

## Reactions of $\text{Mo}(\text{CO})_6$ under biphasic conditions

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MS received 29 April 1993; revised 5 August 1993

**Abstract.** The reaction between molybdenum hexacarbonyl and hydroxide ion under solid-liquid biphasic conditions at room temperature gave  $[(\text{CO})_3\text{Mo}(\text{-OH})_3\text{Mo}(\text{CO})_3]^{3-}$ . Tetrabutylammonium bromide was used as the phase transfer agent. The reaction between hydroxide ion and molybdenum hexacarbonyl under liquid-liquid or solid-liquid biphasic conditions did not give any hydrido complex. Hydroxide ion catalysed substitution reactions of molybdenum hexacarbonyl were studied under solid-liquid and liquid-liquid biphasic conditions. The reaction between molybdenum hexacarbonyl and tetrabutylammonium hydroxide in dichloromethane at room temperature was studied by infrared spectroscopy. Based on the experimental evidence, a mechanism is suggested for the substitution reactions catalysed by the hydroxide ion under biphasic conditions.

**Keywords.** Molybdenum hexacarbonyl; phase transfer catalysis; substitution reactions; nucleophile-carbonyl adduct.

### 1. Introduction

Nucleophilic attack at carbon monoxide centres in metal carbonyls give nucleophile carbonyl adducts  $[\text{M}(\text{CO})\text{-Nu}]^-$ . The nucleophile carbonyl adducts have been characterised as stable complexes and a number of them have been detected as spectrally observable intermediates (Ford and Rokicki 1988). Nucleophile carbonyl adducts are highly reactive and they undergo a variety of reactions, like decarboxylation of  $\text{M-COOH}$  (Pearson and Mauermann 1982; Gross and Ford 1985), decarbonylation of carbon monoxide bound to the metal-nucleophile bond (Bennett and Rokicki 1985; Bryndza *et al* 1985; Darensbourg *et al* 1987), and labilisation of *cis*-ligands by  $-\text{C}(\text{O})\text{Nu}$  to give a coordinatively unsaturated reactive intermediate (Brown and Bellus 1978; Lichtenberger and Brown 1978; Atwood and Brown 1976).

Substitution reactions of metal carbonyls are catalysed by nucleophiles and Lewis bases (Morris and Besolo 1968; Brown and Bellus 1978; Basolo 1981). This kind of enhancement in the ligand substitution in many cases is the result of the formation of nucleophile carbonyl adducts. Group six hexacarbonyls undergo substitution reactions catalysed by sodium borohydride and hydroxide ion (Chatt *et al* 1971). Similar substitution reactions of group six hexacarbonyls were carried out under liquid-liquid biphasic conditions catalysed by hydroxide ions using tetrabutylammonium iodide as the phase transfer agents (Hui and Shaw 1977). We have carried

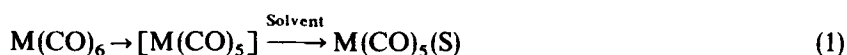
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out the reactions of molybdenum hexacarbonyl under biphase conditions in order to understand the possible mechanism.

## 2. Results and discussion

In general the substitution reactions of group six hexacarbonyls are promoted by heat or UV light (Kirtley 1982). The primary thermal or photo reaction of  $M(CO)_6$  is the dissociation of CO, and it is quite likely that  $M(CO)_5$  is the primary product. If the reaction takes place in a solvent with donor properties, such as tetrahydrofuran or acetonitrile, the 16-electron coordinatively unsaturated pentacoordinate species forms a solvent-stabilised complex. The solvent-metal interaction is usually quite weak and the solvent can be displaced by a better incoming ligand L. Subsequent reactions can displace another CO or the ligand L.

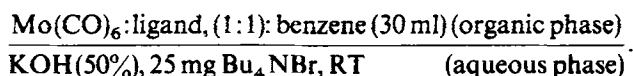


However, under biphase conditions the substitution reactions were catalysed by  $OH^-$  and the reactions were carried out under mild reaction conditions.

