# Solution Structure and Dynamics of Five-Coordinate $d^6$ Complexes

**P. R. Hoffman and K. G. Caulton***

*Contribution No. 2648 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401.* *Received January 20, 1975*

**Abstract:** $MX_2(PPh_3)_3$ (M = Ru, Os; X = Cl, Br) all exhibit square pyramidal ($C_{2v}$) geometry in solution but undergo an intramolecular rearrangement which equilibrates the two phosphorus environments. The rearrangement barrier is higher for Os than Ru, a fact which correlates with the bond length changes which accompany the rearrangement. The barrier for the bromo complex is larger than that of the chloro analog. $RuCl_2(PPh_3)_4$ completely dissociates one phosphine in solution. $RuCl_2(PPh_3)_3$ also dissociates triphenylphosphine to some extent, forming $[RuCl_2(PPh_3)_2]_2$. $OsX_2(PPh_3)_3$ does not exhibit detectable phosphine dissociation. $RuHCl(PPh_3)_3$ also undergoes intramolecular rearrangement, but shows no dissociated phosphine. $RuH(O_2CCH_3)(PPh_3)_3$ shows neither rearrangement nor phosphine dissociation. $RuCl_2(PPh_3)_3$ exchanges with free $PPh_3$ by a dissociative mechanism. $^{31}P$ NMR parameters are reported for all complexes.

Wilkinson and coworkers have synthesized a variety of catalytically active triphenylphosphine (L) complexes of ruthenium(II). $RuHClL_3$[1] and $RuH(O_2CR)L_3$[2] catalyze hydrogenation and olefin isomerization. The former compound also catalyzes hydrosilylation[3] and exchange of the metal-bound and olefinic protons.[4] While early reports showed hydrogenation catalysis when $RuCl_2L_3$ is the charged catalyst, the induction period observed suggests preliminary conversion to $RuHClL_3$; $RuCl_2L_3$ is also observed to catalyze the hydrogenation of oxygen to water.[5] $RuCl_2L_3$ promotes exchange of $D_2$ with OH and NH bonds.[6] Olefin isomerization,[7,8] oxidation of $PPh_3$,[9] and alcoholysis of diarylsilanes[3] are also catalyzed by $RuCl_2L_3$. At elevated temperatures in neat substrate, $RuCl_2L_3$ catalyzes dehydration of tertiary alcohols to the corresponding ether, racemization of RR′HCOH, and H/D interchange of RR′CHOD.[10,11]

Characterization of the equilibria in solution is a prerequisite to any understanding of the mechanism of catalysis. We describe here such a study which includes detailed examination of the energetics and mechanism of the rearrangement of square pyramidal complexes of Ru(II) and Os(II). A portion of this work has appeared as a preliminary communication.[12]

## Experimental Section

Instrumentation and sample handling have been described earlier.[13] Downfield chemical shifts are recorded as *positive*. While this is contrary to most previous papers on $^{31}P$ NMR, it conforms to the recommended convention.[14] Concentrations were calculated from weights of solid complexes and volumes (or weights) of pure solvents. The resulting concentration units are quoted as molarities, neglecting any small volume increase due to the solute. Line widths were read directly from the digitized spectra; the $\nu_{1/2}{}^L$ values in Table III represent only the exchange contribution to the full width at half-height. Error limits represent maximum possible deviations from stated values and were determined as previously described.[13] $RuCl_2L_3$,[15] $RuCl_2L_4$,[15] $RuHClL_3$,[1] $RuH(O_2CMe)L_3$,[2] $RuH_2L_4$,[16] and $RuCl_2[P(OPh)_3]_4$[17] were prepared according to the literature.

At 30° $RuCl_2L_3$ is stable in sealed evacuated tubes in $CHCl_3$ or $CH_2Cl_2$ for months, showing only a tendency to deposit dark crystals (see text). Oxygen reacts instantly with $RuCl_2L_3$ to produce triphenylphosphine oxide, and the absence of a $^{31}P$ NMR peak at +27.7 ppm ($CH_2Cl_2$) due to this product is a useful criterion of purity; phosphine oxide is also produced in some of the syntheses used here, thus providing an alternative source for this resonance. $RuHClL_3$ shows no evidence for reaction with $CH_2Cl_2$ over a period of 12-24 hr at 30°. We find no evidence by $^{31}P$ or $^1H$ NMR, for a second "isomer" of $RuHClL_3$ as described in ref 1.

**$OsCl_2(PPh_3)_3$.** $(NH_4)_2OsCl_6$ (0.10 g) and $PPh_3$ (0.42 g) were refluxed under nitrogen for 115 hr in a solvent mixture composed of 25 ml of *tert*-butyl alcohol and 10 ml of water. After cooling to room temperature, the pale green solid was filtered, washed with three 5-ml portions of $H_2O$, three 5-ml portions of methanol, and three 5-ml portions of hexane. The solid was dried under vacuum. Anal. Calcd for $C_{54}H_{45}Cl_2OsP_3$: C, 61.89; H, 4.30; Cl, 6.78. Found: C, 61.15; H, 4.54; Cl, 6.59. This sample was shown by $^{31}P$ NMR to contain about 10 mol % $PPh_3$. This can be removed by prolonged stirring under hexane at room temperature.

**$RuH_2(PPh_3)_4$ + HBr.** To 0.5 g of $RuH_2L_4$ and 0.34 g of L in a mixture of 40 ml of methanol and 4 ml of THF was added 2 ml of 48% aqueous HBr. After stirring with slight warming for 2 hr under nitrogen, the mixture was cooled and filtered and the solid vacuum dried. Analysis of the purple-brown crystals (C, 62.89; H, 4.53; Br, 13.45) shows them to be a mixture; an infrared absorption at 1913 $cm^{-1}$ is tentatively assigned to $\nu_{RuH}$.

**$[RuCl_2(PPh_3)_2]_n$.** $RuCl_2(PPh_3)_3$ (0.168 g, 0.175 mmol) was slurried in 20 ml of refluxing ethanol under nitrogen for 2 hr. The dark solid was allowed to settle for 15 hr, filtered, and vacuum dried (0.102 g, 84% yield assuming $RuCl_2(PPh_3)_2$). The infrared spectrum of this solid, which appears green when finally divided, is almost identical with that of $RuCl_2(PPh_3)_3$. Anal. Calcd for $C_{36}H_{30}Cl_2RuP_2$: C, 62.07; H, 4.30; Cl, 10.20. Found: C, 62.60; H, 4.51; Cl, 10.08. The filtrate, a rosé color, was taken to dryness, yielding mainly a white solid (0.054 g).

Repetition of the procedure for $RuCl_2(PPh_3)_2$·acetone[18] produced a solid with no ketonic C=O stretching frequency. Anal. Found: C, 63.00; H, 4.58, Cl, 9.39.

Decoupling of the hydride ligand in $RuHCl(PPh_3)_3$ at low temperatures occurs very readily, even to the extent that initial attempts to selectively decouple only phenyl protons were unsuccessful. Reducing decoupling power to a nominal 2.5 W at a "single frequency" (band width less than 5 Hz) centered at $\tau$ 3.0 revealed hydride-phosphorus coupling, but with an anomalously low apparent P-H coupling constant (a value of 25 Hz is observed by $^1H$ NMR). On further reduction in decoupling power (to a limiting value of 0.5 W), the average of the apparent $J_{P-H}$ values increases smoothly toward that observed by $^1H$ NMR.

