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Some Aspects of the Reactivity of Rhodium(I) and Rhodium(II) Tricyclohexylphosphine Derivatives Studied by ESR Spectroscopy.
I. Formation of Paramagnetic $Rh^{II}O_2^-$ Species and Autooxidation of the Coordinated PCy_3 in the Solid State

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The reactivity of $RhCl(PCy_3)_2$ *in the solid state towards* O_2*, CO, and* H_2 *was investigated by ESR and IR spectroscopies and compared with that in solution. The 'decomposition' reaction occurring upon exposure to air produces superoxo species by dioxygen coordination. This leads to the auto-oxidation of the coordinated* PCy_3*, which is partially dissociated from the complex. This behaviour is quite different from that in solution, where a dioxygen adduct is formed. The ability of the complex in activating* O_2 *in the solid state has been related to the existence of polynuclear species.*

No substantial difference has been found for the reactivity of the complex in solution and in the solid state towards CO and H_2*, except that the treatment with CO allowed to evidence Rh(II) impurities contained in the product.*

Introduction

The use of tricyclohexylphosphine (PCy_3) in coordination chemistry is related to the high bulkiness of this ligand, which enables the stabilization of metal complexes in very unusual valence state and coordination numbers [1].

In rhodium chemistry, vivid examples of this ability are documented by the well established formation of Rh(I) and Rh(II) complexes formulated as $RhX(PCy_3)_2$ (X = Cl, Br, I, F) [2] and $RhX'X''(PCY_3)_2$ ($X' = X'' = Cl$; $X' \neq X''$: X = Cl, Br, F, I) [3, 4], even if some aspects of the chemistry of these compounds are unclarified or conflictingly reported. In a previous paper from this laboratory [5], it was reported that solid samples of triphenylphosphine Rh(I) derivatives, containing 'coordinatively unsaturated' metal species, reacted spontaneously with dioxygen giving ESR active species whose content allowed an indirect measurement of the amount of metal species with vacant coordination sites. Due to the important role that even low percentages of this type of very active species can play in determining the overall activity of a catalytic system, their detection and quantitative determination by a very sensitive technique such as ESR was found to be relevant for catalytic investigations. In this context, the study of the reactivity in the solid state of the formally 'coordinatively unsaturated' complex $RhCl(PCy_3)_2$ (I) was of potential interest. Complex (I) in the solid state has been reported to decompose immediately upon exposure to air, and slowly even under inert atmosphere [2], whereas a benzene solution rapidly reacts with dioxygen at room temperature to give almost quantitatively the blue-green diamagnetic adduct *trans*-$RhCl(O_2)(PCy_3)_2$ (II). This different behaviour was not plausible because coordination compounds are generally more stable as solids than in solution and it is likely that, if a 'decomposition' reaction has to take place, it should be more favoured in solution than in the solid state. Another point worthy of being clarified is the problem of the impurities that can contaminate the product. The existence of the equilibria

$$\tfrac{1}{2}[RhCl(PCy_3)_2]_2 \rightleftarrows RhCl(PCy_3)_2 \underset{+C_8H_{14}}{\overset{-C_8H_{14}}{\rightleftarrows}} RhCl(PCy_3)_2(C_8H_{14}) \qquad (1)$$

under synthetic conditions from $[RhCl(C_8H_{14})_2]_2$ and PCy_3 in benzene has been demonstrated by a

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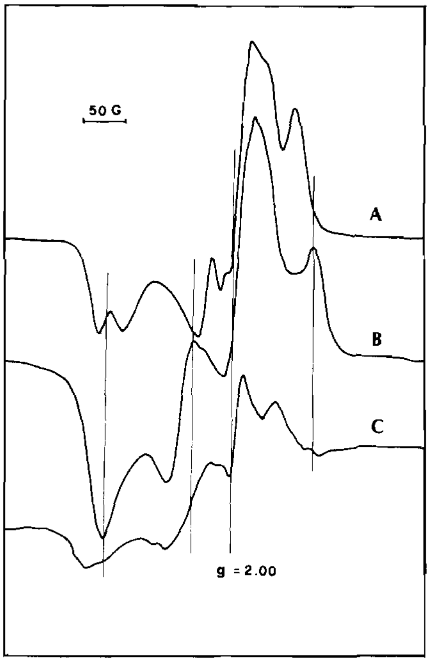


Fig. 1. The X-band ESR powder spectra at room temperature of $RhCl(PCy_3)_2$ after exposure to air in the solid state (room temperature, P 1 atm, 6 h): (A) and (B) samples obtained in different preparative runs (10% and 12% ESR activity, respectively); (C) sample A after 20 days (4% ESR activity).

