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π-ALLYLIC HYDRIDORHODIUM(III) INTERMEDIATES IN THE REACTION OF HYDROGEN CHLORIDE WITH π-ALLYLIC TRIS(TRIFLUOROPHOSPHINE)RHODIUM(I) COMPLEXES

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Summary

Hydrogen chloride reacts with π-allylic tris(trifluorophosphine)rhodium(I) complexes Rh(π-all)$(PF_3)_3$ (all = C_3H_5, cyclohexenyl, 2-methyl-π-allyl, *syn*-1-methyl-π-allyl, 1,1-dimethyl-π-allyl, *syn*-1,2-dimethyl-π-allyl, *syn*-1,3-dimethyl-π-allyl and *syn*-1-ethyl-3-methyl-π-allyl) to yield $[RhCl(PF_3)_2]_2$, PF_3 and the corresponding olefin. An intermediate rhodium(III) π-allyl hydride has been characterised at low temperatures by ^1H and ^{19}F NMR spectroscopy. The direction of hydrogen migration from metal to an asymmetrically coordinated allylic group has been studied and its relevance to transition metal catalysed olefin isomerisation reactions is discussed. $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ reacts with hydrogen and PF_3 to form $RhH(PF_3)_4$ at room temperature and with NO or NOCl to give $Rh(NO)(PF_3)_3$.

Introduction

Oxidative addition reactions of rhodium(I) complexes are well-known [1, 2]. It was of interest to study the reactivity of several recently synthesised π-allylic tris(trifluorophosphine)rhodium(I) complexes [3, 4] towards hydrogen chloride. In particular an attempt has been made to identify π-allylic hydride rhodium species since this type of transition metal complex has been postulated [5] as a possible intermediate in the isomerisation of olefins catalysed by transition metal complexes*. The reactions of $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ with molecular hydrogen, nitric oxide and nitrosyl chloride are also reported.

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* A preliminary account of part of this work has appeared [20].

Results and discussion

The reactions between hydrogen chloride and a series of π-allylic $\text{Rh(PF}_3)_3$ complexes, I-VIII (Fig. 1) have been studied, and the intermediate steps monitored by ^{19}F and ^{1}H NMR spectroscopy. The reactions were performed in vacuo in sealed NMR tubes and the products handled by high vacuum techniques.

When π-allyltris(trifluorophosphine)rhodium(I), $\text{Rh}(\pi\text{-C}_3\text{H}_5)(\text{PF}_3)_3$, is sealed off with hydrogen chloride in an NMR tube held at liquid nitrogen temperature, and the tube immediately inserted into the spectrometer probe precooled to −75°, the ^{19}F NMR spectrum shows, in addition to be expected resonances due to I, a much weaker resonance centred at + 13.9 ppm relative to CCl_3F. The new resonance (Fig. 2) consists of eight lines of equal intensity. The ^{1}H NMR spectrum of the mixture at the same temperature shows an additional broad resonance at τ 28.8 which is characteristic of a transition metal hydride. These results suggest the presence of a π-allylhydrido(trifluorophosphine)rhodium (III) complex, $\text{RhClH}(\pi\text{-C}_3\text{H}_5)(\text{PF}_3)_x$ in the mixture (x is probably 2). The eight line pattern in the ^{19}F NMR spectrum represents the strongest lines of the X part of an $[\text{X}_3\text{A}]_2$ spin system (X = fluorine, A = phosphorus) and arises from spin coupling between fluorine and phosphorus [$^1J(\text{PF}) \approx 1391$ Hz], fluorine and rhodium [$^2J(\text{RhF}) = 20$ Hz], and hydrogen and fluorine [$^3J(\text{FH}) = 8$ Hz]. No extra resonances for the allyl protons in $\text{RhClH}(\pi\text{-C}_3\text{H}_5)(\text{PF}_3)_2$ are observed, but it is likely that these are masked by the stronger allyl resonances of I.

