matsu, R. G. Werth, and I. Sakai for help in collecting and checking the reference data and for WLN assignments, to Miss G. Pesyna for assistance with programs, to Dr. John McGuire for supplying challenging unknowns, and to the National Institutes of Health (GM 16609) for generous financial support.

Activation and Stabilization of Small Molecules by a Chelating Triphosphine–Rhodium(I) Complex. A Correlation of the Chemistry with the Structures of Chlorobis(3-diphenylphosphinopropyl)phenylphosphinerhodium(I) and Its Nitrosyl Derivative[1]

Thomas E. Nappier, Jr.,[2a] Devon W. Meek,*[2a]
Richard M. Kirchner,[2b] and James A. Ibers[2b]

Contribution from the Departments of Chemistry,
The Ohio State University, Columbus, Ohio 43210, and
Northwestern University, Evanston, Illinois 60201. *Received October 31, 1972*

Abstract: The tridentate ligand $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$, L, forms RhLX complexes (X = Cl, Br, I), which are dissociatively stable in nonaqueous solvents. The chloride complex, RhLCl, reacts readily with a variety of small molecules to form five-coordinate, nonionic derivatives, RhLCl·A, where A = BF_3, CO, SO_2, and O_2. The S_2 adduct, RhLCl·S_2, was prepared by treating RhLCl with S_8 in benzene. Cationic complexes of RhLCl were made by two general methods: (1) addition of a positively charged ligand (electrophile), or (2) displacement of the chloride ion by a neutral ligand. The most important difference between the two methods is that rhodium remains Rh(I) in the latter case, whereas in the first case oxidation formally to Rh(III) occurs. For example, the five-coordinate, cationic complexes $[RhLCl\cdot A]^+$ were prepared by treating RhLCl with the cationic reagents H^+, NO^+, N_2Ph^+, and CH_3CO^+. Four- and five-coordinate cations $[RhL(CH_3CN)]^+$, $[RhL(CO)]^+$, and $[RhL(CO)_2]^+$ can be obtained by chloride displacement from RhLCl in polar solvents. The interconversions and chemical reactions of some of the above complexes are presented. The structures of the parent compound, RhLCl, and its nitrosyl derivative, $[RhLCl(NO)][PF_6]$, have been determined from three-dimensional X-ray data collected by counter methods. The yellow parent compound crystallizes in space group C_{2h}^2-$P2_1/m$ of the monoclinic system with two molecules in a unit cell of dimensions $a = 9.312$ (1), $b = 21.187$ (2), $c = 8.851$ (3) Å, and $\beta = 105.39$ (1)°. The observed and calculated densities are 1.36 (1) and 1.38 g cm^{-3}, respectively. Full-matrix least-squares refinement gave a final value of the conventional R factor (on F) of 0.035 for the 2566 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of discrete monomers, and the coordination geometry around the metal is square planar. The molecule has imposed m symmetry. Some important bond lengths in the parent compound are as follows: Rh–P(terminal), 2.288 (1); Rh–P(central), 2.201 (2); and Rh–Cl, 2.381 (2) Å. The nitrosyl derivative crystallizes in space group D_{2h}^{16}-$Pnma$ with four molecules in a unit cell of dimensions $a = 24.350$ (5), $b = 15.196$ (2), and $c = 9.914$ (2) Å. The observed and calculated densities are 1.57 (1) and 1.58 g cm^{-3}, respectively. Full-matrix least-squares refinement gave a final value of the conventional R factor (on F) of 0.055 for the 1282 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of discrete monomers. Addition of a nitrosyl ligand to the parent compound, RhLCl, gives a tetragonal pyramidal coordination around the rhodium atom of $[RhLCl(NO)][PF_6]$, with imposed mirror symmetry as in the parent compound. The nitrosyl ligand itself is bent, with a Rh–N–O bond angle of 131 (1)°. Some important bond lengths in the nitrosyl derivative are as follows: Rh–P(terminal), 2.374 (3); Rh–P(central), 2.282 (4); Rh–Cl, 2.408 (4); and Rh–N, 1.91 (2) Å. The relationship between structure and reactivity is discussed.

Complexes containing a transition metal with a d^8 electronic configuration have been used in many important and diverse chemical reactions involving (1) the homogeneous hydroformylation,[3] oxidation,[4] and hydrogenation[5] of olefins; (2) oxidative-addition reactions;[6] (3) the Lewis basicity of metal complexes;[7] (4) the coordination of small molecules such as O_2 and P_4;[8] and (5) the stabilization of small

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[1] Presented in part at the Winter Meeting of the American Crystallographic Association, Albuquerque, N. M., April 1972, Abstracts, p 45; and at the XIV International Conference on Coordination Chemistry, Toronto, June 1972, Proceedings, p 649. A preliminary communication on part of this chemistry has appeared: T. E. Nappier, Jr., and D. W. Meek, *J. Amer. Chem. Soc.*, **94**, 306 (1972).

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molecular fragments such as S_2 and Se_2.[9] A common feature of all of the above reactions is the coordination of a small molecule substrate to the metal complex. The path and driving force of these reactions depend markedly on the nature of the central metal atom and the surrounding ligands. The ability of the metal to vary its coordination number and the structural geometry of the ligands are also important in determining the nature of the resulting complex. The stereochemistry about d^8 metal ions varies widely. There are examples of tetrahedral and square-planar four-coordinate complexes, as well as ideal and distorted trigonal-bipyramidal and square-pyramidal five-coordinate complexes. In addition to showing a variable coordination number, certain four-coordinate d^8 complexes can often be converted into nominally d^6 six-coordinate complexes, by the addition, sometimes reversible, of a small covalent molecule.

The chemistry of Ir(I), Rh(I), and Co(I) complexes of triphenylphosphine and 1,2-bis(diphenylphosphino)ethane has been investigated extensively,[6-10] and X-ray structure determinations have been performed on key compounds.[11-14] Such d^8 complexes containing monodentate phosphines often yield compounds in which one of the original phosphine ligands is displaced, *e.g.*, treatment of $RhCl(PPh_3)_3$ and $IrCl(PPh_3)_3$ with CO yields $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$, respectively. The remarkable catalytic properties of $RhCl(PPh_3)_3$[5] for hydrogenation and $RhH(CO)(PPh_3)_3$[3b,c] for hydroformylation of olefins depend on dissociation of a triphenylphosphine ligand in solution.[15,16] Higher proportions of terminal aldehydes can be obtained in the hydroformylation of 1-alkenes by increasing the concentration of triphenylphosphine used with the $RhH(CO)(PPh_3)_3$ catalyst, presumably because of an equilibrium involving triphenylphosphine dissociation from the active species.[3b]

To circumvent dissociation of the phosphino groups, we decided to prepare a chelating triphosphine ligand to accomplish simultaneously: (1) a more predictable coordination number and stoichiometry in the resulting d^8 complexes, as the chelate effect should minimize the tendency of one or more phosphino groups to be displaced during a chemical reaction, (2) increased basicity of the rhodium atom, and (3) more control on the stereochemistry of the complexes by using a chelating ligand.

The triphosphine $PhP(CH_2CH_2PPh_2)_2$ fits the above criteria, and it was synthesized.[17] Our initial experiments with Rh(I) complexes showed that the predominant behavior of this ligand did not involve coordination of all three phosphino groups to the same rhodium(I) ion. Instead, one of the terminal phosphino groups bridged to another metal ion and formed polynuclear species such as $[Rh_4(ligand)_3Cl_4]_n$.[18] Apparently, formation of two connected five-membered chelate rings around the planar Rh(I) ion creates too much strain; thus, one end of the ligand prefers to bridge to another metal ion. The strain hypothesis is supported by X-ray results on Rh(I) complexes of the bidentate ligand $Ph_2PCH_2CH_2PPh_2$, which show five-membered chelate rings that have P–Rh–P angles $\cong$83°.[13,14] It is expected that the bite between adjacent phosphorus atoms of $PhP(CH_2CH_2PPh_2)_2$ would also give $\sim$83° P–Rh–P angles in each chelate ring. Thus, the P–Rh–P angle involving the terminal phosphino groups can be no greater than 166°. If this ligand were to form two chelate rings to the same rhodium ion, considerable ring strain or structural distortion of the complex from planarity would result.

In order to achieve a stoichiometry and donor set similar to the Wilkinson catalyst, $RhCl(PPh_3)_3$, and simultaneously to facilitate chelation of both terminal phosphino groups of a triphosphine ligand, trimethylene linkages were incorporated between the phosphorus atoms. According to accurate molecular models, the ligand $PhP(CH_2CH_2CH_2PPh_2)_2$ denoted as L, should bond all three phosphorus atoms to a central metal atom to give a monomeric, square-planar complex of the type RhP_3Cl, *i.e.*, RhLCl.

This paper reports the preparation and characterization of several series of four-, five-, and six-coordinate rhodium complexes with the ligand $PhP(CH_2CH_2CH_2PPh_2)_2$. Also, X-ray structural determinations of the parent compound, RhLCl, and of its five-coordinate nitrosyl derivative are presented.

Results and Discussion of the Chemistry

Four-Coordinate Complexes, RhLX (X = Cl, Br, I). The chloride complex RhLCl is prepared easily in high yields (80–85%) from the 1,5-cyclooctadiene (COD) complex $[Rh(C_8H_{12})Cl]_2$[19] and L in hot ethanol. The bromide compound, RhLBr, is prepared similarly, except for an *in situ* conversion of the COD complex with lithium bromide. Yellow crystals of RhLBr separate cleanly from the ethanol solution. In contrast, the conditions for the preparation of RhLI are more critical. Heating the reaction solution for 15–20 min, as in the chloride or bromide preparations, results in variable mixtures of green, red, orange, and yellow crystals. However, an analytical sample of RhLI having uniform color and crystallinity is obtained by heating the solution for only 2 min, that is, only until it is completely homogeneous. The sensitivity of the iodide complex is reminiscent of the behavior of other tertiary phosphine complexes of rhodium(I) iodide, *e.g.*, difficulties were also encountered in the preparation of $RhI(PPh_3)_3$.[5]

The need for more carefully controlled conditions in the preparation of RhLI is probably due to the higher reactivity of this compound. Even in the solid state the orange iodide complex turns brown after a few months, whereas the yellow chloride, RhLCl, is apparently stable indefinitely in air. The infrared spec-

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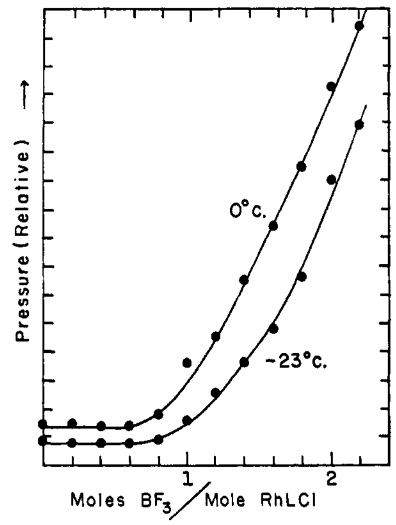
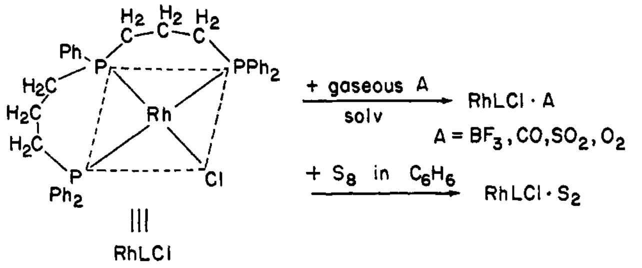


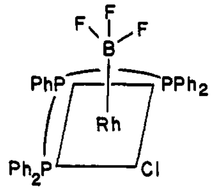
Figure 1. Tensimetric titration of RhLCl with BF_3.

trum of the brown "RhLI" material shows bands at *ca.* 1180 and 880 cm^{-1} which can be attributed to phosphine oxide and coordinated dioxygen, respectively. Consistent with the established reactivity pattern of corresponding Rh and Ir compounds,[13] the solid iridium complex IrLCl[18] shows even greater air sensitivity than RhLCl, reacting with oxygen within a few days.

Five-Coordinate Molecular Complexes, RhLCl·A (A = CO, BF_3, SO_2, O_2, and S_2). The complex RhLCl exhibits a surprisingly strong affinity for small molecules that are Lewis acids. Within the limits of macroscopic detection methods, the solid RhLCl complexes of gaseous molecules show no dissociation at 100° and 0.1 Torr. Also, the compounds do not dissociate when dissolved in inert solvents that are flushed with nitrogen gas. The reaction scheme is given below.



Formation of a stable BF_3 complex of RhLCl establishes the increased basicity of the rhodium atom as compared with $RhCl(CO)(PPh_3)_2$.[20] The strong broad infrared band at *ca.* 1060 cm^{-1} is attributed to the asymmetric B–F stretching vibration of coordinated BF_3.[21] Tensimetric titrations of RhLCl with BF_3 in dichloromethane show sharp breaks only at 1:1 stoichiometry (Figure 1). The ^{19}F nmr spectrum shows a broad resonance at −11.1 ppm from C_6F_6, which coincides with the resonance position of BF_4^-.[22] The ^{11}B nmr spectrum of a 0.1 *M* dichloromethane solution of $RhLCl \cdot BF_3$ shows a weak broad signal at +18.9 ppm from $B(OCH_3)_3$, which is the appropriate position for BF_3 complexes (BF_3·etherate = +18.2 ppm[22]). In considering the nature of the BF_3 association with RhLCl, the only two Lewis base sites are the rhodium and chlorine atoms. As no fluorine or boron coupling to rhodium is observed in the nmr spectra, the data do not permit a definitive assignment of the coordination site. However, on the basis of the numerous other complexes described below that involve Rh–A bonds, we favor a direct rhodium–boron bond in this compound (**1**). This is the first example of a stable BF_3 complex of rhodium. The compound $RhLCl \cdot BF_3$ is sensitive to moisture and crystals suitable for X-ray studies have not been obtained to date.

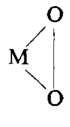


1

The sulfur dioxide compound, $RhLCl \cdot SO_2$, is formed rapidly by bubbling gaseous SO_2 through a slurry of RhLCl in benzene at 30° and ambient pressures. The infrared spectrum of the yellow solid is nearly identical with that of the complex RhLCl except for additional strong bands at 1030 and 1155 cm^{-1}, which are the symmetric and antisymmetric S–O stretching vibrations of a S-bonded SO_2 group. Thus, the SO_2 adduct is formulated as a square-pyramidal complex involving Rh → S electron donation and bonding as in the complexes $MCl(CO)(SO_2)(PPh_3)_2$ (M = Rh and Ir).[11,23]

The tan dioxygen complex, $RhLCl \cdot O_2$, precipitates as dry O_2 is bubbled through a benzene solution of RhLCl. This $RhLCl \cdot O_2$ compound appears to be one of the most stable rhodium–dioxygen complexes known, as the reaction of RhLCl with O_2 is irreversible under practical conditions. No dissociation of O_2 occurs at 80° and 0.05 Torr from the solid adduct. A medium intensity infrared band appears in the dioxygen adduct at 858 cm^{-1} and is assigned to the RhO_2 mode.[13] No bands attributable to a tertiary phosphine oxide group are observed in the infrared spectra of $RhLCl \cdot O_2$ or of any of the complexes obtained subsequently by reactions of $RhLCl \cdot O_2$ with other reagents (see below). On the basis of mass spectra the monomeric complex is favored over a dinuclear complex involving Rh–O–O–Rh bridging, which was found for the O_2 adduct of $RhCl(PPh_3)_3$.[24] The highest *m/e* pattern (700, 701, 702, 703) observed in the mass spectrum is due to the parent ion, RhLCl, and the highest relative abundance peak (*m/e* 700) is due to $RhL^{35}Cl$. Thus, while the parent ion for the dioxygen complex is not observed directly, neither are *fragments* from a dimeric unit, *e.g.*, LRh_2O_4.

