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EXAFS * characterization and spectroscopic FT–IR studies of the reactions of the surface species formed upon adsorption of $Ir_2(\mu\text{-}Cl)_2(COD)_2$ on γ-alumina

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Abstract

The adsorption of $Ir_2(\mu\text{-}Cl)_2(COD)_2$ (**1**) (COD = cyclooctadiene) on alumina has been studied by EXAFS at the LIII edge of Ir. The reactions of the surface complex formed upon adsorption of **1**, with CO and PPh_3 have been investigated by FT–IR spectroscopy. The attachment of **1** on γ-alumina involves the replacement of the bridging chloride ligands by aluminato groups of the support, to form a dimeric surface complex formulated as $Ir_2(\mu\text{-}O\text{-alumina})_2(COD)_2$. The room temperature reaction of this species with CO gives $Ir_2(CO)_4(\mu\text{-}O\text{-alumina})_2$. This tetracarbonyl surface species reacts at room temperature with PPh_3, to give *trans*-$Ir_2(\mu\text{-}O\text{-alumina})_2(CO)_2(PPh_3)_2$. These new surface complexes have considerable potential as precursors for modified iridium-based reforming catalysts.

Introduction

The most common method used in the preparation of reforming catalysts involves the use of adsorbed transition metal salts as precursors of the metallic particles. A new approach consists in the decomposition of organometallic com-

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* EXAFS = extended X-ray absorption fine structure.

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plexes or clusters adsorbed on a support. This yields highly dispersed transition metal particles, and the increased control in the experimental conditions allows a study of the dependence of the catalytic properties with factors such as the particle size [1].

We are engaged in a study of the preparation of reforming catalysts using olefinic transition metal complexes as precursors. We report the results of a study of the adsorption of $Ir_2(\mu\text{-}Cl)_2(COD)_2$ (**1**) (COD = cyclooctadiene) on alumina. When a molecular complex such as **1** is adsorbed on a support, the true nature of the resulting absorbed species is not known, since it cannot be assumed that the molecule remains unaffected through the adsorption process.

The product of the adsorption of **1** on alumina (loading: 2.5% wt. in Ir) has been studied by EXAFS spectroscopy, and the substitution reaction of the adsorbed COD complex with CO, and that of the resulting CO complex with PPh_3, have been studied by FT-IR spectroscopy.

Experimental

The iridium complex **1** was prepared by a published method [2]. Al_2O_3 was obtained from Woelm A.G. (154 m^2/g, 0.28 cm^3/g porous volume). The alumina was pretreated at $200\,^\circ C/10^{-3}$ torr. Dichloromethane and hexane were distilled from CaH_2. IR spectra were recorded on a Perkin–Elmer 1710 FT IR spectrometer.

Adsorption of 1 on alumina (2.5% wt. metal loading). The orange solution of **1** (0.0889) in CH_2Cl_2 (20 ml) was stirred with 2 g of pretreated alumina for 2 h, after which the solution was almost colorless, and the alumina yellow. The adsorption was thus considered complete, and the alumina with the adsorbed complex **2** was filtered off and dried under vacuum. All operations were performed under nitrogen.

Reaction of 2 with CO. **2** (0.3 g) was placed in a Schlenk flask and covered with 5 ml of hexane, and carbon monoxide was bubbled through the suspension for 15 min. The solvent was then decanted and the product **3** was washed with hexane and vacuum dried. Some of **3** was pressed into a thin pellet and its IR spectrum recorded.

Reaction of 3 with PPh_3 **3** (0.1 g) was placed in a Schlenk flask and covered with 5 ml of hexane and PPh_3 (0.007 g; excess) was added to the stirred suspension. After 1 h, the solvent was decanted and the product **4** was washed with hexane and vacuum dried. Some of **4** was pressed into a thin pellet and its IR spectrum taken.

EXAFS data

The X-ray absorption spectra were recorded on the EXAFS I spectrometer at LURE-DCI, using a silicon (331) monochromator, the ring running at 1.85 GeV, 280 mA.

The EXAFS data were extracted from the absorption spectra by means of Victoreen polynomial fittings (P1) of the pre-edge region, fourth order polynomial fittings (P2) in the region beyond the edge, and finally by applying the following normalization expression:

$$\chi(E - E_o) = \frac{\mu(E) - P_2(E)}{P_2(E) - P_1(E)}$$

Where μ is the absorption coefficient.

