

**THE THERMOCHEMISTRY OF $M(\text{CO})_{6-x}\text{L}_x$ ($M = \text{Cr}, \text{Mo}, \text{W}$;
 $L = \text{PIPERIDINE}, \text{PYRIDINE}, \text{PYRAZINE}, \text{PYRAZOLE}, \text{THIAZOLE}$;
 $x = 1, 2, 3$)**

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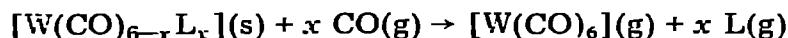
(Received 29 January 1979)

ABSTRACT

A number of $M(\text{CO})_{6-x}\text{L}_x$ complexes ($M = \text{Cr}, \text{Mo}, \text{W}$; $L = \text{piperidine}, \text{pyridine}, \text{pyrazine}, \text{pyrazole}, \text{thiazole}$; $x = 1, 2, 3$) are shown to undergo both disproportionation and substitution in a CO atmosphere, when heated on a thermobalance. Using a DSC, reaction enthalpies have been determined from which enthalpies of formation were calculated. Combined with the sublimation enthalpies of these complexes, individual metal–ligand bond enthalpies were evaluated and discussed.

INTRODUCTION

In our laboratory, thermochemical investigations have been performed on a number of substituted tungsten carbonyls in order to obtain more quantitative data on the strength of the metal–nitrogen bond [1,2]. Heats of reaction have been determined using the DSC method for



Heats of decomposition and heats of iodination of substituted Group VIB metal carbonyls have been measured recently on a microcalorimeter [3]. The metal–nitrogen bond enthalpies evaluated in the various papers differ considerably. This is mainly attributable to the lack of accuracy in the enthalpies of sublimation. Recently, in our laboratory, we have been able to measure vapour pressures using the Knudsen effusion method and thus calculate accurate sublimation enthalpies. Results have been reported for a series of mono-substituted Group VIB metal hexacarbonyls [4].

In this paper, we report on the thermochemical behaviour of the title complexes under CO and N_2 atmospheres. Reaction enthalpies for the displacement of ligand L by CO are determined.

Assuming that the M–C bond strength is constant going from $M(\text{CO})_6$ to $M(\text{CO})_{6-x}$, estimates of the metal–nitrogen bond strength were made. Results are compared with the relevant thermochemical data reported in the literature for nitrogen donor complexes [3].

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EXPERIMENTAL

Preparations

The pyridine, pyrazine, pyrazole and thiazole metal pentacarbonyls were prepared and characterized as previously reported [5,6]. The piperidine complexes were synthesized as follows.

$[M(CO)_5\text{piperidine}]$ ($M = Cr, Mo, W$)

The mono-substituted complexes were prepared from the corresponding $[M(CO)_5X]NEt_4$ complex ($X = Br$ for $M = Cr, W$ and $X = Cl$ for $M = Mo$) [7]. The salt was dissolved in a large excess of piperidine and stirred. After the reaction was complete, excess piperidine was removed under vacuum. The oily residue was dissolved in *n*-hexane. The solution was then filtered and the solvent was removed under reduced pressure. Free piperidine was removed by washing with water and drying with $CaCl_2$. Yield 15%.

$[M(CO)_4(\text{piperidine})_2]$ ($M = Cr, Mo, W$)

The bis product was prepared by refluxing 0.17 mole $M(CO)_6$ in a 200 ml 1 : 1 mixture of piperidine and benzene at 90–100°C for 15 h (Cr, W) or 3 h (Mo). The resulting yellow precipitate was filtered and washed with petroleum ether and *n*-pentane and then dried in vacuum. Yield 50–75%.

$[Mo(CO)_3(\text{piperidine})_3]$

$Mo(CO)_6$ was dissolved in a large excess of piperidine and refluxed at 120°C until conversion was complete (after about 15 h, checked by IR spectra of the CO stretching region). Further purification was carried out as for the bis product. Yield 60%. Note: efforts to prepare the Cr and W complexes thermally failed because the reaction stopped after bis substitution.

Gas chromatography

The gaseous products from the piperidine complexes were qualitatively detected by a gas chromatograph connected to the exit of the thermobalance. The column ($l = 150$ cm, $\phi = 4$ mm) was filled with Chromosorb-W dried in advance at 150°C and loaded with 10% KOH and 30% ethylene glycol. Experimental conditions: injection temperature 250°C, column temperature 250°C, detection temperature 150°C, gasflow 50 ml min⁻¹. The retention time of the products, metal hexacarbonyl about 90 s and piperidine 120 s, enabled a fast measurement and sufficient separation.

Thermochemical measurements

The thermogravimetric measurements were carried out using a Mettler thermobalance type 1. Simultaneously, a DTA signal was monitored with a NiCr/Ni thermocouple. The heating rate was 4 deg min⁻¹ and the gas flow was 10 l h⁻¹.

Reaction enthalpies were determined using a DSC (DuPont type 990). The

dynamic atmosphere was maintained at a flow rate of 5 l h^{-1} and the heating rate was 2 or 5 deg min^{-1} . The sample size was about 5 mg . The area under the DSC thermogram was assumed to be proportional to the reaction enthalpy. The apparatus was calibrated by measuring the enthalpy of fusion of pure indium.

Areas under the thermogram were measured with a Hewlet-Packard digitizer (9864 A) and with a Hewlet-Packard calculator (9810 A). Uncertainty intervals in the reaction enthalpy are expressed as twice the standard deviation of the mean from at least ten measurements.

The baselines of the thermograms were approximated by a straight line drawn between the initial and final reaction temperatures.

