440. *Carbonyl Complexes of Rhodium. Part I. Complexes with Triarylphosphines, Triarylarsines, and Triarylstibines.*

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The preparation and properties of a new series of complexes of rhodium(I) of general formula $[RhL_2(CO)X]$ ($L = Ar_3P, Ar_3As, Ar_3Sb$; $X = Cl, I, SCN$) are described. These compounds are monomeric, non-electrolytes in nitrobenzene, and diamagnetic. They are characterised by a remarkable stability, *e.g.*, the carbonyl group is not affected by cold alkali.

These complexes should be square planar, and measurements of dielectric constant in benzene seem to indicate that they have the *trans*-configuration.

IT has recently been shown [1, 2] that rhodium(I) forms very stable co-ordination compounds which, like those of palladium(II) and platinum(II), are four co-ordinate.

In view of the strong affinity of palladium(II) and platinum(II) for tertiary phosphines and the capacity of these ligands to stabilise low oxidation states of the central metal atom [3, 4] it could be foreseen that rhodium(I), which is isoelectronic with palladium(II), would form stable complexes with tertiary phosphines.

[1] Malatesta and Vallarino, *J.*, 1956, 1867.
[2] Chatt and Venanzi, *Nature*, 1956, **177**, 852.
[3] Malatesta and Angoletta, *Atti Accad. naz. Lincei, Rend. Classe Sci. Fis. mat. nat.*, 1955, VIII, **19**, 43.
[4] *Idem*, *J.*, 1957, 1186.

An ethanolic solution of hydrated rhodium trichloride, on treatment with an excess of an *iso*cyanide[1] or a chelating diolefin,[2] gives, directly, derivatives of rhodium(I), $[Rh(RNC)_4]Cl$ and $[Rh_2(diolefin)_2Cl_2]$, but reduction of a rhodium(III) salt in the presence of a derivative of arsenic(III) gives products which were though to be complexes of rhodium(II).[5] It has recently been found [6] that some of these compounds are diamagnetic, and Nyholm formulates them as mixed salts of rhodium(I) and rhodium(III).

For the preparation of the complexes of rhodium(I) with Group VB donors we used as a starting material tetracarbonyl-$\mu\mu'$-dichlorodirhodium, $[Rh_2(CO)_4Cl_2]$, because it already contains the metal in a +1 oxidation state, and it is the most easily prepared of the carbonyl halides of rhodium.[7]

A cold benzene solution of rhodium carbonyl chloride reacts very readily with triphenylphosphine, both as the solid and in benzene solution. A lively evolution of carbon monoxide occurs and from the solution, on evaporation of most of the solvent at 14 mm. and dilution of the concentrated solution with ethanol or hexane, a yellow crystalline product is obtained which is diamagnetic, does not conduct electricity in nitrobenzene solution, and on the basis of analysis and molecular-weight determination must be formulated as $[Rh(Ph_3P)_2(CO)Cl]$.

Rhodium carbonyl chloride reacts also with other triarylphosphines, and with triarylarsines and triarylstibines, to give products analogous to that obtained with triphenylphosphine. This reaction appears to be fairly general and can be written as:

$$[Rh_2(CO)_4Cl_2] + 4L \longrightarrow 2[RhL_2(CO)Cl] + 2CO \quad (L = Ar_3P,\ Ar_3As,\ or\ Ar_3Sb)$$

The compounds characterised are listed in Table 1. Their thermal stability is considerable: they melt, with decomposition, in the range 150—250°. It is interesting that the arsine-containing complexes have decomposition points which, on average, are about 50° higher than those of the corresponding phosphorus compounds. The general stability of the stibine-containing complexes of rhodium(I) is comparable to that of analogous palladium(II) and platinum(II) derivatives.[8]

TABLE 1. *New complexes of the type* $[RhL_2(CO)Cl]$.

