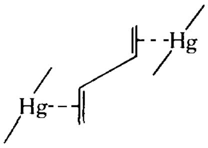
to 40 K followed by cooling to 10 K caused a marked decrease in the intensity of the free butadiene band at 906.0 cm^{-1} and an increase in the intensities of both c and c′ bands. Since this experiment was carried out with a high concentration of $HgCl_2$, it is reasonable to assign the 927.7-cm^{-1} band (c′) to the 2:1 complex, $(HgCl_2)_2(C_4H_6)$. Bands characteristic of the 2:1 complex could not be observed in other regions of the spectra probably because other modes are much less sensitive to the coordination of the second $HgCl_2$ molecule. In the low-frequency region, the Hg–Cl stretching bands of these complexes were observed at 404.5 ($Hg^{35}Cl_2$) and 400.9 cm^{-1} ($Hg^{35}Cl^{37}Cl$). However, no spectral changes were noted by changing the relative concentration of $HgCl_2$. A possible structure of the 2:1 complex may be depicted as



since butadiene retains its symmetric-trans configuration and $HgCl_2$ coordinates to the C═C bond in a side-on fashion.

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The Addition of Alkyl Halides to Rhodium(I) Dithiolene Complexes. The Synthesis, Structure, and Chemical Properties of Rhodium(III) Acyl Species

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Abstract: The Rh(I) complex $[Rh(CO)(PPh_3)(mnt)]^-$ (mnt = maleonitriledithiolate) reacts with alkyl halides R–X (X = I, R = Me, Et, *n*-Pr, *n*-Bu, *n*-$C_{10}H_{21}$; X = Br, R = Bz) to form a series of stable Rh(III) acyl anions. The complexes have been characterized by IR and ^1H NMR spectroscopy, and the structure of a representative member of the series (R = Et) has been determined by single-crystal x-ray diffraction. In all of the complexes (except for R = Me) the α-methylene protons of the acyl ligand are magnetically nonequivalent indicating that the acyl group is bonded to a chiral center which is preserved on the NMR time scale. The structure determination of $(AsPh_4)[RhI(COEt)(PPh_3)(mnt)]$ shows the complex to crystallize in space group $P2_1/a$ ($C_{2h}{}^5$) in a cell of dimensions a = 18.466 (6), b = 13.608 (5), c = 19.088 (8) Å, β = 106.39 (1)° with four molecules per unit cell (ρ_{exptl} = 1.54 (2), ρ_{calcd} = 1.558 g/cm^3). The Rh(III) acyl anion adopts a square pyramidal structure with the acyl group occupying the apical position at a distance of 2.006 (14) Å from the Rh(III) ion. In the base of the square pyramid the Rh–S distances are unequal, reflecting the differing influence of the trans ligands (2.323 (3) Å trans to phosphine vs. 2.269 (3) Å trans to iodide). The structure determination thus affirms the diastereotopic nature of the α-methylene protons in the static structure. Addition of Ag^+ to solutions of the Rh(III) acyl anions results in the removal of iodide and the formation of neutral acyl species in which the α-methylene protons appear magnetically equivalent. Solvent exchange is presumed to ocur rapidly in these systems since neutral five-coordinate complexes can be isolated in the presence of coordinating solvents. Heating solutions of the neutral acyl species in THF or CH_2Cl_2 results in the migration of the R group (R = Me, Et, Bz) from the acyl carbon to one of the sulfur donor atoms of the dithiolene ligand to give S-alkylated Rh(I) complexes of the formula $[Rh(CO)(PPh_3)(R\text{-mnt})]$. The reaction of $[Rh(CO)(PPh_3)(mnt)]^-$ with $OEt_3{}^+$ yields a mixture of the *S*-ethyl complex and the neutral propanoyl species which upon warming in THF converts entirely to the $Rh(CO)(PPh_3)(Et\text{-mnt})$ complex. The dicarbonyl complex $[Rh(CO)_2(mnt)]^-$ is considerably less reactive than its monosubstituted triphenylphosphine derivative.

The formation of rhodium acyl species occurs in a variety of metal promoted and catalyzed reactions ranging from the decarbonylation of aldehydes and acid chlorides[1,2] to ketone syntheses,[3,4] hydroformylation[5,6] and the carbonylation of methanol to acetic acid.[7] In many of these studies the existence of Rh acyl intermediates has been established by observation of the characteristic carbonyl stretch around 1700 cm^{-1} but in others the transient acyl species are proposed based solely on the reaction products. In cases where stable Rh acyl complexes have been synthesized, their characterization has been mainly by IR and NMR spectroscopy.[1,2,8-10] Only one x-ray structure determination of a rhodium acyl complex has been reported to date.[11] Consequently there has been little systematic development of the structure-reactivity relationship for these chemically interesting systems.

In this paper, we report the synthesis and characterization of a series of anionic and neutral rhodium(III) acyl complexes, and the x-ray structure determination of a representative member of this series. These complexes are derived from the anionic Rh(I) dithiolate systems [Rh(CO)L(mnt)]$^-$, where L = CO, PPh$_3$ and mnt = maleonitriledithiolate, first synthesized by Connelly and McCleverty.[12] Although the oxidative addition chemistry of these d^8 complexes was briefly surveyed at the time of this initial report, only poorly characterized adducts of I$_2$, HgCl$_2$, and TCNE were obtained. More recently in our laboratory,[13] the related Rh(I) complexes [Rh(diene)(mnt)]$^-$ (diene = 1,5-COD, NBD) were synthesized, and found to react with methyl iodide and benzyl bromide to yield neutral adducts aklylated at one of the sulfur donor atoms, and not at the metal center as anticipated. These adducts were shown to possess an essentially square planar coordination geometry about the unoxidized Rh(I) ion, and to exhibit fluxional behavior arising in part from inversion at the alkylated pyramidal sulfur.[13]

The notion of coupling the nucleophilicity of the dithiolate sulfur donor atoms with the established reaction chemistry of square planar Rh(I) appealed to us in terms of substrate activation, and prompted us to undertake the present study of the reaction chemistry of these potentially bifunctional complexes, [Rh(CO)L(mnt)]$^-$, with a variety of alkyl halides.

Experimental Section

Materials. Rhodium trichloride hydrate (Matthey Bishop), tetraphenylarsonium chloride, tetraphenylphosphonium chloride (Ventron), triphenylphosphine, alkyl iodides (Eastman), and triethyloxonium hexafluorophosphate (Aldrich) were used as purchased. All solvents were of reagent grade, and were dried and degassed before use.

The sodium salt of maleonitriledithiolate, Na$_2$mnt, was prepared according to the procedure of Davison and Holm.[14] The method of Cleare and Griffith[15] was used to synthesize dichlorodicarbonylrhodate(I), [RhCl$_2$(CO)$_2$]$^-$, as either its AsPh$_4$$^+$ or PPh$_4$$^+$ salt.

Preparation of Complexes. All syntheses were routinely performed under an atmosphere of prepurified nitrogen using modified Schlenk techniques. Elemental analyses were carried out by Micro-Analysis, Inc., Wilmington, Del.

Tetraphenylarsonium Dicarbonyl(maleonitriledithiolato)rhodium(I), (AsPh$_4$)[Rh(CO)$_2$(mnt)]. Sodium maleonitriledithiolate (2.72 g) and (AsPh$_4$)[RhCl$_2$(CO)$_2$] (8.11 g) were dissolved in 200 mL of a 1:1 solution of acetone–ethanol. The solution was stirred for 2 h during which time precipitation of NaCl was observed. Degassed H$_2$O sufficient to dissolve the NaCl was added, and the solution was then reduced in volume using an aspirator pump until a brown precipitate was obtained. This precipitate was filtered, redissolved in a minimum of acetone, and chromatographed on alumina using acetone as eluent. A pale yellow band separated from the brown residue and was collected. Evaporation yielded pale yellow crystals (yield 91%). The tetraphenylphosphonium salt was prepared similarly. Both salts are obtained analytically pure, and the [Rh(CO)$_2$(mnt)]$^-$ anion is readily identified by the characteristic IR bands at 2195 (ν_{CN}) and 2035 and 1985 cm^{-1} (ν_{CO}).