### 2.1 Reactions under liquid-liquid biphase conditions

Hydroxide ions catalyse the substitution reactions of molybdenum hexacarbonyl with ligands. The reactions were carried out under biphase conditions where potassium hydroxide was dissolved in water (aqueous phase) and the reactants (molybdenum hexacarbonyl and ligands) were dissolved in benzene (organic phase). At room temperature (30–33°C) in the absence of hydroxide ions no reaction was detected between molybdenum hexacarbonyl and ligands. Tetrabutylammonium bromide, tetrabutylammonium iodide and cetyltriethylammonium chloride were used as phase transfer agents.

The reaction mixture consists of the following



The reactions were carried out by stirring the reaction mixture rapidly under an argon atmosphere and the progress of the reaction was monitored by IR spectral changes at  $1980\text{ cm}^{-1}$ , which is characteristic of molybdenum hexacarbonyl in solution. The products were isolated from the organic phase by evaporation of the solvent under vacuum. The products were identified from their (CO) stretching bands (Orgel 1962; Kraihanzel and Cotton 1963) as well as from the analytical data (table 1).

The reactions between the ligands 2,2'-bipyridine, *o*-phenanthroline and bis(diphenylphosphino)methane and molybdenum hexacarbonyl in the presence of hydroxide ion were carried out at room temperature under liquid-liquid biphase conditions. The disubstituted products  $Mo(CO)_4(AA)$  (AA = bidentate ligands) (table 2) were isolated and identified in these reactions. Under similar reaction conditions

**Table 1.** Infrared and analytical data of molybdenum carbonyl complexes.

| Complexes  | IR $\nu(\text{CO})$ $\text{cm}^{-1}$ (KBr)                                 | Found (calc.) %  |                |                  |
|--|--|------------------|----------------|------------------|
|  |  | C                | H              | N                |
| $\text{Mo}(\text{CO})_4(\text{dppm})$  | 2010( <i>m</i> ), 1915( <i>sh</i> ),<br>1900( <i>s</i> ), 1860( <i>s</i> ) | 58.9<br>(58.78)  | 3.82<br>(3.72) | —                |
| $\text{Mo}(\text{CO})_4(\text{biPy})$  | 2002( <i>m</i> ), 1915( <i>m</i> ),<br>1870( <i>s</i> ), 1820( <i>vs</i> ) | 45.37<br>(46.15) | 2.13<br>(2.19) | 8.03<br>(7.69)   |
| $\text{Mo}(\text{CO})_4(o\text{-phen})$  | 2005( <i>m</i> ), 1891( <i>sh</i> ),<br>1865( <i>s</i> ), 1844( <i>s</i> ) | 49.27<br>(49.48) | 2.12<br>(2.06) | 7.58<br>(7.21)   |
| $\text{Mo}(\text{CO})_3\text{Py}_3$  | 1886( <i>s</i> ), 1749( <i>vs</i> )  | 51.93<br>(51.79) | 3.42<br>(3.59) | 10.26<br>(10.07) |
| $(\text{Et}_4\text{N})_3[(\text{CO})_3\text{Mo}(\mu\text{-OH})_3\text{Mo}(\text{CO})_3]$ | 1865( <i>s</i> ), 1720( <i>vs</i> , broad)                                 |                  |                |                  |
| $\text{K}_3[(\text{CO})_3\text{Mo}(\mu\text{-OH})_3\text{Mo}(\text{CO})_3]$              | 1868( <i>s</i> ), 1710( <i>s</i> , broad)                                  | 13.41<br>(13.62) | 0.64<br>(0.57) | —                |

