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Bonding Properties of Some Monosubstituted Chromium and Tungsten Hexacarbonyls $M(CO)_5L$ (L = amine, substituted pyridine, azine)

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The photoelectron spectra of a number of $M(CO)_5L$-complexes with M = Cr, W and L = nitrogen donor ligand have been obtained and assigned. The shifts of the free ligand orbitals and the metal d-orbitals upon complexation are discussed in terms of σ- and π-interactions. The ionization potentials of the metal d-orbitals are related to the CO stretching frequencies in the complexes. A combination of the P.E. and U.V. absorption spectra reveals information about unoccupied orbitals. The ^{13}C-NMR chemical shifts were interpreted in terms of changing electron densities.

Introduction

Substituted hexacarbonyls of group VIB metals have been the subject of quite a number of papers in the last few years. Comparison with the hexacarbonyls is possible since vibrational analysis [1], U.V. photoelectron [2, 3], U.V. absorption [4] and N.M.R. studies [5] as well as m.o. calculations [6–8] are known.

U.V. photoelectron spectra [9] and m.o. calculations [10–13] of some mono-substituted hexacarbonyls have been published before. Several conflicting papers [14, 15] over the interpretation of the U.V. absorption spectra have been appeared. The CO stretching region of $M(CO)_5L$ has been described and related to the σ-donating and π-acceptor abilities of the ligand by various authors [16, 17].

In this paper, we report and compare the results of the U.V. photoelectron, U.V. absorption and ^{13}C-N.M.R. spectra for a number of monosubstituted Cr- and W-hexacarbonyls.

Experimental

Preparation

The Cr complexes were prepared according to W. Strohmeier [18] by irradiation of the hexacarbonyl in tetrahydrofuran with a Rayonet type RS from The Southern New England Ultraviolet Company at 3500 Å. Except for 4-X-pyridine (X = Cl, Br), which is unstable at room temperature, the free ligands were added to the solution before irradiation. The THF was removed by evaporation and, if necessary, water was added to precipitate the complex from the oily residue. Excess hexacarbonyl was removed by vacuum sublimation at 35 °C and the resulting crude product was purified by recrystallisation from n-hexane. Large crystals of $Cr(CO)_5L$ (L = pyridine, 4-Cl-pyridine, 4-Br-pyridine, pyrazine and pyridazine) could be obtained by high vacuum sublimation at about 50 °C.

The compounds $W(CO)_5$4-R-pyridine (with R = H, CH_3, Cl, Br) were prepared from the complex $[W(CO)_5Cl]NEt_4$ [19, 20].

The $Fe(CO)_4L$ (L = pyridine, pyrazine) complexes were prepared from $Fe_2(CO)_9$ in THF according to the method described by Cotton [21].

Spectroscopic Measurements

The HeI photoelectron spectra were obtained with a Perkin–Elmer PS-18 photospectrometer equipped with a 2 mm boron nitride discharge capillary. Calibration by a mixture of Xe and Ar was carried out before and after running the spectrum in order to ascertain that no drift had taken place. In some cases partial decomposition could not be avoided, giving rise to additional bands of hexacarbonyl, free ligand and carbon monoxide.

The U.V. absorption spectra were measured with a Cary-14 spectrophotometer in dichloromethane and iso-octane. The I.R. absorption spectra were recorded on a Beckman 4250. ^{13}C N.M.R. spectra were recorded on a CFT-20 Varian instrument.

Results

Photoelectron Spectra

$M(CO)_5L$ (M = Cr, W; L = piperidine, NH_3, $NH(CH_3)_2$, $N(CH_3)_3$)

Ligand orbitals. In the U.V. photoelectron spectrum of the free piperidine molecule the well separat-

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TABLE I. Vertical Ionization Potentials of $M(CO)_5$amine (M = Cr, W) and the Corresponding Free Ligand (values in eV).

	Metal d-orbitals				M–L Bonding (Lone Pair N)
$Cr(CO)_5N(CH_3)_3$[a]		7.45		7.76	10.57
$W(CO)_5N(CH_3)_3$[a]	7.41		7.62	7.96	10.75
$N(CH_3)_3$					8.45
$Cr(CO)_5NH(CH_2)_5$[b]		7.39		7.69	10.50
$W(CO)_5NH(CH_2)_5$[b]	7.35		7.55	7.87	10.59
$NH(CH_2)_5$[b]					8.67
$W(CO)_5NH(CH_3)_2$[a]	7.41		7.62	7.95	11.14
$NH(CH_3)_2$					8.95
$Cr(CO)_5NH_3$		7.56		7.85	–
$W(CO)_5NH_3$[a]	7.54		7.75	8.06	–
NH_3					10.85

[a] Values taken from ref. 10. [b] $NH(CH_2)_5$ is piperidine.

