Inorganica Chimica Acta, 69 (1983) 221–225

Some Aspects of the Reactivity of Rhodium(I) and Rhodium(II) Tricyclohexylphosphine Derivatives Studied by ESR Spectroscopy.
II. Formation of a Paramagnetic Rh(II) Carbonyl Species by Treatment of $RhCl_2(PCy_3)_2$ in the Solid State with Carbon Monoxide

G. VALENTINI, G. BRACA, G. SBRANA

Istituto di Chimica Organica Industriale, Università di Pisa, via Risorgimento 35, 56100 Pisa, Italy

and A. COLLIGIANI

Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R. (National Research Council), via Risorgimento 35, 56100 Pisa, Italy

Received April 27, 1982

The behaviour of $RhCl_2(PCy_3)_2$ in the solid state towards O_2, CO, and H_2 was investigated. Whereas no reaction occurred with dioxygen and dihydrogen, treatment with carbon monoxide led to the formation of $RhCl_2(CO)(PCy_3)_2$, which is the first example of a paramagnetic carbonyl Rh(II) derivative. The product is rather labile but the life-time in the solid state was long enough to allow the spectroscopic study of the decay process. ESR and IR spectra indicated a disproportionation reaction to Rh(I) and Rh(III) carbonyl species.

Introduction

The ability of tertiary phosphines in reducing rhodium(III) either by a two-electron process to rhodium(I), or by a one-electron process to rhodium(II), is well documented [1]. It has been also demonstrated that both mechanisms are generally simultaneously effective, so that Rh(I) derivatives have been recognized to contain Rh(II) impurities [2, 3], as well as Rh(I) and Rh(III) species very often contaminate Rh(II) derivatives [4–6]. It is also known that Rh(II) systems are very reactive precursors for hydrogenation catalysts [7], but no detailed information exists on the transformations which occur during the catalysis.

In the course of our study on the reactivity of $RhCl(PCy_3)_2$, in view of the frequent contamination of Rh(I) derivatives by Rh(II) paramagnetic species, we decided to investigate the stability of $RhCl_2(PCy_3)_2$ and the transformations undergone by action of some small molecules such as dioxygen, carbon monoxide, and dihydrogen.

Experimental

Physical Measurements

E.S.R. and I.R. spectra were recorded using techniques described in the preceding paper. Magnetic susceptibilities were measured at room temperature using the Gouy method, following the procedure given by Figgis and Lewis [8]. $CuSO_4 \cdot 5H_2O$ was used for calibration.

Treatments with Gases

Treatments with O_2, CO and H_2 were carried out as described in the preceding paper.

Purification of Tricyclohexylphosphine

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

Preparation of the Rhodium Complexes

$RhCl_2(PCy_3)_2$ was prepared according to the method described by Moers [9], from $RhCl_3 \cdot 3H_2O$ and PCy_3 in 2-propanol. $RhHCl_2(PCy_3)_2$ [4] and *trans*-$RhCl(CO)(PCy_3)_2$ [9] were prepared according to literature methods.

Results and Discussion

Following the literature procedure [9] we never succeeded in obtaining samples of nominal $RhCl_2(PCy_3)_2$ (I) with a magnetic moment at the solid state of 2.2 BM, accounting for the presence of only Rh(II) paramagnetic species with one unpaired electron in a square planar structure [9]. Our samples, in fact, always showed magnetic moments of 1.70–1.75 BM, accounting only for about 65–70% of Rh(II) paramagnetic species.

0020-1693/83/0000-0000/$03.00

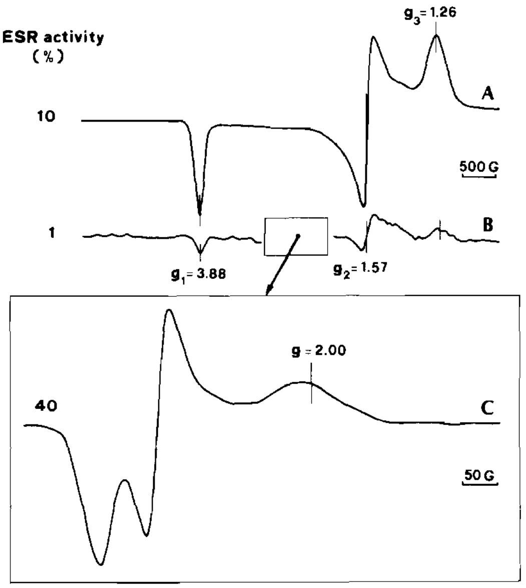

Fig. 1. The X-band ESR powder spectra at room temperature of $RhCl_2(PCy_3)_2$. A - nominal compound; B - after treatment with carbon monoxide at atmospheric pressure for 60 h; C - 'central' part of the spectrum B recorded on a different scale.

