Substituted Metal Carbonyls. Part 9. Solution and Solid-state Decompositions of Diphosphine–Monobridged Molybdenum Carbonyl Dimers

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Abstract

Thermal decomposition of the singly-bridged complexes $Mo_2(CO)_{10}[\mu\text{-}Ph_2P(CH_2)_nPPh_2]$ ($n = 4$, 5, 6) has been studied as hexane, benzene and toluene solutions by infrared monitoring and in the solid state by thermogravimetry and differential scanning calorimetry. The thermal profiles of the three complexes reveal a similar degradation pattern which involves an initial loss of CO followed by phosphine cleavage via a multi-step mechanism. The dimers are stable in boiling hexane but decarbonylate upon prolonged heating in toluene resulting in the *cis*-complexes $Mo(CO)_4(P\text{–}P)$ which are 7-, 8- and 9-membered chelate rings.

Introduction

Whilst the chemistry of bifunctional ligands has been continually attracting attention [1–9], our recent interest has been focused on the diphosphine-bridged dinuclear carbonyls where there is little interaction between the metal centres [10–12]. The stabilizing role of the bridging long-backbone diphosphines is an ill-defined concept compared to that of the analogous complexes with monodentate phosphines [13–16] and chelating diphosphines [17–19]. In our continued effort to establish the relationship between the Gp 6 mononuclear and dinuclear carbonyls [11], we report in this paper the thermal decompositional behaviour of $Mo_2(CO)_{10}(\mu\text{-}P\text{–}P)$ [$P\text{–}P = Ph_2P(CH_2)_nPPh_2$ where $n =$ 4 (dppb), 5 (dpppt) and 6 (dpph)**] in solution and the solid state, the latter of which is studied by thermogravimetric (TG) and differential scanning calorimetric (DSC) techniques.

Experimental

All the preparations and reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The general procedures and instruments used follow that described in earlier reports [11, 20]. The complexes $Mo_2(CO)_{10}(\mu\text{-}P\text{–}P)$ (P–P = dppb, dpppt, dpph) were prepared by the reported method [21]. Sample solutions in hexane, benzene and toluene were refluxed and analysed similar to that described earlier [11]. All thermogravimetric experiments were conducted on a Du Pont 9900 thermal analyser in dry nitrogen. The nitrogen flow was 75 $cm^3\ min^{-1}$ and heating rate 10 °C min^{-1}. The scans were conducted from room temperature to 700 °C. Differential scanning calorimetric experiments were carried out in a self-generated atmosphere on the same instrument and calibrated to have a cell constant of 1.19. The temperature range was from room temperature to 500 °C with the same heating rate of 10 °C min^{-1}. The enthalpy values were generated by computer, with indium as the reference.

Results and Discussion

The TG decomposition profiles of the dppb (**1**), dpppt (**2**) and dpph (**3**) complexes are depicted in Figs. 1a, 2a and 3a respectively. All the complexes are stable below *c.* 120 °C beyond which they display a similar degradation pattern which can be discussed collectively.

The decomposition is essentially composed of three stages, viz. an initial small weight loss in the temperature range *c.* 130–200 °C, an intermediate phase of steep degradation in *c.* 200–400 °C, and a final gradual weight loss in the region *c.* 400–550 °C beyond which no significant change is observed.

The initial loss in weight may be inferred to the evolution of one mole of CO gas; the weight losses observed for the complexes **1**, **2** and **3** are 3.21% (calc. 3.12%) (130–200 °C), 2.80% (calc. 3.07%)

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**dppb: 1,4-bis(diphenylphosphino)butane; dpppt: 1,5-bis(diphenylphosphino)pentane; dpph: 1,6-bis(diphenylphosphino)hexane.

