for recording the ^1H and ^{13}C NMR spectra, to Dr. K. K. Mayer for the mass spectra, and to Prof. J. Fischer for computing facilities. J.W. wishes to thank Prof. H. Brunner for generous support of the experimental part of this work.

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Supplementary Material Available: Tables of full bond lengths and bond angles, hydrogen atom positional parameters, general temperature factor expressions, and structure factors for III and VI and stereoscopic views (Figures 4 and 5) of the unit-cell packing (27 pages). Ordering information is given on any current masthead page.

Oxidative Addition of Dimethylthiocarbamoyl Chloride to $[Rh_2Cl_2(\mu\text{-}CO)(Ph_2PCH_2PPh_2)_2]$, the Facile Interconversion between Chelating η^2 and Bridging Coordination Modes of the $SCNMe_2$ Group, and the Structure of $[Rh_2Cl_2(CO)(SCNMe_2)(Ph_2PCH_2PPh_2)_2][BF_4]\cdot 1.833CH_2Cl_2$

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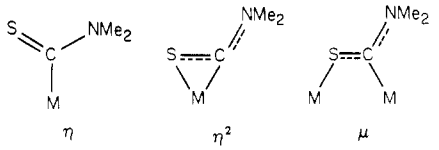
Oxidative addition of $SC(Cl)NMe_2$ to $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (1) (DPM = $Ph_2PCH_2PPh_2$) yields $[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$ (**2**). In the presence of BF_4^- the product of oxidative addition is $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ (**3**). An X-ray structure determination of **3** (space group $P2_1/n$, a = 12.340 (1) Å, b = 32.888 (5) Å, c = 15.374 (2) Å, β = 105.935 (8)°, Z = 4) shows that the $SCNMe_2$ moiety is bound in an η^2 fashion to one metal center. This structure has refined to R = 0.070 and R_w = 0.081 for 4122 observations and 345 parameters varied. The reaction of **3** with Me_3NO results in CO loss, yielding $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (**4**) in which the $SCNMe_2$ group bridges the two metals. Compound **4** reacts with CO to regenerate **3** and reacts with methyl isocyanide to give the analogous isocyanide compound, $[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$ (**5**). The reduction of compound **3** employing BH_4^- was carried out to give the very air-sensitive species $[Rh_2(CO)(\mu\text{-}SCNMe_2)(solvent)(DPM)_2][BF_4]$ (solvent = THF (**6a**), acetonitrile (**6b**)). Compounds **6a** and **6b** react with CO to give $[Rh_2(CO)_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (**7**).

Introduction

We have recently been investigating the chemistry of sulfur-containing heteroallenes[1,2] and related molecules with binuclear systems in order to obtain a better understanding of how these molecules interact with more than one metal center. One such group, which has the ability to coordinate to metals in several ways, is the dimethylthiocarboxamido ligand ($SCNMe_2$). In the presence of a single metal center it can coordinate in either the η^1 mode,[3-5] in which it is bound solely through carbon, or the



η^2 mode,[3-22] in which it is side-on bound through the C–S moiety, and in the presence of two metals the third bonding mode (μ), in which this group bridges the metals, bonding to one metal through carbon and to the other through sulfur, is also possible.[3-5,23-25] Although the second[5,7,9-11,14-20] and third[23-25] modes have been confirmed

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Table I. Infrared Spectral and Conductivity Data

no.	compound	infrared, cm^{-1} ν(CO)	infrared, cm^{-1} ν(CN)	conductivity,[a] Ω^{-1} cm^2 mol^{-1} (10^{-3} M solutions)
2	$[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$	1971,[b] 1988, 2005 (sh)[a]	1615[b]	11.9
3	$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$	1999,[b] 2000[a]	1616[b]	47.4
3a	$[Rh_2Cl_2(^{13}CO)(SCNMe_2)(DPM)_2][BF_4]$	1952[b]	1616[b]	
4	$[Rh_2Cl_2(SCNMe_2)(DPM)_2][BF_4]$		1467[b]	39.8
5	$[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$		1623, 2209 (CNMe)[b]	40.6
6a	$[Rh_2(CO)(SCNMe_2)(THF)(DPM)_2][BF_4]$	1952[c]		
6b	$[Rh_2(CO)(SCNMe_2)(CH_3CN)(DPM)_2][BF_4]$	1957[d]		
7	$[Rh_2(CO)_2(SCNMe_2)(DPM)_2][BF_4]$	1988, 1948[b]	1521[b]	46.9
7a	$[Rh_2(^{13}CO)_2(SCNMe_2)(DPM)_2][BF_4]$	1942, 1902[b]	1521[b]	

[a] CH_2Cl_2 solution. [b] KBr disk. [c] THF solution. [d] CH_3CN solution.

by X-ray structures, no example of the first has yet been reported.

Our interest in the M–C(S)NMe_2 moiety is due to its analogies with metallocarboxylic acid esters (M–C(O)OR) and metallocarboxylic acids themselves (these groups are commonly called alkoxycarbonyls and hydroxycarbonyls, respectively). Metallocarboxylic acids have been proposed to be key intermediates in the homogeneous catalysis of the water gas shift reaction,[26] in the related reactions of metal carbonyls with water to form the related hydrides,[27,28] in the isotopic oxygen exchange of metal carbonyls with H_2O,[29,30] and in the oxidation of CO by metal ions.[31-33] Yet, only a few metallocarboxylic acid complexes have been isolated or characterized,[34-39] owing to the ease with which such complexes extrude CO_2. Complexes containing ligands such as the dimethylthiocarboxamido group are therefore useful models for the transient metallocarboxylic acid intermediates because of the stability of the sulfur-containing species over those containing oxygen. We were particularly interested in the natures of the metallocarboxylic acid and related sulfur-containing complexes in the presence of a second metal center and so undertook a study of the model systems in which the $SCNMe_2$ group was bound in binuclear rhodium complexes. Herein we report the results of this study.

Experimental Section

All solvents were appropriately dried and degassed prior to use under an atmosphere of nitrogen and reactions were routinely carried out under Schlenk conditions with a nitrogen atmosphere. Bis(diphenylphosphino)methane (DPM) was purchased from Strem Chemicals, hydrated rhodium trichloride and tetraethylammonium borohydride from Research Organic/Inorganic Chemicals, and dimethylthiocarbamoyl chloride, which was recrystallized from diethyl ether prior to use, from Aldrich. Except where noted, all reagents were used as received. $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$[40] (1) and MeNC[41] were prepared by the reported procedures. Infrared spectra were recorded by using a Nicolet 7199 Fourier transform interferometer with use of KBr disks or in solution using KBr cells with a 0.5-mm path length. The ^1H NMR spectra were recorded at 200 MHz on a Bruker WP-200 spectrometer, the $^{31}P\{^1H\}$ NMR spectra were recorded at 161.9 MHz on a Bruker WP-400 spectrometer, and the $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra were recorded on a Bruker HFX-90 instrument at 22.6 MHz. ^1H shifts are quoted relative to Me_4Si, ^{31}P shifts are quoted relative to external 85% H_3PO_4, and those for ^{13}C were recorded with respect to CD_2Cl_2 but are quoted relative to Me_4Si. All positive shifts are downfield of the standards. Conductivity measurements were performed on a Yellow Springs Instrument Model 31 employing approximately 1×10^{-3} M solutions in CH_2Cl_2. Elemental analyses were performed within the department or by Canadian Microanalytical Services, Vancouver, Canada.

Preparation of the Complexes. (a) $[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$ (2). Compound 1 (100 mg, 0.093 mmol) and $Me_2NC(S)Cl$ (25 mg, 0.202 mmol) were dissolved in 10 mL of CH_2Cl_2. The resulting dark brown solution was stirred at room temperature for 6 h, with little solution color change. Addition of diethyl ether precipitated a brown-yellow powder which, after two recrystallizations from CH_2Cl_2/Et_2O, gave 2 as a bright yellow powder. The solid was filtered in air and washed with Et_2O; yield 20%. Spectral and conductivity details for 2 and other compounds prepared are summarized in Tables I and II.

(b) $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot n CH_2Cl_2$ (3). Compound 1 (1.0 g, 0.932 mmol) and $SC(Cl)NMe_2$ (0.25 g, 2.2 mmol) were dissolved in 25 mL of CH_2Cl_2, sufficient $NaBF_4$ to form a saturated solution (ca. 250 mg) was added, and the suspension was stirred for 4 h, by which time the color had changed from dark brown to orange-red. The solution was filtered to remove excess $NaBF_4$, and diethyl ether (20 mL) was added to the filtrate, precipitating a crystalline brown-red solid, which was isolated by filtering in air. The product was washed with diethyl ether, dried in vacuo, and recrystallized from CH_2Cl_2/Et_2O; yield 1.02 g, 85%. All samples were found to contain CH_2Cl_2 of solvation, the amount of which varied depending on the exact conditions of crystallization. Anal.[42] Calcd for $C_{54.65}H_{51.3}BCl_{3.3}F_4NOP_4Rh_2S$ (ca. 0.65 CH_2Cl_2 of solvation): C, 50.3; H, 3.9; N, 1.1; S, 2.5; Cl, 8.9. Found: C, 49.2; H, 3.6; N, 1.1; S, 2.8; Cl, 8.6.

