Unique Evidence for a Rh^{III} to Rh^{I} Reduction by Deoxygenation of a Carbonate Moiety to CO_2 by an Out-of-Sphere Phosphane

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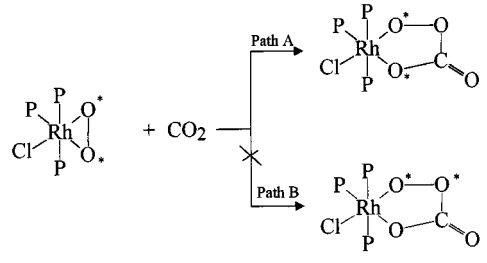
Rh^{III} carbonate generated from either a peroxocarbonate complex $[RhCl(CO_4)(PR_3)_3]$ or $[RhCl_3(PR_3)_3]$ and Na_2CO_3, is reduced to Rh^{I} by deoxygenation of the carbonate moiety to CO_2 by an out-of-sphere phosphane. The reaction takes place in mild conditions and is implied in the catalytic activity shown by Rh^{I} in the oxidation of styrene with O_2/CO_2 mixtures.

Introduction

Transition metal peroxo-carbonates have been known for some time.[1,2] They are usually prepared by reaction of metal dioxygen complexes with CO_2. Accordingly, Rh^{III} peroxocarbonates are easily obtained according to Equation (1). Alternatively, transition metal carbon dioxide complexes can react with dioxygen[3,4] to afford peroxocarbonates.

$$P_3RhCl + O_2 \longrightarrow P_3RhCl(O_2) \xrightarrow{CO_2} P_3RhCl(CO_4) \qquad (1)$$

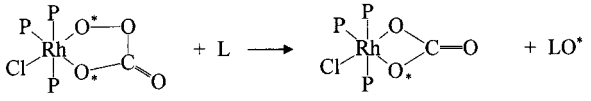
By using labelled species, we have recently shown that CO_2 reacts with $Rh(\eta^2\text{-}O_2)$ complexes by insertion into the O−O bond (Scheme 1, path A), rather than by insertion into the M−O bond (Scheme 1, path B).[5] The reaction pathway has been demonstrated through coupling an IR theoretical study (calculation of the vibrational frequencies of selected bonds of the peroxocarbonate complexes) with experimental vibrational frequencies. The latter match the values calculated for the species obtained assuming CO_2 insertion into the O−O bond (± 2 cm^{-1})[5] better than those of products originating from CO_2 insertion into the M−O bond. This reaction has also been modelled using the Impulse Oscillation Model, IOM,[6−8] which assumes that the vibrations of the metal-dioxygen complex and CO_2 must be synchronised in order for the insertion reaction to occur. IOM unequivocally shows that path A is preferred (up to 92% selectivity) over path B.[9,10]



Scheme 1. Alternative pathways for CO_2 reaction with a Rh dioxygen complex

Very interestingly, the reaction of carbon dioxide metal complexes with dioxygen to afford peroxocarbonates proceeds through the substitution of coordinated CO_2 by dioxygen and subsequent insertion of CO_2 into the O−O bond of the newly formed dioxygen complex.[11]

We have also shown that peroxocarbonates may act as selective one-oxygen transfer agents to an oxophile (Scheme 2).[12−15] By using asymmetrically labelled species, we have demonstrated that the oxygen bonded to the metal is the atom of the peroxo group transferred to the oxophile.[5] The Rh peroxocarbonate is thus converted into a Rh^{III} carbonate complex.



2 **3**

Scheme 2. One-oxygen transfer from the peroxocarbonate moiety to an oxophile

It should be noted that when the peroxocarbonate $[RhCl(CO_4)(PEt_2Ph)_3]$ acts as a one-oxygen transfer agent, the starting Rh^{I} complex $[RhCl(PEt_2Ph)_3]$ is found along with other compounds that undoubtedly originate from the peroxocarbonate. In principle, the Rh^{I} complex could be produced from the peroxocarbonate if the reaction in Equation (1) is reversible.

