

THERMAL DEGRADATION OF THE TRANSITION METAL CARBONYL COMPLEXES

I. TG and DSC of Monodentate Bis-(diphenylphosphino)-methane Substituted Carbonyl Complexes of Chromium, Molybdenum and Tungsten

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The thermal degradation of three monosubstituted hexacarbonyl complexes, $M(\text{CO})_5(\text{dppm})$ (where $M = \text{Cr, Mo and W}$; $\text{dppm} = \text{Bis-(diphenylphosphino)-methane}$) has been studied using TG and DSC technics and their results reported. All the complexes facily lose a carbonyl ligand (CO) below 200 °C. The kinetic analysis on the molybdenum complex suggested a first order dissociation pathway for this decarbonylation process. Dephosphination occurred at high temperature, followed by further decarbonylations. The enthalpy changes associated with the first decarbonylation are reported. The measured kinetic parameters are in good agreement with the literature values on similar systems obtained from solution studies.

Organometallic chemistry has been progressing in a brisk pace in recent years [1, 2]. Such advancement not only bears a fundamental academic interest, because of its linkage to both inorganic and organic chemistry [3–5], but is also relevant to many applied areas such as homogeneous and heterogeneous catalysis [6, 7], laser photolysis [8], and polymer chemistry [9]. Among the thousands of organometallic compounds known, metal carbonyls represent the largest class and their chemistry has been a subject of intense research activities [10–12]. A thorough understanding of the nature of the metal-carbon bond is inevitable before one can utilize such compounds in new industrial application such as chemically modified electrodes [13–15], metal-containing conductive polymers [9] and homogeneous and heterogeneous catalyst [6, 7] which are amongst the most prominent. Data relating to the metal-carbon and metal-phosphorus bond strength in metal carbonyls and phosphines respectively have been measured through a variety of solution kinetic

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and mechanistic studies [16]. Spectroscopic methods such as NMR [17–19] have also been developed in monitoring ligand substitution processes from which invaluable kinetic parameters can be obtained. Most of the classical methods, however, are based on solution techniques, which almost invariably are solvent dependent. Reliable qualitative and quantitative thermochemical study on organometallics in solid state is rare. The utilization of thermal methods in studying coordination complexes containing particularly amino-acids [20, 21], dithiocarbamates [22, 23] and β -diketonates [24, 25] as ligands commenced more than a decade ago. Surprising perhaps, despite the versatility of TG and DSC, their applications to organometallic compounds have been scarcely explored [26, 27].

It is our aim to initiate a programme which allows the thermal study of metal carbonyls through techniques such as TG and DSC to complement other established methods such as calorimetry [28, 29], flash photolysis [30], IR [31], NMR [17–19] and mass spectroscopic techniques [32] which are used extensively in kinetic and mechanistic investigations. We wish to report as part of a series of thermal studies on organometallic complexes, the monosubstituted pentacarbonyl $M(\text{CO})_5(\text{dppm})$ where $M = \text{Cr}, \text{Mo},$ and W . The dppm in these molecules functions as a monodentate ligand despite its bidentate potential. The thermal behaviour of the complexes will be discussed in terms of weight loss, enthalpy changes and activation energy associated with the decomposition steps.

Experimental

Materials

Dppm was purchased from Aldrich Chemicals Co. and was checked for purity by ^{13}C and ^{31}P -NMR before use. Metal hexacarbonyls and trimethylamine N-oxide dihydrate (TMNO) were supplied from Aldrich Chemical Co. and Tokyo Kasai Kogyo Co. Ltd. respectively and used without further purification. The complexes $\text{Cr}(\text{CO})_5(\text{dppm})$ [34, 35] and $\text{W}(\text{CO})_5(\text{dppm})$ [36] have been reported in the literature but their syntheses described in this paper are novel. $\text{Mo}(\text{CO})_5(\text{dppm})$ [37], however, is newly synthesized.