The ESR powder spectrum of the undiluted (I) showed g-factor values typical for a very anisotropic electron distribution around the central rhodium nucleus (Fig. 1, spectrum A). The existence of a g-value at 3.88, and two g-values at 1.57 and 1.26, respectively, fits well with a planar-like structure in the solid state [4] according to the formal coordinative unsaturation of the metal species. However, quantitative ESR measurements on our samples accounted only for about 10% of ESR active species. This low value may be due either to the derivative character of the recorded signals, or to the existence of metal–metal interactions which can cause a decrease of the ESR activity. Because the intensity of the signals did not vary when the spectrum was recorded in benzene solution, we might argue that intermolecular interactions are not responsible for the low ESR activity of the product [5].

In the IR spectrum of (I) two ν(Rh–Cl) absorptions are present at 355 and 344 cm^{-1}, tentatively assignable to two crystalline modifications of the same *trans* isomer, rather than to a *cis* isomer [1,9]. Moreover, the presence in the spectrum of weak absorptions at 1945 and 580 cm^{-1}, assignable to $RhHCl_2(PCy_3)_2$ (II) [literature: ν(Rh–H), 1943 cm^{-1}] [10] indicates that (I) contains some impurities, which would also account for the low magnetic moment of the compound.

Treatment with Dioxygen

Samples of (I) in the solid state were unreactive towards dioxygen. The ESR and IR spectra remained unchanged and no oxidation of tricyclohexylphosphine took place, even when treatments were carried out under pressure.

Treatment with Carbon Monoxide

When solid samples of (I) were exposed to dry CO, even at atmospheric pressure, the colour of the product turned immediately from red-brown to whitish, and significant changes in the ESR and IR spectra were correspondingly observed.

The ESR signals of the anisotropic square planar species (Fig. 1, spectrum A) were very quickly transformed into signals with g-factor values close to 2, indicative of a symmetrization process (Fig. 1, spectra B and C). These ESR modifications are in agreement with a coordination of the CO ligand to the metal through an addition reaction, which does not imply the displacement of any other ligand. Accordingly, no free PCy_3 was recovered by washing the reaction product with n.pentane. Therefore, the product obtained is the first reported example of a paramagnetic carbonyl Rh(II) derivative.

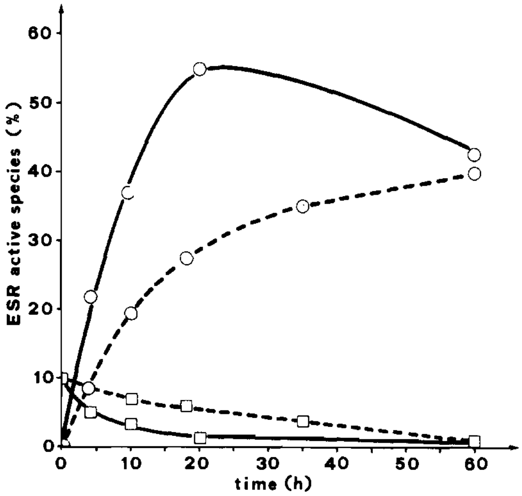

Fig. 2. Effect of CO pressure and exposure time on the concentration of 'anysotropic' (□) and 'symmetric' (○) ESR active species. p_{CO} = 10 atm: solid lines; p_{CO} = 1 atm: dotted lines.

