

U.V.-photoelectron (He I and He II) Studies of $M(\text{CO})_5\text{PR}_3$ ($M = \text{Cr}, \text{W}$ and $R = \text{C}_6\text{H}_{11}, \text{C}_6\text{H}_5, \text{O}-i\text{-C}_3\text{H}_7, \text{OC}_6\text{H}_5$) and $\text{W}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$

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U.V. photoelectron spectra (He I and He II) and ^{13}C NMR spectra of $M(\text{CO})_5\text{PR}_3$ ($M = \text{Cr}, \text{W}$, and $R = \text{C}_6\text{H}_{11}, \text{C}_6\text{H}_5, \text{O}-i\text{-C}_3\text{H}_7, \text{OC}_6\text{H}_5$) are presented and assigned by comparison with the spectra of free PR_3 and $M(\text{CO})_6$. From the PE spectra it could be deduced that σ -donor properties increased in the order PX_3 ($X = \text{F}, \text{Cl}, \text{Br}$) $<$ $\text{P}(\text{OC}_6\text{H}_5)_3 <$ $\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3 <$ $\text{P}(\text{C}_6\text{H}_5)_3 <$ $\text{P}(\text{C}_6\text{H}_{11})_3$ opposite to the π -acceptor properties. Backbonding to a P -donor ligand is stronger than to a pyridine-like ligand. It is shown that σ -interaction in $\text{Cr}(\text{CO})_5\text{L}$ is weaker than in the previously published $\text{Fe}(\text{CO})_4\text{L}$ compounds and that the splitting of the iron e' and e'' orbitals is not a good parameter for π -backbonding. ^{13}C carbonyl resonances are correlated with the σ -donor/ π -acceptor properties of the ligand, whereas in non aromatic PR_3 ligands the ^{13}C resonances are related qualitatively to the reduction of electron density on complexation.

Introduction

The study of He I and II photoelectron spectroscopy of Group VI B hexacarbonyls [1] has been extended to the related monosubstituted complexes $M(\text{CO})_5\text{L}$ [2–11], where L is a substituted pyridine [9], azole [10] or phosphorus trihalide [11]. Conclusions from photoelectron spectra have been used in combination with other spectroscopic data to reveal some aspects concerning the electronic structure.

In this paper we will discuss the He I and II spectra of a series of $M(\text{CO})_5\text{PR}_3$ complexes in comparison with results of earlier published N and P donor complexes. From the photoelectron spectra of the free PR_3 ligands [12–14] it has been concluded that the first IP nearly always arises from the phosphorus lone pair and that electronic as well as steric effects of R influence the ionization potentials. Steric

effects are also important upon complexation of a phosphorus donor ligand [15].

^{13}C NMR spectra of a wide variety of $M(\text{CO})_5\text{L}$ complexes have been published with special emphasis on the relationship between chemical shifts of the carbonyl resonances and σ donation/ π backbonding [16–19]. The difference in ^{13}C NMR resonances between free and complexed ligands will be related to the results obtained from the photoelectron spectra.

Experimental

Preparations

The complexes were prepared by heating hexacarbonyl and the ligand in diglyme at the reflux temperature according to the literature [20, 21]. Excess of hexacarbonyl was removed by vacuum sublimation. The complexes were used without further purification except for the phosphite complexes which were distilled under reduced pressure prior to use.

Physical Measurements

The photoelectron spectra were recorded on a Perkin-Elmer P.S.-18 spectrometer modified with a Helectros He I/He II source. The spectra were calibrated by adding simultaneously a mixture of Ar and Xe into the ionization chamber. A direct inlet probe was used for all complexes. The temperature of the probe was raised until evaporation was sufficient. The liquid phosphite complexes were loaded on Al_2O_3 before inserting into the apparatus.

The ^{13}C NMR spectra were obtained on a Bruker WP80 spectrometer at 20.1 MHz with full proton decoupling.

Results

The spectra of the complexes could be classified in a d-orbital and a ligand and carbon monoxide orbital region.

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TABLE I. Vertical Ionization Potentials (eV) of the Metal d-Orbitals (see also Fig. 1).

