ELSEVIER Journal of Electron Spectroscopy and Related Phenomena 128 (2003) 141–157

JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena

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Preparation of solid-state samples of a transition metal coordination compound for synchrotron radiation photoemission studies

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Received 16 August 2002; received in revised form 21 October 2002; accepted 22 October 2002

Abstract

The aim of this research was to identify a sample preparation method suitable for the study of transition metal complexes by photoemission spectroscopy with synchrotron radiation as the X-ray source, even in the case where the compound is not evaporable. Solid-phase samples of $W(CO)_4$(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane] were prepared according to different methods and their synchrotron radiation XPS spectra measured. The spectra acquired from samples prepared by spin coating show core level peaks only slightly broader than the spectrum recorded from UHV evaporated samples. Moreover, for these samples the reproducibility of the binding energy values is excellent. The dependence of the spin coating technique on parameters such as solvent and solution concentration, spinning speed and support material was studied. The same preparation method also allowed the acquisition of valence band spectra, the main peaks of which were clearly resolved. The results suggest that use of the spin coating technique may allow us to reveal small differences in core level binding energies due to ligand substitution.

Keywords: Synchrotron radiation; Sample preparation; Transition metal complexes; Spin coating; Photoemission spectroscopy; Tungsten carbonyl phosphine

1. Introduction

Transition metal coordination compounds (TMCCs) play a relevant role in many applications of modern chemistry, such as homogeneous catalysis and bioinorganic chemistry. Their importance is mainly due to the endless possibilities of varying the chemical environment around the metal atom, which is the site where the catalytic reaction takes place. This variation may affect both the steric distribution of the ligands around the metal and the electron densities on the metal and the ligands. The clearest demonstration of this dependence is given by the fact that small variations of the structure of a ligand can turn an efficient catalyst into an inert complex.

Photoemission spectroscopy, particularly photoemission from core levels (XPS), provides an important contribution to the evaluation of the electron

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0368-2048/02/$ – see front matter
PII: S0368-2048(02)00272-4

density both on the metal and on the ligands, and indeed its application to TMCCs has been well known for the last 30 years [1]. However, in order to detect very small differences in core level binding energies (BEs), which can be associated with small variations in the structure of the complex, it is necessary to acquire XPS spectra with a very high energy resolution (≈0.1 eV).

The use of synchrotrons as X-ray sources has given new life to photoemission spectroscopy, allowing incomparable energy resolution and photon energy tunability within a very wide continuous range. However, up to now the application of synchrotron radiation XPS to TMCCs has been limited to complexes which can be evaporated to the gas phase [2], and these are very few compared with the total of TMCCs. The inherent insulating nature of these compounds causes broadening and shifting of their photoemission peaks when they are acquired from solid-state samples. Moreover, the shift depends on the distance between the molecule and the conducting support, i.e. the layer in which the photoemitting molecule is lying, thus giving rise to differential charging [3]. Such problems were much less severe in early XPS spectrometers, which used X-ray sources delivering a high divergence beam, because the X-ray flux density was considerably more uniform than in modern systems, the monochromatized sources of which deliver smaller spots [4]. Moreover, in the XPS process itself, there are often sufficient stray, low-energy electrons from Bremsstrahlung and other processes to partially neutralize the charge centres. On the other hand, when a monochromator is used, we have a relatively electron-clean environment around the sample [5], and only recently some monochromatized spectrometers have been modified to minimize charge broadening [6]. However, problems due to differential charging become unacceptable if synchrotron radiation is used as the source, owing to its brightness and the dependence of the photon flux on time.

To obtain useful information, and particularly to exploit the high-resolution characteristics of synchrotron light in the application to solid-state TMCC samples, a charge neutralizing technique is required that completely eliminates this differential charging on the surface.

Several systems have been applied to solve the problem of differential charging on solid, nonconducting samples, such as evaporation of thin gold layers on TMCC samples [7], or the use of a low kinetic energy electron flood gun [4,6]. Unfortunately, neither of these methods is a general solution, since they often lead to sample decomposition. Several articles have reported XPS measurements of TMCC where the samples were prepared by brushing the thin sample powder on a conducting support [8] or dipping the support in a solution of the sample [1b]. However, these techniques can only be applied for traditional X-ray source experiments, and they cannot solve the differential charging problem when synchrotron light is used, as we show in the present paper.

In 1976, Bancroft et al. published a paper on the solid-state broadening effect for XPS studies of tin organometallic compounds [9]. They clearly demonstrated that, even with a traditional X-ray source, the only method for acquiring XPS spectra from solid-state TMCC samples with characteristics similar to those obtained from gas-phase samples is the in situ UHV evaporation of the compound on a conducting support. Analogous results were reported by Lichtenberger et al. for chromium, molybdenum and tungsten complexes [10]. Unfortunately, this technique is feasible only for evaporable compounds.

Several recent publications report comparisons of XPS measurements on solid-state TMCC samples, where the authors rationalize quite small differences in BE (≈0.1 eV) without taking into account the poor overall resolution of their experimental system (≈0.8 eV for nonmonochromatized sources, plus ≈1.0 eV due to differential charging), even if the obtained data appear to be reproducible over time and measurement sets.

In the present paper we report a study of the dependence of broadening effects on the sample preparation method. We acquired synchrotron radiation XPS spectra from samples of a TMCC prepared by various techniques, either traditional (brushing and dipping) or more innovative (spin coating), and compared the results with data published in the literature for gas-phase samples or nonsynchrotron radiation X-ray sources. The main goal was to identify a procedure which would minimize differential charging, thus allowing the acquisition of synchrotron radiation XPS spectra from solid-state samples even for nonevaporable TMCCs. With the same technique it would also be feasible to acquire XPS spectra using monochromatized X-ray sources in order to measure core level BE with higher resolution.

2. Experimental

2.1. General

All the reactions and manipulations were routinely performed under an argon atmosphere using standard Schlenk tube techniques. $W(CO)_6$ (Strem), 1,2-bis-(diphenylphosphino)ethane (dppe) (Strem), bis(2-methoxyethyl)ether (diglyme) and all other chemicals were reagent grade and were used as received from the commercial suppliers. The compound $W(CO)_4(dppe)$ was prepared according to the procedure reported in the literature [11] with slight modifications (vide infra).

2.2. Instrumental

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL EX400 spectrometer operating at 399.77, 100.54 and 161.82 MHz, respectively. ^1H chemical shifts are reported relative to tetramethylsilane; ^{13}C chemical shifts are reported relative to the solvent peak (for $CDCl_3$ δ 77.0); ^{31}P chemical shifts are reported relative to 85% H_3PO_4 as external standard, with downfield shifts taken as positive. Infrared spectra were recorded in Nujol mull on a FT-IR Perkin-Elmer System 2000 spectrometer.

