482. *Carbonyl Complexes of Rhodium. Part II.* Complexes with Triaryl Phosphites.*

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The preparation and properties of complexes [$RhL_2(CO)Cl$] and [RhL_3Cl] (L = triaryl phosphite) are described. These compounds are monomers, non-electrolytes, and diamagnetic. The complexes [$RhL_2(CO)Cl$] are similar to, but less stable than, the analogous compounds with triarylphosphines. On treatment with an excess of triaryl phosphite they give complexes of the type [RhL_3Cl]. The complexes [$RhL_2(CO)Cl$] react with sodium thiocyanate, losing carbon monoxide and giving compounds [$Rh_2L_4(SCN)_2$] which are diamagnetic, non-electrolytes, and have a binuclear structure with bridging thiocyanate groups.

The triaryl derivatives of tervalent phosphorus, arsenic, and antimony react (cf. Part I *) with tetracarbonyl-μμ′-dichlorodirhodium thus:

$$[Rh_2(CO)_4Cl_2] + 4L \longrightarrow 2[RhL_2(CO)Cl] + 2CO$$
$$(L = Ar_3P,\ Ar_3As,\ \text{and}\ Ar_3Sb)$$

Triaryl phosphites used in this reaction gave two series of compounds: [$RhL_2(CO)Cl$] and [RhL_3Cl] where $L = (PhO)_3P$, $(p\text{-}C_6H_4Me{\cdot}O)_3P$, or $(p\text{-}C_6H_4Cl{\cdot}O)_3P$). The former, which are formally analogous to the products isolated with triphenylphosphine, can be prepared by using the stoicheiometric amount of triaryl phosphite, and the latter by using an excess of phosphite.

That triarylphosphines do not give compounds [RhL_3Cl] even under very drastic conditions is in agreement with the previous observation that triaryl phosphites with metal carbonyls tend to give products poorer in carbon monoxide than those obtained by reaction with triarylphosphines.

The compounds of both series, [$RhL_2(CO)Cl$] and [RhL_3Cl], are non-electrolytes in nitrobenzene solution, monomeric, and diamagnetic. The complexes prepared, and their properties, are listed in the Table.

Triaryl phosphite complexes of rhodium(I).

Complex	Decomp. pt.	
[$Rh\{(C_6H_5{\cdot}O)_3P\}_2(CO)Cl$]	160—170°	Pale yellow needles
[$Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_2(CO)Cl$]	170—176	Pale yellow needles
[$Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_2(CO)Cl$]	180—185	Yellow plates
[$Rh\{(C_6H_5{\cdot}O)_3P\}_3Cl$]	170—180	Yellow needles
[$Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_3Cl$]	166—167	Yellow needles
[$Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_3Cl$]	183—186	Pale yellow needles
[$Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_3(SCN)$]	150—170	Yellow prisms
[$Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_3(SCN)$]	158—160	Yellow prisms
[$Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_3I$]	135—136	Orange prisms
[$Rh_2\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_4(SCN)_2$]	150—175	Yellow prisms

Compounds [RhL_3Cl] are stable to dilute aqueous acid and strong base, and to boiling concentrated hydrochloric acid. They do not possess reducing properties and are not attacked by strong reducing agents such as hypophosphorous acid in aqueous alcohol, hydrazine hydrate in ethanol, or metals (magnesium, zinc, and cadmium). They do not react with aromatic amines or pyridine, but are decomposed by aryl *iso*cyanides with formation of tetra*iso*cyanorhodium(I) salts.

The chlorine in the compounds [RhL_3Cl] can be replaced by iodine or thiocyanate in acetone solution by means of sodium iodide or thiocyanate respectively. These derivatives are analogous to the corresponding chlorides, but the iodide is less stable. The solid does not alter on storage for several months, but its solutions, when exposed to the air, become brown within a few hours.

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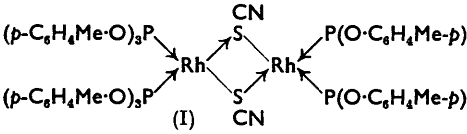
* Part I, 1957, 2287.

The complexes $[RhL_2(CO)Cl]$ behave analogously to the corresponding phosphine complexes, but are more reactive towards triaryl phosphites and sodium thiocyanate. With the former they lose carbon monoxide and give $[RhL_3Cl]$. They react with a suspension of sodium thiocyanate in acetone in the cold: carbon monoxide is liberated and, when $[Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_2(CO)Cl]$ is used as a starting material, a yellow crystalline product can be isolated; this is a non-electrolyte in nitrobenzene solution and diamagnetic, has the composition $[Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_2(SCN)]$, and must be formulated as a dimer with bridging thiocyanate groups (cf. I). Molecular-weight determinations are not reliable because of the very low solubility of this product. The formulation is, however, supported by the infrared spectrum. It is known [2] that in the thiocyanato-complexes of platinum(II) terminal thiocyanate groups absorb in the region of 2100—2150 cm.$^{-1}$, while bridging thiocyanate groups absorb between 2150 and 2182 cm.$^{-1}$. Compound (I) has a strong absorption band at 2150 cm.$^{-1}$ while in the monomeric complex $[Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_3(SCN)]$, in which the thiocyanate group is certainly terminal, does not absorb in this region but has a strong absorption band at 2092 cm.$^{-1}$.



