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Thermal Behaviour of the Materials $[MCl_2(PMe_3)_4]$ and $[MCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3]$ (M = Mo, W; PMe_3 = Trimethylphosphine)

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Abstract

Thermal decomposition of the six-coordinate 16-electron compounds $[MCl_2(PMe_3)_4]$ (M = Mo, W; PMe_3 = trimethyl phosphine) has been studied by means of TG and DTA techniques. In addition a similar study has been carried out over the seven-coordinate 18-electron complexes $[MCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3]$ (M = Mo, W; CN-t-Bu = tert-butyl isocyanide) recently obtained in our laboratory by reaction between the former 16-electron complexes and tert-butyl isocyanide.

Well-crystallized compounds $[MCl_2(PMe_3)_4]$ are stable in air for several hours. However, they are thermally labile and decompose even in an inert atmosphere removing phosphine at temperatures below 200 °C. The seven-coordinate compounds here studied are also unstable at relatively low temperatures. In the latter compounds tert-butyl isocyanide ligand is more weakly bonded to the metal than the other ligands. The two trimethyl phosphines are in almost opposite positions and they are removed at higher temperatures.

The experiments in an inert atmosphere leads to the production of metal dichloride which decomposes at higher temperatures. On the other hand, thermal decomposition in air occurs forming metal dioxides and/or trioxides.

Introduction

Organometallic chemistry has been progressing at 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], activation of small molecules (CO, N_2, CO_2, ...) [9, 10] and polymer chemistry [11]. Data relating to the metal–carbon and metal–phosphorus bond strength in metal carbonyls and phosphine complexes have been measured through a variety of solution kinetic and mechanistic studies [12]. Furthermore spectroscopic methods such as NMR have been applied to study substitution processes of some ligands by others [13–15]. It is not common, however, to find qualitative and quantitative thermochemical studies about organometallic compounds in the solid state. In the last decades thermal methods have been used to study coordination complexes, particularly those containing aminoacids [16, 17], dithiocarbamates [18, 19] and β-diketones [20, 21] as ligands. Amazingly, although thermogravimetry (TG) and differential thermal analysis (DTA) are very versatile techniques, their application to the study of organometallic compounds has been scarcely attempted [22–24].

Our interest in the thermal study of organometallic compounds aims to relate composition, structure and material processing with those properties suitable for various technological applications. An essential part of research on new materials is the synthesis and characterization of heterogeneous catalysts for chemical reactions [25]. In this field, the study of processes to generate effective particles from organometallic precursors, particularly the conditions of decomposition and/or reduction, is a feature still not explored.

In fact there is a challenge to get a better design on the system itself in addition to that originated by extension to more complex systems (e.g. bimetallic catalysts) with undubious interest by their applications [26].

Our aim is to begin a programme of thermal study about organometallic compounds of Mo and W by means of techniques such as TG and DTA in order to carry out a more complete characterization of these compounds, in addition to other extensively used techniques such as IR [9, 10, 27] and NMR [9, 10, 13–15] spectroscopies. These processes could also lead to the production of materials with technological applications: pigments, inhibitors against corrosion, catalysts containing oxides of these elements or metallic particles, etc. We wish to report in this paper a part of such thermal studies about six-coordinate phosphine complexes of Mo^{II} and W^{II} as well as seven-coordinate compounds obtained from the former ones which likewise contain tert-butyl isocyanide ligands.

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Experimental

Materials and General Procedure

Elemental microanalysis were carried out by Mikroanalitisches Labor Pascher, Remagen (F.R.G.) and Butterworth Laboratories Ltd., Middlesex (U.K.). IR absorption spectra were recorded using a Pye Unicam SP3-300 spectrophotometer with a PC Multitech Popular 500 for controlling the scanning conditions and data treatment. The techniques used were KBr pellets, dispersion in Nujol or solution. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded by means of a Varian XL-200 and a Jeol GSX-270 spectrometer using the most suitable deutered solvent in each case (C_6D_6, $CDCl_3$, CD_3COCD_3).

