the final difference Fourier map the highest residuals were in the vicinity of the unaccounted for solvent (0.8 e Å^{-3}), the carboxyethyl group (0.4 e Å^{-3}), and the toluene molecule (0.4 e Å^{-3}). A typical carbon in earlier syntheses had a density of ca. 3.0 e Å^{03}.

The final positional parameters of the individual non-hydrogen atoms and the phenyl carbons are given in Tables IV and V, respectively. The derived hydrogen parameters, a table of anisotropic thermal parameters and the observed and calculated structure amplitudes are available.[63]

Description of Structure. The unit cell of [Rh_2Cl_2(CO)(μ-SCNC(S)N(Ph)C(O)OEt)(DPM)$_2$]·0.5C_7H_8 (14) consists of four discrete complex molecules and two toluene molecules that are severely disordered about the 2(*d*) inversion centers. There are no unusual contacts between any of these molecules.

The overall geometry of the complex, shown in Figure 1, is quite typical for DPM-bridged binuclear complexes, in that the bridging diphosphine ligands are bound in the mutually trans positions on each metal with the other ligands bound essentially perpendicular to the metal–phosphine plane.[64] Parameters within the Rh–DPM framework are not particularly unusual and are comparable to those observed in several related complexes already reported by this group.[1,2,54,55] The metal–metal separation 2.799 (4) Å) is representative of a normal Rh–Rh single bond, falling within the range reported in related Rh–Rh bonded systems (2.7566 (9)–2.8415 (7) Å).[65,66] This metal–metal bond is substantiated by the intraligand P–P separations (average 3.04 (2) Å) which are significantly longer than the Rh–Rh separation, suggesting mutual attraction of the metals. Inclusion of the metal–metal bond in describing the metal geometries yields a quasioctahedral coordination about both metals much as was observed in the closely related CS_2 condensation product [Rh_2Cl_2(CO)(C_2S_4)(DPM)$_2$].[1] The coordination geometry about Rh(1) is comprised of the mutually trans phosphorus atoms of the DPM ligands, a terminal chloro ligand, the Rh–Rh bond, and two interactions with S(2) and C(4) of the bridging isothiocyanate moiety (vide infra) whereas the geometry about Rh(2) is comprised of the mutually trans phosphines, a terminal chloro and carbonyl ligand, the Rh–Rh bond, and one interaction with S(1) of the isothiocyanate group. Distortions from ideal octahedral geometry of each Rh center seems to result primarily from the strain imposed by the bridging isothiocyanate group.

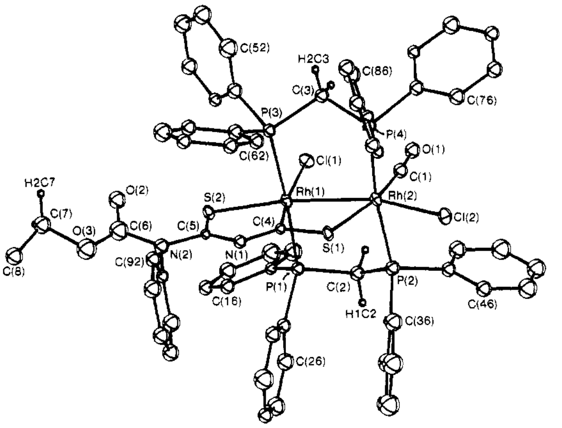

Figure 1. Perspective view of the [Rh_2Cl_2(CO)(μ-SCNC(S)N(Ph)C(O)OEt)(DPM)$_2$] molecule showing the numbering scheme. The numbering of the phenyl carbons starts at the carbon atom bound to the phosphorus and increases sequentially around the ring. The 20% thermal ellipsoids are drawn, except for the hydrogen atoms, C7, and C8, which are drawn artifically small.

Both terminal Rh–Cl distances are significantly longer than is normally observed for such bonds, where distances such as those reported in *trans*-[RhCl(CO)L_2]$_2$ (L_2 = $Ph_2PCH_2PPh_2$ (2.3875 (9) Å),[54] $Ph_2AsCH_2AsPh_2$ (2.370 (3) Å)[67]) are more typical. These

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Table V. Derived Parameters for the Rigid Groups at [$Rh_2Cl_2(CO)(\mu$-SCNC(S)N(Ph)C(O)OEt)(DPM)$_2$]·0.5C_7H_8

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(11)	0.3244 (15)	−0.1536 (8)	0.3735 (13)	2.5 (8)	C(61)	0.0322 (10)	−0.1775 (11)	0.0604 (15)	3.9 (9)
C(12)	0.3942 (14)	−0.1756 (11)	0.3654 (14)	5.6 (11)	C(62)	0.0018 (14)	−0.1336 (9)	0.0157 (14)	3.8 (9)
C(13)	0.4261 (11)	−0.2119 (11)	0.4253 (19)	5.9 (11)	C(63)	−0.0747 (15)	−0.1234 (8)	0.0107 (14)	3.8 (9)
C(14)	0.3882 (15)	−0.2262 (9)	0.4932 (15)	4.8 (10)	C(64)	−0.1209 (9)	−0.1571 (11)	0.0503 (16)	3.6 (9)
C(15)	0.3184 (15)	−0.2043 (10)	0.5013 (13)	3.6 (9)	C(65)	−0.0905 (15)	−0.2011 (9)	0.0950 (16)	5.9 (12)
C(16)	0.2864 (11)	−0.1679 (9)	0.4414 (17)	3.3 (9)	C(66)	−0.0140 (16)	−0.2113 (8)	0.1001 (14)	4.0 (10)
C(21)	0.2472 (16)	−0.0564 (8)	0.3703 (15)	3.2 (9)	C(71)	0.2634 (11)	−0.1245 (10)	−0.1327 (12)	3.5 (9)
C(22)	0.1793 (14)	−0.0299 (11)	0.3515 (13)	4.2 (10)	C(72)	0.2959 (14)	−0.1728 (8)	−0.1496 (14)	2.7 (9)
C(23)	0.1580 (12)	0.0085 (10)	0.4069 (19)	7.0 (13)	C(73)	0.3427 (13)	−0.1763 (8)	−0.2131 (16)	4.9 (11)
C(24)	0.2047 (17)	0.0203 (9)	0.4812 (16)	3.7 (9)	C(74)	0.3571 (12)	−0 1315 (11)	−0.2597 (13)	3.8 (9)
C(25)	0.2726 (15)	−0.0063 (11)	0.5000 (13)	5.6 (12)	C(75)	0.3246 (14)	−0.0832 (9)	−0.2428 (14)	4.3 (10)
C(26)	0.2938 (11)	−0.0446 (10)	0.4445 (18)	4.8 (11)	C(76)	0.2778 (13)	−0.0797 (8)	−0.1793 (16)	4.3 (9)
C(31)	0.2947 (16)	0.0342 (8)	0.2212 (18)	3.5 (9)	C(81)	0.1169 (11)	−0.0871 (10)	−0.1178 (14)	2.8 (9)
C(32)	0.3274 (12)	0.0511 (11)	0.3007 (18)	5.7 (12)	C(82)	0.0931 (13)	−0.0353 (9)	−0.1078 (13)	2.7 (8)
C(33)	0.3023 (17)	0.0973 (12)	0.3362 (13)	6.1 (12)	C(83)	0.0269 (14)	−0.0173 (7)	−0.1538 (16)	3.8 (10)
C(34)	0.2444 (18)	0.1265 (9)	0.2921 (20)	7.7 (14)	C(84)	−0.0155 (11)	−0.0512 (11)	−0.2098 (14)	4.4 (10)
C(35)	0.2116 (13)	0.1096 (11)	0.2126 (20)	7.3 (13)	C(85)	0.0083 (14)	−0.1031 (10)	−0.2199 (14)	4.5 (10)
C(36)	0.2368 (15)	0.0635 (12)	0.1771 (13)	4.9 (10)	C(86)	0.0745 (15)	−0.1210 (7)	−0.1739 (17)	5.1 (11)
C(41)	0.4185 (12)	−0.0035 (12)	0.1464 (15)	3.4 (9)	C(91)	−0.0494 (14)	−0.0962 (8)	0.3019 (16)	2.6 (8)
C(42)	0.4792 (18)	−0.0381 (8)	0.1496 (16)	4.9 (11)	C(92)	−0.1169 (15)	−0.0906 (9)	0.2494 (13)	3.8 (10)
C(43)	0.5465 (13)	−0.0210 (12)	0.1238 (18)	6.7 (13)	C(93)	−0.1614 (11)	−0.0461 (12)	0.2565 (15)	5.4 (11)
C(44)	0.5531 (12)	0.0306 (13)	0.0947 (17)	6.2 (12)	C(94)	−0.1384 (14)	−0.0071 (8)	0.3162 (18)	4.5 (10)
C(45)	0.4924 (18)	0.0652 (8)	0.0915 (16)	6.1 (12)	C(95)	−0.0709 (16)	−0.0127 (9)	0.3687 (14)	4.7 (10)
C(46)	0.4251 (14)	0.0481 (10)	0.1173 (16)	3.9 (10)	C(96)	−0.0264 (11)	−0.0573 (11)	0.3615 (14)	4.7 (10)
C(51)	0.1363 (15)	−0.2609 (7)	0.0825 (19)	3.8 (10)	C(101)[c]	0.4910 (29)	−0.0441 (19)	0.5504 (39)	19 (3)
C(52)	0.0975 (13)	−0.2870 (12)	0.0133 (14)	5.9 (12)	C(102)	0.5155 (27)	−0.0504 (13)	0.4711 (46)	15 (2)
C(53)	0.0942 (13)	−0.3421 (13)	0.0122 (15)	5.4 (11)	C(103)	0.5245 (25)	−0.0063 (32)	0.4207 (14)	19 (3)
C(54)	0.1297 (16)	−0.3711 (7)	0.0802 (20)	5.4 (11)	C(111)	0.4811 (62)	−0.0930 (41)	0.6062 (83)	19
C(55)	0.1685 (13)	−0.3449 (11)	0.1494 (15)	4.3 (10)	C(112)	0.5326 (57)	−0.1062 (27)	0.4390 (96)	19
C(56)	0.1718 (12)	−0.2898 (11)	0.1505 (13)	2.8 (8)	C(113)	0.5515 (53)	−0.0132 (68)	0.3329 (31)	19