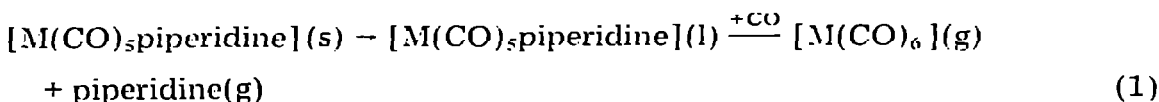
Auxiliary data

The following auxiliary enthalpies were used in evaluating the experimental results: $H_f^0(\text{CO}, \text{g}) = -110.5$ (ref. 8); $H_f^0(\text{piperidine}, \text{g}) = -47.0$ (ref. 9); $H_f^0(\text{pyridine}, \text{g}) = 140.7$ (ref. 10); $H_f^0(\text{pyrazine}, \text{g}) = 196.1$ (ref. 11); $H_f^0(\text{pyrazole}, \text{s}) = 118.5$ (ref. 12); $H_f^0[\text{Cr}(\text{CO})_6, \text{g}] = -908$ (ref. 13); $H_f^0[\text{Mo}(\text{CO})_6, \text{g}] = -915$ (ref. 13); $H_f^0[\text{W}(\text{CO})_6, \text{g}] = -884$ (ref. 13); $H_f^0(\text{Cr}, \text{g}) = 397$ (ref. 14); $H_f^0(\text{Mo}, \text{g}) = 660$ (ref. 15); $H_f^0(\text{W}, \text{g}) = 850$ (ref. 15); $\Delta H_{\text{subl}}[\text{Cr}(\text{CO})_5\text{piperidine}] = 93.5$ (ref. 4); $\Delta H_{\text{subl}}[\text{Mo}(\text{CO})_5\text{piperidine}] = 94.5$ (ref. 4); $\Delta H_{\text{subl}}[\text{W}(\text{CO})_5\text{piperidine}] = 106.4$ (ref. 4); $\Delta H_{\text{subl}}[\text{Cr}(\text{CO})_5\text{pyridine}] = 103.2$ (ref. 4); $\Delta H_{\text{subl}}[\text{Mo}(\text{CO})_5\text{pyridine}] = 102.0$ (ref. 4); $\Delta H_{\text{subl}}[\text{W}(\text{CO})_5\text{pyridine}] = 109.7$ (ref. 4); $\Delta H_{\text{subl}}[\text{Cr}(\text{CO})_5\text{pyrazine}] = 99.7$ (ref. 4); $\Delta H_{\text{subl}}[\text{W}(\text{CO})_5\text{pyrazine}] = 108.4$ (ref. 4); $\Delta H_{\text{subl}}[\text{Cr}(\text{CO})_5\text{pyrazole}] = 88.4$ (ref. 4); $\Delta H_{\text{subl}}[\text{W}(\text{CO})_5\text{pyrazole}] = 112.5$ (ref. 4); $\Delta H_{\text{subl}}[\text{Cr}(\text{CO})_5\text{thiazole}] = 102.0$ (ref. 4).

RESULTS

$[M(\text{CO})_5\text{piperidine}]$ ($M = \text{Cr}, \text{Mo}, \text{W}$)

The complexes reacted under a CO atmosphere according to



The hexacarbonyl and piperidine products were produced in the gaseous state, so that no residue was expected or detected. Both products were detected qualitatively by gas chromatography. The DTA signal consisted of two steps (see Fig. 1); melting of the complex, directly followed by the substitution reaction. The two steps were not separated quantitatively, consequently the heat of reaction reported (ΔH_r) includes both steps. The data are compiled in Table 1.

Under a N_2 atmosphere, two distinct steps could now be observed in the thermogram (Fig. 2).

In the first step, two distinct DTA signals could be distinguished, these

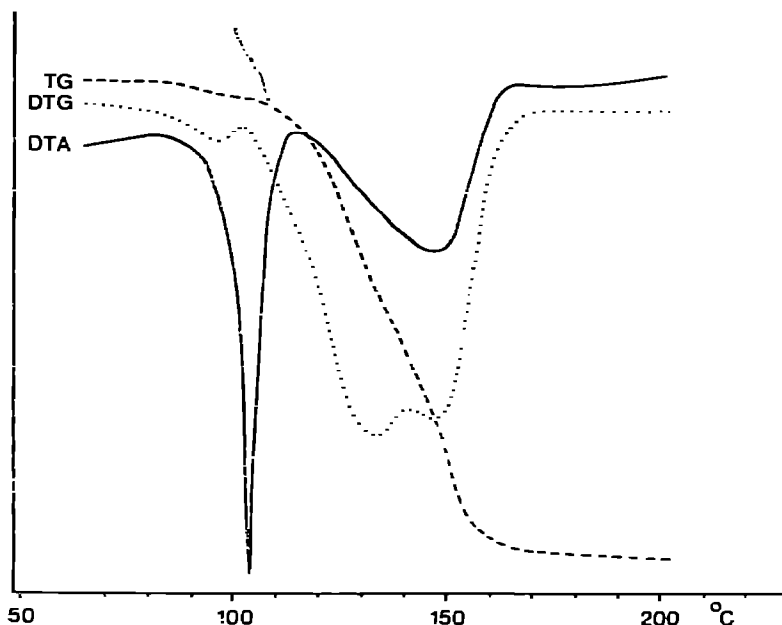
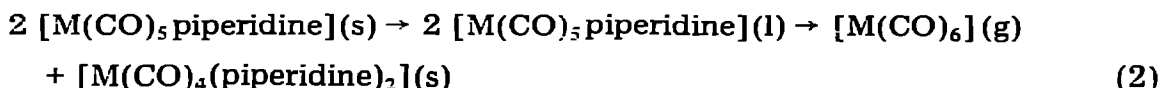


Fig. 1. The thermogram of $[\text{W}(\text{CO})_5\text{piperidine}]$ under CO atmosphere, the conditions are as specified in the experimental section.

being the melting of the complex directly followed by a reaction. Using infrared spectroscopy, the residual reaction product of the first step was found to be $[\text{M}(\text{CO})_4(\text{piperidine})_2]$. Further the weight loss corresponded to the disappearance of metal hexacarbonyl in agreement with the reaction



Chromatographically, only the presence of metal hexacarbonyl could be detected in the dynamic N_2 -atmosphere.