2.3. Preparation of $W(CO)_4(dppe)$

Tungsten hexacarbonyl (1.0 g, 3.0 mmol) and dppe (1.2 g, 3.0 mmol) were added into a Schlenk tube containing 5 ml of diglyme. The reaction mixture was heated at reflux for 45 min, during which time the hexacarbonyl sublimed on the Schlenk walls was periodically returned to the solution by vigorous shaking. The brown solution obtained was cooled to room temperature, yielding a light-yellow solid. Addition of 5 ml of methanol to complete the precipitation of the product was followed by filtration: the solid thus obtained was washed with methanol and dried in vacuo. Yield 76%. ^1H NMR ($CDCl_3$, 25 °C): δ 7.6–7.3 (m, 20H, Ar), 2.59 (m, 4H, CH_2); ^{31}P NMR ($CDCl_3$, 25 °C): δ +40.6 (s, J_{PW} 231.7 Hz); ^{13}C NMR ($CDCl_3$, 25 °C): δ 208.2 (dd, CO *trans* P, $J_{CPtrans}$ 25.4 Hz, J_{CPcis} 6.9 Hz), 201.3 (t, CO *trans* CO, J_{CP} 6.9 Hz), 136.4–128.7 (Ar), 29.9 (m, CH_2). IR (Nujol) 2011, 1909, 1886, 1875 cm^{-1} (ν_{CO}).

2.4. XPS measurements

The samples for XPS were prepared by the following procedures:

(a) *brushing*: ≈50 μg of a very thin powder of the compound was spread onto a clean gold foil, and then rubbed with a quartz rod until a very thin layer intimately pressed on the gold surface was obtained;
(b) *dipping*: ≈2 mg of the compound was dissolved in 10 ml of acetone; a clean gold foil was dipped into the solution and then left to dry in air;
(c) *spin coating*: a solution of the compound at the desired concentration was prepared in the solvent of choice (acetone, chloroform, mesitylene or dichloromethane); a few drops of the solution were then placed on the surface of the support and the spin coater was started for 5 min, at the appropriate spinning rate, until complete evaporation of the solvent. The spin coater used was a Model P6708 from Specialty Coating Systems Inc.;
(d) *UHV evaporation*: thin films of the compound were deposited on a gold foil surface that had been previously cleaned by Ar ion sputtering; evaporation of the compound occurred from a quartz crucible heated at 420 K inside the UHV preparation chamber and the film thickness was determined by a quartz crystal monitor. Compound integrity was verified by off-line evaporation on a thin silicon wafer and subsequent comparison of its infrared spectrum with analogous spectra obtained on solution and spin coated specimens. Samples for XPS measurements were prepared by progressive evaporation of small amounts of compound, and the depositions were precisely controlled by monitoring the

W 4f, P 2p and Au 4f core level intensities for each evaporation. The pressure in the preparation chamber was $<2.0\times10^{-9}$ mbar during preparation.

Each sample was then introduced into the experimental chamber through a load-lock chamber. During all measurements, the experimental chamber pressure was no higher than 2.0×10^{-10} mbar. No evaporation of the compound from the gold support occurred at room temperature in UHV. The sample holder on the manipulator allowed sample cooling at 110 K, as well as gentle warming by a resistance placed behind the sample.

All XPS and UPS spectra were recorded by an angle-integrated Omicron EA 125 HR energy analyzer mounted in the experimental chamber of the VUV-Photoemission beam-line [12] at the Elettra Synchrotron Facility (Trieste-I). The synchrotron radiation beam was normal incident with respect to the surface; photoelectrons were collected with the analyzer axis at 45° to the substrate surface normal.

The photon energy was fixed for all core level spectra at 201.31 eV, which was the best compromise in order to maximize the photoionization cross-sections for both W 4f and P 2p core levels [13]. To ensure high energy resolution and to minimize sample decomposition, the spectra were acquired with a pass energy of 5 eV, and both beam-line slits closed at 10 μm each, thus decreasing the photon flux on the sample. The resulting overall instrumental resolution (photons plus electrons) was 0.10 eV.

2.5. UPS measurements

Valence level spectra of the sample prepared by the spin coating procedure were acquired under the same conditions as for the XPS spectra, but with the photon energy set at 80.25 eV, in order to compare our results with the spectra acquired for analogous complexes in the gas phase and already published in the literature [14], and at 49.18 eV, to detect peak intensity changes induced by cross-section variations. Two spectra were recorded under the same conditions (at 80.25 and 49.18 eV) from the gold supports, as they appear before deposition of the compound, in order to acquire the background spectra to be subtracted from the sample spectra.

2.6. Data analysis

For both XPS and UPS spectra, the sum of several (8–16) rapid, single scan spectra (≈85 s/scan), each recorded on a fresh sample area (≈0.1 mm^2), gave a final spectrum with a higher signal/noise ratio and careful control of the homogeneity of the compound distribution on the sample. Spectra were fitted with a Gaussian–Lorentzian line shape using a nonlinear least-squares procedure, modified to allow the variation of both Gaussian and Lorentzian components for each doublet of peaks present in the spectrum.

For each sample, W 4f and P 2p binding energies were referenced to the Au $4f_{7/2}$ peak at 84.00 eV, thus eliminating any error due to fluctuation of photon energy or electron kinetic energy.

2.7. AFM images

AFM images were recorded with a AFM microscope designed and built by the A. Cricenti group in the ISM laboratories, Rome [15]. The maximum lateral resolution was about 20 nm. In order to optimize the AFM measurements, the images were recorded on samples prepared by spin coating on a steel support mechanically polished down to 0.1 μm roughness.

3. Results and discussion

3.1. Choice of compound

In order to fully evaluate the effects of the preparation method on the quality of the XPS spectra, a careful choice of the model compound had to be made. We chose to carry out the tests on $W(CO)_4$(dppe) samples for the following reasons: (i) W 4f are very narrow core levels, therefore they are particularly suitable for the evaluation of the broadening caused by differential charging; (ii) the P 2p core levels are also useful, because phosphorus-based ligands are widely used in organometallic chemistry and the possibility to visualize their spin–orbit splitting offers a further indication of reduced differential charging; (iii) the room temperature vapor pressure of this compound is low enough to avoid any evaporation in UHV, but the compound can be evaporated by rather moderate heating without thermal decomposition, thus allowing analysis of solid-state, gas-phase and evaporated samples; (iv) the compound is soluble in many common organic solvents and its solutions are quite stable, thus allowing good flexibility of applications; (v) many physico-chemical data on analogous complexes are available in the literature [16]; (vi) several papers have been published on the photoemission spectroscopy of phosphine carbonyl complexes of molybdenum and tungsten, particularly because of the interest in the effect of variation of the phosphine ligand [14,17,18] and the nature of the phosphorus–metal bond [19].

3.2. Comparison of the different preparation methods

The preparation methods were chosen from traditionally used XPS techniques (brushing and dipping) and more innovative methods (spin coating). The latter is commonly used in the deposition of photoresists on semiconductors during the preparation of electronic devices, and the underlying physics has been studied [20]. However, its use for the preparation of samples for photoemission spectroscopy is mainly limited to conjugated polymers [21], whereas its application to the preparation of TMCC samples is still rather uncommon and has not been thoroughly investigated [22]. The last method tested was UHV evaporation, since this technique is known to give the best control of the homogeneity and thickness of the deposited material [9]. Therefore, the samples produced in this way ensured minimization of the differential charging phenomena, and the photoemission spectra should be considered as the optimal results obtainable from solid-state samples.