(c) $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]\cdot n CH_2Cl_2$ (4). Compound 3 (100 mg, 0.077 mmol) and $Me_3NO\cdot 2H_2O$ (18 mg, 0.162 mmol) were dissolved in 10 mL of CH_2Cl_2. The resulting orange-red solution was stirred at room temperature for 1 h, by which time the color had changed to brown. The volume of the solvent was reduced to 2 mL, and 10 mL of Et_2O was slowly added. Filtering the solution in air yielded a green-brown precipitate which was washed with 2–3 mL of 1:1 methanol–diethyl ether to remove excess Me_3NO and then with diethyl ether. Recrystal-

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Table II. NMR Spectral Data

no.	compound	^{1}H, δ	^{13}C{^{31}P-{^{1}H}}, δ	^1J(Rh-C), Hz	^{31}P{^{1}H}, δ	^1J(Rh-P), Hz
2	$[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$	2.05 (s,[a] 3 H), 2.84 (s, 3 H),[b] 3.5 (m, 2 H), 4.4 (m, 2 H)[c]			4.8 (dt) 16.7 (dt)	~117, ~91
3	$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$	2.05 (s, 3 H), 2.84 (s, 3 H),[b] 3.5 (m, 2 H), 4.4 (m, 2 H)[c]	186.0 (d)	81.7	4.8 (dt) 16.7 (dt)	117.6 91.2
4	$[Rh_2Cl_2(SCNMe_2)(DPM)_2][BF_4]$	2.10 (s, 6 H),[b] 3.3 (m, 2 H), 4.1 (m, 2 H)[c]			7.1 (m) 14.9 (m)	106.6 104.2
5	$[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$	2.46 (s, 3 H), 3.01 (s, 3 H),[b] 3.19 (s, 3 H),[d] 3.8 (m, 2 H), 4.1 (m, 2 H)[c]			11.5 (m)	*e*
6a	$[Rh_2(CO)(THF)(SCNMe_2)(DPM)_2][BF_4]$	*f*			14.3 (m) 24.9 (m)	157 125
6b	$[Rh_2(CO)(CH_3CN)(SCNMe_2)(DPM)_2][BF_4]$	1.83 (s, 3 H), 2.65 (s, 3 H),[b] 3.4 (m, 2 H), 3.8 (m, 2 H)[c]			13.6 (m) 25.2 (m)	155 123
7	$[Rh_2(CO)_2(SCNMe_2)(DPM)_2][BF_4]$	1.66 (s, 3 H), 2.85 (s, 3 H),[b] 3.3 (m, 2 H), 3.8 (m, 2 H)[c]	191.3 (d) 199.8 (d)	71.5 55.9	16.4 (m) 23.2 (m)	143 122

[a] Abbreviations: s, singlet, m, multiplet; dt, doublet of triplets; d, doublet. [b] Resonances due to the $SCNMe_2$ protons. [c] Resonances due to the methylene protons of the DPM groups. These appear as an AB quartet in which each peak is further split into quintets due to virtual coupling to all P atoms. [d] Resonance due to CNMe protons. [e] The ^{31}P{^{1}H} NMR spectrum of 5 was recorded at 36.43 MHz only. The Rh-P coupling was not discernible at this frequency. [f] See ref 65.

lization from CH_2Cl_2/Et_2O gave an analytically pure sample containing approximately 0.4 equiv of CH_2Cl_2 of solvation.[42] Anal. Calcd for $C_{53.4}H_{50.8}BCl_{2.8}F_4NP_4Rh_2S$ (n = 0.4): C, 51.12; H, 4.08; N, 1.12; Cl, 7.91. Found: C, 51.60; H, 4.20; N, 1.33; Cl, 8.04.

(d) $[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2][BF_4]$ (5). A solution of 4 was prepared as described above from 3 (100 mg, 0.077 mmol) and $Me_3NO{\cdot}2H_2O$ (18 mg, 0.162 mmol) in 10 mL of CH_2Cl_2. Addition of 10 μL of MeNC (0.17 mmol) changed the color of the solution to orange. The solution was stirred for 30 min, and the volume was reduced to 2 mL. Treatment of this solution with Et_2O precipitated and orange-brown solid which was filtered from the solution in air and washed with diethyl ether; yield 70%.

(e) $[Rh_2(CO)(Solvent)(SCNMe_2)(DPM)_2][BF_4]$. (i) Solvent = THF (**6a**). Compound 3 (100 mg, 0.077 mmol) and $NaBH_4$ (6 mg, 0.159 mmol) were suspended in 5 mL of THF, and the reaction mixture was stirred at room temperature. The solids dissolved slowly over a period of about 2 h, yielding a deep purple, very air sensitive solution of **6a**. (ii) Solvent = CH_3CN (**6b**). Compound 3 (100 mg, 0.077 mmol) and $Et_4N^+BH_4^-$ (22.5 mg, 0.155 mmol) were dissolved in 5 mL of CH_3CN. A vigorous reaction immediately occurred with gas evolution, yielding a deep red-to-purple colored solution of **6b**. Compound **6b** was also very air sensitive so neither it nor **6a** was isolated; their spectral parameters are given in Tables I and II.

(f) $[Rh_2(CO)_2(SCNMe_2)(DPM)_2][BF_4]$ (7). Method i. A solution of compound **6a** was prepared as outlined above. The nitrogen atmosphere in the reaction vessel was replaced with CO, causing an immediate lightening of the solution color to violet. Addition of 10 mL of diethyl ether precipitated a purple microcrystalline solid, 7, which was sufficiently air stable to be filtered in air. Recrystallization from CH_2Cl_2/Et_2O gave a purple product. Samples of 7 stored in air decomposed over a period of a few days to give an unidentified white solid. Samples stored under nitrogen were stable for several weeks. The same reaction could be performed in ethanol, methanol, acetone, acetonitrile, or methylene chloride (employing $Et_4N^+BH_4^-$ as the reductant in the last two solvents).

Method ii. Compound 3 (100 mg, 0.077 mmol) and $NaBH_4$ (8 mg, 0.212 mmol) were degassed in a three-necked round-bottom flask. The nitrogen atmosphere was replaced with CO, and 3 mL of methanol was added. The solids dissolved and reacted to give a purple solution. Cooling to −10 °C quickly precipitated a good yield of **6** as a crystalline, deep purple solid. Anal. Calcd for $Rh_2C_{55}H_{50}BF_4NO_2P_4S$: C, 54.79; H, 4.18; N, 1.16. Found: C, 54.78; H, 4.20; N, 1.16.

Reaction of 4 with CO. A solution of 4 in CH_2Cl_2 was prepared as detailed above and purged with N_2. CO was briefly passed through the solution, causing a color change from brown to orange-red. Comparison of the ^{31}P{^{1}H} NMR spectrum of the reaction mixture with that of an authentic sample of 3 indicated that 3 was the product obtained. Confirmation was obtained from a consideration of the IR spectrum of the solid obtained by treating the solution with diethyl ether and comparing this with an IR spectrum of the authentic sample.

Preparation of ^{13}CO-Labeled Samples. ^{13}CO-labeled samples were prepared by employing ^{13}CO-labeled compound 1 (for 3) and by employing an atmosphere of ^{13}CO for 6.

X-ray Data Collection. Suitable quality, amber single crystals of 3 were grown by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of the complex. Preliminary film data showed that the crystals belonged to the monoclinic system with systematic absences characteristic of the space group $P2_1/n$ (this nonstandard setting of $P2_1/c$ was retained because of a more convenient β angle (105.94° vs. 128.8°)). Accurate cell parameters were obtained by a least-squares analysis of 12 carefully centered reflections chosen from diverse regions of reciprocal space and obtained with use of a narrow X-ray source. Data were collected on a Picker four-circle X-ray diffractometer equipped with a scintillation counter and a pulse height analyzer tuned to accept 90% of the Cu Kα peak. See Table III for pertinent crystal data and the details of data collection.

Structure Solution and Refinement. The structure was solved in space group $P2_1/n$ by using standard Patterson, Fourier, and full-matrix, least-squares techniques. All atoms, including the hydrogens, were ultimately located. Atomic scattering factors for all atoms (hydrogen[43] and others[44]) and anomalous dispersion terms[45] for Rh, Cl, S, and P were taken from the usual sources.

