In our experiments we determined the order of the reaction as well as the activation parameters. The results confirm this hypothesis.

The conclusion agrees well with our previous observations[5] concerning a series of solvates of $Be^{2+}$, including the complex $Be(TMPA)_4^{2+}$.

In this series an increase of steric hindrance leads to a change of the reaction mechanism from $S_N2$ to $S_N1$, accompanied by an increase of the activation parameters.

Steric hindrance, i.e., repulsions between coordinated molecules of TMPA, might be one reason for the variety of mechanisms found for the trivalent non-transition-metal cations $Al^{3+}$, $Ga^{3+}$, and $In^{3+}$. The arrangement of six TMPA molecules around the comparatively small cations $Al^{3+}$, $Ga^{3+}$ is so compact that a heptacoordinated transition state is impossible, thus promoting an $S_N1$ type substitution mechanism. It should be noticed that the exchange rate is faster with $Ga^{3+}$ than with $Al^{3+}$, as can be expected from the increased ionic radius.[28] On the contrary, the relief of the steric strain around the much bigger $In^{3+}$ cation permits a heptacoordinated transition state and therefore an $S_N2$ mechanism.

In conclusion, this mechanistic interpretation agrees with the previous one explaining the increased quadrupolar relaxation rate on passing from $Al^{3+}$ to $In^{3+}$ solvates. Their mutual agreement favors decisively the assumption of the steric strain of the ligands to be the major structural factor in these complexes.

**Acknowledgment.** Financial support from the Centre National de la Recherche Scientifique is gratefully acknowledged. All NMR spectra were recorded on spectrometers of the Groupement Régional de Mesures Physiques de l'Académie de Nancy-Metz. We thank M. Diter for his technical assistance. One of the authors (L.R.) thanks the Deutsche Akademische Austauschdienst for a NATO postdoctoral fellowship grant.

**Registry No.** **1**, 63625-66-1; **2**, 63641-43-0; $^{27}Al$, 7429-90-5; $^{71}Ga$, 14391-03-8; $^{115}In$, 14191-71-0; $Ga^{3+}$, 22537-33-3; $In^{3+}$, 22537-49-1.

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# Interactions between Rhodium(I) Centers in Dimeric Complexes

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The electronic spectra of solutions of the dimeric complexes $[Rh(CO)Cl\{Ph_2P(CH_2)_nPPh_2\}]_2$, $n = 1$, 3, and 4, $Rh_2(CO)_4(O_2CCH_3)_2$, and $Rh_2(CO)_4Cl_2$ are compared with the spectra of $Rh(CO)Cl(PPh_3)_2$, $Rh(CO)_2(O_2C_5H_7)$, and $Rh(CO)_2Cl_2^-$. In dimeric complexes in which the planar Rh(I) units are held in close, face to face proximity there is a pronounced shift of the metal-to-ligand charge-transfer absorption to low energies. The products obtained from reaction of $[Rh(CO)Cl\{Ph_2P(CH_2)_nPPh_2\}]_2$, $n = 1$, 3, or 4, with iodine, tetracyanoethylene (TCNE), and sulfur dioxide are compared with the products obtained from $Rh(CO)Cl(PPh_3)_2$. When the two Rh centers are held closely together Rh(II) products with direct Rh–Rh bonds can form; $[Rh(CO)ClI\{Ph_2PCH_2PPh_2\}]_2$ is an example. In some reactions the Rh–P bonds break and re-form to create higher polymeric products; $[Rh(CO)_2ClI_2\{Ph_2P(CH_2)_nPPh_2\}]_x$, $n = 3$ or 4, and $[Rh(CO)Cl(TCNE)\{Ph_2P(CH_2)_4PPh_4\}]_x$ are examples. In other reactions a substrate attacks only one Rh center while the other Rh center remains four-coordinate; examples of such products are $(TCNE)Rh(CO)Cl\{Ph_2P(CH_2)_3PPh_2\}_2Rh(CO)Cl$ and $O_2SRh(CO)Cl\{Ph_2P(CH_2)_nPPh_2\}_2Rh(CO)Cl$ ($n = 3$ or 4).

## Introduction

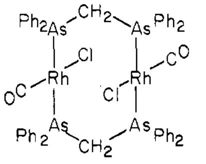
Previous studies from this laboratory have been concerned with the interaction between several metal centers in a single molecule.[1,2] In the present study examples of complexes containing two planar Rh(I) centers which are linked by a variety of bridging ligands are considered. By altering these bridging groups both the distance between the rhodium centers and the relative orientation of the two coordination planes can