All the operations in synthesis and characterization were carried out under an inert atmosphere (dinitrogen or argon), using Schlenk conventional techniques [28]. Thoroughly dried and recently distilled solvents were used after their deoxygenation.

Preparations

PMe_3 [29] and CN-t-Bu [30] ligands, and the compounds $[MCl_2(PMe_3)_4]$ (M = Mo, W) were synthesized by the procedures previously described in the literature [31, 32]. $[MoCl_2(PMe_3)_4]$ was also obtained by a similar path to that used by Richards *et al.* [33] in the synthesis of $[MoCl_2(PMe_2Ph)_4]$.

The compounds $[MCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3]$ (M = Mo, W) were obtained by reaction between the corresponding six-coordinate compound and tert-butyl isocyanide in THF. The synthesis and characterization of the latter compounds have been recently carried out in our laboratory [34]. Some important characterization data are summarized in Table 1. A detailed interpretation of the spectroscopic data can be obtained from refs. 31 and 34.

Thermal Analysis

Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out in a Mettler HE-20 thermoanalyzer system. An amount of sample (10–20 mg) was exactly weighed in the sample container. The thermally inert reference was 15 mg of α-Al_2O_3 previously calcinated at 1300 °C for 5 h. The heating rate was 10 °C/min in every case. Experiments under an inert atmosphere were made using a residual He or Ar flow which also keeps corrosive gases from coming in contact with the balance mechanism.

In order to discover any possible influence of the system on the results further thermogravimetric curves were recorded using a Mettler BE-21 electrobalance and a Desin Microcor III linear temperature programmer. Samples in the same range of weight were used. All the experiments were carried out in this system under a He flow at about 60 cm^3/min keeping all the other conditions identical to that used in the former system.

TABLE 1. Some Analytical and Spectroscopic Data of the Complexes

Compound	Reference	Elemental analysis: obs. (calc.)					^{1}H NMR	IR (cm^{-1})	
		C	H	N	P	Cl	δ (ppm)	ν $P(CH_3)_3$	ν(CN)
$MoCl_2(PMe_3)_4$	31	31.1 (30.6)	7.7 (7.6)			14.5 (15.1)	−8.8 very broad $P(CH_3)_3$	930^a	
$WCl_2(PMe_3)_4$	32	25.7 (25.8)	6.5 (6.44)			12.6 (12.7)	3.8 very broad $P(CH_3)_3$	920^a	
$MoCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3$	34	43.8 (44.3)	7.96 (7.92)	6.34 (7.3)	10.8 (10.9)		1.542,s $CNC(CH_3)_3$ 1.564,d $P(CH_3)_3$	955^b	2045^b 1970
$WCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3$	34	38.4 (38.4)	7.2 (6.9)	6.3 (6.4)	9.2 (9.4)		1.535,s $CNC(CH_3)_3$ 1.637,t $P(CH_3)_3$	950^b	2054^b 1960

^{a}KBr pellets. ^{b}Dispersion in Nujol.

Results and Discussion

[MoCl$_2$(PMe$_3$)$_4$]

The thermogram carried out under an inert atmosphere (Fig. 1a) shows a mass loss at 250 °C, which corresponds to the removal of two phosphine ligands, about 32% of the total mass. At 320 °C further mass loss occurs to reach 48% in agreement with the elimination of another mole of phosphine per mole of complex, probably in the third place of lability. At 450 °C all the phosphine ligands have been removed (approximately 64%). The remaining product is probably $MoCl_2$. This dichloride has a lamellar structure based on the $(Mo_6Cl_8)Cl_4$ unit [35] and decomposes above 530 °C [36]. The last decrease observed in the thermogravimetric curve can be attributed to such a decomposition.

