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π-ALLYLIC COMPLEXES OF RHODIUM(III) AND PLATINUM(II)
IV. CHEMICAL REACTIVITY OF π-ALLYLIC PLATINUM COMPLEXES

H. C. VOLGER AND K. VRIEZE
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.) (The Netherlands)

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SUMMARY

The reactions of $\{[(C_6H_5)_3P]_2Pt(\pi\text{-}C_3H_5)\}^+Cl^-$ and of the π-1,1-dimethylallylic analogue with hydrogen, hydrogen chloride, sulfur dioxide, carbon monoxide, ethene and 1,3-butadiene were studied. With hydrogen and hydrogen chloride the corresponding saturated and unsaturated hydrocarbons were formed respectively.

The reactions with sulfur dioxide and carbon monoxide gave rise to insertion products. The ease of these reactions is ascribed to the very low concentration of the coordinatively unsaturated platinum σ-allyl complex.

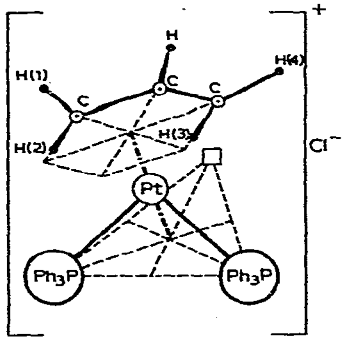
Ethene and 1,3-butadiene yielded small amounts of dimerization products.

INTRODUCTION

Previously[1-3] we reported the general synthesis of bis(triphenylphosphine)-platinum(II) π-allylic complexes by reaction of an allylhalide with the zero-valent tetrakis(triphenylphosphine)platinum in benzene at room temperature.

$$CH_2{=}CH{-}CR_2X + [(C_6H_5)_3P]_4Pt \rightleftarrows \{[(C_6H_5)_3P]_2Pt(\pi\text{-}CH_2{=}CH{=}CR_2)\}^+Cl^- + 2(C_6H_5)_3P$$

The reaction was found to be reversible[1,2]. The structure, configuration (see below) and its uni-univalent electrolytic character were assigned on the basis of molecular weight determinations, electrolytic conductivity measurements and spectroscopic (NMR and IR) data. The temperature-dependent NMR data show, at



−44°, the presence of a stable π-allyl group, which at higher temperatures changes into a dynamic π-allyl group. This process was ascribed to an intramolecular interconversion process proceeding via the σ-allyl form[2,3].

The intermediate formation of a σ-allyl species might well result in high reactivity of the complexes. Hence, the reactions of the platinum π-allylic complexes with hydrogen, hydrogen chloride, carbon monoxide, sulfur dioxide, ethylene and butadiene were investigated. Reactions of some of these reagents were already described for palladium(II) and rhodium(III) π-allylic complexes (Part III) and for zero-valent tetrakis(triphenylphosphine)platinum.

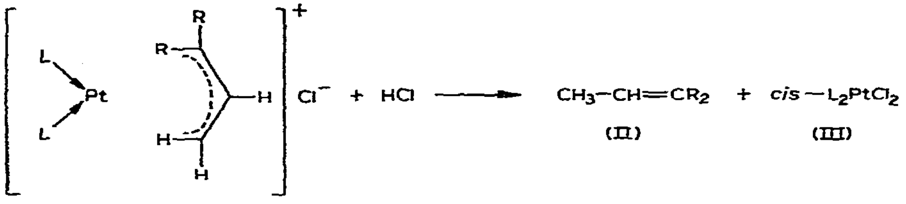
Palladium π-allylic complexes, for instance, may catalyse the carbonylation of allylic compounds[4]. Rhodium(III) π-allylic complexes dimerize ethylene to a mixture of butenes, react with sulfur dioxide to a σ-allyl species containing coordinated SO_2, and with CO give rise to a number of reactions, which finally result in $Rh(CO)ClL_2$ and the corresponding allyl compound[5].

Zero-valent tetrakis(triphenylphosphine)platinum was recently reported to undergo a number of very interesting reactions which lead *e.g.* to the following complexes: $[(C_6H_5)_3P]_2Pt(C_2H_4)$[6,7], $[(C_6H_5)_3P]_3PtSO_2$[8], $[(C_6H_5)_3P]_2Pt(O_2)$[6], $[(C_6H_5)_3P]_3Pt(CO)$[9], $[(C_6H_5)_3P]_2Pt(CO)_2$[9] and $[(C_6H_5)_3P]_2Pt(CO)$[9].

