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Solid State Reactions of $RhCl(PPh_3)_3$: an XPS Study

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Rh(I) complexes frequently used as catalysts reveal from XP spectra systematically the presence of oxidized species on the surface. As a sample system the phenomenon has been studied in greater detail on the Wilkinson compound $RhCl(PPh_3)_3$. XPS data are reported and discussed along with hypotheses on the structure of the oxidized species, taking into account peculiar features showing similarities to Rh(III) species.

A series of solid state reactions, whose behaviour has been followed by means of XPS, is discussed, including air oxygenation, oxygen removal by H_2 under mild conditions, and displacement reactions by strong π-acceptor ligands (CO, C_2H_4) leading to stable Rh(I) substitution products.

Introduction

In the course of a study on XPS characterization of catalytically active rhodium(I) compounds, we re-examined the XPS behaviour of the Wilkinson compound $RhCl(PPh_3)_3$ in the solid state, and observed that in real conditions (that is when the contact with air is not carefully avoided) the compound generally exhibits the presence of oxidized species on the surface in varying amounts. Since surface reactions are presumably important in determining the catalytic properties, we undertook a more detailed investigation on a series of solid state reactions of the Wilkinson compound, following their course by means of XPS. For comparative purposes with significant models we also examined by XPS the behaviour in the solid state of the O_2 adducts of the Wilkinson compound, prepared by literature methods [1, 2].

Our results show that there is a substantial similarity in structure between these pure compounds and the labile species formed by surface oxidation of Wilkinson's complex. In a subsequent note we shall extend the present investigation, and use the results obtained thereby as a contribution to a more general explanation of the surface oxidation phenomena which occur also for other rhodium(I) compounds, and for heterogeneous catalysts based on them.

Experimental

The investigated rhodium compounds $RhCl(PPh_3)_3$ and $RhCl(O_2)(PPh_3)_3$ were prepared according to literature methods and characterized by their chemical and physical properties. XPS measurements were carried out on a VG-ESCA spectrometer equipped with $AlK\alpha_{1,2}$ source (1486.6 eV). Oil diffusion pumps fitted with cold traps produced a vacuum better than 10^{-8} torr, typically between $5 \cdot 10^{-9}$ and $5 \cdot 10^{-10}$ torr.

Calibration was made by the $4f_{7/2}$ gold signal at 84.0 eV (with FWHM = full width at half maximum ~1.8 eV) and sample charging was corrected by referencing to the C1s line of contaminating carbon, taken at 285.0 eV.

Sample treatments were performed in a preparation chamber connected to the sample chamber of the electron spectrometer. The accuracy of the measured binding energies was estimated as ±0.2 eV.

FWHM of XPS signals are reported in parentheses. Curve deconvolution of the Rh 3d spectrum, for the compound $RhCl(PPh_3)_3$, was performed on a GESI microcomputer with a Watanabe WX4671 plotter by adjusting the positions, half-widths, and intensities of the Gaussian-shaped components until a correct fit was obtained.

A Perkin-Elmer 283 B spectrophotometer was used for obtaining spectral data in the range 4000–

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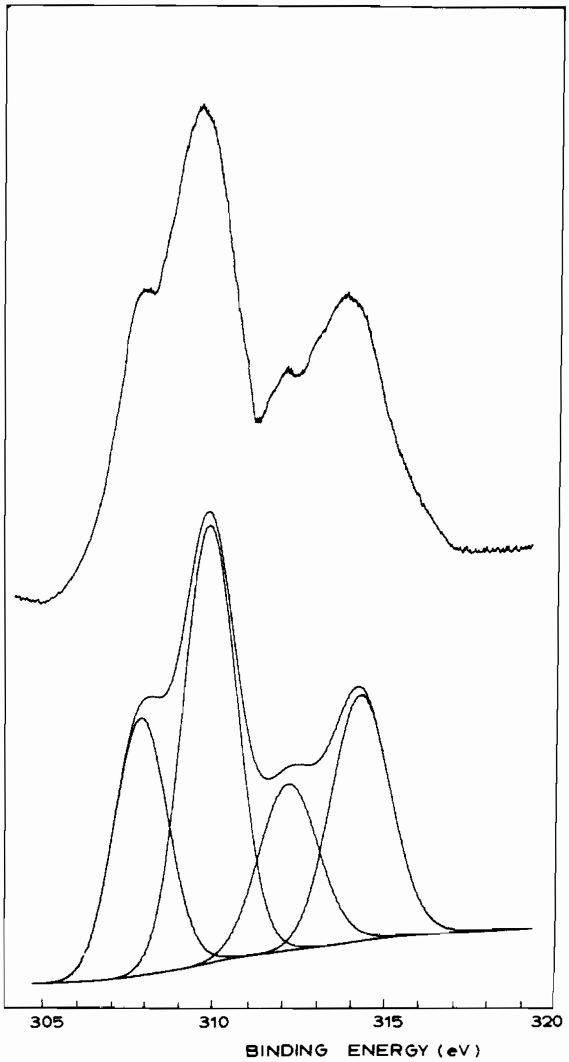