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

compd	$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2]$-$[BF_4]\cdot 1.833CH_2Cl_2$
fw	1403.99
space group	$P2_1/n$ (nonstandard setting of $P2_1/c$; No. 14)
a, Å	12.340 (1)
b, Å	32.888 (5)
c, Å	15.374 (2)
β, deg	105.935 (8)
V, Å^3	5999.1
ρ_{calcd}, g/cm^3	1.554 (Z = 4)
temp, °C	22
radiatn	Cu Kα, $\bar{\lambda}$ = 1.54178 (Ni-filtered)
detector aperture, mm	4 × 4
2θ limits, deg	$2.0 \leq 2\theta \leq 120.0$
scan type	$\theta/2\theta$
2θ scan rate, deg/min	2.0
scan width, deg	symmetrical, $[1.90 + \Delta(\alpha_1 - \alpha_2)]$
bkgd	$3.5° \leq 2\theta \leq 60°$, 10 s $60° < 2\theta \leq 120°$, 20 s
reflcns measd	$\pm h, +k, +l$; 9780
data used ($F^2 \geq 3\sigma(F^2)$)	4122
abs coeff μ, cm^{-1}	86.383
cryst dimens, mm	0.246 × 0.091 × 0.094
range in abs corr factors	0.369–0.560
final no. of parameters refined	345
error in obsv of unit weight	1.775
R	0.070
R_w	0.081

The carbon atoms of all phenyl groups were refined as rigid groups having D_{6h} symmetry, C–C distances of 1.392 Å, and independent isotropic thermal parameters for each atom. The hydrogens were all input to the least-squares program as fixed contributions in their idealized positions by using C–H distances of 0.95 Å and assigning them thermal parameters of 1 Å^2 greater than the B's (or equivalent isotropic B's) of their attached atom; these atoms were not refined. Absorption corrections were applied to the data by using Gaussian integration.[46]

The BF_4^- anion was found to be severely disordered; although peaks could be located in the Fourier maps which were consistent with the known geometry of this group, significant electron density was found in an essentially spherical distribution about the central peak. Attempts to fit this electron density as more than one disordered BF_4^- molecule having fractional occupancies proved unsuccessful, so only one full-occupancy BF_4^- was refined. The resulting thermal parameters of the atoms in this group are rather high, and the B–F distances are less than ideal. However, this problem is not an unusual one with these pseudospherical anions, and the final geometry, although distorted, clearly displays an almost tetrahedral arrangement of fluorine atoms about boron. The occupancy factors of the CH_2Cl_2 molecules were refined; that of molecule 1 (C(7), Cl(3), and Cl(4)) refined to almost 1.0 and so was fixed as a full occupancy in the final cycles, whereas that of molecule 2 ultimately refined to 0.833. The thermal parameters of these solvent molecules were also large, suggesting some slight disorder of these groups. Near the end of refinement the CH_2Cl_2 and BF_4^- groups were removed; however subsequent difference Fourier maps reaffirmed their positions and showed the smeared-out electron density associated with these groups, so they were reinserted and refined as previously.

The final model with 345 parameters refined on 4122 observations converged to R = 0.070 and R_w = 0.081;[47] undoubtedly the badly behaved CH_2Cl_2 and BF_4^- groups hamper the final refinements. However, the complex cation is well-behaved. On a final difference Fourier map the top 20 residuals (0.9–0.6 e Å^{-3}) were in the vicinities of the CH_2Cl_2 molecules, the BF_4^- anion, and the phenyl groups. A typical carbon atom on earlier maps had an electron density of ca. 2.7 e Å^{-3}. The final positional and isotropic thermal parameters of all independent atoms are given in Table IV, and the group parameters are given in Table V. Parameters for the hydrogen atoms and a listing of the structure amplitudes are available.[48]

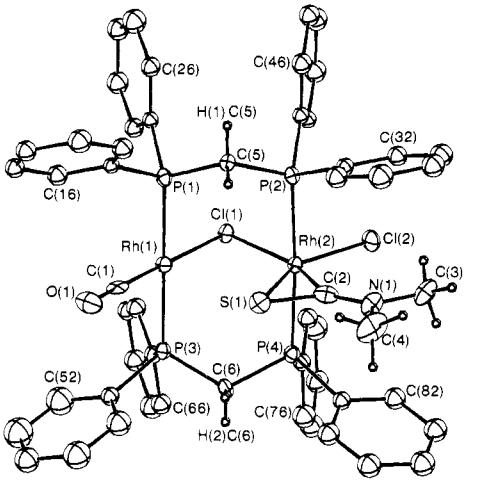


Figure 1. Perspective view of the $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2]^+$ cation showing the numbering scheme. The numbering of the phenyl carbons starts at the carbon atom bound to phosphorus and increases sequentially around the ring; 20% thermal ellipsoids are drawn, except for hydrogen atoms which are shown artificially small.

Description of Structure

$[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ (**3**) crystallizes with ca. 1.83 molecules of CH_2Cl_2 per formula unit in the crystals studied. In other samples which were crystallized under somewhat different conditions the amount of CH_2Cl_2 varied to as low as 0.4 per formula unit. One of the solvent molecules in the present structure has full occupancy and the other has somewhat less than full occupancy (0.833). Both solvent molecules have normal geometries. There are no unusual contacts involving either the solvent molecules, the complex cation, or the BF_4^- anions. The BF_4^- anion is severely disordered and as a result displays a geometry which is distorted from an idealized tetrahedron, with B–F distances ranging from 1.10 (8) to 1.56 (8) Å (see Table VI) and F–B–F angles ranging from 90 (5)° to 133 (9)° (see Table VII). Although the spread in these values is rather large, it is not unexpected considering the disorder, and in spite of the distortions the mean values compare well with reported values.[49]

The complex cation is shown in Figure 1. This cation consists of two rhodium centers bridged by two mutually trans DPM groups, with the Cl, CO, and $SCNMe_2$ ligands bound in the equatorial plane which is approximately perpendicular to the Rh–P vectors. As suggested by the $^{31}P\{^1H\}$ NMR spectrum (vide infra), this complex has two very different rhodium environments. Rh(1) has an essentially square-planar coordination in which the two phosphines are mutually trans and the carbonyl group is trans to the bridging chloro ligand, whereas Rh(2) has a distorted octahedral geometry in which two of the four equatorial sites are occupied by the bridging and terminal chloro ligands and two by the side-on bound $SCNMe_2$ group. This cation represents a rare example of a binuclear

(46) In addition to local programs, the following were used: FASTFO, an adapted version of FORDAP by R. J. Dellaca; BUCILS, University of British Columbia Least-Squares Program; ORFFE for calculating bond lengths, 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.

(47) $R = \sum||F_o| - |F_c|/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_o|)^2/\sum wF_o^2]^{1/2}$.

(48) Supplementary material.

(49) See, for example: Riley, P. E.; Davis, R. E. *Organometallics* **1983**, *2*, 286.

Table IV. Atomic Positional and Thermal Parameters

atom	x[a]	y	z	B, Å^2[b]	atom	x	y	z	B, Å^2
Rh(1)	2036 (1)	974.8 (4)	2963 (1)	3.11	Rh(2)	3979 (1)	1687.7 (4)	3408 (1)	2.75
Cl(1)	4047 (3)	928 (1)	3501 (3)	3.41	Cl(2)	5834 (4)	1802 (2)	3925 (3)	4.71
Cl(3)	6165 (9)	4971 (3)	2735 (9)	16.55	Cl(4)	3894 (8)	4738 (3)	2165 (7)	13.63
Cl(5)	8380 (12)	2120 (5)	2972 (10)	17.94	Cl(6)	9910 (8)	2705 (4)	3864 (9)	13.62
S(1)	2003 (4)	1962 (2)	2899 (4)	4.71	P(1)	2130 (3)	958 (2)	1469 (3)	3.39
P(2)	3968 (4)	1639 (1)	1892 (3)	3.17	P(3)	1935 (3)	985 (2)	4447 (3)	3.37
P(4)	3697 (4)	1701 (2)	4902 (3)	3.29	F(1)	7357 (15)	3422 (5)	2401 (12)	10.50
F(2)	7277 (22)	3393 (7)	3775 (13)	16.51	F(3)	5943 (25)	3652 (7)	2771 (19)	18.58
F(4)	7504 (27)	3973 (7)	3215 (16)	20.60	O(1)	−386 (11)	1037 (6)	2333 (9)	7.20
N(1)	3443 (15)	2620 (5)	3194 (11)	5.26	C(1)	568 (16)	1001 (7)	2589 (10)	4.33
C(2)	3229 (16)	2226 (6)	3202 (12)	4.49	C(3)	4617 (21)	2770 (6)	3492 (16)	6.71
C(4)	2562 (25)	2918 (7)	2931 (20)	9.71	C(5)	2660 (13)	1426 (5)	1128 (12)	3.29
C(6)	2341 (13)	1482 (5)	4964 (12)	3.44	C(7)	5246 (28)	4580 (10)	2447 (28)	15.58
C(8)	8511 (47)	2525 (17)	3440 (26)	18.22	B(1)	7256 (73)	3655 (25)	3035 (58)	17 (2)

[a] Fractional coordinates × 10^4 are given. Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] Equivalent B's are quoted for atoms refined anisotropically.