None of the spectra recorded here shows evidence for broadening by (or coupling to) the quadrupolar nuclei $^{99}Ru$ (13%), $^{101}Ru$ (17%), and $^{189}Os$ (16%).

We find numerous instances of temperature dependent $^{31}P$ chemical shifts. Some of these are evident in Table IV. Of possibly more general interest, we find the chemical shift of triphenylphosphine to be more strongly temperature dependent. In $CH_2Cl_2$, the shift changes from −5.5 ppm at +30° to −8.2 ppm at −79°.

## Results and Discussion

**Solid State Structures.** The structure of $RuCl_2(PPh_3)_3$ was determined[19] sufficiently long ago that it is appropriate to reassess its geometry in the light of recent work on five-

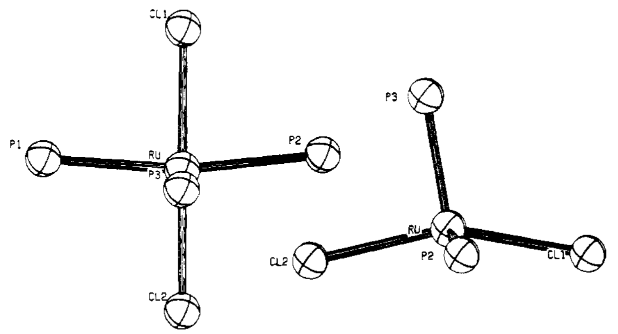
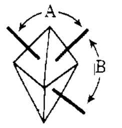
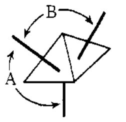
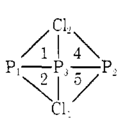


**Figure 1.** Two views of the first coordination sphere of $RuCl_2(PPh_3)_3$. At left, a view from above and perpendicular to the $P_1P_2Cl_1Cl_2$ plane. At right, a view down the $P_2P_1$ line perpendicular to the $Cl_1Cl_2$ line ($P_1$ is hidden behind $P_2$).

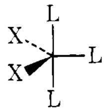
**Table I.** Interplanar Angles for Idealized Five-Coordinate Polyhedra and for $RuCl_2(PPh_3)_3$

| | | | | |
|---|---|---|---|---|
|  | I. Trigonal Bipyramid | | | |
| | $r_a/r_e$[a] | 0.9 | 1.0 | 1.1 |
| | A (deg) | 98.4 | 101.5 | 104.1 |
| | B (deg) | 58.1 | 53.1 | 48.9 |
|  | II. Square Pyramid | | | |
| | $r_a/r_e$[a] | 0.9 | 0 934[b] | 1.0 |
| | A (deg) | 122.0 | 121.2 | 119.8 |
| | B (deg) | 73.7 | 74.4 | 75.7 |
| | III. $RuCl_2(PPh_3)_3$ | | | |
|  | Plane[c] | A (deg) | Plane | B (deg) |
| | 13 | 116.4 | 12 | 74.9 |
| | 46 | 116.5 | 45 | 75.0 |
| | 23 | 125.8 | 14 | 64.7 |
| | 56 | 126.5 | 25 | 81.7 |

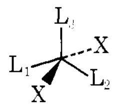
[a] Ratio of apical to equatorial metal–ligand bond lengths. For the square pyramid, an apical-to-basal bond angle of 102° is assumed. [b] This value is taken from the observed structure of $RuCl_2(PPh_3)_3$. [c] Planes not defined on the diagram are as follows: plane 3 is defined by atoms $P_1$, $Cl_1$, and $Cl_2$ while plane 6 is defined by $P_2$, $Cl_1$, and $Cl_2$.

coordinate complexes. The rush of structural studies which resulted from Ibers' review[20] of five-coordinate complexes in 1965 established the numerical superiority of the trigonal bipyramid, particularly for complexes with five monodentate ligands.[21] While authors invariably comment on the near energetic equality of the trigonal bipyramid (TBP) and the square pyramid (SP), the former geometry is usually given preferred status as *the* ground state structure. This generalization is specific to the $d^8$ electronic configuration, which has been shown to favor TBP geometry for electronic reasons.[22] On the other hand, an examination of the literature shows that $d^6$ complexes, *when they can be induced to be five-coordinate,* are best classified as square pyramidal. This is in agreement with second-order Jahn–Teller arguments.[22] For configuration $d^6$, coordination number six predominates, presumably because of the high crystal field stabilization energy associated with a low-spin octahedron. Low-spin octahedral $d^6$ complexes are kinetically inert via SN1 processes for this same reason, and all of the following discussion is relevant to the structure of the intermediate in such SN1 processes.[23] However, five-coordinate complexes are known: $RuCl_2(PPh_3)_3$,[19] $RuHCl(PPh_3)_3$,[24] $RhI_2Me(PPh_3)_2$,[25] $RhHCl_2[P(C_3H_7)_2\text{-}t\text{-}Bu]_2$,[26] $RhHCl(SiCl_3)(PPh_3)_2$.[27] All of these are satisfactorily described as square pyramidal. $M(COR)Cl_2(PPh_3)_2$ (M = Rh,[28,29] Ir[30]) species exhibit molecular weights characteristic of monomers. Finally, $Cr(CO)_5$ in "inert" matrices has a ground state geometry with $C_{4v}$ symmetry.[31]

For complexes of stoichiometry $MX_2L_3$, distinguishing between TBP (I) and SP (II) is difficult because the two



I



II

isomers both possess $C_{2v}$ symmetry. Spectroscopic methods are therefore useless, and a careful analysis of accurate structural parameters is required. Figure 1 shows two views of the coordination sphere of $RuCl_2(PPh_3)_3$ chosen so as to exhibit adherence to and deviations from the two idealized five-coordinate polyhedra. Recently an objective criterion of stereochemistry was proposed based on interplanar angles of the actual coordination polyhedron.[32] Table I displays the values of these parameters for both idealized polyhedra, as well as the values found in solid $RuCl_2(PPh_3)_3$. Two points emerge from these data, as well as from Figure 1. First, $RuCl_2(PPh_3)_3$ is best described as a square pyramid. Some authors have failed to appreciate this fact.[21,33] Second, a distortion is present which favors neither TBP nor SP geometry. The ruthenium atom lies 0.12 Å out of the $P_1P_2P_3$ plane, while it lies in the $Cl_1Cl_2P_3$ plane to within experimental error. We see no ready intramolecular explanation for this result; *o*-phenyl hydrogen interactions (see below) are not at fault.

The most striking aspect of the $RuCl_2(PPh_3)_3$ structure is the pattern of Ru-P bond lengths. While bonds Ru-$P_1$ and Ru-$P_2$ differ by only 3$\sigma$, Ru-$P_3$ is shorter by 0.163 Å than the average of the other two. This pattern contrasts to that found for $d^8$ complexes of formula $MXY(PPh_3)_3$,[21] which are trigonal bipyramidal with three equatorial phosphines.