Tetraphenylphosphonium Carbonyl(triphenylphosphine)(maleonitriledithiolato)rhodium, (PPh$_4$)[Rh(CO)(PPh$_3$)(mnt)]. This complex was prepared by a slight modification of the procedure reported by Connelly and McCleverty.[12] To 4.0 g of (PPh$_4$)[Rh(CO)$_2$(mnt)] in 50 mL of acetone was added 1.8 g of triphenylphosphine in 30 mL of acetone. Immediate gas evolution was observed. After gas evolution had ceased, 100 mL of 2-propanol was added, and the solution was reduced in volume using a rotary evaporator. The yellow precipitate which forms was filtered, washed with ethanol–H$_2$O, and dried in vacuo. A quantitative yield of (PPh$_4$)[Rh(CO)(PPh$_3$)(mnt)] was thus obtained. Characteristic IR bands are 2195 (ν_{CN}) and 1960 cm^{-1} (ν_{CO} broad). No evidence for acetone of crystallization is observed in contrast with Connelly and McCleverty's method.[12]

General Procedure for the Synthesis of Anionic Acyl Complexes of Formula [RhX(COR)(PPh$_3$)(mnt)]$^-$. These complexes were synthesized as their EPh$_4$$^+$ salts (E = P, As) in the following way. A minimum amount of solvent such as acetonitrile, acetone, THF, or methylene chloride was added to 0.2 g of (EPh$_4$)[Rh(CO)(PPh$_3$)(mnt)] and 3 mL of alkyl halide RX to form a homogeneous solution. The reaction was then stirred at room temperature. During the course of the reaction, ν_{CO} of the starting complex at 1960 cm^{-1} decreased in intensity, and an acyl stretching frequency around 1700 cm^{-1} grew in. The reaction solution changed color from yellow to orange, and the reaction was judged complete by the disappearance of the band at 1960 cm^{-1}. Different alkyl halides and the times required for reaction were: MeI, less than 5 min; EtI, 2 h; *n*-PrI, 5 h; *n*-BuI, 6 h; *n*-C$_{10}$H$_{21}$I, 1 day; BzBr, 20 min.

After the reaction was judged complete, an additional 5 mL of solvent and 15 mL of absolute ethanol were added to the orange solution. Evaporation of solvent using an aspirator followed by the addition of *n*-hexane led to the desired product as a brown precipitate. Recrystallization was accomplished using either acetone–ethanol and hexanes or dichloromethane–ether. Yields were ca. 90%. Analytical data follow.

(PPh$_4$)[RhI(COMe)(PPh$_3$)(mnt)]. Calcd for C$_{48}$H$_{38}$OIN$_2$P$_2$RhS$_2$: C, 56.82; H, 3.77; N, 2.76; I, 12.51. Found: C, 56.46; H, 3.39; N, 3.06; I, 12.73.

(PPh$_4$)[RhI(COEt)(PPh$_3$)(mnt)]. Calcd for C$_{49}$H$_{40}$OIN$_2$P$_2$RhS$_2$: C, 57.21; H, 3.91; N, 2.72; I, 12.34. Found: C, 56.69; H, 4.06; N, 3.42; I, 10.64.

(PPh$_4$)[RhI(COPr)(PPh$_3$)(mnt)]. Calcd for C$_{50}$H$_{42}$OIN$_2$P$_2$RhS$_2$: C, 57.59; H, 4.06; N, 2.69; I, 12.17. Found: C, 57.85; H, 4.75; N, 2.54; I, 11.41.

(PPh$_4$)[RhI(COBu)(PPh$_3$)(mnt)]. Calcd for C$_{51}$H$_{44}$OIN$_2$P$_2$RhS$_2$: C, 57.96; H, 4.20; N, 2.65; I, 12.01. Found: C, 58.20; H, 4.33; N, 2.79; I, 11.76.

(AsPh$_4$)[RhI(CO-*n*-C$_{10}$H$_{21}$)(PPh$_3$)(mnt)]. Calcd for C$_{57}$H$_{56}$OAsIN$_2$PRhS$_2$: C, 57.78; H, 4.73; N, 2.36; I, 10.71. Found: C, 58.94; H, 4.93; N, 2.32; I, 10.20.

(PPh$_4$)[RhBr(COBz)(PPh$_3$)(mnt)]·½Me$_2$CO (recrystallized from acetone + hexanes). Calcd for C$_{54}$H$_{42}$OBrN$_2$P$_2$RhS$_2$·½C$_3$H$_6$O: C, 62.48; H, 4.25; N, 2.63; Br, 7.49. Found: C, 62.79; H, 4.29; N, 2.53; Br, 7.29.

Procedure for the Synthesis of Neutral Acyl Complexes [Rh(COR)(PPh$_3$)(mnt)(solvent)]. The following procedure is typical of the synthesis of the neutral acyl complexes. To a solution of 0.5 g of (AsPh$_4$)[RhI(COEt)(PPh$_3$)(mnt)] in 10 mL of CH$_3$CN was added 0.1 g of AgNO$_3$. A precipitate of AgI was formed which was filtered from the reaction solution and washed with CH$_2$Cl$_2$, the latter being combined with the reaction solution. Addition of 15 mL of ethanol followed by concentration of the reaction solution and storage at −10 °C led to the formation of an orange crystalline precipitate. Recrystallization was accomplished from CH$_3$CN–CH$_2$Cl$_2$–ethanol solutions. For the acetyl complex (R = Me), recrystallization from pyridine–CH$_2$Cl$_2$–ethanol solutions led to analytically pure material. Yields are approximately 85%. Analytical data follow.

Rh(COEt)(PPh$_3$)(mnt)(CH$_3$CN). Calcd for C$_{27}$H$_{23}$ON$_3$PRhS$_2$: C, 53.74; H, 3.84; N, 6.96; P, 5.13. Found: C, 53.57; H, 3.85; N, 6.84; P, 4.95.

Rh(CO-*n*-Pr)(PPh$_3$)(mnt)(CH$_3$CN). Calcd for C$_{28}$H$_{25}$ON$_3$PRhS$_2$: C, 54.46; H, 4.08; N, 6.81. Found: C, 54.52; H, 4.08; N, 6.27.

Rh(COMe)(PPh$_3$)(mnt)(C$_5$H$_5$N). Calcd for C$_{29}$H$_{23}$ON$_3$PRhS$_2$: C, 55.51; H, 3.69; N, 6.73. Found: C, 55.44; H, 3.67; N, 6.60.

S-Alkylations. The Synthesis of Carbonyl(triphenylphosphine)(maleonitrile-1-ethylthio-2-thiolato)rhodium, Rh(CO)(PPh$_3$)(Et-mnt). The complex may be prepared in one of three ways. **Method (a).** (AsPh$_4$)[RhI(COEt)(PPh$_3$)(mnt)] (0.22 g) was dissolved in 10 mL of THF–CH$_2$Cl$_2$ (1:1 v/v), and to the solution was added 0.05 g of AgBF$_4$. After removal of the AgI precipitate, the solution was heated at 55 °C for 10 min. Further removal of AgI followed by the addition of ethanol and then removal of solvent using an aspirator pump led to an orange microcrystalline product. Further crystallization occurred upon storing the solution at −10 °C. Prolonged heating leads to decomposition of the product. Yield by this method was ca. 85%. Calcd for C$_{25}$H$_{20}$ON$_2$PRhS$_2$: C, 53.39; H, 3.58; N, 4.98. Found: C, 53.96; H, 3.89; N, 4.86. Characteristic ν_{CO} was observed at 1990 cm^{-1}.

Method (b). Rh(COEt)(PPh$_3$)(mnt)(CH$_3$CN) in THF–CH$_2$Cl$_2$ (1:1 v/v) was heated at 55 °C for 10 min. The reaction solution was treated in the same way as above and the product obtained was identical.

Method (c). To a solution of (AsPh$_4$)[Rh(CO)(PPh$_3$)(mnt)] (0.2 g) in 10 mL of THF was added a slight molar excess of (Et$_3$O)BF$_4$. The infrared spectrum of the solution showed the presence of two species, one the neutral complex alkylated at sulfur and the other the neutral acyl complex described above. Heating of the solution at 55 °C for 10 min allowed the latter complex to rearrange to the former as judged by the disappearance of the acyl carbonyl stretch. Addition of ethanol followed by solvent evaporation and storage at −10 °C led to precipitation of orange microcrystals of Rh(CO)(PPh_3)(Et-mnt).

Characterization of Compounds. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. Most samples were examined as KBr pellets. Routine ^1H NMR spectra were measured on a JEOL MH-100 NMR spectrometer in CD_3CN or $CDCl_3$ solutions with Me_4Si as an internal standard.

