

**THERMAL REACTIONS OF METAL COMPLEXES UNDER  
QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS.  
5. THERMAL BEHAVIOUR OF MOLYBDENUM(0) DINITROGEN  
COMPLEXES IN THE SOLID STATE**

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**ABSTRACT**

Solid-state thermal reactions of *trans*-[Mo(N<sub>2</sub>)(L)(dppe)<sub>2</sub>] were investigated under quasi-isothermal and quasi-isobaric conditions (Q conditions) and under open dynamic conditions (D conditions). (L is a  $\pi$ -accepting ligand selected from CO, N<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CN, and dppe stands for 1,2-bis(diphenylphosphino)ethane.) The results show that *trans*-[Mo(N<sub>2</sub>)(CO)(dppe)<sub>2</sub>]· $\frac{1}{2}$ C<sub>6</sub>H<sub>6</sub> evolves dinitrogen plus  $\frac{1}{2}$ C<sub>6</sub>H<sub>6</sub> at 100–170 °C to produce a five-coordinated intermediate [Mo(CO)(dppe)<sub>2</sub>], which then undergoes disproportionation to produce *cis*-[Mo(CO)<sub>2</sub>(dppe)<sub>2</sub>] and unknown materials. When L is N<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>CN, both the complexes evolve dinitrogen, but they undergo complicated decomposition with no formation of a stable five-coordinated intermediate. The stability of the five-coordinated intermediate [Mo(CO)(dppe)<sub>2</sub>] is attributed to the greater  $\pi$ -accepting ability of CO compared with N<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>N.

**INTRODUCTION**

Low valent metal complexes containing small molecules such as carbon monoxide, ethylene, and dinitrogen have a great importance with respect to the activation of coordinated molecules. The mode of bonding between the metal and the above molecules can be briefly explained by two interactions: the ligand-to-metal  $\sigma$  donation and the metal-to-ligand  $\pi$  back-donation. The ligand activation mainly depends on the magnitude of the latter. In order to determine such metal–ligand interactions, ruthenium(II) ammine complexes containing a variety of  $\pi$ -accepting ligands were prepared and their thermal behaviour was studied in detail; a linear correlation was found between the bond strength of the ruthenium(II) ligand and the magnitude of  $\pi$ -back-bonding [1].

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Molybdenum(0) complexes with phosphine ligands are capable of donating more  $\pi$  electrons to the ligands than ruthenium(II) ammine complexes. It is thus of interest to investigate the thermal behaviour of molybdenum(0) complexes containing  $\pi$ -accepting ligands. This paper deals with the solid-state thermal reactions of molybdenum(0) dinitrogen complexes of the type *trans*-[Mo(N<sub>2</sub>)(L)(dppe)<sub>2</sub>], where L is CO, N<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>CN, and dppe stands for 1,2-bis(diphenylphosphino)ethane.

## EXPERIMENTAL

### *Preparation of complexes*

All preparations were carried out under an atmosphere of dinitrogen or argon using Schlenk apparatus and a glovebox. All solvents were purified by distilling with appropriate drying agents. Dppe was synthesized by published methods [2,3] as colourless needles.

#### *Trans*-[Mo(N<sub>2</sub>)(L)(dppe)<sub>2</sub>] (L = CO, N<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>CN)

*Trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] was prepared by a modification of the known procedure [4] as bright orange crystals. *Trans*-[Mo(N<sub>2</sub>)(CO)(dppe)<sub>2</sub>] · ½C<sub>6</sub>H<sub>6</sub> and *trans*-[Mo(N<sub>2</sub>)(C<sub>6</sub>H<sub>5</sub>CN)(dppe)<sub>2</sub>] were synthesized by the published methods [5–7] as yellow–orange crystals and dark green crystals, respectively.

#### [Mo(CO)(dppe)<sub>2</sub>]

The compound was synthesized by a modification of the known method [6] under an atmosphere of argon. *Trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] (0.5 g (0.5 mmol)) was dissolved in 15 ml of benzene. Benzyl propionate (5 mmol) was added to the solution and the resulting mixture was refluxed for 30 min. During the reflux, the original orange solution changed to black–brown. Hexane (20 ml) was added to the hot solution and then the solution was cooled in an ice bath. The black product thus obtained was collected by filtration and was washed with 5 ml of hexane.