Cr(CO) ₅ P(C ₆ H ₁₁) ₃		7.24	7.41
Mo(CO) ₅ P(C ₆ H ₁₁) ₃		7.44	7.62
W(CO) ₅ P(C ₆ H ₁₁) ₃	7.29	7.47	7.70
Cr(CO) ₅ P(C ₆ H ₅) ₃		7.30	7.50
W(CO) ₅ P(C ₆ H ₅) ₃	7.36	7.55	7.71
Cr(CO) ₅ P(O-i-C ₃ H ₇) ₃		7.61	
W(CO) ₅ P(O-i-C ₃ H ₇) ₃		7.82	
Cr(CO) ₅ P(OC ₆ H ₅) ₃		7.67	
W(CO) ₅ P(OC ₆ H ₅) ₃		7.90	
W(CO) ₅ As(C ₆ H ₅) ₃	7.37	7.60	7.78

d-Orbital Region

In analogy with previous assignments [1–11] the first band system from 7–8 eV is attributed to the metal d-orbitals. The vertical ionization potentials of those orbitals are listed in Table I.

In the spectra measured an intensity increase of these bands was observed in going from He I to He II. This is a common feature for orbitals with a large percentage d-character.

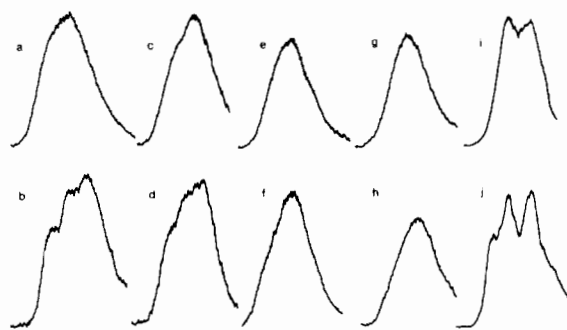


Fig. 1. The metal d-bands of a) Cr(CO)₅P(C₆H₁₁)₃, b) W(CO)₅P(C₆H₁₁)₃, c) Cr(CO)₅P(C₆H₅)₃, d) W(CO)₅P(C₆H₅)₃, e) Cr(CO)₅P(O-i-C₃H₇)₃, f) W(CO)₅P(O-i-C₃H₇)₃, g) Cr(CO)₅P(OC₆H₅)₃, h) W(CO)₅P(OC₆H₅)₃, i) Cr(CO)₅-pyrazine and j) W(CO)₅pyrazine.

The local C_{4v}-symmetry around the metal atom may result in a splitting into e and b₂ components. Moreover, in the W-complexes spin-orbit coupling gives an additional splitting of the E-state according to the double group C_{4v}* [22]. In agreement with this two bands were observed for the P(C₆H₁₁)₃ and P(C₆H₅)₃ chromium and molybdenum pentacarbonyl complexes and three bands for the corresponding tungsten complexes.

The stronger donating ability of the P(C₆H₁₁)₃ and P(C₆H₅)₃ ligands cause the large splitting of the d-orbitals as observed, whereas the complexes of the weaker donating phosphite ligands only showed some broadening of the band (Fig. 1).

TABLE II. Vertical Ionization Potentials (eV) of Bands Belonging to the Ligand Orbitals (see also Fig. 2–6).

