In the formation of the stable square-planar tetraglycine complex, MC^{2-}, dissociation of three protons along with intramolecular rearrangement would be expected to require considerable time before the system can reach equilibrium. This behavior was observed in the potentiometric titration as base was added between $a = 1$ and $a = 4$. The same was true of the back titration for which association of three protons and the reverse intramolecular rearrangement to an octahedral complex occur.

Bis(triphenylphosphine)(π-allyl)rhodium Complexes

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Contribution from Shell Development Company, Emeryville, California.
Received April 17, 1967

Abstract: A series of novel bis(triphenylphosphine)(π-allyl)rhodium complexes is described. The nmr spectra of these compounds not only confirm their structures but also have some interesting features. Coupling is observed between rhodium and the hydrogen of the *central* carbon only of the allyl grouping (and even to the methyl protons in the methallyl complex), whereas only the hydrogens attached to the *terminal* carbons of the allyl grouping are coupled with the phosphorus nuclei. An explanation is given on the basis of simple MO theory. In the presence of excess triphenylphosphine the allyl group stays π-bonded, but rapid exchange occurs between free and complexed triphenylphosphine.

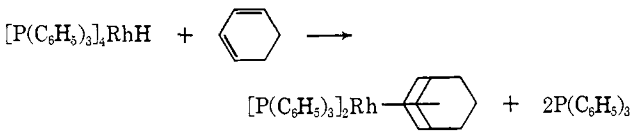
Until very recently allyl complexes of rhodium were unknown. The first example of an allylrhodium compound reported was dichloro(*trans,trans,trans*-1,5,9-cyclododecatrienyl)rhodium.[1] Subsequently, the addition of allyl chloride to chlorotris(triphenylphosphine)rhodium was reported to yield dichlorobis(triphenylphosphine)allylrhodium;[2] the reaction of allyl chloride with chlorodicarbonylrhodium in aqueous methanol was shown to give di-μ-chloro-tetrakis(allyl)-dirhodium[3] from which further derivatives were prepared.[3] Tris(allyl)rhodium finally could be obtained by treating di-μ-chloro-tetrakis(allyl)dirhodium with allylmagnesium chloride.[4] These compounds can be regarded in a formal sense to be derived from rhodium(III). So far only one example of a rhodium(I)–allyl compound has been reported, namely, (cyclooctadiene-1,5)(π-allyl)rhodium.[5] This paper is concerned with the preparation and properties of a series of new rhodium(I)–allyl complexes of the type bis(triphenylphosphine)(π-allyl)rhodium.

Preparation of Bis(triphenylphosphine)(π-allyl)rhodium Complexes. The reaction of chlorotris(triphenylphosphine)rhodium[6] with allylmagnesium chloride in ether solution yields bis(triphenylphosphine)(π-allyl)rhodium according to the equation

$$[P(C_6H_5)_3]_3RhCl + C_3H_5MgCl \longrightarrow [P(C_6H_5)_3]_2Rh(\pi\text{-}C_3H_5) + MgCl_2 + P(C_6H_5)_3$$

After recrystallization from a concentrated benzene solution by addition of diethyl ether the compound can be obtained as a crystalline yellow solid. In the same way bis(triphenylphosphine)(π-methallyl)rhodium and bis(triphenylphosphine)(π-crotyl)rhodium have been prepared.

The addition of a conjugated diolefin to hydridotetrakis(triphenylphosphine)rhodium[7] provides an alternative method for the preparation of bis(triphenylphosphine)(π-allyl)rhodium complexes. Bis(triphenylphosphine)(π-cyclohexenyl)rhodium, bis(triphenylphosphine)(π-cyclooctenyl)rhodium, and bis(triphenylphosphine)(π-crotyl)rhodium have been obtained in this manner from the addition of cyclohexadiene-1,3, cyclooctadiene-1,3, and butadiene, respectively. The reaction, as exemplified for the case of the cyclohexenyl complex, proceeds according to



All bis(triphenylphosphine)(π-allyl)rhodium complexes are yellow crystalline solids, thermally stable to ~170° where decomposition occurs without previous melting. Solvents, especially aromatic hydrocarbons and ethers, are easily incorporated into the crystals and could never be removed completely. The complexes are moderately soluble in aromatic hydrocarbons, sparingly soluble in ethers, and practically insoluble in aliphatic hydrocarbons. The compounds are highly sensitive to air in solution, much less so in the solid state. Protic solvents decompose bis(triphenylphosphine)(π-allyl) complexes in contrast to (cyclooctadiene-1)(π-allyl)rhodium.[5] This reaction has been used to obtain a chemical proof for the structure of the crotyl complex

$$[P(C_6H_5)_3]_2Rh(\pi\text{-}C_4H_7) + H^+ \longrightarrow \{[P(C_6H_5)_3]_2Rh\}^+ + C_4H_8$$

A mass spectroscopic analysis of the gas evolved showed that it contained butene as the only hydrocarbon. The infrared spectra of the bis(triphenylphosphine)(π-allyl)-

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[1] G. Paiaro, A. Musco, and G. Diana, *J. Organometal. Chem.* (Amsterdam), 4, 466 (1965).