**Table I.** Electronic Spectral Data

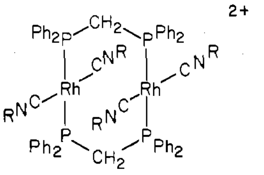
| Complex | $\lambda_{max}$, nm ($\epsilon$) |
|---|---|
| $Rh(CO)Cl(PPh_3)_2$ | 364 (3300), 283 sh (15000), 255 sh (23000) |
| $[Rh(CO)Cl(Ph_2PCH_2PPh_2)]_2$, 4 | 450 (7700), 305 sh (11300) |
| $[Rh(CO)Cl\{Ph_2P(CH_2)_3PPh_2\}]_2$, 5 | 365 (5800), 272 sh (22000), 243 sh (37000) |
| $[Rh(CO)Cl\{Ph_2P(CH_2)_4PPh_2\}]_2$, 6 | 367 (6200), 272 sh (22000), 245 sh (31500) |
| $Rh(CO)_2(C_5H_7O_2)$ | 327 sh (10400), 308 (13600), 361 (20500) |
| $Rh_2(CO)_4(CH_3CO_2)_2$, 7 | 438 (7200), 320 sh (2000), 280 sh (4000), 251 (8600) |
| $Rh_2(CO)_4(CF_3CO_2)_2$ | 410 (6400), 315 (2100), 250 (8600) |
| $Rh_2(CO)_2(CH_3CO_2)_2(Ph_2PCH_2PPh_2)$, 8 | 493 (2700), 420 (3300), 340 sh (4000) |
| $Rh_2(CO)_4(PhN_3Ph)_2$, 9 | 518 (4740), 342 (31000), 245 (44000) |
| $[Bu_4N][Rh(CO)_2Cl_2]$ | 334 (6600), 268 (3900) |
| $Rh_2(CO)_4Cl_2$ | 320 (9000), 260 (14200) |
| $Rh_2(CO)_2(PPh_3)_2Cl_2$ | 400 sh (2400), 350 sh (6550), 333 (8400), 297 (11000), 275 sh (15200), 250 (35000) |
| $[Rh(\textit{cis}\text{-}Ph_2PCHCHPPh_2)_2][Rh(CO)_2Cl_2]$ | 405 (5600), 334 sh (9000), 314 (10700) |
| $Rh(CO)ClI_2(PPh_3)_2$ | 470 sh (3000), 384 sh (12400), 348 (13800), 268 (24000) |
| $Rh_2(CO)_2Cl_2I_2(Ph_2PCH_2PPh_2)_2$ | 650 sh (1130), 525 sh (7500), 435 (12000), 300 sh (25000) |
| $[Rh(CO)ClI_2Ph_2P(CH_2)_3PPh_2]_n$ | 416 sh (6300), 374 sh (10500), 332 (14000), 270 (19100), 265 (19300) |

be varied. The interactions between the rhodium centers are monitored by examining both their electronic spectra and their chemical reactivity.

Examination of a variety of dimers including $[Rh(CNPh)_4]_2^{2+}$,[3] $[Rh(CNR)_4]_2^{2+}$ (R = alkyl),[4] and the ligand-bridged complexes **1**,[1,5] **2**,[1] and **3**[6] have indicated that the



**1**



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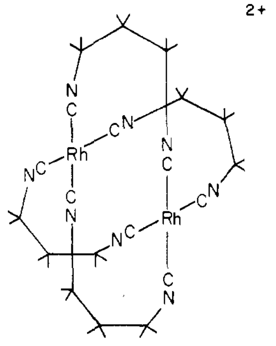


**3**

close, face to face approach of the two rhodium coordination planes cause a pronounced shift of the lowest energy, metal-to-ligand, charge-transfer absorption to lower energy. This shift results from the direct overlap of the out-of-plane metal $d_{z^2}$ and $p_z$ orbitals (with $z$ the out-of-plane direction) and ligand $\pi$ orbitals on one metal with similar orbitals on the other metal center.[1,3] Here we examine this shift with complexes involving other bridging groups and other arrangements in which the rhodium centers are close but the coordination planes lack the face to face orientation required by **1**, **2**, and **3**.

Transannular oxidative addition of halogens to **1**, **2**, and **3** to produce rhodium(II) dimers have been reported.[1,6] Chemical reactions of rhodium dimers in which the rhodium–rhodium separation is varied are described. Particular attention is given to situations in which the rhodium centers are too far apart to allow the formation of directly bonded rhodium(II) dimers but in which the centers are too close together to have the space to accommodate normal addition reactions at both rhodium centers.

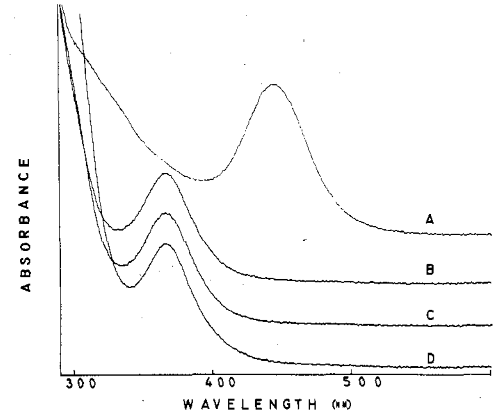
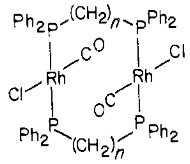


**Figure 1.** Electronic spectra of (A) 0.40 mM $Rh_2(CO)_2Cl_2[Ph_2PCH_2PPh_2]$, (B) 0.40 mM $Rh_2(CO)_2Cl_2[Ph_2P(CH_2)_4PPh_2]_2$, (C) 0.40 mM $Rh_2(CO)_2Cl_2[Ph_2P(CH_2)_3PPh_2]_2$, and (D) 0.8 mM $Rh(CO)Cl(PPh_3)_2$ in chloroform solutions with a cell of 1.0-mm path length.