P(C ₆ H ₁₁) ₃	7.75	9.38	10.3			17.9	19.4	22.9
Cr(CO) ₅ P(C ₆ H ₁₁) ₃	9.16	9.66	10.5	12.5	17.0 ^a	18.3	19.7	23.1
Mo(CO) ₅ P(C ₆ H ₁₁) ₃	9.15	9.75						
W(CO) ₅ P(C ₆ H ₁₁) ₃	9.37	9.80	10.5	12.4	16.8 ^a	18.4	19.7	23.2
P(C ₆ H ₅) ₃	7.97	9.25	10.88	11.76		18.7		22.3
Cr(CO) ₅ P(C ₆ H ₅) ₃	8.77	9.41	10.41	11.2	12.5	16.8 ^a	19.0	22.5
W(CO) ₅ P(C ₆ H ₅) ₃	8.80	9.42	10.50	11.3	12.3	16.8 ^a	18.8	22.7
P(O-i-C ₃ H ₇) ₃	8.76	9.90	10.68	11.3	12.8	18.2	19.4	22.2
Cr(CO) ₅ P(O-i-C ₃ H ₇) ₃	9.70		10.5	11.2	12.7	17.3 ^a	18.3	19.5
W(CO) ₅ P(O-i-C ₃ H ₇) ₃	9.80		10.4	11.2	12.7	17.3 ^a	18.5	19.6
P(OC ₆ H ₅) ₃	8.80	9.47	10.9			19.3		22.8
Cr(CO) ₅ P(OC ₆ H ₅) ₃	8.96	9.46	10.7	11.1	17.2 ^a	19.4		23.4
W(CO) ₅ P(OC ₆ H ₅) ₃	9.07	9.45	10.7	11.1	17.4 ^a	19.6		23.3
As(C ₆ H ₅) ₃	8.11	9.15	10.49	11.8		18.6		22.2
W(CO) ₅ As(C ₆ H ₅) ₃	8.98	9.36	10.45	11.0	12.4	17.9 ^a	19.3	22.3

^aVertical IP of band assigned to carbonyl 4σ-level.

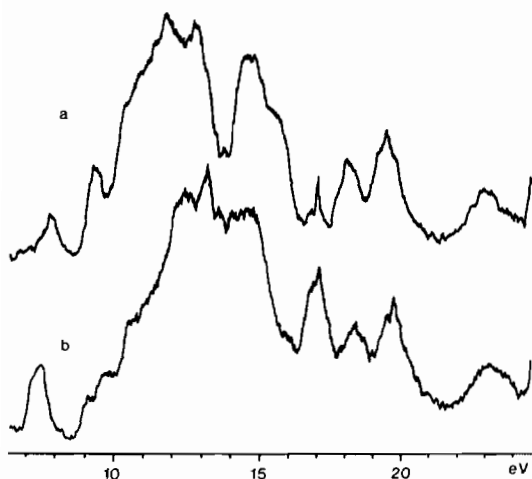


Fig. 2. The He II photoelectron spectra of $\text{P}(\text{C}_6\text{H}_{11})_3$ (top) and $\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_{11})_3$ (bottom).

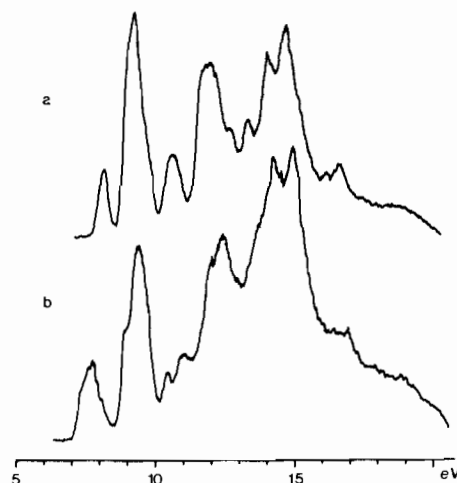


Fig. 4. The He I photoelectron spectra of $\text{As}(\text{C}_6\text{H}_5)_3$ (top) and $\text{W}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$ (bottom).

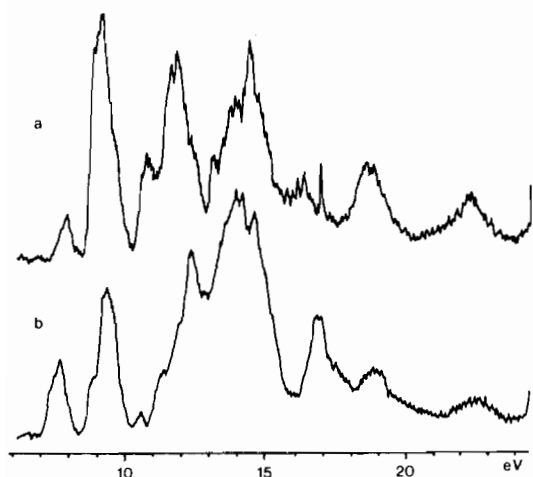


Fig. 3. The He II photoelectron spectra of $\text{P}(\text{C}_6\text{H}_5)_3$ (top) and $\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ (bottom).