Table V

Derived Parameters for the Rigid Groups of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot 1.833CH_2Cl_2$

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.0798 (7)	0.0878 (4)	0.0609 (8)	2.9 (3)	C(51)	0.0511 (9)	0.0926 (5)	0.4556 (9)	3.9 (4)
C(12)	0.0379 (10)	0.1140 (3)	0.0117 (9)	5.1 (5)	C(52)	0.0122 (13)	0.0544 (4)	0.4719 (11)	8.9 (7)
C(13)	−0.0657 (11)	0.1060 (4)	−0.0734 (8)	6.6 (6)	C(53)	−0.0991 (15)	0.0494 (4)	0.4737 (12)	10.3 (9)
C(14)	−0.1273 (8)	0.0718 (4)	−0.0626 (8)	4.9 (5)	C(54)	−0.1717 (9)	0.0826 (6)	0.4592 (11)	7.2 (6)
C(15)	−0.0853 (10)	0.4567 (3)	0.0100 (9)	4.5 (4)	C(55)	−0.1328 (12)	0.1208 (5)	0.4429 (11)	8.8 (7)
C(16)	0.0182 (10)	0.0537 (3)	0.0717 (7)	4.7 (4)	C(56)	−0.0214 (13)	0.1258 (4)	0.4412 (10)	7.1 (6)
C(21)	0.2939 (9)	0.0551 (3)	0.1147 (9)	3.1 (3)	C(61)	0.2747 (9)	0.0606 (3)	0.5221 (8)	3.6 (4)
C(22)	0.3366 (10)	0.0235 (4)	0.1746 (6)	4.3 (4)	C(62)	0.3219 (10)	0.0279 (4)	0.4880 (6)	4.4 (4)
C(23)	0.3875 (10)	−0.0098 (3)	0.1460 (9)	5.3 (5)	C(63)	0.3813 (10)	−0.0018 (3)	0.5463 (9)	4.2 (4)
C(24)	0.3956 (10)	−0.0115 (3)	0.0576 (10)	5.2 (5)	C(64)	0.3936 (10)	0.0011 (4)	0.6389 (8)	5.1 (5)
C(25)	0.3529 (11)	0.0200 (5)	−0.0023 (7)	6.5 (6)	C(65)	0.3465 (11)	0.0338 (4)	0.6730 (6)	6.4 (6)
C(26)	0.3021 (10)	0.0533 (4)	0.0263 (8)	4.3 (4)	C(66)	0.2870 (10)	0.0635 (3)	0.6146 (9)	4.7 (4)
C(31)	0.5083 (8)	0.1356 (3)	0.1597 (8)	3.2 (3)	C(71)	0.4760 (9)	0.1440 (4)	0.5802 (8)	3.6 (4)
C(32)	0.5896 (10)	0.1146 (4)	0.2248 (6)	3.5 (4)	C(72)	0.5628 (11)	0.1208 (4)	0.5642 (7)	4.6 (4)
C(33)	0.6752 (9)	0.0939 (4)	0.2004 (8)	5.4 (5)	C(73)	0.6402 (9)	0.1019 (4)	0.6359 (10)	7.1 (6)
C(34)	0.6794 (9)	0.0942 (4)	0.1109 (10)	5.7 (5)	C(74)	0.6308 (11)	0.1061 (4)	0.7235 (8)	5.7 (5)
C(35)	0.5980 (11)	0.1152 (4)	0.0457 (6)	4.9 (5)	C(75)	0.5440 (13)	0.1293 (5)	0.7395 (7)	6.2 (5)
C(36)	0.5125 (9)	0.1359 (4)	0.0702 (7)	4.7 (4)	C(76)	0.4666 (10)	0.1483 (4)	0.6678 (10)	6.1 (5)
C(41)	0.4085 (11)	0.2144 (3)	0.1418 (9)	3.6 (4)	C(81)	0.3647 (11)	0.2222 (3)	0.5317 (9)	3.8 (4)
C(42)	0.3164 (8)	0.2374 (4)	0.0949 (9)	5.4 (5)	C(82)	0.4671 (8)	0.2419 (4)	0.5674 (9)	5.3 (5)
C(43)	0.3315 (10)	0.2776 (4)	0.0720 (9)	7.1 (6)	C(83)	0.4688 (10)	0.2823 (4)	0.5943 (9)	6.1 (5)
C(44)	0.4387 (13)	0.2947 (3)	0.0961 (10)	6.3 (6)	C(84)	0.3681 (13)	0.3031 (3)	0.5856 (10)	7.0 (6)
C(45)	0.5308 (9)	0.2716 (4)	0.1430 (10)	6.2 (5)	C(85)	0.2657 (10)	0.2834 (4)	0.5500 (10)	6.5 (6)
C(46)	0.5157 (9)	0.2135 (4)	0.1659 (8)	4.6 (4)	C(86)	0.2640 (8)	0.2429 (4)	0.5230 (9)	5.6 (5)

Rigid-Group Parameters

group	x_c[a]	y_c	z_c	δ[b]	ϵ	η
ring 1	−0.0237 (7)	0.0798 (3)	−0.0009 (6)	3.025 (9)	−2.548 (8)	−0.546 (9)
ring 2	0.3448 (6)	0.0218 (3)	0.0862 (6)	0.396 (17)	2.028 (8)	−1.474 (17)
ring 3	0.5938 (6)	0.1149 (2)	0.1353 (6)	0.916 (16)	2.070 (8)	−1.516 (16)
ring 4	0.4236 (7)	0.2545 (3)	0.1190 (6)	−1.653 (8)	−2.968 (8)	−2.843 (8)
ring 5	−0.0603 (8)	0.0876 (3)	0.4574 (6)	0.169 (10)	2.992 (10)	2.843 (9)
ring 6	0.3342 (6)	0.0308 (3)	0.5805 (6)	0.339 (14)	−2.112 (8)	1.324 (15)
ring 7	0.5534 (7)	0.1251 (3)	0.6518 (6)	0.902 (14)	−2.220 (8)	1.513 (13)
ring 8	0.3664 (7)	0.2626 (3)	0.5587 (6)	1.556 (8)	−3.139 (9)	0.298 (8)

[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, and η (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.

rhodium species containing both 4- and 6-coordinate metal centers.[50] These metals can be formally regarded as Rh(I) and Rh(III) with 16- and 18-electron configurations, respectively.

Most parameters within the complex ion are as expected for such a DPM-bridged species, and in particular those parameters involving the DPM ligands themselves are normal. As is often the case, the bridging methylene groups of the diphosphine ligands bend toward the more sterically encumbered side of the complex (that having the $SCNMe_2$ group) to allow the phenyl groups to minimize unfavorable contacts with the relatively large $SCNMe_2$ group. The Rh–P distances fall within the range normally found for these complexes but can be grouped into two pairs; those on Rh(1) (2.319 (5), 2.333 (5) Å) are significantly shorter than those on Rh(2) (2.369 (5), 2.369 (5) Å). Presumably the longer Rh–P distances result because of the more severe steric crowding about Rh(2). A similar disparity in Rh–P distances has been observed in $[Rh_2Cl(CNMe)_2(CF_3C_2CF_3)(DPM)_2]^+$[51] and in $[Rh_2Cl_3(\mu$-

(50) Hoare, R. J.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2141.

(51) Dickson, R. S.; Hames, B. W.; Cowie, M., submitted for publication.

Table VI

(i) Selected Bond Lengths (Å) in $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot 1.833CH_2Cl_2$

Rh(1)-P(1)	2.333 (5)	P(4)-C(6)	1.848 (15)
Rh(1)-P(3)	2.319 (5)	P(1)-C(11)	1.823 (10)
Rh(1)-Cl(1)	2.395 (4)	P(1)-C(21)	1.819 (12)
Rh(1)-C(1)	1.75 (2)	P(2)-C(31)	1.818 (13)
Rh(2)-P(2)	2.369 (5)	P(2)-C(41)	1.834 (12)
Rh(2)-P(4)	2.369 (5)	P(3)-C(51)	1.821 (13)
Rh(2)-Cl(1)	2.509 (4)	P(3)-C(61)	1.823 (11)
Rh(2)-Cl(2)	2.354 (4)	P(4)-C(71)	1.836 (11)
Rh(2)-S(1)	2.407 (5)	P(4)-C(81)	1.835 (12)
Rh(2)-C(2)	1.93 (2)	B(1)-F(1)	1.27 (8)
S(1)-C(2)	1.69 (2)	B(1)-F(2)	1.42 (8)
C(2)-N(1)	1.32 (2)	B(1)-F(3)	1.56 (8)
N(1)-C(3)	1.48 (3)	B(1)-F(4)	1.10 (8)
N(1)-C(4)	1.44 (3)	C(7)-Cl(3)	1.69 (3)
C(1)-O(1)	1.14 (2)	C(7)-Cl(4)	1.69 (3)
P(1)-C(5)	1.805 (17)	C(8)-Cl(5)	1.50 (5)
P(2)-C(5)	1.853 (16)	C(8)-Cl(6)	1.77 (6)
P(3)-C(6)	1.828 (18)		

(ii) Nonbonding Distances (Å)

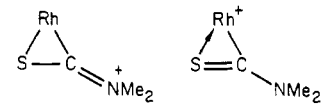
Rh(1)-Rh(2)	3.207 (2)	Rh(1)-S(1)	3.249 (6)

$H)(\mu\text{-CO})(DPM)_2]$,[52] and again the larger values were associated with the more sterically encumbered Rh centers.