General procedure

All reactions were performed under an atmosphere of pure dry nitrogen. Solvents were reagent grade and degassed before used. Proton NMR spectra were recorded either on a Joel FX 900 or a Perkin-Elmer R32 NMR spectrometer at 90 MHz using $\text{Si}(\text{CH}_3)_4$ as internal standard. Phosphorus-31 NMR spectra were recorded on the Joel FX 900 at 36.23 MHz. Chemical shifts are reported in ppm to higher

frequency of external 85% phosphoric acid. The samples were run in deuterated chloroform. Infrared spectra were run on a Perkin-Elmer 1310 Infrared spectrophotometer as solution or a FT-IR Perkin-Elmer 1710 spectrophotometer as KBr disc. Melting points were measured using a Buchi 512 melting point apparatus without calibration. Elemental analyses were performed by the Analytical Service Group of the Department using a Perkin-Elmer Elemental Analyser. Analytical and spectroscopic data are given in Table 1 together with the melting points. The detailed interpretation of the spectroscopic data can be obtained from the references given above [34-37].

Table 1 Microanalytical and spectroscopic data

	Cr(CO) ₅ (dppm)	Mo(CO) ₅ (dppm)	W(CO) ₅ (dppm)
mp	120-122 °C	164 °C	196-197 °C (decomp.)
$\nu \cdot \text{cm}^{-1}$	2050w, 1980w, 1930s ⁽¹⁾	2069m, 1996m, 1932vs (br) ⁽²⁾	2067m, 1986m, 1932vs ⁽²⁾
$\delta(^1\text{H})$ in ppm	7.15-7.57 (m, 2OH) 3.21 (dd, 2H) J (HP _a) = 8 Hz J (HP _b) = 2 Hz ⁽³⁾	7.16-7.54 (m, 2OH) 3.19 (dd, 2H) J (HP _a) = 8.0 Hz J (HP _b) = 2.7 Hz ⁽⁴⁾	7.16-7.53 (m, 2OH) 3.34 (dd, 2H) J (HP _a) = 8 Hz J (HP _b) = 2 Hz ⁽³⁾
$\delta(^{31}\text{P})$ in ppm	48.06 (d, 1P) -25.78 (d, 1P) J (PP) = 90 Hz	28.34 (d, 1P) -24.97 (d, 1P) J (PP) = 112 Hz	10.50 (d, 1P) -24.30 (dt, 1P) J (PP) = 105 Hz J (PW) = 247 Hz
Elemental Analysis	61.7% C, 3.8% H (calcd. = 62.4% C 3.8% H)	58.1% C, 3.5% H (calcd. = 58.1% C 3.6% H)	50.2% C, 3.0% H (calcd. = 50.9% C 3.1% H)

⁽¹⁾ CH₃Cn; ⁽²⁾ KBr disc; ⁽³⁾ Perkin-Elmer R32; ⁽⁴⁾ JOEL FX 90Q

Thermal analysis

The TG runs were conducted on the Shimadzu TG-30 thermal analyser at a heating rate of 10 deg min⁻¹ unless otherwise stated. The atmosphere was flowing nitrogen at 75 cc min⁻¹. For the determination of activation energy, four runs at 2.5, 5, 10 and 20 deg min⁻¹ were realized on the DuPont 9900 thermal analyser. The activation energy was calculated by the method of Wall and Flynn [33] already stored in the computer. DSC experiments were carried out on the DuPont 9900 thermal analyser calibrated to have a cell constant of 1.19. The enthalpy values were generated by the computer with indium as the reference.

Preparation

$\text{Cr}(\text{CO})_5(\text{dppm})$ (I)

Dppm (0.8757 g, 2.27 mmol) was added to a well stirred mixture of $\text{Cr}(\text{CO})_6$ (0.5013 g, 2.27 mmol) and TMNO (0.2593 g, 2.33 mmol) in acetonitrile (30 ml). After 8 hr of stirring, a yellow solution has resulted. The mixture was kept at -15°C for 15 hr and the white microcrystals thus precipitated were filtered off, washed copiously with methanol, and collected. Yield = 0.42 g (32%). The product was recrystallized from dichloromethane (CH_2Cl_2)/methanol (CH_3OH).

