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Tertiary Phosphine Complexes of Rhodium(III) and Rhodium(I)[1,2]

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Phosphorus-31 magnetic resonance spectra are reported for twelve compounds of the type mer–$[(R_nPh_{3-n}P)_3RhCl_3]$, *where R is alkyl and n is 1, 2, or 3. The rhodium-103-phosphorus-31 coupling constant is always larger for a phosphine* trans *to another phosphorus. Coupling between the non-equivalent phosphorus nuclei is also observed. Virtual coupling in the proton magnetic resonance spectra of methyl- and ethyl-phsophine complexes is examined. Visible-ultraviolet spectra are presented.*

Introduction

Phosphorus-31 magnetic resonance has been shown to be a useful tool for the study of coordination compounds,[3-6] especially for those compounds containing a metal which has a reasonable abundance of an isotope with nuclear spin of one-half, or for complexes with several possible stereochemical isomers. Rhodium is of interest for both reasons, *i.e.*, rhodium-103 has a nuclear spin of one-half and is the only naturally occurring isotope of rhodium, and complexes of the type L_3RhCl_3 have two possible isomers: facial (*cis*) and meridional (*trans*). Shaw and coworkers[7-9] have demonstrated the great usefulness of proton magnetic resonance for the structural assignment of isomers of rhodium, iridium, and ruthenium complexes of dimethylphenylphosphine by observation of the methyl « virtual » coupling triplet for *trans* phosphines. Usually, « virtual » coupling is observed only for methyl and sometimes ethylphosphines,[10-12] so that pmr is limited in the range of ligands for which it can furnish relevant data. On the other hand, phosphorus nmr is not limited in this respect.

In this study we report the preparation and phosphorus nmr spectra and other data for twelve compounds of the type *mer*-L_3RhCl_3, where L is a tertiary phosphine. Several cycloocta-1,5-dienerhodium(I) compounds are also reported.

Experimental Section

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee, and by Dr. Franz Kasler, University of Maryland.

Phosphorus-31 nmr measurements were made with a Varian Associates DP-60 spectrometer at 24.3 MHz, as previously described.[13] Chemical shifts (ppm *vs.* H_3PO_4) are accurate to ± 0.4 ppm and coupling constants to ± 8 Hz.

Proton nmr spectra were obtained with a Varian Associates A-60A spectrometer. Spectra in the visible and ultraviolet regions were measured on a Cary Model 14 spectrophotometer.

All tertiary phosphines except commercially available $(C_6H_5)_3P$ and $(C_4H_9)_3P$ were synthesized by the Grignard method from PCl_3, $(C_6H_5)PCl_2$, or $(C_6H_5)_2PCl$. The method of Mann, Wells, and Purdie[14] was used for the preparation of $(CH_3)_3P \cdot AgI$. $Rh_2(C_8H_{12})_2Cl_2$ and $Rh(C_8H_{12})(PPh_3)Cl$ were prepared by the method of Chatt and Venanzi.[15] $Rh(PPh_3)_2(CO)Cl$ was prepared by the method of Chatt and Shaw.[16] All manipulations involving tertiary phosphines were carried out in a nitrogen atmosphere.

mer-Trichlorotris(tripropylphosphine)rhodium(III). Rhodium trichloride trihydrate (2.0 g, 7.6 mmoles), suspended in 75 ml of benzene was stirred magnetically under a nitrogen atmosphere. Tripropylphosphine (4.9 g, 31 mmoles) was injected through a serum cap on a side arm of the flask. The reaction mixture was heated under reflux for 6 hours, then cooled to room temperature. The volume of solution was reduced to about 25 ml by removing solvent at reduced pressure with a rotary evaporator. Petroleum ether (b.p., 90-100°) was added slowly to induce precipitation. The orange solids were removed by filtration, recrystallized from benzene-petroleum ether, washed with petroleum ether, and dried. The product, m.p. 169-171°, (lit., 179-186°) weighed 4.5 g (86%).

The other *mer*-trichlorotris(triorganophosphine)rhodium(III) complexes, except for the trimethylphosphi-

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(2) (a) Taken in part from the Ph. D. Thesis of Robert A. Ference, University of Maryland, 1968; (b) Presented at the Third Middle Atlantic Regional Meeting, ACS, Philadelphia, Feb., 1968, Abstracts of Papers, F9.

