

# INVESTIGATION OF COMPLEXES OF DIPHENYLPHOSPHINE DERIVATIVES BY THERMAL AND OTHER PHYSICO-CHEMICAL METHODS OF ANALYSES

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## Abstract

Six heteroatomic complexes of diphenylphosphine derivatives with heavy metals (Ni, Pd, Pt, Mo and W) were prepared and subjected to elemental spectral and thermal analyses. The different physicochemical methods used indicated the formulae  $[\text{NiCl}_2(\text{dppm})]$ ,  $[\text{PtCl}_2(\text{dppm})]$  and  $[\text{Mo}(\text{CO})_4(\text{dppm})]$  (*dppm*=bis(diphenylphosphine)methane, the *dppm* in these complexes behaving as a bidentate ligand),  $[\text{Pd}(\text{CN})_2(\text{dppm})_2]$  (in which the *dppm* behaves as a monodentate ligand),  $[\text{W}(\text{CO})_4(\text{dppe})_2]$  and  $[\text{Mo}(\text{CO})_4(\text{dppe})_2]$  (*dppe*=1,1-bis(diphenylphosphine)ethene, the *dppe* in these complexes behaving as a bidentate ligand). The thermal analyses (DTA and TG) confirmed these structures. The results of spectral and thermal analyses were compared.

**Keywords:** comparative study, complexes of diphenylphosphine derivatives, thermal analyses

## Introduction

There is much interest in mixed ligand heteroatomic complexes containing diphenylphosphine derivatives as strong field ligands [1-3]. There is also enormous interest and activity in the chemistry of mononuclear metal-phosphine complexes [2]. Large areas of research are concerned with their carbonyl, hydride, organometallic and dinitrogen chemistry. Their catalytic activity in hydroformylation and hydrogenations is of industrial importance and their catalysis of many organic reactions makes them useful in organic syntheses. Binuclear metal-phosphine complexes [4-7] are interesting because they involve a new chemical association with two metals in close proximity. In the present work, some hetero-atomic complexes of Mo, Ni, Pd, Pt and W were prepared [7] and their structures were investigated by various physicochemical methods.

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## Experimental

### Preparation of complexes

The ligand bis(diphenylphosphine)methane(dppm) is a white, air-stable and easily-handled solid capable of forming several types of binuclear complexes. It can also act as a chelating agent forming mononuclear four-membered ring complexes [1–3]. The compound 1,1-bis(diphenylphosphine)ethene(dppe) is a homologue of dppm. The complexes were prepared as follows:

1.  $[\text{Mo}(\text{CO})_4(\text{dppm})]$  (**5**) was prepared by reacting one mole of  $\text{Mo}(\text{CO})_6$  and one mole equivalent of dppm in diglyme or in decane under reflux.

2.  $[\text{PtCl}_2(\text{dppm})]$  (**4**) was prepared by treatment of an aqueous solution of one mole of  $\text{K}_2\text{PtCl}_4$  with one mole equivalent of dppm in acetone at room temperature. The adduct was precipitated as a pink solid, whose elemental analysis was consistent with the formula  $[\text{Pt}(\text{dppm})_2][\text{PtCl}_4]$  [8]. Heating of this salt in  $\text{EtOH}/\text{CHCl}_3$  (1:1) under reflux gave a high yield of crude  $[\text{PtCl}_2(\text{dppm})]$ . The pure complex was readily obtained by extraction of the crude product with  $\text{CH}_2\text{Cl}_2$ .

3.  $[\text{Pd}(\text{CN})_2(\text{dppm})_2]$  (**2**) can be obtained from  $[\text{PdCl}_2(\text{PhCN})_2]$  and dppm [2]. Addition of  $\text{NaCN}$  to a methanolic solution of  $[\text{Pd}(\text{dppm})\text{p}_2']\text{Cl}_2$  gave the colourless crystalline monohapto complex  $[\text{Pd}(\text{CN})_2(\text{dppm})_2]$  [4]. Known salts of the type  $[\text{M}(\text{dppm})_2]\text{Cl}_2$  ( $M = \text{Pt}$  or  $\text{Pd}$ ) were readily prepared from dppm and either  $\text{MCl}$  or  $[\text{MCl}_2\text{NR}_2]$  ( $R = \text{Bu}$ ,  $M = \text{Pt}$ ;  $R = \text{Ph}$ ,  $M = \text{Pd}$ ) [3].

4.  $[\text{NiCl}_2(\text{dppm})]$  (**1**) was prepared from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and dppm in ethanol by warming a mixture of equimolecular amounts. On standing at room temperature, red crystalline needles were obtained.

5.  $[\text{W}(\text{CO})_4(\text{dppe})_2]$  (**3**) and  $[\text{Mo}(\text{CO})_4(\text{dppe})_2]$  (**6**) were prepared by heating  $\text{M}(\text{CO})_6$  [ $M = \text{Mo}$  or  $\text{W}$ ] with 2 mole equivalents of dppe in *n*-decane under reflux for 2 h.