From a quantitative point of view, even after short times of exposure to CO, the coordination of the ligand was accompanied by an increase of the total amount of ESR active species (Fig. 2), this indicating that even species not accounted for in the initial spectrum can contribute to the formation of the more symmetric species. The treatment with CO at atmospheric pressure (Fig. 2, dotted lines) took about 60 h to reduce the amount of the initial anisotropic species down to 1%, this corresponding to the overall appearance of 40% of the 'symmetric' species. At higher CO pressure (10 atm) (Fig. 2, solid lines) an equivalent change occurs within 20 h, accompanied by the formation of 55% of new paramagnetic species. In this case, however, longer exposure times (60 h) did not lead to an improved ESR activity, due to the reduction of the 'central' species in spite of the further reduction of the 'anisotropic' ones. Analogously, samples maintained under inert atmosphere after the CO treatment exhibited a spontaneous decay of the ESR activity, attributable to the disappearance of the symmetrized species. These results, which suggest a relative instability of the Rh(II) carbonyl species, also explain why it was impossible to obtain a percent of paramagnetic carbonyl species accounting for a quantitative transformation of the Rh(II) species present in the starting complex. The life-time of the 'central' paramagnetic species was however long enough to allow the study of their progressive decay and to run ESR and IR monitoring spectra.

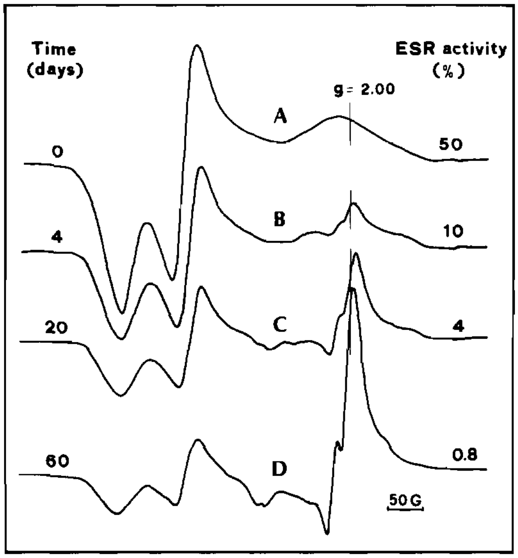

Fig. 3. Central part of the X-band ESR powder spectra of $RhCl_2(PCy_3)_2$ treated with carbon monoxide (10 atm, 15 h): A - immediately recorded after the treatment; B, C, and D - recorded at different time intervals during the storage under inert atmosphere.

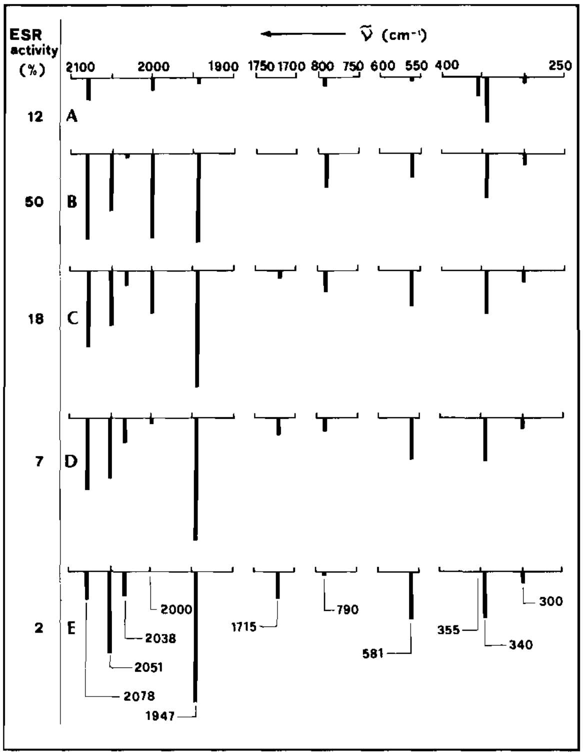

Fig. 4. Histograms of the more significant IR absorptions of samples of $RhCl_2(PCy_3)_2$ treated in the solid state with CO at room temperature: A - after a treatment at atmospheric pressure for 30 min; B - immediately recorded after a treatment at 10 atm for 15 h; C - sample B, after 2 days under argon; D - sample B, after 10 days under argon; E - sample B, after 30 days under argon.

The intensity of the bands is relative to the PCy$_3$ absorption at 1001 cm^{-1}.

TABLE I. Assignments of the Major IR Absorption Bands (cm^{-1}) for Rh(I), Rh(II), and Rh(III) Carbonyl Derivatives (nujol mull, CsI discs).

