

Review

Extraction methods and surface reactions as a convenient methodology for the characterization of surface organometallic species

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Abstract

The characterization of the nature of surface species is a primary requirement for a better insight into surface organometallic chemistry and therefore heterogeneous catalytic processes. To date, the structures of organometallic species formed on the surface of inorganic supports (e.g. mainly oxides such as SiO₂, Al₂O₃, TiO₂, MgO) have been investigated spectroscopically. However, the use of solvent extraction with or without surface reactions as a tool for a more precise characterization of these surface species is becoming a new approach. Extraction tests under various conditions constitute a first probe because the eventual extracted species can be easily characterized by classical methods. Moreover, reactions of the unextracted surface organometallic species with specific reagents may lead to products which can be extracted and characterized as well by classical methods. This approach can give an indirect evidence of the nature of the unextracted organometallic surface species. The nature of surface species can be further substantiated by the synthesis of well defined molecular organometallic models and by the investigation of their reactivity.

Keywords: Extraction methods; Surface reactions; Organometallic species

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1. Introduction

Recently, specific areas of surface organometallic chemistry have attracted increasing attention in both fundamental and applied chemistry [1]. The growing interest is due, in part, to the observation that metal carbonyl clusters interact with the surface groups of many inorganic oxides (SiO_2 , Al_2O_3 , TiO_2 , MgO , zeolites), or even carbon [2–4], affording surface organometallic compounds which may be the origin of catalysts with unusual catalytic activities and selectivities as compared to supported metallic catalysts prepared conventionally [5]. In parallel, it was found that inorganic oxides may be a convenient reaction medium for the selective, high yield preparation under mild conditions of various carbonyl metal clusters and complexes [6–11].

Structural characterization of surface organometallic species is indispensable: (i) to understanding the process of interaction between organometallic compounds and the surface of inorganic supports, (ii) to the study of the relationships between catalytic properties and the nature of the surface organometallic species and therefore, (iii) to a better design of 'hybrid' catalysts.

To date, the structures of supported organometallic species have been deduced mainly spectroscopically. Because of its relative simplicity and wide applicability, infrared spectroscopy has been the technique most used [2]. Diffuse reflectance UV–Vis spectroscopy can also provide some information about the bonding characteristics of supported metal species [12]. ^{13}C NMR solid state spectroscopy [13] and in a few cases ESR [14] and Mössbauer [15] spectroscopies were used to define the chemical environment of the surface metal atoms and their oxidation state. Extended X-ray absorption fine structure (EXAFS) spectroscopy was extensively used to give information on the number and type of neighbouring atoms around a selected absorber metal atom and on interatomic distances; however, the theoretical treatment of

experimental EXAFS results has not become easier yet, and structurally well-defined reference organometallic compounds must be often used [16,17]. X-ray photoelectron spectroscopy (XPS), in favorable cases, was used to reach conclusions regarding the chemical environment and/or oxidation state of the surface species [18]. Ultraviolet photoelectron spectroscopy was also used in order to reach some insight into the chemical bonding [12]. Disadvantages of these X-ray and electron spectroscopies are the requirements of ultra-high vacuum conditions and the possibility of reaching high temperatures under the analysing beam, which could change or even destroy the original structure of the surface organometallic species.

Thermoanalytical methods have also been used to characterize surface species indirectly. The temperature programmed decomposition technique provides information about the stoichiometries of transformations of supported metal carbonyl clusters, whereas the temperature-programmed reduction technique gives indirect information about the oxidation states of surface metal species [12,19].

Preferably, reliance on a combination of spectroscopic and thermoanalytical techniques is necessary for a better identification of the nature and structure of supported organometallic species. An interesting indirect approach is the synthesis and full characterization of molecular organometallic models of surface species, which are organometallic complexes with model ligands mimicking the surface functional groups such as silanols [20–26]. The structure of these models can be determined by classical methodologies including X-ray diffraction for the determination of the molecular structure. Comparison of their spectroscopic properties with those of the surface species provides indirect support for the definition of possible structures of the surface species [27]. However, all the above methods give mainly indirect evidence of the structure of the organometallic surface species.

In the last few years, a relatively simple approach to the characterization of surface-sup-

ported organometallic species has been developed: the use of solvent extraction and surface chemical reaction as a tool for the characterization of surface organometallic species. In this paper, we describe some work done in this area, to show how simple chemical methods may be useful in specific cases to fully characterize the nature of physisorbed and chemisorbed surface organometallic species.

2. Methods of characterization

Organometallic species can be bonded more or less strongly to an inorganic support such as an inorganic oxide, the metal loading of the surface being an important factor in controlling the surface interactions. According to the kind of interaction between the organometallic compound and the support, extraction with or without surface reaction can be carried out. The extracted species can then be easily characterized using classical methods (elemental analysis, infrared, NMR and mass spectroscopies) affording clear information about the nature of the supported organometallic species. Obviously, the 'extraction method' cannot be applied to organometallic species entrapped in the zeolites cages (ship-in-a-bottle species) while it can be used with inorganic oxides such as SiO_2 , Al_2O_3 , TiO_2 and MgO .

2.1. Physisorbed organometallic species

Organometallic species which are not linked chemically to the functional groups of the surface of inorganic oxides are only 'physisorbed'. Since they are only deposited on the surface, they may be extracted with a suitable solvent, with the exception of species entrapped in the zeolites cages. The solvent does not need to be an electron-donor able to act as a ligand, but, it must readily dissolve the organometallic surface species such as a metal carbonyl cluster or an organometallic complex (Table 1).

For example, $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Ru}, \text{Os}$) may

Table 1
Physisorbed organometallic species

Physisorbed species	Solvent for extraction	Reference
$\text{Cr}(\eta^5\text{-C}_5\text{H}_5)_2/\text{SiO}_2$	decane or toluene	[2,31]
$\text{Fe}(\text{CO})_5/\text{SiO}_2$	hexane	[27]
$\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$	hexane	[27]
$[\text{Ru}(\text{CO})_3\text{Cl}_2]_2/\text{SiO}_2$	CH_2Cl_2	[33]
$\text{Ru}_3(\text{CO})_{12}/\text{SiO}_2$	pentane, hexane	[28]
$\text{H}_4\text{Ru}_4(\text{CO})_{12}/\text{SiO}_2$	hexane, CH_2Cl_2	[32,34]
$\text{H}_4\text{Ru}_4(\text{CO})_{12}/\text{TiO}_2$	hexane	[34]
$\text{Ru}_6\text{C}(\text{CO})_{17}/\text{SiO}_2$	pentane	[28]
$[\text{Os}(\text{CO})_3\text{Cl}_2]_2/\text{SiO}_2$	CH_2Cl_2	[35]
$\text{Os}_3(\text{CO})_{12}/\text{SiO}_2$	CH_2Cl_2	[11,20]
$\text{H}_4\text{Os}_4(\text{CO})_{12}/\text{SiO}_2$	hexane, CH_2Cl_2	[11,32]
$\text{K}[\text{H}_3\text{Os}_4(\text{CO})_{12}]/\text{SiO}_2$	acetonitrile	[10,11]
$\text{K}_2[\text{H}_2\text{Os}_4(\text{CO})_{12}]/\text{SiO}_2$	acetonitrile	[11]
$\text{K}_2[\text{Os}_5\text{C}(\text{CO})_{14}]/\text{SiO}_2$	acetonitrile	[11]
$\text{Na}_3[\text{Os}_{10}\text{C}(\text{CO})_{24}]/\text{SiO}_2$	acetonitrile	[11]
$[\text{Rh}(\text{CO})_2\text{Cl}]_2/\text{SiO}_2$	CH_2Cl_2	[9]
$\text{Rh}_4(\text{CO})_{12}/\text{SiO}_2$	CHCl_3 , CH_2Cl_2	[9,21]
$\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$	CHCl_3 , CH_2Cl_2	[9,21]
$\text{Rh}_6(\text{CO})_{16}/\text{Al}_2\text{O}_3$	CHCl_3	[36–38]
$[\text{Ir}(\text{COT})_2\text{Cl}]_2/\text{SiO}_2$	CH_2Cl_2	[29]
$\text{Ir}_4(\text{CO})_{12}/\text{SiO}_2$	CH_2Cl_2 , THF	[39]
$\text{Ir}_6(\text{CO})_{16}/\text{SiO}_2$	CH_2Cl_2	[40]

