# The Phosphorus-31 and Rhodium-103 Nuclear Magnetic Resonance Spectra of Some Rhodium(I) and Rhodium(III) Phosphine Complexes

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**Abstract:** The high resolution $^{31}P$ and $^{103}Rh$ nuclear magnetic resonance spectra of several halide complexes of rhodium(I) with triphenylphosphine and of rhodium(III) with tributylphosphine have been measured in methylene chloride solution. The phosphorus chemical shifts appear to be dependent mainly on the electronegativities of the neighboring atoms. Substitution of various halogens in the complexes has the major influence on the coupling constant between the rhodium atom and the phosphorus atom which is *trans* to the halogen atom. In addition the absorption spectra of the complexes were measured in methylene chloride solution. The rhodium chemical shifts are dependent on the oxidation state of the rhodium atom as well as on the electronegativities of the substituents but are not dependent mainly on the $\Delta E$ term in the Ramsey equation for the shifts.

In a recent note we described the $^{31}P$ and $^{103}Rh$ nuclear magnetic resonance spectra of $Rh((C_6H_5)_3P)_3Cl$ and *trans*-$Rh((C_6H_5)_3P)_2COCl$.[1] The double resonance measurements also allowed a determination of the relative signs of the rhodium–phosphorus and the *cis* phosphorus–phosphorus coupling constants. In the present paper we extend these experiments to other rhodium(I) complexes and to rhodium(III) complexes. Also an attempt is made to measure the electronic absorption spectra of the complexes. The studies are undertaken to understand better the chemical bonding in the complexes and the nature of heavy atom chemical shifts[2–4] for compounds of a second transition series element.

The experimental technique employed is to observe the phosphorus spectrum of the complex and then to determine the rhodium spectrum by double irradiation at the appropriate frequencies which produces a perturbation on the phosphorus spectrum. By this "spin-tickling" method[5] it is possible to determine the rhodium spectra, measurements difficult by direct observation because of the small magnetic moment of the rhodium nucleus ($I$ = $^1/_2$, abundance 100%). In the present case the method is limited to systems in which there is an easily observable nuclear spin coupled to the rhodium nucleus. The low solubility of the complexes in all solvents and the low sensitivity of the phosphorus nucleus to nmr detection made the present experiments more difficult. However, the sensitivity and resolution of the spectra were greatly enhanced by broad band decoupling of the protons in the phosphine ligands.

## Experimental Section

The compounds $Rh((C_6H_5)_3P)_3Cl$ and $Rh((C_6H_5)_3P)_2COCl$ were obtained from Strem Chemicals Inc. and were used without further purification. All preparations were carried out under a nitrogen atmosphere. The compound $Rh((C_6H_5)_3P)_3Br$ was prepared as described by Wilkinson, *et al.*,[6] by adding LiBr to the reaction mixture of the corresponding chloride. Orange crystals of the complex were obtained in 65% yield. Attempts to prepare the analogous iodide complex by the method of the previous authors produced rather poor yields. Better yields, in excess of 50%, were achieved by adding LiI to a hot ethanolic solution of $RhCl_3 \cdot 3H_2O$ and immediately adding a molar excess of triphenylphosphine.[7] After refluxing for 30 min, red-orange crystals of the iodo complex separated. The crystals were washed with ether and dried *in vacuo*. The compound melted at 117°. The compound *mer*-$Rh((C_4H_9)_3P)_3Cl_3$ was prepared as described by Chatt, *et al.*;[8] however, poor yields were obtained due to the high solubility of the complex in ethanol. The orange colored complex melted at 139°. Deep red crystals of the compound $Rh((C_4H_9)_3P)_3Br_3$ were prepared by adding 2.0 g of LiBr to a solution of 0.4 g of rhodium chloride and 1.10 g of tributylphosphine in hot ethanol. After refluxing for several hours the crystals separated on cooling and were washed with ether. The yield was 50% and the compound melted at 136°. Attempts to prepare the compound $Rh((C_4H_9)_3P)_3I_3$ were unsuccessful, possibly due to the reducing influence of the iodide ions in the reaction. The compound $Rh_2((C_4H_9)_3P)_4Cl_6$ was prepared as red-brown prisms and recrystallized from light petroleum ether as described.[8] The yield was 40% and the compound melted at 195° with decomposition.