Rigid-Group Parameters

group	X_c[a]	Y_c	Z_c	δ[b]	ϵ	η
ring 1	0.3563 (9)	−0.1899 (6)	0.4334 (10)	1.471 (20)	−2.500 (17)	2.233 (18)
ring 2	0.2259 (9)	−0.0181 (6)	0.4257 (10)	−1.751 (20)	−2.609 (17)	2.259 (17)
ring 3	0.2695 (10)	0.0804 (7)	0.2567 (11)	1.380 (28)	2.322 (17)	0.707 (25)
ring 4	0.4858 (10)	0.0136 (7)	0.1206 (9)	1.380 (20)	−2.872 (16)	−0.363 (16)
ring 5	0.1330 (8)	−0.3160 (7)	0.0814 (11)	−1.624 (35)	−2.154 (14)	−0.014 (33)
ring 6	−0.0444 (9)	−0.1673 (6)	0.0554 (9)	2.999 (20)	−2.535 (14)	0.077 (18)
ring 7	0.3103 (8)	−0.1280 (7)	−0.1962 (9)	0.136 (15)	2.962 (15)	−0.945 (14)
ring 8	0.0507 (9)	−0.0692 (7)	−0.1638 (9)	2.989 (18)	2.709 (15)	−0.480 (15)
ring 9	−0.0939 (9)	−0.0517 (6)	0.3090 (9)	−1.090 (23)	−2.427 (15)	2.940 (20)
ring 10	0.5000	0.0000	0.5000	0.462 (60)	−2.295 (54)	−1.093 (58)

[a] X_c, Y_c, and Z_c are the fractional coordinates of the centroid of the rigid group. [b] The rigid-group orientation angles δ, ϵ, η (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511. [c] Atoms C(101)-C(103) are the three independent aryl carbon atoms of the toluene molecule (site symmetry 1) and C(111)-C(113) are the disordered methyl carbons, each having $^1/_6$ occupancy.

Rh–Cl distances are, however, comparable to those observed in the closely related complex [$Rh_2Cl_2(CO)(C_2S_4)(DPM)_2$].[1] Thus, the Rh–Cl bond that is trans to the σ-bound carbon atom in these compounds (Rh(1)–Cl(1) = 2.465 (10) Å in 14; 2.442 Å (av) in the C_2S_4 analogue) displays the lengthening that is typical for Cl when opposite a group of high trans influence, and the Rh(2)–Cl(2) bond that is opposite the Rh–Rh bond is extremely long in each case (2.559 (10) Å in 14; 2.518 Å (av) in the C_2S_4 analogue); to our knowledge the only Rh–Cl distance that is longer than that reported for compound 14 was observed in [$RhCl(\eta^1$-$CO_2)(diars)_2$][68] (2.635 (4) Å). While it may be that the metal–metal interaction in the present compound exerts a strong trans influence on the Rh(2)–Cl(2) bond, as has been suggested in a related complex,[69] we cannot rule out steric interactions between the phenyl hydrogens and this Cl atom as being, at least in part, responsible. Phenyl groups 3, 7, and 8 are aimed into the regions around Cl(2) in such a way as to cause lengthening of the Rh(2)–Cl(2) bond (see Figure 1) and several short non-bonded contacts involve these hydrogens and Cl(2) (see Table VI). It is significant, however, that the longer Rh(2)–Cl(2) distance observed in the present case is accompanied by the shorter Rh–Rh bond (compared with 2.811 (3) Å in the C_2S_4 analogue[1]) as would be expected were the trans influence of the Rh–Rh interaction responsible for the lengthening.

Table VI. Selected Interatomic Distances (Å) in [$Rh_2Cl_2(CO)(\mu$-SCNC(S)N(Ph)C(O)OEt(DPM)$_2$]·0.5C_7H_8

(i) Bonding

Rh(1)-Rh(2)	2.799 (4)	C(6)-O(3)	1.28 (5)
Rh(1)-Cl(1)	2.465 (10)	O(3)-C(7)	1.54 (5)
Rh(2)-Cl(2)	2.559 (10)	C(7)-C(8)	1.42 (8)
Rh(1)-P(1)	2.350 (11)	Rh(2)-C(1)	1.88 (4)
Rh(1)-P(3)	2.322 (11)	C(1)-O(1)	1.11 (4)
Rh(2)-P(2)	2.320 (12)	P(1)-C(2)	1.78 (3)
Rh(2)-P(4)	2.329 (11)	P(2)-C(2)	1.81 (3)
Rh(2)-S(1)	2.373 (10)	P(3)-C(3)	1.87 (3)
Rh(1)-S(2)	2.331 (10)	P(4)-C(3)	1.80 (4)
Rh(1)-C(4)	1.92 (3)	P(1)-C(11)	1.84 (2)
S(1)-C(4)	1.64 (3)	P(1)-C(21)	1.80 (3)
C(4)-N(1)	1.36 (3)	P(2)-C(31)	1.79 (3)
N(1)-C(5)	1.30 (3)	P(2)-C(41)	1.83 (3)
C(5)-S(2)	1.72 (3)	P(3)-C(51)	1.82 (2)
C(5)-N(2)	1.42 (3)	P(3)-C(61)	1.86 (2)
N(2)-C(91)	1.46 (4)	P(4)-C(71)	1.84 (2)
N(2)-C(6)	1.41 (5)	P(4)-C(81)	1.82 (2)
C(6)-O(2)	1.16 (5)		

(ii) Nonbonding

Cl(1)-H(52)	2.79	Cl(2)-H(32)	2.74
Cl(2)-H(86)	2.66	Cl(2)-H(72)	2.82

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(68) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914.