Analysis of the complexes gave the following results. Found: C, 68.19%, H, 5.32%; N, 1.76%. Calculated for [Mo(N<sub>2</sub>)(CO)(dppe)<sub>2</sub>] · ½C<sub>6</sub>H<sub>6</sub>: C, 68.09%; H, 5.20%; N, 2.83%. Found: C, 66.02%; H, 5.14%; N, 5.92%. Calculated for [Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>]: C, 65.83%; H, 5.10%; N, 5.90%. Found: C, 69.21%; H, 5.17%; N, 4.15%. Calculated for [Mo(N<sub>2</sub>)(C<sub>6</sub>H<sub>5</sub>CN)(dppe)<sub>2</sub>]: C, 68.22%; H, 5.22%; N, 4.10%. Found: C, 66.58%; H, 5.14%. Calculated for [Mo(CO)(dppe)<sub>2</sub>]: C, 67.09%; H, 5.10%.

Excellent analytical results were not obtained for the complexes *trans*-[Mo(N<sub>2</sub>)(CO)(dppe)<sub>2</sub>] · ½C<sub>6</sub>H<sub>6</sub> and [Mo(CO)(dppe)<sub>2</sub>] because they were unstable in air. However, their compositions were confirmed using IR and <sup>31</sup>P

nuclear magnetic resonance (NMR) spectroscopies of the freshly prepared samples.

### *Derivatographic measurements*

The thermal reactions of the complexes were traced under quasi-isothermal and quasi-isobaric conditions (Q conditions) and under open dynamic conditions (D conditions). Q derivatograms were obtained using a MOM Q derivatograph with a Riken Densi d.c. microvolt meter Model DC 208 and a Riken Densi X-Y recorder Model F-35. D derivatograms were obtained with a MOM derivatograph Typ-OD-102. Measurements of D derivatograms were carried out under a constant flow of dinitrogen at a heating rate of  $1.3^{\circ}\text{C min}^{-1}$ . Finely ground samples of about 100 mg were employed.

### *Spectral measurements*

IR spectra were measured using the KBr disc method with a JASCO Model A-3 IR spectrometer. In the case of air-sensitive complexes, the KBr disc was prepared under a nitrogen atmosphere using a glovebox. Proton decoupled  $^{31}\text{P}$  NMR spectra were monitored in a solution of  $\text{CDCl}_3\text{-CHCl}_3$  or  $\text{C}_6\text{D}_6\text{-C}_6\text{H}_6$  (1:4, v:v) on a JEOL JNM GX-400 spectrometer at 161.7 MHz. 85%  $\text{H}_3\text{PO}_4$  was employed as the external standard.

### *Thin layer chromatography (TLC)*

TLC was conducted using a silica gel plate G made by Merck Ltd. Chloroform or benzene was used as the developing solvent and iodine was employed as the colour-developing reagent. TLC for air-sensitive compounds was carried out under a dinitrogen atmosphere in a glovebox.

## RESULTS AND DISCUSSION

### *Thermal behaviour of $\text{trans-[Mo(N}_2\text{)(CO)(dppe)}_2\text{]} \cdot \frac{1}{2}\text{C}_6\text{H}_6$*

Figure 1 shows Q and D derivatograms of the complex. The mass loss in the figure is expressed in terms of grams per formula weight ( $\text{g FW}^{-1}$ ). Under D conditions, the mass loss of about  $50 \text{ g FW}^{-1}$  takes place between ambient temperature and  $100^{\circ}\text{C}$  where a plateau is obtained. Under Q conditions the mass loss is about  $45 \text{ g FW}^{-1}$  between  $100$  and  $180^{\circ}\text{C}$ . The products obtained at the plateaux of the derivatograms under Q and D conditions are named Q and D products, respectively. The mass losses thus found are smaller than that ( $67 \text{ g FW}^{-1}$ ) calculated for  $\text{N}_2 + \frac{1}{2}\text{C}_6\text{H}_6$ . This is due to the fact that part of the  $\text{N}_2 + \frac{1}{2}\text{C}_6\text{H}_6$  in the complex may be lost

