

Donor Properties of Diphosphine Ligands in Tungsten Carbonyl Complexes: Synchrotron Radiation XPS Measurements and DFT Calculations

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Synchrotron radiation XPS measurements of W 4f and P 2p core level binding energies in the series W(CO)₄(P–P) (P–P = dpmm (1), dppe (2), dppp (3), dppb (4), dmpe (5), F-dppe (6); dpmm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dmpe = 1,2-bis(dimethylphosphino)ethane, F-dppe = 1,2-bis(bis(pentafluorophenyl)phosphino)ethane) are reported. The results are interpreted in terms of effects of the chelate ring size and of the nature of substituents of the P atoms. The trend of XPS data show an excellent agreement with the results of DFT calculations, obtained by the Δ SCF approach. Further analysis of the Kohn–Sham eigenvalues calculated at the ground-state level has assessed the role played by the initial state effects.

Introduction

Recent literature reports on homogeneous transition-metal-based catalysts employing diphosphine ligands provide increasing evidence that the electronic and steric properties of the phosphine play a key role in determining the catalytic properties of the complexes.¹ For monodentate phosphines a number of parameters have been established² to describe steric and electronic properties, even if some controversial points still remain, such as the extent of metal–phosphorus π -back-bonding.^{2c,3} On the other hand, despite some remarkable recent reports,^{1i,4} stereoelectronic effects of diphosphine ligands⁵ are not equally well understood, partly because

electronic and steric factors appear to be strictly correlated. A crucial effect on the reactivity of metal–diphosphine compounds appears to be played by the chain length connecting the two phosphorus atoms, which has been interpreted in some cases as favoring a certain geometry of an intermediate of the catalytic cycle^{1d,6} and in others as allowing partial dissociation of the chelate ring, thus providing an available coordination site;⁷ however, the variation of the metal–phosphorus bond nature as a consequence of the diphosphine chain length variation should be also taken into account. An attempt to correlate the steric effects—and particularly the chelate effects—of bidentate phosphines with the metal–phosphorus bond nature has been made by Lichtenberger and Jatcko,⁸ who employed gas-phase

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UPS spectroscopy to evaluate the electronic mapping in a series of molybdenum and tungsten diphosphine complexes; however, the need of using evaporable compounds severely limited the number of examples studied. A previous investigation on a series of tungsten mono- and diphosphine complexes by UPS spectroscopy had been reported by Bancroft et al.;⁹ the results were mainly interpreted in terms of W–P bond nature, whereas the effect of chelation was neglected.

The longstanding application¹⁰ of photoelectron spectroscopy, both of core level (XPS) and of valence band (UPS), to transition-metal coordination compounds has gained new life by the use of synchrotrons as X-ray sources; incomparable energy resolution and photon energy tunability have made feasible a more precise evaluation of the variations of the binding energies (BEs)—and therefore of the electron densities—depending on the substitution of ligands in the complex. An early application of synchrotron radiation (SR) in UPS and XPS spectroscopy has been reported by Bancroft and co-workers, who showed how the high resolution can evidence fine effects in ligand substitution within a series of tungsten carbonyl phosphine complexes.¹¹ However, such studies were necessarily limited to volatile compounds of monodentate phosphines.

The limitation of the feasibility of SR XPS to complexes which can be evaporated in the gas phase¹² has been recently overcome by our group with the setup of a sample preparation method which produces a thin and homogeneous layer of a transition-metal compound on a conducting, inert support.¹³ The solid-phase samples prepared by that technique minimize the differential charging effects due to the inherent insulating nature of these compounds, and their synchrotron radiation XPS spectra show a reduced broadening and shifting and an excellent reproducibility. Using this method, it is feasible to observe very slight differences in the BE that would otherwise be undetectable by traditional XPS.

The interpretation of XPS spectra can be assisted by quantum-chemical calculations; in fact, theory may be useful to discuss the results in terms of electronic effects. For this reason we have calculated the core electron binding energies by means of a method based on the density functional theory (DFT), which has proven¹⁴ very accurate and computationally economic for application to large transition-metal compounds.

