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Alkyl Group Migration in Rhodium Carbonyl Dithiolates and the Molecular Structure of Carbonyl(triphenylphosphine)(1-(ethylthio)maleonitrile-2-thiolato)rhodium, Rh(CO)(PPh₃)(Et-mnt)

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The alkyl group migration between the acyl carbon atom and a sulfur donor atom of a series of rhodium carbonyl dithiolates has been explored by synthesis, spectroscopic characterization, and X-ray structure determination of the typical S-alkylated complex Rh(CO)(PPh₃)(Et-mnt) (mnt = maleonitriledithiolate; Et-mnt = the S-ethylated derivative). The neutral rhodium(III) acyl complexes Rh(COR)LL'(mnt) where L = PPh₃ and PEt₃ and L' = pyr, C₆H₁₁NH₂, and Sol are prepared by the reaction of [Rh(CO)L(mnt)]⁻ with RX followed by removal of X⁻ with Ag⁺ and the addition of L'. Heating of these neutral acyl complexes in THF or CHCl₃ solution leads in certain cases to the S-alkylated derivatives Rh(CO)(PPh₃)(R-mnt) (R = Et, *n*-Pr, Bz) and the corresponding PEt₃ complex where R = Et. The migration was followed in both the forward and reverse directions by IR and NMR spectroscopies, and in one case where L = PPh₃, L' = pyr, and R = Et an equilibrium mixture of the two Rh species was obtained. The complex Rh(CO)(PPh₃)(Et-mnt) was examined by single-crystal X-ray methods and refined by standard procedures to final agreement factors *R* and *R'* of 3.73 and 5.14%. The geometry of the complex is square planar with the alkylated sulfur donor cis to the carbonyl ligand. The alkylated S donor is pyramidal, and the bond distances and angles are as expected. The S-alkylated complex is a Rh(I) system, and hence the alkyl group migration takes place with an internal redox reaction in which an electron pair of the dithiolate ligand serves in a complementary way to the electron pair of the Rh(III)/Rh(I) couple. The mechanism of the alkyl group migration is proposed as a succession of two 1,2 shifts with a rhodium(III) alkyl carbonyl dithiolate as an intermediate.

Introduction

During the last several years we have been investigating the reactions of alkyl halides with rhodium(I) complexes of maleonitriledithiolate (mnt).¹⁻⁴ Initially, we observed that the diolefin derivatives [Rh(NBD)(mnt)]⁻ and [Rh(COD)(mnt)]⁻ (NBD = norbornadiene; COD = 1,5-cyclooctadiene) react only with activated alkyl halides such as MeI and BzBr to form S-alkylated products¹ in which the d⁸ Rh(I) center is maintained. Subsequently, we found that the carbonyl-containing derivatives [Rh(CO)L(mnt)]⁻ (L = PPh₃, PEt₃) react with a wide variety of alkyl halides to form series of stable, well-characterized acyl complexes of Rh(III) in which the 1,2-dithiolate nature of the mnt ligand is preserved.^{2,3}

Single-crystal structure determinations of two of the acyl complexes^{2,4} have shown the Rh(III) ion to be pentacoordinated in a square-pyramidal arrangement with the acyl ligand in each case occupying the unique apical position. In the case where halide ion of the RX substrate remains coordinated to the Rh(III) center, the acyl complexes are anionic and exhibit chiral integrity on the NMR time scale as evidenced by the magnetic nonequivalence of the α -methylene protons of RC(O)- ligand. When the halide ion is removed by substitution or by reaction with Ag⁺BF₄⁻, neutral complexes are produced. In the course of investigating these neutral acyl complexes, we found that under certain conditions a migration of the R group occurs from the carbonyl carbon of the acyl ligand to one of the sulfur donors of the mnt ligand. This unusual rearrangement, which corresponds to the controlled migration of an alkyl group within the coordination sphere, is the subject of the present paper. We describe herein the complete characterization of the S-alkylated products and the reactions leading to their formation.

Experimental Section

Procedures and Materials. All reactions were carried out under a nitrogen atmosphere by using modified Schlenk techniques. ¹H NMR spectra were measured on JEOL MH-100 NMR spectrometer, and infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. All solvents were of analytical grade and were dried and degassed before use.

Rhodium trichloride hydrate (Matthey Bishop), tetraphenylarsonium chloride (Ventron), triethylphosphine (Strem), alkyl halides, triphenylphosphine, tetra-*n*-butylammonium chloride (Eastman), and

triethylxonium hexafluorophosphate (Aldrich) were used as purchased. The Rh(I) anions [Rh(CO)(PPh₃)(mnt)]⁻ and [Rh(CO)(PEt₃)(mnt)]⁻, their acyl derivatives [RhX(COR)(PPh₃)(mnt)]⁻ and Rh(COR)(PEt₃)₂(mnt), and the S-alkylated complex Rh(CO)(PPh₃)(Et-mnt) were prepared according to the previously reported procedures.²⁻⁴

Preparation of Neutral Acyl Complexes Rh(COR)LL'(mnt). Rh(COMe)(PPh₃)(mnt)(CH₃CN). To a solution of [(*n*-Bu)₄N]⁺[Rh(COCH₃)(PPh₃)(mnt)]⁻ generated in situ by the addition of 1 mL of CH₃I to 0.5 g of [(*n*-Bu)₄N]⁺[Rh(CO)(PPh₃)(mnt)]⁻ in 10 mL of CH₃CN was added slowly 0.115 g of AgNO₃ in 5 mL of CH₃CN. A precipitate of AgI was formed and was filtered off. After addition of ethanol, the filtrate was concentrated on a rotary evaporator affording a brown crude product. Dissolution of the crude product in CH₃CN results in the crystallization of the desired pure orange complex (85% yield). Anal. Calcd for C₂₆H₂₁N₃OPS₂Rh: C, 52.98; H, 3.59; N, 7.13; P, 5.25. Found: C, 52.80; H, 3.63; N, 7.18; P, 5.25.

The propionyl and butyryl analogues of this neutral acetyl species may be prepared in a similar way. These complexes have been reported previously following slightly different synthetic procedures.² Attempts to isolate in pure form the corresponding triethylphosphine derivatives Rh(COR)(PEt₃)(mnt)(CH₃CN), where R = Me, Et, Bz, and the phenylacetyl species Rh(COCH₂Ph)(PPh₃)(mnt)(CH₃CN) did not succeed.

Rh(COR)LL'(mnt), Where L = PPh₃, PEt₃ and L' = C₅H₅N, C₆H₁₁NH₂. These complexes were prepared similarly except that the crude brown products were recrystallized from CH₂Cl₂-EtOH-L' solutions to afford the desired complexes Rh(COR)LL'(mnt). Yields are approximately 70%. Analytical data follow.

Rh(COCH₃)(PEt₃)(C₅H₅N)(mnt). Anal. Calcd for C₁₇H₂₃N₃OPS₂Rh: C, 42.24; H, 4.80; P, 6.41. Found: C, 42.16; H, 5.01; P, 6.47.

Rh(COEt)(PPh₃)(C₅H₅N)(mnt). Anal. Calcd for C₃₀H₂₅N₃OPS₂Rh: C, 56.17; H, 3.93; P, 4.83. Found: C, 56.27; H, 4.27; P, 5.10.

Rh(COEt)(PPh₃)(C₆H₁₁NH₂)(mnt). Anal. Calcd for C₃₁H₃₃N₃OPS₂Rh: C, 56.28; H, 5.03; P, 4.68. Found: C, 56.17; H, 5.40; P, 5.08.

Rh(CO-*n*-Pr)(PPh₃)(C₅H₅N). Anal. Calcd for C₃₁H₂₇N₃OPS₂Rh: C, 56.80; H, 4.15; P, 4.72. Found: C, 56.33; H, 4.20; P, 5.19.

Rh(COCH₂Ph)(PPh₃)(C₆H₁₁NH₂)(mnt). Anal. Calcd for C₃₆H₃₅N₃OPS₂Rh: C, 59.74; H, 4.87; N, 5.81; S, 8.86. Found: C, 59.22; H, 5.11; N, 5.75; S, 8.84.