## Results and Discussion

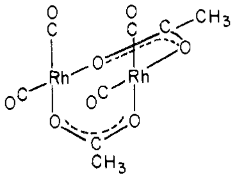
**Electronic Spectra.** The electronic spectra of chloroform solutions of $Rh(CO)Cl(PPh_3)_2$ and the related dimers **4**, **5**, and **6** are reproduced in Figure 1 and presented in numerical form in Table I. The dimeric structures of **4**, **5**, and **6** and the trans disposition of their phosphine ligands have been established previously.[7] Since no x-ray structural data are available for these species, we have estimated the Rh–Rh separation in **4**, **5**, and **6** from examination of Corey–Pauling–Koltum space filling models.[8] For **4** this distance is expected to be about 2.8 Å, but structural studies of other dimers of second-row transition metals with this bridging ligand have metal–metal distances ranging from 2.7[9] to 3.2 Å.[10] In **5** the two rhodium coordination planes are held roughly parallel to one another with a 4.5–5 Å separation while in **6** that separation increases to between 5 and 6 Å. These bridging ligands effectively restrict closer approach of the two metals.[11] Returning to the spectra in Figure 1, the lowest energy transition at 365 nm in the spectrum of $Rh(CO)Cl(PPh_3)_2$ has been assigned as a transition from the highest filled metal d orbital (the $d_{z^2}$ orbital) to an empty, largely ligand localized, $\pi$ orbital composed of contributions from the out-of-plane $p(\pi^*)$ or d ligand orbitals.[12] Of these phosphine bridged dimers only **4** shows a significant shift of the low-energy absorption. We will refer to such absorptions as proximity shifted charge-transfer absorptions. The shift in this absorption band may be readily explained by the molecular orbital interaction shown in Figure 2.[1,3] Overlap of the two filled metal $d_{z^2}$ orbitals in the dimer and of the two empty ligand $\pi_z$ orbitals results in a narrowing of the energy gap between the highest filled metal orbital and the lowest empty ligand $\pi_z$ orbital. The narrowing of this gap produces the shift of the metal-to-ligand charge-transfer absorption to lower energies. The lack of a proximity shift in **5** and **6** is not unexpected since at the rather large rhodium–rhodium sep-



4, *n* = 1
5, *n* = 3
6, *n* = 4

arations involved in these species, overlap of the out-of-plane orbitals is expected to be very small. Unfortunately with this series of compounds it has not been possible to explore the effect of rhodium–rhodium separations in the range 3.4–4.5 Å. Distances in this range might have been obtained using bis(diphenylphosphino)ethane as a bridging ligand, but this ligand preferentially forms the monomeric chelate Rh(CO)Cl($Ph_2PCH_2CH_2PPh_2$).[7]

In Figure 2 the spectra of chloroform solutions of monomeric dicarbonyl(acetylacetonato)rhodium(I)[13] and dimeric dicarbonyl(acetato)rhodium(I)[14] are compared. We believe that the acetylacetonato and acetato ligands individually would provide comparable crystal field and metal–ligand charge-transfer spectra. Thus the low-energy band seen at 438 nm in the spectrum of dicarbonyl(acetato)rhodium(I) is again attributed to a proximity shift of a metal-to-ligand ($d_{z^2} \rightarrow \pi_{p_z}$) charge-transfer band, which in the absence of the second rhodium center occurs at about 320 nm. Since dicarbonyl(acetato)rhodium(I) does show the effects of close proximity of the rhodium centers, this complex probably has the structure **7**, which should, with the exception of the lack of axial carbonyl groups, be similar to the structure of $Os_2(CO)_6(O_2CCH_3)_2$.[15] Unlike the cations $Rh(CNR)_4^+$ and **3** the neutral complex **7** shows no tendency to undergo association in solution. It obeys Beer's law in dichloromethane solution over the concentration range 10–0.1 mM. Addition of bis(diphenylphosphino)methane to **7** produces another ligand-bridged dimer to which we assign the structure **8**. Again this complex shows low-energy transitions which are attributed to the proximity shifted, ligand-to-metal charge-transfer absorptions. Dimeric dicarbonyl(trifluoroacetato)rhodium(I)[14] has an electronic spectrum which is similar to that of **7** and consequently it probably has a similar structure. Another complex to which we assign a related structure is the triazeno complex **9**.[16] This complex exhibits an infrared spectrum similar to that of **7** and a proximity shifted metal-to-ligand charge-transfer absorption at 518 nm.



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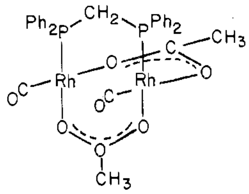

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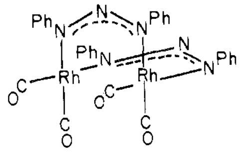

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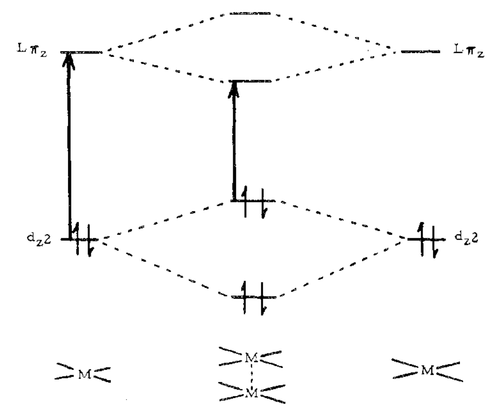


**Figure 2.** A molecular orbital diagram showing the interaction of the metal $d_{z^2}$ orbitals and ligand $\pi_z$ orbitals. The *z* axis is perpendicular to the coordination plane and along the M–M vector in the dimeric species.

