

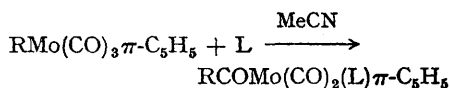
## The Carbonyl Insertion Reactions of Alkyltricarbonyl- $\pi$ -cyclopentadienylmolybdenum

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THE reaction of methylpentacarbonylmanganese with ligands has been extensively studied,<sup>1</sup> and recently it has been shown that these reactions involve a methyl migration.<sup>2</sup> Related carbonyl insertion reactions of methyldicarbonyl- $\pi$ -cyclopentadienyliron<sup>3</sup> and methyltricarbonyl- $\pi$ -cyclopentadienylmolybdenum<sup>4</sup> have been reported but nothing is known about the mechanism of these reactions.

We have found that a variety of alkyltricarbonyl- $\pi$ -cyclopentadienylmolybdenum complexes reacts with phosphorus-containing ligands to afford the corresponding acyl complexes in high yield.



(L = PR<sub>3</sub> where R<sup>1</sup> = alkyl, alkoxy, aryl group; R = Me, Et, PhCH<sub>2</sub>, CH<sub>2</sub>=CH·CH<sub>2</sub>)

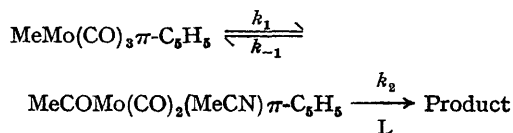
Kinetic measurements established that the relative reactivities of the alkyltricarbonyl- $\pi$ -cyclopentadienylmolybdenum complexes towards phosphorus ligands is Et > Me > PhCH<sub>2</sub> > CH<sub>2</sub>=CH·CH<sub>2</sub>. The rate of reaction is solvent dependent; reaction proceeds *ca.* 10<sup>3</sup> times faster in MeCN than in tetrahydrofuran.

The reactions in MeCN of, for example, MeMo(CO)<sub>3</sub> $\pi$ -C<sub>5</sub>H<sub>5</sub> with the various phosphorus ligands

all proceed at the same rate and the rates are independent of ligand concentration, demonstrating the rate-determining formation of a reactive intermediate, which rapidly reacts with the ligand. Surprisingly the corresponding arsenic or sulphur ligands, *e.g.*, As[OCH<sub>2</sub>]<sub>3</sub>CMe and S(Bu<sup>t</sup>)<sub>2</sub> do not react, demonstrating selectivity by the reaction intermediate which is probably due to kinetic, rather than steric, factors.

Acetonitrile is a good donor solvent and therefore the intermediate formed in these reactions are likely to be complexes of the type RCOMo(CO)<sub>2</sub>(MeCN) $\pi$ -C<sub>5</sub>H<sub>5</sub> (I). However, the <sup>1</sup>H n.m.r. spectrum of, for example, MeMo(CO)<sub>3</sub> $\pi$ -C<sub>5</sub>H<sub>5</sub> in CD<sub>3</sub>CN shows no evidence for the formation of an acyl complex (I; R = Me).

This observation demonstrates that in the Scheme  $k_{-1} > k_1$ :



When the reacting ligand L is of the type PR<sub>3</sub> then  $k_2 \gg k_{-1} > k_1$ , whereas when L is AsR<sub>3</sub> or SR<sub>2</sub>  $k_{-1} > k_1 > k_2$ . It is important to note that methylpentacarbonylmanganese reacts in donor solvents

with  $\text{AsR}_3$  ligands, and therefore differences observed here are peculiar to the molybdenum system.

The carbonyl insertion reaction effectively involves migration of an alkyl group from the metal-to-carbon of co-ordinated carbon monoxide. The

reactivity sequence mentioned indicates the importance of an intramolecular 1,2 shift with little or no charge separation. Reactivity is determined by the strength of the carbon-to-transition metal  $\sigma$ -bond in the complex  $\text{RMo}(\text{CO})_3\pi\text{-C}_6\text{H}_5$ .

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