The second step turned out to be mainly a decomposition reaction according to



Both the residual weight of the metal and the chromatographic detection of

TABLE I

Results of the substitution reaction of piperidine by CO

	T_i	T_{p1}	T_p	T_f	ΔH_r
$\text{Cr}(\text{CO})_5\text{piperidine}$	62	73	149	170	85 ± 8
$\text{Mo}(\text{CO})_5\text{piperidine}$	48	78	112, 129	143	108 ± 8
$\text{W}(\text{CO})_5\text{piperidine}$	80	104	146	169	101 ± 8

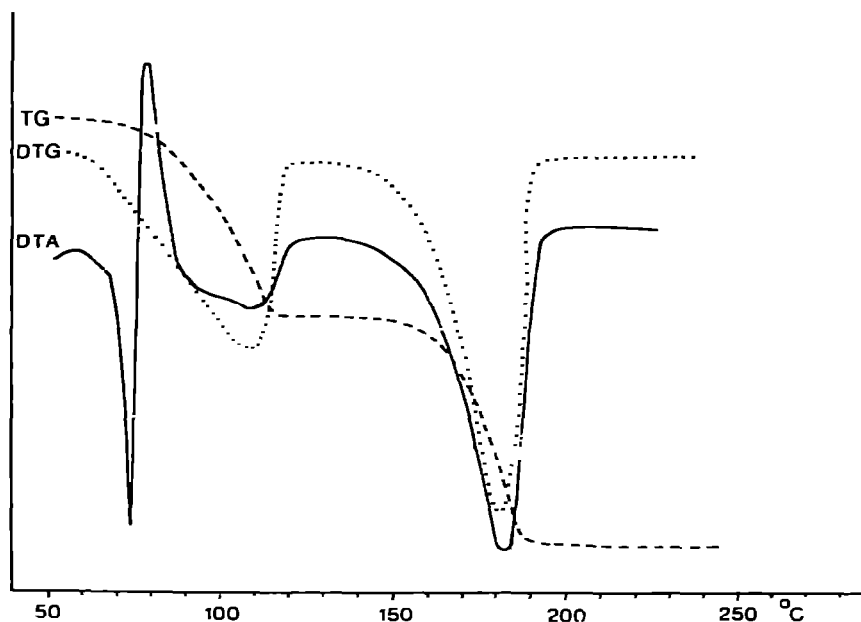


Fig. 2. The thermogram of $[\text{Mo}(\text{CO})_5\text{piperidine}]$ under N_2 atmosphere, the conditions are as specified in the experimental section.

piperidine confirmed this assumption. This second step, however, could not be analyzed quantitatively since this reaction occurred concurrently with substitution of piperidine by free CO. This free CO originated from reaction (3). Indeed, the presence of some metal hexacarbonyl was detected in the gas phase during the second step.

So only the quantitative results of the disproportionation reaction including melting of the complex are gathered in Table 2.

Disproportionation may also occur under a CO atmosphere. However, as this alternative route led to the same products as produced in eqn. (1) this did not affect the determined reaction enthalpy. It may explain the additional features in the DTA curves as observed for some mono-substituted complexes under a CO atmosphere. An example of the competition between the two pathways is shown by the DTA curve of $[\text{Mo}(\text{CO})_5\text{piperidine}]$ in Fig. 3 (compare with Fig. 1).

TABLE 2

Results of the reaction under N_2 atmosphere

	T_i	T_{p1}	T_p	T_f	ΔH_r	T_i	T_p	T_f
$\text{Mo}(\text{CO})_5\text{piperidine}$	60	76	81	110	129	22 ± 6	129	184 198
$\text{W}(\text{CO})_5\text{piperidine}$	82	101	110	122	135	27 ± 6	165	197 216

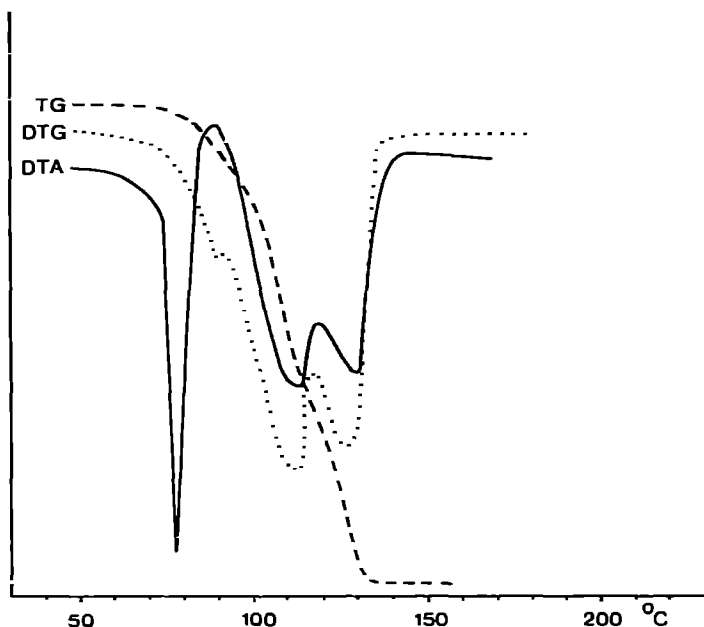
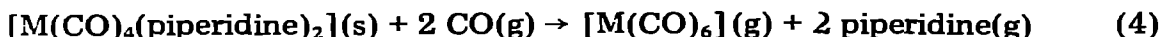


Fig. 3. The thermogram of $[\text{Mo}(\text{CO})_5\text{piperidine}]$ under CO atmosphere, the conditions are as specified in the experimental section.

$[\text{M}(\text{CO})_4(\text{piperidine})_2]$ ($M = \text{Cr}, \text{Mo}, \text{W}$)

Under a CO atmosphere, both the thermogram and the DTA curve showed one step (see Fig. 4) corresponding to



Evidently, the di-substituted complexes do not melt before the reaction. The residual weight was negligible. The thermodynamic data are summarized in Table 3.