In an attempt to demonstrate if such a hypothesis holds or not, we have carefully investigated the reaction and have unequivocally shown that $[RhCl(PEt_2Ph)_3]$ originates from Rh^{III} carbonate $[RhCl(CO_3)(PEt_2Ph)_3]$, through an unprecedented carbonate deoxygenation to carbon dioxide promoted by an external phosphane. We describe in this paper some properties of Rh peroxocarbonate **2** and the reduction

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of carbonate **3** to $[RhCl(PEt_2Ph)_3]$. The latter reaction has also been performed using an external carbonate source (Na_2CO_3, Ag_2CO_3) and a Rh^{III} chloride complex.

Results and Discussion

Rh^{III} peroxocarbonate was prepared by reaction of $[RhCl(PEt_2Ph)_3(O_2)]$ with CO_2 at 240 K in toluene[4,5] according to Equation (1). The pure compound is quite stable at low temperature (below 240 K) in the solid state for several days or for several minutes at a temperature as high as 340 K (see Experimental Section). Conversely, in solution above 250 K, or in the solid state at 323 K in the presence of an external phosphane, or any other species that may interact with the Rh centre, it readily reacts and transfers one oxygen atom to an oxophile to afford the carbonate complex **3** (Scheme 2). It is worth recalling that olefins and tetrahydrofuran can be oxidised in this way under mild conditions by Rh peroxocarbonates.[13]

When pure **2** is dissolved in CH_2Cl_2 at 250 K, the ^{31}P NMR spectrum unequivocally shows the conversion of the peroxocarbonate (Figure 1, spectrum A) into a number of other species (Figure 1, spectrum B). These have all been identified by comparison with the spectra of authentic samples. Resonances a−g have been assigned as follows: (a) assigned to the $O{=}PEt_2Ph$ species; (b) and (e) assigned to the *mer*-$RhCl(CO_3)(PEt_2Ph)_3$ species; (c) and (f) assigned to the *mer*-$RhCl(CO_4)(PEt_2Ph)_3$ species; (d and g) assigned to the *mer*-$RhCl_3(PEt_2Ph)_3$ species (see Experimental Section).

It is evident from these data that **2** behaves differently whether it is pure or is in the presence of external ligands or a solvent. Moreover, the fact that a coordinated phosphane is not oxidised (we recall that pure **2** is stable up to 345 K), demonstrates that the O-transfer process is intermolecular, not intramolecular.

The reactivity in the solid state and in solution find a common basis of interpretation. However, in solution the oxygen transfer is promoted by the solvent, which causes the phosphane dissociation (Scheme 3, path a).

The out-of-sphere phosphane formed in solution attacks the peroxo group affording carbonate and phosphane oxide (Scheme 3, path a). The latter may be found free in solution or coordinated to Rh, according to the nature of solvent.