A final point relates to the origin of the square pyramidal geometry. LaPlaca and Ibers[19] note that the close approach of one *o*-phenyl hydrogen to the metal effectively blocks this potential coordination site and causes the complex to be five-coordinate. We concur that steric effects, possibly those described by these authors, prevent Ru(II) from achieving its usual coordination *number* of six. However, it would be incorrect to attribute the square pyramidal coordination *geometry* to *o*-phenyl hydrogen interactions. Such an argument reverses the cause and effect: a square pyramidal geometry is favored by the $d^6$ configuration, and the resulting "open" side of the coordination polyhedron provides a natural site for packing a phenyl ring in the solid state. The proton NMR at 220 MHz ($CH_2Cl_2$, 20°) shows the usual pair of phenyl multiplets (ortho, and meta plus para) with intensities 2:3; there is no evidence for a long-lived interaction of any phenyl groups with the metal.

$RuHCl(PPh_3)_3$ also possesses inequivalent phosphine ligands.[24] The basic geometry is the same as that of $RuCl_2(PPh_3)_3$ with some distortion resulting from the small hydride ligand. One Ru-P bond is again significantly shorter than the other two. Here any argument for distortions away from $C_{3v}$ symmetry based on the assumption that three triphenylphosphine ligands are too large to fit in equivalent positions around ruthenium is untenable. $HRhCOL_3$, $HIrNOL_3^+$, $HRuNOL_3$, and $HCoN_2L_3$ all possess equivalent phosphines.[21] The origin of the observed distortion in $RuHCl(PPh_3)_3$ must therefore lie in the electronic requirements of the $d^6$ configuration.

In spite of the fact that $RuH(O_2CCH_3)(PPh_3)_3$ is six-coordinate (bidentate acetate) in the solid state,[34] the structure bears a close relationship to those of $RuCl_2L_3$ and $RuHClL_3$; the pattern of the three Ru-P bond lengths and the three PRuP angles are similar. The hydride is trans to one of the carboxylate oxygens. The Ru-O distances are both long and, as a result of the small (57.6°) angle ORuO, the acetate has been termed "pseudo-monodentate". Our NMR data show this description to be somewhat misleading. The structure of the formate analog also exhibits all the features of the acetate discussed here.[35]

**Solution.** Present knowledge of the solution behavior of $RuH(O_2CCH_3)L_3$ is due entirely to the work of Wilkinson et al.[2] There is no evidence for ionic dissociation in solution. "Reliable" molecular weights in the range 400-500 are said to imply phosphine dissociation (eq 1). However, the hydride resonance is a quartet ($J_{P-H}$ = 25 Hz) due to coupling to *three* equivalent phosphines. In summary, it is stated[2] that it is "... possible that the carboxylate group becomes unidentate ..." in solution and that the catalytic activity of the complex is "... most readily interpreted in terms of square Ru(II) with *trans*-$PPh_3$ groups and H *trans* to the carboxylate group".

$$RuH(O_2CR)(PPh_3)_3 \rightleftharpoons RuH(O_2CR)(PPh_3)_2 + PPh_3 \qquad (1)$$

$RuCl_2L_3$ has been little studied in solution due to a lack of suitable spectroscopic probes. Molecular weights in the range 409-433 are said to indicate considerable phosphine dissociation.[15] James and Markham recently described the results of an equilibrium study in benzene and *N,N*-dimethylacetamide using the electronic spectrum as a probe.[36] The derived thermodynamic parameters imply 80% dissociation of one phosphine in a $10^{-3}$ *M* benzene solution at 25°.

The proton NMR of $RuHClL_3$ consists of a sharp quartet down to −60 °. It has been stated that the complex exhibits "little dissociation" of phosphine ligand.[1] Dissociation to produce a "kinetically significant" amount of a trans square planar monomer is suggested, however.

**$RuCl_2L_{3,4}$.** The reactions of $PPh_3$ with commercial "ruthenium trichloride hydrate" are puzzling. Reaction in methanol with a 6:1 $PPh_3$:Ru ratio produces different products at reflux temperature ($RuCl_2(PPh_3)_3$) and room temperature ($RuCl_2(PPh_3)_4$). The reaction chemistry of both tris and tetrakis complexes appears to be the same, but the structure of the latter is unknown. Both are dark solids which form solutions with similar colors.

The $^{31}P$ NMR spectrum of $RuCl_2L_4$ at 30° in $CHCl_3$ shows (Figure 1 of ref 12) peaks at the chemical shift of $RuCl_2(PPh_3)_3$ (see below) and $PPh_3$ with relative intensities 3:1. Both resonances are broadened, although the origin of the broadening is different for the two compounds. This indicates "complete" dissociation of one phosphine from $RuCl_2(PPh_3)_4$, and brings up the question of the exact nature of "$RuCl_2(PPh_3)_4$" in the solid state. There are no confirmed examples of nonhydridic five- or six-coordinate complexes with four triphenylphosphine ligands; even $RhCl(PPh_3)_3$ shows puckering characteristic of crowding among the phosphines.[37] We therefore tentatively propose that $RuCl_2(PPh_3)_4$ does not have four-coordinated phosphines in the solid, but instead contains $RuCl_2(PPh_3)_3$ molecules and "lattice $PPh_3$". Comparable situations exist for $LiI{\cdot}5Ph_3PO$[38] and $Ni(C_6H_8N_2)_6Cl_2$.[39] In support of this idea, we note that *Dq* values for octahedral Ru(II) are large, shifting d-d transitions toward the ultraviolet. As a result, $RuCl_2(PR_3)_4$ (R = alkyl),[40] $Ru_2X_3(PR_3)_6{}^+$,[41] and $RuCl_2[P(OPh)_3]_4$[17] are all yellow or colorless. $RuCl_2(PPh_3)_4$, even in the solid state, is dark brown (the color of $RuCl_2L_3$); such low transition energies are more characteristic of the orbital energies found in coordination number five. A crystal structure determination should prove interesting.

A set of observed and calculated $^{31}P$ NMR spectra for $RuCl_2L_3$ is shown in Figure 2. The major pattern observed at low temperatures is characteristic of the solid state structure of $RuCl_2L_3$ (inequivalent phosphines). The inequivalent phosphorus sites interchange more rapidly at elevated temperatures, and a single (though still slightly broadened) line is observed at +30°. Line shape analysis yields rate constants which vary over 5 orders of magnitude. An Arrhenius plot appears in Figure 3. The activation parameters derived from a least-squares treatment of this plot and a plot of the Eyring equation appear in Table II. The values of log *A* and $\Delta S^{\ddagger}$ are consistent with this being an intramolecular process. This evidence for intramolecularity is particularly important in view of the presence of $[RuCl_2L_2]_2$ (see below) in solution. This excludes the plausible alternative bond breaking mechanism for site exchange (eq 2). Site

$$RuCl_2L_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RuCl_2L_2 + L \qquad (2)$$