Confirmation of the assignment of the new π-allylhydrido complex comes from the observation that the ^{19}F NMR spectrum of the products of the reaction between I and deuterium chloride at −75° simplifies to the expected mirror image pattern of lines for an $[\text{X}_3\text{A}]_2$ spin system split further by the ^{103}Rh nucleus (Fig. 2).

As the temperature is raised above −75° the resonances in the ^{19}F NMR spectrum assigned to $\text{RhClH}(\pi\text{-C}_3\text{H}_5)(\text{PF}_3)_2$ gradually diminish in intensity and finally disappear at −50°. Similar behaviour is observed in the ^{1}H NMR spectrum

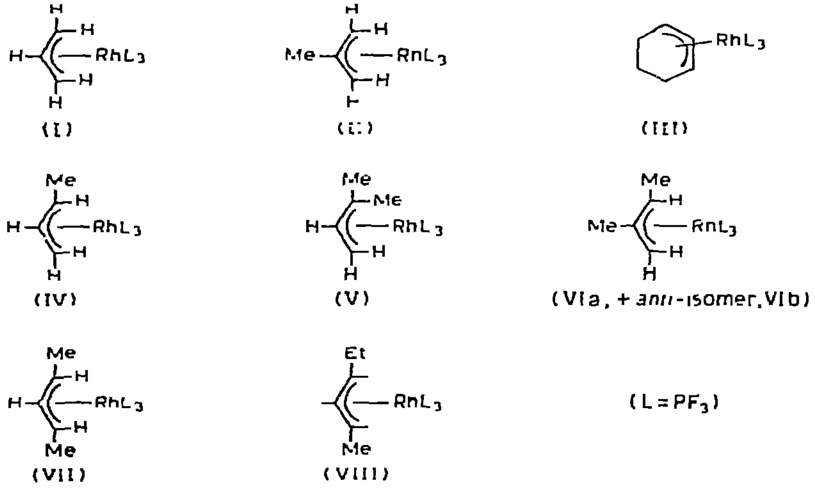


Fig. 1. π-Allylic tris(trifluorophosphine)rhodium complexes I-VIII.

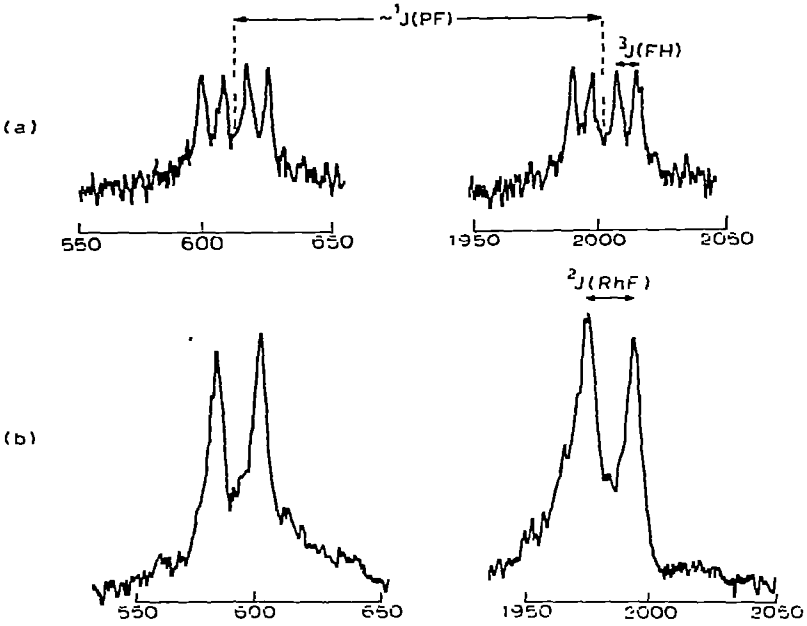


Fig. 2. The ^{19}F NMR spectra of the products of the reactions at −75° between I and (a) hydrogen chloride, (b) deuterium chloride in CCl$_3$F solution. The scale is in Hz relative to CCl$_3$F.

