and Liberman[16] for Cu Kα_1 radiation. This agreement also indicates that the specimen was substantially free of inversion twinning.

A single crystal of $Th[N(Si(CH_3)_3)_2]_3CH_3$ was examined by the X-ray diffraction method and found to be isomorphous with the $Th[N(Si(CH_3)_3)_2]_3BH_4$ complex reported here. The methyl derivative has cell dimensions a = 18.68 (1) and 8.537 (6) Å. Weissenberg patterns of the two isomorphs showed intensities that were visually the same. The crystals of the methyl derivative were too poor in quality to be used for collecting a suitable set of intensity data.

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Registry No. $ClTh[N(SiMe_3)_2]_3$, 51700-07-3; $ClU[N(SiMe_3)_2]_3$, 69517-42-6; $MeTh[N(SiMe_3)_2]_3$, 69517-43-7; $MeU[N(SiMe_3)_2]_3$, 69517-44-8; $BH_4Th[N(SiMe_3)_2]_3$, 69532-06-5; $BH_4U[N(SiMe_3)_2]_3$, 69532-07-6; $NaN(SiMe_3)_2$, 1070-89-9; $ThCl_4$, 10026-08-1; UCl_4, 10026-10-5.

Supplementary Material Available: Data processing formulas and the listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Further Studies of Diphosphine- and Diarsine-Bridged Rhodium Complexes

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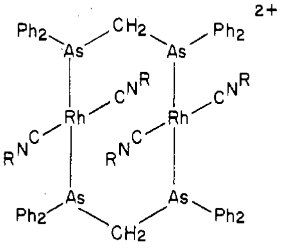
A convenient, new route to the diphosphine-bridged dimers $[Rh_2(CNR)_4(Ph_2PCH_2PPh_2)_2]^{2+}$ via the addition of the diphosphine and the isocyanide to [(1,5-cyclooctadiene)RhCl]$_2$ is described. The analogous diarsine-bridged dimers $[Rh_2(CNR)_4(Ph_2AsCH_2AsPh_2)_2][BPh_4]_2$ are best prepared by adding an isocyanide to $Rh_2(CO)_2Cl_2(Ph_2AsCH_2AsPh_2)_2$ followed by precipitation of the cation with sodium tetraphenylborate. Oxidative addition of iodine to $[Rh_2(CNR)_4(Ph_2AsCH_2AsPh_2)_2]^{2+}$ produces rhodium(II) complexes, $[Rh_2I_2(CNR)_4(Ph_2AsCH_2AsPh_2)_2]^{2+}$, with direct Rh–Rh bonds. Addition of disulfides to $[Rh_2(CNR)_4(Ph_2PCH_2PPh_2)_2]^{2+}$ can produce two different products. With trifluoromethyl disulfide, rhodium(II) dimers, $[Rh_2(SCF_3)_2(CNR)_4(Ph_2PCH_2PPh_2)_2]^{2+}$, are formed while with phenyl disulfide, pentafluorophenyl disulfide, and phenyl diselenide, rhodium(III) monomers, $[Rh(SR)_2(CNR)_2(Ph_2PCH_2PPh_2)]^+$ or $[Rh(SePh)_2(CNR)_2(Ph_2PCH_2PPh_2)]^+$, are obtained. Addition of disulfides and diselenides to $Rh(CNR)_4^+$ produces six-coordinate rhodium(III) species, *trans*-$[Rh(SR)_2(CNR)_4]^+$ or *trans*-$[Rh(SePh)_2(CNR)_4]^+$.

Introduction

Recent studies from our laboratory have been concerned with the chemical and physical properties of complexes containing two rhodium atoms.[1-4] Here we describe some additional studies in this area. The preparation of the diarsine-bridged complexes **1** and a comparison of these with their diphosphine-bridged counterparts **2**[2] are presented. Oxidation of **2** and similar dimers, including **1** as shown here, with iodine (and bromine) produces Rh(II) dimers with direct Rh–Rh bonds.[2] However the role of the ligand in promoting such transannular oxidative additions is not clear, since unbridged Rh(II) dimers, $Rh_2(CNR)_8X_2^{2+}$, may readily be prepared either by addition of halogen to $Rh(CNR)_4^+$ or by reacting $Rh(CNR)_4^+$ with $Rh(CNR)_4X_2^+$.[1] We now show that trifluoromethyl disulfide undergoes transannular oxidative addition to **1** to produce $[Rh_2(CNR)_4(Ph_2PCH_2PPh_2)_2(SCF_3)_2]^{2+}$ whereas no comparable Rh(II) species is obtained in the absence of a bridging ligand. Other aspects of the addition of disulfides to mononuclear and binuclear Rh(I) compounds are described. Previous studies have shown that disulfides can add to very reactive monomeric Rh(I) compounds to produce Rh(III) thiolate complexes.[5]