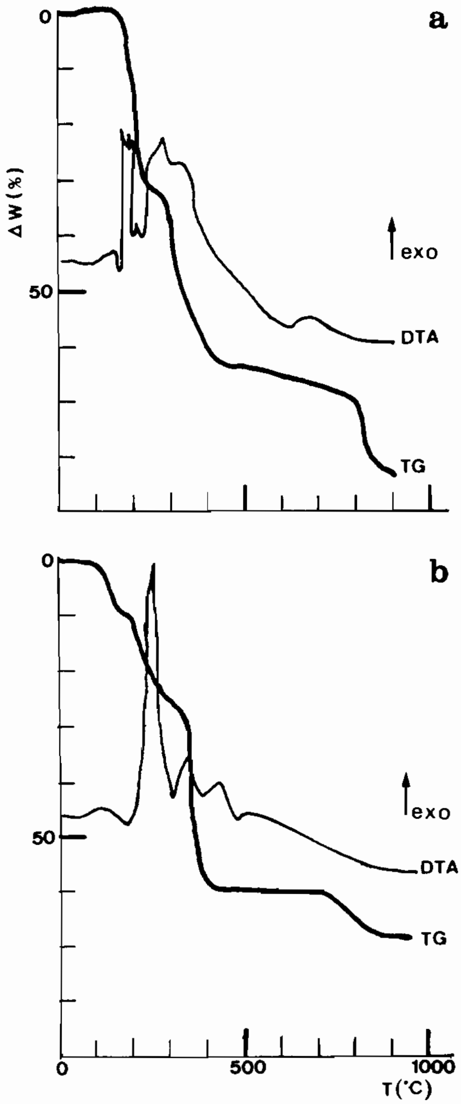

Fig. 1. Mass loss and DTA curves of $[MoCl_2(PMe_3)_4]$: (a) in inert atmosphere; (b) in air.

The DTA curve shows a small endothermic peak at 180 °C which is probably due to the melting and is immediately followed by two broad exothermic bands with some structure over the temperature interval 320–450 °C. They can be attributed to decomposition of the PMe_3 ligand during its elimination. This interpretation is in agreement with recent works by Chan *et al.* [24] with carbonyl complexes containing other phosphines.

The molybdenum compound decomposes under air in a more complex way (Fig. 1b). Thermal decomposition occurs at a lower temperature compared to in an inert atmosphere. The thermogram shows a mass loss between 150 and 220 °C to reach a value of 16% due to the removal of a bonded phosphine. At about 350 °C 57.7% of the total mass has been lost and at 450 °C the mass loss reaches a value of 61% approximately. This seems to point to the formation of MoO_2Cl_2 first and then $MoOCl_2$. An intermediate mass plateau from about 500–700 °C is observed because in this range of temperature $MoOCl_2$ is stable. On further heating a mass loss is observed at 950 °C to reach a value of 69.5%, corresponding to the formation of MoO_3 which sublimes at these temperatures.

The DTA curve shows a small endothermic effect at 175 °C which can correspond to the removal of phosphine. The important exothermic effects recorded at higher temperatures are due to the removal of trimethylphosphine with simultaneous decomposition of the ligand and subsequent oxidation to MoO_3. The sublimation of the last compound is indicated by an endothermic effect.

[WCl$_2$(PMe$_3$)$_4$]

The TG curve in an inert atmosphere is shown in Fig. 2a. A pronounced mass loss occurs between 180 and 550 °C. Curve inflections are observed at 210 and 300 °C, corresponding to losses of 27% and 40.8% which can be explained by the elimination of two and three moles of trimethylphosphine per mole of complex respectively. At 575 °C the mass loss reaches 54.40% while the last trimethylphosphine ligand is probably removed. On further heating the dichloride, WCl_2, is produced but decomposes showing the last change in the thermogram with a deflection point at about 650 °C.

The DTA curve at low temperatures is very similar to that found for the analogous complex of Mo. A small endothermic peak is immediately followed by very intense and complex exothermic effects in two temperature regions, 180–210 and 300–400 °C. No thermal effect associated with the decomposition of WCl_2 is observed probably due to its weakness.