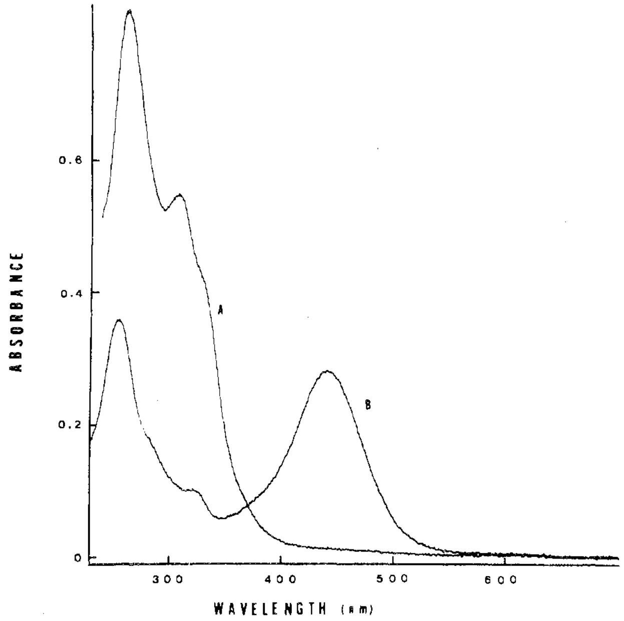
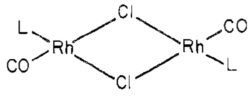


**Figure 3.** Electronic spectra of (A) 0.8 mM $Rh(O_2C_5H_7)(CO)_2$ and (B) 0.4 mM $Rh_2(O_2CCH_3)_2(CO)_4$ in dichloromethane solutions with a cell of 1.0-mm path length.



10, L = CO
11, L = $PPh_3$

The halogen bridged dimers **10** and **11** also contain two planar rhodium centers. These dimers are folded along the chloride bridging ligands so that the dihedral angle between the two rhodium coordination planes is 122° for **10** in the solid state[17] and probably very nearly the same for **11**. Measurements of the dipole moment of **10** in cyclohexane solution[18] and the relative intensity of the infrared carbonyl stretching modes of **10**[19] indicate that this dimer retains its folded nature when it dissolves. Because of this folding the rhodium–rhodium separation is rather small, 3.12 Å in **10**.[17] There has been considerable discussion about the possibility of intramolecular metal–metal bonding in **10**.[17,20,21] The electronic spectra of dichloromethane solutions of $Rh_2Cl_2(CO)_4$ and

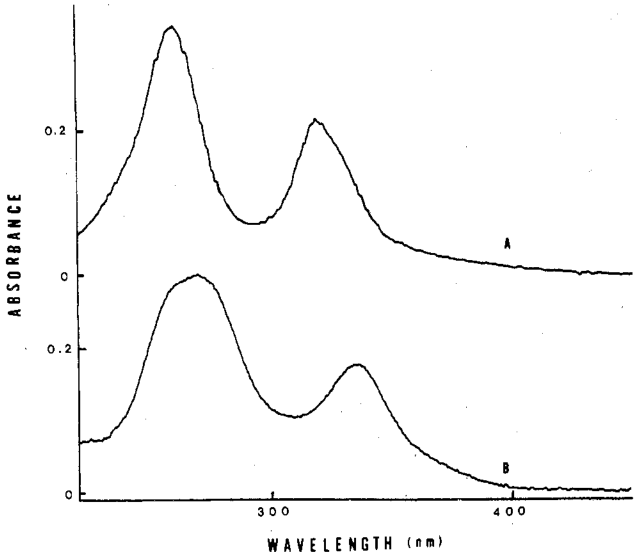


**Figure 4.** Electronic spectra of (A) 0.25 mM $Rh_2(CO)_4Cl_2$ and (B) 0.50 mM $[(n\text{-}C_4H_9)_4N][Rh(CO)_2Cl_2]$ in dichloromethane solutions with a cell of 1.0-mm path length.

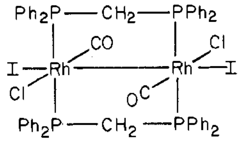
$Rh(CO)_2Cl_2^-$ are compared in Figure 3. Both spectra are similar and no pronounced proximity shift is observed. Of course for such a dimer, the orientation of the two coordination planes prevents appreciable out-of-plane orbital overlap between the two metal centers, and consequently the lack of a proximity shift is expected.

Finally, the salt $[Rh(cis\text{-}Ph_2PCHCHPPh_2)_2][Rh(CO)_2Cl_2]$[22] is considered. In chloroform solution this complex is reported to be a nonelectrolyte and to have a molecular weight (determined by osmometry) in the range 1200–1300.[7,21] In acetonitrile solution this compound behaves as a 1:1 electrolyte.[21] This compound has been examined to determine whether any direct rhodium–rhodium interaction is present in poorly ionizing solvents. The electronic spectra of this salt are the same in several solvents (dichloromethane, chloroform, acetonitrile). These spectra are the sum of the spectrum of the cation (reproduced in ref 23) and the anion (Figure 3). Indeed models indicate that the phenyl groups of the cation effectively block the rhodium from approach by the anion. The low electrical conductivity of this salt in chloroform must arise from ion pairing which does not produce any close rhodium–rhodium contact. Both $[Ph_4As][Rh(CO)_2Cl_2]$ and $(n\text{-}Bu_4N)[Rh(CO)_2Cl_2]$ are nonconductors in chloroform.