In our present studies we propose to verify the effect of a variation either of the diphosphine chain length or of the substituents on phosphorus atoms on metal and phosphorus core level BEs and to obtain quantitative

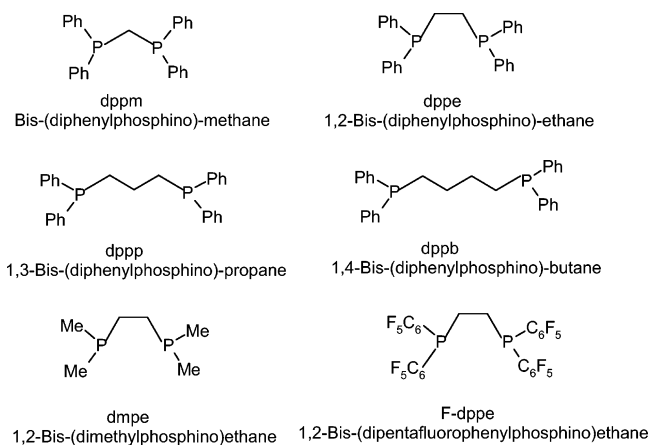


Figure 1. Structures of the six diphosphines used for the synthesis of the compounds under investigation.

information on the donor properties of the phosphine employed: such properties will determine whether a complex will behave as an active catalyst rather than an inert object.

Here we report the investigation on a series of tungsten carbonyl complexes with chelating diphosphines by synchrotron radiation XPS and by DFT calculations: the differences of measured and calculated BEs have been used to estimate the variations of electron densities caused by the different donor abilities of the phosphine. The complexes under investigation are the octahedral derivatives $W(CO)_4(P-P)$ ($P-P =$ dppm (**1**), dppe (**2**), dppp (**3**), dppb (**4**), dmpe (**5**), F-dppe (**6**); dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dmpe = 1,2-bis(dimethylphosphino)ethane, F-dppe = 1,2-bis(bis(pentafluorophenyl)phosphino)ethane) (see Figure 1): compounds **1–4** provide a series in which the effect of chain length variation is examined, whereas for complexes **2**, **5**, and **6** the substituents on phosphorus are changed while maintaining the same chelate ring size.

Although most of these complexes could be evaporated without decomposition, we have chosen them in order to compare our solid-state results with previous higher resolution and accurately calibrated gas-phase studies⁹ and to demonstrate the feasibility of this approach to solid-state samples of nonvolatile organometallic compounds.

Experimental Section

General Considerations. All the reactions and manipulations were routinely performed under an argon atmosphere by using standard Schlenk tube techniques. Bis(2-methoxyethyl) ether (diglyme) and all other chemicals were reagent grade and were used as received by commercial suppliers.

The compound $W(CO)_4(dppe)$ was prepared according to the previously reported procedure.¹⁵

Instrumentation. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a JEOL EX400 spectrometer operating at 399.77,

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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 (δ 77.0 for CDCl_3), and ^{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 mulls on a FT-IR Perkin-Elmer System 2000 spectrometer.

Synthesis of the Complexes. (a) Preparation of $\text{W}(\text{CO})_4(\text{dppm})$. Tungsten hexacarbonyl (0.52 g, 1.4 mmol) and dppm (0.54 g, 1.4 mmol) were added into a Schlenk tube containing 5 mL of diglyme. The reaction mixture was heated at reflux for 75 min, during which time the hexacarbonyl that sublimed on the Schlenk walls was periodically returned to the solution by vigorous shaking. The yellow-brown solution obtained was cooled to room temperature; addition of 5 mL of methanol caused precipitation of yellow crystals, which were filtered, washed with methanol, and dried in vacuo. Yield: 71%. ^1H NMR (CDCl_3 , 25 °C): δ 7.5–7.2 (m, 20H, Ar), 4.89 (t, 2H, CH_2 , $J_{\text{HP}} = 9.1$ Hz); ^{31}P NMR (CDCl_3 , 25 °C): δ -23.3 (s, $J_{\text{PW}} = 202.2$ Hz). ^{13}C NMR (CDCl_3 , 25 °C): δ 210.3 (m, CO trans P), 202.8 (t, CO trans CO, $J_{\text{CP}} = 7.3$ Hz), 136–128 (Ar), 52.2 (t, CH_2 , $J_{\text{CP}} = 14.0$ Hz).