For the formation enthalpy of the di-substituted complexes we have data from two independent pathways, i.e. substitution according to reaction (4) and disproportionation of $[\text{M}(\text{CO})_5\text{piperidine}]$ according to reaction (2). This enables us to calculate the formation enthalpy in two entirely different ways. As is shown below, the two ways gave concordant results to within

TABLE 3

Results of the substitution reaction of piperidine by CO

	T_i	T_p	T_f	ΔH_f
$\text{Cr}(\text{CO})_4(\text{piperidine})_2$	68	153	164	119 ± 8
$\text{Mo}(\text{CO})_4(\text{piperidine})_2$	85	153	170	164 ± 12
$\text{W}(\text{CO})_4(\text{piperidine})_2$	118	155	181	141 ± 12
$\text{Mo}(\text{CO})_3(\text{piperidine})_3$	58	133	148	138 ± 20

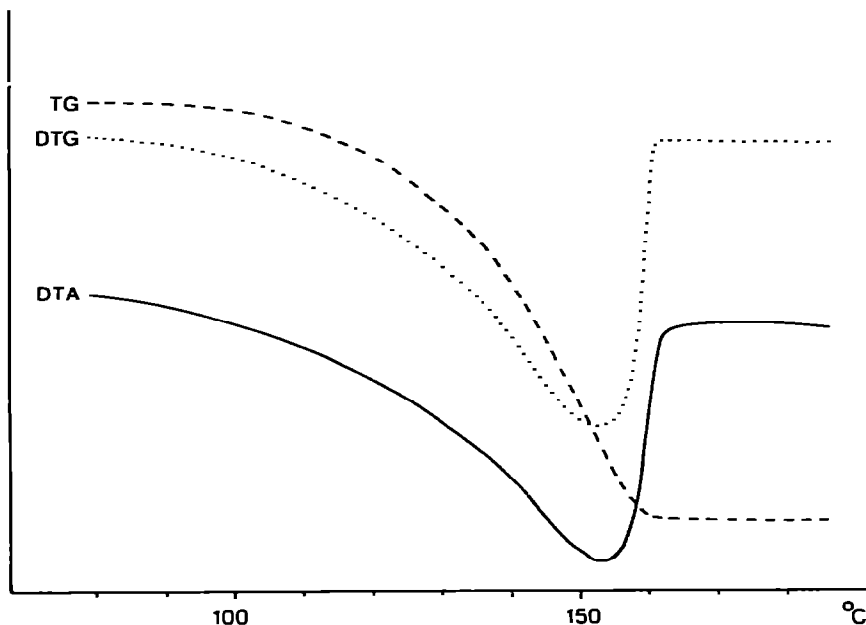


Fig. 4. The thermogram of $[\text{Mo}(\text{CO})_4(\text{piperidine})_2]$ under CO atmosphere, the conditions are as specified in the experimental section.

experimental error, thus giving support to the results obtained.

Using $\Delta H_r(1) = \Delta H_r(2) + \Delta H_r(3)$ in kJ mole^{-1} ; Mo: $2(108 \pm 8) = 164 \pm 12 + 2(22 \pm 6)$ and W: $2(101 \pm 8) = 141 \pm 12 + 2(27 \pm 6)$ where $\Delta H_r(1)$ is the substitution enthalpy of two mole $[\text{M}(\text{CO})_5\text{piperidine}]$, $\Delta H_r(2)$ is the

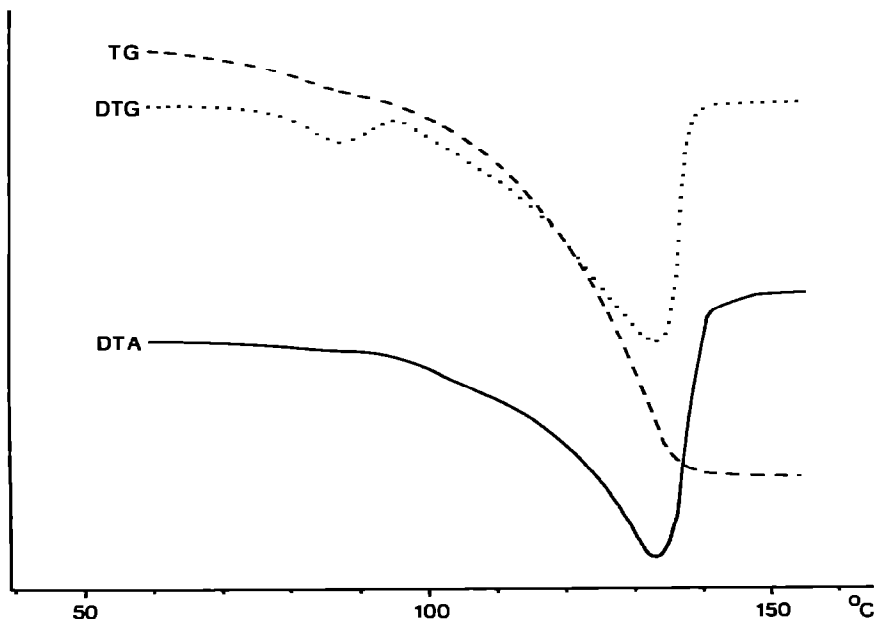
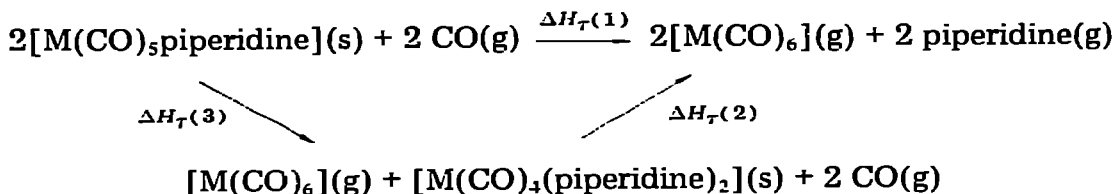


Fig. 5. The thermogram of $[\text{Mo}(\text{CO})_3(\text{piperidine})_3]$ under CO atmosphere, the conditions are as specified in the experimental section.

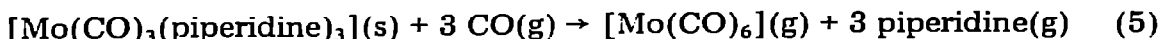
substitution enthalpy of one mole $[M(CO)_4(\text{piperidine})_2]$ and $\Delta H_T(3)$ is the disproportionation of two mole $[M(CO)_5\text{piperidine}]$.



Scheme 1

$[Mo(CO)_3(\text{piperidine})_3]$

It could be deduced from the thermogram of $[Mo(CO)_3(\text{piperidine})_3]$ under a CO atmosphere (see Fig. 5) that no melting occurred and that CO substitution took place according to



The DTA signal showed a small thermal effect at about 70°C followed by the main step with τ maximum at 130°C . With infrared, it could be demonstrated that the sample at 80°C consisted mainly of $[Mo(CO)_4(\text{piperidine})_2]$ indicating a stepwise conversion from the tri- to the di-substituted complex. The results are presented in Table 3.

