Journal of Organometallic Chemistry, 87 (1975) 341—346

FLUOROPHOSPHINE COMPLEXES OF RHODIUM

VI*. REACTION OF DI-μ-CHLOROTETRAKIS(TRIFLUOROPHOSPHINE)-DIRHODIUM(I) WITH MONO- AND DI-OLEFINS

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(Received October 14th, 1974)

Summary

$[RhCl(PF_3)_2]_2$ (I) reacts with conjugated dienes to form the yellow complexes $[RhCl(PF_3)_2diene]_n$ (diene = 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene) which are unstable thermally and in solution. I forms an isolable complex with acrylonitrile and acts as a homogeneous catalyst for the isomerisation of 1-decene to 2-decene.

Several diene complexes of rhodium are known [1-3]. Chlorobis(cyclooctene)rhodium(I) has been shown to react with various 1,3-dienes to afford complexes of the type $RhCl(diene)_2$ (e.g., diene = 1,3-butadiene, 1,3-pentadiene, and 2-methyl-1,3-butadiene) [4]. These complexes are moderately stable in the solid state, but decompose rapidly on heating or in solution. $RhCl(PPh_3)_3$ reacts with 1,3-butadiene to give $RhCl(C_4H_6)(PPh_3)_2$ [5], while $[RhCl(CO)_2]_2$ and 1,3-cyclohexadiene give the 1/1 complex $Rh_2Cl_2(CO)_4(C_6H_8)$, which on attempted sublimation readily reforms the starting materials [6]. There is a report of a hexafluorobutadiene carbonyl rhodium complex $RhCl(C_4F_6)(CO)_2$ in which the metal atom is part of an unsaturated perfluoroheterocycle [5].

We find that the red complex di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I), $[RhCl(PF_3)_2]_2$ [7,8], reacts readily with an excess of butadiene at room temperature to give a yellow crystalline solid formulated as $[RhCl(C_4H_6)(PF_3)_2]_n$ (II) on the basis of elemental analysis and a careful study of the reaction stoichiometry. Complex II is stable at room temperature but attempted high-vacuum sublimation results in decomposition and the regeneration of $[RhCl(PF_3)_2]_2$ and butadiene. The mass spectrum of II shows no parent ion but mass peaks corresponding to both the $C_4H_6^+$ and $[RhCl(PF_3)_2]_2^+$ molecular ions are observed. II also rapidly decomposes in solution.

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* For part V see ref. 17.

In a similar way 1,3-pentadiene reacts with $[RhCl(PF_3)_2]_2$ to afford the yellow crystalline solid $[RhCl(C_5H_8)(PF_3)_2]_n$ (III) which is moderately stable in the solid state at room temperature.

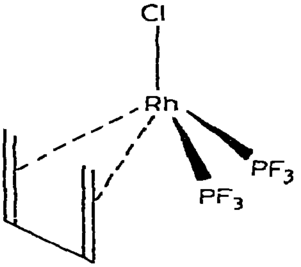
The reaction between $[RhCl(PF_3)_2]_2$ and an excess of 2-methyl-1,3-butadiene in vacuo at 0° gives initially a yellow crystalline solid (after removal of excess diene at −78°), but when this solid is allowed to warm to room temperature an immediate decomposition occurs, yielding $[RhCl(PF_3)_2]_2$ and 2-methyl-1,3-butadiene. The formation of one molecule of the diene per rhodium atom together with the initial reaction stoichiometry suggests that the unstable yellow complex is $[RhCl(C_5H_8)(PF_3)_2]_n$.

All the above reactions therefore may be represented by the equation:

$$[RhCl(PF_3)_2]_2 + 2n \text{ diene} \rightleftharpoons 2\,[RhCl(\text{diene})(PF_3)_2]_n$$

the position of equilibrium being dependent on the nature of the diene.

It has not been possible to determine whether the dienerhodium complexes are monomeric or dimeric in view of their ready dissociation both in solution and in the mass spectrometer. However, a monomeric complex would be expected to have the structure shown below in which the coordination round the metal atom approximates to a square pyramid. This type of structure has been established for $RhCl(C_4H_6)_2$ by a single crystal X-ray crystallographic study [9,10].