be deposited at room temperature on silica by impregnation from a pentane or dichloromethane solution. Evaporation of the solvent affords physisorbed $[\text{M}_3(\text{CO})_{12}]$ which may be quantitatively re-extracted with pentane or dichloromethane, the process of simple physisorption being reversible [20,28]. Similarly, physisorbed $[\text{Ir}(\text{cyclooctene})_2\text{Cl}]_2$ is obtained by stirring a dichloromethane solution of this Ir(I) complex with silica, followed by evaporation of the solvent. The physisorbed species $[\text{Ir}(\text{cyclooctene})_2\text{Cl}]_2$ can be easily re-extracted with dichloromethane [29]. $[\text{Fe}_3(\text{CO})_{12}]$ is deposited on silica by sublimation [27,30] and may be quantitatively extracted with hexane, confirming that it is just physisorbed [27]. Similarly, silica physisorbed metallocenes (e.g. $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2]$, $\text{M} = \text{Cr}, \text{Fe}$) can be extracted with decane or toluene [2,31]. This kind of behaviour was observed for various neutral metal carbonyl clusters and complexes deposited on silica, alumina, titanium oxide and magnesium oxide (Table 1) [9,11,20,21,27–29], [31–40].

The extraction method proved to be very useful to establish that a surface organometallic species is physisorbed. For example, impregnation of $\eta\text{-Al}_2\text{O}_3$ with a chloroform solution of $[\text{Rh}_6(\text{CO})_{16}]$, followed by evaporation of the solvent, affords a powder which infrared spectrum resembles, in the carbonyl region, that of the original cluster but is not identical. It was not clear if this modification was due only to a weak interaction between $[\text{Rh}_6(\text{CO})_{16}]$ and the surface or to the formation of a substituted species such as $[\text{Rh}_6(\text{CO})_{16-n}\text{Y}_n]$ (Y = donor groups of the surface). Extraction with chloro-

form led to a quantitative recovery of $[\text{Rh}_6(\text{CO})_{16}]$, indicating that the cluster was simply physisorbed, retaining its integrity on the surface [38].

Besides, when a solution of $[\text{Rh}_4(\text{CO})_{12}]$ is adsorbed on silica previously dehydroxylated at 500°C, the infrared spectrum of the silica powder, obtained after evaporation of the solvent, suggests the transformation of the Rh_4 cluster into $[\text{Rh}_6(\text{CO})_{16}]$; this was easily confirmed by extraction of $[\text{Rh}_6(\text{CO})_{16}]$ with chloroform [21]. Thermal treatment of physisorbed $[\text{M}_3(\text{CO})_{12}]$ (M = Ru, Os) with hydrogen affords ph-

Table 2
Chemisorbed organometallic species attached to the support by ion-pairing

Chemisorbed species	Salt used for extraction via ion-exchange reaction	Extracted species	Reference
$[\text{CpW}(\text{CO})_3]^-/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}][\text{CpW}(\text{CO})_3]$	[42]
$[\text{HFe}_3(\text{CO})_{11}]^-/\text{Al}_2\text{O}_3$	$[\text{Et}_4\text{N}]\text{Cl}$ in hexane	$[\text{Et}_4\text{N}][\text{HFe}_3(\text{CO})_{11}]$	[27]
$[\text{HFe}_3(\text{CO})_{11}]^-/\text{ZnO}$	$[\text{Et}_4\text{N}]\text{Cl}$ in hexane	$[\text{Et}_4\text{N}][\text{HFe}_3(\text{CO})_{11}]$	[27]
$[\text{HFe}_3(\text{CO})_{11}]^-/\text{MgO}$	$[\text{Et}_4\text{N}]\text{Cl}$ in hexane	$[\text{Et}_4\text{N}][\text{HFe}_3(\text{CO})_{11}]$	[27]
$[\text{HRu}_3(\text{CO})_{11}]^-/\text{Al}_2\text{O}_3$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}][\text{HRu}_3(\text{CO})_{11}]$	[43]
$[\text{HRu}_3(\text{CO})_{11}]^-/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}][\text{HRu}_3(\text{CO})_{11}]$	[44]
$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-/\text{Al}_2\text{O}_3$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$	[44,45]
$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$	[44]
$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-/\text{TiO}_2$	$[\text{Bu}_4\text{N}]\text{Br}$ in THF	$[\text{Bu}_4\text{N}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$	[34]
$[\text{Ru}_6(\text{CO})_{18}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_6(\text{CO})_{18}]$	[44]
$[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}/\text{Al}_2\text{O}_3$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$	[44]
$[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$	[44]
$[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in acetone	$[(\text{Ph}_3\text{P})_2\text{N}][\text{H}_3\text{Os}_4(\text{CO})_{12}]$	[6]
$[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in acetone	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Os}_5\text{C}(\text{CO})_{14}]$	[6]
$[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in acetone	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$	[6]
$[\text{H}_3\text{RuOs}_3(\text{CO})_{12}]^-/\text{Al}_2\text{O}_3$	$[\text{AsPh}_4]\text{Cl}$ in THF	$[\text{AsPh}_4][\text{H}_3\text{RuOs}_3(\text{CO})_{12}]$	[46]
$[\text{RhH}_2(\text{PMe}_3)_4]^+/\text{SiO}_2$	$[\text{Bu}_4\text{N}]\text{Cl}$ in nitromethane	$[\text{RhH}_2(\text{PMe}_3)_4]\text{Cl}$	[8]
$[\text{Rh}_5(\text{CO})_{15}]^-/\text{Al}_2\text{O}_3$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF	$[(\text{Ph}_3\text{P})_2\text{N}][\text{Rh}_5(\text{CO})_{15}]$	[47]
$[\text{Rh}_5(\text{CO})_{15}]^-/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF or $\text{K}[\text{CH}_3\text{CO}_2]$ in methanol	$[(\text{Ph}_3\text{P})_2\text{N}][\text{Rh}_5(\text{CO})_{15}]$ or $\text{K}[\text{Rh}_5(\text{CO})_{15}]$	[47]
$[\text{Rh}_6(\text{CO})_{15}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in CH_2Cl_2	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Rh}_6(\text{CO})_{15}]$	[47]
$[\text{Rh}_{12}(\text{CO})_{30}]^{2-}/\text{Al}_2\text{O}_3$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF or $\text{K}[\text{CH}_3\text{CO}_2]$ in methanol	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Rh}_{12}(\text{CO})_{30}]$ or $\text{K}_2[\text{Rh}_{12}(\text{CO})_{30}]$	[47]
$[\text{Rh}_{12}(\text{CO})_{30}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF or $\text{K}[\text{CH}_3\text{CO}_2]$ in methanol	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Rh}_{12}(\text{CO})_{30}]$ or $\text{K}_2[\text{Rh}_{12}(\text{CO})_{30}]$	[47]
$[\text{Hlr}_4(\text{CO})_{11}]^-/\text{Al}_2\text{O}_3$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in methanol	$[(\text{Ph}_3\text{P})_2\text{N}][\text{Hlr}_4(\text{CO})_{11}]$	[48]
$[\text{Hlr}_4(\text{CO})_{11}]^-/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF or methanol	$[(\text{Ph}_3\text{P})_2\text{N}][\text{Hlr}_4(\text{CO})_{11}]$	[49]
$[\text{Ir}_6(\text{CO})_{15}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF or methanol	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ir}_6(\text{CO})_{15}]$	[49]
$[\text{Ir}_8(\text{CO})_{22}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF or methanol	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ir}_8(\text{CO})_{22}]$	[49]
$[\text{Pt}_6(\text{CO})_{12}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Pt}_6(\text{CO})_{12}]$	[7]
$[\text{Pt}_9(\text{CO})_{18}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Pt}_9(\text{CO})_{18}]$	[7]
$[\text{Pt}_{12}(\text{CO})_{24}]^{2-}/\text{MgO}$	$[\text{Bu}_4\text{N}]\text{Br}$ in acetone	$[\text{Bu}_4\text{N}]_2[\text{Pt}_{12}(\text{CO})_{24}]$	[7]
$[\text{Pt}_{15}(\text{CO})_{30}]^{2-}/\text{MgO}$	$[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in THF	$[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Pt}_{15}(\text{CO})_{30}]$	[50]

