Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. Part X.[1] Five-co-ordinate Rhodium(I) Complexes of *ortho*-Vinylphenyl Phosphines and Arsines

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Rhodium(I) complexes of three ligands, tris-*o*-vinylphenyl-phosphine (tvpp) and -arsine (tvpa) and phenyl (bis-*o*-vinylphenyl)phosphine (dvpp), have been prepared. All complexes are five-co-ordinate with the empirical formula RhXL, the bis(vinylphenyl) compounds being dimeric with bridging halogen atoms. The tris(vinylphenyl)-arsine rhodium complexes, although apparently structurally similar to those of the phosphine show an unexpected ease of displacement of the olefin groups by many ligands (*e.g.* CO or PPh_3). The iodo-complex adopts a dimeric halogen-bridged structure with one free olefin group. The halogen bridges in these complexes are easily split by both ordinary σ-type ligands and those which form ($\sigma + \pi$) double bonds, forming five-co-ordinate monomeric species. The relative tendencies of these polydentate ligands to form five-co-ordinate rhodium(I) complexes is discussed.

THIS study of the synthesis and reactions of the rhodium(I) complexes of tris-olefin tertiary-phosphine and -arsine groups, which are potential quadridentate ligands, is of interest for comparison with the behaviour of the related d^8 platinum(II) complexes of these ligands.[1] Earlier work[2] with *o*-vinylphenyldiphenylphosphine showed that chelation is possible and we hoped to attach all three double bonds to the metal atom. While our work was in progress Clark and Hartwell[3] showed that tris(but-3-enyl)phosphine stabilises rhodium(I) with the co-ordination of all three olefinic groups as reported here. However, they reported that their compound was a 1 : 1 electrolyte in methanol; similar measurements on RhBr(tvpp) indicate a molecular conductivity of 24 Ω^{-1} cm^2 mol^{-1} at 10^{-3}M in methanol. This is only about one third of that expected for a 1 : 1 electrolyte; but the addition of a small excess (1·1 mol) of triphenylphosphine to the solution causes a slow increase in conductivity, reaching a final value of 55 Ω^{-1} cm^2 mol^{-1}. The cation produced can be isolated as the $[Rh(tvpp)PPh_3]^+$ BPh_4^- salt by addition of sodium tetraphenylborate; this is a normal 1 : 1 electrolyte in acetone. The same cation is formed by the chloro- and iodo-complexes. I.r. spectra of these ions are similar to those of (tvpp)-RhBr, with additional bands due to PPh_3; the products are assigned a closely similar structure with PPh_3 replacing the halogen atom in the axial position. The equilibrium in methanol and the reaction with PPh_3 is summarised by the equation

$$L{\cdot}RhBr + MeOH \rightleftharpoons L{\cdot}Rh(MeOH)^+ + Br^- \xrightarrow{PPh_3} L{\cdot}Rh(PPh_3)^+ + Br^-$$

(Pyridine can replace triphenylphosphine).

The complexes of tris(*o*-vinylphenyl)arsine react similarly except that: (i) on adding $AsPh_3$ to (tvpa)-RhCl in methanol, the molecular conductivity changes from 19 to 37 Ω^{-1} cm^2 mol^{-1} instantaneously: both

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[1] Part IX, D. I. Hall and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, 1491.

[2] (*a*) M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *Inorg. Chem.*, 1968, **7**, 556; (*b*) M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organometallic Chem.*, 1967, **10**, 301.

[3] P. W. Clark and G. E. Hartwell, *Inorg. Chem.*, 1970, **9**, 1948.

these values are lower than those for the phosphine complex; (ii) the solution of (tvpa)RhCl in methanol, initially almost colourless, becomes intensely yellow on the addition of $AsPh_3$ or pyridine. No such colour change occurs for the phosphine complex. On adding $NaBPh_4$, the white ionic salt $[Rh(tvpa)AsPh_3]^+$ BPh_4 is precipitated.

