X-ray Photoelectron Spectroscopy as a probe of Rhodium-ligand interaction in ionic liquids

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Abstract

We use X-ray photoelectron spectroscopy (XPS) to identify the interaction between the rhodium atom and phosphine ligands in six 1-octyl-3-methylimidazolium-based ionic liquids ([C_8C_1Im][X]). The formation of a mono-phosphine rhodium complex based upon addition of triphenylphosphine (PPh_3) is confirmed by XPS in all ionic liquids studied herein. Due to the electron donation effect of the ligand, the rhodium atom becomes more negatively charged and thus exhibits a lower measured binding energy. The influence of the anion basicity on the formation of different types of rhodium complexes is also investigated. By introducing a biphosphine ligand, a chelated diphosphine rhodium complex is formed in ionic liquids with more basic anions and verified by both XPS and Infrared Spectroscopy (IR). The measured Rh 3d binding energies are correlated to the reaction selectivity of a hydroformylation reaction which inspires a method to design a metal catalyst to control the chemical reaction towards desired products in the future.

Introduction

Homogeneous catalysis is a large field of activity in the area of ionic liquids and has attracted lots of interests over the past decade.[1-4] Since ionic liquids exhibit a wide range of fascinating properties, *i.e.* low volatility and excellent solvating ability, they have shown huge potential for the replacement of the traditional organic solvents.[2, 5] As has been reported previously, many ionic liquids can dissolve organometallic compounds, allowing them to act as suitable solvents for transition metal based catalysis.

In many cases, they have been found to be better solvents when compared to traditional organic solvents, as well as water.[1] Ionic liquids have been successfully applied to many homogeneous catalytic reactions such as hydrogenation,[6] hydroformylation,[3] oxidation,[3] oligomerization[3] as well as coupling reactions, *i.e.* Heck reaction[7, 8] and Suzuki reaction.[8, 9] Using ionic liquids as reaction solvents can usually give rise to a different chemical activity of the system[10-17] and thus an acceleration[8, 9] or better selectivity towards the desired products,[18, 19] which renders them more valuable. An excellent example is the rhodium catalysed hydroformylation reaction. Rhodium based catalysts have been successfully applied to hydroformylation reactions in a biphasic ionic liquid/scCO_2 systems where the catalyst was firstly dissolved in ionic liquid phase and the product was extracted by scCO_2.[20-22] In the case of reactions catalysed by (Acetylacetonato)dicarbonylrhodium(I) ([Rh(acac)$(CO)_2$]), a potential problem is that the catalyst can be also extracted out of the ionic liquid phase. To overcome such problem, phosphine ligands were always added into the system to enhance the solubility of the catalyst in ionic liquid phase. This procedure aimed to avoid the leaching of the rhodium catalyst from the ionic liquid phase primarily. Unexpectedly, the reaction selectivity was somehow controlled; different phosphine ligands show different reaction selectivity towards the desired linear product.

Due to the low volatility of ionic liquids, XPS has been applied to characterise the elemental composition and subtle binding energy shifts of samples since 2005, when the Licence group measured the reduction of Pd(II) to Pd(0) in 1-ethyl-3-methylimidazolium ethylsulfate ($[C_2C_1Im][EtSO_4]$) by XPS.[23-25] It not only opened the door for the analysis of ionic liquid-based solutions by XPS but provided with an opportunity to further understand the processes involved when a metal catalyst is dissolved in ionic liquids, *i.e.* the metal-ligand interaction and the solute-solvent interaction[26]. Since then, there have been lots of publications from all over the world focusing on the use of XPS to analyse ionic liquid-based metal catalytic systems.[27, 28] In 2006, Maier *et al.* used angle resolved XPS (ARXPS) to analyse a platinum catalyst in $[C_2C_1Im][EtSO_4]$ and for the first time showed surface enrichment of the cation of the catalyst.[29] In 2008, Neatu *et al*. proved the chemical state of Au in an ionic liquid mixture using an XPS Au 4f high resolution spectrum together with Extended X-ray Absorption Fine Structure (EXAFS) measurements. In the same year, Nguyen *et al.* investigated the reduction of Fe in halometallate-based ionic liquids with the anions $[FeCl_4]^-$ and $[Fe_2Cl_7]^-$.[30] In 2009, Tao *et al.* analysed the presence of Pd(II) nanoparticles in ionic liquid-based catalytic systems on sepiolite.[31] Shortly after, the Licence group monitored the *in situ* electrochemical generation of an Fe(III) species in an ionic liquid system using XPS with a special EC-XPS set up.[32] In 2010, the same group also investigated the *in situ* dissolution of copper into ionic liquids by XPS.[33] Later in the same year, Kolbeck *et al.* investigated the ligand effect on the surface composition of Rh-containing ionic liquid systems by XPS.[34] In the same year, Apperley *et al.* analysed chloroindate-based ionic liquids by XPS together with EXAFS and found that there is indium chloride power suspended in the neutral tetrachloroindate ionic liquid.[35] Recent studies have highlighted that the XPS signals can act as reporters to tune the electronic environment of metal atoms in halometallate-based ionic liquids[36, 37] and as probes of solvent-solute interactions in ionic liquid-based palladium systems[26, 38]