### Microanalyses of the products

Microanalyses for C, H, N and halogen, and molecular weight determinations on the pure crystalline products were performed by the Microanalytical Center at Cairo University. The microanalysis data led to the general formulae given above for compounds **1–6** (Table 1).

### IR spectra

The IR spectra of the solid products **1–6** were measured by the KBr disc technique (at the same microanalytical unit) in the range  $250\text{--}4000\text{ cm}^{-1}$ , using a Perkin-Elmer model 1650 FI-IR instrument.

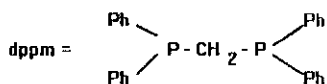
**Table 1** Elemental analyses and some properties of complexes of Mo, W, Ni, Pd and Pt

Complex	<i>m.p.</i>	Colour	MW	C	H	N	Cl
1	>210	wine-red	513.7 (500)	58.39 (58.29)	4.29 (4.28)	–	18.82 (13.72)
2	–	white	930.4 (938)	64.98 (64.45)	4.72 (4.69)	2.95 (3.0)	–
3	178-180	purple	1213.7 (1200)	55.36 (55.4)	3.65 (3.65)	–	–
4	>230	white	650 (660)	46.15 (46.12)	3.38 (3.37)	–	10.90 (10.90)
5	189-192	yellow	591.0 (591.9)	58.78 (58.76)	3.71 (3.68)	–	–
6	181-184	yellow	1037.0 (1037.88)	64.74 (64.72)	4.23 (4.20)	–	–

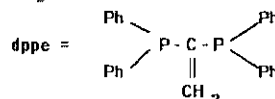
The values in parentheses are the found values.

1=[NiCl<sub>2</sub>(dppm)], 2=[Pd(CN)<sub>2</sub>(dppm)<sub>2</sub>], 3=[W(CO)<sub>4</sub>(dppe)<sub>2</sub>],

4=[PtCl<sub>2</sub>(dppm)], 5=[Mo(CO)<sub>4</sub>(dppm)], 6=[Mo(CO)<sub>4</sub>(dppe)<sub>2</sub>]



bis(diphenylphosphine)methane



1,1-bis(diphenylphosphine)ethene

### Thermal analyses (DTA and TG)

The DTA and TG studies were made with a conventional thermal analyser (Shimadzu system, Shimadzu 30 series thermal analysis instrument). The mass losses (from 5 mg sample) and heat responses of the changes in the samples were measured in the range from ambient temperature up to 500°C. The heating rate was 10°C min<sup>-1</sup> in both TG and DTA in an inert argon atmosphere.

### NMR spectra

The <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra of some of the investigated heteratomic complexes and the original ligands were scanned with a 200 MHz Varian Gemini 200 spectrometer. The solvent used was dimethylsulfoxide and the spectra extended from 0 to 15 ppm. The chemical shifts δ of different protons were assigned. The effects of complexation on the chemical shifts were studied [8].

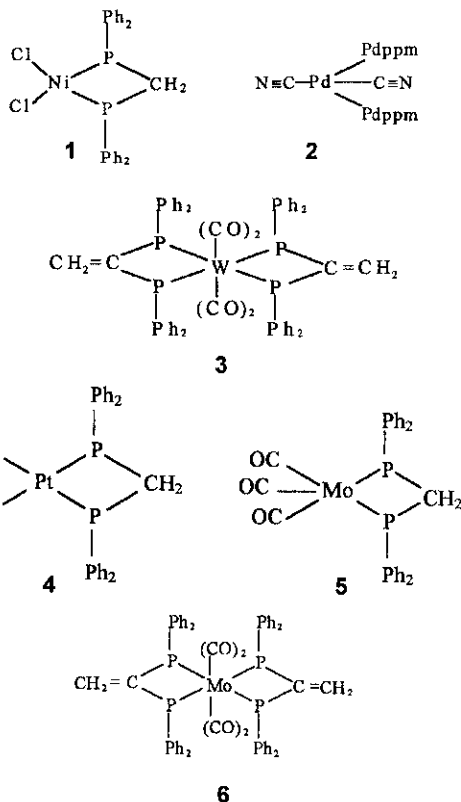
## Mass spectra

The mass spectra of the ligands and the complexes were recorded with the EI technique (70 eV) on a Hewlett Packard MS-5988 GC-Mass instrument in the Microanalytical Center, Cairo University.

## Results and discussion

The structures of the prepared complexes of dpmm and dppe were studied by means of NMR, mass spectra and thermal analyses. The correlations between the various results and especially the thermal and mass fragmentations, and consequently the confirmation of the proposed structures, were the main objects of this work.