The chloro bridge is unsymmetrical, with the bond to Rh(1) being significantly shorter. This shorter distance (Rh(1)–Cl(1) = 2.395 (4) Å) is normal and compares closely with that observed in $[Rh_2(CO)_2(\mu\text{-Cl})(DPM)_2]^+$,[53] in which the Cl ligand also bridges two metals which are not bonded to each other. The unusually long Rh(2)–Cl(1) distance (2.509 (4) Å) can be rationalized in terms of the high trans influence of C(2) and can be contrasted with the above Rh(1)–Cl(1) distance and with the normal, terminal Rh(2)–Cl(2) distance (2.354 (4) Å) on the same metal. A similar variation in metal–chlorine bond lengths has been observed in other $SCNMe_2$ complexes[5,11,14] and also in another binuclear complex containing both 4- and 6-coordinate rhodium centers.[50]

The geometry of the η^2-dimethylthiocarboxamido ligand compares well with other structurally characterized examples.[5,7,9-11,14-16,20] This group is essentially planar, with the largest deviation from the least-squares plane (0.013 Å) being for C(2).[48] Similarly, the S(1)–C(2)–N(1)–C(3) and S(1)–C(2)–N(1)–C(4) torsion angles of −179 (2)° and 3 (3)°, respectively, confirm the near planarity of this group. The rhodium–carbon bond length of 1.93 (2) Å is intermediate between those values previously reported for $SCNMe_2$ complexes of rhodium (1.90 (2), 2.00 (2) Å),[11,14] and the Rh(2)–S(1) distance (2.407 (5) Å), although comparable to other metal–sulfur distances for these ligands (range 2.387 (2)–2.469 (4) Å), is fractionally shorter than the two determinations involving rhodium (2.419 (5), 2.432 (5) Å).[11,14] The angle subtended by this ligand at Rh(2) (44.3 (6)°) is acute but represents a normal value for such a side-on bound group.

Within the $SCNMe_2$ ligand itself, the geometry is consistent with significant partial double bond character in the S(1)–C(2) and C(2)–N(1) bonds. Thus, the S(1)–C(2) distance (1.69 (2) Å) is comparable to the C–S double bond in ethylenethiourea[54] although it is longer than those in CS_2[55] and COS[56] (ca. 1.55 Å). The C(2)–N(1) distance (1.32 (2) Å) is typical for a C–N bond having partial double bond character and is certainly much shorter than a normal C–N single bond of about 1.47 Å.[54] Other $SCNMe_2$ complexes have displayed rather similar values (S–C range 1.61 (1)–1.69 (1) Å; C–N range 1.28 (2)–1.32 (3) Å). These S–C and C–N distances indicate the importance of the two tautomers, shown below, in the structure of **3**.



The importance of the first in the present structure is obvious from a consideration of the parameters around N(1); first, the atoms about N(1) are planar, and second, C(3) and C(4) are eclipsed with respect to S(1) and Rh(2). Had the C(2)–N(1) bond been single, we would have expected a pyramidal geometry about N(1) and also a twisting of the NMe_2 group about the C(2)–N(1) bond to allow these methyl groups to avoid contacts with S(1) and Cl(2) (see Figure 2). Both N(1)–Me distances are normal for single bonds and are obviously significantly longer than that of C(2)–N(1), which, as noted, has multiple bond character. All angles within the $SCNMe_2$ ligand are essentially as one might expect on the basis of the above description; the angles about N(1) are all close to 120° and the S(1)–C(2)–N(1) angle (132 (2)°) is comparable to the values previously reported.

Although the $SCNMe_2$ moiety is clearly bound to only one of the metal centers, this group is in such a position that movement to the bridging site would require very little rearrangement; the nonbonded Rh(1)–S(1) distance is only 3.249 (6) Å. The orientation of the $SCNMe_2$ group with regard to Rh(1) is clearly shown in Figure 2. This close nonbonded contact between Rh(1) and S(1) provides a rationalization for the facile interconversion of the η^2 and μ forms of this ligand (vide infra).

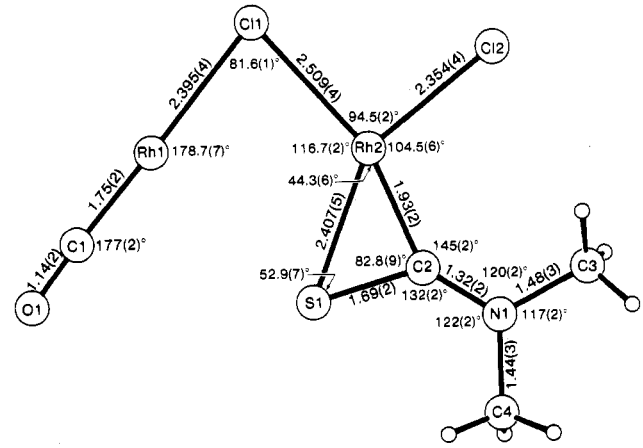


Figure 2. Inner coordination sphere of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2]^+$ in the approximate plane of the metals and the $SCNMe_2$ group. Some relevant bond lengths and angles are shown.

Discussion of Results

The majority of complexes containing the dialkylthiocarboxamido ligands ($SCNR_2$) has been prepared either by displacement of Cl^- from $SC(Cl)NMe_2$ by a metal carbonyl anion[6,8] or by oxidative additon of molecules of the type $SC(X)NMe_2$ (X = Cl,[3-5,8,12,13,17] S_2CNMe_2,[3,4,13] $N(Ph)(SNMe_2)$,[13] SMe,[13] H[25]) to a variety of metal centers. Other preparative routes, including sulfur abstraction from

(52) Sutherland, B. R.; Cowie, M. *Inorg. Chem.*, in press.
(53) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.
(54) "International Tables for X-ray Crystallography"; Macgilvray, C. H., Rieck, G. D., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. III, Table 4.2.
(55) Herzberg, G. "Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand: New York, 1945.
(56) Callomar, M. J.; Thompson, H. W. *Proc. R. Soc. London, Ser. A*, **1959**, *222*, 431.

Table VII. Selected Angles (Deg) in $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot 1.833CH_2Cl_2$

(a) Bond Angles

P(1)-Rh(1)-P(3)	179.4 (2)	Rh(2)-C(2)-N(1)	145 (2)	C(5)-P(1)-C(11)	103.9 (6)
C(1)-Rh(1)-Cl(1)	178.7 (7)	S(1)-C(2)-N(1)	132 (2)	C(5)-P(1)-C(21)	106.3 (7)
C(1)-Rh(1)-P(1)	90.3 (5)	C(2)-N(1)-C(3)	120 (2)	C(11)-P(1)-C(21)	98.6 (5)
C(1)-Rh(1)-P(3)	89.5 (5)	C(2)-N(1)-C(4)	122 (2)	C(5)-P(2)-C(31)	103.7 (6)
Cl(1)-Rh(1)-P(1)	90.7 (2)	C(3)-N(1)-C(4)	117 (2)	C(5)-P(2)-C(41)	103.9 (6)
Cl(1)-Rh(1)-P(3)	89.5 (2)	Rh(1)-Cl(1)-Rh(2)	81.6 (1)	C(31)-P(2)-C(41)	102.5 (6)
P(2)-Rh(2)-P(4)	176.1 (2)	Rh(1)-C(1)-O(1)	177 (2)	C(6)-P(3)-C(51)	102.2 (7)
Cl(1)-Rh(2)-Cl(2)	94.5 (2)	Rh(1)-P(1)-C(5)	112.7 (6)	C(6)-P(3)-C(61)	107.0 (6)
Cl(1)-Rh(2)-S(1)	116.7 (2)	Rh(1)-P(3)-C(6)	111.0 (6)	C(51)-P(3)-C(61)	103.8 (6)
Cl(2)-Rh(2)-C(2)	104.5 (6)	Rh(2)-P(2)-C(5)	112.4 (6)	C(6)-P(4)-C(71)	104.4 (6)
S(1)-Rh(2)-C(2)	44.3 (6)	Rh(2)-P(4)-C(6)	111.8 (6)	C(6)-P(4)-C(81)	103.1 (7)
Cl(1)-Rh(2)-P(2)	87.9 (2)	P(1)-C(5)-P(2)	117.4 (9)	C(71)-P(4)-C(81)	105.0 (5)
Cl(1)-Rh(2)-P(4)	89.5 (2)	P(3)-C(6)-P(4)	118.0 (9)	Cl(3)-C(7)-Cl(4)	112 (2)
Cl(2)-Rh(2)-P(2)	91.3 (2)	Rh(1)-P(1)-C(11)	116.0 (4)	Cl(5)-C(8)-Cl(6)	116 (2)
Cl(2)-Rh(2)-P(4)	91.8 (2)	Rh(1)-P(1)-C(21)	117.7 (4)	F(1)-B(1)-F(2)	105 (6)
S(1)-Rh(2)-P(2)	90.3 (2)	Rh(2)-P(2)-C(31)	121.5 (4)	F(1)-B(1)-F(3)	96 (6)
S(1)-Rh(2)-P(4)	88.3 (2)	Rh(2)-P(2)-C(41)	111.1 (4)	F(1)-B(1)-F(4)	133 (9)
C(2)-Rh(2)-P(2)	91.7 (6)	Rh(1)-P(3)-C(51)	113.8 (4)	F(2)-B(1)-F(3)	90 (5)
C(2)-Rh(2)-P(4)	89.8 (6)	Rh(1)-P(3)-C(61)	117.7 (4)	F(2)-B(1)-F(4)	115 (7)
Rh(2)-S(1)-C(2)	52.9 (7)	Rh(2)-P(4)-C(71)	118.9 (4)	F(3)-B(1)-F(4)	106 (7)
Rh(2)-C(2)-S(1)	82.8 (9)	Rh(2)-P(4)-C(81)	112.1 (4)		