$\text{Mo}(\text{CO})_5(\text{dppm})$ (II)

$\text{Mo}(\text{CO})_6$ (0.5072 g, 1.92 mmol) and TMNO (0.2103 g, 1.89 mmol) were stirred in acetonitrile (30 ml) at 28°C for 15 min, yielding a clear yellow solution. Upon addition of dppm (0.7299 g, 1.90 mmol), a light brown solution had resulted. After 1 hr of vigorous stirring, a milky suspension thus formed was filtered. The white solid obtained was washed with methanol and recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. Yield = 0.68 g (56%).

$\text{W}(\text{CO})_5(\text{dppm})$ (III)

$\text{W}(\text{CO})_6$ (0.5003 g, 1.42 mmol) and TMNO (0.1577 g, 1.42 mmol) were mixed in acetonitrile (30 ml). Dppm (0.5463 g, 1.42 mmol) was added to the resulting yellow mixture. After 5 hr of vigorous stirring, the mixture was evaporated under vacuum to 10 ml, followed by addition of CH_3OH (10 ml). The white microcrystalline precipitate was filtered, collected and recrystallised from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. Yield = 0.4526 g (45%).

Results and discussion

$\text{Cr}(\text{CO})_5(\text{dppm})$ (I)

TG—In Fig. 1, the weight loss at about 190° corresponds to the expulsion of one CO ligand (obsd. 4.5%; calcd. 4.9%). Another weight loss was observed at about 250° which may be attributed to the expulsion of the next most labile CO ligand (obsd. 4.5%; calcd. 4.9%). From 300 to 360° the dppm ligand is eliminated extremely rapidly (obsd. 67.9%; calcd. 66.7%) and the weight remains fairly constant until 700° . Two of the remaining three CO ligands (obsd. 9.2%; calcd. 9.7%) are eliminated between 700 and 1000° to give $\text{Cr}(\text{CO})$ obsd. 13.0%; calcd. 13.9%).

DSC—Fig. 2 shows that $\text{Cr}(\text{CO})_5(\text{dppm})$ melts at 126.3° . The endothermic peaks at 190° and 278.7° with enthalpies 24.6 and 30.0 kJ mol^{-1} respectively are