(69) Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 1229.

Table VII. Selected Angles (deg) in $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt(DPM)_2]\cdot 0.5C_7H_8$

(i) Bond Angles			
Rh(2)-Rh(1)-P(1)	93.4 (3)	Cl(2)-Rh(2)-S(1)	90.2 (3)
Rh(2)-Rh(1)-P(3)	93.0 (2)	Cl(2)-Rh(2)-C(1)	104.0 (11)
Rh(1)-Rh(2)-P(2)	91.4 (3)	Rh(2)-C(1)-O(1)	174 (3)
Rh(1)-Rh(2)-P(4)	93.9 (3)	Rh(2)-S(1)-C(4)	96.6 (12)
P(1)-Rh(1)-P(3)	172.2 (4)	Rh(1)-C(4)-S(1)	115 (2)
P(2)-Rh(2)-P(4)	171.3 (4)	S(1)-C(4)-N(1)	121 (3)
Cl(1)-Rh(1)-P(1)	85.4 (4)	Rh(1)-C(4)-N(1)	123 (2)
Cl(1)-Rh(1)-P(3)	89.8 (4)	C(4)-N(1)-C(5)	115 (3)
S(2)-Rh(1)-P(1)	89.4 (4)	N(1)-C(5)-S(2)	124 (3)
S(2)-Rh(1)-P(3)	85.9 (4)	C(5)-S(2)-Rh(1)	93.9 (11)
C(4)-Rh(1)-P(1)	97.4 (10)	N(1)-C(5)-N(2)	118 (3)
C(4)-Rh(1)-P(3)	88.3 (10)	S(2)-C(5)-N(2)	118 (3)
Cl(2)-Rh(2)-P(2)	86.2 (4)	C(5)-N(2)-C(6)	129 (4)
Cl(2)-Rh(2)-P(4)	91.1 (4)	C(5)-N(2)-C(91)	114 (2)
S(1)-Rh(2)-P(2)	94.7 (4)	C(6)-N(2)-C(91)	117 (2)
S(1)-Rh(2)-P(4)	93.5 (4)	N(2)-C(6)-O(2)	119 (5)
C(1)-Rh(2)-P(2)	85.7 (12)	N(2)-C(6)-O(3)	112 (5)
C(1)-Rh(2)-P(4)	87.0 (12)	O(2)-C(6)-O(3)	129 (5)
Rh(1)-Rh(2)-Cl(2)	160.4 (3)	C(6)-O(3)-C(7)	111 (4)
Rh(1)-Rh(2)-S(1)	70.6 (2)	O(3)-C(7)-C(8)	97 (5)
Rh(1)-Rh(2)-C(1)	95.2 (11)	Rh(1)-P(1)-C(2)	107.6 (12)
Rh(2)-Rh(1)-Cl(1)	93.5 (2)	Rh(2)-P(2)-C(2)	108.9 (12)
Rh(2)-Rh(1)-S(2)	161.2 (3)	Rh(1)-P(3)-C(3)	109.3 (12)
Rh(2)-Rh(1)-C(4)	77.7 (10)	Rh(2)-P(4)-C(3)	111.1 (13)
S(2)-Rh(1)-Cl(1)	105.3 (3)	P(1)-C(2)-P(2)	113 (2)
S(2)-Rh(1)-C(4)	83.6 (10)	P(3)-C(3)-P(4)	114 (2)
(ii) Torsion Angles			
P(1)-Rh(1)-Rh(2)-P(2)	−2.3 (4)	C(5)-N(2)-C(6)-O(2)	−9 (7)
P(1)-Rh(1)-Rh(2)-P(4)	170.8 (4)	C(5)-N(2)-C(6)-O(3)	180 (3)
P(3)-Rh(1)-Rh(2)-P(2)	−177.9 (4)	N(1)-C(5)-N(2)-C(91)	−15 (3)
P(3)-Rh(1)-Rh(2)-P(4)	−4.8 (4)	S(2)-C(5)-N(2)-C(91)	163 (2)
S(1)-Rh(2)-Rh(1)-C(4)	0.0 (10)	O(2)-C(6)-N(2)-C(91)	165 (3)
Rh(1)-C(4)-S(1)-Rh(2)	0.0 (18)	O(3)-C(6)-N(2)-C(91)	−6 (4)
Rh(1)-C(4)-N(1)-C(5)	1 (4)	C(7)-O(3)-C(6)-O(2)	2 (8)
Rh(1)-S(2)-C(5)-N(1)	−4 (3)	C(7)-O(3)-C(6)-N(2)	172 (4)
N(1)-C(5)-N(2)-C(6)	159 (4)	C(6)-O(3)-C(7)-C(8)	175 (6)
S(2)-C(5)-N(2)-C(6)	−23 (5)		

As noted, the coordination geometries about both metals are completed by the bridging group that has resulted from condensation and rearrangement of the original isothiocyanate ligands. This condensed fragment binds to the metals yielding one five-membered and one four-membered metallacycle as shown clearly in Figure 2. Therefore the present complex looks much like the C_2S_4 analogue,[1] apart from CO_2Et and Ph moieties in the former. Otherwise, most differences between these two complexes seem to result from the smaller covalent radius of N compared to S, resulting, for example, in a smaller five-membered ring in the isothiocyanate product.

The head-to-tail condensation of the EtOC(O)NCS and PhNCS groups, which resulted in formation of the N(1)–C(5) bond, has also been accompanied by migration of the ethoxycarbonyl moiety from N(1) to N(2), much as was observed in $[RhCl(PPh_3)_2(SC(N(C(O)OEt)_2NCSC(NC(O)OEt)S)]$,[11] in which a condensation of three SCNC(O)OEt groups occurred. This migration in the present compound has resulted in the formation of a new isothiocyanate group, SCNR (where R = C(S)N(Ph)C(O)OEt), which is bound between the two metals and is carbon bound to one rhodium center and sulfur bound to the other, much as we propose for the initial 1:1 isothiocyanate adducts (vide infra), and similar to that observed for CS_2 in a binuclear platinum complex.[70] This is only the second reported structure involving an isothiocyanate group and is the first in which this group bridges two metals. Apart from the ethoxycarbonyl and phenyl groups, the metal isothiocyanate unit is quite planar; only N(2) is significantly displaced (0.14 (3) Å) from the Rh(1)Rh(2)S(1)C(4)N(1)C(5)S(2)N(2) least-squares plane.[63] Exo to the metallacycle rings significant twists from this plane occur, so the torsion angles about the N(2)–C(5) and the N(2)–C(6) bonds are ca. 19° and 8°, respectively (see Table VII), allowing O(2) to avoid unfavorable contacts with S(2). In addition, the phenyl group is twisted from the above least-squares plane by ca. 87° in order to minimize contacts with the rest of the ligand. As was the case for the C_2S_4 analogue,[1] the parameters within the isothiocyanate unit suggest extensive delocalization. The C–S bonds (1.64 (3) and 1.72 (3) Å) are comparable to those in ethylene thiourea (1.71 Å)[71] although they are longer than those in COS[72] and CS_2[73] (ca. 1.55 Å), and

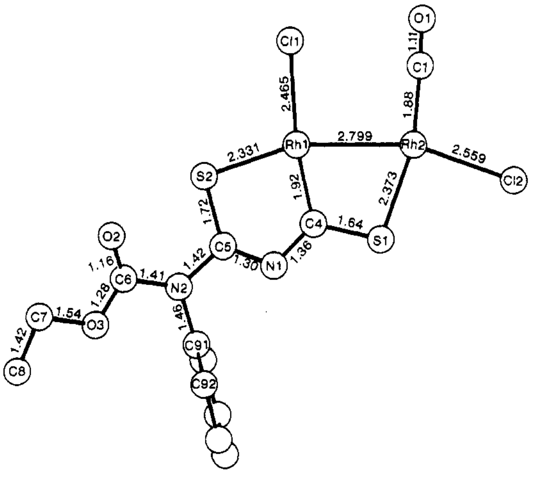

Figure 2. Inner coordination sphere of $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]$ in the approximate plane of the metals and the isothiocyanate ligand. Some relevant bond lengths are shown.