Fig. 1. Rh 3d photoelectron spectrum from nominal RhCl-$(PPh_3)_3$.

400 cm^{-1}, using the potassium bromide pellet technique.

The ESR measurements were carried out as previously reported [3].

Results

The Wilkinson compound $RhCl(PPh_3)_3$ has been previously investigated in XPS by other authors [4–8] and binding energy values for the rhodium $3d_{5/2,3/2}$ levels are reported at about 307.8–312.5 eV.

In repeated XPS measurements on the Wilkinson compound we found that samples handled in air always showed double rhodium 3d signals, with a second band component for each peak at higher binding energy values, indicative of the presence of oxidized species. Deconvolution of Rh 3d signals is reported in Fig. 1.

Binding energy values characteristic of the oxidized species are reproduced constantly; on the other hand, the intensity of the high b.e. component varies, depending on preparation procedures, air exposure conditions and ageing of samples. Even in the presence of variable amounts of oxidized species in the XP spectra, the bulk composition of the sample still corresponded satisfactorily to nominal rhodium(I).

Therefore, we concluded that the observed presence of oxidized species is to be regarded as a surface phenomenon, and we decided to further investigate such surface effects, whose elucidation should contribute to a better understanding of structure and activity of Rh(I) catalysts.

Our investigation was aimed at two main objectives: firstly to determine and interpret the chemical nature of the oxidized species present at the surface. Several alternatives can be in fact considered to this regard, since the oxidized surface species could be simply a dioxygen adduct of the initial Rh(I) species, or a paramagnetic rhodium(II) labile species [3], or a rhodium(III) species resulting from oxidative addition. Since several forms of solid adducts of reaction products from the Wilkinson compound and molecular oxygen have been reported [1, 2, 10, 11], we undertook an XPS study of the most representative of such adducts.

Our second objective was a re-examination of the reactivity of the Wilkinson compound in the solid state with respect to molecular oxygen and other simple gaseous reagents, such as H_2, CO, C_2H_4. In fact, while the reactivity of the Wilkinson compound has been the subject of numerous and extensive studies in solution [9, 12–14], the knowledge of its reactivity in the solid state is much more limited [5, 15], although one can probably expect no significant qualitative differences.

Furthermore, we examined for the Bennett monomeric O_2 adduct [1], the same reactions as for the Wilkinson compound.

The oxidized species revealed by XPS on the surface of solid Wilkinson's complex is characterized by XPS b.e. values for the Rh $3d_{5/2,3/2}$ levels, at 309.7–314.4 eV: these data are too high for typical rhodium(I) species which, to a first approximation, should be excluded on XPS evidence. The data are not selective enough for rhodium(II) paramagnetic species, or rhodium(III) oxidative reaction products.

The existence and the general instability of such Rh(II) species have been investigated by ESR [3, 16, 17]. On the other hand, contrarily to the cases of iron and cobalt [18], very few examples of Rh(II) superoxo derivatives are known [19].

TABLE I. Binding Energies and FWHM[a] (in eV)[b] of Rh 3d Levels from the Wilkinson Compound (both Pure and after Various Treatments), and from some Reference Compounds.

