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Bonding Properties of $W(CO)_5(4R\text{-}Py)$ ($R = CH_3$, H, Cl, Br, CH_3CO and CN)

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Vibrational, ^{13}C NMR, electronic absorption and photoelectron spectra of the complexes $W(CO)_5(4R$-Pyridine) are discussed in terms of the influence of variation of R on the trans carbonyl and the extent of π-bonding between tungsten and the pyridine ligand. Enthalpies of reaction are determined for the reaction

$$W(CO)_5(4R\text{-}Py)(s) + CO(g) \rightarrow W(CO)_6(g) + 4R\text{-}Py(g).$$

The decrease of reaction enthalpy on going from $R = CH_3$ to $R = CN$ is ascribed to a weakening of the W–pyridine bond.

Introduction

Monoderivatives $W(CO)_5L$ have already been studied by various authors and attention has been paid to the spectroscopic and thermal properties of amine compounds[1–4]. Raman data have been reported for some complexes[3,5]. The infrared spectra of these amine compounds show only small variations in CO stretching frequencies which have been ascribed to the lack of an appreciable π-bonding between the metal and the amines.

Dennenberg and Darensbourg[4] studied the thermal decomposition reactions of $W(CO)_5$–amines from which the complexes of amines with large pK_a values appeared to be most stable. However, for unsaturated heterocyclic amines, the pK_a value is found to be an irrelevant quantity, because their complexes are more stable than those containing saturated amines with comparable pK_a values. This behaviour has been ascribed to a W–L π-bond in these complexes. The absorption spectra of the complexes $W(CO)_5(4R$-Py) have recently been determined by Wrighton[6,7] and our results are in close agreement with his data.

The purpose of this investigation is a description of the bonding properties of the complexes $W(CO)_5$ (4R-Py) by a systematic study of the spectroscopic (IR, Raman, ^{13}C NMR, UV) and thermodynamic properties in relation to the $W(CO)_5$(piperidine) complex and the earlier investigated complexcs, *trans*-$PtCl_2(C_2H_4)(4R\text{-}Py)$[10,11].

Experimental

Preparation

The compounds $W(CO)_5(4R$-Py) were prepared from the complex $[W(CO)_5Cl]NEt_4$[8]. This salt was dissolved directly in pyridine (for R = H and CH_3) or in benzene with addition of the ligand (for R = Cl, Br, CH_3CO or CN). $NaBPh_4$ was added to all solutions to increase the reaction rate and the yield. After stirring for several hours, addition of water gives a precipitate of a mixture of $W(CO)_5(4R$-Py) and $W(CO)_4(4R\text{-}Py)_2$. Excess $W(CO)_6$ was removed from the solid by vacuum sublimation at about 50°C. $W(CO)_5(4R$-Py) ($R = CH_3$, H, Cl or Br) was extracted from the residue with n-hexane. Recrystallization from hexane resulted in yellow products[9].

For $R = CH_3CO$ or CN the precipitate was washed with n-hexane to remove $W(CO)_4(4R\text{-}Py)_2$. The residue was recrystallized from ether and gave yellow–brown products. The analytical data are listed in Table I.

Physical Measurements

IR spectra for the solid compounds and CH_2Cl_2 solutions were recorded on a Beckmann IR-12 spectro-

TABLE I. Analytical Data for $W(CO)_5L$.

L	% C		% H	
	calc	exp.	calc	exp.
$4CH_3$-Py	31.65	31.87	1.68	1.78
Py	29.78	30.36	1.24	1.48
4Cl-Py	28.81	29.54	.96	1.09
4Br-Py	24.90	25.50	.83	.93
$4CH_3CO$-Py	32.26	33.22	1.57	1.75
4CN-Py	30.84	30.61	.93	.90

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photometer. Raman spectra were obtained with a Coderg PH 1 spectrophotometer with dc detection. The 6471 Å line of a CRL-52 Kr$^+$ laser was used as the exciting line. Raman spectra were recorded for solids and CH_2Cl_2 solutions (dp measurements).

^{13}C NMR spectra were recorded in deuterated benzene at 20 MHz on a Varian CFT-20 spectrometer with full proton decoupling. After pulsing for about 16 hours some complexes partly decomposed. Electronic absorption spectra were obtained with a Cary-14 spectrophotometer. Extinction coefficients were determined in CH_2Cl_2. The spectra were analyzed with a Gaussian curve fitting program. Photoelectron spectra were run on a Perkin Elmer PS-18 instrument, equipped with a 584 Å (21,21 eV) He discharge source.