**Table 2.** Substitution reactions of  $\text{Mo}(\text{CO})_6$  under biphase conditions.

| Ligand              | Cond. | L/M <sup>#</sup> | Time<br>(h) | Product (yield %)   |
|---------------------|-------|------------------|-------------|---|
| Dppm                | A     | 1                | 6           | $\text{Mo}(\text{CO})_4(\text{dppm})$ (82)  |
| 2,2'-Bipyridine     | A     | 1                | 6           | $\text{Mo}(\text{CO})_4(\text{biPy})$ (76)  |
| 1,10-Phenanthroline | A     | 1                | 8           | $\text{Mo}(\text{CO})_4(o\text{-phen})$ (72)  |
| 2,5-Norbornadiene*  | A     | 1                | 12          | —   |
|                     | A     | 5                | 12          | —   |
| 1,5-Cyclooctadiene* | A     | 5                | 12          | —   |
| 2,2'-Bipyridine     | B     | 1                | 8           | $\text{Mo}(\text{CO})_4(\text{biPy})$ (84)  |
| 1,10-Phenanthroline | B     | 1                | 10          | $\text{Mo}(\text{CO})_4(o\text{-phen})$ (78)  |
| 2,5-Norbornadiene   | B     | 1                | 16          | $(\text{Et}_4\text{N})_3[(\text{CO})_3\text{Mo}(\mu\text{-OH})_3\text{Mo}(\text{CO})_3]$ (44) |
|                     | B     | 5                | 16          | $(\text{Et}_4\text{N})_3[(\text{CO})_3\text{Mo}(\mu\text{-OH})_3\text{Mo}(\text{CO})_3]$ (42) |
| 1,5-Cyclooctadiene  | B     | 5                | 16          | $(\text{Et}_4\text{N})_3[(\text{CO})_3\text{Mo}(\mu\text{-OH})_3\text{Mo}(\text{CO})_3]$ (47) |

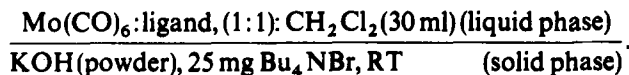
PTC =  $\text{Bu}_4\text{NBR}$ ; \*Most of the  $\text{Mo}(\text{CO})_6$  recovered unreacted from the organic phase: A =  $\text{C}_6\text{H}_6/\text{KOH}(50\%)$ ; B =  $\text{CH}_2\text{Cl}_2/\text{KOH}(\text{powder})$ ; Dppm = *bis*(diphenylphosphino)methane; <sup>#</sup>Molar ratio

1,5-cyclooctadiene and 2,5-norbornadiene did not give any substituted product even though the analogous complexes are known (Bennett *et al* 1961).

## 2.2 Reactions under solid-liquid biphase conditions

Substitution reactions of molybdenum hexacarbonyl with ligands catalysed by hydroxide ion and the reaction between molybdenum hexacarbonyl and hydroxide ion were studied under solid-liquid biphase conditions. Under these conditions the hydroxide ion was extracted into the organic phase using tetrabutylammonium bromide (dichloromethane was used as solvent). Even though crown ethers and cryptates were used in the solid-liquid extractions, in the present study quarternary ammonium salts were successfully used for the solid-liquid extractions.

The reaction mixture consists of the following:



The reactions were carried out by stirring the reaction mixture under argon atmosphere at room temperature. The ligands 2,2'-bipyridine and *o*-phenanthroline were reacted with molybdenum hexacarbonyl to give the disubstituted products (table 2).

The ligands 1,5-cyclooctadiene and 2,5-norbornadiene did not react with molybdenum hexacarbonyl. However, analysis of the liquid phase after 16 h of reaction showed the absence of the band at  $1980\text{ cm}^{-1}$ , characteristic of molybdenum hexacarbonyl. The work-up of the solid phase gave a yellow complex.

The reaction between molybdenum hexacarbonyl and hydroxide ion was also studied at room temperature under solid-liquid biphasic conditions. The reaction mixture consisting of molybdenum hexacarbonyl, potassium hydroxide powder and catalytic amounts of tetrabutylammonium bromide (phase transfer agent) in dichloromethane was stirred under argon atmosphere for 16 h. The solid phase gave a yellow complex after further work-up.

The yellow complexes which were isolated exhibited similar spectral and chemical properties. They were highly air-sensitive and pyrophoric in nature. They were identified as  $(\text{Et}_4\text{N})_3[(\text{CO})_3\text{Mo}(\mu\text{-OH})_3\text{Mo}(\text{CO})_3]$  from their chemical and spectral properties. This complex has two strong (CO) stretching bands at  $1865$  and  $1720\text{ cm}^{-1}$  (figure 1).