Compound	Rh $3d_{5/2}$	Rh $3d_{3/2}$
$RhCl(PPh_3)_3$	308.0(2.3)	312.7(2.5)
	309.7(2.3)	314.4(2.5)
$RhCl(PPh_3)_3^{+} O_2$ (room temperature, 5 hrs, 100 kPa)	309.7(2.9)	314.4(3.7)
O_2 treatment followed by H_2 (100 °C, 18 hrs, 100 kPa)	308.0(2.8)	313.0(3.4)
$RhCl(PPh_3)_3^{+}$ X-ray (~7 hrs, 480 W)	308.8(4.6)	313.5(4.7)
$RhCl(PPh_3)_3$ heated *in vacuo* (60 °C, 18 hrs, 0.13 Pa)	309.1(4.8)	313.6(5.3)
$RhCl(PPh_3)_3^{+} H_2$ (100 °C, 18 hrs, 100 kPa)	308.2(2.5)	312.7(2.8)
H_2 treatment followed by O_2 (room temperature, 5 hrs, 100 kPa)	309.7(3.1)	314.4(3.8)
$RhCl(PPh_3)_3^{+}CO$ (100 °C, 18 hrs, 100 kPa)	309.2(2.8)	314.0(3.2)
$RhCl(PPh_3)_3^{+}CO$ (room temperature, 10 hrs, 300 kPa)	308.9(2.3)	313.5(2.5)
$RhCl(PPh_3)_3^{+} C_2H_4$ (100 °C, 18 hrs, 100 kPa)	308.9(2.5)	313.6(3.0)
Rh metal	307.2[c]	312.1[c]
$RhCl_3 \cdot 3H_2O$	310.2(2.0)	315.2(2.6)
trans-$RhCl(CO)(PPh_3)_2$	308.9(2.0)	313.6(2.3)
$[Rh(CH_3COO)_2]_2$	309.0(2.1)	313.9(2.8)
$RhCl(PPh_3)_3$	310.0(2.6)	315.0(3.2)

[a] FWHM = full width at half maximum, in parentheses. [b] C1s = 285.0 eV. [c] Ref. (5).

Taking into account the difficult rationalization of the oxygen-metal interactions, we used XPS and ESR results to clarify this matter. All prepared samples of the Wilkinson catalysts proved to be essentially ESR inactive. From a rough calculation of the amount of metal species present at the surface and involved in the oxidation phenomenon (Fig. 2 spectrum A), and taking into account of the very high sensitivity of the ESR technique, it is possible to conclude that the main interaction of O_2 with rhodium does not give rise to Rh(II) species.

From our observations, in the course of XPS measurements, it turned out clearly that the oxidized species is labile, and its formation reversible, under our experimental conditions. Further information on the nature of bonded O_2 was obtained from our XPS study on the modifications of the surface species, due to the treatment with small molecules. In Table I binding energies and FWHM in electron volts are given from Rh $3d_{5/2,3/2}$ levels from $RhCl(PPh_3)_3$ treated in various ways and from some reference compounds. Figure 2 shows the related XP spectra.

If a solid sample of nominal $RhCl(PPh_3)_3$ (spectrum A) is treated at room temperature with O_2 (100 kPa, 5 hrs), the result is an increase of the surface concentration of the species at higher b.e. values (spectrum B), *i.e.* Rh $3d_{5/2}$ 309.7 eV (FWHM = 2.9), implying that surface oxidation tends to become nearly complete. Subsequent treatment of the latter product with H_2 (100 kPa, 18 hrs, 100 °C), in order to evaluate the possible reversibility of the bonded O_2, showed only a residual signal at higher b.e. values together with a signal at b.e. at 308.0 eV (FWHM = 2.8 eV), as expected for Rh(I) species (spectrum C). This result can be attributed to the formation of stable oxidized species resulting from the O_2 treatment, possibly containing $OPPh_3$ as ligand. Accordingly the IR spectrum shows a band at 1120 cm^{-1}, characteristic of the P=O stretching [20], together with other ligand bands.

If $RhCl(PPh_3)_3$ samples are kept for a long time (~7 hrs) under an X-ray source, a b.e. shift in the XPS patterns of the surface species is observed, *i.e.* a conversion of species containing rhodium at higher b.e. into species at lower b.e. does apparently occur (spectrum D). Since a similar behaviour (spectrum E) is also observed when the sample is heated *in vacuo* (0.13 Pa, 18 hrs, 60 °C), it can possibly result from a thermal alteration of a surface equilibrium of the type:

$$RhCl(PPh_3)_3 + O_2 \rightleftarrows RhCl(O_2)(PPh_3)_3$$

even if a contribution from different pathways cannot be excluded.