Table 3

Chemisorbed organometallic species weakly linked to the support which acts as a donor ligand via the surface hydroxyl or oxo groups

Chemisorbed species	Donor solvent or specific reagent used for extraction	Extracted derivative	Reference
$\text{Ru}(\text{CO})_2\text{Cl}_2(\text{HOSi}\equiv)_2$	pyridine, tetrahydrofuran, ethanol or acetone	$\text{Ru}(\text{CO})_2\text{Cl}_2(\text{solvent})_2$	[33]
$\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\equiv)$	pyridine, acetonitrile, tetrahydrofuran, ethanol or acetone	$\text{Ru}(\text{CO})_3\text{Cl}_2(\text{solvent})$	[33]
$\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\equiv)$	bipyridine in CH_2Cl_2	$\text{Ru}(\text{CO})_2\text{Cl}_2(\text{bipyridine})$	[51]
$\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\equiv)$	$[\text{Co}(\text{CO})_4]^-$ in THF	$[\text{RuCo}_3(\text{CO})_{12}]^-$	[51]
$\text{Os}(\text{CO})_3\text{Cl}_2(\text{HOSi}\equiv)$	pyridine, acetonitrile, tetrahydrofuran, ethanol or acetone	$\text{Os}(\text{CO})_3\text{Cl}_2(\text{solvent})$	[35]

ysisorbed $[\text{H}_4\text{M}_4(\text{CO})_{12}]$ which is easily extracted with hexane or dichloromethane [32].

Moreover, recently, a few anionic osmium clusters have been generated by reductive carbonylation of silica-supported $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ in the presence of alkali carbonates (e.g. $\text{K}[\text{H}_3\text{Os}_4(\text{CO})_{12}]$, $\text{K}_2[\text{H}_2\text{Os}_4(\text{CO})_{12}]$, $\text{K}_2[\text{Os}_5\text{C}(\text{CO})_{14}]$ and $\text{Na}_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$) [10,11]. All these clusters are simply deposited on the silica surface, because they can be extracted with rather polar solvents (e.g. acetonitrile and acetone) necessary to solubilize them.

2.2. Chemisorbed organometallic species

When $[\text{Fe}_3(\text{CO})_{12}]$ is supported on alumina by sublimation, it cannot be extracted successively with hexane [27] and therefore it is not simply physisorbed. Infrared evidence suggests that it reacts with the surface $-\text{OH}$ groups to give the anion $[\text{HFe}_3(\text{CO})_{11}]^-$ which can be extracted only by ion-exchange techniques, suggesting that the counter-cation is an aluminium

acidic surface site (and not a surface $[\text{H}_3\text{O}]^+$ species). This anion interacts chemically with the surface and therefore is a 'chemisorbed' species. Once extracted, it can be fully characterized by classical methods.

Organometallic 'chemisorbed' species may be divided into three types depending on the kind of chemical interaction between the organometallic moiety and the support:

(i) neutral species with basic ligands [41] or anions [6,7,27,34,42–50] which interact with the Lewis acidic sites of inorganic oxides (e.g. Al^{3+} , Mg^{2+}) and cations [8] which are attached to the surface by ion pairing (Table 2),

(ii) organometallic moieties weakly linked to the surface hydroxyl or oxo groups (presence of a weak dative bond between the organometallic species and the support which acts as a ligand via the surface hydroxyl or oxo groups; Table 3) [33,35,51],

(iii) organometallic moieties covalently linked to the surface oxy groups (presence of a covalent bond between the organometallic species

Table 4

Chemisorbed organometallic species covalently linked to the support which acts as a ligand via the surface oxy groups

Chemisorbed species	Specific reagent used to cleave the metal-support covalent bond	Extracted derivative	Reference
$[\text{Os}(\text{CO})_2(\text{OMg}-)_4]^{2-}$	HCl (aq)	$[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$	[52]
$[\text{M}(\text{CO})_x(\text{OSi}\equiv)_2]_n$ (M = Ru, Os; x = 2,3)	HCl (aq)	$[\text{M}(\text{CO})_2\text{Cl}_4]^{2-}$ and $[\text{M}(\text{CO})_3\text{Cl}_3]^-$ (M = Ru, Os)	[53]
$\text{HO}_3(\text{CO})_{10}(\text{OSi}\equiv)$	HF (aq)	$\text{HO}_3(\text{CO})_{10}(\text{OH})$	[54]
$\text{HO}_3(\text{CO})_{10}(\text{OSi}\equiv)$	HCl (aq)	$\text{HO}_3(\text{CO})_{10}\text{Cl}$	[55]
$\text{HO}_3(\text{CO})_{10}(\text{OSi}\equiv)$	$\text{Na}_2\text{CO}_3(\text{aq})$ or $\text{K}_2\text{CO}_3(\text{aq})$	$\text{HO}_3(\text{CO})_{10}(\text{OH})$	[56]
$(\text{PMe}_3)_3\text{Rh}(\text{OSi}\equiv)$	H_2 followed by $[\text{Bu}_4\text{N}]\text{Cl}$	$[\text{RhH}_2(\text{PMe}_3)_4]\text{Cl}$	[8]
$[\text{Rh}(\text{CO})_2(\text{OMg}-)(\text{HOMg})]$	HCl (aq)	$[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$	[57]
$[\text{Rh}(\text{CO})_2(\text{OMg}-)(\text{HOMg})]$	$\text{CO} + \text{H}_2\text{O}$	$[\text{Rh}_6(\text{CO})_{16}]$	[38,57]
$[\text{Rh}(\text{CO})_2(\text{OAl}=(\text{HOAl}))]$	$\text{CO} + \text{H}_2\text{O}$	$[\text{Rh}_6(\text{CO})_{16}]$	[38]
$\text{Cp}^* \text{Ir}(\text{OSi}\equiv)(\text{Ph})(\text{PMe}_3)$	$\text{HC}\equiv\text{CCO}_2\text{Et}$	$\text{Cp}^* \text{Ir}(\text{C}\equiv\text{CCO}_2\text{Et})(\text{Ph})(\text{PMe}_3)$	[58]
$\text{Cp}^* \text{Ir}(\text{OSi}\equiv)(\text{Ph})(\text{PMe}_3)$	<i>p</i> -nitrophenol	$\text{Cp}^* \text{Ir}(p\text{-OC}_6\text{H}_4\text{NO}_2)(\text{Ph})(\text{PMe}_3)$	[58]