Prior to Fourier transformation of the EXAFS data, a Kaiser window was applied in order to minimize the ripples arising from the fact that a limited range of k is taken in the FT. The contribution to the EXAFS signal of scatterers lying in a limited range of distances was isolated by back-transforming over that same range in the space of the phases.

In order to extract structural information from EXAFS data, the isolated contributions were fitted by introducing the appropriate parameters in the EXAFS formula, and then refining the simulation by least squares procedure.

Results and discussion

EXAFS studies

The well characterized pure complex $Ir_2(\mu\text{-}Cl)_2(COD)_2$ (**1**) was used as the reference and the starting point for the elucidation of the EXAFS spectrum of the alumina adsorbed species in **2**. The crystal structure of **1** has been reported [2], so its interatomic distances are available (Table 1). With this information available, an analysis of the EXAFS spectrum of **1** provides the necessary phase and amplitude functions to be transferred to the problem of the adsorbed complex.

The raw EXAFS spectrum of **1**, obtained above the LIII absorption edge of Ir, was filtered through a Kaiser window ranging from 30 to 770 eV, and Fourier transformed (Fig. 1).

The modulus of the FT can be regarded as a pseudo-radial function centered at the absorbing atom (Ir). The positions of the peaks are modified with respect to the true distances owing to the phase shifts. The intensity of the peaks depends on the number of scatterers and their nature; it diminishes when the distance increases, owing to the attenuation factors $1/kR^2$ and $\exp(-\Gamma R/k)$, which take into account the mean free path of the ejected photoelectron.

The two intense peaks observed at 1.7 and 2.1 Å, are due to the scattering from the four sp^2 carbon atoms of the COD molecule, and from the two bridging chlorine atoms, respectively. Owing to the fact that the differences between the back-scattering phase of carbon and chlorine are close to π, the FT function vanishes in the region between the two maxima. This accounts for the apparently clean separation of these two contributions. In order that this spectrum can be used as a reference in the analysis of the EXAFS of the adsorbed complex, these two oscillatory compo-

Table 1

Interatomic distances in **1** and adsorbed species, as reported in ref. 1 and obtained from EXAFS analysis. All values are in Å

	N	$Ir_2(\mu\text{-}Cl)_2(COD)_2$ RDX data [1]	N	$Ir_2(\mu\text{-}Cl)_2(COD)_2$ EXAFS	N	Adsorbed complex
Ir–C(sp^2)	4	2.085	4	2.09 [b]	4	2.09
Ir–Cl	2	2.395	2	2.40 [b]	–	–
Ir–Ir	1	2.910	1	2.91	1	2.92
Ir–C(sp^3)	4	3.049 [a]	4	3.04	4	3.04
Ir–O	–	–	1	–	2	2.12

[a] Average value of 4 Ir–C distances. [b] Value used in the extraction of the Ir–C phase shift and amplitude functions.

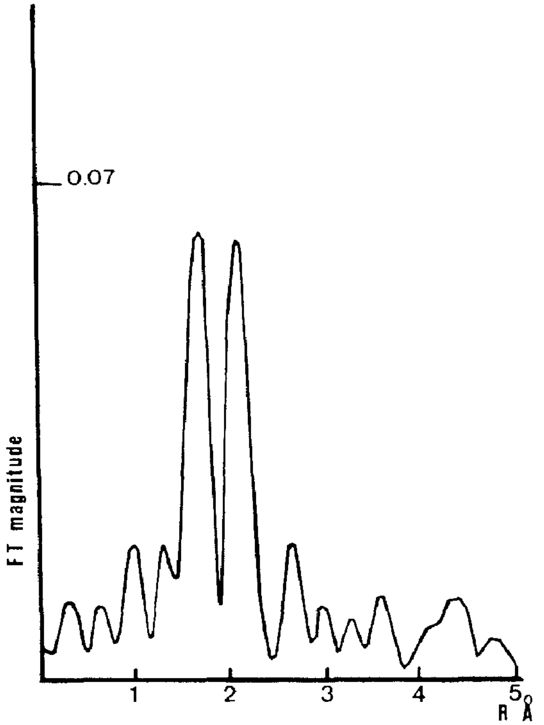

Fig. 1. Modulus of the Fourier transform obtained from the spectrum of $Ir_2(\mu\text{-}Cl)_2(COD)_2$, with a Kaiser window ranging from 30–770 eV.