The real solid Wilkinson catalysts, when exposed to H_2 (100 kPa, 18 hrs, 100 °C), show in the Rh 3d spectra an increase of the concentration of the species at lower b.e. (spectrum F), *i.e.* 308.2 eV

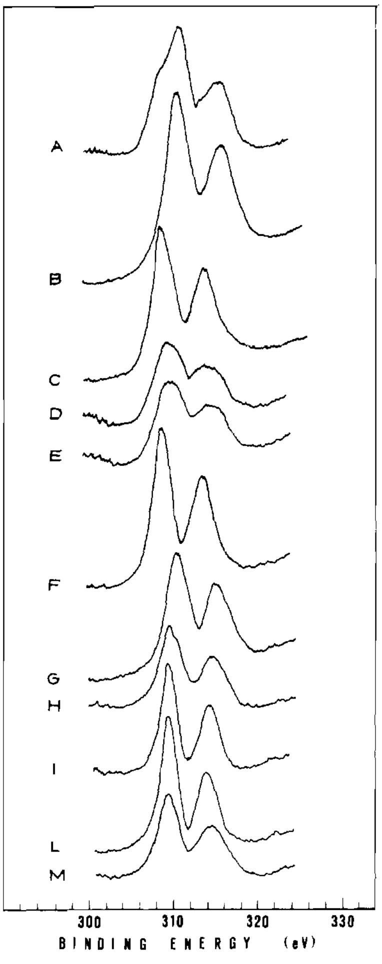

Fig. 2. Rh 3d photoelectron spectra from nominal RhCl-$(PPh_3)_3$ and after various treatments. (A) nominal complex, (B) after O_2 (room temperature, 5 hrs, 100 kPa), (C) sample (B) after H_2 (100 °C, 18 hrs, 100 kPa), (D) after X-ray (~7 hrs, 480 W), (E) heated *in vacuo* (60 °C, 18 hrs, 0.13 Pa), (F) after H_2 (100 °C, 18 hrs, 100 kPa), (G) sample (F) after O_2 (room temperature, 5 hrs, 100 kPa), (H) after CO (100 °C, 18 hrs, 100 kPa), (I) after CO (room temperature, 10 hrs, 300 kPa), (L) *trans*-$RhCl(CO)(PPh_3)_2$, (M) $RhCl(PPh_3)_3$ after C_2H_4 (100 °C, 18 hrs, 100 kPa).

(FWHM = 2.5 eV). This corresponds to the displacement of O_2 by H_2 although an oxidative addition reaction between H_2 and Rh(I) cannot be excluded in principle [5]. In our case, however, no spectroscopic evidence was found for this type of reaction, and the formation of substantial amounts of $RhClH_2(PPh_3)_2$, white or pale yellow in colour [9], was not observed; instead there is a persistence of the burgundy-red colour of the reaction product, probably neat $RhCl(PPh_3)_3$.

Further treatment of the latter product with O_2 (100 kPa, 5 hrs, room temperature) leads to an increase of the concentration of the surface oxygen containing species at higher b.e. values (spectrum G), *i.e.* 309.7 eV (FWHM = 3.1 eV).

By CO treatment (100 kPa, 18 hrs, 100 °C), of the real Wilkinson catalysts a carbonylation product is easily formed, probably $RhCl(CO)(PPh_3)_2$, as suggested both by the colour change from burgundy-red to yellow, and by XP spectral patterns which take a more simple shape with a single band (b.e. at 309.2 eV, and FWHM = 2.8 eV (spectrum H)). Accordingly, the IR spectrum shows the appearance of a carbonyl band at 1965 cm^{-1} (nujol mull; literature 1961 cm^{-1} [21]).

The surface reaction seems to be incomplete under our experimental conditions; however, if the CO treatment is carried out at higher pressure (300 kPa, 10 hrs, room temperature) a quantitative transformation occurs, identical on the evidence of the IR and XPS spectra (spectrum I) to those of an authentic sample of *trans*-$RhCl(CO)(PPh_3)_2$ (spectrum L).