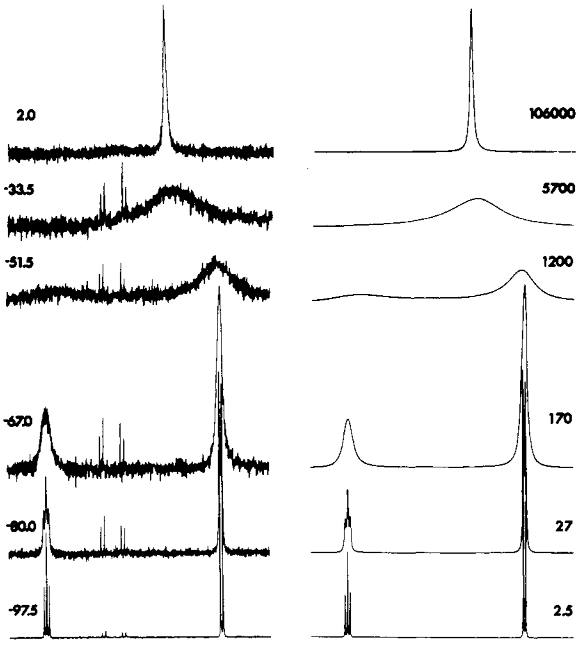


**Figure 2.** Observed (left) and calculated $^{31}P\text{-}\{H\}$ spectra of $RuCl_2(PPh_3)_3$ in $CH_2Cl_2$ (0.05 *M*). Spectra are labeled with degrees and rate constants, respectively. The AB pattern is due to $[RuCl_2(PPh_3)_2]_2$ (see text).

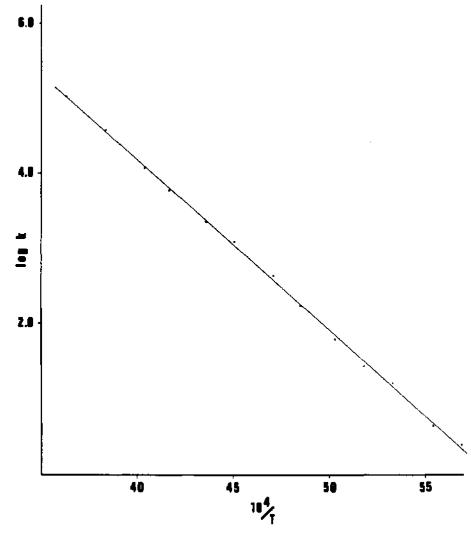


**Figure 3.** Arrhenius plot for intramolecular site exchange in $RuCl_2(PPh_3)_3$.

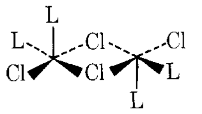
Table II. Activation Parameters for Phosphine Site Exchange

| | Log *A* | $E_a$ (kcal/ mol) | $\Delta H^{\ddagger}$ (kcal/ mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|---|
| $RuCl_2(PPh_3)_3$ | 13.3 (5) | 10.4 (4) | 10.0 (4) | 0.9 (21) |
| $RuHCl(PPh_3)_3$ | 15.2 (6) | 13.9 (6) | 13.4 (6) | 9.4 (26) |
| $OsCl_2(PPh_3)_3$ | 12.7 (5) | 11.5 (6) | 11.0 (6) | −2.3 (23) |
| $OsBr_2(PPh_3)_3$ | 13.3 (4) | 12.6 (5) | 12.0 (5) | 0.4 (20) |

exchange by a bimolecular process is also excluded by the observation that the line shape (at −50°) of $RuCl_2L_3$ with added equimolar $PPh_3$ is not altered from that shown in Figure 2.

$RuCl_2L_3$ dissociates phosphine ligand detectably in $CHCl_3$, $CH_2Cl_2$, and toluene. This is evident at all temperatures as a resonance due to free ligand as well as by resonances 50–60 ppm downfield from 85% $H_3PO_4$. In $CHCl_3$ at 30°, a solution 0.076 *M* in ruthenium contains 85% undissociated $RuCl_2L_3$. The same is true for a 0.05 *M* solution in $CH_2Cl_2$. In toluene at 30°, however, a solution 0.01 *M* in ruthenium is only 41% undissociated $RuCl_2L_3$. In order to more closely simulate catalytic conditions, a $^{31}P$ NMR spectrum was recorded on a $7 \times 10^{-4}$ *M* solution of $RuCl_2L_3$ in $CH_2Cl_2$ at 30°. The spectrum exhibited only the peaks found in more concentrated solutions.

The sharp AB pattern observed at low temperatures (Figure 2) has an integrated intensity equal to twice that of the free ligand signal and is attributed to a species of formula $[RuCl_2L_2]_n$. Since a monomer based on tetrahedral or planar geometry would produce only a $^{31}P$ singlet, a monomer is excluded. Monomeric $RuCl_2L_2$ would be a 14-electron species. Although one can write monomeric *five-coordinate* structures by invoking coordinated solvent, halocarbons and particularly toluene have never been shown to occupy coordination sites. We therefore discount this explanation. The simplest explanation for the observed spectrum is a halide-bridged structure with two square pyramids sharing a basal edge (III).[42] The anion $Ni_2Cl_8^{4-}$ possesses such a structure.[43] Assuming no coupling across the halide bridges, an AB spin system results. An alternative structure based on a pair of trigonal bipyramids sharing an axial-equatorial edge is inconsistent with the ground state geometry favored by the d$^6$ configuration.



III

An attempt was made to prepare a pure sample of $[RuCl_2(PPh_3)_2]_2$ by refluxing $RuCl_2L_3$ in a solvent which dissolves L but not $RuCl_2L_3$. When $RuCl_2L_3$ is slurried in boiling ethanol, a dark solid of empirical formula $RuCl_2L_2$ is indeed produced. Attempts to synthesize Wilkinson's $RuCl_2L_2$·acetone produced a material of the same stoichiometry. Unfortunately, these solids are not soluble in any common solvents; the material may be polymeric.

With the demonstration that $RuCl_2L_3$ dissociates to a dimer, the thermodynamic data of James and Markham become suspect.[36] These authors *assumed* dissociation to a monomer (eq 2) and derived equilibrium constants and thermodynamic functions. While we do not deny the possible kinetic importance of "$RuCl_2L_2$", we find it to have no spectroscopically detectable population in solution. Our efforts to determine thermodynamic parameters for eq 3 have been frustrated by precipitation at low temperature. Even at 25°, sealed evacuated tubes of $RuCl_2L_3$ slowly form dark crystals over a period of weeks. Although material sufficient for elemental analysis has not been obtained, solids of composition $[RuCl_2L_2]_n$ obtained by alternative methods are also insoluble in $CHCl_3$ once formed.

$$2RuCl_2L_3 \rightleftarrows [RuCl_2L_2]_2 + 2L \qquad (3)$$

Site exchange also occurs for $[RuCl_2L_2]_2$. Thus, solutions of $RuCl_2L_3$ show only two broad humps in the region +50 to +60 ppm at 30° (see Figure 1 of ref 12). It is clear from Figure 2, however, that site exchange in the molecule $RuCl_2L_3$ is independent of site exchange in $[RuCl_2L_2]_2$, since coalescence of apical and basal sites of the former actually occurs around (or through) the AB pattern of the latter. This is particularly evident at −33.5°, where the AB pattern is still sharp.