These data suggest that the addition of a donor ligand to a solution of RhCl(tvpa) produces a new neutral species. This can be isolated by recrystallisation of RhCl(tvpa) from acetone–light petroleum in the presence of an excess of the ligand, $AsPh_3$ or pyridine, and has the formula RhCl(tvpa) (ligand); this product reverts to RhCl(tvpa) in the absence of the free ligand. The complex RhCl(tvpa)(ligand) shows i.r. absorption bands at 926 and 971 cm^{-1} (δCH), characteristic of a free vinyl group. The C=C stretch has not been observed but it is usually very weak in systems of this type.[4]

TABLE 1

Compound	Colour	M.p.[a]	C	H	N	Halide	ν(C=C), (cm^{-1})
RhCl(tvpa)	Pale yellow	239	55·7 (55·2)	4·5·(4·1)		6·9 (6·8)	1270s
RhCl(CO)(tvpa)	Yellow	247	54·6 (54·5)	4·2 (3·8)		7·8 (6·4)	
RhCl(tvpa)py	Orange	252	56·3 (57·9)	4·3 (4·3)	2·3 (2·3)		1250m
$RhCl(tvpa)AsPh_3$	Orange	217	61·1 (60·9)	4·4 (4·4)		4·5 (4·3)	1251m
RhBr(tvpa)	Yellow	244	50·7 (50·8)	3·9 (3·7)		14·0 (14·1)	1270s
RhBr(tvpa)py	Dark yellow		53·3 (53·9)	4·3 (3·8)	2·0 (2·2)	13·2 (12·4)	1252m
$RhBr(tvpa)AsPh_3$	Orange	208	58·4 (57·8)	4·6 (4·2)		9·6 (9·2)	1251m
RhI(tvpa)	Dark red	215	47·2 (47·0)	3·7 (3·5)		20·5 (20·7)	1252m
RhI(tvpa)py	Orange	150[b]	50·7 (50·2)	4·0 (3·8)	2·0 (2·0)	18·5 (18·3)	1252m
$RhI(tvpa)AsPh_3$	Red	207					
RhCl(dvpp)	Yellow	244	57·7 (58·4)	4·2 (4·2)		8·3 (7·8)	1255m
RhCl(CO)(dvpp)	Bright yellow	243	57·5 (57·5)	4·6 (4·0)		7·7 (7·4)	1256m
$RhCl(dvpp)PPh_3$	Bright yellow	147[c]	67·4 (67·2)	5·1 (4·8)		5·0 (5·0)	1254m,br
RhCl(dvpp)py	Yellow	260	61·9 (61·0)	5·0 (4·6)	2·9 (2·6)	5·8 (6·7)	
$RhCl(dvpp)_2$	Cream	268	66·2 (68·9)	5·0 (5·0)		4·4 (4·6)	
RhBr(dvpp)	Yellow	254					
RhBr(dvpp)CO	Yellow						
$RhBr(dvpp)PPh_3$	Yellow	184[c]	63·3 (63·3)	4·9 (4·5)		10·8 (10·5)	1250m
RhBr(dvpp)py	Yellow		56·2 (56·3)	4·4 (4·2)	2·4 (2·4)	13·2 (13·9)	
RhI(dvpp)	Orange	262	48·4 (48·6)	3·5 (3·5)		22·7 (23·3)	1253m
RhI(dvpp)CO	Brown	150[b]	47·8 (48·3)	3·6 (3·4)		22·2 (22·2)	1256m
RhI(dvpp)py	Yellow	290	52·0 (52·0)	4·0 (3·9)	2·1 (2·2)	19·2 (20·3)	1251br
$RhI(dvpp)PPh_3$	Yellow	182[c]	59·0 (59·6)	4·4 (4·3)		15·8 (15·7)	
$[Rh(PPh_3)(tvpp)]BPh_4$	White	160	77·4 (77·4)	6·0 (5·5)			1264m
$[Rh(py)(tvpp)]BPh_4$	Cream	132	75·2 (75·6)	5·8 (5·5)	1·6 (1·7)		1266m
$[Rh(py)(tvpa)]BPh_4$	Pale yellow	157	72·0 (71·9)	5·7 (5·2)	1·5 (1·6)		1266m

[a] All compounds show a greater or lesser degree of decomposition on melting. [b] Decomposes without melting. [c] Loses triphenylphosphine. Calculated analytical figures in parentheses.

The equilibria involved here are:

$$\begin{tikzcd}
{[RhX(tvpa)]^\circ} \arrow[r, shift left, "MeOH"] \arrow[d, shift left, "AsPh_3"'] & {[Rh(MeOH)(tvpa)]^+ \; X^-} \arrow[l, shift left] \arrow[d, shift left, "AsPh_3"] \\
{[RhX(tvpa)AsPh_3]^\circ} \arrow[r, shift left, "-X^-"] \arrow[u, shift left] & {[Rh(tvpa)AsPh_3]^+} \arrow[l, shift left, "+X^-"] \arrow[u, shift left]
\end{tikzcd}$$