For each sample, the quality of the spectrum was evaluated on the basis of the BE of the core level peaks, since a higher BE indicates higher charging, and of the Gaussian FWHM (Γ), since a less homogeneous deposition of the molecules on the surface—upon a statistical distribution—leads to a broader peak, i.e. a higher Γ. Moreover, a full comparison with the results reported by other authors is meaningful only on the basis of Γ, whereas BEs are more affected by differences in the experimental setup.

3.3. W 4f measurements

The W 4f XPS spectra of the compound $W(CO)_4$(dppe), acquired for samples prepared by different methods, are shown in Fig. 1. The doublet peaks due to the original compound can be observed at about 163 and 165 eV kinetic energy (KE). The second doublet at much lower KE (158–160 eV) is related to a molecular species with the tungsten atom in a higher oxidation state and is produced by decomposition of the original compound during sample preparation. Its intensity depends on the sample preparation procedure, but it does not change upon beam exposition.

On the other hand, the compound was shown to decompose upon beam exposition, thus leading to a third, very large doublet at about 162 and 164 eV. In order to minimize the latter decomposition, we reduced both the photon flux on the sample and the acquisition time for each single point of the scan, thus obtaining very quick single scans.

The spectra obtained by this procedure were analyzed by peak fitting, thus allowing the identification of the components contributing to the total spectrum, and a more precise measurement of the KE, intensity and width of the single components. An example of the fit is shown in Fig. 2, which shows the W 4f core level spectrum obtained from the sample prepared by spin coating from a CH_2Cl_2 solution. Three components can be identified: the first and most intense is due to the W 4f atoms in the original complex, $W(CO)_4$(dppe) [W $4f_{5/2}$ KE = 163.143(6) eV, $\Gamma = 0.680(14)$ eV]. The second, broader component [W $4f_{5/2}$ KE = 162.176(282) eV, $\Gamma = 1.265(633)$ eV] is related to the species originating from sample decomposition upon beam exposition, whereas the third component [W $4f_{5/2}$ KE = 158.546(75) eV, $\Gamma = 1.301(138)$ eV] is related to decomposition of the compound during sample preparation. The intensity of the second component is only 10% of that of the signal of the original compound. However, when several scans are acquired on the same spot of the sample (thus leading to progressive compound decomposition upon beam exposition), we observe a reduction of the component relative to the original compound and a corresponding increase of the second component, which at the same time becomes much broader. With

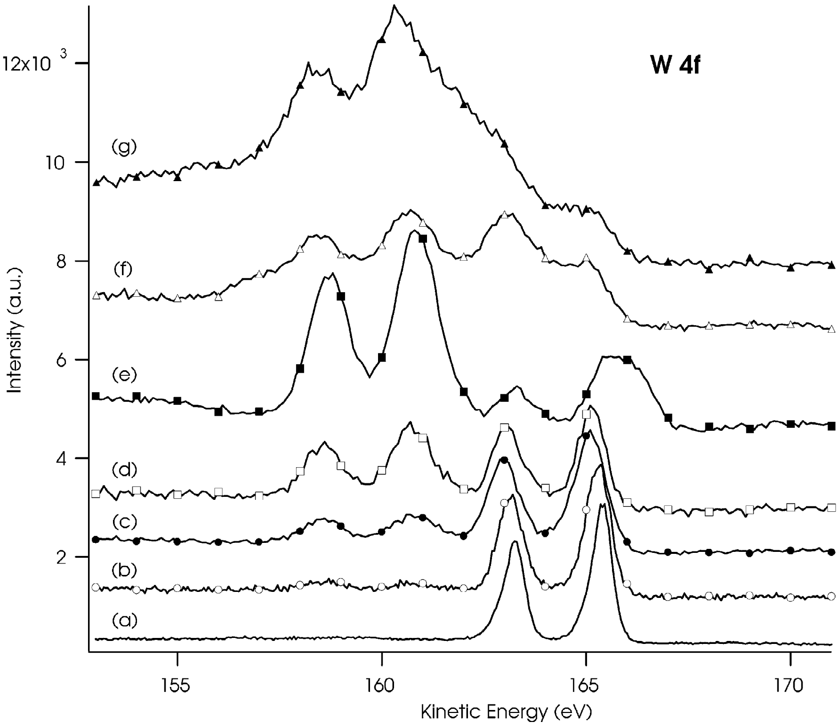

Fig. 1. W 4f core level spectra of W(CO)$_4$(dppe) samples prepared by different methods: (a) UHV evaporation; (b) spin coating from a CH_2Cl_2 solution; (c) spin coating from a $CHCl_3$ solution; (d) spin coating from a $(CH_3)_2CO$ solution; (e) spin coating from a 1,3,5-$C_6H_3(CH_3)_3$ solution; (f) dipping into a $(CH_3)_2CO$ solution; (g) brushing.

this experimental setup (which delivers $\approx 1.6\times 10^{11}$ photons/s), the W(CO)$_4$(dppe) lifetime, as measured by monitoring the reduction in intensity of the peaks related to the original compound upon beam exposition, was about 9 min.

For all three components we optimized the values of the lorentzian width (=0.063 eV), the branching ratio (=1.333) and the spin–orbit splitting (=2.151 eV). These results are reasonably in agreement with the data reported in the literature [14,23], therefore the same values were used for the peak fitting of all the other W 4f spectra.

The results of the fit for the spectra obtained from samples prepared by different methods (brushing, dipping and spin coating) and by spin coating from solutions in different solvents (mesitylene, acetone, chloroform and dichloromethane) are summarized in Table 1. For each preparation are listed the W 4f$_{5/2}$ KE obtained by peak fitting, the W 4f$_{7/2}$ BE derived from the W 4f$_{7/2}$ KE and referenced to the Au 4f$_{7/2}$ BE at 84.00 eV and Γ; the 2σ fitting error is also reported in parentheses for each value. In the same table, we also list for comparison the corresponding values for two other preparation methods reported in the literature: a spectrum obtained by brushing the same compound, but using a monochromatized X-ray gun instead of synchrotron radiation [17], and a spectrum obtained with synchrotron radiation for *cis*-W(CO)$_4$(PMe$_3$)$_2$ in the gas phase [14].

The W 4f spectra reported in Fig. 1 clearly show that brushing and dipping are unsuitable for the preparation of samples for synchrotron radiation XPS, because of their broadness and the uncertain determination of BE. Moreover, the bad quality of the spectra makes any peak fitting meaningless, therefore the corresponding values are missing from Table 1. However, it should be emphasized that samples prepared by the same methods would be suitable for XPS with a traditional X-ray source, although with a lower resolution.