$[M(CO)_5\text{pyridine}]$ ($M = \text{Cr}, \text{Mo}, \text{W}$)

These complexes behaved in a similar manner under CO and N_2 atmospheres as the mono-substituted piperidine complexes.

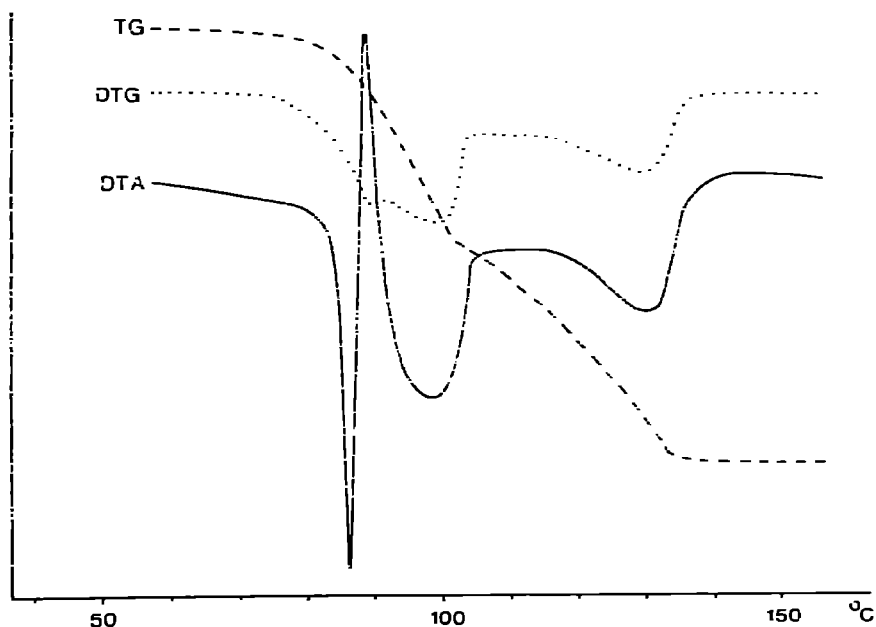


Fig. 6. The thermogram of $[Mo(CO)_5\text{pyridine}]$ under CO atmosphere, the conditions are as specified in the experimental section.

TABLE 4

Results of the substitution reaction of pyridine by CO

	T_i	T_{p1}		T_p	T_f	ΔH_r
Cr(CO) ₅ pyridine	87	98		128	142	75 ± 6
Mo(CO) ₅ pyridine	79	87	90	98	129	57 ± 3 ^a
W(CO) ₅ pyridine	95	109	116	85	165	83 ± 10

^a This enthalpy consists of ΔH (disproportionation of [Mo(CO)₅pyridine]) = 30 ± 2 kJ mole⁻¹ and ΔH (substitution of [Mo(CO)₄(pyridine)₂]) = 5.1 ± .1 kJ mole⁻¹.

Special attention was warranted by the thermogram of [Mo(CO)₅pyridine] under a CO atmosphere. Two separate steps were observed (see Fig. 6 in comparison with Figs. 1 and 3). Both infrared spectroscopy of the residual reaction product and the weight loss corresponded to a disproportionation reaction. The reaction enthalpy of the first step agreed to within experimental error with the enthalpy of disproportionation observed under a N₂ atmosphere. Thus it is evident that disproportionation is much faster than substitution after the [Mo(CO)₅pyridine] has melted under a CO atmosphere. The second step is due to substitution of the bis substituted product. The results are tabulated in Table 4.

[M(CO)₅pyrazine] (M = Cr, W)

For these complexes, during the first stage of the observed thermogram (see Fig. 7) the melting and reaction steps could not be distinguished. The

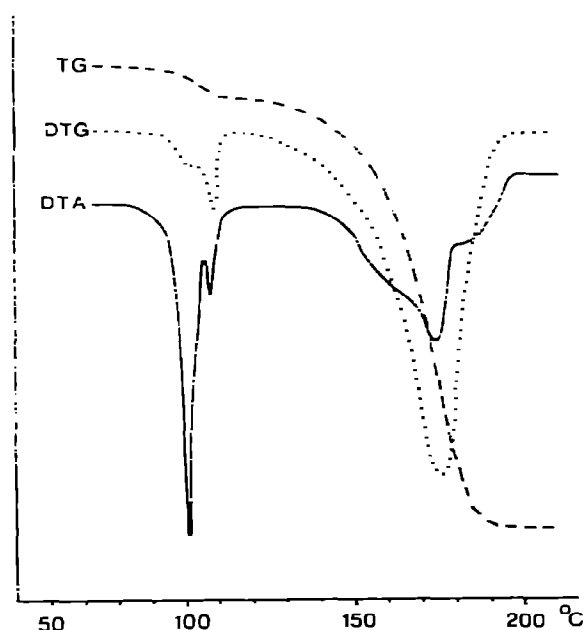


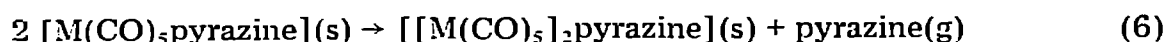
Fig. 7. The thermogram of [W(CO)₅pyrazine] under CO atmosphere, the conditions are as specified in the experimental section.

TABLE 5

Results of the reaction of $M(\text{CO})_5$ pyrazine under CO atmosphere

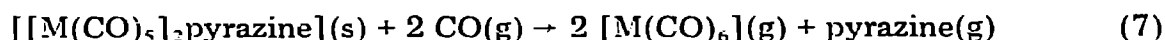
	T_i	T_{p1}	T_p	T_f	ΔH_{r1}	T_i	T_p	T_f	ΔH_{r2}
Cr(CO) ₅ pyrazine	75	86	95	103	23 ± 2	148	158	168	9 ± 4
W(CO) ₅ pyrazine	85	101	108	118	23 ± 1	157	175	195	41 ± 4

same reaction occurred both under CO and N₂ atmosphere and it is therefore evident that CO was not involved in this reaction. The loss of weight, 40 a.u., is equal to half the weight of one pyrazine molecule indicating that reaction (6) took place.