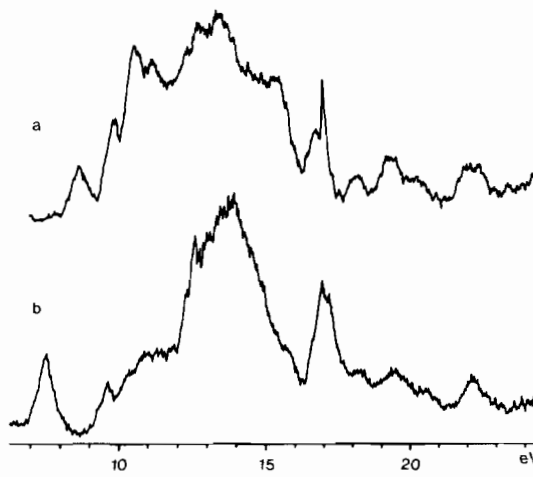


Fig. 5. The He II photoelectron spectra of $\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$ (top) and $\text{Cr}(\text{CO})_5\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$ (bottom).

Ligand and Carbon Monoxide Orbitals

The ionization potentials in this region between 8–24 eV are listed in Table II. Because the carbonyl bands are expected above 13 eV in analogy with the metal hexacarbonyls the features between 8 and 13 eV could unambiguously be assigned to phosphorus ligand orbitals.

The spectra of the complexes in this region showed a direct correspondence with spectra of the free ligands, so the assignment was made accordingly. This is nicely demonstrated in Figs. 2–6 for $\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$, $\text{W}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$, $\text{Cr}(\text{CO})_5\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$ and $\text{W}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$ respectively.

The intense band between 13–15 eV is a combination of the carbonyl 5σ and 1π orbitals and phosphorus ligand orbitals. The carbonyl 4σ orbital could

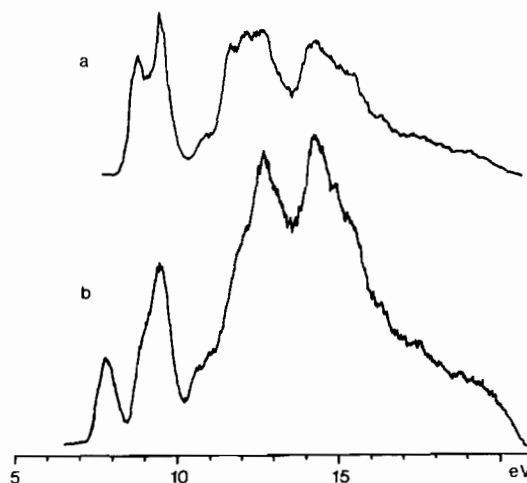


Fig. 6. The He I photoelectron spectra of $\text{P}(\text{OC}_6\text{H}_5)_3$ (top) and $\text{W}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$ (bottom).

TABLE III. ^{13}C NMR Chemical Shifts of $\text{M}(\text{CO})_5\text{PR}_3$ and Free PR_3 in CDCl_3^a Relative to TMS with J(P-C) in Brackets.

								CO(ax)		CO(eq)		
$\text{P}(\text{C}_6\text{H}_{11})_3$	31.2	(12)	30.7	(11)	27.3	(10)	26.2					
$\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_{11})_3$	36.9	(15)	29.5		27.7	(10)	26.2	221.5	(7)	218.5	(13)	
$\text{Mo}(\text{CO})_5\text{P}(\text{C}_6\text{H}_{11})_3$	35.8	(14)	29.8		27.5	(10)	26.1	210.6	(21)	207.4	(9)	
$\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_{11})_3$	36.4	(19)	29.9		27.4	(10)	26.0	198.9	(18)	198.3	(7)	
$\text{P}(\text{C}_6\text{H}_5)_3$	137.3	(12)	133.7	(20)	128.6		128.4	(7)				
$\text{Cr}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$	134.9	(37)	132.6	(11)	130.1	(2)	128.5	(10)	221.7	(6)	216.7	(12)
$\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$	135.4	(42)	133.0	(12)	130.2		128.7	(10)	199.1	(22)	197.3	(7)
$\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$			65.1	(12)	23.9	(4)						
$\text{Cr}(\text{CO})_5\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$			69.6	(6)	23.9	(4)		220.5	(6)	216.4	(22)	
$\text{W}(\text{CO})_5\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$			69.8	(5)	23.8	(4)		198.7	(37)	196.1	(11)	
$\text{P}(\text{OC}_6\text{H}_5)_3$	151.4	(3)	129.4		123.9		120.4	(7)				
$\text{Cr}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$	151.2	(9)	129.9		125.3		121.2	(5)	218.5		214.3	(21)
$\text{W}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$	151.3	(6)	129.9		125.3		121.3	(5)	196.5	(44)	194.2	(10)