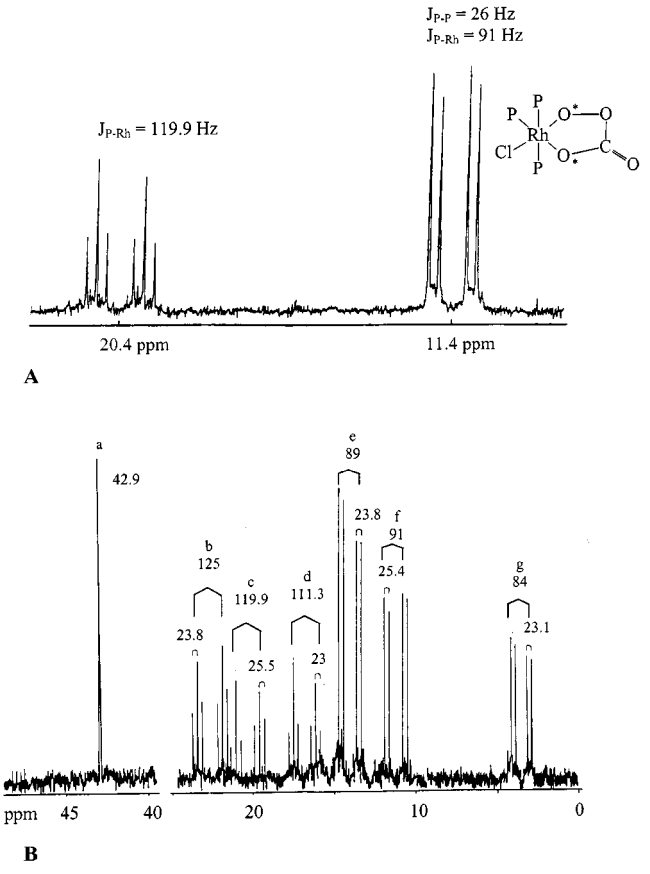
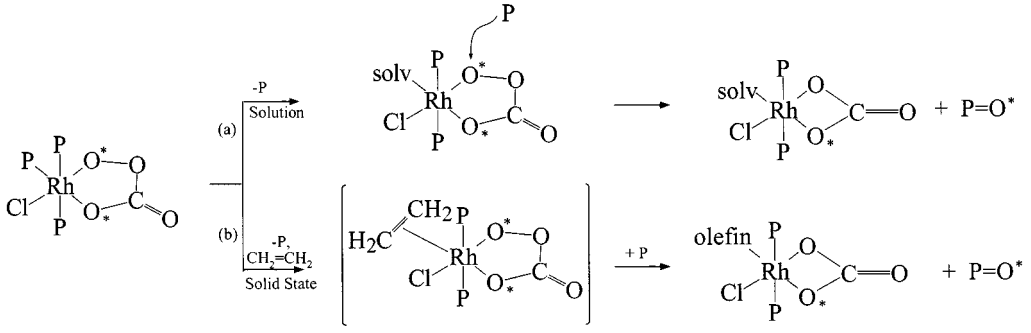
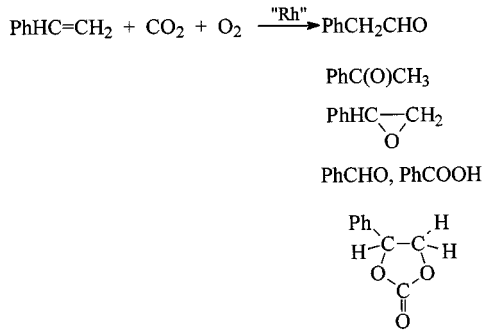


Figure 1. Spectrum A: ^{31}P NMR spectrum (213 K, CD_2Cl_2) of $[RhCl(CO_4)(PEt_2Ph)_3]$; spectrum B: ^{31}P NMR (CD_2Cl_2) spectrum of the solution from A warmed to 250 K

However, when solid Rh peroxocarbonate is warmed to 340 K with an equimolar amount of ethylene, phosphane is slowly released and then rapidly oxidised by the peroxocarbonate to Et_2PhPO (Scheme 3, path b). The selectivity of phosphane oxidation with respect to ethylene is 100%, as demonstrated by the gas-phase analysis which does not show the presence of ethylene oxidation products. The role of ethylene is therefore that of favouring the phosphane release from the Rh coordination sphere. Conversely, if more reactive olefins like styrene are used, in excess with respect to the stoichiometric ratio and under CO_2/O_2 atmosphere, they can be oxidised in solution by Rh peroxocarbonates (Scheme 4).



Scheme 3. Reactivity of $[RhCl(CO_4)(PR_3)_3]$ in solution (path a) and in the solid state in the presence of ethylene (path b)