Figure 2b shows the thermal decomposition under air which basically occurs in two steps. In the first one trimethyl phosphine is removed with decomposition. At 250 °C the mass loss is consistent with

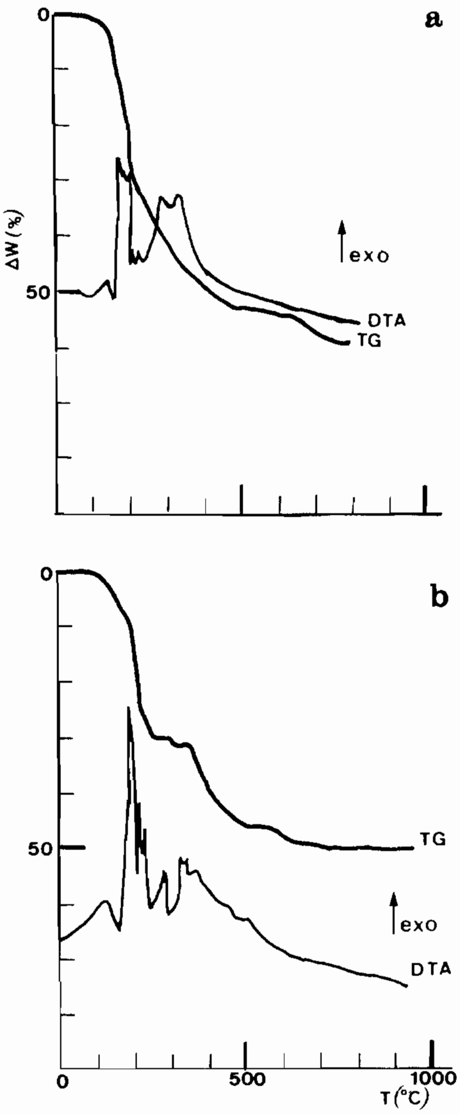

Fig. 2. Mass loss and DTA curves of $[WCl_2(PMe_3)_4]$: (a) in inert atmosphere; (b) in air.

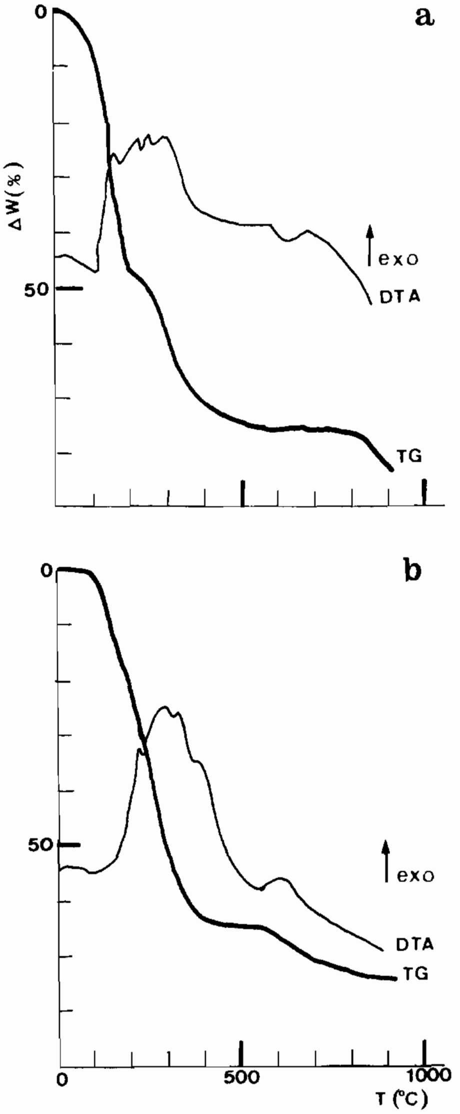

Fig. 3. Mass loss and DTA curves of $[MoCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3]$: (a) in inert atmosphere; (b) in air.