and the support which acts as a ligand; Table 4) [8,38,52–58].

In all three cases, selective surface reactions followed by extraction often allow an indirect characterization of the nature of the surface species.

(i) One of the simplest chemisorption modes of a metal carbonyl on a metal oxide involves the formation of a Lewis acid–base adduct, the basic oxygen of a carbonyl group interacting with a Lewis acidic site of the surface [42]. An example is alumina chemisorbed $[\text{CpFe}(\text{CO})_4]$ which can be extracted from the surface using a basic solvent like pyridine [41].

When the supported organometallic species is an anion interacting with the Lewis acidic sites of inorganic oxides, it may be easily removed by the ion-exchange technique. Typically, this technique consists in the extraction of the supported anionic species with a solution of a salt of a bulky organic cation dissolved in an organic solvent. Many examples are reported in the literature (Table 2). Thus, the alumina chemisorbed $[\text{HFe}_3(\text{CO})_{11}]^-$ species reported above may be extracted with a hexane solution of $[\text{Et}_4\text{N}]\text{Cl}$ [27]. Similarly, magnesium oxide chemisorbed $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$ and $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ [6], magnesium oxide chemisorbed $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ [47], and alumina chemisorbed $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ [44,45] may be extracted with a dichloromethane or tetrahydrofuran solution of $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$.

The first example of a cationic organometallic complex, $[\text{RhH}_2(\text{PMe}_3)_4]^+$, attached to a siloxy anionic group $[\equiv\text{SiO}]^-$ of the silica surface by ion pairing has been given recently. This cation can be easily extracted from the surface by ion-exchange with $[\text{Bu}_4\text{N}]\text{Cl}$ dissolved in nitromethane. Its characterization in solution and in the solid state has confirmed the nature of the surface species proposed on the basis of surface spectroscopic characterization [8].

(ii) An organometallic moiety may be weakly linked to the surface hydroxyl groups which act as donor ligands. These functional surface

groups may be easily replaced by good donor solvents (e.g. ethers, nitriles, alcohols, amines), allowing extraction of the supported species (Table 3).

For example, two silica chemisorbed ruthenium species of this type, $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{HOSi}\equiv)_2]$ and $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\equiv)]$, formed during the reductive carbonylation of silica-supported RuCl_3 , have been identified by ‘ligand exchange reaction’. In contrast to the related physisorbed $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ and $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{H}_2\text{O})]$, which may be easily extracted with a non-donor solvent like dichloromethane, these two species cannot be extracted with non-donor solvents at room temperature, suggesting that they are linked to the surface, probably via silanol groups. As expected, extraction with donor solvents (e.g. pyridine, tetrahydrofuran, ethanol) affords $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{solvent})_2]$ and $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{solvent})]$, respectively [33].

Similarly, the osmium carbonyl surface species obtained by reductive carbonylation of silica-supported OsCl_3 has been identified as $[\text{Os}(\text{CO})_3\text{Cl}_2(\text{HOSi}\equiv)]$ since it can be extracted with donor solvents but not with dichloromethane, in contrast to physisorbed $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ which can be easily extracted with this latter non-donor solvent [35].

However it should be added that a supported species which can be only extracted with donor solvents is not necessarily bound to the surface hydroxyl groups. As reported above in the case of physisorbed anionic clusters, it might be a physisorbed cluster only soluble in polar donor solvents (Table 1). In addition, some physisorbed surface organometallic species can be polymeric (e.g. $[\text{M}(\text{CO})_x(\text{OH})_2]_n$ where $x = 2, 3$ and $\text{M} = \text{Ru}, \text{Os}$) and therefore not soluble in non-donor solvents [59]. In these latter cases, further chemical and physico-chemical characterization of the species extracted with donor solvents may reveal the true nature of the surface species.

(iii) The third kind of chemisorbed organometallic species is that anchored to the

surface for instance via covalent bonds with surface oxy groups. This kind of species cannot be extracted by simple treatment with solvents. Cleavage of either the bond M–OS (S = Si, Al, Ti or Mg) or the bond MO–S by a surface reaction is necessary (Table 4). For instance, examples of this kind of supported species include surface species such as $[\text{HM}_3(\text{CO})_{10}\text{OS}]$ and $[\text{M}(\text{CO})_x(\text{OS})_2]_n$ ($x = 2, 3$; M = Ru, Os; S = Si, Al or Mg) which are formed by thermal treatment of physisorbed $[\text{M}_3(\text{CO})_{12}]$ [60].

The structure and nature of the silica chemisorbed species $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$ have been suggested by a series of spectroscopic methods (Infrared [20,61–63], Raman [64] and EXAFS [65,66]). However, none of these methods allowed a clear choice between two potential structures: $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$ and $[\text{Os}_3(\text{CO})_{10}(\text{OSi}\equiv)_2]$. Comparison of the solid state ^{13}C NMR spectrum of the silica chemisorbed species with that of model compounds was in agreement with a structure such as $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$ [67]. However, it was impossible to find a spectroscopic method for direct evidence of the presence of a hydrogen bridging ligand. Indirect evidence was originated by the lack of hydrogen evolution in the surface reaction between $[\text{Os}_3(\text{CO})_{12}]$ and the silica surface, to give the silica-anchored trimeric species, [20] and by the close characteristics of the infrared spectra of this surface species and some organometallic models $[\text{HOs}_3(\text{CO})_{10}\text{OSiR}_3]$ (R = Ph, Et) [24]. Only the reaction of $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$ with HF (aq) and HCl (aq), respectively, presented simple and clear evidence of the presence of the bridging hydrogen. In the presence of excess HF (aq), silicon–oxygen bonds are cleaved affording H_2SiF_6 and liberating $[\text{HOs}_3(\text{CO})_{10}\text{OH}]$ [54]. It was later found that in the presence of HCl (aq), osmium–oxygen bonds are cleaved and $[\text{HOs}_3(\text{CO})_{10}\text{Cl}]$ is obtained [55], while under basic conditions (e.g. aqueous solution of sodium carbonate), $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$ can also be converted into $[\text{HOs}_3(\text{CO})_{10}\text{OH}]$ [56]. In contrast to $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$, both

$[\text{HOs}_3(\text{CO})_{10}\text{OH}]$ and $[\text{HOs}_3(\text{CO})_{10}\text{Cl}]$ can be easily extracted with dichloromethane and therefore the presence of a hydrogen bridging ligand was identified by classical methods (^1H NMR spectroscopy).