(3) J. F. Nixon and A. Pidcock, « Annual Review of NMR Spectroscopy », E. F. Mooney, ed., Vol. 2, Academic Press, New York, N. Y., 1969, pp. 345-422.

(4) S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, *8*, 1716 (1969).

(5) R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, *8*, 2115 (1969).

(6) J. W. Dawson and L. M. Venanzi, *J. Amer. Chem. Soc.*, *90*, 7229 (1968).

(7) P. R. Brookes and B. L. Shaw, *J. Chem. Soc. (A)*, 1079 (1967).

(8) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, 1407 (1966).

(9) J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. (A)*, 1787 (1966).

(10) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(11) E. W. Randall D. Shaw, *Mol. Phys.*, *10*, 41 (1965).

(12) H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, *89*, 533 (1967).

(13) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, *6*, 1133 (1967).

(14) F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937).

(15) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(16) J. Chatt and B. L. Shaw, *Chem. Ind.*, 931 (1960); 290 (1961).

Table I. Analytical Data for L_3RhCl_3 Compounds

L	mp	Calculated C	Calculated H	Calculated Cl	Found C	Found H	Found Cl
Bu_3P	141-142 (139-142)[a]	—	—	—	—	—	—
Pr_3P	169-171 (179-186)[a]	46.99	9.22	15.41	46.89	9.15	15.38
Et_3P	114-117 (114-117)[a]	38.34	8.06	18.86	38.41	8.19	18.69
Me_3P	235-260	24.70	6.23	24.31	24.91	6.39	24.14
Bu_2PhP	156-158	57.56	7.95	12.14	57.47	7.98	11.98
Pr_2PhP	176-178	54.58	7.27	13.43	54.30	7.31	13.35
Et_2PhP	183-184 (183-196)[a]	50.90	6.42	15.02	51.07	6.41	15.14
Me_2PhP	230-232 (218-224)[a]	46.21	5.34	17.03	46.08	5.34	16.86
$BuPh_2P$	137-138	61.57	6.15	11.36	61.67	6.22	11.25
$PrPh_2P$	145-146	60.44	5.76	11.89	60.63	5.79	11.89
$EtPh_2P$	133-135 (>200)[a]	59.20	5.33	12.48	59.30	5.20	12.45
$MePh_2P$	170-173	57.83	4.86	13.13	58.11	5.07	13.06

[a] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 2508 (1964).

Table II. Analytical Data for Tertiary Phosphine Complexes of the Type $LRh(C_8H_{12})Cl$

L		Calculated C	Calculated H	Calculated Cl	Found C	Found H	Found Cl
PPh_3	140-145 (146)[a]	—	—	—	—	—	—
$PPrPh_2$	106-108	58.17	6.17	7.47	58.08	6.10	1.33
$PEtPh_2$	123-125	57.34	5.92	7.69	57.09	5.79	7.46
$PMePh_2$	118-122	56.45	5.65	7.94	56.27	5 51	8.15
PEt_2Ph	99-105	52.37	6.61	—	50.87	6.43	—
PEt_3	117-120	46.10	7.48	9.72	45.93	7.50	9.59

[a] Ref. 15

ne compound, were prepared in a similar manner. Melting points and analytical data for these complexes are given in Table I.

Several of these complexes could also be prepared in good yield by the reaction of the tertiary phosphine with a suspension of trichlorotris(acetonitrile)rhodium(III), $Rh(NCCH_3)_3Cl_3$, in dry benzene.

mer-Trichlorotris(trimethylphosphine)rhodium(III). A suspension of $RhCl_3 . 3H_2O$ (2.0 g, 7.6 mmoles) and $Me_3P . AgI$ (8.0 g, 25.7 mmoles) in 75 ml of dry benzene was stirred under a nitrogen atmosphere while being heated in an oil bath at 70° for 2 hours, then under reflux for 16 hours. After cooling, silver iodide was removed by filtration. The filtrate was exaporated to about 20 ml volume and petroleum ether (90-100°) added to induce precipitation. The brilliant orange crystals were removed by filtration, washed with petroleum ether, and recrystallized from benzene-petroleum ether.