(b) Preparation of $\text{W}(\text{CO})_4(\text{dppp})$. In a Schlenk tube containing 5 mL of diglyme, 0.52 g of tungsten hexacarbonyl (1.4 mmol) and 0.61 g of dppp (1.4 mmol) were added. The reaction mixture was heated at reflux for 30 min, and then the resulting yellow-green solution was cooled to room temperature. After addition of 5 mL of methanol a pale yellow solid was obtained, which was filtered, washed with methanol, and dried in vacuo. Yield: 77%. ^1H NMR (CDCl_3 , 25 °C): δ 7.5–7.3 (m, 20H, Ar), 2.56 (m, 4H, PCH_2), 2.00 (m, 2H, CH_2). ^{31}P NMR (CDCl_3 , 25 °C): δ +0.4 (s, $J_{\text{PW}} = 223.0$ Hz). ^{13}C NMR (CDCl_3 , 25 °C): δ 205.7 (m, CO trans P), 203.1 (t, CO trans CO, $J_{\text{CP}} = 7.4$ Hz), 138–128 (Ar), 31.1 (m, PCH_2), 20.2 (s, CH_2).

(c) Preparation of $\text{W}(\text{CO})_4(\text{dppb})$. Tungsten hexacarbonyl (0.52 g, 1.4 mmol) and dppb (0.64 g, 1.4 mmol) were added into a Schlenk tube containing 5 mL of diglyme. The reaction mixture was heated at reflux for 35 min, the yellow-brown solution obtained was cooled to room temperature, and addition of 5 mL of methanol caused precipitation of light yellow crystals, which were filtered, washed with methanol, and dried in vacuo. Yield: 81%. ^1H NMR (CDCl_3 , 25 °C): δ 7.5–7.3 (m, 20H, Ar), 2.6 (bm, 4H, PCH_2), 2.0–1.7 (m, 4H, CH_2). ^{31}P NMR (CDCl_3 , 25 °C): δ 11.3 (s, $J_{\text{PW}} = 230.9$ Hz). ^{13}C NMR (CDCl_3 , 25 °C): δ 205.4 (m, CO trans P), 202.9 (t, CO trans CO, $J_{\text{CP}} = 7.4$ Hz), 138–128 (Ar), 31.2 (m, PCH_2), 23.5 (s, CH_2).

(d) Preparation of $\text{W}(\text{CO})_4(\text{dmpe})$. In a Schlenk tube containing 5 mL of diglyme were added 0.74 g of tungsten hexacarbonyl (2.0 mmol) and 0.30 g of dmpe (2.0 mmol). The reaction mixture was heated at 130 °C for 5 h, and then the resulting yellow solution was cooled to room temperature. Pale yellow crystals were obtained; precipitation was completed by addition of pentane. The product was filtered, washed with methanol, and dried in vacuo. Yield: 46%. ^1H NMR (CDCl_3 , 25 °C): δ 3.64–3.50 (m, 4H, CH_2), 1.60 (d, 12H, CH_3 , $J_{\text{HP}} = 6.5$ Hz). ^{31}P NMR (CDCl_3 , 25 °C): δ 9.0 (s, $J_{\text{PW}} = 222.0$ Hz). ^{13}C NMR (CDCl_3 , 25 °C): δ 209.1 (dd, CO trans P, $J_{\text{CPtrans}} = 22.1$, $J_{\text{CPcis}} = 5.5$ Hz), 201.6 (t, CO trans CO, $J_{\text{CP}} = 7.4$ Hz), 31.8 (m, CH_2), 19.1 (d, CH_3 , $J_{\text{CP}} = 25.8$ Hz).

(e) Preparation of $\text{W}(\text{CO})_4(\text{F-dppe})$. Tungsten hexacarbonyl (0.35 g, 1.0 mmol) and F-dppe (0.76 g, 1.0 mmol) were added into a Schlenk tube containing 8 mL of diglyme. The reaction mixture was heated at reflux for 90 min, the yellow-brown solution obtained was cooled to room temperature, and addition of 5 mL of methanol caused precipitation of a light gray solid, which was filtered, washed with methanol and with methylene chloride, and dried in vacuo. Yield: 38%. ^1H NMR (CDCl_3 , 25 °C): δ 2.94 (m, 4H, CH_2). ^{31}P NMR (CDCl_3 , 25 °C): δ +17.3 (s, $J_{\text{PW}} = 264.4$ Hz). ^{13}C NMR data were not obtained due to low solubility.