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[70] Cameron, T. S.; Gardner, P. A.; Grundy, K. R. *J. Organomet. Chem.* **1981**, *212*, C19.

[71] Macgillavry, C. H., Rieck, G. D., Eds.; "International Tables for X-ray Crystallography"; Kynoch Press, Birmingham, England, 1974; Vol. III, Table 4.2.

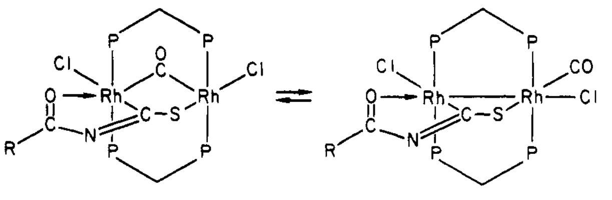
[72] Herzberg, G. "Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand; New York, **1945**.

the C–N bonds within the metallacycle (1.30 (3) and 1.36 (3) Å) are typical for partical double-bond character and are much shorter than a typical C–N single bond (1.47 Å).[71] Two of the distances involving the exocyclic nitrogen atom N(2) are somewhat shorter than a normal single bond, although this difference is not significant; the N(2)–C(91) distance on the other hand is exactly as expected for a single bond.

The length of the bridging C–S bond in compound 14 (1.64 (3) Å) is similar to that observed in the C_2S_4 product (1.66 (3) Å) and also to that in the other structurally characterized isothiocyanate complex $[Ni(CH_3C(CH_2PPh_2)_3](\eta^2\text{-}SCNPh)]$ (1.68 (2) Å).[15] Although the two isothiocyanate species differ in the coordination mode of the isothiocyanate ligands (the former is bridging whereas the latter is η^2 bound), the C–S moiety seems to be rather insensitive to this difference.

Discussion of Results

(i) The 1:1 Reactions with Benzoyl and Ethoxycarbonyl Isothiocyanates. The addition of an equimolar amount of either ethoxycarbonyl isothiocyanate (SCNC(O)OEt) or benzoyl isothiocyanate(SCNC(O)Ph) to compound 1 yields $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(O)R)(DPM)_2]$ (R = OEt (3), Ph (4)) in about 90% yield. Based on their elemental analyses, on a consideration of their spectral parameters, and on their subsequent chemistry (vide infra), we can establish that in each case the isothiocyanate molecule has inserted into the Rh–Rh bond of compound 1. In the solid state neither compound shows a terminal carbonyl stretch but instead displays a medium intensity infrared band at ca. 1710 cm^{-1} which shifts to ca. 1670 cm^{-1} when ^{13}CO-substituted compound 1 is used. The shift upon ^{13}CO substitution clearly establishes that this stretch is not due to the isothiocyanate carbonyl group. In fact, no stretch that is clearly attributable to this organic carbonyl moiety is observed. The low carbonyl stretch, although unusual for a "conventional" carbonyl group, is well in line with those reported for carbonyl moieties that bridge two metals not bonded to each other (ketonic carbonyls);[55] in the present case the ketonic carbonyl has resulted from isothiocyanate insertion into the Rh–Rh bond of 1. The analogous insertion of acetylenes into the Rh–Rh bond of 1 to give ketonic carbonyl species is a well-documented transformation.[55] We propose that in these complexes the isothiocyanate molecule is bridging the two metals and is bound to one through the S atom and to the other via the isothiocyanate carbon atom. A similar binding mode for the related CS_2 molecule has already been reported[70] (and again this has resulted from heteroallene insertion into a metal–metal bond) but more importantly the structure reported herein for compound 14 unambiguously establishes this bonding mode for an isothiocyanate molecule (vide supra). The absence of an observable stretch for the organic carbonyl moiety suggests to us that this carbonyl group is coordinated to the metal, and certainly the coordination of such carbonyl groups in benzoyl and ethoxycarbonyl isothiocyanates has been observed.[11,23]



A B

In solution, the infrared spectra of compounds 3 and 4 show additional bands at 2023 and 2010 cm^{-1}, respectively, which disappear upon crystallization. These bands are very close to those observed in compound 14 and in $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$ (2030 cm^{-1})[1] and indicate the presence of a terminal carbonyl ligand. The disappearance of these bands upon crystallization and their reappearance in solution, together with the bridging carbonyl band, suggest the following equilibrium between the carbonyl-bridged species A and that containing a terminal CO group (B). The $^{31}P\{^1H\}$ NMR spectra of compounds 3 and 4 consist of broad unstructured signals in the region 11–12 ppm, which are temperature invariant over the range +20 to −80 °C. Likewise the $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra consist of a broad peak at ca. 199 ppm; although this is normally the region associated with terminal carbonyl groups, the ^{13}C resonances of ketonic carbonyls have also been observed in this region.[55] Both sets of NMR spectra are consistent with the above dynamic behavior. The ^1H NMR spectrum shows the DPM methylene resonances as broad unresolved patterns but with the peak envelopes essentially as is normally seen in related DPM-bridged complexes, but interestingly the resonances due to the ethyl group are well resolved, presumably since this group is well removed from the sites affected by the fluctionality. This structure proposed for isomer B is analogous to those observed for $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$[1] and compound 14.

The iodo analogue of compound 1, $[Rh_2I_2(\mu\text{-}CO)(DPM)_2]$ (2), also reacts with 1 equiv of EtOC(O)NCS to yield $[Rh_2I_2(CO)(\mu\text{-}SCNC(O)OEt)(DPM)_2]$ (5), a species having only a terminal carbonyl stretch (2001 cm^{-1}) both in solid and solution. The $^{31}P\{^1H\}$ NMR spectrum of this product is a well-resolved AA′BB′XY pattern, which, together with the IR spectrum and the lack of conductivity, suggests that it has a structure analogous to isomer B shown above for the chloro species. Complexes in which a bridging carbonyl ligand is not accompanied by a metal–metal bond are still not common[55,74–77] and the subtle factors which favor this carbonyl geometry are not yet understood, although it seems that slight changes, such as the exchange of Cl for I in compound 3 to give 5, are enough to destabilize this carbonyl geometry. Such a change can be rationalized on the basis of steric arguments; the larger iodo group on the more crowded rhodium center presumably forces the carbonyl group from the bridging position to the terminal site on the other metal.

The carbonyl-bridged forms of compounds 3 and 4 (isomer A) have a coordinatively unsaturated, 16-electron rhodium center, suggesting the possibility of coordinating a two-electron donor at this metal. Consequently, reacting a suspension of 3 in CH_2Cl_2 with CO yields a clear yellow solution, the $^{31}P\{^1H\}$ NMR spectrum of which shows the presence of two species 6 and 7 whose molar ratios vary with reaction time (vide infra). The first species, whose spectrum is typical of an AA′BB′XY spin system, appears to be a simple CO adduct of 3 as diagrammed below. This species displays carbonyl stretches in an infared spectrum of the solid at 1968 and 1700 cm^{-1} (1912 and 1665 cm^{-1} in ^{13}CO-substituted product) and shows two resonances in the $^{13}C\{^1H\}$ NMR spectrum of an enriched sample, at 191.5 and 228.6 ppm, consistent with a terminal and a bridging carbonyl group. These ^{13}C resonances were not ^{31}P decoupled so the former appears as an approximate doublet of triplets (J_{Rh-C} = 70 Hz; $J_{P-C} \simeq$ 7 Hz) and the latter is

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[73] Callomar, M. J.; Thompson, M. W. *Proc. R. Soc. London, Ser. A* **1959**, *222*, 431.