nents must be separated. The oscillations due to the chlorine shell can be isolated by using the spectrum of K_2IrCl_6 as a reference to obtain the amplitude and phase functions of the Ir–Cl pair, and the crystallographic data for Ir–Cl distances (2 × 2.40 Å) in the EXAFS formula. These oscillations can then be subtracted from the original spectrum, thus eliminating the interference between the oscillations due to the Ir–C and Ir–Cl pairs.

The FT of this difference spectrum must display all the features present in the FT of the original spectrum, with the exception of the peak due to the chlorine shell. We can also expect an enhancement of the Ir–C peak owing to the elimination of the interference caused by the chlorine contribution.

When this subtraction was performed directly, with no correction in the k-space, a residual contribution remained in the region ranging from 2 to 2.5 Å. This is due to the fact that the Ir–Cl oscillations are not in phase because of the incomplete chemical transferability of phases from the K_2IrCl_6 (Ir^{IV} to the complex (Ir^{I})). This can be easily verified by superimposing the imaginary parts of the calculated and the experimental spectra. A misfit of the peaks in the region between 2 and 2.5 Å (Ir–Cl) is observed (Fig. 2).

As has been previously noted [3] chemical transferability can be ensured by shifting the k space in the calculated spectrum by use of the expression $k' = (k^2 + 0.262\Delta E_0)^{1/2}$ where ΔE_0 corresponds to the redefinition of the energy origin of the photoelectron.

Figure 3 shows the modulus of the Fourier transform corresponding to the difference spectrum obtained by taking a ΔE_0 of -7 eV and two Ir–Cl distances of

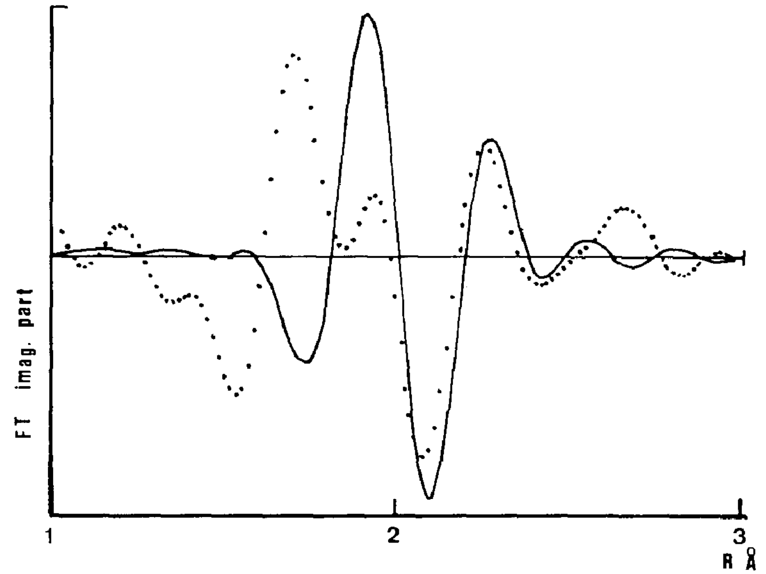

Fig. 2. Imaginary parts of the Fourier transforms of the experimental spectrum (······) and the calculated one corresponding to the Ir–Cl contribution (———) showing the misfit attributed to incomplete phase function transferability between K_2IrCl_6 and the complex (see text).

2.40 Å. From this spectrum we have calculated the amplitude and phase for the Ir–C pair, using the crystallographic Ir–C distances. Additionally, the presence of a second Ir–C shell in the complex (the sp^3 carbon atoms of COD), offers the possibility of testing these Ir–C phase functions.