	ν(Rh–H)	ν(CO)	δ(CO)
$RhHCl_2(CO)(PCy_3)_2$		2078	790
	2100[a]	2020[a]	
$RhCl_2(CO)(PCy_3)_2$		2000	720 ?
trans-$RhCl(CO)(PCy_3)_2$ (III)		1947	581
		1941[b]	
		1947[c]	582[c]

[a] In benzene solution, ref. 4. [b] Ref. 9. [c] Ref. 15.

In Fig. 3 the central part of the ESR spectrum is reported after a CO treatment at 10 atm for 15 h (spectrum A), and compared with the spectra of the same sample recorded at different time intervals there after (spectra B, C, and D). The slow transformation of the paramagnetic species into ESR inactive ones is shown to take place through the intermediate formation of more symmetric species. This behaviour indicates that the geometry of the system in the solid state is not particularly rigid, and some rearrangements can take place. The most relevant IR absorptions of the product obtained by a treatment with CO of a few minutes are reported in histogram fashion in Fig. 4, spectrum A, and the assignments to the different metal species are summarized in Table I.

In comparison with the IR spectrum of (I), new absorptions appeared in the 2100–1900 cm^{-1} region together with a band at 790 cm^{-1}, whereas the former band of the doublet at 355 and 340 cm^{-1} [ν(Rh–Cl)] was shifted down to 300 cm^{-1}. The dominant absorptions in the carbonyl region were at 2078 and 2000 cm^{-1}, with a minor band at 1947 cm^{-1}. The first band was recognized to be peculiar to $RhHCl_2(CO)(PCy_3)_2$, formed by reaction with CO of the hydrido-impurity (II). This was demonstrated by a separate experiment in which an authentic sample of (II) was treated with CO (5 atm, 2 h) in the solid state (see Table I). The product did not show any evident band assignable to ν(Rh–H), probably blurred due to its weak intensity.

The absorption at 1947 cm^{-1}, which is accompanied by a weak band at 581 cm^{-1}, is indicative of the presence of *trans*-$RhCl(CO)(PCy_3)_2$ (III) (see Table I). These assignments are in agreement with the large increase in CO stretching frequencies on going from Rh(I) to Rh(III) carbonyl species, as previously observed and explained for different phosphine ligands [11, 12]. In this context, the intermediate frequency at 2000 cm^{-1} can be reasonably attributed to a Rh(II) carbonyl derivative. The more significant IR absorptions of the product obtained by treatment of (I) with CO (10 atm, 15 h) are reported in Fig. 4, as shown in the spectra recorded immediately (spectrum B) and at different time intervals thereafter (spectra C–E).

The modification of the IR band pattern and the corresponding change of the ESR activity (see left-hand row in Fig. 4), give significant information on the transformations undergone by the Rh(II) and Rh(III) carbonyl species. The paramagnetic $RhCl_2(CO)(PCy_3)_2$ [ν(CO) at 2000 cm^{-1}] rapidly decays, probably through a disproportionation reaction, to give Rh(I) and Rh(III) carbonyl species (eq. 1), as demonstrated by the increase of the intensity of the band at 1947 cm^{-1}, due to *trans*-$RhCl(CO)(PCy_3)_2$, and by the appearance of new absorptions at 2051 and 2038 cm^{-1}, respectively. The band at 2051 cm^{-1} can be attributed to $RhCl_3(CO)(PCy_3)_2$, according to Usón [13] [ν(CO) 2060 cm^{-1}, KBr].

$$2RhCl_2(CO)(PCy_3)_2 \longrightarrow \underset{(III)}{RhCl(CO)(PCy_3)_2} + RhCl_3(CO)(PCy_3)_2 \quad (1)$$