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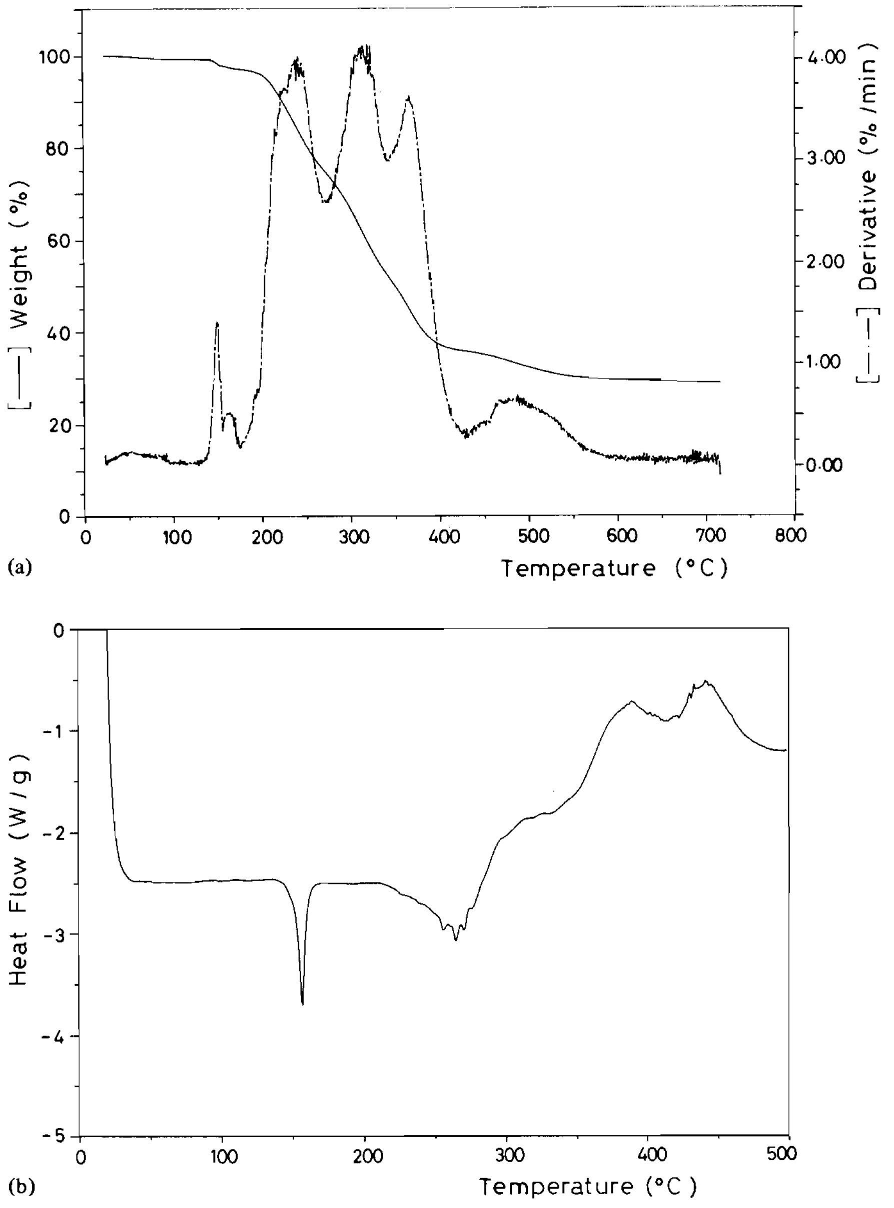
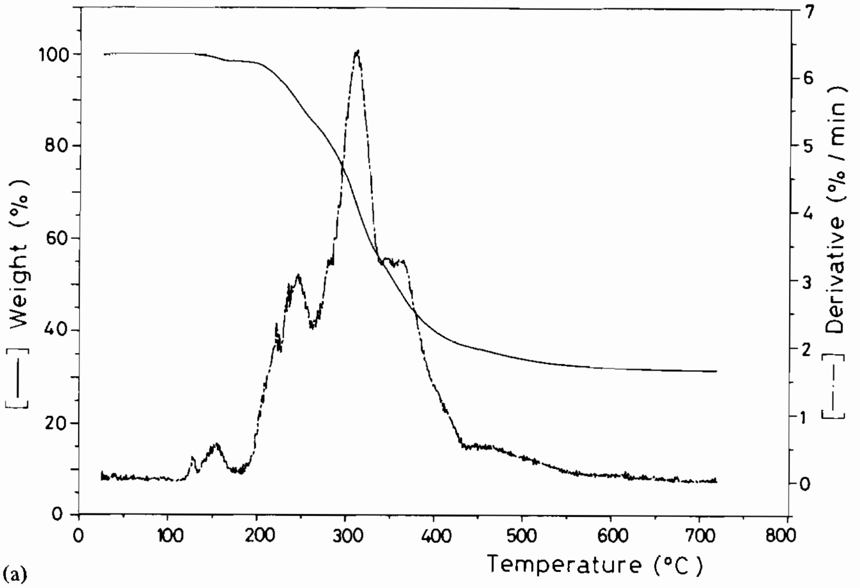