and new resonances assignable to 1-propene appear above −50°. A sharp doublet characteristic of $[RhCl(PF_3)_2]_2$ undergoing intermolecular exchange with trifluorophosphine is observed in the ^{19}F NMR spectrum [6, 7] and $[RhCl(PF_3)_2]_2$ may be isolated and characterised. The overall reaction can therefore be represented by eqn. 1. When an excess of hydrogen chloride is used the 1-propene formed

$$Rh(\pi\text{-}C_3H_5)(PF_3)_3 + HCl \rightarrow \tfrac{1}{2}[RhCl(PF_3)_2]_2 + C_3H_6 + PF_3 \qquad (1)$$

slowly undergoes Markownikoff addition to form isopropyl chloride. The reaction between the other π-allylic complexes, II-VIII, and hydrogen chloride were studied in a similar manner, and all proceed according to the general equation 2.

$$Rh(\pi\text{-allylic})(PF_3)_3 + HCl \rightarrow \tfrac{1}{2}[RhCl(PF_3)_2]_2 + \text{olefin} + PF_3 \qquad (2)$$

The olefinic products, which were all identified by ^{1}H NMR spectroscopy, are shown in Table 1. Subsequent reaction with excess hydrogen chloride is found to be fastest for olefins which can give rise to tertiary carbonium ion intermediates. In the reaction between II and hydrogen chloride the 2-methyl-1-propene formed reacts immediately with excess hydrogen chloride to form tert-butyl chloride while VI and hydrogen chloride afford 2-chloro-2-methylbutane. Since the latter could arise by rapid Markownikoff addition of hydrogen chloride to either of the possible olefinic products, 2-methyl-2-butene or 2-methyl-1-butene, an unambiguous assignment of the olefins initially formed is not possible in this case.

TABLE 1

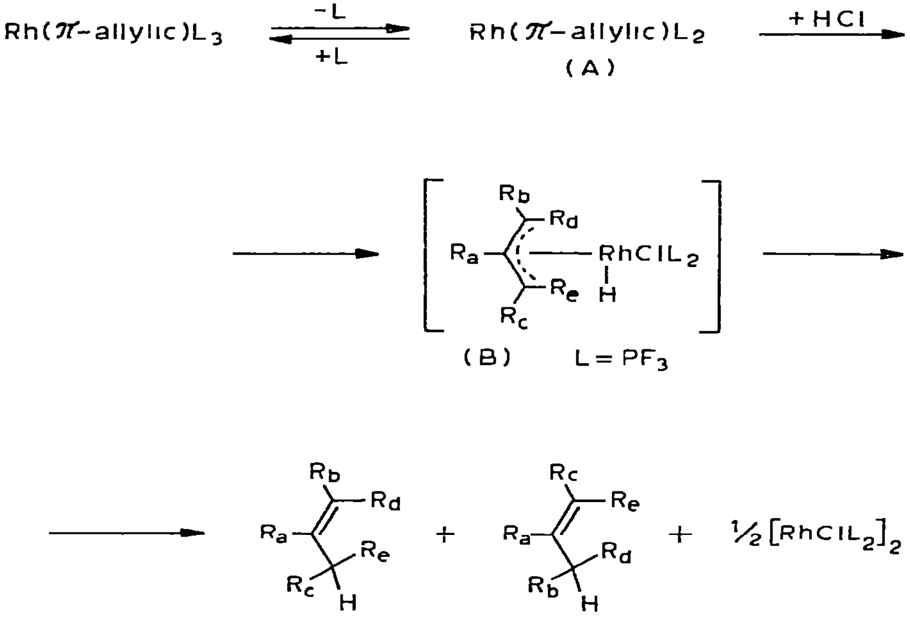
OLEFINIC PRODUCTS OF THE REACTIONS BETWEEN COMPLEXES I-VII AND HYDROGEN CHLORIDE

Complex	Olefinic products
I	1-Propene
II	2-Methyl-1-propene[a]
III	Cyclohexene
IV	1-Butene + 2-butene
V	3-Methyl-1-butene + 2-methyl-2-butene[a]
VI	2-Methyl-2-butene[a, b] + 2-methyl-1-butene[a, b]
VII	2-Pentene
VIII	2-Hexene + 3-hexene

[a] Identified as Markownikoff addition product with excess HCl. [b] See text.