**Chemical Behavior.** The chemical reactions of the dimers **4**, **5**, and **6** have been examined in order to ascess the effects of increasing distance between the rhodium centers. Transannular oxidative addition accompanied by rhodium–rhodium bond strengthening has been established for **1**, **2**, and **3** and was anticipated for **4**. With **5** and **6**, the bridging phosphine prevents the close approach necessary for transannular oxidative addition and creates a small vacant space between the two rhodium atoms. However, the space between the two rhodium centers does not appear to be sufficiently large enough to accommodate normal oxidative additions at both rhodium atoms.

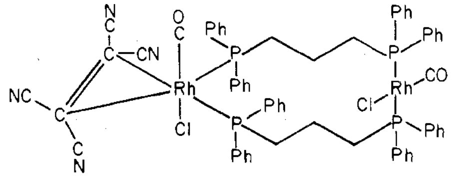
The reactions of the dimeric rhodium complexes **4**, **5**, and **6** toward a variety of reagents are compared with similar reactions of $Rh(CO)Cl(PPh_3)_2$. Neither $Rh(CO)Cl(PPh_3)_2$ nor the dimers react with dihydrogen, dioxygen, or diphenyl disulfide. Reactions with iodine, tetracyanoethylene, and sulfur dioxide at 25 °C have been examined in detail largely by titrations which have been monitored by infrared spectroscopy in the region of the carbon monoxide stretching frequencies. In favorable cases the products have been isolated and characterized.

Iodine reacts with $Rh(CO)Cl(PPh_3)_2$ ($\nu$(CO) 1983 $cm^{-1}$) in a 1:1 molar ratio to form $Rh(CO)ClI_2(PPh_3)_2$ ($\nu$(CO) 2085 $cm^{-1}$).[24] Titration of **4** with iodine indicates that only 1 mol of iodine reacts with 1 mol of dimer. During the titration $\nu$(CO) for the dimer at 1970 $cm^{-1}$ decreases and a new $\nu$(CO) at 2023 $cm^{-1}$ grows in intensity. The product is formulated as the Rh(II) dimer **12**. The small increase in $\nu$(CO) upon oxidation is consistent with the formation of a Rh(II) product.[1] Additional evidence for the difference in oxidation studies between **6** and $Rh(CO)ClI_2(PPh_3)_2$ comes from the electronic spectra of these two complexes. The spectrum of **6** displays intense absorption at lower energy than found for the Rh(III) complex. Titration of **5** with iodine results in the growth of a new CO stretching frequency at 2085 $cm^{-1}$, and the growth of this band is complete after 2 mol of iodine has been added to 1 mol of dimeric **5**. The shift of $\nu$(CO) and the electronic spectrum of a solution of the product indicate that a Rh(III) complex has been formed. It has not been possible to isolate a crystalline product from this reaction. However, molecular weight measurements on the amorphous solid precipitated from solutions of **5** and 2 mol of iodine indicate that the product is probably a mixture of polymers $[Rh(CO)ClI_2Ph_2P(CH_2)_3PPh_2]_n$ where $n$ is in the range 3–4. Titration of **6** with iodine cannot be effectively monitored due to the formation of a brown microcrystalline solid. The solid exhibits $\nu$(CO) at 2088 $cm^{-1}$ and analyses as $[Rh(CO)ClI_2Ph_2P(CH_2)_4PPh_2)]_n$. Since the product has no solubility in common solvents we suspect that it is highly polymerized through bridging phosphines.



**12**

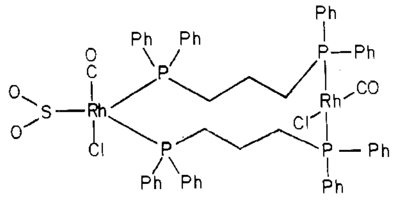
Tetracyanoethylene reacts with $Rh(CO)Cl(PPh_3)_2$ to give $Rh(CO)Cl(C_6N_4)(PPh_3)_2$ ($\nu$(CO) 2075, $\nu$(CN) 2230 $cm^{-1}$).[25] Titration of **4** with tetracyanoethylene reveals no change in $\nu$(CO) up to a 2:1 molar ratio of tetracyanoethylene to dimer. Titration of **5** with tetracyanoethylene reveals a growth of a new carbonyl stretching frequency to 2076 $cm^{-1}$. All spectral changes are complete when the tetracyanoethylene to dimer ratio is 1:1. The product has been isolated as a yellow crystalline solid with $\nu$(CO) at 2076 and 1963 $cm^{-1}$ and $\nu$(CN) at 2231 and 2220 $cm^{-1}$ in a Nujol mull. In chloroform the product has a molecular weight which is consistent with the addition of one tetracyanoethylene to one dimer. We propose that the product has structure **13** in which tetracyanoethylene has added to only one of the two rhodium centers.