Chloro (triethylphosphine) (cycloocta-1,5-diene)rhodium(I). To a solution of $Rh_2(C_8H_{12})_2Cl_2$ (1.0 g, 2.0 mmoles) in 50 ml of dichloromethane was added 2.0 ml of triethylphosphine. The flask was stoppered and stirred magnetically for 30 minutes. The solution was evaporated to about 5 ml volume at 15 torr, methanol added, and evaporation continued until precipitation occurred. The orange solid was removed by filtration, washed with hexane, and air dried. The distinctive odor of cycloocta-1,5-diene remained even after several washings. Attempted recrystallization from ethanol led to considerable decomposition.

Petroleum ether (90-100°) was used to precipitate the Et_2PhP and $MePh_2P$ complexes. Analytical data for the rhodium(I) compounds are given in Table II.

Results and Discussion

The reaction of $RhCl_3 . XH_2O$ with tertiary phosphines in the manner described gives mainly one isomer with the formula L_3RhCl_3. By varying conditions and stoichiometries, other products[7,17] such as ionic compounds, dimers, and another isomer of L_3RhCl_3 can be produced in generally smaller yields. In this discussion we deal only with the major product. The phosphorus nmr spectra of the purified principal isomer unequivocally confirm the meridional structure (Figure 1 b) for these compounds. This structure had been proposed by Chatt[18] on the basis of dipole moment measurements and been confirmed by Shaw[7] on the basis of proton nmr for the dimethylphenylphosphine complex. The facial (or *cis*) compounds have three equivalent phosphorus atoms and should therefore produce only one peak in the ^{31}P nmr spectrum. The meridional (or *trans*) structure has two equivalent pho-

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[17] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1674 (1969).

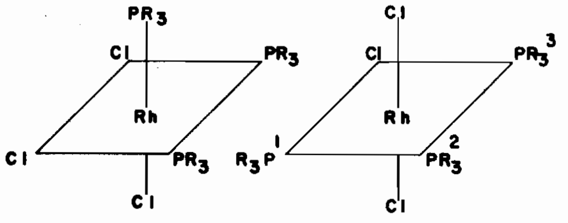
[18] J. Chatt, A. E. Field, and B. L. Shaw, *J. Chem. Soc.*, 3371 (1963).

Table III. Phosphorus-31 NMR Data for L_3RhCl_3 Compounds[a]

L	J_{Rh-P2}	$J_{Rh-P1,3}$	J_{P-P}	δ_P	δ_{P2}	$\delta_{P1,3}$	Δ_{P2}	$\Delta_{P1,3}$
Bu_3P	114(5)	84(1)	21(3)	+32.3 [b]	−14.7(.2)	+0.7(.1)	−47.0	−31.6
Pr_3P	115(2)	84(3)	19(2)	+33 [b]	−14.2(.1)	+1.1(.3)	−47.2	−31.9
Et_3P	109(11)	84(2)	—	+20.4 [b]	−20.0(.3)	−4.3(.2)	−40.4	−24.7
Me_3P	103(3)	82(4)	22(2)	+62 [b]	−7.6(.4)	+8.6(.2)	−69.6	−53.4
Bu_2PhP	113(2)	84(3)	19(3)	+26.2 [b]	−12.7(.2)	+0.7(.2)	−38.9	−25.5
Pr_2PhP	115(7)	85(2)	20(3)	+27.7 [c]	−12.7(.2)	+0.8(.1)	−40.4	−26.9
Et_2PhP	108(7)	84(4)	13(2)	+16 [b]	−17.5(.2)	−3.9(.3)	−33.5	−19.9
Me_2PhP	112(8)	86(4)	20(4)	+46 [b]	−4.4(.3)	+5.5(.2)	−50.4	−40.5
$BuPh_2P$	120(8)	85(5)	18(1)	+17.1 [b]	−15.9(.2)	−7.4(.1)	−33.0	−24.5
$PrPh_2P$	117(7)	85(6)	14(4)	+17.6 [c]	−16.0(.2)	−6.8(.2)	−33.6	−24.4
$EtPh_2P$	116(5)	85(2)	14(3)	+12 [b]	−20.0(.2)	−9.4(.3)	−32.0	−21.4
$MePh_2P$	—	—	—	+26 [b]	+3.4(.2)	+6.8(.2)	−22.6	−19.2