the removal of two PMe_3 ligands. In the second step combustion mainly occurs. The curve inflections recorded at 480 and 650 °C represent mass losses of 45% and 48%; they seem to point out the formation of the oxochlorides $WOCl_3$ and WO_2Cl_2 respectively. Formation of WO_3 has been observed although not studied in detail in our experiment because of the complexity of a variety of phases which can be formed at higher temperatures. These apparently non-stoichiometric phases have been studied by Magneli [37] and are now known to be composed of a large number of stoichiometric phases.

The DTA curve shows the complexity of thermal decomposition. The exothermic peaks are very intense due to decomposition of the ligand while it is removed. The displacement of chlorine by oxygen also appears to be a complex process as indicated by the structure of the exothermic band in the diagram.

$[MoCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3]$

A rather pronounced mass loss is observed at 180 °C in the thermogram recorded under an inert atmosphere (Fig. 3a). This effect seems to correspond to the removal of tert-butyl isocyanide ligands (mass loss observed 44%, compared to the calculated 43.8%). At higher temperatures ranged between 200–400 °C a new mass loss is observed reaching a value of 70.5%. Trimethylphosphine ligands are being removed in this range of temperatures. At 380 °C the mass loss corresponds exactly to the removal of two phosphines in addition to the loss of the isocyanides. These results point out that the M–C bond is more labile compared to the M–P bond, in agreement with that found in similar complexes [M(CO)$_5$L] (where M = Mo, W; L = monodentate diphosphines) through some solution kinetic investigations [38].

Actually, structural studies carried out from NMR spectra [34] show that trimethylphosphine ligands are placed in approximately *trans* positions. The tert-butyl isocyanide ligand *cis* to the phosphines is likely more labile owing to its competition for π electrons with its *trans* counterpart. The mass loss curve shows a last effect, attributed to the decomposition of MoCl$_2$. In summary, the thermal decomposition of this complex occurs in two main steps. These steps are basically elimination and decomposition of tert-butyl isocyanide ligands in the first one and trimethylphosphine in the second as indicated by the two exothermic peaks in the DTA curve.

When the atmosphere in the furnace is air the thermal study (Fig. 3b) shows a pronounced change in the mass loss curve in the range from 190 to 400 °C associated with the elimination of the polyatomic ligands and the oxidation of tungsten forming oxochlorides. At 400 °C the mass loss is 64.5% in agreement with the calculated value taking into account the formation of MoO$_2$Cl$_2$, 64.9%. At 500 °C the effect on the mass loss curve suggests the formation of MoOCl$_2$ (the mass loss reaches a value of 67.3% close to the calculated value 67.8%). The last effect on the thermogram can be associated with the formation of MoO$_3$ and other oxides with close stoichiometry. MoO$_3$ sublimes above 900 °C.

The important exothermic peaks on the DTA diagram corroborate our earlier interpretation.

[WCl$_2$(PMe$_3$)$_2$(CN-t-Bu)$_3$]

The thermal decomposition of this compound under inert atmosphere is likely a complex process, but the TG curve is not well resolved into different steps (Fig. 4a). The range of decomposition temperatures is lower than was found for the analogous molybdenum complex. The TG curve shows a very pronounced loss in the range from 150 to 400 °C corresponding to the removal of tert-butyl isocyanide and trimethylphosphine ligands. The dichloride, WCl$_2$, probably decomposes at higher temperatures. The mass loss at 800 °C reaches a value of 70%, which points to the formation of metal or metal carbides. The calculated mass losses are 70%, 71% and 71.8% for WC, W$_2$C and W, respectively. The referred carbides would contain carbon produced during thermal decomposition of the organic ligands. This last suggestion is corroborated by the exothermic peaks associated with the elimination of the ligands.