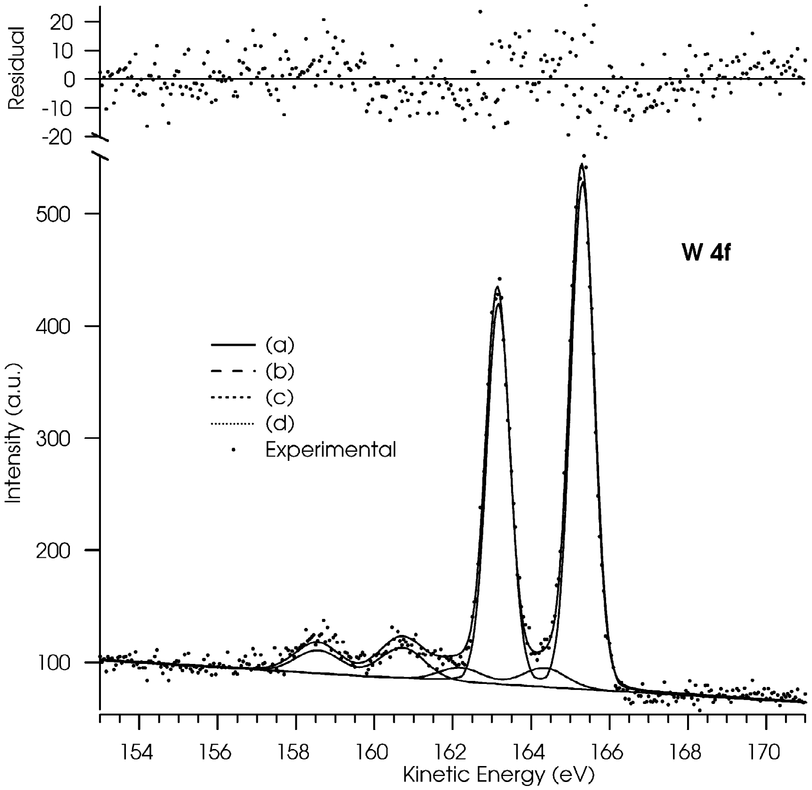

Fig. 2. Experimental W 4f core level spectra of W(CO)$_4$(dppe) samples prepared by spin coating from a CH_2Cl_2 solution and its fit: (a) overall fitted spectrum; (b) spectrum of the first component; (c) spectrum of the second component; (d) spectrum of the third component. The residual shown is the difference between the experimental and overall fitted spectra.

Spectra obtained from spin coated samples (Fig. 1(b)–(e)) are strongly dependent on the solvent used for the solution, both for the BE and FWHM of the peaks related to the original compound and for the amount of decomposed compound at lower KE. As shown in Table 1, the best results are obtained with more volatile solvents [i.e. $CH_2Cl_2 > (CH_3)_2CO \approx CHCl_3$]. On the other hand, the good BE peak fitting result for the sample from mesitylene solution is not fully reliable for the detection of the simultaneous presence of other overlapped signals. The best results from the spin coated sample (i.e. from CH_2Cl_2 solution) are clearly not comparable to those from gas-phase samples, where the FWHM is so narrow to allow the resolution of the vibrational fine structure due to W–CO stretching and the detection of broadening due to ligand field splitting [14]. However, spin coated samples approach the results for UHV evaporated samples, with a very small shift towards higher BE and a more pronounced increase of Γ. Moreover, the same spin coated samples give far more resolved spectra than those reported from samples prepared by brushing and with a monochromatized X-ray gun [17].

The results obtained for the spin coating technique appear to be dependent on other parameters in addition to the solvent: the spinning rate, which has to be as fast as possible to minimize the thickness of the deposited compound on the surface [20], treatment and material of the support on which to deposit the compound (see below in the discussion of the AFM results) and the concentration of the starting solution. Tests carried out to explore the consequences of sample cooling at 110 K, as well as gentle warming at 390 K, did not show significant effects on W 4f BE and Γ. Only a slight increase in

Table 1
W 4f KEs, BEs[a] and Gaussian widths (Γ) for W(CO)$_4$(dppe) samples prepared by different methods (in eV)

Preparation method	W $4f_{5/2}$ KE	W $4f_{7/2}$ BE	Γ
UHV evaporation	163.264(8)	31.028(8)	0.493(11)
Spin coating from a CH_2Cl_2 solution	163.143(6)	31.118(6)	0.680(15)
Spin coating from a $CHCl_3$ solution	162.994(13)	31.312(13)	0.751(30)
Spin coating from a $(CH_3)_2CO$ solution	163.010(8)	31.305(8)	0.765(19)
Spin coating from a 1,3,5-$C_6H_3(CH_3)_3$ solution	163.259(28)	30.996(28)	0.836(71)
Dipping in a $(CH_3)_2CO$ solution	n.a.	n.a.	n.a.
Brushing	n.a.	n.a.	n.a.
Brushing; monochromatized X-ray gun[b]	n.a.	31.2	1.5
Gas phase synchrotron radiation XPS[c]	n.a.	36.400(20)	0.320(5)

[a] BEs are referenced to the Au $4f_{7/2}$ BE at 84.00 eV.
[b] Ref. [17].
[c] *cis*-W(CO)$_4$(PMe$_3$)$_2$ [14].

peak intensity was observed as a result of sample warming, probably due to partial degassing of the surface from small co-adsorbed molecules (i.e. H_2O, CO, CO_2, solvent, etc.).

The influence of the concentration of the starting solution on the quality of the W 4f spectra was investigated in the case of samples prepared by spin coating from dichloromethane solutions. The results of the peak fitting of such spectra are listed in Table 2, where the W $4f_{5/2}$ KE, W $4f_{7/2}$ BE and Γ corresponding to solutions with concentrations between 0.058 and 0.469 mmol/l are reported. For each sample obtained from a different concentration, a second spectrum was acquired with both entrance and exit beam-line slit widths increased from 10 to 20 μm, thus increasing the photon flux on the sample by a factor of ≈5. Although a greater number of photons accelerates decomposition of the compound, a comparison between spectra at higher and lower photon fluxes gives a useful indication of the amount of differential charging present on the sample, since charging phenomena are roughly proportional to the number of photons impinging on the sample.

The results reported in Table 2 show that the W 4f BE decreases on increasing the dilution of the starting solution, until a concentration of 0.127 mmol/l is reached. Further dilution does not give a subsequent improvement. The effect on Γ is not as

Table 2
W 4f KEs, BEs[a] and Gaussian widths (Γ) for W(CO)$_4$(dppe) samples prepared by spin coating from CH_2Cl_2 solution at different concentrations and at different slit openings

Conc. (mmol/l)	Slit					
	10/10 μm			20/20 μm		
	W $4f_{5/2}$ KE (eV)	W $4f_{7/2}$ BE (eV)	Γ (eV)	W $4f_{5/2}$ KE (eV)	W $4f_{7/2}$ BE (eV)	Γ (eV)
0.469	162.618(5)	31.290(5)	0.676(9)	162.482(12)	31.426(5)	0.905(39)
0.234	162.680(4)	31.195(4)	0.697(13)	162.602(10)	31.273(10)	0.891(45)
0.127	162.760(4)	31.104(4)	0.666(10)	162.775(11)	31.089(11)	0.816(47)
0.058	162.743(9)	31.129(9)	0.655(23)	162.728(14)	31.144(14)	0.659(43)

[a] BEs are referenced to the Au $4f_{7/2}$ BE at 84.00 eV.

evident. The W 4f BE dependence on the concentration is clearly related to the thickness of the layer deposited on the support. Confirmation for this comes from a comparison of the results obtained at 10/10 and 20/20 μm. For both 0.469 and 0.234 mmol/l solutions, a greater photon flux results in an increase in W 4f BE and Γ; that is a strong evidence of differential charging occurring on the sample. On the other hand, there is no significant effect on W 4f BE of the slit opening for both 0.127 and 0.058 mmol/l solutions, thus confirming that differential charging is minimized in these cases.