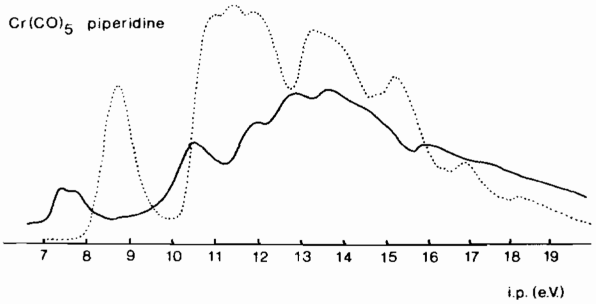

Figure 1. The He I photoelectron spectra of piperidine (-------) and $Cr(CO)_5$ piperidine (———).

TABLE II. Energy Shift for Lone Pairs in $M(CO)_5$amine (values in eV).

Amine	Stabilization Lone Pair		Ionisation Potential Free Ligand	pK_a Free Ligand
	M = W	M = Cr		
$N(CH_3)_3$	2.30	2.12	8.45	9.81
$NH(CH_2)_5$[a]	1.92	1.83	8.67	11.12
$NH(CH_3)_2$	2.19		8.95	10.73

[a] Piperidine.

ed band at 8.67 eV can be attributed to the nitrogen lone pair. The bands at 10.9 eV and lower energy belong to the σ-skeleton.

Upon complexation this lone pair orbital will be stabilized by mixing with the d_{z^2} orbital, *viz.*, 1.83 eV and 1.93 eV in the Cr- and W-complex, respectively (see Figure 1 and Table I).

As is shown in Table II, evidently no relationship exists between the σ-donating ability (pK_a values), the ionization potentials of the lone pair in the free ligand and the stabilization energy upon complexation. Clearly other factors must be involved.

A general increase of the ionization potentials of the σ-skeleton by at least 0.8 eV suggests that a positive charge on the piperidine ligand is created by the donation of this lone pair. This is also confirmed by the ^{13}C-N.M.R. results.

The ionization potentials of the CO ligand were, as expected, found above 13 eV.

Metal orbitals. The two bands with highest energy are assigned to the metal d-orbitals. On substitution in the octahedral complexes the local symmetry is lowered to C_{4v} and the degeneracy of the t_{2g} orbitals is partly lifted giving an $e(d_{xz}, d_{yz})$ and a b_2 (d_{xy}) orbital.

The choice between which band belongs to the e and which to the b_2 species could, for the Cr-complexes, be made by looking at the relative intensities. The energy difference (Δπ) between e and b_2 represents the difference in π-acceptor properties of the amines and carbon monoxide.

On going down group VIB, spin–orbit coupling increases and the results are visible in the spectra. It is, however, possible to distinguish between the contribution of the spin–orbit coupling and that of the difference in π-acceptor properties by the following relations taken from ref. 22:

$$\epsilon_o = \epsilon_e - \tfrac{1}{2}\zeta$$

$$\epsilon_\pm = \tfrac{1}{2}(\epsilon_e + \tfrac{1}{2}\zeta + \epsilon_{b_2}) \pm \tfrac{1}{2}\sqrt{(\epsilon_e + \tfrac{1}{2}\zeta - \epsilon_{b_2})^2 + 2\zeta^2}$$

The results of these calculations are summarized in Table III.

TABLE III. Ionization Potentials of the d-orbitals of $W(CO)_5$ amine Corrected for Spin–Orbit Coupling (values in eV).

	e	b_2	ζ
$W(CO)_5N(CH_3)_3$	7.50	7.74	0.24
$W(CO)_5NH(CH_2)_5$[a]	7.42	7.68	0.25
$W(CO)_5NH(CH_3)_2$	7.50	7.74	0.24
$W(CO)_5NH_3$	7.63	7.88	0.23

[a] $NH(CH_2)_5$ = piperidine.

