INVESTIGATION OF NOVEL ORGANOMETALLICS BY THERMAL SPECTROSCOPIC METHODS

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Abstract

The photolysis of $W(CO)_6$ in CH_2Cl_2 produces $(CO)_5WCH_2Cl_2$. The high reactivity of $(CO)_5WCH_2Cl_2$ (1) was exploited to synthesize a vinylidene complexes via the acetylene–vinylidene rearrangement. The addition of a terminal acetylene ($H-C \equiv C-COOCH_3$) to a solution of (1) produced the η^2-acetylene-pentacarbonyltungsten complex $(CO)_5W(\eta^2-HC \equiv C-COOCH_3)$ in good yield. The production of the vinylidene complex $(CO)_5W=C=CH-COOCH_3$ in equilibrium with the acetylene complex in the reaction medium was verified experimentally by reaction with excess imine. The heterocyclic organometallic compound of tungsten obtained was separated and purified and its structure was studied by IR, ^1H NMR, ^{13}C NMR and mass spectrometry in comparison with the thermal analysis and elemental analysis data. The final aim of this investigation is the development of a new alternative route to a β-lactame with antibacterial activity.
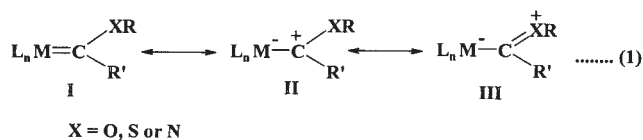
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Introduction

The first planned synthesis and characterization of a stable transition metal carbene complex were described by Fischer and Maasböl [1]. A whole series of new preparation routes have subsequently been developed. Several hundred carbene complexes have been isolated, characterized [2–4] and studied [5]. Stable Fischer carbene complexes can be depicted in three mesomeric structural formulae (I–III). The higher the electronegativity of the heteroatom substituent *X*, the smaller the *X–C* bond order. Conversely, increase in the π-donor ability of *X* is associated with an increase in the stability of Fischer carbene complexes. These Fischer carbene complexes are thermally stable up to temperatures higher than 100°C.

Fischer carbene complexes react in several ways [2] and typical modes, as indicated by the formula,

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$$L_nM=C\begin{smallmatrix}\nearrow XR\\\searrow R'\end{smallmatrix} \longleftrightarrow L_n\overset{-}{M}-\overset{+}{C}\begin{smallmatrix}\nearrow XR\\\searrow R'\end{smallmatrix} \longleftrightarrow L_n\overset{-}{M}-C\begin{smallmatrix}\nearrow \overset{+}{X}R\\\searrow R'\end{smallmatrix} \quad .... (1)$$

I   II   III

X = O, S or N

where a=substituent, b=addition of a nucleophile, c=insertion of reaction, d=at carbene side-chain, and e=oxidation or reduction of the metal.

$$L_nM=C\begin{smallmatrix}\nearrow XR\\\searrow R'\end{smallmatrix}$$
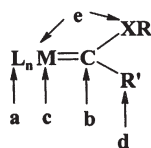
Fischer *et al*. [6] showed that the reaction of monosubstituted vinylidene complexes $(CO)_5W=C=CHR$ with N,N-diethylaminoprop-1-ene produce 3-amino-substituted cyclobutenylidene complexes, which undergo rearrangement to produce cyclic complexes of tungsten. The reactions of disubstituted vinylidene complexes of tungsten and chromium with electron-rich alkynes to produce stable cyclo-butenylidene complexes have also been investigated by Fischer *et al*. [7]. The stabilization of the cyclobutenylidene complexes is attributed to the presence of the π-electron-donor substituents in position 3.

The present work has the chief aim of the preparation of some novel vinylidene organometallics. The prepared vinylidene complexes were exploited in the synthesis of novel complexes containing cyclic carbene ligands (e.g. azetidinylidene complexes) and aminocarbene complexes via reaction with some imines. The mechanisms of these reactions were studied by different methods. The structures of the organometallics obtained were investigated by different physico-chemical methods of analysis in comparison with mass and thermal analyses (TG, DTG and DTA). The final aim was to find a new route for preparation of biologically reactive tungsten organometallics.

