Dimeric Rhodium(I) and Rhodium(II) Complexes with Bridging Phosphine or Arsine Ligands

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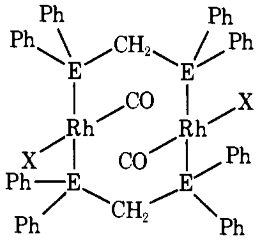
Abstract New ligand-bridged complexes of Rh(I) of the type $(RNC)_2Rh(Ph_2PCH_2PPh_2)_2Rh(CNR)_2{}^{2+}$ (R = CH_3, n-C_4H_9, C_6H_{11}, t-C_4H_9) have been prepared and isolated as their crystalline hexafluorophosphate or tetraphenylborate salts. The dimeric formulation for these complexes has been established by measurement of the equivalent conductance over a range of concentrations. Infrared spectra indicate that only terminal isocyanide ligands are present. ^1H NMR spectra confirm their composition and indicate that the complexes are diamagnetic. The electronic spectra of these dimers and the related species $Rh(CO)X(Ph_2ECH_2EPh_2)_2Rh(CO)X$ (E = P, X = Cl; E = As, X = Cl or Br) are reported. In comparison with elated monomers, an electronic transition of the monomers is shifted to lower energies in the dimers. The origin of this shift is discussed. These dimeric rhodium(I) complexes are oxidized by iodine to dimeric, diamagnetic rhodium(II) dimers. These rhodium(II) complexes have been isolated in crystalline form and characterized by infrared, proton magnetic, and electronic spectra and by electrical conductivities in solution.

The chemistry of rhodium is dominated by the occurrence of planar, four-coordinate Rh(I) complexes and six-coordinate Rh(III) complexes.[1] In recent years the ability of rhodium complexes to interconvert between these two oxidation states has been utilized in the development of a variety of homogeneous catalysts for hydrogenation and hydroformylation.[2] This area of rhodium chemistry has been developed in the main using various phosphine ligands. Recent investigations have indicated that the chemistry of rhodium complexes of nonphosphine ligands may vary considerably from the well-known chemistry found with phosphine ligands. The rhodium isocyanide cations, $(RNC)_4Rh^+$, have been shown to undergo self association, presumably through direct metal-metal bonding, in solution.[3] Although the association of planar d^8 complexes through metal-metal bonds in the solid state has been encountered for some time,[4] similar self association of planar d^8 complexes in solution is, at present, rare.[5] Secondly, some isocyanide complexes of Rh(I) and Rh(III) have also been shown to form dimers of formally Rh(II) (eq 1).[6]

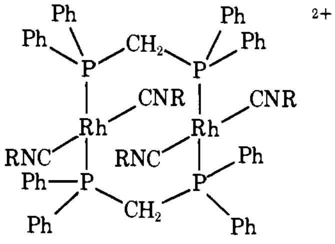
$$(RNC)_4Rh^+ + (RNC)_4RhX_2{}^+ \rightleftarrows (RNC)_8Rh_2X_2{}^{2+} \quad (1)$$
$$(R = \text{alkyl group, } X = \text{halide})$$

These diamagnetic Rh(II) complexes are also believed to contain direct rhodium-rhodium bonds.

It remains to be seen if other rhodium complexes with small ligands undergo similar forms of association. Analogous association of phosphine complexes of rhodium is probably limited by the steric bulk of most phosphines.[7] Most phosphines can prohibit the close approach of two rhodium centers which is necessary for direct metal-metal bonding. However, the bidentate group 5 donors bis(diphenylphosphino)methane and bis(diphenylarsino)methane are known to have the appropriate geometry to span two metal atoms.[8-12] These ligands might be expected to be useful in the construction of binuclear complexes of rhodium. In fact, one group of binuclear Rh(I) complexes of structure type **1** has been prepared.[13] X-ray structural data on complex **1a** is available.[12] The complex contains two planar rhodium(I) units bridged by the diarsine ligand. The related dimers **1b** and **1c** are isomorphous with **1a** and presumably have the same basic structure. The rhodium-rhodium bond length in **1a** is 3.396 Å. This distance is fairly long when it is compared with other rhodium-rhodium bond lengths. The metal-metal bond length in Rh(II) dimers ranges from 2.3 to 2.9 Å.[14-16] The rhodium-rhodium distances in various rhodium cluster compounds which require direct rhodium-rhodium bonds to account for their diamagnetism also fall into this range.[11,17-23] Nevertheless both physical and chemical consequences of the proximity of the rhodium centers in **1a** can be demonstrated. This article explores effects of the rhodium-rhodium interaction in the complexes of type **1**. For additional information a new series of bridged complexes of type **2** has been synthesized.



1a, E = As; X = Cl
1b, E = As; X = Br
1c, E = P; X = Cl



2a, R = CH_3
2b, R = n-C_4H_9
2c, R = c-C_6H_{11}
2d, R = t-C_4H_9

Experimental Section

Preparation of Compounds. Methyl isocyanide,[24] *tert*-butyl isocyanide,[24] $Rh_2(CO)_2Cl_2(Ph_2PCH_2PPh_2)_2$,[13] $Rh_2(CO)_2Cl_2(Ph_2AsCH_2AsPh_2)_2$,[13] and $Rh_2(CO)_2Br_2(Ph_2AsCH_2AsPh_2)_2$[13] were prepared by the reported procedures. Tetrakis(alkyl isocyanide)rhodium(I) salts were prepared by treating a methanolic slurry of 1,5-cyclooctadienerhodium chloride dimer[26] with an excess of isocyanide and adding a salt of the appropriate anion to the methanol solution to precipitate the desired complex. The properties of these salts of $(RNC)_4Rh^+$ agree with those previously reported.[27-30] Cyclohexyl isocyanide (Aldrich), n-butyl isocyanide (Aldrich), bis(diphenylphosphino)methane (PCR), and bis(diphenylarsino)methane (Strem) were obtained from commercial sources and utilized without further purification.