Another example of chemisorbed species strongly bonded to the surface is the silica-anchored species $[\text{M}(\text{CO})_x(\text{OSi}\equiv)_2]_n$ ($x = 2, 3$; M = Ru, Os) [20,28] which cannot be extracted with non-donor solvents (in contrast to physisorbed $[\text{M}(\text{CO})_3\text{Cl}_2]_2$) or even with donor solvents (in contrast to $[\text{M}(\text{CO})_3\text{Cl}_2(\text{HOSi}\equiv)]$ [33,35]. This lack of extraction suggests the presence of a covalent bond between the 'M(CO)_x' moiety and the silica surface, although a deposited polymeric structure $[\text{M}(\text{CO})_x(\text{OH})_2]_n$ cannot be excluded. After reaction with HCl, these surface organometallic species may be extracted with ethanol or with a dichloromethane solution of $[\text{PPN}]\text{Cl}$, allowing a simple and clear determination of the number of CO ligands per metal atoms. In fact, $[\text{M}(\text{CO})_2\text{Cl}_4]^{2-}$ and $[\text{M}(\text{CO})_3\text{Cl}_3]^-$ are obtained for $x = 2$ and 3, respectively [53]. Therefore, remarkably, a simple surface reaction with HCl is a convenient, precise and alternative method to the more conventional temperature-programmed decomposition technique [19], to determine the number of CO ligands in this kind of osmium surface species. Similarly, surface species such as $[\text{Os}(\text{CO})_2(\text{OMg})_4]^{2-}$ and $[\text{Rh}(\text{CO})_2(\text{OMg})(\text{HOMg})]$ react with HCl affording $[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$ and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$, respectively, which can be easily extracted [52,57].

3. Extraction and reactivity as methods for the characterization of surface organometallic species

3.1. Extraction method

A first approach to the understanding of the nature of unknown surface organometallic

species is their extraction working in the following order:

(i) treatment with non-donor solvents (e.g. pentane, dichloromethane) will extract only physisorbed non-ionic and non-polymeric surface organometallic complexes or clusters;

(ii) treatment with donor solvents (e.g. acetonitrile, tetrahydrofuran, ethanol) will extract polymeric, anionic and cationic surface organometallic species or clusters physisorbed on the surface as well as chemisorbed species weakly bonded to the surface hydroxyl or oxo groups via donor bonds;

(iii) treatment with an organic solution of a salt of a large organic cation will extract, via the ion-exchange technique, chemisorbed anionic or cationic organometallic species and clusters bonded to the surface by ionic interactions;

(iv) species remaining on the support after the above treatments might be a chemisorbed compound anchored to the surface via covalent bonds with surface oxy groups. Therefore, selective cleavage of the bond M–OS (M = Metal; S = Si, Al, Ti, Mg, etc) by acids or bases may be tried, followed by extraction with a solvent or by ion-exchange technique; the extracted species can then be characterized using classical methods.

Such an approach may allow in specific cases the separation and characterization of a mixture of surface species or the detection of minor amounts or even traces of a surface organometallic species.

For example, when silica-supported $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ is treated with K_2CO_3 (molar ratio $\text{K}_2\text{CO}_3:\text{Os} = 10:1$) and heated at 150°C under CO for 1 h, extraction with dichloromethane and acetonitrile affords $[\text{HOs}_3(\text{CO})_{10}\text{OH}]$ and $\text{K}[\text{H}_3\text{Os}_4(\text{CO})_{12}]$, respectively [68]. After the extractions, the carbonyl bands typical of silica-anchored $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$, a potential intermediate species, could not be detected in the infrared spectrum of the resulting silica powder, because some osmium (II) carbonyl surface species were still present. The infrared absorptions of these

latter species could hide the carbonyl absorptions of minor amounts of $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$ [68]. The presence of this latter on the surface was indirectly confirmed, by treating the silica powder for 24 h with a mixture of H_2O and dichloromethane, a process which should convert surface $[\text{HOs}_3(\text{CO})_{10}\text{OSi}\equiv]$ into physisorbed $[\text{HOs}_3(\text{CO})_{10}\text{OH}]$. It turned out in fact that some $[\text{HOs}_3(\text{CO})_{10}\text{OH}]$ was formed, as shown by infrared and ^1H NMR spectroscopies of the product which went into the organic phase [68]. Therefore, by this approach, which involves extraction and specific surface chemical reactions, traces of an intermediate surface species were detected, although in a mixture with other surface species present in much larger amounts.

3.2. Surface chemical reactivity as an indirect method of determination of organometallic surface species nature

Classical methods of structure determination of a new compound rely heavily on the formation of derivatives of known composition [51]. This technique also proved to be useful for the characterization of surface-supported organometallic species. For instance, as reported above, a simple surface reaction with an acid such as HCl can give direct information on the nature of an organometallic species strongly bonded to the surface, like $[\text{Os}(\text{CO})_2(\text{OMg})_4]^{2-}$ or $[\text{Rh}(\text{CO})_2(\text{OMg})(\text{HOMg})]$ (Table 4) [52,57].

Because surface organometallic species can be considered to belong to the molecular state, their reactivity is characterized by elementary steps typical of molecular organometallic chemistry, including reversible ligand binding, oxidative addition, reductive elimination, protonation, heterolytic metal–carbon bond cleavage, electrophilic C–H bond activation and insertion into metal–carbon bonds [69]. This reactivity can be used as an indirect method to study the nature of surface species.

For instance, the behavior of $[\text{Rh}_6(\text{CO})_{16}]$ chemisorbed on alumina and magnesium oxide

surfaces differs from that of the cluster supported on silica. On silica, the infrared spectrum of adsorbed $[\text{Rh}_6(\text{CO})_{16}]$ is identical with that obtained in solution, suggesting that $[\text{Rh}_6(\text{CO})_{16}]$ is physisorbed, keeping its integrity on the surface. In fact, $[\text{Rh}_6(\text{CO})_{16}]$ is recovered quantitatively by extraction of the silica powder with chloroform [21]. On alumina and on magnesium oxide a very fast oxidation and cleavage of the rhodium cage can occur, already at room temperature. The relative intensity and position of the carbonyl absorption bands of the 'oxidized' rhodium species are similar to those of Rh^{I} complexes of the type $[\text{Rh}(\text{CO})_2\text{X}]_2$ where $\text{X} = \text{Cl}$, suggesting the presence of surface $\text{Rh}^{\text{I}}(\text{CO})_2$ groups chemically bonded to the support by AlO-Rh or MgO-Rh bonds, also because these species cannot be extracted by treatment with different solvents. In agreement with this hypothesis, these rhodium surface species react with $\text{CO} + \text{H}_2\text{O}$ giving back $[\text{Rh}_6(\text{CO})_{16}]$, as expected for a rhodium(I) carbonyl species [38]. The formation of $[\text{Rh}(\text{CO})_2(\text{OMg})(\text{HOMg})]$ surface species was also confirmed by reaction with HCl which affords $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$, easily extracted [57].