We have briefly investigated exchange of free and coordinated phosphine at 30° in $CH_2Cl_2$ solutions containing the $RuCl_2L_3$–$[RuCl_2L_2]_2$ equilibrium system. Since the $RuCl_2L_3$ singlet is significantly broadened by intramolecular site exchange, it is not possible to detect intermolecular exchange broadening on this signal. Moreover, since addition of L decreases the concentration of $[RuCl_2L_2]_2$ according to eq 3, line width measurements on the dimer are also impossible. Our measurements have therefore been limited to the line width of free L. Table III summarizes the results. If exchange occurs by an associative mechanism (eq 4),

$$RuX_2L_3 + L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} RuX_2L_4 \qquad (4)$$

then $\tau_L^{-1}$, the inverse lifetime of the ligand, is given by $k_2[RuX_2L_3]$. If, on the other hand, a dissociative process is operative (eq 2), $\tau_L^{-1}$ is given by eq 5. The experiments in

$$\tau_L^{-1} = k_1([RuX_2L_3]/[L]) \qquad (5)$$

Table III were carried out with $[RuX_2L_3]$ in the range 0.04–0.05 *M* and [L] varied over a wide range. The dependence of $\tau_L^{-1}$ clearly rules out an associative mechanism[44] and the constancy of the derived values of $k_1$ in the last column of Table III supports a dissociative mechanism.[45] This is the only evidence we have for monomeric $RuCl_2L_2$, which may be a 14-electron species. The nature of this experiment makes determination of $k_{-1}$, and therefore the equilibrium constant for eq 2, impossible. It must be emphasized that we never directly observe $RuCl_2L_2$ spectroscopically, but its existence as a kinetically important species is implied by the concentration dependence of phosphine exchange. We do feel that our kinetic measurements actually refer to eq 2, while the thermodynamic measurements of James and Markham do not. Our work directly demonstrates eq 3. While this describes the overall stoichiometry, the mechanism must involve eq 2 followed by dimerization of the resultant monomer (eq 6) or reaction with $RuCl_2L_3$ (eq 7).

$$2RuCl_2L_2 \longrightarrow [RuCl_2L_2]_2 \qquad (6)$$

$$RuCl_2L_2 + RuCl_2L_3 \longrightarrow [RuCl_2L_2]_2 + L \qquad (7)$$

Equation 2 certainly has an extremely small equilibrium constant. Finally, consistent with these mechanistic conclusions, no trace of a $^{31}P$ resonance due to the molecule $RuCl_2L_4$ is observed even when $[L]/[RuCl_2L_3] = 6$.

**$RuCl_xBr_{2-x}L_3$.** The spectrum of a sample of "$RuBr_2L_3$" prepared according to the literature[15] is shown in Figure 4A. It is apparent that the literature synthesis produces a mixture of three species, $RuBr_2L_3$, $RuBrClL_2$, and $RuCl_2L_3$, in a mole ratio of 4.9:4.7:1. While the synthesis was performed with a Br/Cl ratio of 6:1, the corresponding ratio of coordinated halides in the product is only 2:1. The $^{31}P$ NMR spectrum of a $CH_2Cl_2$ solution 0.08 *M* in

Table III. Kinetic Data at 30°

| [L] | [L]/[RuCl$_2$L$_3$] | $\nu_{1/2}{}^{L}$ (Hz) | $\tau_L{}^{-1}$ (sec$^{-1}$) | $\tau_L{}^{-1}\cdot$[L]/[RuCl$_2$L$_3$] (sec$^{-1}$) |
|---|---|---|---|---|
| 0.0079[a] | 0.171 | 9.5 | 30 | 5.1 |
| 0.0077 | 0.188 | 7.6 | 24 | 4.5 |
| 0.0145 | 0.324 | 7.0 | 22 | 7.1 |
| 0.0351 | 0.615 | 4.6 | 14 | 8.8 |
| 0.0519 | 1.04 | 2.7 | 8.6 | 9.0 |
| 0.2942[b] | 5.94 | 0.31 | 1.0 | 5.7 |

[a] In 0.0463 *M* RuCl$_2$L$_2$; no added L. [b] In 0.0495 *M* RuCl$_2$L$_4$ + 0.2610 *M* L.

"RuBr$_2$L$_3$" and 0.58 *M* in tetrabutylammonium bromide is shown in Figure 4B. The upfield resonance is due to the dichloride. The extreme downfield peak increases most in intensity, so it is assigned as the dibromide. Substitution of chloride by bromide thus shifts the $^{31}$P resonance downfield.

If the equilibria among the three RuCl$_x$Br$_{2-x}$L$_3$ species were statistical, Figure 4B would exhibit a RuBr$_2$L$_3$:RuBrClL$_3$ ratio of 7:1. This spectrum, as well as the initial failure of the literature preparation to produce pure RuBr$_2$L$_3$, is indicative of enhanced stability of the chloride containing species relative to the bromide species. It has been shown that solvation plays a key role in determining relative stabilities of halide complexes of rhodium and iridium.[46] The trends observed here therefore may not indicate relative bond strengths.

The low temperature spectrum of an RuCl$_x$Br$_{2-x}$L$_3$ mixture shows at least three AB quartets due to [RuCl$_x$Br$_{2-x}$L$_2$]$_2$. This confirms that this species is indeed a dihalide and not a salt such as [RuXL$_2$]X.

As an alternative route to RuBr$_2$L$_3$, the reaction of RuH$_2$L$_4$ with excess HBr was investigated. The products consist mainly of the RuBr$_2$L$_3$-[RuBr$_2$L$_2$]$_2$ equilibrium system, with about 16% of the ruthenium as RuHBrL$_3$; the latter compound was identified by the similarity of its spectrum to that of the hydrido chloro compound (see below).

**OsCl$_2$L$_3$.** This is a new compound, although a brief report of the bromo analog exists.[47] Reduction of (NH$_4$)$_2$OsCl$_6$ and PPh$_3$ with N$_2$H$_4$ under reflux produces only yellow (octahedral) complexes with infrared spectra suggesting coordinated dinitrogen. Reduction with the phosphine alone succeeds if the solvent is chosen carefully. *tert*-Butyl alcohol is employed as solvent in order to avoid carbonyl abstraction from the solvent. The lack of solubility of (NH$_4$)$_2$OsCl$_6$ in this alcohol necessitates addition of water to the reaction mixture; without it, (NH$_4$)$_2$OsCl$_6$ is unchanged after 48 hr reflux in the pure alcohol. The reaction is slow, passing through several diamagnetic intermediates. The product shows no tendency to add dinitrogen at 1 atm.