$[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$. A solution of 0.132 g (0.343 mmol) of bis(diphenylphosphino)methane in 10 ml of acetone was added to a solution of 0.247 g (0.327 mmol) of $[(n\text{-}C_4H_9\text{-}$

$NC)_4Rh][BPh_4]$ in 10 ml of acetone. The blue violet solution was filtered and 15 ml of 1-propanol was added to the filtrate. The solvent was removed from the mixture through the use of a rotary evaporator. Evaporation was stopped when purple crystals of the product began to separate. The product was collected by filtration and purified by recrystallization from acetone/1-propanol followed by vacuum drying (yield 0.19 g, 60%): conductivity $\Lambda = 59$ cm^2 equiv^{-1} ohm^{-1}; ^{1}H NMR in dimethyl-d_6 sulfoxide τ (intensity) 9.29 (9, broad multiplet) *n*-butyl, 7.85 (1) methylene, 3.16, 2.89, 2.67, 2.31 (20) phenyl. Anal. Calcd for $C_{118}H_{120}B_2N_4P_4Rh_2$: C, 72.85; H, 6.22; N, 2.88. Found: C, 72.48; H, 6.87; N, 2.98.

$[(C_6H_{11}NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$. This complex which forms red crystals was obtained from $[(C_6H_{11}NC)_4Rh][BPh_4]$ by the procedure described above: conductivity $\Lambda = 63$ cm^2 equiv^{-1} ohm^{-1}. Anal. Calcd for $C_{123}H_{128}B_2N_4P_4Rh_2$: C, 73.83; H, 6.29; N, 2.73. Found: C, 73.66; H, 6.39; N, 3.33.

$[(t\text{-}C_4H_9NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][PF_6]_2$. This complex was obtained as red crystals from $[(t\text{-}C_4H_9NC)_4Rh][PF_6]$ by the procedure outlined above: conductivity $\Lambda = 98$ cm^2 equiv^{-1} ohm^{-1}; ^{1}H NMR in dimethyl-d_6 sulfoxide, τ (intensity) 9.27 (9) *tert*-butyl, 7.95 (1) methylene, 2.67 (6), 2.35 (4) aromatic multiplet. Anal. Calcd for $C_{70}H_{80}F_{12}N_4P_6Rh_2$: C, 52.54; H, 5.05; N, 3.51; P, 11.64. Found: C, 52.84; H, 5.17; N, 3.84; P, 11.27.

$[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$. This salt which forms red crystals was prepared from $[(CH_3NC)_4Rh][BPh_4]$ by the procedure described above: conductivity $\Lambda = 63$ cm^2 equiv^{-1} ohm^{-1}. Anal. Calcd for $C_{106}H_{96}B_2N_4P_4Rh_2$: C, 71.63; H, 5.44; N, 3.15. Found: C, 71.10; H, 5.20; N, 3.36.

$[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][PF_6]_2$. Methyl isocyanide (0.3 ml, 5 mmol) was added to a slurry of 0.247 g (0.5 mmol) of 1,5-cyclooctadienerhodium(I) chloride dimer in 15 ml of methanol. To this solution a solution of 0.162 g (1.0 mmol) of ammonium hexafluorophosphate in 5 ml of methanol was added. The gray precipitate of $[(CH_3NC)_4Rh][PF_6]$ was collected by filtration and washed with methanol and dichloromethane. This gray solid was suspended in 50 ml of acetone and 0.384 g (1 mmol) of bis(diphenylphosphino)methane was added. The mixture was heated under reflux for 15 min. During heating most of the gray solid dissolved and a blue violet solution formed. The solution was filtered to remove any unreacted material and 15 ml of 1-propanol was added to the filtrate. The solvent was removed by distilation until crystals of the product began to form. The solution was then allowed to cool, and the product was collected by filtration, washed with methanol and diethyl ether, and vacuum dried: conductivity $\Lambda = 93$ cm^2 equiv^{-1} ohm^{-1}; ^{1}H NMR in acetonitrile-d_3, τ (intensity) 7.49 (3) methyl, 6.07 (1) methylene, 2.51, 2.29 (10 phenyl multiplet). Anal. Calcd for $C_{58}H_{56}F_{12}N_4P_6Rh_2$: C, 48.76; H, 3.95; N, 3.92. Found: C, 48.62; H, 3.93; N, 4.05.

$[(CH_3NC)_2Rh(PPh_3)_2][PF_6]$. Triphenylphosphine (0.262 g, 1.0 mmol) was added to a slurry of 0.206 g (0.50 mmol) of $[(CH_3NC)_4Rh][PF_6]$ in 5 ml of acetone. The mixture was heated under reflux for 30 min and filtered. Ten milliliters of 1-propanol was added to the filtrate and the solvent was removed from this mixture through the use of a rotary evaporator until yellow crystals of the product formed. These were collected by filtration, washed with methanol, and recrystallized from dichloromethane-methanol, yield (0.30 g, 70%): conductivity, $\Lambda = 98$ cm^2 equiv^{-1} ohm^{-1}; ^{1}H NMR in chloroform-*d*, τ (intensity) 7.54 (3) methyl, 2.48 (15) phenyl. Anal. Calcd for $C_{40}H_{36}F_6N_2P_3Rh$: C, 56.22; H, 4.25; N, 3.29. Found: C, 55.82; H, 4.30; N, 3.24.