[2] M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborne, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

[3] J. Powell and B. L. Shaw, *ibid.*, 236 (1966).

[4] J. Powell and B. L. Shaw, *ibid.*, 323 (1966).

[5] A. Kasahara and K. Tanaka, *Bull. Chem. Soc. Japan*, 39, 634 (1966).

[6] F. H. Jardine, J. A. Osborne, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

[7] K. C. Dewhirst, to be published.

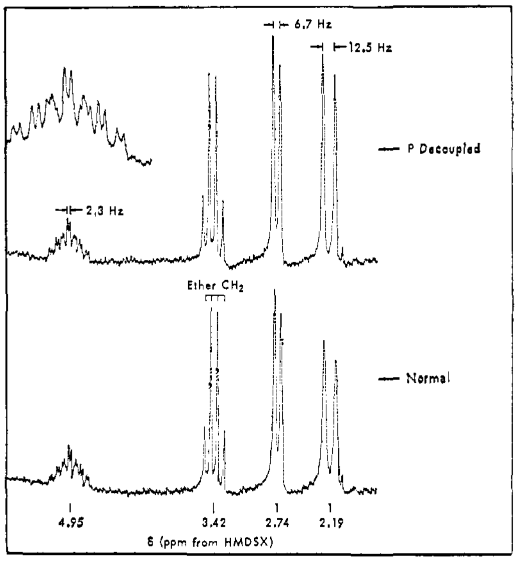

Figure 1. 100-MHz nmr spectra of bis(triphenylphosphine) (π-allyl)rhodium in C_6H_5Cl at ambient temperature (~30°).

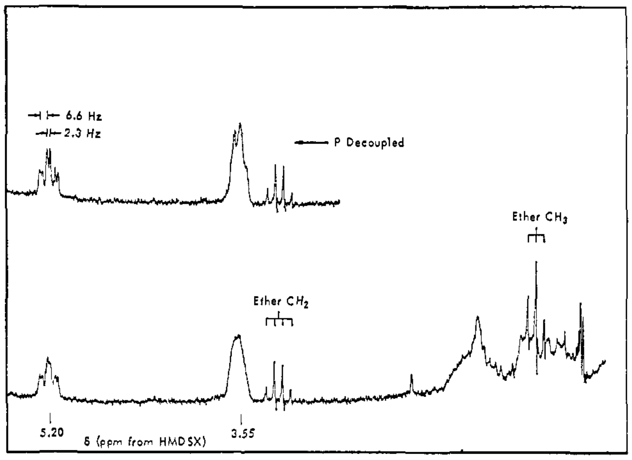

Figure 2. 100-MHz nmr spectra of bis(triphenylphosphine)(π-cyclohexenyl)rhodium in C_6H_5Cl at ambient temperature (~30°).

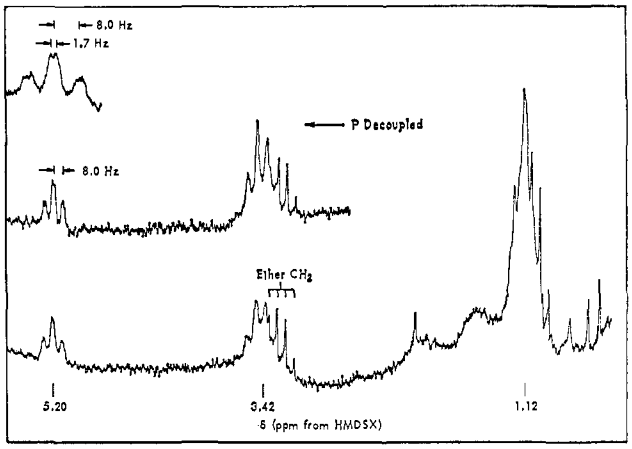

Figure 3. 100-MHz nmr spectra of bis(triphenylphosphine)(π-cyclooctenyl)rhodium in C_8H_5Cl at ambient temperature (~30°).