As reported above, the nature of the silica chemisorbed cluster $[\text{HOS}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ has been confirmed by its reaction with HF or H_2O and with HCl to generate $[\text{HOS}_3(\text{CO})_{10}(\text{OH})]$ and $[\text{HOS}_3(\text{CO})_{10}\text{Cl}]$, respectively [54–56]. Obviously, one can distinguish silica-anchored $[\text{HOS}_3(\text{CO})_{10}(\text{OSi}\equiv)]$ from silica-physisorbed $[\text{HOS}_3(\text{CO})_{10}(\text{OH})]$ because the former cannot be extracted with solvents, whereas the latter can be easily extracted with dichloromethane [68].

$[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ reacts on the silica surface affording a species characterized as $[(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2]$ ($\text{X} = \text{H}, \text{Si}\equiv$) [70–74]. Reaction of this surface-anchored species with PMe_3 followed by H_2 yields $[\text{RhH}_2(\text{PMe}_3)_4]^+$ which can be quantitatively extracted from the surface by ion-exchange with $[\text{Bu}_4\text{N}]\text{Cl}$ in nitromethane [8]. Since the related complex $[\text{ClRh}(\text{PMe}_3)_3]$ is known to react with

H_2 in solution to give $[\text{RhH}_2(\text{PMe}_3)_4]\text{Cl}$ [75], it is likely that the reaction of $[(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2]$ ($\text{X} = \text{H}, \text{Si}\equiv$) with excess PMe_3 leads to the intermediate formation of a surface analogue of $[\text{ClRh}(\text{PMe}_3)_3]$, i.e. $[(\equiv\text{SiO})\text{Rh}(\text{PMe}_3)_3]$ [8]. In fact, reaction of $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ with silica, followed by treatment with excess PMe_3 , affords $[(\equiv\text{SiO})_2\text{Rh}(\text{PMe}_3)_3(\eta^1\text{-C}_3\text{H}_5)]$ and $[(\equiv\text{SiO})\text{Rh}(\text{PMe}_3)_3]$ along with propene and 1,5-hexadiene [76,77].

The reaction of CO with the species obtained on the surface by interaction of $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ with silica, titania and alumina is another example of indirect characterization. As a first step, coordination of CO to these chemisorbed organometallic species is accompanied by a shift of the coordinated allyl ligands of the type $\eta^3\text{-}\eta^1$ [78]. Then, on surfaces with low proton content (silica dehydroxylated in vacuum at 400°C , alumina, titania), 1,5-hexadiene is produced quantitatively by reductive coupling of two allyl ligands, with simultaneous formation of the well known surface-bound dicarbonylrhodium(I) species. In the presence of a high concentration of surface protons (silica dehydroxylated in vacuum at 200°C), there are two reaction pathways: (i) formation of propene by reaction of an allyl ligand with a surface proton, and (ii) insertion of CO into the metal-carbon bond to give the acyl complex $[(\text{CH}_2=\text{CHCH}_2\text{C}(\text{O}))\text{Rh}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\text{SiO})(\text{SiOX})]$, as detected by infrared spectroscopy. The acyl ligand may undergo reductive elimination with an allyl ligand, giving the minor product 1,6-heptadien-4-one, or nucleophilic attack by a surface hydroxyl, with transfer of 3-butenolate to the silica support (extracted as methyl-3-butenolate). The final organometallic product is again the dicarbonylrhodium(I) fragment bound to the surface [78]. This surface reactivity is similar to that of the homogeneous analogue $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}]_2$. In fact, the first step is formation of $[\text{Rh}(\eta^1\text{-C}_3\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(\text{CO})\text{Cl}]$, with a $\eta^3\text{-}\eta^1$ allyl ligand shift, followed by reductive elimination of 1,5-

hexadiene or insertion of CO to give an acyl-rhodium complex. This latter eliminates 1,6-heptadien-4-one with formation of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [78]. This very similar behaviour is an indirect evidence of the nature of the surface organometallic species.

In the same way, the surface reactivity of chemisorbed carbonyl ruthenium species, obtained by depositing $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{THF})]$ on silica, alumina and magnesium oxide, was used to determine their structure; in particular, the reaction of these chemisorbed species with bipyridine and $[\text{Co}(\text{CO})_4]^-$ was investigated [51].

Bipyridine (bpy) is known to react with $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{THF})]$ in solution to yield $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{bpy})]$ [79]. Addition of bipyridine as a solution in dichloromethane to the ruthenium carbonyl species supported on silica resulted in the loss of 1 equiv. of CO/Ruthenium atom and in the formation of $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{bpy})]$ which could be extracted with dichloromethane (Table 3) [51]. In contrast, the reaction of bipyridine with the ruthenium carbonyl species obtained either on alumina or magnesium oxide did not give $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{bpy})]$ but a species which could not be extracted with dichloromethane [51]. Both results are consistent with a weak donor interaction corresponding to the structure $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{OSi}\equiv)]$ on silica (similar to $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{THF})]$) and with a covalent bonding with the surface corresponding to the structure $[\text{Ru}(\text{CO})_3(\text{HOS})(\text{OS})_2]$ ($\text{S} = \text{Al}, \text{Mg}$) on alumina and magnesium oxide.

Besides, it is known that $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{THF})]$ reacts with $[\text{Co}(\text{CO})_4]^-$ in THF to yield $[\text{RuCo}_3(\text{CO})_{12}]^-$ [80]. The ruthenium carbonyl species supported on silica afforded as expected $[\text{RuCo}_3(\text{CO})_{12}]^-$ in the presence of $[\text{Co}(\text{CO})_4]^-$ (Table 3) while the ruthenium carbonyl species supported on alumina or magnesium oxide did not react. These observations are in agreement with a ruthenium carbonyl species strongly bound to the surface of alumina or of magnesium oxide [51].

Recently, chemical reactivity as a structural tool has also been used to characterize a

' $\text{Cp}^*\text{Ir}(\text{Ph})(\text{PMe}_3)$ ' species (where Cp^* is $\eta^5\text{-C}_5\text{Me}_5$ ligand) supported on silica, obtained by treatment of silica with $[\text{Cp}^*\text{Ir}(\text{OH})(\text{Ph})(\text{PMe}_3)]$ [58]. The ^{13}C CPMAS NMR spectrum of the surface species was carried out but the broadness of the signals prevented an unambiguous assignment. Evidence that the iridium complex was chemisorbed by a covalent Ir–OSi bond and not simply hydrogen-bonded to the silica surface, was obtained by monitoring the reactions of $[\text{Cp}^*\text{Ir}(p\text{-NHC}_6\text{H}_4\text{Me})(\text{Ph})(\text{PMe}_3)]$ and $[\text{Cp}^*\text{Ir}(\text{OSiMe}_2\text{Bu})(\text{Ph})(\text{PMe}_3)]$ with the silanol groups of silica (dried under vacuum at 200°C to remove surface water) which led to the same silica-bound chemisorbed species, liberating in parallel one equivalent of free *p*-toluidine or HOSiMe_2Bu respectively. The silica-bound iridium species reacted also with phenols to produce equilibrium ratios of $[\text{Cp}^*\text{Ir}(\text{OSi}\equiv)(\text{Ph})(\text{PMe}_3)]$ and the corresponding aryloxo complex which can be extracted with an organic solvent.