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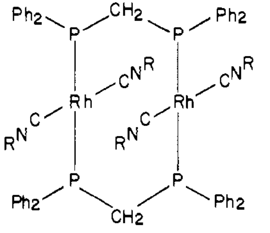

2

Experimental Section

Preparation of Compounds. Bis(diphenylphosphino)methane and bis(diphenylarsino)methane were obtained from Strem Chemicals, and the disulfides were also obtained from commercial sources. The following compounds were obtained by established routes: $[(1,5\text{-}C_8H_{12})RhCl]_2$,[6] $Rh_2(Ph_2AsCH_2AsPh_2)_2(CO)_2Cl_2$,[7] $(C_6F_5S)_2$.[8] Only representative syntheses are reported in cases where the substituents on the isocyanides may be varied.

$[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$. *n*-Butyl isocyanide (0.31 mL, 3.2 mmol) was added dropwise to a briskly stirred slurry of 0.40 g (0.81 mmol) of $[(1,5\text{-}C_8H_{12})RhCl]_2$ and 0.63 g (1.6 mmol) of bis(diphenylphosphino)methane in 30 mL of methanol. The stirring

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was continued for 30 min after the addition of the isocyanide was completed, whereupon the blue-violet solution was filtered. A solution of 0.56 g (1.6 mmol) of sodium tetraphenylborate in 10 mL of methanol was added to the filtrate. The deep blue precipitate was collected by filtration and washed with methanol. Purification was accomplished by recrystallization from acetone/1-propanol; yield 1.14 g (72%). The product was identified by comparison of electronic, infrared, and NMR spectra with the spectra of an authentic sample prepared as described previously.[2]

$[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2AsCH_2AsPh_2)_2][BPh_4]_2\cdot(CH_3)_2CO$. n-Butyl isocyanide (0.068 mL, 0.72 mmol) was added dropwise to a rapidly stirred slurry of 0.23 g (0.18 mmol) of $Rh_2(CO)_2Cl_2(Ph_2AsCH_2AsPh_2)_2$ in 10 mL of methanol. After being stirred for 20 min, the blue-violet solution was filtered, and a solution of 0.13 g (3.8 mmol) of sodium tetraphenylborate in 5 mL of methanol was added. The deep violet precipitate was removed by filtration and washed with methanol. The solid was dissolved in 30 mL of acetone and the solution was filtered. After the addition of 15 mL of 1-propanol, the volume of the solution was reduced under vacuum by the use of a rotary evaporator until dark blue-violet crystals of the product formed. These were collected by filtration, washed with 1-propanol and methanol, and vacuum dried; yield 0.24 g (63%). The infrared spectrum contained a sharp band at 1725 cm^{-1} due to the lattice acetone. ^1H NMR (CH_3CN solution): δ 6.6–7.8 (phenyl multiplet), 3.6 (methylene of diarsine), 2.68 (α-methylene of isocyanide), 1.82–1.60 (remaining isocyanide protons). Anal. Calcd for $C_{121}H_{126}As_4B_2N_4Rh_2O$: C, 66.68; H, 5.82; N, 2.57. Found: C, 66.78; H, 5.83; N, 2.52.

$[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2AsCH_2AsPh_2)_2I_2][BPh_4]_2$. A solution of 17.6 mg (6.93×10^{-5} mol) of iodine in 5 mL of acetone was added to a solution of 126.4 mg (5.95×10^{-5} mol) of $[(n\text{-}BuNC)_4Rh_2(Ph_2AsCH_2AsPh_2)_2][BPh_4]_2$ in 5 mL of acetone. The brown solution was filtered, and 10 mL of 1-propanol was added to the filtrate. The solvent was removed by vacuum evaporation until the product crystallized. The brown crystals were collected by filtration, washed with 1-propanol and methanol, and vacuum dried; yield 118 mg (83%). ^1H NMR (CD_3CN solution): δ 8.0–6.6 (phenyl multiplet), 4.5 (methylene of diarsine), 3.1 (α-methylene of isocyanide), 1.4–0.9 (remaining isocyanide protons). Anal. Calcd for $C_{118}H_{120}As_4B_2I_2N_4Rh_2$: C, 59.67; H, 5.09; I, 10.69. Found: C, 59.90; H, 5.13; I, 11.20.