This binuclear product was characterized by elemental and infrared analyses [16]. The pyrazine in the complex bridges the two pentacarbonyl moieties.

This binuclear complex was stable at quite elevated temperatures. However, it reacted under a CO atmosphere, before melting, as indicated by the second stage of the thermogram (see Fig. 7) according to



The residual weight was again negligible.

The enthalpies of reactions (6) and (7) could be determined independently. In reaction (6), a metal–nitrogen bond was broken and another formed. In reaction (7), two metal–nitrogen bonds were broken and two metal–carbonyl bonds formed. The sum of both reactions represents the heat of substitution. All these data are collected in Table 5.

Other $[M(\text{CO})_5L]$ complexes

These complexes reacted in a similar manner to the mono-substituted metal hexacarbonyls of piperidine. All relevant thermochemical data are collected in Table 6.

TABLE 6

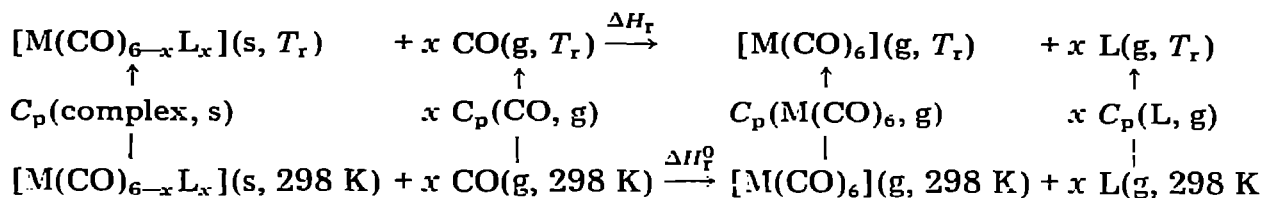
Results of the substitution reaction of $M(\text{CO})_5L$ under CO atmosphere

	T_i	T_{p1}	T_p	T_f	ΔH_r
Cr(CO) ₅ pyrazole	55	78	143	153	84 ± 6
W(CO) ₅ pyrazole	77	94	138	156	58 ± 6
Cr(CO) ₅ thiazole	62	83	115	136	84 ± 6

DISCUSSION

Justification of the method

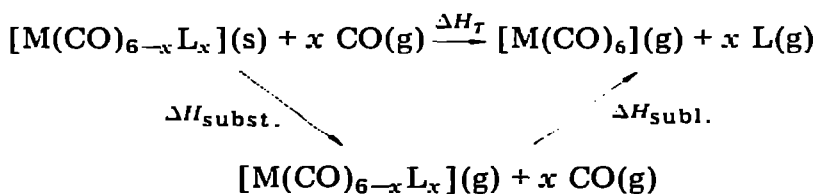
In order to deduce relevant data from the measurement, several assumptions and approximations have to be made. Reaction enthalpies under standard conditions are obtained from Scheme 2.



Scheme 2

The reaction temperature, T_r , is a mean value since a temperature range is involved. In the case of the mono-substituted complexes, the scheme is complicated by melting of the complex before the reaction. In most cases, no accurate specific heat data of the substituted complexes and of the ligands were available. The assumption was made that specific heats of reactants and products were equal and that Kirchoff's corrections were negligible. An estimation of the error involved can be made by approximating $C_p(\text{M}(\text{CO})_{6-x}\text{L}_x, \text{s})$ by $C_p(\text{M}, \text{s}) + (6-x) C_p(\text{CO}, \text{g}) + x C_p(\text{L}, \text{l})$. Specific heat data on piperidine and pyridine both in the liquid and gaseous state are available in the literature [9,17,18] as well as $C_p(\text{M}(\text{CO})_6, \text{g})$ and $C_p(\text{CO}, \text{g})$ [13,8]. The correction turns out to be about 5 kJ mole^{-1} and about the same for all mono-substituted piperidine and pyridine metal hexacarbonyls, when the reaction temperature is raised by 100 K.

Taking into account these considerations, the enthalpy of substitution in the gas phase, ΔH_{subst} can be calculated from



Scheme 3

Another source of systematic error may be introduced by the construction of the baseline of the thermogram during the reaction, since the initial and final reaction temperature are not well defined and the baseline before and after the reaction may shift.

In order to calculate the metal–nitrogen bond enthalpy $D(\text{M–N})$ in the mono-substituted complex, it is necessary to know the metal–carbonyl bond enthalpy derived from the reaction $[\text{M}(\text{CO})_6](\text{g}) \rightarrow [\text{M}(\text{CO})_5](\text{g}) + \text{CO}(\text{g})$. This enthalpy is unknown. Thus we approximated $D(\text{M–CO})$ to one sixth of the disruption enthalpy of the metal hexacarbonyl according to $[\text{M}(\text{CO})_6](\text{g}) \rightarrow \text{M}(\text{g}) + 6 \text{CO}(\text{g})$.

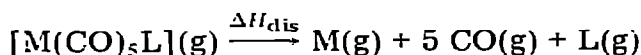
The thermochemical data

The enthalpies of formation of the metal hexacarbonyls, carbon monoxide and the ligands are known from the literature (see auxiliary data). The previously unknown enthalpy of sublimation of pyrazole was measured by us with a Knudsen effusion cell [4], $\Delta H_{\text{subl}}(\text{pyrazole}) = 71.8 \pm 1.0$ kJ mole⁻¹ in the temperature range 250–275 K. The orifice diameter was 0.1 mm. The enthalpy of sublimation, ΔH_{subl} for all the mono-substituted complexes involved have been published recently [4]. Thus with the assumptions made earlier on the reaction enthalpy, ΔH_r , it is possible to calculate the enthalpy of formation of the mono-substituted complexes from the equations

$$H_f[\text{M}(\text{CO})_5\text{L}, \text{s}] = H_f[\text{M}(\text{CO})_6, \text{g}] + H_f(\text{L}, \text{g}) - H_f(\text{CO}, \text{g}) - \Delta H_r$$

$$H_f[\text{M}(\text{CO})_5\text{L}, \text{g}] = H_f[\text{M}(\text{CO})_5\text{L}, \text{s}] + \Delta H_{\text{subl}}[\text{M}(\text{CO})_5\text{L}]$$