L	Decomp. pt.		L	Decomp. pt.	
Ph_3P	195—200°	Yellow prisms	$(p\text{-}C_6H_4Cl)_3As$	230—245°	Yellow prisms
$(p\text{-}C_6H_4Me)_3P$	190—195	Deep yellow prisms	Ph_3Sb	151—153	Purple-red prisms
$(p\text{-}MeO{\cdot}C_6H_4)_3P$	193—195	Yellow prisms	$(p\text{-}C_6H_4Me)_3Sb$	156—158	Red needles
$(p\text{-}C_6H_4Cl)_3P$	190—195	Yellow needles	$(p\text{-}C_6H_4Cl)_3Sb$	160—162	Orange-red plates
Ph_3As	242—245	Yellow prisms	Ph_3P [a]	190—195	Yellow plates
$(p\text{-}C_6H_4Me)_3As$	235—242	Deep yellow prisms	Ph_3P [b]	188—194	Yellow prisms
$(p\text{-}MeO{\cdot}C_6H_4)_3As$	235—240	Yellow prisms			

[a] Iodide. [b] Thiocyanate.

Another notable feature of the complexes $[RhL_2(CO)Cl]$ is their chemical inertness. They are not attacked by boiling dilute solutions of acids and bases, boiling concentrated hydrochloric acid, or cold alcoholic alkali hydroxides. The last, when hot, decompose the complexes with formation of amorphous brown products. These rhodium(I) derivatives do not tend to oxidise spontaneously and do not reduce silver nitrate or mercuric chloride. Their aqueous-alcoholic suspensions are not reduced by hypophosphorous acid, nor are their alcoholic suspensions by metallic magnesium or hydrazine hydrate. The chlorine atom in these compounds is fairly strongly bound. A benzene solution of silver perchlorate in the cold becomes cloudy only after several minutes. This chlorine atom is not replaced by bromine or iodine when an acetone solution is boiled with lithium bromide or iodide, but it is replaced by prolonged boiling of an acetone solution with an excess of sodium iodide or

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[5] Dwyer and Nyholm, *J. Proc. Roy. Soc., New South Wales*, 1942, **75**, 122.
[6] See Nyholm, Proc. Solvay Conference, Brussels, 1956.
[7] Hieber and Lagally, *Z. anorg. Chem.*, 1943, **251**, 98.
[8] Chatt and Wilkins, *J.*, 1953, 70.

thiocyanate, probably because in this case the reaction is favoured by precipitation of sodium chloride. By this method the compounds [Rh($Ph_3P)_2$(CO)I] and [Rh($Ph_3P)_2$(CO)(SCN)] were obtained. The iodo-complex is less stable than its chloro-analogue, especially in solution, where it becomes brown within a few hours.

The difficulty encountered in replacing the chlorine atom by iodine is rather surprising. Rhodium(I) has its *d*-orbitals immediately under the valency shell filled, and gives strongly covalent complexes, very similar to those of palladium(II) and platinum(II) and therefore one would have expected the chlorine atoms to be quickly replaced by bromine and iodine, as happens with the complexes of palladium(II) and platinum(II).

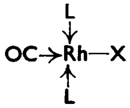
The most striking feature of the complexes of type [RhL_2(CO)Cl] is the stability of the carbon monoxide–metal bond. The complexes can be recovered in almost quantitative yield after 2 hours' boiling in xylene with an excess of ligand, L, or after boiling of a chloroform solution with an excess of pyridine or *p*-toluidine. The direct replacement of carbon monoxide from these complexes does not appear possible. The displacement of carbon monoxide by another ligand, when it occurs, is always accompanied by a complete change in the nature of the complex. This displacement occurs with triarylphosphites and aryl *iso*cyanides, thus:

$$[\mathrm{Rh(Ar_3P)_2(CO)Cl}] + 3(\mathrm{ArO})_3\mathrm{P} \longrightarrow [\mathrm{Rh\{(ArO)_3P\}_3Cl}] + \mathrm{CO} + 2\mathrm{Ar_3P}$$