$[RhCl(PF_3)_2]_2$ reacts with an excess of the activated monoolefin acrylonitrile to give a yellow crystalline solid which on the basis of analytical data and the reaction stoichiometry is formulated as $[RhCl(PF_3)_2(C_3H_3N)]_n$. This compound which decomposes without melting at 100° and is insoluble in common organic solvents, is related to the previously reported compound $RhCl(C_3H_3N)_2$ [4].

$[RhCl(PF_3)_2]_2$ does not form any isolable complexes with simple olefins, e.g., propene, butene, etc., [11,12], but it does catalyse the isomerisation of 1-decene to 2-decene in toluene solution. The rate of isomerisation is very slow at room temperature, but occurs at a convenient rate above 80°. The isomerisation reaction affords *cis*-2-decene initially and this is subsequently isomerised to the *trans*-isomer. After a 20% conversion of 1-decene the *cis/trans* ratio of 2-decene is 3/1 decreasing to 1/3 at 75% conversion. Some limited kinetic data are available for this isomerisation process.

The reaction rates were studied over a catalyst concentration range 0.015 to 0.045 *M* (see Experimental section). Plots of log C_t/C_0 versus time (where C_0 is the initial 1-decene concentration and C_t the concentration at time t) for different temperatures and catalyst concentrations gave reasonably good straight lines (e.g., see Fig. 1), but an extrapolation of the data points did not go through the origin.

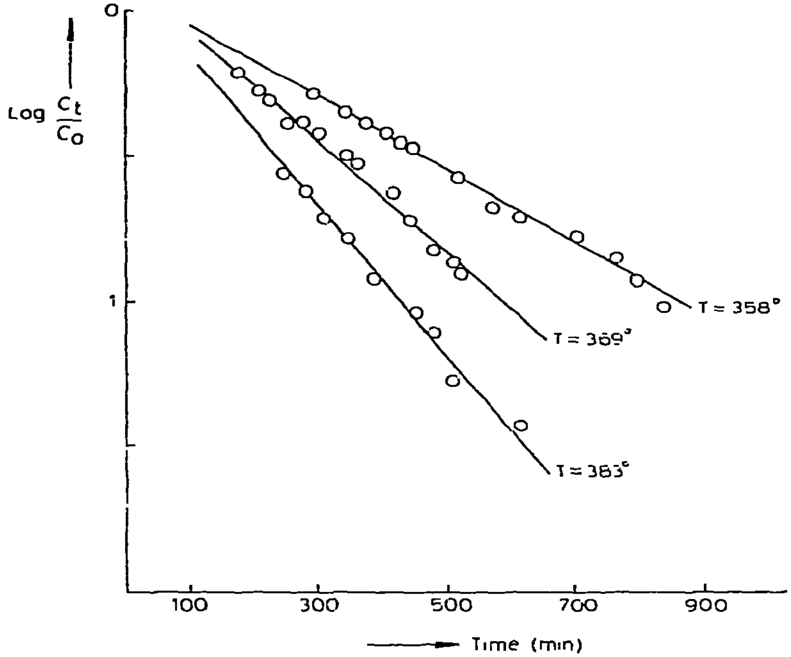


Fig. 1.

Variable temperature studies were made at a fixed catalyst concentration of 0.015 *M* and a plot of $\log_{10} k$ versus $1/T$ gave an activation energy of about 40 kJ mol^{-1}. A value of 100 kJ mol^{-1} was obtained by Wilkinson et al. for the activation energy for the isomerisation of 1-pentene to 2-pentene catalysed by $RhH(CO)(PPh_3)_3$ [13]. Many rhodium complexes catalysing the isomerisation of olefins require a co-catalyst (e.g., HCl or H_2) which initiates reaction by the formation of metal hydrido intermediates [14], but $RhCl(PPh_3)_3$ is also an active isomerisation catalyst at 80° without added activators [15].