The complex $RhLCl \cdot O_2$ undergoes reactions that are characteristic of



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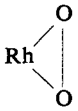
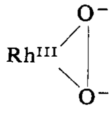
units (M = Ir(I), Rh(I), Pd(0), Pt(0)). For example, it reacts rapidly at 25° with SO_2 and NO_2 to give coordinated sulfate and dinitrate complexes, respectively. It reacts more slowly with carbon monoxide to form the carbonate complex. The yellow sulfate complex, $RhLCl(SO_4)$, exhibits infrared bands characteristic of bidentate $SO_4{}^{2-}$ groups[25,26] at 1250, 1240, 1147, and 640 cm^{-1}, while the 858-cm^{-1} peak due to the symmetric


$$Rh\langle{}^{O}_{O}|$$

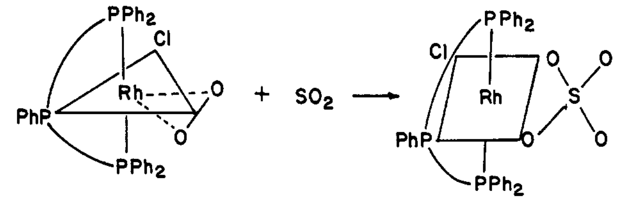
unit[13] in $RhLCl \cdot O_2$ has disappeared. Similarly, the infrared bands (Nujol) of $RhLCl(CO_3)$ at 1630 (m, sh) and 1600 (vs, br) are indicative of bidentate coordination by a $CO_3{}^{2-}$ group, and they occur at positions comparable to the carbonate bonds in the rhodium and iridium complexes of $CH_3C(CH_2PPh_2)_3$.[27] The preparation of $RhLCl(CO_3)$ represents one of only a few cases where carbon monoxide is oxidized by a rhodium dioxygen complex.[25-27]

The reaction of $RhLCl \cdot O_2$ with nitrogen dioxide, NO_2 (N_2O_4), is not as straightforward as expected. For example, in one case the pale orange solid, which precipitates in low yields (<20%) from an ethanol solution, has strong, broad infrared absorptions (*ca.* 1500 and 1260 cm^{-1}, Nujol) characteristic of coordinated nitrate groups.[25,26] In another experiment the solvent was removed *in vacuo* from the reaction mixture; in this case the infrared spectrum of the orange powder indicated that the product was a mixture of NO_x compounds. Although the analytical data are consistent with the dinitrate formulation, $RhLCl(NO_3)_2$, the complicated infrared spectrum suggests the presence of other nitrogen–oxygen groups, *e.g.*, nitro, nitrito, and/or nitrosyl. A strong peak at 1370 cm^{-1} is assigned to an ionic nitrate group, and the conductance (73 cm^2/(ohm mol), a uni-univalent electrolyte in nitromethane) also shows the ionic nature of the compound.

In forming the $RhLCl(SO_4)$ complex the addition sequence of reagents is very important. The dioxygen complex reacts within seconds with sulfur dioxide at 25°, whereas if one bubbles O_2 through a solution of $RhLCl \cdot SO_2$, no sulfate complex is formed within 1 hr. Valentine, *et al.*,[23] found that the $IrCl(PPh_3)_3 \cdot O_2$ compound also reacts with sulfur dioxide much faster than the corresponding SO_2 complex reacts with molecular oxygen. The inertness of $RhLCl \cdot SO_2$ toward dioxygen (*i.e.*, no formation of sulfate complex) also attests to the stability of the SO_2 adduct in solution at 25°. The reactions of SO_2, NO_2, and CO in solution with the dioxygen complexes could be interpreted as a nucleophilic attack on the Lewis acids by the peroxide linkage of


$$Rh^{III}\langle{}^{O^-}_{O^-}|$$

with cleavage of the O–O bond, *e.g.*, **2** + $SO_2 \rightarrow$ **3**.



2 **3**

The disulfur complex $RhLCl \cdot S_2$ was prepared by treating a solution of S_8 with RhLCl. The infrared spectrum (Nujol) of the orange-brown solid shows a new band at 546 cm^{-1}, which is coincidentally in the region expected for a coordinated phosphine sulfide group.[28] However, the mass spectrum of $RhLCl \cdot S_2$ shows no peaks (*m/e*) higher than those of RhLCl; in addition, a peak at *m/e* 64 was observed, and no peaks attributable to phosphine sulfide fragments were detected. Stabilization of S_X fragments has been accomplished recently with other rhodium and iridium compounds.[9] For example, cleavage of S_8 rings by $RhCl(PPh_3)_3$ results in displacement of two phosphine groups and gives the tetrameric $[RhCl(PPh_3)S_3]_4$.[9b] On the other hand, $[Ir(dpe)_2]^+$ (dpe = 1,2-bis(diphenylphosphino)ethane) abstracts the S_2 fragment from S_8 without loss of dpe to give $[Ir(dpe)_2S_2]^+$.[29] In the latter complex the S_2 unit is π bonded to Ir in the same manner as is O_2 in the analogous dioxygen complexes.[13] By analogy, we propose that $RhLCl \cdot S_2$ contains a π-bonded S_2 fragment; thus, these O_2 and S_2 complexes probably have similar overall structures, *e.g.*, **2**.

The carbonyl frequency of RhLCl(CO) (1956 cm^{-1}, Nujol; 1957 cm^{-1}, CH_2Cl_2) is difficult to interpret in terms of a structure as there are no similar $RhCl(CO)P_3$ complexes. The carbonyl bands for *trans*-$RhCl(CO)(PPh_3)_2$ (1960 cm^{-1})[30] and *cis*-$RhCl(CO)(Ph_2PCH_2CH_2PPh_2)$ (2010 cm^{-1})[31a] have been discussed in connection with the "softening of the metal by a third phosphine" in rhodium complexes of $CH_3C(CH_2PPh_2)_3$.[27] The carbonyl absorption is expected to decrease if a third phosphine is added to either four-coordinate carbonyl complex above; thus, the observed carbonyl frequency for RhLCl(CO) seems to exclude a structure with CO trans to Cl. From the known arrangement of L in RhLCl and $RhLCl(NO)^+$, the RhLCl(CO) complex could have a tetragonal pyramidal geometry similar to that observed for $RhLCl(NO)^+$. However, a trigonal bipyramid is tentatively proposed on the basis that it is the predominant geometry observed for five-coordinate complexes of cobalt, rhodium, and iridium that can be assigned definitively the d^8 electronic configuration.[31b] The steric requirements of the triphosphine ligand probably require that it span axial–equatorial–axial sites of a trigonal bipyramid. Thus the chloride and carbonyl ligands probably occupy the equatorial positions of a distorted trigonal bipyramid, *e.g.*, **4**.

Five-Coordinate Cations, $[RhLCl \cdot A']^+$ (A′ = H, NO, N≡NPh, and CH_3CO). Five-coordinate cationic complexes of RhLCl are obtained relatively easily by adding

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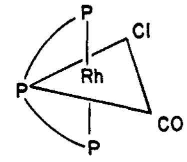
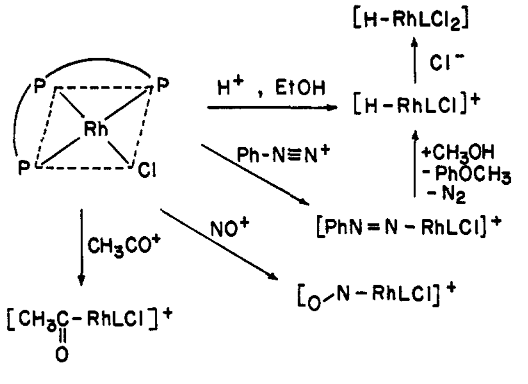


4

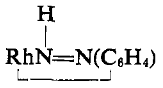
BF_4^- or PF_6^- salts of NO^+, PhN_2^+, CH_3CO^+, and H^+, as shown below. Addition of NO^+, PhN_2^+, CH_3CO^+, and H^+ could be viewed as an oxidative addition, or, more appropriately, as a Lewis acid association[32] of the electrophile with the Lewis base, RhLCl.



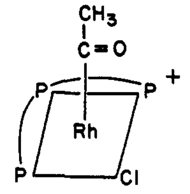
Addition of acids with large counterions, *e.g*,, aqueous solutions of HPF_6 and HBF_4, to RhLCl forms the stable hydride $[RhLClH]^+$ (ν(Rh–H) 2175 cm^{-1} for the BF_4^- salt, 2162 cm^{-1} for the PF_6^- salt). Both salts crystallize with one molecule of ethanol which may be coordinated at the sixth position of the metal. Addition of lithium chloride to an ethanol–dichloromethane solution of the PF_6^- complex gave $RhLCl_2H$, which has also been prepared by adding HCl to RhLCl (*vide infra*). From the low conductance of $RhLCl_2H$ it can be argued that $[RhLClH]^+$ has a strong affinity for chloride ion; perhaps this also indicates that the five-coordinate hydride cation has a strong tendency to become six coordinate, either through solvation or addition of a halide ion.

The nitrosyl complexes $[RhLCl(NO)][PF_6]$ and $[RhLCl(NO)][BF_4]$, which are prepared by adding RhLCl to methanol solutions of $NOPF_6$ and $NOBF_4$, have strong infrared N–O stretching frequencies at 1692 and 1699 cm^{-1}, respectively. The N–O absorption occurs in the range usually cited for bent M–N–O linkages.[33] In fact, the structure of $[RhLCl(NO)]^+$ is a square pyramid with a Rh–N–O angle of 131° (*vide infra*). The structural determination of $[RhLCl(NO)]^+$ confirms that discrete five-coordinate complexes result from addition of Lewis acids directly to rhodium in the RhLCl complex. Also, the basal plane of the complex remains relatively fixed, *i.e.*, a square-pyramidal coordination geometry seems to be favored in the five-coordinate complexes, especially for the formally Rh(III) cases.

Addition of PhN≡N⁺ to RhLCl in dichloromethane–methanol gives bright orange crystals which have properties consistent with those expected for the metal-phenylazo cation $[RhLCl(N_2Ph)]^+$.[34] The nature of the bonding by the PhN_2^+ group is especially interesting in view of the unusual products obtained by treating diazonium salts with *trans*-$IrCl(CO)(PPh_3)_2$.[35a] Rearrangements occur to give iridium tetrazene and *o*-carbon phenylazo complexes.[35] The infrared spectrum of $[RhLCl(N_2Ph)][PF_6]$ contains two new medium intensity peaks at 1561 and 1627 cm^{-1}. No new infrared bands are observed in the 3100–3200-cm^{-1} region, thus excluding formation of an *o*-phenylene Rh–carbon linkage of the type[35a]



Acylation of RhLCl with $CH_3CO^+BF_4^-$ [36] produces the cation $[RhLCl(CH_3CO)]^+$ cation, 5, in excellent yield. The infrared spectrum shows a ketonic absorption at 1704 cm^{-1} and the proton nmr has a methyl resonance at τ 7.94 in CD_2Cl_2. Also, the conductance of the compound in nitromethane is consistent with a 1:1 electrolyte.



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Four-Coordinate Cations, $[RhL(A)]^+$ (A = CO, CH_3CN). An infrared spectrum of RhLCl(CO) dissolved in dichloromethane shows a very weak band at *ca.* 2020 cm^{-1} in addition to the very strong band at 1956 cm^{-1}. The intensity of the 2020-cm^{-1} band increases in nitromethane, where the conductance (Λ_M = 32) suggests partial ionization. The four-coordinate cation $[RhL(CO)]^+$ (ν(CO) 2026 cm^{-1}, CH_2Cl_2 solution) is isolated easily by adding $NaPF_6$ to a 1:1 acetone–dichloromethane solution of RhLCl(CO). Addition of $NaPF_6$ to a solution of RhLCl(CO) under 1 atm of carbon monoxide gives the solid dicarbonyl complex $[RhL(CO)_2][PF_6]$ (ν(CO) 2037, 1980 cm^{-1}). The dicarbonyl cation loses carbon monoxide slowly in the solid state and rapidly in solution to give monocarbonyl $[RhL(CO)][PF_6]$. The solid monocarbonyl (ν(CO) 2025 cm^{-1}, Nujol) can be obtained from this solution if the excess CO is removed by bubbling nitrogen or argon gas through the solution. The interconversion between the four-coordinate $[RhL(CO)]^+$ and the five-coordinate $[RhL(CO)_2]^+$ cations appears to be completely reversible at 25° and ambient pressures.

Additional information about the mono- and dicarbonyl equilibrium was obtained from the infrared spectrum of $[RhL(CO)][PF_6]$ in dichloromethane under carbon monoxide pressure. The monocarbonyl exhibits one strong peak at 2026 cm^{-1}; after 6 hr at 56 psi CO pressure a second peak at ~1980 cm^{-1}

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(32) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

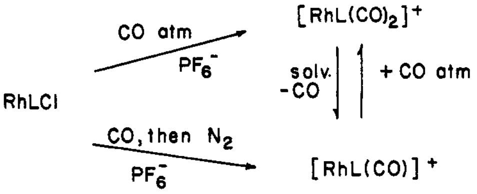
(33) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); **8**, 1282 (1969); D. M. P. Mingos and J. A. Ibers, *ibid.*, **9**, 1105 (1970).

(34) Complexes with both BF_4^- and PF_6^- anions have been isolated; the BF_4^- complex crystallizes with 1 mol of solvent (CH_2Cl_2), whereas the PF_6^- complexes are usually unsolvated after pumping at 25° for 3 hr at 0.1 Torr. Solvent inclusion appears to be general for *all* the BF_4^- complexes reported in this study, whereas usually the corresponding PF_6^- salt did not contain solvent molecules after pumping.

(35) (a) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **94**, 645 (1972); (b) G. W. Parshall, *ibid.*, **89**, 1822 (1967).

(36) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 72, 73.

appears at ~50% of the intensity of the major peak, which has shifted to 2029 cm^{-1} and decreased somewhat in intensity. When the carbon monoxide pressure is increased to 80 psi, the two carbonyl peaks remain at the same positions, and the intensity of the 1980-cm^{-1} band has increased to ~70% of the intensity of the 2029-cm^{-1} band. These experiments show that the position of the equilibrium can be shifted significantly toward the dicarbonyl complex under carbon monoxide pressure.