Preparation of S-Alkylated Complexes Rh(CO)L(R-mnt). Rh(CO)(PEt₃)(Et-mnt). [(*n*-Bu)₄N]⁺[Rh(CO)(PEt₃)(mnt)]⁻ (0.58 g) in 15 mL of THF was allowed to react with EtI (2 mL) for 2 h to yield the corresponding acyl anion [RhI(COEt)(PEt₃)(mnt)]⁻. Addition of 0.22 g of AgBF₄ resulted in the formation of a precipitate of AgI

which was filtered from the solution. After addition of ethanol, the solution was concentrated on a rotary evaporator to give the crude neutral acyl complex Rh(COEt)(PEt₃)(mnt)(THF). The neutral species was dissolved in 15 mL of THF and was heated at 70 °C for 15 min, allowing the acyl complex to rearrange to the S-alkylated species. Addition of ethanol followed by solvent evaporation led to the formation of a crude brown product which was recrystallized from THF-EtOH affording 0.24 g of pure material (72%). Anal. Calcd for C₁₃H₂₀N₂OPS₂Rh: C, 37.33; H, 4.82; P, 7.40. Found: C, 37.08; H, 5.00; P, 7.23.

Rh(CO)(PPh₃)(*n*-Pr-mnt). This complex was similarly prepared. Anal. Calcd for C₂₆H₂₂N₂OPS₂Rh: C, 54.17; H, 3.85; P, 5.37. Found: C, 53.84; H, 4.28; P, 5.01.

Rh(CO)(PPh₃)(PhCH₂-mnt). The crude neutral acyl complex Rh(COCH₂Ph)(PPh₃)(mnt)(THF) (0.28 g) was dissolved in 10 mL of CH₂Cl₂. The solution was then heated at 55 °C for 20 min. Addition of ethanol followed by evaporation led to the formation of a brown precipitate, whose IR spectrum revealed the presence of both starting material and product. Addition of hexanes to the filtrate, which was separated from the brown precipitate, followed by storage at -10 °C yielded a pure orange crystalline product. Anal. Calcd for C₃₀H₂₂N₂PS₂ORh: C, 57.70; H, 3.55; N, 4.49; P, 4.96. Found: C, 57.61; H, 3.61; N, 4.51; P, 5.01.

Monitoring Alkyl Group Migration. Measured amounts of either a neutral acyl complex Rh(COR)LL'(mnt) or an S-alkylated species and a neutral ligand L' such as C₂H₅N, C₆H₁₁NH₂, etc. were dissolved in chloroform, CH₂Cl₂, or THF in an NMR tube. The tube was sealed with a septum under 1 atm of nitrogen and was heated at 70 °C until the reaction reached equilibrium. During the time of heating, the IR or NMR spectrum of the solution (the latter only in CDCl₃) was taken from time to time. To obtain the solution IR spectra, we transferred part of the solution each time from the NMR tube to an appropriate cell for measuring the spectrum.

Crystal Structure Analysis of Carbonyl(triphenylphosphine)(1-ethylthio)maleonitrile-2-thiolato)rhodium(I). **Data Collection and Reduction.** The complex Rh(CO)(PPh₃)(Et-mnt) was prepared, and crystals suitable for an X-ray structure analysis were grown from acetone solution. Precession photographs showed that the crystals belong to the triclinic system, and the observed systematic absences of $h + k = 2n + 1$ indicated that a C-centered cell had been chosen. The space group was thus either C1 or C $\bar{1}$, corresponding to alternative settings of the primitive triclinic space groups. The C-centered cell had dimensions refined from the setting angles of 12 high-angle reflections ($(\sin \theta)/\lambda > 0.312$) of $a' = 23.400$ (6) Å, $b' = 11.988$ (4) Å, $c' = 9.119$ (2) Å, $\alpha' = 86.345$ (25)°, $\beta' = 106.6678$ °, and $\gamma' = 93.032$ (32)°, while the reduced primitive cell constants were $a = 11.988$ Å, $b = 12.861$ Å, $c = 9.119$ Å, $\alpha = 103.369$ °, $\beta = 93.665$ °, and $\gamma = 114.706$ °. The reduced cell is related to the C-centered cell by the transformation $a = -b'$, $b = 1/2a' + 1/2b'$, $c = c'$. The C-centered cell was used throughout the structure determination; assumption of the centrosymmetric possibility C $\bar{1}$ was confirmed by the successful refinement of the structure. An experimental density of 1.51 (2) g/cm³ obtained by the flotation method agrees with the calculated value of 1.529 g/cm³ for $Z = 4$ in the C-centered unit cell.

The crystal used for photographs and data collection had dimensions of 0.35 × 0.28 × 0.30 mm and was mounted along the b^* axis. Intensities were measured on a Picker FACS-1 diffractometer by the θ - 2θ scan technique at a scan rate of 1°/min with the scan ranging from 0.7° below the $K\alpha_1$ peak to 0.7° above the $K\alpha_2$ peak. Background counts of 10 s were measured at each end of the scan. Attenuator foils were automatically inserted when the intensity of the diffracted beam reached 10000 counts/s. The pulse-height analyzer was set for a 90% window centered on Mo $K\alpha$ radiation.

Data were collected to a maximum 2θ value of 45° from the hemisphere with $l \geq 0$. Three standard reflections were monitored every 77 observations. The intensities of the standards varied less than 3% throughout data collection. In the data collection, systematically absent reflections having $h + k = 2n + 1$ were not measured. The intensities of a total of 3448 reflections were thus gathered. The values of I and $\sigma^2(I)$ were obtained by using the expressions previously described.⁶ The value of p used in the expression for the variance was chosen as 0.04.⁷ The intensity I and $\sigma^2(I)$ were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections. This led to 3264 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. Owing to the small linear absorption coefficient ($\mu_{Mo} = 9.31$ cm⁻¹), no absorption correction was performed.

Solution and Refinement of the Structure

The position of the rhodium atom was determined from a Patterson map. Subsequent difference Fourier maps yielded the sites of the remaining nonhydrogen atoms.⁸ The structure was refined by a least-squares procedure in which the function minimized as $\sum w(|F_o| - |F_c|)^2$ where the weights used were $w = 4F_o^2/\sigma^2(F_o^2)$. In the refinements, only the reflections with $F_o^2 > 3\sigma(F_o^2)$ were included. Scattering factors for the nonhydrogen atoms were those of Cromer and Mann,⁹ while the hydrogen scattering factor was taken from Stewart et al.¹⁰ The rhodium, phosphorus, and sulfur atoms were treated for anomalous dispersion by using the values of $\Delta f'$ and $\Delta f''$ tabulated by Cromer and Lieberman.¹¹ The phenyl rings were treated as rigid groups in the refinements on the assumption that all the carbon and hydrogen atoms are in the same plane and that $d(C-C) = 1.392$ Å and $d(C-H) = 0.95$ Å. The refinement with anisotropic thermal parameters for the Rh, P, S, C, N, and O nongroup atoms, variable isotropic thermal parameters for the phenyl carbon atoms, and fixed isotropic temperature factors of 6.0 Å² for the phenyl hydrogens led to convergence with discrepancy indices R and R' of 0.0484 and 0.0903, respectively, and an estimated standard deviation in an observation of unit weight of 4.13. Because of this high value and the discrepancy between the weighted and unweighted R factors, an analysis of the weighting scheme was carried out. The analysis revealed a dependence of the weighted residual on the magnitude of F_o with poorest agreement obtained for both weak and extremely strong reflections.