Crystal Structure Analysis of Tetraphenylarsonium Iodopropanoylmaleonitriledithiolato(triphenylphosphine)rhodium(III). Data Collection and Reduction. Brown crystals of [$AsPh_4$][RhI(COEt)(PPh_3)(mnt)] suitable for single-crystal x-ray diffraction study were grown at −10 °C from dichloromethane-ether solution. On the basis of Weissenberg and precession photographs it was established that the crystals belong to the monoclinic system. The observed systematic absences of $k = 2n + 1$ for $0k0$ and $h = 2n + 1$ for $h0l$ establish the space group as $P2_1/a$ which is a nonstandard setting of $P2_1/c$ (C_{2h}^5).[16] The lattice constants at 22 °C were determined from a least-squares refinement of the setting angles of 12 high angle reflections ($\sin\theta/\lambda \geq 0.300$).[17] The reflections were carefully centered, using Mo $K\alpha_1$ radiation (λ 0.709 261 Å), on a Picker FACS-1 diffractometer equipped with a graphite monochromator. The lattice constants are a = 18.466 (6) Å, b = 13.608 (5), Å, c = 19.088 (8) Å, and β = 106.39 (1)°. An experimental density of 1.54 (2) g/cm^3 determined by the flotation method agrees with a value of 1.558 g/cm^3 calculated for $Z = 4$.

The mosaicity of the crystal used for intensity measurements was examined by means of the narrow source, open counter ω scan technique.[18] The full widths of these scans were acceptably low, ranging from 0.20 to 0.35°. The crystal dimensions were approximately 0.09 × 0.11 × 0.62 mm, and the crystal was mounted with the b^* axis coincident with the ϕ axis of the diffractometer.

Intensities were measured by the θ–2θ scan technique. The takeoff angle for the x-ray tube was 3.0°. The scan was from 0.7° below the $K\alpha_1$ peak to 0.7° above the $K\alpha_2$ peak. The scan rate was 1°/min, and backgrounds were counted for 10 s at each end of the scan range for data with $2\theta \leq 35°$ and for 20 s for data with $35° < 2\theta \leq 40°$. Attenuator foils were automatically inserted when the intensity of the diffracted beam reached 10 000 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 40° from the quadrant with $k \geq 0$ and $l \geq 0$. Three standard reflections were monitored every 77 observations. The intensities of the standards varied by less than ±3% throughout data collection. A total of 4742 reflections was observed. The values of I and $\sigma^2(I)$ were obtained using the expressions previously described.[19] The value of p used in the expression for the variance was chosen as 0.04.[20] Values of I and $\sigma^2(I)$ were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections. Because of the small linear absorption coefficient (μ_{Mo} = 2.62 cm^{-1}), no absorption correction was performed.

Of the 260 reflections systematically absent as a result of the a glide, all had $F_o^2 < 3\sigma(F_o^2)$ and only five had $F_o^2 > 2\sigma(F_o^2)$. The equivalent reflections $h0l$ and $\bar{h}0l$ were averaged before final computations. An agreement factor of 2.7% for the 178 reflections measured twice was obtained. The final data set thus consisted of 4564 independent reflections of which 2557 had $F_o^2 \geq 3\sigma(F_o^2)$.

Solution and Refinement of the Structure. The structure was solved by standard heavy atom methods. A three-dimensional Patterson function map was computed, and from it the positions of the Rh and I atoms were determined. A least-squares refinement of the positional and thermal parameters of these atoms together with a single scale factor led to discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.60 and 0.50, respectively. Although initially reversed, the assignments of the Rh and I positions were quickly corrected. All remaining nonhydrogen atoms in the structure were located from a succession of difference Fourier syntheses based on the phases of previously located and refined atoms.[21]

The complete trial structure of 56 nonhydrogen atoms was refined by a least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. In these refinements only the reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were included. Scattering factors for neutral Rh, I, As, S, P, C, N, and O were those of Cromer and Mann.[22] The scattering factor table for hydrogen was that of Stewart et al.[23] The effects of anomolous dispersion for Rh, I, and As were included in the calculation of $|F_c|$; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Lieberman.[24] The phenyl rings were treated as rigid groups in the refinements assuming D_{6h} symmetry and d(C–C) = 1.392 Å. Each group atom was assigned its own variable isotropic thermal parameter, while all nongroup atoms were allowed to vary according to an anisotropic thermal model. In the final cycles of refinement, contributions from all of the phenyl ring hydrogen atoms were included in F_c based on d(C–H) = 0.95 Å and

Table I. Final Positional and Thermal Parameters for ($AsPh_4$)[RhI(COEt)(PPh_3)(mnt)]

Atom	x	y	z	β_{11}[a,b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	−0.106 43 (5)[c]	0.204 11 (7)	0.225 17 (5)	37.2 (4)	57.6 (7)	28.8 (3)	−12.0 (4)	7.53 (28)	−8.6 (4)
Rh	−0.209 99 (5)	0.058 21 (7)	0.187 85 (5)	22.7 (4)	37.2 (7)	19.1 (3)	0.8 (4)	7.6 (3)	−0.7 (4)
As	0.324 86 (7)	0.014 11 (10)	0.437 28 (7)	24.4 (5)	59.9 (11)	24.0 (5)	0.2 (6)	8.2 (4)	0.8 (6)
S1	−0.162 13 (18)	−0.004 28 (28)	0.305 08 (16)	31.2 (14)	69. (3)	20.3 (12)	−0.9 (17)	6.0 (10)	5.7 (16)
S2	−0.315 30 (16)	−0.033 50 (24)	0.176 43 (16)	22.7 (12)	47.1 (25)	23.7 (12)	−0.8 (14)	8.0 (10)	6.6 (14)
P	−0.270 91 (17)	0.138 95 (24)	0.080 05 (17)	23.9 (13)	31.3 (23)	22.5 (12)	0.8 (14)	12.5 (10)	−1.1 (14)
O	−0.185 3 (4)	−0.063 2 (6)	0.078 5 (5)	27. (3)	75. (7)	38. (4)	13. (4)	7. (3)	−20. (5)
C1	−0.154 5 (7)	−0.034 0 (8)	0.139 3 (7)	43. (7)	27. (9)	23. (5)	−13. (6)	7. (5)	−12. (5)
C2	−0.076 4 (6)	−0.063 2 (11)	0.180 4 (7)	16. (5)	118. (14)	38. (6)	34. (7)	−10. (4)	−22. (8)
C3	−0.039 6 (7)	−0.121 0 (13)	0.131 5 (9)	30. (6)	133. (16)	66. (8)	37. (8)	5. (6)	−42. (10)
N2	−0.395 9 (8)	−0.225 9 (10)	0.265 8 (7)	67. (7)	102. (13)	36. (5)	−30. (8)	21. (5)	4. (7)
N1	−0.199 2 (8)	−0.210 8 (11)	0.419 8 (7)	84. (8)	110. (14)	36. (6)	26. (8)	23. (6)	26. (7)
S1C1	−0.227 3 (7)	−0.091 6 (9)	0.309 3 (7)	34. (6)	57. (11)	19. (5)	17. (6)	10. (5)	9. (6)
S1C2	−0.210 7 (8)	−0.157 8 (12)	0.371 8 (9)	48. (7)	66. (13)	42. (7)	−1. (8)	24. (6)	−4. (8)
S2C1	−0.293 5 (8)	−0.102 8 (9)	0.256 1 (7)	39. (6)	47. (10)	23. (5)	0. (7)	19. (5)	7. (6)
S2C2	−0.349 7 (9)	−0.171 6 (11)	0.262 1 (7)	51. (8)	48. (12)	14. (5)	9. (7)	11. (5)	−3. (6)

Group	x_c[d]	y_c	z_c	ϕ	θ	ρ	B, Å^2
PR1	−0.415 28 (28)	0.0426 (4)	−0.034 92 (26)	0.549 (4)	−3.031 (5)	−2.592 (4)	0.0 (0)
PR2	−0.331 50 (28)	0.3421 (5)	0.127 93 (28)	−0.703 (8)	2.326 (6)	2.502 (8)	0.0 (0)
PR3	−0.180 5 (3)	0.1864 (3)	−0.038 46 (28)	−1.840 (6)	−2.680 (4)	−1.876 (5)	0.0 (0)
AsR1	0.369 0 (3)	−0.1007 (4)	0.594 0 (3)	1.676 (6)	−2.924 (5)	2.015 (5)	0.0 (0)
AsR2	0.393 10 (26)	0.2345 (5)	0.484 9 (3)	2.843 (27)	−1.757 (5)	1.636 (27)	0.0 (0)
AsR3	0.141 4 (3)	0.0325 (4)	0.375 44 (28)	−0.039 (6)	−2.528 (5)	−3.071 (6)	0.0 (0)
AsR4	0.387 3 (3)	−0.0748 (5)	0.305 2 (3)	0.610 (6)	2.645 (6)	−1.501 (6)	0.0 (0)

[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 Carbon Atoms[a]