M(CO)₅L (M = Cr, W; L = pyridine, 4-R-pyridine, 2-R-pyridine, 2,4-R-pyridine, pyrazine, pyridazine)

Ligand orbitals. The electronic structure of $M(CO)_5$pyridine can be studied in comparison with the free ligand for which various papers have been published [23, 24]. The generally accepted assignment of the photoelectron spectra of the free ligand shows a_1(nitrogen lone pair), $a_2(\pi)$ and $b_1(\pi)$ orbitals as the highest filled orbitals. The $b_1(\pi)$ orbital with a large electron density on the nitrogen atom will be more stabilized upon complexation than the $a_2(\pi)$ orbital since the latter has nodes through the N- and γ-position. In contrast to the $a_2(\pi)$ orbital, b_1 possesses the correct symmetry for mixing with metal d-orbitals. Thus the change of the $a_2(\pi)$ orbital energy will give us indications about the relative charge shifts in the ligand on complexation. On these grounds we have assigned the band at 10.39 eV in the Cr-complex to the $a_2(\pi)$ orbital and the band at 11.46 eV to the $b_1(\pi)$ plus the σ(M–N) orbital in the complex. The greater intensity of the latter band suggests the presence of two orbitals here (see also $Fe(CO)_4$-pyridine). This assignment corresponds to stabilization energies of 0.60 eV and 0.90 eV for $a_2(\pi)$ and $b_2(\pi)$, respectively.

The shifts of the ligand lone pair and π-orbitals are in general somewhat larger in the corresponding W-complexes.

A comparison with the energy levels of several alkyl substituted pentacarbonyl pyridine complexes [25] confirms this assignment. For instance, an electron releasing methyl substituent at the γ-position of the pyridine ring especially destabilizes the $b_1(\pi)$ orbital because of its high electron density at this position. This effect is enhanced when stronger electron releasing groups such as tertiary butyl are used. The $a_2(\pi)$ and the σ(M–N) bands are less affected.

In $Cr(CO)_5$-α-picoline, however, the $a_2(\pi)$ and b_1-(π) are equally destabilized since both orbitals have electron density at the α-position. When, finally the

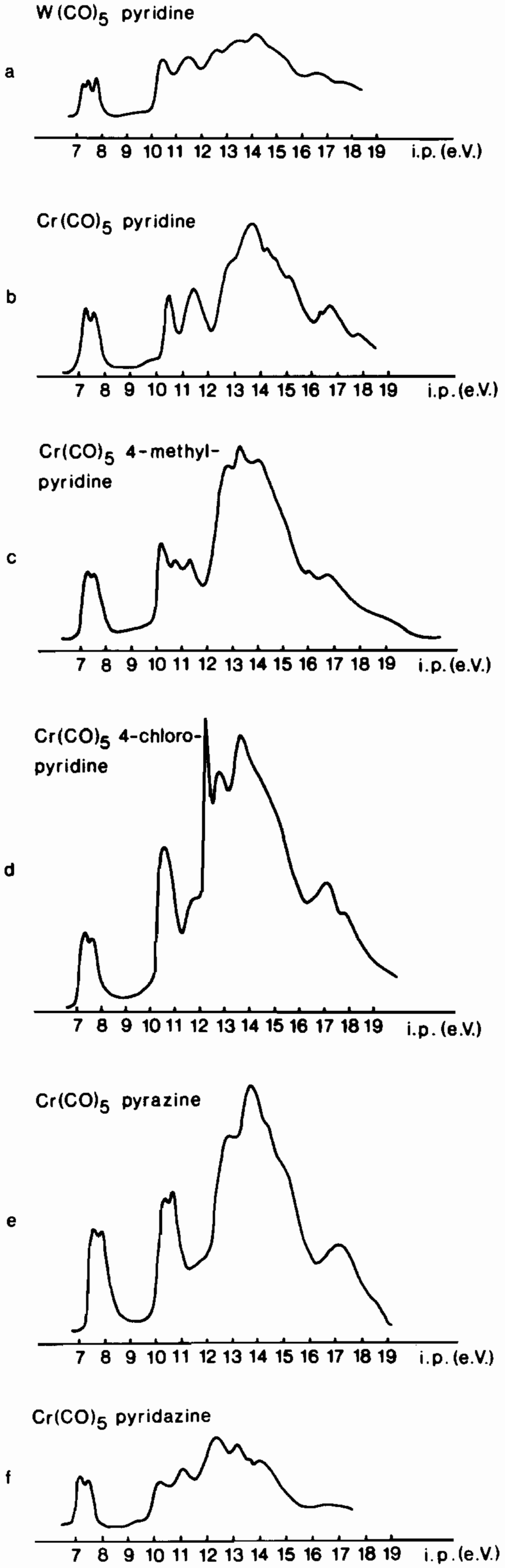

Figure 2. The He I photoelectron spectra of a) $W(CO)_5$ pyridine; b) $Cr(CO)_5$ pyridine; c) $Cr(CO)_5$4-methylpyridine; d) $Cr(CO)_5$ 4-Cl-pyridine; e) $Cr(CO)_5$pyrazine; f) $Cr(CO)_5$pyridazine.