OsCl$_2$L$_3$ shows no evidence for dissociation of triphenylphosphine in CH$_2$Cl$_2$ at 30°. Some samples (see Experimental Section) gave acceptable analyses for OsCl$_2$L$_3$ but showed observable amounts of PPh$_3$ in solution. Since the chloride analysis precludes the phosphine being present as such, it may be that OsCl$_2$L$_4$ is present in the solid. The $^{31}$P spectrum in CH$_2$Cl$_2$ at 30° is a singlet (4.3 Hz broad). Site exchange is slowed at reduced temperatures and an AX$_2$ pattern is evident by about −60°. There is no evidence for other osmium-phosphine complexes between −69 and +30°. Kinetic analysis as for RuCl$_2$L$_3$ yields the parameters shown in Table II. The results of a similar study of OsBr$_2$L$_3$ appear in Table II. Refluxing this compound in methanol for 3 hr brings about partial conversion to *mer*-OsHBr(CO)(PPh$_3$)$_3$,[48] identified by ir and $^{31}$P NMR. RuCl$_2$L$_3$ has been shown to decarbonylate many solvents.[49]

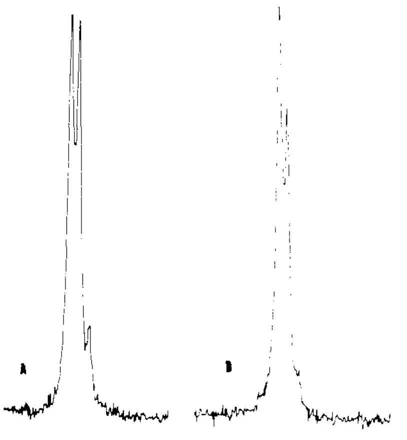


Figure 4. (A) "RuBr$_2$(PPh$_3$)$_3$" in CHCl$_3$ at 30°; (B) 0.08 *M* "RuBr$_2$(PPh$_3$)$_3$" and 0.58 *M* N(*n*-Bu)$_4$Br in CHCl$_3$ at 30°. Horizontal bar indicates 100 Hz.

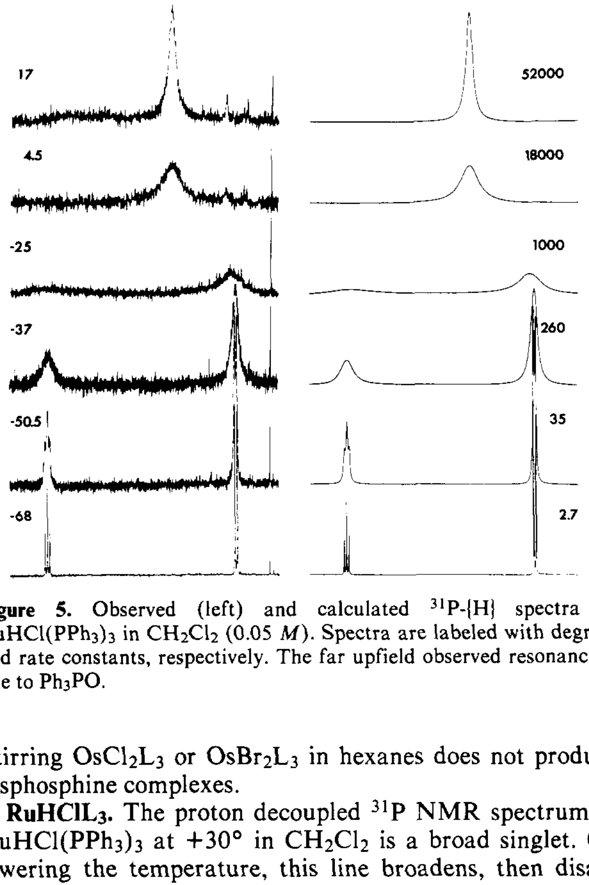


Figure 5. Observed (left) and calculated $^{31}$P-{H} spectra of RuHCl(PPh$_3$)$_3$ in CH$_2$Cl$_2$ (0.05 *M*). Spectra are labeled with degrees and rate constants, respectively. The far upfield observed resonance is due to Ph$_3$PO.

Stirring OsCl$_2$L$_3$ or OsBr$_2$L$_3$ in hexanes does not produce bisphosphine complexes.

**RuHClL$_3$.** The proton decoupled $^{31}$P NMR spectrum of RuHCl(PPh$_3$)$_3$ at +30° in CH$_2$Cl$_2$ is a broad singlet. On lowering the temperature, this line broadens, then disappears and an AX$_2$ pattern develops and sharpens (Figure 5). A static spectrum is achieved by −68°. At this temperature no resonances due to free PPh$_3$ or any other complexes are evident. Consistent with this, refluxing RuHClL$_3$ in methanol does not produce any bisphosphine species.

Selective decoupling of only the phenyl protons at −77° allows determination of $^2J_{\mathrm{P_aH}}$ = 30.7 and $^2J_{\mathrm{P_eH}}$ = 21.4 Hz. This yields a weighted average of 24.5, compared to a value of 25 measured by proton NMR at 220 MHz and 20° in CH$_2$Cl$_2$. At 30°, selective decoupling does not resolve the averaged $J_{\mathrm{P-H}}$ in the $^{31}$P spectrum due to the magnitude of the exchange broadening.

Line shape analysis as for RuCl$_2$L$_3$ yields the activation parameters shown in Table II. An intramolecular process is indicated by the log *A* and $\Delta S^\ddagger$ values,[50] although these are significantly larger than those for RuCl$_2$L$_3$, OsCl$_2$L$_3$, and OsBr$_2$L$_3$. It has been shown recently that solvation can alter

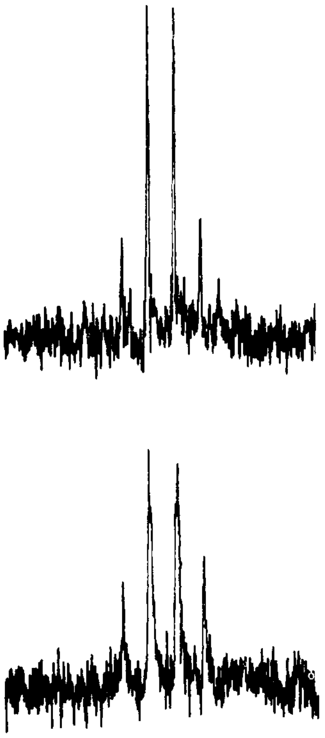


Figure 6. The 220-MHz $^1$H NMR spectra of $RuHCl(PPh_3)_3$ and $RuH(O_2CCH_3)(PPh_3)_3$ (bottom) in $CH_2Cl_2$. Only the high field resonance due to the hydride proton is shown. Calibration bar is 50 Hz.

$\Delta S^\ddagger$ values by 10 eu.[51] While this may be significant for $RuHClL_3$, we are presently unable to provide a detailed explanation.

**$RuH(O_2CMe)L_3$.** The proton-decoupled $^{31}$P NMR spectrum of $RuH(O_2CMe)(PPh_3)_3$ at +30° in $CH_2Cl_2$ (in which it is inactive) and in THF (in which it is catalytically active) is an $AX_2$ pattern consistent with the solid state structure. The value of $^2J_{PP'}$ is typical of cis stereochemistry on Ru(II). There is no spectroscopic evidence for free phosphine or any other metal complex (signal/noise ratio of 95:1). The spectrum is unchanged on lowering the temperature to −72°.