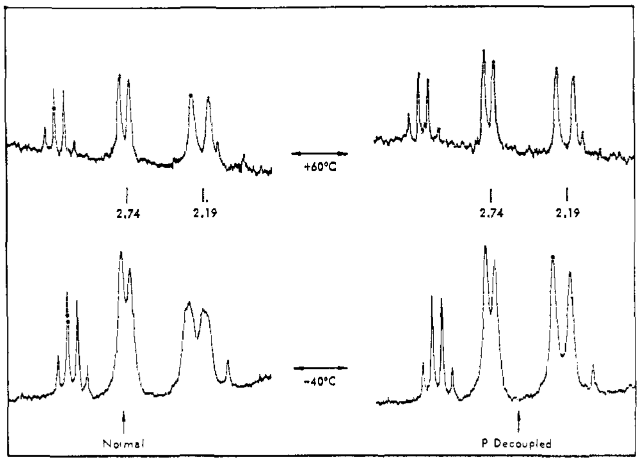

Figure 4. Upfield portion of 100-MHz nmr spectra of bis(triphenylphosphine)(π-allyl)rhodium in C_6H_5Cl as a function of temperature.

rhodium complexes are dominated by the bands of complexed triphenylphosphine and are not useful for obtaining structural information.

Nmr Spectra of Bis(triphenylphosphine)(π-allyl)rhodium Complexes. Confirmation of the structures of these complexes was obtained from their nmr spectra. Figures 1–3 show the spectra of bis(triphenylphosphine)(π-allyl)rhodium, bis(triphenylphosphine)(π-cyclohexenyl)rhodium, and bis(triphenylphosphine)(π-cyclooctenyl)rhodium, and Table I summarizes the parameters. The proton chemical shifts and proton–proton coupling constants are very similar to those found in other π-allyl complexes. The first interesting feature is the coupling between the rhodium nucleus and the hydrogen on the central carbon of the allyl group and to that proton only. As will be shown below, this coupling is indicative of a fairly strong σ-type interaction between rhodium and the central carbon. The small coupling between the hydrogens, H_A and H_B, attached to the terminal carbon atoms of the allyl grouping is manifested only in a line broadening; sharpening of the respective proton doublets occurs upon irradiation of the phosphorus nuclei at their resonance frequency (double irradiation). The lines for H_A are slightly broader (smaller peak intensity) than those for H_B, and this is probably due to a slightly larger interaction of H_A with the rhodium nucleus. This interaction is too small to be detectable as a splitting of the resonance lines and hence this Rh–H coupling cannot be greater than about 0.5 Hz. The broadening caused by coupling is only slightly dependent on temperature (Figure 4). The chemical shift of the phosphorus (δ_P *ca.* −43) upon complexation shows considerable change from free triphenylphosphine (δ_P −9).[8] Unfortunately not enough is known about phosphorus chemical shifts to permit an interpretation of this result to be made.

Bis(triphenylphosphine)(π-methallyl)rhodium has a very interesting nmr spectrum in deuteriobenzene (Figure 5). Essentially the same spectrum is obtained in chlorobenzene. The nmr parameters are also given in Table I. Some peculiarities in the spectrum will be noted. The resonance of the methyl group is split into a doublet by coupling of the methyl hydrogens with the rhodium nucleus. This coupling is about as strong as the coupling between rhodium and the H on this carbon in the other bis(triphenylphosphine)(π-allyl)rhodium complexes even though the effect is transmitted through

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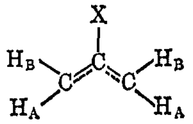
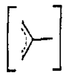
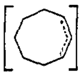
[8] Both in C_6H_5Cl solution. In THF solution δ_P for triphenylphosphine is +7.

Table I. Nmr Parameters for the Allyl Grouping in Bis(triphenylphosphine)(π-allyl)rhodium Complexes[a]



	δ_{H_A}, ppm	δ_{H_B}, ppm	δ_X, ppm	δ_P, ppm	J_{XH_A}, Hz	J_{XH_B}, Hz	$J_{H_AH_B}$, Hz	J_{RhX}, Hz
$[(C_6H_5)_3P]_2Rh$ 	2.19	2.74	4.95	−43	12.5	6.7	~0	2.3
$[(C_6H_5)_3P]_2Rh$ 	2.27	2.46	1.62 (CH_3)	−42			~0	2.1
$[(C_6H_5)_3P]_2Rh$ 		3.55	5.20	−46		6.6	~0	2.3
$[(C_6H_5)_3P]_2Rh$ 		3.42	5.20	−41		8.0	~0	1.7

[a] Chlorobenzene solution at ~30°.

an additional bond. This pronounced effect again can be accounted for by a strong σ-type interaction between the rhodium and the π electrons of the central carbon of the allyl group. The phosphorus nuclei are coupled to the protons on the terminal carbon atoms H_A and H_B of the allyl grouping. For the H_B protons this shows up only as a line broadening; the lines again are sharpened by phosphorus decoupling. For the H_A protons at δ 2.24 the multiplet contains three lines with $J_{PH_A+PH_A'}$ = 6.60 Hz (for an AA'XX' system).