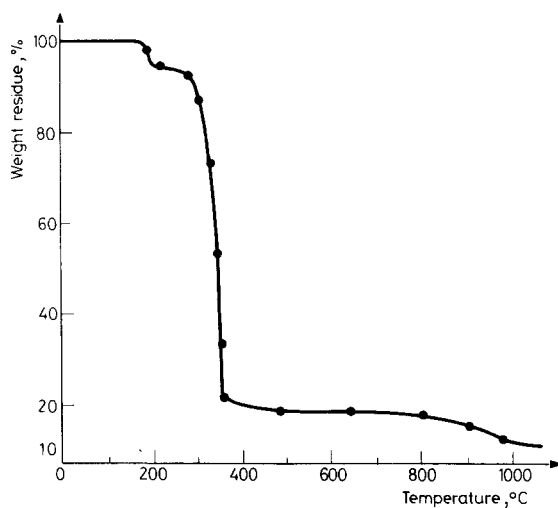


Fig. 1 TG curve of $\text{Cr}(\text{CO})_5(\text{dppm})$

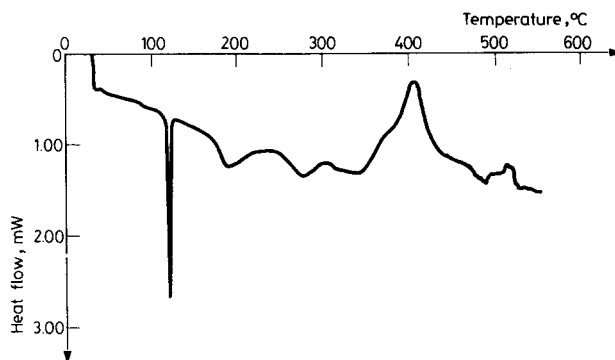
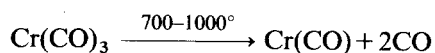
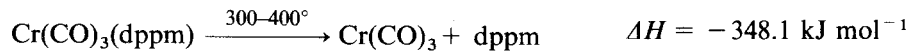
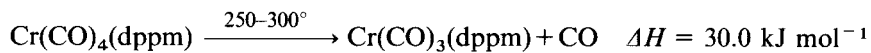
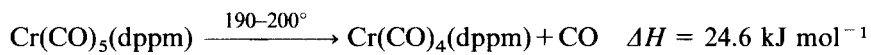


Fig. 2 DSC curve of $\text{Cr}(\text{CO})_5(\text{dppm})$

consistent with the two consecutive losses of CO ligands. The energy released by the decomposition of dppm ligand is $348.1 \text{ kJ mol}^{-1}$



Mo(CO)₅(dppm) (II)

TG—The TG thermogram (Fig. 3) shows a rapid weight loss between 180 to 200° which corresponds to the elimination of one Co ligand (observed 4.8%; calculated 4.5%). The steep weight loss which followed up to 425° is consistent with the rapid decomposition of the ligand (obsd. 61.9%; calcd. 62.0%). Two of the remaining four CO ligands are expelled between 400 and 850° (obsd. 10%; calcd. 9%). The weight % remaining at 1000° is consistent with the residue $\text{Mo}(\text{CO})_2$ (obsd. 23.5%; calcd. 24.5%).

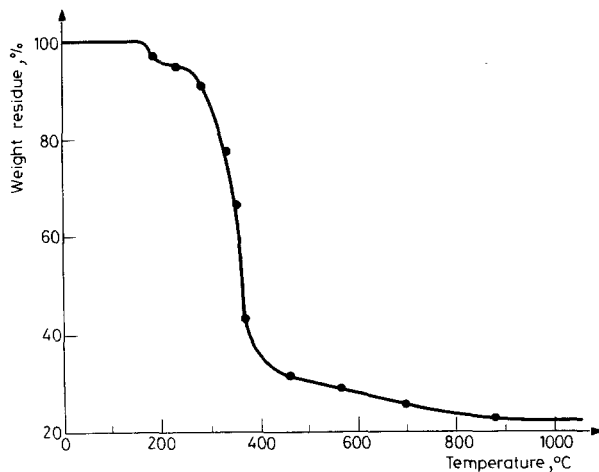


Fig. 3 TG curve of $\text{Mo}(\text{CO})_5(\text{dppm})$

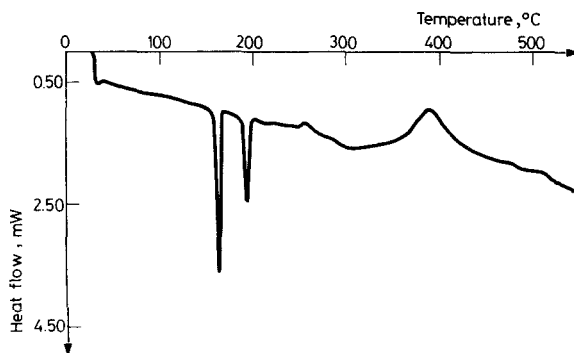
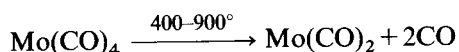
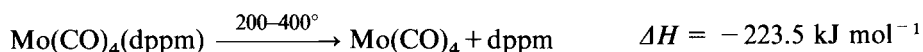
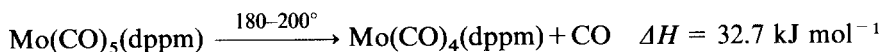