When the amplitude functions $A(k)$ are to be used with compounds where the distance R is similar to that in the reference, it is normally fruitful to extract $A(k)$ as the product $f(k)\exp(-2\sigma^2k^2)\exp(-\Gamma R/k)$. The differences in the Debye–Waller factor (σ) can then be introduced in the fitting procedure by means of a term $\Delta\sigma$. However, when the distances in the reference species are very different from those in the species to be analysed, the factor $\exp(-\Gamma R/k)$ must be taken into account. The way to proceed in this case is to compensate this factor in $A(k)$, multiplying by $\exp(\Gamma R_{\text{ref}}/k)$ and reentering it in the fitting procedure, with the appropiate value of R. This is the case when we want to use the amplitude functions deduced from the first Ir–C shell to calculate the second shell. We have assumed a value of gamma of 2.5 $Å^{-2}$, close to that obtained in related systems [4].

Figure 4 shows a comparison between the FT (imaginary part and module) of the experimental spectrum and that calculated by using the set of distances reported in Table 1. The amplitude and phase functions for the Ir–Ir pair were obtained from a 10% wt. Ir/alumina catalyst formed of large Ir crystallites as evidenced by electron microscope imaging.

We should emphasize the fact that the two peak pattern seen between 2.5 and 3 Å arises from the interference between the Ir–C(sp^3) and Ir–Ir contributions, and either of these two contributions would individually produce a more intense signal, centered at R values differing slightly from those found in the experimental spectrum. This interference pattern is well explained in our reconstruction by using Ir–C and Ir–Ir distances essentially identical to those found in the reported single crystal X-ray study.

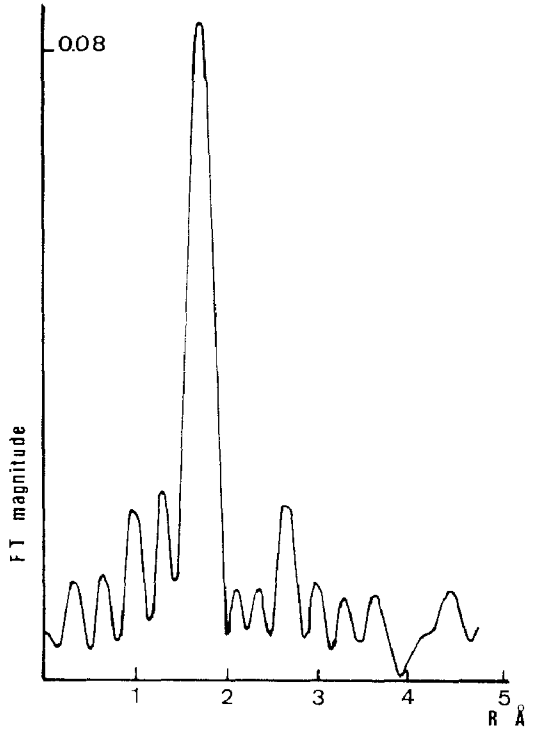

Fig. 3. Modulus of the Fourier transform of the difference spectrum obtained by substracting the Ir–Cl contribution from the experimental spectrum of $Ir_2(\mu\text{-}Cl)_2(COD)_2$ (ΔE_0 –7 eV).

Adsorbed complex

Figure 5 shows the FT modulus of the spectrum of the alumina-adsorbed complex recorded under the conditions used for the pure complex **1**. The first thing

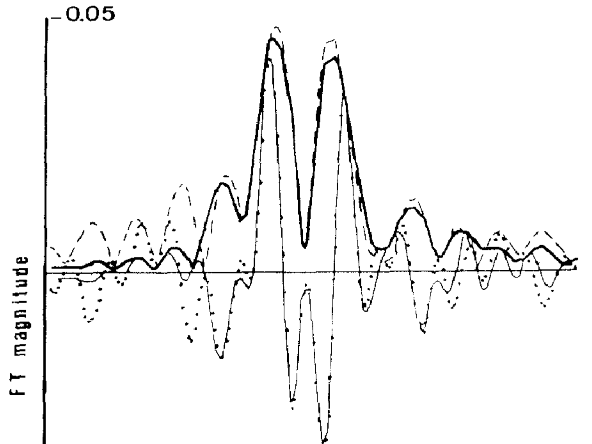

Fig. 4. Modulus and imaginary part of: Experimental spectrum of $Ir_2(\mu\text{-}Cl)_2(COD)_2$: (— — —) modulus; (· · · · · ·) imag. part, and calculated spectrum: (▬▬) modulus, (———) imag. part.