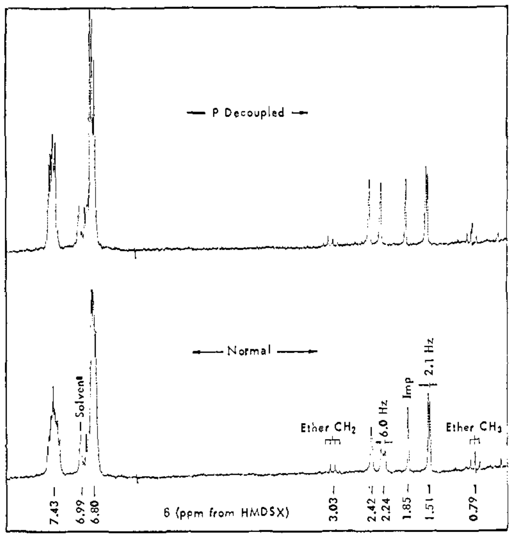
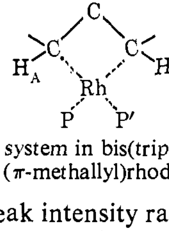


Figure 5. 100-MHz nmr spectra of bis(triphenylphosphine)(π-methallyl)rhodium in C_6H_6 at ambient temperature (~30°).



AA'XX' spin system in bis(triphenylphosphine)-(π-methallyl)rhodium

The fact that the peak intensity ratios are not 1:2:1 (the outer lines are higher than the central one) indicates that $J_{PP'} > J_{H_AH_A'}$ (there is no evidence in the literature for strong coupling between the A protons in other π-allyl complexes). In view of the results for the π-crotyl compound (discussed below), it is likely that $J_{PH_A'} = J_{P'H_A} \approx 6.0$ Hz and $J_{PH_A} = J_{P'H_A'} \approx 0$. Bis(triphenylphosphine)(π-methallyl)rhodium is the case in which these phenomena (coupling of the phosphorus nuclei to H_A and H_B *and to these protons only* and coupling of the rhodium to the methyl protons *and to these protons only*) are most pronounced. It is interesting to note that this is in contrast to the results obtained with the (π-methallyl)rhodium(III) complex dichlorobis(triphenylphosphine)(π-methallyl)rhodium, $[P(C_6H_5)_3]_2Rh(\pi\text{-}C_4H_7)Cl_2$, where the protons H_A and H_B are coupled with the rhodium as well as with the phosphorus nuclei.[9]

The normal and P-decoupled spectra of bis(triphenylphosphine)(π-crotyl)rhodium in chlorobenzene are shown in Figure 6. It is obvious from the methyl doublets (J = 6.4 and 5.8 Hz) at δ 0.82 and 0.94, respectively, that two isomers are present. Proton–proton decoupling experiments permitted the remainder of the multiplets to be assigned to the proper isomer. The nmr parameters obtained are given in Table II. A comparison with the corresponding, separated complexes with $CO(CO)_3$[10] is included. The chemical shifts in the later complexes were measured relative to benzene and cannot be readily compared with those for the rhodium complexes. Corresponding spin–spin coupling constants agree as well as could be expected considering the different natures of the complexes. A comparison of the normal with the P-decoupled spectrum shows that only *one* of the phosphorus nuclei in each isomer is coupled appreciably with proton A (J = 5.8 Hz at δ_A 2.01 and J = 6.6 Hz at δ_A 2.15). A much smaller, unresolved coupling, probably of both P nuclei to proton B, can also be detected. No difference in P chemical shifts in the two isomers was noted.

It has been shown for transition metal (π-allyl) complexes containing group V donor ligands, *e.g.*, triphenylphosphine, that the π-allyl group might under certain circumstances be converted to a σ-allyl group or a

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(9) H. C. Volger and K. Vrieze, *J. Organometal Chem.* (Amsterdam), 6, 297 (1966).

(10) D. W. Moore, H. B. Jonassen, T. B. Joyner, and A. J. Bertrand, *Chem. Ind.* (London), 1304 (1960).