One possible mechanism for the $[RhCl(PF_3)_2]_2$ catalysed olefin isomerisation of olefins would involve coordination of the olefin to the rhodium followed by a hydrogen migration from carbon to metal to give a π-allyl hydride intermediate which then could undergo a hydride shift to the less substituted carbon atom. We have shown elsewhere the feasibility of the latter process [11,12] and the reversible equilibrium between coordinated propene and a π-allyl metal hydride has been demonstrated by Bönnemann [16] in a nickel complex. We have not, however, been successful in detecting this type of intermediate in solutions of $[RhCl(PF_3)_2]_2$ and terminal olefins even using NMR spectroscopy at temperatures as low as −75°.

Experimental

Reactions were carried out and complexes handled either in vacuo or under an atmosphere of dry nitrogen gas. Solvents were dried and freshly distilled under dinitrogen before use. IR spectra were recorded in the 4000-400 cm^{-1} range on a Perkin—Elmer 457 spectrometer. Elemental analyses were carried out by

Mrs. A. Olney of this department. Mass spectra were recorded on an A.E.I. MS9 spectrometer.

In the catalytic studies toluene and 1-decene were freshly distilled under dinitrogen from sodium wire and KOH respectively. $[RhCl(PF_3)_2]_2$ was sublimed in vacuo immediately before use. Samples were extracted using a syringe and analysed by GLC using a Varian—Aerograph 500 D with flame ionisation detector. The 9′ column used was packed with 5% β,β'-oxydipropionitrile on Chromosorb G.

Reaction between $[RhCl(PF_3)_2]_2$ and 1,3-butadiene

$[RhCl(PF_3)_2]_2$ (0.200 g, 0.318 mmol) was sealed off in an evacuated glass ampoule with 1,3-butadiene (0.300 g, 5.55 mmol) and the mixture shaken at room temperature. After cooling the ampoule to − 78° the volatile products were fractionated to give a trace of PF_3, and unreacted 1,3-butadiene (0.269 g, 4.97 mmol). The combining ratio C_4H_6/Rh is therefore 0.91/1.

The yellow solid residue was washed with a 1/1 mixture of butadiene and chloroform and gave yellow crystals (0.140 g), m.p. 60° (dec.). Found: C, 14.5; H, 2.0. $C_4ClH_6F_6P_2Rh$ calcd.: C, 13.04; H, 1.63%. IR spectrum: 3080m, 3040m, 3020w, 2950m, 1435m, 1240w, 1220w, 1200w, 1000w, 972w, 930s, 892(sh), 875vs, 851vs, 795w cm^{-1} (nujol and hexachlorobutadiene mulls). The mass spectrum showed peaks at both m/e = 628 and m/e = 54, corresponding to $[RhCl(PF_3)_2]_2^+$ and $C_4H_6^+$ respectively.

Reaction between $[RhCl(PF_3)_2]_2$ and 1,3-pentadiene

A mixture of $[RhCl(PF_3)_2]_2$ (0.175 g, 0.278 mmol) and an excess of 1,3-pentadiene (0.235 g, 3.45 mmol) was kept at 0° for 2 h after which time yellow crystals had formed on the side of the ampoule. In a similar way to that described above, removal of the volatile products yielded a trace of PF_3, and pentadiene (0.192 g, 2.82 mmol) and left a pale yellow solid residue (0.174 g), m.p. 60°. Found: C, 16.2; H, 2.1. $C_5ClH_8F_6P_2Rh$ calcd.: C, 15.66; H, 2.08%. IR spectrum: 3080w, 3040m, 2995w, 2960w, 1730w, 1500w, 1200w, 1038w, 971m, 930s, 920(sh), 872s, 855s, 555s, 528s cm^{-1} (nujol and hexachlorobutadiene mulls). The mass spectrum showed peaks assignable to both $[RhCl(PF_3)_2]_2^+$ (628) and $C_5H_8^+$ (68). The ratio of C_5H_8 to rhodium is 1.13/1.