TABLE IV. Vertical Ionization Potentials of $M(CO)_5$ imine (M = Cr, W) and the Corresponding Free Ligand (values in eV).

	Metal d-orbitals				$a_2(\pi)$	$b_1(\pi)$	M–N Bonding Lone Pair N	Other Lone Pair
$Cr(CO)_5$ pyridine		7.29		7.61	10.39	11.46	11.46	
$W(CO)_5$ pyridine	7.20		7.42	7.77	10.42	11.41	11.41	
pyridine					9.79	10.51	9.67	
$Cr(CO)_5$ 4-picoline		7.29		7.60	10.21	10.72	11.32	
$W(CO)_5$ 4-picoline	7.17		7.43	7.79	10.22	10.79	11.39	
4-picoline					9.58	9.94	9.46	
$Cr(CO)_5$ 2-picoline		7.28		7.60	9.88	10.91	11.25	
2-picoline					9.25	10.29	9.39	
$Cr(CO)_5$ 4-tert.butylpyr.		7.18		7.51	10.02	10.45	11.26	
4-tert.butylpyridine					9.48	9.80	9.39	
$Cr(CO)_5$ 2,4-lutidine		7.23		7.49	9.81	10.55	11.09	
2,4-lutidine					8.98	9.80	9.15	
$Cr(CO)_5$ 4-Cl-pyridine		7.34		7.65	10.52	10.52	11.66	12.23
$W(CO)_5$ 4-Cl-pyridine	7.33		7.55	7.89	10.59	10.59	11.68	12.24
4-Cl-pyridine					10.11	10.11	10.11	11.75
$Cr(CO)_5$ 4-Br-pyridine		7.34		7.67	10.38	10.38	11.37	11.43
$W(CO)_5$ 4-Br-pyridine	7.31		7.51	7.86	10.42	10.42	11.38	11.47
4-Br-pyridine					9.82	9.82	9.82	11.00
$Cr(CO)_5$ pyrazine		7.62		7.93	10.72	–	–	10.41
pyrazine					10.18[a]	11.77[b]	9.63	11.35
$Cr(CO)_5$ pyridazine		7.22		7.51	11.15	–	–	10.28
pyridazine					10.61[c]	11.3[c]	9.31	11.3

[a] b_{2g} symmetry. [b] b_{1g} symmetry. [c] The main axis of rotation is in the plane of the ring perpendicular to the N–N bond.

shifts of these orbitals in $Cr(CO)_5$-γ-picoline and in $Cr(CO)_5$-α-picoline relative to $Cr(CO)_5$ pyridine are summed, the results fit the shifts in the corresponding orbitals in $Cr(CO)_5$-2,4-lutidine.

In free 4-X-pyridine (X = Cl, Br) the $b_1(\pi)$ is destabilized relative to free pyridine and merges with the other two bands in one broad band. This has been explained by the mixing with the filled p-orbital of the halogen atom perpendicular to the pyridine ring. The next very sharp peak at 11.75 eV (X = Cl) and 11.00 eV (X = Br) has been assigned to the p-orbital of the halogen atom in the pyridine plane but perpendicular to the z-axis [23]. On symmetry grounds this orbital is not allowed to mix. The filled p_z-orbital of the X-atom will have a lower energy and will participate in the σ-bond. The large stabilization of the very sharp peak upon complexation is an indication of a through-bond interaction with the $M(CO))_5$ moiety *via* the pyridine ring. In comparison with the pyridine complex, however, the 4-X-pyridine complexes show a much smaller lowering of the $b_1(\pi)$ ring orbital upon complexation since part of its electron density in the ring is transfered to the halogen atom. The merging of $a_2(\pi)$ and $b_1(\pi)$ remains after complexation, as is indicated by the intensity of the band (see figure 2d).

In pyrazine [26] a strong through-bond interaction exists between the two nitrogen lone pairs. The bands at 9.63 eV and 11.35 eV have been assigned to a plus combination (n_+) and a minus combination (n_-), respectively. Both combinations participate in the M–N bond in the complex, but to a different extent. Thus different shifts were found for n_+ (0.78 eV) and for n_- (>1.6 eV). The energy change of $a_2(\pi)$ of the ligand is 0.54 eV which is of the same order of magnitude as in the pyridine complexes.