$[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2PCH_2PPh_2)_2I_2][BPh_4]_2$. A solution of 0.0198 g (7.78×10^{-5} mol) of iodine in 5 ml of acetone was added to a solution of 0.151 g (7.76×10^{-5} mol) of $[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ in 15 ml of acetone. This brown solution was filtered and 10 ml of 1-propanol was added to the filtrate. The volume of the solution was reduced through the use of a rotary evaporator until the product began to crystallize. The brown crystals were collected by filtration and washed with methanol. Purification was achieved by recrystallization from acetone/1-propanol (yield 0.14 g, 82%): conductivity $\Lambda = 62$ cm^2 equiv^{-1} ohm^{-1}. Anal. Calcd for $C_{118}H_{120}B_2I_2N_4P_4Rh_2$: C, 64.44; H, 5.50; I, 11.54; N, 2.55. Found: C, 64.68; H, 5.28; I, 10.87; N, 2.29.

$[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2I_2][BPh_4]_2$. A solution of 0.0254 g (0.10 mmol) of iodine in 7 ml of dichloromethane was added to a solution of 0.177 g (0.10 mmol) of $[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ in 10 ml of dichloromethane. The resulting brown solution was filtered and cyclohexane was added dropwise to precipitate the product as brown crystalline flakes (yield 0.16 g, 80%): conductivity $\Lambda = 61$ cm^2 equiv^{-1} ohm^{-1}; ^{1}H NMR in dimethyl-d_6 sulfoxide, τ (intensity), 6.87 (3) methyl, 4.95 (1) methylene, 3.15, 2.86, 2.51 (10) phenyl multiplets. Anal. Calcd for $C_{106}H_{96}B_2I_2N_4P_4Rh_2$: C, 62.68; H, 4.76; N, 2.76. Found: C, 62.84; H, 5.15; N, 2.89.

$[(C_6H_{11}NC)_4Rh_2(Ph_2PCH_2PPh_2)_2I_2][BPh_4]_2$. This complex was obtained as dark brown crystals by the procedure described for the preparation of $[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2I_2][BPh_4]_2$: conductivity $\Lambda = 60$ cm^2 equiv^{-1} ohm^{-1}. Anal. Calcd for $C_{126}H_{128}B_2I_2N_4P_4Rh_2$: C, 65.70; H, 5.60; I, 11.02; P, 5.38. Found: C, 65.96; H, 5.54; I, 11.00; P, 5.20.

$(CO)_2Rh_2(Ph_2AsCH_2AsPh_2)_2Br_2I_2$. A solution of 0.026 g (0.10 mmol) of iodine in 5 ml of dichloromethane was added to a solution of 0.14 g (0.103 mmol) of $(CO)_2Rh_2(Ph_2AsCH_2AsPh_2)_2Br_2$ in 8 ml of dichloromethane. The solution was filtered and cyclohexane was added to precipitate the product as black crystals. These were collected, washed with cyclohexane, and vacuum dried (yield 0.090 g, 56%). Anal. Calcd for $C_{52}H_{44}As_4Br_2I_2O_2Rh_2$: C, 38.55; H, 2.74; total halogen, 25.54; mol wt, 1620. Found: C, 38.61; H, 2.32; total halogen, 25.84; mol wt, 1750.

$(CO)_2Rh_2(Ph_2AsCH_2AsPh_2)_2Br_4$. One and a half milliliters of a solution of 0.1 ml of bromine in 20 ml of dichloromethane was added to a solution of 0.206 g (0.151 mmol) of $(CO)_2Rh_2(Ph_2AsCH_2AsPh_2)_2Br_2$ in minimum volume of dichloromethane. The solution was filtered and 15 ml of methanol was added to the filtrate. The solvent was removed by distillation until black crystals of the product formed. The product was collected and recrystallized from methanol/dichloromethane (yield 116 g, 70%). Anal. Calcd for $C_{52}H_{44}As_4Br_4O_2Rh_2$: C, 40.83; H, 2.91; Br, 20.95. Found: C, 40.97; H, 3.16; Br, 21.40.

Physical Measurements. Conductivities were determined for 5×10^{-4} equiv/l. solutions in nitromethane with an Industrial Instruments conductivity bridge. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Proton magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL-MH-100 spectrometer operating at 100 MHz; tetramethylsilane was the internal standard. Electronic spectra were recorded on a Cary 17 spectrophotometer. Molecular weights were measured in chloroform solution using a Mechrolab vapor pressure osmometer.

Results

Synthesis and Characterization of Rh(I) Dimers. The phosphine bridged Rh(I) dimers **2** are readily prepared by the addition of bis(diphenylphosphino)methane to a solution of the tetrakis(alkylisocyanide)rhodium salt in either dichloromethane or acetone. The progress of the substitution reaction is readily apparent since the rhodium(I) isocyanide cations are yellow or red in dilute solution while the dimers **2** are blue or violet. Elemental microanalytical data for the hexafluorophosphate or tetraphenylborate salts of these new cations are recorded in the experimental section. Electrical conductivity data for these salts indicate that they are electrolytes in solution. The dimeric formulation for these cations has been established from measurements of the equivalent conductivities of these salts over a range of concentrations. The slopes, B, of the linear plots of $\Lambda_0 - \Lambda_e$ vs. $\sqrt{C_e}$, where Λ_e is the equivalent conductivity, Λ_0 is the equivalent conductivity at infinite dilution, and C_e is the equivalent concentration, are sensitive to the electrolyte type.[31] For a group of hexafluorophosphate salts of 1:2 electrolyte type in nitromethane solution the slopes B range from 250 to 300 cm$^{1/2}$ equiv$^{-1/2}$ ohm^{-1} while for 1:1 electrolytes B is found to be near 150 cm$^{1/2}$ equiv$^{-1/2}$ ohm^{-1}.[32,33] For the hexafluorophosphate salts of **2a** and **2d**, B is 280 and 300 cm$^{1/2}$ equiv$^{-1/2}$ ohm^{-1}, respectively.