[a] Values in parentheses are standard deviations; coupling constants are in Hz; chemical shifts are in ppm relative to 85% H_3PO_4. [b] S. O. Grim and W. McFarlane, *Nature, 208,* 995 (1965). [c] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem. 32,* 781 (1967).

sphorus atoms (P_1, P_3) and a different third phosphorus atom (P_2). This compound should give rise to two peaks of 2 : 1 relative intensity. In addition, each of the peaks should be split into a doublet by rhodium-103. A representative spectrum is shown in Figure 2 which clearly confirms the latter situation. Of special interest here is the additional splitting (*ca.* 20 Hz) observed on the large doublet caused by phosphorus-phosphorus coupling with P_2. Since this splitting is detected for the large doublet, the small doublet arising from P_2 should be split additionally into triplets due to the equivalent P_1 and P_3 atoms. This unfortunately could not be resolved with our instrumentation. This phosphorus-phosphorus coupling[19] was the first such coupling directly observed from the ^{31}P spectra of coordination compounds, a field which has had active interest lately.[3,19-24] No phosphorus-phosphorus coupling is observed for the triethylphosphine complex and the ^{31}P spectrum of the diphenylmethylphosphine complex consists of only two broad lines, *i.e.*, the rhodium phosphorus coupling is not detected. The mechanism for collapse of the P-P and Rh-P coupling, respectively, in these two compounds is unknown at this time. Ligand exchange could be responsible for the collapsing of the P-P doublet in the triethylphosphine compound. This would imply the mean lifetime, τ, of the complex would be between $\sqrt{2}/20$ sec and $\sqrt{2}/85$ sec, since $^1J_{Rh-P1,3}$ (85 Hz) is observed although $^2J_{P-P}$ (estimated to be *ca.* 20 Hz by analogy with the other compounds) is not. However, this is not a satisfactory explanation for the collapse of J_{Rh-P} in the diphenylmethylphosphine complex; since if the mean life is shorter than $\sqrt{2}/85$ sec (which is implied by the $J_{1,3}$ signal being a singlet instead of the expected doublet) then one would *not* expect to see two distinct peaks for $P_{1,3}$ and P_2, which have a chemical shift difference of only 3.4 ppm (83 Hz). Rapid exchange which would cause collapsing of $J_{Rh-P1,3}$ would also cause averaging of the $P_{1,3}$ and P_2 chemical shifts.



(1a) (1b)

Figure 1a. facial-L_3RhCl_3; 1b, meridional-L_3RhCl_3

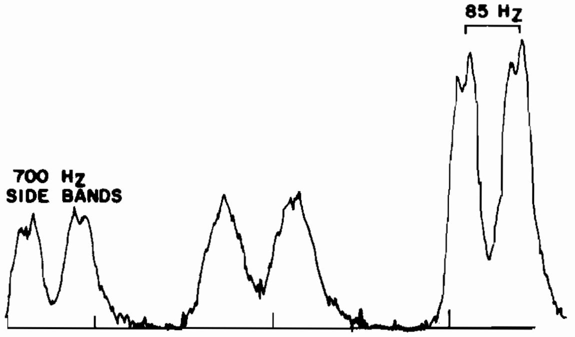


Figure 2. Phosphorus-31 nmr spectrum of mer-trichlorotri(tripropylphosphine)rhodium(III).

The phosphorus nmr data are listed in Table III for the rhodium(III) compounds. The coordination chemical shifts, $\Delta = \delta_{complex} - \delta_{phosphine}$, are also listed for convenience. First, it is observed that J_{Rh-P} is always greater for phosphorus *trans* to chlorine (*ca.* 110 Hz) then for phosphorus *trans* to phosphorus (*ca.* 85 Hz). We suggest this is due to increased Rh-P interaction due to increased Rh-P π-bonding when phosphorus is *trans* to chlorine, similar to the situation in platinum(II) *cis* and *trans* isomers.

At the present, this is a rather controversial explanation and others[3,25,26] prefer to invoke only polarization and σ-effects for explaining the magnitudes of these couplings. However, neither hypothesis can be proved unequivocally from current data and theory. Se-

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(19) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Letters, 2,* 205 (1966).