(b) Torsion Angles

Rh(1)-Cl(1)-Rh(2)-Cl(2)	179.8 (2)	Rh(2)-S(1)-C(2)-N(1)	177 (2)	S(1)-C(2)-N(1)-C(4)	3 (3)
Rh(1)-Cl(1)-Rh(2)-S(1)	0.3 (2)	Rh(2)-C(2)-N(1)-C(3)	-5 (4)	S(1)-C(2)-N(1)-C(3)	-179 (2)
Rh(1)-Cl(1)-Rh(2)-C(2)	0.2 (17)	Rh(2)-C(2)-N(1)-C(4)	177 (2)		

a dithiocarbamate ligand,[16,18,20] alkylation of an η^2-methyl isothiocyanate ligand,[19] attack of an amine on a thiocarbonyl unit,[21] and addition of SH^- to an isocyanide ligand,[22] have also been used. We have utilized the route involving oxidative addition of $SC(Cl)NMe_2$ to a metal substrate, namely $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (1). This reaction yields a brown solution whose $^{31}P\{^1H\}$ NMR spectrum shows the presence of only one detectable, phosphorus-containing compound (2). Attempts to isolate 2 give it in only low yields as a bright yellow powder. This low yield appears to be due to facile reversal of the reaction upon precipitation. If, however, $NaBF_4$ is added to the above reaction mixture, a clear, red-orange solution results which has the same $^{31}P\{^1H\}$ NMR spectrum as that of 2 (see Figure 3). From this solution $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ (3) can be isolated in high yield. The $^{31}P\{^1H\}$ NMR spectra of 2 and 3 are consistent with two very different rhodium environments within the complexes, as was confirmed in the crystal structure of 3 (vide supra). A computer simulation[57] of the $^{31}P\{^1H\}$ NMR spectrum of compound 3 is shown together with the observed spectrum in Figure 3. This spectrum can be analyzed on the basis of an AA'BB'XY spin system with parameters $\delta(P_A) = 4.8$, $\delta(P_B) = 16.7$, $^1J_{Rh_X-P_A} = 117.6$ Hz, $^1J_{Rh_Y-P_B} = 91.2$ Hz, $^2J_{P_A-Rh_X-P_{A'}} = 300$ Hz, $^2J_{P_B-Rh_Y-P_{B'}} = 350$ Hz, $^2J_{P_A-C-P_B} = 23.8$ Hz, and $^4J_{P_A-P_{B'}} = 2.1$ Hz. All other couplings were set to zero. This spectrum is quite insensitive to changes in the values of $^2J_{P-Rh-P}$ so these parameters were arbitrarily set to the values given, which are in the range previously reported for such couplings.[58] The value of $|^2J_{P_A-C-P_B} + {}^4J_{P_A-P_{B'}}|$ can be obtained directly from the experimental spectrum, being the difference in frequency between the two smaller peaks of each "triplet". In fact the positions of these bands do not change as long as $|^2J_{P_A-C-P_B} + {}^4J_{P_A-P_{B'}}|$ is held constant; variations in the two individual couplings lead only to alterations in the intensities of the sidebands with respect to the central peak. By using the ^{13}CO-enriched compound 1, it is possible to identify the low-field

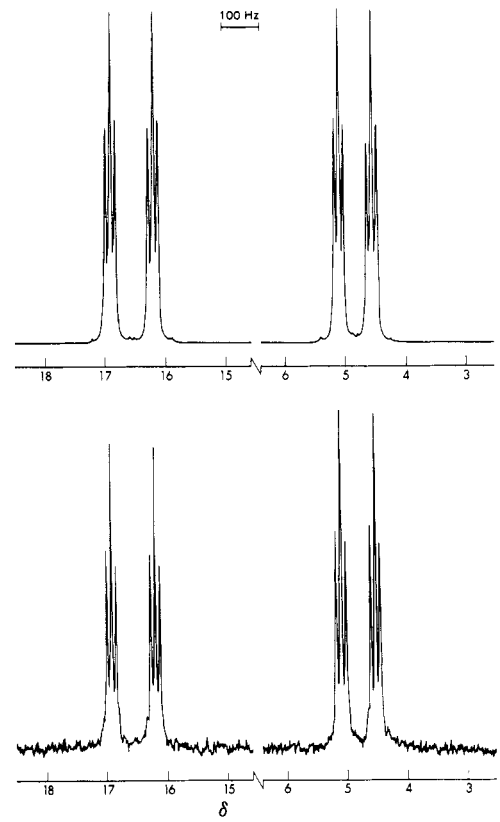
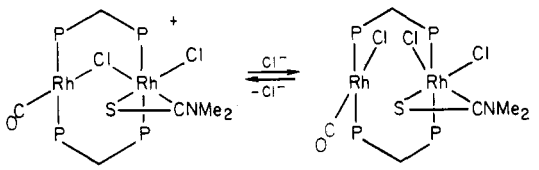


Figure 3. Simulated (top) and experimental $^{31}P\{^1H\}$ NMR spectra of $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2]^+$ recorded at 161.9 MHz.

^{31}P resonance as the one due to the phosphorus nuclei on the CO-containing end of the molecule (P(1) and P(3)) since this resonance is further split into doublets with $J_{P-C} = 13.5$ Hz. The $^{13}C\{^{31}P\{^1H\}\}$ NMR spectrum of this ^{13}CO-enriched sample consists of a doublet at $\delta = 186.0$ ($J_{Rh-C} = 81.7$ Hz), typical of a terminal carbonyl bound to rhodium.[59,60]

(57) Simulations of the $^{31}P\{^1H\}$ NMR spectra were obtained by using LAOCOON III; see: Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.
(58) Mague, J. T., DeVries, S. H. *Inorg. Chem.* **1980**, *19*, 3743.
(59) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246.
(60) Gansow, O. A.; Vernon, W. D. *Top. Carbon-13 NMR Spectrosc.* **1976**, *2*, Chapter 5.

It seems that on the NMR time scale compounds **2** and **3** are essentially identical, yet there are significant differences in the two compounds. Compound **3** has a conductivity consistent with its being a 1:1 electrolyte whereas that for **2** is much less than that expected for a 1:1 electrolyte, suggesting some association of the Cl^- anion with the complex cation. In addition, their infrared spectra differ in the carbonyl region. The carbonyl stretches for **3** in the solid and in CH_2Cl_2 solution are essentially identical (1999 and 2000 cm^{-1}, respectively), suggesting the same structure in both phases. However, for **2** the solid-state IR spectrum has ν(CO) at 1971 cm^{-1}, and the solution spectrum has two bands—a strong one at 1988 cm^{-1} and a shoulder at 2005 cm^{-1}. We suggest that in the solid state **2** has the Cl^- anion coordinated to give $[Rh_2Cl_3(CO)(SCNMe_2)(DPM)_2]$, as shown below. The carbonyl stretch



3 **2**

for this species is, as expected, lower than for the cationic species **3**. In the solution infrared spectrum we see two species which we suggest are in equilibrium; the shoulder at 2005 cm^{-1} presumably corresponds to the cationic species **3** (but with Cl^- counterion) since the position of this band is similar to that observed with the BF_4^- anion, and the major peak at 1988 cm^{-1} we believe is due to the neutral species **2** or to something closely related to **2**. It may be that in solution **2** exists not with the Cl^- anion actually coordinated but as a close ion pair with the cationic complex; this would explain the position of the 1988-cm^{-1} band between those observed for the cationic species **3** and neutral species **2** (in the solid). Dissociation of Cl^- from **2** probably occurs because of steric crowding about Rh(2). When this occurs the chloro ligand on the other metal moves to the bridging position to give Rh(2) the 18-electron, pseudooctahedral environment favored for rhodium in the +3 oxidation state.