The ^{1}H NMR spectra of the cations **2** are reported in the experimental section. Resonances (with the correct intensity ratios) arising from the isocyanide alkyl groups, the methylene groups of the diphosphine ligands and from the phenyl groups are observed. The ^{1}H NMR spectra indicate that these dimeric cations are diamagnetic.

The infrared spectra of the complexes show absorptions

Table I. Infrared Stretching Frequencies from Rhodium Complexes

Compound	$\nu(\mathrm{C{\equiv}O})$, cm^{-1} chloroform solution	$\nu(\mathrm{C{\equiv}O})$, cm^{-1} solid
$(\mathrm{CO})_2\mathrm{Rh}_2\mathrm{Cl}_2(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$	1973	1963
$(\mathrm{CO})_2\mathrm{Rh}_2\mathrm{Cl}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$	2034	
$(\mathrm{CO})_2\mathrm{Rh}_2\mathrm{Br}_2(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$	1968	1965, 1923 sh
$(\mathrm{CO})_2\mathrm{Rh}_2\mathrm{Br}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$	2025	2023
$(\mathrm{CO})_2\mathrm{Rh}_2\mathrm{Br}_4(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$	2024	2028
$(\mathrm{CO})\mathrm{RhCl}(\mathrm{PPh}_3)_2$	1976	
$(\mathrm{CO})\mathrm{RhClI}_2(\mathrm{PPh}_3)_2$	2085	
$(\mathrm{CO})\mathrm{RhCl}(\mathrm{AsPh}_3)_2$	1973	
$(\mathrm{CO})\mathrm{RhClI}_2(\mathrm{AsPh}_3)_2$	2080	
	$\nu(\mathrm{C{\equiv}N^-})$, cm^{-1} acetone solution	$\nu(\mathrm{C{\equiv}N^-})$, cm^{-1} solid
$[(\mathrm{CH}_3\mathrm{NC})_2\mathrm{Rh}(\mathrm{PPh}_3)_2][\mathrm{PF}_6]$	2176	2173
$[(\mathrm{CH}_3\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2][\mathrm{PF}_6]_2$	2174	2175, 2149
$[(\mathrm{CH}_3\mathrm{NC})_4\mathrm{Rh}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2][\mathrm{BPh}_4]_2$	2215	2207
$[(n\text{-}\mathrm{C}_4\mathrm{H}_9\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2][\mathrm{BPh}_4]_2$	2160	2165, 2146
$[(n\text{-}\mathrm{C}_4\mathrm{H}_9\mathrm{NC})_4\mathrm{Rh}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2][\mathrm{BPh}_4]_2$	2201	2195, 2177 sh
$[(\mathrm{C}_6\mathrm{H}_{11}\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2][\mathrm{BPh}_4]_2$	2141	2157, 2136
$[(\mathrm{C}_6\mathrm{H}_{11}\mathrm{NC})_4\mathrm{Rh}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)][\mathrm{BPh}_4]_2$	2180	2175, 2161
$[(t\text{-}\mathrm{C}_4\mathrm{H}_9\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2][\mathrm{PF}_6]_2$	2150, 2125	2152, 2122

Table II. Electronic Spectra of Rhodium Complexes

Compound	$\lambda_{\mathrm{max,\,nm}}$ (ϵ_{max}) at 25 °C
$\mathrm{Rh}(\mathrm{CO})\mathrm{Cl}(\mathrm{PPh}_3)_2$[a]	410 sh (570), 364 (3300), 283 sh (16 300), 255 (23 900)
$\mathrm{Rh}_2(\mathrm{CO})_2\mathrm{Cl}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2$[a]	417 (7200), 301 (13 700), 255 sh (3400)
$\mathrm{Rh}(\mathrm{CO})\mathrm{Cl}(\mathrm{AsPh}_3)_2$[a]	400 sh (640), 357 (3700), 297 (11 600), 257 (27 700)
$\mathrm{Rh}_2(\mathrm{CO})_2\mathrm{Cl}_2(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$[a]	466 (8200), 292 (16 900), 240 (48 100)
$\mathrm{Rh}_2(\mathrm{CO})_2\mathrm{Br}_2(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$[a]	463 (7200), 297 (15 400)
$(\mathrm{CH}_3\mathrm{NC})_2\mathrm{Rh}(\mathrm{PPh}_3)_2{}^+$ [b]	458 (220), 400 (6400), 350 sh (3200), 317 (15 000)
$(\mathrm{CH}_3\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2{}^{2+}$	573 (12 200), 340 sh (5800), 316 (18 000)
$(n\text{-}\mathrm{C}_4\mathrm{H}_9\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2{}^{2+}$ [b]	560 (16 500), 338 sh (7700), 320 (18 100)
$(\mathrm{C}_6\mathrm{H}_{11}\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2{}^{2+}$ [b]	550 (11 000), 340 sh (7400), 322 (14 700)
$(t\text{-}\mathrm{C}_4\mathrm{H}_9\mathrm{NC})_4\mathrm{Rh}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2{}^{2+}$ [b]	523 (22 000), 337 (14 300), 320 (20 200)
$(\mathrm{CO})_2\mathrm{Rh}_2\mathrm{Br}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$[a]	580 (4500), 462 (15 000), 390 sh (12 700), 334 (19 500), 267 (28 500)
$(\mathrm{CH}_3\mathrm{NC})_4\mathrm{Rh}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2{}^{2+}$ [b]	498 (16 400), 437 (38 600), 380 sh (9300), 338 (16 200), 267 (47 700)
$(n\text{-}\mathrm{C}_4\mathrm{H}_9\mathrm{NC})_4\mathrm{Rh}_2\mathrm{I}_2(\mathrm{Ph}_2\mathrm{PCH}_2\mathrm{PPh}_2)_2{}^{2+}$ [b]	500 (18 800), 441 (41 600), 340 (18 200), 270 (48 700)
$(\mathrm{CO})_2\mathrm{Rh}_2\mathrm{Br}_4(\mathrm{Ph}_2\mathrm{AsCH}_2\mathrm{AsPh}_2)_2$[c]	430 (23 000), 348 (35 000), 260 (35 000)