(20) M. Lenzi and R. Poilblanc, *C. R. Acad. Sci. Paris, Ser. C,* 263, 674 (1966).

(21) C. H. Barlow, J. F. Nixon, and J. R. Swain, *J. Chem. Soc. (A),* 1082 (1966).

(22) D. G. Hendricker, R. E. McCarley, R. W. King, and J. G. Verkade, *Inorg. Chem., 5,* 639 (1966).

(23) A. Pidcock, *J. Chem. Soc. (D),* 92 (1968).

(24) S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem., 7,* 161 (1968).

(25) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. (A),* 1707 (1966).

(26) L. M. Venanzi, *Chem. Brit.,* 162 (1968).

Table IV. Phosphorus-31 NMR Data for Tertiary Phosphine Complexes of Rhodium(I) [a]

Compound	J_{Rh-P} (Hz)	δ_P (ppm)	δ_{Rh-P} (ppm)	Δ(ppm)
$Rh(PPh_3)_2(CO)Cl$	129(8)	+8 [b]	−29.3(.3)	−37.3
$Rh(PPh_3)(C_8H_{12})Cl$	152(4)	+8 [b]	−30.8(.2)	−38.8
$Rh(PPrPh_2)(C_8H_{12})Cl$	152(4)	+17.6 [c]	−26.1(.2)	−43.7
$Ph(PEtPh_2)(C_8H_{12})Cl$	153(8)	+12 [b]	−28.4(.2)	−40.4
$Rh(PMePh_2)(C_8H_{12})Cl$	150(3)	+26 [b]	−17.7(.2)	−43.7
$Rh(PEt_2Ph)(C_8H_{12})Cl$	149(3)	+16 [b]	−22.8(.1)	−38.8
$Rh(PEt_3)(C_8H_{12})Cl$	146(4)	+20.4 [b]	−21.4(.2)	−41.8

[a] Values in parentheses are standard deviations. [b] S. O. Grim and W. McFarlane, *Nature, 208*, 995 (1965). [c] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem., 32*, 781 (1967).

Table V. Proton NMR Data for Methyl- and Ethyl-substituted Phosphine Complexes of Rhodium(III)

Compound	Group	τ (ppm)	J (Hz)	Comments
$Rh(PMe_3)_3Cl_3$	Triplet	8.37	7.2 [a]	Five lines, triplet
	Doublet	8.43	10.7	and.doublet superimposed.
$Ph(PMe_2Ph)_3Cl_3$	Phenyl	2.7		
	Triplet	8.08	8.6 [b]	
		(8.04) [c]		
	Doublet	8.75	11.4	
		(8.79) [c]	(11.2) [c]	
$Rh(PMePh_2)_3Cl_3$	Phenyl	2.7		
	Triplet	7.88	7.2 [a]	Four lines, triplet
	Doublet	8.03	10.5	and doublet overlap.

	Comments
$Rh(PEt_3)_3Cl_3$	Methylene multiplet; τ 7.5-8.0. Two quintets, almost superimposed; τ 8.83, $J_A = 7.0$ [d].
$Rh(PEt_2Ph)_3Cl_3$	Phenyl; τ 2.7 Methylene multiplet; τ 6.5-8.5. Quintet; τ 9.02, $J_A = 7.2$ [d] (τ 8.95, $J_A = 7.4$ [e]). Two overlapping triplets: τ 9.69, $^3J_{P-H} = 14.5$ $^3J_{H-H} = 7.4$ (τ 9.70, $^3J_{P-H} = 14.8$ $^3J_{H-H} = 7.4$ [e]).
$Ph(PEtPh_2)_3Cl_3$	Phenyl; τ 2.7 Methylene multiplet; τ 6.5-8.1. Complex methyl multiplet; τ 8.5-9.9. (Includes three prominent lines, separation 7.4).