$[(C_6H_{11}NC)_4Rh(SCF_3)_2][BPh_4]$. Trifluoromethyl disulfide was bubbled through a solution of 0.27 g of $[(C_6H_{11}NC)_4Rh][BPh_4]$ in 10 mL of dichloromethane. After the infrared spectrum of the yellow solution indicated that none of the starting rhodium complex remained, the solution was filtered, and ether was slowly added to precipitate the yellow crystalline product, yield 80%. Anal. Calcd for $C_{54}H_{64}BF_6N_4RhS_2$: C, 61.13; H, 6.08; N, 5.28; S, 6.04. Found: C, 60.96; H, 5.98; N, 5.20; S, 6.58.

$[(C_6H_{11}NC)_4Rh(SC_6H_5)_2][BPh_4]$. A solution of 0.10 g (0.46 mmol) of phenyl disulfide in 5 mL of dichloromethane was added to a solution of 0.19 g (0.25 mmol) of $[(C_6H_{11}NC)_4Rh][BPh_4]$ in 15 mL of dichloromethane. After the solution was heated under reflux for 1 h, it was filtered, and 10 mL of 1-propanol was added to the filtrate. The volume of this solution was reduced under vacuum on a rotary evaporator until orange crystals of the product formed. These were collected by filtration and washed with 1-propanol and ether; yield 70%. Anal. Calcd for $C_{64}H_{74}BN_4RhS_2$: C, 71.36; H, 6.92; S, 5.95. Found: C, 71.30; H, 7.44; S, 6.69.

$[(n\text{-}C_4H_9NC)_4Rh(SC_6F_5)_2][BPh_4]$. A solution of 0.102 g (0.256 mmol) of pentafluorophenyl disulfide in 5 mL of acetone was added to a solution of 0.174 g (0.231 mmol) of $[(n\text{-}BuNC)_4Rh][BPh_4]$ in 10 mL of acetone. The brown solution was filtered and evaporated to 5 mL. After the addition of 10 mL of 1-propanol the solution was stored at −10 °C. The orange crystals which formed were collected by filtration and washed with methanol. Purification was achieved by recrystallization from acetone/1-propanol; yield 0.128 g (48%). Anal. Calcd for $C_{56}H_{54}BF_{10}N_4RhS_2$: C, 58.34; H, 4.90; S, 5.56. Found: C, 58.59; H, 4.76; S, 5.64.

$[(n\text{-}C_4H_9NC)_4Rh(SeC_6H_5)_2][BPh_4]$. Orange plates of the compound were prepared from phenyl diselenide by the method used for $[(n\text{-}C_4H_9NC)_4Rh(SC_6F_5)_2][BPh_4]$ in 91% yield. Anal. Calcd for $C_{56}H_{66}BN_4RhSe_2$: C, 63.05; H, 6.24; Se, 14.80. Found: C, 63.81; H, 6.40; Se, 14.95.

$[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2(SCF_3)_2][PF_6]_2$. Trifluoromethyl disulfide was bubbled through a slurry of 0.15 g of $[(CH_3NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ in 15 mL of acetonitrile. After the blue solution had turned orange and all the solid had dissolved, the solution was filtered, and ether was added dropwise to the filtrate in order to precipitate orange crystals of the product. These were removed by filtration and washed with ether; yield 70%. ^1H NMR (CD_3CN solution): δ 7.64 (phenyl multiplet), 4.60 (CH_2), 2.46 (CH_3). Anal. Calcd for $C_{60}H_{56}F_{18}N_4P_6Rh_2S_2$: C, 44.19; H, 3.46; N, 3.44; S, 3.93. Found: C, 44.25; H, 3.62; N, 3.54; S, 4.23.