In this study, we extend the use of XPS as an effective technique to investigate the rhodium-ligand interaction in ionic liquids. The ligand effect on the electronic environment at the rhodium centre for $[Rh(acac)(CO)_2]$ is explored. The formation of phosphine rhodium complex based upon the addition of phoshine ligands is confirmed by XP spectra. The influence of the basicity of the anion on the formation of different types of rhodium complexes is also investigated. The reaction selectivity of such catalytic system due to different types of metal-ligand interaction is correlated to the measured binding energies of Rh $3d_{5/2}$.

Experimental methods

Materials: All chemicals were obtained from Sigma-Aldrich or Alfa Aesar and were used as received except for 1-methylimidazole, which was distilled over calcium hydride prior to use. Lithium bis[(trifluoromethane)sulfonyl]imide was obtained from 3M and used as received. All ionic liquids investigated in this study were prepared in our laboratory using established synthetic protocols, $[C_8C_1Im][OAc]$,[39] $[C_8C_1Im]Cl$,[40] $[C_8C_1Im][BF_4]$,[41]

$[C_8C_1Im][TfO]$,[42] $[C_8C_1Im][PF_6]$,[40] and $[C_8C_1Im][Tf_2N]$.[43] The structures of the individual cations and anions investigated in this study are shown in Table S1.

Unless otherwise stated, all ionic liquids were characterised by ^1H and ^{13}C NMR; spectra were recorded on a Bruker DPX-300 spectrometer at 300 and 75 MHz respectively as solutions in $CDCl_3$ and DMSO-d_6. When anion exchange was one of the synthetic steps, ion chromatographic analysis showed that halide concentration < 10 ppm. No halide signal was observed by XPS analysis, *i.e.*, the concentration was below the limit of detection in every case. Full data for all materials studied in this work appears in the supplementary information.

Sample preparation: In this study, Rh-containing ionic liquid-based samples were prepared using PPh_3 and 1,1'-Bis(diphenylphosphino)ferrocene (dppf) as ligands. Moreover, since the rhodium catalyst shows limited and slow solubility in ionic liquids, dichloromethane was added into the mixture to speed up solvation processes.[44, 45] The addition of dichloromethane allows full contact of the catalyst and ionic liquids as they are both dissolved in dichloromethane. Dichloromethane can then be removed, firstly under rotary evaporator and then under high vacuum at room temperature for more than 12 hours, to give Rh-containing ionic liquid based samples. It must be noted that the signal to noise ratio of the Rh 3d spectrum is relatively low when compared to the other spectra. This is due to the relatively low concentration of $[Rh(acac)(CO)_2]$ in the ionic liquid solution, *i.e.* lower than 0.02 atomic % in all cases.