The neutral species **2**, containing Rh(I)/Rh(III) centers, is the expected product if oxidative addition occurs at one metal center. We rule out the possibility of oxidative addition at both metals to give a Rh(II)/Rh(II) system since the carbonyl stretch in the solid is more consistent with a Rh(I) species (for example, it is very similar to the value of 1968 cm^{-1} observed for *trans*-$[RhCl(CO)(L_2)]_2$, L_2 = $Ph_2PCH_2PPh_2$,[40] $Ph_2AsCH_2AsPh_2$[61]).

In the infrared spectra of **2** and **3** the C–N stretches for the $SCNMe_2$ group (1615 and 1616 cm^{-1}, respectively) are almost identical, suggesting similar bonding of these groups, and both are in the region typical for a η^2-bound $SCNMe_2$ group (1570–1650 cm^{-1}).[5] Of course the X-ray structure determination unambiguously establishes this bonding mode for **3** (vide supra). The ^1H NMR spectra of **2** and **3** are also identical, showing two methyl resonances at 2.05 and 2.84 ppm, as is typically observed for an η^2-$SCNMe_2$ group.[5] The two resonances indicate that rotation about the C–N bond is restricted, probably due to the multiplicity of this bond (vide supra) and possibly also because of steric interactions with the other ligands, particularly with the phenyl groups.

It is of interest to note that the oxygen-containing analogue, $OC(Cl)NMe_2$, does not react with **1** even after refluxing in THF for several days.

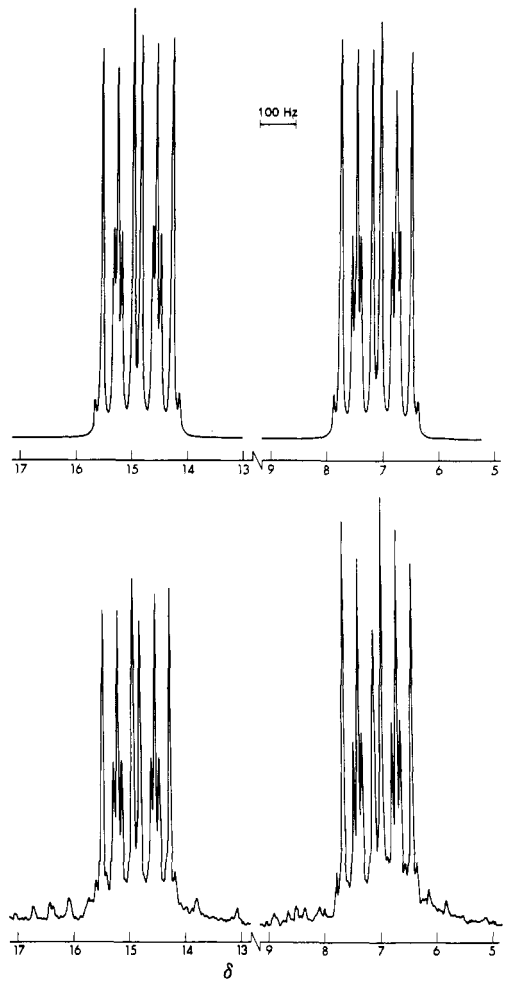
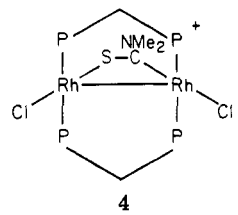


Figure 4. Simulated (top) and experimental $^{31}P\{^1H\}$ NMR spectra of $[Rh_2Cl_2(SCNMe_2)(DPM)_2]^+$ recorded at 161.9 MHz.

Compound **3** reacts smoothly with Me_3NO resulting in carbonyl loss, generating the A-frame species **4**. The

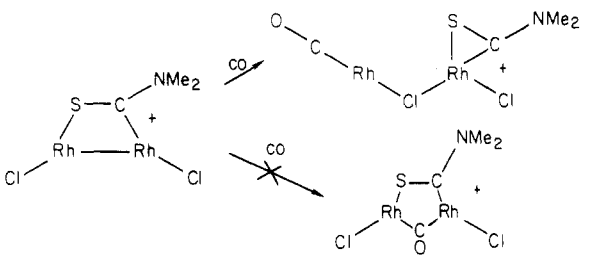


4

infrared spectrum of **4** not only confirms that CO loss has occurred but also indicates a change in the bonding mode of the $SCNMe_2$ group: the C–N stretch of this group drops to 1467 cm^{-1}, a region typical of bridging $SCNMe_2$ groups (1460–1520 cm^{-1}).[5] In the ^1H NMR spectrum there is only one signal (integrating to six hydrogens) at δ = 2.10, implying rotation about the C–N bond that makes both methyls equivalent on the NMR time scale. This rotation is consistent with the observed drop in the C–N stretch. The $^{31}P\{^1H\}$ NMR spectrum of **4** (see Figure 4) can be simulated as an AA′BB′XY pattern, also shown in the figure. The derived parameters are $\delta(P_A)$ = 7.1, $\delta(P_B)$ = 14.9, $^1J_{Rh_X-P_A}$ = 104.2 Hz, $^1J_{Rh_Y-P_B}$ = 106.6 Hz, $^2J_{P_A-Rh_X-P_{A'}}$ = 300 Hz, $^2J_{P_B-Rh_Y-P_{B'}}$ = 350 Hz, $^2J_{P_A-C-P_B}$ = 67.9 Hz, and $^4J_{P_A-P_{B'}}$ = 15.7 Hz, with all other couplings of 0 Hz. As was the case for spectrum of compound **3**, little effect is observed when the $^2J_{P-Rh-P}$ values are altered. The value of $|^2J_{P_A-C-P_B} + {}^4J_{P_A-P_{B'}}|$ can be obtained from the experimental spectrum, being the frequency difference between the outer peaks of each 5-line multiplet (the spectrum can roughly

(61) Mague, J. T.; Mitchner, J. P. *Inorg. Chem.* **1969**, *8*, 119.

Scheme I

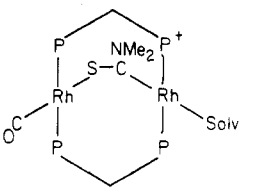


be described as two resonances (P_A and P_B), each of which consists of two closely spaced 5-line multiplets).

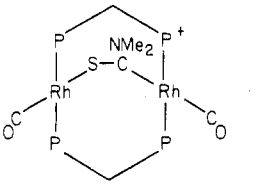
Compound **4** is structurally analogous to the acetylene-bridged species $[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$;[62] both have terminal halide ligands, a bridging group, and an accompanying Rh–Rh bond. This hexafluoro-2-butyne adduct reacted with CO to yield the unusual species $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)(DPM)_2]$,[51] in which CO had inserted into the Rh–Rh bond, and suggested to us the possibility that **4** might react likewise. However, the reaction of **4** with CO does not give the product of CO insertion into the Rh–Rh bond, $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}SCNMe_2)(DPM)_2]^+$, as shown in Scheme I, but instead regenerates **3**, suggesting that CO attack occurs at the terminal site adjacent to the sulfur atom instead of at the bridging site. Attack at the other rhodium center to give an isomer of **3** in which CO is adjacent to the $CNMe_2$ end of the $SCNMe_2$ ligand is presumably not favored since the methyl groups block this coordination site. Similarly, **4** reacts with methyl isocyanide to give $[Rh_2Cl_2(CNMe)(SCNMe_2)(DPM)_2]^+$ (**5**), which is assumed to be structurally analogous to **3** but with CNMe instead of CO. The $^{31}P\{^1H\}$ and ^1H NMR spectra of **5** are similar to those of **3** (apart from the additional methyl resonance in the ^1H NMR of **5**), and the infrared spectrum shows the C–N stretch of the terminal isocyanide at 2209 cm^{-1} and that of the $SCNMe_2$ group at 1623 cm^{-1}, showing that the latter group is η^2-bound to one metal center.

The facile interconversion between the chelating and bridged bonding modes of the $SCNMe_2$ ligand, although unusual, is not surprising under the circumstances. A consideration of the structure of **3** indicates that the sulfur atom in the chelate form is only 3.249 (6) Å away from the other Rh center. Upon CO loss from **3** it takes very little movement of the $SCNMe_2$ group to give the bridging structure, which is needed to satisfy the otherwise electron-deficient Rh(1). Similarly CO or CNMe attack at Rh(1) forces the $SCNMe_2$ group of the bridging site and back to the initial η^2 mode as observed for **3**.