The removal of several very intense reflections (111, 201, 222, 130, 220 and 200) from the refinement procedure, the elimination of a number of duplicate reflections not previously removed, and the use of a new weighting scheme in which $w = 4F_o^2/\sigma^2(F_o^2)$ for $F_o \geq 144$ and $w = (144/F_o) * 4F_o^2/\sigma^2(F_o^2)$ for $F_o < 144$ led to significantly better results with final discrepancy indices R and R' of 0.0373 and 0.0514. The estimated standard deviation of an observation of unit weight was 1.91. A difference map showed no peak higher than approximately 20% of the height of a typical carbon atom in the structure. The parameters obtained from the refinement with $R = 0.0373$ and $R' = 0.0514$ are thus taken as the final parameters of the structure and are given in Table I. The derived group atom positions are presented in Table II, and root-mean-square amplitudes of vibration for the anisotropically refined atoms are given to Table III. A tabulation of the observed and calculated structure factors used in the final refinements is included in the supplementary material.¹²

Results and Discussion

Synthesis of Neutral Acyl Complexes. The removal of halide ion X⁻ from the acyl anions [RhX(COR)L(mnt)]⁻, where X⁻ = Br⁻, I⁻ and L = PPh₃, PEt₃, by reaction with Ag⁺ in THF and CH₃CN led to the formation of the neutral acyl species Rh(COR)L(mnt)(Sol),^{2,4} where Sol = solvent. For L = PPh₃ and Sol = CH₃CN, analytically pure complexes Rh(COR)(PPh₃)(mnt)(CH₃CN) were isolated for R = Me, Et, and *n*-Pr and have been reported previously.² However, for Sol = THF, only impure complexes of formula Rh(COR)L(mnt)(THF) can be obtained, and these samples appear to be contaminated with trace amounts of the S-alkylated species Rh(CO)L(R-mnt) (vide infra). The formula Rh(COR)L(mnt)(THF) was assigned to these neutral acyl complexes because their NMR spectra exhibit the presence of THF and their IR spectra show the ν_{CO} band at ca. 1710 cm⁻¹.

Recrystallization of Rh(COR)L(mnt)(Sol) in the presence of the neutral ligand L' = C₂H₅N or C₆H₁₁NH₂ resulted in the substitution of L' for solvent and the formation of the new acyl complex Rh(COR)LL'(mnt). On the basis of the structures of the analogous acyl complexes which have been determined by X-ray crystallography, we assign these neutral acyl complexes a five-coordinate, square-pyramidal geometry. While each of the neutral acyl species reveals similar ν_{CO} stretches at ca. 1700 cm⁻¹, their ¹H NMR spectra differ significantly in the region of the α -methylene protons of the acyl group. For L = PPh₃ and L' = CH₃CN and C₂H₅N, the α -methylene protons of the R group are magnetically equivalent. However, for L = PPh₃ and L' = C₆H₁₁NH₂, magnetic nonequivalence of the α -methylene protons is observed. For example, the ¹H NMR spectrum of Rh-

Table I. Final Positional and Thermal Parameters for Rh(CO)(PPh₃)(Et-mnt)^c

atom	x	y	z	$\beta_{11}^{a,b}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.526944 (14)	0.313562 (27)	0.06279 (4)	12.54 (9)	56.1 (3)	90.6 (6)	-5.05 (11)	7.87 (16)	6.72 (29)
P	0.43981 (5)	0.22577 (9)	0.08392 (12)	12.49 (23)	51.7 (9)	93.1 (16)	-2.3 (3)	9.8 (5)	-1.4 (9)
S2	0.61373 (5)	0.41071 (9)	0.05172 (14)	15.14 (25)	57.2 (9)	130.8 (18)	-5.4 (4)	10.5 (5)	13.3 (10)
S1	0.57427 (5)	0.26642 (11)	0.31822 (14)	16.62 (27)	94.0 (12)	103.0 (17)	-7.7 (4)	7.6 (5)	17.4 (11)
OC1	0.49561 (22)	0.3505 (4)	-0.1414 (6)	18.8 (11)	82 (4)	114 (8)	-13.2 (17)	2.7 (23)	17 (5)
O	0.48140 (20)	0.3748 (4)	-0.2696 (5)	32.8 (12)	171 (5)	123 (7)	-24.4 (19)	-0.6 (21)	44 (4)
C1	0.65183 (23)	0.3386 (5)	-0.0620 (6)	21.5 (12)	116 (5)	114 (7)	-4.6 (20)	21.0 (24)	8 (5)
C2	0.66204 (28)	0.2161 (5)	-0.0154 (7)	32.8 (16)	84 (5)	176 (10)	7.6 (22)	22 (3)	-11 (5)
S2C1	0.66281 (20)	0.3894 (4)	0.2363 (5)	14.7 (10)	57 (4)	131 (7)	-3.1 (15)	8.4 (22)	-10 (4)
S2C2	0.71983 (24)	0.4435 (4)	0.2617 (6)	18.0 (13)	76 (4)	173 (9)	-8.6 (19)	9.8 (26)	-26 (5)
S2N	0.76503 (24)	0.4890 (5)	0.2739 (7)	22.8 (13)	140 (6)	282 (12)	-22.1 (23)	19 (3)	-47 (7)
S1C1	0.64370 (20)	0.3312 (4)	0.3465 (5)	15.6 (10)	58 (4)	109 (7)	0.0 (15)	1.3 (21)	-15 (4)
S1C2	0.68295 (22)	0.3194 (4)	0.4990 (6)	20.1 (12)	69 (4)	126 (8)	2.1 (17)	9.6 (27)	-21 (4)
S1N	0.71378 (22)	0.3100 (4)	0.6209 (6)	27.0 (12)	114 (5)	136 (8)	9.7 (19)	-6.8 (26)	-34 (5)
group ^d	x_c	y_c	z_c	ϕ	θ	ρ			
Ph1	0.36328 (10)	0.36928 (17)	0.24016 (24)	-1.1613 (20)	-2.7619 (19)	2.4028 (22)			
Ph2	0.45662 (8)	-0.00751 (15)	0.28126 (21)	1.3146 (18)	-2.5595 (17)	2.5065 (21)			
Ph3	0.35210 (9)	0.15738 (18)	-0.24150 (24)	0.1003 (19)	2.8731 (17)	-2.1950 (20)			

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Values of the thermal parameters have been multiplied by 10^4 . ^c Standard deviations of the least significant figures are given in parentheses. ^d The parameters for refinement of a rigid group have been previously defined (see R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965)). Group thermal parameters B were not refined.

Table II. Derived Parameters for Group Atoms^a

atom	x	y	z	$B, \text{\AA}^2$
PC11	0.39580 (12)	0.30892 (24)	0.1682 (3)	3.12 (8)
PC12	0.33370 (12)	0.30118 (26)	0.1216 (3)	4.60 (10)
PC13	0.30118 (10)	0.3615 (3)	0.1935 (4)	5.34 (12)
PC14	0.33077 (13)	0.42965 (28)	0.3121 (4)	5.06 (11)
PC15	0.39287 (13)	0.43738 (26)	0.3587 (3)	5.00 (11)
PC16	0.42539 (10)	0.37702 (26)	0.2868 (3)	4.01 (9)
PC21	0.44970 (12)	0.09572 (18)	0.2004 (3)	2.90 (8)
PC22	0.49665 (11)	0.02930 (22)	0.1998 (3)	3.32 (8)
PC23	0.50357 (11)	-0.07393 (21)	0.2806 (3)	3.84 (9)
PC24	0.46355 (13)	-0.11074 (18)	0.3621 (3)	3.99 (9)
PC25	0.41660 (12)	-0.04432 (23)	0.3628 (3)	4.26 (10)
PC26	0.40968 (11)	0.05891 (21)	0.2819 (3)	3.61 (9)
PC31	0.38689 (13)	0.18560 (22)	-0.09643 (26)	2.97 (8)
PC32	0.37469 (14)	0.07367 (20)	-0.1300 (3)	3.64 (9)
PC33	0.33990 (15)	0.04545 (20)	-0.2751 (3)	4.96 (11)
PC34	0.31730 (15)	0.12916 (27)	-0.38658 (28)	5.42 (12)
PC35	0.32951 (15)	0.24109 (24)	-0.3530 (3)	5.29 (12)
PC36	0.36430 (14)	0.26931 (18)	-0.2079 (3)	4.20 (10)

^a PC11, PC21, and PC31 carbon atoms are attached to P. Carbon atoms in each benzene ring are numbered consecutively such that PC11 is para to PC14, etc.