Atom	x	y	z	B, Å^2
PR1C1	−0.3558 (4)	0.0831 (5)	0.0192 (3)	2.46 (24)
PR1C2	−0.3502 (3)	−0.0123 (5)	−0.0052 (4)	2.98 (25)
PR1C3	−0.4098 (4)	−0.0527 (4)	−0.0593 (4)	4.2 (3)
PR1C4	−0.4748 (4)	0.0022 (6)	−0.0891 (4)	3.97 (28)
PR1C5	−0.4803 (4)	0.0975 (6)	−0.0646 (4)	4.7 (3)
PR1C6	−0.4208 (4)	0.1380 (4)	−0.0105 (4)	4.3 (3)
PR2C1	−0.3054 (5)	0.2552 (5)	0.1052 (5)	2.79 (25)
PR2C2	−0.3486 (5)	0.2523 (6)	0.1543 (5)	6.9 (4)
PR2C3	−0.3747 (5)	0.3392 (8)	0.1770 (4)	8.4 (5)
PR2C4	−0.3576 (5)	0.4291 (6)	0.1506 (5)	5.8 (4)
PR2C5	−0.3144 (5)	0.4320 (5)	0.1015 (5)	5.5 (3)
PR2C6	--0.2883 (4)	0.3450 (7)	0.0788 (4)	4.5 (3)
PR3C1	−0.2189 (4)	0.1683 (6)	0.0133 (4)	2.98 (25)
PR3C2	−0.2584 (3)	0.1985 (6)	−0.0567 (4)	3.97 (28)
PR3C3	−0.2200 (4)	0.2165 (6)	−0.1085 (3)	4.6 (3)
PR3C4	−0.1421 (4)	0.2045 (6)	−0.0903 (4)	4.22 (28)
PR3C5	−0.1025 (3)	0.1744 (6)	−0.0202 (4)	4.1 (3)
PR3C6	−0.1409 (4)	0.1563 (6)	0.0316 (3)	4.1 (3)
AsR1C1	0.3502 (5)	−0.0591 (6)	0.5246 (4)	3.46 (26)
AsR1C2	0.4257 (4)	−0.0708 (6)	0.5637 (5)	5.0 (3)
AsR1C3	0.4444 (4)	−0.1124 (7)	0.6331 (5)	6.7 (4)
AsR1C4	0.3877 (6)	−0.1423 (7)	0.6634 (4)	6.2 (4)
AsR1C5	0.3123 (5)	−0.1305 (7)	0.6243 (5)	6.1 (4)
AsR1C6	0.2935 (3)	−0.0889 (7)	0.5549 (5)	4.7 (3)
AsR2C1	0.3656 (4)	0.1406 (5)	0.4639 (5)	3.55 (27)
AsR2C2	0.3830 (5)	0.2033 (7)	0.4133 (3)	5.1 (3)
AsR2C3	0.4106 (5)	0.2972 (6)	0.4343 (5)	5.7 (3)
AsR2C4	0.4206 (5)	0.3285 (5)	0.5059 (5)	5.5 (4)
AsR2C5	0.4032 (5)	0.2658 (7)	0.5564 (4)	5.7 (4)
AsR2C6	0.3756 (5)	0.1719 (6)	0.5354 (4)	4.6 (3)
AsR3C1	0.2196 (3)	0.0244 (6)	0.4010 (4)	3.26 (26)
AsR3C2	0.1783 (5)	−0.0439 (5)	0.3512 (4)	4.5 (3)
AsR3C3	0.1001 (4)	−0.0358 (6)	0.3257 (4)	4.4 (3)
AsR3C4	0.0632 (3)	0.0406 (7)	0.3499 (5)	5.0 (3)
AsR3C5	0.1044 (5)	0.1089 (6)	0.3996 (5)	6.3 (4)
AsR3C6	0.1826 (5)	0.1008 (6)	0.4252 (4)	4.8 (3)
AsR4C1	0.3614 (5)	−0.0391 (7)	0.3620 (4)	3.59 (28)
AsR4C2	0.4086 (5)	−0.1208 (7)	0.3730 (4)	5.6 (3)
AsR4C3	0.4345 (5)	−0.1566 (6)	0.3162 (6)	8.0 (4)
AsR4C4	0.4132 (6)	−0.1106 (8)	0.2483 (5)	6.6 (4)
AsR4C5	0.3660 (6)	−0.0289 (8)	0.2373 (4)	6.8 (4)
AsR4C6	0.3401 (5)	0.0069 (6)	0.2941 (5)	5.6 (3)

[a] PR*i*Cl or AsR*i*Cl carbon atoms are attached to P or As, respectively. Carbon atoms in each benzene ring are numbered consecutively such that -C4 is para to -C1.

Table III. Root-Mean-Square Amplitudes of Vibration (Å)[a]

Atom	Min	Intermed	Max
I	0.192 (2)	0.236 (2)	0.267 (1)
Rh	0.172 (2)	0.188 (2)	0.193 (1)
As	0.191 (3)	0.204 (2)	0.237 (2)
S1	0.181 (6)	0.224 (6)	0.260 (5)
S2	0.175 (8)	0.194 (5)	0.226 (5)
P	0.154 (10)	0.173 (7)	0.214 (4)
O	0.171 (25)	0.223 (13)	0.318 (14)
C1	0.119 (36)	0.217 (24)	0.271 (20)
C2	0.087 (48)	0.233 (27)	0.397 (18)
C3	0.140 (52)	0.273 (22)	0.448 (20)
S1C1	0.163 (27)	0.186 (33)	0.275 (18)
S2C1	0.140 (46)	0.216 (24)	0.262 (17)
S1C2	0.217 (41)	0.250 (25)	0.297 (17)
S2C2	0.140 (36)	0.209 (26)	0.293 (22)
N1	0.207 (28)	0.304 (26)	0.395 (16)
N2	0.209 (33)	0.272 (18)	0.372 (18)

[a] Measured along the principal axes of the thermal ellipsoids.

isotropic temperature factors 1 Å^2 greater than those of their respective carbon atoms. This refinement of 229 variables proceeded smoothly to convergence, yielding final discrepancy indices R_1 and R_2 of 0.0400 and 0.0437 for 2557 reflections included in the calculation. The estimated standard deviation of an observation of unit weight was 1.24 e$^-$.

A final difference Fourier map showed no peaks higher than approximately 20% of the height of a typical carbon atom in the structure. Attempts to locate the propanoyl hydrogen atoms were largely unsuccessful probably because of the large anisotropic thermal motion of the methyl and methylene carbon atoms. The parameters obtained from the refinement which converged with $R_1 = 0.0400$ are thus taken as the final parameters of the structure, and are given in Table I. The derived carbon atom positions are presented in Table II, and root mean square amplitudes of vibration of the anisotropically refined atoms are given in Table III. A listing of the observed and calculated structure factors is included with the supplementary material for the paper.[25]

Results and Discussion

Synthetic Studies. The Rh(I) dithiolene anion [Rh(CO)$_2$(mnt)]$^-$ was synthesized as its AsPh$_4^+$ or PPh$_4^+$ salt through the reaction of Na$_2$(mnt) with the respective salt of [RhCl$_2$(CO)$_2$]$^-$. This procedure gives significantly higher yields than the previously reported synthesis[12] (>90% vs. 48% based on Rh). Substitution of triphenylphosphine proceeds quantitatively to give [Rh(CO)(PPh$_3$)(mnt)]$^-$ as described previously.[12] Both of these Rh(I) mnt complexes react rapidly with MeI to form the respective anionic acetyl complex [RhI(COMe)L(mnt)]$^-$. However, the product complex with L = CO is unstable in solution, and slowly decomposes on standing. The nature of this decomposition is under study, as it may relate to the Rh(I) catalyzed carbonylation of methanol.[7]

With primary alkyl iodides, only the triphenylphosphine complex [Rh(CO)(PPh$_3$)(mnt)]$^-$ reacts completely to give well-characterized products according to eq 1.

$$[\mathrm{Rh(CO)(PPh_3)(mnt)}]^- + \mathrm{R\text{-}I} \rightarrow [\mathrm{RhI(COR)(PPh_3)(mnt)}]^- \quad (1)$$

The greater reactivity of this complex relative to that of the dicarbonyl system can be understood in terms of the better σ donor and poorer π acid properties of PPh$_3$ relative to CO, and consequently the greater nucleophilicity of this complex for reaction with alkyl halide substrates. The reaction between [Rh(CO)(PPh$_3$)(mnt)]$^-$ and R-I where R = Et, *n*-Pr, *n*-Bu, and *n*-C$_{10}$H$_{21}$ leads in all cases to the formation of an anionic acyl complex having the general formula [RhI(COR)(PPh$_3$)(mnt)]$^-$. A similar reaction with benzyl bromide also occurs, yielding a phenylacetyl species. The formation of the acyl ligand in these complexes requires the metal center to undergo a formal two-electron oxidation to Rh(III). This can be envisioned formally in terms of the oxidative addition of R-I followed by the "migratory insertion" of CO. However, mechanistic details regarding the formation of these complexes are not yet established (vide infra). The acyl complexes are five-coordinate, as determined by the x-ray structural results described below, and they are most readily characterized by the broad acyl stretch ν_{CO} in the region 1695-1685 cm^{-1}.

