Bonding Properties of Group VIB Metal Pentacarbonyl Azole Complexes Studied by Electronic Absorption, Photoelectron, 13C NMR and Vibrational Spectroscopy

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The electronic absorption, photoelectron, 13C NMR and vibrational spectra of a series of M(CO)5L complexes (M = Cr, W and L = imidazole, pyrazole, isoxazole, thiazole and isothiazole) are reported and assigned. The results are used to interpret the σ and π-bonding between the metal and the nitrogen donor ligand. The metal–azole bond is compared with the metal–pyridine and –pyrazine bond in the corresponding complexes.

Introduction

The spectroscopic properties of group VI B monosubstituted hexacarbonyls have already been studied by various authors [1–4]. Weis and Beck [5] reported the preparation of tungsten pentacarbonyl imidazole and pyrazole without a chromatographic purification. The dipole moments of a series of substituted pyrazole and imidazole metal pentacarbonyls have been measured [6]. Pannell *et al.* concluded that within a series of substituted thiazole and isothiazole metal pentacarbonyls coordination exclusively occurs via the nitrogen atom [7]. A number of Cr(II) complexes with pyrazole and imidazole have been characterized by Mani and Scapacci [8].

The vibrational and electronic absorption spectra, the magnetic properties and the pK$_a$ values of the free azoles as well as of various azole complexes of M(II) have been published [9–11]. The He I photoelectron spectra of the azoles have been measured and assigned [12–15]. 13C NMR spectra of the free azoles have been reported [16–18]. Pugmire and Grant described the effect of proton coordination on the 13C resonances of pyrazole and imidazole.

In this article the results of the electronic absorption, the photoelectron (He I/He II), the 13C NMR and the vibrational spectra of chromium and tungsten pentacarbonyl azole complexes are reported while the bonding properties are discussed in relation to the corresponding pyridine and azine compounds [19].
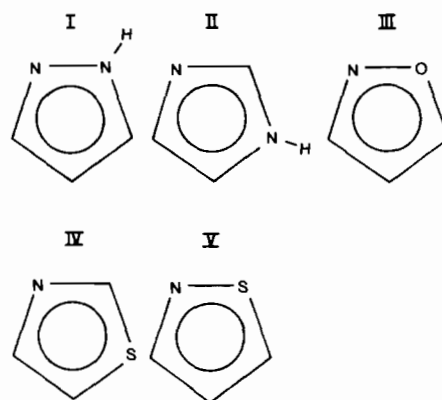

Fig. 1. I Pyrazole, II imidazole, III isoxazole, IV thiazole, V isothiazole.

Experimental

Preparations

The complexes were prepared according to Strohmeier [20] by irradiation of the group VI B hexacarbonyl in tetrahydrofuran at 3000 Å. The source was a Rayonet type RS from the Southern New England Ultraviolet Company. The crude products were purified by chromatography (see below). The eluent was evaporated after the separation and the products were washed with n-pentane or n-hexane. All procedures were performed oxygen free. Purity was checked by elemental analysis and by IR spectroscopy.

Ia Cr(CO)5L (L = pyrazole; I in Figure 1): Column: Silicagel; Eluent: ether

Ib W(CO)5pyrazole: Column: Silicagel; Eluent: 80% ether and 20% n-pentane

IIa Cr(CO)5L (L = imidazole; II in Figure 1): as Ia

IIb W(CO)5 imidazole: as Ia

IIIa Cr(CO)5L (L = isoxazole; III in Figure 1): Column: Silicagel; Eluent: 50% ether and 50% benzene

IVa Cr(CO)5L (L = thiazole; IV in Figure 1): as Ia

Va Cr(CO)5L (L = isothiazole; V in Figure 1): Column: Al2O3; Eluent: CH2Cl2

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TABLE I. Electronic Transitions of $Cr(CO)_5L$ (kK) in CH_2Cl_2 and Their Assignment. The values of ϵ_{max} are given in brackets.