Reaction enthalpies (ΔH_r) for the reaction

$$W(CO)_5(4R\text{-}Py)(s) + CO(g) \rightarrow W(CO)_6(g) + 4R\text{-}Py(g)$$

have been determined by Differential Scanning Calorimetry, DSC (Dupont type 990). The apparatus was calibrated by the heat of fusion of pure indium at its melting point (156 °C).

All reactions were carried out under a dynamic carbon monoxide atmosphere (5 lh^{-1}) at a heating rate of 2 °C min^{-1}.

Confirmation of the substitution reaction was obtained by carrying out the experiment on a thermobalance (Mettler, type TA 1).

The measured ΔH_r values are the mean of at least ten DSC scans (Figure 3). Uncertainties are expressed as the standard deviations (σ) of the mean values. For the determination of the standard enthalpies of formation ($\Delta^s H^o_f$) at 25 °C of $W(CO)_5(4R\text{-}Py)$, specific heat data, sublimation and/or evaporation enthalpies were needed for all reactants and products.

For L = $4CH_3$-pyridine or pyridine all these data are known from the literature[29–33] and $\Delta^s H^o_f$ could be calculated (see Table IX for these auxiliary data).

Results and Discussion

Infrared and Raman Spectra

In Table II the IR and Raman results are presented for the skeletal vibrations (200–650 cm^{-1}) and the carbonyl stretching modes (1800–2200 cm^{-1}). The assignments given, assuming C_{4v} symmetry, are based on the results of Young *et al.*[5] and on a comparison of IR and Raman data. Mostly the solution data are used in order to avoid solid state effects.

The changes in carbonyl stretching frequencies are small. The largest variation is found for the *trans*-CO stretching mode (A_1^1) which shifts to higher frequency on going from an electron releasing (*e.g.* CH_3) to an electron withdrawing (*e.g.* CN) substituent in the pyridine ring. This shift is ascribed to an increase of metal–pyridine π-bonding because σ-bonding effects hardly influence this vibration (see ref. 5).

In the metal–carbon stretching region only three bands ($2A_1$ and E) are observed in solution, the ν(W–C) with B_1 symmetry being too weak to be observed. From the two A_1 vibrations, which are fully polarized in the Raman spectra, the band with higher frequency is assigned to the metal–*trans*-carbonyl stretching mode, in accordance with Young[5].

Both ν(W–C) and δ(WCO) vibrations show hardly any frequency shift when the substituent R is varied (Table II).

The spectra of these compounds are compared with the results for $W(CO)_5$(piperidine). There is a close correspondence between the spectra although ν(CO) (A_1^1) is somewhat lower in $W(CO)_5$(piperidine)

TABLE II. Assignment of Bands for the Vibrations Which are Most Sensitive to Metal–Ligand Interactions (in approximate description)[a].

L Assignment[b] (cm^{-1})	$4CH_3$-Py	Py	4Cl-Py	4Br-Py	$4CH_3CO$-Py	4CN-Py	Piperidine
ν(W–N)	254	202[c]	246	234[c]	253[c]	212[c]	208[d]
ν(W–C)(E)	370	372	370	372	372	370	370
ν(W–C)(A_1^2)[d]	432	435	430	436	433	434	432[e]
ν(W–C)(A_1^1)[d]	477	475	477	478	475	473	488[e]
δ(WCO)	544	550	–	540	–	546	553
δ(WCO)	591	592	593	591	593	593	591
δ(WCO)	603	603	603	603	603	602	605
ν(CO)(A_1^1)	1895	1896	1897	1900	1903	1906	1891
ν(CO)(E)	1935	1931	1934	1935	1936	1939	1924
ν(CO)(B_1)	1975	1978	1975	1980	1980	1982	1969
ν(CO)(A_1^2)	2074	2076	2077	2077	2077	2079	2074

[a] These data are for CH_2Cl_2 solutions, unless otherwise stated. [b] A_1^1 is related to the carbonyl *trans* with respect to the pyridine ligand. A_1^2 is related to the *cis* carbonyls[5]. [c] Solid state. [d] Raman data for CH_2Cl_2 solutions.

than in the corresponding pyridine complexes due to the absence of π-bonding.

The W–pyridine stretching vibrations, which could only be observed in the infrared because of the low polarizability of the W–N bond[10] show the same irregular dependence on the substituent R as found in the complexes *trans*-$PtCl_2(C_2H_4)$(4R-Py)[10]. From this we may conclude that, just as for the Pt complexes, the W–pyridine π-backbonding increases on going from R = CH_3 to R = CN.