**13**

A yellow solid precipitates as tetracyanoethylene is added to **6**. This solid analyzes as $[Rh(CO)Cl(C_6N_4)Ph_2P(CH_2)_4PPh_2]_n$. The infrared spectrum of the solid shows $\nu$(CN) at 2200 $cm^{-1}$ and $\nu$(CO) at 2100 $cm^{-1}$. The solid does not dissolve in common organic solvents. Consequently it probably is an extended polymer with phosphine bridges and tetracyanoethylene coordinated to each rhodium.

Addition of sulfur dioxide to $Rh(CO)Cl(PPh_3)_2$ produces $Rh(CO)Cl(PPh_3)_2SO_2$[26] ($\nu$(CO) 2035, $\nu$(S–O) 1208, 1053 $cm^{-1}$) which has been characterized by an x-ray structure determination.[27] This product readily loses sulfur dioxide on heating. Addition of sulfur dioxide to **5** has led to the isolation of **14**. This complex has $\nu$(CO) at 2020 (2001 sh) and 1971 (1983 sh) cm$^{-1}$ and $\nu$(S–O) at 1237 and 1065 cm$^{-1}$. When a Nujol mull of the sample is gently warmed, the infrared absorptions at 2020, 1237, and 1065 cm$^{-1}$ decrease in intensity as sulfur dioxide is lost and the complex is converted back to **2**. Addition of sulfur dioxide to **6** produces a new complex which, as a solid, has $\nu$(CO) at 2024 and 1968 and $\nu$(S–O) at 1220 and 1060 cm$^{-1}$. The product is more thermally labile than **14**, and it has not been possible to obtain analytical data for this compound. Addition of sulfur dioxide to **4** produces new carbonyl absorptions at 2023 and 1996 cm$^{-1}$, but it has not been possible to isolate a pure adduct from solution.



**14**

The reactions of the dirhodium complexes which have been observed fall into three categories. One class of reaction, which has been previously mentioned, involves transannular oxidative addition with the formation of Rh(II) dimers. The formation of **12** is an example. Another class involves examples where the normal reactivity of a rhodium site is diminished in the dimeric complex. Examples include the lack of reaction of **4** with tetracyanoethylene, the observation that only one rhodium site in **5** reacts with tetracyanoethylene, and the observation that only 1 mol of sulfur dioxide adds to **5** and **6**. We suspect that in all cases the lack of reactivity results from the inability of the unreactive rhodium center to readjust its coordination geometry to the arrangement necessary to bind the substrate. From examination of analogous monomers, it appears that the phosphine ligands or other ligands must fold back to accommodate binding of sulfur dioxide or tetracyanoethylene. Because of the constraints of the ring system of which the rhodium center is a part, this folding may be inhibited. Alternately these complexes may have ligands arranged so that the approach of either sulfur dioxide or tetracyanoethylene to the second rhodium is sterically hindered by the phenyl groups of the phosphine ligands.

The third class of reactions result in the formation of what appear to be higher polymers. We presume that these reactions occur by opening the cyclic rhodium dimers at the Rh–P bonds. Reassembly of the Rh–P bonds could produce either higher polymers or monomers with chelating diphosphines. In the reactions so far examined higher polymerization appears to result.

A potential class of reactions which was not observed would involve simultaneous substrate binding to both rhodium atoms. With the dimeric complexes **4**, **5**, and **6** the small size of the cavity between the two metals may discourage entry of substrate between the two metals and favor substrate attack on the outer surface of the rhodium coordination sphere.

## Experimental Section

**Preparation of Compounds.** Phosphine ligands were obtained from Strem Chemicals and used as received. The following materials were obtained by established routes: $Rh(CO)Cl(PPh_3)_2$,[28] $Rh_2(CO)_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}_2$ ($n$ = 1, 3, 4),[7] $[Rh(cis\text{-}Ph_2PCHCHPPh_2)_2][Rh(CO)_2Cl_2]$,[22] $Rh_2(CO)_4Cl_2$,[29] $Rh_2(CO)_2(PPh_3)_2Cl_2$,[30] $Rh_2(CO)_4(O_2CCH_3)_2$,[14] $Rh(C_6H_7O_2)(CO)_2$,[13] and $Rh_2(CO)_4(O_2CCF_3)_2$.[31]

**$(PhN_3Ph)_2Rh_2(CO)_4$.** A solution of 0.51 g (2.6 mmol) of diphenyltriazene in 30 mL of hot hexane was added to a solution of 0.66 g (2.6 mmol) of $(C_5H_7O_2)Rh(CO)_2$ in 30 mL of boiling hexane. The solution was heated under reflux for 15 min and then taken to dryness (to ensure removal of acetylacetone) on a rotary evaporator. Under nitrogen the resulting red solid was dissolved in boiling hexane and filtered. The filtrate was cooled to −10 °C and stored for 24 h. The red crystalline product was collected by filtration, yield 0.52 g, 57%. Further purification was effected by recrystallization from pentane. Anal. Calcd for $C_{14}H_{10}N_3O_2Rh$: C, 47.35; H, 2.84; N, 11.83. Found: C, 47.66; H, 3.21; N, 11.97. In cyclohexane solution the infrared spectrum has carbonyl stretching frequencies of 2086, 2059, and 2023 cm$^{-1}$. The product appears to be the same as the dimeric material of the same composition previously obtained by carbonylation of $(Ph_2N_3)RhC_6H_{12}$.[16]