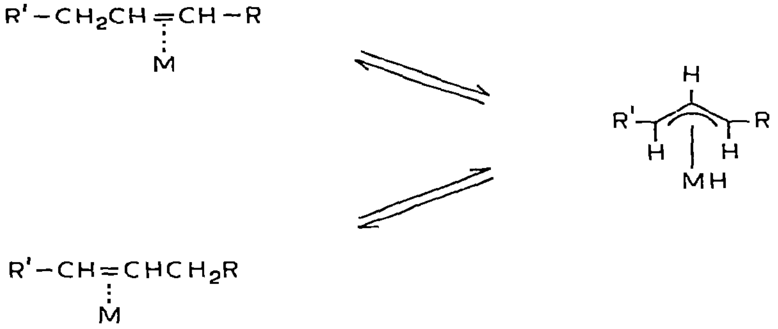
The reactions between complexes I-VIII and hydrogen chloride most likely proceed via unstable π-allylic hydridorhodium(III) intermediates, although this has been established positively only for complex I. The most likely mechanism (see Scheme 1) involves an initial ligand dissociation step to afford the coordinatively unsaturated species A which undergoes oxidative addition with hydrogen chloride giving the 6-coordinate intermediate B. In the final step a hydrogen migration from rhodium to the allylic ligand produces $[RhCl(PF_3)_2]_2$ and olefin. In reactions involving complexes containing a symmetric π-allylic ligand, only one olefinic product is observed in each case as expected. The propene formed by addition of deuterium chloride to I, as expected, contains deuterium only in the terminal position. In the case of the asymmetric π-allylic complexes IV and VIII, roughly 1/1 mixtures of isomeric olefins are obtained,

SCHEME 1

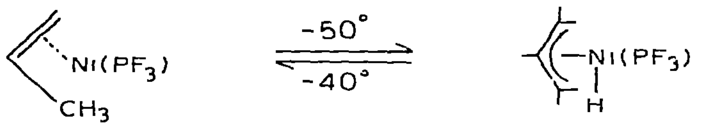


indicating that hydrogen atom migration to both terminal carbon atoms of the π-allylic ligand occurs almost equally. In the reaction between V and hydrogen chloride, the formation of a 2/1 mixture of 2-methyl-2-butene and 3-methyl-1-butene suggests there is some preferential migration to the least-substituted terminal carbon atom.

These observations establish for the first time the feasibility of hydrogen atom migration from a transition metal to either end of an asymmetrically coordinated π-allylic group. This type of 1,3-hydrogen shift is the essential step which has been postulated to occur in transition metal catalysed olefin isomerisation reactions involving a π-allylic transition metal hydride intermediate [5].



Further support for this mechanism comes from the work of Bonnemann [8] who has shown recently that an equilibrium exists at low temperatures between a propenenickel(0) complex and the corresponding π-allylhydridonickel(II) compound:



There is a growing body of other indirect evidence for the participation of π-allylic hydridometal intermediates in this type of reaction from several recent studies on homogeneous systems involving iron carbonyl complexes containing tritiated 1-octene [9], deuterated 1,4-cyclohexadiene [10], deuterated allyl alcohol [11], deuterated ethyl-1-pentene [12], *exo* and *endo* alcohols [13] and also in certain heterogeneous systems (e.g., zinc oxide [14]).