XPS Data Collection: All XP spectra were recorded using a Kratos Axis Ultra spectrometer employing a focused, monochromated Al Kα source ($h\nu$ = 1486.6 eV), hybrid (magnetic/electrostatic) optics, hemispherical analyser and a multi-channel plate and delay line detector (DLD) with a X-ray incident angle of 30° and a collection angle, θ, of 0° (both relative to the surface normal). X-ray gun power was set to 100 W. All spectra were recorded using an entrance aperture of 300×700 μm with a pass energy of 80 eV for survey spectra and 20 eV for high-resolution spectra. The instrument sensitivity was 7.5×10^5 counts s^{-1} when measuring the Ag $3d_{5/2}$ photoemission peak for a clean Ag sample recorded at a pass energy of 20 eV and 450 W emission power. Ag $3d_{5/2}$ full width half maximum (FWHM) was 0.55 eV for the same instrument settings. Binding energy calibration was made using Au $4f_{7/2}$ (83.96 eV), Ag $3d_{5/2}$ (368.21 eV) and Cu $2p_{3/2}$ (932.62 eV). The absolute error in the acquisition of binding energies is ±0.1 eV, as quoted by the instruments manufacturer (Kratos); consequently, any binding energies within 0.2 eV can be considered the same, within the experimental error. Charge neutralisation methods were not required (or employed) in the measurement of these data. Sample stubs were earthed *via* the instrument stage using a standard BNC connector.

Samples were prepared by placing a small drop (≈ 20 mg) of the ionic liquid into a depression on a stainless steel sample stub (designed for powders) or on a standard stainless steel multi-sample bar (both Kratos designs). The ionic liquid samples were presented as thin films (approx. thickness 0.5-1 mm), thereby avoiding experimental complications associated with variable sample height. Initial pumping to high vacuum pressure was carried out in a preparation chamber immediately after thin film preparation to avoid significant absorption of volatile impurities. Pumping of ionic liquids was carried out with care as the high viscosities associated with these samples meant that significant bubbling due to removal of volatile impurities was observed. The pumping down process was consequently carried out slowly to avoid contamination of the UHV chamber by bumping/splashing of the ionic liquid samples. The preparation chamber pressure achieved was $\approx 10^{-7}$ mbar. Pumping-times varied (1-3 hr total) depending upon the volume, volatile impurity content and viscosity of the sample, *i.e.*, viscous ionic liquids were found to require longer pumping times. The samples were then transferred to the main analytical vacuum chamber. The pressure in the main chamber remained $\leq 1 \times 10^{-8}$ mbar during all XPS measurements, suggesting that all volatile impurities, such as water, are removed, leading to high purity samples.[46]

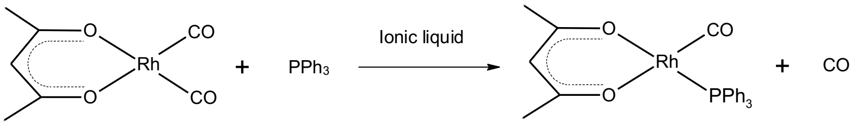
Information Depth of XPS: The information depth (ID) of XPS experiments may be defined as the depth, within the sample, from which 95% of the measured signal will originate. ID is assumed to vary mainly with cos θ, where θ is the electron emission angle relative to the surface normal. Values of λ are typically in the range of 1-3 nm.[47] If we assume that the inelastic mean free path (λ) of photoelectrons in organic compounds is of the order of ~3 nm, at the kinetic energies employed here we can estimate ID in this geometry, when $\theta = 0°$, ID = 7-9 nm. Consequently these data may be considered as representative of the bulk composition and do not reflect any local enhancements of concentration at the near surface region.

XPS Data Analysis: For data interpretation, a linear spline background subtraction was used. Relative Sensitivity Factors (RSF) were taken from the Kratos Library and were used to determine atomic percentages.[48] Peaks were fitted using GL(30) lineshapes; a combination of a Gaussian (70%) and Lorentzian (30%).[47] This lineshape has been used consistently in the fitting of XP spectra, and has been found to match experimental lineshapes in ionic liquid systems. The FWHM of each component was initially constrained to $0.8 \leq \text{FWHM} \leq 1.5$ eV. XP spectra for $[C_8C_1Im][A]$ ionic liquid solutions were charge corrected by setting the measured binding energy of the aliphatic C 1s component ($C_{aliphatic}$ 1s) to 285.0 eV. This procedure has been shown to be robust for all samples when alkyl substituents on charge carriers are large (*i.e.*, when $n \geq 8$).[49-51] A fitting model has been developed for charge referencing samples where the anion is $[OAc]^-$.[26]

