

New complexes of rhodium(I) with conjugated diolefins or other compounds containing activated double bonds

In a previous note¹ we reported on the preparation and structure of the complex $(C_4H_6)_2RhCl$, containing two molecules of butadiene coordinated to a central atom of monovalent rhodium. A method of preparation of such a complex consisted in reacting $RhCl_3$ with cyclooctene, and subsequently treating the brown complex so obtained, $(C_3H_{14})_2RhCl$ (I), with liquid butadiene. The last reaction proceeds rapidly and with high yield.

In continuation of our work, we have examined the reaction of (I) with various conjugated diolefins and also with some compounds containing activated double bonds. We have obtained by this route, under very mild conditions, a series of complexes of monovalent rhodium, resulting from the total or partial replacement of cyclooctene in (I) by new ligands. In this note we wish to report briefly on the preparation and properties of these new complexes.

On reacting, at about -10° , (I) and the *trans* isomer of 1,3-pentadiene, a yellow microcrystalline powder is obtained, which can be recrystallized by dissolving in petroleum ether at 0° and cooling at -78° . Elemental analysis is in accord with the formula $(C_5H_8)_2RhCl$ (II). In the crystalline state, this complex can be kept at room temperature, under nitrogen, for several days. Its solutions in organic solvents, however, decompose rapidly, even in an inert atmosphere. *E.g.*, from solutions of (II) in benzene, acetone, or chloroform, left at room temperature under nitrogen, a red-brown precipitate forms after 5–10 min, the composition of which has not yet been determined. (II) reacts rapidly with 1,5-cyclooctadiene, giving, in practically quantitative yields, the known complex² $(C_8H_{12})_2Rh_2Cl_2$ and furthermore free pentadiene (*trans* isomer) in a ratio of two molecules per atom of rhodium. Analogously, $(CO)_4Rh_2Cl_2^{2-}$ is obtained on reaction of (II) with CO, and $[(C_6H_5)_3P^-]_3RhCl^+$ on reaction with $(C_6H_5)_3P$, together with free pentadiene.

Also the *cis* isomer of pentadiene reacts with (I), giving a crystalline complex, which was found to be unstable above about -10° . The complex is still under examination.

Isoprene and 2,3-dimethylbutadiene react rapidly at 0° with (I) to give complexes in which only one molecule of cyclooctene has been replaced by the diolefin. Elemental analyses of these complexes are in accord with the formulae $(C_3H_{14})(C_5H_8)RhCl$ (III) and $(C_3H_{14})(C_6H_{10})RhCl$ (IV), respectively.

On reacting with cyclooctadiene both (III) and (IV) give $(C_8H_{12})_2Rh_2Cl_2$, setting free the diolefin and cyclooctene. (III) and (IV) were found to be slightly more stable, either in solution or in the crystalline state, than the complex $(C_4H_6)_2RhCl$ reported in the previous note and the above complex (II) as well. On reaction with *p*-toluidine in petroleum ether, (III) and (IV) give complexes in which one molecule of *p*-toluidine is substituted for one molecule of cyclooctene, of formula $(p\text{-toluidine})(C_5H_8)RhCl$ (V) and $(p\text{-toluidine})(C_6H_{10})RhCl$ (VI), respectively. (V) and (VI) give on reaction with cyclooctadiene the known complex² $C_8H_{12}RhCl(p\text{-toluidine})$, monomeric, together with isoprene or 2,3-dimethylbutadiene, in a ratio of one molecule per atom of rhodium.

Even performing the reaction between (I) and isoprene or 2,3-dimethylbutadiene above 0° , *e.g.* in the boiling diolefin, it was not possible to obtain complexes

containing two molecules of diolefin per atom of rhodium. Complexes of this type, however, of formula $(C_5H_8)_2RhCl$ (VII) and $(C_6H_{10})_2RhCl$ (VIII), could be obtained by reacting the complex containing butadiene, $(C_4H_6)_2RhCl$, with liquid isoprene or 2,3-dimethylbutadiene respectively, at 0° . The behaviour of (VII) and (VIII) in the reactions with CO, cyclooctadiene, or $(C_6H_5)_3P$ is analogous to that of (II).

Conjugated diolefins containing functional groups also react readily with (I). From methyl sorbate, *e.g.*, a complex is obtained, $(C_7H_{10}O_2)_2RhCl$ (IX), which forms a brick-red microcrystalline powder, fairly stable at room temperature under nitrogen, and, for some time, also in the air. (IX) is slightly soluble in petroleum ether, more soluble in benzene. In solution, it is much more stable than, *e.g.* (II) or (III), no formation of precipitate being observed even after many hours. On reaction with cyclooctadiene or $(C_6H_5)_3P$, (IX) gives two molecules of methyl sorbate per atom of rhodium and, $(C_3H_{12})_2Rh_2Cl_2$ or $[(C_6H_5)_3P]_3RhCl$ respectively.