RESULTS

Hydrogen chloride

Treating a concentrated solution of (I) in chloroform with gaseous hydrogen chloride produces the corresponding unsaturated hydrocarbon (II) and *cis*-bis(triphenylphosphine)platinum dichloride (III) in nearly quantitative yield; *e.g.* for $R=CH_3$ 2-methyl-2-butene (85%) was obtained:

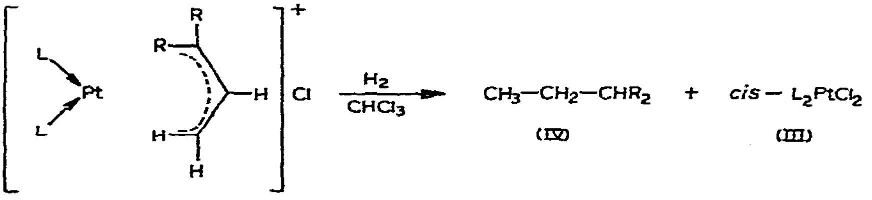


(I)

The reaction can be described as a protonation of the allyl group (presumably via the platinum atom) followed by decomposition of the intermediate π-olefin complex.

Hydrogen

Hydrogen of one atmosphere is consumed at room temperature by a solution



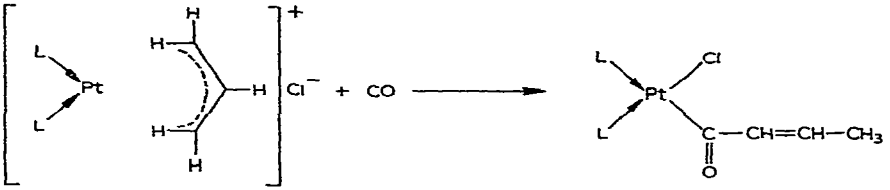
(I)

of (I) in chloroform to give the corresponding saturated hydrocarbon and *cis*-bis(triphenylphosphine)platinum dichloride (III) in high yields; besides, small amounts of the unsaturated hydrocarbon (II), triphenylphosphine and platinum metal are formed.

It seems conceivable that the reaction proceeds via a bis(triphenylphosphine)-π-olefinplatinum hydride chloride [or an isomeric bis(triphenylphosphine)-σ-alkylplatinum chloride], which either reacts with hydrogen to yield (IV) and L_2PtHCl or decomposes into (II) and L_2PtHCl. The latter complex is known to react with chloroform to yield *cis*-L_2PtCl_2 (III). Part of the saturated hydrocarbon may originate from the platinum-metal-catalysed hydrogenation of (II).

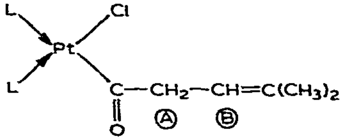
Carbon monoxide

A solution of (I) in chloroform consumed one equivalent of carbon monoxide (one atm) in fifteen hours at 20° with quantitative formation of a carbonyl insertion product, which, unlike the starting material, does not exhibit electrical conductivity. The product consisted of a one-to-one mixture of (*cis*-2-butenoyl)- and (*trans*-2-butenoyl)bis(triphenylphosphine)platinum chlorides (V):



(I) (R=H) (V)

The dimethyl-substituted complex (I, R = CH_3) yields (VI) as the sole product:



(VI)

In both cases the thermodynamically most stable product is obtained[10]; for the unsubstituted π-allyl complex (I, R = H) the insertion is apparently followed by double-bond isomerization.

Structures (V) and (VI) are assigned on the basis of NMR and IR spectroscopic evidence*. The IR spectrum of (V) shows stretching frequencies for the double bond and carbonyl group at 1650 cm^{-1} and 1630 cm^{-1}, respectively; the former frequency is about equal to that observed for croton aldehyde (1648 cm^{-1}); the latter is characteristic of a platinum(II)-carbonylalkyl group[11,12]. The NMR spectrum of (V) shows a pattern characteristic of a propenyl group (Table 1).

Some less intensive high field signals may be attributed to the allyl carbonyl complex, in which the double bond may be coordinated to the metal.

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* Products (V) and (VI) are depicted tentatively in the *cis* configuration.