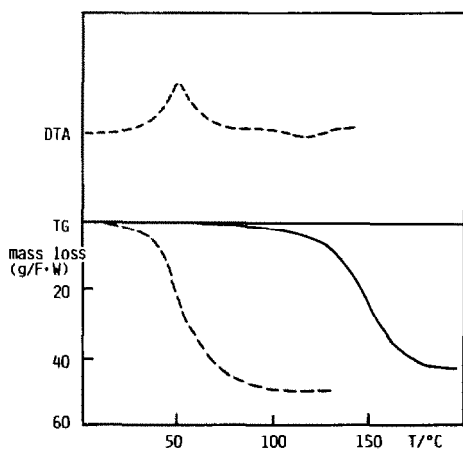


Fig. 1. Q (—) and D (---) derivatograms of  $trans\text{-}[\text{Mo}(\text{N}_2)(\text{CO})(\text{dppe})_2] \cdot \frac{1}{2}\text{C}_6\text{H}_6$ .

during the sampling procedure because, as mentioned in the experimental section, the complex is unstable in air. Although the reaction temperature and the mass loss of the complex under Q conditions are different from those observed under D conditions, Q and D products are identical as determined by IR spectroscopy and elemental analyses. Figure 2 shows the IR spectra of the complex and the Q product. The C–O ( $\nu(\text{CO})$ ) and N–N ( $\nu(\text{NN})$ ) stretching vibrations are shown. As seen from the figure,  $\nu(\text{NN})$  is not detected for the product, indicating that it does not contain  $\text{N}_2$ . The stretching vibrations  $\nu(\text{CO})$  of the complex appear at 1716 and 1817  $\text{cm}^{-1}$ . Those of the product appear at 1782 and 1857  $\text{cm}^{-1}$ , and are identical with those of  $cis\text{-}[\text{Mo}(\text{CO})_2(\text{dppe})_2]$  (1786 and 1852  $\text{cm}^{-1}$ ) [8]. This implies that the product consists of  $cis\text{-}[\text{Mo}(\text{CO})_2(\text{dppe})_2]$ . This implication also receives support from the following facts. Firstly, the signals of the  $^{31}\text{P}$  NMR

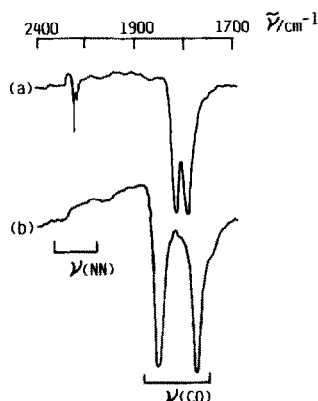


Fig. 2. IR spectra of  $trans\text{-}[\text{Mo}(\text{N}_2)(\text{CO})(\text{dppe})_2] \cdot \frac{1}{2}\text{C}_6\text{H}_6$  (a) and the Q product (b).

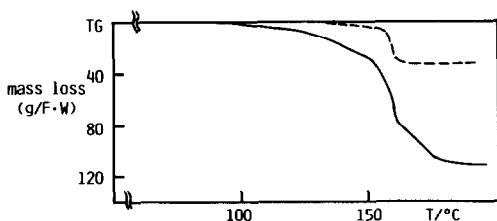


Fig. 3. Q derivatograms of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] (—) and *trans*-[Mo(N<sub>2</sub>)(C<sub>6</sub>H<sub>5</sub>CN)(dppe)<sub>2</sub>] (---).