Table III. Root-Mean-Square Amplitudes of Vibration (\AA)^a

atom	min	intermed	max
Rh	0.1623 (7)	0.1816 (7)	0.2255 (6)
P	0.1708 (17)	0.1887 (16)	0.2023 (16)
S1	0.1877 (17)	0.1951 (17)	0.2868 (16)
S2	0.1700 (17)	0.2059 (16)	0.2503 (15)
OC1	0.183 (7)	0.196 (8)	0.299 (7)
O	0.200 (6)	0.251 (5)	0.414 (6)
C1	0.189 (7)	0.236 (7)	0.298 (7)
C2	0.238 (7)	0.262 (7)	0.293 (7)
S1C1	0.175 (7)	0.207 (6)	0.237 (6)
S1C2	0.200 (7)	0.223 (7)	0.248 (6)
S1N	0.199 (7)	0.262 (6)	0.328 (6)
S2C1	0.182 (7)	0.214 (6)	0.231 (6)
S2C2	0.187 (8)	0.252 (7)	0.270 (7)
S2N	0.203 (8)	0.324 (7)	0.355 (7)

^a Measured along the principal axes of the thermal ellipsoids.

(COCH₂Ph)(PPh₃)(C₆H₁₁NH₂)(mnt) in CDCl₃ reveals an AB quartet for the α -methylene protons at 3.57 ppm with $\Delta\delta(\text{AB}) = 0.26$ ppm and $J(\text{AB}) = 17$ Hz. The analogous propionyl derivative Rh(COEt)(PPh₃)(C₆H₁₁NH₂)(mnt) also exhibits the magnetic nonequivalence of the α -methylene protons. The

ν_{CO} stretches and ¹H NMR data of these neutral acyl species are given in Table IV.

Syntheses of S-Alkylated Complexes. The S-alkylated complexes Rh(CO)L(R-mnt) were prepared by heating a THF or CHCl₃ solution of Rh(COR)L(THF)(mnt) or Rh(COR)L(CH₃CN)(mnt) (vide supra). The yield depended mainly on the extent of completeness of the rearrangement. With R = Et and *n*-Pr, the rearrangement is near quantitative and the yield is high. For R = CH₃ and PhCH₂, however, the reaction is not complete and only a very low yield of the complex can be obtained by partial recrystallization methods. The reaction of [Rh(CO)(PPh₃)(mnt)]⁻ with Et₃O⁺ to synthesize Rh(CO)(PPh₃)(Et-mnt) has been previously reported.²

The complexes are most readily characterized by a carbonyl stretching frequency in the region 2000–1990 cm⁻¹ (Table IV). The NMR spectrum of Rh(CO)(PET₃)(Et-mnt) in CDCl₃ exhibits a quartet at δ 3.42 and a triplet at δ 1.46 consistent with S attachment. The results from the NMR measurements of other species are in agreement with S attachment as well and are summarized in Table IV. As determined by the X-ray structural analysis (vide infra) the complexes are four-coordinate square-planar Rh(I) d⁸ systems.

Alkyl Group Migration from Acyl Carbon to Sulfur. Heating of Rh(COR)L(L')(mnt), where L = PPh₃, PET₃ and L' = THF, CH₃CN, C₂H₅N, C₆H₁₁NH₂, in THF, CHCl₃, or CH₂Cl₂ solution results in at least partial formation of the S-alkylated species Rh(CO)L(R-mnt) via the migration of the alkyl group from the acyl carbon atom to one of the sulfur donor atoms of the mnt group. For convenience, we will call this process the forward alkyl group migration. In some cases, e.g., where L' = THF, CH₃CN, L = PPh₃, and R = Et, *n*-Pr, the migration is very nearly complete, and Rh(CO)L(R-mnt) can be isolated easily (see Experimental Section). The S-alkylated species generated by heating the solutions of the acyl complexes are characterized by comparing their ν_{CO} and ¹H NMR spectra with those of the pure S-alkylated species isolated independently. In Figure 1, spectra a–c show the progress of the forward alkyl group migration of Rh(COEt)(PPh₃)-(C₅H₅N)(mnt) in CDCl₃ in the presence of 1 extra equiv of C₅H₅N. During the course of migration, the acyl carbonyl stretches at 1692 (s) and 1764 (w) cm⁻¹ of Rh(COEt)-(PPh₃)(C₅H₅N)(mnt) gradually decrease in intensity, and the carbonyl stretch at 2000 cm⁻¹ characteristic of Rh(CO)-(PPh₃)(Et-mnt) grows in (Figure 1b). The reaction reaches equilibrium for this system (vide infra), and no further changes

Table IV. ¹H NMR Data and Carbonyl Stretching Frequencies

complex	chemical shift data (δ) ^a					ν _{CO} ^c
	R group ^{b,f}			other resonances, assignments, etc.		
	α-CH ₂ -	β-CH ₂ -	-CH ₃			
Rh(CO)(PPh ₃)(Me-mnt)			2.96 s	7.5 m (Ph)		1997 ^d
Rh(CO)(PPh ₃)(Et-mnt)	3.38 q		1.46 t	7.4 m (Ph)		2000 ^e
Rh(CO)(PPh ₃)(<i>n</i> -Pr-mnt)	3.28 b	1.84 m	1.07 t	7.4 m (Ph)		2000 ^e
Rh(CO)(PPh ₃)(PhCH ₂ -mnt)	4.54 s			7.4 m (Ph)		1997 ^d
Rh(CO)(PEt ₃)(Me-mnt)			2.86 s	g		1996 ^e
Rh(CO)(PEt ₃)(Et-mnt)	3.42 q		1.46 t	1.94 m, 1.19 m (PEt ₃)		1993 ^e
Rh(COMe)(PPh ₃)(CH ₃ CN)(mnt)			2.20 b	7.4 m (Ph); 1.98 s (CH ₃ CN)		1718 ^d
Rh(COEt)(PPh ₃)(C ₅ H ₅ N)(mnt)	2.42 q		0.76 t	8.04 d (pyr α-H); 7.20 m (aromatic)		1764, 1692 ^e
Rh(COEt)(PPh ₃)(C ₆ H ₁₁ NH ₂)(mnt)	2.28 q		0.63 t	7.42 m (Ph); 3.0-0.8 (C ₆ H ₁₁ NH ₂)		1773, 1687 ^e
Rh(CO- <i>n</i> -Pr)(PPh ₃)(C ₅ H ₅ N)(mnt)	2.41 t	1.32 m	0.68 t	8.05 d (pyr α-H); 7.8 m (aromatic)		1705 ^e
Rh(COCH ₂ Ph)(PPh ₃)(C ₅ H ₅ N)(mnt)	3.63 s			8.06 d (pyr α-H); 7.2 m (aromatic)		1709 ^e
Rh(COCH ₂ Ph)(PPh ₃)(C ₆ H ₁₁ NH ₂)(mnt)	3.57 s			7.6 m (Ph); 3.1-0.75 (C ₆ H ₁₁ NH ₂)		1708 ^e
Rh(COMe)(PEt ₃)(C ₅ H ₅ N)(mnt)			2.21 s	1.85 m, 0.99 m (PEt ₃); 8.66 d (pyr α-H); 7.5 m (pyr β- and γ-H)		1703 ^e
Rh(COEt)(PEt ₃)(CH ₃ CN)(mnt)	2.39 q		0.85 t	h		1766, 1706 ^e

^a In CDCl₃. ^b The R group in Rh(CO)L(R-mnt) or Rh(COR)LL'(mnt). ^c In cm⁻¹. ^d KBr pellet. ^e In chloroform. ^f The coupling constants, $J_{\alpha\beta}$ and $J_{\beta\gamma}$ are all 7 Hz. ^g The complex was not isolated and was generated in situ by heating the corresponding acyl species Rh(CO-Me)(PEt₃)(C₅H₅N)(mnt) in CDCl₃. ^h The complex was not isolated and was generated in situ from the reaction of CH₃CN with Rh(CO)-(PEt₃)(Et-mnt) in CDCl₃.