The results of the elemental analyses of the complexes, together with some of their properties, are shown in Table 1. These data are in good agreement with previously reported findings [6–8]. The proposed structures of the prepared complexes, as suggested by the results of the microanalyses and the IR, NMR and mass spectra, may be tentatively given as follows:



The  $^{31}\text{P}$  NMR spectrum [12] of complex **1** exhibits a distinct peak at  $\delta (P)=41.3$ , and **2** gives two peaks, at  $(PA)=16.9$  and  $\delta (PA)=269$  ppm. A noteworthy feature of the  $^1\text{H}$  NMR spectra of **3**, **5** and **6** is the presence of a 'virtual triplet' with the extremely large N-doublet separation of 50 Hz. This separation is equal to  $^3J(\text{P}-\text{C}\equiv\text{C}-\text{H})$  *cis*  $^3J(\text{P}-\text{C}\equiv\text{C}-\text{H})$  *trans*, which are both probable and positive.

The  $^{31}\text{P}$ -( $^1\text{H}$ ) NMR spectra [12] of these complexes showed one singlet at  $\delta = 63.9$  ppm and  $^{194}\text{Pt}$  satellites,  $^1J(\text{PtP})=3080$  Hz; and another singlet at  $\delta=2.57$  ppm assigned to methyl protons coupled to  $^{195}\text{Pt}$ ; and  $^4J(\text{PtH})=6$  Hz. The methylene protons exhibited coupling to phosphorus, the singlet becoming a triplet of triplets  $^3J(\text{PH})=11$  Hz.

The IR spectrum of complex **2** contains the  $\nu(\text{C}=\text{N})$  band at  $2122\text{ cm}^{-1}$ . The IR spectra [12] of **3**, **5** and **6** revealed bands at 2018–2020, 1918–1920, 1895–1910 and 1850–1879  $\text{cm}^{-1}$ , assigned to  $\nu\text{CO}$  frequencies of different kinds. The far-IR spectrum of **4** showed two bands in the vicinity of  $300\text{ cm}^{-1}$ , assigned to  $\nu(\text{PtCl})$  modes consistent with the presence of the *cis*  $\text{PtCl}_2$  group.

The mass spectra of the complexes gave molecular ion peaks (**1**,  $m/e = 500$ , **2**,  $m/e = 936$ , **3**,  $m/e = 1205$ , **4**,  $m/e = 656$ , **5**,  $m/e = 592$ , **6**,  $m/e = 1035.5$ ), with isotopic distribution patterns in agreement with the proposed molecular and structural formulae (**1–6**). In addition to the molecular information, intense patterns were observed that were consistent with the consecutive losses of up to two  $\text{Cl}^-$  ligands from the Ni complex **1** and the Pt complex **5**; two  $\text{CN}^-$  ligands from the Pd complex **2**; two CO ligands from the W and Mo complexes **3** and **6**; and four CO ligands from the Mo complex **5**.

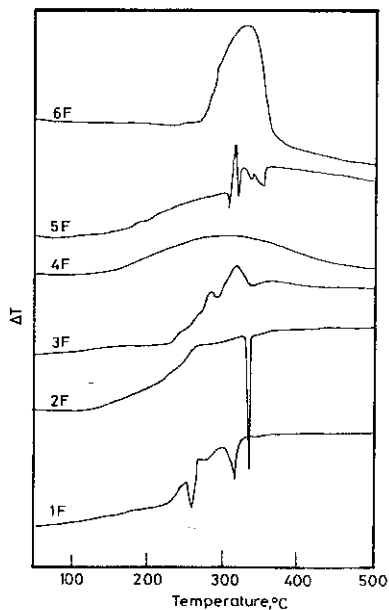
In order to confirm the mass changes indicated in the mass spectra of these complexes, their thermal analyses were performed. Another aim of these thermal analyses was to establish the thermal stabilities of the proposed structures [13].

### Thermal analyses (TG and DTA)

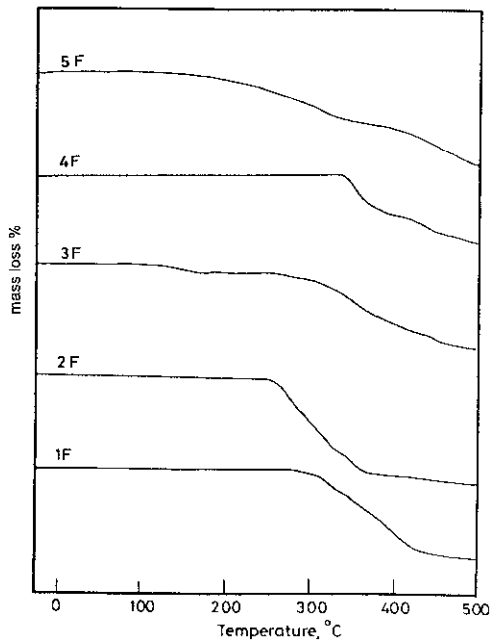
The DTA curve for the Ni complex **1** is presented in Fig. 1. This curve displays an exothermic base shift up to  $250^\circ\text{C}$  due to an increase in heat capacity, followed by two sharp endotherms at 260 to  $320^\circ\text{C}$ . These endotherms refer to the start of consequent mass losses of  $\text{Cl}_2$  and 2  $\text{C}_6\text{H}_5$  fragments (Table 2) (calculated mass loss = 44.19% and estimated mass loss = 44.0%) up to  $500^\circ\text{C}$ , as given by TG (Fig. 2a).