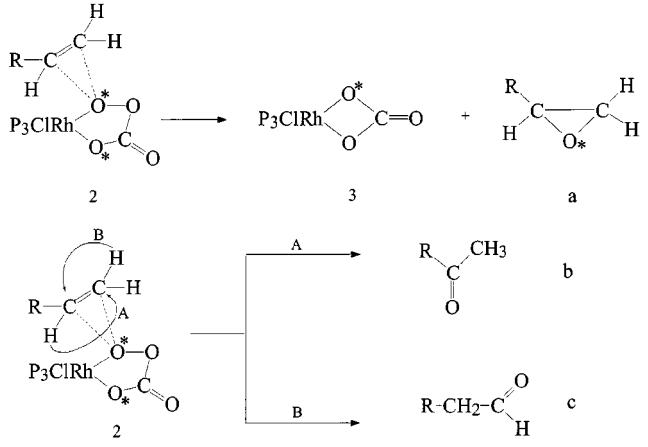


Scheme 4. Reaction of styrene with a CO_2/O_2 mixture promoted by Rh^{I}

Styrene is converted into a mixture of phenylacetaldehyde, phenylmethylketone and styrene epoxide, as major products, along with benzaldehyde which is produced by the cleavage of the styrene C−C double bond by O_2. It is worth noting that Rh peroxocarbonates and Rh dioxygen complexes show a different behaviour towards styrene oxidation.[5,13−18] While the dioxygen complex causes the cleavage of the double bond [Equation (2)], the peroxo-carbonate promotes a one-oxygen transfer to the olefin, mimicking mono-oxygenase enzymes (Scheme 4).

$$RHC{=}CH_2 + O_2 \longrightarrow RHCO + H_2CO \qquad (2)$$

The formation of the ketone and phenylacetaldehyde can be explained assuming a hydrogen shift promoted by the metal centre (Scheme 5).



Scheme 5. Formation of ketone and terminal aldehyde by H-migration promoted by Rh^{I}

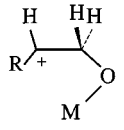
In such an oxidation reaction, if Rh complexes stabilised by monodentate P ligands are used, the catalyst has a lifetime of less than one hour. In fact, the reaction with the olefin releases the phosphane, which is easily oxidised according to Equation (3):

$$\underset{\mathbf{2}}{(PEt_2Ph)_3RhCl(CO_4)} + \text{olefin} \longrightarrow (\text{olefin})(PEt_2Ph)_2RhCl(CO_3) + P{=}O \qquad (3)$$

The phosphane oxidation can go on in the presence of an excess of olefin until complex **2** is totally converted into other species that are not active catalysts. The use of bidentate phosphanes or chelating nitrogen ligands, like dipyridyl or phenanthroline, stabilises the catalyst for up to two to three hours,[14,16] after which it has been converted into inactive species. The mechanism of deactivation of the catalyst when monodentate or bidentate ligands are used is quite different. In the case of monodentate ligands, as we have reported above, the oxidation of the dissociated phosphane causes the destruction of the catalyst [Equation (3)], whereas in the case of bidentate ligands, ligand scrambling causes the destruction of the active catalytic species as shown in Equation (4). In fact, the square-planar moiety "$Rh(L\text{-}L)_2$" (where L-L is a bidentate phosphane) is not active in catalysis as it does not promote the formation of the peroxocarbonate because two *cis*-positions are not available. Similarly, the olefin complex does not coordinate either dioxygen or CO_2.

$$2\,Rh(L\text{-}L)Cl + n\,(\text{olefin}) \longrightarrow \underset{\mathbf{5}}{Rh(L\text{-}L)_2Cl} + \underset{\mathbf{6}}{Rh(\text{olefin})_nCl} \qquad (4)$$

Compound **5** has been isolated from the reaction solution and its nature confirmed by comparison with an authentic sample. As reported above, the oxygen transfer reaction assumes a particular importance when olefins or ethers are used,[13] affording useful products. Peroxocarbonates can therefore be used to promote the transfer of a single oxygen atom of the original dioxygen molecule to an oxophile. The reaction path and products are reported in Scheme 5. In the case of an olefin, carbocation **6** could be the intermediate[13] that generates epoxides, aldehydes and ketones. The oxygen transfer reaction has been also modelled using IOM.[17,18] Very interestingly, if styrene is used (Scheme 4), the calculated distribution of products is very close to the experimental one.