The ^{1}H NMR spectra of the Rh acyl anions are particularly informative regarding their structure in solution. The results of these measurements are summarized in Table IV. The α-methylene protons of the acyl ligand in all of the complexes formed from R-I exhibit complicated splitting patterns in the region δ 3.5-2.2, and they are found to be magnetically nonequivalent. Removal of spin-spin splitting due to the β protons by either spin decoupling or the use of an R group without β protons leads to the appearance of the α-methylene proton resonance as an AB quartet. This is illustrated in Figure 1a for the phenylacetyl complex. This observation contrasts with

Table IV. ^{1}H NMR Data and Carbonyl Stretching Frequencies for Rhodium Complexes

	Chemical shift data (δ)[b]					Coupling constant data (Hz)[c]			
Complex[a]	α-Methylene protons	Other $-CH_2-$	$-CH_3$	Aromatic protons	$\Delta\delta_{AB}$	J_{AB}	$J_{\alpha\beta}$	$J_{\psi\omega}$	ν_{CO}[d]
$[RhI(COMe)(PPh_3)(mnt)]^-$			2.56 (s)	7.5 (m)					1690
$[RhI(COEt)(PPh_3)(mnt)]^-$	2.95 (m)[e,f]		0.76 (t)	7.5 (m)	0.54	17	7		1690, 1758
$[RhI(CO\text{-}n\text{-}Pr)(PPh_3)(mnt)]^-$	2.99 (m)[e,f]	1.29 (m)	0.72 (t)	7.6 (m)	0.48	17	7	7	1687
$[RhI(CO\text{-}n\text{-}Bu)(PPh_3)(mnt)]^-$	2.98 (m)[e,f]	1.22 (m)	0.74 (t)	7.5 (m)	0.44	16	7	7	1687
$[RhI(CO\text{-}n\text{-}C_{10}H_{21})(PPh_3)(mnt)]^-$[g]	2.96 (m)[e,f]	1.22 (m)	0.84 (t)	7.5 (m)	0.40	16	7	5	1685
$[RhBr(COBz)(PPh_3)(mnt)]^-$[h]	4.42 (q)[f,i]			7.5 (m)	0.69	17			1695
$[Rh(COEt)(PPh_3)(mnt)(CH_3CN)]$[j]	2.45 (q)		0.78 (t)	7.5 (m)			7		1702, 1764
$[Rh(CO\text{-}n\text{-}Pr)(PPh_3)(mnt)(CH_3CN)]$[k]	2.51[l]	1.29[l]	0.69[l]	7.4 (m)			l	l	1707
$[Rh(COMe)(PPh_3)(mnt)(C_5H_5N)]$[k]			2.19 (s)	7.4 (m)					1705
$[Rh(CO)(PPh_3)(Me\text{-}mnt)]$			2.96 (s)	7.5 (m)					1997
$[Rh(CO)(PPh_3)(Et\text{-}mnt)]$	3.38 (q)		1.46 (t)	7.4 (m)			7		1990
$[Rh(CO)(PPh_3)(Bz\text{-}mnt)]$[k]	4.54 (s)			7.4 (m)					1997

[a] Except where noted, all anionic complexes have PPh_4^+ as the counterion. [b] All NMR spectra are of CD_3CN solutions except where noted: s = singlet, t = triplet, q = quartet, and m = multiplet. $\Delta\delta_{AB}$ is the chemical shift difference between the α-methylene protons. The value given in the first column corresponds to the average of the α-methylene proton chemical shifts when the two protons are magnetically nonequivalent. [c] J_{AB} is the coupling constant between the diastereotopic α-methylene protons. $J_{\psi\omega}$ is the coupling constant between the terminal methyl protons and the adjacent methylene protons. [d] KBr pellet; in cm^{-1}. [e] Upon irradiation of the β proton resonances, the multiplet collapsed to an AB quartet. [f] The spectrum revealed the presence of small amounts of the corresponding neutral acyl species. [g] $AsPh_4^+$ salt. [h] Isolated as a CH_2Cl_2 solvate. CH_2Cl_2 resonance observed at δ 5.45. [i] An AB quartet. Chemical shift for the benzyl protons in the neutral acyl complex was δ 3.80. [j] Measured in a 1:1 $CD_3CN/CDCl_3$ solution. Resonance of the CH_3CN protons derived from the complex overlapped with the CHD_2CN resonance in the solvent. [k] $CDCl_3$ solution. [l] Peaks broad, spin–spin splitting was not resolved. Chemical shift for CH_3CN protons was δ 1.99.

results reported previously for other rhodium acyl complexes by Shaw and co-workers,[10] and by Baird et al.[1] The diastereotopic nature of the α-methylene protons indicates that the acyl group is bonded to a chiral center which must be preserved on the NMR time scale, and which of necessity resides at the metal ion in these systems.

Neutral Acyl Complexes. Reaction of the acyl anions $[RhI(COR)(PPh_3)(mnt)]^-$ with Ag^+ results in the removal of the coordinated iodide and the formation of neutral Rh(III) acyl complexes. When the reaction is carried out in the presence of coordinating solvents such as acetonitrile and pyridine, analytically pure five-coordinate complexes can be isolated. These complexes have the acyl stretch shifted to higher frequencies by approximately 10 cm^{-1}. The ^{1}H NMR spectra of the neutral acyl complexes in both acetonitrile-d_3 and $CDCl_3$ reveal that the α-methylene protons in these species are magnetically equivalent. Solvent exchange is thus presumed to occur rapidly so that the different magnetic environments of the α-methylene protons in the five-coordinate structures are equilibrated. In these complexes, the acyl, phosphine, and dithiolate ligands are thought to occupy basal positions of a square pyramid (vide infra) with solvent coordination in the apical position. An alternative possibility is that in solution the neutral acyl complexes adopt symmetric six-coordinate structures with two bound solvent molecules.

The resonances for the α-methylene protons in the neutral acyl complexes are given in Table IV. They are observed at slightly higher fields than their resonances in the corresponding anions. With the neutral phenylacetyl complex, the α-methylene protons appear as singlets at δ 3.80 and 3.69 as illustrated in Figure 1f. The two singlets, of which the lower field one is more prominent, probably arise from the existence of different conformers in which rotation about the Rh–acyl bond is restricted by nonbonded interactions. Significant concentrations of the neutral acyl species occur in solutions of the anionic acyl complex into which polar solvents such as D_2O have been introduced. The equilibrium between the anionic and neutral phenylacetyl species is indicated in Figures 1b and 1c. Similar observations are made with solutions of the other acyl anions as well. The implication of these observations is that coordination of the halide ion is relatively weak in the Rh(III) acyl anion complexes.

The neutral acyl complex is readily converted back to the anionic species by the addition of X^- to its solutions. Figure 1g shows that the addition of sufficient bromide to the neutral complex results in a methylene proton resonance identical with that observed in the ^{1}H NMR spectrum of the initial anionic complex. Equation 2 summarizes the interconversion of anionic and neutral acyl complexes.

$$[RhX(COR)(PPh_3)(mnt)]^- \underset{X^-}{\overset{Ag^+}{\rightleftharpoons}} [Rh(COR)(PPh_3)(mnt)(sol)_x] \qquad (2)$$

$$sol = CH_3CN,\ C_5H_5N;\ x = 1$$

The analytical results for the neutral acyl complexes indicate that in the presence of coordinating solvent, these complexes are isolated as pentacoordinate species. However, while the isolated five-coordinate structures of the neutral and anionic acyl complexes may be similar, their properties in solution, especially with respect to exchange, differ significantly. The former probably exchange solvent rapidly while the latter maintain their sense of chirality on the NMR time scale and exist in the NMR slow exchange limit.

The Solid State Structure of $[RhI(COEt)(PPh_3)(mnt)]^-$. The crystal structure of $[AsPh_4][RhI(COEt)(mnt)(PPh_3)]$ consists of the packing of discrete cations and anions as illustrated in Figure 2. The closest intermolecular hydrogen···nonhydrogen atom contacts (excluding the propanoyl hydrogen atoms) are: PR2H6···O, 2.60 Å; AsR2H5···N2, 2.68 Å; AsR3H6···N1, 2.53 Å; and AsR3H3···N2, 2.75 Å. The closest intermolecular H···H contacts are: AsR2H5···AsR4H3, 2.51; AsR2H5···AsR3H3, 2.60; PR1H5···PR3H4, 2.60; and PR2H2···AsR1H4, 2.56 Å. All of the intermolecular contacts appear normal and are therefore not tabulated completely.