Fig. 1. $Mo_2(CO)_{10}[\mu\text{-}Ph_2P(CH_2)_4PPh_2]$: (a) TG curve, (b) DSC curve.

(120–205 °C) and 3.35%(calc. 3.02%) (130–175 °C), respectively. A similar mode of decarbonylation was observed in the related mononuclear pentacarbonyl with a dangling diphosphine, i.e. $Mo(CO)_5(\eta^1\text{-dppm})$ ($\text{dppm} = Ph_2PCH_2PPh_2$) [22]. The difference is that the latter decarbonylation results in the stable chelate $Mo(CO)_4(\eta^2\text{-dppm})$ which shows a higher resistivity to further decomposition than the present apparent intermediate $[Mo_2(CO)_9(\mu\text{-P–P})]$. As a result, rapid disintegration is observed in all the complexes **1**, **2** and **3** over the range *c*. 200–400 °C which is judged to be a multi-staged phosphine cleavage process. The recorded percentage residues of 28.9, 31.8 and 31.6% for **1**, **2** and **3** are higher than that expected for pure metal (21.4, 21.0 and 20.7% respectively); this is indicative of incomplete deligation as a consequence of the strength of the Mo–CO bonds in highly-substituted carbonyls.

It is noteworthy that for all the complexes decarbonylation should occur prior to dephosphination. This is in apparent disagreement with the general notion that L in $M(CO)_5(L)$ would dissociate more readily than not only the carbonyls in the same complex but also those in $M(CO)_6$ [23, 24]. Though the observed decarbonylation is not as



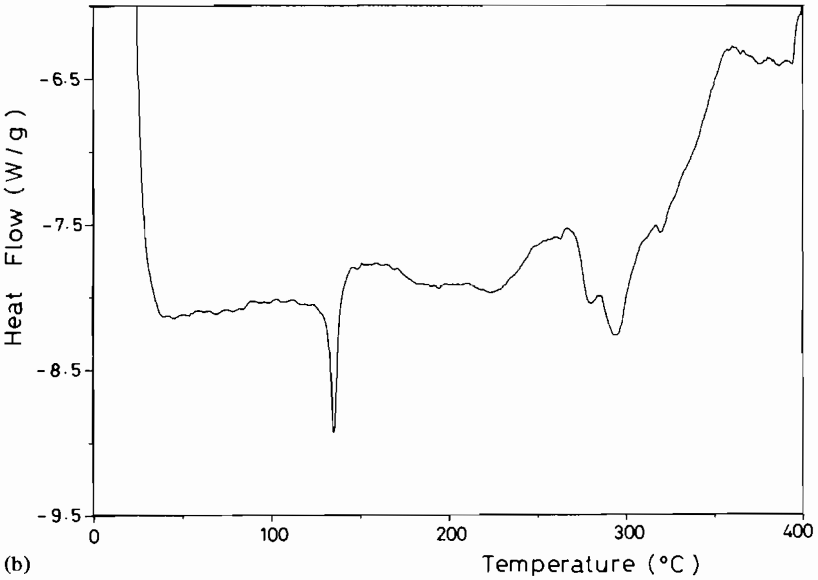
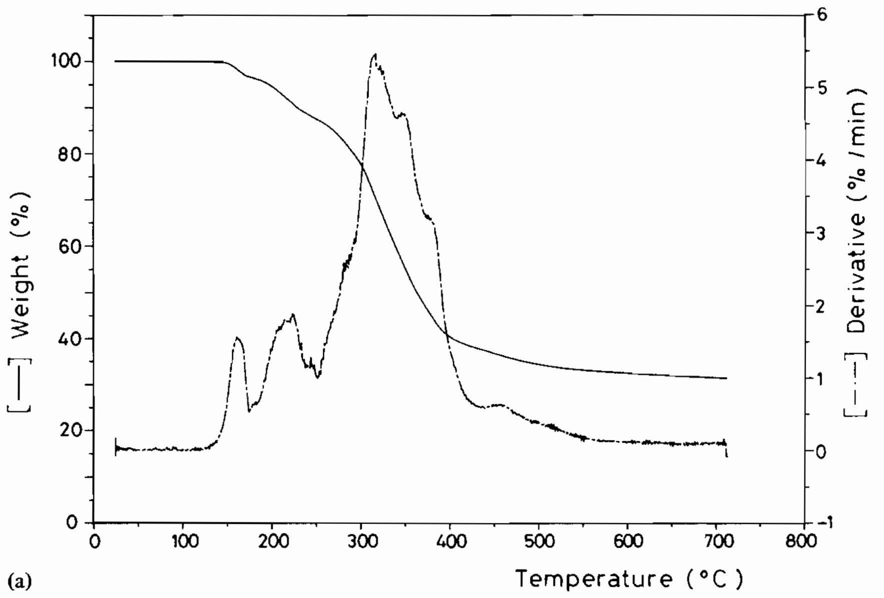