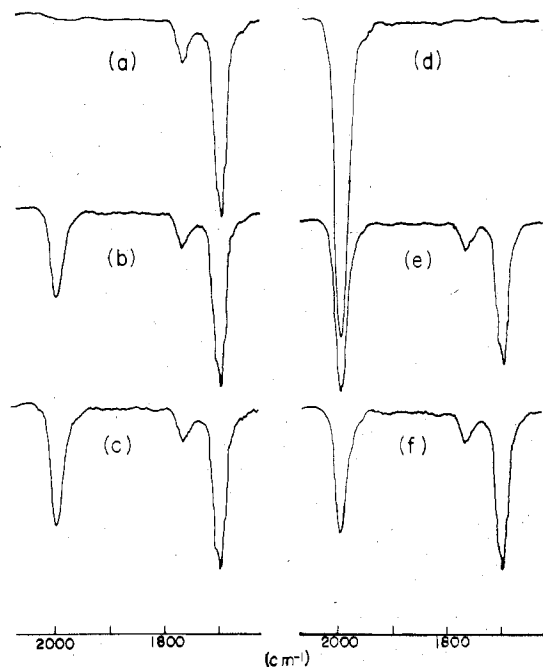
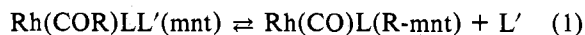


Figure 1. (a) IR spectrum of 0.052 M Rh(COEt)(PPh₃)(C₅H₅N)(mnt) and 0.052 M pyridine in CDCl₃ in the region 2100-1600 cm⁻¹. (b) Spectrum after heating at 70 °C for 10 min. (c) Spectrum after heating at 70 °C for 30 min; the spectrum remained essentially the same on further heating at 70 °C. (d) IR spectrum of 0.053 M Rh(CO)(PPh₃)(Et-mnt) and 0.106 M pyridine in CDCl₃. (e) Spectrum after heating for 30 min at 70 °C. (f) Spectrum after heating for 50 min at 70 °C; no significant changes observed on further heating at the same temperature.

in intensities of both species are observed after the solution is heated at 70 °C for 30 min (Figure 1c). The ¹H NMR spectra of the reaction solution are in agreement with the results observed by IR spectroscopy. Before the CDCl₃ solution was heated, Rh(COEt)(PPh₃)(C₅H₅N)(mnt) shows chemical shifts of the ethyl group at δ 2.42 (q) and 0.76 (t). When the solution is heated, the intensities of these resonances decrease, and the decreases are accompanied by the appearance of new resonances at δ 3.38 (q) and 1.46 (t) which are identified as those of the ethyl protons in Rh(CO)-(PPh₃)(Et-mnt) from independent isolation and characterization. Again, the relative intensities of all the resonances stop

changing after the solution is heated for 30 min, indicating that an equilibrium is established but that the reaction is slow on the NMR time scale. Similar results are also observed by IR and NMR spectroscopies of the other neutral acyl complexes. The alkyl group migration can thus be summarized by eq 1. The reverse migration from the S-alkylated species



to the neutral acyl complex will be discussed further below. Evidence for the dissociation of the coordinated L' to free ligand in going from Rh(COR)LL'(mnt) to Rh(CO)L(R-mnt) can be found in the NMR spectra of the reaction solutions. For example, when the CDCl₃ solution of Rh(CO-*n*-Pr)(PPh₃)(C₅H₅N)(mnt) is heated, the chemical shift at δ 8.05 (d) for the α protons of the coordinated C₅H₅N in the neutral acyl complex decreases in intensity, and the concentration of free pyridine which appears at δ 8.45 (d) increases. Similar observations are also made on heating the CDCl₃ solutions of other acyl pyridine complexes. A possible discrepancy may exist in these observations in that solvent exchange is slow on the NMR time scale, while equivalency of the α-methylene protons of the acyl ligand suggests rapid equilibration. We had previously said that equilibration of these diastereotopic protons by a strictly intramolecular pathway not involving solvent or ligand exchange does not appear to be feasible, thereby giving rise to the possible discrepancy.² However, an alternative explanation of the α-methylene proton equivalency in the neutral systems is accidental degeneracy of their resonances.

The extent of the forward migration varies significantly from one acyl complex to another and depends on the nature of R, L', and L. With L' = CH₃CN and THF, Rh(COEt)-(PPh₃)L'(mnt) and Rh(CO-*n*-Pr)(PPh₃)L'(mnt) in CHCl₃ are quantitatively converted to Rh(CO)(PPh₃)(Et-mnt) and Rh(CO)(PPh₃)(*n*-Pr-mnt), respectively, upon heating. The corresponding acetyl and phenylacetyl complexes, however, show little tendency to rearrange to the S-alkylated species. The same trend is also observed in the analogous triethylphosphine complexes. The tendency for the acyl complexes to convert to the S-alkylated species is thus Et ≫ CH₃, Bz.

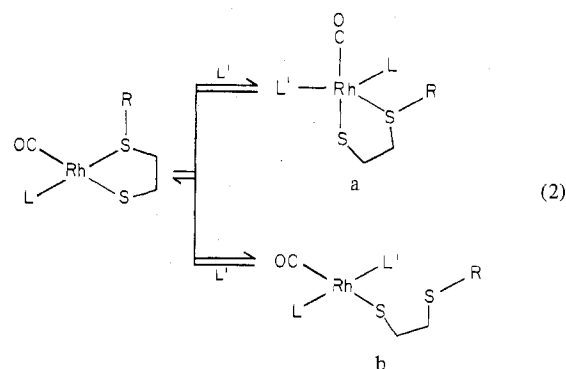
The stability of the neutral acyl complex relative to the corresponding S-alkylated species also appears to be proportional to the coordinating ability of the ligand L'. Thus the tendency for the formation of S-alkylated species from Rh(COEt)(PPh₃)L'(mnt) is in the order L' = THF > CH₃CN

$\gg C_5H_5N, C_6H_{11}NH_2 \gg I^-$, which is approximately the reverse order of their coordinating ability. While the rearrangement from $Rh(COEt)(PPh_3)(THF)(mnt)$ to $Rh(CO)(PPh_3)(Et-mnt)$ is quantitative, no S-alkylated species is observed when solutions of $[RhI(COEt)(PPh_3)(mnt)]^-$ are heated. In general, the acyl anions $[RhI(COR)(PPh_3)(mnt)]^-$ and the neutral systems $Rh(COR)(PEt_3)_2(mnt)$ are relatively stable to heating, and no significant rearrangement is observed with the exception of $Rh(COCH_2C\equiv CH)(PEt_3)_2(mnt)$ which will be discussed later.

Alkyl Group Migration from Sulfur to Acyl Carbon. Addition of a neutral ligand L' , where $L' = CH_3CN, C_5H_5N, C_6H_{11}NH_2$, etc., to a chloroform solution of $Rh(CO)L(R-mnt)$ followed by heating leads to the formation of the neutral acyl species $Rh(COR)LL'(mnt)$. In this reaction, the alkyl group attached to the sulfur donor atom trans to the phosphine ligand migrates to the carbonyl carbon and a new ligand, L' , coordinates to the metal center to yield the corresponding neutral acyl complex. This reaction is the reverse of the alkyl group migration from the acyl carbon to a sulfur atom of the mnt ligand and is represented by the reverse reaction of eq 1. Similar to the forward alkyl group migrations, these "reverse migrations" are best followed by IR and NMR spectroscopies. During the reaction, the concentration of $Rh(COR)LL'(mnt)$ increases at the expense of the S-alkylated species $Rh(CO)L(R-mnt)$. Figure 1d for example shows the carbonyl stretch of $Rh(CO)(PPh_3)(Et-mnt)$ in $CDCl_3$ in the presence of 2 equiv of pyridine. When the $CDCl_3$ solution is heated for 30 min, two new stretches at 1692 and 1764 cm^{-1} appear, indicating the formation of the acyl species $Rh(COEt)(PPh_3)(C_5H_5N)(mnt)$ as illustrated in Figure 1e. Further heating leads finally to the equilibrium mixture of $Rh(COEt)(PPh_3)(C_5H_5N)(mnt)$ and $Rh(CO)(PPh_3)(Et-mnt)$ as indicated in Figure 1f. The ratios of $Rh(CO)(PPh_3)(Et-mnt)$ to $Rh(COEt)(PPh_3)(C_5H_5N)(mnt)$ in Figure 1c,f are equal within experimental error, showing that a true equilibrium exists in this system, having been approached from the two limiting starting materials. The changes in NMR spectra during a "reverse migration" from S-alkylated species to neutral acyl complex are the reverse of those found for the corresponding forward alkyl group migration. For example, $Rh(CO)(PPh_3)(n-Pr-mnt)$ has chemical shifts at δ 3.28 (br), 1.84 (m), and 1.07 (t) in $CDCl_3$. When the solution is heated with added pyridine, the intensities of these peaks decrease, and three other resonances at δ 2.41 (t), 1.32 (m), and 0.68 (t), corresponding to the chemical shifts of $Rh(CO-n-Pr)(PPh_3)(C_5H_5N)(mnt)$, appear in the NMR spectrum. Similar changes are observed with other S-alkylated complexes.