The nmr spectra were recorded on a Bruker HFX90-MHz variable frequency spectrometer. The rhodium spectra were measured by applying a small irradiation field to a second set of transmitter coils in the probe. The latter field was supplied by a Schmondl frequency synthesizer which was externally locked to the 1-MHz master crystal of the spectrometer. A third irradiation field was applied at the proton frequencies in order to decouple the ligand protons, thus improving the resolution and signal to noise ratio of the phosphorus spectra. All results are reported for a field strength such that the proton signal from TMS would be observed exactly at 90 MHz. The rhodium chemical shifts are reported for this field strength relative to the frequency which has been reported for rhodium metal.[9] The latter frequency (nominally chosen to be 2.840104 MHz) corresponds to the center of the resonance reported for rhodium metal and is corrected to the field strength of the present experiments by measuring the chemical shift of $D_2O$ from TMS. For room temperature measurements the samples were sealed in 13-mm spinning sample tubes, while those measured at lower temperatures were sealed in 5-mm tubes. A capillary of 85% $H_3PO_4$ was sealed in the tubes as an external reference. The compounds were dissolved in the minimum quantity of spectrograde methylene chloride unless otherwise noted and the solutions were purged with nitrogen gas.

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[1] T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, 91, 3378 (1969). The rhodium frequencies which were reported for the two complexes are incorrect. The frequencies are low by a constant amount of 590 Hz. The corrected chemical shifts for these compounds may be found in Table I.

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[3] R. Freeman, G. R. Murray, and R. E. Richards, *Proc. Roy. Soc.*, **455**, 242 (1957).

[4] (a) T. H. Brown, E. B. Whipple, and P. H. Verdier, *Science*, **140**, 178 (1963); (b) *J. Chem. Phys.*, 38, 3029 (1963); (c) in "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963.

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[9] P. B. Sogo and C. D. Jeffries, *Phys. Rev.*, **98**, 1316 (1955).

Table I. Nmr Spectral Parameters for Rhodium Complexes in Methylene Chloride Solution

| Compound | Temp, °K | $\delta P_1$,[a] ppm | $\delta P_2$, ppm | $J$(Rh–$P_1$),[b] Hz | $J$(Rh–$P_2$), Hz | $J$($P_1$–$P_2$), Hz | $\delta$Rh,[a] ppm |
|---|---|---|---|---|---|---|---|
| $Rh((C_6H_5)_3P)_3Cl$ | 305 | −31.5[d] | −48.0 | −142 | −189 | −38 | −1291 |
| $Rh((C_6H_5)_3P)_3Br$ | 280 | −29.8 | −46.8 | −141 | −192 | −37 | −1230 |
| $Rh((C_6H_5)_3P)_3I$ | 260 | −27.1 | −43.2 | −139 | −194 | −36 | −1104 |
| $Rh((C_6H_5)_3P)_2COCl$[c] | 305 | −29.1 |  | −124 |  |  | −1003 |
| $Rh((C_4H_9)_3P)_3Cl_3$ | 305 | +0.5 | −15.1 | −84 | −113 | −23 | −4146 |
| $Rh((C_4H_9)_3P)_3Br_3$ | 305 | +7.8 | −13.7 | −84 | −108 | −23 | −3709 |
| $Rh_2((C_4H_9)_3P)_4Cl_6$ | 305 |  | −37.8 |  | −115 |  | −4354 |