Selective decoupling of the phenyl protons produces a $^{31}$P spectrum which exhibits coupling of each phosphorus environment to the hydride ligand with coupling constants $^2J_{P_e\text{-}H} = 25.8$, $^2J_{P_a\text{-}H} = 28.4$ Hz. Since the hydride resonance has been reported to be a quartet,[2,52] we have reinvestigated the high-field NMR. The 220-MHz spectrum at 20° in $CH_2Cl_2$ is shown in Figure 6, along with that of $RuHCl(PPh_3)_3$. The amplitudes of the quartet peaks of the hydrido acetate are not 1:3:3:1. The central peaks have shoulders on their interior sides, identifying this pattern as a doublet of triplets with deceptively similar $J_{PH}$ values. The proton NMR therefore accurately reflects the stereochemical rigidity of this complex. The osmium analog also exhibits near degeneracy of these coupling constants.[52]

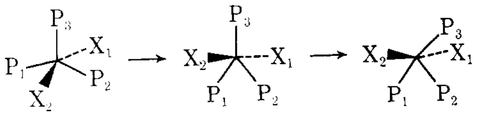
Phosphine dissociation by $RuH(O_2CCH_3)(PPh_3)_3$ is spectroscopically undetectable. The low solution molecular weights are thus erroneous. Nevertheless, from the standpoint of catalytic activity, $RuH(O_2CCH_3)(PPh_3)_3$ could obtain an open coordination site if the carboxylate group became monodentate in solution. However, such a five-coordinate complex should exhibit nonrigid behavior similar to that observed for the other Ru(II) species studied here. The observed rigidity of $RuH(O_2CCH_3)(PPh_3)_3$ is therefore highly suggestive of coordination number six persisting in solution. The catalytic activity exhibited by this complex must therefore result from very small concentrations of relatively high energy species. The solution structure of $RuH(O_2CCH_3)(PPh_3)_3$, with bidentate acetate, contrasts to that of $Rh(O_2CPh)(PPh_3)_3$, which has a monodentate carboxylate group in the solid.[53]

**$RuCl_2[P(OPh)_3]_4$.** For comparison purposes, we have investigated the solution properties of $RuCl_2[P(OPh)_3]_4$ which is formally similar to $RuCl_2(PPh_3)_4$ and is prepared from $RuCl_2(PPh_3)_3$ by addition of $P(OPh)_3$. This complex shows only a single resonance in $CH_2Cl_2$ at +30 and −92°. This establishes an exclusive trans stereochemistry for the product prepared in this manner, as well as the absence of phosphite dissociation. While electronic factors may be significant, it is worth noting that the smaller cone angle[54] (121°) of $P(OPh)_3$ relative to $PPh_3$ (145°) is sufficient to rationalize the persistence of the six-coordinate complex $RuCl_2[P(OPh)_3]_4$ in solution.

**Rearrangement Mechanism and Energetics.** The log $A$ and activation entropy parameters for $RuCl_2L_3$, $OsCl_2L_3$, and $OsBr_2L_3$ are all equal within experimental error. In view of the structural similarity of these molecules, this result is expected and suggests that the $\Delta S^\ddagger$ values determined here are meaningful, and not mere artifacts. The large temperature range over which rate data are obtainable is partly responsible. All three molecules exhibit near-zero activation entropies. The averaging process is thus intramolecular.

The possible "modes of rearrangement" of square pyramidal polyhedra have been enumerated for the general case of an $MX_5$ species.[55] If we assume a model with no population of an intermediate with three equatorial phosphines or with one apical and two cis equatorial ones, a single "observable process" exists for an $MX_2L_3$ species. Using $^{31}$P NMR, one cannot discriminate between a physical process which (a) interchanges $L_3$ (structure II) with either basal phosphorus leaving the other phosphorus and the X groups unmoved (ea) and (b) one which sequentially permutes $L_1$, $L_2$, and $L_3$ while leaving the X groups unmoved (trans eea).

Berry pseudorotation is the physical process often used to account for equilibration of axial and equatorial nuclei in TBP species.[56] In cases studied to date, the energy surface for rearrangement has an absolute minimum at the TBP structure and either a maximum or a local minimum at the SP geometry. Berry pseudorotation, which corresponds to the trans eea mode for an $MX_2L_3$ species, also effects the permutations observed in this work. A new feature of $MX_2(PPh_3)_3$ (M = Ru, Os) species is that the square pyramid is the ground state and the trigonal bipyramid is the transition state.



This characteristic reveals a new feature of rearrangements of five-coordinate complexes. Previous analyses of trends in rearrangement parameters gave no consideration to changes in bond length in creating the transition state. This is because nothing is known about a d$^8$ square pyramid. For the d$^6$ case, grossly inequivalent metal-phosphorus bond lengths characterize the square pyramidal ground state. The transition state, on the other hand, has $X_1$ and $X_2$ precisely trans and has three equivalent phosphorus nuclei.[57] Energetically, the most demanding feature of such a rearrangement is probably the stretching and compression of Ru–P bonds. If metal–phosphorus bond stretching is a major factor in the rearrangement a correlation should, and does, exist between activation parameters and vibrational force constants. The osmium compound has higher values of $E_a$, $\Delta H^‡$, and $\Delta G^‡$ at all temperatures; at 200°K, the ratio of rate constants for $RuCl_2L_3$ and $OsCl_2L_3$ is $10^2$. Although metal–phosphorus force constants are unknown for isostructural complexes of ruthenium and osmium, comparison is possible for bonds to ligands Cl, O, N, and CO. In every instance force constants are larger for osmium than ruthenium.[58-60] We see no reasonable argument based on size effects (compare $M[P(OR)_3]_5{}^{n+}$ complexes[56]) due to the very similar radii of ruthenium and osmium. The steric contribution to the barrier may be large,[61] but it is certainly the same for the two $MCl_2L_3$ species.

Values of $E_a$, $\Delta H^‡$, and $\Delta G^‡$ (at temperatures below 500°K) are higher for $OsBr_2L_3$ than for the chloro analog. This is viewed as a "site preference" effect in the trigonal bipyramidal transition state. $\sigma$-Bonding ligands prefer to occupy apical positions in a TBP. $\pi$-Acidity leads to preference for equatorial sites.[62] Since bromide is a stronger $\pi$-acid than chloride, it destabilizes trigonal bipyramidal $OsX_2L_3$ for X = Br relative to X = Cl.

Values of $E_a$, $\Delta H^‡$, and $\Delta G^‡$ (below 400°K) are higher for $RuHClL_3$ than for $RuCl_2L_3$. This cannot be a transition state effect since hydride should prefer an apical position in a TBP more than chloride.[63] It must be concluded that $RuHClL_3$ has a lower ground state energy, possibly steric in origin. Since a square pyramid does not possess the requisite $C_{3v}$ symmetry the "tetrahedral edge traverse" mechanism[64] does not smoothly produce the permutation observed for $RuHClL_3$. The possibility remains, however, that the physical pathway utilized by $RuHClL_3$ differs from that of the dihalo species.