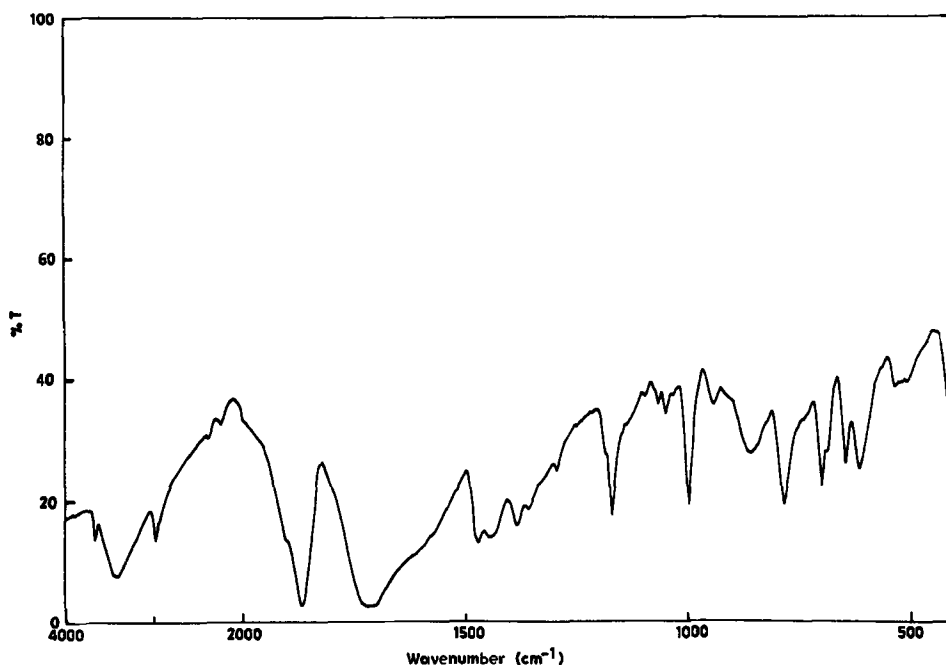


Figure 1. IR spectrum of  $(\text{Et}_4\text{N})_3[(\text{CO})_3\text{Mo}(\mu\text{-OH})_3\text{Mo}(\text{CO})_3]$ .

The aqueous solution of this complex reacts rapidly with pyridine at room temperature and gives a yellow precipitate. The yellow precipitate obtained in aqueous solution was isolated and identified as  $\text{Mo}(\text{CO})_3\text{Py}_3$  from its (CO) stretching bands as well as from analytical data. The potassium salt  $\text{K}_3[(\text{CO})_3\text{Mo}(-\text{OH})_3\text{Mo}(\text{CO})_3]$  was isolated from the solid phase as follows: the solid phase was dissolved in water and gave a yellow precipitate on addition of sufficient quantity of ethanol. The precipitate was filtered and dried under vacuum to give the yellow complex  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$ .

Hieber *et al* (1959) have studied the reaction between molybdenum hexacarbonyl and potassium hydroxide in refluxing ethanol and methanol. On refluxing molybdenum hexacarbonyl with potassium hydroxide in ethanol they isolated  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$ , whereas in methanol they isolated the complex  $\text{K}_3[(\text{CO})_3\text{Mo}(-\text{OH})_2(\text{OMe})\text{Mo}(\text{CO})_3]$ . Sartorelli *et al* (1971) reported the IR spectral data for the complex  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$ . The complex isolated either as potassium or as tetraethylammonium salt of the anion  $[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]^{3-}$  has spectral and chemical properties similar to those reported in the literature.