Assignment	imidazole	pyrazole	isoxazole	thiazole	isothiazole
$^1E_a \leftarrow {}^1A_1$(LF)	24.9(3200)	24.7(3300)	25.0(3100)	24.6(2650)	24.3(2900)
π^*(L) $\leftarrow$ d(Cr)			33.3(sh)	29.4(sh)	27.9(2800)
$^1E_b \leftarrow {}^1A_1$(LF)					31.0(sh)
π^*(CO) $\leftarrow$ d(Cr)	$39.7(2.8 \times 10^4)$	$39.8(2.2 \times 10^4)$	$40.5(3.1 \times 10^4)$	$41.7(2.5 \times 10^4)$	$40.8(2.7 \times 10^4)$
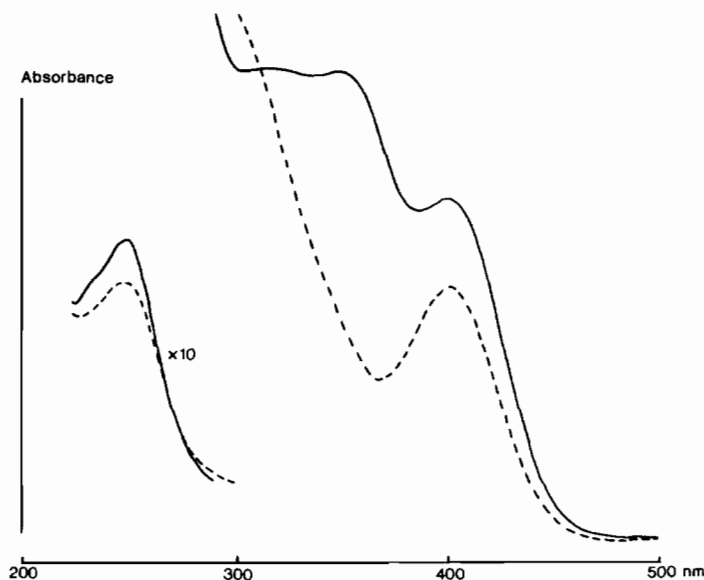
Fig. 2. Electronic absorption spectrum of $Cr(CO)_5$ (isoxazole) in iso-octane (———) and dichloromethane (------).

Spectroscopic Measurements

The electronic absorption spectra were obtained with a Cary-14 spectrophotometer for the solid compounds in diffuse reflection and in CH_2Cl_2 solution.

The photoelectron spectra were recorded on a Perkin-Elmer P.S. 18 spectrometer modified with an Helectros He I/He II source. Calibration was performed before and after the measurement. Thermal decomposition of $W(CO)_5$pyrazole, Cr- and $W(CO)_5$ imidazole caused improper P.E. spectra.

^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer.

The Raman spectra were measured with a Coderg PH-1. The 6471 Å line of a CR 500 K Kr laser was used as the exciting line. The spectra were obtained from the solid in a tube at about $-160\ ^\circ$C in order to avoid decomposition.

The infrared spectra were recorded on a Beckman IR-12 or Beckman IR 4250 spectrophotometer in both nujol and kel-F mulls. The far infrared region was obtained with a Beckman IR-11 as nujol mull in a polyethylene cell.

Results

Electronic Absorption Spectra

In Table I the energies and intensities of the observed transitions are collected. The spectrum of $Cr(CO)_5$ isoxazole is shown in Figure 2.

The assignment is straightforward. The band at 25.0 kK is assigned to the $^1E_a \leftarrow {}^1A_1$ LF transition [21]. The relatively high intensity is not uncommon for this type of complexes and is attributed to a considerable delocalisation of the metal e-orbital. So this transition has some charge transfer character [1].

The solvatochromic band is assigned to a transition from the metal to the lowest empty π^*-orbital of the ligand. The shift of this MLCT band to higher energy in more polar solvents confirms this assignment. In imidazole and pyrazole the lowest unoccupied π^*-orbital has a relatively high energy. Accordingly the MLCT band in the complexes of these ligands is obscured by the very intense transitions to the CO ligands.

TABLE IIa. Vertical Ionization Potentials and Their Assignment of the Free Azoles (values in eV).

	π_3	π_2	σ_N	σ_S
pyrazole	9.15	9.88	10.7	
isoxazole	10.20	11.38	11.38	
thiazole	9.50	10.24	10.48	12.77
isothiazole	9.62	10.26	10.80	12.42

TABLE IIb. Vertical Ionization Potentials and Their Assignment of the $Cr(CO)_5$(azole) Complexes (values in eV).