The assignment of the highest filled orbitals of pyridazine [26] corresponds to that of pyrazine, *viz.* two lone pair nitrogen combinations at 9.31 and 11.3 eV and two π-orbitals at 10.61 (a_2) and 11.3 eV (b_1). The lowering of the C_{2v} symmetry of the free ligand upon complexation causes the two pairs of orbitals to become indistinguishable by recombination of the m.o.'s. However, we may expect a general

TABLE V. Ionization Potentials of the d-orbitals of W(CO)$_5$-imine Corrected for Spin–Orbit Coupling (values in eV).

	e	b$_2$	ζ
W(CO)$_5$pyridine	7.29	7.57	0.27
W(CO)$_5$4-picoline	7.30	7.61	0.31
W(CO)$_5$4-Cl-pyridine	7.42	7.71	0.29
W(CO)$_5$4-Br-pyridine	7.38	7.63	0.27
W(CO)$_6$	8.45	8.45	0.17

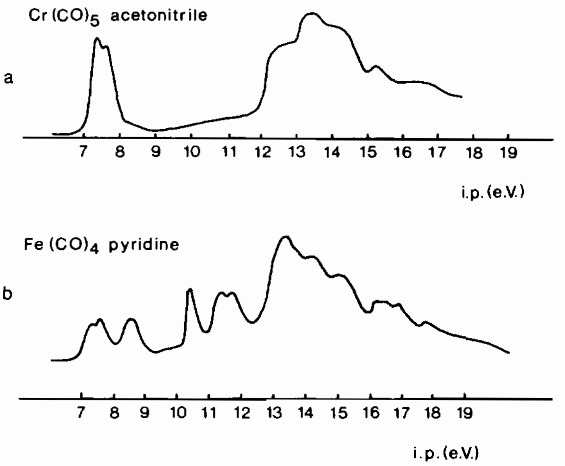

Figure 3. The He I photoelectron spectra of a) Cr(CO)$_5$acetonitrile; b) Fe(CO)$_4$pyridine.

stabilization upon complexation. It seems reasonable to assign the band at 10.28 eV in the complex to the lone pair orbital on the nitrogen atom not bonded to the metal atom. The former a$_2$(π) orbital is shifted 0.54 eV to lower energy which is in agreement with the shifts in the pyridines. The other two bands will be highly stabilized since they have large densities on the nitrogen next to the M(CO)$_5$ moiety. Their position in the spectrum is thus obscured by the CO orbitals.

Metal orbitals. The two lowest ionization potentials will arise from the metal d-orbitals as is shown in Table IV.

Just as in the amine complexes, the corresponding W-complexes show spin–orbit coupling for which a correction could be calculated (see Table V). The corrected ionization potentials of the e and b$_2$ orbitals are about equal for Cr and W and the difference $\epsilon_e - \epsilon_{b_2}$ ($=\Delta\pi$) does not change significantly. From Table V we see a large increase in the coupling constant compared to W(CO)$_6$. This may be attributed to a smaller delocalisation of the metal orbitals in the substituted complexes.

Cr(CO)$_5$acetonitrile

The spectrum is shown in Figure 3. The splitting of the metal d-orbitals is somewhat smaller than in the corresponding amine and imine complexes. Unfortunately no separate ligand orbitals could be observed since these orbitals are obscured by the σ- and π-orbitals of the CO ligands. Cr(CO)$_5$CH$_3$CN: 7.36 eV (e), 7.61 (b$_2$), 12.5, 13.3 and 15.3 eV.

Fe(CO)$_4$L (L = pyridine, pyrazine)

In contrast to the group VIB imines the Fe(CO)$_4$L complexes have different local symmetries, *viz.* C$_{3v}$. The eight metal d-electrons occupy e″ (d_{xz}, d_{yz}) and e′ (d_{xy}, $d_{x^2-y^2}$). The spectrum is shown in Figure 3 and the ionization potentials are tabulated in Table VI. The energy difference between e′ and e″ decreases from 1.26 eV in Fe(CO)$_5$ to 1.0 eV in Fe(CO)$_4$L. The ligand orbitals in the complex do not differ significantly from Cr(CO)$_5$L.

^{13}C-NMR Spectra

The ^{13}C-NMR chemical shifts are shown in Tables VIIa and VIIb for the amine and the imine series.