The W–pyridine frequencies are about 30 cm^{-1} lower than for the Pt–pyridine vibrations, however, which means that the pyridines are more strongly bonded in the Pt than in the W complexes.

Electronic Absorption and Photoelectron Spectra

In an earlier study of the complexes *trans*-$PtCl_2(C_2H_4)$(4R-Py)[11] a relation was found between the platinum to pyridine charge transfer transition and the ^{13}C chemical shift of the *ortho*-carbon atoms of the pyridine ring. In order to investigate the possible existence of this relationship in other pyridine complexes we studied the absorption spectra of the $W(CO)_5$(4R-Py) compounds. The results are compiled in Table III.

Before discussing the charge transfer transitions, we will comment on the first spin allowed ligand field transition of these complexes in relation to photoelectron spectra.

Although the absorption spectra of some complexes $W(CO)_5L$ have been described in the literature[5, 15, 18] various explanations have been given in terms of a stabilization or destabilization of the orbitals involved with respect to $W(CO)_6$. Therefore photoelectron data, which give us the absolute values of the filled levels in the Koopmans approximation, are used in relation to the absorption spectra. Photoelectron spectra have been reported for $W(CO)_6$[16], $W(CO)_5NH_3$ and $W(CO)_5(NHMe_2)$[17] and were determined for $W(CO)_5$(Py) and $W(CO)_5$(Pip) in our laboratory.

The first ionization potential is connected with the highest occupied *d* orbital which is degenerate in the case of $W(CO)_6$ (t_{2g} symmetry) apart from some spin–orbit coupling[16]. For the mono derivatives of $W(CO)_6$ a splitting of this level into e and b_2 levels is observed. A further splitting of the e level can result from spin–orbit interaction (Table IV). It is clear from the lowering of the IP's that all the occupied *d* orbitals in $W(CO)_5$(amine) are destabilized with respect to $W(CO)_6$ (e more than b_2) (Fig. 1). This

TABLE III. Electronic Transitions in $W(CO)_5L$ (energies in kK). The values of ε_{max} in CH_2Cl_2 are given in brackets. The bands below the solid line are only found in iso-octane solution and mainly represent W→π^*(CO) transitions.

L Assignment	4CH_3-Py	Py	4Cl-Py	4Br-Py	4CH_3CO-Py	4CN-Py	Piperidine[a]
$d \rightarrow d$(S→T)	22.3(250)	23.2(390)	22.4(170)	22.5(260)	22.6(1600)	22.7(1400)	22.6(560)
$d \rightarrow d$(S→S)[b]	25.3(2400)	25.5(2700)	25.3(2000)	25.2(2000)			24.7(3400)
$d \rightarrow \pi^*$(Py)	30.3(5200)	29.9(3900)	29.0(3400)	28.7(4400)	25.2(7200)	24.8(6600)	
					29.5(780)	29.9(390)	29.2(1000)
$d \rightarrow \pi^*$(CO)[c]	34.5	34.5	35.1	35.3	36.4	35.3	
	38.9		41.2	40.8	42.7	40.8	
	44.1	47.6	45.5	44.8	45.5		

[a] Benzene solution. [b] This band often shows a shoulder at higher energy like piperidine. [c] Iso-octane solution. No curve fitting analysis has been applied.

TABLE IV. Ionization Potentials, pK_a Values and Electronic Transition Energies for $W(CO)_5L$.

Compound	IP (eV)			pK_a	Δ(kK)[c]
$W(CO)_6$[17]		8.56			32.2[14]
$W(CO)_5(NH_3)$[17]	7.54[a]	7.75[a]	8.06[b]	9.2	24.5[d]
$W(CO)_5(NHMe_2)$[17]	7.41	7.62	7.95	10.8	24.7
$W(CO)_5$(Pip)	7.35	7.55	7.87	11.12	24.7
$W(CO)_5$(Py)	7.22	7.45	7.79	5.17	25.5

[a] IP's originating from the e levels (see text). [b] IP originating from the b_2 level. [c] Δ refers to the energy of the first spin allowed electronic transition. [d] M. Wrighton, *Inorg. Chem., 13,* 905 (1974).