### 2.3 Infrared spectral studies

Molybdenum hexacarbonyl was treated with tetrabutylammonium hydroxide in dichloromethane. The reaction mixture was stirred rapidly under argon atmosphere at room temperature and the progress of the reaction was followed by recording the IR spectra of the aliquots, at different time intervals. There was a significant change in the carbonyl stretching frequencies of the reaction mixture (figure 2). The results are summarised in table 3.

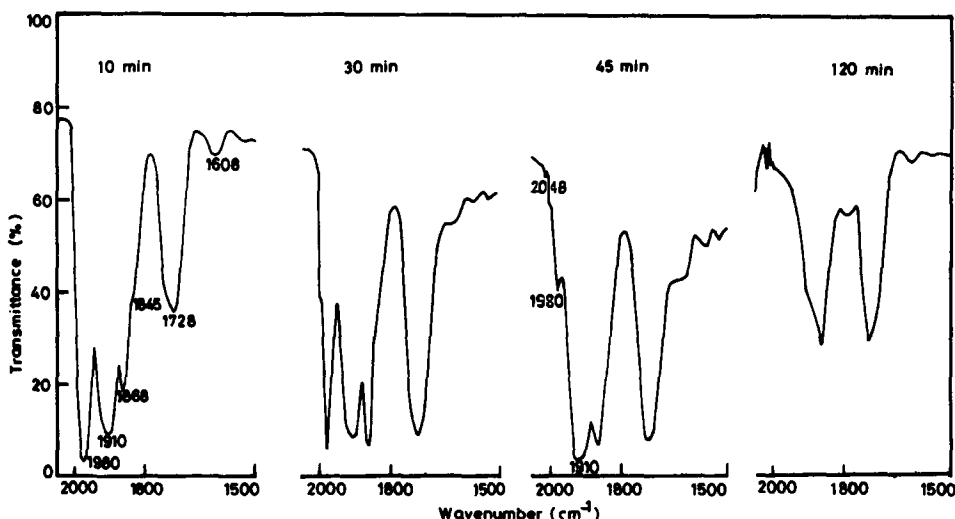


Figure 2. IR spectra of aliquots drawn from the reaction mixture of  $\text{Mo}(\text{CO})_6$  and BuNOH in dichloromethane at intervals of time.

Table 3. Infrared spectral data (dichloromethane solution).

| Complex  | Frequency<br>( $\text{cm}^{-1}$ ) | Assignment                          |
|--|-----------------------------------|-------------------------------------|
| [Mo(CO) <sub>5</sub> COOH] <sup>-</sup>  | 1608                              | $\nu(\text{CO}); \eta^1\text{COOH}$ |
|  | 1845                              | $\nu(\text{CO})$                    |
| [Mo(CO) <sub>5</sub> OH] <sup>-</sup>  | 1910                              | $\nu(\text{CO})$                    |
|  | 2048                              |                                     |
| Mo(CO) <sub>6</sub>  | 1980                              | $\nu(\text{CO})$                    |
| [(CO) <sub>5</sub> Mo( $\mu$ -OH) <sub>3</sub> Mo(CO) <sub>3</sub> ] <sup>3-</sup> | 1868                              | $\nu(\text{CO})$                    |
|  | 1728                              |                                     |

Table 4. Substitution reactions of Mo(CO)<sub>6</sub> catalysed by Bu<sub>4</sub>NOH.

| Ligand              | Solvent         | Time<br>(h) | Product*<br>(yield %) |
|---------------------|-----------------|-------------|-----------------------|
| 1,10-Phenanthroline | Benzene         | 8           | 57                    |
|                     | Dichloromethane | 2           | 82                    |
|                     | Tetrahydrofuran | 3           | 88                    |
|                     | Methanol        | 10          | —                     |
| 2,2'-Bipyridine     | Tetrahydrofuran | 3           | 76                    |
| DPPM                | Tetrahydrofuran | 3           | 61                    |

Mo(CO)<sub>6</sub> – 0.2 mmol; ligand – 0.2 mmol; Bu<sub>4</sub>NOH – 0.01 mmol; reaction temperature = 30°C; \*isolated yield; DDPM = bis(diphenylphosphino) methane.