Results and Discussion

Formation of the mono-phosphine rhodium complex

It is well known that $[Rh(acac)(CO)_2]$ can react with phosphine ligands at room temperature in ionic liquids and thus form a new rhodium catalytic system, as according to Scheme 1.[34, 52]



Scheme 1 Reaction of [Rh(acac)(CO)$_2$] with PPh$_3$ in ionic liquids

The coordination of the phosphine ligand to the rhodium centre affects its electronic environment and thus reflects the shift of its measured binding energy. One equivalent of a phosphine ligand, PPh$_3$, was added to the Rh-containing ionic liquid solution and the new system was analysed by XPS.

Figure S1 shows a survey XP spectrum for a solution of [Rh(acac)(CO)$_2$] dissolved in [C$_8$C$_1$Im][Tf$_2$N]. This ionic liquid solution will be used as a case study to describe the principal XPS features. XPS signals were observed for all expected elements, as was the case for each of the ionic liquid solutions presented herein. Previous XPS studies of ionic liquids from various groups have shown the presence of impurities in the near-surface region of ionic liquids that could not be detected using NMR or other bulk sensitive techniques.[23, 53-56] Figure S1a shows no indication of any impurities present in the solution.

The regions due to elements in the ionic liquid are shown in Figures S1b-f; the Rh 3d region is shown in Figure S1g. All components fitted are labelled in Figures S1b-f, and have previously been identified.[49] The XP spectra given in Figures S1b-f are qualitatively the same as those recorded for simple [C$_8$C$_1$Im][Tf$_2$N],[49] within the experimental error (see Table S2 in the Supplementary Information). This observation demonstrates that the Rh solute does not affect the electronic environment of the bulk ionic liquid sufficiently to influence the ionic liquid XPS binding energies, as expected as the Rh solute is in low concentrations (for detection of XPS binding energy shifts) in all cases.

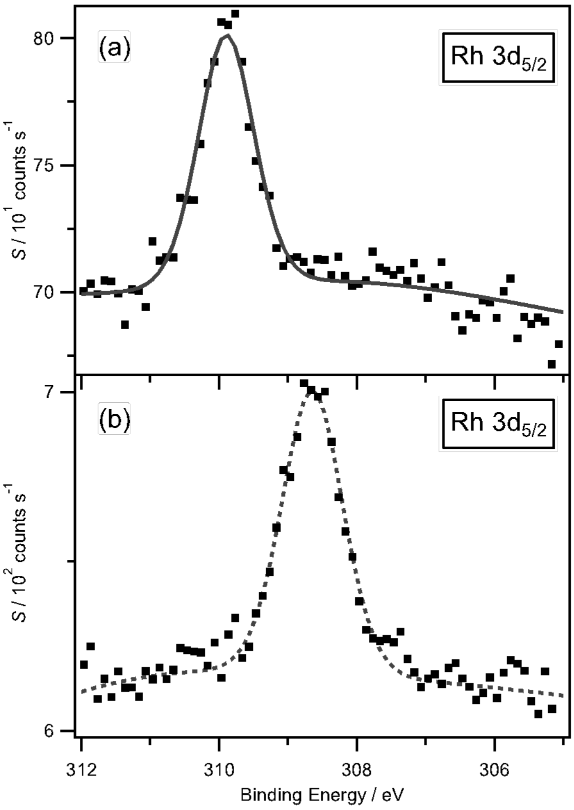


Figure 1 XP spectra of Rh $3d_{5/2}$ for [Rh(acac)(CO)$_2$] in [C_8C_1Im][Tf_2N] (a) and [Rh(acac)(CO)$_2$] plus PPh_3 in [C_8C_1Im][Tf_2N] (b). All XP spectra were charge corrected by referencing the $C_{aliphatic}$ 1s component to 285.0 eV.