It should be pointed out that the W 4f BE obtained for the 0.127 mmol/l concentration is very close to the value shown in Table 1, although the two W 4f KEs are different. The reason for this lies in the use of slightly different photon energies for the two experimental data sets, which are compensated by referencing to Au $4f_{7/2}$ BE at 84.00 eV. As far as the precision of the measured BE is concerned, it is important to underline that the value reported in parentheses is the 2σ error caused by the uncertainty in the fitting procedure. The generally small value, particularly for the W 4f core level, is related to the high precision available for the determination of the KE of the peak, on the basis of the experimental data set. On the other hand, the reproducibility in the acquisition of the experimental result is the parameter we need to maximize in order to allow the use of this technique to detect the BE shift for two different complexes. We have found that, using the spin coating technique under the most optimal conditions, the W 4f spectra are reproducible within ±20 meV.

3.4. P 2p measurements

Analogous XPS spectra of the P 2p core levels recorded from samples prepared using the same techniques as in Fig. 1 are shown in Fig. 3. In this case the peaks related to decomposed compounds are

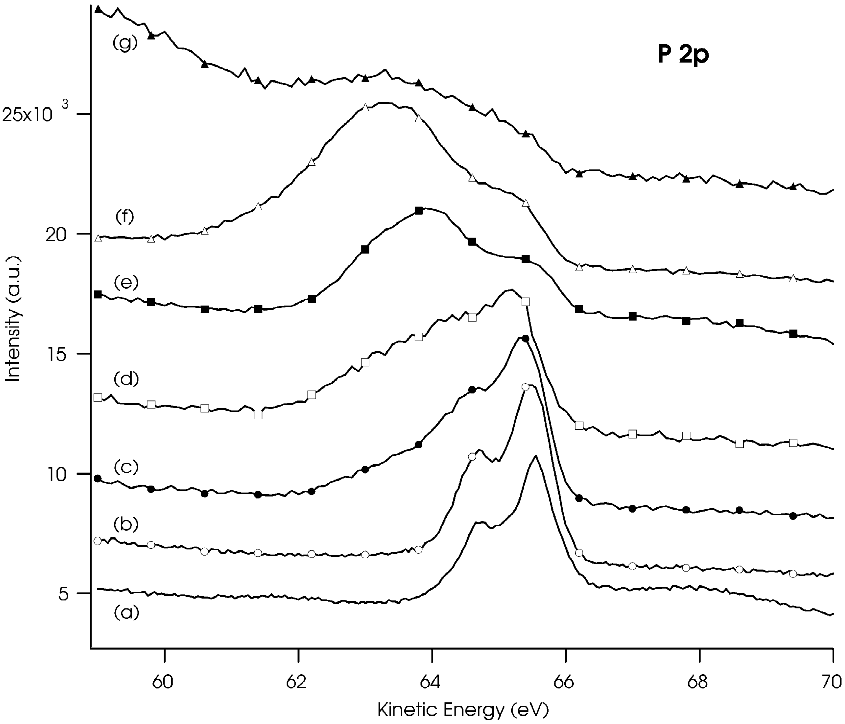

Fig. 3. P 2p core level spectra of W(CO)$_4$(dppe) samples prepared by different methods: (a) UHV evaporation; (b) spin coating from a CH_2Cl_2 solution; (c) spin coating from a $CHCl_3$ solution; (d) spin coating from a $(CH_3)_2CO$ solution; (e) spin coating from a 1,3,5-$C_6H_3(CH_3)_3$ solution; (f) dipping into a $(CH_3)_2CO$ solution; (g) brushing.

not as separated as in the case of the W 4f core level, but their presence leads to an overall broadening of the doublet centered around 65 eV. The broad shoulder at about 68 eV in Fig. 3(a), obtained from a sample prepared by UHV evaporation, is assigned to a gold Auger transition, made more evident by the low coverage of the gold surface from compound deposition.

As in the case of W 4f, an example of a fitted spectrum is shown in Fig. 4, with the P 2p core level peak fitting of the spectrum obtained from the sample prepared by spin coating from a CH_2Cl_2 solution. Also for P 2p peaks, the spectrum can be reproduced by a three-component fitting, with the most intense component [P $2p_{1/2}$ KE = 64.655(88) eV, Γ = 0.603(105) eV] being correlated with the original compound. Although the fitting errors for the other two components [P $2p_{1/2}$ KE = 63.948(10.782) eV, Γ = 1.174(7.966) eV and P $2p_{1/2}$ KE = 64.262(1.345) eV, Γ = 0.752(1.338) eV] are much greater, on the basis of their intensities we can assign the second component to the compound decomposed under beam exposition and the third component to the compound decomposed during sample preparation. The best values obtained by peak fitting for the lorentzian width (= 0.120 eV), the branching ratio (= 2.000) and the spin–orbit splitting (= 0.860 eV) are in agreement with analogous data reported in the literature [24], therefore the same values were used for the peak fitting of all the other P 2p spectra.

The results of peak fitting for all the P 2p spectra obtained from different preparation methods are listed in Table 3. As in Table 1, we also list for comparison the corresponding values published for $W(CO)_4$(dppe), with a monochromatized X-ray gun [17], and for *cis*-$W(CO)_4(PMe_3)_2$ with synchrotron radiation in the gas phase [14].

Fig. 3 shows that the conclusions drawn for the W 4f core level spectra are confirmed for the P 2p peaks: brushing, dipping and spin coating from a mesitylene solution are not suitable techniques for the preparation of samples for synchrotron radiation XPS. Spin coated samples lead to much more defined spectra, but only the use of a CH_2Cl_2 solution allows us to approach the shape of the peaks