Reaction between $[RhCl(PF_3)_2]_2$ and 2-methyl-1,3-butadiene

When a mixture of $[RhCl(PF_3)_2]_2$ (0.128 g, 0.204 mmol) and 2-methyl-1,3-butadiene (0.471 g, 6.91 mmol) was kept at 0° for 30 min large yellow crystals formed on the sides of the ampoule. 2-Methyl-1,3-butadiene (0.442 g, 6.49 mmol) could be pumped away from the sample held at −78° (combining ratio C_5H_8/Rh is therefore 1.03/1).

When the yellow solid was warmed from −78° to room temperature it immediately decomposed to afford $[RhCl(PF_3)_2]_2$ (0.099 g, 0.157 mmol) and 2-methyl-1,3-butadiene (0.030 g, 0.440 mmol) leaving behind a trace of yellow oil. Thus the unstable yellow solid has the formula $[RhCl(C_5H_8)_{1.08}(PF_3)_2]_n$.

Reaction between $[RhCl(PF_3)_2]_2$ and acrylonitrile

$[RhCl(PF_3)_2]_2$ (0.200 g, 0.318 mmol) and acrylonitrile (0.406 g, 7.65 mmol) held at room temperature for 10 min gave a yellow solution. Removal of the volatile products yielded a trace of PF_3, unreacted acrylonitrile (0.368 g, 6.94 mmol) and left behind a yellow solid which after washing with ether gave a yellow microcrystalline solid (0.170 g), m.p. 100° (dec.). Found: C, 10.9; H, 1.7; N, 3.7. $C_3ClH_3F_6NP_2Rh$ calcd.: C, 9.76; H, 0.82; N, 3.79%. IR spectrum 2260m, 1730w, 1175s, 1025w, 930m, 880(sh), 855vs, 555s cm^{-1} (nujol mull). The ratio of C_3H_3N/Rh was 1.12/1.

Catalytic studies

In a typical experiment toluene (18.0 ml) was distilled in vacuo into a 100 ml round bottomed flask containing a known weight of $[RhCl(PF_3)_2]_2$. The flask was attached to a nitrogen line and fitted with a condenser. Samples for GLC analysis were withdrawn via a serum cap. 1-Decene (2.0 ml) was syringed into the flask to initiate the reaction and the temperature was carefully controlled. The results are summarised below:

(a) Catalyst concentration 1.5×10^{-2} mol l^{-1}; 1-decene concentration 5.3×10^{-1} mol l^{-1}.

Temperature 383 K.

Time (min), % 2-decene; 182, 24; 244, 44; 276, 47; 303, 51; 340, 54; 347, 67; 374, 62; 449, 65; 476, 67; 506, 72; 617, 76.

(b) Catalyst concentration 1.5×10^{-2} mol l^{-1}; 1-decene concentration 5.3×10^{-1} mol l^{-1}.

Temperature 358 K.

Time (min), % 2-decene; 289, 25; 339, 31; 373, 33; 404, 35; 431, 37; 446, 38; 515, 44; 568, 49; 615, 51; 698, 54; 758, 58; 792, 61; 834, 65.

(c) Catalyst concentration 1.5×10^{-2} mol l^{-1}; 1-decene concentration 5.3×10^{-1} mol l^{-1}.

Temperature 369 K.

Time (min), % 2-decene; 186, 20; 205, 24; 220, 27; 277, 33; 300, 35; 340, 39; 360, 41; 413, 47; 434, 51; 451, 57; 471, 57; 510, 58; 522, 60.

(d) Catalyst concentration 3.4×10^{-2} mol l^{-1}; 1-decene concentration 5.3×10^{-1} mol^{-1}.

Temperature 383 K.

Time (min), % 2-decene; 55, 12; 72, 16; 107, 26; 129, 34; 172, 37; 188, 43; 207, 52; 224, 56; 289, 60; 319, 71; 369, 73.

(e) Catalyst concentration 4.4×10^{-2} mol l^{-1}; 1-decene concentration 5.3×10^{-1} mol^{-1}.

Temperature 383 K.

Time (min), % 2-decene; 53, 19; 81, 25; 99, 32; 114, 38; 131, 45; 148, 52; 166, 54; 197, 65; 213, 67; 230, 69; 249, 73; 289, 76.

Acknowledgement

We thank the S.R.C. for financial support (for BW).

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