TABLE 1

NMR DATA OF (*cis*-2-BUTENOYL)- AND (*trans*-2-BUTENOYL)BIS(TRIPHENYLPHOSPHINE)PLATINUM CHLORIDES

	H_A		H_B		H_C	H_D		H_E		H_F
δ(ppm)	4.05		4.95		2.10	4.60		5.09		2.10
J(c/s)		17(H_A–H_B)		7(H_B–H_C)			10(H_D–H_E)		7(H_E–H_F)	

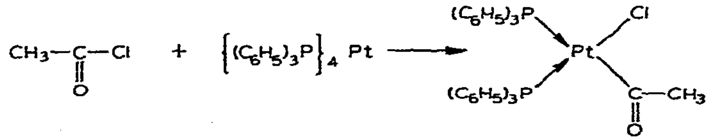
The IR spectrum of the 4-methyl-3-pentenoyl complex (VI) shows frequencies at 1660 cm^{-1} and 1650 cm^{-1} for the carbonyl and double bond; the NMR spectrum shows signals at 1.99 ppm [CH_2(A), doublet, $J(CH_2–H_B)=7$ c/s], 5.01 ppm [H_B, triplet, $J(CH_2–H_B)=7$ c/s], 1.02 ppm (CH_3, singulet) and 1.50 ppm (CH_3, singulet).

The remarkably high field signals of the two methyl groups may indicate coordination of the double bond to the metal (five coordination).

The reaction conditions for the insertion of carbon monoxide are mild as compared with those necessary for the conversion of $[(C_2H_5)_3P]_2Pt(CH_3)Cl$ into $[(C_2H_5)_3P]_2Pt[C(O)CH_3]Cl$[11,12]. The difference may be caused by the fact that the interaction of CO with the platinum alkyl compound has to proceed via the five-coordinated $[(C_2H_5)_3P]_2(CO)Pt(CH_3)Cl$. This reaction path is energetically unfavourable as compared with the possible formation of the four-coordinated σ-intermediate in the allyl complexes $[L_2(CO)Pt(CH_2–CH=CH_2)]^+Cl^-$. For both types of processes, the end products are formed by *cis*-ligand migration of the allyl group towards CO[13].

The course of the insertion reaction, *i.e.* substitution of the least substituted carbon atom [compare (VI)] is consistent with that encountered with palladium(II) π-allylic complexes[4]. The formation of the intermediate $Pt–CH_2–CH=C(CH_3)_2$ may be sterically more favourable relative to $Pt–C(CH_3)_2–CH=CH_2$; at any rate the latter is energetically less favourable.

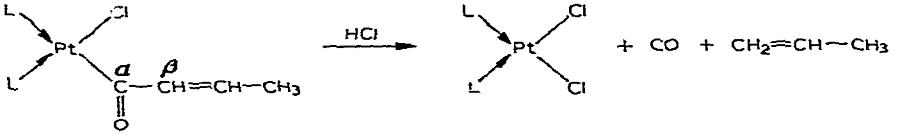
We have attempted to synthesize similar insertion products starting from tetrakis(triphenylphosphine)platinum (VII) and acid chlorides. With acetyl chloride, bis(triphenylphosphine)acetylplatinum chloride (VIII) [ν(C=O) 1710 cm^{-1}] was formed:



(VII) (VIII)

We have not succeeded in synthesizing (V) from (VII) and either 2- or 3-butenoic acid chloride. From the results of several experiments carried out under a variety of conditions we conclude that the product composition is very sensitive with respect to solvent, temperature, reaction time and excess of acid chloride.

In an attempt to generate an acid chloride (or an aldehyde) by treating the insertion products (V) or (VI) with hydrochloric acid only carbon monoxide, the unsaturated hydrocarbon and *cis*-L_2PtCl_2 [$L=(C_6H_5)_3P$] were isolated.



(V) (III)

The reaction may proceed by simultaneous protonation of the carbonyl group and coordination of the chloride ion at the fifth coordination site. Enhanced backbonding from platinum to carbon would bring about a weakening of the C_α–C_β bond. The intermediate complex will decompose into carbon monoxide and the unsaturated hydrocarbon.

Ethylene

Bis(triphenylphosphine)-π-allylplatinum chloride, dissolved in benzene, reacts very slowly with ethylene (25 atm). GLC and mass-spectrometric analysis of the gas and liquid phases indicate the presence of 1,3-butadiene and butenes.

