Five-co-ordinate Rhodium(I) Complexes with Three Metal–Olefin Bonds

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Summary One-to-one complexes of the ligands (*o*-styryl)$_3$P and (*o*-styryl)$_3$As with RhX (X = Cl, Br, I) have been prepared: their properties indicate a pentaco-ordinate trigonal bipyramidal structure with the three olefin groups occupying the three trigonal (C_3), and the halogen and phosphorus (or arsenic) atoms the apical, positions.

THE announcement by van der Ent and van Soest[1] of a pentaco-ordinate iridium(I)–ethylene complex of formula $IrCl(C_2H_4)_4$ prompts us to report the preparation, properties, and possible structure of a rhodium(I) complex containing the potentially quadridentate ligand tri-*o*-styrylphosphine.

Reaction of equimolar quantities of biscyclo-octa-1,5-diene-$\mu\mu'$-dibromodirhodium(I) and tri-*o*-styrylphosphine in chloroform at 25° gives a yellow crystalline 1 : 1 : 1 complex of rhodium, halogen, and ligand. The complex is monomeric in chloroform and a non-conductor in acetone solution.

I.r. spectra (Nujol mull) show disappearance of the carbon–carbon stretching frequency of the free ligand at 1627 cm^{-1} and the appearance of a new, very strong band at 1267 cm^{-1}, observed in other metal–olefin complexes, which has been assigned[2] to a combination of ν (C=C) and δ (CH$_2$). Raman spectroscopy confirms the absence of a free vinyl group in the solid state, the region 1590—1800 cm^{-1} being free from emission bands.

N.m.r. spectra (CDCl$_3$)show only three proton resonances in the region expected for vinyl groups co-ordinated to a metal atom (see Table 1): it has been shown earlier that the β-vinylic protons in [Ph$_2$P(*o*-styryl)]$_2$RhCl absorb[3] at τ 5·8 and 6·8. No change in the spectrum occurs on cooling to —62°. Addition of an excess of triphenylphosphine to the solution does not affect the resonance of the vinyl protons, indicating that the co-ordinated olefin groups are not displaced; no new products can be isolated from reactions

TABLE 1. *N.m.r. absorptions*

	Phenyl	α	β-*cis*	β-*trans*	*J*(*cis*)	*J*(*trans*)
(*o*-Styryl)$_3$P	2·1—2·7	2·5	4·85	4·45	11·2	17·8
Area	5		1	1		
(*o*-Styryl)$_3$PRhBr	2·1—2·6	3·78	5·45	6·6		
Area	4	1	1	1	8·7	11·7

with this ligand or with carbon monoxide. The chelate diarsine *o*-phenylenebisdimethylarsine does react, however.

With the exception of iodo(tristyrylarsine)rhodium(I), the behaviour of the other complexes is similar to that of the bromo-phosphine described above (see Table 2).

TABLE 2. *Physical properties of complexes* RhX(*o*-styryl)$_3$L

X	L	Colour	M.p.[a]
Cl	P	Cream	282°
Br	P	Buff	277°
I	P	Yellow	dec. at 236°
Cl	As	Yellow	239°
Br	As	Buff	244°
I	As	Red	dec. at 190°

[a] With decomposition.

Satisfactory analyses for carbon, hydrogen, and halogen have been obtained in all cases.

Two obvious structures suggest themselves for a five-co-ordinate complex RhX·P(*o*-styryl)$_3$. The first is a square pyramid with an apical phosphorus atom, the four square positions being occupied by the halogen and the three olefin groups. This would involve two different types of vinyl groups, namely *cis* and *trans* to the halide. I.r., Raman, and n.m.r. studies, however, suggest that only one type of vinyl group is present. The other likely shape is a trigonal bipyramid with apical halogen and phosphorus atoms. The centres of the carbon–carbon bonds in the three vinyl groups are presumably in the equatorial plane, the three C=C bonds being approximately perpendicular to it. Preliminary *X*-ray studies[4] are consistent with this structure. Thus the molecule would have C_3 symmetry and the spectral properties would be explained satisfactorily.

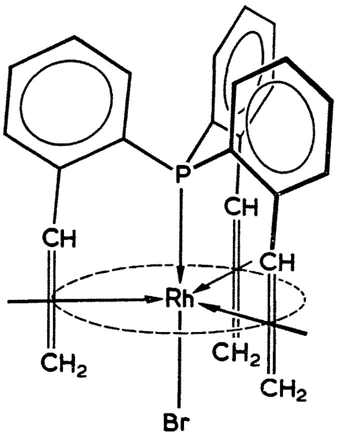

FIGURE. *Suggested structure of* [Rh·P(*o*-styryl)$_3$Br].

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