	Metal d-orbitals	π_3	π_2	$\sigma(MN)$
pyrazole	7.40 7.71	10.32	10.80	
isoxazole	7.42 7.65	10.92	11.85	
thiazole	7.36 7.63	10.3	11.2	12.0
isothiazole	7.32 7.63	10.3	10.8	

In the absorption spectrum of $Cr(CO)_5$isothiazole a band at 31.0 kK is observed. A similar band has been found for $M(CO)_5$pyridine and has been assigned to a LF $^1E_b \leftarrow \, ^1A_1$ transition [21]. Depending on the resolution of the spectra the other complexes showed a shoulder in this region.

Apart from transitions to the π^*-carbonyl orbitals other transitions such as $\pi \rightarrow \pi^*$ transitions of the ligand contribute to the strong featureless band at about 40 kK.

Photoelectron Spectra

The vertical ionization potentials of the free azole ligands and their complexes are presented in Table II.

A representative spectrum of the complexes is shown in Figure 5. These spectra agree with those of other monosubstituted group VI B hexacarbonyls [19]. The first band assigned to the metal d-orbitals is mostly split in an e- and b_2-level.

A comparison between the spectra of the free azoles and their complexes shows in general a simple one to one correspondence. The first three bands in the spectra of the free ligands, which are well separated have been attributed to one σ-orbital and two π-orbitals. The σ-orbital is mainly concentrated on the nitrogen and represents the lone pair orbital which will form the coordinated σ-bond to the metal.
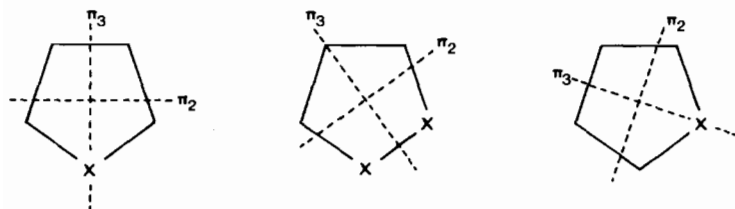
From the literature it is known that this orbital is strongly stabilized on coordination, *viz.* from 1.5 to 2.1 eV [19]. The two occupied π-orbitals (π_2, π_3) of the free ligands both possess a nodal plane. The stabilization of these two orbitals on coordination will mainly be determined by the positive charge created on the ligand. This effect is largest for those orbitals which have a large electron density on the coordinated nitrogen atom. Besides these ligand π-orbitals may interact with the occupied metal d-orbitals which results in an additional stabilization. The stabilization of the ligand π_2 and π_3-orbital is estimated to range from 0.5 to 1.0 eV [19].

For the pyrazole complex the vibrational fine structure of the band belonging to the π_3-orbital and the envelop of both π-orbital bands showed but little deviations from the spectra of the free ligands. Both π-orbitals are shifted by about 1.1 eV to lower energy. The band belonging to the metal–nitrogen σ-orbital is obscured by carbonyl bands. Since the nitrogen lone pair of the free ligand has been found at 10.7 eV, this orbital must be stabilized by at least 1.4 eV.

For the chromium pentacarbonyl complexes of isoxazole, thiazole and isothiazole a similar situation is observed. The more electronegative S and O atoms will increase the ionization potentials of the π-orbitals with respect to free pyrazole. This causes in free isoxazole a coincidence of the nitrogen lone pair orbital and the π_2-orbital. The respective stabilizations of π_2 and π_3 are 0.5 and 0.7 eV in both the isothiazole and isoxazole complex. The shifts of the π_2 and π_3 bands in the thiazole complex with respect to the free ligand are 1.0 and 0.8 eV respectively. The shifts of the π-bands in the isoxazole, isothiazole and thiazole complexes are significantly smaller than those in the pyrazole complex. We attribute this to a relatively high electron density of the π-orbitals on the O and S atom with respect to the coordinating nitrogen atom.