**$Rh_2(Ph_2PCH_2PPh_2)(CO)_2(O_2CCH_3)_2\cdot C_6H_6$.** A solution of 60.4 mg (0.157 mmol) of bis(diphenylphosphino)methane in 5 mL of benzene was added to a filtered solution of 67.9 mg (0.156 mmol) of $Rh_2(CO)_4(O_2CCH_3)_2$ in 15 mL of benzene. The resulting red solution was evaporated to a volume of 7 mL under a stream of nitrogen. The red crystalline product was collected by filtration, washed with benzene and ether, and vacuum dried, yield 68 mg, 53%. Anal. Calcd for $C_{36}H_{34}O_6P_2Rh_2$: C, 52.75; H, 4.07; P, 7.35; mol wt, 764. Found: C, 52.17; H, 3.96; P, 7.37; mol wt, 800. In a Nujol mull the complex has $\nu$(CO) at 2061 and 1985 cm$^{-1}$. The proton magnetic resonance spectrum consists of a broad multiplet at $\tau$ 2.5 with a sharp spike due to benzene of solution at 2.64, a complex methylene multiplet centered at 6.5 and a broad methyl resonance at 8.24. The breadth of the methyl resonance is consistent with the existence of two methyl environments with nearly the same chemical shift.

**$Rh_2\{Ph_2PCH_2PPh_2\}_2(CO)_2Cl_2I_2$.** A solution of 22 mg (0.087 mmol) of iodine in 10 mL of dichloromethane was added to a solution of 96 mg (0.087 mmol) of $Rh_2\{Ph_2PCH_2PPh_2\}_2(CO)_2Cl_2$ in 30 mL of hot dichloromethane. The brown solution was filtered and 15 mL of cyclohexane was added and the solvent volume was reduced by means of a rotary evaporator. The brown solid which formed was collected by filtration, washed with cyclohexane, and vacuum dried, yield 50%. Anal. Calcd for $C_{52}H_{44}Cl_2I_2O_2P_4Rh_2$: C, 46.08; H, 3.27; P, 9.14. Found: C, 47.09; H, 3.59; P, 8.66.

**$[Rh\{Ph_2P(CH_2)_4PPh_2\}(CO)ClI_2]_n$.** A solution of 68.3 mg (0.269 mmol) of iodine in 10 mL of dichloromethane was added to a solution of 156 mg (0.131 mmol) of $Rh_2\{Ph_2P(CH_2)_4PPh_2\}_2(CO)_2Cl_2$ in 10 mL of dichloromethane. The brown, microcrystalline precipitate was collected by filtration, washed with dichloromethane and vacuum dried, yield, 113 mg, 51%. The product appears to have almost no solubility in dichloromethane, benzene, acetone, or methanol. Anal. Calcd for $C_{29}H_{28}ClI_2OP_2Rh$: C, 41.14; H, 3.33; I, 29.98. Found: C, 40.49; H, 3.34; I, 30.21.

**$R_2\{Ph_2P(CH_2)_3PPh_2\}_2(CO)_2Cl_2(C_6N_4)$.** A solution of 20.6 mg (0.161 mmol) of tetracyanoethylene in 7 mL of dichloromethane was added to a solution of 173 mg (0.155 mmol) of $Rh_2\{Ph_2P(CH_2)_3PPh_2\}_2(CO)_2Cl_2$ in 7 mL of dichloromethane. The gradual addition of ether to this solution caused the product to precipitate as yellow crystals. These were collected by filtration, washed with ether, and vacuum dried, yield 138 mg, 72%. Anal. Calcd for $C_{62}H_{52}Cl_2N_4O_2P_4Rh_2$: C, 57.92; H, 4.08; Cl, 5.51; N, 4.36; mol wt, 1286. Found: C, 57.65; H, 3.97; Cl, 4.92; N, 4.54; mol wt, 1200.

**$[Rh\{Ph_2P(CH_2)_4PPh_2\}(CO)Cl(C_6N_4)]_x$.** A solution of 42.7 mg (0.334 mmol) of tetracyanoethylene dissolved in 5 mL of dichloromethane was added to a solution of 167 mg of $Rh_2\{Ph_2P(CH_2)_4PPh_2\}_2(CO)_2Cl_2$ in 5 mL of dichloromethane. After the mixture stood for 1 h, the yellow precipitate was collected by filtration, washed with dichloromethane, and vacuum dried, yield 74 mg, 37%. The product appears to have almost no solubility in dichloromethane, benzene, acetone, or methanol. Anal. Calcd for $C_{35}H_{28}ClN_4OP_2Rh$: C, 58.31; H, 3.91; N, 7.77. Found: C, 58.32; H, 4.07; N, 7.97.

**$Rh_2\{Ph_2P(CH_2)_3PPh_3\}_2(CO)_2Cl_2SO_2\cdot 1.5CH_2Cl_2$.** Sulfur dioxide was passed through a solution of 157 mg of $Rh_2\{Ph_2P(CH_2)_3PPh_3\}_2(CO)_2Cl_2$ in 7 mL of dichloromethane. The yellow-green solution was filtered and ether was slowly added to the filtrate. The deep yellow crystals which gradually formed were collected by filtration, washed with ether, and dried in air, yield 142 mg, 87%. In addition to phenyl resonances at $\tau$ 2.63 and methylene resonances at 7.80 the proton magnetic resonance spectrum has a resonance at 4.53 due to lattice trapped dichloromethane. Anal. Calcd for $C_{56}H_{52}Cl_2O_4P_4Rh_2S$: C, 51.19; **H**, 4.10; S, 2.38; mol wt, 1221. Found: C, 51.18; H, 4.12; S, 1.77; mol wt, 1090.