(I)

The preceding three types of rhodium(I)–phosphite complex should have square planar configuration, and $[RhL_2(CO)Cl]$ should exist in *cis*- and *trans*-forms. It is probable that they have *trans*-configuration, in analogy with the similar derivatives of phosphines and arsines (Part I).

EXPERIMENTAL

Carbonylbis(triphenyl Phosphite)chlororhodium(I), $[Rh\{(Ph{\cdot}O)_3P\}_2(CO)Cl]$.—A solution of triphenyl phosphite (4 mmols.) in benzene (50 ml.) was added to a solution of tetracarbonyldichlorodirhodium (1 mmol.) in benzene (20 ml.). Carbon monoxide was evolved and the colour of the solution changed from orange to yellow. The solution was taken to dryness at 15 mm., giving a yellow oil which was washed with ethanol. This was treated in chloroform with charcoal, filtered, and diluted with ethanol. Crystals slowly separated. The *complex* was purified further by reprecipitation from chloroform with ethanol (Found: P, 8·0; Rh, 12·95%; *M*, cryoscopic in 2·3% benzene solution, 770. $C_{37}H_{30}O_7ClP_2Rh$ requires P, 7·9; Rh, 13·1%; *M*, 787). It is soluble in methylene chloride, chloroform, benzene, and nitrobenzene, moderately soluble in acetone and ethyl ether, insoluble in methanol, ethanol, and hexane. It is diamagnetic.

The following were prepared and purified analogously:

*Carbonylbis(tri-*p*-tolyl phosphite)chlororhodium*(I), $[Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_2(CO)Cl]$ (Found: P, 6·4; Rh, 11·5%; *M*, cryoscopic in 2·2% benzene solution, 865. $C_{43}H_{42}O_7ClP_2Rh$ requires P, 7·1; Rh, 11·8%; *M*, 871), $\chi_m = -464 \times 10^{-6}$.

*Carbonylbis(tri-*p*-chlorophenyl phosphite)chlororhodium*(I), $[Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_2(CO)Cl]$ (Found: P, 6·4; Rh, 10·4; CO, 3·0%; *M*, cryoscopic in 2·4% benzene solution, 990. $C_{37}H_{24}O_7Cl_7P_2Rh$ requires P, 6·2; Rh, 10·4; CO, 2·8%; *M*, 994), $\chi_m = -474 \times 10^{-6}$.

*Attempted Reaction of Carbonylbis(tri-*p*-chlorophenyl Phosphite)chlororhodium with* p*-Toluidine and Pyridine*.—The complex (0·1 g.) in chloroform (10 ml.) and an excess of *p*-toluidine were refluxed for 10 min. The solution was cooled and on dilution with ethanol a crystalline product was obtained (0·075 g.) which did not contain nitrogen and evolved carbon monoxide on addition of aryl*iso*cyanides. It was identical with the starting material, as shown by its infrared spectrum.

The starting material was also recovered unchanged after being boiled with pyridine in chloroform and identified by its infrared spectrum.

*Reaction of Carbonylbis(tri-*p*-chlorophenyl Phosphite)chlororhodium with* p*-Tolyl* iso*Cyanide*.—*p*-Tolyl *iso*cyanide was added to the complex suspended in ethanol. Carbon monoxide was

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[1] Malatesta and Sacco, *Ann. Chim. (Italy)*, 1954, **44**, 134.

[2] Chatt and Duncanson, *Nature*, 1956, **178**, 997.

evolved and the starting material dissolved, giving a brown-red solution. On addition of sodium perchlorate in ethanol a violet crystalline product separated, which in boiling benzene gave yellow $[Rh(p\text{-}C_6H_4Me{\cdot}NC)_4]ClO_4$ (Found: N, 8·5; Rh, 15·2. Calc. for $C_{32}H_{28}O_4NClRh$: N, 8·3; Rh, 15·35%).