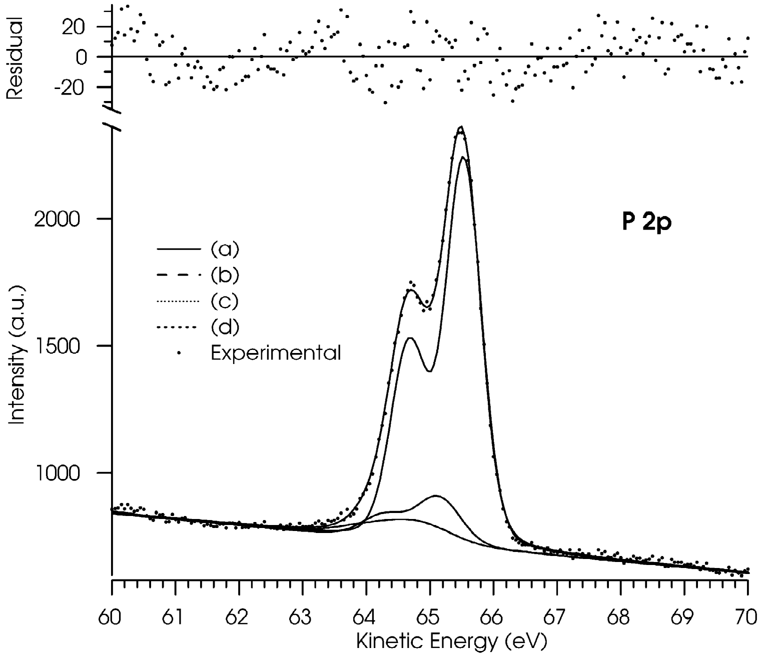

Fig. 4. Experimental P 2p core level spectra of $W(CO)_4$(dppe) samples prepared by spin coating from a CH_2Cl_2 solution and its simulation by fitting: (a) overall fitted spectrum; (b) spectrum of the first component; (c) spectrum of the second component; (d) spectrum of the third component. The residual shown is the difference between the experimental and overall fitted spectra.

Table 3
P 2p KEs, BEs[a] and Gaussian widths (Γ) for W(CO)$_4$(dppe) samples prepared by different methods (in eV)

Preparation method	P 2p$_{1/2}$ KE	P 2p$_{3/2}$ BE	Γ
UHV evaporation	64.693(6)	130.869(6)	0.592(18)
Spin coating from a CH_2Cl_2 solution	64.655(88)	130.876(88)	0.603(105)
Spin coating from a $CHCl_3$ solution	64.394(408)	131.182(408)	0.767(239)
Spin coating from a $(CH_3)_2CO$ solution	65.545(181)	131.040(181)	0.615(112)
Spin coating from a 1,3,5-$C_6H_3(CH_3)_3$ solution	64.539(29)	130.986(29)	0.939(63)
Dipping in a $(CH_3)_2CO$ solution	n.a.	n.a.	n.a.
Brushing	n.a.	n.a.	n.a.
Brushing; monochromatized X-ray gun[b]	n.a.	131.4	n.a.
Gas-phase synchrotron radiation XPS[c]	n.a.	136.760(80)	0.500(30)

[a] BEs are referenced to the Au 4f$_{7/2}$ BE at 84.00 eV.
[b] Ref. [17].
[c] *cis*-W(CO)$_4$(PMe$_3$)$_2$ [14].

obtainable by UHV evaporation. Moreover, the evident splitting between the P 2p$_{1/2}$ and P 2p$_{3/2}$ components is further evidence of the very good resolution [24], although, for this core level, the peaks related to decomposed complexes are more overlapped with those of the original compound, thus increasing the overall broadening. One more consequence of the overlapped peaks is the increased difficulty in the peak fitting procedure, which leads to greater 2σ errors. Spin coated samples from a CH_2Cl_2 solution give, in this case, the same P 2p BE and Γ of UHV evaporation, and the lowest Γ of the spin coated samples. The P 2p Γ is very close to the W 4f Γ reported in Tables 1 and 2, which is reasonable, since the Gaussian FWHM derives from the instrumental resolution and from the residual differential charging, and these are the same for both core levels. The P 2p spectrum from the CH_2Cl_2 spin coated sample is really very good when compared with that recorded from an analogous gas-phase sample [14], both in overall appearance (Fig. 4), and Γ (Table 3). No experimental data have been reported for the P 2p FWHM from samples prepared by brushing and with a monochromatized X-ray gun [17], but it seems reasonable to presume a FWHM close to that reported for W 4f (≈1.5 eV), and therefore much higher than the 0.6 eV we report.

3.5. AFM images

In order to observe the real distribution of the molecules on the substrate, we acquired AFM images of a sample obtained by spin coating deposition from a dilute dichloromethane solution on a carefully polished steel substrate. Two images are shown in Fig. 5, acquired before (a) and after (b) the deposition of the compound. A comparison of the two images allows us to reveal the disappearance of the long diagonal stripes (Fig. 5(a)), which are the residual structure due to the mechanical polishing of the surface. After compound deposition, the surface appears more uniform with the exception of small grains of compounds, one of which is shown in the A–A′ section, the height of which ranges between 4 and 12 nm. We observed a clear decrease of both the height and number of grains as the concentration of the spin coated solution decreased. The regular surface upon deposition as shown in Fig. 5(b), compared with the structures in the naked support shown in Fig. 5(a), is good evidence of the suitability of the spin coating technique. The core level peak broadening in comparison with the spectrum obtained by UHV evaporation arises from the residual inhomogeneity of the molecular distribution, and mostly from the presence of small sample grains and

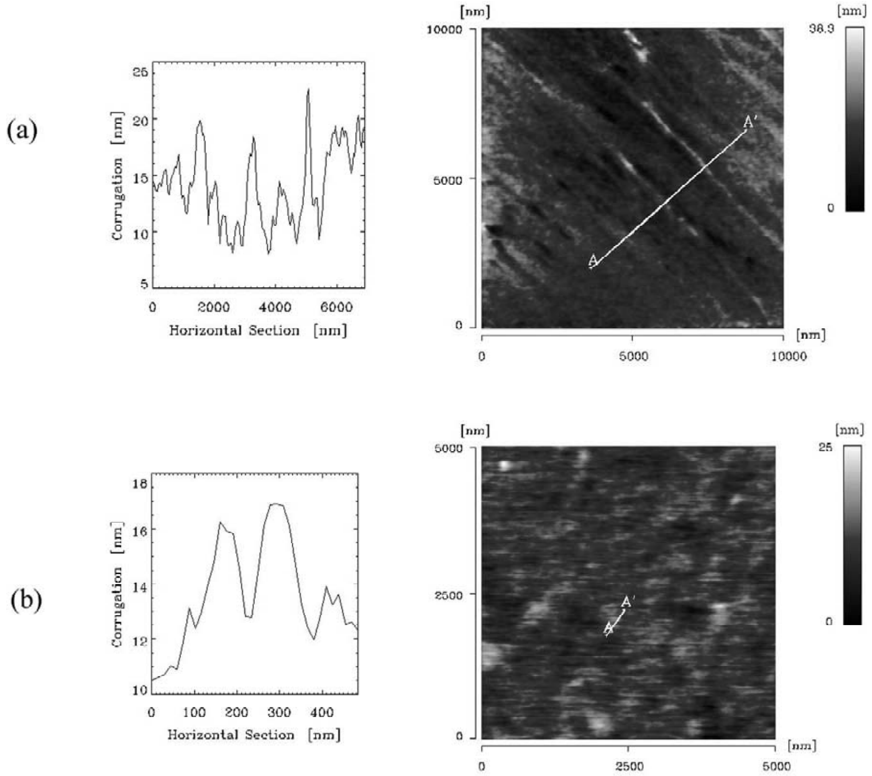

Fig. 5. AFM images of a stainless steel plate acquired (a) before and (b) after the spin coating deposition of W(CO)$_4$(dppe) from a dilute CH$_2$Cl$_2$ solution.

from the irregularity of the metallic support surface. The number and size of sample particles are minimized by an increase in dilution, and would probably be further reduced by using suitable microfilters on the solution before spin coating. The problem of the irregularity of the metallic support has to be minimized by control of the support polishing. The support shown in Fig. 5(a) underwent careful polishing down to 0.1 μm roughness, and, indeed, no structures evidenced in the A–A′ section exceed 12 nm. However, since a W(CO)$_4$(dppe) molecule has a size of $10.5\times8.6\times11.2$ Å [based on Mo(CO)$_4$(dppe) structural data [25], as no data are available for W(CO)$_4$(dppe)], even the shallow valleys shown in Fig. 5(a) allow the formation of at least 13–14 layers before being completely filled by the sample.