Evidence of a strong silica–iridium interaction was further confirmed by comparison of the reactions of the silica-supported species with those of the analogous monomeric iridium hydroxo and triflate compounds ($[\text{Cp}^*\text{Ir}(\text{OR})(\text{Ph})(\text{PMe}_3)]$, $\text{R} = \text{H}$ and Tf). The reactions with (i) phenols, (ii) dimethyl acetylene dicarboxylate and (iii) alkyne ethyl propionate were investigated. It turned out that the reactivity of the silica-bound species was intermediate between that of the hydroxide and that of the triflate [58].

4. Conclusion

In conclusion, we have proposed an appropriate methodology, based on simple extraction processes, with or without involvement of chemical reactions of the surface organometallic species, as a useful way to determine the nature and the structure of specific organometallic surface species and to probe the nature of the 'organometallic species–inorganic support' in-

teraction. In addition, the investigation of specific surface reactions can give further information on the nature of the surface species and can be used as a straightforward structural tool. Therefore this approach is expected to develop rapidly in the next few years, also because applications with supports different from simple inorganic oxides, for example carbon where some spectroscopy methods cannot be easily applied, may also emerge.

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References

- [1] B.C. Gates, *Chem. Rev.*, 95 (1995) 511.
- [2] A. Zecchina and C.O. Areal, *Catal. Rev.-Sci.Eng.*, 35 (1993) 261.
- [3] J.J. Venter and M.A. Vannice, *J. Mol. Catal.*, 56 (1989) 117.
- [4] J.M. Basset, J.P. Candy, A. Choplin, M. Leconte and A. Théolier, in R. Ugo (Ed.), *Aspects of Homogeneous Catalysis*, Kluwer, Dordrecht, 1990, Vol. 7, 85.
- [5] (a) A.K. Smith, A. Théolier, J.M. Basset, R. Ugo, D. Commereuc and Y. Chauvin, *J. Chem. Soc., Chem. Commun.*, (1978) 2590; (b) D. Commereuc, Y. Chauvin, F. Hugues, J.M. Basset and D. Olivier, *J. Chem. Soc., Chem. Commun.*, (1980) 154; (c) T. Okuhara, K. Kobayashi, T. Kimura, M. Misono and Y. Yoneda, *J. Chem. Soc., Chem. Commun.*, (1981) 1114; (d) S.D. Jackson, R.B. Moyes, P.B. Wells and R. Whyman, *J. Catal.*, 86 (1984) 342; (e) C. Dossi, A. Fusi, E. Grilli, R. Psaro, R. Ugo and R. Zanon, *J. Catal.*, 123 (1990) 181; (f) M. Ichikawa, *Adv. Catal.*, 38 (1992) 283.
- [6] H.H. Lamb, A.S. Fung, P.A. Tooley, J. Puga, T.R. Krause, M.J. Kelley and B.C. Gates, *J. Am. Chem. Soc.*, 111 (1989) 8367.
- [7] B.C. Gates, *J. Mol. Catal.*, 86 (1994) 95, and references cited therein.
- [8] S.L. Scott, P. Dufour, C. Santini and J.M. Basset, *J. Chem. Soc., Chem. Commun.*, (1994) 2011.
- [9] D. Roberto, R. Psaro and R. Ugo, *Organometallics* 12 (1993) 2292.
- [10] D. Roberto, E. Cariati, R. Psaro and R. Ugo, *Organometallics*, 13 (1994) 734.
- [11] D. Roberto, E. Cariati, R. Ugo and R. Psaro, *Inorg. Chem.*, 35 (1996) 2311.
- [12] H. Knozinger, in B.C. Gates, L. Gucci and H. Knozinger (Eds.), *Metal Clusters in Catalysis*, Elsevier, Amsterdam, 1986, p. 123.
- [13] L. Reven, *J. Mol. Catal.*, 86 (1994) 447.
- [14] A.V. Shvets, A.L. Tarasov, V.B. Kazansky and H. Knözinger, *J. Catal.*, 86 (1984) 223.
- [15] K. Lázár, K. Matusek, J. Mink, S. Dobos, L. Gucci, L. Markó, A. Vizi-Orosz and W.M. Reiff, *J. Catal.*, 87 (1984) 163.
- [16] B.C. Gates and D.C. Koningsberger, *CHEMTECH*, (1992) 300.
- [17] D.C. Koningsberger and R. Prins (Eds.), *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, Wiley, New York, 1988.
- [18] (a) B.G. Frederick, G. Apai and T.N. Rhodin, *J. Am. Chem. Soc.*, 109 (1987) 4797; (b) M. Kawai, M. Uda and M. Ichikawa, *J. Phys. Chem.*, 89 (1985) 1654; (c) R. Zanon and R. Psaro, *Spectrochim. Acta (A)*, 43 (1987) 1497.
- [19] C. Dossi, A. Fusi, R. Psaro and G.M. Zanderighi, *Appl. Catal.*, 46 (1989) 145.
- [20] R. Psaro, R. Ugo, G.M. Zanderighi, B. Besson, A.K. Smith and J.M. Basset, *J. Organomet. Chem.*, 213 (1981) 215.
- [21] A. Théolier, A.K. Smith, M. Leconte, J.M. Basset, G.M. Zanderighi, R. Psaro and R. Ugo, *J. Organomet. Chem.*, 191 (1980) 415.
- [22] A. Vizi-Orosz and L. Marko, *Transition Met. Chem.*, 7 (1982) 216.
- [23] J. Evans and B.P. Gracey, *J. Chem. Soc., Dalton Trans.*, (1982) 1123.
- [24] L. D'Ornelas, A. Choplin, J.M. Basset, L.Y. Hsu and S.G. Shore, *Nouv. J. Chim.*, 9 (1985) 155.
- [25] J. Puga, T.P. Fehlner, B.C. Gates, D. Braga and F. Grepioni, *Inorg. Chem.*, 29 (1990) 2376.
- [26] A. Vizi-Orosz, R. Ugo, R. Psaro, A. Sironi, M. Moret, C. Zucchi, F. Ghelfi and G. Palyi, *Inorg. Chem.*, 33 (1994) 4600.
- [27] F. Hugues, J.M. Basset, Y. Ben Taarit, A. Choplin, M. Primet, D. Rojas and A.K. Smith, *J. Am. Chem. Soc.*, 104 (1982) 7020.
- [28] G.M. Zanderighi, C. Dossi, R. Ugo, R. Psaro, A. Théolier, A. Choplin, L. D'Ornelas and J.M. Basset, *J. Organomet. Chem.*, 296 (1985) 127.
- [29] D. Roberto, E. Cariati, R. Psaro and R. Ugo, *Organometallics*, 13 (1994) 4227.
- [30] Y. Iwasawa, M. Yamada, S. Ogasawara, Y. Sato and H. Huroda, *Chem. Lett.*, (1983) 621.
- [31] F.J. Kard, C. Wu, W.T. Reichle and N.J. Maraschin, *J. Catal.*, 60 (1979) 68.
- [32] C. Dossi, R. Psaro, D. Roberto, R. Ugo and G.M. Zanderighi, *Inorg. Chem.*, 29 (1990) 4368.
- [33] D. Roberto, R. Psaro and R. Ugo, *J. Organomet. Chem.*, 451 (1993) 123.
- [34] S. Uchiyama and B.C. Gates, *J. Catal.*, 110 (1988) 388.
- [35] D. Roberto, R. Psaro and R. Ugo, *J. Mol. Catal.*, 86 (1994) 109.