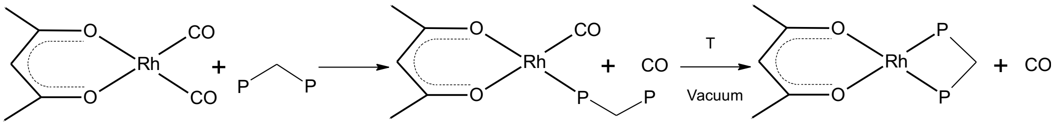
A comparison of the Rh $3d_{5/2}$ high resolution spectra of [Rh(acac)(CO)$_2$] and the new PPh_3-containing rhodium complex are shown in Figure 1. The Rh 3d high resolution spectrum is composed of a doublet peak which originates from the 3d orbital with a spin-orbital coupling energy difference of 4.74 eV,[57] and area ratio of $3d_{5/2}$: $3d_{3/2}$ is 3:2 (see Figure S2g), as expected from theory. In this study, unless otherwise stated, the $3d_{5/2}$ component is selected to ensure valid comparisons, simply because the intensity for this component is greater. The XP spectra indicate how the Rh $3d_{5/2}$ binding energies shift upon the addition of the ligand. The measured binding energy of Rh $3d_{5/2}$ for the [Rh(acac)(CO)$_2$] solution is 309.9 eV which is consistent with that obtained in literature for solid [Rh(acac)(CO)$_2$].[58, 59] The measured binding energy of Rh $3d_{5/2}$ for the ligand-containing solution is 308.7 eV which is 1.2 eV lower than that of the reference [Rh(acac)(CO)$_2$] solution. This observation suggests that the ligand is coordinated to the rhodium centre. Phosphine ligands are well known to be electron donors.[60] The electronic donating effect of the ligand gives rise to a rhodium centre in a more electron rich environment Moreover, CO is considered as a strong PI-acceptor ligand. The elimination of one CO group leads to further negatively charged rhodium centre, which is observed at a lower binding energy.

The ligand-containing ionic liquid solutions were prepared in a range of different

$[C_8C_1Im]^+$-based ionic liquids with commonly used anions. The measured binding energies of Rh $3d_{5/2}$ in all $[C_8C_1Im]^+$-based ionic liquids are the same (see Table S2), which indicates that ionic liquid components are spectators and have no impact on the electronic environment of the rhodium centre. This observation suggests that ionic liquids have no impact on inner sphere electronic change at the metal centre and may be considered as spectators in neutral solute systems.

Investigation of the chelated diphosphine rhodium complex

Since there is the coordination between $[Rh(acac)(CO)_2]$ and phosphine ligands,[34, 52] the presence of a diphoshine ligand, *i.e.* 1,1'-bis(diphenylphosphino)-ferrocene (dppf), could result in a more complicated coordination scenario.[61] Upon addition of the phosphine ligand, immediately, the first CO group within $[Rh(acac)(CO)_2]$ will be substituted to form a mono-phosphine rhodium complex. However, by simply heating or evacuating, the second CO group could eventually be substituted to form a diphosphine rhodium complex, see Scheme 2.



Scheme 2 Reaction of $[Rh(acac)(CO)_2]$ with a diphosphine ligand in ionic liquids

As has been reported previously in our group, the basicity of the anion is a key factor in determining the charge transferred from the anion to the cation, and thus the measured binding energy for cation-based components.[26, 49-51] It also influences the physical or chemical properties of the ionic liquids, *i.e.* dipolarity or polarisability.[62] Consequently, it is assumed that during the processes of CO group substitution using ionic liquids as the reaction solvents, a degree of reactive control could be afforded by carefully selecting/tuning of the reaction solvent.

Three dppf-containing solutions in ionic liquids with anions of different basicity, *i.e.* $[C_8C_1Im][Tf_2N]$, $[C_8C_1Im][TfO]$ and $[C_8C_1Im][OAc]$, were prepared and analysed by XPS. As shown in Figure 2(a), in ionic liquids anions of low basicity, *i.e.* $[C_8C_1Im][Tf_2N]$, XPS data suggests that only a mono-phosphine rhodium complex is formed with a measured binding energy of Rh $3d_{5/2}$ at 308.7 eV, which is consistent with those obtained for PPh_3-containing solutions. This observation was confirmed by Infrared (IR) Spectroscopy. In the IR spectrum, only one CO group stretching vibration[63] at 2012 cm^{-1} was observed for the dppf-containing solution in $[C_8C_1Im][Tf_2N]$, which replaced the two CO stretching vibrations for $[Rh(acac)(CO)_2]$ (2075, 2015 cm^{-1}).