^{31}P NMR study, together with the formation of a product formulated as $[RhCl(PCy_3)_2]_n$ [ν(Rh–Cl) 275 cm^{-1}, br] from a supersaturated solution [2]. Notwithstanding, the product obtained from the synthesis is indicated as $RhCl(PCy_3)_2$, except that the existence of the monomer–dimer equilibrium was invoked to explain, for example, the low reaction rate with nitrogen [2].

In order to get some elucidations on the nature and behaviour of '$RhCl(PCy_3)_2$', and on the nature of the contaminating impurities, a combined ESR and IR study was performed on the reactivity of the complex in solution and in the solid state towards O_2, CO and H_2.

Experimental

Physical Measurements

ESR spectra were recorded on a Varian E112 Century Series Spectrometer at X-band, provided with a standard rectangular cavity, and magnetically modulated as 100 kHz. Unless otherwise indicated, all samples were undilute powders. The concentration of paramagnetic species was estimated from the intensity of the signals by comparison with those of $CuSO_4 \cdot 5H_2O$ standard samples, and the *g*-values were determined with respect to the *g*-values of standard samples.

IR spectra were recorded using a Perkin-Elmer 283 B spectrophotometer in the region 4000–200 cm^{-1}, the samples being supported as Nujol mulls between CsI discs. Spectra in benzene solution were recorded in the region 400–200 cm^{-1} in 0.5 mm polyethylene molded cells (Barnes Engineering Co.).

Purification of tricyclohexylphosphine

PCy_3 (Strem Chemicals) was recrystallized from methanol under argon just before use.

Preparation of the Rhodium Complexes

$RhCl(PCy_3)_2$ was prepared according to van Gaal's procedure [2] from $[RhCl(C_8H_{14})_2]_2$ and PCy_3 in benzene solution, using acetone as non-solvent. $RhCl(O_2)(PCy_3)_2$ [2], $RhCl_2(PCy_3)_2$ [3], $RhHCl_2(PCy_3)_2$ [4], $RhCl(CO)(PCy_3)_2$ [3], and $[RhCl(C_8H_{14})_2]_2$ [6] were prepared according to literature methods.

Treatments with Gases

Treatments with dry O_2, CO or H_2 were carried out at room temperature and atmospheric pressure on samples contained in quartz ESR tubes without stirring. In the experiments carried out at higher gas pressure, the tubes were put into an autoclave.

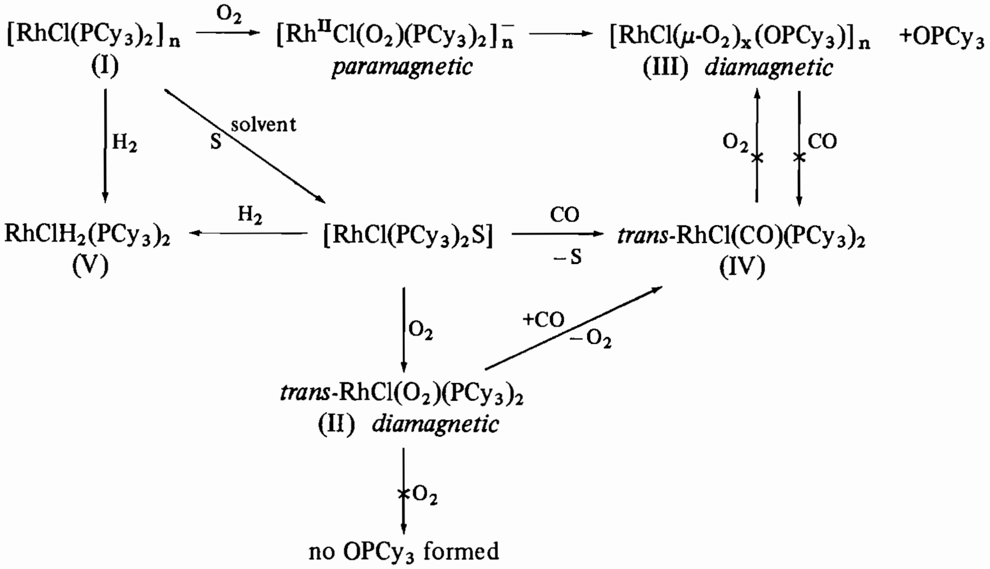
The samples were always handled rigorously in an argon atmosphere. The solvents were carefully purified and degassed before use.