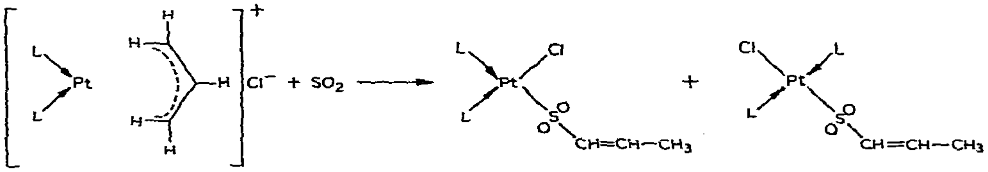
The conversion was very low.

1,3-*Butadiene*

Bis(triphenylphosphine)-π-allylplatinum chloride, dissolved in benzene, reacts with butadiene. Heptenes and octenes could be detected by mass-spectrometric analysis; the yields were very low. According to the IR spectrum the recovered complex was identical with (I, R = H).

Sulfur dioxide

On bis(triphenylphosphine)-π-allylplatinum chloride (I, R = H) being reacted with liquid sulfur dioxide at room temperature, two sulfur-containing complexes differing in solubility in liquid SO_2 are formed. The complexes are in equilibrium with each other; on treatment of each of the complexes with SO_2 a mixture of the two complexes was obtained. According to the elemental analysis, the complexes appear to be 1 : 1 SO_2 adducts; they are considered to be *cis,trans* isomers of the insertion product (XII):



(I) (XII)

The structure was assigned on the basis of the following evidence: the complexes do not show electrical conductivity in solution; mass-spectrometric analysis of the two complexes showed the presence of a $C_3H_5SO_2$ fragment, which suggests the occurrence of SO_2 insertion. The location of the double bond in (XII) is deduced from the presence of the C=C stretching frequency (1630 cm^{-1}) and the absence of the CH and CH_2 out of plane deformations in the 910–1000 cm^{-1} region. The characteristic SO_2 absorptions were present at 1210–1220 and 1060–1065 cm^{-1}, indicating the presence of metal–sulfur–carbon bonds[14]. The poor solubility of the complexes in the appropriate solvents made it impossible to produce NMR spectra.

The dimethyl-substituted π-allyl platinum complex (I, $R = CH_3$) gives also rise to the formation of a 1 : 1 adduct; the structure with respect to *cis* or *trans* configuration and the manner of attachment of the dimethylpropenyl moiety to the sulfur atom is not known.

Although insertion reactions of SO_2 in metal–alkyl bonds are reported[14,15], no example is known of insertion in metal–π-allyl bonds. Interesting in this respect are the observations of Wojcicki, who found insertion of SO_2 in $(CO)_5Mn{-}CH_2{-}CH{=}C(CH_3)_2$, yielding $Mn{-}S(O)_2{-}C(CH_3)_2{-}CH{=}CH_2$, whereas $(CO)_4Mn$(π-allyl) complexes do not exhibit any reactivity[16]. It may well be that the reactivity of our π-allylplatinum complexes is due to the dynamic character of the allyl group.

An attempt to obtain complex (XII) starting from tetrakis(triphenylphosphine)platinum (VII) and $CH_2{=}CH{-}CH_2{-}SO_2Cl$ led to a mixture of *cis*-bis(triphenylphosphine)platinum dichloride and a compound with the composition $\{[(C_6H_5)_3P]_2PtCl_2\}_2SO_2$. The latter complex was quantitatively obtained from *cis*-$[(C_6H_5)_3P]_2PtCl_2$ and SO_2. The IR spectrum of the complex is almost equal to that of *cis*-$[(C_6H_5)_3P]_2PtCl_2$, except for the rather intense absorption bonds due to the SO_2 group (1090–1100 cm^{-1}). The sulfur atom is most likely to be bonded to be both platinum atoms.

EXPERIMENTAL PART*

The NMR spectra were measured in $CDCl_3$ with a Varian HA 100 spectrometer; TMS was used as internal reference.

Conductivities were measured with a Philips Philoscope G.M. 4249 using Pt electrodes. Dichloromethane was used as the solvent.

The synthesis of bis(triphenylphosphine)-π-allylplatinum chloride and the dimethyl-substituted derivative and their NMR spectra have been described in Part I[2].