XPS Spectra. The samples for XPS were prepared by the spin-coating technique as described elsewhere:¹³ a few drops of a solution of the desired complex in CH_2Cl_2 (0.085 mmol/L) were placed on the carefully polished surface of a gold foil (roughness ≤ 0.1 μm ; 0.5 μm diamond suspension as polishing medium), and the spin coater was started for 5 min, at a spinning rate of 3000 rpm, until complete evaporation of the solvent. The spin coater used was a Model P6708 from Specialty Coating System Inc. The dependence of the overall spectrum on several parameters during the sample preparation (spin speed rate, solution concentration, gold foil roughness) and the necessary characteristics of the support have already been reported in a previous paper.¹³ The deposition of the complexes by this technique was shown to be homogeneous enough to minimize the differential charging, leading to no drifting peaks upon changing of photon flux. The thickness of the layer was estimated to be around a few monolayers, but the Au 4f signal from the underlying gold foil was always detectable and was even more intense than the W 4f signal. Each sample was introduced into the experimental chamber through a load-lock chamber; during all measurements, the experimental chamber pressure was not higher than 2.0×10^{-10} mbar. No evaporation of the complexes from all the solid-state samples has been observed at room temperature in UHV.

The XPS spectra were recorded by the angle-integrated Omicron EA 125 HR energy analyzer mounted in the experimental chamber of the VUV-photoemission beam line¹⁵ 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.¹⁶ 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 were closed at 10 μm each, thus decreasing the photon flux on the sample. The instrumental resolution was estimated by a Fermi edge spectrum acquired with the same setting of the core level spectra. The resulting resolution was never worse than 0.10 eV, with an estimated photon energy contribution of ≈ 45 meV, and the remaining uncertainty was attributed to the analyzer.

XPS Data Analysis. The sum of several (8 ÷ 16) quick, single-scan spectra (~ 85 s/scan), each recorded on a fresh sample area (~ 0.1 mm^2), gave a final spectrum with higher signal/noise ratio and, at the same time, a careful control of the homogeneity of the compound distribution on the sample. Spectra were fit 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, the BEs from W 4f and P 2p final spectra were referenced to the Au 4f_{7/2} peak at 84.00 eV acquired before and after the series of single scans, thus eliminating any error due to fluctuation of photon energy or electron kinetic energy. The BEs obtained by the fit calculation are given in the present work with a 95% interval confidence shown in parentheses. Such interval confidence provides an evaluation only of the precision of the fit calculation on the basis of its standard deviation; on the other hand, the reproducibility of the BEs could be obtained by the comparison of several (not less than five) samples of different batches of the same compound, measured during different beam times, and it was within ± 30 meV.

DFT Calculations. The calculations of core electron BEs have been performed in terms of the so-called ΔSCF approach,

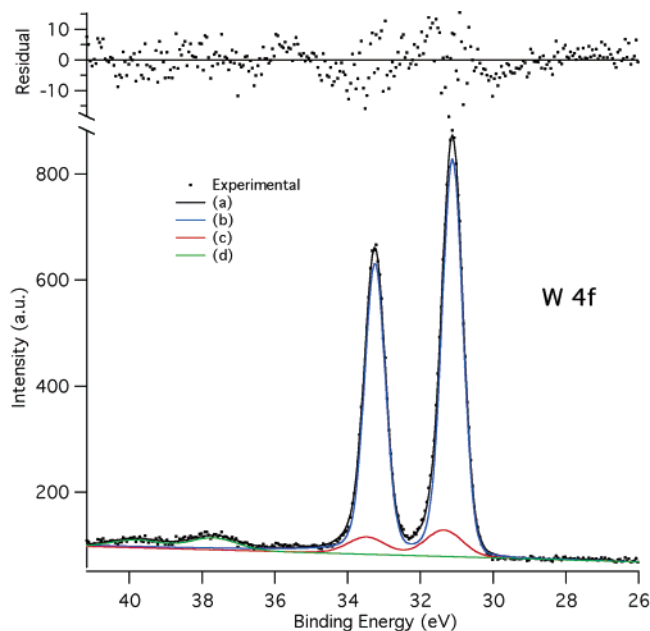


Figure 2. Experimental W 4f spectrum of $W(CO)_4(dppe)$ (2) and its simulation by fitting: (a) overall fitted spectrum; (b) spectrum of the first component; (c) spectrum of the second component; (d) spectrum of the third component. The residual shown is the difference between the experimental and overall fitted spectra.