Fig. 2. $Mo_2(CO)_{10}[\mu\text{-}Ph_2P(CH_2)_5PPh_2]$: (a) TG curve, (b) DSC curve.

facile as that in $Mo(CO)_5(\eta^1\text{-dppm})$, the stabilizing influence of the diphosphines in these monobridged systems cannot be ignored.

The DSC scans for **1**, **2** and **3** are shown in Figs. 1b, 2b and 3b, respectively which are in general agreement to the TG findings. A common characteristic feature belongs to the very clean endotherms centering at *c.* 157, 136 and 183 °C for **1**, **2** and **3**, respectively. These endotherms correspond to the concurrent melting and decarbonylation; the enthalpic changes estimated for the integrated area are 45, 30 and 47 kJ mol^{-1} for **1**, **2** and **3** respectively. These low values lend further support to the lability of the initial Mo–CO bond cleavages.

Thermal decomposition of the complexes in refluxing hexane, benzene and toluene is monitored by the infrared changes of the solutions during a duration of 18 h. These dimers are essentially indifferent to boiling hexane. In benzene partial decomposition occurs upon prolonged reflux. The predominant decomposition product is the *cis*-chelate $Mo(CO)_4(P\text{–}P)$. Complete decomposition is attained only upon overnight heating in toluene. All the complexes decarbonylate at a comparable rate and with nearly identical infrared changes. A typical