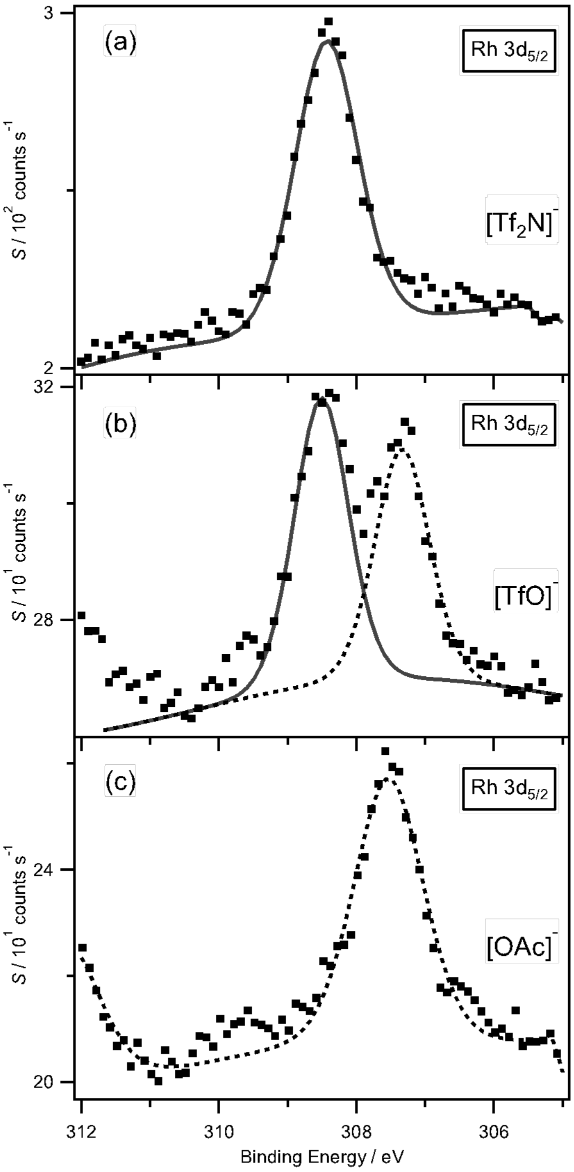


Figure 2 XP spectra of Rh $3d_{5/2}$ for $[Rh(acac)(CO)_2]$ plus dppf in $[C_8C_1Im]^+$-based ionic liquids (a) $[Tf_2N]^-$, (b) $[TfO]^-$ and (c) $[OAc]^-$. All XP spectra were charge corrected by referencing the $C_{aliphatic}$ 1s component to 285.0 eV.

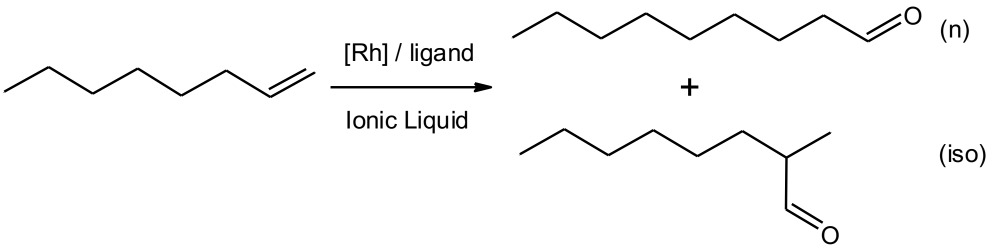
In ionic liquids with anions of high basicity, *i.e.* $[C_8C_1Im][OAc]$, it is apparent that only a diphosphine rhodium complex is formed, with a measured binding energy of Rh $3d_{5/2}$ at 307.5 eV, see Figure 2c. Moreover, in the IR spectrum, no CO group stretching vibration was observed, confirming the formation of a chelated diphosphine rhodium complex.