Results and Discussion

The reactivity of $RhCl(PCy_3)_2$ (I) and related products towards O_2, CO and H_2 in the solid state is shown in Scheme 1, together with the already reported reactivity in solution.

Treatment with Dioxygen

When solid samples of the lilac powder (I) were exposed to dioxygen, they turned immediately into a light-brown product (III). Whereas the dioxygen adduct (II) obtained in benzene solution is practically diamagnetic, the disappearance of the lilac colour in the solid state resulted in the appearance of ESR signals which grew very rapidly and reached a maximum (about 10% of ESR active species) within a few hours of exposure to dioxygen. The percentage of ESR active species and the shape of the signals (Fig. 1, spectra A and B) were slightly different for separately synthesized samples, but substantially the same for different samples of the same preparative run. The ESR spectra are consistent with paramagnetic species of nearly axial symmetry (*g*-factor value near 2), to which a superoxo structure



Scheme 1

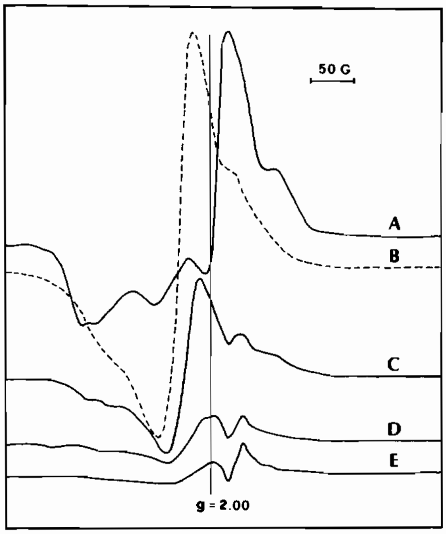


Fig. 2. The X-band ESR spectra at room temperature of $RhCl(PCy_3)_2$ after exposure to air in the solid state (see before): (A) initial sample (10% ESR activity); (B) sample A just after the addition of benzene (10% ESR activity); (C), (D), and (E) sample B after 0.5, 1.0, and 1.5 h, respectively (2.0, 0.7, and 0.3% ESR activity, respectively).

of the type $Rh^{II}O_2^-$ can be assigned, according to that previously reported for other rhodium systems [6–8].

The life-time of the paramagnetic species formed from (I) was of several months, the species with a higher symmetry disappearing more rapidly than the others (Fig. 1, spectrum C). The overall decaying rate was unaffected *in vacuo*, whereas a slight increase was observed if the samples were gently warmed. On the contrary, a very rapid disappearance of the ESR signals occurred when a few drops of benzene were added, giving a concentrated solution. In this case, the decay proceeded through the initial formation of more symmetric intermediates (Fig. 2, spectrum B), leaving after a few minutes a weak residual ESR signal (about 0.3% of ESR active species) of simplified shape (Fig. 2, spectra C, D and E). In every case, the decay process was irreversible and it was impossible to re-generate paramagnetic species from decayed solid or liquid samples by further treatment with dioxygen, even under pressure.

It seems pertinent to note, at this point, that $RhCl(PPr^i_3)_2$, a strict analogue of (I), reacts easily with O_2 in n-pentane giving *trans*-$RhCl(O_2)(PPr^i_3)_2$, closely comparable to (II) [9]. This product exhibits a weak unresolved ESR signal very similar to that observed for our samples (see Fig. 1, spectrum C). In our opinion these paramagnetic species are $Rh^{II}O_2^-$ impurities generated in the initial step of decomposition of the dioxygen adduct which leads to a slow partial oxidation of the phosphine ligand. This seemed not to be the case with the tricyclohexylphosphine complex (II): when a solid sample of (II) was treated with O_2 at 5 atm for 24 h, in fact, no colour change or $OPCy_3$ formation was observed. Correspondingly, the product did not show any ESR activity, thus suggesting that the different oxygenating ability of (I) in solution and in the solid state can probably be ascribed to the different nature of