Experimental

Materials

Pentane and dichloromethane were distilled from CaH_2 under an atmosphere of nitrogen or argon. The silica gel used for chromatography (Fa. J. T. Baker, silica gel for flush chromatography) was nitrogen or argon-saturated. All chemical reactions were carried out under a nitrogen or argon atmosphere with the use of Schlenk techniques. The yields refer to the analytically pure compounds and were not optimized. All organic reagents were prepared as in recommended procedures [8, 9].

Spectroscopic instruments

IR spectra were recorded on a FTIR-spectrophotometer, (Biorad company: FT570) with CaF_2 cells at Konstanz University. The following abbreviations are used in the text in the IR explanations: vs=very strong, s=strong, m=medium, sh=shoulder, and w=weak.

^1H NMR spectra

The ^1H NMR spectra were recorded on a Bruker WM250 instrument, with $Si(CH_3)_4$ as internal standard and $CDCl_3$ as solvent in Konstanz University. The following abbreviations are used in the text: s=singlet, d=doublet, t=triplet, m=multiplet, and br=broad.

Mass spectra

The mass spectra were recorded on a Finniggan MAT312-EI instrument, at Konstanz University.

Thermal analyses

The thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analyses (DTA) of the prepared heterocyclic tungsten organometallics were performed by using a conventional thermal analyzer (TG-50, DTA-50 H; Shimadzu system, Shimadzu 30 series) in an inert atmosphere of nitrogen. The heating rate was $10°C\ min^{-1}$.

Elemental analyses

Elemental analyses were performed with a CHN-Analyzer (CHN-ORAPID; Heraeus Company) at Konstanz University, and some of them were repeated in the Microanalytical Centre, at Cairo University.

General procedures

Preparation of pentacarbonyl(dichloromethane)tungsten complexes

Hexacarbonyltungsten, $W(CO)_6$ (2.84 mmol) in 300 ml CH_2Cl_2 was irradiated with UV light under stirring in a nitrogen gas stream to sweep away carbon monoxide, using a photoreactor cooled to $-80°C$, until all the $W(CO)_6$ had been converted to $(CO)_5WCH_2Cl_2$ (after about 90 min) which has been detected by IR spectroscopy.

IR of $(CO)_5WCH_2Cl_2$ at 230 K: $\nu_{(CO)}$=2076 w, 1934 vs, 1880 m cm^{-1} (where w=weak, vs=very strong, m=medium, s=strong and sh=sharp).

Preparation of pentacarbonyl (η^2-methylcarboxyacetylene)tungsten (i↔ii)

To a freshly prepared solution of $(CO)_5WCH_2Cl_2$ 0.497 g (5.976 mmol) of methylcarboxyacetylene was added at $-80°C$ with stirring. The temperature was gradually raised to $-40°C$ (at $10°C\ min^{-1}$) and the solution was carefully evaporated under vacuum.

IR of $(CO)_5W=C=CH-COOCH_3$ (at 233 K): $\nu_{(CO)}$=2076 s, 1974 vs, 1934 sh cm^{-1}.

Preparation of pentacarbonyl [1-propyl-3-carboxylmethyl-4-phenyl-benzylidene-2-ylidene]tungsten (iii) (Z_8Fr_1)

0.82 g (5.572 mmol) of N-isopropyliminobenzylidene was added with stirring to the highly concentrated solution of the acetylene complex (i) at –30°C. The reaction was followed by IR spectroscopy until peaks of acetylene complexes were no longer observed. The solution was gradually warmed to room temperature. The solvent was removed under vacuum to give a brown oily product (iii).

Purification of the reaction product (iii) was carried out by chromatography on silica gel at –30°C. Elution with pentane gave first the unreacted $W(O)_6$ and then the unreacted imine. Continued elution with pentane/CH_2Cl_2 (10:3) gave a yellow band containing complex (Z_8Fr_1); this was characterized via its IR, mass, ^{1}H NMR and ^{13}C NMR spectra and elemental analysis for C, H and N. W was analyzed by ICP-AES after digestion of the complex in a microwave system. The *m.p.* of Z_8Fr_1 was found to be 148°C.