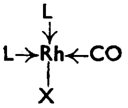
$$[\mathrm{Rh(Ar_3P)_2(CO)Cl}] + 4\mathrm{ArNC} \longrightarrow [\mathrm{Rh(ArNC)_4}]\mathrm{Cl} + \mathrm{CO} + 2\mathrm{Ar_3P}$$

The second reaction occurs particularly easily and can be carried out very quickly and quantitatively by mixing in the cold the solid complex with an excess of liquid *iso*cyanide, which also acts as a solvent. It has been used for the volumetric determination of carbon monoxide in the above compounds.

(I)



$$\mathrm{OC}\rightarrow\underset{\underset{\textstyle \mathrm{L}}{\uparrow}}{\overset{\overset{\textstyle \mathrm{L}}{\downarrow}}{\mathrm{Rh}}}-\mathrm{X}$$



$$\mathrm{L}\rightarrow\underset{\underset{\textstyle \mathrm{X}}{|}}{\overset{\overset{\textstyle \mathrm{L}}{\downarrow}}{\mathrm{Rh}}}\leftarrow\mathrm{CO}$$

(II)

In analogy to the tetraco-ordinated complexes of palladium(II) and platinum(II), the compounds [RhL_2(CO)Cl] should have square planar configuration and the rhodium atom dsp^2 hybridisation. On this basis our complexes should, at least in principle, be capable of existing in a *trans*-form (I) and a *cis*-form (II). In each case, however, only one form could be obtained and this does not appear to change on repeated recrystallisation from different solvents.

In an attempt to establish the geometrical configuration of the products which were isolated, the dielectric constant of a benzene solution of several of these compounds was measured at 25° and from this an approximate dipole moment was calculated by Jensen's approximate formula.[9] The values obtained for these moments are listed in Table 2.

TABLE 2. *Approximate dipole moments* (μ, D) *of the complexes* [Rh{(p-X·$C_6H_4)_3$M}$_2$(CO)Cl].

X	H	Me	Cl	OMe
M = P	3·15	3·1	2·5	4·0
M = As	3·2	3·6	2·9	Unknown

The dipole moments are all rather low for co-ordination compounds and consequently little value can be attributed to the absolute figures obtained, in view of the uncertainties about the contributions of the electron and atom polarisation. The relative moments of the bonds Rh–PR_3, Rh–AsR_3, Rh–CO, and Rh–Cl are not known, but one can, as a first approximation, assume that they do not differ appreciably from those of the corresponding bonds to platinum(II). The complex *cis*-[Pt$(CO)_2Cl_2$] has $\mu = 4{\cdot}65$ D,[10] and the *cis*-[Pt$(R_3M)_2Cl_2$] (M = P, As, or Sb) have $\mu = 10$—11 D.[11] From these figures one would

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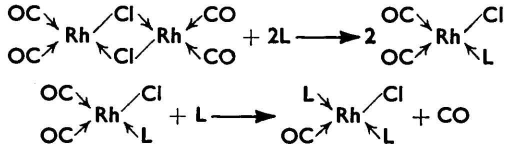
[9] Jensen, *Z. anorg. Chem.*, 1936, **229**, 250.

[10] Chatt and Williams, *J.*, 1951, 3061.

[11] Chatt and Wilkins, *J.*, 1952, 4300.

expect dipole moments of the order of 3—3·5 D for the *trans*-isomer (I), and 8—9 D for the *cis*-isomer (II). The values given in Table 2 come within the range of a *trans*-isomer.

This conclusion is also supported by the possible reaction mechanism based on the assumption that the *trans*-effect [12] is operative in complexes of rhodium(I):



The lower stability of the iodo-complex $[Rh(Ph_3P)_2(CO)I]$ is also in agreement with this configurational assignment and the relative position of these two halide ions in the *trans*-effect scale.