The thermogram in Fig. 4b (recorded under air) shows a large mass loss, being 51% at 250 °C. This effect can be associated with removal of tert-butyl isocyanide and trimethylphosphine ligands, being tungsten oxidized. The calculated mass loss is 50.7% if WOCl$_2$ is formed. Between 250 and 370 °C there is a small mass loss probably associated with the formation of WO$_2$Cl$_2$ (at 370 °C 56% of the total mass has been lost in agreement with the calculated value for the formation of WO$_2$Cl$_2$). At 500 °C another mass loss to reach 64.7% is recorded likely owing to the formation of WO$_2$ and WO$_3$ or, perhaps, intermediate phases of various stoichiometry (Magnéli's phases). Thermal decomposition with simultaneous oxidation is indicated by the exothermic peaks found in the DTA curve at 275 and 380 °C. The final displacement of chlorine by oxygen is indicated by an exothermic peak at 500 °C.

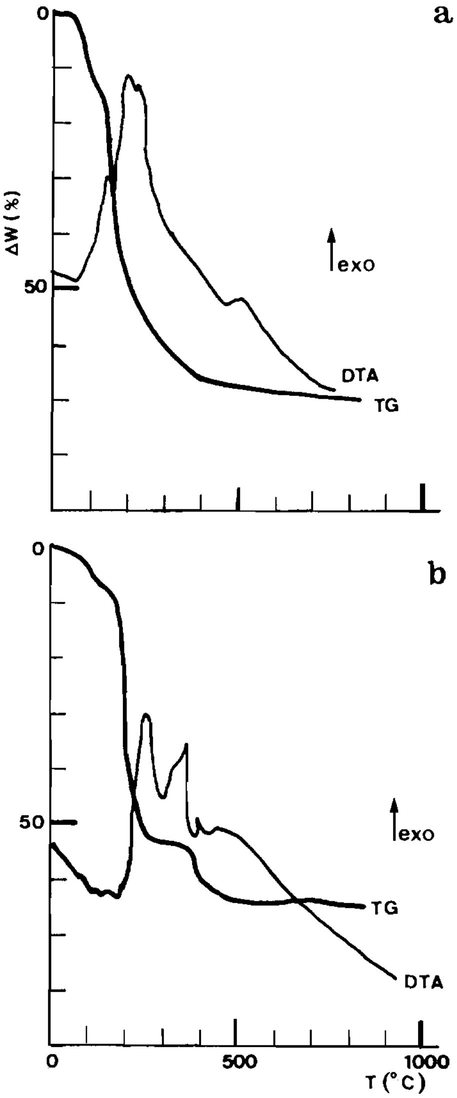

Fig. 4. Mass loss and DTA curves of [WCl$_2$(PMe$_3$)$_2$(CN-t-Bu)$_3$]: (a) in inert atmosphere; (b) in air.

Conclusions

The thermal study of the six-coordinate compounds $[MCl_2(PMe_3)_4]$ shows that decomposition under an inert atmosphere begins at temperatures below 200 °C. This thermal decomposition leads to the removal and cracking of trimethylphosphine, forming the metal dichloride at 450 °C ($MoCl_2$) or 575 °C (WCl_2). Both these dihalides decompose at higher temperatures. If the thermal decomposition takes place under air a lower decomposition temperature is observed. Then two major decomposition reactions take place. In a first step elimination of a part of the trimethylphosphine ligands occurs and in a second one the remaining phosphine is removed being the metal oxidized to the formation of oxochlorides. A last and smaller effect is observed due to the formation of MO_2, MO_3 or intermediate phases (the so-called Magnéli's phases).

Analogous conclusions can be extracted from the data about thermal decomposition of the seven-coordinate compounds of Mo and W, $[MCl_2(PMe_3)_2(CN\text{-}t\text{-}Bu)_3]$. In addition, the study carried out under an inert atmosphere shows a stronger metal–phosphine bond than the metal–tert-butyl isocyanide bond in agreement with previous data in the literature [38].

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