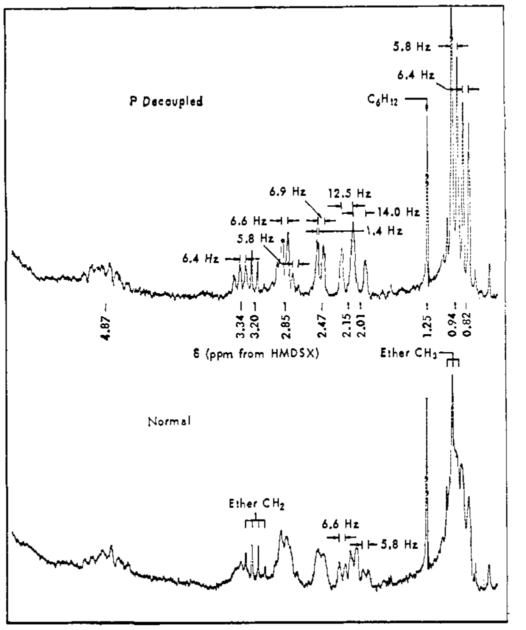
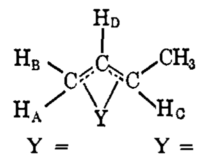
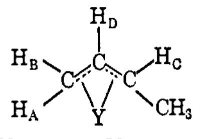


Figure 6. 100-MHz nmr spectra of bis(triphenylphosphine)(π-crotyl)rhodium isomers in C_6H_5Cl at 60°.

"dynamic" allyl group ($\delta_{H_A} = \delta_{H_B}$),[11] an effect that is likely to be temperature dependent.[9] In this connection it was of interest to study the temperature dependence of the nmr spectrum. Practically no change was detected over a temperature range of −30 to 120°, which means that the allyl group stays π-bonded (see Figure 4, for example).

Table II. Nmr Parameters for Bis(triphenylphosphine)(π-crotyl)rhodium[a]

				
	Y = Rh[P(C$_6$H$_5$)$_3$]$_2$	Y = Co(CO)$_3$	Y = Rh[P(C$_6$H$_5$)$_3$]$_2$	Y = Co(CO)$_3$
δ_{CH_3}	0.94		0.82	
δ_A	2.15		2.01	
δ_B	2.85		2.47	
δ_C	~2.9		3.35	
δ_D	~4.9		~4.9	
δ_P	−40		−40	
$J_{CH_3\text{-}HC}$	5.8	6.5	6.4	7.0
J_{AB}	<1	<0.2	<1	0.6
J_{AC}	<1		<1	
J_{AD}	12.5	10.5	14.0	12.3
J_{BC}	<1	<0.2	1.4	1.6
J_{BD}	6.6	6.3	6.9	7.1
J_{CD}	~12	10.5	~6	6.8
J_{PH_A}	6.6		5.8	

[a] δ values in ppm; J values in Hz.

The effect of adding free triphenylphosphine to the solutions of the complexes was also investigated. The nmr spectra obtained, *e.g.*, upon successive additions of a saturated solution of triphenylphosphine in tetrahydrofuran to the deuteriobenzene solution of the π-methallyl complex, are shown in Figures 7 and 8. The spectrum obtained upon the addition of a large excess of triphenylphosphine to the same complex in dichlorobenzene solution is given in Figure 9. There is no evidence in these spectra for the formation of a σ-allyl or of a "dynamic" allyl form; the features of the π-allyl group are preserved. Instead, a sharpening of the lines for H_A and H_B and a broadening of those for the phenyl protons occur. No separate spectrum from the phenyl protons of the free triphenylphosphine can be detected, but the chemical shifts of these protons approach those of the free ligand with increasing concentration. Also, only a single chemical shift of phosphorus is found, which, with increasing ligand concentration, changes gradually from that characteristic of the complexed ligand to that characteristic of the free ligand. From these observations it is concluded that complexed ligands exchange rapidly with free triphenylphosphine in solution, the rate of exchange increasing with increasing concentration of free triphenylphosphine. This rapid exchange accounts for the increased averaging of the phosphorus chemical shifts and also leads to a sharpening of the lines for H_A and H_B.