which consists of calculating the BEs as the total energy difference between the ground-state molecule and the ion obtained after the core electron has been removed; thus, two separate calculations are necessary. The BEs calculated at the Δ SCF level contains both initial and final state effects: initial effects are of the inductive type and are derived essentially from the electron density over the atomic site where core ionization occurs; on the other hand, final state effects, namely relaxation, are a consequence of the response of the electrons to the core hole formation, which are quite strong for core ionization. Therefore, in general BEs are modulated not only by the electron density of a specific atomic site but also by the capability of the electrons to screen the core hole. As in the present work we suggest employing experimental BEs to probe the electron density of the complexes under study, it is important to verify that the BE trend is mainly governed by the inductive effects. For this reason it is very useful to also extract from the theory information pertaining to only initial states. This can be done by simply monitoring the Kohn–Sham (KS) eigenvalue of the core state calculated at the ground-state level, which is not affected by relaxation. For this reason we have inserted in Tables 1 and 2 also the KS eigenvalue for comparison. The Δ SCF calculations have been performed by solving the KS equations for both initial and final states, employing the LCAO method implemented in the ADF program.¹⁷ We have employed a TZ basis set for W, while for other atoms a DZP set has been employed. The VWN¹⁸ exchange–correlation potential has been employed in all calculations. The geometries of all the complexes have been optimized for all diphosphine ligands, and the BE calculations have been performed on the optimized structures.

Results

An example of a W 4f XPS spectrum of the compound $W(CO)_4(dppe)$ is shown in Figure 2, together with the results of the peak fitting analysis, which allows the

Table 1. W 4f Binding Energies of $W(CO)_4(L-L)^a$

complex	L–L	exptl W 4f _{7/2} BE (eV)	calcd	
			W 4f BE Δ SCF (eV)	W 4f BE – ϵ (eV)
1	dppm	31.123(7)	46.58	38.91
2	dppe	31.118(6)	46.57	38.92
3	dppp	31.081(6)	46.54	38.89
4	dppb	31.136(4)	46.52	38.88
5	dmpe	31.296(8)	46.65	38.74
6	F-dppe	31.931(90)	47.38	39.58

^a Calculated values are reported at both the Δ SCF level and as KS eigenvalues (– ϵ).

identification of the components contributing to the total spectrum, and a more precise measurement of KE, intensity, and width of the single components. The overall spectrum has been simulated by the convolution of three components. The first and most important doublet, being due to the W 4f atoms in the original complex (W 4f_{7/2} BE = 31.118(6) eV), is overlapped with two other signals correlated to two different decomposition products: the second one upon beam exposition (W 4f_{7/2} BE = 31.368(451) eV) and the third one due to oxidation during the sample preparation (W 4f_{7/2} BE = 37.718(353) eV). The identification of the three components has been suggested by the observation of a sequence of spectra acquired on the same spot, where the progressive intensity decrease of the first component is accompanied by the parallel increase of the second, broader component.¹³ In contrast, the third component remains unchanged upon beam exposition, but its intensity depends on the procedure adopted during sample preparation. The acquisition procedure of the spectra has been optimized in order to minimize the amount of the second component (i.e.: the decomposition upon beam exposition), which was calculated to be less than 10% of the original complex. The whole spectrum shows an excellent separation among the peaks, with an unprecedented overall resolution for a solid-state sample prepared in air.

The list of the W 4f_{7/2} BEs for complexes 1–6, calculated on the basis of the corresponding KEs, is shown in Table 1 with the 95% interval confidence given in parentheses.

Analogously, the P 2p spectrum of $W(CO)_4(dppe)$ is shown in Figure 3. Although the P 2p separation among the three components is much smaller than in the case of the W 4f core level, we can assign them on the basis of their relative intensities, with the three components correlated to the original complex (P 2p_{3/2} BE = 130.876(21) eV), to the compound decomposed upon beam exposition (P 2p_{3/2} BE = 131.386(796) eV), and to the complex decomposed during the sample preparation (P 2p_{3/2} BE = 131.180(233) eV), respectively. As for the W4f case, the three components have been assigned on the basis of the evolution of the spectrum upon beam exposition. A further weak and broad shoulder at about 126.6 eV of BE has been identified as an Auger peak of the gold foil underlying the sample. Also in this case, the resolution between the peaks is nearly comparable to that of the best spectra reported in the literature for phosphine-containing gas-phase samples.¹¹

The P 2p_{3/2} BEs for all six complexes, calculated on the basis of the corresponding KEs, is shown in Table 2 with the 95% interval confidence given in parentheses.