Compounds containing double bonds activated by negative groups also react with (I). For instance, from dimethyl maleate and acrylonitrile yellow crystalline complexes have been obtained of formula $(C_6H_8O_4)_2RhCl$ (X) and $(C_3H_3N)_2RhCl$ (XI), respectively. (XI) is practically insoluble in benzene, petroleum ether, chloroform. Unlike the preceding compounds, it does not react, at room temperature, with cyclooctadiene or $(C_6H_5)_3P$.

Several other complexes of monovalent rhodium have been obtained by this route, which have not been so far completely characterized and which therefore will be described in the final paper.

The above results, however, are sufficient to show that complex (I), easily obtainable, is an useful intermediate for the synthesis of a vast class of compounds of rhodium, which are not easily obtainable by other ways.

All the above compounds are diamagnetic. In complexes (II)–(IX) the coordination of the diolefin is most probably of the same type as that observed in the compound $(C_4H_6)_2RhCl$, previously described¹, and obtained by the same route. That "butadiene-type" ligands are present in these complexes is clearly shown, (a) by the reactions with cyclooctadiene or $(C_6H_5)_3P$, each of which sets the diolefin free from the complex, and (b) by the infrared spectra of (II)–(IX), which indicate the absence of free C=C bonds, but include bands in the region 1460–1480 cm^{-1} , which are characteristic of the complexed conjugated double bonds (see *e.g.* refs. 5 and 6). Similar bands are present in the known complex⁷ $C_4H_6Fe(CO)_3$, in some diolefin complexes of V, Mo or Mn recently described⁸ and also in the complex $(C_4H_6)_2RhCl$ described by us¹.

In the infrared spectrum of (XI) the band characteristic of the non-complexed vinyl group is absent, which indicates that the π electrons of the double bond are involved in the bonding to Rh. On the other hand, the band of the nitrile group is present, though slightly shifted [2235 cm^{-1} in the spectrum of liquid acrylonitrile, 2250 cm^{-1} in that of (XI)].

Analogously, in the IR spectrum of (X), the band of the free C=C bonds is absent, which is at about 1645 cm^{-1} in liquid dimethyl maleate, while the band of the $>C=O$ ester groups is present, which has almost the same position as in liquid dimethyl maleate (~ 1730 cm^{-1}). Hence, also in this case, the π electrons of the C=C bond are involved in the bonding to Rh.

TABLE I

SOME PROPERTIES OF THE LL'RhCl COMPLEXES (L, L' = organic ligands)

Ligand		Formula	Colour	Melting or decomposition temp. (°C)	Typical bands in the I.R. spectrum (cm ⁻¹)
L	L'				
butadiene	butadiene	RhCl(C ₄ H ₆) ₂	pale yellow	40 ^a	1474, 1464, 1432, 1365
cyclooctene	cyclooctene	Rh(C ₈ H ₁₄) ₂	brown	140 ^a	1458, 1439, 1350
pentadiene	pentadiene	RhCl(C ₅ H ₈) ₂	pale yellow	40 ^a	1475, 1456, 1442, 1376
isoprene	cyclooctene	RhCl(C ₅ H ₈)(C ₈ H ₁₄)	light brown	105-106 (dec.)	1479, 1464, 1446, 1371
2,3-dimethyl-butadiene	cyclooctene	RhCl(C ₆ H ₁₀)(C ₈ H ₁₄)	light brown	114-115 (dec.)	1464, 1446, 1375
isoprene	<i>p</i> -toluidine	RhCl(C ₅ H ₈)(C ₇ H ₉ N)	yellow green	145 ^a	1468, 1453, 1379
2,3-dimethyl-butadiene	<i>p</i> -toluidine	RhCl(C ₆ H ₁₀)(C ₇ H ₉ N)	yellow green	152 ^a	1467, 1452, 1380
isoprene	isoprene	RhCl(C ₅ H ₈) ₂	pale yellow	125 ^a	1464, 1455, 1445, 1368
2,3-dimethyl-butadiene	2,3-dimethylbutadiene	RhCl(C ₆ H ₁₀) ₂	pale yellow	140 ^a	1472, 1455, 1433, 1380
methyl sorbate	methyl sorbate	RhCl(C ₇ H ₁₀ O ₂) ₂	red	118-122 (dec.)	1720, 1461, 1444, 1435, 1378
methyl maleate	methyl maleate	RhCl(C ₆ H ₈ O ₄) ₂	yellow	108-113 (dec.)	1730, 1467, 1455, 1440, 1384
acrylonitrile	acrylonitrile	RhCl(C ₃ H ₃ N) ₂	yellow	120 ^a	2250, 1462, 1360

^a Decompose without melting.

Some of these complexes are now being investigated by X-ray techniques, in order to reach definitive conclusions about their structure.

Table I summarizes, for the sake of clarity, some characteristics of the complexes obtained. More detailed information concerning the preparation as well as the properties and structure of the above compounds will be reported in a subsequent paper.

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