Fig. 4 DSC curve of $\text{Mo}(\text{CO})_5(\text{dppm})$

DSC—The first endothermic peak at 164.95° in Fig. 4 is very sharp which represents the melting of the complex. The second endothermic peak at 193.67° confirms the expulsion of one CO ligand as indicated by TG. The low enthalpy

value for this process (32.7 kJ mol^{-1}) suggests that the first CO ligand to be expelled was very labile. The broad exothermic peak between 300 and 425° can be attributed to the decomposition of the dppm ligand. The energy involved in this step is $-233.5 \text{ kJ mol}^{-1}$.



W(CO)₅(dppm) (III)

TG—The first weight loss step at 200° in Fig. 5 suggests the expulsion of one CO ligand (obsd. 4.5%; calcd. 4.0%). The step belonging to the loss of dppm (obsd. 55.5%; calcd. 54.2%) is different to that of $\text{Mo}(\text{CO})_5(\text{dppm})$ in that the process extends over a larger temperature range up to 650° . The intermediate complex $\text{W}(\text{CO})_4$ gives off two more CO ligands (obsd. 8.0%; calcd. 7.9%) from 700 to 900° . The residue is $\text{W}(\text{CO})_2$ (obsd. 32.0%; calcd. 33.9%).

DSC—The endothermic peak at 198° observed in Fig. 6 is due to two overlapping reactions: the melting of the complex and the elimination of one CO ligand at about 200° . The enthalpy for the two processes is 91.0 kJ mol^{-1} but it would be very

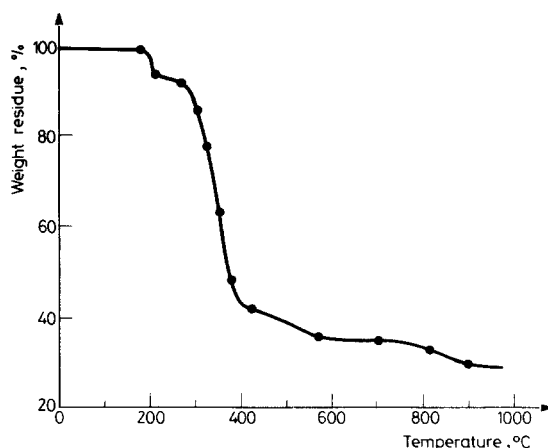


Fig. 5 TG curve of $\text{W}(\text{CO})_5(\text{dppm})$

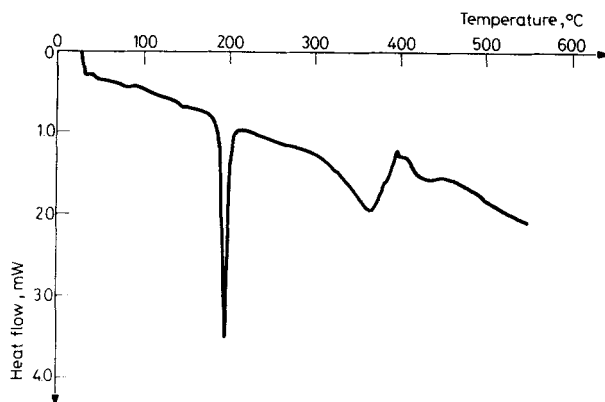
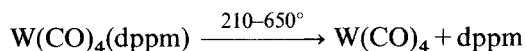
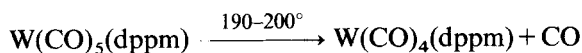
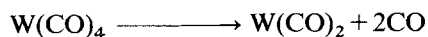


Fig. 6 DSC curve of $W(CO)_5(dppm)$

difficult to determine the two enthalpies separately. The decomposition of dppm of this complex from 325 to 450° is demonstrated by an endothermic reaction ($\Delta H = 154.6 \text{ kJ mol}^{-1}$) followed immediately by an exothermic peak ($\Delta H = -81.0 \text{ kJ mol}^{-1}$) which suggests that the breakdown mechanism of the dppm ligand in this case is more complex than that of I and II. The overall enthalpy for the step is taken to be the sum of the two enthalpies, i.e., 73.6 kJ mol^{-1} .