It is also interesting to note that the treatment of solid samples with CO resulted not only in the displacement of the labile O_2 ligand at the surface, but also of one triphenylphosphine group per Rh atom, which is quantitatively recovered by extraction with n-pentane at room temperature, according to eqns. (1) and (2).

$$RhCl(O_2)(PPh_3)_3 + CO \rightarrow$$

$$RhCl(CO)(PPh_3)_2 + PPh_3 + O_2 \qquad (1)$$

$$RhCl(PPh_3)_3 + CO \rightarrow RhCl(CO)(PPh_3)_2 + PPh_3 \qquad (2)$$

It has been reported [22] that $[RhCl(PPh_3)_2]_2$ in carefully dried benzene reacts with dioxygen to give a product formulated as $RhCl(O_2)(PPh_3)_2$, partly similar in structure to the Bennett O_2 complex $RhCl(O_2)(PPh_3)_3$ [1]; this complex furthermore reacts with alcohols to give $RhCl(CO)(PPh_3)_2$, plus another dimeric carbonyl product recovered after washing the carbonyl product with n-pentane. This latter product did not show any IR absorption characteristic of $OPPh_3$.

If the 'real' solid Wilkinson compound is treated with C_2H_4 (100 kPa, 18 hrs, 100 °C) a product, probably $RhCl(C_2H_4)(PPh_3)_2$, is almost quantitatively formed as indicated by a colour change from burgundy-red to yellow, and by XP spectra showing a simpler pattern and b.e. at 308.9 eV (FWHM = 2.5 eV) [15] (spectrum M).

The above reactions, whenever carried out with more active reagents like CO and C_2H_4, produce the same final product as obtained from the pure Wilkinson compound. Therefore they confirm the lability of the oxidized species and also the possibility of

TABLE II. Binding Energies and FWHM[a] (in eV)[b] of Rh 3d Levels from the Bennett Monomeric Compound $RhCl(O_2)(PPh_3)_3 \cdot 2CH_2Cl_2$, both Pure and after Various Treatments.

Treatment	Rh $3d_{5/2}$	Rh $3d_{3/2}$
none	309.7(2.4)	314.3(2.8)
heated *in vacuo* (50 °C, 18 hrs, 0.13 Pa)	309.2(4.4)	313.5(4.7)
X-ray (~7 hrs, 480 W)	309.2(4.5)	313.6(5.0)
H_2 (70 °C, 18 hrs, 100 kPa)	308.2(2.5)	313.2(2.6)
CO (70 °C, 18 hrs, 100 kPa)	309.4(3.0)	314.3(3.4)
C_2H_4 (70 °C, 18 hrs, 100 kPa)	309.3(2.9)	314.4(3.3)

[a] FWHM = full width at half maximum, in parentheses. [b] Cls = 285.0 eV.

reverting to the pure Wilkinson compound; however, the latter step cannot be isolated if a subsequent irreversible reaction, such as those with CO or C_2H_4, takes place.

At this point, in order to better identify the structure of the oxidized surface species, we compared its XPS behaviour and solid state reactivity with those of pure dioxygen adducts in bulk form. The reactivity of the Rh–O_2 complexes has not been extensively studied so far [1, 2, 11, 13, 22, 23], and only very few references on solid samples have been published until now [22, 23]. Of the various Wilkinson oxygenation products described in the literature, we considered mainly the compounds described by Bennett [1] and by Atlay [2]; we carried out more extensive XPS investigations on the Bennett monomeric compound, because of its better reproducibility in preparation and knowledge of its structural data. In any case the two oxygenated compounds seem to display exactly the same XPS behaviour.

We have not considered the dimeric product $[RhCl(O_2)(PPh_3)_2]_2$ reported in [11] which is less likely as a model for our surface oxygenated product, because of its more complex structure implying a more complicated formation pathway, and because of its loss of phosphine and presumable lower O_2 lability. Table II shows the binding energies and FWHM (in eV) for Rh $3d_{5/2,3/2}$ levels from $RhCl(O_2)(PPh_3)_3 \cdot 2CH_2Cl_2$ treated in different ways. Figure 3 reports the corresponding XP spectra.