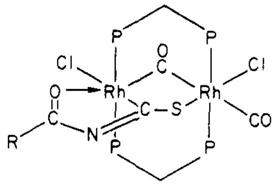
[74] Olmstead, M. M.; Hope, M.; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502.

[75] Brown, M. P.; Keith, A. N.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chim. Acta* **1979**, *34*, L223.

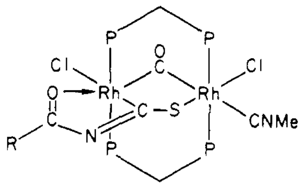
[76] Mague, J. T.; DeVries, S. M. *Inorg. Chem.* **1982**, *21*, 1632.

[77] Oberdorfer, F.; Balbach, B.; Ziegler, M. L. *Z. Naturoforsch.* **1982**, *876*, 157.

a complex multiplet which roughly appears as a broad triplet, indicating that the coupling to both Rh centers is approximately the same ($J_{Rh-C} \simeq 45$ Hz). The second product (7) was identified as $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(DPM)_2][Cl]$[57] based on a comparison of its $^{31}P\{^1H\}$ NMR, $^{13}C\{^1H\}$ NMR, and infrared spectra (ν(CO) = 2004, 1960, and 1868 cm^{-1}) with those of the same complex having either BPh_4^- or $RhCl_2(CO)_2^-$ anions.[78] Compound **6** could not be isolated in the pure form since all samples were contaminated by compound **7** in varying amounts. In the reaction of the benzoyl isothiocyanate analogue **4** with CO no carbonyl adduct similar to **6** is observed; instead only starting material and the tricarbonyl species **7** appears. After prolonged exposure to CO only **7** is observed and ultimately both compounds **3** and **4** react under excess CO with isothiocyanate displacement to give compound **7**. It appears that the coordinatively unsaturated, 16-electron rhodium center is required for the reaction with CO since the analogous species **14**, which has a bridging isothiocyanate group but a terminal CO and therefore two 18-electron rhodium centers, is unreactive toward CO. Similarly, the iodo compound **5**, which also has 18-electron configurations at both metals, does not react with CO. This is somewhat surprising since we would have expected that the coordinated carbonyl group of the isothiocyanate group would be readily displaced by carbon monoxide as has previously been reported in similar compounds.[11] Consistent with this observation, no stretch attributable to an uncoordinated ethoxycarbonyl moiety is observed in the reaction of **3** with CO; it seems that the vacant site of isomer A is the favored site of CO addition.



6, R = OEt

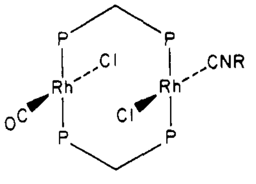


8, R = OEt
9, R = Ph

Compounds **3** and **4** also react with 1 equiv of MeNC to give compounds **8** and **9**, respectively, in 100% yield (from NMR). These products have similar $^{31}P\{^1H\}$ NMR spectra to compound **6** and their infrared spectra show the presence of ketonic carbonyl groups (ν(CO) = 1668 cm^{-1} (**8**) and 1656 cm^{-1} (**9**)) and terminal isocyanide ligands (ν(CN) = 2229 cm^{-1} (**8** and **9**)). The carbonyl bands, which shift to ca. 1623 cm^{-1} in ^{13}CO-labeled samples, are at very low frequencies even for ketonic carbonyls but are not without precedent; $[Pt_2Cl_2(\mu\text{-}CO)(DPM)_2]$, which has been shown to contain a ketonic carbonyl group,[75] has the carbonyl stretch at 1638 cm^{-1}. The $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra of **8** and **9** consist of a doublet of doublets at ca. 233 ppm as expected for a bridging carbonyl group which is coupled to two chemically inequivalent Rh nuclei (see Table II).

The geometries shown for compounds **6**, **8**, and **9** have the terminal CO and CNMe groups trans to the bridging carbonyl group. This is based on our postulated structures for compounds **3** and **4** (isomer A) shown earlier. Previous studies on analogous doubly bridged A-frame species[55,66,79] have shown that in each case the carbonyl group occupies the enclosed bridging site leaving vacant coordination sites in the trans positions. It is one of these sites in **3** and **4** at which we postulated CO or CNMe coordination occurs yielding **6**, **8**, and **9**. However the spectroscopic evidence is equally consistent with the isomer in which the terminal CO and CNMe ligands are cis to the bridging CO group, and this isomer cannot be ruled out.

(ii) Reactions with Methyl and Phenyl Isothiocyanates. The reactions of compound **1** with methyl and phenyl isothiocyanates proceed in a very different manner to those described for the ethoxycarbonyl and benzoyl analogues. For these nonactivated isothiocyanates no simple 1:1 adduct is observed, instead $^{31}P\{^1H\}$ NMR spectra of reaction solutions show a complex mixture of species at all isothiocyanate:compound **1** molar ratios. Varying the amounts of isothiocyanate does not seem to alter these spectra significantly. When the reaction mixture of compound **1** and phenyl isothiocyanate is allowed to stand for several days, a yellow solid (**10**) precipitates in low yield; however, the $^{31}P\{^1H\}$ NMR spectrum of the remaining mother liquor does not differ appreciably from that initially observed. The infrared spectrum of **10** exhibits bands at 1971 and 2165 cm^{-1}, attributable to a terminal carbonyl and isocyanide group, respectively, and this together with a comparison of its spectral parameters with the MeNC analogue **11** (vide infra) suggests the formulation diagrammed below. Although the trans geometry is shown, we cannot rule out the possibility that the CO and CNMe groups are mutually cis. Both the very low solubility of **10** and its carbonyl stretch are reminiscent of the closely related species, *trans*-$[RhCl(CO)(DPM)]_2$ (ν(CO) = 1968 cm^{-1}).[80] In the reaction of compound **1** with MeNCS no precipitate is obtained, yet the $^{31}P\{^1H\}$ NMR spectrum of a fresh reaction mixture is rather similar to that observed in the PhNCS reaction. However, after several days, a complex multiplet due to a new species (**11**) appears at δ 20.0 in the $^{31}P\{^1H\}$ NMR spectrum. Although this species was not isolated, it can be identified as $[Rh_2Cl_2(CO)(CNMe)(DPM)_2]$ (**11**) based on a comparison of its $^{31}P\{^1H\}$ NMR and infrared (ν(CO) = 1970 cm^{-1} and ν(CN) = 2169 cm^{-1}) spectra with those of an authentic sample prepared by the 1:1 reaction of $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (**1**) with MeNC.[81] It seems that both the PhNC (**10**) and the MeNC (**11**) complexes appear slowly with time, although the former is insoluble and precipitates from solution and so is not observed in the solution spectra. The analogous reactions of $[Pd_2Cl_2(DPM)_2]$ with methyl and phenyl isothiocyanates seem to proceed in a manner similar to those reported above; in these reactions the solutions are reported to contain several species from which the isocyanide complexes $[Pd_2Cl_2(\mu\text{-}CNR)(DPM)_2]$ (R = Me, Ph) slowly precipitate in low yields.[37]



10, R = Ph
11, R = Me

The only species that we have identified in our reactions with MeNCS and PhNCS are the final isocyanide products **10** and **11**, so we can make no definitive statement regarding the mode of isocyanide production. However, two routes seem probable, either involving sulfur abstraction from 1 equiv of isothiocyanate, or involving disproportionation of a condensed isothiocyanate moiety $(SCNR)_2$.