$$\Delta H = 73.6 \text{ kJ mol}^{-1}$$



All three complexes $Cr(CO)_5(dppm)$ (I), $Mo(CO)_5(dppm)$ (II), and $W(CO)_5(dppm)$ (III) readily lose their first CO ligand between 180–200°. The low enthalpies for these endothermic processes (24.6 kJ mol^{-1} for I, 32.7 kJ mol^{-1} for II and $<91.1 \text{ kJ mol}^{-1}$ for III) suggest a high lability for the metal-carbon bond. The relative magnitude for the enthalpies (ΔH) measured is in good agreement with that reported in a recent pyrolysis experiment [8] on metal hexacarbonyls which cited an increasing metal-carbon bond dissociation energy from chromium to molybdenum to tungsten.

The fact that the cleavage of the metal-carbon bond occurs prior to that of the metal-phosphorus bond in the complexes studied in this work is consistent with that

found in similar systems $M(\text{CO})_5L$ (where $M = \text{Cr}, \text{Mo}$ and W , $L =$ monodentate diphosphines) through some solution kinetics investigations [38]. The carbonyl ligand cis to the phosphine is probably the most labile owing to its competition for π electrons with its trans counterpart. The present study however cannot ascertain the exact nature of the resultant species whether it be a pentacoordinate 16-electron square pyramidal intermediate, or a saturated stable 18 electron octahedral species.

After the initial loss of CO, the second cleavage occurs readily at the metal-phosphorus site in II and III in the temperature range of about 300–450°. The exothermic process in II ($\Delta H = -223.5 \text{ kJ mol}^{-1}$) is thermodynamically more favourable than that found in III ($\Delta H = 74.6 \text{ kJ mol}^{-1}$). The production of the species $M(\text{CO})_4$ instead of $M(\text{CO})_3(\text{dppm})$ for Mo and W reinforces the conception that metal-carbonyl bond lability is extremely sensitive to the electron environment of the metal coordination sphere. The initial loss of CO apparently strengthened the remaining metal-carbon bonds. This can be understood since, after partial decomposition, there would be less competition for π electrons between the carbonyl ligands which are renowned for strong π electron acceptors.

For I, the TG curve suggests a concomitant loss of CO and phosphine in the temperature range of 250–360° after the initial loss of a CO ligand at about 200°. The DSC thermogram, however, is able to differentiate the two processes, an endothermic cleavage of CO at 279° ($\Delta H = 32.0 \text{ kJ mol}^{-1}$) and an exothermic peak at 338° ($\Delta H = -348.1 \text{ kJ mol}^{-1}$).

It is interesting to note that, despite a common notion of labile metal-carbon bond and unstable carbonyl complexes, complete cleavage of the metal-carbon bonds was not observed in any of the three complexes studied. At 1000°, the residues were $\text{Cr}(\text{CO})$, $\text{Mo}(\text{CO})_2$ and $\text{W}(\text{CO})_2$ respectively. Latest work by Smith et al. [8] showed that prolonged laser pyrolysis on $\text{Cr}(\text{CO})_6$ failed to yield any metal

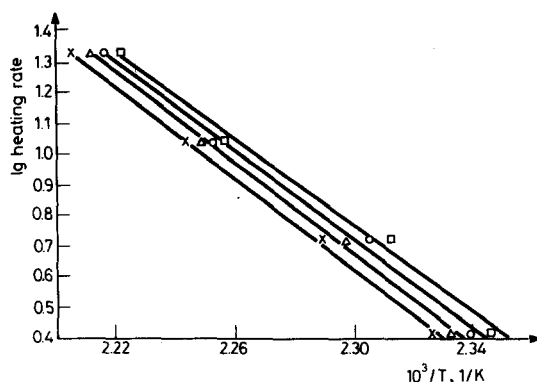


Fig. 7 Wall and Flynn [33] plot for $\text{Mo}(\text{CO})_5(\text{dppm})$

particles, which tends to agree with our findings. On the contrary, $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ lead ultimately to the complete deliganded metal particles, which are not observed under our conditions.