Reaction of Carbonylbis(*tri*-p-*tolyl Phosphite*)*chlororhodium with Sodium Thiocyanate.*—Solid sodium thiocyanate (0·15 g.) was added to the complex (0·4 g.) suspended in acetone (15 ml.); there was gas evolution and the solid changed in appearance. The mixture was boiled for 10 min. and then the solvent evaporated at 15 mm. The residual solid was extracted with chloroform; the solution was filtered and diluted with ethanol. Crystals separated at once, and were filtered off, washed with ethanol, and purified by reprecipitation with ethanol from a chloroform solution (yield 0·3 g.). They were *tetrakis*(*tri*-p-*tolyl phosphite*)-*μμ′-dithiocyanatodirhodium*, $[\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_4Rh_2(SCN)_2]$ [Found: C, 59·2; H, 5·1; N, 1·8%; *M*, cryoscopic in 0·66% benzene solution, 1400 (not very reliable because of low solubility). $C_{86}H_{84}O_{12}N_2S_2P_4Rh_2$ requires C, 59·65; H, 4·9; N, 1·6%; *M*, 1731]. It is appreciably less soluble than the other compounds described. It is diamagnetic. It does not evolve carbon monoxide when treated with aryl *iso*cyanides, even at 100°.

Tris(*triphenyl Phosphite*)*chlororhodium*(I), $[Rh\{(Ph{\cdot}O)_3P\}_3Cl]$.—Triphenyl phosphite (8 mmols.) was added to a solution of tetracarbonyldichlorodirhodium (1 mmol.) in benzene. The solution was evaporated to a small volume at 15 mm. and diluted with ethanol. The *complex* obtained was recrystallised from chloroform by addition of ethanol (yield 1·75 g.) (Found: P, 8·4; Rh, 9·55%; *M*, cryoscopic in 3·4% benzene solution, 1035. $C_{54}H_{45}O_9ClP_3Rh$ requires P, 8·7; Rh, 9·6%; *M*, 1069). It is slightly less soluble than its carbonyl analogue. It is diamagnetic.

The following were prepared and purified analogously:

Tris(*tri*-p-*tolyl phosphite*)*chlororhodium*(I), $[Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_3Cl]$ (Found: P, 7·7; Rh, 8·7%; *M*, cryoscopic in 3·0% benzene solution, 1100. $C_{63}H_{63}O_9ClP_3Rh$ requires P, 7·8; Rh, 8·6%; *M*, 1195), $\chi_m = -746 \times 10^{-6}$.

Tris(*tri*-p-*chlorophenyl phosphite*)*chlororhodium*(I), $[Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_3Cl]$ (Found: Cl, 25·95; P, 6·7; Rh, 7·5%; *M*, cryoscopic in 8% bromoform solution, 1410. $C_{54}H_{36}O_9Cl_{10}P_3Rh$ requires Cl, 25·7; P, 6·7; Rh, 7·5%; *M*, 1379), $\chi_m = -396 \times 10^{-6}$.

An attempted reaction of tris(tri-*p*-chlorophenyl phosphite)chlororhodium with *p*-toluidine, as described for the carbonyl compound, gave unchanged starting material (infrared spectrum).

Tris(*tri*-p-*tolyl Phosphite*)*thiocyanatorhodium*(I), $[Rh\{(p\text{-}C_6H_4Me{\cdot}O)_3P\}_3(SCN)]$.—The chloro-complex (0·4 g.) and sodium thiocyanate (0·3 g.) in acetone were refluxed for 15 min., then taken to dryness under reduced pressure, and the residual solid was extracted with chloroform. The solution was filtered and diluted with ethanol. A crystalline *product* was obtained (0·31 g.), which was purified as its chloro-analogue (Found: N, 1·3; S, 2·8%; *M*, cryoscopic in 1·2% benzene solution, 1233. $C_{64}H_{63}O_9NSP_3Rh$ requires N, 1·15; S, 2·6%; *M*, 1218). It is diamagnetic.

Tris(*tri*-p-*chlorophenyl Phosphite*)*thiocyanatorhodium*(I), $[Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_3(SCN)]$.—This *compound* was prepared and purified as its *p*-tolyl analogue (yield 0·5 g. from 0·6 g.) (Found: N, 1·15; S, 2·45%. $C_{55}H_{36}O_9NCl_9SP_3Rh$ requires N, 1·0; S, 2·3%). It is diamagnetic.

Tris(*tri*-p-*chlorophenyl Phosphite*)*iodorhodium*(I), $[Rh\{(p\text{-}C_6H_4Cl{\cdot}O)_3P\}_3I]$.—This complex, prepared and purified analogously to the corresponding thiocyanate (yield 0·2 g. from 0·3 g. of chloro-complex and 0·15 g. of sodium iodide) (Found: C, 43·8; H, 2·65%; *M*, cryoscopic in 1·6% benzene solution, 1410. $C_{54}H_{36}O_9Cl_9IP_3Rh$ requires C, 44·0; H, 2·5%; *M*, 1475), is diamagnetic.

Conductance Measurements.—None of the compounds described shows electric conductance in 10^{-3}M-nitrobenzene solution at 20°.

Infrared Spectra.—The compounds were finely ground and suspended in Vaseline. Their infrared spectra were taken with a Perkin-Elmer spectrophotometer (type 21), a rock-salt prism and cell being used. No compensation was made for the absorption of the Vaseline.

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