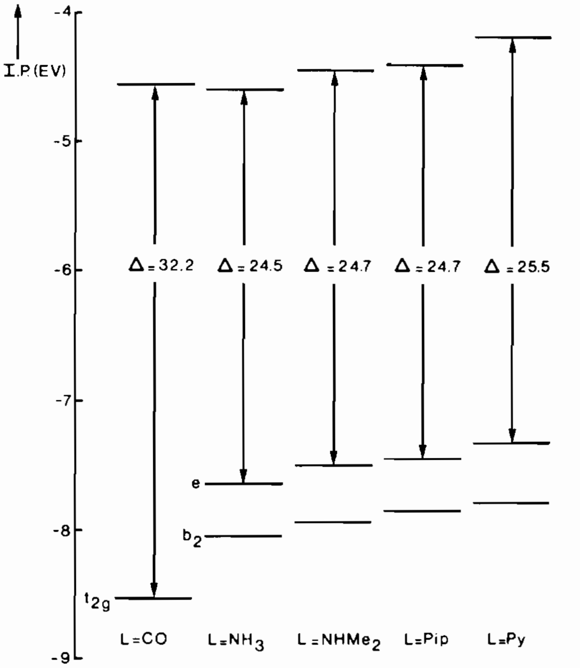

Figure 1. The energy level scheme of $W(CO)_6$ and $W(CO)_5L$ based on PES measurements and the first spin allowed ligand field transition.

is ascribed to an increase of the electron density on W when CO is replaced by the amine ligand[17].

Thus in the saturated amine complexes, $W(CO)_5(NH_3)$, $W(CO)_5(NHMe_2)$ and $W(CO)_5(Pip)$ the IP's decrease with an increase of pK_a (Table IV). However, the low first IP of the pyridine complex cannot easily be explained in terms of the pK_a value of pyridine. Presumably, the π-electrons of pyridine interact with the electrons of tungsten causing the observed decrease of the first IP with respect to the other amine complexes.

A combination of these PES results with the energies of the first spin allowed electronic transition (at about 25 kK) shows that the lowest unoccupied level of the $W(CO)_5$(amine) complexes is only slightly shifted with respect to $W(CO)_6$ (Figure 1).

Only for the pyridine complex does this level appear to be more destabilized. A complete MO calculation, however, is needed for conclusive explanation of these results.

Apart from the ligand field bands in these spectra a metal to pyridine charge transfer transition is found for the pyridine complexes which is easily recognized by the following properties:

(i) Its dependence on R; a red shift is obtained by decreasing the basicity of the pyridine ligand[11, 12].

(ii) The blue shift of this band in a more polar solvent[13], which does not affect the *d–d* transitions.

(iii) The band is not observed in $W(CO)_6$[14, 15] and $W(CO)_5$(piperidine).

The observed red shift of this CT band on going from R = CH_3 to R = CN agrees with the results for the corresponding complexes *trans*-$PtCl_2(C_2H_4)$(4R-Py)[10].

^{13}C NMR

The carbon-13 NMR spectra of the complexes $W(CO)_5$(4R-Py) have been obtained in C_6D_6. The results which are collected in Table V are compared with the values for free 4R-pyridine in CH_2Cl_2. Also the data for $W(CO)_5$(piperidine) have been added. The ^{13}C spectra of the complexes have also been measured in $CDCl_3$ and in deuterated acetone. In the more polar solvents downfield shifts were observed for the carbonyl resonances as well as for the pyridine ring. This solvent effect, however, is rather small (about 1.3 ppm).

TABLE V. ^{13}C NMR Chemical Shifts for $W(CO)_5L$ in C_6D_6[a].

L Assignment	$4CH_3$-Py	Py	4Cl-Py	4Br-Py	$4CH_3CO$-Py	4CN-Py[c]	Piperidine
C-2	155.3	155.6	156.2	156.0	156.6	155.8	59.4
C-2 (free lig.)[b]	149.1	149.5	150.6	151.1	150.3	150.4	47.9
C-3	126.3	125.1	125.6	128.6	122.8	–	28.0
C-3 (free lig.)[b]	124.0	123.3	123.7	127.3	120.7	125.1	27.7
C-4	149.3	136.5	145.2	134.0	142.4	124.3	22.0
C-4 (free lig.)[b]	146.1	135.3	143.3	132.7	142.1	119.9	25.9
CO-*cis*	199.5	199.3	199.1	199.1	199.2	198.8	199.2
CO-*trans*	202.5	202.2	201.9	201.8	202.2	–	202.5

[a] The chemical shifts were measured relative to benzene: $\delta_{TMS} = \delta_{C_6D_6} - 128.0$ ppm. [b] The NMR spectra of the free ligands were recorded in CH_2Cl_2, except for piperidine (in C_6D_6). [c] This complex gave a very bad spectrum because of its low solubility.