X = Cl, Br

The structure of the ligand in the complexes $[RhX(tvpa)AsPh_3]^\circ$, [RhX(tvpa)(py)], and RhX(tvpa)(CO) is different from that in RhX(tvpa): the ' carbon–carbon stretch ' of the co-ordinated olefin,[5] a very strong band at 1270 cm^{-1} in RhCl(tvpa), is of medium intensity at 1251 cm^{-1} in $RhCl(tvpa)AsPh_3$. This may be due to a change in the angle between the C=C and As–Rh bonds caused by a change in (olefin)–Rh–(olefin) angle from 120 to 180° if the geometry of the trigonal-bipyramidal rhodium co-ordination sphere [6] of RhCl(tvpa) changes to a square-planar arrangement with an axial ligand in the complex $RhCl(tvpa)AsPh_3$ (see Figure 1). Both types of geometry are known [7,8] for Rh^I. The change in ν(C=C) could then be due to the use by the rhodium of different orbitals for bonding in the two cases. Support for this view is provided by the behaviour of RhCl(tvpa) towards chelating ligands such as bipyridyl when it yields RhCl(tvpa)(bipyridyl); the i.r. spectrum of the latter is similar to that of RhCl(tvpa) (pyridine) but it is a 1 : 1 electrolyte in solution, *viz.* $[Rh(tvpa)(bipy)]^+ Cl^-$. If the rhodium–olefin bonding in RhCl(tvpa)py were the same as in RhCl(tvpa), then it would be expected that the second nitrogen present in bipyridyl would also displace an olefin group and that the olefinic ligand would then behave as a bidentate group.

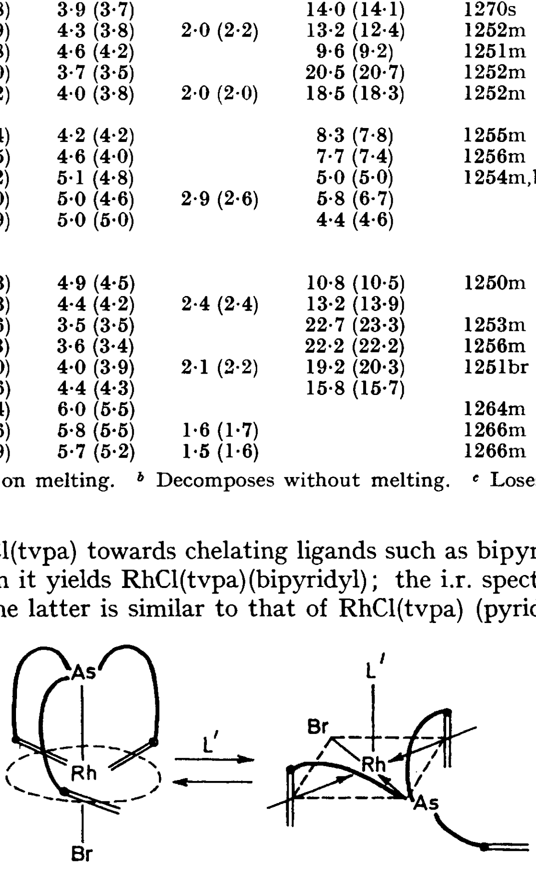

FIGURE 1

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[4] W. R. Kneen, Ph.D. Thesis, University of London, 1967.

[5] J. Hiraishi, D. Finseth, and F. A. Miller, *Spectrochim. Acta*, 1969, **25***A*, 1657.

[6] D. I. Hall and R. S. Nyholm, *Chem. Comm.*, 1970, 488.

[7] S. J. LaPlaca and J. A. Ibers, *Acta Cryst.*, 1965, **29**, 511.

[8] A. Immirzi and G. Allegra, *Acta Cryst.*, 1969, **B25**, 120.

The interpretation of the ^1H n.m.r. spectra of the $-CH{=}CH_2$ groups is less straightforward. The compounds RhCl(tvpa)(CO), RhBr(tvpa)(C_5H_5N), and RhI(tvpa)(C_5H_5N) in the presence of an excess of pyridine, in spite of the fact that they show *two* C–C stretching frequencies in the i.r. spectrum, have only *three* vinyl proton absorption bands in the n.m.r. spectrum; the chemical shifts τ are approximately equal to $\frac{1}{3}\tau$ (free ligand) plus $\frac{2}{3}\tau$ [RhX(tvpa)], the lines being slightly broadened. Hence these compounds have the vinyl groups in dynamic equilibrium, two being bonded to the rhodium and one free at any given moment. Presumably this exchange occurs by a process similar to that postulated in the compound $PtBr_2$(tvpa).[1] The compound RhCl(tvpa)(C_5H_5N) has a more complex spectrum showing eight absorption lines between τ 5·5 and 6·4, which are resolvable as the β-proton resonances of three vinyl groups, two of which are identical. However, as neither set of lines corresponds with those in RhCl(tvpa), these cannot be explained as being due to ' free ' and ' co-ordinated ' vinyl groups.