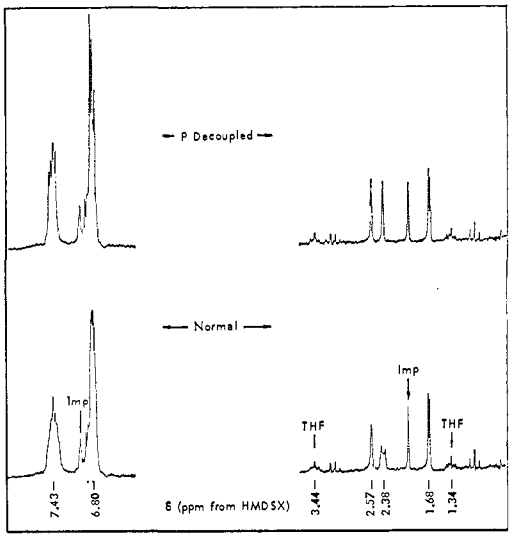


Figure 7. 100-MHz nmr spectra of bis(triphenylphosphine)(π-methallyl)rhodium in C_6D_6 at ambient temperature (~30°) with a small added amount of THF saturated with triphenylphosphine.

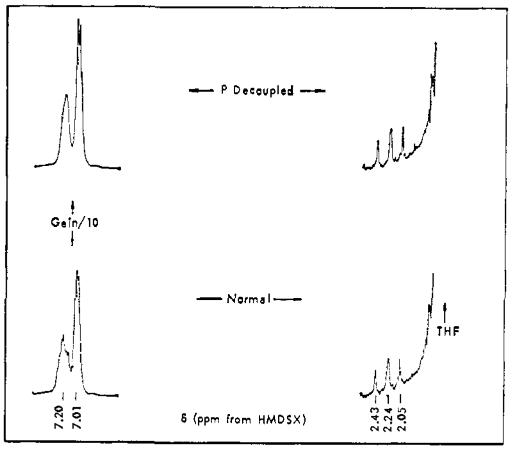


Figure 8. 100-MHz nmr spectra of bis(triphenylphosphine)(π-methallyl)rhodium in C_6D_6 at ambient temperature (~30°) with a large added amount of THF saturated with triphenylphosphine.

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[11] (a) J. W. C. Chien and H. C. Dehm, *Chem. Ind.* (London), 745 (1961); (b) J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Commun.*, 78 (1965).

Table III

Phosphorus	Rhodium	Allyl	MO
$\psi_1' = \frac{1}{\sqrt{2}}(\varphi_1' + \varphi_2')$	$4d_{z^2}$, 5s	$\psi_1 = \frac{1}{2}(\varphi_1 + \sqrt{2}\varphi_2 + \varphi_3)$	σ type
$\psi_2' = \frac{1}{\sqrt{2}}(\varphi_1' - \varphi_2')$	$4d_{xz}$	$\psi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3)$	π type
	$4d_{yz}$	$\psi_3 = \frac{1}{2}(\varphi_1 - 2\varphi_2 + \varphi_3)$	. . .

Discussion

The nmr spectra show clearly that, in these bis(triphenylphosphine)(π-allyl)rhodium complexes, the allyl grouping maintains a typical, symmetrical π structure under a variety of experimental conditions. This result and the spin-spin coupling data observed can be understood, at least qualitatively, on the basis of simple MO theory and the assumption that the couplings arise by Fermi contact interactions.[12]

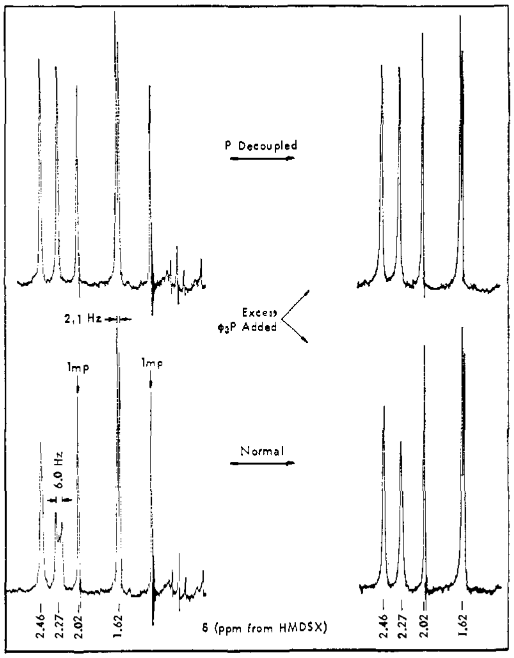

Figure 9. 100-MHz nmr spectra of bis(triphenylphosphine)(π-methallyl)rhodium in C_6H_5Cl at ambient temperature ($\sim$30°) with a large excess of added triphenylphosphine.