A dichloromethane solution of RhLCl was also examined under CO pressure. At 55 psi of CO the only infrared peak observed in the carbonyl region was the 1960-cm^{-1} absorption of RhLCl(CO). At 80 psi of CO, however, the 1960-cm^{-1} peak is soon replaced by strong peaks at ~2030 and 1970 cm^{-1} which may be attributed to the dicarbonyl complex. Thus, even in the presence of chloride the mono- and dicarbonyl equilibrium is established at ~80 psi of carbon monoxide.

The equilibrium between the rhodium carbonyl cations can be compared with the similar cobalt(I) complex.[18] Only the five-coordinate, dicarbonyl [CoL(CO)$_2$][PF$_6$] can be isolated and is dissociatively stable in both the solid state (ν(CO) 1933, 2009 cm^{-1}, Nujol) and in dichloromethane solution (ν(CO) 1952, 2007 cm^{-1}). These rhodium and cobalt dicarbonyl cations provide another comparison[37] of similar d^8 complexes in which the Co(I) complex exhibits a greater tendency to be five coordinate than does the corresponding Rh(I) complex.

The chloride ion in RhLCl can also be displaced by strongly coordinating solvents, *e.g.*, acetonitrile. The cation [RhL(CH$_3$CN)][PF$_6$] crystallizes readily from a hot methanol–acetonitrile (95:5) solution of NaPF$_6$ and RhLCl. This yellow solid shows the characteristic infrared bands of coordinated acetonitrile at 2295 and 2328 cm^{-1}.

Oxidative-Addition Products, RhLCl(X)(Y), XY = Cl$_2$, Br$_2$, I$_2$, HCl, H$_2$, and CH$_3$I. Generally, four-coordinate Rh(I) and Ir(I) phosphine complexes readily undergo oxidative-addition reactions with XY molecules to give six-coordinate M(III) complexes.[6] Oxidative-addition reactions also occur with RhLCl and provide some particularly interesting insight into the bulkiness of the coordination environment around rhodium and lead to some interesting trends. For example, the small molecules H$_2$, HCl, and Cl$_2$ readily add to RhLCl to give the six-coordinate complexes RhLClH$_2$, RhLCl$_2$H, and RhLCl$_3$, respectively. Also the tribromide and triiodide complexes, RhLBr$_3$ and RhLI$_3$, are obtained by adding Br$_2$ and I$_2$ to RhLCl in the presence of bromide and iodide, respectively. The conductivity data on the RhLH$_2$Cl, RhLCl$_2$H, RhLCl$_3$, and RhLBr$_3$ complexes indicate that they are essentially nonelectrolytes, whereas a plot of equivalent conductance against the square root of the equivalent concentration for RhLI$_3$ gave a slope of 58 in nitromethane, which is approximately one-third the value for a 1:1 electrolyte.[38] The appreciable conductance of RhLI$_3$ and the isolation of the stable five-coordinate cations [RhLCl(A)]$^+$ (*vide supra*) suggests that crowding becomes important when three bulky groups are bonded to rhodium, in addition to the ligand L.

We have been unable to isolate the expected six-coordinate product, RhLClBr(C$_7$H$_7$), when benzyl bromide is mixed with RhLCl. Even the reaction of methyl iodide requires very careful conditions to obtain the oxidative-addition product RhLCl(CH$_3$)I. The latter complex was isolated by using purified methyl iodide as a solvent and keeping the reaction mixture in the dark. The problem of adding alkyl halides does not seem to be related to an inherent instability of a rhodium–carbon bond, as the [RhLCl(CH$_3$CO)]$^+$ cation was obtained readily by alkylation of RhLCl with [CH$_3$CO][BF$_4$]. The results of all the synthetic work suggest that one group adds readily to give a five-coordinate cation, nominally of Rh(III); however, addition of the second group seems to be restricted. As will be discussed in more detail in the X-ray section that follows, the triphosphine ligand provides some close intramolecular contacts, of the order of 2.8 Å, which block somewhat one site of the coordination sphere. The structure of [RhLCl(NO)]$^+$ also provides an excellent rationale for the chemical results, as it shows that the sixth site is blocked even more effectively by hydrogen atoms on the phenyl groups of L in that area.

Six-Coordinate Hydrides. The dihydride, RhLClH$_2$, is a pale yellow solid that is stable in air and shows no tendency to lose molecular hydrogen in the solid state (25° and 0.1 Torr) or in benzene solution. The dissociative stability of the dihydride may account for the fact that it does not function as a hydrogenation catalyst for cyclohexene or 1-pentene in dichloromethane at 25° with either 1 or 7 atm of hydrogen pressure. The stability and catalytic inactivity of RhLClH$_2$ resemble the striking decrease in activity that was noticed when the phenyl groups of the Wilkinson catalyst were replaced by ethyl substituents.[39] The decreased activity of the RhCl(PR$_3$)$_3$ complexes (R = alkyl) probably results from the increased stability of the Rh–H bonds in the RhClH$_2$(PR$_3$)$_3$ compounds after treatment with H$_2$. In fact, the latter complexes do not lose molecular hydrogen as readily as the analogous arylphosphine complexes. The ligand L possesses the inductive effects of one phenyldialkyl- and two diphenylalkylphosphine ligands, in addition to the chelate effect.

The RhLClH$_2$ complex is coordinatively saturated (*i.e.*, six-coordinate Rh(III) = 18 e case). Without expansion of the coordination number of rhodium or chloride dissociation to [RhLH$_2$]$^+$, an olefin substrate can not bond to rhodium to provide a facile pathway for hydride transfer from rhodium to the olefin. A terminal phosphino group could possibly dissociate to provide a vacant site for olefin coordination to

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(37) L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, **93**, 6671 (1971).

(38) T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **8**, 146 (1969); R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964); A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(39) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1054 (1968).

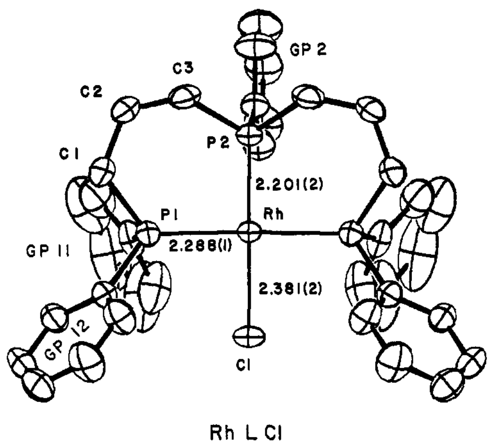
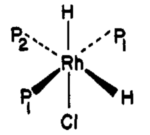


Figure 2. Perspective view of RhLCl approximately down the x axis with the 50% probability ellipsoids shown. The mirror plane is coplanar with atoms Cl, Rh, P(2), and phenyl group G(P2). Methylene and phenyl hydrogen atoms are not shown.

RhLClH$_2$; however, throughout the chemical and spectroscopic work on these RhLCl complexes, we have seen no evidence for dissociation of one of the phosphino groups. Thus, this system tends to provide some indirect support for the proposed[39,40] mechanism for homogeneous catalytic hydrogenation of olefins by the Wilkinson catalyst. It is thought that the RhClH$_2$(PPh$_3$)$_3$ complex (**6**) loses one triphenylphosphine



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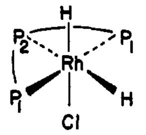

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ligand (P$_2$) to produce the five-coordinate intermediate RhClH$_2$(PPh$_3$)$_2$ which then adds an olefin molecule. In RhLCl the stability of the chelate ring prevents dissociation of any phosphino group—particularly the central phosphorus atom—from the analogous hydrogen adduct, RhLClH$_2$ (**7**). Although chelation and concomitant lack of phosphine dissociation may be the most important factors for the noncatalytic behavior of RhLClH$_2$, clearly the contributions of electronic and steric factors are not negligible, but it is difficult at present to assess their relative contributions.

If H$_2$ is added to RhLCl in dichloromethane instead of benzene at 25° and 1 atm, the resultant product is RhLCl$_2$H (ν(Rh–H) 2195 cm^{-1}), not the expected dihydride, RhLClH$_2$. The same monohydride is also obtained when RhLCl is treated in dichloromethane with 100 psi of H$_2$ for 3 hr, or if chloride ion is added to the [RhLClH]$^+$ cation. These reactions indicate that a chlorine atom has been abstracted from the dichloromethane solvent during the reaction.

Results and Discussion of the Structures of RhLCl and [RhLCl(NO)][PF$_6$]

Concomitant with the chemical studies already discussed, a series of crystal structure studies is being carried out in an attempt to relate chemical reactivity to structure. Here we present the results of the first two such structural studies: the crystal structures of the parent complex RhLCl and its five-coordinate derivative [RhLCl(NO)][PF$_6$]. The choice of the parent complex was clearly dictated by our desire to study the structural changes it undergoes in forming various complexes. The choice of the NO derivative was dictated partly by stability and availability and partly by the abundance of structural data on a variety of NO complexes of d^8 systems.

RhLCl. The crystal structure of the parent compound, Rh[C$_6$H$_5$P(CH$_2$CH$_2$CH$_2$P(C$_6$H$_5$)$_2$)$_2$]Cl, consists of discrete monomers. A perspective view of a single molecule with the atom labeling scheme is given in Figure 2. Selected bond distances and angles are given in Table I. The molecule has imposed mirror symmetry, with the Rh, Cl, P(2), and phenyl group G(P2) atoms lying on the mirror plane.

The geometry of the coordination polyhedron about the rhodium atom of the parent compound is approximately square planar. As can be seen in Table II, the rhodium atom is located 0.138 (1) Å from the weighted least-squares plane defined by the coordinating atoms. The Rh(I)–P(terminal) bond distances are 0.087 (2) Å longer than the Rh(I)–P(central) bond distance. In addition, these Rh(I)–P distances are shorter than those in comparable structures, as can be seen in Table III. Presumably this is due to the phosphine donor atoms with their linking propyl chain in the ligand L being more basic than in triphenylphosphine. Steric restrictions of the ligand are presumably also important but are difficult to assess. The Rh(I)–Cl distance of 2.381 (2) Å compares well with other similar Rh(I)–Cl distances given in Table III, indicating that this distance is not sensitive to change in other ligand groups.

The bond angles within the coordination polyhedron show only a slight deviation from the values expected for square-planar geometry. The deviations from the expected bond angle values of 180° for P(1)–Rh–P(1)′ (171.12 (5)°) and P(2)–Rh–Cl (178.82 (5)°) result from the rhodium atom being slightly above the plane formed by the ligand donor atoms.

There are two short intramolecular contacts in the parent compound. They are the Cl–H(6)(GP12) distance at 2.81 Å and the Rh–H(6)(GP2) distance at 2.80 Å. These contacts occur across one of the two vacant axial coordination positions of the rhodium atom, as shown by the dashed lines in Figure 3. From this we anticipate that in chemical reactions of RhLCl, the ligand L would hinder coordination at one of the two axial sites.

[RhLCl(NO)][PF$_6$]. When the parent compound undergoes Lewis acid ligand association to form the nitrosyl complex, the nitrosyl group attaches itself to the unhindered axial coordination site of the original compound, giving five-coordinate square pyramidal geometry about the rhodium atom (Figure 4). Interestingly, the basic geometry found for the ligands of the parent compound is not changed. The nitrosyl complex has the same imposed mirror symmetry as the parent compound, with the nitrosyl group lying on the mirror plane. The major change in geometry from the parent compound is that with the attachment of the NO group; the rhodium atom is located an additional 0.12 Å above the basal coordination plane.

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(40) (a) P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Amer. Chem. Soc.*, **94**, 3240 (1972); (b) S. Siegel and D. Ohrt, *Inorg. Nucl. Chem. Lett.*, **8**, 15 (1972).

Table I. Selected Distances (Å) and Angles (deg) for RhLCl and [RhLCl(NO)][PF$_6$]

	RhLCl	[RhLCl(NO)][PF$_6$]		RhLCl	[RhLCl(NO)][PF$_6$]
Rh–P(1)	2.288 (1)	2.374 (3)	Rh–P(1)–C(1)	119.8 (1)	113.5 (4)
Rh–P(2)	2.201 (2)	2.282 (4)	Rh–P(1)–C(1)(GP11)	118.7 (1)	115.7 (2)
Rh–Cl	2.381 (2)	2.408 (4)	Rh–P(1)–C(1)(GP12)	110.5 (1)	113.6 (2)
Rh–N		1.909 (15)	Rh–P(2)–C(3)	118.1 (1)	116.7 (4)
P(1)–C(1)	1.834 (4)	1.810 (11)	Rh–P(2)–C(1)(GP2)	112.5 (2)	111.9 (4)
P(1)–C(1)(GP11)	1.833 (4)	1.823 (7)	Rh–N–O		131.0 (1.4)
P(1)–C(1)(GP12)	1.822 (4)	1.814 (6)	P(1)–Rh–P(2)	90.73 (2)	90.34 (8)
P(2)–C(3)	1.827 (4)	1.829 (11)	P(1)–Rh–Cl	89.18 (2)	88.01 (8)
P(2)–C(1)(GP2)	1.836 (6)	1.797 (9)	P(1)–Rh–P(1)′	171.12 (5)	170.49 (13)
C(1)–C(2)	1.532 (6)	1.525 (14)	P(1)–Rh–N		94.67 (7)
C(2)–C(3)	1.522 (6)	1.523 (15)	P(2)–Rh–Cl	178.82 (5)	159.30 (15)
N–O		1.081 (16)	P(2)–Rh–N		96.43 (5)
P(1)–P(2)	3.195 (1)	3.302 (4)	N–Rh–Cl		104.3 (5)
P(1)–Cl	3.279 (1)	3.322 (4)	P(1)–C(1)–C(2)	116.5 (3)	115.7 (7)
P(1)–N		3.16 (1)	C(1)–C(2)–C(3)	113.8 (4)	113.8 (9)
P(2)–N		3.13 (1)	C(2)–C(3)–P(2)	114.7 (3)	116.3 (7)
Cl–N		3.42 (2)	C(3)–P(2)–C(3)′	98.6 (3)	98.7 (5)

Dihedral Angles in the Ligand, L

Atoms defining dihedral angle	Dihedral angle	
	RhLCl	[RhLCl(NO)]$^+$
Rh–P(1)–C(1)–C(2)	44.9 (4)	60.0 (9)
P(1)–C(1)–C(2)–C(3)	62.9 (5)	72.7 (11)
C(1)–C(2)–C(3)–P(2)	71.2 (4)	68.9 (11)
C(2)–C(3)–P(2)–Rh	61.0 (3)	55.5 (9)

Phenyl Group Distances (Å) and Angles (deg) for RhLCl[a]

		Unweighted mean			Unweighted mean
G(P11)			G(P11)		
C(1)–C(2)	1.384 (5)	1.384 (5)	C(1)–C(2)–C(3)	120.4 (4)	120.3 (4)
C(2)–C(3)	1.390 (6)		C(2)–C(3)–C(4)	120.2 (4)	
C(3)–C(4)	1.384 (7)		C(3)–C(4)–C(5)	119.9 (4)	
C(4)–C(5)	1.367 (6)		C(4)–C(5)–C(6)	120.1 (4)	
C(5)–C(6)	1.393 (6)		C(5)–C(6)–C(1)	120.7 (4)	
C(6)–C(1)	1.386 (5)				
G(P12)			G(P12)		
C(1)–C(2)	1.384 (6)	1.385 (7)	C(1)–C(2)–C(3)	120.4 (7)	120.2 (7)
C(2)–C(3)	1.379 (9)		C(2)–C(3)–C(4)	120.3 (7)	
C(3)–C(4)	1.352 (12)		C(3)–C(4)–C(5)	121.6 (6)	
C(4)–C(5)	1.411 (12)		C(4)–C(5)–C(6)	117.4 (7)	
C(5)–C(6)	1.390 (7)		C(5)–C(6)–C(1)	121.1 (6)	
C(6)–C(1)	1.393 (7)				
G(P2)			G(P2)		
C(1)–C(2)	1.384 (8)	1.379 (10)	C(1)–C(2)–C(3)	120.9 (7)	120.4 (7)
C(2)–C(3)	1.376 (10)		C(2)–C(3)–C(4)	121.0 (6)	
C(3)–C(4)	1.366 (11)		C(3)–C(4)–C(5)	119.1 (6)	
C(4)–C(5)	1.376 (10)		C(4)–C(5)–C(6)	120.1 (7)	
C(5)–C(6)	1.389 (8)		C(5)–C(6)–C(1)	121.0 (6)	
C(6)–C(1)	1.381 (8)				

[a] The phenyl groups in [RhLCl(NO)][PF$_6$] were refined as rigid bodies. Rigid body and derived parameters are given in Table VII.