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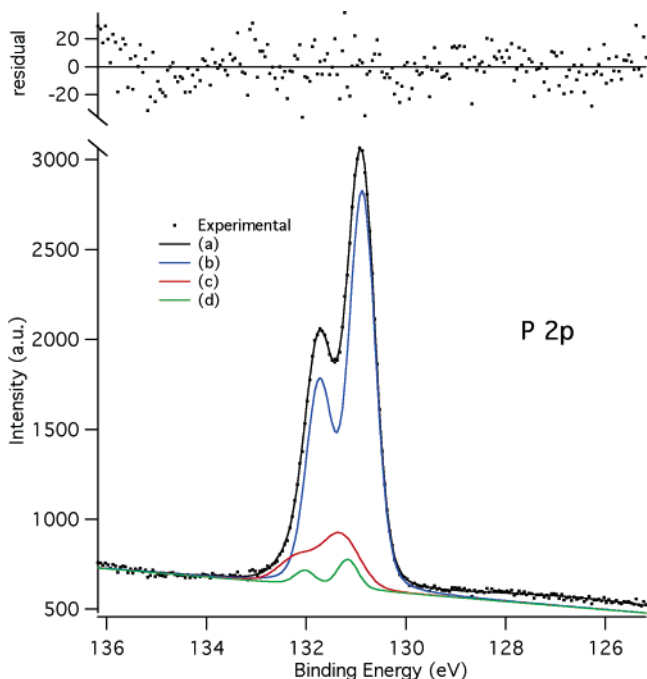


Figure 3. Experimental P 2p spectrum of $W(CO)_4(dppe)$ (**2**) and its simulation by fitting: (a) overall fitted spectrum; (b) spectrum of the first component; (c) spectrum of the second component; (d) spectrum of the third component. The residual shown is the difference between the experimental and overall fitted spectra.

Table 2. P 2p Binding Energies of $W(CO)_4(L-L)^a$

complex	L-L	exptl P 2p _{3/2} BE (eV)	calcd	
			P 2p BE Δ SCF (eV)	P 2p _{3/2} BE - ϵ (eV)
1	dppm	131.058(8)	138.96	124.21
2	dppe	130.876(21)	138.77	124.02
3	dppp	130.828(6)	138.69	123.94
4	dppb	130.801(14)	138.69	123.93
5	dmpe	131.285(26)	138.96	123.83
6	F-dppe	132.378(105)	140.00	125.24

^a Calculated values are reported at both the Δ SCF level and as KS eigenvalues ($-\epsilon$).

We can analyze the W4f data reported in Table 1 by separating the effect on the BEs induced by (i) variation of the substituents on phosphorus atoms and (ii) variation of chain length between phosphorus atoms. (i) Comparison of BEs for compounds **2**, **5**, and **6** reveals that the nature of substituents on phosphorus atoms of $R_2P(CH_2)_2PR_2$ is relevant in determining BEs ($R = Ph, Me, C_6F_5$). (ii) The modification of the chain length only causes a slight variation of BE, almost within the instrumental reproducibility (Table 1, entries 1–4).

As evidenced by the results reported in Table 2, the P2p BEs follow the same trends observed for the W 4f data; i.e., the effect of the substitution on the phosphorus atoms causes more important BE differences than does the variation of chain length, except for the BE of dppm complex **1**, which is significantly higher than for complexes **2**–**4**.

The results of DFT calculations of W 4f and P 2p core BEs are also reported in Tables 1 and 2, respectively. It is well-known¹⁴ that in DFT the calculated absolute binding energies are affected by errors due to the presence of spurious electronic self-interaction terms. However, these errors remain practically constant along

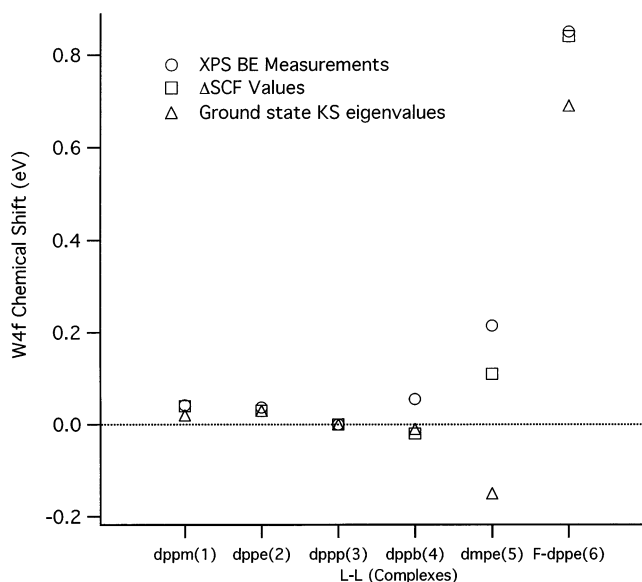


Figure 4. W 4f BE chemical shifts of complexes **1**–**6** referenced to the $W(CO)_4(dppp)$ (**3**) BE: XPS experimental measurements, Δ SCF calculations, and ground-state KS eigenvalues.