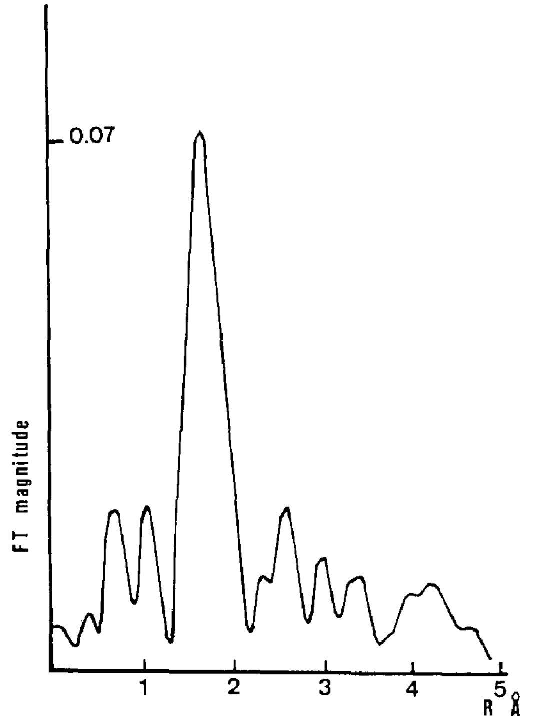

Fig. 5. Modulus of the Fourier Transform obtained in the case of the absorbed complex. Kaiser window: 30–770 eV.

that can be seen by comparing this curve with that for the pure complex (Fig. 1) is that upon adsorption the chlorine atoms disappear from the environment of the iridium atoms.

In Fig. 6 the imaginary part of this FT is superimposed on the imaginary part of the FT function corresponding to the difference spectrum, obtained by subtracting the Ir–Cl contribution from the spectrum of the pure complex (vide supra). The close similarity between these two curves up to 3 Å shows unambiguously that the chlorine has been displaced from the molecule. It also suggests that the COD ligand has been retained upon adsorption. This view is reinforced by the fact that the interference pattern observed in the region 2.5–3 Å in the case of the pure complex is also present in the spectrum of the adsorbed species. As has been previously shown (vide supra), this pattern is due to interference between the Ir–C(sp^3) and the Ir–Ir distances.

The filtered EXAFS spectrum (Fig. 7) obtained by back-transforming the FT data in the range 1.5 to 2.9 Å is in phase with that calculated by assuming Ir–C distances of 2.08 Å, but its amplitude envelope cannot be explained in terms of this assumption even if the DW * factor is increased. Because the chlorine atoms have been lost from the iridium coordination sphere, it seems logical to consider that they have been replaced by other ligands, namely oxygen atoms coming from the alumina surface, and so we introduced Ir–O distances into the fitting procedure. As

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* DW = Debye–Waller factor.

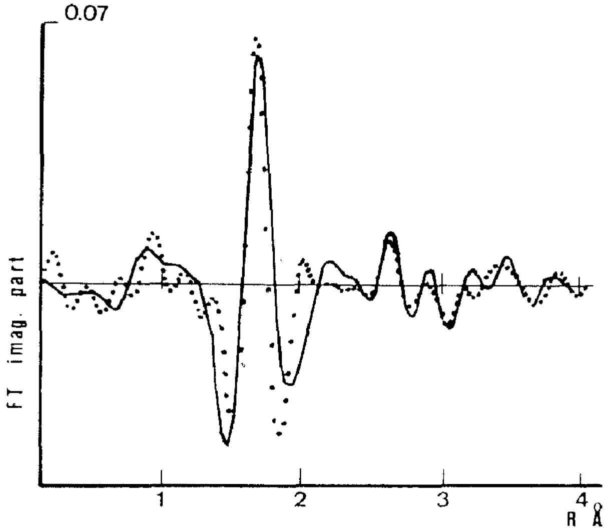

Fig. 6. Superposition of the imaginary parts of the FT obtained in the case of the pure complex (······) and the adsorbed complex (———).

a suitable reference for Ir–O amplitude and phase functions, PtO_2 was used. This is possible because the central atom phase functions of Pt and Ir are very similar.