[a] Dichloromethane solution. [b] Acetonitrile solution. [c] Chloroform solution.

which are characteristic of the various constituents of the complexes and the anions present. The frequencies of the isocyanide stretching vibrations for these and other complexes are recorded in Table I. These data indicate that only terminal isocyanide ligands are present. The observed isocyanide stretching frequencies occur in the range (2200–2130 cm^{-1}) in which most Rh(I) isocyanide complexes exhibit CN stretching frequencies.[27-30] For a complex with the geometry shown by **2**, two isocyanide stretching frequencies, with B_{1u} and B_{2u} symmetry, are predicted if the complex assumes idealized D_{2h} symmetry. For many of the complexes of type **2** the isocyanide stretching region does contain two distinct absorptions in the 2200–2130 cm^{-1} region.

Electronic Spectra of Rhodium(I) Complexes. The electronic spectral data are compiled in Table II. All of the complexes examined obey Beer's law over the concentration range 5–0.05 mM. The monomeric complexes $\mathrm{Rh}(\mathrm{CO})\mathrm{Cl}(\mathrm{PPh}_3)_2$, $\mathrm{Rh}(\mathrm{CO})\mathrm{Cl}(\mathrm{AsPh}_3)_2$, and $\mathrm{Rh}(\mathrm{CNCH}_3)_2(\mathrm{PPh}_3)_2{}^+$, in contrast to $(\mathrm{RNC})_4\mathrm{Rh}^+$,[3] show no tendency to associate in solution. Similarly the ligand bridged complexes of type **1** or **2** do not show any signs of further association or dissociation which would result from the changes in complex concentration.

Comparison of the electronic spectra of the ligand bridged dimers with the spectra of related monomers clearly demonstrates that the proximity of the two metal coordination spheres results in a significant alteration in the spectra of the rhodium chromophores. In Figure 1 the electronic spectrum of **1a** is compared with the spectrum for the corresponding monomer *trans*-$\mathrm{Rh}(\mathrm{CO})\mathrm{Cl}(\mathrm{AsPh}_3)_2$. In Figure 2 a comparison is made between **2a** and the related monomer $(\mathrm{CH}_3\mathrm{NC})_2\mathrm{Rh}(\mathrm{PPh}_3)_2{}^+$. Similar effects are seen in both cases. The low energy transitions of the monomeric complexes are shifted to lower energies in the dimeric complexes. The shift for the case of **1a** is 6500 cm^{-1} while in **2a** the shift is 7500 cm^{-1}. The higher energy features in the electronic spectrum are largely unaltered. These observations are related to the spectral changes which accompany the self association of $(\mathrm{RNC})_4\mathrm{Rh}^+$ [3] and ion pairing between $(\mathrm{RNC})_4\mathrm{Pt}^{2+}$ and $\mathrm{Pt}(\mathrm{CN})_4{}^{2-}$.[5] Increasing self association of $(\mathrm{PhNC})_4\mathrm{Rh}^+$ results in the growth of electronic absorptions at 568 and 727 nm. These absorptions have been assigned to electronic transitions at the dimer $[(\mathrm{PhNC})_4\mathrm{Rh}]_2{}^{2+}$ and the trimer $[(\mathrm{PhNC})_4\mathrm{Rh}]_3{}^{3+}$, respectively. Along with the increase in intensity of the absorptions due to the dimer and trimer, the low energy transition of the monomer $(\mathrm{PhNC})_4\mathrm{Rh}^+$ at 411 nm decreases in intensity as the total rhodium concentration in solution increases and the extent of association increases Our observation of a single low energy transition for dimeric **2** strengthens the assignment of the band

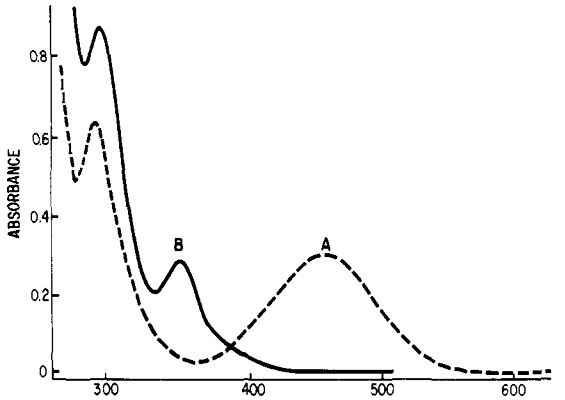


Figure 1. The electronic spectrum of: A, a 0.37 mM dichloromethane solution of $(CO)_2Rh_2Cl_2(Ph_2AsCH_2AsPh_2)_2$, and B, a 0.74 mM dichloromethane solution of $(CO)RhCl(AsPh_3)_2$. Each solution is contained in a 1.0-mm pathlength cell.

at 568 nm to the dimeric species in the $[(PhNC)_4Rh^+]_n$ system.