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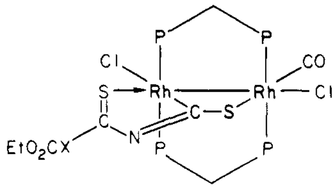
[80] Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* 1969, *8* 119.
[81] Gibson, J. A. E.; Dickson, R. S.; Cowie, M., unpublished results.

We tend to favor the former process for this binuclear system based on our observations with other isothiocyanate groups (vide infra) and with a related binuclear iridium system.[3] If, as is observed with the EtOC(O)NCS complex **3**, subsequent condensation of MeNCS or PhNCS ligands occurs with C–N bond formation to yield a species like that shown for species E in Scheme I (shown later), it is difficult to envision facile isocyanide formation; in the more common condensation mode in which C–S bond formation occurs, one can readily understand isocyanide formation (vide supra). Furthermore, in some very analogous chemistry involving the binuclear iridium complex $[IrCl(CO)(DPM)]_2$, we have observed that reaction with 1 equiv of either MeNCS or PhNCS yields stoichiometrically the sulfido-bridged isocyanide species $[Ir_2Cl_2(CO)_2(CNR)(\mu\text{-}S)(DPM)_2]$ by sulfur–carbon bond cleavage of the isothiocyanate molecule.[3] Assuming that the iridium system can serve as a model for the rhodium chemistry, we suggest that a similar process may be occurring with rhodium. However, the rhodium chemistry is obviously more complex since a mixture of products is obtained in this case and further studies are needed to unravel the natures of these unidentified species.

(iii) Isothiocyanate Condensation Products. Having obtained the 1:1 isothiocyanate adducts **3** and **4** and having established that they are capable of reacting with small molecules such as CO and CNMe, we thought that they might also be capable of reacting with additional heteroallene molecules. It seemed that this would be a potential route to a variety of condensation products containing heteroallene molecules and that such products could yield valuable information regarding these ligand coupling reactions. Compound **3**, the ethoxycarbonyl isothiocyanate adduct, does, in fact, react with a variety of isothiocyanates and CS_2 to yield single isolable products, which are shown by their elemental analyses and their conductivity and spectroscopic data to be of the form $[Rh_2Cl_2(CO)(SCNC(O)OEt)(SCX)(DPM)_2]$ (X = NC(O)OEt (**12**), NMe (**13**), NPh (**14**), NC(O)Ph (**15**), and S (**16**)). Compound **12** can also be prepared directly from **1** by reacting with two or more equivalents of EtOC(O)NCS. In no case was further reaction with these heteroallenes, to yield compounds containing more than two of these groups, observed even in the presence of large excesses of the ligand. Interestingly, the benzoyl isothiocyanate adduct **4** does not react further with heteroallenes. The spectral parameters of compounds **12–16** are all very similar; their infrared spectra display a carbonyl stretch at ca. 2025 cm^{-1} which shifts to ca. 1980 cm^{-1} when ^{13}CO-substituted compound **1** is used, and all show the carbonyl stretch of the ethoxycarbonyl moiety in the region 1700–1800 cm^{-1}; in compounds **12** and **15** two organic carbonyl stretches are observed, one for each carbonyl group. These data indicate that all compounds contain a terminal carbonyl ligand and that the organic carbonyl moiety of the ethoxycarbonyl isothiocyanate group is no longer coordinated to one of the metals as suggested for compound **3** (vide supra). The $^{31}P\{^1H\}$ NMR spectra of compounds **12–16** are also very similar and are as expected for complexes in which the two chemically different rhodium environments render the phosphorus nuclei on each metal chemically inequivalent. Similar spectra have been successfully analyzed[2] as AA′BB′XY spin systems, as suggested for the present compounds. A typical $^{31}P\{^1H\}$NMR spectrum (for compound **15**) is shown in the supplementary material.[43] Similarly, the $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra for these species also resemble each other, displaying a doublet due to the terminal carbonyl group at ca. 190 ppm with rhodium–carbon doupling of ca. 70 Hz, and the ^1H NMR spectra show all of the required resonances which integrate according to the formulations given; for compound **12** two sets of ethyl resonances are observed showing that these groups are chemically inequivalent.

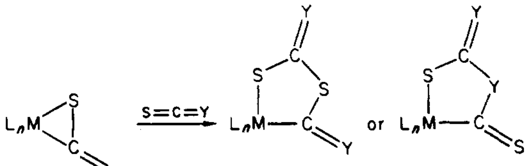
Although the above data show that all compounds are similar and that they contain two heteroallene units, they do not unambiguously establish whether condensation of these units has occurred. However, the X-ray structure determination of compound **14** does clearly establish that condensation has occurred, and, based on the very close similarities between the spectral parameters for compounds **12–16**, we propose that all have the structures



12, X = NC(O)OEt
13, X = NMe
14, X = NPh
15, X = NC(O)Ph
16, X = S

shown. As noted earlier, these structures are very close to that reported[1] for the CS_2 condensation product $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$, and again this C_2S_4 species has rather similar spectral parameters to those of compounds **12–16**. However, these compounds are not the expected products of isothiocyanate condensation reactions and are unusual in two important details; first, the condensation mode involves C–N bond formation rather than the normal C–S bond formation, and second, the ethoxycarbonyl moiety has migrated from the EtOC(O)NCS group, which was originally coordinated in compound **3**, to the added heteroallene molecule.

In sulfur-containing heteroallenes (S=C=Y) there seems to be a marked tendency, especially with the group 8 metals, to coordinate through sulfur instead of through Y and the resulting condensation products almost invariably involve C–S bond formation as shown for isomer III.[49]