In the case of $[C_8C_1Im][TfO]$, since the basicity of $[TfO]^-$ lies in between that of $[Tf_2N]^-$ and $[OAc]^-$, the XP spectrum indicates two different Rh electronic environments showing binding energies at 308.6 eV and 307.4 eV respectively, see Figure 2b. The higher binding energy is very similar, certainly within the experimental error to that obtained for the singly coordinated dppf-containing complex in $[Tf_2N]^-$-based solution. The lower binding energy is consistent to that obtained for the chelated bidentate dppf-containing in $[OAc]^-$-based solution. It suggests that both mono- and chelated diphosphine rhodium complexes are formed in [C_8C_1Im][TfO]. The results in this section suggest that ionic liquids can impact upon the coordination of a ligand to the rhodium centre in [Rh(acac)$(CO)_2$], specifically the substitute of the second CO group. It must be noted that the ratio of monodetate and bidentate complexes is roughly 1:1, as shown in Figure 2b. As has been stated in the sample preparation section, in all cases, samples were under high vacuum for at 12 hours. Consequently, it is expected that Figure 2b shows the final state of the formation of diphosphine rhodium complex in [C_8C_1Im][TfO]. The reason why the substitution of the second CO group stopped at a certain extent is still unknown to the best of our knowledge. However, it is worth further future work on more carefully comparison of the formation of bidentate complexes at different point.

As has been stated in the sample preparation section, the signal to noise ratio of the Rh 3d spectrum is relatively low when compared to the other spectra. This is due to the low concentration of catalyst in the ionic liquid solution. Although the acquisition time of the Rh 3d spectrum is much longer than that of other cases, it contains unexpected increase of the background in the spectrum, as shown in Figure 2b, 2c and 3b. However, to the best of our knowledge, this is mainly due to the lower signal to noise ratio of the Rh 3d spectrum. Consequenly, these types of increase of background were not discussed in this paper.

An outlook of the correlation of reaction selectivity and binding energy

As mentioned earlier, ionic liquids can be used as solvents for hydroformylation reactions.[3] When different phosphine ligands are applied to the [Rh(acac)$(CO)_2$] catalysed hydroformylation of 1-octene in ionic liquids (see Scheme 3), they are found to improve the solubility of the catalyst, and also show different reaction selectivity towards the desired linear product, *i.e.* n-nonanal, *e.g.* 79% upon addition of dppf as ligand compared to that of 72% with PPh_3 as ligand.[19]



Scheme 3 The hydroformylation of 1-octene in ionic liquid

The reason different phosphine ligands show different reaction selectivity towards the desired linear product in the hydroformylation reaction may be due to the formation of different rhodium complexes in ionic liquids. The formation of different types of rhodium complexes by addition of different ligands, *i.e.* PPh_3 and dppf, in ionic liquids with anions of high basicity, *i.e.* [C_8C_1Im][OAc], has been illustrated in this study.

Figure 3 shows the Rh $3d_{5/2}$ high resolution XP spectra for the solutions of [Rh(acac)$(CO)_2$] plus two ligands with a 1:1 molar equivalent (catalyst : ligand) in [C_8C_1Im][OAc]. It is evident that the measured Rh $3d_{5/2}$ binding energies for both solutions are lower than that obtained for [Rh(acac)(CO)$_2$] (309.9 eV, see Table S2). This suggests that both of the ligands have coordinated to the rhodium centre and thus influenced its electronic environment. The binding energy of Rh $3d_{5/2}$ for the dppf-containing solution (see Figure 3b) is 1.2 eV lower when compared to that obtained for the PPh$_3$-containing solution (see Figure 3a). The lower binding energy of Rh $3d_{5/2}$ for the dppf-containing solution means that the corresponding Rh centre is more electron rich when compared to the PPh$_3$-containing analogue. XPS data can thus be used to quantify the difference in the amount of charge transferred to the rhodium centre. It provides with an outlook in the future work to correlate the reaction selectivity of a certain chemical reaction to the measured binding energy of a certain metal atom of a catalyst.