The nitrosyl group itself is bent, with a Rh–N–O bond angle of 131 (1)°. The rhodium–nitrogen distance is 1.91 (2) Å. This nitrosyl ligand is close in character to the bent nitrosyl ligands that have metal–nitrogen–oxygen angles of about 120°. A bent nitrosyl can be formally considered to be NO$^-$.[41] In the X-ray structures of five other similar iridium and osmium complexes, the NO group is bent and is located in the apical position of the square-pyramidal geometry.[41]

The Rh(III)–P and Rh(III)–Cl bond distances in the nitrosyl complex are longer than in the parent complex, a direct consequence of increasing the coordination number from four to five. Just as in the parent compound there are also close contacts in the region of the remaining vacant axial coordination site. The nitrosyl complex H(2)(GP2)–Rh and H(6)(GP12)–Cl intramolecular contact distances (the same distances as shown by dotted lines in Figure 3 for the parent compound) at 2.78 and 2.68 Å, respectively, are about the same magnitude as the corresponding contacts in the parent compound.

The Ligand, L. The chelating nature of the ligand allows a planar tridentate configuration of phosphorus atoms about the rhodium atom. In both the parent and nitrosyl complexes, the Rh–P distances trans to each other are longer. In the similar Wilkinson compound, RhCl(P(C$_6$H$_5$)$_3$)$_3$, where there is no chelating ligand, two of the Rh–P distances are also longer than the

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(41) B. A. Frenz and J. A. Ibers, *M.T.P. Int. Rev. Sci., Phys. Chem.*, Series 1, **11**, 33 (1972).

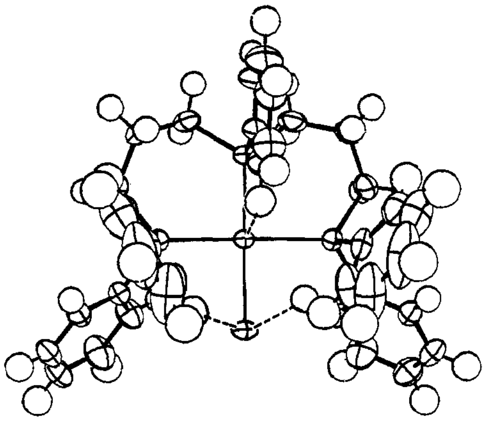

Figure 3. Perspective view of a single molecule of RhLCl showing the steric hindrance about a vacant axial coordination site. Close intramolecular contact distances are indicated by dotted lines. The 50% probability ellipsoids are shown with the hydrogen atoms as open circles. This is a view from the opposite direction of Figure 2.

Table II. Distances of Atoms from Various (Weighted Least-Squares) Planes[a]

		a. RhLCl	b. [RhLCl-(NO)]PF_6
1	P(1)	−0.0436 (9)	0.065 (3)
	P(1)′	−0.0436 (9)	0.065 (3)
	P(2)	0.0997 (14)	−0.154 (4)
	Cl	0.1150 (15)	−0.178 (4)
	Rh	0.138 (1)	0.255 (4)
2	Rh	0.0385 (4)	0.091 (1)
	P(1)	−0.1358 (9)	−0.100 (3)
	P(1)′	−0.1358 (9)	−0.100 (3)
	P(2)	0.0096 (14)	−0.319 (4)
	Cl	0.0205 (15)	−0.343 (4)
3	P(1)		
	P(1)′		
	P(2)		
	Rh	0.172 (1)	0.194 (4)

Equations of the Planes Are of the Form $AX + BY + CZ = D$ (Crystal Coordinates)

	A	B	C	D
1a	9.212	0.0000	−1.079	0.5060
b	24.010	0.0000	1.651	2.234
2a	9.213	0.0000	−1.109	0.5975
b	24.009	0.0000	1.652	2.069
3a	9.106	0.0000	−0.5139	0.5140
b	24.29	0.0000	0.7171	2.638

[a] All perpendicular distances are in Å. The direction of the rhodium is defined to be positive. Brackets enclose those atoms defining the plane.

third.[42] This suggests that there must be an electronic effect, for example, the trans influence of P being greater than Cl, which combined with the chelating nature of the ligand gives these two long and one short Rh–P distances.

As discussed above, the Rh–P distances in the present compound are shorter than in comparable Rh(I) structures. The effect of shortening the Rh–P bonds should result in longer P–C bonds to the phenyl rings and propyl chain, an opening of the Rh–P–C angles, and consequently a closing of the C–P–C angles as previously discussed by Mason and Towl[43] for triphenylphosphine ligands. This type of distortion is found in RhLCl with its shorter Rh–P bonds, and, to a lesser degree, is found also in [RhLCl(NO)][PF_6].

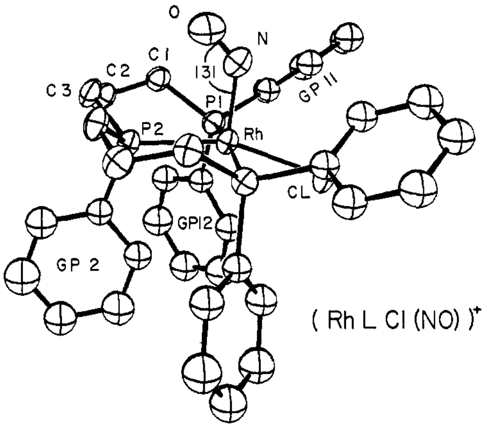

Figure 4. Perspective view of [RhLCl(NO)]$^+$ approximately down the *y* axis. Rh, P(2), Cl, N, and O lie on the mirror plane. The 50% probability ellipsoids are shown. Hydrogen atoms are not shown.

Table III. Comparison of Similar Rh(I) Complexes

	RhLCl	RhCl-$(PPh_3)_3$[a]	Rh(CS)-$Cl(PPh_3)_2$[b]	Rh(C_2F_4)-$Cl(PPh_3)_2$[a]	Rh(CO)-$H(PPh_3)_3$[c]
Rh–P(1)	2.288 (1)[d]	2.320 2.331 [e]	2.335 (2)	2.374 (8) 2.370 (8)	2.336 (8) 2.316 (9) 2.315 (8)
Rh–P(2)	2.201 (2)	2.210	2.337 (2)	2.375 (8)	
Rh–Cl	2.381 (2)	2.383	2.386 (3)		

[a] P. B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Commun.*, 1367 (1969). [b] J. L. DeBoer, D. Rogers, A. C. Skapski, and P. G. H. Troughton, *Chem. Commun.*, 756 (1966). [c] S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965). [d] All distances in Å with estimated standard deviations of the least significant figure in parentheses. [e] Bond distances are from a more recent personal communication, standard deviations unknown.

The carbon atoms of the propyl chain linking the phosphorus atoms exhibit the gauche conformation, while each bidentate ligand-metal moiety has the chair conformation. Bond distances and angles within the P(1)–C(1)–C(2)–C(3)–P(2) linkage are not unusual. The C–C–C bond angles in this propyl chain are about those expected (115°) from nonbonded interactions.

A combination of the chelating nature of the ligand and the effect of the short Rh(I)–P distances in the case of the parent compound results in P–P chelate bite distances that are shorter than the comparable P–P nonbonded distances (3.45 and 3.47 Å) in $RhCl(P(C_6H_5)_3)_3$.[42] This short bite distance causes a strain within the propyl linkage which is relieved by various amounts of twisting about the bonds. As can be seen in Table I, there is a 26 and 17° range in the values for the dihedral angles in this part of the ligand for the parent and nitrosyl complexes, respectively. The larger range of values for the parent complex results from the effect of shorter Rh(I)–P distances.

Intermolecular Contact Distances and Packing. There are two short intermolecular contacts in the parent compound, the Cl–H(32)″ distance of 2.66 Å and the H(12)–H(4)(GP12)″ distance of 2.21 Å. In the nitrosyl complex there is one short intermolecular contact, the Cl–H(6)(GP2)″ distance of 2.72 Å. Recall that these are idealized hydrogen atom positions.

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[42] P. B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Commun.*, 1367 (1969).

[43] R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970).

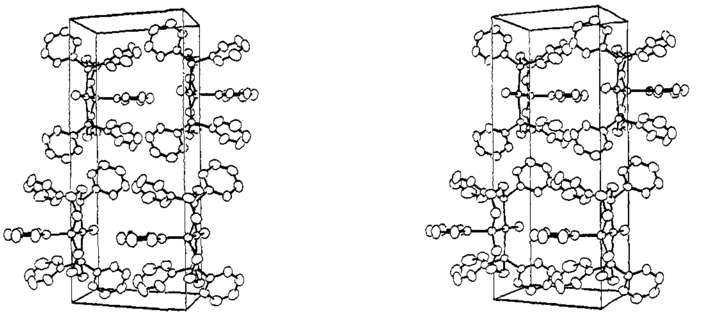

Figure 5. Stereoscopic view approximately down the *z* axis with the outline of one unit cell of RhLCl indicated. Hydrogen atoms are not shown.

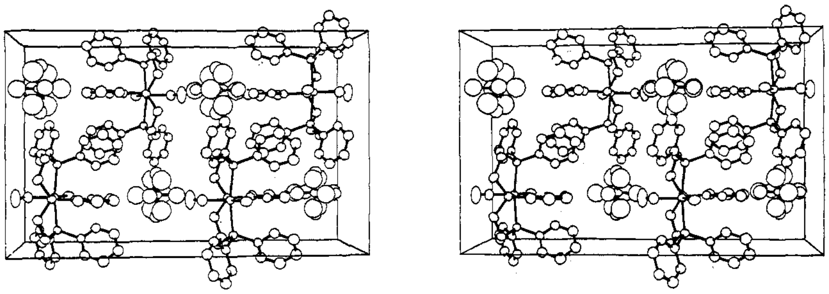

Figure 6. Stereoscopic view approximately down *z* axis with the outline of one unit cell of [RhLCl(NO)][PF_6] indicated. Hydrogen atoms are not shown.

Packing diagram stereoscopic views are given in Figures 5 and 6 for RhLCl and [RhLCl(NO)][PF_6], respectively.

Conclusions

On the basis of the dramatically increased stability of the five-coordinate adducts of small molecules (*e.g.*, BF_3, SO_2, O_2), the rhodium(I) chloride complex of the chelating triphosphine $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$, RhLCl resembles the reactions of $IrCl(CO)(PPh_3)_2$ and $IrCl(PPh_3)_3$ more closely than other rhodium–arylphosphine complexes. Similarly, RhLCl·O_2 reacts with SO_2, NO_2, and CO much more rapidly than other rhodium(I) complexes of arylphosphines. The stability of the dihydride $RhLClH_2$ and the tendency of RhLCl to undergo oxidative-addition reactions are comparable to the more basic iridium(I)–triphenylphosphine complexes and rhodium(I) complexes of alkyl–phosphines. The combined inductive and chelation effects increase the apparent nucleophilic and basic nature of RhLCl significantly over that of $RhCl(PPh_3)_3$.

The several complexes of RhLCl isolated in this study can be classified into one of three groups, based on whether RhLCl acts as an acid or base toward a given substrate. Class I contains the six-coordinate Rh(III) complexes that are formed by oxidative addition to RhLCl, *e.g.*, the reactions of Cl_2, Br_2, I_2, H_2, HCl, and CH_3I. Class II contains the five-coordinate cations obtained from RhLCl acting as a base toward electrophilic reagents, *e.g.*, H^+, CH_3CO^+, NO^+, and $N{\equiv}NPh^+$. These species are all probably square-pyramidal complexes of nominally Rh(III), as found in the crystal structure of [RhLCl(NO)][PF_6]. Class III contains the carbonyl complexes RhLCl(CO) and $[RhL(CO)_2]^+$ in which rhodium is accepting two electrons from each ligand to attain the 18 e configuration (thereby functioning as a σ acid). Clearly, however, the metal also acts as a π donor to the CO ligand. For the class III complexes, the structure is probably a distorted trigonal bipyramid as rhodium is formally Rh(I), a d^8 ion.

Assignment of the BF_3 and SO_2 adducts to one of the three classes is more difficult. Rhodium is functioning as a σ donor to the Lewis acids. However, what is the appropriate oxidation state for rhodium? Assignment of an oxidation state to rhodium in the five-coordinate SO_2 and BF_3 adducts is somewhat of a semantic problem and is subject to one's prejudice. For example, is it more correct as $M^I \cdot SO_2$ or as $M^{III} \cdot (SO_2{}^{2-})$? On the basis of the square-pyramidal structure of $IrCl(CO)(SO_2)(PPh_3)_2$,[11] we favor a square-pyramidal structure for the RhLCl·SO_2 and RhLCl·BF_3 cases, even though this may imply a d^6 electronic configuration for rhodium.

The structures of the O_2 and S_2 complexes probably resemble the trigonal-bipyramidal (or distorted octahedral) structures of $[IrX(O_2)(CO)(PPh_3)_2]$ (X = Cl,[11] I[42]), $[M(O_2)(dpe)_2]^+$ (M = Ir, Rh; dpe = $Ph_2PCH_2CH_2PPh_2$),[13,44] and $[Ir(S_2)(dpe)_2]^+$.[29] As discussed above for the BF_3 and SO_2 adducts, assignment of an oxidation state for rhodium in the O_2 and S_2 complexes becomes a prejudiced exercise. In fact, even assigning the coordination number of rhodium as five or six in the S_2 and O_2 compounds is arbitrary.