$[(n\text{-}C_4H_9NC)_2Rh(Ph_2PCH_2PPh_2)(SPh)_2][BPh_4]$. A solution of 0.102 g (0.46 mmol) of phenyl disulfide in 5 mL of acetone was added to a solution of 0.195 g (0.100 mmol) of $[(n\text{-}C_4H_9NC)_4Rh_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ in 10 mL of acetone. The solution was heated under reflux for 1 h, 10 mL of 1-propanol was added, and the solution was filtered. Acetone was distilled from the solution until crystals of the product appeared. After being cooled, the solution was filtered, and the deep rose crystalline product was washed with 1-propanol and methanol. Purification was achieved by recrystallization from acetone/1-propanol; yield 0.193 g (81%). Anal. Calcd for $C_{71}H_{70}BN_2P_2RhS_2$: C, 71.59; H, 5.92; S, 5.38. Found: C, 72.11; H, 6.21; S, 5.06.

$[(n\text{-}C_4H_9NC)_2Rh(Ph_2PCH_2PPh_2)(SC_6F_5)_2][BPh_4]$. Yellow needles of this compound were obtained with the method described for $[(n\text{-}C_4H_9NC)_2Rh(Ph_2PCH_2PPh_2)(SPh)_2][BPh_4]$ in 33% yield. Anal. Calcd for $C_{71}H_{60}BF_{10}N_2P_2RhS_2$: C, 62.20; H, 4.41. Found: C, 62.46; H, 4.60.

$[(n\text{-}C_4H_9NC)_2Rh(Ph_2PCH_2PPh_2)(SePh)_2][BPh_4]$. Brown plates of this material were obtained from phenyl diselenide by the method used for $[(n\text{-}C_4H_9NC)_2Rh(Ph_2PCH_2PPh_2)(SPh)_2][BPh_4]$ in 60% yield. Anal. Calcd for $C_{71}H_{70}BN_2P_2RhSe_2$: C, 66.37; H, 5.49; N, 2.18. Found: C, 65.66; H, 5.36; N, 2.25.

Physical Measurements. Infrared spectra were recorded on a Beckman IR-12 spectrometer. Proton magnetic resonance spectra were obtained with a JEOL MH-100 spectrometer with tetramethylsilane as internal standard while ^{31}P NMR spectra were recorded at 40.5 MHz with a JEOL PS-100 pulsed Fourier transform spectrometer with external 85% phosphoric acid as reference. Conductivities were determined by the use of an Industrial Instruments conductivity bridge with 10^{-3} M acetonitrile solutions.

Results and Discussion

The phosphine-bridged dimers have been prepared previously by the reaction of the diphosphine with $[(RNC)_4Rh]^+$.[2] A similar substitution reaction with bis(diphenylarsino)methane in place of its phosphine analogue was not successful. Apparently the weaker arsine donor will not replace the isocyanide ligands. Two new routes to such bridged complexes have been devised. The addition of an isocyanide to a methanolic slurry of 1,5-cyclooctadienerhodium(I) chloride dimer and bis(diphenylphosphino)methane produces purple or violet solutions of $[(RNC)_4Rh_2(Ph_2PCH_2PPh_2)_2]^{2+}$, and these cations may be isolated by precipitation as the hexafluorophosphate or tetraphenylborate salts. A similar procedure with bis(diphenylarsino)methane does yield $[(RNC)_4Rh_2(Ph_2AsCH_2AsPh_2)_2]^{2+}$ but some $[(RNC)_4Rh]^+$ forms also, and the separation of these two cations can be difficult. A better route to the preparation of $[(RNC)_4Rh_2(Ph_2AsCH_2AsPh_2)_2]^{2+}$ involves the gradual addition of an isocyanide to the preformed dimer $Rh_2(Ph_2AsCH_2AsPh_2)_2(CO)_2Cl_2$.[7] The purple or blue-violet cations which are formed in methanol solution have been crystallized as tetraphenylborate salts.