spectrum of the Q product appear at 67.9 and 47.6 p.p.m. and closely resemble those (68.0 and 47.7 p.p.m.) of *cis*-[Mo(CO)<sub>2</sub>(dppe)<sub>2</sub>]. Secondly, the *R<sub>f</sub>* value for TLC of the Q product is the same as that of *cis*-[Mo(CO)<sub>2</sub>(dppe)<sub>2</sub>]. From the above results, it is conceivable that the product mainly consists of *cis*-[Mo(CO)<sub>2</sub>(dppe)<sub>2</sub>] with unknown materials. Consequently, the thermal reaction of *trans*-[Mo(N<sub>2</sub>)(CO)(dppe)<sub>2</sub>] may proceed as follows: the complex first evolves N<sub>2</sub> +  $\frac{1}{2}$ C<sub>6</sub>H<sub>6</sub> to form a five-coordinated complex [Mo(CO)(dppe)<sub>2</sub>], which then undergoes disproportionation to produce *cis*-[Mo(CO)<sub>2</sub>(dppe)<sub>2</sub>] and unknown materials. A similar disproportionation was detected in the thermal reaction of [Mo(CO)(dppe)<sub>2</sub>] which was prepared as a reference compound.

#### *Thermal behaviour of trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] and *trans*-[Mo(N<sub>2</sub>)(C<sub>6</sub>H<sub>5</sub>CN)(dppe)<sub>2</sub>]

Figure 3 shows Q derivatograms of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] and *trans*-[Mo(N<sub>2</sub>)(C<sub>6</sub>H<sub>5</sub>CN)(dppe)<sub>2</sub>]. In the Q derivatogram of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>], a gradual mass loss is seen between 130 and 170°C, where a plateau is obtained. The product at the plateau shows no IR band due to  $\nu$ (NN), and analytical results indicate that the product does not contain any nitrogen. The mass loss at the plateau corresponds to about 110 g FW<sup>-1</sup>, which is about twice as large as that (56 g FW<sup>-1</sup>) calculated for 2 moles of dinitrogen. The <sup>31</sup>P NMR spectrum of the product gives many unidentified signals together with the signal (-12 p.p.m.) due to free dppe. Therefore it is conceivable that the complex evolves 2 moles of dinitrogen followed by subsequent complicated decomposition.

In the Q derivatogram of *trans*-[Mo(N<sub>2</sub>)(C<sub>6</sub>H<sub>5</sub>CN)(dppe)<sub>2</sub>], the mass loss of about 28 g FW<sup>-1</sup> occurs between 130 and 150°C, where a plateau is obtained. The IR spectrum of the product obtained at the plateau shows no band due to  $\nu$ (NN), indicating that the product does not contain dinitrogen. In addition, the mass loss (about 28 g FW<sup>-1</sup>) corresponds to that of 1 mole of dinitrogen (28 g FW<sup>-1</sup>). These results seemingly imply that the complex evolves dinitrogen to produce a five-coordinated species [Mo(C<sub>6</sub>H<sub>5</sub>CN)(dppe)<sub>2</sub>]. However, detailed IR and <sup>31</sup>P NMR spectra mea-

surements and TLC of the product show that it does not consist of a single component, but several species. Therefore the product was not well characterized.

## SUMMARY

When heated, *trans*-[Mo(N<sub>2</sub>)(L)(dppe)<sub>2</sub>] evolves coordinated dinitrogen in the first stage to produce a transient five-coordinated intermediate [Mo(L)(dppe)<sub>2</sub>]. When L is CO, the five-coordinated intermediate is stable enough to be isolated. However, when L is N<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>CN, the isolation of a five-coordinated intermediate is unsuccessful because the intermediate undergoes further complicated decomposition with the cleavage of the phosphine ligands.

The stability of the five-coordinated intermediate [Mo(CO)(dppe)<sub>2</sub>] may be attributed to the greater  $\pi$ -accepting ability of CO compared with that of N<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>CN. When CO is coordinated to molybdenum(0), the excess electron density on the metal is moved to the CO moiety by the large  $\pi$ -back-donation from the  $d\pi$  orbital of molybdenum(0) to the  $p\pi^*$  orbital of the CO ligand, which probably stabilizes the five-coordinated intermediate. In contrast, when the ligands N<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CN with less  $\pi$ -accepting ability are coordinated to the metal, the excess electron density on the metal is only slightly moved to the ligands, which may make the five-coordinated intermediate unstable.

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