Therefore, these observations introduce the problem of the choice of the material for the support. The use of carefully polished stainless steel plates fulfills the need for a rigid and flat support, which is necessary for the use of the spin coater. Moreover, stainless steel allows good and rather easy polishing of the surface. A final gold coating ensures a high chemical inactivity towards the sample, although it is well known that a gold surface may also react with the phosphine ligand [26]. Moreover, the Au 4f core levels are very suitable as a reference for other core level BEs.

3.6. UPS measurements

Valence level spectra of the sample prepared by the best spin coating procedure were acquired at 49.18 and 80.25 eV photon energy. After subtraction of a Gaussian tail as background caused by secondary electrons, the Au valence level spectra were subtracted from the W(CO)$_4$(dppe) spectra until the Fermi edge completely disappeared. The final spectra are shown in Fig. 6, with the single components obtained by peak fitting. The BE and overall FWHM

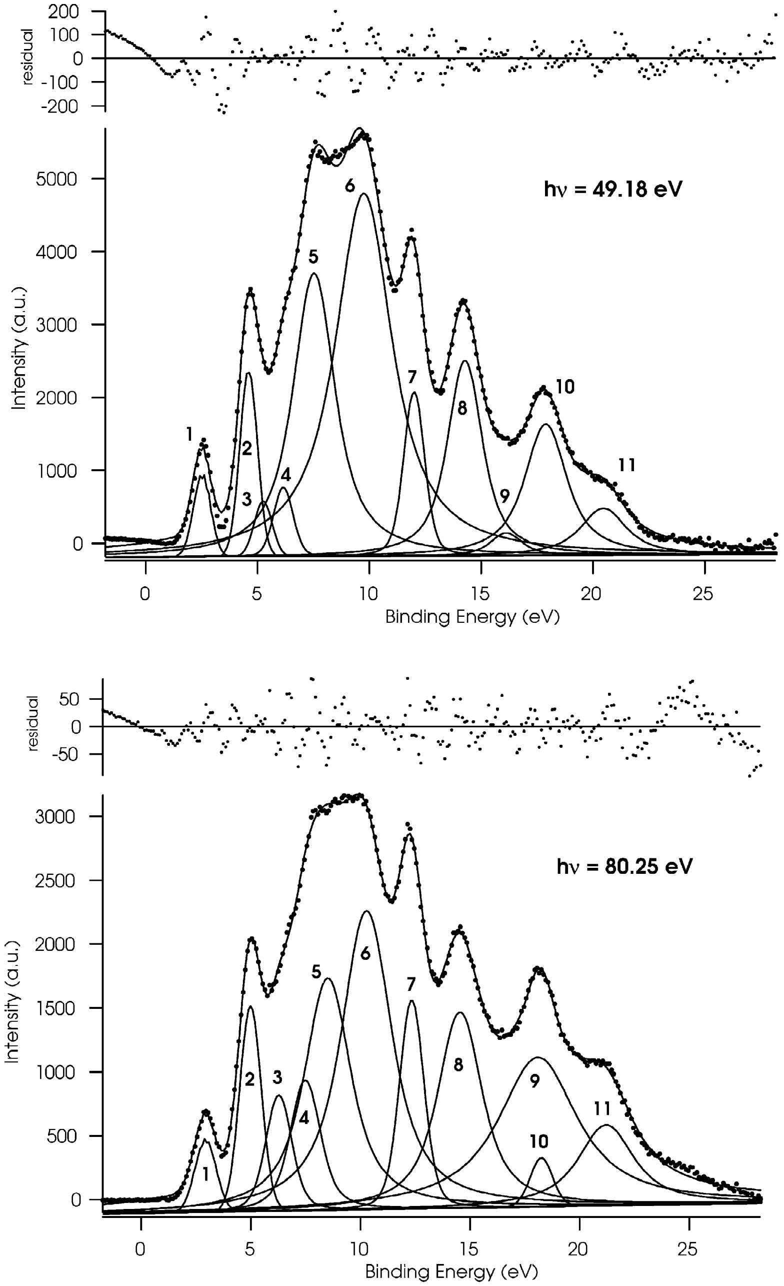

Fig. 6. Valence level spectra of a $W(CO)_4$(dppe) sample prepared by spin coating from a dilute CH_2Cl_2 solution, with 49.18 eV (a) or 80.25 eV (b) photon energy. The single peaks obtained by fitting are shown as dotted lines.

resulting from the fitting procedure for both photon energies are listed in Table 4. An overview spectrum of the valence band for gas-phase samples of $W(CO)_4$(dppe) with synchrotron radiation is not available in the literature, but we list in Table 4 some gas-phase data reported for *cis*-$W(CO)_4(PMe_3)_2$ with synchrotron radiation [14], and for $W(CO)_4$(dppm) [dppm = 1,2-bis(diphenylphos-

Table 4
Valence band BEs and Gaussian widths (Γ) for $W(CO)_4$(dppe) samples prepared by spin coating from a dilute CH_2Cl_2 solution (in eV) compared with literature data

Peak	Assignment	$h\nu = 49.18$ eV			$h\nu = 80.25$ eV			Literature data		
		BE	Γ	Δ^a	BE	Γ	Δ^a	BE	Γ	Δ^a
11	Satellite 2	20.42	2.42	17.95	21.17	3.00	18.27	26.14^b	2.33^b	19.01
10	Satellite 1	17.85	2.23	15.37	18.22	1.20	15.32	23.60^b	2.13^b	16.47
9	C 2s	16.08	1.69	13.61	18.06	4.30	15.16	21.86^b	1.35^b	14.73
8	Valence shake-up	14.23	1.84	11.76	14.50	2.39	11.60	18.66^b	2.80^b	11.53
7	4σ (CO)	11.96	1.10	9.49	12.30	1.32	9.40	16.50^b	1.00^b	9.37
6	$5\sigma + 1\pi$ (CO) $+\sigma$ (C–H)	9.71	3.04	7.24	10.24	2.74	7.34	14.47^c	n.a.	7.34
5	σ (P–C)	7.48	2.24	5.01	8.47	2.50	5.57	12.67^c	n.a.	5.54
4	σ (P–C)	6.11	1.03	3.63	7.45	1.62	4.55	11.22^c	n.a.	4.09
3	σ (W–P)	5.21	0.93	2.73	6.24	1.39	3.34	10.62^c	n.a.	3.49
2	π (Phenyl)	4.56	0.93	2.08	4.96	1.16	2.06	9.74^c	n.a.	2.61
1	W 5d	2.47	0.92	–	2.90	1.14	–	7.13^b	0.50^b	–