The interconversion between the acyl complex and the corresponding S-alkylated species via the migration of an alkyl group within the coordination sphere is thus established by independent studies of both acyl and S-alkylated systems. The interconversion reaction involves changes in both the rhodium oxidation state and the coordination geometry. As the migration proceeds from the acyl complex to the S-alkylated species, the complex changes from a Rh(III) d^6 system to a Rh(I) d^8 species. This change is accompanied by a change of the coordination geometry from a five-coordinate square pyramid in the acyl system to a four-coordinate square-planar arrangement in the S-alkylated species (vide infra). The change in rhodium oxidation state is compensated within the complex by a redox reaction of the coordinated ligands which for the forward reaction is best described in terms of an oxidation of the dithiolate ligand to a monothioether moiety. Clearly, the accessibility of the Rh(I) and Rh(III) oxidation states in these systems is complemented by the oxidized and reduced forms of the ligand array as the alkyl group migration takes place.

Based on the observation that mixtures of the neutral acyl complex and the S-alkylated species were obtained in certain systems starting with either complex, the notion of equilibrium 1 was formulated. This equilibrium suggested that the addition of excess L' to the solution of the S-alkylated species could serve to drive the reverse migration of the alkyl group. However, when this notion was tested, it was found that another reaction took place instead of the reverse migration. For $L' =$ pyridine and $C_6H_{11}NH_2$, this competing reaction became significant when the ratio of L' to rhodium complex exceeded 10:1; for $L' = PPh_3, PEt_3$, and I^- , the competing reaction was observed to predominate even at low concentrations of L' . The IR spectra of the products of this reaction all exhibit a ν_{CO} at $\sim 1960\text{ cm}^{-1}$ which is about 40 cm^{-1} lower than the corresponding S-alkylated species. The NMR spectra of the new species generated from the reactions of $Rh(CO)L(Et-mnt)$ for $L = PPh_3$ and PEt_3 with PPh_3 as L' in $CDCl_3$ show chemical shifts for the ethyl groups at δ 2.25 (q), 1.24 (t) and δ 2.58 (br), 1.30 (t), respectively. The resonances of the α -methylene protons shift to upper field by approximately 1 ppm relative to the corresponding complexes $Rh(CO)L(Et-mnt)$. The low ν_{CO} and the NMR data are consistent with either an addition reaction to form a five-coordinate complex $Rh(CO)LL'(R-mnt)$, a, or a substitution reaction to form b as shown in eq 2. The other possibility



of L' attacking the R group of $Rh(CO)L(R-mnt)$ to form $Rh(CO)L(mnt)$ and RL'^+ is ruled out by the fact that the resonances of the Et group after the reaction do not show coupling with phosphorus.

Solid-State Structure of $Rh(CO)(PPh_3)(Et-mnt)$. The crystal structure of $Rh(CO)(PPh_3)(Et-mnt)$ consists of discrete molecules arranged in the C-centered triclinic unit cell as illustrated in Figure 2. The closest intermolecular hydrogen...hydrogen contacts (excluding the methyl hydrogens) are as follows: H12...H13, 2.52 Å; H22...H32, 2.58 Å; H35...H34, 2.68 Å. The closest intermolecular hydrogen...nonhydrogen contacts are as follows: H34...S2N, 2.61 Å; H14...S1C2, 2.86 Å; H14...S1N, 2.73 Å; H35...PC14, 2.87 Å; H23...PC32, 2.83 Å; H26...S2N, 2.89 Å. All the intermolecular contacts appear to be normal and are not tabulated.

The structure determination reveals that the ethyl group is bound to one of the sulfur donor atoms in the mnt ligand as expected and that the complex is square planar with the triphenylphosphine ligand trans to the alkylated sulfur atom. From these results, it is established that the S-alkylated complex is a four-coordinate Rh(I) d^8 system in agreement with the conclusions drawn from the previous IR and NMR studies.² A stereoview of the coordination geometry is presented in Figure 3, and the important interatomic distances and angles for the structure are given in Table V.

The present structure is thus similar to that of the previously reported system $Rh(COD)(Me-mnt)$ ¹ which was prepared from the reaction of MeI with $Rh(COD)(mnt)$. In that reaction, the methyl group, rather than coordinating to the

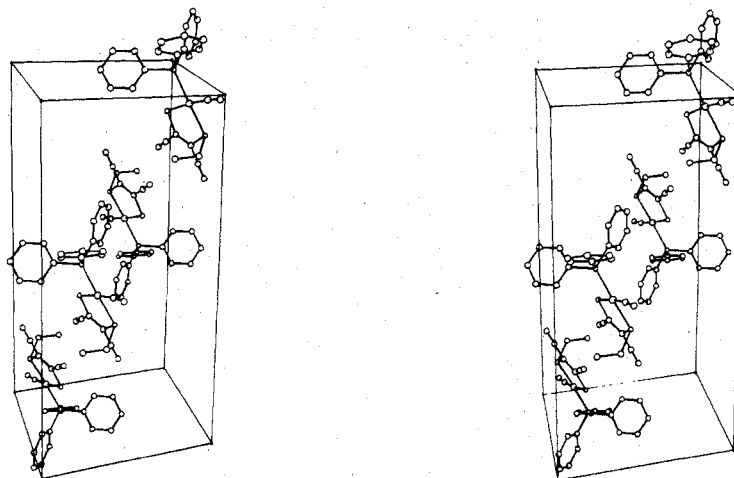


Figure 2. Packing diagram of Rh(CO)(PPh₃)(Et-mnt). The orientation of the unit cell is such that *b* is horizontal and *a* is vertical.

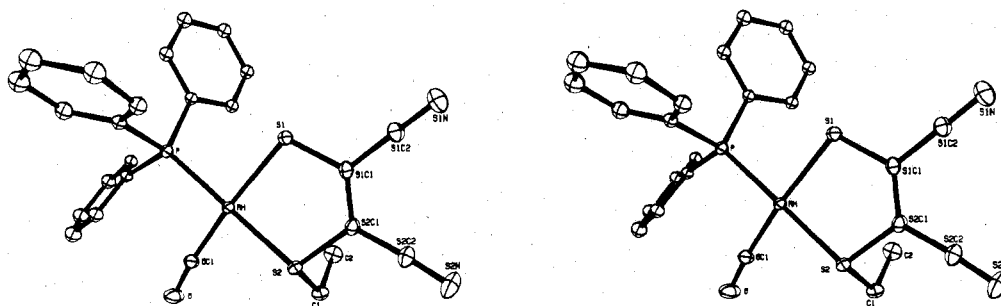


Figure 3. Perspective view of Rh(CO)(PPh₃)(Et-mnt). The thermal ellipsoids correspond to 50% probability distributions.

Rh center to form a rhodium(III) complex, binds to one of the sulfur donor atoms of the mnt ligand, and the complex thus remains as a square-planar d⁸ system.