The carbonyl frequencies of the substituted W(CO)$_5$L complexes occur at lower field than in W(CO)$_6$[19] (δ^{13}C(CO) = 192.1 ppm) and the *trans* carbonyl is more deshielded than the *cis* carbonyls. This behaviour[19–23] can be ascribed to changes in the local paramagnetic shielding constant σ_p[24]:

$$\sigma_p = -\text{const}\,\frac{<r_{2p}^{-3}>}{\Delta E}\,(Q_{AA} + \sum_{A \neq B} Q_{AB}) \qquad (1)$$

Both ΔE[20] and Q_{AB}[22] can be determining factors as well as the increase in π-backbonding to CO[21,23]. In Table V the ^{13}C NMR results of both piperidine and 4R-pyridine complexes are collected. These data show hardly any shift for both *cis* and *trans*-carbonyls when piperidine is replaced by pyridine and when the substituent R is varied. Thus any π-backbonding from W to pyridine hardly influences the ^{13}C NMR shifts of the carbonyls. This result is in agreement with the vibrational spectra.

The ^{13}C resonances of the piperidine and pyridine ring, especially of the carbon-2 atoms, are shifted downfield with respect to the free ligands.

For the piperidine ligand, the electron density in the ring is reduced by the σ-bond formation with W, causing a large downfield shift for the *ortho* carbon atom (11.5 ppm). On the other hand, the carbon-2 atom of pyridine shows a smaller downfield shift (6 ppm) due to its much weaker σ-bond (pK_a = 5.17) compared with piperidine (pK_a = 11.12). However, π-backbonding may also contribute to the shifts of pyridine because, if the difference in σ-bond strength is the only factor, one would expect the same trend for the other atoms of the pyridine ring with respect to the piperidine ligand (Table VI).

Furthermore, although the difference in pK_a between 4CH$_3$-pyridine (6.02) and 4CN-pyridine (1.10) is of the same order as between piperidine (11.12) and pyridine (5.17), the differences in shifts for the carbon-2 atom with respect to the free ligands are much smaller on going from R = CH$_3$ to R = CN than when piperidine is replaced by pyridine.

TABLE VI. ^{13}C NMR Shift Differences between Free and Complexed Ligand[a].

Assignment Complex	C-2	C-3	C-4	pK_a[25]
W(CO)$_5$(piperidine)	+11.5	+ .3	−3.9	11.12
W(CO)$_5$(pyridine)	+ 6.1	+1.8	+1.2	5.17
W(CO)$_5$(4CH$_3$-Py)	+ 6.2	+2.3	+3.2	6.02
W(CO)$_5$(4CN-Py)	+ 5.4	–	+4.4	1.10

[a] Downfield shifts are indicated by +; upfield shifts by −.

Just as for the *trans*-PtCl$_2$(C$_2$H$_4$)(4R-Py)[11] complexes, a relationship has been found between these carbon-2 chemical shifts and the charge transfer transition $(\Delta E)_{CT}$ which moves to lower energy on going from R = CH$_3$ to R = CN. The δ^{13}C(C-2) also shifts downfield in that order.

Thermochemistry

The thermochemical properties of the W(CO)$_5$(4R-Py) compounds were investigated in order to attempt to correlate the influence of variation of R on the W–N bond strength.

To obtain reliable enthalpies of reaction the reactants and products have to be well-defined. In Tables VII and VIII the results of the reaction on the thermobalance under N$_2$ as well as under CO atmosphere are given. Here T_i, T_p and T_f, respectively, represent the initial, peak and final temperatures (in °C) of the reaction. Sometimes two peak temperatures are found; the first one normally being the melting point.

Under N$_2$ atmosphere several reaction steps are indicated by the thermogram (Figure 2). The following reactions may occur:

TABLE VII. Results of the Decomposition of W(CO)$_5$L under a Dynamic N$_2$ Atmosphere (5 lh^{-1}). Heating Rate 4 °C min^{-1}.

Compound	T_i(°C)[a]	T_{P_1}(°C)[a]	T_{P_2}(°C)[a]	T_f(°C)[a]	Weight of Tungsten Residue (%)	pK_a
W(CO)$_5$(4CH$_3$-Py)	97	119	187	210	33	6.02
W(CO)$_5$(Py)	95	117	185	200	48	5.17
W(CO)$_5$(4Cl-Py)	119	131	169	196	56	3.82
W(CO)$_5$(4Br-Py)	127	166	194	229	76	3.75
W(CO)$_5$(4CH$_3$CO-Py)	102	117	150	203	75	3.51
W(CO)$_5$(4CN-Py)	123	157	225	239	103	1.00

[a] For explanation see text.

TABLE VIII. Results for the Substitution by CO under a Dynamic CO Atmosphere (5 lh^{-1}). Heating Rate 4°C min^{-1}.