The spectra were assigned by comparison with the free ligand [27] and with other substituted hexacarbonyls [5, 28].

U.V. Absorption Spectra

The combination of photoelectron and U.V. absorption results gives us the opportunity of calculating the energies of low-lying unoccupied orbitals.

The U.V. absorption spectra of the free ligand [29–31] and of some of these complexes [9, 15] have been published and assigned. Apart from ligand field bands a metal to ligand charge-transfer transition is observed as is shown in Table VIII. The blue shift of this band in W complexes in a more polar solvent [20, 32] was also observed for the analogous Cr complexes which indicates a lowering of the polarity of the excited state. The first ligand field band was assigned to a $E \leftarrow {}^1A_1$ transition from d_{xz}, d_{yz} to the

TABLE VI. Vertical Ionization Potentials of Fe(CO)$_4$L (values in eV).

	e″		e′	a$_2$ (π)	b$_1$ (π)	M–N bonding	Lone Pair
Fe(CO)$_4$pyridine	7.3	7.58	8.53	10.39	11.33	11.70	
Fe(CO)$_4$pyrazine	7.5	7.72	8.76	10.72			10.45

TABLE VIIa. ^{13}C-NMR Chemical Shifts of $Cr(CO)_5L$ in $CDCl_3$[a] (in ppm) Relative to TMS.

L	C-2	C-3	C-4	C-5	C-6	α	γ	CO(ax)	Co(eq)
pyridine	155.6	128.3	134.6					220.4	214.0
4-picoline	154.6	125.7	149.2				20.5	220.7	214.3
4-tert•butylpyridine	154.9	122.0	161.9				30.0[b]	220.5	214.4
2,4-lutidine	162.4	127.8	149.3	122.1	155.5	27.7	20.3	221.2	214.4
4-Cl-pyridine	155.7	125.2	146.0					220.4	214.0
4-Br-pyridine	155.6	128.3	134.7					–	214.0
pyrazine	149.8	145.7						–	213.7
pyridazine		151.4	126.7	128.1	157.3			–	214.4
piperidine[c]	58.2	28.1	22.7					220.4	214.6

[a] $\delta_C^{CDCl_3} = 76.9$ ppm. [b] C directly bonded to ring, other ^{13}C resonance of 4R at 34.7 ppm. [c] Recorded in benzene $\delta_C^{C_6D_6} = 128$ ppm.

Note: for ^{13}C-NMR results of W-complexes see ref. 20.

TABLE VIIb. ^{13}C-NMR Chemical Shifts of Free Ligand in $CDCl_3$[a] (in ppm) Relative to TMS.

	C-2	C-3	C-4	C-5	C-6	α	γ
pyridine	149.9	123.7	135.8				
4-picoline	149.6	124.6	146.9				20.8
4-tert•butylpyridine	148.8	119.7	158.8				29.6
2,4-lutidine	157.0	123.0	146.1	120.7	147.9	23.2	19.7
4-Cl-pyridine	150.3	123.8	143.6				
4-Br-pyridine	150.1	126.8	132.5				
pyrazine	144.1	144.1					
pyridazine		150.6	125.6	125.6	150.6		
piperidine[c]	47.9	27.7	25.6				

[a] $\delta_C^{CDCl_3} = 76.9$ ppm. [b] C directly bonded to ring, other ^{13}C resonance of 4R at 33.6 ppm. [c] Recorded in benzene $\delta_C^{C_6D_6} = 128$ ppm.

TABLE VIII. Electronic Transitions of $Cr(CO)_5L$ in Isooctane (kK).

L	d → d		d → π*(L)
pyridine	25.7	29.8	25.7
4-picoline	23.9	30.5	26.9
2-picoline	24.8	30.1	27.3
4-tert.butylpyridine	24.0	30.0	26.8
2,4-lutidine	23.9	30.5	27.5
4-Cl-pyridine	24.8	29.9	24.8
4-Br-pyridine	24.8	29.4	24.8
pyrazine	24.8	–	21.6
pyridazine	24.2	–	21.8
piperidine[a]	24.0	–	–

[a] Benzene solution.

Note: for U.V. results of W-complexes see ref. 20.

antibonding d_{z^2}. Often a second ligand field transition with lower intensity appears at higher energy. These transitions are insensitive to changes in the polarity of the solvent. Within the series of complexes there is a fair constancy of the ligand field. With respect to the ligand field transition $^1T_{1g} \leftarrow {}^1A$ of $M(CO)_6$ a substantial red shift is noticed. However, the destabilization of the occupied e orbitals more than compensates for this shift.