A detailed analysis of the molecular parameters for the present structure shows the rhodium-ligand bond lengths to be in accord with those expected for a Rh(I) species. The Rh-CO bond length of 1.830 (5) Å agrees with values of 1.80–1.83 Å found in the other Rh(I) systems^{15–17} while the Rh-S bond lengths of 2.312 (1) and 2.322 (1) Å are within the range of 2.27–2.37 Å²¹⁴ observed in other rhodium-thiolate and -thioether structures. The oxidation state of Rh does not appear to be a major factor in influencing the Rh-S bond lengths, whereas in certain cases such as [Rh(COEt)I-(PPh₃)(mnt)]⁻², the nature of the trans ligand does. In the present structure, such an influence does not appear to be observed, but it should be noted that the sulfur donors are themselves quite different, one being a thioether and the other a conjugated thiolate, thus precluding direct comparison. The difference in the trans ligands also makes unmeaningful a comparison of the Rh-S bond lengths involving the two different types of sulfur donor. The observed distances of 2.312 and 2.322 Å for the thioether and thiolate donors, respectively, do not differ greatly and are in reasonable agreement with the corresponding values of 2.290 (2) and 2.303 (2) Å in the related Rh(COD)(Me-mnt) structure.¹ Contradictory results, however, may be found in the literature for metal-thioether and metal-thiolate linkages within the same molecule. For example, in Ru(CO)(C₅H₅)(SC₅H₃(Me)S-C₆H₄Me)¹³ the ruthenium-thioether linkage is 0.06 Å shorter than the ruthenium-thiolate distance, whereas in Rh(MeSC₂H₂S)₃^{14a} the rhodium-thiolate bonds are shorter by 0.04 Å. The Rh-P bond length of 2.297 (1) Å in the present structure is also in the expected range of 2.22–2.36 Å for Rh(I) complexes.¹⁸

The preference to have the triphenylphosphine trans to the alkylated sulfur in the present structure may be rationalized by two factors: (i) electronically, PPh₃, a better electron donor

Table V. Important Intramolecular Distances (Å) and Angles (deg) for Rh(CO)(PPh₃)(Et-mnt)^a

Rh-OC1	1.830 (5)	Rh-P	2.2967 (13)
Rh-S1	2.3217 (13)	Rh-S2	2.3115 (14)
S1-S1C1	1.721 (5)	S2-S2C1	1.756 (5)
S2-C1	1.829 (6)	OC1-O	1.143 (6)
S1C1-S1C2	1.433 (7)	S2C1-S2C2	1.416 (7)
S1C2-S1N	1.141 (6)	S2C2-S2N	1.144 (7)
S1C1-S2C1	1.354 (7)	P-PC11	1.818 (4)
P-PC21	1.8162 (25)	P-PC31	1.8275 (25)
C1-C2	1.515 (8)		
S1-Rh-S2	87.86 (5)	S1-Rh-P	90.82 (4)
S2-Rh-OC1	88.17 (15)	P-Rh-OC1	93.29 (15)
S1-Rh-OC1	175.32 (16)	S2-Rh-P	176.25 (4)
Rh-S1-S1C1	103.06 (16)	Rh-S2-S2C1	104.29 (16)
Rh-S2-C1	110.85 (18)	C1-S2-S2C1	100.79 (23)
Rh-P-PC11	114.27 (10)	Rh-P-PC21	114.60 (10)
Rh-P-PC31	115.47 (11)	PC11-P-PC21	104.36 (15)
PC11-P-PC31	103.42 (14)	PC21-P-PC31	103.27 (12)
Rh-OC1-O	173.6 (5)	S2-C1-C2	114.7 (4)
S1-S1C1-S2C1	124.8 (3)	S1-S1C1-S1C2	115.6 (4)
S2C1-S1C1-S1C2	119.6 (4)	S2-S2C1-S1C1	119.9 (3)
S2-S2C1-S2C2	115.8 (4)	S1C1-S2C1-S2C2	124.1 (4)
S1C1-S1C2-S1N	179.4 (6)	S2C1-S2C2-S2N	176.3 (6)

^a Errors are estimated from the full variance-covariance matrix except for those values involving group refined atoms, in which case only the variances were used.

and poorer π acid than CO, is better suited for ligation trans to the thioether donor than to the thiolate sulfur atom; (ii) the steric interaction between the bulky PPh₃ and the alkyl group is minimized with the alkyl group attached to the sulfur atom trans to PPh₃ rather than cis to it. It is interesting to note that in this steric arrangement with the ethyl group three atoms away from the phenyl groups, the projection of the ethyl group along S-Rh-P axis is such that the ethyl group is staggered between two phenyl rings to further reduce any nonbonded interactions.

Table VI. Equations of Best Least-Squares Planes and Deviations (Å) of Atoms from Them

Plane 1: Rh, P, OC1, S1, S2			
	$1.039X - 1.052Y - 0.388Z - 0.193 = 0$		
Rh	0.0089 (3)	OC1	0.087 (6)
P	-0.055 (1)	S2	-0.068 (1)
S1	0.005 (1)	C1	1.528 ^a
Plane 2: Rh, P, OC1, S1, S1C1, S2, S2C1			
	$1.043X - 1.052Y - 0.385Z - 0.195 = 0$		
Rh	0.0089 (3)	OC1	0.081 (6)
P	-0.058 (1)	S1C1	-0.053 (4)
S1	0.013 (1)	S2C1	-0.041 (5)
S2	-0.065 (1)	C1	1.530 ^a

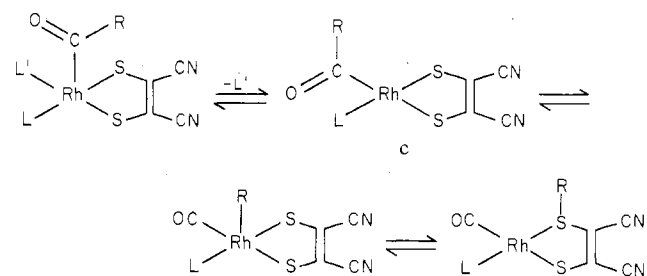
^a Not included in the least-squares plane.

The bond distances and angles within the mnt ligand agree with those observed in the Rh(COD)(Me-mnt) structure.¹ Despite the near equality of the two Rh-S bond lengths, the S-C distances within the chelate ring differ significantly, 1.721 (5) and 1.756 (5) Å, with the larger value involving the alkylated sulfur as expected. The alkylated sulfur is pyramidal with the ethyl group 1.53 Å out of the least-squares coordination plane given by the equation $1.039X - 1.052Y - 0.388Z - 0.192 = 0$. Other least-squares planes and deviations of the atoms from them are given in Table VI.

Intimate Mechanism of the Alkyl Migration Reaction. With regard to the mechanism of this controlled alkyl group migration within the coordinate sphere, two basically different pathways can be postulated: (i) two successive 1,2 migrations from the carbonyl carbon atom to the rhodium metal and then to the sulfur donor, or the reverse of this sequence; (ii) a direct 1,3 migration between the acyl carbon atom and the sulfur donor. The latter corresponds to a 1,3-sigmatropic shift and involves a cyclic four-membered transition state, while the former is based on the formation of a rhodium(III) alkyl carbonyl intermediate to accomplish the migration.

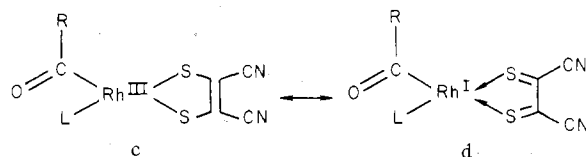
In nearly all cases, monitoring the forward or reverse alkyl group migrations by IR spectroscopy revealed no detectable species other than the S-alkylated and acyl complexes. However, when attempts were made to generate the acyl complex Rh(COCH₂Ph)(PEt₃)(THF)(mnt) by removing the coordinated Br⁻ from [RhBr(COCH₂Ph)(PEt₃)(mnt)]⁻ in THF by using Ag⁺, we observed in the IR spectrum the postulated benzylcarbonylrhodium(III) intermediate which reveals a carbonyl stretch at 2075 cm⁻¹, in addition to the expected acyl complex and a small amount of the S-alkylated species. The ¹H NMR spectrum of a CDCl₃ solution of the mixture obtained by addition of ethanol to the THF solution further verified the existence of the Rh^{III}-CH₂Ph species. The resonances of α-methylene protons of the benzyl group exhibit a complicated splitting pattern in the range δ 3.5–5.0 due to the diastereotopic nature of the α-methylene protons which split each other to an AB quartet and the spin-spin coupling by Rh and phosphorus atoms. Addition of I⁻ to the solution reduces the complicated pattern to an AB quartet, indicating the re-formation of the acyl anion [RhI(COCH₂Ph)(PEt₃)(mnt)]⁻ in agreement with the results observed from IR spectroscopy.