**Magnetic Resonance Parameters.** These are summarized in Table IV. The axial–equatorial chemical shift differences observed in $RuCl_2L_3$ is exceptionally large (51.6 ppm). The differences observed for $RuHClL_3$ (55.6 ppm) and $RuH(O_2CMe)L_3$ (33.9 ppm) are also large. It is unlikely that this large difference is related to the short axial Ru–P bond distance, since $[RuCl_2L_2]_2$ and both $OsX_2L_3$ species have axial–equatorial separations less than 10 ppm. The chemical shifts of the osmium compounds lie close to that of free L (−5.4 ppm). For both $OsX_2L_3$ species, the axial resonance is upfield of the equatorial resonance, reversing the pattern found in the ruthenium complexes.

## Conclusion

A dissociated ligand is spectroscopically detectable only in the case of $RuCl_2L_3$ (and $RuCl_2L_4$). The decreased dissociation on passing from Ru(II) to Os(II) is consistent with trends observed for $RhL_3Cl$,[65] and $IrL_3Cl$,[66] and also for the pair $HRhCOL_3$-$HIrCOL_3$.[67,68] For complexes of formula $M(Ph_2PCH_2CH_2PPh_2)(CO)^+$ [13] and $M(CO)_2L_2Cl$[69] (M = Rh, Ir), the tendency to bind carbon monoxide is Ir > Rh. The third-row complex generally is "tighter" than the second-row analog. Decreased dissociation on passing from $RuCl_2L_3$ to $RuHClL_3$ follows from the latter molecule being less crowded; predictably the structure of the hydrido chloride shows bending of the three phosphines toward the hydride. Crowding in $RuH(O_2CMe)L_3$ is predicted to be intermediate between that in the dichloride and the hydrido chloride.

$RuHClL_3$ and $RuH(O_2CCH_3)L_3$, both active hydrogenation catalysts, show no detectable dissociation of phosphine. The acetate complex must dissociate to be catalytically active, however. This work therefore stands as a brutal reminder that "spectroscopically undetectable" species are real, possibly central features of catalytic systems. It may be common that catalytically active species (i.e., the catalyst, as opposed to the catalyst precursor) are undetectable (at least by NMR), and the phrase "kinetically significant concentrations" takes on added meaning.

Table IV. $^{31}P$ NMR Parameters[a]

| | Chemical shift (ppm)[b] | Temp, °C | $^2J_{PP}$ (Hz) |
|---|---|---|---|
| $RuCl_2(PPh_3)_3$ | 40.9 | 30 | |
| | 75.7, 24.1 | −97 | 30.5 |
| $RuClBr(PPh_3)_3$ | 42.8 | 30 | |
| | 79.0, 25.9 | −93 | 30.5 |
| $RuBr_2(PPh_3)_3$ | 43.8 | 30 | |
| | 80.0, 27.4 | −88 | 30.5 |
| $OsCl_2(PPh_3)_3$ | −3.9 | 30 | |
| | −7.2, −1.3 | −79 | 13.4 |
| $OsBr_2(PPh_3)_3$ | −5.3 | 30 | |
| | −9.0, −0.45 | −80 | 13.4 |
| $RuHCl(PPh_3)_3$ | 59.0 | 30 | |
| | 94.0, 38.4 | −74 | 29.0 |
| $RuHBr(PPh_3)_3$ | 93.8, 38.6 | −88 | 29.3 |
| $RuH(O_2CCH_3)(PPh_3)_3$ | 77.6, 43.8[c] | 30 | 27.5 |
| | 78.1, 44.3 | 30 | 27.5 |
| | 78.0, 43.6 | −83 | 27.5 |
| $[RuCl_2(PPh_3)_2]_2$ | 58.8, 53.0 | −97 | 41.5 |
| $[RuBr_2(PPh_3)_2]_2$ | 61.6, 55.0 | −88 | 41.5 |
| $RuCl_2[P(OPh)_3]_4$ | 110.7 | 30 | |
| | 114.2 | −92 | |
| *mer*-$OsHBr(CO)(PPh_3)_3$ | −12.3, +4.2 | 30 | 11.0 |

[a] In $CH_2Cl_2$ unless otherwise noted. [b] When two values are listed for an $AX_2$ pattern, the first refers to the unique (apical) ligand. [c] In THF.

A final comment deserves mention simply because it explains so many of the observations made here. The great steric bulk of triphenylphosphine appears to be a feature which dominates the chemistry of these Ru(II) and Os(II) complexes. Iron(II) is not known to form $FeCl_2(PPh_3)_3$. Five-coordination is atypical for Ru(II) and Os(II). The conversion of $RuCl_2L_3$ to $RuCl_2[P(OPh)_3]_4$ makes this clear, as does the analogous transformation of $RuHClL_3$ to $RuHCl[P(OPh)_3]_4$.[70] In the absence of four equivalents of smaller phosphines, six-coordinate dimers of stoichiometry $L_3RuX_3RuL_3{}^+X^-$ invariably form. Oxidation of $Ru_3(CO)_{12}$ with $SnCl_4$ produces $(OC)_3RuCl_3Ru(SnCl_3)(CO)_2$.[71] It therefore appears reasonable to attribute the unusual coordination number observed for $MX_2(PPh_3)_3$ (M = Ru, Os) to the steric requirements of triphenylphosphine. The dissociation of $RuCl_2L_3$ to the dimer replaces $PPh_3$ by bridging halide. This implies the presence of even three triphenylphosphine ligands in a five- or six-coordinate nonhydridic complex is unfavorable. The dissociative dimerization[65] of $RhCl(PPh_3)_3$ also supports this contention. Indeed there is a remarkable similarity between the $RuCl_2L_3$-$[RuCl_2L_2]_2$ equilibrium system and that of $RhClL_3$-$[RhClL_2]_2$.[65] The occurrence of intermolecular phosphine exchange by a dissociative mechanism ($RuCl_2L_3$) is evidence for the difficulty of binding three triphenylphosphine ligands to a five-coordinate complex. Moreover, the lack of any significant participation by an associative pathway merely reiterates the obvious. In summary, it is important to recognize that triphenylphosphine is a very atypical phosphine, although it may be precisely this steric factor which optimizes its effect as a catalyst "promoter".

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# Nuclear Magnetic Resonance Studies of Planar Low-Spin Complexes of Cobalt(II) with Schiff Bases. *N,N'*-Ethylenebis(salicylideneiminato)cobalt(II) in Noncoordinating Solvents

**Kouto Migita,* Masamoto Iwaizumi, and Taro Isobe**

*Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan.*

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**Abstract:** Isotropic proton NMR shifts have been measured for low-spin salicylaldehyde Schiff base complexes of cobalt(II) in $CDCl_3$. The isotropic shifts are shown to arise from both dipolar and contact interaction of comparable magnitude. This appreciable contact contribution is attributable to spin delocalization involving M ← L π charge transfer out of the highest filled π MO. From the mode of the interaction between the cobalt ion and the ligand, it is concluded that the cobalt(II) complexes have an electronic ground state with the unpaired electron in the $d_{yz}$ orbital.

The electronic structure of the *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) complex, Co(salen), has been widely investigated by electronic spectroscopy,[1] ESR spectroscopy,[1,2] and other methods.[3] It is known that in coordinating solvents, such as pyridine, piperidine, etc., the complex forms a five-coordinate, square pyramidal species with the solvent molecules, and it possesses an electronic ground state having an unpaired electron in the $d_{z^2}$ level.[1b,c,2b,4] In