In order to ensure the chemical transferability, a ΔE_0 was applied to these Ir–O (Pt–O) phases. This factor was changed stepwise in each run of the fitting procedure. The best solution was obtained for ΔE_0 −7 eV, and it involves four Ir–C distances at 2.07 Å and two Ir–O distances at 2.12 Å (see Table 1). No ΔE_0 was necessary for the Ir–C phases as obtained from the $IrCl_6(COD)_2$ reference. A $\Delta\sigma^2$ of 0.0001 $Å^2$ with respect to the reference was used.

Thus the EXAFS analysis indicates that reasonable formulation for the adsorbed iridium complex is $Ir_2(COD)_2(\mu\text{-}O\text{-alumina})_2$, the stereochemical structure of which is shown in Fig. 9A.

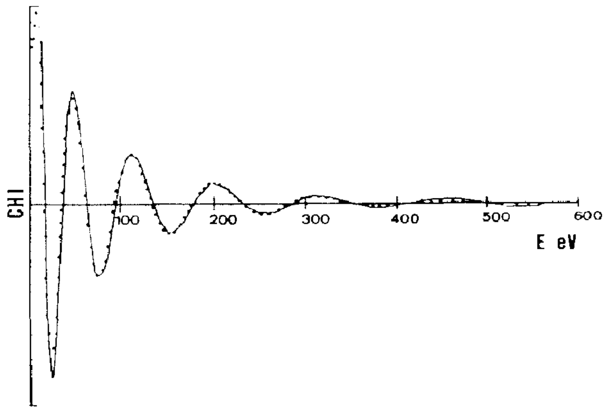

Fig. 7. Fit of the back-transformed first shell of the adsorbed complex with the parameters reported in Table 1.

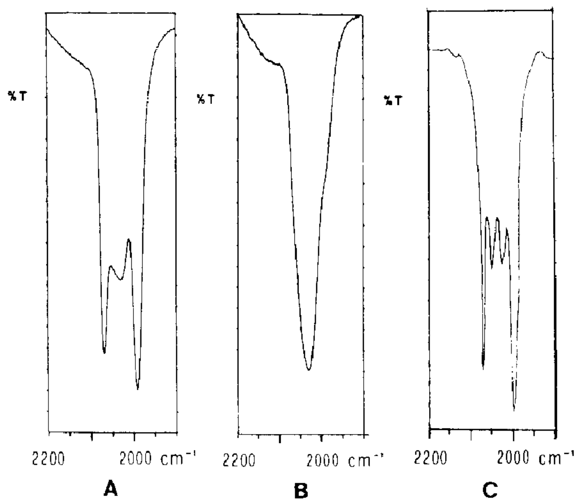

Fig. 8. (A) FT–IR spectrum obtained after reaction of the adsorbed complex with CO (**2**). (B) FT–IR spectrum obtained after reaction of **2** with PPh_3. (C) FT–IR spectrum obtained after bubbling CO through a CH_2Cl_2 solution of $Ir_2(\mu\text{-}(OCH_3))_2(COD)_2$.

Reactivity of the supported species

The adsorbed species reacted very rapidly with CO at room temperature and 1 atm of pressure, as indicated by IR spectroscopy (Fig. 8A). The spectrum of the CO-treated supported iridium complex, **2**, exhibits intense CO absorptions at 2069, 2030 and 1990 cm^{-1}, in a region characteristic of terminal CO ligands. The implication is that the COD ligand is readily displaced by CO to form a dimeric tetracarbonyl, such as that in Fig. 9B, that we formulate as $Ir_2(CO)_4(\mu\text{-}O\text{-alumina})_2$ on the basis of its IR spectrum and the structure of the precursor $Ir_2(COD)_2(\mu\text{-}O\text{-alumina})_2$.

The three-band structure of the IR spectrum arises from the coupling of the two *cis*-$Ir(CO)_2$ groups forming a dihedral angle. This feature confirms the dimeric nature of the carbonyl species. The dimeric structure could also be inferred by analogy to the COD precursor, which has been shown to be a dimer by EXAFS (vide supra). If dissociation has ocurred, we would have a single $Ir(CO)_2$ system, which would give rise to only two bands in the IR spectrum. The position of the IR bands is well within the normal range for Ir^I [5]. For Ir^{III} carbonyls there are bands above 2100 cm^{-1}, and in the case of bridging carbonyls the bands appear at much lower frequency; thus, these possibilities are ruled out.