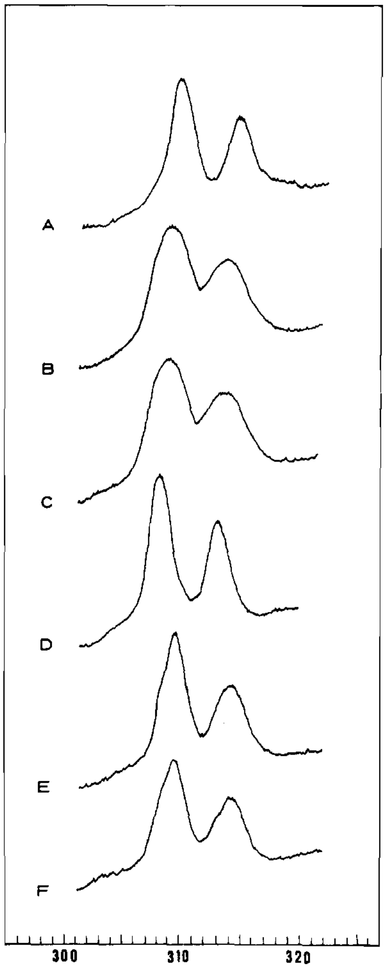

Fig. 3. Rh 3d photoelectron spectra from $RhCl(O_2)(PPh_3)_3 \cdot 2CH_2Cl_2$ pure and after various treatments. (A) pure compound, (B) heated *in vacuo* (50 °C, 18 hrs, 0.13 kPa), (C) after X-ray (~7 hrs, 480 W), (D) after H_2 (70 °C, 18 hrs, 100 kPa). (E) after CO (70 °C, 18 hrs, 100 kPa), (F) after C_2H_4 (70 °C, 18 hrs, 100 kPa).

XPS data of the dioxygen adduct exhibit Rh $3d_{5/2,3/2}$ b.e. values quite analogous to the surface oxidized species of the Wilkinson compound (spectrum A), *i.e.* 309.7(2.4)–314.3(2.8) eV. These values appear to be in agreement with Rh(III) species rather than with Rh(I) systems; in fact, Rh(III) b.e.s are usually reported around 310.0 eV [4–7] and Rh(I) b.e.s around 308.0 eV [4–8]. Besides, the Bennett compound reveals a certain reactivity under the experimental conditions of our XPS measurements, which is substantially similar, at least qualitatively, to that of the oxidized solid Wilkinson compound. In fact upon heating $RhCl(O_2)(PPh_3)_2 \cdot 2CH_2Cl_2$ *in vacuo* (0.13 Pa, 18 hrs, 50 °C) a change in the XP spectrum is observed (spectrum B), leading practically to the same final situation as exhibited from heat treatment of the solid 'real' Wilkinson compound. A similar behaviour is also observed when a sample of the Bennett compound is kept for a long time (~7 hrs) under X-ray irradiation (spectrum C): the result can be possibly explained as a thermal dissociation of the adduct of the same kind as observed for the Wilkinson system.

$$RhCl(O_2)(PPh_3)_3 \cdot 2CH_2Cl_2 \rightleftarrows RhCl(PPh_3)_3 + O_2 + 2CH_2Cl_2$$

The Bennett compound after exposure to H_2 (100 kPa, 18 hrs, 70 °C) shows in the Rh 3d spectra a complete transformation into a species with lower 3d b.e. values, *i.e.* 308.2(2.5)–313.2(2.6) eV (spectrum D), which are very similar to the species obtained from the pure Wilkinson compound. Moreover a colour change is also observed, from pale-yellow to the red colour of the pure Wilkinson compound.

By CO treatment (100 kPa, 18 hrs, 70 °C) of the Bennett adduct a carbonylation product is partially formed (spectrum E), which shows Rh 3d b.e. values at 309.4(3.0)–314.3(3.4) eV with signal broadening, indicative of incomplete reaction. The same behaviour is observed (spectrum F) when a solid sample of the Bennett compound is treated with C_2H_4 (100 kPa, 18 hrs, 70 °C), the resulting spectrum showing Rh 3d b.e. values of 309.3(2.9)–314.4(3.3) eV. The different extent of the reaction with CO or C_2H_4 shown by the Bennett compound with respect to the Wilkinson complex can be due either to the lower temperature used in the treatment of the former product because its lower m.p., or to the fact that the Bennett solid species in bulk form is possibly more stable than the dispersed species on the Wilkinson real surface.