**Physical Measurements.** Molecular weights were measured in chloroform solution using a Mechrolab vapor pressure osmometer.

The standard was $Rh(CO)Cl(PPh_3)_2$. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. A Cary 17 spectrophotometer was used to obtain the electronic spectra.

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**Registry No.** **4**, 22427-58-3; **5**, 58719-46-3; **6**, 58675-42-6; **7**, 27341-80-6; **8**, 63428-33-1; **9**, 36126-17-7; **10**, 14523-22-9; **11**, 34676-63-6; **12**, 63428-32-0; **13**, 63428-31-9; **14**, 63493-70-9; $Rh(CO)Cl(PPh_3)_2$, 15318-33-9; $Rh(CO)_2(C_5H_7O_2)$, 14874-82-9; $Rh_2(CO)_4(CF_3CO_2)_2$, 14522-94-2; $[Bu_4N][Rh(CO)_2Cl_2]$, 14593-70-5; [Rh(*cis*-$Ph_2PCHCHPPh_2)_2][Rh(CO)_2Cl_2]$, 23301-91-9; $Rh(CO)ClI_2(PPh_3)_2$, 63492-80-8; $[Rh(CO)ClI_2Ph_2P(CH_2)_3PPh_2]_m$, 63428-81-9; $[Rh\{Ph_2P(CH_2)_4PPh_2\}(CO)ClI_2]_n$, 63428-79-5; $[Rh\{Ph_2P(CH_2)_4PPh_2\}(CO)Cl(C_6N_4)]_x$, 63428-77-3.

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# Photochemical Synthesis of *cis*-Chlorobis(ethylenediamine)(ethylenediaminium)rhodium(III) Chloride, *cis*-$[Rh(en)_2(enH)Cl]Cl_3{\cdot}2H_2O$

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Ligand field photolysis of $Rh(en)_3^{3+}$ in acidic, chloride media leads to the formation of the monodentate ethylenediamine complex *cis*-$Rh(en)_2(enH)Cl^{3+}$ as the sole photolysis product. The quantum yield for this process is relatively insensitive to acid concentration ($1\ M > [H^+] > 10^{-8}\ M$) and has a value of $\sim$0.040 mol/einstein. In basic solution (pH >8), the photolysis product is the deprotonated complex *cis*-Rh(en)$_2$(mono-en)$Cl^{3+}$. There is no evidence for secondary photochemical or thermal reactions with pH is ≤10. These results are discussed in the context of previous mechanistic interpretations of the photochemistry of rhodium(III) amine complexes.

Ligand field photolysis of rhodium(III) amine complexes in aqueous solution customarily leads to photoaquation of one of the ligands in the complex[1] resulting in a monoaquo species. Subsequent reactions are not observed spectroscopically since further reaction is usually limited to $H_2O$ exchange.[2] Some of the literature systems are illustrated by eq 1 and 2.

$$\mathrm{Rh(NH_3)_5L^{n+}} \xrightarrow[\mathrm{LF}]{h\nu} \mathrm{Rh(NH_3)_5H_2O^{3+}} + \mathrm{L} \tag{1}$$

$L = NH_3$,[3] substituted pyridines,[4] organonitriles,[4] Cl[5]

$$trans\text{-}\mathrm{RhA_4Cl_2^+} \xrightarrow[\mathrm{LF}]{h\nu} trans\text{-}\mathrm{RhA_4(H_2O)Cl^{2+}} \tag{2}$$

$A_4 = (NH_3)_4$,[6] $(en)_2$,[6] cyclam[6]

There have been mechanisms proposed for some photochemical[7-10] and thermal[11,12] reactions of transition metal complexes in which the bidentate ethylenediamine appears in the product as the monodentate ethylenediaminium ligand. Of these reactions, the only isolated solid for a $d^6$ metal system has been *cis*-$[Co(en)_2(enH)Cl]Cl_3{\cdot}H_2O$[5] which was characterized by elemental analysis and electronic spectroscopy. In addition, there have been some photochemical studies of Rh(III)[13,14] and Co(III)[15,16] complexes of ethylenediamine in which a monodentate ethylenediamine ligand has been proposed as an intermediate in the photosubstitution process. Some of these researchers[13,15,16] have proposed mechanisms in which the labilized end of an ethylenediamine undergoes an edge displacement of a chloro ligand.

The different modes of reactivity of the monodentate ethylenediamine ligand, which apparently either exist as stable species[7-12] or undergo rechelation through edge displacement of an adjacent chloro ligand,[13-16] must be a result of subtle changes in the complexes which were studied or must be indicative of an incorrect mechanistic description in some of the earlier work. The tendency of hexaammine-, pentaammine-, and *trans*-dichlorotetraaminerhodium(III) species to undergo photosubstitution at only one coordination site led us to study the ligand field photochemistry of tris(ethylene-