#### 2.4 Tetrabutylammonium hydroxide catalysed substitution reactions of molybdenum hexacarbonyl

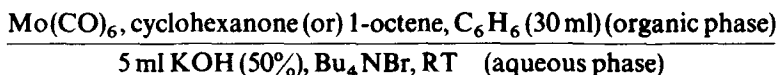
On stirring the reaction mixture consisting of molybdenum hexacarbonyl and ligands in the presence of catalytic amounts of tetrabutylammonium hydroxide at room temperature, molybdenum hexacarbonyl undergoes substitution reactions to yield the corresponding ligand-substituted products (table 4).

Among the solvents used, tetrahydrofuran and dichloromethane were found to be better solvents than benzene. In methanol no reaction was detected at room temperature. In the absence of tetrabutylammonium hydroxide no reaction was detected between molybdenum hexacarbonyl and the ligands at room temperature. Addition of tetrabutylammonium bromide instead of tetrabutylammonium hydroxide does not catalyse the reaction.

#### 2.5 Studies on the reduction of cyclohexanone and 1-octene under liquid–liquid biphasic conditions

Studies on the stoichiometric reductions of cyclohexanone and 1-octene were carried out under liquid–liquid biphasic condition. The reaction mixture consists of the

following:



The reaction mixture was stirred under argon atmosphere at room temperature. The organic phase was analysed by gas liquid chromatography at intervals of the reaction. Results showed no cyclohexanol or octane formation even after 12 h of the reaction period. These results suggest that the hydrido complexes were not involved as an intermediate in the reaction between molybdenum hexacarbonyl and hydroxide ion under biphasic conditions. The hydrido complex of molybdenum hexacarbonyl acts as the reductant; it reduces the ketones and the unsaturated olefins (Gibson *et al* 1985; Tooley *et al* 1986).

## 2.6 Mechanism

The following observations were made from studies on the reactions of molybdenum hexacarbonyl with various ligands and hydroxide ion under biphasic conditions.

Analysis of the reaction products under biphasic conditions showed that the reaction between molybdenum hexacarbonyl and hydroxide ion did not give any hydrido complex. One might expect the formation of  $[\text{Mo}(\text{CO})_5\text{H}]^-$  or  $[\text{Mo}_2(\text{CO})_{10}\text{H}]^-$  by the elimination of  $\text{CO}_2$  from the adduct  $[\text{Mo}(\text{CO})_5\text{COOH}]^-$  either under solid-liquid or liquid-liquid biphasic conditions.

The absence of a hydrido complex as an intermediate in the reaction between molybdenum hexacarbonyl and hydroxide ion is supported by the following observations: (i) The reaction between  $\text{Mo}(\text{CO})_6$  and  $\text{OH}^-$  under biphasic conditions gave the complex  $[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]^{3-}$ ; (ii) analysis of the aqueous phase showed  $\text{CO}_3^{2-}$  to be absent. It should have been present if  $\text{CO}_2$  had been eliminated from the adduct in the formation of the hydrido complex; (iii) studies on the reduction of cyclohexanone and 1-octene also suggested that the hydrido complex was not involved as an intermediate in the reactions; (iv) IR spectral studies on the reaction between molybdenum hexacarbonyl and tetrabutylammonium hydroxide showed the formation of  $[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]^{3-}$  and not the hydrido complex; (v) in an  $^{18}\text{O}$  labelling experiment under biphasic conditions at  $70^\circ\text{C}$ , Darensbourg *et al* (1980) observed that  $\text{CO}_2$  elimination was very slow and that  $[\text{Mo}_2(\text{CO})_{10}\text{H}]^-$  derivatives were formed rather slowly and with poor yields.