The two lowest energy transitions of the three different monomers can be confidently identified as spin forbidden and spin allowed, metal-to-ligand charge-transfer transitions. Similar patterns of low energy transitions have been identified as $d_{z^2} \rightarrow a_{2u}(\pi^*)\ {}^1A_{1g} \rightarrow {}^3A_{2u}$ and $d_{z^2} \rightarrow a_{2u}(\pi^*)\ {}^1A_{1g} \rightarrow {}^1A_{2u}$ transitions for planar complexes with D_{4h} symmetry and either four phosphine[34] or four isocyanide[35] donors. By analogy then the low energy transitions in $Rh(CO)Cl(PPh_3)_2$, $Rh(CO)Cl(AsPh_3)_2$, and $(CH_3NC)_2Rh(PPh_3)_2{}^+$ are identified as $d_{z^2} \rightarrow \pi^*$ metal to ligand charge transfer absorptions.

Within the series of complexes of type 2, the position of the lowest energy electronic transition is sensitive to the isocyanide alkyl substituent. This absorption band moves to lower energy in the following order: *tert*-butyl (523 nm) > cyclohexyl (550) > *n*-butyl (560) > methyl (573). This order is also the order of decreasing physical size of the isocyanide substituents. In order to accommodate large isocyanide ligands, three distortions can take place within the geometry of **2**. The two adjacent isocyanide ligands may bend away from one another, the two metal coordination planes may twist away from an eclipsed orientation, and the rhodium-rhodium distance may lengthen. We suspect that the spectral changes seen in the series **2a-d** result from lengthening of the rhodium-rhodium distance.

Oxidation to Produce Rh(II) Complexes. In view of the formation of dimeric Rh(II) complexes via eq 1, it was expected that the Rh(I) dimers **1** and **2** should undergo chemical oxidation to produce Rh(II) dimers. Examples of halogen oxidation, particular with iodine, which do produce Rh(II) complexes are described below. More extensive studies of oxidative-additions to these Rh(I) dimers are in progress and will be described in a subsequent publication.

Titrations of these dimeric Rh(I) complexes with iodine have been used as a preliminary means of establishing the stoichiometry of the oxidation. These titrations have been monitored by observing the CO or CN stretching frequencies. Oxidative halogen addition results in an increase in the CO or CN stretching frequency since the extent of metal to ligand backbonding is decreased as the formal metal oxidation state increases. The titration of **2a** with iodine is representative of the behavior of **2a**, **2b**, and **2c**. As the mole ratio of iodine to **2a** increases from 0 to 1 the intensity of the absorption at 2174 cm^{-1} due to **2a** decreases and a new absorption at 2214 cm^{-1} grows in intensity. All of the starting Rh(I) dimer has been consumed when the iodine to **2a** ratio reaches 1 since the initial absorbance at 2174 cm^{-1} vanishes at that ratio. Further increases in the iodine to **2a** ratio do not alter the isocyanide stretching region.

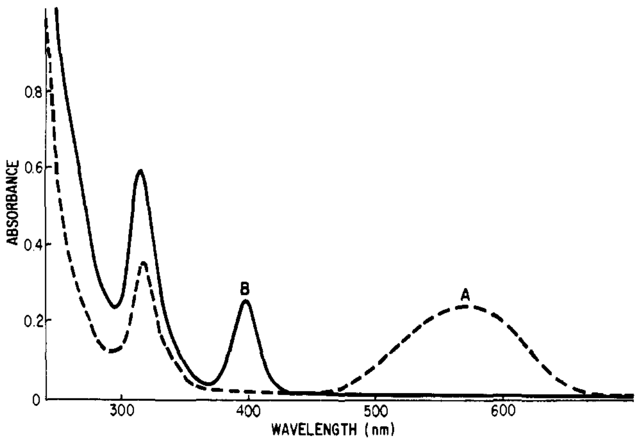
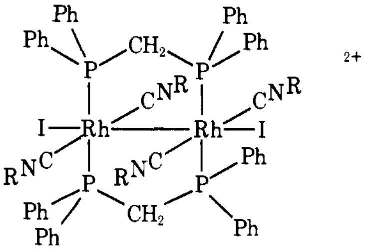


Figure 2. The electronic spectrum of: A, a 0.20 mM acetonitrile solution of $[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][PF_6]_2$, and B, a 0.40 mM acetonitrile solution of $[(CH_3NC)_2Rh(PPh_3)_2][PF_6]$. Each solution is contained in a 1.0-mm pathlength cell.

The products of the iodine oxidation of **2a-c** have been isolated as brown crystalline solids **3a**, **3b**, and **3c**. The elemental microanalytical data confirm the stoichiometry of iodine addition that was indicated by the titration data. Except for the shifts in the isocyanide stretching frequencies, the infrared spectra of the iodine oxidation products closely resemble the spectra of **2a**, **2b**, and **2c**. The shift of the isocyanide stretching frequency of **3** relative to the Rh(I) counterpart **2** is in the range 35-50 cm^{-1}. In contrast oxidation of a Rh(I) isocyanide complex to a Rh(III) isocyanide complex results in an increase in the range 65-80 cm^{-1}. Thus the smaller shift upon oxidation of **2** by iodine is consistent with the formation of a Rh(II) product. Similarly the Rh(II) dimers produced by eq 1 show an increase 35-50 cm^{-1} in their isocyanide stretching frequencies relative to the appropriate Rh(I) complexes.

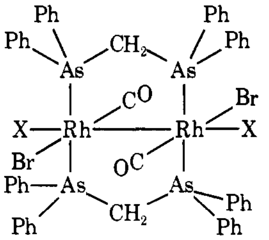
These data and the data which follow suggest that the iodine oxidation products have the structures shown below. The basic



3a, R = CH_3
3b, R = n-C_4H_9
3c, R = C_6H_{11}

structure of the Rh(I) dimers remains intact except that iodine has added to the axial rhodium coordination sites. The electrical conductivities of **3a**, **3b**, and **3c** in nitromethane solution are nearly the same as measured for **2a**, **2b**, and **2c**, respectively. Consequently the iodide is firmly bound in the rhodium coordination sphere. The proton magnetic resonance spectra of the Rh(II) dimers **3** indicate that they are diamagnetic, and consequently a direct rhodium-rhodium bond is present.