If the geometry shown in Figure 10 (based on structure determinations of other π-allyl complexes, *e.g.*, $[(\pi\text{-allyl})PdCl]_2)$[13] is assumed for these complexes, in which the plane of C_1, C_2, C_3, and X is inclined at some angle θ (near 90°) to that of the Rh and P nuclei, then the MO's can be constructed from the set of interacting orbitals shown in Table III. Here, φ_1, φ_2, and φ_3 are the p_z orbitals centered on C_1, C_2, and C_3, respectively, ψ_1 and ψ_2 being then symmetric and antisymmetric (with respect to the *yz* plane) π MO's, respectively, of the π-allyl group. Similarly, ψ_1' and ψ_2' are the symmetric and antisymmetric MO's for P_1 and P_2 constructed from the lone-pair orbitals φ_1' and φ_2' centered on P_1 and P_2.

The metal–ligand bonding can include both σ (dative bonding) and π (back bonding) types. A combination of the symmetric orbitals, ψ_1', $4d_{z^2}$, 5s, and ψ_1, leads to a σ-type MO, whereas a combination of the antisymmetric ones, ψ_2', d_{xz}, and ψ_2, leads to a π-type MO.

The π-type MO has a nodal plane through Rh, C_2, and X, and therefore is not expected to give rise to any Rh coupling or to any P–X coupling. On the other hand, this MO is very likely responsible for the observed coupling of P to the H's on C_1 and C_3. The difference in size of J_{PH_A} ($\sim$6 Hz) and J_{PH_B} ($\sim$0) can be assumed to be due to an unsymmetrical relationship of P to H_A and H_B. It is known that, in other organic complexes, a *trans* J_{PH} is larger than a *cis* one.[14] This fact suggests that each P should be coupled only to the hydrogen (H_A) *anti* to it and not to the hydrogens H_A and H_B *syn* to it. The observations of J_{PH} are fully in accord with this expectation. The downfield shift of H_B relative to H_A suggests that H_B is nearer to its *syn* P than is H_A. We conclude, then, that the plane of C_1, C_2, C_3, and X is inclined at some angle θ, greater than 90° (see Figure 10), to that of the Rh, P_1, and P_2 nuclei.

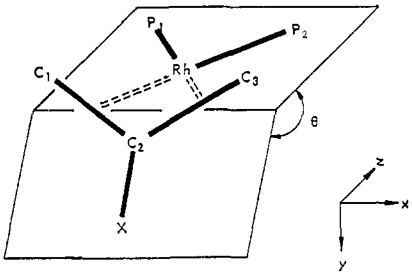

Figure 10. Assumed geometry of bis(triphenylphosphine)(π-allyl)rhodium complexes.

The σ-type MO can give rise to J_{RhX} provided that the 5s orbital of Rh is used in its construction. This MO could also give rise to J_{PX}, but such couplings would be expected to be smaller than J_{RhH} ($\sim$2 Hz) because of the extra bond between the nuclei. It is not surprising, then, that no J_{PX} was detected. The smaller coefficients for φ_1 and φ_3 relative to that for φ_2 in ψ_1 would suggest that the contribution by the σ-type MO to J_{PH_A} and J_{PH_B} should be even less than its contribution to J_{PX}, and hence negligible. We conclude then that the σ-type MO gives rise only to J_{RhX} and the π-type one only to J_{PH}.

If the above conclusion is valid, then the change in J_{RhX} from one complex to another could be used to determine the change in the amount of dative bonding.

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(12) E. Fermi, *Z. Physik*, **60**, 320 (1930).

(13) A. E. Smith, *Acta Cryst.*, **18**, 331 (1965).

(14) J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964); C. A. Reilly, unpublished results.

Similarly, the change in $J_{\mathrm{PH_A}}$ might be used to determine the change in the amount of back bonding (assuming no change in geometry). Unfortunately, values for $J_{\mathrm{PH_A}}$ are not always readily available because of averaging by rapid interchange of triphenylphosphine ligands.

The values for J_{RhX} in the π-allyl, π-cyclohexenyl, and π-cyclooctenyl complexes are 2.3, 2.3, and 1.7 Hz, respectively, indicating that the degree of dative bonding, *i.e.*, shift of electronic density from the ligand to the metal atom, is about the same in all three complexes. In the π-methallyl complex, $J_{\mathrm{RhX}} = 2.1$ Hz, *i.e.*, about the same as in the above three complexes in spite of the fact that the coupling takes place through an extra bond. This suggests that the dative bonding in the π-methallyl complex is stronger than in the others, and is consistent with the increased dative bonding expected because of the electron-donating character of the methyl group on C_2.[15]

The nmr data for the dynamic form of the π-allyl group in other complexes suggest very strongly that rapid reorientation of the terminal methylene groups occurs about the C_1–C_2 and the C_2–C_3 bonds.[16] This means that the bonding between the allyl ligand and the metal is largely localized between C_2 and the metal, *i.e.*, that the bonding occurs mainly *via* a σ-type MO. However, in the rhodium complexes studied here, the nmr data suggest that π bonding may be more important; conversion to a dynamic form would then be less likely. Indeed, thermal energy does not bring about such a change, nor does the presence of an excess of free triphenylphosphine; instead, the more loosely bound triphenylphosphine ligands undergo exchange.