$^a \delta_{\text{C}}^{\text{CDCl}_3}$ 76.9 ppm.

readily be assigned by its high intensity in the He II spectra. The low intensity in the He I spectrum is due to the analyzer discrimination at low kinetic energy. The vertical ionization potential varied between 16.8 and 17.9 eV which is somewhat lower than that in the free carbonmonoxide (19.68 eV). The bands with higher IP, all attributed to phosphorus ligand orbitals, show a stabilization with respect to the free ligand.

^{13}C NMR

^{13}C resonances from the carbonyls and from the phosphorus ligands are gathered in Table III. The carbonyl resonances were shifted downfield with respect to the parent metal hexacarbonyls in agreement with previous observations. In accordance with literature we assigned $\delta_{\text{CO}}(\text{trans}) > \delta_{\text{CO}}(\text{cis})$. The assignment of the ^{13}C resonances for the coordinated phosphorus ligands was straight forward in comparison with the free ligands. The *cis* J($^{183}\text{W}-^{13}\text{C}$) constants only raised between 125 and 127 eV for all complexes.

Discussion

The bonding properties of these monosubstituted pentacarbonyls can best be described in terms of the σ -donating abilities of the ligands and π -backbonding. The expected order of donating properties of the ligands is $\text{P}(\text{OC}_6\text{H}_5)_3 < \text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3 < \text{P}(\text{C}_6\text{H}_5)_3$. This is reflected in the results in various ways:

a) For all the complexes studied a significant destabilization of the occupied metal d-orbitals was

measured with respect to the metal hexacarbonyls. This destabilization shows that a net electron shift occurs towards the metal carbonyl. Especially the trend in the $d(b_2)$ ionization potential will reflect the charge on the metal and thus the net donating properties of L in the expected order, since this d-orbital is directed into the plane of the equatorial carbonyls and will not interact with the phosphorus ligand. $\text{As}(\text{C}_6\text{H}_5)_3$ closely resembles $\text{P}(\text{C}_6\text{H}_5)_3$ within this series.

b) For a series of complexes in which steric effects play only a minor role it could be demonstrated that a low ionization potential of the lone pair is stabilized to a larger extent. For $\text{P}(\text{C}_6\text{H}_{11})_3$ this stabilization was about 1.5 eV, whereas for $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$ it was estimated to range from 0.8 to 1.2 eV. This confirms the stronger σ -bonding properties of $\text{P}(\text{C}_6\text{H}_{11})_3$. The high intensity of the first band in the photoelectron spectrum of $\text{P}(\text{OC}_6\text{H}_5)_3$ as well as the small shift upon coordination proved that the phosphorus lone pair orbital was overlapped by a band from the phenyl π -orbitals. In agreement with the much higher lone pair ionization potential, PX_3 (X = F, Cl, Br) [11] possesses lower electron donating properties than the phosphites. Comparison of the spectra of $\text{P}(\text{C}_6\text{H}_{11})_3$ and $\text{P}(\text{C}_6\text{H}_5)_3$ with those of $\text{P}(\text{CH}_3)_3$ chromium pentacarbonyl [2] showed that the $\text{P}(\text{CH}_3)_3$ lone pair was stabilized to a similar extent upon complexation although the IP in the free $\text{P}(\text{CH}_3)_3$ ligand was found much higher. This may be due to steric effects since the cone angles of $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{CH}_3)_3$ are 170° , 145° and 118° respectively [15]. This stabilization of the

lone pair upon complexation is smaller for phosphorus ligands than for nitrogen ligands [9, 10], indicating that σ -donation is less important for phosphorus ligands.

c) A stronger electron donating capacity of the ligand is accompanied by an increase in the π -backbonding to the five carbonyls. This is reflected in the photoelectron spectrum by a destabilization of the carbonyl 4σ level with respect to the metal hexacarbonyl. The same will happen to the 5σ and 1π carbonyl levels; however these IP's are more difficult to locate due to strong overlapping bands. A corresponding trend is observed, but in reversed order, for the stabilization of the low lying orbitals of the phosphorus ligands upon coordination.