It is interesting to note that during a related study using π-allylic tris(trifluorophosphine)cobalt(I) complexes [15, 16] we find that the reactions with hydrogen chloride are very much slower than the analogous rhodium compounds. This probably reflects the much easier intermolecular phosphine exchange process which is known to occur in the rhodium series [3, 4].

Reactions of I with molecular hydrogen, nitric oxide and nitrosyl chloride

Complex I reacts smoothly at room temperature with a mixture of hydrogen and trifluorophosphine (total pressure 1 atmosphere) to yield 1-propene and hydridotetrakis(trifluorophosphine)rhodium in high yield (eqn. 3). In the absence of PF_3 only moderate yields of $RhH(PF_3)_4$ result together with 1-propene, propane and an uncharacterised black solid which probably contains metallic rhodium. It is interesting to note that the analogous cobalt complex shows no reaction with hydrogen under similar conditions.

$$Rh(\pi\text{-}C_3H_5)(PF_3)_3 \xrightarrow[25^\circ]{H_2/PF_3} RhH(PF_3)_4 + C_3H_6 \qquad (3)$$

Both nitric oxide and nitrosyl chloride react with I at room temperature to from the dark yellow volatile liquid complex nitrosyltris(trifluorophosphine)-rhodium, $Rh(NO)(PF_3)_3$ (eqn. 4). The structure of this compound, which was first prepared by Kruck and Lang [17] by a different route, has been reported recently [18].

$$\begin{aligned} &Rh(\pi\text{-}C_3H_5)(PF_3)_3 \xrightarrow{NO} Rh(NO)(PF_3)_3 \\ &Rh(\pi\text{-}C_3H_5)(PF_3)_3 \xrightarrow{NOCl} Rh(NO)(PF_3)_3 + [RhCl(PF_3)_2]_2 \end{aligned} \qquad (4)$$

Experimental

The π-allylic tris(trifluorophosphine)rhodium complexes were made by published methods [3, 4] and purified prior to use. The reactions between π-allylic tris(trifluorophosphine)rhodium(I) complexes and hydrogen chloride were studied by sealing the reactants in NMR tubes and monitoring the course of the reactions using ^{19}F and ^1H NMR spectroscopy. ^1H and ^{19}F NMR spectra were recorded using a Varian HA100 NMR spectrometer operating at 100 MHz and 94.1 MHz respectively.

Olefinic products were identified by comparison of their ^1H NMR spectra with authenic samples. The dimeric rhodium(I) complex $[RhCl(PF_3)_2]_2$, which was also a product of the reactions, was isolated after the reactions were complete and characterised by comparison of its melting point and infrared spectrum [6, 7].

Deuterium chloride was prepared by dropping deuterium oxide on to phosphorus pentachloride and was purified by fractiohation. Its purity was checked by infrared spectroscopy.

The reaction between I and hydrogen chloride

Complex I (0.114 g, 0.279 mmol) and HCl (0.010 g, 0.274 mmol) were sealed with CCl_3F in vacuo in an NMR tube at liquid nitrogen temperature and inserted into the NMR spectrometer probe precooled to −75°. The ^{19}F spectrum of the solution showed, in addition to resonances assigned to I, a new resonance, [$\Phi_F = 13.9$ ppm, $^2J(RhF) = 20$, $^1J(PF) \approx 1391$, $^3J(FH) = 8$ Hz], assigned to the complex $RhClH(\pi\text{-}C_3H_5)(PF_3)_2$. The ^1H NMR spectrum at this temperature showed, in addition to the resonances of I, a broad high field resonance (τ 28.8). At room temperature the final ^{19}F NMR spectrum consisted only of a very sharp doublet [$\Phi_F = 19.0$ ppm, $^1J(PF) = 1385$ Hz] characteristic of $[RhCl(PF_3)_2]_2$ undergoing intermolecular exchange with trifluorophosphine [6, 7]. The ^1H

NMR spectrum showed only resonances assignable to 1-propene. Removal of the highly volatile products and solvent under reduced pressure afforded $[RhCl(PF_3)_2]_2$ (0.062 g, 0.099 mmol).