Similar oxidative-additions to the Rh(I) dimers of structure **1** are possible. An iodine titration of **1b** in dichloromethane solution indicates the formation of a Rh(II) dimer. As the mole ratio of iodine to **1b** increases from 0 to 1, the intensity of the carbonyl stretching frequency of **1b** at 1968 cm^{-1} decreases and a new carbonyl band appears at 2025 cm^{-1}. When this mole ratio reaches 1 the band at 1968 cm^{-1} has totally disappeared and the only carbonyl band present is the one at 2025 cm^{-1}. The product of this reaction has been isolated as a black microcrystalline solid. Oxidation of **1b** with bromine similarily produces a rhodium(II) dimer. These products are believed to have structure **4**. The infrared spectra of **4a** and **4b** are similar to that of **1b**. The increase in the carbonyl stretching frequency



4a, X = Br
4b, X = I

in **4a** and **4b** relative to **1b** is ca. 60 cm^{-1}. In contrast the carbonyl stretching frequency increases by 100 cm^{-1} when iodine is added to $Rh(CO)Cl(AsPh_3)_2$ or $Rh(CO)Cl(PPh_3)_2$ to form the Rh(III) products $Rh(CO)ClI_2(AsPh_3)_2$ or $Rh(CO)ClI_2(PPh_3)_2$. In dichloromethane solution both **4a** and **4b** are nonelectrolytes. The molecular weight of **4b** in chloroform solution substantiates the dimeric formulation.

The electronic spectra of these rhodium(II) complexes are reported in Table II. These spectra show a number of similarities. In particular all of the iodide complexes show intense absorption in the 430-465 nm region. For comparison $I_2Rh_2(CNC_6H_{11})_8{}^{2+}$, which is formed via eq 1, shows an absorption at 452 nm with an extinction coefficient of 25 000. This absorption band and the weaker shoulder found at lower energies in some of the complexes are probably due to iodide-to-metal charge transfer, since in the bromide analogues $Br_2Rh_2(CNC_6H_{11})_8{}^{2+}$ and **4a** this transition is shifted to higher energies (415 and 430 nm, respectively).

Discussion

A number of dimeric complexes containing two d^8 metal ions are known. For many of these the metal-metal distance is within bonding range but the details of the nature of metal-metal interaction are subject to considerable uncertainty.[36] For the dimeric rhodium(I) complexes **1** and **2** the molecular orbital approaches developed for $[(RNC)_4PtPt(CN)_4]^{2+}$ and for $[(RNC)_4Rh]_2{}^{2+}$ [3] appear to be applicable. A qualitative molecular orbital diagram for the construction of **2** from two hypothetical $(RNC)_2Rh(PR_3)_2{}^+$ fragments is shown in Figure 3. The principal metal-metal interaction is expected to involve the out-of-plane metal σ orbitals (d_{z^2} and p_z). The d_{z^2} orbitals of the planar monomers, labeled $1a_g$, are filled (and may well be the highest filled molecular orbitals if some[37,38] of the calculations[39] for $Pt(CN)_4{}^{2-}$ can be applied to $(RNC)_4Rh^+$ and $(RNC)_2Rh(PPh_3)_2{}^+$) while the p_z orbitals are empty. In addition, the diagram includes interactions between the empty ligand π levels and phosphorous d orbitals of b_{1u} symmetry, which are expected to be the lowest empty molecular orbitals in the monomers. For the dimers the levels $1a_g$ and $1b_{1u}$ are doubly occupied. The low energy electronic transitions which dominate the visible spectra of the dimers of type **2** are spin allowed transitions from $1b_{1u}$ to $2a_g$. Due to the orbital interaction the splitting between the $1b_{1u}$ and $2a_g$ levels must be smaller in the dimers than the splitting between the $1a_g$ and $1b_{1u}$ levels in the monomer. Mixing of the three a_g states and also of the three b_{1u} states can result in an overall attractive interaction between the two rhodium ions in these dimers. Of course for these ligand bridged dimers it is not certain that the direct rhodium-rhodium interaction is attractive, but in view of the attractive forces in $[(RNC)_4Rh]_2{}^{2+}$ it is also likely to be attractive in **2**. The electronic spectral shifts in $Rh(CO)Cl(EPh_3)_2$ and **1** can be explained similarly.

It should be noted that there exists a series of halo-bridged Rh(I) dimers (including $[(OC)_2RhCl]_2$[40] and $(1,5\text{-}C_8H_{12})RhCl_2Rh\{P(OC_6H_5)_3\}_2$[41]) which have shorter rhodium-rhodium distances than that found in **1a**. Studies of the physical or chemical effects of the proximity of the two metals in such dimers are limited and further investigations are warranted. It is reported that $[\{(p\text{-}CH_3C_6H_4)_3P\}_2RhCl]_2$ reacts with hydrogen at only one end to give $[\{(p\text{-}CH_3C_6H_4)_3P\}_2RhCl]_2H_2$.[42] We suspect that the relative orientation of the two metal coordination spheres as well as the distance between the metal ions determine the extent of interaction between them.