The π -acceptor properties of the corresponding ligands decrease in the reverse order compared with the σ -donor abilities, however to a much lesser extent. The splitting of the d-orbitals can be used as the best parameter for the π -backbonding properties of the ligand. The π -backbonding from the metal d(e)-orbital into the empty phosphorus 3d-orbitals will be greater when the splitting decreases. Although the resolution in the d-orbital region was poor the expected reversed order of the ligands could be deduced (Fig. 1).

In particular, in the cases of the tungsten complexes accurate determination of the splitting in the d-band is hardly possible because of the asymmetry of the envelopes and the differences in intensity of the individual transitions. Hall *et al.* [7] made a deconvolution by fitting the bands with asymmetric Gaussian peaks with equal intensities. For $\text{W}(\text{CO})_6$ however the intensity ration is 1:2.7 and not 1:2 as expected. Also in the spectra of the $\text{W}(\text{CO})_5$ N-donor complexes a deviation from the expected 1:1:1 intensity ratio could be obtained since here the peaks are well separated (Fig. 1 i-f). So with some hesitation we can say that this splitting appears to be smaller for $\text{W}(\text{CO})_5$ P-donor complexes than for the analogous N-donor complexes suggesting a reduced spin-orbit coupling for the former complexes. This is in agreement with the obtained larger delocalization of the metal d-electrons into the phosphorus 3d ligand orbitals.

When the bonding properties of the phosphorus ligands are compared with N-donor ligands, the latter must be divided into imines and amines. In general the nitrogen lone pair of pyridine and azole like ligands possess higher ionization potentials than the phosphines and phosphites under study. The net effect of σ -donation and π -backbonding as observed from the ionization potential of the metal d(b_2) orbitals showed however that these ligands fall inbetween the phosphines and phosphites. This may readily be explained by smaller π -backbonding properties of imines, which was supported experimentally by a larger d-orbital splitting (Fig. 1). The

differences between the photoelectron spectra of the amine complexes and the corresponding phosphorus ligand complexes is not well understood just as the differences between amine and imine complexes [9] are not well understood. Hybridisation and steric effects may complicate a comparison.

The conclusions from photoelectron spectroscopy are in close agreement with those of the force constants calculated by the Cotton-Kraihanzel method [24-26]. The ν_{CO} A_1^1 is significantly higher in a metal pentacarbonyl complex with a P-donor than with a N-donor ligand suggesting a higher π -backbonding ability for the P ligand. The force constant of the carbonyl bond *trans* to L is also higher for a phosphorus complex than for a nitrogen donor complex. This again is an affirmation of the better σ -donor abilities of the N-ligand and of the better delocalization of the metal d-electrons towards the phosphorus ligand.

With respect to the NMR results, Bodner [26] suggested that the *cis* carbonyl ^{13}C chemical shift data for $\text{M}(\text{CO})_5\text{L}$ derivatives would indicate a net donation of electron density from the ligand to the $\text{M}(\text{CO})_5$ moiety. Variation of this effect will be partly compensated by a distribution over the carbonyl moiety which may be regarded a buffer. When the ionization potential of the chromium d(b_2)-orbital, a parameter for the electron density on the metal, is plotted against the *cis* carbonyl ^{13}C chemical shift reasonable correlation for the various N [9, 10, 19] and P-donor complexes is obtained. The correlation with ^{13}C chemical shift data of the *trans* carbonyl was less pronounced. Although the ionization potentials of the tungsten metal d-orbitals are not well pin pointed due to spin-orbit coupling it is clear that a relationship between these values and the chemical shift seems less obvious. Both the *cis* and *trans* carbonyl ^{13}C chemical shifts of the $\text{W}(\text{CO})_5$ N-donor [19] complexes are observed at lower field with respect to the $\text{W}(\text{CO})_5$ P-donor complexes, whereas the d-orbital ionization potentials of the N-donor complexes are between those for the phosphine and phosphite complexes. So it seems that the π -system alone rather than the net effect of σ and π -bonding dominates the carbonyl ^{13}C chemical shifts in the W complexes. The stronger delocalisation of the π -electrons towards the ligand L will reduce backbonding to the carbonyls.