Hydrogenation

Bis(triphenylphosphine)-π-(1,1-dimethylallyl)platinum chloride (500 mg) was added to chloroform (20 ml) which had been saturated with hydrogen (1 atm). The reaction mixture was kept in contact with hydrogen for forty eight h. In the gas phase isopentane was detected by means of GLC (flame ionization technique) (85%); the net observed gas uptake was very small. The precipitate formed in the reaction mixture was found to be *cis*-bis(triphenylphosphine)platinum dichloride (m.p. 287°, lit.[17]: 310–312°)(yield 90%). The IR spectra of the product and an authentic sample could be superimposed.

Similarly, bis(triphenylphosphine)-π-allylplatinum chloride was equilibrated with hydrogen; propane was detected as the major product besides a small amount of

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* With Miss M. Gronert and J. W. F. M. Lemmers.

propene. *Cis*-bis(triphenylphosphine)platinum dichloride was obtained in an 85% yield.

Hydrogen chloride

Bis(triphenylphosphine)-π-allylplatinum chloride (500 mg) was added to a saturated solution (20 ml) of gaseous hydrogen chloride in chloroform. On standing a white precipitate of *cis*-bis(triphenylphosphine)platinum dichloride was formed; yield 85%, m.p. 309–310° (lit.[17]: 310–312°). Very often incorporation of chloroform in the precipitate was observed. It was removed by heating at 100° *in vacuo*. (Found: C, 54.6; H, 3.88; Cl, 8.8; P, 7.9. $C_{36}H_{30}Cl_2P_2Pt$ calcd.: C, 54.71; H, 3.80; Cl, 8.97; P, 7.84%.)

Carbon monoxide

A solution of 500 mg of bis(triphenylphosphine)-π-allylplatinum chloride in 20 ml of chloroform was equilibrated at room temperature with carbon monoxide (1 atm). One equivalent of carbon monoxide was consumed; on evaporation of the solvent a white precipitate of bis(triphenylphosphine)(2-butenoyl)platinum chloride was isolated. (Found: C, 58.1; H, 4.39; Cl, 4.36; P, 7.6; Pt, 24.9. $C_{40}H_{35}ClOP_2Pt$ calcd.: C, 58.29; H, 4.28; Cl, 4.30; P, 7.52; Pt, 23.67%.)

IR spectrum: ν(C=O) 1630 cm^{-1}, ν(C=C) 1650 cm^{-1}; compare: $[(C_2H_5)_3P]_2Pt[CH_3C(O)]Cl$ ν(C=O) 1629 cm^{-1} (ref. 11) and $[(C_6H_5)_3P]_3Pt(CO)$ ν(C=O) 1903 cm^{-1} (ref. 12).

Mass-spectrometric analysis showed large amounts of CO: fragments like C_3H_5CO were not observed. The NMR data have been summarized in Table 1.

Under similar conditions a "carbonyl" complex was obtained from bis(triphenylphosphine)-π-(1,1-dimethylallyl)platinum chloride. (Found: C, 59.3; H, 4.54; Cl, 4.71; P, 8.3; Pt, 25.0. $C_{42}H_{39}ClOP_2Pt$ calcd.: C, 59.2; H, 4.6; Cl, 4.1; P, 7.3; Pt, 22.9%.)

IR spectrum: ν(C=O) and ν(C=C) 1660 and 1650 cm^{-1}.

Decomposition of carbonyl insertion products by HCl

A solution of 500 mg of bis(triphenylphosphine)(2-butenoyl)platinum chloride in 20 ml of chloroform was saturated with HCl. On standing overnight a white precipitate of *cis*-$[(C_6H_5)_3P]_2PtCl_2$ is formed: in the gas phase carbon monoxide and propene were detected by mass-spectroscopical analysis.

Reaction of $[(C_6H_5)_3P]_4Pt$ with acetyl chloride

One equivalent of acetyl chloride dissolved in benzene was added to a solution of $[(C_6H_5)_3P]_4Pt$ in benzene. A white precipitate of bis(triphenylphosphine)acetylplatinum chloride was formed. (Found: C, 57.8; H, 4.2; Cl, 4.6; P, 8.1. $C_{38}H_{33}ClOP_2Pt$ calcd.: C, 57.18; H, 4.17; Cl, 4.44; P, 7.76%.)

IR spectrum: ν(C=O) 1620, 1600 cm^{-1} (mull).