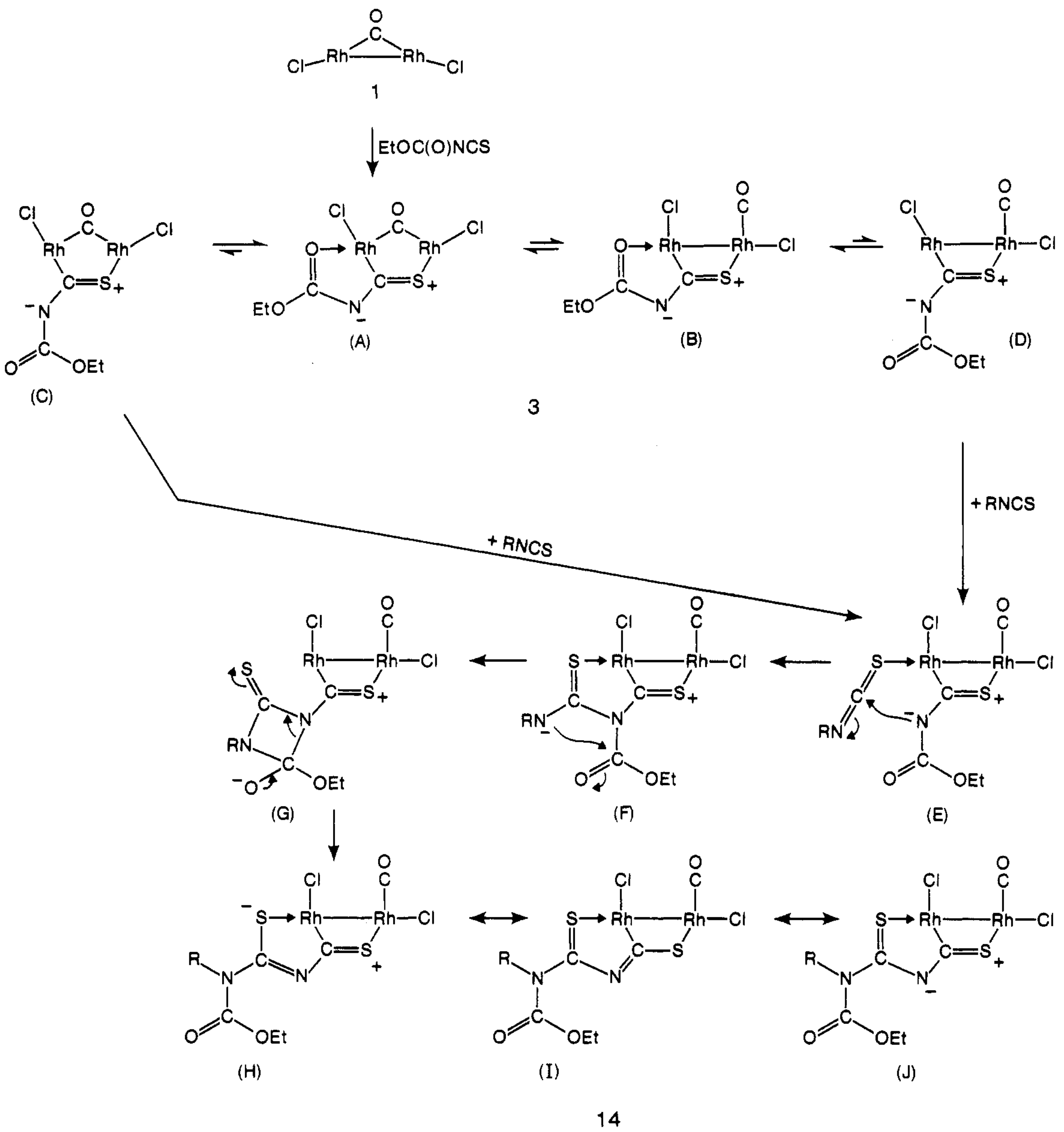


III IV

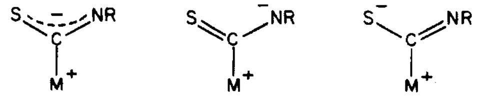
The alternate isomer, resulting from C–Y bond formation (IV), has not previously been unambiguously established in the condensation of two heteroallene molecules, although such a species has been postulated as in intermediate in the condensation of three EtOC(O)NCS molecules.[11] However, in this latter condensation of three ligands we feel that the conventional isomer III cannot be ruled out as the first condensation product (vide infra). Nevertheless, the structure of compound **14** is the first to establish unambiguously the C–N condensation mode for isothiocyanate molecules, at least for the case involving two such molecules. It was therefore of interest to attempt to establish why C–N bond formation results for this binuclear complex whereas the related mononuclear reactions proceed so frequently by C–S bond formation.

(iv) A Plausible Mechanism for Condensation and Migration. In mononuclear 1:1 isothiocyanate adducts the isothiocyanate molecule is generally coordinated to the metal in a side-on fashion through the C–S bond.[8-15]

Scheme I



However, it has been suggested[11] that the "active" intermediate in subsequent condensation reactions is the zwitterionic form, shown below for V, in which the ligand is η^1 bound through carbon. Although this coordination mode has not been established for isothiocyanates, it has been observed for the closely related CO_2 molecule.[68] On the basis of this postulated intermediate and the relative stabilities of the contributing resonance forms VI and VII,



V VI VII

the tendency for these species to undergo condensation reactions at sulfur rather than at nitrogen can be rationalized. Structure VI should be unstable with respect to VII owing to the S–C π bond being weaker than that involving nitrogen and carbon, by virtue of poorer overlap between the carbon 2p and the sulfur 3p or 3d orbitals. As a consequence the sulfur atom should be more nucleophilic and should therefore be susceptible to electrophilic attack by another S=C=NR molecule with concomitant C–S bond formation. However, in binuclear systems in which the C–S moiety bridges the two metals, the binding of the second metal to sulfur significantly influences the relative tendencies of the sulfur and nitrogen atoms to function as nucleophiles. First, the resulting four-membered $\overline{\text{M–C–S–M}}$ metallacycle in the binuclear species is less strained than the three-membered $\overline{\text{M–C–S}}$ one in mononuclear compounds, tending to favor sulfur coordination and to reduce the importance of the η^1 bonding mode in the subsequent reactivity of the former. Furthermore, coordination to the second metal in our systems, it seems, lowers the nucleophilicity of sulfur owing to the formal positive charge on this atom as is suggested by a consideration of the structure of the binuclear isothiocyanate complex 14. In this compound the short C(4)–S(1) bond suggests the importance of resonance structures H and J with the resulting charge on sulfur, as is shown at the bottom of Scheme I. Although the structure of the important first product (3) in the condensation reactions has not been determined crystallographically, we feel that it should closely resemble that of 14. The major difference in these structures, at least as far as the isothiocyanate ligand is concerned, should be due to replacement of the coordinated organic carbonyl group with the thiocarbonyl moiety in **14** (see Scheme I). This should result in an increased importance of the structure analogous to J for compound **3**, owing to the more favourable C=O bond compared to C=S, and should therefore increase the nucleophilicity of nitrogen, by virtue of its formal negative charge, leading to C–N bond formation (vide infra).

In order for condensation with other heteroallene molecules to occur, we suggest that prior coordination of these groups to one of the metals is necessary; a similar conclusion was reached by Itoh and co-workers in their related mononuclear chemistry.[11] In solution, compound **3** exists as isomers A and B on Scheme I, of which only A has a vacant coordination site. However, heteroallene coordination at this site should lead to condensation via C–S bond formation, which is not observed; it seems that the reduced nucleophilicity of S(1) does not allow this conventional condensation mode to occur. Instead, for the observed product to be obtained, condensation of the second heteroallene at the other metal center must occur. Such a vacant coordination site does result if dissociation of the coordinated ethoxycarbonyl group in A and B occurs to give C and D, respectively. The concentrations of C and D in solution must be small since no infrared stretch corresponding to the free ethoxycarbonyl group is observed. Coordination of the second heteroallene (an isothiocyanate molecule in the example shown) at this vacant site on either C or D would lead to structure E which then has an appropriate geometry for nucleophilic attack by nitrogen at the heteroallene carbon atom to give structure F. That prior coordination of the second heteroallene is necessary is suggested by the failure of species such as allene, carbon dioxide, phenyl isocyanate, and methyl isocyanate to react with compound **3**; we would expect these molecules to have a lower tendency to coordinate to Rh than do their sulfur-containing analogues. Next we suggest that nucleophilic attack of the nitrogen of the second isothiocyanate molecule at the carbonyl carbon occurs with subsequent N–C bond formation (structure G). The resulting four-membered 1,3-diazetidine ring will be highly strained, so it may be that in order to alleviate some of this strain the sulfur atom becomes detached from the metal as shown. Finally, by the electron reorganization shown, cleavage of the original C–N bond results in a 1,3 shift of the ethoxycarbonyl group to give the final product **14**.

The structure of compound **14**, which is also, as noted, an isothiocyanate adduct of compound **1**, can be described by a combination of the resonance structures shown for H, I, and J. As such, compound **14** should also be capable of additional isothiocyanate coordination and subsequent condensation. However, this is not the case; no further reaction of **14** is observed. The reason for this difference in the chemistry of **3** and **14** is again probably attributable to the replacement of the coordinated organic carbonyl group in the former by the thiocarbonyl moiety in the latter. In compound **14** the most important single resonance structure is that of H, as evidenced by the short C(S)–N(1) and C(4)–S(1) bonds, whereas in compound **3** we suggest that the structures corresponding to A and B are most important. As a result, the isothiocyanate nitrogen of compound **3** should be more nucleophilic than that of **14**, and the tendency of the latter to undergo condensation reactions should consequently be lower. But more importantly, the sulfur atom in **14** should be more tightly bound to Rh than the oxygen atom in **3** and we suggest that as a result no vacant site is available for coordination of the additional isothiocyanate molecule, and therefore no subsequent reaction of **14** is observed.