Elemental analyses: $C_{19}H_{17}O_7NW$, M_w=555.2

Calc.	C=41.10	H=3.05	N=2.52
Found	40.87	3.12	2.92
	40.78	3.16	2.74

IR (pentane, 298 K) $\nu_{(CO)}$=1944 vs syn., $\nu_{(CO)}$=1925 vs isomer, ν=2067 m cm^{-1};
  (CH_2Cl_2, 298 K) $\nu_{(CO)}$=1929 vs syn., $\nu_{(CO)}$=2066 sharp cm^{-1}.
Mass spectra 555 [M^+], 527 [M^+–CO], 494 [M^+–2CO], 471 [M^+–3CO],
  443 [M^+–4CO], 415 [M^+–5CO], 382 [M^+–6CO], 372 [M^+–CH_2–6CO],
  346 [M^+–6CO–$COCH_3$], 302 [M^+–6CO–$COCH_3$–isopropyl],
  131 [M^+–$(CO)_5WC_2C_6H_5$], 115 [M^+–$(CO)_5WC_2C_6H_5$–1/2O_2],
 77 [M^+–$(CO)_5WC$–CH_3CHO–$CH_3CHCH(CH_3)_2$].
^{1}H NMR 7.1–7.41[s, 5H, Aryl], 5.25–5.97[d, 1H*, CH], 4.01–4.46[s, 6H, isopropyl],
  3.35–3.9[s, 1H, CH_3–isopropyl], 1.1–1.41[1H, CH_3–C]
^{13}C NMR 200[(CO)*trans*], 195.2[*cis*(CO)], 132.09, 129.3, 128.72, 176.94(aryl),
  71.96–76.89(PhC), 61.06(CH), 56.137 (CH_3COOCH_3),
  50.93(CHNH.isopropyl), 21.13, 19.39, 19.11(CH_3CHCH_3).

Results and discussion

Increasing attention has recently been paid to photochemical reactions, which often occur clearly and readily at low-temperatures. The photogeneration of $M(CO)_5L$ has been extensively studied [10–12]. Virtually every metal carbonyl can generate a reactive intermediate through the loss of one CO ligand. This may be attributed to the fact that the lowest photoexcited states are those resulting from π-σ^* transitions, which weaken the M–CO bond. The resulting 16-electron fragment, $M(CO)_5$, is very reac-

tive and reacts avidly with any available donor to form the species M(CO)$_5$L, as given by the following equation:

$$M(CO)_6 \xrightarrow{\text{hv, } -CO} [M(CO)_5] \xrightarrow{L} M(CO)L \qquad (2)$$
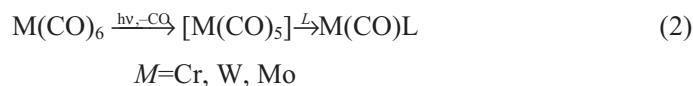
$$M=\text{Cr, W, Mo}$$

Photolysis of a solution of M(CO)$_6$ (M=Cr, W, Mo) in a polar solvent produces a pentacarbonylmetal–solvent complex. The stability of the M(CO)$_5$–solvent complex depends on the nature and the π-donor ability of the ligand used. The extraction of carbon monoxide by another electron pair donor is a reversible process. A nitrogen stream was therefore used to sweep the carbon monoxide out and thus drive the reaction to completion. The progress of the reaction can be followed by IR spectroscopy in the $\nu_{(C=O)}$ region, using small samples that are periodically taken from the reaction vessel. The IR absorption of the M(CO)$_5$–complex (three signals) is at lower frequency than for the corresponding M(CO)$_6$ (one signal in the CO stretching region), due to the higher metal–ligand back-bonding the latter. The smaller the signal of M(CO)$_6$, the greater the amount of M(CO)$_5$L formed. The reaction may be completed by photolysis for about 90 min at –80°C. The stability of (CO)$_5$MCH$_2$Cl$_2$ [M=Cr, Mo, W] decreases in the sequence W>Cr>Mo. Accordingly, the present work was concentrated on the W complexes.