Discussion

Whereas carbon monoxide is a good π-acceptor, the amines are unable to participate in π-interaction. In $M(CO)_5$-amine, therefore, the difference between the b_2 metal d-orbital (with π-back bonding to the four equatorial CO ligands) and the less stable e orbital (with interactions with the two equatorial and the axial CO) represents the stabilization by CO due to π-acceptor properties. The general increase of the ionization potentials of the ligand orbitals in the amine series after complexation suggests a positive charge on the ligand. This is confirmed by the downfield shifts of the ^{13}C-NMR resonances of C-2 and C-3 of piperidine upon complexation, showing a lowering of the electron density in the ring.

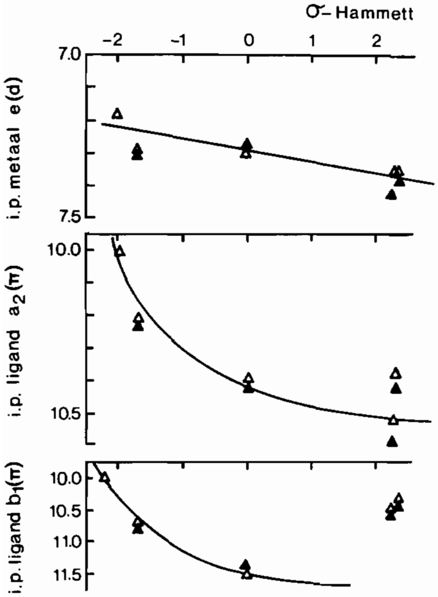

Figure 4. Plot of the ionization potential of $a_2(\pi)$, $b_1(\pi)$ and e(d) in $M(CO)_5$4R-pyridine (△ = Cr and ▲ = W) *versus* the σ-Hammett parameter of R.

The metal–imine bond is complicated by the additional presence of π- and π*-orbitals on the nitrogen donor ligand, which may interact with the metal d-orbitals. It is striking that the stabilization of the lone pair of the imine ligands upon complexation is similar to the stabilization energy of the piperidine ligand although these ligands have very different pK_a-value. An explanation cannot yet be given.

Compared to piperidine a smaller downfield shift of the ^{13}C resonances of the imine ligand upon complexation is noticed, which may be attributed to the smaller σ-donating ability of the sp^2-hybridised imine ligand. The magnitude of the ^{13}C-NMR shift upon complexation of the carbon ring atoms clearly diminishes as the carbon atom is further apart from the $M(CO)_5$ moiety. Recently the ^{13}C-NMR chemical shifts of pyridine and γ-picoline of some low spin d^6 complexes have been interpreted in terms of σ-donating and π-backbonding probes [33]. As a result the ^{13}C changes at the γ-carbon may provide a quantitative measure of electron density changes from one species to another. Indeed the upfield shift of 1.2 ppm at the γ-position in $Cr(CO)_5$ pyridine is in agreement with π-backbonding tendencies. In 4-methyl and 4-tertiary butyl pyridine complexes, however, downfield shifts are observed (2.3 ppm and 3.1 ppm respectively) consistent with less π-backbonding. The upfield shift of the methyl carbon in $Cr(CO)_5$ γ-picoline indicates a charge increase, while for the tertiary butyl group a downfield shift is observed. The absence of ^{13}C-NMR data of similar 4-X-pyridine (X = Cl, Br) complexes and the

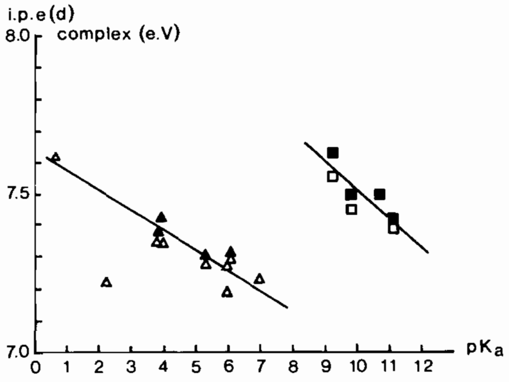

Figure 5. Plot of the ionization potential of the metal e(d) in $M(CO)_5L$ (□, △ = Cr and ■, ▲ = W) *versus* the pK_a of ligand L (□, ■ = amine and △, ▲ = imine).

complexity of the halogen–carbon bond make a simple interpretation of the shifts impossible.