Compound	T_i(°C)	T_{p1}(°C)	T_{p2}(°C)	T_f(°C)	Weight of Residue (%)	ΔH_r[a] (Kcal mol^{-1})	σ[b]	pK_a
$W(CO)_5(4CH_3\text{-}Py)$	98	141	165	181	1.29	33.78	1.39	6.02
$W(CO)_5(Py)$	82	116	165	185	1.85	24.18	.83	5.17
$W(CO)_5(4Cl\text{-}Py)$	110	134	144	189	2.52	23.83	2.30	3.82
$W(CO)_5(4Br\text{-}Py)$	110	167	187	216	17.1	–	–	3.75
$W(CO)_5(4CH_3CO\text{-}Py)$	90	121	155	192	15.2	–	–	3.51
$W(CO)_5(4CN\text{-}Py)$	109	158	–	200	4.29	21.51	1.37	1.00

[a] ΔH_r is the reaction enthalpy of the substitution reaction. [b] σ is the standard deviation from the mean value.

$$2W(CO)_5(4R\text{-}Py) \xrightarrow{N_2} W(CO)_4(4R\text{-}Py)_2 + W(CO)_6\uparrow \quad (1)$$

$$W(CO)_4(4R\text{-}Py)_2 \xrightarrow{N_2} W\downarrow + 4CO\uparrow + 2(4R\text{-}Py) \quad (2)$$

$$W(CO)_5(4R\text{-}Py) \xrightarrow{N_2} W\downarrow + 5CO\uparrow + (4R\text{-}Py) \quad (3)$$

$$W(CO)_5(4R\text{-}Py) + CO \xrightarrow{N_2} W(CO)_6\uparrow + (4R\text{-}Py) \quad (4)$$

The carbon monoxide in reaction (4) may originate from reaction (2) or (3). Sublimation of the $W(CO)_5$ (4R-Py) will not be important, because different heating rates did not affect the percentage of residue.

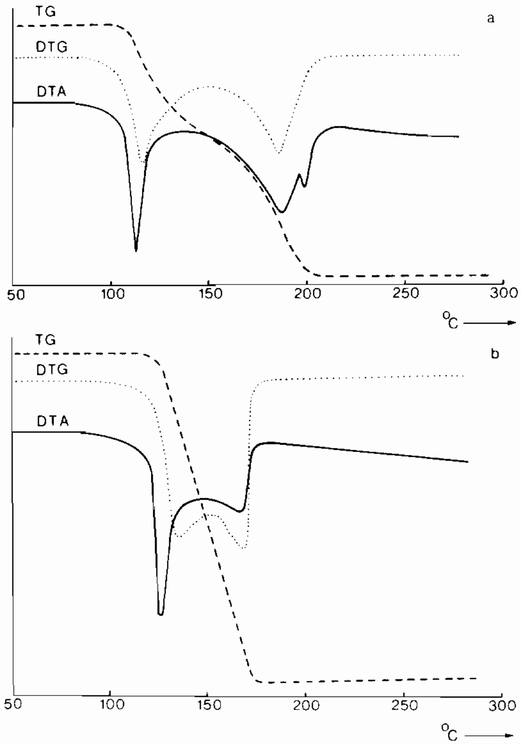

Figure 2. The thermogram of $W(CO)_5(4CH_3\text{-}Py)$ under N_2 atmosphere (a) and under CO atmosphere (b).
TG = thermogravimetry curve; DTG = derivative of the thermogravimetry curve; DTA = differential thermal analysis. Heating rate is 4°C min^{-1}.

The residue, expressed in the original amount of tungsten can only be metallic tungsten. Thus, if the percentage of W is lower than 50%, reaction (4) will certainly occur together with (1) and (2). When the percentage of W is more than 50%, reaction (3) is of importance together with (1) and (2). When the basicity of the pyridine ligand is decreased, reaction (3) becomes more important (Table VII). This may be caused by the weaker σ-bond between W and N in these complexes.

Thus, the decomposition of the complexes under N_2 atmosphere cannot be used for the determination of reaction enthalpies. The substitution reaction of L by CO in these complexes has therefore recently been investigated in our laboratory[26] and good results for the reaction enthalpies (ΔH_r) have been obtained in the case of L = CH_3CN [27] and piperidine[28].

This same substitution reaction has been used for $W(CO)_5(4R\text{-}Py)$:

$$W(CO)_5(4R\text{-}Py)(s) + CO(g) \rightarrow W(CO)_6(g) + 4R\text{-}Py(g) \quad (5)$$

Evidence for the occurrence of this reaction was obtained by thermobalance measurements. In addition to $W(CO)_6$, $4CH_3$-pyridine and piperidine were detected by gas chromatography.