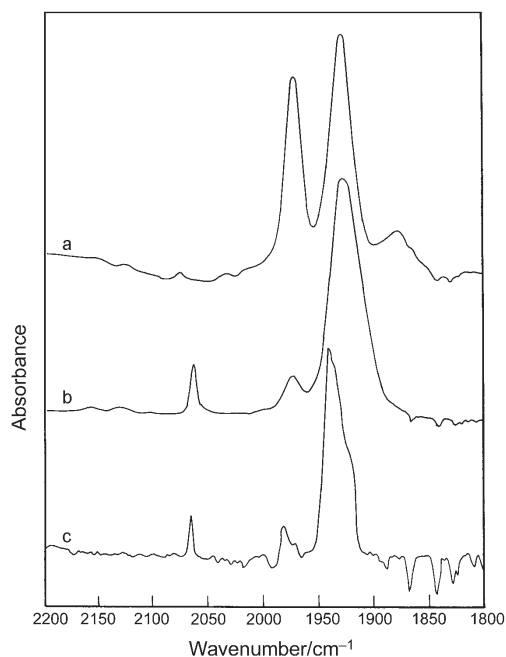**Fig. 1** a – Spectra of complex (i) (CO)$_5$W(η^2-HC≡CH–COOCH$_3$); b – Spectra of complex (iii) Z$_8$Fr$_1$, in CH$_2$Cl$_2$ at RT; c – Spectra of complex (iii) Z$_8$Fr$_1$, in pentane

Spectroscopic results and discussion

The IR spectrum of the complex $(CO)_5W(\eta^2\text{-}HC\equiv C\text{-}COOCH_3)$ in Fig. 1 revealed only two signals in the $\nu_{(C=O)}$ region (2087 m, 1932 vs cm^{-1}); but no 1650 w cm^{-1} band for $\nu_{(C=C)}$ vibration. The ^{1}H NMR spectrum was consistent with the composition of the η^2-acetylene–metal complex. The CH signals ($\delta\cong6.0$–3.8) appeared at lower field than those for the corresponding free alkyne ($\delta\cong3.1$) This may indicate that the $C\equiv C$ bond is weakened by coordination to tungsten. The presence of the vinylidene complexes $(CO)_5W=C=CH\text{-}COOCH_3$ (ii)   with the acetylene complex $(CO)_5W(\eta^2\text{-}HC\equiv C\text{-}COOCH_3)$ (i) in the reaction medium was verified experimentally by its reaction with isopropylimine, as explained by the equilibrium (i↔ii) to give the heterocyclic azetidinylidene complex (iii):
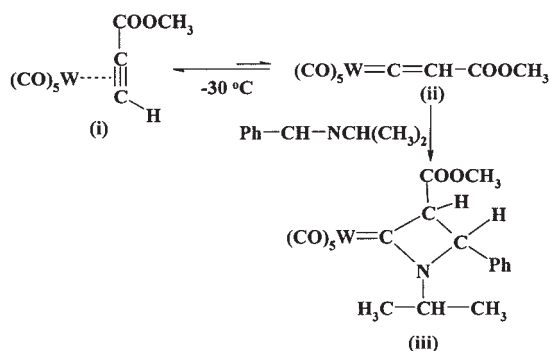
The IR spectra of the complex (iii) in Figs 1b and 1c exhibit two signals in the $\nu_{(C=O)}$ region at 2067 m and 1944 vs cm^{-1} in pentane, and at 2067 and 1930 vs cm^{-1} and in CH_2Cl_2 similarly as for the previously prepared azetidivinylidene complexes obtained by Abd-El-Zaher El-Abiad [13].
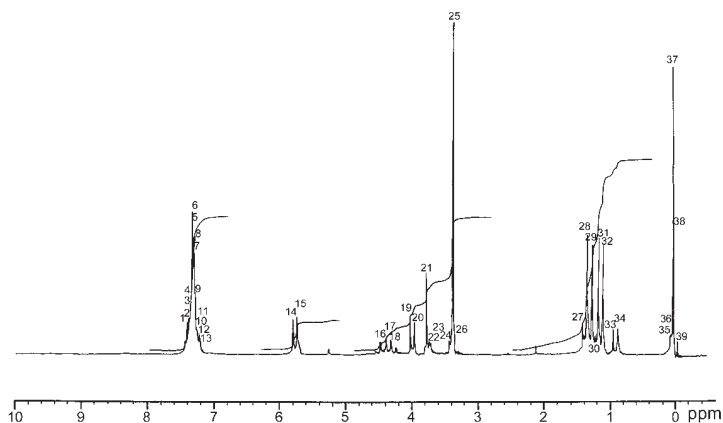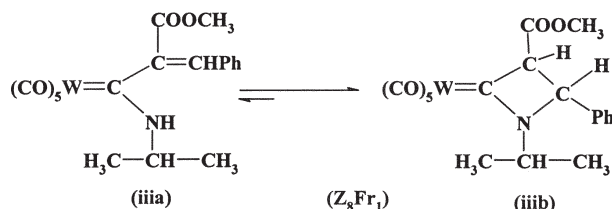

