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SUBSTITUTED METAL CARBONYLS.
Part XVII. * Thermal decarbonylation and chelation of $M(CO)_5(\eta^1\text{-dppf})$ and $Fe(CO)_4(\eta^1\text{-dppf})$ [where M = Cr, Mo, W; dppf = $(Ph_2PC_5H_4)_2Fe$]

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ABSTRACT

Thermal decarbonylation of the unidentate complexes $M(CO)_5(\eta^1\text{-dppf})$ (M = Cr, Mo, W) and $Fe(CO)_4(\eta^1\text{-dppf})$ results in ring closure to form the corresponding chelates. The reactions have been followed by IR and NMR spectroscopy in refluxing acetonitrile, tetrahydrofuran, hexane and heptane solutions and in solid-state by thermogravimetric (TG) and differential scanning calorimetric (DSC) means. The solid-state decompositions have been emulated in Schlenk flasks and the chelates formed have been isolated and analysed. Decarbonylations of the W and Fe complexes are found to be the least facile. A kinetic study by the Flynn and Wall method suggests that only the Fe complex follows a first order dissociative mechanism.

INTRODUCTION

Chemical and thermal studies of the Group 6 metal pentacarbonyls bearing a difunctional ligand coordinated in a unidentate fashion have attracted considerable interest largely because of their high reactivity towards many electrophiles and their possible link to many catalytic processes [2]. The thermal and photochemical instabilities of these compounds have prompted their use as precursors for many carbonyl substrates. One of the most documented reactions for these complexes is decarbonylation, followed by ring closure, or chelation [3]. A wealth of information is currently available on the solution characteristics for this process, but in contrast, the chemical, kinetic and mechanistic properties are relatively less understood in their solid state. Realising the importance of many organometallic materials

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in their solid state in many catalytic or other surface phenomena, we initiated a programme to study the TG and DSC of these complexes bearing a pendant diphosphine [4]. It is generally believed that the chelation mechanism is dependent not only on the nature of the central metal but also the local geometry of the difunctional ligand. In this paper, we examine the thermal properties of $M(CO)_5(dppf)$ ($M = Cr$, Mo, W) and $Fe(CO)_4(dppf)$ with the ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) in its pendant state. Our recent findings [5] suggested that dppf is characterised by a flexible bite which enables it to act in the bridging, chelating and unidentate modes.

EXPERIMENTAL

All preparations were carried out in standard Schlenk flasks under dry argon or nitrogen atmosphere according to the methods previously described [5]. Solvents used were of reagent or AnalaR grade and were dried and deoxygenated before use. The identity and purity of the samples were checked by IR and NMR spectroscopy and microanalyses. The general procedures and instruments used follow those described in our earlier report [6]. Decarbonylation in solution for each complex was carried out in acetonitrile, hexane, heptane and tetrahydrofuran similarly to the methods described earlier [7].

All TG experiments were conducted on a DuPont 9900 thermal analyser in dry nitrogen. The nitrogen flow was 75 $cm^3\ min^{-1}$ and the heating rate was 10 °C min^{-1}. The scans were conducted on a sample quantity of approximately 2 mg from 25 °C to 600°C. A multi-heating rate kinetics method, devised by Flynn and Wall [8], was used to determine the activation energy (E_{act}) by using the system software of the analyser. Four runs at 2.5, 5, 10 and 15 °C min^{-1} were realised on the DuPont 9900 analyser. Using the selected values of conversion (20, 30, 40, 50 and 60%) within the first decarbonylation step, the temperature (K) at that conversion level is measured for each thermal curve. A plot of the log of the heating rate versus the reciprocal temperature at constant conversion was prepared from which E_{act} was calculated from the slope.

DSC experiments were carried out under nitrogen with the same flow and heating rates as that of TG. The temperature ranges from 25 to 300°C. The enthalpies were generated by computer, with indium as the reference. The solid-state decomposition was emulated in Schlenk flasks using a 0.1 g sample. The heating was done under a dynamic nitrogen atmosphere from room temperature to the point indicated by the TG profile at which the first step of weight loss is complete.

RESULTS AND DISCUSSION

Conversion of the unidentate $M(CO)_5(dppf)$ ($M = Cr$, Mo, W) and $Fe(CO)_4(dppf)$ to the chelates $M(CO)_4(dppf)$ and $Fe(CO)_3(dppf)$ can be conveniently monitored by their IR and TLC changes in CH_3CN, hexane, heptane and THF solutions. The decarbonylation is most facile for the Mo complex, with significant formation of the chelate upon overnight reflux in hexane and THF and near quantitative yields in CH_3CN and heptane. The W complex on the other hand shows the highest resistance, with the starting material mostly recovered even in refluxing heptane. This observation is in full accord with the expected relative strengths of the metal–carbon bonds [9]. The more stringent conditions employed for the Fe and W reactions resulted in a trace quantity of the dimeric $Fe_2(CO)_8(\mu\text{-dppf})$ and $W_2(CO)_{10}(\mu\text{-dppf})$ respectively. The commonly acknowledged accelerating effect of donor solvents towards decarbonylation was not apparent in the present study except in the case of W where the unidentate complex survives in refluxing heptane but partially collapses to give the chelate in refluxing CH_3CN. For a quantitative evaluation of these decompositions, each complex is subjected to TG (and its derivative DTG) and DSC analyses.