The DTA curve of the Pd complex **2** reveals a distinct exothermic base shift from  $80^\circ\text{C}$  up to  $208^\circ\text{C}$ , due to an increase in heat capacity of the compound. This is followed by a finite endotherm at  $290^\circ\text{C}$ , which points to the consecutive mass losses of phosphine fragments, together with cyanogen gas  $(\text{CN})_2$ , as indicated by TG (Fig. 2), from  $180^\circ\text{C}$  up to  $500^\circ\text{C}$  (calcd. mass loss 47.7%, estimd. 47.0%).

The DTA curve of the W complex **3** (Fig. 1) starts with an exothermic base shift due to an increase in heat capacity up to  $210^\circ\text{C}$ , followed by two consecutive



**Fig. 1** DTA of complexes: 1: nickel complex, 2: palladium complex, 3: tungsten complex, 4: platinum complex, 5,6: molybdenum complexes



**Fig. 2** TG of complexes: 1: nickel complex, 2: palladium complex, 3: tungsten complex, 4: platinum complex, 5: molybdenum complex

**Table 2** Thermal analyses of complexes

Compound	Temperature/ °C	Mass loss/ %	DTA features
<b>1</b>	25–250	–	exothermic base shift endotherms
	250–320	44.19 (44.0) Cl <sub>2</sub> +2C <sub>6</sub> H <sub>5</sub>	
<b>2</b>	80–208	–	exothermic base shift finite endotherm
	290	47.7 (47.0) dppm+(CN) <sub>2</sub>	
<b>3</b>	180–210	–	exothermic base shift consecutive exotherms
	294–320	6.92 (6.60)	
	142–308	3CO	
	308–400	19.78 (20) methylene group	
	408–500	17.63 (17.0) phenylphosphine group	
<b>4</b>	120–500	36.7 (36.0) P(Ph) <sub>2</sub> CH <sub>2</sub> Cl <sub>2</sub> active radical +Cl <sub>2</sub> (9)	very broad exotherm
<b>5</b>	25–220	–	exothermic base shift series of endotherms
	280–324	–	
	188–260	4.73 (4.4) CO	
	260–308	9.46 (9.0) 2CO	
	308–500	31.0 (31.0) phenylhydrazine group	
<b>6</b>	25–250	–	endothermic base shift broad exotherm
	284–460	–	

The values in parentheses are estimated values

exothermic peaks centred at 294°C and 320°C. These exotherms may refer to the cleavage of three CO groups at 142 to 308°C (calcd. 6.92%, estimd.=6.6%) as indicated by TG (Fig. 2). This is followed by mass loss starting at 308°C, corresponding to the ethylene group (calcd. 19.78%, estimd. 20%), followed by loss of the phenylphosphine group starting at 408°C (calcd.=17.63%, estimd. 17.0%) up to 500°C.

The DTA curve of the Pt complex **4** (Fig. 1) shows only a very broad exotherm from 120°C up to 500°C, which may refer to the mass loss (Fig. 2) of P(Ph)<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub>

fragments as active radicals together with  $\text{Cl}_2$  gas from  $400^\circ\text{C}$  up to  $560^\circ\text{C}$  (calcd. 36.27%, estimd. 36.0%).

The DTA curve of the Mo complex **5** (Fig. 1) demonstrates a distinct exothermic base shift up to  $220^\circ\text{C}$ , followed by a finite endotherm at  $280^\circ\text{C}$  and a series of exotherms and endotherms at 284, 290, 296, 310 and  $324^\circ\text{C}$ . The first is due to the increase in heat capacity of **5** and the other endotherms may indicate consecutive mass losses (Fig. 5b) of 3 CO ligands from 188 to  $260^\circ\text{C}$  (calcd. 4.73%, estimd. 4.4%) and two CO ligands at 260 to  $308^\circ\text{C}$  (calcd. 9.46%, estimd. 9.0%). This is immediately followed by the loss of a phenylhydrazine group (calcd. 31.0%, estimd. 31.0%), as suggested by the TG curve (Fig. 2).

The W complex **6** gives DTA and TG curves with similar behaviour to those of **5** (Figs 1 and 2, Table 2).

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