The ligand ^{13}C chemical shifts, in particular the carbons close to the coordinating phosphorus, are shifted to lower field upon complexation of $\text{P}(\text{C}_6\text{H}_{11})$ and $\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3$. This has also been observed for $\text{M}(\text{CO})_5$ N-donor complexes. Photoelectron spectra showed that a significant electron shift from L to $\text{M}(\text{CO})_5$ occurred and we tentatively ascribed this to a reduction of the diamagnetic shielding. Changes in ^{13}C chemical shifts of $\text{P}(\text{OC}_6\text{H}_5)_3$ are much smaller upon coordination, whereas in the

complexes of $P(C_6H_5)_3$ the carbon directly attached to the phosphorus is shifted upfield. Apart from a reduction of electron density in these P-donor ligands the interaction of the aromatic π -system with the empty phosphorus d-orbitals [13] will undergo significant changes. It may be due to the latter factor that such a variation in different behaviour is observed.

Recently the He I photoelectron spectra of $Fe(CO)_4L$ ($L = P(C_6H_5)_3$ or $As(C_6H_5)_3$) have been published [27]. Except of course for the bands ascribed to the metal d-orbitals the spectra resemble the corresponding groups VI B metal pentacarbonyls. The differences of the metal d-bands are directly related to the number of metal valence electrons and the coordination number. In analogy with the group VI B metal pentacarbonyls variation in the ionization potential of the band belonging to the d-orbitals in the equatorial plane will chiefly represent the net charge effect of σ -donation and π -backbonding of ligand L in the Fe-complexes. The destabilization of this band upon substitution of CO by $P(C_6H_5)_3$ is 1.1 eV in the iron complex, about 0.2 eV larger than in the chromium complex. Furthermore the ligand orbitals, in particular the coordinating lone pair, are more stabilized in the iron complex. In agreement with group VI B metal pentacarbonyls it was deduced that the net donating properties decrease on going from $P(C_6H_5)_3$ to pyridine.

However, the π -backbonding properties deduced from the reduction of the splitting between e' and e'' in $Fe(CO)_5$ upon monosubstitution deviated. It was concluded that π -backbonding increases in the order $P(C_6H_5)_3 < pyridine < CO$ which is in contrast to our results and contrary to the generally accepted order. The splitting of e' and e'' will reach a lower limit for $Fe(CO)_4N(CH_3)_3$, because no π interaction between Fe and $N(CH_3)_3$ is possible. The splitting is 1.04 eV the same as in $Fe(CO)_4$ pyridine [9], showing that this is not a good parameter for the π -backbonding properties of L.

Conclusions

The σ -donating properties of PR_3 are stronger than the π -acceptor properties. The net charge effect on the metal increases in the order: $P(OC_6H_5)_3 < P(O-i-C_3H_7)_3 < P(C_6H_5)_3 \sim As(C_6H_5)_3 < P(C_6H_{11})_3$ paralleling the σ -donating properties, while π -acceptor properties decrease. Bulky R-groups will reduce the interaction between the metal and the ligand due to steric hindrance. The π -acceptor properties of phosphorus donor ligands are better than those of nitrogen donor ligands such as pyridine and piperidine. The relative donor properties cannot be estimated unambiguously from photoelectron spectra.

The ^{13}C chemical shift of the carbonyls correlate with both the net charge effect of σ and π -interaction of L for the chromium complexes or with

only the π -acceptor properties of L for the tungsten complexes. The downfield ^{13}C chemical shift of non aromatic R groups is in accordance with an electro-density reduction upon complexation.

σ -interaction in the corresponding $Fe(CO)_4L$ complexes seems to be stronger, the splitting of the iron $d(e')$ and $d(e'')$ does not seem to be a good parameter for the π -acceptor properties of L.

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