Physical characteristics of these diarsine-bridged dimers are reported in Tables I and II. These data indicate that the analogous diphosphine- and diarsine-bridged dimers have similar structures. The infrared spectra indicate that only terminal isocyanide ligands are present and also exhibit bands characteristic of the arsine ligands and the tetraphenylborate anions. The isocyanide stretching vibrations occur in the range 2200–2130 cm^{-1}, characteristic for Rh(I) compounds.[9-11] The electronic spectra of the diarsine-bridged dimers reveal the proximity-shifted metal-to-ligand ($d_{z^2} \rightarrow \pi^*$) charge-transfer absorptions which are a characteristic feature of face-to-face dimeric d^8 complexes[2,3,12] with acceptor ligands. Thus, the

Table I. Physical Properties

compd[a]	color	ν(CN),[b] cm^{-1}	Λ_M,[c] cm^2 mol^{-1} ohm^{-1}
$[(CH_3NC)_4Rh_2(dam)_2][BPh_4]_2$	blue	2196, 2172	186
$[(n\text{-}C_4H_9NC)_4Rh_2(dam)_2][BPh_4]_2$	blue-violet	2166, 2144	176
$[(C_6H_{11}NC)_4Rh_2(dam)_2][BPh_4]_2$	rose	2162, 2131	178
$[(t\text{-}C_4H_9NC)_4Rh_2(dam)_2][BPh_4]_2$	rose	2151, 2125	185
$[(n\text{-}C_4H_9NC)_4Rh(SCF_3)_2][BPh_4]$	yellow	2255	88
$[(C_6H_{11}NC)_4Rh(SCF_3)_2][BPh_4]$	yellow	2254	
$[(n\text{-}C_4H_9NC)_4Rh(SC_6F_5)_2][BPh_4]$	yellow	2250	80
$[(n\text{-}C_4H_9NC)_4Rh(SC_6H_5)_2][BPh_4]$	orange	2247	85
$[(C_6H_{11}NC)_4Rh(SC_6H_5)_2][BPh_4]$	orange	2228	85
$[(n\text{-}C_4H_9NC)_4Rh(SeC_6H_5)_2][BPh_4]$	orange	2241	87
$[(CH_3NC)_4Rh_2(dpm)_2(SCF_3)_2][PF_6]_2$	orange	2214	278[d]
$[(n\text{-}C_4H_9NC)_4Rh_2(dpm)_2(SCF_3)_2][BPh_4]_2$	orange	2197	185
$[(n\text{-}C_4H_9NC)_2Rh(dpm)(SC_6F_5)_2][BPh_4]$	yellow	2230	
$[(n\text{-}C_4H_9NC)_2Rh(dpm)(SC_6H_5)_2][BPh_4]$	red	2233	80
$[(n\text{-}C_4H_9NC)_2Rh(dpm)(SeC_6H_5)_2][BPh_4]$	brown-violet	2222	82
$[(n\text{-}C_4H_9NC)_4Rh_2(dam)_2I_2][BPh_4]_2$	brown	2199	168
$[(C_6H_{11}NC)_4Rh_2(dam)_2I_2][BPh_4]_2$	brown	2181	195

[a] dam = $(C_6H_5)_2AsCH_2As(C_6H_5)_2$; dpm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$. [b] As Nujol mulls. [c] In acetonitrile solution. [d] Conductivity for PF_6^- salts are always higher than for BPh_4^- salts. For comparison, in acetonitrile $[(CH_3NC)_4Rh_2(dpm)_2][PF_6]$ has $\Lambda_M = 276$.

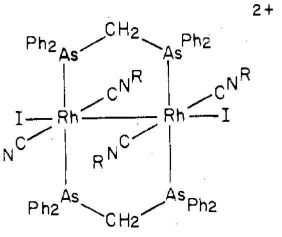
Table II. Electronic Spectra of Rhodium Complexes in Acetonitrile Solution