[a] $\Delta = (BE_{peak} - BE_{W\ 5d})$.
[b] *cis*-$W(CO)_4(PMe_3)_2$ [14].
[c] Fig. 2(b) of Ref. [18f] for $W(CO)_4$(dppm).

phino)methane] with a He lamp [18f]. However, the BE values from gas-phase samples are not readily comparable with solid-phase samples, because, for the latter, it is necessary to also take into account the work function Φ (which is not readily calculable for our system), whereas $\Phi = 0$ for a gas. Therefore, we have also listed in the same table the BE difference between each peak and the W 5d peak [$\Delta = (BE_{peak} - BE_{W\ 5d})$], since the W 5d peak is one of the most separated and recognizable peaks. The peak fitting was started on the basis of the peaks whose presence was clearly evident from the shape of the overall spectrum, thus leading to a first, rather good agreement. Only during the refining procedure, and particularly by comparison with the gas-phase results, did we realize the necessity of adding more peaks (namely peaks 3 and 9), thus obtaining better agreement between real and fitted spectra, and with the data reported in the literature.

Although for the UPS spectra the fitting procedure gave poorer agreement and larger fitting errors than for the core level spectra, the results shown in Fig. 6 and Table 4 are surprisingly encouraging. After subtraction of the secondary electrons Gaussian baseline and of the gold background, the structures in the valence band are rich and well defined, and they are reproducible with a change in photon energy. Moreover, the agreement with the reported gas-phase results is rather good, as the Δ comparisons show for most of the peaks. Also, a visual comparison between our 80.25 eV spectrum and the He lamp spectrum of $W(CO)_4$(dppm) [18f] confirms the reliability of the spectrum. In any case, it should be taken into account that we are looking at a spectrum of a solid-state sample prepared in air: the presence of small co-adsorbed molecules (although partially subtracted together with the background) and the intrinsic broadening due to solid-state effects hardly make it comparable to the resolution obtained in the gas phase. As a matter of fact, only a few examples of TMCC valence band spectra from solid-state samples can be found in the literature [10], and, as far as we know, none of the reported samples were prepared in air. On the other hand, we found papers reporting the valence band spectra from UHV evaporated samples, since preparation in air had given unacceptable results [27]. Nevertheless, the spectrum we obtained from the spin coating sample is suitable to identify most of the peaks in the valence band of $W(CO)_4$(dppe).

In order to shed light on the decomposition mechanism on beam exposition, a series of scans

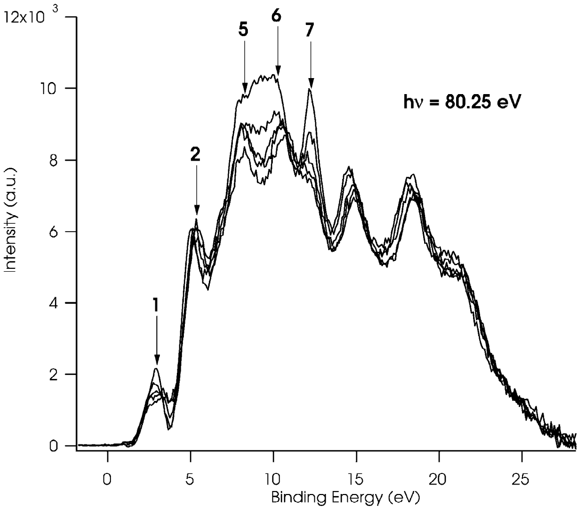

Fig. 7. Sequence of valence level spectra of a W(CO)$_4$(dppe) sample prepared by spin coating from a dilute CH_2Cl_2 solution, acquired on the same sample spot, with 80.25 eV photon energy (top spectrum, first scan; bottom spectrum, last scan).

was acquired on the same sample spot, each one lasting about 70 s for a photon flux of $\approx 5.1 \times 10^{11}$ photons/s. The sequence of single scans (Fig. 7) shows a strong decrease in intensity in the region between 8 and 12 eV, which corresponds to peaks 5, 6 and 7, as confirmed by peak fitting of the single scans. The same fit showed a general broadening of all peaks, but particularly of peak 1. Identification of peaks 6 and 7 as CO-based orbitals [peak 6, $5\sigma + 1\pi$ (CO); peak 7, 4σ (CO)] allows us to propose an hypothesis for sample decomposition based on the loss or the transformation of the carbonyls. Such decomposition can be caused by interaction of the compound either with high energy photons or with electrons photoemitted from vicinal molecules, as has already been observed for other metal carbonyls under synchrotron radiation exposure [28]. The broadening of peak 1 (i.e. W 5d orbitals) can be easily explained by the formation of several W-containing species with different coordination environments, as observed for the broadening of the W 4f core level. It is not as easy to formulate any hypothesis about the fate of the coordination of the phosphine ligand, because of little evidence of the corresponding peak. However, it appears that the phenyl rings of the phosphine (peak 2) are not significantly affected by decomposition.

4. Conclusions

Solid-state samples of W(CO)$_4$(dppe) were prepared by different methods in order to record synchrotron radiation photoemission spectra with very low broadening caused by differential charging. For each preparation method, the XPS spectra of the W 4f and P 2p core levels were acquired and their BE and Gaussian FWHM measured. Samples prepared by brushing or by dipping gave unacceptable spectra, whereas those obtained by the spin coating preparation method showed much better resolution. We found that the best results are obtained by spin coating at a high spinning rate and from dilute solutions in low boiling solvents. AFM images of the metallic support before and after sample spin coating show significant homogeneity in the distribution of the molecules, and stress the importance of a starting support with very low roughness. Spectra obtained by spin coating under optimal conditions gave core level BE and Gaussian FWHMs very close to those acquired by the best known method for the preparation of solid-state samples, e.g. evaporation of a thin film of the compound in UHV.

The sample prepared by the same method also gave UPS spectra that were suitable for identifying the main characteristics of the valence band. This was confirmed by comparison with the gas-phase spectra of analogous compounds, although solid-state effects introduce unavoidable peak broadening. However, the availability of solid-state samples for synchrotron radiation UPS opens up several possibilities in the field of advanced techniques in the study of transition metal coordination compounds, such as resonant photoemission [2].

Therefore, spin coating has been shown to be a suitable method for the preparation of samples for synchrotron radiation photoemission spectroscopy, and most likely even for transition metal complexes which cannot be evaporated. It seems therefore that the spectra so obtained could be used to detect core level BE shifts related to small modifications in the structure of the compound.

Acknowledgements

We are deeply grateful to all colleagues, researchers and technicians of the Istituto Struttura della Materia (National Council for Research) for their suggestions, support and encouragement. We thank Sincrotrone Trieste S.C.p.A. for financial support through a Basic Research Project and for the purchase of the spin coater instrument.

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