All the samples show a rapid loss in weight corresponding to CO expulsion as their first step. The formation of the chelate at this stage is best illustrated in Fig. 1 which shows the TG profiles of $Mo(CO)_5(dppf)$ and an authentic sample of $Mo(CO)_4(dppf)$. Subsequent degradation is complex but inevitably involves the cleavage of the dppf ligand via a multi-step

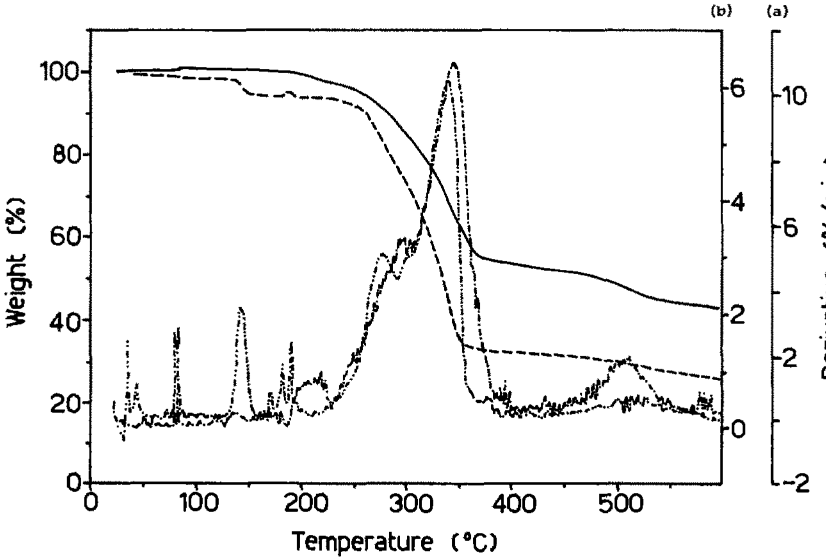

Fig. 1. (a) $Mo(CO)_5(dppf)$; (i) TG (- - - - - -) and (ii) DTG (– · · – · · –). (b) $Mo(CO)_4(dppf)$: (i) TG (———) and (ii) DTG (· – · – ·).

TABLE 1

TG and DSC data for the decarbonylation and chelation of $M(CO)_5$(dppf) (M = Cr, Mo, W) and $Fe(CO)_4$(dppf) to their corresponding chelates

	M			
	Cr	Mo	W	$Fe(CO)_4$(dppf)
Temp. range (°C)	133–176	126–159	148–206	165–220
Obs. (Est.) wt. loss (%)	4.0(3.8)	4.0(3.5)	3.3(3.2)	3.7(3.9)
Obs. (DSC registered) m.p. (°C)	138–139(144)	128–133(145)	158–159(164)	161–164(169)
ΔH(chelation) (kJ mol^{-1})	+36.4 [a]	+47.6 [a]	−27.1	[b]

[a] Concurrent with melting.

[b] Unable to be measured due to subsequent decompositon of the chelate.

pathway. The temperature range at which decarbonylation occurs and the estimated and observed weight losses are listed in Table 1. The Mo complex decomposes notably at the lowest temperature range with the sharpest drop in weight and gives rise to a flat trough suggesting the high stability of the Mo chelate. The relative instabilities of the W and Fe chelates are reflected in the poor demarcation of their TG and DTG curves. A comparison of these data with those of the related $M(CO)_5$(dppm) (dppm = bis(diphenylphosphino)methane) [4] revealed a slightly higher kinetic stability of the latter with respect to the initial decarbonylation. The thermodynamic stability of the dppm family is also evident in their preparations when the dppm unidentates can be synthesised conveniently with better yields. The steric crowding around the pendant phosphine site in the dppm complexes has been invoked to explain such stability [10]. The expected *trans* (or *anti*) disposition of the phosphinated Cp rings makes the pendant phosphine site vulnerable for nucleophilic attack on the acidic $[M(CO)_5]$ or labile $M(CO)_5$(solvent). Related to this, methylation of the pendant phosphine in the present dppf complexes occurs steadily at room temperature in ether suspension whilst failure was met in our attempt to methylate the corresponding dppm species [11].