Table VIII shows that only 70% of $W(CO)_5(4Br\text{-}Py)$ and 73% of $W(CO)_5(4CH_3CO\text{-}Py)$ had reacted so that for these compounds, ΔH_r of the substitution reaction (5) could not be determined. The residues found for the other complexes expressed as percentage of the original amount indicate that another reaction also occurs, *e.g.* for $W(CO)_5(4CN\text{-}Py)$ to an extent of about 12%.

Using the data in Table IX ΔH_r can be reduced to standard conditions and the enthalpy of formation ($\Delta^s H^\circ_f$) for $W(CO)_5(Py)$ can be calculated. When the same Kirchhoff corrections (1.48 Kcal mol^{-1}) and the same sublimation enthalpy for the complex (7.3 Kcal mol^{-1}) are used in the case of $W(CO)_5(4CH_3\text{-}Py)$ a value of -192.7 Kcal mol^{-1} is calculated for the

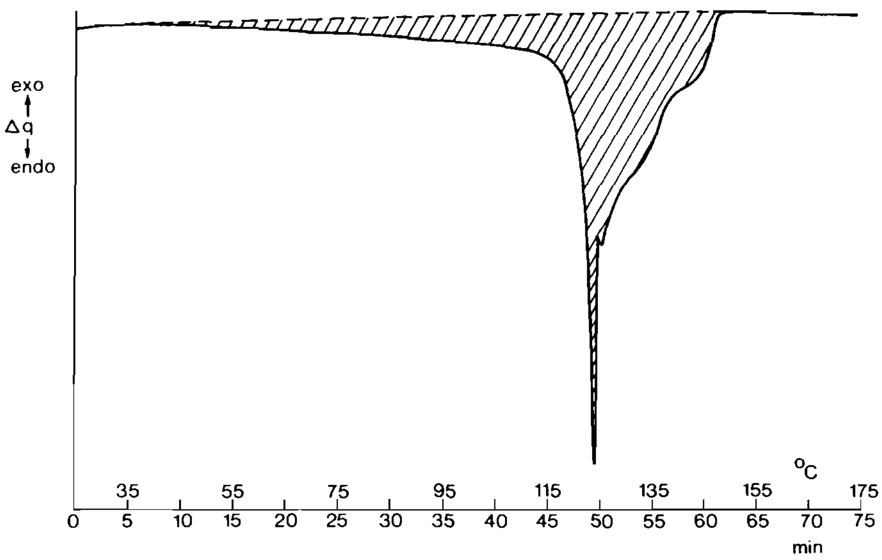

Figure 3. The DSC curve of $W(CO)_5(4CH_3\text{-}Py)$ under CO atmosphere (heating rate 2° C min^{-1}). The shaded area is used in the determination of ΔH_r.

$\Delta^{s}H^{\circ}_{f}$ of this latter compound with –173.9 Kcal mol^{-1} for $W(CO)_5(Py)$. The dissociation enthalpies of the W–N bonds (D(W–N)) for these two complexes, which are a measure for the tungsten–nitrogen bond energies, can be determined from the decomposition reaction in the gas phase[34]:

$$W(CO)_5(4R\text{-}Py)(g) \rightarrow W(g) + 5CO(g) + 4R\text{-}Py(g) \quad (6)$$

In Table IX $\Delta H(W\text{–}L)$ refers to the sum-total of the W–ligand dissociation enthalpy contributions in gaseous $W(CO)_5(4R\text{-}Py)$ at 25 °C.

Now, according to our spectroscopic results, the W–CO bond hardly changes with variation of the nitrogen base and variations of $\Delta H(W\text{–}L)$ can therefore be ascribed to differences in the W–N bond strength. Besides, approximate values for the dissociation enthalpies of the W–N bonds (D(W–N)) can be calculated by assuming that each W–carbonyl bond in the $W(CO)_5$ moiety has the same average dissociation enthalpy contribution as in $W(CO)_6$ (42.6 Kcal mol^{-1})[30]. These values are compared with the results for $W(CO)_5$(piperidine)[28].

Approximately the same D(W–N) values are found

TABLE IX. W–N Bond Enthalpy Contributions[a]. Auxiliary data for calculating $\Delta^{s}H^{\circ}_{f}$ and ΔH°_{r} are given in the lower part of the table.