[a] J apparent (J_A) is defined as the line separation in the triplet, which is 3.6 Hz; $^2J_{P-H}$ is 7.2 Hz. [b] J_A is 4.3. [c] Ref. 7. [d] J_A is one fourth the separation of the outermost lines of the quintet. [e] Ref. 11.

cond, it is noted that the chemical shift of P_2 is always downfield from that of P_1, P_3. Simple screening effects as outlined earlier for platinum *cis* and *trans* compounds[13] would predict that the phosphorus which is behaving as the better π-acceptor would receive the larger electronic charge, have the higher shielding, and occur at higher field. On this basis, the ^{31}P chemical shift in *cis*-$(R_3P)_2MCl_2$ would be greater than in *trans*-$(R_3P)_2MCl_2$ (M = Pt, Pd) and the chemical shift of P_2 should be higher than that of P_1, P_3 in $(R_3P)_3MCl_3$ (M = Rh, Ir). This is true for platinum[13] and iridium[27] (third transition series), but the opposite is true of rhodium and palladium[28] (second transition series). The reasons for this are not obvious at this time although it is clear that the simple diamagnetic screening effects are not predominant; and presumably paramagnetic and neighboring atom effects are more important.

Third, there is a slight detectable difference in the magnitude of J_{Rh-P} with basicity of the phosphines. The averages of J_{Rh-P2} for Ph_2RP, PhR_2P, and R_3P are 117.7, 112.0, and 110.2, respectively, which is the same trend observed for the platinum compounds,[13] *i.e.*, the least basic phosphine results in the largest metal phosphorus coupling. However, the errors in these measurements are approximately the same size as the differences of the measurements, so the reliability of th trend is not great.

Fourth, the coordination chemical shift for all the compounds is negative. This downfield shift with respect to the phosphines is expected due to the decreased electron density on the phosphorus in the decreased electron dnsity on the phosphorus in the coordination compounds. However, there are some exceptions to this rule, *viz.*, iridium(III) phosphine complexes and some tungsten(0) phosphite complexes. In general the downfield shift is less with heavier elements. The coordination shifts (absolute value) are largest for the methylphosphines, which have unusually high free ligand chemical shifts (compared to other alkyl phosphines), probably partly due to smaller bond angles and larger s- character of the lone pair, with the result that the methylphosphine rehybridization upon complex formation is more extensive than for the other tertiary posphines. The coordination

[27] S. O. Grim and R. A. Ference, to be published.
[28] S. O. Grim and R. L. Keiter, to be published.