The structural results presented here correlate well with the preliminary model building and with chemical reactivity. They confirm that the tridentate ligand L occupies three of the coordination sites about Rh(I). They confirm that NO^+ is attached directly to the metal and that the resultant complex $RhLCl(NO)^+$ is best interpreted as a $Rh^{III}(NO^-)$ complex. A comparison of the two results indicates that the change in RhL environment on going from the four-coordinate

(44) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

parent complex to the five-coordinate NO derivative is minimal. Structural results on both complexes indicate considerable crowding of the sixth potential site on the Rh atom. They thus provide a structural rationalization for the fact that oxidative addition of bulky ligands, such as benzyl bromide, to RhLCl cannot be accomplished, at least by methods tried to date.

The design of the ligand $PhP(CH_2CH_2CH_2PPh_2)_2$ favors coordination of all three phosphino groups to a transition metal. Throughout the reactions reported in this study, the phosphine ligand functioned as a tridentate and remained bonded to the metal. Thus, one can carry out unusual chemical reactions on the metal site with three coordination sites effectively occupied and without changing the number of phosphine donors.

Experimental Section

Reagents and Characterization. All solvents were reagent grade and were thoroughly degassed before use. Further purification of solvents and reagents, if necessary, was by standard methods. The ligand, $PhP(CH_2CH_2CH_2PPh_2)_2$,[18] was used as a stock benzene solution (1 mmol = 4.1 ml). Complexes were prepared routinely in degassed solvents and isolated under a nitrogen atmosphere; the solid complexes were generally air stable (except where noted). Conductivity measurements were made at *ca.* 23° on $\sim10^{-3}$ *M* nitromethane solutions (dried with Linde 4A molecular sieves) and results are given in cm²/(ohm mol). Nmr measurements were made on Varian HA-100 and Jeol MH-100 instruments operating at 38°. Infrared spectra were taken on Perkin-Elmer 337 grating and Beckman IR-9 spectrometers as Nujol mulls between KBr plates (unless otherwise specified) and are listed as cm^{-1}.

Infrared spectra of solutions under gas pressures up to 80 psi were obtained using 0.2 or 1.0 mm sodium chloride cavity infrared cells type "E" (Barnes Engineering Co., Stamford, Conn.) sealed with an O-ring to a specially constructed, compact, portable gas manifold.[45] With dichloromethane as a solvent and a compensating cell, the 0.2-mm cell showed no strong absorptions in the region 1850–2250 cm^{-1}.

Preparation of the Ligand Bis(3-diphenylphosphinopropyl)phenylphosphine, L. 1. Bis(3-hydroxypropyl)phenylphosphine.[46] Phenylphosphine (27.2 g, 0.247 mol) and hexane (250 ml) were placed in a three-necked, 1000-ml flask containing a sintered glass frit and a stopcock on the bottom. The flask was also equipped with a reflux condenser, mechanical stirrer, and a pressure-equalizing addition funnel. Butyllithium (0.494 mol, 313 ml of a 1.6 *M* hexane solution) was added at room temperature over a 30-min period; then the resultant slurry was refluxed 1 hr. After the solution cooled to room temperature, the hexane was removed from the yellow solid $C_6H_5PLi_2$ by vacuum filtration; then 300 ml of tetrahydrofuran was added to the flask. Oxetane (assuming 95% $C_6H_5PLi_2$, 0.469 mol, 30.4 ml) in 50 ml of tetrahydrofuran was added at a rate to maintain a gentle reflux, and the resultant slurry was refluxed 1 additional hr. After cooling, approximately 75% of the tetrahydrofuran was removed by vaporization *in vacuo* and replaced with an equal volume of diethyl ether. With vigorous stirring 200 ml of aqueous saturated ammonium chloride was added cautiously, after which the aqueous layer was extracted with three 100-ml portions of ether; the combined ether layers were dried overnight over anhydrous sodium sulfate. The mixture was filtered and the ether was removed *in vacuo;* the waxy residue was heated at 120° for 24 hr *in vacuo* (0.1 Torr) to remove the volatile components. At room temperature the product (47.4 g, 0.209 mol, 85%) is a viscous pale yellow liquid. The yields based on phenylphosphine from three other experiments were 82, 79, and 73%.

The infrared spectrum of the neat oil showed a strong OH absorption at 3340 cm^{-1}. The ^1H nmr spectrum ($CDCl_3$) of the compound consisted of broad peaks at τ 2.25–2.92 (phenyl protons, relative intensity 5.0), 5.19 (hydroxyl protons, intensity 2.0), 6.46 ($-CH_2O$ protons, intensity 3.6), and 8.32 ($-PCH_2CH_2-$ protons, intensity 7.7), all consistent with the formula $C_6H_5P(CH_2CH_2CH_2OH)_2$.

2. Bis(3-hydroxypropyl)phenylphosphine Oxide. The above oil, $C_6H_5P(CH_2CH_2CH_2OH)_2$ (47.4 g), was dissolved in 100 ml of acetone and placed in an ice bath. A solution of hydrogen peroxide (23 ml of 30% aqueous H_2O_2 in 46 ml of acetone) was added slowly with stirring so that the temperature of the reaction mixture did not rise above 35°. After the acetone was removed *in vacuo*, the remaining water was removed as the benzene azeotrope. The remainder of the benzene was removed by vacuum distillation and the oily residue was carefully heated to 120° for 18 hr to remove the volatile components. The product (50.2 g, 0.207 mol, 99%) is a pale yellow viscous oil. The yields on this reaction for three other preparations were ~100, 97, and 91%.

Strong and broad infrared absorptions are observed at 3350 and 1170 cm^{-1}; the first is due to OH and the latter is assigned to the P=O stretching frequency. The ^1H nmr spectrum ($CDCl_3$) is similar to that of the previous compound except for the resolution of the CH_2O protons: τ 2.00–2.75 (broad, C_6H_5, relative intensity 5.0), 5.05 (singlet, OH, intensity 1.7), 6.41 (triplet, $J \cong 6$ Hz, CH_2O, intensity 3.5), and 7.58–8.67 (broad multiplet, $-PCH_2CH_2-$, intensity 7.5).

3. Bis(3-chloropropyl)phenylphosphine Oxide. A solution of the oil from part 2, $(C_6H_5)P(O)(CH_2CH_2CH_2OH)_2$ (50.2 g), in 100 ml of dichloromethane was added slowly (to avoid excessive HCl effervescence) to a refluxing solution of phosphorus pentachloride (104 g, 20% excess) in 200 ml of carbon tetrachloride. The HCl was removed continually by a stream of nitrogen and trapped in aqueous NaOH along with the dichloromethane not retained by the reflux condenser. The solution is red-orange when all of the phosphine oxide has been added and turns black while refluxing an additional 6 hr. The solution was cooled and most of the volatile compounds (CCl_4, $POCl_3$, CH_2Cl_2) were removed *in vacuo.* The black waxy residue was hydrolyzed with aqueous $NaHCO_3$ and extracted with three 100-ml portions of benzene and two 100-ml portions of dichloromethane. The combined extracts are treated with *ca.* 100 g of activated charcoal; subsequent removal of the solvent *in vacuo* yields a brown solid. Extraction of this solid with 150 ml of ether in a Soxhlet apparatus yielded 36.2 g of a pale yellow solid; a further crop of darker crystals (4.7 g) was obtained by evaporating the ether extracts. Total yield, 40.9 g, 0.147 mol, 71%; mp 78–79°. *Anal.* Calcd for $C_{12}H_{17}Cl_2OP$: C, 51.63; H, 6.14; P, 11.10; Cl, 25.40. Found: C, 51.52; H, 6.08; P, 11.36; Cl, 25.30.

The OH absorption due to the alcohol from part 2 above is absent in the infrared spectrum, but the P=O absorption is strong and broad at 1190 cm^{-1}. The ^1H nmr spectrum ($CDCl_3$) is also similar to that of the previous compounds except for the absence of the OH peak: τ 1.92–2.58 (broad, C_6H_5, relative intensity 5.0), 6.40 (broad, $-CH_2Cl$, intensity 3.7), and 7.91 (broad, $-PCH_2CH_2-$, intensity 8.1).

4. Bis(3-diphenylphosphinopropyl)phenylphosphine Oxide. A solution of $(C_6H_5)_2PLi$ was prepared by adding 0.3 mol of butyllithium (190 ml of a 1.6 *M* hexane solution) to 0.3 mol of diphenylphosphine (55.8 g) in 200 ml of tetrahydrofuran over 30 min at 0°. This solution was stirred 1 hr at room temperature and then added slowly (1 hr) to a solution of $(C_6H_5)P(O)(CH_2CH_2CH_2Cl)_2$ (40.9 g in 250 ml of tetrahydrofuran) at 0°. The solution was stirred 1 hr at 0°, allowed to warm to room temperature, and then stirred for 18 hr. The solution was heated almost to the refluxing temperature (*ca.* 60°) for a few minutes; after cooling, the solution was hydrolyzed with 100 ml of ethanol and the solvent removed *in vacuo.* The product was dissolved in 200 ml of benzene and chromatographed on an alumina column (100 g, grade III, Woelm neutral), eluting with 600 ml of benzene. The benzene was removed *in vacuo* at *ca.* room temperature; the last volatile components were removed by heating the compound at 130° (~0.1 Torr) for 12 hr. The product (80.6 g, 95.3%) is a pale yellow viscous oil. The yield was 59.2% when the reaction time was only 4 hr; this was increased to 82.6% at 12 hr and 90.2% at 18 hr.

The infrared spectrum showed the strong broad P=O frequency at 1190 cm^{-1}. The ^1H nmr spectrum consisted of two broad resonances at τ 2.33–2.91 (C_6H_5) and 7.70–8.53 (CH_2); the relative intensity ratio is 25:11.4 which compares favorably with the expected ratio of 25:12.

5. Bis(3-diphenylphosphinopropyl)phenylphosphine, the Ligand L. Hexachlorodisilane, Si_2Cl_6 (26.2 ml, 0.154 mol, 10% excess) was added to a solution of $(C_6H_5)P(O)(CH_2CH_2CH_2P(C_6H_5)_2)_2$ (80.6 g) in 200 ml of benzene. The resultant solution changed from pale yellow to orange as it was refluxed 1 hr; the small amount of HCl evolved was trapped in NaOH solution. After cooling to room temperature, the solution was hydrolyzed very carefully with 200 ml of 30% aqueous NaOH. The reaction, which forms a large

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(45) We thank Dr. K. Barefield for suggestions on construction of the pressure infrared cell.

(46) K. Issleib and H. Roloff, *Chem. Ber.*, **98**, 2091 (1965).

amount of thick white precipitate, is very exothermic and requires cooling. After *ca.* 2 hr stirring part of the precipitate dissolved and the aqueous layer became more mobile. The aqueous layer was extracted three times with 100-ml portions of benzene. The combined benzene fractions were dried overnight with anhydrous Na_2SO_4. After filtering, removing the benzene *in vacuo*, and heating to 130° (0.1 Torr) for 12 hr, a viscous pale yellow oil was obtained (76.3 g, 99%). The yields on three other preparations were 99, 93.2, and 86.2%. The yield in this step appears to be related to how well the white precipitate is broken up; otherwise, it is virtually quantitative.

The total yield of ligand L after the five synthetic steps, calculated on the basis of $C_6H_5PH_2$, is 55%. The infrared spectrum is virtually identical with that of the preceding compound except for the absence of the strong P=O band; the ^1H nmr chemical shifts and relative intensities are also similar to those of the preceding phosphine oxide, *i.e.*, 4, and consistent with the formula $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$.

6. Tris(benzyl bromide) Derivative of the Ligand Bis(3-diphenylphosphinopropyl)phenylphosphine. The tris(benzyl bromide) derivative was prepared by refluxing 0.5 mmol of $(C_6H_5)P[CH_2CH_2CH_2P(C_6H_5)_2]_2$ (2.05 ml of benzene solution) in 50 ml of ethanol with 0.5 ml of benzyl bromide for 30 min. The solution was reduced to 20 ml and 50 ml of benzene was added slowly. The resultant white solid was washed with benzene and dried *in vacuo*, yield 0.51 g, 94%. *Anal.* Calcd for $C_{57}H_{58}Br_3P_3$: C, 63.62; H, 5.43. Found: C, 63.85; H, 5.34.

Synthesis of Metal Complexes. A. RhLCl. To a boiling slurry of $[Rh(COD)Cl]_2$[19] (COD = 1,5-cyclooctadiene) (0.5 g, 2 mmol Rh) in 100 ml of ethanol was added 8.2 ml of the benzene solution of the ligand L (2 mmol). On addition of the ligand solution all of the $[Rh(COD)Cl]_2$ dissolved quickly and yellow crystals began separating from the solution in minutes. The volume of the solution was reduced to *ca.* 80 ml over the 15–20 min reaction period. After the solution cooled to room temperature, the solid was collected and washed with 2 ml of ethanol and 5 ml of diethyl ether and dried with a nitrogen stream on a sintered-glass frit, yield ~1.2 g, ~83%, mp (under N_2) 227–229° dec. *Anal.* Calcd for $C_{36}H_{37}ClP_3Rh$: C, 61.68; H, 5.28; Cl, 5.07. Found: C, 62.16; H, 5.33; Cl, 5.26.

B. RhLBr. The bromide complex was prepared similarly except that $[Rh(COD)Cl]_2$ was refluxed for 5 min in ethanol with a tenfold excess of lithium bromide before adding the ligand solution, yield of yellow needles 86%. *Anal.* Calcd for $C_{36}H_{37}BrP_3Rh$: C, 58.00; H, 4.97; Br, 10.73. Found: C, 59.24; H, 5.34; Br, 10.28.

C. RhLI. The iodide complex was prepared similarly from $[Rh(COD)I]_2$[19] except that the solution was refluxed only 2 min after adding the ligand solution. Orange flakes began crystallizing as the solution was cooled at ~0° for 30 min. The crystals were collected and washed with 3 ml of cold ethanol and dried in a nitrogen stream, yield 83%. *Anal.* Calcd for $C_{36}H_{37}IP_3Rh$: C, 54.56; H, 4.67; I, 16.03. Found: C, 54.39; H, 4.54; I, 15.88.

D. RhLCl(CO)·CH₂Cl₂. Carbon monoxide was bubbled through a dichloromethane solution (10 ml) of RhLCl (0.35 g, 0.5 mmol) for 30 min, followed by 30 min of bubbling with nitrogen. Petroleum ether (65–110°) was added slowly until the solution became cloudy. The resultant solution was treated with six 5-ml portions of petroleum ether at 6 hr intervals. The resultant orange crystals were washed on the frit with 2 ml of diethyl ether and dried, yield 0.32 g, 88%; infrared ν(CO) 1956 (Nujol), 1957 (CH_2Cl_2); Λ_M = 32. *Anal.* Calcd for $C_{38}H_{39}Cl_3OPh_3Rh$: C, 56.04; H, 4.83; Cl, 13.08. Found: C, 56.23; H, 4.56; Cl, 14.04.