On the other hand, changing the substituent X on the benzene ring, in *para*-position to the donor atom M, should not appreciably change the dipole moment if the complex has *trans*-configuration. The differences observed are too small to be caused by a *cis*-configuration in the complex. These results could be explained by assuming that in benzene solution an equilibrium is established between the two isomers, consisting mainly of the *trans*-form, but containing small amounts of *cis*-form which vary with the nature of the donor atom M and the *para*-group X. The existence of such equilibria in benzene solution for complexes of the type $[PtL_2Cl_2]$ and $[PdL_2Cl_2]$, where $L = R_3P$, R_3As, or R_3Sb,[8, 11] is well known, and in these cases the equilibrium position varies with the nature of R.

EXPERIMENTAL

Tetracarbonyl-μμ'-dichlorodirhodium(I) $[Rh_2(CO)_4Cl_2]$.—This was prepared by Hieber and Lagally's method [7] and purified by extracting the mixture with boiling hexane, filtering the hot solution, and cooling it to −20°. The product separated in long orange-red needles (Found: CO, 29·3; Rh, 53·0. Calc. for $C_4O_4Cl_2Rh_2$: CO, 28·8; Rh, 52·9%).

Carbonylbis(triphenylphosphine)chlororhodium(I) $[Rh(Ph_3P)_2(CO)Cl]$.—Triphenylphosphine (0·90 g., 3·5 mmols.) was added to a solution of tetracarbonyldichlorodirhodium(I) (0·225 g., 0·58 mmols.) in benzene (60 ml.). A lively reaction occurred with evolution of carbon monoxide (palladous chloride test). The solution was evaporated to a small volume at 15 mm. and then diluted with ethanol (40 ml.). A yellow crystalline product gradually separated; it was filtered off, washed with ether, and dried (1·05 g.). Recrystallisation was effected by dissolving the crude product in chloroform and diluting the solution with ethanol (yield 0·80 g.) (Found: CO, 3·9; Cl, 5·1; P, 9·1; Rh, 15·1%; *M*, cryoscopic in 2·5% nitrobenzene solution, 740. $C_{37}H_{30}OClP_2Rh$ requires CO, 4·05; Cl, 5·1; P, 9·0; Rh, 14·9%; *M*, 691). $\chi_M = -513 \times 10^{-6}$. The *complex* is very soluble in methylene chloride and chloroform, soluble in carbon tetrachloride, benzene and its homologues, and nitrobenzene, slightly soluble in acetone and ethyl ether, and insoluble in methanol, ethanol, and hexane.

This compound is also obtained by using the stoicheiometric amount of triphenylphosphine or a larger excess.

Attempted reaction with an excess of triphenylphosphine. The complex (0·3 g.) and triphenylphosphine (0·5 g.) in xylene (15 ml.) were refluxed for 2 hr. After cooling, methanol (40 ml.) was added. Crystals slowly separated, and were filtered off, washed with ether, and purified as described for the starting material (yield 0·25 g.). They constituted starting material, as shown by the infrared spectrum.

Attempted reaction with lithium bromide and lithium iodide. The complex (0·6 g.) in acetone (50 ml.) was boiled for 15 min. with lithium bromide (0·1 g.). There was no apparent colour change. The solution was evaporated to a small volume at 15 mm. pressure and diluted with methanol. The starting material was thus recovered (0·4 g.) and identified by its infrared spectrum.

When this reaction was carried out with lithium iodide instead of lithium bromide, a brown

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[12] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456, and references quoted therein.

solution was obtained, but on dilution with methanol the unchanged starting material was recovered (0·3 g.) and identified by its infrared spectrum.

Attempted reaction with p-*toluidine and pyridine.* The complex (0·15 g.) in chloroform (10 ml.) was refluxed for 30 min. with *p*-toluidine (0·15 g.). On dilution with methanol crystals separated (0·12 g.); these did not contain nitrogen and the infrared spectrum was identical with that of the starting material.