- [36] M. Primet, J.-M. Basset, M.V. Matthieu and M. Prettre, *J. Catal.*, 28 (1973) 368.
- [37] K.L. Watters, R.F. Howe, T.P. Chojnacki, C.M. Fu, R.L. Schneider and N.B. Wong, *J. Catal.*, 66 (1980) 424.
- [38] A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bilhou-Bougnol and W.F. Graydon, *Inorg. Chem.*, 18 (1979) 3104.
- [39] R. Psaro, C. Dossi, A. Fusi, R. Della Pergola, L. Garlaschelli, D. Roberto, L. Sordelli, R. Ugo and R. Zanoni, *J. Chem. Soc. Faraday Trans.*, 88 (1992) 369.
- [40] D. Roberto, E. Cariati, R. Psaro and R. Ugo, *J. Organomet. Chem.*, 488 (1995) 109.
- [41] C. Tessier-Youngs, F. Correa, D. Ploch, R.L. Burwell Jr. and D.F. Shriver, *Organometallics*, 2 (1983) 898.
- [42] H.H. Lamb, B.C. Gates and H. Knozinger, *Angew. Chem., Int. Ed. Engl.*, 27 (1988) 1127.
- [43] J.J. Bergmeister, III and B.E. Hanson, *J. Organomet. Chem.*, 352 (1988) 367.
- [44] R. Pierantozzi, E.G. Valagene, A.F. Nordquist and P.N. Dyer, *J. Mol. Catal.*, 21 (1983) 189.
- [45] V. Kuznetsov, A.T. Bell and Y.I. Yermakov, *J. Catal.*, 65 (1980) 374.
- [46] J.R. Budge, J.P. Scott and B.C. Gates, *J. Chem. Soc., Chem. Commun.*, (1983) 342.
- [47] S. Kawi, Z. Xu and B.C. Gates, *Inorg. Chem.*, 33 (1994) 503.
- [48] S. Kawi, J.R. Chang and B.C. Gates, *J. Phys. Chem.*, 97 (1993) 5375.
- [49] S. Kawi and B.C. Gates, *Inorg. Chem.*, 31 (1992) 2939.
- [50] J.R. Chang, D.C. Koningsberger and B.C. Gates, *J. Am. Chem. Soc.*, 114 (1992) 6460.
- [51] J.J. Bergmeister, III and B.E. Hanson, *Inorg. Chem.*, 29 (1990) 4055.
- [52] R. Psaro, C. Dossi and R. Ugo, *J. Mol. Catal.*, 21 (1983) 331.
- [53] E. Cariati, D. Roberto and R. Ugo, *Organometallics*, submitted.
- [54] C. Dossi, A. Fusi, M. Pizzotti and R. Psaro, *Organometallics*, 9 (1990) 1994.
- [55] D. Roberto, M. Pizzotti and R. Ugo, *Gazz. Chim. Ital.*, 125 (1995) 133.
- [56] E. Cariati, E. Lucenti, D. Roberto and R. Ugo, unpublished results.
- [57] C. Dossi, R. Psaro and R. Ugo, *J. Organomet. Chem.*, 359 (1989) 105.
- [58] T.Y. Meyer, K.A. Woerpel, B.M. Novak and R.G. Bergman, *J. Am. Chem. Soc.*, 116 (1994) 10290.
- [59] E. Cariati, E. Lucenti, M. Pizzotti, D. Roberto and R. Ugo, unpublished results.
- [60] R. Psaro and R. Ugo, in B.C. Gates, L. Gucci and H. Knozinger (Eds.), *Metal Clusters in Catalysis*, Elsevier, Amsterdam, 1986, p. 427.
- [61] B. Besson, B. Moraweck, A.K. Smith, J.M. Basset, R. Psaro, A. Fusi and R. Ugo, *J. Chem. Soc., Chem. Commun.*, (1980) 569.
- [62] M. Deeba and B.C. Gates, *J. Catal.*, 67 (1981) 303.
- [63] S.L. Cook, J. Evans, G.S. McNulty and G.N. Greaves, *J. Chem. Soc., Dalton Trans.*, (1986) 7.
- [64] M. Deeba, B.J. Streusand, G.L. Schrader and B.C. Gates, *J. Catal.*, 69 (1981) 218.
- [65] N. Binstead, J. Evans, G.N. Greaves and R.J. Price, *Organometallics*, 8 (1989) 613.
- [66] F.B.M. Duivenvoorden, D.C. Koningsberger, Y.S. Uh and B.C. Gates, *J. Am. Chem. Soc.*, 108 (1986) 6254.
- [67] T.H. Walter, G.R. Fraunhoff, J.R. Shapley and E. Oldfield, *Inorg. Chem.*, 27 (1988) 2561.
- [68] E. Cariati, D. Roberto and R. Ugo, *Gazz. Chim. Ital.*, in press.
- [69] S.L. Scott and J.-M. Basset, *J. Mol. Catal.*, 86 (1994) 5.
- [70] M.D. Ward, T.V. Harris and J. Schwartz, *J. Chem. Soc., Chem. Commun.*, (1980) 357.
- [71] M.D. Ward and J. Schwartz, *J. Mol. Catal.*, 11 (1981) 397.
- [72] H.C. Foley, S.J. DeCanio, K.D. Tau, K. J. Chao, J.H. Onuberko, C. Dybowski and B.C. Gates, *J. Am. Chem. Soc.*, 105 (1983) 3074.
- [73] P. Dufour, C. Houtman, C.C. Santini, C. Nédez, J.-M. Basset, L. Y. Hsu and S.G. Shore, *J. Am. Chem. Soc.*, 114 (1992) 4248.
- [74] H.E. Fischer, S.A. King, C.E. Bronniman and J. Schwartz, *Langmuir*, 9 (1993) 391.
- [75] R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, *J. Chem. Soc., Dalton Trans.*, (1980) 511.
- [76] S.L. Scott, C. Crippen, C.C. Santini and J.-M. Basset, *J. Chem. Soc., Chem. Commun.*, (1995) 1875.
- [77] S.L. Scott, J.-M. Basset, G.P. Nicolai, C.C. Santini, J.P. Candy, C. Lecuyer, F. Quignard and A. Choplin, *New J. Chem.*, 18 (1994) 115.
- [78] P. Dufour, S.L. Scott, C.C. Santini, F. Lefebvre and J.-M. Basset, *Inorg. Chem.*, 33 (1994) 2509.
- [79] M.I. Bruce and F.G.A. Stone, *J. Chem. Soc. A*, (1967) 1238.
- [80] P.C. Braunstein, J. Rose, Y. Dusauso and J.P.C. Mangeot, *R. Hebd, Seances Acad. Sci.*, 294 (1982) 967.