It is interesting that the benzoyl isothiocyanate adduct **4** does not undergo heteroallene condensation reactions as are observed for **3**. Both compounds **3** and **4** should be similar in their tendencies to dissociate the coordinated ethoxycarbonyl moiety generating the vacant coordination site, such as in structures C and D of Scheme I. Both species should therefore have comparable abilities to coordinate the second heteroallene molecule. The major difference between **3** and **4**, we suggest, may lie in the greater ability of the benzoyl group to delocalize electron density compared with the ethoxycarbonyl group. In compound **4** the structures analogous to C and D will have the negative charge on nitrogen effectively delocalized over the benzoyl moiety, whereas the ethoxycarbonyl group cannot delocalize the charge extensively because the carbonyl group is strongly conjugated with the lone-pair electrons on the ethoxy group. As a result, the electron density on nitrogen and therefore its nucleophilicity are higher for the ethoxycarbonyl isothiocyanate adduct that for the benzoyl analogue. This lower nucleophilicity of the latter presumably is sufficient to inhibit the condensation reaction in compound **4**. It is also possible that steric differences between the two isothiocyanate molecules play some part in the observed reactivity difference.

Scheme I, which shows the addition of isothiocyanates to compound **3**, can apply equally well for CS_2 addition. Therefore, compound **3** reacts with CS_2 to give $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)SC(O)OEt)(DPM)_2]$ (**16**). The mechanisim for this reaction is presumably like that shown in Scheme I replacing RNCS in this scheme by CS_2.

We have noted earlier that this paper presents the first clear example of a condensation reaction involving two isothiocyanate molecules which proceeds by C–N bond formation. Although Itoh and co-workers postulated such an intermediate in their mononuclear chemistry,[11] based on a very careful study, we feel that our additional data suggest that their reactions may proceed by C–S bond formation in the first condensation step, and certainly this possibility cannot be ruled out. It is our contention that the first step in the mononuclear chemistry involves C–S bond formation via the η^1-SCNR intermediate noted earlier. Once the sulfur end of the isothiocyanate molecule is "tied up" with the second molecule then subsequent condensation reactions must occur at nitrogen if they are to occur. In the mononuclear chemistry then, one observes condensation of benzoyl isothiocyanate at sulfur to give the 2:1 product but no further reaction occurs since the nitrogen atom of the original isothiocyanate molecule is not nucleophilic enough. With the ethoxycarbonyl isothiocyanate molecule, the analogous 2:1 product reacts further with C–N bond formation since the nitrogen of this ligand is sufficiently nucleophilic for condensation at this atom to occur. The difference between our binuclear chemistry and the related mononuclear chemistry is that in the former a second metal center "ties up" the sulfur atom of the coordinated isothiocyanate ligand so condensation, if it is to occur, must proceed through nitrogen via C–N bond formation. Whether or not condensation at this nitrogen occurs for both the binuclear and the mononuclear chemistry depends on the nuclephilicity of this nitrogen. Thus our 1:1 isothiocyanate complexes are analogous to the 2:1 mononuclear ones of Itoh and co-workers and our 2:1 ethoxycarbonyl isothiocyanate product compares with their 3:1 adduct.

Conclusions

Organic isothiocyanates are shown to diplay three distinct reactivity modes with the binuclear complex

$[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$, depending on the nature of the isothiocyanate molecule itself. The first mode observed for the so-called activated isothiocyanates EtOC(O)NCS and PhC(O)NCS involves formation of 1:1 adducts in which the isothiocyanate ligand bridges the metal, bound by carbon to one and by sulfur to the other metal center. The ethoxycarbonyl isothiocyanate adduct, in turn, reacts further with a variety of heteroallenes yielding unusual condensation products that have resulted from C–N bond formation by nucleophilic attack of the nitrogen atom of the coordinated EtOC(O)NCS ligand at carbon of the incoming heteroallene molecule. In addition, these condensation reactions are accompanied by a 1,3 shift of the ethoxycarbonyl moiety to either the nitrogen of the added isothiocyanate molecule or to one of the sulfur atoms if CS_2 is the added heteroallene. With the nonactivated PhNCS and MeNCS molecules a third reactivity mode, yielding the corresponding isocyanide ligands, is observed.

This study is significant in several aspects. It is believed to be the first in which all three types of reaction products have been isolated and characterized for the same metal system; in particular isolation of the 1:1 ethoxycarbonyl isothiocyanate adduct is an important development since it allows the preparation of a variety of heteroallene condensation products, which prove useful for delineating the reaction mechanism. This study is also the first in which the coupling of *two* isothiocyanate molecules by C–N, rather than by C–S, bond formation is clearly established. A scheme is presented for these two-metal-center induced coupling reactions that can be applied, with slight modifications, to related mononuclear chemistry and is therefore attractive in that it outlines a unified approach to heteroallene coupling reactions.

The presence of the second metal center in these reactions has a very significant effect on the chemistry as compared with that displayed by the mononuclear analogues. Coordination of the heteroallene sulfur atom by the second metal lowers its nucleophilicity with the result that subsequent condensation reactions occur at nitrogen rather than at sulfur. This modification of reactivity by the second metal center has obvious relevance to organic synthesis. So, for example, in this study we observe the syntheses of a variety of new isothiocyanate molecules by the coupling of the ethoxycarbonyl isothiocyanate molecule with other heteroallenes followed by the 1,3 shift of the ethoxycarbonyl group.

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Supplementary Material Available: A figure of the $^{31}P\{^1H\}$ NMR spectrum of compound **15** and tables of anisotropic thermal parameters, the derived hydrogen parameters, least-squares planes, and the observed and calculated structure factor amplitudes for $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]\cdot 0.5C_7H_8$ (11 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of (Chlorovinyl)nickel Complexes: An Unusual Symmetrization Reaction. X-ray Crystal Structure of $[Ni(CCl{=}CCl_2)_2(PMe_2Ph)_2]$

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The oxidative addition of $CCl_2{=}CCl_2$, $CCl_2{=}CHCl$, *trans*-CHCl=CHCl, and $CH_2{=}CCl_2$ to $[Ni(PPh_3)_n]$, prepared in situ from $NiCl_2$, PPh_3, and $NaBH_4$, gives square-planar *trans*-$[NiCl(chlorovinyl)(PPh_3)_2]$. The addition takes place at the less hindered C–Cl bond, with retention of geometry. The PPh_3 ligand is replaced by dppe in $[NiCl(C_2Cl_3)(PPh_3)_2]$ giving $[NiCl(C_2Cl_3)dppe]$ whereas the action of N-donor bidentate ligands gives a symmetrization reaction, forming $[NiCl_2(LL)]$ and $[Ni(C_2Cl_3)_2(LL)]$ (LL = 2,2′-bpy and *o*-phen). The ligand bpy may be replaced by phosphines like PMe_2Ph and PEt_3 in the trichlorovinyl complex. The crystal structure of *trans*-$[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$ (monoclinic, space group $P2_1/c$, $a = 9.203$ (2) Å, $b = 16.005$ (3) Å, $c = 9.604$ (2) Å, $\beta = 114.79$ (3)°, $Z = 2$) shows the presence of the anti and syn isomers in the solid. The Ni–P bond distance and the mean Ni–C bond distance are 2.201 (1) and 1.91 (1) Å, respectively. ^{31}P and ^{13}C NMR spectra indicate that similar amounts of syn and anti isomers are present in solution.

Introduction

The reaction of polyhaloethylenes with low-valent transition-metal complexes of Ni, Pd, and Pt gives different types of compounds. The reaction between fluorinated olefins and M(0) complexes leads initially to the compounds $[M(olefin)L_2]$ which contain a rigid σ-bonded three-membered ring and which can become the σ-alkenyl complexes $[MX(fluorovinyl)L_2]$.

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