Reaction of $[(C_6H_5)_3P]_4Pt$ with 3-butenoyl chloride

One equivalent of 3-butenoic acid chloride dissolved in benzene was added to a solution of tetrakis(triphenylphosphine)platinum in benzene at 20°. A white precipitate was formed, which, according to the IR spectrum, consisted mainly of *cis*-bis(triphenylphosphine)platinum dichloride.

A similar result was obtained using 2-butenoyl chloride.

Sulfur dioxide

Left undisturbed for twenty-four h at room temperature, a solution of bis(triphenylphosphine)-π-allylplatinum chloride in liquid sulfur dioxide yielded a precipitate (A); on evaporation of the solvent the filtered solution yielded complex (B). [Found (A): C, 54.2; H, 4.08; Cl, 5.0; P, 6.3; S, 2.85; (B): C, 54.6; H, 4.32; Cl, 4.21; P, 7.4; S, 2.74. $C_{39}H_{35}ClO_2P_2PtS$ calcd.: C, 54.45; H, 4.10; Cl, 4.12; P, 7.20; S, 3.73%.)

The IR spectra of (A) and (B) showed characteristic absorptions of the SO_2 group at 1210 and 1220 cm^{-1} (asym. SO_2) and at 1060 and 1065 cm^{-1} (sym. SO_2) (compare ref. 14).

Similarly, bis(triphenylphosphine)-π-(1,1-dimethylallyl)platinum chloride yielded two SO_2-containing products.

The insoluble complex appears to be $\{[(C_6H_5)_3P]_2PtCl_2\}_2SO_2$. (Found: C, 53.3; H, 3.95; Cl, 6.81; P, 7.4; S, 2.25. $C_{72}H_{60}Cl_4O_2P_4Pt_2S$ calcd.: C, 52.56; H, 3.68; Cl, 8.61; P, 7.53; S, 1.95%.)

The product was identical with the one obtained from *cis*-$[(C_6H_5)_3P]_2PtCl_2$ and SO_2 (see below).

The soluble product (C) appeared to be the 1:1 adduct. (Found: C, 52.5; H, 4.11; Cl, 3.85; P, 7.4; S, 2.99. $C_{41}H_{39}ClO_2P_2PtS$ calcd.: C, 55.44; H, 4.43; Cl, 3.99; P, 6.97; S, 3.61%.)

The IR spectrum of (C) showed characteristic bands at 1230 and 1060 cm^{-1} (asym. and sym. SO_2 modes).

Reaction of tetrakis(triphenylphosphine)platinum with allylsulfonyl chloride

One equivalent of allylsulfonyl chloride[18] dissolved in benzene was added to a solution of $[(C_6H_5)_3P]_4Pt$ in benzene. On standing a precipitate of *cis*-$[(C_6H_5)_3P]_2$-$PtCl_2$ was formed. (Found: C, 55.6; H, 3.97; Cl, 8.0; P, 8.5; S, 0.62. $C_{36}H_{30}Cl_2P_2Pt$ calcd.: C, 54.71; H, 3.80; Cl, 8.97; P, 7.84%.)

Synthesis of $\{[(C_6H_5)_3P]_2PtCl_2\}_2SO_2$

After standing for twenty four h a solution of *cis*-$[(C_6H_5)_3P]_2PtCl_2$ and liquid SO_2 was concentrated, washed with water and dried. Evaporation of the solvent yielded $\{[(C_6H_5)_3P]_2PtCl_2\}_2SO_2$. (Found: C, 52.7; H, 4.03; Cl, 8.7; P, 7.6; S, 2.18. $C_{72}H_{60}Cl_4O_2P_4Pt_2S$ calcd.: C, 52.56; H, 3.68; Cl, 8.61; P, 7.53; S, 1.95%.)

Reaction with ethylene

Ethylene (25 atm) was equilibrated with a stirred solution of 1.52 g of bis(triphenylphosphine)-π-allylplatinum chloride in 25 ml of benzene at 20°. No pressure change was observed during a period of one hundred h. According to GLC analysis the gas phase contained, besides ethene, 1,3-butadiene, 1-butene and butane.

Reaction with butadiene

1,3-Butadiene was passed through an heterogeneous solution of 570 mg of bis(triphenylphosphine)-π-allylplatinum chloride in 40 ml of benzene. After standing for forty-eight h heptenes and octenes were identified in the gas phase according to mass-spectrometric and GLC analysis.

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