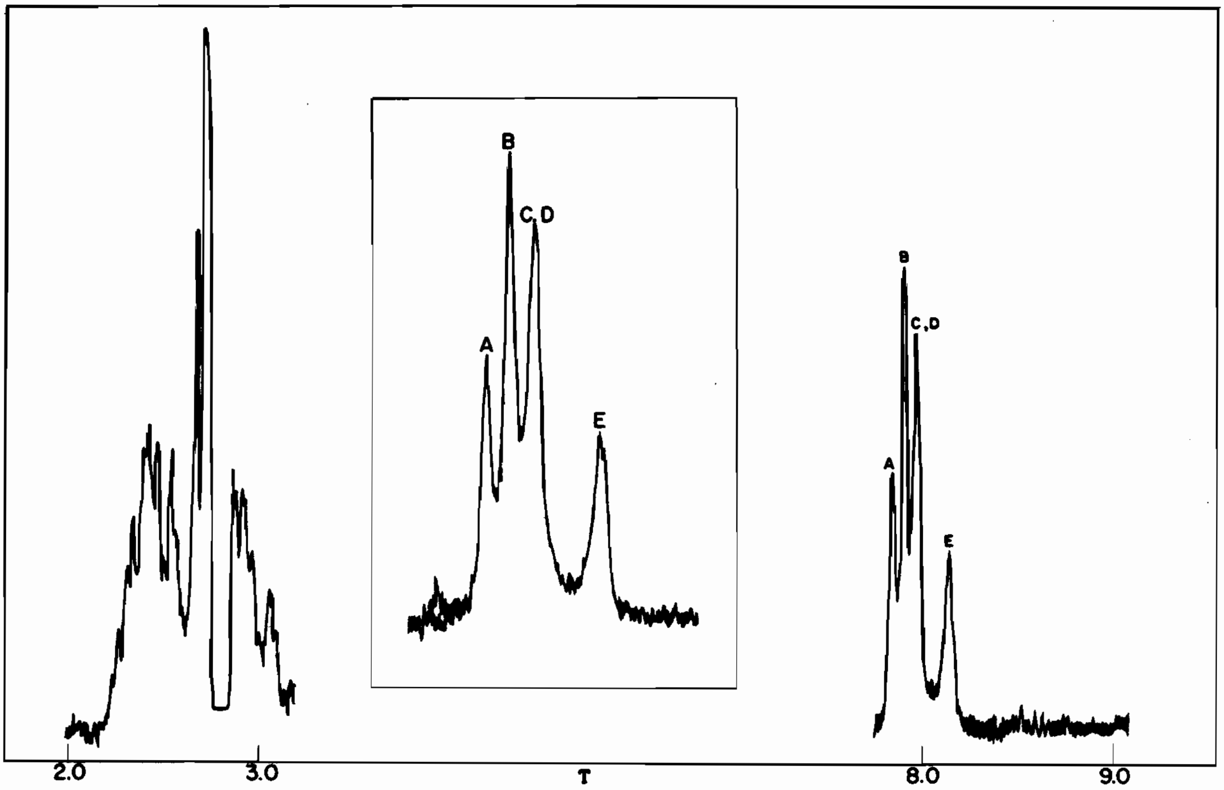

Figure 3. Proton nmr spectrum of mer-Trichlorotris(methyldiphenylphosphine)rhodium(III).

shifts (absolute value) decrease in the series $R_3P > R_2PhP > RPh_2P$ as is the case for platinum(II) compounds.

Phosphorus-31 nmr data for $Rh(PPh_3)_2COCl$ and several $Rh(PR_3)(C_8H_{12})Cl$ compounds are listed in Table IV. It is interesting to note that the ratio of the average of $J_{Rh\text{-}P_2}$ (113 Hz) in the rhodium(III) compounds to the average of $J_{Rh\text{-}P}$ (147 Hz) for the rhodium(I) compounds is 0.70. This is close to 0.67 expected for the ratio of 1/6 s-character in octahedral d^2sp^3 to 1/4 s-character in square dsp^2 hybridization and similar to the experimental platinum-phosphorus results for analogous Pt^{IV} and Pt^{II} compounds.[25,26,29] This fact can be offered in support of σ-only effects but is also consistent with π-bonding theories, since phosphorus would be expected to πbond better with Rh^I than with Rh^{III}.

Proton magnetic resonance spectra. The chemical shift and coupling constant data for the compounds are listed in Table V. The spectra for dimethylphenylphosphine[7] and diethylphenylphosphine[11] complex have been discussed previously. The former's methyl region is a doublet due to the methyl group on P_2 split by phosphorus and a sharp 1 : 2 : 1 triplet due to the « virtually » coupled methyl groups on P_1, P_3. These two are well separated and integrate in the proper 1:2 ratio. For mer-trichlorotris(methyldiphenylphosphine)-rhodium(III), the same pattern is observed but the inner peaks of doublet and triplet are coincidental (Figure 3). For *mer*-trichlorotris(trimethylphosphine)-rhodium(III) the doublet and triplet overlap (Figure 4). The A and E peaks are assigned to the doublet and B, C and D are assigned to the triplet. These assignments give $J_{Rh-P_2} = 10.7$ Hz and J_{Rh-P_1}, $J_{Rh-P_3} = 7.2$ Hz, which are about the same as for the other methylphosphine complexes.

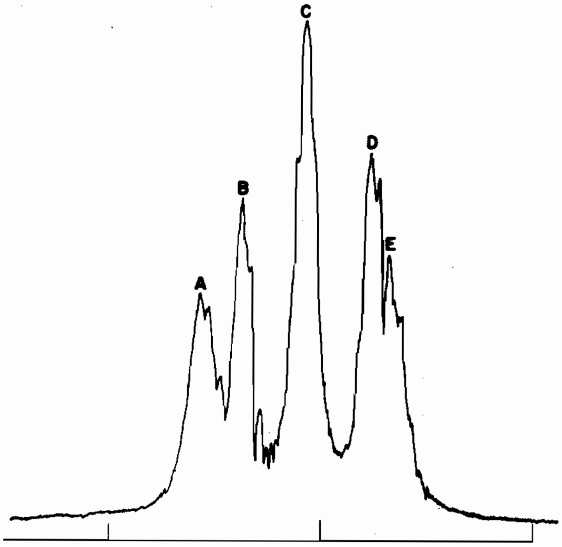

Figure 4. Proton nmr spectrum of mer-Trichlorotris(trimethylphosphine)rhodium(III).