It was mentioned earlier that the solubility and spectra of the compound RhI(tvpa) differ markedly from those of the other halides of Rh^I of the same formula and from that of the compound RhI(tvpp). The reason for this now seems clear. RhI(tvpa) exists in the solid state as a dimer with iodine bridges and with one free olefin group, the i.r. spectrum of the ligand being almost identical with that in RhX(tvpa)$AsPh_3$. Naturally, the dimer is less soluble than the monomeric chloride and bromide. The complexes RhI(tvpa)L are in all respects similar to the corresponding chloro- and bromo-complexes.

To extend and clarify the conclusions of this work a pair of potential terdentate ligands, phenylbis(*o*-vinylphenyl)-phosphine and -arsine (dvpp and dvpa) were synthesised in order to compare their complexes with those of tris(*o*-vinylphenyl)arsine, in which we believe that the ligand behaves as a terdentate group. Unfortunately the complexes of dvpa with Rh^I could not be obtained in a pure state. The ligand dvpp forms insoluble microcrystalline dark yellow or red complexes of stoicheiometry LRhX, with i.r. spectra closely resembling those of RhCl(tvpa)$AsPh_3$ and RhI(tvpa); absorptions due to free vinyl groups are, of course, absent. As it is difficult to understand why the square-planar rhodium(I) species should be insoluble, we propose that these compounds be formulated as dimers having the same structure as $[RhI(tvpa)]_2$.

The dihalide bridges are split by two-electron ligands, as is usual for halogen-bridged rhodium(I) dimers[9] to give monomers of formula (dvpp)RhClL′, with the expected greater solubility as compared with the original dimers. The compounds crystallise as bright yellow solids which lose the two-electron ligand above 150°, or on recrystallisation from a large volume of solvent. When treated with bipyridyl the dimers give the ionic species $[Rh(bipy)(dvpp)]^+ Cl^-$ similar to those derived from RhCl(tvpa).

The ^1H n.m.r. spectra of the dvpp–pyridine adducts give the same pattern as those of RhX(tvpa)L (see Table 2), but the chemical shifts are greater; the $-CH{=}CH_2$ spectrum is due to *co-ordinated* vinyl groups only. The chemical shifts are greater than those observed in RhX(tvpa) complexes, implying once more that the bonding, and by inference the geometry, are different.

TABLE 2

	Chemical shift (τ)			Coupling constants (Hz)	
Compound	α [a]	*cis*-β	*trans*-β	*J*(*cis*)	*J*(*trans*)
RhCl(tvpa)	3·72	5·52	6·60	9·2	12·0
RhBr(tvpa)	3·78	5·41	6·66	9·0	12·4
RhCl(tvpa)py [b]	4·09	5·94 5·58	5·83 6·26	9·3 9·5	11·0 13·0
RhBr(tvpa)py [b]	4·21	5·96	5·76	7·7	11·5 [c]
RhI(tvpa)py	4·40	5·97	5·77	10·0	13·0 [c]
RhCl(tvpa)CO	4·0	5·57	5·97	9·6	13·2 [c]
RhCl(dvpp)PPh_3	3·99	6·4 [d]	7·28		10·5 [c]
RhBr(dvpp)PPh_3	3·92	6·3 [d]	7·22		12·8 [c]
RhCl(dvpp)py	4·50	5·84	7·12	8·4	11·2 [c]
RhCl(CO)(dvpp)	4·07	5·80	6·67	8·4	10·8
RhBr(CO)(dvpp)	4·14	5·80	6·80	8·4	11·0
RhI(CO)(dvpp)	4·13	5·60	6·83	8·2	11·0

[a] Complex multiplet: can be rationalised as a double doublet of close doublets. [b] In presence of an excess of two-electron ligand. [c] Peaks all broadened by *ca.* 5 Hz. [d] Peak width 40 Hz: single.

All spectra recorded at 34° in $CDCl_3$.