The DSC plots reveal a characteristic endothermic peak corresponding to the melting process followed by an exotherm which represents the chelation step. The exothermic step represents the summation of two enthalpic terms, decarbonylation and coordination of the pendant phosphine site. The formation of the chelate via decarbonylation of the unidentate complex is best illustrated by comparing the DSC plots of $Mo(CO)_5$(dppf) and $Mo(CO)_4$(dppf) in Fig. 2. The melting points recorded uncalibrated by a melting point apparatus and from the DSC profiles and the chelation enthalpy values are listed in Table 1. This general pattern however does not apply to $Fe(CO)_4$(dppf) in which the exothermic peak is ill-defined, thus suggestive of the poor stability of the chelate $Fe(CO)_3$(dppf). Among the Group 6

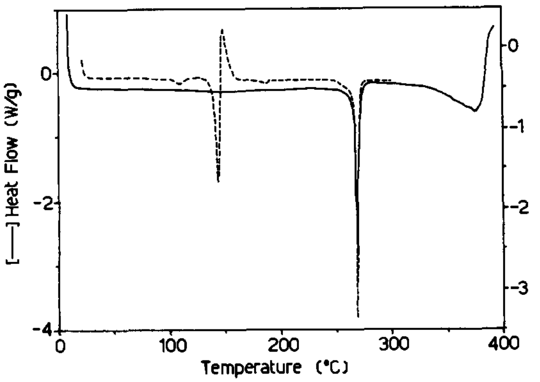

Fig. 2. DSC curves of $Mo(CO)_5(dppf)$ (- - - - - -) and $Mo(CO)_4(dppf)$ (———).

metals, the chelation enthalpy values of the Cr and Mo complexes cannot be quantified because of the merge of the two enthalpy terms.

Modelling experiments were carried out in Schlenk flasks to emulate the thermal decomposition as determined by TG. The samples were heated under a nitrogen stream from ambient to the temperature indicated by TG/DTG at which the first step of weight loss is completed. The solid residue was then subjected to ^{1}H and ^{31}P NMR analyses in $CDCl_3$. The results proved conclusively that the chelates are the sole product in the Group 6 reactions, though an unknown side product is formed in the course of the iron decomposition.

As all the complexes undergo facile decarbonylation below 200 °C, a kinetic study was carried out on this step by plotting log(heating rate) versus the reciprocal of the temperature for five decompositional percentages in the range 20–60% within this step based on the method of Flynn and Wall [8]. The best result was obtained for the iron complex (Fig. 3) in which a near parallel plot within this chelation step strongly supports a first-order kinet-

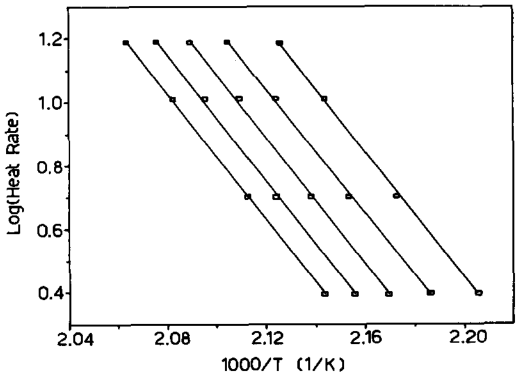

Fig. 3. Flynn and Wall plot of $Fe(CO)_4(dppf)$.

ics. The narrow E_{act} range of 177–184 kJ mol^{-1} with an average value of 180 kJ mol^{-1}, which is in good agreement with the computed bond dissociation energy (184.5 kJ mol^{-1}) and the experimentally derived enthalpy of activation (174.3 kJ mol^{-1}) for the first decarbonylation of $Fe(CO)_4(PPh_3)$ [12], lends further support to a first-order dissociative mechanism. Similar experiments on the Group 6 complexes yield some fairly inconsistent E_{act} ranges of 211–388 (mean = 276) (M = Cr), 328–344 (mean = 336) (M = Mo) and 239–279 (mean = 255) (M = W) kJ mol^{-1} with an unusually high activation barrier for a Group 6 metal carbonyl. These data, coupled with the erratic non-parallel Flynn and Wall plots, infer a non-first-order kinetics, which is in stark contrast to the dppm analogues. A second-order associative ring closure mechanism [13], which is found in some other Group 6 carbonyls with sterically unrestrictive ligands and large metals, is also unlikely to be operative here due to the bulk of the dppf group. The disposition and orientation of the pendant phosphine with respect to the metal centre probably account for the different behaviour of the dppm and dppf complexes. Unlike that in dppm [14], the free phosphine in the titled dppf complexes is expected to be *trans* to the coordinated phosphine in a fashion similar to that found in the structurally characterised free dppf [15] and many of its complexes [16]. Chelation in this case would be preceded by the twisting of the Cp–Fe–Cp centroids which is not a prerequisite for the dppm complexes. This complication in the ring closure mechanism is likely to be less severe in an Fe sphere which has a sterically less demanding trigonal bipyramidal geometry.

CONCLUSION

There is no conclusive evidence to suggest that the many dppm chelates in the literature enjoy a higher thermodynamic stability compared to their dppf counterparts, though some slight structural strains are noted in some of the latter. Our results with the dppm and dppf carbonyls point to their kinetic differences in the decarbonylation and chelation. Future uses of solid-state thermal techniques such as TG, DTG and DSC are likely to contribute towards a better understanding of these and other related diphosphine complexes.

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