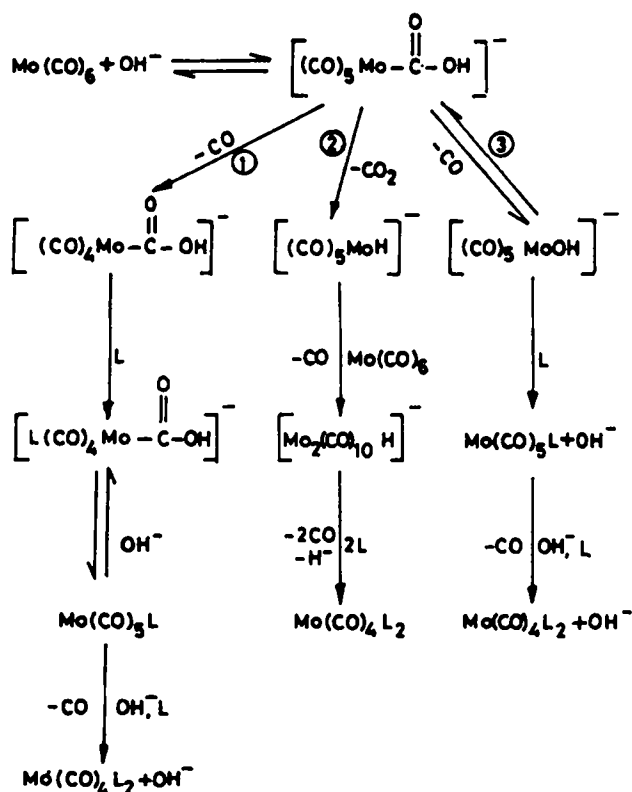
These experimental observations showed that  $[\text{Mo}(\text{CO})_5\text{COOH}]^-$  did not eliminate  $\text{CO}_2$  and substitution reactions under biphasic conditions did not operate through the formation of a hydrido complex (scheme 1).

## 3. Experimental

All reactions were carried out in a dual argon vacuum Schlenk line under argon atmosphere. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer. The products were identified by analytical and IR spectral data.

### 3.1 Materials

All the solvents were purified according to the literature procedure. Molybdenum hexacarbonyl (Fluka) was used without further purification. *Bis*(diphenylphosphino)



Scheme 1. Mechanism of substitution reactions of  $\text{Mo(CO)}_6$  catalysed by hydroxide ions.

methane (Alfa Inorganics) was recrystallised from methanol. 2,2'-bipyridine and 1,10-phenanthroline (Merck) were recrystallised from hexane. Tetrabutylammonium bromide (Aldrich) and tetrabutylammonium hydroxide 40% solution (Merck) were used as such. 2,5-Norbornadiene and 1,5-cyclooctadiene (Merck) were distilled before use.

### 3.2 Preparation of complexes

**3.2a Tetracarbonyl-2,2'-bipyridinemolybdenum(0)  $\text{Mo(CO)}_4(\text{bipy})$ :** *Procedure 1* –  $\text{Mo(CO)}_6$  (1 g, 3.8 mmol), 2,2'-bipyridine (0.63 g, 4 mmol) and tetrabutylammonium bromide (0.025 g) were added to a mixture of benzene (20 ml) and 50% aqueous KOH (5 ml). The reaction mixture was stirred at room temperature for about 6 h. At the end of the reaction, the contents were filtered and the precipitate was washed with water and dried under vacuum to give the complex (1.05 g, 76%).

*Procedure 2* –  $\text{Mo(CO)}_6$  (1 g, 3.8 mmol), 2,2'-bipyridine (0.63 g, 4 mmol) and tetrabutylammonium bromide (0.025 g) were added to a mixture of dichloromethane (30 ml) and KOH powder (2 g). The reaction mixture was stirred rapidly at room temperature for 8 h. After completion of the reaction KOH was filtered off and the solvent was



removed under reduced pressure to give the complex. The complex was washed with water and dried under vacuum to give  $\text{Mo}(\text{CO})_4(\text{bipy})$  (1.16 g, 84%).

*Procedure 3* –  $\text{Mo}(\text{CO})_6$  (500 mg, 1.9 mmol), 2,2'-bipyridine (0.32 g, 2 mmol) and tetrabutylammonium hydroxide (0.026 g, 0.1 mmol) were added to tetrahydrofuran (30 ml). The reaction mixture was stirred rapidly at room temperature for 3 h. The solvent was evaporated under vacuum after completion of the reaction and the residue was washed with water and dried under vacuum to give the complex  $\text{Mo}(\text{CO})_4(\text{bipy})$  (520 mg, 76%).