All the three complexes undergo facile metal-carbon bond cleavage below 200° and a more detailed study of this step was carried out on complex II. The plot of \log (heating rate) vs. $1/T$ for four different % decomposition within the first CO deligandation step based on the method of Wall and Flynn [33] is shown in Fig. 7. The slopes of the plots were calculated by the computer to give activation energies (E^*) between 137.6 and 143.6 kJ mol^{-1} . Such consistency further suggests that this step proceeds by a simple first order metal-carbon bond scission mechanism. Moreover, an average E^* value of 141.2 kJ mol^{-1} is close to the literature values found for $\text{Mo}(\text{CO})_6$ ($E^* = 132.6 \text{ kJ mol}^{-1}$ in decalin) [39], $\text{Mo}(\text{CO})_5(\text{dppm})$ ($E^* = 120.1 \text{ kJ mol}^{-1}$ in octane) [40] and $\text{Cr}(\text{CO})_5(\text{dppm})$ ($E^* = 141.0 \text{ kJ mol}^{-1}$ in octane) [38] which are indicative of a simple $S_{\text{n}}1$ dissociative process as opposed to the associative mechanism.

Conclusion

The present study demonstrated the sequential cleavages of the metal-ligand bonds during the decomposition of the three monosubstituted pentacarbonyl complexes of chromium, molybdenum and tungsten. All complexes facilely lose a molar equivalent of carbon monoxide below 200° via a first order dissociative process. In all cases the residues remaining at 1000° contain at least one carbonyl ligand. It has been shown that the TG and DSC techniques can provide invaluable qualitative and quantitative information on the decomposition pattern of Group VI substituted metal carbonyls. Thermal analysis is particularly useful when applied to insoluble systems. Results obtained are compatible with those from classical solution techniques. This work will be extended to related carbonyl systems.

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Zusammenfassung — Der thermische Abbau von drei monosubstituierten Hexacarbonyl-Komplexen des Typs $M(\text{CO})_5(\text{dppm})$ ($M = \text{Cr}, \text{Mo}$ oder W ; $\text{dppm} = \text{Bis}(\text{-diphenylphosphino)-methan}$) wurden mittels TG und DSC untersucht. Alle diese Komplexe geben unterhalb 200°C leicht einen Carbonylliganden (CO) ab. Die für den Molybdänkomplex ausgeführte kinetische Analyse deutet auf einen Dissoziationsverlauf erster Ordnung für diesen Decarbonylierungsprozeß hin. Bei hohen Temperaturen erfolgt Dephosphinierung, gefolgt von weiterer Decarbonylierung. Die sich auf den ersten Decarbonylierungsschritt beziehenden Enthalpieänderungen werden angegeben. Die gemessenen kinetischen Parameter stimmen gut mit Literaturwerten ähnlicher Systeme überein.

Резюме — Методом ТГ и ДСК изучено термическое разложение трех монозамещенных гексакарбонильных комплексов $M(\text{CO})_5(\text{dppm})$, где $M = \text{Cr}, \text{Mo}$ и W ; $\text{dppm} = \text{бис-дифенилфосфино-метан}$. При температуре ниже 200° комплексы легко теряют карбонильный

лиганд. Кинетический анализ реакции разложения молибденового комплекса указывает на первый порядок реакции декарбонилирования. Потеря фосфорорганического лиганда протекает при более высокой температуре, за которой следует дальнейшее декарбонилирование. Приведено изменение энтальпии, связанное с первичной реакцией декарбонилирования. Полученные кинетические параметры хорошо согласуются с литературными значениями, найденными для подобных систем в растворе.