a series of analogous molecules; therefore, they are practically canceled if relative differences are considered. For this reason it is more convenient to discuss the theoretical BEs in terms of shifts. With regard to the W4f core level, the comparison among the XPS measurements, the Δ SCF calculations, and the KS eigenvalues shows the same trend for all three methods, with the exception of **5**, which gives a rather high Δ SCF BE but the lowest KS eigenvalue. This finding indicates that the dmpe ligand is less effective in screening the core hole, and therefore, in **5** the relaxation plays a minor role with respect to the other series terms. The same trend is found for the P 2p BE (Table 2): in this case the differential relaxation detected in **5** is even more pronounced than in W, due to the vicinity of the P atom to the methyl groups.

The comparison between theory and experiment of W 4f BE for all six complexes is better visualized in Figure 4, where the BE values are reported in terms of shifts relative to $W(CO)_4(dppp)$ (**3**), taken as reference. The experimental slight BE decrease on going from **1** to **3**, followed by an increase which is very pronounced on going from **5** to **6**, is very well reproduced by the Δ SCF values, apart for a minor discrepancy in the ordering between **3** and **4**.

An analogous comparison for the P 2p core level BEs is shown in Figure 5. The significant decrease of BE from dppm to dppe is confirmed in both experimental and theoretical data, whereas the differences among compounds **2**–**4** are just above the uncertainty related to both methods. As observed for W 4f data, also P 2p BEs increase significantly for compounds **5** and **6**, with a rather good agreement between experimental and theoretical results.

Discussion

Photoemission spectroscopy can in principle be considered as the most suitable technique to probe electronic properties of a series of ligands as a function of

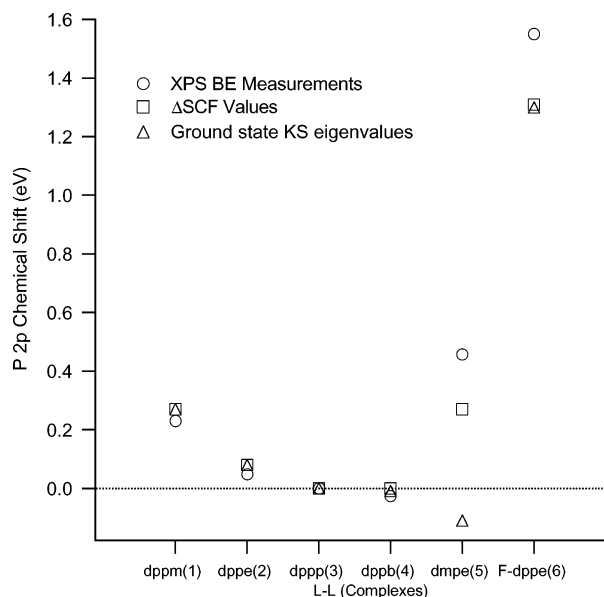


Figure 5. P 2p BE chemical shifts of complexes **1–6** referenced to the $W(CO)_4(dppp)$ (**3**) BE: XPS experimental measurements, Δ SCF calculations, and ground-state KS eigenvalues.

substituents. A number of studies are present in the literature, which report on photoemission measurements on series of coordination compounds, either on the valence shell (UPS) or on the core levels (XPS).^{11,12} However, to detect the small BE variation induced by minor modifications in the ligand structure, it is necessary to turn to instrumental techniques with very high energy resolution power, such as the SR photoemission.