Using pyridine (0·5 ml.) instead of *p*-toluidine, under the same conditions, gave starting material (0·1 g.), identified by its infrared spectrum.

Reaction with tri-p-*chlorophenyl phosphite.* The complex (0·2 g.) in chloroform (10 ml.) and tri-*p*-chlorophenyl phosphite (0·1 g.) were boiled for a few minutes. The solution was taken to dryness at 15 mm. and the residual yellow oil was washed with hexane, then dissolved in benzene, and the solution diluted with hexane. Crystals (0·11 g.) were obtained which, from the infrared spectrum, were starting material.

This reaction, with 2 mols. of tri-*p*-chlorophenyl phosphite per mole of complex, gave a mixture of yellow crystalline products (as shown under a microscope), still containing carbon monoxide, which was evolved on addition of aryl *iso*cyanides.

Using 3 mols. of tri-*p*-chlorophenyl phosphite per mole of complex under the above conditions, gave *tris-*(p-*chlorophenyl phosphite*)*chlororhodium*, $[Rh\{(p\text{-}Cl{\cdot}C_6H_4{\cdot}O)_3P\}_3Cl]$ (0·7 g. from 0·6 g.) (Found: P, 6·9; Rh, 7·6. $C_{54}H_{36}O_9Cl_{10}P_3Rh$ requires P, 6·7; Rh, 7·5%). Its infrared spectrum is identical with that of the product obtained by direct reaction of tri-*p*-chlorophenyl phosphite and rhodium carbonyl chloride which will be described later.

Reaction with p-*tolyl* iso*cyanide.* *p*-Tolyl *iso*cyanide (1 mmole) was added to the solid complex (0·1 mmole); a gas was evolved immediately and the reaction was taken to completion by warming the mixture to 50—60° for 2 min. The gas evolved was measured in a Lunge's burette filled with mercury (Found: 2·18 ml., 0·0965 mmol.), and identified as pure carbon monoxide (palladous chloride test and ammoniacal cuprous chloride).

The reaction mixture was dissolved in ethanol (40 ml.) and filtered after treatment with charcoal. On addition of sodium perchlorate in ethanol violet crystals separated which, in boiling benzene, gave yellow plates of *tetra*-p-*tolyl*iso*cyanorhodium*(I) *perchlorate* (Found: N, 8·5; Rh, 15·5. $C_{32}H_{28}O_4N_4ClRh$ requires N, 8·3; Rh, 15·35%).

Carbonylbis(*triphenylphosphine*)*iodorhodium*(I) $[Rh(Ph_3P)_2(CO)I]$.—The corresponding chloride (0·4 g.) and sodium iodide (0·2 g.) in acetone (20 ml.) were refluxed for 30 min. The solution was taken to dryness at 15 mm. The solid residue was extracted with benzene, and the solution filtered. Diluting this solution with hexane gave crystals slowly (0·3 g.). The new *complex* was purified by dissolving it in hot benzene and reprecipitating it with hexane (Found: C, 56·5; H, 3·8; I, 16·3. $C_{37}H_{30}OIP_2Rh$ requires C, 56·8; H, 3·9; I, 16·2%). It is diamagnetic, and less soluble than its chloro-analogue. It is stable in the crystalline state but its solutions darken within a few hours.

Carbonylbis(*triphenylphosphine*)*thiocyanatorhodium*(I) $[Rh(Ph_3P)_2(CO)(SCN)]$.—This *compound* was prepared analogously to the iodide, from the corresponding chloride (0·6 g.) and sodium thiocyanate (0·3 g.) in acetone (50 ml.), and purified as its chloro-analogue (yield 0·45 g.). It is diamagnetic (Found: N, 2·15; S, 4·7; CO, 3·7%; *M*, cryoscopic in 2·2% bromoform solution, 730. $C_{38}H_{30}ONSP_2Rh$ requires N, 2·0; S, 4·5; CO, 3·9%; *M*, 713). It appears to be much less soluble than its chloro-analogue.

