### 389. *Alkyls and Aryls of Transition Metals. Part V. Rhodium Derivatives.*

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ORGANO-DERIVATIVES of the general type $[MX_lR_nL_n]$, where M is a transition metal, X a halogen, R an alkyl or an aryl group, and L a mono- or bi-dentate tertiary phosphine, have been prepared from all of the metals of Group VIII [1,2] including iridium.[3] Of these metals, rhodium has proved the most intractable and here we describe attempts to obtain organo-derivatives of rhodium derived from halides of the types $[RhX_3(PR_3)_3]$ and $[RhClCO(PR_3)_2]$ by reaction with Grignard or lithium reagents. No alkyl or aryl derivative of rhodium was known, but a stable hydride $[RhHCl_2(AsMePh_2)_3]$ had been reported,[4] and so no particular difficulty was expected in preparing a corresponding organic derivative. Nevertheless all attempts to obtain methyl, phenyl, *o*-tolyl, or mesityl derivatives from the above two halides have proved unsuccessful. It has been found, however, that 1-naphthylmagnesium bromide reacts with $[RhBr_3L_3]$ (L = PPr^n_3 or PEt_2Ph) to give small yields of an unusual five-co-ordinated complex $[RhBr(1\text{-naphthyl})_2L_2]$ of surprisingly high stability. These complexes are monomeric, diamagnetic, and their dipole moments are ~3 D. They were shown to be 1-naphthyl derivatives by reaction with deuteroacetic acid which produced 1-deuteronaphthalene, and by thermal decomposition giving 1,1'-binaphthyl. The dipole moments are lower than would be expected if the tertiary phosphine molecules were in *cis*-positions at right angles to each other. Thus *cis*-$[PtMe_2(PEt_3)_2]$ has a moment of 5·55 D,[5] and that of *cis*-$[PtCl_2(PEt_3)_2]$ is 10·9 D.[6] The phosphine molecules must, therefore, be in approximately *trans*-positions and certainly neither can be *trans* to the negatively charged bromine atom. On this basis, and by taking into account the steric requirements of the ligands, only the arrangements shown in the Figure are possible. It has been shown that, in *trans*-$[Co(mesityl)_2(PEt_2Ph)_2]$, the bulky phosphine ligands on either side of the cobalt atom produce an approximately spherical structure with a deep groove around it (like a yo-yo)
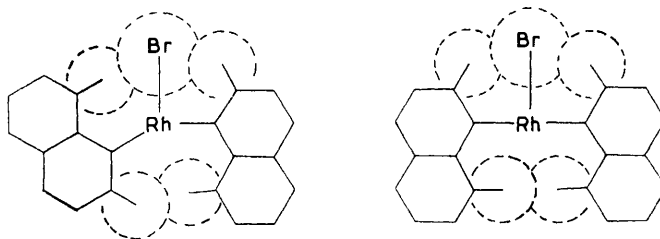
Possible models of $[RhBr(1\text{-naphthyl})_2(PR_3)_2]$. The tertiary phosphine molecules lying approximately above and below the rhodium atom have been omitted for clarity. The broken lines indicate the van der Waals surfaces of the bromine and contact hydrogen atoms.

and that the mesityl groups fill the groove completely.[7] The above rhodium complexes will have a similar structure, with the bromine and naphthyl groups filling the groove. This can be done with either an approximately square pyramidal or trigonal bipyramidal arrangement of ligands (see Figure). The dipole moment of such molecules would be

[1] Chatt, *Record of Chemical Progress*, 1960, **21**, 147, and references therein.
[2] Chatt and Shaw, *J.*, 1961, 285, and references therein.
[3] Chatt and Shaw, unpublished results.
[4] Lewis, Nyholm, and Reddy, *Chem. and Ind.*, 1960, 1386.
[5] Chatt and Shaw, *J.*, 1959, 705.
[6] Chatt and Wilkins, *J.*, 1952, 4300.
[7] Owston and J. M. Rowe, *J.*,1963, in the press.

about 2—3 D. The fact that the observed values are slightly higher suggests that the Br–Rh–P angles are rather greater than 90° as are the Br–Pt–P angles in *trans*-[PtHBr(PEt₃)₂].[8]