It is remarkable that the stabilization of π_3 is larger than or equal to that of π_2 for pyrazole, isoxazole and isothiazole, whereas for thiazole the opposite is found. This is also related to the electron density distribution of both orbitals in the ring. A closer look at the pictures of the π-orbital with their nodal planes confirms this assumption. For the pyrazole, isoxazole and isothiazole ligand (Figure 3):

Figure 3. π-Orbitals.
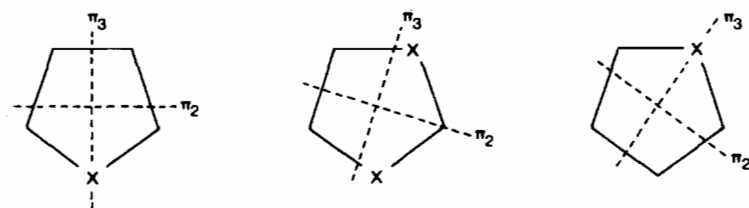
Fig. 4. π-Orbital for thiazole.
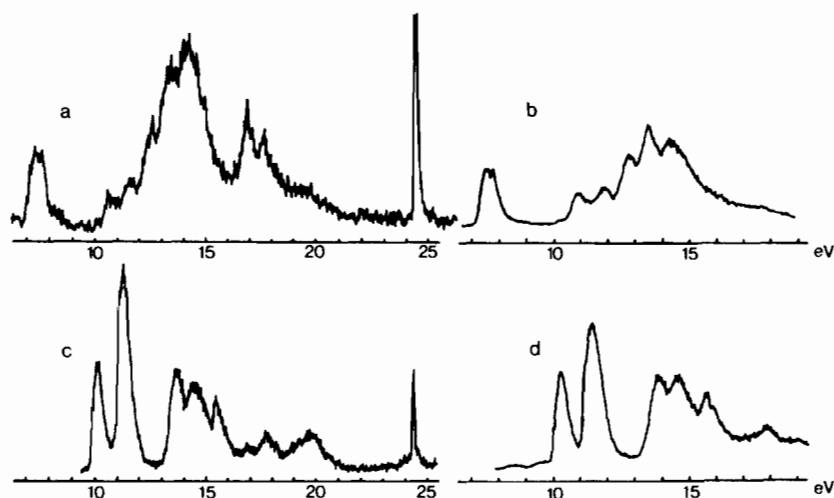
Fig. 5. The photoelectron spectra of $Cr(CO)_5$ (isoxazole) (a, He II and b, He I) and of free isoxazole (c, He II and d, He I).

for thiazole (Figure 4).

In these schemes the dotted line represents a nodal plane and X an arbitrary group which is electronegative with respect to a C–H element in the ring. The changes of the nodal plane orientation are described for heteroatoms at the 1.2 and 1.3 position. Because of the inequivalence of the two hetero groups the real situation is somewhere in between. This scheme of the π-orbitals is confirmed by calculations in the literature [14].

The stabilization of the coordinating lone pair of the ligand will reflect the strength of σ-donation, so 4Cl-pyridine and thiazole have about the same pK_a (3.88 and 2.52 respectively) and also the same ionization potential of the nitrogen lone pair in the free ligand (10.1 and 10.5 eV respectively). It is therefore expected that the lone pair orbitals of both ligands shift by same amount of 1.5 eV on coordination [19]. As a result the band at 12.0 eV in the thiazole complex is assigned to the Cr–N σ-orbital.

The He II spectra of all the complexes show an intensity increase of the metal d-band with respect to the ligand bands. This is very characteristic [22] and confirms the proposed assignment. The relative increase of bands with ionization potentials higher than 13.0 eV must be ascribed chiefly to analyzer discrimination of low kinetic photoelectrons [23]. In the He II spectra a strong band at 17.0 eV is observed. In analogy with the band at 17.8 eV in the

He II spectrum of $Cr(CO)_6$ it is assigned to the 4σ carbonyl level. A long tail to lower energy is observed. Though azole bands may also contribute in this range the five 4σ carbonyl levels will split by the local C_{4v} symmetry of he $M(CO)_5$ moiety. These will reduce to $2xa_1$, b_1 and e with $2xa_1$ at lower energy.

^{13}C NMR Measurements

The ^{13}C NMR spectra of the complexes were obtained in $CDCl_3$, in which solution, however, Cr-(CO)$_5$isothiazole and to a less extent the thiazole complex decomposed before measurements could be completed. The results are collected in Table III together with the free ligand resonances from the literature [16–18].