The following compounds were prepared and purified analogously to the carbonylbis(triphenylphosphine)chlororhodium:

Carbonylbis(*tri*-p-*tolylphosphine*)*chlororhodium*(I) $[Rh\{(p\text{-}C_6H_4Me)_3P\}_2(CO)Cl]$ (Found: Cl, 4·75; P, 7·95; Rh, 13·6; CO, 3·7%; *M*, cryoscopic in 3·0% nitrobenzene solution, 722. $C_{43}H_{42}OClP_2Rh$ requires Cl, 4·6; P, 8·0; Rh, 13·3; CO, 3·6%; *M*, 775). $\chi_M = -480 \times 10^{-6}$.

Carbonylbis(*tri*-p-*methoxyphenylphosphine*)*chlororhodium*(I) $[Rh\{(p\text{-}MeO{\cdot}C_6H_4)_3P\}_2(CO)Cl]$ (Found: Cl, 4·05; P, 7·1; Rh, 11·7%; *M*, cryoscopic in 1·1% benzene solution, 822. $C_{43}H_{42}O_7ClP_2Rh$ requires Cl, 4·1; P, 7·1; Rh, 11·8%; *M*, 871). $\chi_M = -574 \times 10^{-6}$.

Carbonylbis(*tri*-p-*chlorophenylphosphine*)*chlororhodium*(I) $[Rh\{(p\text{-}C_6H_4Cl)_3P\}_2(CO)Cl]$ (Found: Cl, 27·9; P, 7·1; Rh, 11·65%; *M*, cryoscopic in 1·4% benzene solution, 813. $C_{37}H_{24}OCl_7P_2Rh$ requires Cl, 27·65; P, 6·9; Rh, 11·5%; *M*, 898). $\chi_M = -426 \times 10^{-6}$.

Carbonylbis(*triphenylarsine*)*chlororhodium*(I) $[Rh(Ph_3As)_2(CO)Cl]$ (Found: Cl, 4·7; As, 19·0; Rh, 13·2; CO, 3·4%; *M*, cryoscopic in 1·3% benzene solution, 769. $C_{37}H_{30}OClAs_2Rh$ requires Cl, 4·55; As, 19·2; Rh, 13·2; CO, 3·6%; *M*, 779). $\chi_M = -325 \times 10^{-6}$.

*Carbonylbis(tri-*p*-tolylarsine)chlororhodium*(I) $[Rh\{(p\text{-}C_6H_4Me)_3As\}_2(CO)Cl]$ (Found: Cl, 4·2; As, 17·4; Rh, 12·0%; *M*, cryoscopic in 1·6% benzene solution, 835. $C_{43}H_{42}OClAs_2Rh$ requires Cl, 4·1; As, 17·4; Rh, 11·9%; *M*, 863). $\chi_M = -488 \times 10^{-6}$.

*Carbonylbis(tri-*p*-methoxyphenylarsine)chlororhodium*(I) $[Rh\{(p\text{-}MeO\cdot C_6H_4)_3As\}_2(CO)Cl]$ (Found: Cl, 3·7; As, 15·75; Rh, 10·9%; *M*, cryoscopic in 1·1% nitrobenzene solution, 928. $C_{43}H_{42}O_7ClAs_2Rh$ requires Cl, 3·7; As, 15·6; Rh, 10·7%; *M*, 959). $\chi_M = -552 \times 10^{-6}$.

*Carbonylbis(tri-*p*-chlorophenylarsine)chlororhodium*(I) $[Rh\{(p\text{-}C_6H_4Cl)_3As\}_2(CO)Cl]$ (Found: Cl, 25·8; As, 15·3; Rh, 10·4%; *M*, cryoscopic in 1·0% benzene solution, 968. $C_{37}H_{24}OCl_7As_2Rh$ requires Cl, 25·2; As, 15·2; Rh, 10·4%. *M*, 986). $\chi_M = -394 \times 10^{-6}$.