Compound	$\Delta^{s}H^{\circ}_{f}$[b]	$\Delta^{subl}H^{\circ}_{f}$[b]	$\Delta H(W\text{–}L)$	D(W–N)	ΔH°_{r}(corrected)	pK_a
$W(CO)_5(4CH_3\text{-}Py)$	–192.7	7.3[c]	280.9	70.4	32.3	6.02
$W(CO)_5(Py)$	–173.9	7.3[c]	271.3	60.8	22.7	5.17
$W(CO)_5(Pip)$	–222.5	12.7	269.6	59.1	23.4	11.12

Auxiliary data[a] (ref.) (ref.)
$\Delta^{g}H^{\circ}_{f}(Py)$ = 33.63(29); $\Delta^{s}H^{\circ}_{f}(W(CO)_6)$ = –229.5(30)
$\Delta^{g}H^{\circ}_{f}(4CH_3\text{-}Py)$ = 24.43(29); $\Delta^{subl}H^{\circ}_{f}(W(CO)_6)$ = 18.3(20)
$\Delta^{g}H^{\circ}_{f}(CO)$ = –26.41(31); $\Delta^{g}H^{\circ}_{f}(W)$ = 203.1(36)

$C_p(W(CO)_5(Py)) = -3.07 + \frac{368}{1000} \cdot T$ cal deg^{-1} mol^{-1} [c];
$C_p(Py)(g)$: ref. 33; $C_p(CO)(g)$: ref. 31;
$C_p(W(CO)_6)(g)$: ref. 31.

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[a] All values are given in Kcal mol^{-1}. [b] $\Delta^{s}H^{\circ}_{f}$ and $\Delta^{g}H^{\circ}_{f}$ are the standard enthalpies of formation at 25 °C in the solid and gaseous state respectively. $\Delta^{subl}H^{\circ}_{f}$ is the standard enthalpy of sublimation at 25 °C. [c] Determined in our laboratory[32].

for the pyridine and piperidine complexes, although the pK_a values are quite different (5.17 and 11.2 respectively)[25] for these ligands. Therefore, both σ-bonding and π-backbonding must contribute to the W–N bond in $W(CO)_5(Py)$. The higher D(W–N) value of $W(CO)_5(4CH_3\text{-}Py)$ can be explained by the stronger W–N σ-bond.

For the other complexes sublimation enthalpies have not been measured and enthalpies of formation and heat capacity data for the gaseous ligands are also not available. Thus D(W–N) values cannot be obtained in these cases. Since, however, the products and reactants probably possess similar structures and since the range of reaction temperatures is narrow, the measured ΔH_r values (Table VIII) will reflect the differences in W–N bond strengths[35]. When the basicity of the pyridine ligand decreases, the ΔH_r value becomes lower, due to the weakening of the W–N bond. The differences between the pyridine, 4Cl-pyridine and 4CN-pyridine complexes are small, however. This means that the decrease in σ-bonding is largely compensated by an increase in π-bonding by the better acceptor ability of the ligand.

Conclusions

In this article spectroscopic and thermal properties of $W(CO)_5(4R\text{-}Py)$ are compared with the results for $W(CO)_5$(piperidine) and *trans*-$PtCl_2(C_2H_4)(4R\text{-}Py)$.

The presence of π-backbonding from W to 4R-pyridine is evidenced by the specific variation of the W-pyridine stretching frequency with R which has also been found for the Pt–pyridine vibration in *trans*-$PtCl_2(C_2H_4)(4R\text{-}Py)$[10]. Furthermore, the reaction enthalpy (ΔH_r) of the substitution of L by CO in $W(CO)_5L$ hardly changes on going from L = piperidine to L = pyridine, a result which is also explained by the influence of π-backbonding to pyridine in the pyridine complex.

The same holds for the variation of the ^{13}C NMR shift of the carbon-2 atoms of the piperidine and pyridine ring.

Hardly any influence of π-backbonding from W to pyridine can be deduced from the spectroscopic data of the carbonyls in $W(CO)_5(4R\text{-}Py)$ as demonstrated by the invariance of CO stretching, ν(W–C) and δ(WCO) frequencies and ^{13}C NMR shifts of the carbonyls.

All absorption spectra of the $W(CO)_5(4R\text{-}Py)$ compounds possess a charge transfer band from W to 4R-Py, which shifts to lower energy on going from R = CH_3 to R = CN just as for *trans*-$PtCl_2(C_2H_4)(4R\text{-}Py)$[10].

A relationship is found between the variation of $(\Delta E)_{CT}$ and the change of the ^{13}C chemical shift of the carbon-2 atom in the pyridine ring in agreement with the results for the Pt-complexes[11].

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