

INFRA-RED SPECTRA OF SUBSTITUTED,  
CARBONYLS OF IRON  $X_2Sn[\pi-C_5H_5Fe(CO)_2]_2$   
AND  
GROUP VI TRANSITION METALS  $M(CO)_n(PPh_3)_2X_2$

THIS THESIS HAS BEEN ACCEPTED FOR  
THE DEGREE OF .....  
AND A COPY MAY BE PLACED IN THE  
UNIVERSITY LIBRARY.  
BY

FRANCIS NJAGI MBOGO

UNIVERSITY OF NAIROBI  
LIBRARY

A Thesis Submitted in Partial Fulfilment  
For a Degree of Master of Science in the  
University of Nairobi.

JULY 1986

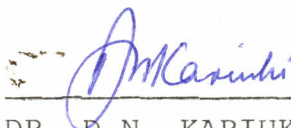
THIS THESIS IS MY ORIGINAL WORK AND HAS NOT BEEN  
PRESENTED FOR A DEGREE IN ANY OTHER UNIVERSITY.



---

FRANCIS NJAGI MBOGO

THIS THESIS HAS BEEN SUBMITTED FOR EXAMINATION  
WITH OUR APPROVAL AS UNIVERSITY SUPERVISORS:



---

DR. D.N. KARIUKI  
DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF NAIROBI.



---

DR. N.C. DESAI  
DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF NAIROBI.

(i)

ABSTRACT

Three series of transition metal carbonyls compounds namely:  $X_2Sn[\pi-C_5H_5Fe(CO)_2]_2$  ( $X = Cl, Br, I, CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_5$  and  $C_6H_5$ ),  $M(CO)_{n=2,3}(PPh_3)_2X_2$  ( $M = Mo, W; X = Cl, Br$ ) and  $M(CO)_{n=2,3}(PPh_3)_2Cl.Br$  ( $M = Mo, W$ ), have been studied. The compounds were prepared either using literature methods or modification of methods for similar compounds. All these compounds were found to be air-sensitive especially in solution and were synthesized in an inert atmosphere or on a vacuum line which was constructed for this work. The vacuum line was also used for recrystallisation of the compounds and also for cold-finger sublimation.

Samples of the carbonyl derivatives of the first series  $X_2Sn[\pi-C_5H_5Fe(CO)_2]_2$  were obtained in reasonable yield and purity with exception of the methyl derivative. Group VI metal derivatives  $M(CO)_{n=2,3}(PPh_3)_2X_2$  and  $M(CO)_{n=2,3}(PPh_3)_2Cl.Br$  were obtained in low yields but the crystals were reasonably pure.

Characterisation of the compounds was done by elemental analysis of the metal, carbon and

(ii)

halogen, using standard procedures. The results obtained were in good agreement with those expected. The only exception was the methyl derivative  $(\text{CH}_3)_2 \text{Sn}[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ .

Infrared spectra of the carbonyl stretching region were also used to characterise the compounds. The spectra studied were run in KBr pellets and in solution. Assignments of the carbonyl bands of Group VI metal derivatives,  $\text{M}(\text{CO})_{n=2,3}(\text{PPh}_3)_2\text{X}_2$  have not been reported but crystal data for a few of these compounds or analogous compounds have been reported. The crystal structures reported showed that the compounds have a capped octahedron structure, where the metals (molybdenum and tungsten) have a coordination number of seven. From the spectral similarities of these compounds it was possible to speculate on the structures of the rest of the compounds. On the basis of these structural and spectral data, assignments of the carbonyl bands were made. The tricarbonyl compounds  $\text{M}(\text{CO})_3(\text{PPh}_3)_2\text{X}_2$  showed three bands which have been assigned on the basis of  $\text{C}_s$ -symmetry. For the dicarbonyls  $\text{M}(\text{CO})_2(\text{PPh}_3)_2\text{X}_2$ , two bands were observed and these were assigned on the basis of  $\text{C}_2$ -symmetry.

(iii)

The spectral data of the mixed carbonyl halides  $M(\text{CO})_{n=2,3}(\text{PPh}_3)_2 \text{Cl.Br}$  were found to be similar to those of the compounds  $M(\text{CO})_{n=2,3}^-(\text{PPh}_3)_2\text{X}_2$ . This implies that the structures of the two sets of compounds are similar.

The crystal structures reported for some of the compounds of the series  $\text{X}_2\text{Sn}[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  indicate that the structures of these compounds vary with the nature of the substituent on the tin atom. Point groups  $\text{C}_{2v}$ ,  $\text{C}_1$ ,  $\text{C}_s$  and  $\text{C}_2$  were considered. The variation of the frequencies and the intensity patterns of the four bands was used to speculate on the possible reasons for the differences in:

- (a) the structures of alkyl or aryl and halogen substituted derivatives,
- (b) the donor - acceptor properties of the substituent on the tin atom and their effects on the multiple bond formation to the tin and iron atoms,
- (c) the effect of the physical state; whether the compounds are in solution or in the solid state.

Observation of four bands rules out the  $\text{C}_{2v}$  symmetry. For compounds of  $\text{C}_s$  symmetry, the

frequencies,  $\nu$ , of the bands should decrease in the order  $\nu_{A'(1)} > \nu_{A'(2)} > \nu_{A''(1)} \approx \nu_{A''(2)}$ , while the intensities,  $I$ , should decrease in the order  $I_{A'(2)} > I_{A''(1)} > I_{A'(1)} > I_{A''(2)}$ . For  $C_1$  symmetry, the frequencies,  $\nu$ , decrease in the series  $\nu_{A(1)} > \nu_{A(2)} > \nu_{A(3)} > \nu_{A(4)}$ , while the intensities,  $I$ , should decrease in the series,  $I_{A(1)} \approx I_{A(2)} > I_{A(3)} \approx I_{A(4)}$ . For  $C_2$  symmetry, the frequencies,  $\nu$ , should decrease in the order,  $\nu_{A(1)} > \nu_{B(1)} > \nu_{A(2)} > \nu_{B(2)}$ , while the intensities,  $I$ , of the bands alternate,  $I_{A(1)} > I_{B(1)} > I_{A(2)} > I_{B(2)}$ .

Band assignments of Group VI metal derivatives and mixed halide analogues were made. The present work has shown that when crystal data is not available, infrared spectral studies can be used to predict structures of analogous compounds. Assignments of carbonyl bands in the series  $X_2Sn(\pi-C_5H_5Fe(CO)_2)_2$  was completed by assigning carbonyl frequencies of compounds on the basis of  $C_2$ -symmetry. These compounds  $X_2Sn(\pi-C_5H_5Fe(CO)_2)_2$  were found to exist in all the three possible symmetries  $C_1$ ,  $C_s$  and  $C_2$  while in solution but the dominant symmetry in the solid state was found to be  $C_2$ .