Due to tautomeric proton exchange the shifts of C-3,5 in free pyrazole and of C-4,5 in free imidazole average. In agreement with the reduction in the ligand symmetry upon coordination three different ^{13}C resonances were observed. So coordination of these ligands does not only involve the formation of the metal nitrogen bond but also the permanent protonation of the second nitrogen in the ring. According to Pugmire et al. [16] protonation of a nitrogen atom in a five-membered heterocycle causes an upfield shift of 9.0 ppm at the α-position. Indeed a resulting upfield shift was observed for pyrazole C-5 and imidazole C-2,5 resonances. All the other ligand ^{13}C resonances were shifted downfield upon com-

TABLE III. ^{13}C NMR Chemical Shifts of Cr(CO)$_5$L and Free L in CDCl$_3$[a] Relative to TMS.

	C-2	C-3	C-4	C-5	CO(ax)	CO(eq)
pyrazole		133.2	104.4	133.2		
Cr(CO)$_5$(pyrazole)		146.2	107.4	131.1	220.6	214.1
W(CO)$_5$(pyrazole)		146.3	106.8	130.2	201.4	196.8[b]
imidazole	126.1		135.0	135.0		
Cr(CO)$_5$(imidazole)	116.8		138.6	133.7	220.8	215.0
isoxazole		148.6	103.0	157.3		
Cr(CO)$_5$(isoxazole)		155.3	106.3	160.2	220.6	214.0
thiazole	117.8		142.1	151.9		
Cr(CO)$_5$(thiazole)	120.2		148.0	157.1	–	–

[a] $\delta_C^{CDCl_3} = 76.9$ ppm. [b] *cis* J(^{183}W–^{13}CO) = 130 Hz.

plexation, in particular the resonances from the carbon atoms next to the coordinating nitrogen.

The ^{13}C carbonyl resonances were shifted downfield with respect to the hexacarbonyls with δCO-(*trans*) > δCO(*cis*) just as has been found for the corresponding pyridine and amine complexes.

Vibrational Analysis

The azole ligands retain a local C$_s$-symmetry after complexation, so a simple one to one correspondence between the vibrations of the free and complexed ligand is expected. Complete vibrational analyses of the free ligand are known from the literature [24–30].

The ligand vibrations hardly change in going from the chromium to the tungsten complex and even in comparison with M(II)–azole complexes [8–11] the vibrations do not shift much. In particular the in-plane vibrations show shifts to higher frequencies.

The presence of hydrogen bonding in the solid state spectra of free pyrazole and imidazole and its absence in the corresponding solid state spectra of the complexes cause a significant shift.

Vibrations from the M(CO)$_5$ moiety hardly change going from one to another azole ligand. The carbonyl stretching vibrations in the solid state both in Raman and IR are tabulated in Table IV and assigned according to reference 31. In particular due to the high resolution of the Raman spectra frequently splittings of bands were observed which are ascribed to strong intermolecular coupling.

The observed frequencies in the range from 500 to 70 cm^{-1} are gathered in Table V. The assignment of the metal carbon stretching vibration is according to Young *et al.* [3]. In some cases shoulders and splittings due to the solid state could be observed. The CMC bending vibrations, the metal–nitrogen

TABLE IV. Carbonyl Stretching Frequencies (in cm^{-1}) and Assignment of Cr(CO)$_5$(azole) Complexes in the Solid State, Relative Intensities in Parenthesis.

		A$_1^2$		B$_1$		E		A$_1^1$		
Cr(CO)$_5$(pyrazole)	R	2078(m)	2074(m)	1988(m)	1980(m)	1943(w)		1906(s)	1883(m)	
	IR	2085(m)	2080(m)		1975(sh)	1945(s)		1910(s)	1887(s)	1870(s)
Cr(CO)$_5$(imidazole)	R	2067(m)		1977(m)	1964(s)			1893(w)	1856(s)	
	IR	2074(m)		1976(sh)		1935(s)	1905(s)	1880(m)	1855(m)	
Cr(CO)$_5$(isoxazole)	R	2076(m)		1976(s)				1904(m)		
	IR	2073(m)				1943(s)	1919(m)			
Cr(CO)$_5$(thiazole)	R	2076(m)	2071(w)	1985(s)	1961(m)	1940(w)		1908(w)	1894(s)	
	IR	2073(m)			1968(sh)	1940(s)	1920(s)		1890(sh)	
Cr(CO)$_5$(isothiazole)	R	2074(m)		1977(s)				1885(m)	1863(s)	
	IR	2074(m)				1943(s)	1921(m)	1894(sh)	1873(m)	

TABLE V. Infrared Frequencies in the Range from 70 to 500 cm^{-1} and the Assignment of ν_{CrC} and ν_{CrN} of Cr(CO)$_5$(azole) in the Solid State.