The most important feature of the structure determination is the geometry of the anionic acyl complex. The coordination geometry about rhodium is square pyramidal with the propanoyl group occupying the apical position. A view of the coordination geometry is presented in Figure 3, while important intramolecular distances and angles for the structure are given in Table V.

The square pyramid observed here is the preferred coordination geometry for low spin pentacoordinate d^6 metal ions. The steric bulk of the PPh_3 ligand coupled with the established tendency of σ-bonded carbon atoms to weaken any possible

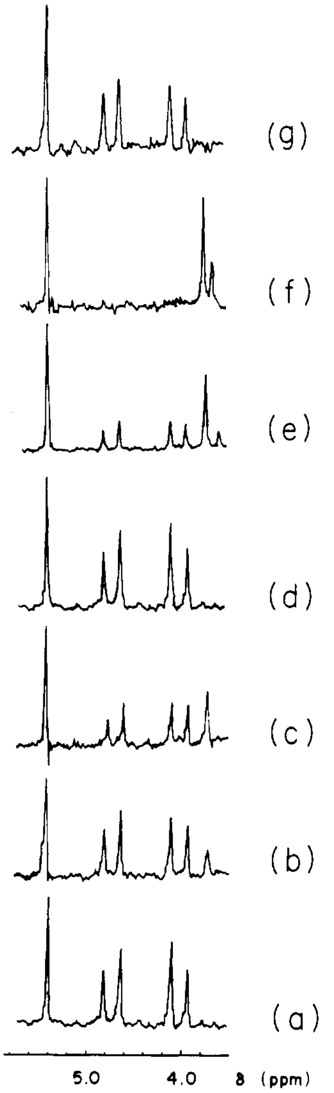


Figure 1. (a) ^1H NMR spectrum of 20 mg of $(PPh_4)[RhBr(COBz)(PPh_3)(mnt)]\cdot\frac{1}{2}CH_2Cl_2$ dissolved in 0.4 mL of CD_3CN in the region of the α-methylene protons (the resonance at δ 5.45 is assignable to CH_2Cl_2); (b) spectrum after the addition of 0.07 mL of D_2O; (c) the same sample after the addition of another 0.07 mL of D_2O; (d) repeat of (a); (e) spectrum of the complex after the addition of 0.5 equiv of $Ag(NO_3)$ and removal of the AgBr precipitate; (f) spectrum after the addition of excess $Ag(NO_3)$ and removal of precipitate; (g) spectrum after adding excess LiBr to the sample used for (f) and removal of precipitate.

Table V. Important Intramolecular Distances and Angles for $(AsPh_4)[RhI(COEt)(PPh_3)(mnt)]$[a]

Atoms	Distance, Å	Atoms	Distance, Å
Rh–C1	2.006 (14)	Rh–I	2.709 (1)
Rh–S1	2.323 (3)	Rh–S2	2.269 (3)
Rh–P	2.324 (3)	C1–O	1.205 (15)
C1–C2	1.488 (16)	C2–C3	1.519 (23)
S1–S1C1	1.709 (14)	S2–S2C1	1.737 (13)
S1C1–S1C2	1.457 (20)	S2–S2C2	1.427 (21)
S1C2–N1	1.138 (21)	S2C2–N2	1.144 (21)
S1C1–S2C1	1.360 (16)	P–PR1C1	1.832 (7)
P–PR2C1	1.820 (8)	P–PR3C1	1.842 (9)
As–AsR1C1	1.884 (7)	As–AsR2C1	1.890 (7)
As–AsR3C1	1.876 (6)	As–AsR4C1	1.895 (9)

Atoms	Angle, deg	Atoms	Angle, deg
C1–Rh–S1	96.4 (4)	C1–Rh–S2	98.5 (4)
C1–Rh–P	94.0 (4)	C1–Rh–I	99.5 (4)
S1–Rh–P	169.6 (1)	S2–Rh–P	89.3 (1)
S1–Rh–I	88.1 (1)	S2–Rh–I	162.0 (1)
S1–Rh–S2	88.5 (1)	P–Rh–I	90.9 (1)
Rh–C1–O	119.1 (9)	Rh–C1–C2	118.0 (9)
O–C1–C2	122.9 (12)	C1–C2–C3	110.4 (11)
Rh–S1–S1C1	102.6 (4)	Rh–S2–S2C1	103.5 (5)
S1–S1C1–S1C2	118.7 (9)	S2–S2C1–S2C2	115.6 (9)
S1–S1C1–S2C1	122.6 (10)	S2–S2C1–S1C1	122.1 (11)
S1C1–S1C2–N1	178.3 (15)	S2C1–S2C2–N2	178.3 (15)
S1C2–S1C1–S2C1	118.7 (12)	S2C2–S2C1–S1C1	122.3 (12)
Rh–P–PR1C1	118.6 (3)	PR1C1–P–PR2C1	103.2 (4)
Rh–P–PR3C1	119.9 (3)	PR2C1–P–PR3C1	106.5 (4)
Rh–P–PR2C1	107.2 (3)	PR1C1–P–PR3C1	100.0 (3)
AsR1C1–As–AsR-2C1	105.3 (3)	AsR1C1–As–AsR-3C1	109.8 (4)
AsR1C1–As–AsR-4C1	114.6 (4)	AsR2C1–As–AsR-3C1	108.9 (3)
AsR2C1–As–AsR-4C1	110.6 (4)	AsR3C1–As–AsR-4C1	107.6 (3)

[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.

trans ligation[26-28] most probably accounts for the absence of a sixth ligand in the coordination sphere. Examples of the structural influence of σ-bonded carbon atoms include $[RhCl_2(C_8H_{15}O_2)(4\text{-}Me(py))]_2$ by Evans et al.[26] and the acetyl complex $[Rh_2I_4(CO)_2(\mu\text{-}I)_2(COMe)_2]^{2-}$.[11] The latter, which is the only other rhodium acyl structure determined to date, shows the Rh–I distance trans to the acetyl ligand to be 0.322 (3) Å greater than the corresponding distance in the cis position.

The Rh–C distance of 2.006 (14) Å in the present structure is shorter than nearly all reported Rh–C σ bonds,[11,26,28,29] and indicates the probability of back-bonding from the appropriate

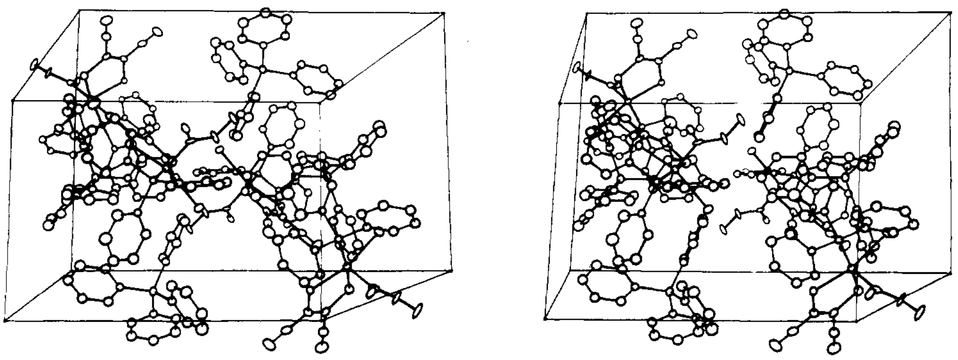


Figure 2. Packing diagram of $(AsPh_4)[RhI(COEt)(PPh_3)(mnt)]$. The orientation of the unit cell is such that *a* is horizontal and *b* is vertical.