The triphenylphosphine adducts show different n.m.r. patterns: all the lines are broad, the β-*cis* proton showing a single peak of width *ca.* 40 Hz at τ 6·2. The broad resonances can probably be ascribed to slow triphenylphosphine exchange. Cooling of the solution, however, does not cause splitting of the resonance band.

The action of carbon monoxide at atmospheric pressure on the dimeric species $[RhX(dvpp)]_2$ gives monomeric species of formula RhX(CO)(dvpp) which exhibit carbonyl stretching frequencies outside the normal range for rhodium(I) (see Table 3), implying a greater apparent oxidation state of the metal than; for example, that exhibited by *trans*-RhCl(CO)$(PPh_3)_2$.

TABLE 3

Infrared absorptions of carbonyl groups

	(cm^{-1})
RhCl(CO)(dvpp)	2048
RhBr(CO)(dvpp)	2049
RhI(CO)(dvpp)	2020
RhCl(CO)(tvpa)	2008 2033
RhI(CO)(tvpa)	2018

The i.r. band assigned to ν(C=C) does not differ greatly in frequency or strength between $[RhX(dvpp)]_2$ and RhX(dvpp)L′; it appears in complexes as a medium-intensity absorption at 1250—1256 cm^{-1}, implying that RhX(dvpp)L′ and RhX(tvpa)L′ are very similar. Clark and Hartwell[3] assign a band at 1236 cm^{-1} to ν(C=C), and they state that an *X*-ray structure indicates that the carbon–carbon and phosphorus–rhodium bonds are

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[9] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

mutually perpendicular in their complex $(CH_2{=}CHCH_2CH_2)_3PRhCl$. A crystal-structure determination is in progress to decide the exact geometry of our compound $RhCl(tvpa)AsPh_3$, the structure of RhBr(tvpp) having been described recently.[10]

The carbonyl group in RhX(dvpp)CO is unusually labile: it is displaced by pyridine slowly in the cold (and quickly on heating under reflux) and instantaneously by triphenylphosphine, to give the complexes RhCl(dvpp)L′. This is in contrast to the situation in four-co-ordinate rhodium(I) complexes, where the reaction

$$(PPh_3)_3RhCl + CO \longrightarrow trans\text{-}(PPh_3)_2Rh(CO)Cl + PPh_3$$

proceeds entirely to the right at 1 atmosphere of CO pressure.

The marked tendency of the complexes RhX(dvpp) to exist as five-co-ordinate dimers is unusual: where rhodium(I) halogeno-complexes exist as dimers, it is usually in order to attain four-co-ordination, as in $[(diene)RhX]_2$. The compound $[RhX(dvpp)]_2$ appears to be the first example of a five-co-ordinate rhodium(I) species with bridging halogens.

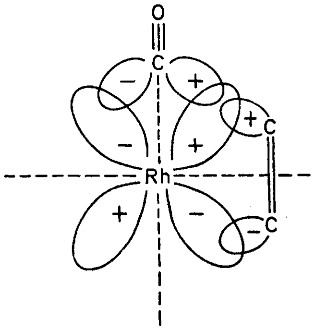

FIGURE 2

The reason for this is probably explained by the nature of the ligands: donation by the metal from the d_{xz} to the π^* orbitals of the vinyl groups of dvpp removes electron density from the metal, presumably making the acceptance of the pair of electrons of a donor ligand easier, in this case to such an extent that a non-bonding pair of electrons from a covalently bound chlorine is basic enough to form a bond. Thus support is found for Hartley's assertion [11] that the π-component of a metal–olefin bond is more important than the σ-component because the π-back-donation removes electron density from the metal, allowing co-ordination of a fifth ligand. When a full positive charge is present, five-co-ordination becomes normal for rhodium(I).[12] In the same way, the unusual behaviour of the carbonyls can be explained by considering the back-donation from the d_{xz} orbital to the π^* orbitals of the carbonyl group, shown in Figure 2. This process is normally invoked to explain the lowering of frequency of the C–O vibration.

The same process can explain the lability of the carbonyl group toward bases such as pyridine and triphenylphosphine: under normal conditions, the rhodium–carbon bond is strengthened by the synergic effect of the back-donation, and if this effect is weakened, the stronger σ-donation of pyridine or triphenylphosphine than that of carbon monoxide favours replacement. Studies are at present in hand to determine whether this reaction occurs by an associative or a dissociative mechanism.