		ν_{CrN}	ν_{CrC} A$_1^2$	B$_1$	E	A$_1^1$
Cr(CO)$_5$(pyrazole)	R	100 129 231	393(s)	417(w)	456(w)	482(m)
	IR	88 103 209 228	386(m)	412(m)	442(s)	—
Cr(CO)$_5$(imidazole)	R	not measured 191 236	396(s) 403(m)		446(w)	500(m)
	IR	——(150) 189 214 232 236	390(sh)	417(m)	444(s)	
Cr(CO)$_5$(isoxazole)	R	not measured (200) 236	394(s)	418(w)	452(w)	481(s)
	IR	88 98 189 208	386(m)	411(m)	437(s)	477(w)
Cr(CO)$_5$(thiazole)	R	74 87 100 113 130 142 189 216	394(s)	413(w)	447(w)	481(m) 490(m)
	IR	100 184 198 207	388(w)	412(m)	440(s)	
Cr(CO)$_5$(isothiazole)	R	76 98 109 120 128 179 224	391(s) 400(m)	412(w)	440(w) 446(w)	496(m)
	IR	110 113 176 181	386(sh)	408(m)	436(s)	480(w)

stretching vibration, two bending vibrations of the azole ring with respect to the M(CO)$_5$ moiety and two NMC bendings are expected in the far infrared region. From those vibrations the metal–nitrogen stretching vibration will have the highest frequency. A complete assignment in these vibrations was impossible, however.

The assignment of the metal–nitrogen stretching vibration in this type of complexes has been limited to a very few papers. Our assignment is based on the following results:

1. Hutchinson *et al.* [32] made an assignment in M(CO)$_5$(quinuclidine) with ν_{MN} = 185, 170 and 168 cm^{-1} for M = Cr, Mo and W respectively.

2. Meester *et al.* [4] concluded that W–N vibrations could only be observed in infrared for a series of W(CO)$_5$(pyridine) complexes in the range from 200 to 250 cm^{-1}.

3. A study of the Resonance Raman spectra of M(CO)$_{4-x}$(PR$_3$)$_x$L (L = diimine) [33, 34] revealed a strong enhancement of a broad band in this region. The strong coupling of this band with the L ← M charge transfer transition confirmed the assignment.

4. In this range no vibrations from the ligand or the M(CO)$_5$ moiety occur.

The very low intensity of the metal–nitrogen stretching vibration in the Raman spectrum is in accordance with a low polarizability of the bond. Also here splittings due to solid state effects were observed. The differences between the vibrations were very large in some cases and this indicates that other vibrations are also present in this region.

A complete one to one correspondence between all vibrations and their assignment of the free and coordinated ligands is available on request.

Discussion

The spectroscopic results will be discussed in terms of electron donating and withdrawing abilities of the ligand with respect to each other and in relation to the corresponding substituted pyridine and pyrazine complexes.