Fig. 2 ^{1}H NMR spectrum of complex (iii), Z_8Fr_1, in CDCl$_3$ at *RT*

The ^{1}H NMR spectrum (Fig. 2) showed that the cycloaddition reactions proceeded with high regio selectivity and that two isomers (iiia) and (iiib) were produced as an inseparable mixture of diastereomers:

(iiia) (Z$_8$Fr$_1$) (iiib)

In the ^{1}H NMR spectrum of this mixture, the C–CHPh proton of the major isomer (Z$_8$Fr$_1$) gave a doublet at δ=5.781 ppm (J=4.5 Hz). The signal of the NCH(CH$_3$)$_2$ proton of the major product appeared at δ=4.46. The ^{13}C NMR spectrum of Z$_8$Fr$_1$ gave signals for W=C at 267.2, CO *trans* at 200, CO *cis* at 195.2, aryl carbons at 132.09, 129.3, 128.72 and 127.94; C–Ph at 71.96, C–H at 61.06, and CH$_3$ at 21.13 ppm.

The equilibrium between vinylidene and acetylene complexes

The presence of vinylidene complexes (CO)$_5$W=C=CR (ii) in the reaction medium in equilibrium with acetylene complexes (CO)$_5$W (η-HC≡CR) (i) was verified by reaction with imine [6], although the signals of the vinylidene complex were absent in the IR, ^{1}H NMR and ^{13}C NMR spectra. This observation can be explained in view of either (a) the very fast conversion of (ii) to (i) (faster than the NMR time-scale) or (b) the slow conversion of (ii) to (i), so that (ii) is present in only very low concentration (<3%) [6]. Hypothesis (b) is preferred because of the appearance of (i) only regardless of the measuring temperature (50 to 0°C).

The presence of an equilibrium between (i) and (ii) was confirmed by addition of an equimolecular amount of imine to (i) dissolved in CD$_2$Cl$_2$ at –20°C. The ^{1}H NMR spectrum indicated that complex (i) totally, disappeared within the half-lifetime for isomerization of (i)→(ii) at –20°C, i.e. in less than 25 s [8]. Vinylidene complex (ii) is characterized by its high reactivity [9–11]. Addition of two equivalents of imine to complex (ii) therefore gave two cyclo complexes (iiia) or (iiib). (iiib) is known as an azetidinylidene complex (closed cycle), which is formed via a cycloaddition reaction between the C=C double bond in the vinylidene complex and the N=C double bond in the imine. The alkenyl(phenylimino)carbene, the open complex (iiia), is formed by a 1,3-hydrogen shift in the azetidinylidene complexes in the presence of excess imine and ring-opening. The complexes are soluble in polar solvents, e.g. CH$_2$Cl$_2$, and insoluble in pentane. The IR spectra of (iiia) and (iiib) are similar. The ^{13}C NMR spectra of both forms are similar to those of other carbene complexes [6, 8]. All low-field signals for the carbene carbon atom were recorded at ca δ=270 for the azetidinylidene tungsten complex and recorded at δ=260 ppm for the alkenyl(phenylamino)carbene