Discussion

The Wilkinson compound in real conditions, *i.e.* exposed to the air, shows an easy extensive surface oxidation. On XPS evidence, rhodium seems to be present in the oxidized species as Rh(III), considering that Rh(I) species may be excluded in a first approximation. In fact, we found b.e. values $3d_{5/2}$ at 309.7 eV more similar to those usually reported in the literature for the oxidation state (+3) of the rhodium [4–7], (*e.g.* 310.2 for $RhCl_3 \cdot 3H_2O$ and 310.0 for $RhCl_3(PPh_3)_3$). Furthermore, the presence of Rh(II) ESR active species is ruled out by ESR measurements. On the other hand, the actual oxidation number of the Rh atom may not be definite on the ground of Rh b.e. values only, and conventional coordination numbers and integral oxidation states may be inadequate in this case for the discussion of oxygen bonding.

Even considering the support of structural data, some ambiguities often arose in the literature about the assignment of the formal oxidation number of metals bound to dioxygen. For rhodium derivatives, for example, the Bennett complex bis[chloro(dioxygen)tris(triphenylphosphine)rhodium] was reported in a preliminary communication as a distorted octahedral complex of Rh(III) with a chelating peroxide ion [10], whereas in the subsequent paper [11] the same complex is formulated as a Rh(I) derivative where the two dioxygen molecules act both as π-bonded ligands and chelating peroxo groups. The analogous monomeric compounds $RhCl(O_2)(PPh_3)_3 \cdot 2CH_2Cl_2$ and $RhCl(O_2)(PPr^i_3)_2$ are also reported as Rh(I) peroxo derivatives [1, 17], on the ground of crystallographic characterization of the Rh–O as well as the O–O bond lengths, which indicate a side ways coordination of the dioxygen molecule. On the other hand, the dioxygen adduct recently reported by Atlay *et al.* [2] is formulated as a Rh(III) complex on the basis of IR data.

Beside the XP spectrum discussed above, we also obtained indications on the actual structure of the oxidized species from an assessment of its surface reactivity in the solid state, characterized by easy reconversion to the pure Wilkinson species and by qualitative analogy with the behaviour of solid Bennett compound, possibly modified and made more reactive by dispersion on the surface. The study of reactions in solid state is of interest also with regard to possible interpretation of the catalytic behaviour, and our preliminary results can be summarized by stating that: i) reaction with O_2 occurs in an easy way, and does not lead primarily to irreversible oxidation products; ii) the particular facility in the subsequent reaction with H_2 indicates a considerable H_2 activation in mild conditions; iii) irreversible formation of new stable complexes occurs only with reagents having a much stronger affinity for Rh(I) such as CO or C_2H_4. Thus, the presence of oxidized species on the surface does not necessarily inhibit the activity of Rh(I) catalysts. At this point, our results have brought two new pieces of evidence on the electronic structure of the surface oxidation product of the Wilkinson compound and of the Bennett dioxygen adduct. The former regards the electron density at the rhodium atom as revealed by the chemical shifts on the XPS b.e. values, and the latter regards the lability and reversibility of the surface reactions.

While certainly contributing to the elucidation of the electronic structure, these findings do not lead to the unambiguous assignment of a formal oxidation state to the Rh atom, since the b.e. values fall in the range typical of Rh(III), whereas the considerable oxygen lability is more consistent with a Rh(I) formulation, and the statement of a labile Rh(I) species with electron density at the Rh atom comparable with that of Rh(III) can show the inadequacy of the concept of formal integral oxidation state in the present case. As far as the chemistry of Rh(I) is concerned, the difference between easily reactive Rh(I) compounds such as the Wilkinson complex, subject to surface alterations in mild conditions, and stable Rh(I) compounds, such as carbonyl derivatives not showing any well developed reactivity of the same kind, are worthy of further interest.

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