The stabilization of the coordinated lone pair of the azole complexes could only be measured for Cr(CO)$_5$(thiazole) (1.5 eV). The σ-donation of thiazole is smaller than of pyridine (the pyridine lone pair is stabilized by 1.8 eV in Cr(CO)$_5$(pyridine). This is in agreement with their basicities. Also the ionization potentials of metal d-orbitals in the azole complexes are higher than for Cr(CO)$_5$(pyridine) as a result of a larger transfer of electron density from the pyridine ligand to the metal. The trend in the photoelectron spectroscopic results of pyridine and azole complexes can be explained by a smaller σ-interaction of the azoles with respect to pyridine.
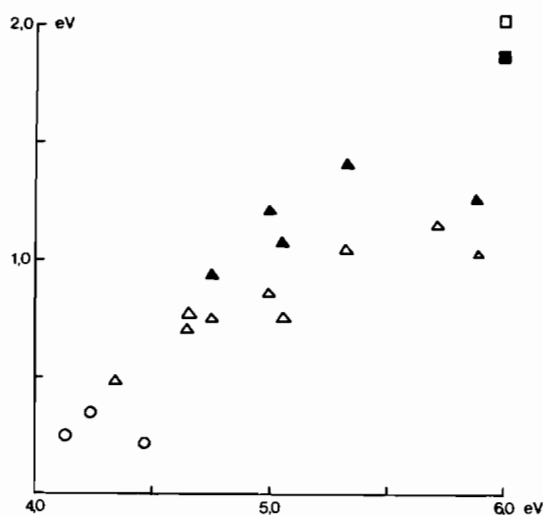
Fig. 6. Plot of the energy (in eV) of the lowest π^*-orbital of the free ligand L *versus* the destabilization energy (in eV) upon formation of $M(CO)_5L$ ($\square$, $\triangle$, $\circ$ = Cr; $\blacksquare$, $\blacktriangle$, = W and $\square$, $\blacksquare$ = CO; $\triangle$, $\blacktriangle$ = subst. pyridine or azine; $\circ$ = azole).

The destabilization energy of the unoccupied π^*-level of the ligand is a measure of the π-interaction of this level with the occupied metal d_{xz} and d_{yz} orbitals. It can be estimated from the ionization potentials derived from the P.E. spectra and from the energy of the corresponding MLCT transition from the absorption spectra. For all azole ligands a destabilization of the lowest π^*-orbitals was found. Within the series of unsaturated nitrogen donor ligands destabilization appeared to be larger for ligands with a lower lying π^*-orbital in the free molecule (Figure 6). From this a smaller π-back bonding for azoles than for pyridine and pyrazine could be derived.

The same conclusion could be deduced from the considerable differences in energy between the d-orbitals of the pyrazine and azole complexes. The ionization potentials of the d-orbitals are 7.6 eV for $Cr(CO)_5$(pyrazine) and 7.3–7.4 eV for $Cr(CO)_5$-(azole), whereas the σ-donations expressed by their basicity are about the same. This indicates that back bonding to the pyrazine π^*-orbital is stronger than to the corresponding orbital of the azoles.

The splitting of the t_{2g} level upon substitution of the hexacarbonyl is a measure of the difference in π-back bonding between the ligand L and CO. This splitting is always about the same when L is a nitrogen donor ligand and therefore not a very sensitive parameter for the back bonding abilities of L.

From the P.E. spectra it was shown that the carbonyl 4σ level shifts from 17.8 to 17.0 eV upon substitution of the hexacarbonyl by an azole. The net electron density donated by the azole is partly distributed by an increased back bonding to the resulting carbonyls. Accordingly carbonyl orbitals desta-

bilize and azole orbitals are bound stronger in the complex.

The ^{13}C NMR chemical shifts of the CO's were rather insensitive to differences in σ-donor and π-acceptor properties within a series of N-donor metal pentacarbonyl complexes. No conclusion could be drawn from the *cis* $J(^{183}W-^{13}CO)$ coupling constant in $W(CO)_5$(pyrazole). This constant turns out to be rather insensitive to changes of L and is in between $W(CO)_6$ (126 Hz) and $W(CO)_5$(cyclohexylamine) (132 Hz) [35]. The downfield shift of the ligand ^{13}C resonances may also be interpreted in terms of an overall release of electron density in the ring upon complexation. A similar effect was observed for a series of pyridine complexes.

The shift of the azole modes to higher frequency upon complexation and the similarity with $M(II)$ azole complexes also indicate a net release of electron density from the azole ring. Besides in-plane modes in the low frequency region may mix with the metal–nitrogen stretching vibration.

Conclusions

The spectroscopic properties of the group VI B metal pentacarbonyl azole complexes closely resemble the related pyridine and azine complexes. Electron density is transfered from the azole ring to the metal pentacarbonyl moiety, showing that σ-donation is much more important than π-back bonding. It may be stated that the σ-donor ability of the azoles studied is smaller than pyridine. It is also concluded that π-interaction of the occupied metal d_{xz} and d_{yz} with the lowest ligand π^*-orbital is less strong than with pyridine and azine.

Acknowledgements

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