Similar experiments employing an excess of hydrogen chloride afforded not 1-propene but isopropyl chloride, formed by Markownikoff addition of hydrogen chloride to 1-propene.

In all the following experiments the course of the reaction was monitored by ^1H and ^{19}F NMR spectroscopy. Reactions were complete after 24 h.

The reaction between I and deuterium chloride

The reaction between I (0.202 g, 0.495 mmol) and deuterium chloride (0.017 g, 0.466 mmol) was studied in a similar way. At −75°, the ^{19}F NMR spectrum showed, in addition to the spectrum of I, a new resonance [Φ_F = 13.7 ppm, $^2J(RhF)$ = 19, $^1J(PF)$ = 1390 Hz] assigned to the complex $RhCl(^2H)(\pi\text{-}C_3H_5)(PF_3)_2$. On warming to room temperature the ^{19}F NMR spectrum finally consisted only of a sharp doublet [Φ_F = 18.2 ppm, $^1J(PF)$ = 1364 Hz], characteristic of $[RhCl(PF_3)_2]_2$ undergoing intermolecular exchange with trifluorophosphine. The ^1H NMR spectrum showed only resonances assignable to $[3\text{-}^2H_1]$-1-propene.

Reaction between II and hydrogen chloride

Complex II (0.050 g, 0.118 mmol) and hydrogen chloride (0.006 g, 0.165 mmol) were sealed with CCl_3F in vacuo in an NMR tube. The ^{19}F NMR spectrum of the products was similar to that described above while the ^1H NMR spectrum showed only resonances assignable to tert-butyl chloride and 2-methyl-1-propene. Removal of the highly volatile products and solvent under reduced pressure afforded $[RhCl(PF_3)_2]_2$ (0.028 g, 0.045 mmol).

Reaction between IV and hydrogen chloride

Complex IV (0.060 g, 0.142 mmol) and hydrogen chloride (0.016 g, 0.439 mmol) were sealed in with CCl_3F in vacuo in an NMR tube. The ^{19}F NMR spectrum of the products was similar to that above, while the ^1H NMR spectrum consisted only of resonances assignable to roughly equimolar amounts of 1-butene and 2-butene. Removal of the highly volatile products and solvent under reduced pressure afforded $[RhCl(PF_3)_2]_2$ (0.032 g, 0.059 mmol).

Reaction between V and hydrogen chloride

Complex V (0.039 g, 0.089 mmol) and hydrogen chloride (0.005 g, 0.137 mmol) were sealed with CCl_3F in vacuo in an NMR tube. The ^{19}F NMR spectrum of the products was similar to that above and the ^1H NMR spectrum showed only resonances assignable to 3-methyl-1-butene and 2-chloro-2-methylbutane. Removal of the highly volatile products and solvent under reduced pressure afforded $[RhCl(PF_3)_2]_2$ (0.024 g, 0.038 mmol).

Reaction between VI and hydrogen chloride

A roughly equimolar mixture of isomers VIa and VIb (0.041 g, 0.094 mmol) and hydrogen chloride (0.005 g, 0.137 mmol) were sealed with CCl_3F in vacuo in an NMR tube. The ^{19}F NMR spectrum was similar to that described above and the ^{1}H NMR spectrum showed only resonances assignable to 2-chloro-2-methylbutane. Removal of the highly volatile products and solvent under reduced pressure afforded $[RhCl(PF_3)_2]_2$ (0.024 g, 0.038 mmol).