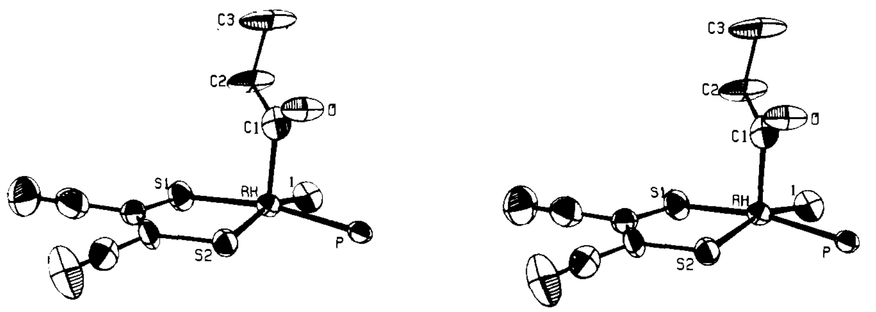


Figure 3. A stereoview of the inner coordination geometry of $[\mathrm{RhI(COEt)(PPh_3)(mnt)}]^-$. The phenyl rings are omitted for clarity. The thermal ellipsoids correspond to 50% probability distributions.

d_π orbital of the Rh(III) center to the π^* orbital of the acyl ligand. The shortening of an Fe-C σ bond in a ferrelactone ring has recently been rationalized by Churchill and Chen in a similar way.[30] A tabulation of Rh(III)-C σ-bond distances has been presented by Collman et al.[28] All values are in the range 2.05-2.26 Å, except for 1.97 Å in the chelating carbene complex $\mathrm{RhI_3(CO)(CPhN(Me)C(Ph)NMe)}$ where metal → ligand back-bonding undoubtedly occurs.[31]

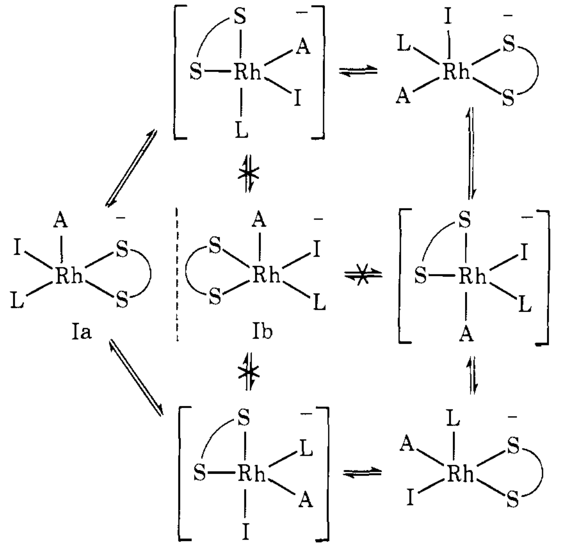
The Rh-S bond lengths within the chelate ring differ significantly, 2.269 (3) vs. 2.323 (3) Å, and the difference clearly relates to the nature of the trans ligand in the base of the square pyramid. For comparison, Rh-S bond lengths in structures containing S donor chelates are: 2.290 and 2.303 (2) Å in Rh(COD)(Me-mnt),[13] 2.369 and 2.322 (3) Å in $\mathrm{Rh(MeSC_2H_2S)_3}$,[32] and 2.333 and 2.316 (3) Å in $\mathrm{Rh(sacsac)_3}$.[33] The shorter Rh-S distance in the present structure is trans to iodide which appears weakly coordinated based on the ease with which it is removed in solution from the coordination sphere. The Rh-I distance of 2.709 (1) Å is slightly longer than the range of 2.65-2.69 Å observed for most Rh(III)-iodide distances.[34] It is, however, shorter than the 2.813 (1) Å value for Rh-I trans to methyl in the six-coordinate complex $\mathrm{RhI(Me)[C_2(DO)(DOBF_2)]}$,[28] and the 3.001 (2) Å value for Rh-bridging iodide trans to the acetyl ligand in $[\mathrm{Rh_2I_4(CO)_2(\mu\text{-}I)_2(COMe)_2}]^{2-}$.[11]

All other molecular parameters in the structure appear normal and they are given in Table V. The propanoyl ligand is oriented so as to minimize nonbonded repulsions with the triphenylphosphine ligand and rotation about the Rh-acyl bond appears restricted. However, the thermal ellipsoids of the α and β carbon atoms of the acyl ligand (see Figure 3 and Table III) show evidence of anisotropic thermal motion in the crystal corresponding to twisting of the ligand about the Rh-C bond.

Structures of the Acyl Complexes in Solution. The solid state structure of the propanoyl complex establishes the square pyramidal coordination geometry for the anionic systems. As the magnetic nonequivalence of the α-methylene protons indicates, the Rh(III) ion is indeed located at a center of dissymmetry. However, the question of whether or not the five-coordinate structure adopted by the anions is static in solution is unanswered. While stereochemical nonrigidity in five-coordinate systems is well established,[35-37] the propensity of a given complex to exhibit fluxional behavior depends on the relative energies of the ground state and transition state structures in the rearrangement process. A d^6 metal ion in the square pyramidal geometry should be significantly more stable than in a trigonal bipyramidal coordination, and hence stereochemical nonrigidity via a series of square pyramid (SP) ⇌ trigonal bipyramid (TBP) interconversions might not be expected on the NMR time scale.

If, however, one presumes such a sequence to occur rapidly, the restriction that the bidentate mnt ligand must always span axial-equatorial positions in the intermediate TBP preserves the chiral integrity of the acyl anion complex as shown in Scheme I. (The S···S distance of 3.204 Å in the propanoyl complex is among the largest bite distances reported for 1,2-dithiolene structures,[38] and it accommodates a S-Rh-S bond angle of only 88.5 (1)°. Significant strain would therefore be imposed on any TBP intermediate in which the mnt ligand is required to span two equatorial positions.)

Scheme I. Proposed Intramolecular Rearrangements of Acyl Anions via SP ⇌ TBP Interconversions



A = acyl ligand; L = $\mathrm{PPh_3}$; Ia and Ib are enantiomers.

For the neutral acyl complexes, exchange of solvent in the coordination sphere occurs readily and the different magnetic environments of the α-methylene protons in the SP arrangement are averaged on the NMR time scale. While the possibility of octahedral coordination in solutions of strongly coordinating solvents such as DMF and $\mathrm{CH_3CN}$ cannot be dismissed, the crystalline products isolated from these solutions are consistent solely with five-coordinate structures. In actuality solvated octahedral structures are closely related to discrete SP structures undergoing rapid solvent exchange. Solvation effects in poorly coordinating solvents are undoubtedly weak, and exchange in these solutions is rapid.

Alkyl Group Migrations. Heating methylene chloride or THF solutions of the neutral acyl complexes for R = Me, Et, and Bz results in the formation of Rh(I) species via alkyl group migration from the acyl carbon atom to one of the sulfur donor atoms of the mnt ligand. The neutral S-alkylated complexes are characterized by a carbonyl stretching frequency of ~1990 cm^{-1} and NMR spectra which show chemical shifts for the α protons at δ 2.96, 3.38, and 4.54 consistent with S-attachment for R = Me, Et, and Bz, respectively (see Table IV). For comparison, the resonances of the α protons of a number of thioether and S-alkylated complexes are at δ 2.87 and 2.23 for *mer*-$RhCl_3(PhSMe)_3$,[39a] δ 3.71 and 2.96 for *mer*-$RhCl_3(PhSEt)_3$,[39b] δ 2.70 for Rh(COD)(Me-mnt),[13] δ 2.64 for Rh(NBD)(Me-mnt),[13] δ 4.36 for both Rh(COD)(Bz-mnt) and Rh(NBD)(Bz-mnt),[13] δ 2.36 for $[Ni(Me_2S_4C_4Ph_4)]$,[39] and δ 4.20 for $[Pt(Bz_2S_4C_4Ph_4)]$.[39] The S-alkylated complexes found in the present study are thus directly analogous to the previously reported systems [(diene)Rh(R-mnt)] where diene = 1,5-COD, NBD and R = Me, Bz.[13] When solutions of the neutral acyl complexes in coordinating solvents such as acetonitrile are heated, no alkyl group migration is observed. The controlled transfer of alkyl groups within the coordination sphere has intriguing implications in terms of catalysis, especially if bifunctional complexes such as the present ones containing nucleophilic lone pairs on the sulfur donor atoms and reactive d^8 metal centers are employed.

An attempt to further verify the nature of the S-alkylated complexes was made by reacting $[Rh(CO)(PPh_3)(mnt)]^-$ with Et_3O^+ in CH_2Cl_2-THF solutions. It is known that reactions of trialkyloxonium cations with metal complexes lead to one of several possibilities:[40] (a) oxidative addition or alkylation of the metal, (b) alkylation of a coordinated ligand, (c) halogen abstraction, or (d) one-electron oxidation. While it was hoped that (b) would predominate in the present instance because of the nucleophilicity of the sulfur lone pairs, a mixture of products corresponding to the neutral propanoyl complex and the *S*-ethyl complex was obtained. These products could be separated and characterized, or converted entirely to the *S*-ethyl species by further heating of the reaction solution, as indicated in eq 3.

$$[Rh(CO)(PPh_3)(mnt)]^- + OEt_3^+ \longrightarrow \begin{array}{l} [Rh(CO)(PPh_3)(Et\text{-}mnt)] \\ + [Rh(COR)(PPh_3)(mnt)(sol)_x] \end{array} \Big]^{\Delta} \quad (3)$$

The nature of the migration of the alkyl group in the neutral acyl complexes is under intensive study. Direct 1,3-migration from the acyl carbon atom to the sulfur donor is feasible, as is a sequence of successive 1,2-migrations. Stereochemical tests will help to determine the nature of this migration.