compd[a]	λ_{max}, nm (ϵ_{max}) [at 25 °C]
$[(CH_3NC)_4Rh_2(dam)_2][BPh_4]_2$	588 (13 000), 324 (17 000), 277 sh (17 000)
$[(n\text{-}C_4H_9NC)_4Rh_2(dam)_2][BPh_4]_2$	575 (12 400), 323 (18 700), 273 sh (15 500), 260 sh (21 600)
$[(C_6H_{11}NC)_4Rh_2(dam)_2][BPh_4]_2$	551 (11 000), 381 (2000), 325 (18 300)
$[(t\text{-}C_4H_9NC)_4Rh_2(dam)_2][BPh_4]_2$	515 (9600), 321 (14 400), 306 (18 100)
$[(n\text{-}C_4H_9NC)_4Rh_2(dam)_2I_2][BPh_4]_2$	514 (15 500), 465 (25 900), 395 (8900), 346 (19 800)
$[(C_6H_{11}NC)_4Rh_2(dam)_2I_2][BPh_4]_2$	515 (16 000), 467 (20 000), 410 sh (10 000), 350 (21 000)
$[(C_6H_{11}NC)_4Rh(SPh)_2][BPh_4]$	460 sh (1500), 353 (28 800)
$[(n\text{-}C_4H_9NC)_4Rh(SPh)_2][BPh_4]$	470 sh (1290), 360 (30 300)
$[(n\text{-}C_4H_9NC)_4Rh(SePh)_2][BPh_4]$	480 (1260), 359 (46 300)
$[(n\text{-}C_4H_9NC)_4Rh(SC_6F_5)_2][BPh_4]$	450 (1330), 359 (36 900)
$[(n\text{-}C_4H_9NC)_2Rh(dpm)(SPh)_2][BPh_4]$	500 (3500), 340 (29 400)
$[(n\text{-}C_4H_9NC)_2Rh(dpm)(SePh)_2][BPh_4]$	520 (2400), 417 sh (2400), 342 (32 200)
$[(CH_3NC)_4Rh_2(dpm)_2(SCF_3)_2][PF_6]_2$	500 sh (1100), 427 (42 700), 337 (24 600), 268 (46 000)
$[(n\text{-}C_4H_9NC)_4Rh_2(dpm)_2(SCF_3)_2][BPh_4]_2$	550 sh (540), 423 (14 600), 400 sh 13 000), 334 (18 400)

[a] dam = $(C_6H_5)_2AsCH_2As(C_6H_5)_2$; dpm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$.

lowest energy band reported for each complex of type **1** in Table II is responsible for the blue to violet color of these dimers. As in the case with **2**, this charge-transfer absorption is sensitive to the isocyanide ligand substituent.[2] As the bulk of the substituent decreases from *tert*-butyl through cyclohexyl and *n*-butyl to methyl, this absorption moves to lower energies because the two metal centers are allowed to approach one another more closely, and the overlap between the orbitals involved increases. The proton magnetic resonance spectra of the dimers, **1**, show resonances characteristic of their components. The electrical conductivities of acetonitrile solutions of **1** are consistent with their formulation as 1:2 electrolytes.

Iodine reacts with **1** to produce diamagnetic Rh(II) dimers **3**. Titration of **1** with iodine in acetone and dichloromethane has been monitored by infrared spectroscopy in the region 2300–2000 cm^{-1}. During the titration, the isocyanide stretching bands due to **1** disappear as a new absorption grows in at ca. 40 cm^{-1} higher energy. For R = methyl, *n*-butyl, and cyclohexyl, the titration is complete after the addition of 1 mol of iodine to 1 mol of **1**. Further addition of iodine even in refluxing acetone produces no further changes. The products of iodine oxidation have been isolated as brown microcrystalline solids. These solids exhibit isocyanide stretching frequencies that are ca. 40 cm^{-1} higher than those of the starting materials. In contrast, Rh(III) isocyanide complexes generally show an increase in the isocyanide stretching frequencies of ca. 70 cm^{-1}. The electronic spectra of the Rh(II) cations **3** are similar to their diphosphine-bridged analogues.[2] The electrical conductivity of these salts in acetone are consistent with the presence of 1:2 electrolytes and indicate that the iodide ions are coordinated to rhodium.



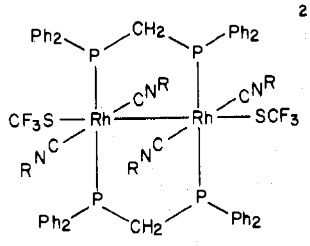
3

The dimers of type **1** and **2** with *tert*-butyl groups have properties which indicate that their structures are strained due to the eclipsed position of the bulky isocyanide substituents. Neither complex undergoes a smooth oxidation with iodine to give a Rh(II) dimer, **3**. Rather, upon titration with iodine, an uptake of 2 mol of iodine/mol of dimer is required to complete all spectral changes. The products appear to be mixtures of Rh(III) species with ν(CN) of ca. 2230 cm^{-1}. These have not yet been separated into pure products. Their formation involves a conversion of the diphosphine and diarsine ligands from a bridging mode to a chelating form. Since oxidation of **1** and **2** to Rh(II) species is anticipated to result in a shortening of the Rh–Rh distance from 3.5 to 2.8 Å, the bulk of the isocyanide substituents appears to prohibit formation of **3** with R = *tert*-butyl. Additionally, dilute (0.05 mM) acetonitrile solutions of **1** and **2** with *tert*-butyl substituents are markedly more oxygen sensitive (turning from violet to yellow in 1 or 2 h in air) than their counterparts with smaller isocyanide substituents.