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Scheme 6. Formula of compound **6**

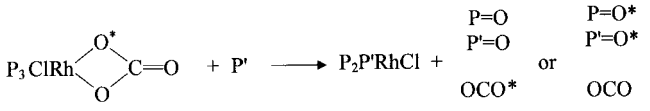
When peroxocarbonates react as oxidant towards an external phosphane or, in general when they act as one-oxygen transfer agents, as reported above, the carbonate is formed, as demonstrated by spectroscopic techniques (IR, NMR). The ^{31}P NMR spectrum shows a doublet of doublets (dd) at $\delta = 14.2$ ($J_{P\text{-}P} = 23.8$ Hz, $J_{P\text{-}Rh} = 89$ Hz) and a doublets of triplets (dt) at $\delta = 22.7$ ($J_{P\text{-}Rh} = 125$ Hz). These signals are also found in the ^{31}P spectrum when a solution of **2** in CD_2Cl_2, prepared at 240 K, is heated to room temperature. Interestingly, when the oxygen transfer occurs from the peroxocarbonate to the external phosphane, the

final reaction mixture shows the presence of a ^{31}P signal that can be attributed to $[RhCl(PEt_2Ph)_3]$.[19]

The formation of this species might be explained in terms of a reversible dissociation of CO_2 from the peroxocarbonate to afford the dioxygen complex that may give back $[RhCl(PEt_2Ph)_3]$ [Equation (1)]. We have tried to prove this hypothesis by GC-MS analysis and found that dioxygen is not detected. Conversely, CO_2 is released and, if labelled O_2 is used in the synthesis of the peroxocarbonate, a semi-labelled ^{18}O species is formed. Moreover, if a phosphane is added to the Rh carbonate formed from the peroxocarbonate after oxygen-transfer to the external oxophile, phosphane oxide is formed together with $[RhCl(PEt_2Ph)_3]$ [Equation (5)].

$$\underset{\mathbf{3}}{P_3ClRh(CO_3)} + P \longrightarrow \underset{\mathbf{4}}{P_3RhCl} + P{=}O + CO_2 \qquad (5)$$

This behaviour suggests that CO_2 could originate from a mechanism in which the carbonate is implicated in the phosphane oxidation. As a matter of fact we have performed a number of reactions which have clearly demonstrated that the "Rh^{III} carbonate ion" system can transfer one oxygen atom to the phosphane with formation of phosphane oxide and CO_2. The amount of CO_2 has been evaluated by a GC of the gas phase. The GC-MS spectrum of the gas phase also shows that if the carbonate has one ^{18}O oxygen atom that is used for binding the CO_3^{2-} moiety to the metal, the resulting CO_2 has ca. 50% of ^{18}O, as does the phosphane oxide (Scheme 7).



Scheme 7. Carbonate deoxygenation by an external phosphane ligand

The conversion of the carbonate to CO_2 with oxygen transfer to a substrate is reminiscent of the reaction of inorganic carbonates which form CO_2 and the metal oxide when heated at high temperature [Equation (6)].

$$MCO_3 \xrightarrow{1000\text{-}1200\ K} MO + CO_2 \qquad (6)$$
$$M = Ca, Mg$$

The release of CO_2 from coordinated carbonate complexes is not a trivial process. To the best of our knowledge, it has not been documented in the literature with phosphane as the reducing agent. It is known that hydrogen at high temperature and pressure is able to deoxygenate carbonates into carbon dioxide. In fact, $CoCO_3$ has been used for the synthesis of $Co_2(CO)_8$ with H_2 at 673 K.[20] Therefore, we decided to investigate if an external carbonate ion could itself undergo the deoxygenation reaction under mild conditions. We have thus reacted $[RhCl_3(PEt_2Ph)_3]$ with Na_2CO_3 or Ag_2CO_3 in the presence of a free phosphane. Interestingly, the reaction occurs at 353 K according to Equation (7) and (8), respectively.