The energy of $a_2(\pi)$ and $b_1(\pi)$ in γ-substituted pyridine complexes, however, could be related to the σ-Hammett parameters of the substituents. As expected, it turned out that a greater donor ability increases the orbital energies as is shown in Figure 4. As stated before, the $b_1(\pi)$ orbitals in $Cr(CO)_5$4-X-pyridine (X = Cl, Br) interact with the p-orbitals of the X-atom and will fall outside the trend in this series.

These trends can also be compared with trends in the photoelectron spectra of 4-R-pyridine oxide [34, 35] and 4-R-pyridine boranes [36]. The decrease in energy of the $a_2(\pi)$ orbital is: $BH_3 > M(CO)_5 > O$ whereas for $b_1(\pi)$ the sequence $BH_3 > O > M(CO)_5$ is found.

Though not so pronounced, the same trend is found in the energies of the metal d-orbitals.

The ionization potentials of the metal d-orbitals in these complexes depend on the σ- and π-bonding properties of the ligands. Neglecting differences in the π-interactions within a series of nitrogen donor ligands, the d-orbital energy is expected to shift to higher energy with a larger σ-donating ability of the ligand. Within the series of amines or the imines this relation holds (see Figure 5).

The fact that the difference between e and b_2 is constant upon complexation can be explained by assuming an interaction of the occupied $b_1(\pi)$ ligand orbital with occupied d_{xz} and d_{yz} metal orbital combinations of the right symmetry, which, in turn, can mix with the empty $b_1(\pi^*)$ ligand orbital cancelling any mutual energy change.

We reject the possibility of hyperconjugation in the metal–amine bond, a backdonation to the antibonding σ^*_{NH}, for two reasons:

Firstly the impossibility of hyperconjugation in $Cr(CO)_5N(CH_3)_3$ which follows the trend in the amine series. Secondly, the lowering of the NH stretching frequency [38] can be explained by a larger polarization of the N–H bond [39].

The lower ionization potentials of the metal d-orbitals in the imine series with respect to the amine series are surprising, however. Since the imine ligands have low lying empty π-orbitals a relative stabilization of the d-orbitals should be expected.

This anomaly is also found in the amine- and 4-R-pyridine boranes [26, 36]. The anomaly in behaviour of the d-orbitals may be explained either in terms of σ- or π-bonding. The susceptibility of the metal towards formally sp^2 and sp^3 hybrid orbitals may be quite different as is indicated by the stabilization of the lone pairs. Alternatively an extra donation of the filled $b_1(\pi)$ orbital to the empty metal p-orbital may be assumed.

For the $Fe(CO)_4L$ complexes, on the other hand, the following conclusions may be drawn: Since the σ- and π-system does not alter significantly in the xy-plane, the shift of the ionization potential of the e′ orbital must be attributed to an increase of the negative charge on the metal atom. This shift is larger than in the corresponding Cr-complexes. In contrast to e′, the position of the e″ orbital (d_{xz}, d_{yz}) is significantly influenced by the π-system. The decrease in energy difference (Δ) upon complexation can be explained in terms of a smaller π-backbonding in imines relative to CO. The decrease of Δ matches quite well the $\Delta\pi$ in $Cr(CO)_5L$.

The carbonyl stretching frequencies give information about the bonding in the molecule mainly from changes in the π-backbonding. Trends in the ionization potentials of the orbitals d_{xz} and d_{yz} which are directly involved in the π-backbonding must be manifested by trends in the CO stretching frequencies. Within the imine series a higher energy of the e orbital is accompanied by a lowering of the *trans* CO vibrational frequencies. In the amine series the lack of low lying π^* orbitals in L makes the e orbital more susceptible to interaction with the π^* of CO causing an extra decrease in this frequency.

The energy of the lowest lying empty orbitals $b_1(\pi^*)$, calculated from photoelectron and U.V. absorption results, reveal, in the imine series, a large destabilization upon complexation due to the π-backbonding. This destabilization increases with a smaller difference between $b_1(\pi^*)$ of the free ligand and the metal e-orbital of the $M(CO)_5$ moiety. Thus the π-acceptor ability increases with decreasing energy of $b_1(\pi^*)$ in the imine free ligand.

Conclusion

With the usual σ- and π-interaction parameters a completely satisfactory explanation for the metal to ligand bonding mechanism could not be obtained. For instance, the pK_a values and the ionization potentials of the lone pairs of the free ligands turned out not to be good parameters for describing the σ-bond system. The existence of π-interactions between the imines and the $M(CO)_5$ moiety is indicated.

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