[a] The chemical shifts are calculated from $\delta X = (\nu_r - \nu_s)/\nu_r \times 10^6$, where $\nu_r$ and $\nu_s$ are the resonant frequencies of reference and sample, respectively, at a field strength such that the proton signal from TMS would be observed at 90 MHz. For $\delta$P, $\nu_r$ is the frequency of 85% $H_3PO_4$, and for $\delta$Rh $\nu_r$ is the frequency nominally calculated for rhodium metal (2.840104 MHz). [b] For the sign determination and absolute sign convention see ref 1. [c] Measured in chloroform solution. [d] Accuracy of the measurements, $J(X) = \pm 1.0$ Hz, $\delta P = \pm 0.1$ ppm, $\delta Rh = \pm 1.0$ ppm.

The visible–uv spectra obtained on a Cary-14 spectrometer were measured in methylene chloride solutions which were purged with nitrogen gas. Only the lowest frequency observed bands are reported. More intense bands were observed in all the complexes at higher frequencies but these are not reported because they are most likely associated with charge transfer and are not due to transitions within the d orbitals of the rhodium atoms. For the rhodium(I) complexes a possible third weak band was observed as a shoulder on the charge-transfer bands; however, it is not reported because of the difficulty in accurately determining its position.

## Results and Discussion

The phosphorus and rhodium chemical shifts as well as the various rhodium–phosphorus and phosphorus–phosphorus coupling constants are reported in Table I. A negative chemical shift for either nucleus indicates that the phosphorus or rhodium resonance occurs at a higher frequency and therefore the nucleus is less shielded than in the reference. The temperature dependence of the spectrum of $Rh((C_6H_5)_3P)_3Br$ has been determined over the range from 235 to 280°K. The phosphorus and rhodium chemical shifts were found to have a temperature dependence which is not greater than +0.02 ppm/°K and −1 ppm/°K, respectively. The latter value agrees with that found recently for another rhodium complex.[10] A more detailed temperature-dependent nmr study of these compounds will be reported later. For the purpose of the following discussion the effect of temperature on the chemical shifts is found to be smaller than the shifts between the compounds.

The phosphorus spectra of the rhodium(I) compounds support a square-planar structure for all the triphenylphosphine complexes. The spectra of the tristriphenylphosphinerhodium(I) complexes consist of four lines at high field, due to the mutually *trans* phosphorus atoms (labeled $P_1$) and six lines at lower field due to the *cis* phosphorus atom (labeled $P_2$). The structure of the lines arises from a large rhodium–phosphorus coupling superimposed upon the smaller phosphorus–phosphorus coupling of the nonequivalent phosphorus atoms. As the temperature is raised or as excess triphenylphosphine is added to the solutions, the multiplet patterns collapse and eventually only a single phosphorus line is observed. While the chloro complex could be studied at room temperature the bromo complex had to be cooled below 283°K and the iodo complex below 263°K before the multiplet splittings were well resolved. These observations are in agreement with the proposed dissociation of the tristriphenylphosphine complexes into a triply coordinated rhodium species and unassociated triphenylphosphine.[6] The spectrum of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) consists of a doublet due to rhodium–phosphorus coupling.[1,11]

The phosphorus spectra of the tristributylphosphinerhodium(III) complexes again consists of four lines at high field and two low-field triplets.[11] The coupling scheme is analogous to that found for the tristriphenylphosphinerhodium(I) complexes and the labeling scheme is the same. The spectra support the meridional structure proposed by Chatt and others for the rhodium(III) complexes.[8] The phosphorus spectrum of the compound $Rh_2((C_4H_9)_3P)_4Cl_6$ consists of a doublet due to rhodium–phosphorus coupling. This as well as the other spectra were verified by double irradiation at the rhodium frequencies, which in this case showed a triplet for the rhodium spectrum. Based on that fact and the large rhodium–phosphorus coupling constant a dimer structure is proposed in which there are two bridging chlorine atoms and four phosphorus atoms *trans* to the bridging chlorine atoms. However, this does not rule out an alternative structure. This proposed structure is inconsistent with the large value found for the molecule's dipole moment in benzene solution,[8] an observation confirmed in this laboratory. Attempts to measure the phosphorus nmr spectrum in benzene solution were unsuccessful because of the compound's low solubility in that solvent.