$$(PEt_2Ph)_3RhCl_3 + Na_2CO_3 + P' \rightarrow (PEt_2Ph)_3RhCl + 2\,NaCl + P'{=}O + CO_2$$
$$P' = PCy_3 \qquad (7)$$

$$(PEt_2Ph)_3RhCl_3 + Ag_2CO_3 + 2\,P' \rightarrow 1/2\,[(PEt_2Ph)_2RhCl]_2 + 2\,(PEt_2Ph)AgCl + P'AgCl + P'{=}O + CO_2$$
$$P' = PEt_2Ph,\ PCy_3 \qquad (8)$$

In Equation (7), NaCl was isolated by extraction with water, and the Rh^I complex was isolated by recrystallisation from pentane. The latter has been characterised by elemental analysis, and its spectroscopic properties compared with those of an authentic sample. If PCy_3 is added as external phosphane, $O{=}PCy_3$ is the most abundant phosphane oxide, with minor amounts of $O{=}PEt_2Ph$. A limited degree of phosphane scrambling is observed (ca. 10%). Equation (7) represents a quite unique and interesting reaction, if one considers that the release of CO_2 from Na_2CO_3 requires high temperatures (>1000 K).[21] Ag_2CO_3 behaves in the same way. However, coordination to Rh lowers the decomposition temperature of the carbonate by more than 600 K. This finding rationalizes the behaviour of peroxocarbonate **2** and elucidates the reaction pathway relevant to Rh catalysis in styrene oxidation-carbonation,[12–15] allowing us to propose the cycle represented in Figure 2 for the Rh^I–Rh^{III} cyclic conversion.

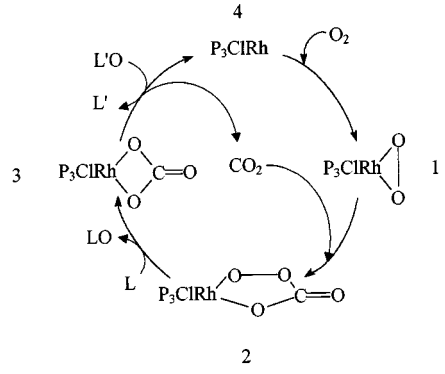


Figure 2. Double one-oxygen transfer to two different substrates from an O_2 molecule mediated by a Rh^I–Rh^{III}–Rh^I shuttle with the intermediacy of peroxocarbonate moiety; a ligand (P, L) scrambling is also observed

At the same time, the reduction of Rh^{III} to Rh^I explains the catalytic role of the metal. In fact, without reduction to Rh^I, only a stoichiometric reaction is observed in the O-transfer to the olefin from the peroxocarbonate complex. The observed turnover number. which is higher than one, can be interpreted only on the basis of a $Rh^{III} \rightarrow Rh^I$ reduction and reactivation of the catalyst.

Conclusions

The unprecedented deoxygenation of a carbonate ion to CO_2 in the presence of Rh^{III} has been observed. This finding represents an interesting new piece of chemistry demon-

strating that coordination of the carbonate anion allows the lowering of its decomposition temperature by more than 600 °C. However, this finding allows us to rationalise the catalytic role of Rh^{I} in the oxidation of styrene to styrene epoxide and other one-oxygen transfer products in an O_2/CO_2 atmosphere, with the intermediacy of peroxocarbonate−carbonate−carbon dioxide complexes.

Experimental Section

General: Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen or CO_2 atmosphere by using vacuum line techniques. All solvents were dried as described in the literature[22] and stored under dinitrogen. CO_2 (≥99.95%) and O_2 (≥99.98%) were purchased from Air Liquide Spa. The $RhCl(PR_3)_3$ complexes were prepared from $[RhCl(C_2H_4)]_2$ (Aldrich) and the corresponding phosphanes (Aldrich) according to previously reported experimental procedures.[4] The synthesis of $RhCl[^{18}O^{16}OC(^{16}O)^{18}O](PEt_2Ph)_3$ has been described previously.[5]