[12, 13]. The difference in signals (in ppm) between these isomers reflects the higher donor ability of the N atom in the open system isomer than in the closed one.

Factors affecting formation of open and closed complexes

Formation of the alkenyl(phenylamino)carbene complex iiia from azetidinylidene complexes depends on two important factors: excess imine, and the rate of increase of reaction completion. Experimentally, it was found that rapid chromatographic separation of the product from the excess imine gives the closed form (iiib), while leaving the product in excess imine overnight leads to the open form (iiia); this is known as the imine rearrangement. The rapid increase in reaction completion on temperature increase from lower $-80°C$ to room temperature leads to the formation of the closed form (iiib). A gradual temperature increase in excess imine leads to form of open formation (iiia).

Thermal analyses of the heterocyclic tungsten azetidinylidene complex (Z_8Fr_1)

The proposed structure of the heterocyclic tungsten compound (Z_8Fr_1) as suggested by the elemental analysis, ^1H NMR, ^{13}C NMR spectra, etc., is given by structure (iii). The TG data are given in Fig. 3a and Table 1, and the DTA data are given in Fig. 3b and Table 2. The first TG mass loss (78.5%) in the temperature range 106–410°C is due to the loss of $(CO)_5W=C=CHPh$ (calculated 78.9%) as five carbonyl groups is evolved separately or collectively losed together with the vinylidene part. At 411–624°C CO_2 is evolved (7.6 as compared with the calculated 7.93%) from decom-
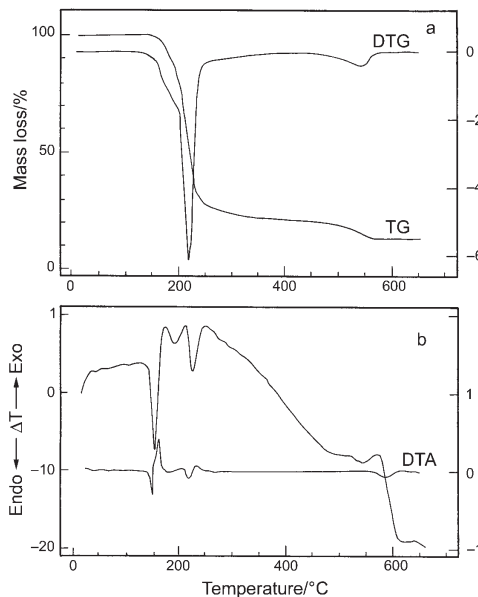

Fig. 3 Thermal analyses of complex (iii), Z_8Fr_1; a – TG and DTG; b – DTA

position of the side-chain $COOCH_3$ in the form (iiib). The third loss (12.6%) is due to the loss of tertiarybutylamine $(CH_3)_3C–NH_2$ (calculated 13.33%). The proposed scheme of this TG loss is:
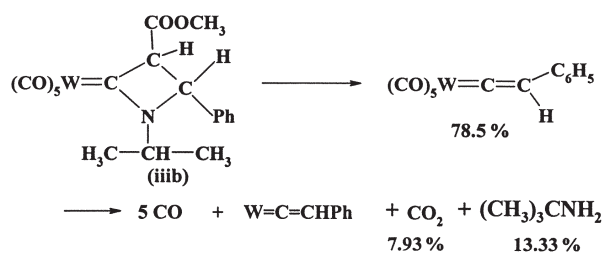