EXPERIMENTAL

Solvents were AnalaR grade and used as supplied with the exception of ether, which was dried over sodium. Tris-(*o*-vinylphenyl)-phosphine and -arsine were prepared as described previously.[1] Biscyclo-octa-1,5-diendi-μ-chloro-dirhodium(I) and the corresponding bromo- and iodo-complexes were prepared by the literature method.[9]

Phenylbis(o-*vinylphenyl*)*phosphine*.—A Grignard reagent prepared in ether from *o*-bromostyrene (30 g, 0·1639 mol) was treated at 0° under nitrogen during 1 h with phenyldichlorophosphine (14·7 g, 0·082 mol) in ether. The solution was heated under reflux for 1 h. Hydrolysis with 10% ammonium chloride solution, followed by evaporation of the ether layer and recrystallisation of the residue from ether–methanol gave the white *ligand* (17·1 g, 66%), m.p. 99°.

Phenylbis(o-*vinylphenyl*)*arsine*.—This was prepared similarly from phenyldichloroarsine (18·3 g); [13] yield 65%.

Chloro[*phenylbis*(o-*vinylphenyl*)*phosphine*]*rhodium*(I) *Dimer*.—A solution of biscyclo-octa-1,5-diendi-μ-chloro-dirhodium(I) $[(cod)RhCl]_2$ (0·87 g, 1·77 mmol) in dichlormethane (10 ml) was treated at 293 K with a solution of phenylbis(*o*-vinylphenyl)phosphine (1·11 g, 3·54 mmol) in dichloromethane (10 ml). Orange tabular crystals were deposited, which were crushed and dried at 0·001 Torr at 330 K to remove solvent. This gave a yellow *powder* (1·45 g, 91%).

Chloro(*carbonyl*)[*phenylbis*(o-*vinylphenyl*)*phosphine*]*rhodium*(I).—$[RhCl(dvpp)]_2$ (1·45 g, 1·60 mmol) suspended in dichloromethane (20 ml) was frozen to 77 K and the flask evacuated. The flask was connected to a bladder containing carbon monoxide and allowed to warm to room temperature. Stirring for 0·5 h gave a clear solution, to which light petroleum (40 ml) was added. The filtered solution was distilled under reduced pressure to 20 ml, giving yellow *prisms* (1·41 g, 90%).

Chloro(*triphenylphosphine*)[*phenylbis*(o-*vinylphenyl*)*phosphine*]*rhodium*(I).—*Method A*. $[RhCl(dvpp)]_2$ (0·20 g, 0·22 mmol) and triphenylphosphine (0·13 g, 0·49 mmol) were stirred together in dichloromethane (15 ml) at 298 K until the initial suspension cleared (1 h). Light petroleum (30 ml) was added and the filtered solution with evaporated to 10 ml. The dichloromethane *solvate* which precipitated was recrystallised from acetone–light petroleum giving greenish-yellow *irregular crystals* (0·26 g, 87%).

Method B. RhCl(CO)(dvpp) (0·30 g, 0·62 mmol) in acetone (10 ml) was treated with triphenylphosphine (0·20 g, 0·76 mmol) in acetone (2 ml). Gas was evolved. On

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[10] C. Nave and M. R. Truter, *Chem. Comm.*, 1971, 1253.

[11] F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799, and references therein.

[12] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.

[13] (*a*) P. J. Gaston, personal communication; (*b*) R. L. Barker, E. Booth, W. E. Jones, and F. N. Woodward, *J. Soc. Chem. Ind.*, 1949, **68**, 277.

addition of light petroleum and evaporation, the *complex* was precipitated as above (0·37 g, 84%).

Chloro[tris(o-*vinylphenyl)arsine]rhodium*(I).—[(cod)RhCl]$_2$ (0·8 g, 1·63 mmol) in dichloromethane (8 ml) was added to tris(*o*-vinylphenyl)arsine in dichloromethane (4 ml). The mixture was set aside at 273 K overnight; yellow crystals formed. Recrystallisation from dichloromethane–ethanol gave primrose *needles* (1·07 g, 61%).

Chloro(triphenylarsine)[tris(o-*vinylphenyl)arsine]rhodium*-(I).—RhCl(tvpa) (0·6 g, 1·15 mmol) was suspended in acetone (20 ml) and triphenylarsine (0·42 g, 1·37 mmol) in acetone (5 ml) was added. The solid dissolved and light petroleum (20 ml) was added to the orange solution. On evaporation, the solution gave orange-yellow *prisms* (0·67 g, 70%). This complex could not be recrystallised in the absence of triphenylarsine (see text).

We acknowledge financial support (to D. I. H.) from the Department of Trade and Industry.

[1/1858 *Received*, 11*th October*, 1971]