E. RhLI(CO). Carbon monoxide was bubbled for 20 min through 20 ml of a dichloromethane solution of RhLI (0.35 g). Heptane (30 ml) was added slowly to induce crystallization. After 24 hr at −10°, the yellow crystals were collected and washed with 2 ml each of ethanol and diethyl ether, yield 0.34 g, 94%; infrared ν(CO) 1937 (Nujol). *Anal.* Calcd for $C_{37}H_{37}IOP_3Rh$: C, 54.13; H, 4.55; I, 15.47. Found: C, 54.32; H, 4.43; I, 15.63.

F. RhLCl·BF₃. A 100-ml flask containing 0.35 g of RhLCl was attached to a vacuum line and evacuated. Dry benzene (20 ml) was condensed into the flask and then warmed to *ca.* 25°, partially dissolving the RhLCl. The solution was frozen and boron trifluoride (0.5 mmol) was condensed into the flask. The flask was again warmed to room temperature and stirred for 1 hr. An orange precipitate formed immediately as the solids melted. The resultant slurry was frozen and the benzene sublimed away, yield 0.38 g, 99%; infrared ν(B–F) 1060 vs, br; ^{19}F nmr, −11.1 ppm (C_6F_6); ^{11}B nmr, +18.9 ppm ($B(OCH_3)_3$). *Anal.* Calcd for $C_{36}H_{37}BClF_3P_3Rh$: C, 56.21; H, 4.85; Cl, 4.62; F, 7.42. Found: C, 50.36;[47] H, 4.68; Cl, 4.66; F, 7.89.

G. RhLCl·SO₂. A slurry of 0.35 g of RhLCl in 30 ml of benzene was treated for 30 min with bubbling SO_2; when 30 ml of petroleum ether (65–110°) was added slowly, yellow crystals began forming. After 3 hr at 0°, the crystals were collected, washed with ether, and dried *in vacuo* at 56° for 12 hr, yield 0.38 g, 99%; infrared ν(SO) 1030, 1155 vs (Nujol). *Anal.* Calcd for $C_{36}H_{37}ClO_2P_3RhS$: C, 56.49; H, 4.88; Cl, 4.64; S, 4.18. Found: C, 57.61; H, 4.90; Cl, 5.45; S, 4.62.

H. RhLCl·O₂. Dry oxygen gas was bubbled through a slurry of RhLCl (0.35 g) in 20 ml of benzene for 30 min. The solution changed from yellow to orange and light brown microcrystals separated. The crystals were collected and washed with 2 ml of benzene and 2 ml of ether, yield 0.35 g, 97%; infrared $\nu(RhO_2)$ 858 m (Nujol). *Anal.* Calcd for $C_{36}H_{37}ClO_2P_3Rh$: C, 58.98; H, 5.15; Cl, 4.84. Found: C, 59.68; H, 5.14; Cl, 4.64.

I. RhLCl·S₂. A solution of 0.032 g of recrystallized sulfur in 20 ml benzene was added dropwise to a solution containing 0.35 g of RhLCl in 10 ml of dichloromethane. The volume of the solution was reduced to 10 ml with an aspirator. After 30 min the resultant orange-brown crystals were collected and washed with 2 ml each of cold ethanol and diethyl ether, yield 0.19 g, 50%; infrared $\nu(RhS_2)$ 546 m. *Anal.* Calcd for $C_{36}H_{37}ClP_3RhS_2$: C, 56.49; H, 4.88; Cl, 4.64; S, 8.38. Found: C, 57.30; H, 4.89; Cl, 4.90; S, 8.28.

J. RhLCl(SO₄). Gaseous SO_2 was bubbled through a slurry of 0.25 g of RhLCl·O_2 in 20 ml of benzene for 20 min. The color of the mixture changed from light brown to yellow. The excess SO_2 was removed by bubbling nitrogen through the slurry for 15 min. The yellow microcrystals, which separated, were filtered and washed with 2 ml each of ethanol and diethyl ether, yield 0.23 g, 85%; infrared $\nu(SO_4)$ 1250, 1240, 640 (Nujol). *Anal.* Calcd for $C_{36}H_{37}ClO_4P_3RhS$: C, 54.22; H, 4.68; S, 4.02. Found: C, 54.45; H, 4.61; S, 3.91.

K. RhLCl(CO₃). A solution of RhLCl·O_2 (0.25 g) in dichloromethane (20 ml) was stirred vigorously at ambient pressure under a carbon monoxide atmosphere for 24 hr. Ethanol (10 ml) was added and the dichloromethane was removed on a rotary evaporator. The resultant pale yellow crystals were collected and washed with 2 ml each of cold ethanol and diether ether, yield 0.09 g, 33%; infrared $\nu(CO_3)$ 1630 sh, 1600 vs, br, 1260 m (Nujol). *Anal.* Calcd for $C_{37}H_{37}ClO_3P_3Rh$: C, 58.37; H, 4.90; Cl, 4.67. Found: C, 58.34; H, 4.92; Cl, 4.82.

L. Reaction of RhLCl·O₂ with NO₂ (N₂O₄). (a) A dichloromethane solution of RhLCl·O_2 (0.25 g in 20 ml) was stirred for 2 hr with 0.1 ml of N_2O_4 at 25°. Ethanol (20 ml) was added and the volume was reduced to 15 ml under a stream of nitrogen (2 hr). The resultant orange powder was collected and dried, yield ~50 mg. The infrared spectrum (Nujol, Halocarbon) showed absorptions at 1500 (vs, br) and 1260 (s, br) cm^{-1}. (b) The dioxygen complex RhLCl·O_2 was generated by bubbling dried oxygen gas through a slurry of RhLCl (0.35 g) in benzene (20 ml) for 2 hr. The remaining benzene was removed *in vacuo* and replaced with 25 ml of dichloromethane maintained at −10°. The slurry was treated with N_2O_4 at this temperature for 30 min, and then the excess N_2O_4 was removed *in vacuo* by a water aspirator. Ethanol (10 ml) was added and the solvent was removed slowly (1 hr) *in vacuo*. The orange powder was dried at 25° for 24 hr at 0.05 Torr, yield 0.37 g; infrared 1630 m, 1550 s, sp, 1510 vs, 1370 s, 1320 s, 1260 m, and 1220 m (Nujol, Halocarbon); Λ_M = 73. *Anal.* Calcd for $C_{36}H_{37}ClN_2O_6P_3Rh$: C, 52.38; H, 4.52; N, 3.40. Found: C, 52.26; H, 4.44; N, 3.47.

M. [RhL(CO)₂][PF₆]. Carbon monoxide was bubbled through a suspension of 0.35 g of RhLCl and 0.1 g of $NaPF_6$ in 20 ml of 1:1 dichloromethane–acetone for 30 min. The solution was filtered and 80 ml of petroleum ether was added slowly over 20 min under a CO atmosphere. After 24 hr at 0° the pale yellow microcrystals were collected and recrystallized from dichloromethane and petroleum ether under a CO atmosphere, yield 0.39 g, 91%; infrared ν(CO) 1960, 2040 vs (Nujol), 2026 (CH_2Cl_2, observed CO effervescence on dissolution); Λ_M = 76. *Anal.* Calcd for $C_{38}H_{37}$-

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(47) Other workers have also experienced difficulty obtaining accurate carbon analyses in some polyphosphine complexes of heavy metals. For example, see ref 27, p 2162 and their references 10, 14, 15, and 17. On the basis of our experience this problem becomes acute in the presence of both boron and fluorine. (Personal communication, M. H. W. Laboratories, Garden City, Mich.)

Table IV. Crystal Data and Data Collection Details

	RhLCl	[RhLCl(NO)][PF_6]
	Crystal Data	
a	9.312 (1) Å	24.350 (5) Å
b	21.187 (2) Å	15.196 (2) Å
c	8.851 (3) Å	9.914 (2) Å
β	105.39 (1)°	
Z	2	4
d_{obsd}	1.36 (1) g cm^{-3}	1.57 (1) g cm^{-3}
d_{calcd}	1.38 g cm^{-3}	1.58 g cm^{-3}
Space group	$C_{2h}{}^2$-$P2_1/m$ or $P2_1$	$D_{2h}{}^{16}$-$Pnma$ or $P2_1ma$
Imposed symmetry	m	m
Color	Yellow	Light green
Habit	Flat parallelepiped	Hexagonal needle
Bounding faces	$\{100\}$, $\{010\}$, $\{10\bar{2}\}$	$\{100\}$, $\{101\}$, $\{010\}$
Dimensions	0.7 × 0.25 × 0.43 mm	0.17 mm long × 0.030 mm cross-section
Absorption coefficient Cu K$\bar{\alpha}$	57.1 cm^{-1}	66.9 cm^{-1}
Crystal volume	0.0076 mm^3	0.0012 mm^3
Range of transmission coefficients	0.268–0.670	0.66–0.69 (no correction made)
	Data Collection	
Radiation	Cu K$\bar{\alpha}$	Cu K$\bar{\alpha}$
Filter	1.0-mil Ni postfilter	1.0-mil Ni prefilter
Takeoff angle	1.9°	2.3°
Aperture	6.4 × 6.4 mm, 32 cm from counter	6.4 × 6.4 mm, 32 cm from counter
Scan speed	2°/min $2\theta < 50°$ 1°/min $2\theta > 50°$	1°/min $2\theta < 68°$ 0.5°/min $2\theta > 68°$
Method	θ–2θ scans	θ–2θ scans
Scan width	$-0.6°$ (α_1) to $+0.7°$ (α_2) $2\theta < 60°$ $-0.65°$ (α_1) to $+0.65°$ (α_2) $2\theta > 60°$	$-0.8°$ (α_1) to $+0.7°$ (α_2)
Background time	10 sec $2\theta < 45°$ 20 sec $2\theta > 45°$	20 sec $2\theta < 45°$ 40 sec $45° < 2\theta < 68°$ 100 sec $2\theta > 68°$
Standards	6 every 200 reflections	6 every 75 reflections
Maximum deviation of standards	2.5σ	4σ
2θ limit	63.5°	90°
Number of data	3530 (including 501 Friedel pairs)	2058 (including 256 Friedel pairs)
p	0.03	0.04
Number of unique data for which $F_o{}^2 > 3\sigma(F_o{}^2)$	2566	1282

Table V. Course of the Refinements

Set no.	Conditions	—RhLCl—		[RhLCl(NO)]-[PF_6]	
		R	R_w	R	R_w
1	Isotropic (no H), rigid phenyl groups, rigid F_6 group	0.108	0.140	0.087	0.107
2	No H atoms, nongroup atoms anisotropic, individual B's on group atoms	0.061	0.081	0.073	0.094
3	Same as 2, but with 2 partial F_6 groups, center tied to P position, occupancy varied			0.069	0.090
4	H contributions added	0.058	0.075	0.058	0.081
5	Same as 2 but with variable extinction parameter			0.058	0.078
6	Same as 4 but with no rigid groups and all nonhydrogen atoms anisotropic and variable extinction parameter	0.035	0.046		
7	Same as 5 but with H contributions added			0.055	0.066

$F_6O_2P_4Rh$: C, 52.64; H, 4.31; F, 13.16. Found: C, 52.14; H, 4.30; F, 12.88.

N. [RhL(CO)][PF_6]. The same procedure was followed as in (M) except that the yellow solid was recrystallized after sweeping the dichloromethane solution with N_2 or argon for 30 min after CO addition, yield 0.37 g, 86%; infrared ν(CO) 2025 vs (Nujol), 2026 (CH_2Cl_2); $\Lambda_M = 75$. *Anal.* Calcd for $C_{37}H_{37}F_6OP_4Rh$: C, 52.97; H, 4.45; F, 13.60. Found: C, 52.96; H, 4.21; F, 14.13.

O. [RhL(CH_3CN)][PF_6]. A slurry of 0.35 g of RhLCl, 0.1 g of $NaPF_6$, and 1 ml of acetonitrile in 20 ml of methanol was heated to reflux for 15 min. The hot solution was filtered and cooled at 0° for 18 hr. The resultant yellow crystals were washed with 2 ml each of methanol and diethyl ether and dried under nitrogen, yield 0.32 g, 76%; infrared ν(C≡N) 2295, 2328 w (Nujol); $\Lambda_M = 74$. *Anal.* Calcd for $C_{38}H_{40}F_6NP_4Rh$: C, 53.57; H, 4.73; N, 1.64. Found: C, 53.66; H, 4.52; N, 1.52.

P. [RhLCl($N_2C_6H_5$)][BF_4]·CH_2Cl_2. A solution of 0.1 g of $C_6H_5N_2{}^+BF_4{}^-$ in 20 ml of methanol was added to 0.35 g of RhLCl in 5 ml of dichloromethane. Orange crystals were obtained when the solution was concentrated quickly on a rotary evaporator. The crystals were collected, washed with 2 ml each of cold ethanol and diethyl ether, and dried, yield 0.34 g, 70%; $\Lambda_M = 79$. *Anal.* Calcd for $C_{43}H_{44}BCl_3F_4N_2P_3Rh$: C, 52.79; H, 4.53; Cl, 10.90; N, 2.86. Found: C, 52.99; H, 4.56; Cl, 9.60; N, 2.71.

Q. [RhLCl($C_6H_5N_2$)][PF_6]. This complex was prepared in a manner similar to the above $BF_4{}^-$ salt by using $C_6H_5N_2{}^+PF_6{}^-$, yield 0.29 g, 67%; $\Lambda_M = 80$. *Anal.* Calcd for $C_{42}H_{42}ClF_6N_2P_4Rh$: C, 53.00; H, 4.46; N, 2.94. Found: C, 52.83; H, 4.38; N, 2.76.

R. [RhLCl(NO)][PF_6]. A solution of 0.1 g of $NO^+PF_6{}^-$ in 10 ml of methanol was added to 0.35 g of RhLCl in 20 ml of warm benzene. The green crystals which formed immediately were filtered, washed with benzene and diethyl ether (2 ml each), and dried, yield 0.36 g, 82%; infrared ν(NO) 1692 vs (Nujol); $\Lambda_M = 80$. *Anal.* Calcd for $C_{36}H_{37}ClF_6NOP_4Rh$: C, 49.33; H, 4.26; N, 1.60. Found: C, 49.36; H, 4.42; N, 1.40.

S. [RhLCl(NO)][BF_4]·1.5C_6H_6. This compound was prepared analogously to the above $PF_6{}^-$ salt using $NO^+BF_4{}^-$, yield 0.21 g, 75%; infrared ν(NO) 1699 (Nujol); $\Lambda_M = 77$. *Anal.* Calcd for $C_{45}H_{46}BClF_4NOP_3Rh$: C, 56.83; H, 4.96; Cl, 3.79; N, 1.50. Found: C, 57.48; H, 4.86; Cl, 3.88; N, 1.48.