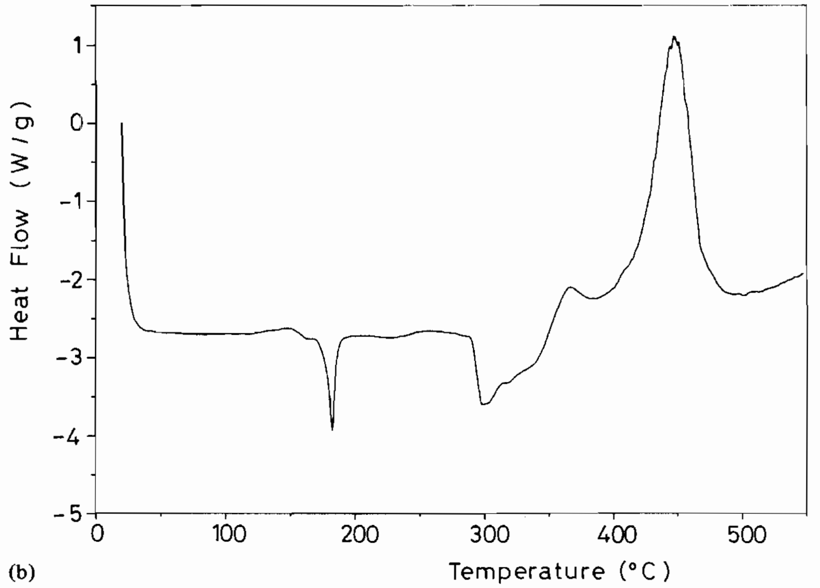


Fig. 3. $Mo_2(CO)_{10}[\mu\text{-}Ph_2P(CH_2)_6PPh_2]$: (a) TG curve, (b) DSC curve.

run is sketched in Fig. 4 which represents the spectral changes of $Mo_2(CO)_{10}(\mu\text{-dpph})$ in toluene over a period of 18 h. The conversion to the *cis*-tetracarbonyl chelate is complete after 18 h refluxing. Similar conversion was observed earlier for $Mo_2(CO)_{10}(\mu\text{-dpppp})$ [dpppp = $Ph_2P(CH_2)_3PPh_2$] [11]. Refluxing in toluene also leads to the deposit of some insoluble metallic residue and a soluble by-product with an IR absorption at *c.* 1970 cm^{-1} which could be the isomeric *trans*-$[Mo(CO)_4(\mu\text{-}P\text{—}P)]_n$. There is however no indication for the generation of $Mo(CO)_6$ or any bridging carbonyl species.

There is insufficient evidence to suggest that the solid state and solution decompositions follow the same mechanistic pathway. However, based on the inhibiting behaviour of CO gas on the breakdown of $Mo_2(CO)_{10}(\mu\text{-dpppp})$ [11], and the CO liberation at the onset of the decompositions described above, it is probable that, like many substitution processes in the Gp 6 mononuclear carbonyls [25–28], a dissociative process predominates in the decomposition of the titled complexes.

Decomposition of $Mo_2(CO)_{10}(\mu\text{-}P\text{—}P)$ in both solid and solution states has demonstrated unequivocally that the variation in the length of the

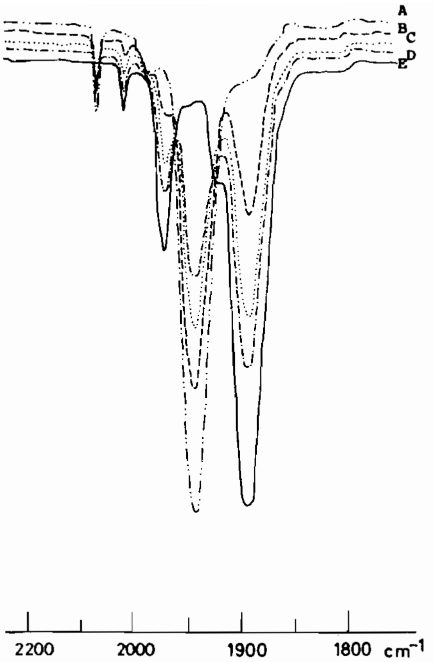


Fig. 4. Infrared spectral changes in the carbonyl region of $Mo_2(CO)_{10}[\mu\text{-}Ph_2P(CH_2)_6PPh_2]$: A, before refluxing (– ·· –); after B, 2 h (– – –); C, 4 h (·······); D, 6 h (– · · –); E, 18 h (——) refluxing in toluene.

hydrocarbon backbone of the phosphine has little effect on either the mechanism or the rate of the decompositional process. Despite the seemingly unfavourable conformation in the 8- and 9-membered rings, chelates such as *cis*-$Mo(CO)_4(\eta^2\text{-}P{-}P)$ (P–P = dpppt and dpph) constitute the major isolable products in these bridge-cleavage decarbonylation reaction. The fact that cyclization is preferred rather than the formation of the *trans* open-chain structures lends further support to the theory that large chelate rings can be stabilized by bulky substituents such as phenyls and t-butyls on the coordinating ligands [19, 29, 30].

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