Reaction between VII and hydrogen chloride

Complex VII (0.035 g, 0.080 mmol) and hydrogen chloride (0.005 g, 0.137 mmol) were sealed with CCl_3F in vacuo in an NMR tube. The ^{19}F NMR spectrum was similar to that described above and the ^{1}H NMR spectrum showed only resonances assignable to 2-pentene. Removal of the highly volatile products and solvent under reduced pressure afforded $[RhCl(PF_3)_2]_2$ (0.020 g, 0.032 mmol).

Reaction between VIII and hydrogen chloride

Complex VIII (0.082 g, 0.182 mmol) and hydrogen chloride (0.009 g, 0.247 mmol) were sealed with CCl_3F in vacuo in an NMR tube. The ^{19}F NMR spectrum showed the expected resonances due to $[RhCl(PF_3)_2]_2$ and the ^{1}H NMR spectrum showed only resonances assignable to roughly equimolar amounts of 2-hexene and 3-hexene. Removal of the highly volatile products and solvent under reduced pressure afforded $[RhCl(PF_3)_2]_2$ (0.050 g, 0.080 mmol).

Reaction between III and hydrogen chloride

Complex III (0.120 g, 0.268 mmol) was condensed into a Schlenk tube with HCl (a large excess). On warming to room temperature an immediate reaction occurred, with the formation of a red solid. Subsequent fractionation afforded PF_3 and excess HCl (not separated) at −196°, cyclohexene (0.021 g, 0.256 mmol) at −78°, and at −45° a red volatile solid, $[RhCl(PF_3)_2]_2$ (0.072 g, 0.115 mmol).

Reaction between I, hydrogen, and trifluorophosphine

Complex I (0.265 g, 0.650 mmol) and trifluorophosphine (0.391 g, 4.44 mmol) were condensed into a large Schlenk tube (volume 200 ml), and sufficient hydrogen admitted to give a total pressure of 1.1 atmospheres at room temperature. The tube was shaken at this temperature for 16 h and after careful removal of excess hydrogen with the tube cooled to −196°, fractionation afforded a mixture of trifluorophosphine and 1-propene and a colourless volatile liquid, $RhH(PF_3)_4$ (0.257 g, 0.564 mmol, 86% based on I). The product was identified by comparison with an authentic sample of $RhH(PF_3)_4$.

Reaction between I and hydrogen

Complex I (0.106 g, 0.260 mmol) was condensed into a Schlenk tube (volume 200 ml), and a pressure of hydrogen of 1 atmosphere admitted at room temperature. The tube was shaken at this temperature for 4 h. Fractionation afforded a mixture of 1-propene and propane (not separated) at −196°, and at −78° a colourless volatile liquid, $RhH(PF_3)_4$ (0.032 g, 0.070 mmol, 26.9% based on I). A black solid remained in the tube.

Reaction between I and nitric oxide

Complex I (0.049 g, 0.120 mmol) and NO (0.016 g, 0.533 mmol) were sealed in vacuo, and kept at room temperature for 10 days. Repeated fractionation after this time afforded unreacted I (0.20 g, 0.049 mmol) at −36.5°, and at −78° a dark yellow volatile liquid, tris(trifluorophosphine)nitrosylrhodium(−I), $Rh(PF_3)_3(NO)$ (0.019 g, 0.048 mmol) (40%). Infrared spectrum: 1810vs, 926vs, 900vs, 890(sh), 860vs cm^{-1} (vapour phase). This spectrum is identical with that reported for $Rh(PF_3)_3(NO)$ in the literature [18, 19]. An uncharacterised brown solid remained in the ampoule.

Reaction between I and nitrosyl chloride

Complex I (0.050 g, 0.122 mmol) and ClNO (0.007 g, 0.107 mmol) were sealed in vacuo, and allowed to warm slowly to room temperature. Fractionation afforded unreacted I (0.025 g, 0.061 mmol), $Rh(PF_3)_3(NO)$ (0.010 g, 0.025 mmol) and $[RhCl(PF_3)_2]_2$ (0.004 g, 0.006 mmol). The black solid remaining in the ampoule was not characterised further.

Acknowledgements

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