^{31}P NMR spectra were obtained at 81 MHz with a Varian XL-200 instrument. ^{31}P chemical shifts are referred to 85% H_3PO_4 using the high-frequency-positive convention. FTIR spectra were recorded using a Bruker 113V Fourier transform interferometer. Frequencies are accurate to ±1 cm^{-1}. Solid samples were studied as Nujol mulls (Nujol was previously dried over sodium wire and deoxygenated with argon). GC analyses were performed with a HP 5890 Series II gas chromatograph equipped with an Alltech-Heliflex AT-1000 capillary column (30 m × 0.00025 m, 0.2 μm thickness). GC-MS analysis was carried out with a gas chromatograph SHIMADZU 17 A-1000 (capillary column: 30 m × 0.00025 m, 0.25 μm thickness) detector linked to a SHIMADZU GCMS-QP 5050 mass spectrometer. GC analysis of gaseous phases was carried out with a gas chromatograph DANI equipped with a Carbowax column 3 m × 2.1 mm (ID) and TCD detector.

Study on the Thermal Stability of $(PEt_2Ph)_3RhCl(CO_4)$: a) Solid $[RhCl(CO_4)(PEt_2Ph)_3]$ (0.050 g, 0.07 mmol) was heated at 338 K for 10 min. under a dinitrogen atmosphere into Cell (a) (Figure 3) that was then connected to a GC and the gas phase analysed with a TCD. The GC analysis showed the absence of CO_2. The IR analysis of the solid showed that no reaction had occurred.
b) Analogous results were obtained when C_2H_4 was admitted into the cell and the system heated for 1−2 min. at 340 K. A longer reaction time produced a conversion of the Rh complex (see below).

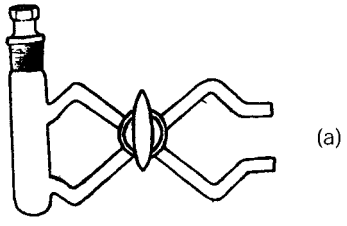


Figure 3. Apparatus used for the analysis of the gas phase in equilibrium with a solid

Conversion of $[RhCl(CO_4)(PEt_2Ph)_3]$ in CD_2Cl_2: A solution of **2** in CD_2Cl_2 was prepared at 213 K and the NMR spectrum recorded (Figure 1, spectrum A). The solution was heated to 250 K for 20 min. and the ^{31}P NMR spectrum recorded at this temperature (Figure 1, spectrum B). Heating produced the oxygen transfer to the phosphane. The following compounds were identified: *trans*-$RhCl(CO)(PEt_2Ph)_2$: δ = 26.0 (d, $J_{P\text{-}Rh}$ = 128.7 Hz); *mer*-$RhCl_3(PEt_2Ph)_3$: δ = 3.7 (dd, $J_{P\text{-}Rh}$ = 84 Hz, $J_{P\text{-}P}$ = 23.1 Hz), 16.9 (dt, $J_{P\text{-}Rh}$ = 111.3 Hz); *mer*-$RhCl(CO_3)(PEt_2Ph)_3$: δ = 14.2 (dd, $J_{P\text{-}Rh}$ = 89 Hz, $J_{P\text{-}P}$ = 23.8 Hz), 22.7 (dt, $J_{P\text{-}Rh}$ = 125 Hz); O=PEt_2Ph: δ = 42.9.

Reaction of $[RhCl(CO_4)(PEt_2Ph)_3]$ with PEt_2Ph: a) Solid **2** was heated with an equimolar amount of PEt_2Ph at 320 K under dinitrogen. The IR spectrum of the mixture showed the appearance of phosphane oxide (1150 cm^{-1}) within 4 hours and the formation of Rh^{III} carbonate (IR band at 1660 cm^{-1}), which was isolated from the mother mixture.

b) Compound **2** in CH_2Cl_2 solution was treated with an equimolar amount of PEt_2Ph at room temperature under dinitrogen. The solution was monitored at intervals of time by GC and GC/MS. The formation of phosphane oxide was clearly demonstrated to be a product of the oxidation process.