Inspection of the coupling constant data in Table I indicates that all of the coupling constants are larger for complexes of rhodium(I) than for those of rhodium(III). Moreover, for compounds of both oxidation states the rhodium–phosphorus coupling is always larger for a phosphorus *trans* to a halogen, $J$(Rh–$P_2$), than for the phosphorus atoms *cis* to that halogen, $J$(Rh–$P_1$). At the present time there is considerable controversy about the various factors which influence the metal–phosphorus coupling in similar complexes.[12] It is agreed that the coupling constants depend on the electronic distributions in the vicinity of both nuclei; and, since the contact term is predicted to dominate the coupling, increased s character of the valence orbitals on either atom should lead to an increase in the coupling constant.[13] Therefore $\sigma$-bond

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(13) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 40, 1714 (1964).

effects should be predominant.[14] However, others have argued that greater $\pi$ bonding may also indirectly increase the coupling constant by strengthening the bond.[11] The larger coupling constants for the rhodium(I) complexes can be predicted almost as well by either mechanism. A larger fraction of both s and $\pi$ character of the rhodium bonding orbitals is predicted for the lower valence complexes. Likewise, the larger value of $J(\text{Rh–P}_2)$ than $J(\text{Rh–P}_1)$ can possibly be explained by either a directed inductive effect of the halogen atom or by the predicted greater $\pi$ character of the phosphorus *trans* to the halogen atom.

Whatever the actual mechanism effecting the coupling constants may be, our results indicate that the halogen atoms exhibit a directed influence on the coupling in the rhodium complexes. The substitution of various halogens has a more pronounced effect on the coupling of the phosphorus *trans* to the halogen, $J(\text{Rh–P}_2)$, than of those *cis* to that halogen. Moreover, for the rhodium(III) complexes, $J(\text{Rh–P}_2)$ is largest in the chloride complex while for the rhodium(I) complexes, it is smallest in the chloride complex. In contrast to this influence of the halogen on the couplings, the substitution of a carbonyl for a phosphine group produces a marked decrease on the coupling constants of the phosphorus atoms *cis* to the carbonyl group.

The factors which influence the $^{31}$P chemical shifts in similar complexes are little better understood than those effecting the coupling constants. In this study the phosphorus shielding appears to be mainly sensitive to the electronegativities of the neighboring atoms. As less electronegative halogens are substituted in the complexes, all the phosphorus resonances are shifted to higher field. This effect may or may not be directional in character; in the rhodium(III) complexes the phosphorus atom *trans* to a halogen is shifted to a considerably less extent than are those *cis* to that halogen. However, a similar trend is not obvious in the rhodium(I) complexes.

The $^{103}$Rh chemical shifts in Table I are found to vary over a range of approximately 3500 ppm. For the phosphine complexes in this study, the rhodium chemical shifts are more strongly dependent on the valence of the rhodium atom than on the ligand environment. If the central atom resides in a "strong" ligand field the chemical shielding parameter may be approximately expressed as a sum of diamagnetic and paramagnetic contributions by[15]