mer-Trichlorotris(diethylphenylphosphine)rhodium-(III) has in the methyl region a quintet (rel. intensity = 2) from the « virtually » coupled methyl groups

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(29) F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 2700 (1968).

on $P_{1,3}$ and two overlapping triplets (rel. int. = 1) from the methyl groups on P_2 which are split by phosphorus (14.5 Hz) and by the methylene protons (7.4 Hz). The methylene region is very complex. The methyl regions of the triethylphosphine complex arising from the $P_{1,3}$ ligands and the P_2 ligands are superimposed to give a broad quintet with some additional fine structure (Figure 5). The spectrum was not analyzed. It is clear from these latter two spectra that ^{31}P magnetic resonance is more advantageous for structural assignments than is pmr at 60 MHz without double resonance techniques.

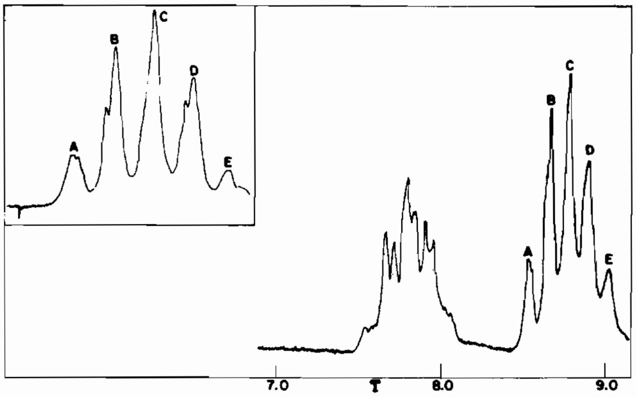

Figure 5. Proton nmr spectrum of mer-Trichlorotris(-triethylphosphine)rhodium(III).

Electronic absorption spectra. The electronic spectra in the 4000-7000 Å region generally have one broad symmetrical band in the region of 4190-4480 Å (Table IV) and an intense charge transfer band beginning about 4000 Å. It is noted that the energy for the long wavelength band for the methylphosphines (Me_3P, Me_2PhP, and $MePh_2P$) is about 300 to 900 cm^{-1} greater than for the other alkylphosphines in the same series. Further, the values for the butyl, propyl, and ethyl members of a particular series are generally constant within the limits of experimental error (±10 Å, ±50 cm^{-1}). Except for the methylphosphines mentioned above, the transition energies fall into three ranges: R_3P(22910-22990 cm^{-1}), R_2PhP-(22780-22880 cm^{-1}), and RPh_2P (22320-22370 cm^{-1}), which indicates a ligand order influenced by basicities, *i.e.*, the most basic phosphines have the largest energies. Except for the methylphosphines, the transition energies for the tertiary phosphines are intermediate between water ($Rh(H_2O)_3Cl_3$, 21310 cm^{-1})[30] and ammonia ($Rh(NH_3)_3Cl_3$, 23400 cm^{-1}).[31] It is clear that small differences in π-bonding abilities by the phosphorus ligands cannot be determined by electronic spectra of rhodium(III) complexes, since the order determined here is distinctly a σ-donor order.

Table VI. Electronic Absorption Spectra of L_3RhCl_3 Compounds

L	λ(Å)	ε_{max}(lit/mole-cm)
PBu_3	4350	630
PPr_3	4360	630
PEt_3	4350	630
PMe_3	4190	630
PBu_2Ph	4390	950
PPr_2Ph	4370	610
PEt_2Ph	4370	630
PMe_2Ph	4270	670
$PBuPh_2$	4480	910
$PPrPh_2$	4480	1000
$PEtPh_2$	4470	840
$PMePh_2$	4410	750

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(30) E. Blasius and W. Preetz, *Z. Anorg. Allgem. Chem.*, 335, 1 (1965).

(31) H. H. Schmidtke, *Z. Anorg. Allgem. Chem.*, 339, 103 (1965).