

## TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS .....	vi
LIST OF TABLES .....	viii
LIST OF FIGURES .....	ix
LIST OF SCHEMES .....	x
INTRODUCTION .....	1
THEORY .....	7
EXPERIMENTAL .....	25
RESULTS AND DISCUSSION .....	37
SUMMARY .....	62
REFERENCES .....	64

SUMMARY

$M(CO)_5(CNR)$  ( $M = Cr, Mo$  and  $W$ ;  $R = t$ -butyl and cyclohexyl) complexes have been successfully synthesized by photochemical routes and the yields of the reactions are higher than those obtained from the conventional thermal reaction. Electronic and infrared absorption spectral data for these complexes are reported. The first absorption band in the electronic spectra of these complexes appears in the ultraviolet region, with a maximum at about 345 nm and the band is assigned to the lowest ligand field spin-allowed transition,  ${}^1A_1(e^4b_2^2) \longrightarrow {}^1E(e^3b_2^2a_1)$ . The CN stretching frequency of the complexes is found to be higher than that of the free ligand (ca. 2160 vs 2140  $cm^{-1}$ ).

The photochemical reactivity of the complexes have been investigated by irradiating the complexes in the presence of excess pyridine or piperidine at 364 nm in vacuo. Photosubstitution of CNR (in the complexes) by pyridine or piperidine was observed with a rather high quantum efficiency,  $\Phi \approx 0.4-0.8$ . This reveals that photodissociation of CNR from the complexes is an important primary photoprocess among the decay processes from the ligand field state. The observation of the photodissociation of CNR from the complexes in high quantum yield while the photodissociation of CO from the complexes was not observed also indicates that the  $M \text{ --- } CNR$  bonding is weaker than the  $M \text{ --- } CO$  one, at least in its excited state, and this is consistent with the nature of bonding in the  $M(CO)_5(CNR)$  complexes which have been reported that CO has much greater

$\pi$ -accepting ability than CNR. The results also show the metal dependence on the quantum yields in a decreasing pattern as ;