In the case of the neutral acyl complex derived from the reaction of propargyl bromide with [Rh(CO)(PEt₃)(mnt)]⁻ + PEt₃, we found additional evidence for a stable rhodium(III) alkyl carbonyl. When a saturated chloroform solution of Rh(COCH₂CCH)(PEt₃)₂(mnt) was heated at 50 °C, rearrangement from the acyl complex to the corresponding carbonylalkylrhodium(III) species was observed as evidenced by the appearance of a carbonyl stretch at 2060 cm⁻¹ at the expense of the two acyl carbonyl bands of Rh-(COCH₂CCH)(PEt₃)₂(mnt) at 1728 and 1672 cm⁻¹. The

Scheme I

rearrangement was complete within 1 h, and no other carbonyl stretch was found in the IR spectrum of the solution. However, when this chloroform solution was heated at higher temperature, e.g., 70 °C, two new ν_{CO} bands at 1990 and 1960 cm⁻¹ grew in, and the ν_{CO} band at 2060 cm⁻¹ decreased in intensity. The species at 1990 cm⁻¹ is undoubtedly the corresponding S-alkylated complex Rh(CO)(PEt₃)(HCCCH₂-mnt), while the 1960-cm⁻¹ species is most likely the product from the further reaction of Rh(CO)(PEt₃)(HCCCH₂-mnt) with PEt₃ (vide supra).

The observation of the rhodium(III) alkyl carbonyl species in these two special cases and the fact that the migration of the alkyl group from the rhodium(III) alkyl species to the S-alkylated species occurs in the Rh(COCH₂C≡CH)-(PEt₃)₂(mnt) system support the notion of a successive 1,2 migration mechanism as shown in Scheme I. That the forward migration takes place only very slowly in MeCN suggests the necessity of forming a highly unsaturated intermediate or one that readily dissociates a ligand for the migration to occur and thus adds further support to the proposal of successive 1,2 migrations. Species c, which is a tetracoordinate rhodium(III) acyl complex, represents such a highly unsaturated intermediate, and it might be stabilized in this sequence by the well-established dithiolate ↔ dithione resonance structures of the 1,2-dithiolene ligands^{19,20}—i.e., species c is stabilized by the resonance structure d.



While both the alkylation and dealkylation of a sulfur donor ligand^{21–23} and the insertion and “deinsertion” of carbonyl²⁴ are well-known processes, the present rhodium carbonyl dithiolates appear unique in having both processes occurring or, at the very least, accessible within the same systems. The migration of the R group within the coordination sphere of these complexes involves internal oxidative addition and reductive elimination reactions in which an electron pair of the dithiolate ligand serves in a complementary way to the electron pair of the Rh(I)/Rh(III) couple. The alkyl group migration reactions of these Rh dithiolates thus have interesting implications in the area of two-substrate activation.

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Registry No. Rh(CO)(PPh₃)(Me-mnt), 70728-71-1; Rh(CO)-(PPh₃)(Et-mnt), 63159-27-3; Rh(CO)(PPh₃)(*n*-Pr-mnt), 70728-72-2; Rh(CO)(PPh₃)(PhCH₂-mnt), 70728-73-3; Rh(CO)(PEt₃)(Me-mnt), 70728-74-4; Rh(CO)(PEt₃)(Et-mnt), 70774-45-7; Rh(COMe)-(PPh₃)(CH₃CN)(mnt), 70728-75-5; Rh(COEt)(PPh₃)(C₆H₅N)(mnt), 70728-76-6; Rh(COEt)(PPh₃)(C₆H₁₁NH₂)(mnt), 70728-77-7; Rh-

(CO-*n*-Pr)(PPh₃)(C₅H₅N)(mnt), 70728-78-8; Rh(COCH₂Ph)(PPh₃)(C₅H₅N)(mnt), 70728-79-9; Rh(COCH₂Ph)(PPh₃)(C₆H₁₁NH₂)(mnt), 70728-80-2; Rh(OMe)(PEt₃)(C₅H₅N)(mnt), 70728-81-3; Rh(COEt)(PEt₃)(CH₃CN)(mnt), 70728-82-4; [(*n*-Bu)₄N][Rh(CO)(PPh₃)(mnt)], 29985-52-2; [(*n*-Bu)₄N][Rh(CO)(PEt₃)(mnt)], 70728-83-5.

Supplementary Material Available: A listing of observed and calculated structure factors for Rh(CO)(PPh₃)(Et-mnt) (20 pages). Ordering information is given on any current masthead page.

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ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plotting program. All computations were performed on an IBM 360/65 computer.

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Pentagonal-Bipyramidal Complexes. Synthesis and Characterization of Aqua(nitrato)[2,6-diacetylpyridinebis(benzoic acid hydrazone)]cobalt(II) Nitrate and Diaqua[2,6-diacetylpyridinebis(benzoic acid hydrazone)]nickel(II) Nitrate Dihydrate

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The reaction of 2,6-diacetylpyridinebis(benzoic acid hydrazone), DAPBH, with Co(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O yields the pentagonal-bipyramidal complexes [Co(DAPBH)(H₂O)(NO₃)]⁺NO₃⁻ (I) and [Ni(DAPBH)(H₂O)₂]²⁺(NO₃⁻)₂·2H₂O (II), respectively. The infrared spectra suggested differences in the interaction of the metal with DAPBH and also the presence of a coordinated nitrate in I but not in II. Complex I crystallizes in the monoclinic space group *P*₂₁/*n*, with four molecules per cell. The unit cell dimensions are *a* = 7.361 (2), *b* = 17.423 (5), and *c* = 19.876 (5) Å with β = 97.86 (2)°. Complex II crystallizes in the orthorhombic space group *Pbca*, with eight molecules per cell. The cell dimensions are *a* = 24.624 (3), *b* = 15.942 (7), and *c* = 14.589 (3) Å. Intensity data for both complexes were measured by using Mo Kα radiation. The structures were determined by the heavy-atom method and refined by least-squares techniques to an unweighted residual of 0.035 for I and 0.059 for II. The cations in both complexes are pentagonal bipyramids. The DAPBH ligand is in the equatorial plane and one monodentate nitrate and one water molecule are in the axial positions of I, with two water molecules axially coordinated in II. The equatorial plane distances are as follows: Co-N of 2.194, 2.203, and 2.190 Å; Co-O of 2.150 and 2.229 Å; Ni-N of 2.018, 2.090, and 2.178 Å; Ni-O of 2.282 and 2.477 Å. The large difference in the Ni-O bond lengths is attributed to Jahn-Teller distortions in the Ni²⁺ case and explains the differences in the infrared spectra of I and II.

Introduction

The role that seven-coordinate intermediates play in the substitution reactions of six- and eight-coordinate complexes and in the oxidative-addition reactions of five-coordinate species has stimulated interest in complexes with high coordination numbers.^{1,2} A further impetus came from our early reports that the then relatively rare pentagonal-bipyramidal (PB) complex could be stabilized by planar pentadentate ligands such as DAPSC (2,6-diacetylpyridinebis(semicarbazone)) or DAPPH (2,6-diacetylpyridinebis(2'-pyridylhydrazone)).³⁻⁷ A number of other seven-coordinate complexes have now been synthesized by utilizing either planar⁸ or macrocyclic pentadentate ligands⁹ and their structures have been determined by X-ray diffraction techniques.

Although the majority of the PB complexes of DAPSC and DAPPH are relatively regular, large distortions were observed in the high-spin Cr(DAPSC)(H₂O)₂³⁺ and Ni(DAPSC)-

(H₂O)₂²⁺ cations.^{3,6} These distortions could be explained on the basis of the Jahn-Teller¹⁰ theorem, the observed spin state, and the expected splitting of the d orbitals in a PB field.¹¹ Since the Cr(III) and Ni(II) complexes represented the first examples of Jahn-Teller distortions in a PB field, we decided to synthesize other seven-coordinate Ni(II) complexes to explore in greater detail these distortions. Furthermore, to investigate the general utility of planar pentadentate ligands in stabilizing PB complexes, we prepared a series of ligands derived from the reaction of 2,6-diacetylpyridine with various acid hydrazides. The donor properties of these planar pentadentate hydrazone ligands should be dependent upon the nature of the parent acid hydrazone. Our present study demonstrates that PB Co(II) and Ni(II) complexes of 2,6-diacetylpyridinebis(benzoic acid hydrazone), DAPBH, can be prepared. In addition, the Ni(II) complex was found to be distorted in a manner which is very similar to that found in