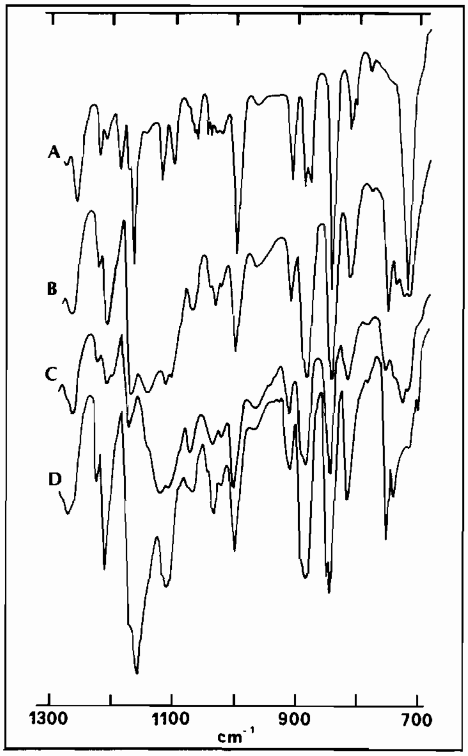


Fig. 3. IR spectra (nujol mull, CsI) of $RhCl(PCy_3)_2$: (A) under argon; (B) after air exposure; (C) residue of sample B after washing with n-pentane; (D) soluble part of sample B recovered from the n-pentane solution.

the dioxygen intermediates formed in the first step of the reaction. In connection with the formation of the oxygenated species (III), significant changes in the IR spectra were observed. The spectrum of (I) recorded rigorously under argon (Fig. 3, spectrum A) shows the typical band pattern of coordinated PCy_3 with major absorptions at 1173, 1001, 850, and 721 cm^{-1} and a band at 280 cm^{-1} of the Rh–Cl stretching. After the contact with dioxygen, new absorptions appear due to the formation of considerable amounts of tricyclohexylphosphineoxide (characteristic absorptions at 1158 cm^{-1}, $\nu(P{=}O)$ [8], and at 756 cm^{-1}), whereas the $\nu(Rh{-}Cl)$ is shifted to 315 cm^{-1} (Fig. 3, spectrum B). Particularly in the 1200–1100 cm^{-1} region the spectrum appears to be very crowded so that it is impossible to decide if the $OPCy_3$ is free or bound to the metal. Besides, the masking effect of the combined absorptions of PCy_3 and $OPCy_3$ does not evidence the presence of absorptions due to coordinated oxygen. However, the absence of the band at 993 cm^{-1}, assignable to a $\nu(O{-}O)$ of a peroxo species, which is well evident in the spectrum of (II) [2], confirmed that the reaction of (I) with dioxygen in the solid state or in solution leads to different oxygenated products.

Part of the $OPCy_3$ formed in the solid samples can be extracted by washing with n-pentane (Fig. 3, spectrum D), and part remains still coordinated to the metal in an insoluble product (Fig. 3, spectrum C). Because it has been found [8] that the $\nu(P{=}O)$ in the tricyclohexylphosphine complexes shifts to lower frequency by about 40 cm^{-1} with respect to the free ligand, the absorption at 1120 cm^{-1} can be reasonably attributed to coordinated $OPCy_3$.

The P/Rh ratio found for the insoluble product accounts for the dissociation of about one $OPCy_3$ mol per Rh atom and suggests, together with the shift of $\nu(Rh{-}Cl)$ to higher frequencies, the possible formation of polynuclear μ-oxo species. On the other hand, the ability in oxidizing coordinated PCy_3 in the solid state appeared a very striking and surprising feature of (I), which gives only traces of $OPCy_3$ when the reaction with dioxygen is carried out in benzene solution. This apparently conflicting behaviour can probably be interpreted taking into account the different nature of the system in solution and in the solid state. In solution, due to the coordinative intervention of the solvent which leads to the formation of mononuclear species, the interaction of O_2 with the metal seems to be weak enough. Accordingly the presence of $\nu(O{-}O)$ at high frequency (993 cm^{-1}), indicating a strong O–O bond, and the X-ray data for analogous systems [9], confirmed that in this case we are in the presence of an 'oxygen adduct' in which a real activation of the ligand in a superoxidic form does not take place. On the contrary, the situation in the solid state, wherein polynuclear species are predominant, may be also conducive to the activation of the dioxygen molecule leading to ESR active $Rh^{II}O_2^-$ species, more reactive for the transfer of oxygen to coordinated PCy_3. Accordingly it has been found that in the catalytic oxidation of the coordinated triphenylphosphine in rhodium complexes occurred in the solid state only when ESR active superoxide species were formed [5].

Treatment with Carbon Monoxide

By reaction of (I) with CO in benzene solution, the yellow complex $RhCl(CO)(PCy_3)_2$ is reported to be formed [2]. Spectroscopic data suggest that the product is substantially *trans*-$RhCl(CO)(PCy_3)_2$ (IV), identical to the product obtained from $RhCl_3 \cdot 3H_2O$, CO, and PCy_3 in ethanolic solution according to Moers' method [3].