Table 1 Thermal analysis of complex (iii), Z_8Fr_1

Temperature range/°C	Mass loss/%	Proposed fragment
106–410	79.15 (78.9)	$(CO)_5W=C=CHQ$
411–624	8.27 (7.93)	CO_2
>624	12.50 (13.33)	$CH_3-\underset{\underset{NH_2}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_3$
	100.02 (100.13)	

The DTA (Table 2) shows first a very sharp endothermic peak in the temperature range 13.8–163.6 which is complete at 152°C with $E_a=–270$ J g^{-1} which may be due to the loss of the 78.5% of the complex (iiib). This is followed by two small sharp endothermic peaks in the range 176.9–210.2°C ($E_a= –98.0$ J g^{-1}). These two peaks may be due to the loss of CO_2 via decomposition of $COOCH_3$ group and NH_2 tertiaryamine. The final broad endothermic peak at 516.3–569.8°C ($E_a= –33.34$ J g^{-1}) and the steep endothermic base shift at 579.2–650°C ($E_a= –200$ J g^{-1}) may be due to the thermal decomposition of $(CO)_5W=C=CHPh$ into 5CO and W=C=CHPh.

Five glass transitions are observed in the thermal treatment of complex (iii) in the temperature range 25–650°C, which may point to thermal aggregates of crystalline rearrangements of the complex due to its thermal decomposition.

Mass spectrum of (Z_8Fr_1)

The heterocyclic compound (Z_8Fr_1) displays mass weightof 555 (Fig. 4), which confirm the molecular mass calculated (555.2) from the general formula $C_{19}H_{17}O_7NW$ found by elemental analysis. It undergoes the loss of 5CO from the pentacarbonyl part of the compound, and of one CO_2 coming from the decomposition of the $COOCH_3$ side-chain. Some possible fragments could not be identified by thermal analysis but they were easily detected by mass spectrometry, e.g. $(CO)_5WC_2$

Table 2 DTA description of Z_8Fr_1

Temperature range/°C	Peak at/°C	E_a/J g^{-1}	Description	Glass transition/mW	
133.9–168.6	152	–270	very sharp endothermic peak	132.97–137.21	4.863
176.9–210.2	193.6	–52.8	small endothermic peak	186.7–215.9	–0.218
215.6–243	225.6	–98.0	sharp endothermic peak	217.8–221.7	0.295
516.3–567.8	544.9	–33.34	broad small endothermic peak	544–561	0.416
579.7–650	620.0	–200	steep endothermic base shift	579–605.9	–11.255

(M^+348), C_6H_5 (M^+77), $CH_3CHO+CH_3$–$NHCH(CH_3)_2$ (M^+117), $HCOOCH_3+CH_3NHCH(CH_3)_2$ (M^+133),
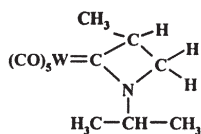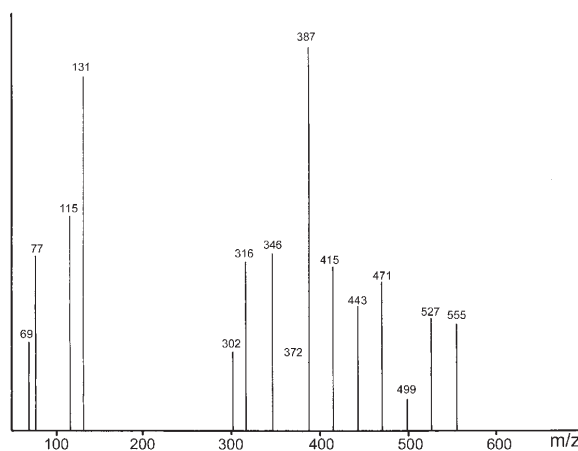

(M^+,443), etc.

Fig. 4 Mass spectra of heterocyclic organometallic complex (iii), Z_8Fr_1

The mass spectral data are therefore in good agreement with the thermal analysis data. The carbonyl groups of complex (iii) are readily split off followed by decomposition of the carboxylic group. The final stage involves complete thermal decomposition of the ring structure of the heterocyclic part and liberation of the benzene ring.

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