*Reaction of Carbonylbis(triphenylarsine)chlororhodium with Tri-*p*-chlorophenyl Phosphite.*—The reaction was carried out as described for the triphenylphosphine derivative. (1) With 1 or 2 mols. of tri-*p*-chlorophenyl phosphite a mixture of crystalline products was obtained, which evolved carbon monoxide with aryl *iso*cyanides. (2) With 3 mols. of phosphite tris(tri-*p*-chlorophenyl phosphite)chlororhodium was obtained, as shown by its infrared spectrum.

Carbonylbis(triphenylstibine)chlororhodium(I) $[Rh(Ph_3Sb)_2(CO)Cl]$.—This *complex* was prepared analogously to the triphenylphosphine derivative and purified by dissolving the crude product in methylene chloride and reprecipitating it with di*iso*propyl ether (Found: Cl, 4·1; Sb, 28·0; Rh, 11·55%; *M*, cryoscopic in 0·98% benzene solution, 795. $C_{37}H_{30}OClSb_2Rh$ requires Cl, 4·1; Sb, 27·9; Rh, 11·8%; *M*, 872·5). $\chi_M = -248 \times 10^{-6}$. It is more soluble than the corresponding phosphine and arsine derivatives.

The following were prepared and purified as described for their phenyl analogue:

*Carbonylbis(tri-*p*-tolylstibine)chlororhodium*(I) (Found: Cl, 3·65; Sb, 26·0; Rh, 10·5%; *M*, cryoscopic in 2·1% benzene solution, 965. $C_{43}H_{42}OClSb_2Rh$ requires Cl, 3·7; Sb, 25·45; Rh, 10·8%; *M*, 957). $\chi_M = -605 \times 10^{-6}$.

*Carbonylbis(tri-*p*-chlorophenylstibine)chlororhodium*(I) (Found: Cl, 22·7; Sb, 22·7; Rh, 9·3%; *M*, cryoscopic in 1·6% benzene solution, 968. $C_{37}H_{24}OCl_7Sb_2Rh$ requires Cl, 23·0; Sb, 22·6; Rh, 9·5%; *M*, 1079). $\chi_M = -342 \times 10^{-6}$.

Reaction of Carbonylbis(triphenylstibine)chlororhodium(I) *with Tri-*p*-chlorophenyl Phosphite.*—This reaction was carried out as for the corresponding phosphine derivative. (1) With 1 or 2 mols. of phosphite a mixture of yellow and orange products was obtained. From this repeated recrystallisation gave pure tris(tri-*p*-chlorophenyl phosphite)chlororhodium. (2) With 3 mols. of phosphite, tris(tri-*p*-chlorophenyl phosphite)chlororhodium was obtained in good yield. These products were identified by their infrared spectra.

Conductivity Measurements.—None of the compounds described conducts electricity in a 10^{-3} molal nitrobenzene solution at 20°.

Magnetic Moments.—These were determined by a Gouy balance at 20°.

Dipole Moments.—The dielectric constants of benzene solutions of the tertiary phosphine and arsine derivatives were measured at 25° on an apparatus kindly made available by Dr. J. Chatt, Akers Research Laboratories, Imperial Chemical Industries Limited, The Frythe, Welwyn, Herts. From the values of the dielectric constants the dipole moments were calculated by Jensen's approximate formula.[9]

Infrared Spectra.—The compounds were finely ground and suspended in Vaseline. Their infrared spectra were determined with a Perkin-Elmer (type 21) spectrophotometer with a rock-salt prisms and cell. No compensation was made for the absorption of the Vaseline. The author is indebted to Istituto di Chimica Industriale del Politecnico-Milano, for these measurements.

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