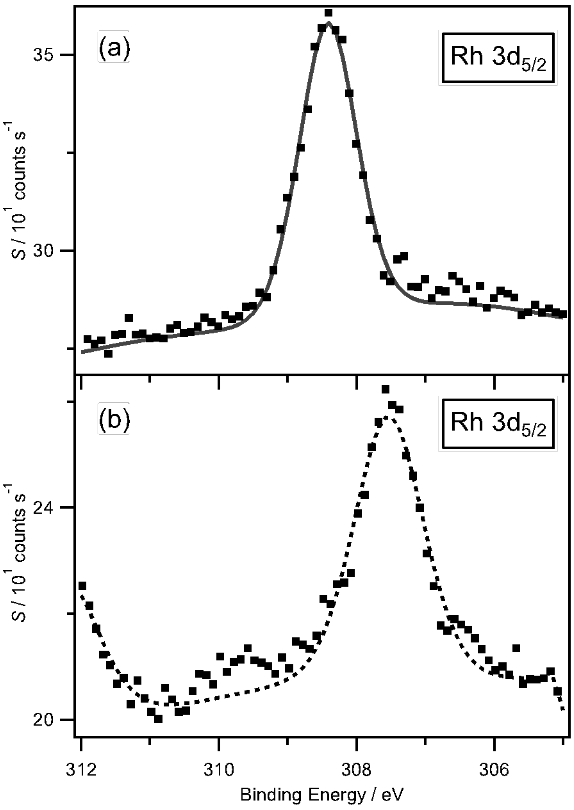


Figure 3 XP spectra of Rh $3d_{5/2}$ for [Rh(acac)(CO)$_2$] plus PPh$_3$ (a) and dppf (b) in [C$_8$C$_1$Im][OAc]. All XP spectra were charge corrected by referencing the C$_{\text{aliphatic}}$ 1s component to 285.0 eV.

Conclusions

In this study, XPS has been used as an effective method for the analysis of ionic liquid-based metal catalyst solutions. Rh-containing ionic liquid-based solutions, with a variety of ligands, for the use in hydroformylation reactions were analysed and the reaction selectivity data were correlated to the binding energies of the Rh centre. The differences in electronic environment were quantified for different Rh centres in solution. Moreover, the formation of Rh-containing complexes was monitored by XPS. In the case of the mono-phosphine ligand, *i.e.* PPh_3, the binding energies of Rh 3d for all Rh-containing solutions are the same, within the experimental error. In the case of diphosphine ligands, *i.e.* dppf, the influence of anion basicity on the formation of the diphosphine rhodium complex was discussed and confirmed by XPS in conjunction with IR spectrocopy. It was concluded that in ionic liquids with anions of low basicity, *i.e.* $[Tf_2N]^-$, only a mono-phosphine rhodium complex can be formed; but in ionic liquids with anions of high basicity, *i.e.* $[OAc]^-$, only a diphosphine rhodium complex is observed.

XPS can also be used to quantify the difference in the amount of charge transferred to the metal centre. The reaction selectivity for the hydroformylation reaction was correlated to the measured binding energies for the Rhodium centres of the catalytic systems. It provides with an outlook in the future work to correlate the reaction selectivity of a certain chemical reaction to the measured binding energy of a certain metal atom of a catalyst. Based upon this outlook, it is worth to employ more types of phosphine ligands in the future work, *e.g.* $P(Me)_3$ and dppe. It also inspired the idea of designing a metal catalyst to enhance reaction selectivity for the future work.

Acknowledgements

We thank the EPSRC (EP/K005138/1), General project of Science and Technology Research Project of Liaoning Provincial Department of Education (L2015461) and China Postdoctoral Science Foundation funded project (2015M571344) for financial support. PL acknowledges the EPSRC for the award of an ARF (EP/D073014/1). SM acknowledges Shenyang Ligong University for the award of an Open Fund of the Key Discipline (4771004kfx18). The authors are grateful to Dr Emily F. Smith for helpful discussions and critical advice.

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