The organorhodium compounds described here are the only known five-co-ordinate complexes of rhodium(III). The metal will have d^2sp^2 hybridisation; since it is normally six-co-ordinate it can be described as electron deficient, and so should be liable to attack by nucleophilic reagents. The complexes must, therefore, owe their stability to the very compact arrangement of ligands around the metal atom, which completely shield it from attacking reagents in spite of its electron deficiency. In this way the organorhodium complexes are very closely similar to the planar dimesityl and bispentachlorophenyl derivatives of iron and cobalt of the types, *trans*-[M(mesityl)₂(PR₃)₂]. Here the *ortho*-substituents are especially effective in shielding the octahedral oppositions of the metal atom from attack,[2,7] and impose the low-spin planar configuration which is otherwise unknown amongst complexes of those metals with monodentate ligands.

Experimental.—*Bromodi*-1-*naphthylbis*-(*tri*-*n*-*propylphosphine*)*rhodium*(III). A benzene solution of tribromotris(tri-n-propylphosphine)rhodium(III), made by treating an ethanolic solution of commercial rhodium trichloride with the phosphine,[9] was added to an excess (100%) of a solution of 1-naphthylmagnesium bromide in tetrahydrofuran. The mixture was stirred for 30 min., cooled to 0°, and hydrolysed with ice-cold dilute hydrobromic acid. The organic layer was immediately separated, dried (Na₂SO₄), and evaporated to dryness. Naphthalene was sublimed from the residue under a vacuum (0·5 mm.) at 50° and the remaining solid chromatographed on neutral alumina in benzene to afford the pure *product* (3%) as an off-white powder, m. p. 137—139° [Found: C, 60·45; H, 7·5; Br, 9·5%; *M* (cryoscopically in benzene), 707 (3·025% solution). C₃₅H₂₉BrP₂Rh requires C, 60·2; H, 7·45; Br, 10·55%; *M*, 758], also prepared from μ-dibromotetrabromotetrakis(tri-n-propylphosphine)dirhodium(III) [9] in 1% yield.

Bromodi-1-*naphthylbis*(*diethylphenylphosphine*)*rhodium*(III). This was similarly prepared from tribromotris(diethylphenylphosphine)rhodium(III) and recrystallised from ethyl acetate in 10% yield as pale pink plates, m. p. 144—146° [Found: C, 62·9; H, 5·7; Br, 9·5%; *M* (cryoscopically in benzene), 726 (2·035% solution). C₃₀H₂₉BrP₂Rh requires C, 62·5; H, 5·8; Br, 10·4%; *M*, 770].

The *complex* [RhBr(1-naphthyl)₂(PPrⁿ₃)₂] was heated with deuteroacetic acid in dry benzene for 48 hr. at 60° in a sealed tube. The product was warmed under a vacuum in a flask attached to a cold trap and yielded a white crystalline sublimate which was identical (infrared spectrum) with 1-deuteronaphthalene obtained by reaction of 1-naphthyl-lithium with deuterium oxide.[10] When the complex [RhBr(1-naphthyl)₂(PEt₂Ph)₂] was heated under a vacuum in a sublimation block decomposition occurred with the formation of a white crystalline sublimate or colourless oil on the cooler parts of the tube. This was identical (infrared spectrum) with 1,1′-binaphthyl obtained from 1-naphthylmagnesium bromide and anhydrous cupric bromide.[11]

Dipole moments of [RhBr(1-naphthyl)₂L₂] in benzene at 25°.*

	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	$_TP$	$_EP$	$_oP$	μ (D)
RhBr(1-naphthyl)₂(PPrⁿ₃)₂ {	1·842	1·950	—	—	—	—	—	—
	2·814	1·991	—	(0·47)	(433·9 †)	(209·7)	192·7 †	3·1 †
RhBr(1-naphthyl)₂(PEt₂Ph)₂ {	2·562	2·361	—	—	—	—	—	—
	2·799	2·325	—	(0·47)	494·8 †	(213·0)	249·8 †	3·5 †

* For the meaning of the symbols see ref. 5. † Calculated by using estimated values of densities and refractivities (see Part I of this series [5]).

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[8] Owston, Partridge, and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 246.
[9] Chatt, Johnson, and Shaw, unpublished results.
[10] Goubeau, Luther, Feldmann, and Brandes, *Chem. Ber.*, 1953, **86**, 214.
[11] Schoepfle, *J. Amer. Chem. Soc.*, 1923, **45**, 1566.