Mechanism of Acyl Formation. It was noted above that the formation of the acyl ligand corresponds formally to the oxidative addition of R-X (or R^+) to Rh(I) followed by "migratory insertion" of CO. The mechanism of acyl formation, however, is not yet established. Initial alkylation could occur at either the metal center or at the sulfur donor atom. The former seems most probable in view of the alkyl migrations mentioned above. Moreover, addition of iodide to solutions of the neutral *S*-ethyl complex failed to lead to the formation of the propanoyl anion complex. However, preliminary results with R = Me and Bz, which will be published separately,[41] seem at variance with the results for R = Et. Tests are in progress in which the phosphine ligand blocks accessibility to the Rh(I) center in order to establish if initial S-alkylation can lead to acyl formation.

Monitoring of the reaction between EtI and [Rh(CO)-$(PPh_3)(mnt)]^-$ by IR spectroscopy reveals no evidence for the formation of a Rh-Et complex. A Rh(III)-alkyl complex would be anticipated to have ν_{CO} greater than ~2050 cm^{-1}, but no such band is observed. Another example of acyl formation without direct observation of a Rh(III) alkyl carbonyl as an intermediate is in the carbonylation of methanol using $RhI_2(CO)_2^-$ + HI as the catalyst system.[42] Similarly, a number of decarbonylation studies of Rh-acyl systems have failed to observe directly the existence of intermediate Rh(III) alkyl carbonyl species.[1,2] However, evidence for the formation of a Rh(III)-Me intermediate in the reaction of MeI with $RhCl(CO)(PPh_3)_2$ has been reported by Doueck and Wilkinson,[8] and recent studies in our laboratory show a Rh(III)-Et intermediate in the reaction of EtI with the triphenyl phosphite complex $[Rh(CO)(P(OPh)_3)(mnt)]^-$.[43]

Clearly, the formation of the acyl ligand in the present systems, the migration of the alkyl groups within the coordination sphere, and the reactivity of the acyl ligand are all avenues of future inquiry in these systems.

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Supplementary Material Available: Listing of observed and calculated structure factors for $(AsPh_4)[RhI(COEt)(PPh_3)(mnt)]$ (16 pages). Ordering information is given on any current masthead.

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Reactions of Atomic (^{1}D) Sulfur: Synthesis of *B*-Mercaptocarboranes and *B*-Disulfidocarboranes

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Abstract: The reactions of atomic sulfur (^{1}D), generated by the gas phase photolysis of carbonyl sulfide, with the small closo carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ were studied and found to be a convenient method of preparing the corresponding *B*-mercaptocarboranes, including: 2-SH-1,5-$C_2B_3H_4$, 2-SH-1,6-$C_2B_4H_5$, 5-SH-2,4-$C_2B_5H_6$, 1-SH-2,4-$C_2B_5H_6$, and 3-SH-2,4-$C_2B_5H_6$. In addition, the photolytic decomposition of the *B*-mercapto derivatives of 2,4-$C_2B_5H_7$ results in the formation of several isomers containing boron bonded bridging disulfide groups: 5,5′-S_2-(2,4-$C_2B_5H_6$)$_2$, 1,1′-S_2-(2,4-$C_2B_5H_6$)$_2$, and 3,3′-S_2-(2,4-$C_2B_5H_6$)$_2$.

The use of atomic species as synthetic reagents has seen a resurgence in recent years mainly due to the development of high temperature methods,[1] and these techniques are now widely used[2] for those elements, particularly the transition metals, which vaporize as monoatomic species. Alternatively, a number of atomic species which may be useful for synthetic purposes, but impossible or difficult to generate using high temperatures, may be generated with the use of photochemical techniques.

In particular, Gunning and Strausz[3] have shown in a series of papers that sulfur atoms in the ^{1}D excited state may be produced by the photolysis of carbonyl sulfide at 2537 Å. Their studies have also revealed that these sulfur atoms are extremely reactive and undergo reactions reminiscent of single methylene. For example, ^{1}D sulfur atoms readily insert[4] into the C–H bonds of an alkane to form the corresponding mercaptan. Although the reactions of ^{1}D sulfur atoms with a wide variety of organic compounds have been studied, there has been little application to the synthesis of inorganic compounds. Recent studies in this laboratory have shown that atomic sulfur is a useful reagent for the synthesis of inorganic and organometallic compounds, and we now wish to report our studies of the reaction of sulfur ^{1}D atoms with the small closo carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$.

Experimental Section

All reactions and operations were performed using standard high vacuum techniques except where otherwise indicated. All photochemical reactions were performed in a cylindrical quartz tube (30 × 7 cm diameter) equipped with a greaseless stopcock. Attached to the bottom of the reactor was a small cold finger which was shielded to prevent photolysis of the liquid phase. The radiation source was a Griffin-Rayonet photochemical reactor equipped with 16 2537-Å lamps. Gas–liquid chromatography was conducted on a homemade evacuatable chromatograph equipped with a gas density detector and using 6 ft × 0.25 in., 20% tricresylphosphate (TCP) on Chromosorb W (60/80 mesh) column. Chromatographic retention volumes, R_v, are relative to 2,4-$C_2B_5H_7$ = 1.0. Preparative thin layer chromatography was conducted on silica gel plates (Brinkman) in air. Melting points were determined by Stock's ring method.

Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on either a Varian HA-100 spectrometer or a JEOL PS-100 pulse Fourier transform spectrometer and are presented in Tables I and II, respectively. The ^{11}B chemical shifts were measured relative to an external $BF_3{:}O(C_2H_5)_2$ (0 ppm) standard, while ^{1}H shifts are relative to external Me_4Si. Infrared spectra (Table III) were obtained on a Perkin-Elmer Infracord spectrophotometer. Mass spectra were recorded on a Perkin-Elmer RMU-6E mass spectrometer.

The 1,5-dicarba-*closo*-pentaborane(5) (1,5-$C_2B_3H_5$), 1,6-dicarba-*closo*-hexaborane(6) (1,6-$C_2B_4H_6$), and 2,4-dicarba-*closo*-heptaborane(7) (2,4-$C_2B_5H_7$) were purchased from Chemical Systems, Inc., and purified by vacuum line fractionation or GLC before use. Carbonyl sulfide (COS) was purchased from Matheson Gas Products. All solvents were reagent grade.

Reaction of 1,5-$C_2B_3H_5$ and ^{1}D Sulfur Atoms. A 10.0-mmol mixture of 1,5-$C_2B_3H_5$ and COS in approximate 2:1 mole ratio was irradiated for 1 h at 35 °C while the cold finger of the photolysis reactor was maintained at 0 °C. During this time the tube became coated with a fine white deposit. The tube was then opened and the volatile material fractionated through a −95 °C trap to remove unreacted COS and 1,5-$C_2B_3H_5$. The material retained at −95 °C was further purified by gas chromatography on the TCP column at 108 °C to give 2.3 mg of 2-SH-1,5-$C_2B_3H_4$, R_v = 1.70. The mass spectrum shows a three-boron pattern with a cutoff at *m/e* 94 corresponding to the formula $^{12}C_2{}^{11}B_3{}^{32}S^1H_5$. This compound slowly decomposes in the liquid phase and an accurate melting point could not be obtained.

Reaction of 1,6-$C_2B_4H_6$ and ^{1}D Sulfur Atoms. In a typical reaction, a mixture of 9.9 mmol of 1,6-$C_2B_4H_6$ and 3.9 mmol of COS was irradiated for 3.5 h at 35 °C with the cold finger on the reactor maintained at 0 °C. As in the 1,5-$C_2B_3H_5$ reaction, the tube became coated with a fine white powder. The tube was then opened to the vacuum line and the volatile material was separated by trap-to-trap fractionation. The material retained at −78 °C was purified by GLC on the TCP column at 112 °C to give 3.0 mg of 2-SH-1,6-$C_2B_4H_5$, R_v = 5.0. The yield was 1.5% based on 1,6-$C_2B_4H_6$ consumed. The mass spectrum shows a four-boron pattern with a cutoff at *m/e* 106 corresponding to the formula $^{12}C_2{}^{11}B_4{}^{32}S_1{}^1H_6$. The melting point is −6.5 °C.

Reaction of 2,4-$C_2B_5H_7$ and ^{1}D Sulfur Atoms. A mixture of 10.6 mmol of 2,4-$C_2B_5H_7$ and 2.3 mmol of COS was irradiated for 2.5 h at 35 °C, while the cold finger of the reaction tube was maintained at 25 °C. The tube was opened to the vacuum line and the volatile materials were separated by trap-to-trap fractionation. The material retained in a −63 °C trap, but passing a −30 °C trap, consisted of a mixture of compounds of the formula $C_2B_5H_7S$ (25.4 mg, 8.8% yield, based upon 2,4-$C_2B_5H_7$ consumed). The isomers were separated by