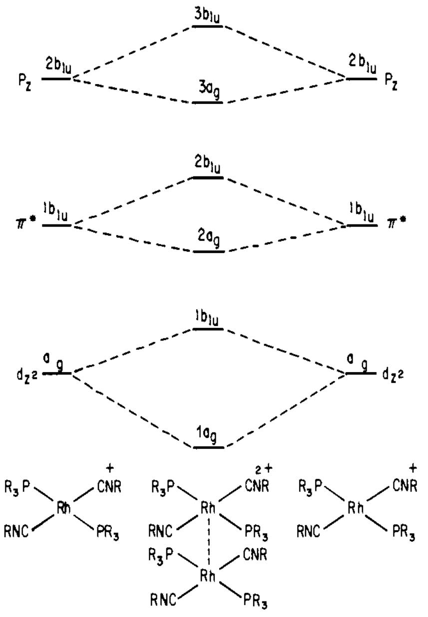
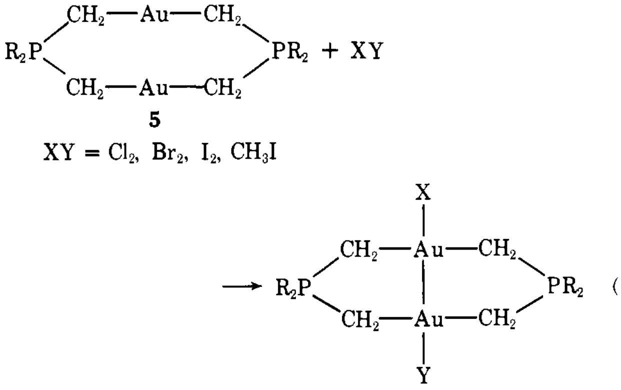


Figure 3. A partial molecular orbital diagram for the interaction of two planar $(RNC)_2Rh(PR_3)_2{}^+$ units.

Because of their diamagnetism, the rhodium(II) dimers are expected to contain a direct rhodium-rhodium bond. Almost certainly the oxidation of the ligand bridged rhodium(I) complexes by halogen results in a shortening of the rhodium-rhodium distances. The chemical bonding in rhodium(II) dimers has been a subject of some controversy. The range of rhodium-rhodium bond lengths in these compounds is quite large. For rhodium(II) acetate, which has the shortest rhodium-rhodium bond distance in this group, it has been suggested that the bond is short because a triple bond exists between the two metals.[14,15] Others maintain that the rhodium-rhodium bond in this compound is a single bond.[43] The availability of a new group of rhodium(II) dimers with isocyanide and phosphine ligands greatly increases the number of known Rh(II) dimers and presents further opportunities for studying the metal-metal bonding between transition metal ions with d^7 electronic configurations.

The oxidative-addition of iodine to the dimeric rhodium(I) complexes **1** and **2**, is an example of transanular bond strengthening within an eight-membered ring. Such oxidative coupling of atoms in a medium sized ring has been observed in a few other cases. The cyclic gold(I) complexes **5** are oxidized by halogens and methyl iodide to give gold(II) complexes **6** (eq 2).[44,45] Such interactions are not restricted to the tran-



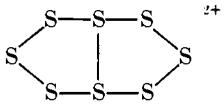
5

XY = Cl_2, Br_2, I_2, CH_3I

(2)

6

sition metals. Oxidation cyclooctasulfur produces the bicyclic cation 7.[46] Further examples of such transanular oxidations



7

and oxidative-additions may be anticipated.

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Photochemistry of Transition Metal Hydride Complexes. 1. Photoinduced Elimination of Molecular Hydrogen from $[IrClH_2(PPh_3)_3]$ and $[IrH_3(PPh_3)_3]$

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Abstract: Although $[IrClH_2(PPh_3)_3]$, *mer*-$[IrH_3(PPh_3)_3]$, and *fac*-$[IrH_3(PPh_3)_3]$ will not lose hydrogen under a variety of thermal conditions, irradiation with ultraviolet light readily induces elimination of H_2. Irradiation of $[IrClH_2(PPh_3)_3]$ with ultraviolet light or sunlight gives formation of $[IrCl(PPh_3)_3]$ with a 254-nm quantum yield of 0.56 ± 0.03. Irradiation of *mer*-$[IrH_3(PPh_3)_3]$ and *fac*-$[IrH_3(PPh_3)_3]$ leads to H_2 loss with subsequent formation of internally metallated $[\overline{Ir(C_6H_4P}Ph_2)(PPh_3)_2]$. The results reported herein suggest that photoinduced elimination of H_2 is a general process for di- and polyhydride complexes of iridium. The lack of production of HD upon photolysis of an $[IrClH_2(PPh_3)_3]$–$[IrClD_2(PPh_3)_3]$ mixture demonstrates that the photoelimination of H_2 from $[IrClH_2(PPh_3)_3]$ proceeds in a concerted fashion. A molecular orbital description of the complexes is proposed, and the photoactive excited state is believed to involve population of an iridium-H_2 antibonding orbital. The $[IrClH_2(PPh_3)_3]$–$[IrCl(PPh_3)_3]$ system is an attractive model for hydrogen storage and energy storage.

Transition metal hydride complexes have become an important class of compounds in inorganic and organometallic chemistry, and the field has expanded tremendously since the 1955 report[1] of the first thermally stable hydride complex, $[Re(\eta^5\text{-}C_5H_5)_2H]$. Many reviews have been published[2-7] describing the properties of metal hydrides, and in a recent literature survey[8] of the three catalytically important metals, ruthenium, rhodium and iridium, over 2000 known hydride complexes were uncovered. Transition metal hydrides play a key role in many homogeneous catalytic reactions, are useful synthetic intermediates, have promise as hydrogen and energy storage systems, and have been proposed[9] as important intermediates for obtaining molecular hydrogen from water.

In spite of the very large number of known hydride complexes and their importance in homogeneous catalysis, relatively few photochemical investigations have been conducted