In the results of SR XPS measurements we are now reporting, W 4f and P 2p BEs in the series $W(CO)_4(L-L)$ appear to be (i) strongly influenced by the substituents on phosphorus atoms but (ii) only slightly influenced by the chain length connecting the phosphorus atoms. The latter effect is in fact detectable only in P 2p BEs, whereas the BE shifts obtained for the W 4f core level are comparable to instrumental reproducibility. Then, it appears that the chelate ring size has a minor influence on the P–W bond nature of these compounds, despite the change of natural bite angle^{1a} in the series from dppm (four-membered chelate ring) to dppb (seven-membered chelate ring). It must also be noted that such small BE chemical shifts can be partially ascribed to the “buffer” effect of the $W(CO)_4$ fragment, which is expected to attenuate differences in the donating properties of phosphines by corresponding variations in the extent of W–CO π -bond. Lichtenberger and Jatcko, who also reported⁸ minor changes in the UPS data of $M(CO)_4(dmpm)$ and $M(CO)_4(dmpe)$ ($M = Mo, W$; $dmpm = bis(dimethylphosphino)methane$, $dmpe = bis(dimethylphosphino)ethane$) interpreted such results in terms of “phosphine twist”: i.e., the capability of phosphines to accommodate the geometric constraints while maintaining as much of the M–P bond as possible, resulting in a slightly bent metal–phosphine bond.

Conversely, the pronounced effect of the substituents on phosphorus atoms as evidenced by both experimental and calculated values deserves a deeper discussion, mainly regarding the relative donor capability of phenyl- and methylphosphines. Particularly relevant to this

issue are studies by Bancroft and co-workers,^{11,19} who reported UPS measurements on the series $W(CO)_5-(PMe_nPh_{3-n})$ and $W(CO)_4(R_2P(CH_2)_nPR_2)$, and the trend in W 5d BEs and in the stabilization energy of the phosphorus lone pair on coordination. These authors deduced that phenylphosphines are slightly stronger donors than methylphosphines: although they take into account the possible differential relaxation effects, they concluded that in this case the BE shifts are related to the real relative molecular orbital energies.

The XPS and Δ SCF results we are reporting in Figures 4 and 5 show a behavior similar to the W 5d data reported by Bancroft, with the phenylphosphine complex BE (**2**) lower than the corresponding methylphosphine (**5**) value. Indeed, dmpe is less effective in screening the core hole, and this is the reason its experimental and Δ SCF values are high in the series. This effect can be ascribed to the methyl groups, which are less effective as electron reservoirs to screen the core hole with respect to the phenyl group. In fact, the π electrons of the phenyl moiety are expected to be much more polarizable and therefore able to screen the core hole than the more rigid σ electrons of the methyl group.

However, the results obtained by taking into account only the initial state effect (i.e., the ground-state KS eigenvalue) indicate an opposite behavior. The trend evidenced in Figures 4 and 5 indicates that for dmpe in the ground state the W atom is the least positive in the series, as a consequence of a higher electron density on the metal: i.e., of the enhanced donor properties of the methyl substituents. On the other hand, it is known that relaxation effects in core level BE shifts can be much higher than in the valence band;²⁰ this should account for the discrepancy between our ground-state results and W 4f BE data as well as Bancroft’s W 5d measurements. The same considerations can be applied to the P atom, with an enhanced intensity due to the proximity of the P atom to the substituted moieties. We wish to point out that the very satisfactory agreement between the trends of XPS and Δ SCF results supports the validity of both methods, thus confirming the reliability of KS results as well.

Finally, it is worth noting the very strong effect found for **6** in comparison to **2**, which is entirely ascribed to the initial state effect caused by the high F electronegativity. Although such behavior could be easily foreseen, the excellent agreement of predictions based on the fluorine inductive effect, experimental measurements, and theoretical calculations is a further proof of the validity of the methods used.

However, our results suggest that it is safe to use XPS measured BEs to extract information about electron densities only within a homologous series of compounds: as a matter of fact, the trend given by XPS and Δ SCF data is perfectly confirmed by KS eigenvalues in the series **1–4**, whereas measurements on the dmpe compound **5** should be considered within a series of alkyl-substituted phosphines, where analogous trends in Δ SCF and KS calculations are expected.

(19) Puddephatt, R. J.; Dignard-Bailey, L.; Bancroft, G. M. *Inorg. Chim. Acta* **1985**, *96*, L91.

(20) Carlson, T. A., *Photoelectron and Auger Spectroscopy*; Plenum: New York, 1975; p 74.

Conclusions

In the present paper we have reported the first example of application of SR XPS measurements on a series of solid-state coordination compounds. In the compounds $W(CO)_4(P-P)$, the W 4f and P 2p BE measurements allow an evaluation of the relative donor capability of the chelating diphosphines, as a function of chelate ring size and substituents on phosphorus. The chain length between the phosphorus atoms has only a minor effect on the P and W electron density, whereas the nature of substituents has an important influence on both core levels. A comparison between experimental BEs and DFT-based calculations results has shown an

excellent agreement in the trends, thus confirming the feasibility of the techniques used.

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