The exposure to CO of (I) in the solid state, even at atmospheric pressure, resulted in an immediate change of the colour to whitish. After a treatment under pressure (3 atm, 10 h) the final product showed the typical IR spectrum of (IV) [$\nu(CO)$: 1947 cm^{-1}; $\delta(CO)$: 581 cm^{-1}; $\nu(Rh{-}Cl)$: 305 cm^{-1}]. The presence of minor carbonyl bands at 2078, 2051, and 2000 cm^{-1} can be associated with the presence of Rh(II) and Rh(III) impurities able to react with CO (see later).

The carbonyl compound obtained was fairly stable in the solid state and no colour change or spectroscopic modifications were observed after prolonged exposure to O_2 under pressure. Besides, it is interesting to outline that also (II) reacts in the solid state with CO under pressure to give (IV), the easy displacement of the coordinated O_2 confirming once again the weak Rh–O bonding. On the contrary, the oxygenated complex (III) does not react with CO (3 atm, 15 h).

Treatment with Dihydrogen

When the complex (I) is treated with H_2 in benzene, it undergoes an oxidative addition giving $RhH_2Cl(PCy_3)_2$ (V), which is easily separated by precipitation with n-hexane [4]. Spectroscopic information indicates that the complex is characterized by a square pyramidal structure with the phosphine *trans* to each other and the chlorine in an axial situation [4]. Formally the same product is reported to be obtained by refluxing a toluene solution of $[RhCl(C_8H_{14})_2]$ and PCy_3 [10]. However, conflicting data are reported for the most relevant IR absorptions of the two products, particularly in the Rh–H region, thus suggesting that the nature of the product is dependent on the preparative route. In fact, van Gaal's product exhibits a band of medium intensity at 2120 cm^{-1}, together with a shoulder at 2165 cm^{-1} [4], probably suggesting the presence of two isomeric forms of the product, whereas Vrieze's compound shows only a single absorption at 2150 cm^{-1} [10].

By treatment of solid (I) with H_2 at atmospheric pressure for 16 h, a yellow product with an IR spectrum identical to (V) was obtained. Therefore, the reactivity of the complex (I) towards H_2 resulted to be practically the same either in solution or in the solid state.

Presence of Impurities

Small amounts of $RhCl_2(PCy_3)_2$, variable in the different preparative runs, always contaminated our samples of (I), in agreement with that previously reported [2]. The ESR technique provided a very useful tool to detect these paramagnetic impurities. Moreover, when the direct determination was impossible due to sensitivity limits, the enhancement of the ESR signal on treating the solid samples with CO (see next paper) allowed us to measure concentrations as low as 0.5% of Rh(II) ESR active species in our samples.

Another impurity in (I) was evidenced by the presence in the IR spectrum of a weak absorption at 1945 cm^{-1}, not assignable to a carbonyl species also being present in samples obtained using only hydrocarbon solvents. This impurity seems to be the hydrido complex $RhHCl_2(PCy_3)_2$ (VI), already cited as a decomposition product of (I) in solution [2]. The preparation of (VI) from $[RhCl(C_8H_{14})_2]$ and PCy_3 in toluene at 20 °C [ν(Rh–H) at 1943 cm^{-1}] has been reported by James [11]. Formally the same product was obtained by van Gaal through oxidative addition of gaseous HCl to an acetone suspension of (I) [4]. In this case the product does not show any IR absorption in the ν(Rh–H) region and spectroscopic evidence on its hydridic nature was gathered through a deuterium exchange reaction which allowed us to assign a band of δ(Rh–H) at 587 cm^{-1} (350 and 335 cm^{-1} in the deuteriated product) [4]. This suggests that with different procedures isomers of (VI) are formed. When a nominal sample of (VI), prepared according to [4], was treated in the solid state with CO at atmospheric pressure, its IR spectrum showed correspondingly a strong absorption at 2078 cm^{-1}, which was also found as a minor absorption in the spectrum of (I) after treatment with CO.

We can suppose that these hydrido-impurities are generated through an *ortho*-metallation process, which is rather likely for (I) due to the existence in the complex of two driving factors in C–H bond activation, *i.e.* bulkiness of the ligands and coordinative unsaturation [10].

Conclusions

The study of the reactivity in the solid state towards O_2, CO, and H_2 of transition metal complexes with vacant coordination sites, such as $RhCl(PCy_3)_2$, may give useful information on the nature of chemical activation of these small molecules. The interactions in absence of solvent, quite different from those observed in solution, may also open new perspectives on the use, in heterogeneous phase, of transition metal complexes widely used as homogeneous catalysts.

Furthermore, the use of ESR and IR techniques can be relevant in solving some problems related to the presence of impurities in the products investigated.

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