The reaction of **3** with borohydride reducing agents was undertaken in order to determine whether reduction would occur preferentially at the metal centers or at the $SCNMe_2$ ligand; examples related to both have been observed. For example, reaction of a somewhat analogous compound, *trans*-$[RhCl(CO)(DPM)]_2$, with BH_4^- has been reported to yield the unusual dimer, $[Rh(CO)(DPM)]_2$, a reactive species which displays a rich chemistry with small molecules and which is a catalyst precursor for hydrogenation, hydroformylation, and water gas shift chemistry.[63] Although reduction of a chelating $SCNMe_2$ ligand has not been reported, reduction of the related SCSMe unit to give a thiocarbonyl ligand is a known transformation.[64] In the reaction of **3** with 2 equiv of BH_4^- per dimer we find that reduction occurs at the metals. This reaction occurs instantly at room temperature in a variety of solvents such as CH_2Cl_2, acetone, MeOH, EtOH, and acetonitrile but more slowly in THF. However, only in the latter two solvents are single products reproducibly obtained; in all other solvents tried, reactions repeated under seemingly identical conditions give rise to either different products or to different mixtures of products. Surprisingly, no matter what solvent is used or what the products are, subsequent reaction with CO always yields the same single product (vide infra). We have at this time only studied the reductions in THF and acetonitrile (yielding compounds **6a** and **6b**, respectively) in detail. All reduction products are extremely air sensitive and cannot be isolated as solids. Nevertheless, the infrared and NMR spectra of the products in THF and acetonitrile solutions as well as a characterization of the subsequent product obtained on reaction with CO allow us to propose structures for these species. The $^{31}P\{^1H\}$ NMR spectra of **6a** and **6b** indicate the presence of only one species in each case. These spectra are very similar to each other and also closely resemble the AA'BB'XY pattern obtained for compound **4**. Both **6a** and **6b** show a single carbonyl stretch at ca. 1955 cm^{-1} in solution; unfortunately no band attributable to the C–N stretch of the $SCNMe_2$ group can be detected in either case. In most samples of **6b**[65] no hydride resonances can be detected in the ^1H NMR spectra; however, in some samples small amounts (<5%) of two hydride species are observed (vide infra).[66] These NMR spectra show two resonances for the methyl groups, which although at higher field than usually observed for complexes of $SCNMe_2$[5] are not unreasonable. These data suggest that compounds **6a** and **6b** are not hydrides and on the basis of the above information we propose the structures shown below. These structures are consistent with the observation that different products having a broad range in colors are obtained in the different solvents (green (EtOH, MeOH), red (acetone, CH_2Cl_2), purple (acetonitrile, THF)). Furthermore, it is consistent that for such species the solvents which have the greater coordinating ability yield products which are more stable and therefore more readily handled.



6a, Solv = THF
6b, Solv = CH_3CN



7

We expect that the first step in the reaction with BH_4^- is the formation of the dihydride, $[Rh_2H_2(CO)(SCNMe_2)(DPM)_2][BF_4]$, which then reductively eliminates H_2 to give compound **6** as the solvated species. Although small amounts of two hydride complexes were observed in the ^1H NMR spectra of some preparations of compound **6b**, it is not clear whether either of these resonances is due to the above dihydride. We are presently investigating this reaction further and will attempt the

(62) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682.
(63) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.
(64) Collins, T. J.; Roper, W. R.; Town, K. G. *J. Organometal. Chem.* **1976**, *121*, C41.
(65) The reduction of **3** by $NaBH_4$ has repeatedly failed in THF-d_8 while having succeeded in parallel attempts in nondeuterated THF although both solvents were dried and degassed. Presumably small amounts of impurities in the deuterated solvent are responsible.
(66) The hydride resonances, which integrate as approximately 2:1, appear as doublets of triplets: (i) $\delta = -16.32$, $^1J_{Rh-H} = 36$ Hz, $^2J_{P-H} = 10$ Hz; (ii) $\delta = -13.72$, $^1J_{Rh-H} = 28$ Hz, $^2J_{P-H} = 9$ Hz.

reduction under H_2 in an attempt to isolate this dihydride (a similar approach, it seems, has succeeded in isolating the initial dihydride in the reduction of *trans*-[RhCl(CO)(DPM)]$_2$).[67]

As noted earlier, the reaction of **6a**, **6b**, or any of the related reduction products in other solvents with CO yields the same single species which, on the basis of its spectral parameters, its elemental analysis, and its conductivity, we have identified as $[Rh_2(CO)_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (**7**). This species displays carbonyl stretches at 1988 and 1948 cm^{-1}, which shift to 1942 and 1902 cm^{-1} when the product is labeled with ^{13}CO, and a C–N stretch for the $SCNMe_2$ group at 1521 cm^{-1}, suggesting the bridging mode for this group (vide supra). The infrared spectrum of **7** does not change when $NaBD_4$ is used instead of $NaBH_4$ nor are any resonances observed in the ^1H NMR spectrum of the BH_4^- reduction product which can be attributed to a metal hydride species. The $^{31}P\{^1H\}$ NMR spectrum is qualitatively very similar to that of compound **4**, suggesting a species of similar geometry, and when ^{13}CO-labeled sample is used both sets of ^{31}P resonances are split by ^{13}C, indicating that the two carbonyls are on different metals. Furthermore, the $^{13}C\{^{31}P\{^1H\}\}$ NMR spectrum, which consists of two doublets (δ = 199.8 and 191.3 ppm, $^1J_{Rh-C}$ = 55.9 and 71.5 Hz, respectively) with no ^{13}C–^{13}C coupling, confirms this conclusion. On the basis of these data and the conductivity, which indicates that **7** is a 1:1 electrolyte, we propose the structure shown earlier. This structure is analogous to those of **6a** and **6b** in which CO has displaced the weakly coordinated solvent molecules. It is clear that whatever the unknown species are in the reductions of **3** in solvents other than THF and CH_3CN, their reactions with CO convert these unstable species into the air-stable dicarbonyl, **7**, probably again via displacement of the weakly coordinating solvent molecules. Unlike compound **4**, which also has a bridging $SCNMe_2$ group but which shows only one methyl resonance in the ^1H NMR, compound **7** displays two methyl resonances at 1.66 and 2.85 ppm, indicating hindered rotation about the C–N bond for the latter. This observation is consistent with the higher C–N stretching frequency observed for **7** (see text and Table I).

Conclusions

We have prepared $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]$ (**3**) by the oxidative addition of $SC(Cl)NMe_2$ to $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ in the presence of $NaBF_4$. Although the $SCNMe_2$ group in compound **3** is side-on bound through sulfur and carbon to only one metal center, this group is oriented such that the sulfur atom is close to the second metal, suggesting that its interconversion between chelating and bridging coordination modes should be possible. Such facile interconversion has been observed by us in two reactions. First, reversible carbonyl loss from compound **3** yields $[Rh_2Cl_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (**4**), and second, reduction of **3** by BH_4^- yields $[Rh_2(CO)(\mu\text{-}SCNMe_2)(DPM)_2(solvent)][BF_4]$ (**6**); both species **4** and **6** have bridging $SCNMe_2$ groups. Another compound, $[Rh_2(CO)_2(\mu\text{-}SCNMe_2)(DPM)_2][BF_4]$ (**7**), also having a bridging $SCNMe_2$ moiety, can be obtained from **6** upon reaction with CO. This facile interconversion between η^2 and μ bonding modes of the $SCNMe_2$ group suggests that an analogous process may be possible with metallocarboxylic acids and their esters, which in turn suggests that CO_2 and related substrates may display reactivities in multinuclear complexes different from those in mononuclear ones, owing to the several bonding modes possible in the former group.

Further studies on the very reactive compound **6** seem warranted, as do studies on the hydrido species, $[Rh_2H_2(CO)(SCNMe_2)(DPM)_2][BF_4]$, which we assume is an intermediate in the reduction of compound **3** to **6**. Complexes which contain hydrido ligands together with metallocarboxylic acid and related moieties are of obvious interest owing to the possible involvement of such species as intermediates in the reduction of CO_2 to alkyl species. However, owing to the very labile nature of such species, their sulfur-containing analogues should prove invaluable in aiding with their characterization. For these reasons, studies on the above complexes are continuing and are being extended to include model systems which more closely resemble the desired metallocarboxylic acid intermediates.

Acknowledgment. We thank NSERC (Canada) and the University of Alberta for support of this research, the University of Alberta for a scholarship to J.A.E.G., and Prof. J. T. Mague for supplying us with a copy of LAOCOON III, the NMR simulation program, and for helpful discussions.

Registry No. 1, 73680-37-2; **2**, 89321-53-9; **3**, 89321-56-2; **3a**, 89321-66-4; **4**, 89321-58-4; **5**, 89321-60-8; **6a**, 89321-62-0; **6b**, 89321-68-6; **7**, 89321-64-2; **7a**, 89321-70-0.

Supplementary Material Available: Tables listing the anisotropic thermal parameters, the derived hydrogen parameters, least-squares planes, and the observed and calculated structure factor amplitudes for $[Rh_2Cl_2(CO)(SCNMe_2)(DPM)_2][BF_4]\cdot 1.833CH_2Cl_2$ (16 pages). Ordering information is given on any current masthead page.

(67) Woodcock, C.; Eisenberg, R. "Abstracts of Papers", 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983; INOR 253.