The disulfides, trifluoromethyl disulfide, pentafluorophenyl disulfide, and phenyl disulfide, add readily to $(RNC)_4Rh^+$ to give the pale yellow to orange cations *trans*-$(RNC)_4Rh(SR)_2^+$. The weaker oxidant *n*-butyl disulfide does not add to $(n\text{-}BuNC)_4Rh^+$. These oxidative additions result in an increase of ν(CN) of ca. 80 cm^{-1}. The products have been isolated as their tetraphenylborate salts, and these have electrical conductivities characteristic of 1:1 electrolytes. The trans stereochemistry is established by the observation of only a single isocyanide stretching frequency. Phenyl diselenide reacts similarly with $(n\text{-BuNC})_4\text{Rh}^+$ to yield *trans*-$(n\text{-BuNC})_4\text{Rh(SePh)}_2^+$.

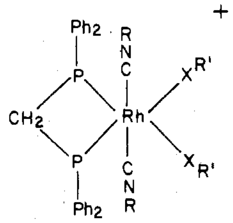
No evidence for the formation of Rh(II) complexes from $(\text{RNC})_4\text{Rh}^+$ has been found in these disulfide oxidations. Infrared observation during the oxidation of $(\text{RNC})_4\text{Rh}^+$ to $(\text{RNC})_4\text{Rh(SR)}_2^+$ shows only the presence of these two cations. Mixing solutions of $(\text{RNC})_4\text{Rh}^+$ and $(\text{RNC})_4\text{Rh(SR)}_2^+$, unlike the situation with $(\text{RNC})_4\text{Rh}^+$ and $(\text{RNC})_4\text{RhX}_2^+$ (X = Br or I),[4] produces no infrared or electronic spectral changes. A possible cause for the lack of formation of Rh(II) species with thiolate ligands has been described in a previous discussion of the mechanism of the reaction between Rh(I) and Rh(II) isocyanide complexes.[13]

However, Rh(II) species are formed by the reaction of **2** (R = *n*-butyl or methyl) and trifluoromethyl disulfide. The products are formulated as the dimers **4**. The elemental analysis as well as the increase of ν(CN) upon the preparation of **4** are consistent with the formation of a Rh(II) rather than a Rh(III) product. The proton magnetic resonance spectrum of **4a** indicates that the product is diamagnetic and that all isocyanide ligands reside in a single environment.



4a, R = CH_3
b, R = $n\text{-C}_4\text{H}_9$

In contrast phenyl disulfide, pentafluorophenyl disulfide and phenyl diselenide react with **2** to yield rhodium(III) complexes. These reactions have been carried out in refluxing acetone solution and are somewhat slower than the oxidations with iodine or trifluoromethyl disulfide. The products exhibit ν(CN) at frequencies that are both characteristic of rhodium(III) species and higher than the phosphine-bridged rhodium(II) dimers that have been prepared. The observation of only a single, sharp isocyanide stretching frequency indicates that the isocyanide ligands are mutually trans. The ^{31}P NMR spectra of these products are also indicative of rhodium(III) species. For $[(n\text{-C}_4\text{H}_9\text{NC})_2\text{Rh}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\text{SeC}_6\text{H}_5)_2]^+$ in acetone solution, a doublet at 13.45 ppm downfield from 85% external phosphoric acid with $^1J_{\text{P-Rh}}$ = 73.54 Hz is observed while for $[(n\text{-C}_4\text{H}_9\text{NC})_2\text{Rh}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\text{SeC}_6\text{H}_5)_2]^+$ a similar doublet at 22.09 ppm with $J'_{\text{P-Rh}}$ = 75.07 Hz has been observed. These simple spectra contrast with the more complex spectra characteristic of AA′A″A‴XX′ systems which are observed for **2**, other binuclear Rh(I) complexes, and the dimeric Rh(II) complexes **3** and **4**.[14] Additionally, the Rh–P coupling constants are typical of Rh(III) species. Rhodium(III) complexes typically have $^1J(^{31}\text{P}-^{103}\text{Rh})$ in the range 60–100 Hz while Rh(I) complexes display $^1J(^{31}\text{P}-^{103}\text{Rh})$ in the range 114–160 Hz.[15]