At the same time, in agreement with the well known instability of Rh(III) hydrido carbonyl species [4, 5], $RhHCl_2(CO)(PCy_3)_2$ produced by carbonylation of the impurity (II), loses HCl giving (III), as demonstrated by the disappearance of the bands at 2078 and 790 cm^{-1} and the contemporary growth of the band pattern of (III) even after the complete disappearance of the paramagnetic carbonyl species. Furthermore the appearance and the growth of new broad absorption at 1715 cm^{-1}, probably assignable to a ν(CO) of a polynuclear (μ-CO) species, suggests that other decay pathways are also possible. Disproportionation reactions are not unusual in rhodium chemistry [1], but sometimes they proceed too quickly to be monitored, especially when carried out in solution. Thus, in our case, when a benzene solution of (I) was exposed to CO in the ESR cavity (atmospheric pressure and room temperature) an immediate disappearance of the original ESR signal was observed and the yellowish product recovered by solvent evaporation showed IR and residual ESR spectra very similar to those of the decayed product, after the formation in the solid state of the paramagnetic $RhCl_2(CO)(PCy_3)_2$. However, the transformation of the Rh(II) carbonyl intermediate appeared to be complete in solution, as demonstrated by the absence of IR bands at 2078, 2000, and 790 cm^{-1} and by the very weak residual signal in the ESR spectrum (0.002% of ESR active species). On the other hand, the addition of few drops of benzene to a solid sample of paramagnetic $RhCl_2(CO)(PCy_3)_2$ resulted in a very rapid decay of the ESR activity, giving products with the same spectroscopic properties as those obtained in the above experiment in solution. On the basis of our findings, we conclude that the addition of CO to $RhCl_2(PCy_3)_2$ leads to a five-coordinated square-pyramidal Rh(II) carbonyl derivative whose instability causes a disproportionation reaction to take place. This is also in agreement with the rapid isomerization in solution of the acetyl complex $RhCl_2(COMe)(PPh_3)_2$, the unique example of a square-pyramidal rhodium derivative, to a hexacoordinated methyl derivative [14]. Another point worthy being outlined is that the formation of polynuclear (μ-CO) species seems to be peculiar of solid samples, whereas in solution the decay process is probably too fast and bridging situations are not favoured.

Treatment with Dihydrogen

The product (I) proved to be completely inert towards dihydrogen, even under pressure. No ESR or IR changes were observed even after prolonged treatments.

Conclusions

The reaction in the solid state of transition metal complexes with small molecules is an interesting potential way for obtaining and studying labile derivatives, not detectable in the presence of solvents. An example of this possibility is given by the reaction of $RhCl_2(PCy_3)_2$ with carbon monoxide which leads to the formation of long-living paramagnetic $RhCl_2(CO)(PCy_3)_2$, not otherwise obtainable. A more diffuse recourse to the ESR technique in the detection and study of the nature of impurities in transition metal complexes at 'catalytic' level is also indicated.

Acknowledgements

The present work was carried out under the research program 'Progetto Finalizzato Chimica Fine e Secondaria' of C.N.R., Rome (Section Ab). We thank Dr. G. Dell'Amico for magnetic measurements and helpful discussion.

References

1 M. A. Bennett and P. A. Longstaff, *J. Am. Chem. Soc., 91,* 6266 (1969).
2 J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A),* 1711 (1966).
3 C. Busetto, A. D'Alfonso, F. Maspero, G. Perego, and A. Zazzetta, *J. Chem. Soc., Dalton Trans.,* 1828 (1977).
4 H. L. M. Van Gaal, J. M. J. Verlaak, and T. Posno, *Inorg. Chim. Acta, 23,* 43 (1977).
5 C. Masters and B. L. Shaw, *J. Chem. Soc. (A),* 3679 (1971).
6 H. D. Empsall, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* 1980 (1974).
7 B. R. James, 'Homogeneous Hydrogenation', Wiley, New York, 1973, p. 285.
8 N. B. Figgis and J. Lewis, in 'Modern Coordination Chemistry', J. Lewis and R. G. Wilkins, Eds., Interscience, New York, N.Y., 1960, p. 416.
9 F. G. Moers, J. A. M. De Jong, and P. M. H. Beaumont, *J. Inorg. Nucl. Chem., 35,* 1915 (1973).
10 B. R. James, M. Preece, and S. D. Robinson, *Inorg. Chim. Acta, 34,* L 219 (1979).
11 J. Chatt and B. L. Shaw, *J. Chem. Soc. (A),* 1437 (1966).
12 D. M. Adams, *J. Chem. Soc.,* 1771 (1964).
13 R. Usón, P. Lahuerta, D. Carmona, and L. A. Oro, *Trans. Met. Chem., 5,* 327 (1980).
14 D. A. Slack, D. L. Egglestone, and M. C. Baird, *J. Organo-Metal. Chem., 146,* 71 (1978).
15 H. L. M. Van Gaal and F. L. A. Van den Bekerom, *J. Organometal. Chem., 134,* 237 (1977).