Experimental Section

Preparation *via* the Grignard Method. In a Schlenk tube 5 g of chlorotris(triphenylphosphine)rhodium[6] (~5.5 mmoles) is suspended in 30 ml of dry ether under nitrogen or argon. To the mixture is added 6 mmoles of the corresponding allylmagnesium chloride solution with stirring at room temperature. The suspension gradually turns from red to yellow and the reaction is completed in ~24 hr. The mixture is filtered by suction (in an inert atmosphere); the solid is dissolved in benzene or toluene and filtered again by gravity. The filtrate, which may vary in color from yellow to red, is concentrated to 5–10 ml; then the same volume of ether is added. Yellow crystals precipitated which are filtered, washed with little ether and a hydrocarbon solvent (*e.g.*, hexane), and finally dried, yield ~3 g (~80%).

If the reaction is carried out with bromotris(triphenylphosphine)-rhodium and the corresponding allylmagnesium bromide, a practically pure product can be obtained by simply filtering the reaction mixture. All impurities are soluble in ether.

Anal. Calcd for bis(triphenylphosphine)(π-allyl)rhodium, $C_{39}H_{35}P_2Rh$: C, 70.0; H, 5.2; P, 15.4; Rh, 9.3. Found: C, 71.1; H, 5.5; P, 15.5; Rh, 9.5. Calcd for bis(triphenylphosphine)-(π-methallyl)rhodium, $C_{40}H_{37}P_2Rh$: C, 70.4; H, 5.5; P, 15.1; Rh, 9.1. Found: C, 71.1; H, 5.7; P, 14.4; Rh, 8.5.

Preparation from Hydridotetrakis(triphenylphosphine)rhodium. (a) Reaction with Cyclic Diolefins. A Schlenk tube is charged in an inert atmosphere with 5 g of hydridotetrakis(triphenylphosphine)-rhodium[7] and 20–30 ml of the diene, and the mixture is stirred at room temperature until a clear solution results (0.5–1 hr). The diene is then stripped off under reduced pressure and the residue treated with 5 ml of ether, whereupon yellow crystals precipitate which are washed with a little ether and more hydrocarbon solvent and dried, yield 2.5–3 g (80–95%).

Anal. Calcd for bis(triphenylphosphine)(π-cyclohexenyl)rhodium, $C_{42}H_{39}P_2Rh$: C, 71.1; H, 5.6; P, 14.5; Rh, 8.7. Found: C, 69.9; H, 5.4; P, 13.9; Rh, 8.2. Calcd for bis(triphenylphosphine)(π-cyclooctenyl)rhodium, $C_{44}H_{43}P_2Rh$: C, 71.8; H, 5.7; P, 14.0; Rh, 8.4. Found: C, 70.9; H, 6.0; P, 13.0; Rh, 8.0.

(b) Reaction with Butadiene. A glass pressure vessel is charged with 5 g of hydridotetrakis(triphenylphosphine)rhodium[7] in an inert atmosphere. About 30 ml of butadiene is condensed on it, and the closed vessel is kept stirred (magnetically) at a temperature of ~40° for ~12 hr. A clear yellow solution is obtained which is cooled rapidly to $-78°$; yellow crystals precipitate which are filtered quickly, washed with a minimum of ether and more hydrocarbon solvent, and finally dried, yield ~2 g (~70%).

Anal. Calcd for bis(triphenylphosphine)(π-crotyl)rhodium, $C_{40}H_{37}P_2Rh$: C, 70.4; H, 5.5; P, 15.1; Rh, 9.1. Found: C, 69.8; H, 5.6; P, 15.4; Rh, 8.8.

Nmr Spectra. All nmr spectra were obtained on a Varian HR-100 spectrometer equipped with a field-frequency lock similar to that described by Elleman, Manatt, and Pearce.[17] The spectrometer was operated in the frequency-sweep mode. The P decoupling was done with an NMR Specialties SD-60 spin decoupler locked to an audiooscillator. Proton chemical shifts are quoted in ppm downfield from external hexamethyldisiloxane and P chemical shifts in ppm from external trimethyl phosphate.

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