Reaction of Solid $[RhCl(CO_4)(PEt_2Ph)_3]$ with C_2H_4: Solid $[RhCl(CO_4)(PEt_2Ph)_3]$ (0.05 g, 0.07 mmol) was stirred at room temperature under a C_2H_4 atmosphere. The reaction was monitored by GC analysis of the equilibrium gas. No ethylene oxidation products were detected in the gas or solid phase, while in the solid phase phosphane oxide [^{31}P NMR: δ = 42.9 (s)] appeared after a couple of days. After a week the solid completely changed its appearance and the reaction was stopped and the solid analyzed by ^{31}P NMR spectroscopy. The residual solid was a mixture of compounds which had a ^{31}P spectrum close to that shown in Figure 1B. If an inert gas was used instead of ethylene, the complex lasted for a much longer time under the same experimental conditions.

Reaction of $(PEt_2Ph)_3RhCl(CO_4)$ with Styrene: Styrene (0.1 mL) in THF (2 mL) was added to **2** (0.100 g, 0.16 mmol) under a CO_2/O_2 atmosphere (10:1 v/v) and the solution stirred at room temperature. At intervals of 30 min., a sample was withdrawn and analysed by GC/MS. The presence of the following products was ascertained: benzaldehyde, phenylacetaldehyde, phenyl methyl ketone and styrene epoxide in a molar ratio 1:3:3:5. Benzoic acid and styrene carbonate were also present.

Reaction of $[RhCl_3(PEt_2Ph)_3]$ with Na_2CO_3: $[RhCl_3(PEt_2Ph)_3]$ (0.200 g, 0.3 mmol) was dissolved in toluene (5 mL) and a stoichiometric amount of Na_2CO_3 (0.031 g, 0.3 mmol) and free phosphane (0.050 g, 0.3 mmol) added. The reaction mixture was heated to 353 K. After 1 hour the GC analysis of the gas phase revealed the presence of CO_2 while in solution the free phosphane and phosphane oxide were detected. After 24 h, the amount of CO_2 in the gas phase increased to almost reach a CO_2/Rh ratio of 0.5. CO_2 was also present in solution. The total amount of released CO_2 allowed us to estimate when the reaction had reached completion. NaCl separated from the solution and was isolated by filtration. Its mass was 95% of the expected stoichiometric amount. From the mother solution 0.150 g of crude $[RhCl(PEt_2Ph)_3]$ was isolated, which was then crystallised from pentane. − $C_{30}H_{45}ClP_3Rh$ (636.97): calcd. C 56.57, H 7.12, Cl 5.57, P 14.59; found C 56.03, H 7.01, Cl 5.61, P 15.03.

Reaction of $(PEt_2Ph)_3RhCl_3$ with Ag_2CO_3: $[RhCl_3(PEt_2Ph)_3]$ (0.140 g, 0.2 mmol) was dissolved in CH_3CN (3 mL) and a stoichiometric amount of Ag_2CO_3 (0.050 g, 0.2 mmol) and PEt_2Ph (0.030 g, 0.2 mmol) were added. The reaction mixture was heated to 353 K. After 1 hour the GC analysis of the gas phase revealed

the presence of CO_2. After 24 h the gas phase showed an increased amount of CO_2 and from the solution a whitish-yellow solid separated, which was filtered, washed with pentane and dried in vacuo. It was analyzed as $AgCl(PEt_2Ph)$. From the solution $[RhCl(PEt_2Ph)_2]_2$ was isolated together with $O{=}PEt_2Ph$. The dimer was characterized by elemental analysis and its spectroscopic properties were compared to an authentic sample. – $C_{18}H_{33}AgClP$ (423.75): calcd. C 51.01, H 7.85, P 7.30, Cl 8.36; found C 50.85, H 7.54, P 7.10, Cl 8.16. – $C_{40}H_{60}Cl_2P_4Rh_2$ (941.54): calcd. C 51.03, H 6.42, Cl 7.53, P 13.16; found C 50.90, H 7.70, Cl 8.01, P 7.03.

In one run we used PCy_3 as the external phosphane. This was essentially totally converted into $O{=}PCy_3$. The isolated Rh complexes showed that some phosphane scrambling also took place and mixed phosphane species were obtained. The exchange did not exceed 10–15%, as demonstrated by ^{31}P NMR spectroscopy.

Acknowledgments

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