5a, XR′ = SPh, R = *n*-Bu
b, XR′ = SePh, R = *n*-Bu

These data suggest that the oxidation products from these reactions are the monomeric cations **5**. In order for these rhodium(III) cations to form, the diphosphine has had to change from a bridging ligand to a chelating one. We have previously reported other cases in which similar changes from bridging to chelating coordination occur for diphosphines.[3] However, at the present time it does not appear possible to predict the circumstances which will cause diphosphines to undergo these changes, and further studies of this phenomenon appear warranted. It is possible that the higher temperatures used in the addition of phenyl disulfide, pentafluorophenyl disulfide, and phenyl diselenide were responsible for the fragmentation of the dimeric species so that Rh(III) monomers resulted. However, attempts to convert $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}_2(\text{dpm})_2\text{I}_2]^{2+}$ into a Rh(III) monomer by treatment with iodine in refluxing acetone under the conditions used for disulfide addition resulted only in the recovery of the starting Rh(II) dimers.

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Registry No. $[(\text{CH}_3\text{NC})_4\text{Rh}_2(\text{dam})_2][\text{BPh}_4]_2$, 69420-76-4; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}_2(\text{dam})_2][\text{BPh}_4]_2$, 69420-78-6; $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}_2(\text{dam})_2][\text{BPh}_4]_2$, 69420-80-0; $[(t\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}_2(\text{dam})_2][\text{BPh}_4]_2$, 69420-82-2; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}(\text{SCF}_3)_2][\text{BPh}_4]$, 69420-84-4; $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}(\text{SCF}_3)_2][\text{BPh}_4]$, 69420-86-6; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}(\text{SC}_6\text{F}_5)_2][\text{BPh}_4]$, 69420-88-8; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}(\text{SC}_6\text{H}_5)_2][\text{BPh}_4]$, 69420-90-2; $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}(\text{SC}_6\text{H}_5)_2][\text{BPh}_4]$, 69420-92-4; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}(\text{SeC}_6\text{H}_5)_2][\text{BPh}_4]$, 69420-94-6; $[(\text{CH}_3\text{NC})_4\text{Rh}_2(\text{dpm})_2(\text{SCF}_3)_2][\text{PF}_6]_2$, 69420-96-8; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}_2(\text{dpm})_2(\text{SCF}_3)_2][\text{BPh}_4]_2$, 69420-98-0; $[(n\text{-C}_4\text{H}_9\text{NC})_2\text{Rh}(\text{dpm})(\text{SC}_6\text{F}_5)_2][\text{BPh}_4]$, 69421-00-7; $[(n\text{-C}_4\text{H}_9\text{NC})_2\text{Rh}(\text{dpm})(\text{SC}_6\text{H}_5)_2][\text{BPh}_4]$, 69421-02-9; $[(n\text{-C}_4\text{H}_9\text{NC})_2\text{Rh}(\text{dpm})(\text{SeC}_6\text{H}_5)_2][\text{BPh}_4]$, 69421-04-1; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}_2(\text{dam})_2\text{I}_2][\text{BPh}_4]_2$, 69421-06-3; $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}_2(\text{dam})_2\text{I}_2][\text{BPh}_4]_2$, 69421-08-5; $[(1,5\text{-C}_8\text{H}_{12})\text{RhCl}]_2$, 12092-47-6; $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{dam})_2$, 23299-75-4; $[(\text{C}_6\text{H}_{11}\text{NC})_4\text{Rh}][\text{BPh}_4]$, 61160-75-6; $[(n\text{-BuNC})_4\text{Rh}][\text{BPh}_4]$, 61160-72-3; $[(\text{CH}_3\text{NC})_4\text{Rh}_2(\text{dpm})_2][\text{BPh}_4]_2$, 61160-79-0; $[(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}_2(\text{dpm})_2][\text{BPh}_4]_2$, 61160-70-1; trifluoromethyl disulfide, 372-64-5; phenyl disulfide, 882-33-7; pentafluorophenyl disulfide, 1494-06-0; phenyl diselenide, 1666-13-3.

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