$$\sigma = A - \frac{B}{\Delta E} \tag{1}$$

where $A$ is the diamagnetic contribution, $\Delta E$ is the "average" value of the electronic excitation energy for the first low-lying excited states of the atom, and the term $B$ indicates the product of physical constants with matrix elements of the type $\langle\Psi_0|\sum_i l_i|\Psi_n\rangle$ and $\langle\Psi_0|\sum_i r^{-3}l_i|\Psi_n\rangle$, where $\Psi_0$ and $\Psi_n$ are the wave functions of the ground and excited states, $l_i$ is the angular momentum operator for electron $i$, and $r$ is its distance from the nucleus. The paramagnetic contribution is usually greater than the diamagnetic contribution for all but the lightest atoms, but a very careful analysis is required to separate the various contributions. It is perhaps more illustrative to consider the effects on the rhodium shielding parameter with substitution of different halogens in a series of complexes. The results in Table I indicate that the rhodium atom is more shielded in both oxidation states as one goes down the series of halogen substituents in these complexes. This roughly parallels the influence on the phosphorus shifts for the same compounds. A similar trend has recently been observed for several halogen series of platinum(II) complexes with various donor ligands.[16] As has been done for other transition metal complexes, an attempt was made to determine the influence of the $\Delta E$ term on the platinum shielding parameters.[16] In that case the shielding seemed to be dependent mainly on the other terms in eq 1.

The electronic absorption spectra of the rhodium(I) and rhodium(III) phosphine complexes have not as yet been characterized. A detailed analysis of the absorption spectra is beyond the scope of this work but it is reasonable to expect that in a halogen series of metal complexes with the same donor ligands the absorption spectra should exhibit the same general features. In Table II the observed frequencies of the bands are listed for most of the complexes. The band numbers refer only to the relative order of the band positions; this order is thought to be quite good within an oxidation state but it is not meant to imply that the same order is carried over between oxidation states. More intense bands which were observed at higher frequencies are not included in this table because it is questionable whether these are ligand field bands.

**Table II.** Lowest Frequency Bands in the Electronic Absorption Spectra of Rhodium Phosphines Dissolved in Methylene Chloride at 300°K

| Compound | Band number 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $\text{Rh}((\text{C}_6\text{H}_5)_3\text{P})_3\text{Cl}$ | 2.77[a] | 3.48 | | |
| $\text{Rh}((\text{C}_6\text{H}_5)_3\text{P})_3\text{Br}$ | 2.67 | 3.32 | | |
| $\text{Rh}((\text{C}_6\text{H}_5)_3\text{P})_3\text{I}$ | 2.60 | 3.15 | | |
| $\text{Rh}((\text{C}_6\text{H}_5)_3\text{P})_2\text{COCl}$ | 2.74 | 3.18 | | |
| $\text{Rh}((\text{C}_4\text{H}_9)_3\text{P})_3\text{Cl}_3$ | 2.35[b] | 3.08 | 3.38 | 4.73 |
| $\text{Rh}((\text{C}_4\text{H}_9)_3\text{P})_3\text{Br}_3$ | 2.16 | 2.89 | 3.21 | 4.67 |

[a] Frequencies reported in units of $10^4$ cm$^{-1}$. [b] There is no direct correspondence between the band numbers of the two oxidation states.

A red shift of all the absorption bands is found as bromine and iodine atoms are substituted for chlorine atoms in the complexes. Then as expected the ligand field splittings are most likely in the order Cl > Br > I. If the $\Delta E$ term in eq 1 is the dominant factor in determining the rhodium chemical shifts, the rhodium atoms should be the most shielded in the chloride complex for a series of tris tertiary phosphine complexes. However, the rhodium resonance occurs at the lowest field in the chloride complexes, possibly indicating that the other

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(15) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 1079.

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contributions to the paramagnetic shielding, *B*, mainly determine the rhodium chemical shifts. This parallels the result found for similar platinum complexes.[16] Likewise, substitution of the carbonyl group for a phosphine group in the rhodium(I) complexes seems to produce a red shift in the absorption spectra. If the $\Delta E$ term is dominant, then the rhodium nucleus should be less shielded in the carbonyl complex than in the tris-triphenylphosphine complex. The carbonyl complex is observed at higher field, again indicating a greater dependence of $\sigma$ on the other terms in eq 1.

Obviously an estimate of the other factors which could effect the paramagnetic shielding of the rhodium and phosphorus nuclei is difficult at this time. These experimental results may, however, give some insight into the shielding mechanism. Further experimental, as well as theoretical, studies are in progress in the hope of further understanding these parameters.