T. [RhLCl(CH_3CO)][PF_6]. A solution of 0.35 g of RhLCl and 0.3 g of $NaPF_6$ in 30 ml of 2:1 ethanol–CH_2Cl_2 was treated with a solution of 0.3 ml of 50% aqueous HBF_4 in 3 ml of acetic anhydride. The volume of the solution was reduced to 15 ml by distillation and pale yellow needles separated from the solution. The hot solution was filtered, and the crystals were washed with 3 ml each of ethanol and diethyl ether, and dried; yield 0.40 g, 89%;

Table VI. Positional and Thermal Parameters for Rh{$C_6H_5P(CH_2CH_2CH_2P(C_6H_5)_2)_2$}Cl and [Rh{$C_6H_5P(CH_2CH_2CH_2P(C_6H_5)_2)_2$}Cl(NO)][$PF_6$]

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				RhLCl					
Rh	0.08109 (4)[b]	0.25000	0.10224 (4)	0.00801 (5)	0.00134 (1)	0.00640 (6)	0.0	0.00215 (4)	0.0
P(1)	0.06225 (10)	0.35768 (4)	0.10292 (10)	0.00950 (11)	0.00134 (2)	0.00934 (13)	−0.00009 (4)	0.00204 (10)	−0.00008 (4)
P(2)	0.04779 (15)	0.25000	−0.15339 (14)	0.01042 (17)	0.00164 (3)	0.00703 (17)	0.0	0.00280 (14)	0.0
Cl	0.11169 (16)	0.25000	0.38703 (14)	0.01545 (20)	0.00235 (3)	0.00680 (16)	0.0	0.00352 (15)	0.0
C(1)	0.1182 (5)	0.4041 (2)	−0.0468 (5)	0.0173 (7)	0.0017 (1)	0.0124 (6)	−0.0012 (2)	0.0039 (5)	0.0004 (2)
C(2)	0.0650 (5)	0.3801 (2)	−0.2157 (5)	0.0204 (7)	0.0020 (1)	0.0104 (6)	−0.0012 (2)	0.0046 (6)	0.0009 (2)
C(3)	0.1258 (5)	0.3154 (2)	−0.2405 (5)	0.0154 (6)	0.0025 (1)	0.0090 (6)	−0.0009 (2)	0.0052 (5)	0.0005 (2)
G(P11) C(1)	0.1653 (4)	0.4011 (2)	0.2771 (4)	0.0106 (5)	0.0015 (1)	0.0100 (5)	−0.0005 (2)	0.0022 (4)	−0.0004 (2)
C(2)	0.3054 (4)	0.3800 (2)	0.3572 (5)	0.0101 (5)	0.0024 (1)	0.0172 (8)	0.0001 (2)	0.0009 (5)	−0.0015 (2)
C(3)	0.3888 (5)	0.4128 (3)	0.4869 (6)	0.0124 (6)	0.0031 (1)	0.0208 (9)	−0.0004 (2)	−0.0030 (6)	−0.0018 (3)
C(4)	0.3322 (6)	0.4670 (2)	0.5372 (5)	0.0182 (7)	0.0026 (1)	0.0146 (7)	−0.0018 (2)	−0.0001 (6)	−0.0020 (2)
C(5)	0.1940 (6)	0.4883 (2)	0.4586 (5)	0.0199 (8)	0.0021 (1)	0.0142 (7)	−0.0001 (2)	0.0033 (6)	−0.0019 (2)
C(6)	0.1103 (5)	0.4556 (2)	0.3283 (5)	0.0147 (6)	0.0018 (1)	0.0117 (6)	0.0007 (2)	0.0014 (5)	−0.0005 (2)
G(P12) C(1)	−0.1294 (4)	0.3815 (2)	0.0865 (6)	0.0090 (5)	0.0015 (1)	0.0191 (8)	0.0002 (2)	0.0012 (5)	−0.0014 (2)
C(2)	−0.2116 (6)	0.4197 (3)	−0.0318 (6)	0.0179 (8)	0.0029 (1)	0.0196 (9)	0.0024 (3)	−0.0028 (7)	−0.0014 (3)
C(3)	−0.3572 (8)	0.4346 (4)	−0.0381 (10)	0.0170 (11)	0.0042 (2)	0.0403 (20)	0.0042 (4)	−0.0092 (11)	−0.0036 (5)
C(4)	−0.4199 (6)	0.4132 (4)	0.0735 (15)	0.0094 (7)	0.0038 (2)	0.0837 (39)	0.0014 (3)	0.0042 (13)	−0.0043 (7)
C(5)	−0.3391 (8)	0.3760 (3)	0.1998 (13)	0.0183 (10)	0.0033 (2)	0.0775 (31)	0.0012 (4)	0.0265 (15)	0.0005 (6)
C(6)	−0.1944 (6)	0.3594 (2)	0.2011 (8)	0.0136 (7)	0.0024 (1)	0.0412 (17)	0.0012 (2)	0.0121 (9)	0.0018 (4)
G(P2) C(1)	−0.1500 (6)	0.2500	−0.2612 (6)	0.0111 (7)	0.0018 (1)	0.0087 (8)	0.0	0.0012 (6)	0.0
C(2)	−0.1992 (8)	0.2500	−0.4231 (7)	0.0160 (10)	0.0040 (2)	0.0095 (9)	0.0	0.0005 (7)	0.0
C(3)	−0.3489 (9)	0.2500	−0.4980 (8)	0.0198 (12)	0.0044 (3)	0.0124 (10)	0.0	−0.0054 (9)	0.0
C(4)	−0.4532 (8)	0.2500	−0.4148 (9)	0.0141 (10)	0.0032 (2)	0.0196 (14)	0.0	−0.0036 (9)	0.0
C(5)	−0.4069 (7)	0.2500	−0.2537 (9)	0.0102 (8)	0.0034 (2)	0.0216 (14)	0.0	0.0016 (8)	0.0
C(6)	−0.2559 (7)	0.2500	−0.1776 (8)	0.0116 (8)	0.0024 (2)	0.0132 (10)	0.0	0.0008 (7)	0.0
				[RhLCl(NO)][PF_6]					
Rh	0.1143 (1)	0.2500	−0.4634 (1)	0.0012 (1)	0.0026 (1)	0.0051 (2)	0.0	0.0003 (1)	0.0
P(1)	0.1223 (1)	0.0943 (2)	−0.4651 (3)	0.0012 (1)	0.0027 (1)	0.0068 (3)	0.0000 (1)	0.0002 (1)	0.0001 (2)
P(2)	0.1155 (2)	0.2500	−0.2333 (4)	0.0014 (1)	0.0032 (2)	0.0056 (5)	0.0	0.0006 (2)	0.0
Cl	0.1480 (2)	0.2500	−0.6918 (4)	0.0023 (1)	0.0040 (2)	0.0057 (5)	0.0	0.0012 (2)	0.0
N	0.0363 (6)	0.2500	−0.4825 (15)	0.0016 (3)	0.0054 (9)	0.0087 (21)	0.0	0.0008 (7)	0.0
O	0.0040 (6)	0.2500	−0.4078 (16)	0.0016 (3)	0.0152 (15)	0.0150 (22)	0.0	0.0002 (7)	0.0
P(F)	0.4136 (2)	0.2500	0.3277 (5)	0.0025 (1)	0.0032 (3)	0.0207 (9)	0.0	0.0016 (3)	0.0
C(1)	0.0835 (4)	0.0409 (7)	−0.3327 (11)	0.0015 (2)	0.0031 (6)	0.0078 (14)	−0.0003 (3)	0.0003 (5)	0.0000 (8)
C(2)	0.0990 (4)	0.0665 (7)	−0.1890 (11)	0.0017 (2)	0.0033 (6)	0.0091 (16)	−0.0003 (3)	0.0008 (5)	0.0008 (8)
C(3)	0.0806 (5)	0.1587 (7)	−0.1492 (10)	0.0018 (2)	0.0041 (6)	0.0064 (15)	−0.0004 (3)	0.0010 (5)	0.0008 (8)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The numbers given here are estimated standard deviations in the least significant figures. Parameters fixed by symmetry considerations have no estimated standard deviation.

Table VII. Group and Derived Parameters for $[Rh\{C_6H_5P(CH_2CH_2CH_2P(C_6H_5)_2)_2\}Cl(NO)][PF_6]$

Group	x_c[a]	y_c	z_c	δ	ϵ	η
G(P11)[b]	0.0751 (2)	−0.0062 (3)	−0.7263 (5)	0.548 (4)	2.855 (4)	−2.173 (4)
G(P12)	0.2467 (2)	0.0275 (3)	−0.4324 (4)	−0.377 (5)	2.506 (5)	0.109 (6)
G(P2)	0.2385 (3)	0.2500	−0.1215 (8)	1.571	−1.907 (6)	1.571
G(FA)	0.4136	0.2500	0.3277	−1.571	1.900 (8)	1.571
G(FB)	0.4136	0.2500	0.3277	−1.571	−1.905 (20)	1.571

Group atom	Derived group atoms				Derived phenyl group hydrogen atoms[c]			
	x	y	z	B, Å^2	Atom	x	y	z
G(P11) C(1)	0.0959 (3)	0.0392 (4)	−0.6149 (6)	2.9 (2)				
C(2)	0.1103 (3)	−0.0487 (4)	−0.6361 (6)	3.7 (2)	H(2)	0.1356	−0.0790	−0.5732
C(3)	0.0895 (3)	−0.0941 (3)	−0.7475 (7)	4.2 (3)	H(3)	0.0995	−0.1570	−0.7635
C(4)	0.0543 (3)	−0.0516 (4)	−0.8377 (6)	4.0 (3)	H(4)	0.0387	−0.0843	−0.9175
C(5)	0.0398 (3)	0.0363 (4)	−0.8165 (6)	4.1 (3)	H(5)	0.0140	0.0666	−0.8810
C(6)	0.0606 (3)	0.0817 (3)	−0.7051 (7)	3.3 (2)	H(6)	0.0501	0.1446	−0.6907
G(P12) C(1)	0.1923 (2)	0.0556 (5)	−0.4447 (7)	3.0 (2)				
C(2)	0.2048 (2)	−0.0180 (5)	−0.3661 (7)	3.9 (3)	H(2)	0.1751	−0.0502	−0.3182
C(3)	0.2592 (3)	−0.0461 (4)	−0.3537 (7)	5.1 (3)	H(3)	0.2685	−0.0977	−0.2958
C(4)	0.3011 (2)	−0.0006 (5)	−0.4200 (8)	4.7 (3)	H(4)	0.3404	−0.0195	−0.4094
C(5)	0.2886 (2)	0.0730 (5)	−0.4987 (7)	4.7 (3)	H(5)	0.3189	0.1062	−0.5456
C(6)	0.2343 (3)	0.1011 (4)	−0.5110 (7)	3.7 (3)	H(6)	0.2255	0.1537	−0.5680
G(P2) C(1)	0.1843 (3)	0.2500	−0.1680 (11)	3.0 (3)				
C(2)	0.2278 (4)	0.2500	−0.2599 (8)	3.3 (3)	H(2)	0.2204	0.2500	−0.3588
C(3)	0.2820 (3)	0.2500	−0.2135 (10)	4.9 (4)	H(3)	0.3133	0.2500	−0.2792
C(4)	0.2927 (3)	0.2500	−0.0750 (12)	4.9 (4)	H(4)	0.3318	0.2500	−0.0417
C(5)	0.2492 (5)	0.2500	0.0170 (8)	5.9 (5)	H(5)	0.2572	0.2500	0.1162
C(6)	0.1950 (4)	0.2500	−0.0295 (10)	4.4 (4)	H(6)	0.1643	0.2500	0.0366
G(FA) F(1)	0.4750 (2)	0.2500	0.3792 (13)	11.9 (8)				
F(2)	0.3522 (2)	0.2500	0.2763 (13)	8.6 (6)				
F(3)	0.3927 (5)	0.2500	0.4786 (4)	9.4 (6)				
F(4)	0.4346 (5)	0.2500	0.1769 (4)	14.9 (10)				
F(5)	0.4136 (6)	0.1460	0.3278 (15)	7.6 (4)				
G(FB) F(1)	0.3523 (4)	0.2500	0.3801 (30)	14 (2)				
F(2)	0.4749 (4)	0.2500	0.2755 (30)	5 (1)				
F(3)	0.3985 (9)	0.3235	0.2213 (7)	16 (2)				
F(4)	0.4287 (9)	0.3235	0.4342 (7)	17 (2)				

Derived Hydrogen Atom Positions[c] for $Rh\{C_6H_5P(CH_2CH_2CH_2P(C_6H_5)_2)_2\}Cl$

Atom	x	y	z	Atom	x	y	z
H(11)[d]	0.2314	0.4055	−0.0174	GP(12) H(2)	−0.1684	0.4354	−0.1166
H(12)	0.0819	0.4489	−0.0419	H(3)	−0.4197	0.4626	−0.1231
H(21)	0.0933	0.4117	−0.2884	H(4)	−0.5280	0.4243	0.0766
H(22)	−0.0476	0.3775	−0.2444	H(5)	−0.3849	0.3588	0.2829
H(31)	0.2377	0.3161	−0.1921	H(6)	−0.1335	0.3316	0.2895
H(32)	0.1077	0.3073	−0.3558				
G(P11) H(2)[e]	0.3479	0.3401	0.3222	G(P2) H(2)	−0.2223	0.2500	−0.0573
H(3)	0.4925	0.3967	0.5454	H(3)	−0.1212	0.2500	−0.4867
H(4)	0.3948	0.4907	0.6315	H(4)	−0.3817	0.2500	−0.6187
H(5)	0.1523	0.5281	0.4943	H(5)	−0.5625	0.2500	−0.4699
H(6)	0.0077	0.4715	0.2710	H(6)	−0.4828	0.2500	−0.1893

[a] x_c, y_c, and z_c are the fractional coordinates of the group center; δ, ϵ, η (in radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965); S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965). [b] G(P11) and G(P12) are the two phenyl rigid-body groups attached to P(1); G(P2) is the phenyl rigid-body group attached to P(2); G(FA) and G(FB) are rigid-body groups associated with the PF_6 disorder model. [c] Hydrogen atoms were assigned temperature factors equal to those of the carbon atom to which each hydrogen atom is attached. [d] Hydrogen atom H(1_) is attached to C(1), H(2_) to C(2), and H(3_) to C(3). [e] Hydrogen atom H(2) is attached to C(2), etc.

infrared ν(CO), 1704 vs (Nujol); $\Lambda_M = 79$. *Anal.* Calcd for $C_{38}H_{40}ClF_6OP_4Rh$: C, 51.31; H, 4.53; Cl, 3.99. Found: C, 51.43; H, 4.52; Cl, 4.14.

U. **$[RhLClH][BF_4]\cdot C_2H_5OH$.** A solution of RhLCl (0.35 g) in dichloromethane (15 ml) and ethanol (5 ml) was treated with 50% aqueous HBF_4 (1 ml), and then the dichloromethane was removed on a rotary evaporator. The pale yellow crystals were collected from the cold solution, washed with 2 ml each of ethanol and diethyl ether, and dried, yield 0.31 g; infrared ν(OH) 3400 m, br, ν(Rh–H) 2175 w (Nujol); $\Lambda_M = 83$. *Anal.* Calcd for $C_{38}H_{44}BClF_4OP_3Rh$: C, 54.64; H, 5.33; Cl, 4.25; F, 9.11; P, 11.14. Found: C, 50.88;[47] H, 5.38; Cl, 4.28; F, 9.23; P, 10.97.