The displacement of COD from the adsorbed species parallels the behaviour we have observed for the model compound $Ir_2(\mu\text{-}OCH_3)_2(COD)_2$ in solution [6]. The

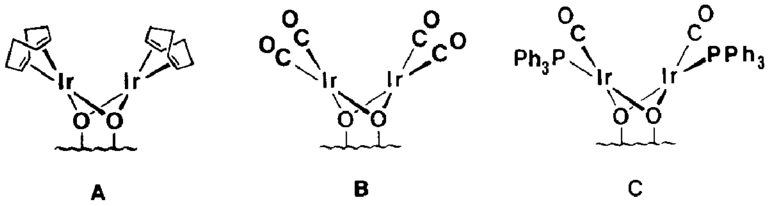

Fig. 9. A, B, C: proposed models for the surface complexes **1**, **2** and **3**, respectively.

IR spectrum of a CH_2Cl_2 solution of $Ir_2(OCH_3)_2(COD)_2$ through which CO had been bubbled, exhibits bands at 2068(st), 2046(w), 2022(w) and 1997(st) cm^{-1} (Fig. 8B). The intense bands at 2068 and 1997 cm^{-1} closely match those at 2069 and 1990 cm^{-1} in the spectrum of the adsorbed species, and the main difference is that the two weaker peaks at 2046 and 2022 cm^{-1} in the spectrum of the model appear as a single broader band in the supported species.

The supported carbonyl species was found to react with PPh_3 at room temperature to form an alumina-supported phosphine adduct **3**. The IR spectrum (Fig. 8C) shows a single peak at 2030 cm^{-1} which is consistent with **3** being a *trans*-disubstituted iridium dimer on the surface. It is formulated as $Ir_2(CO)_2(PPh_3)_2(\mu\text{-}O\text{-alumina})_2$, and shown in Fig. 9C.

Conclusions

When **1** is adsorbed in Al_2O_3 the chloride bridges are replaced by oxygen bridges provided by aluminato ligands from the support, hydrogen chloride presumably being evolved. The adsorbed species remains dimeric and the COD ligands are not displaced. The EXAFS results would also be consistent with a bis-μ-hydroxo (instead of a "bis-μ-aluminato") species, because only the fragment $Ir_2(\mu\text{-}O)_2(COD)_2$ was used in the fitting of the spectrum. However, the iridium is strongly bound to the surface: it is not even partially desorbed by solvents; this suggests to us that at least one of the bridges is an "aluminato" ligand from the surface.

We conclude that when molecules containing hydrolyzable ligands (including binary metal chlorides) are adsorbed on a "hydroxo surface" (such as alumina) these ligands can be displaced to give metal–oxygen bonds containing surface species. In our system this is a very ready process, proceeding rapidly even at low temperatures. However, in the case of alumina-supported $RhCl_3 \cdot 3H_2O$, as reported by Koningsberger et al. [7], the chlorides remain coordinated to the rhodium until the alumina is heated.

When a stable complex is adsorbed on a support, it should form a single, simple adsorbed species. However, the surface may react with it, and this should always be taken into account. The formation of a single adsorbed species favours a more uniform behaviour upon further treatment (reduction, syntering, etc.). It is important to start with well characterized materials in studies of metal particle growth and metal-support interactions.

Catalysis studies on Ir/Al_2O_3 prepared from **2** show that metallic particles of small size are formed upon treatment with hydrogen at 200 °C [8]. This process can be visualized as follows: the Ir–O bonds are broken when the metal is reduced by hydrogen and the COD ligands are eliminated by thermolysis, allowing the iridium atoms to come together and form crystallites. Thus, the temperature of formation of crystallites from adsorbed organometallic complexes will depend on the lability of the ligands, with more labile ligands being lost at lower temperatures, formation of crystallites should be favoured.

We have shown that surface species can be modified through simple chemical reactions. Thus, the reactions of the surface species can be exploited as a strategy for the modification of catalysts by introducing new elements in a controlled way. This includes reactions of the adsorbed species with other metal complexes ultimately to give bimetallic catalysts.

Acknowledgment

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