From the formation enthalpy of the complex and the ligands, the sum of the metal–ligand bond enthalpies can be deduced. This total disruption enthalpy is defined by



The contribution of the metal–nitrogen bond enthalpy to the total disruption enthalpy could be calculated from the relationship $D(\text{M–N}) = \Delta H_{\text{dis}} - 5 D(\text{M–CO})$. If the results are evaluated in this way, the measured reaction enthalpy is thought to consist of

$$\Delta H_r = \Delta H_{\text{subl}}[\text{M}(\text{CO})_5\text{L}] + \Delta H_{\text{subst}}[\text{M}(\text{CO})_5\text{L}]$$

(see Scheme 3) with $\Delta H_{\text{subst}}[\text{M}(\text{CO})_5\text{L}] = D(\text{M–N}) - D(\text{M–CO})$.

All the measured and calculated data from the mono-substituted complexes are collected in Table 7.

TABLE 7
Data for mono-substituted complexes

	ΔH_r	H_f (solid)	H_f (gas)	ΔH_{dis}	$D(\text{M–N})$
Cr(CO) ₅ piperidine	85 ± 8	–930	–836	634	99
Mo(CO) ₅ piperidine	108 ± 8	–960	–865	926	166
W(CO) ₅ piperidine	101 ± 8	–922	–815	1066	173
Cr(CO) ₅ pyridine	75 ± 6	–732	–629	614	79
Mo(CO) ₅ pyridine	57 ± 3	–721	–619	867	107
W(CO) ₅ pyridine	83 ± 10	–716	–606	1044	151
Cr(CO) ₅ pyrazine	32 ± 5	–633	–534	575	40
W(CO) ₅ pyrazine	64 ± 4	–641	–533	1027	134
Cr(CO) ₅ pyrazole	84 ± 6	–691	–603	638	103
W(CO) ₅ pyrazole	58 ± 6	–641	–529	1017	124
Cr(CO) ₅ thiazole	84 ± 6	^a	^a	624	89

^a Because no data on H_f (thiazole) are available in the literature, these values could not be calculated.

TABLE 8

Data for di- and tri-substituted complexes

	ΔH_r	H_f (solid)	ΔH_{subl}	$D(\text{M-N})$
$\text{Cr}(\text{CO})_4(\text{piperidine})_2$	119 ± 8	-900	110	112
$\text{Mo}(\text{CO})_4(\text{piperidine})_2$	164 ± 12	-952	110	179
$\text{W}(\text{CO})_4(\text{piperidine})_2$	141 ± 12	-898	114	191
$\text{Mo}(\text{CO})_3(\text{piperidine})_3$	138 ± 20	-863	118	159
$\text{Mo}(\text{CO})_4(\text{pyridine})_2$	^a	-467	113	123

^a Calculated from the disproportionation reaction of $[\text{Mo}(\text{CO})_5\text{pyridine}]$, see note in Table 4.

Determination of the sublimation enthalpies of the di- and tri-substituted complexes with the Knudsen effusion method failed. Estimates of these sublimation enthalpies could be made, however, by assuming a linear relationship between dipole moment and sublimation enthalpies. Using data from ref. 4, illustrated in Fig. 2, it was calculated that $\Delta H_{\text{subl}} = 4.2 \mu + 75$. In addition, Strohmeier [19] showed that the additivity rule of partial dipole moments is an acceptable approximation. From the measured ΔH_r , the estimated ΔH_{subl} and the cycle in Scheme 3, the following relationships were deduced.

$$\text{M}(\text{CO})_4\text{L}_2 : D(\text{M-N}) = \frac{1}{2} [\Delta H_r - \Delta H_{\text{subl}} + 2 D(\text{M-CO})]$$

$$\text{M}(\text{CO})_3\text{L}_3 : D(\text{M-N}) = \frac{1}{3} [\Delta H_r - \Delta H_{\text{subl}} + 3 D(\text{M-CO})]$$

$D(\text{M-CO})$ was again approximated to one sixth of the decomposition of metal hexacarbonyl in the gas phase. The results are presented in Table 8. A comparison between the $D(\text{M-N})$ of the mono-, di- and tri-substituted complexes revealed that the di-substituted complexes had a somewhat higher metal-nitrogen bond enthalpy. This may, however, be due to the assumptions made.

Recently, Skinner et al. published the enthalpies of formation of a number of pyridine and acetonitrile substituted Group VIB metal carbonyls [3]. Although these complexes nicely extend our series, unfortunately their complexes are not the same as our complexes. So a direct comparison of the results is not possible. In Table 9, we collected the solid state formation enthalpies that were measured by Skinner et al., and the sublimation enthalpies

TABLE 9

Data for substituted complexes from the literature

	H_f (solid) ^a	H_f (gas)	$D(\text{M-N})$
$\text{Cr}(\text{CO})_4(\text{pyridine})_2$	-505	-392	100
$\text{Mo}(\text{CO})_3(\text{pyridine})_3$	-275	-153	149
$\text{W}(\text{CO})_3(\text{pyridine})_3$	-250	-124	177

^a Ref. 3.

estimated from the dipole moment of the complexes. From these data and $D(\text{M}-\text{CO})$ we calculated $D(\text{M}-\text{N})$. The calculated values of $D(\text{M}-\text{N})$ of ref. 3 are somewhat higher than our values. However, Skinner's values fitted well within the observed trends: $[\text{Cr}(\text{CO})_5\text{pyridine}]$, $[\text{Cr}(\text{CO})_4(\text{pyridine})_2]$ [3], $[\text{Mo}(\text{CO})_5\text{pyridine}]$, $[\text{Mo}(\text{CO})_4(\text{pyridine})_2]$ and $[\text{Mo}(\text{CO})_5\text{pyridine}]$, $[\text{Mo}(\text{CO})_4(\text{pyridine})_2]$, $[\text{Mo}(\text{CO})_3(\text{pyridine})_3]$ [3].