V. **$[RhLClH][PF_6]\cdot C_2H_5OH$.** This complex was prepared in a manner similar to the above BF_4^- salt by using HPF_6, yield 0.34 g; infrared ν(OH) 3480 m, ν(Rh–H) 2162 w (Nujol); $\Lambda_M = 76$. *Anal.* Calcd for $C_{38}H_{44}ClF_6OP_4Rh$: C, 51.07; H, 4.97; Cl, 3.97; F, 12.77; P, 13.89. Found: C, 51.25; H, 5.08; Cl, 4.08; F, 11.09; P, 13.88.

W. **$RhLCl_3$.** For 5 min chlorine gas was bubbled through a solution of 0.35 g of RhLCl in 20 ml of dichloromethane. After adding 20 ml of ethanol the dichloromethane was distilled off and the volume of the solution reduced to 15 ml. The solution was cooled to 25°, and the resultant yellow-orange crystals were collected and washed with 2 ml each of ethanol and diethyl ether, yield 0.36 g, 94%; $\Lambda_M = 5$. *Anal.* Calcd for $C_{36}H_{37}Cl_3P_3Rh$: C, 55.99; H, 4.83; Cl, 13.79. Found: C, 55.84; H, 4.90; Cl, 13.58.

X. **$RhLI_3$.** A slurry of RhLCl (0.35 g), $LiI\cdot 3H_2O$ (0.5 g), and iodine (0.15 g) in ethanol (15 ml) and dichloromethane (15 ml) was stirred for 12 hr; the resultant red-orange crystals were collected, washed with 2 ml each of ethanol and diethyl ether, and dried, yield 0.48 g, 92%; $\Lambda_M = 55.7$. *Anal.* Calcd for $C_{36}H_{37}I_3P_3Rh$: C, 41.30; H, 3.57; I, 36.40. Found: C, 41.36; H, 3.62; I, 36.14.

Y. $RhLBr_3$. A solution of RhLCl (0.35 g), lithium bromide (0.2 g), and bromine (0.1 ml) in 30 ml of 1:1 ethanol–dichloromethane was stirred at ~40° for 20 min. The solution was evaporated under a nitrogen stream to 15 ml and cooled to give fibrous pale orange crystals; they were collected and washed with 2 ml each of ethanol and diethyl ether, yield 0.38 g, 84%; $\Lambda_M = 8.9$. *Anal.* Calcd for $C_{36}H_{37}Br_3P_3Rh$: C, 47.74; H, 4.12; Br, 26.49. Found: C, 47.61; H, 4.07; Br, 26.65.

Z. $RhLCl_2H$. Hydrogen chloride gas was bubbled for 3 min through a solution of RhLCl (0.35 g) in dichloromethane (15 ml). Ethanol (15 ml) was added and the dichloromethane was distilled off. The pale yellow crystals were collected and washed with 2 ml each of ethanol and ether, yield 0.33 g, 90%; infrared ν(Rh–H) 2193 (Nujol); $\Lambda_M = 6$. *Anal.* Calcd for $C_{36}H_{38}Cl_2P_3Rh$: C, 58.61; H, 5.20; Cl, 9.62. Found: C, 58.67; H, 5.21; Cl, 9.50.

AA. Reactions of RhLCl with H_2. A dichloromethane solution (50 ml) of RhLCl (1.0 g) was stirred for 24 hr under a hydrogen atmosphere at 750 Torr; the resultant pale yellow microcrystals were filtered and washed with 1 ml each of ethanol and diethyl ether, yield 0.52 g; infrared 2195 w (Nujol). *Anal.* Calcd for $RhLClH_2$, $C_{36}H_{39}ClP_3Rh$: C, 61.47; H, 5.59; Cl, 5.05. Found: C, 58.61; H, 5.30; Cl, 9.93. Calcd for RhLCl·HCl, $C_{36}H_{38}Cl_2P_3Rh$: C, 58.61; H, 5.20; Cl, 9.62.

A slurry of 0.35 g of RhLCl in 25 ml of benzene was stirred under 100 psi of hydrogen in a Parr bomb for 2 hr. The resultant pale yellow powder was collected and washed with 2 ml each of benzene and diethyl ether, yield 0.25 g; infrared 2162 m, 1858 s (Nujol). *Anal.* Found: C, 61.31; H, 5.50; Cl, 5.00.

A solution of RhLCl (0.70 g) in dichloromethane (25 ml) was stirred for 3 hr under 100 psi of hydrogen in a Parr bomb. The solvent was removed on an aspirator and the yellow solid was dried *in vacuo*; infrared 2195 w, 1965 br w, 1834 w (Nujol).

BB. $RhL(CH_3)ClI$. A solution of freshly distilled (from molecular sieves) methyl iodide (5 ml) and RhLCl (0.35 g) was stirred 5 min and the solvent removed *in vacuo*. The pale yellow solid had dark red impurities on the surface. This red material was removed by stirring the solid in 5 ml of cold benzene, filtering, washing with 2 ml of cold benzene and 2 ml of diethyl ether, and drying, yield 0.29 g. *Anal.* Calcd for $C_{37}H_{40}ClIP_3Rh$: C, 52.69; H, 4.78; Cl, 4.21; I, 15.06. Found: C, 52.88, 53.00; H, 4.65, 4.77; Cl, 4.41; I, 10.59, 10.66.

Collection and Reduction of X-Ray Intensity Data. Preliminary photographic methods (Weissenberg and precession) on both compounds led to approximate cell constants and to probable space groups. Data collection procedures closely paralleled those described previously from this laboratory[48,49] and were carried out on a Picker FACS-1 computer-controlled diffractometer. Details of the crystal data and data collection are given in Table IV.

Solution and Refinement of the Structures. The crystal structure of the parent complex RhLCl was determined by Patterson methods[50] and was refined by successive Fourier and least-squares calculations on the assumption that the correct space group is $P2_1/m$ and that the molecule has imposed m symmetry. The crystal structure of [RhLCl(NO)][PF_6] was solved through direct methods, using the 296 highest E values. It was refined in a similar manner on the assumption that the space group is *Pnma* and that the ions have imposed m symmetry. In these calculations atomic scattering factors for the neutral nonhydrogen atoms were taken from the usual tabulation[51] while scattering factors for H were those of Stewart, *et al.*[52] Anomalous dispersion effects were included in the calculation of F_c using the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer.[53] The course of the refinements is given in Table V. There R is defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_w as $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and only those reflections having $F_o^2 > 3\sigma(F_o^2)$ were used. When the phenyl rings were treated as rigid groups the C–C distance was taken to be 1.397 Å. The rigid body constraint on the phenyl groups of the parent compound was discontinued after a difference Fourier synthesis showed that the individual isotropic rigid body model did not account satisfactorily for the large anisotropic thermal motion of one of the phenyl groups. When fixed contributions of the H atoms were added, it was assumed that the C–H distance was 1.0 Å, that the H–C–H angle in the methylene groups was 109.5°, while the H atom was assigned the isotropic B value of the C atom to which it was attached. In the nitrosyl complex the F_6 portion of the PF_6 group was assumed to be a rigid, octahedral group with a P–F distance of 1.58 Å. Ultimately difference maps indicated disorder in the F_6 portion, and refinement was continued with two partial F_6 groups, with each center tied to the P (of the PF_6) position.

Table VIII. Root-Mean-Square Amplitudes of Vibration (Å) along the Principal Axes

RhLCl	Min	Intermed	Max
Rh	0.1519 (7)	0.1745 (6)	0.1808 (6)
P(1)	0.174 (1)	0.185 (1)	0.200 (1)
P(2)	0.158 (2)	0.193 (2)	0.206 (2)
Cl	0.154 (2)	0.231 (2)	0.252 (2)
C(1)	0.179 (6)	0.217 (6)	0.275 (5)
C(2)	0.169 (6)	0.224 (6)	0.296 (6)
C(3)	0.161 (6)	0.231 (5)	0.262 (5)
G(P11)C(1)	0.177 (5)	0.198 (5)	0.215 (5)
C(2)	0.196 (5)	0.219 (6)	0.281 (6)
C(3)	0.188 (6)	0.263 (6)	0.332 (6)
C(4)	0.175 (6)	0.273 (6)	0.303 (6)
C(5)	0.178 (6)	0.259 (6)	0.291 (6)
C(6)	0.193 (5)	0.208 (5)	0.263 (5)
G(P12)C(1)	0.172 (6)	0.190 (5)	0.285 (5)
C(2)	0.211 (6)	0.237 (6)	0.359 (7)
C(3)	0.192 (8)	0.288 (8)	0.482 (11)
C(4)	0.183 (8)	0.289 (9)	0.578 (13)
C(5)	0.195 (8)	0.279 (8)	0.538 (11)
C(6)	0.201 (6)	0.237 (6)	0.394 (8)
G(P2)C(1)	0.176 (8)	0.204 (7)	0.222 (7)
C(2)	0.183 (9)	0.271 (8)	0.301 (9)
C(3)	0.172 (9)	0.317 (10)	0.344 (10)
C(4)	0.198 (8)	0.272 (9)	0.329 (10)
C(5)	0.203 (8)	0.279 (9)	0.293 (9)
C(6)	0.201 (8)	0.235 (8)	0.247 (8)
[RhLCl-(NO)][PF_6]	**Min**	**Intermed**	**Max**
Rh	0.155 (3)	0.175 (2)	0.193 (2)
P(1)	0.176 (5)	0.182 (5)	0.194 (5)
P(2)	0.158 (8)	0.195 (6)	0.211 (6)
Cl	0.153 (8)	0.215 (6)	0.270 (5)
N	0.190 (26)	0.238 (22)	0.251 (20)
O	0.221 (21)	0.274 (20)	0.422 (21)
P(F)	0.195 (8)	0.254 (7)	0.336 (7)
C(1)	0.18 (2)	0.20 (2)	0.22 (2)
C(2)	0.17 (2)	0.22 (2)	0.24 (2)
C(3)	0.15 (2)	0.22 (2)	0.25 (2)

In both refinements the appropriate centrosymmetric space group was assumed. Evidence that this assumption is justified in both cases includes the general excellence of the agreement between $(|F_o| - |F_c|)^2$ as a function of F_o, scattering angle, and Miller indices which shows no unusual trends. The error in an observation of unit weight is 2.01 for the parent complex and 2.13 e for the nitrosyl. The corresponding values of the extinction coefficients are 1.6 (9) × 10^{-5} and 4.9 (6) × 10^{-8} e^{-2}. The maximum heights on the final difference Fourier maps are 1.1 (5) and 1.0 (1) e/Å^3, respectively. In each case these are less than one-fourth

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(49) R. M. Kirchner and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 1095 (1973).

(50) In addition to various local programs, those used in this work include modifications of Johnson's ORTEP thermal ellipsoid program and Zalkin's FORDAP Fourier program. Our local least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.

(51) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in press, Table 2.2A.

(52) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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of the height of a typical C atom in previous difference maps. For the parent complex of the 313 reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$, only one had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. Using the same criterion for the nitrosyl complex, two of the 405 reflections omitted from the refinement had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. The final percentage of F_6 group F-A was 70 (2)%, and hence that of F_6 group F-B was 30 (2)%.

Table VI lists the positional and thermal parameters for the nonhydrogen atoms that were refined anisotropically, along with the standard deviations as estimated from the inverse matrix. Table VII lists the group parameters for the nitrosyl complex along with the positional parameters that may be derived therefrom. The calculated positions of the H atoms are also given in Table VII. Table VIII lists the root-mean-square amplitudes of vibration of those atoms refined anisotropically. The final values of $10|F_o|$ and $10|F_c|$ in electrons for the parent and the nitrosyl complexes have been deposited.[54]

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(54) Tables of the structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-73-4194. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Studies in Stereochemistry. XLIII. Racemizations and Solvolyses of Cyclopropanes through Carbanion–Carbonium Ion Intermediates[1,2]

Ernest W. Yankee, Florin D. Badea,[3] Norman E. Howe, and Donald J. Cram*

Contribution Number 3045 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California 90024.

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Abstract: Optically pure (+)- and (−)-methyl 1-cyano-2,2-diphenylcyclopropanecarboxylate ((+)- and (−)-**1**) were prepared. Racemizations (first-order rate constant, k_r) and solvolyses (first-order rate constant, k_s) of (+)- and (−)-**1** were studied. In benzene and dry dimethylformamide only racemization was observed. In methanol at 100°, $k_r/k_s > 10^2$. At 150° in methanol (±)-**1** gave 46% methyl 2-cyano-4,4-diphenyl-4-methoxybutanoate and 36% 1,1-diphenylpropene-3-carbonitrile. In acetic acid at 100°, $k_r/k_s \sim 0.5$, and olefin was the main solvolysis product. In acetic acid–0.1 *M* *p*-toluenesulfonic acid, $k_r/k_s \sim 4$ at 100°. At 50° in formic acid, $k_r/k_s \sim 15$. In dimethylformamide, racemization was catalyzed by, and was first order in, free bromide ion from 0.0132 to 0.0380 *M* LiBr. In acetic acid, the racemization–solvolysis reactions were *p*-toluenesulfonic acid catalyzed and followed H_0. Values of $(k_r + k_s)^{rel}$ at 126° were: benzene, 1; dimethylformamide, 5; methanol, 20; acetic acid, 25; dimethylformamide–0.1 *M* LiBr, 74; acetic acid–0.17 *M* *p*-toluenesulfonic acid, ~250; formic acid, 2×10^4. Activation enthalpies ($\Delta H^{\ddagger}$, kcal/mol) were 30.4 in benzene, 27.7 in dimethylformamide, 25.5 in methanol, 25.9 in acetic acid, and 22.9 in dimethylformamide–0.1 *M* LiBr. An isokinetic plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ ($\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta\Delta S^{\ddagger}$) was linear, $\Delta H_0^{\ddagger} \sim 36$ kcal/mol and $\beta = 762°$. For solvolyses of secondary benzyl systems, $\beta = 760°$. In formic acid at 126°, $\Delta H^{\ddagger} = 22.9$ kcal/mol. The point for formic acid was far from falling on the isokinetic plot. The medium effects and changes in distribution of activation energies between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ suggest the racemization reaction occurs through carbanion–carbonium ion reorganization (rotation about methylene-to-cyanoacetate bond), and collapse. Bromide ion catalysis is interpreted as involving interception of ion pairs equilibrating with starting material. The carbanion produced reorganizes and collapses to liberate bromide ion. In formic acid or acetic acid–*p*-toluenesulfonic acid, racemization is interpreted as involving protonation of ion pairs equilibrating with starting material. The carbonium ion produced reorganizes and collapses to liberate a proton. The products of solvolysis are interpreted as arising from the ion pairs by either capture by solvent, or by proton transfers from and to solvent.

Appropriately substituted ethylenimines and oxides undergo thermal cleavage to give zwitterions.[4] Although solvolysis-like products have been reported for photolysis of cyclopropane compounds,[5] the usual thermal cleavage assumes a homolytic course.[6] With one carbon of a cyclopropane ring substituted with negative- and another with positive-charge distributing substituents (*e.g.*, as in methyl 2,2-dimethyl-1-benzenesulfonylcyclopropanecarboxylate), products of racemization, solvolysis, and ring expansion were ob-

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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