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# Formation and Fluorine-19 Nuclear Magnetic Resonance Spectra of the Polyfluorosulfuric Acids, $H(SO_3)_nF$. Existence of the Polyfluorosulfuric Acids in $SbF_5$–$HSO_3F$

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**Abstract:** Direct evidence for the formation of the polyfluorosulfuric acids, $HS_2O_6F$, $HS_3O_9F$, . . . , $HS_7O_{21}F$, in solutions of $SO_3$ in $HSO_3F$ or $HSO_3F$–$SO_2ClF$ has been obtained by the observation of separate $^{19}F$ nmr signals from each of these species at low temperature. Recent evidence for the formation of these acids in $HSO_3F$–$SbF_5$ systems is shown to be incorrect.

The Raman and room temperature $^{19}F$ nmr spectra of solutions of $SO_3$ in $HSO_3F$ have been studied previously[1] and the results have been interpreted as providing evidence for the formation of the polyfluorosulfuric acids $H(SO_3)_nF$. New lines that appear in the Raman spectrum on addition of $SO_3$ to $HSO_3F$ could be satisfactorily interpreted as being due to the formation of $HS_2O_6F$ and $HS_3O_9F$ and further changes in the Raman spectrum at high $SO_3$ concentrations indicated, but did not prove, the existence of higher members of the series of polyfluorosulfuric acids. On addition of $SO_3$ to $HSO_3F$, only a single line was observed in the room temperature $^{19}F$ nmr spectrum, but it showed a large shift to low field with increasing concentration of $SO_3$. This large shift could only be reasonably interpreted as indicating the formation of a series of polyfluorosulfuric acids, but separate signals from the different acids were not obtained.

A recent $^{19}F$ nmr and Raman spectroscopic study by Commeyras and Olah[2] of concentrated solutions of $SbF_5$ in $HSO_3F$ has provided evidence for the formation of $SbF_6^-$ and $Sb_2F_{11}^-$ anions in these systems. The formation of these anions had not been observed in the more dilute solutions previously investigated by Thompson, *et al.*,[3] in which it was shown that the following equilibria are set up.

$$SbF_5 + 2HSO_3F \rightleftarrows H_2SO_3F^+ + SbF_5(SO_3F)^-$$

$$2SbF_5 + 2HSO_3F \rightleftarrows H_2SO_3F^+ + (SbF_5)_2SO_3F^-$$

In order to account for the formation of $SbF_6^-$ and $Sb_2F_{11}^-$, Commeyras and Olah proposed the following additional equilibria, including the formation of the polyfluorosulfuric acids $HS_2O_6F$ and $HS_3O_9F$.

$$HSO_3F \rightleftarrows SO_3 + HF$$

$$SbF_5 + HF \rightleftarrows HSbF_6$$

$$2SbF_5 + HF \rightleftarrows HSb_2F_{11}$$

$$SO_3 + HSO_3F \leftrightarrows HS_2O_6F$$

$$2SO_3 + HSO_3F \leftrightarrows HS_3O_9F$$

In support of this scheme they attributed lines at approximately −69 and −32 Hz from $HSO_3F$ in their 56.4 MHz $^{19}F$ nmr spectra to the species $HS_2O_6F$ and $HS_3O_9F$, respectively. The scheme seems unlikely as there is no evidence for any appreciable dissociation of fluorosulfuric acid into $SO_3$ and HF.[4] Furthermore it has been shown that $SbF_6^-$ and $Sb_2F_{11}^-$ are also formed in the $SbF_5$–$H_2O$ and $SbF_5$–$H_2SO_4$ systems in solution in $SO_2$.[5] Hence it is clear that the additional fluoride required to convert $SbF_5$ to $SbF_6^-$ or $Sb_2F_{11}^-$ need not come from dissociation of the $HSO_3F$, and it has been demonstrated that the $SbF_6^-$ and $Sb_2F_{11}^-$ can arise *via*

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