From $\Delta H_{\text{subst}} [\text{M}(\text{CO})_5\text{L} = D(\text{M}-\text{N}) - D(\text{M}-\text{CO})]$, a direct comparison between the metal-nitrogen and the metal-carbonyl bond enthalpies can be made in the mono-substituted complexes. Except for $\Delta H_{\text{subst}} [\text{Mo}(\text{CO})_5\text{-piperidine}]$, all the substitution enthalpies turned out to be negative. So it is concluded that, in general, $D(\text{M}-\text{CO}) > D(\text{M}-\text{N})$.

In agreement with ref. 3, we found that $D(\text{Cr}-\text{N}) < D(\text{Mo}-\text{N}) < D(\text{W}-\text{N})$. This observation is quite general [20]. Because piperidine is able to form only a σ -bond, this trend can be ascribed to an increase in the σ -bond strength on descending Group VIB. It should, however, be realized that the $D(\text{M}-\text{N})$ is evaluated from the metal in its ground state. Just like the $D(\text{M}-\text{CO})$ of the hexacarbonyls, the strength of the metal-nitrogen bond in the complex is related to the metal in its hypothetical valence state [21].

The $\text{p}K_{\text{a}}$ -value of L or the ionization potential of the nitrogen lone pair is often used to describe the σ -donating properties within a series of ligands. Evidently thiazole ($\text{p}K_{\text{a}} = 2.4$; i.p. = 10.5 eV) and pyrazole ($\text{p}K_{\text{a}} = 2.5$; i.p. = 10.7 eV) are expected to form a weaker σ -bond than pyridine ($\text{p}K_{\text{a}} = 5.2$; i.p. = 9.67 eV) or piperidine ($\text{p}K_{\text{a}} = 11.2$; i.p. = 8.67 eV), whereas the $D(\text{Cr}-\text{N})$ values are 89, 103, 79 and 99 kJ mole^{-1} , respectively. This means, that an obvious relation between σ -donating parameters such as $\text{p}K_{\text{a}}$ and ionization potentials and the chromium-nitrogen bond enthalpy does not exist. In agreement with the low basicity of pyrazine ($\text{p}K_{\text{a}} = 0.65$), a low value of 40 kJ mole^{-1} is found for $D(\text{Cr}-\text{N})$ in $\text{Cr}(\text{CO})_5$ pyrazine. Apart from other effects, π -bonding between metal and ligand may disturb such a relationship. Within the limited series studied, $D(\text{W}-\text{N})$ decreases when the σ -donating properties of L become smaller.

CONCLUSIONS

The enthalpy of substitution and disproportionation could be determined for a series of Group VIB metal carbonyls, which enables us to estimate the M-N bond enthalpy. It is indicated that $D(\text{M}-\text{N})$ slightly increases going from mono-, di- to tri-substituted complexes. It is shown that $D(\text{M}-\text{N}) < D(\text{M}-\text{CO})$ and, within the assumptions made that $D(\text{Cr}-\text{N}) < D(\text{Mo}-\text{N}) < D(\text{W}-\text{N})$. The $\text{p}K_{\text{a}}$ and ionization potential of the nitrogen lone pair are not proper parameters to describe the trend of $D(\text{Cr}-\text{N})$ in contrast with $D(\text{W}-\text{N})$.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. K. Cavell for critical reading of the manuscript and useful suggestions. Mr. J.M. Ernsting is thanked for experimental assistance.

REFERENCES

- 1 R.H.T. Bleijerveld and K. Vrieze, *Inorg. Chim. Acta*, 19 (1976) 195.
- 2 M.A.M. Meester, R.C.J. Vriens, D.J. Stufkens and K. Vrieze, *Inorg. Chim. Acta*, 19 (1976) 95.
- 3 F.A. Adedeji, J.A. Connor, Ch.P. Demain, J.A. Martinho-Simoes, H.A. Skinner and M.T. Zafarani Moattar, *J. Organomet. Chem.*, 149 (1978) 333.
- 4 H. Daamen, J.M. Ernsting and A. Oskam, *Thermochim. Acta*, accepted for publication.
- 5 H. Daamen and A. Oskam, *Inorg. Chim. Acta*, 26 (1978) 81.
- 6 H. Daamen, A. Oskam, D.J. Stufkens and H.W. Waaijers, *Inorg. Chim. Acta*, 34 (1979) 253.
- 7 E.W. Abel, I.S. Butler and J.G. Reid, *J. Chem. Soc.*, (1963) 2008.
- 8 J. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer Verlag, Berlin and Heidelberg, 1973.
- 9 D.W. Scott, *J. Chem. Thermodyn.*, 3 (1971) 649.
- 10 J.D. Cox, A.R. Challoner and A.R. Meetham, *J. Chem. Soc.*, (1954) 265.
- 11 J. Tjebbes, *Acta Chem. Scand.*, 16 (1962) 916.
- 12 A.F. Bedford, P.B. Edmondson and C.T. Mortimer, *J. Chem. Soc.*, (1962) 2927.
- 13 G. Pilcher, M.J. Ware and D.A. Pittam, *J. Less Common Met.*, 42 (1975) 223.
- 14 D.D. Wagman, W.H. Evans, V.B. Parker, I. Hallow, S.M. Bailey and R.H. Schumm, *Natl. Bur. Stand. (U.S.)*, Tech. Note 270-4, 1969, U.S. Government Printing Office, Washington, D.C.
- 15 D.R. Stull and H. Prophet, *JANAF Thermochemical Tables*, NSRDS-NB 37, U.S. Government Printing Office, Washington D.C., June 1971.
- 16 H. Daamen, D.J. Stufkens and A. Oskam, to be published.
- 17 E.W. Washburn (Ed.), *International Critical Tables*, National Research Council of the U.S.A., McGraw-Hill, New York, 1926.
- 18 J.P. McCullough, D.R. Douslin, J.F. Messerly, I.A. Hossenlapp, T.C. Kincheloe and G. Waddington, *J. Am. Chem. Soc.*, 79 (1957) 4289.
- 19 W. Strohmeier and W. Langhäuser, *Z. Phys. Chem. N. F.*, 28 (1961) 268.
- 20 H.A. Skinner, *J. Chem. Thermodyn.*, 10 (1978) 309.
- 21 D.R. Lloyd and E.W. Schlag, *Inorg. Chem.*, 8 (1969) 2544.