3.2b *Tetracarbonyl-1,10-phenanthroline molybdenum(0)*  $\text{Mo}(\text{CO})_4(o\text{-phen})$ : This complex was also prepared by procedures 1–3 as discussed for the complex  $\text{Mo}(\text{CO})_4(\text{bipy})$ .

3.2c *Tetracarbonylbis(diphenylphosphino)methane molybdenum(0)*  $\text{Mo}(\text{CO})_4(\text{dppm})$ : *Procedure 4* –  $\text{Mo}(\text{CO})_6$  (1 g, 3.8 mmol), bis(diphenylphosphino)methane (1.5 g, 4 mmol) and tetrabutylammonium bromide (0.025 g) were added to a mixture of benzene (20 ml) and 50% aqueous KOH (5 ml). The reaction mixture was stirred rapidly for about 6 h. At the end of the reaction the organic phase was separated and evaporated under vacuum. The complex obtained was recrystallised from 1:1 dichloromethane and methanol to give  $\text{Mo}(\text{CO})_4(\text{dppm})$  (1.96 g, 82%).

*Procedure 5* –  $\text{Mo}(\text{CO})_6$  (0.5 g, 2 mmol), bis(diphenylphosphino)methane (0.75 g, 2 mmol) and tetrabutylammonium hydroxide (0.026 g, 0.1 mmol) were reacted in tetrahydrofuran (30 ml) for about 3 h. At the end of the reaction the solvent was evaporated under reduced pressure, and the solid obtained was recrystallised from 1:1 dichloromethane and methanol to give the complex  $\text{Mo}(\text{CO})_4(\text{dppm})$  (0.68 g, 61%).

3.2d *Potassium-hydroxobis(tricarbonyl)molybdenum(0)*  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$   $\text{Mo}(\text{CO})_6$  (1.5 g, 5.7 mmol) and tetrabutylammonium bromide (0.025 g) were added to dichloromethane (30 ml) and KOH powder (2 g). The reaction mixture was stirred rapidly under an argon atmosphere at room temperature for about 16 h. At the end of the reaction the solid phase was dissolved in water, and 50 ml of ethanol added to this solution to give a precipitate. The precipitate was filtered, washed with ethanol and dried to give the complex  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$  (0.70 g, 47%).

The tetraethylammonium salt was isolated by the addition of tetraethylammonium bromide solution to the reaction mixture to give the complex  $(\text{Et}_4\text{N})_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$  (0.95 g, 43%).

3.2e *Tricarbonyltris(pyridine)molybdenum(0)*  $\text{Mo}(\text{CO})_3\text{Py}_3$ : *Procedure 6* – This complex was prepared under solid-liquid biphasic conditions as described for the preparation of  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$ . 2 ml of pyridine was added slowly with stirring during a period of 5 to 10 min to the aqueous solution obtained by dissolving the residue remaining after evaporation of dichloromethane. Addition of pyridine gives a yellow precipitate which was filtered and washed with water and dried under vacuum to give  $\text{Mo}(\text{CO})_3\text{Py}_3$ .

*Procedure 7* – Tricarbonyltris(pyridine)molybdenum(0) was also prepared from  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_3\text{Mo}(\text{CO})_3]$  or  $\text{K}_3[(\text{CO})_3\text{Mo}(\text{OH})_2(\text{OMe})\text{Mo}(\text{CO})_3]$  250 mg of

the complex was dissolved in water and 1 ml of pyridine was added with stirring for about 15 min at room temperature. On addition of pyridine a yellow precipitate was obtained which was filtered, washed with water and dried to give the complex  $\text{Mo}(\text{CO})_3\text{Py}_3$ .

### Acknowledgements

One of us (TC) is thankful to the Indian Institute of Technology, Madras and the Council of Scientific & Industrial Research, New Delhi for financial support.

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