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MÖSSBAUER STUDIES OF SOME CYCLOPENTADIENYLIRON DERIVATIVES

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SUMMARY

Mössbauer parameters are compared with carbonyl IR stretching frequencies for cyclopentadienyliron derivatives.

INTRODUCTION

Complexes of general formula $(\pi\text{-}C_5H_5)Fe(CO)(L)R$ [$R=$alkyl or aryl group; $L=PPh_3$ or $P(n\text{-}Bu)_3$] react very rapidly with sulfur dioxide to give insertion products having an *S*-sulfinato structure[1]. The relative rates of insertion depend on the nature of L, and increase in the order $CO > PPh_3 > PBu_3$, which is consistent with an electrophilic attack of SO_2 on the complex[2]. Similar behaviour has been also observed for the reactions of these complexes with carbon monoxide[3]. We have studied the Mössbauer spectra of these complexes to provide information about the oxidation state of the iron atom, the symmetry of its electronic environment and, the nature of the chemical bonds involved[4].

EXPERIMENTAL

The complexes were prepared by previously described methods[1,3].

A 2-mCi source of ^{57}Co in Pt was used in a Mössbauer apparatus constructed in our laboratories. The velocity profile, generated by a function generator and controlled by a standard negative feedback circuit, was sinusoidal. A 256-channel analyzer, operating in time mode and synchronized with the motion, stored the spectrum.

The samples used as absorbers were prepared from microcrystalline powders which were pulverized and gently compressed in a polyethylene or aluminium container, being approximatively 10 mm thick and 12.5 mm in diameter.

The calibration of the motion was determined with the aid of the hyperfine structure of an iron foil enriched in the ^{57}Fe isotope and with the standard disodiumpentacyanonitrosylferrate(II) to which shifts (mm/sec) were referred.

The spectra were recorded at room temperature, and Mössbauer parameters were evaluated by the least squares method to fit the experimental curves.

RESULTS AND DISCUSSION

The Mössbauer parameters of the complexes are summarized in Table 1, which also lists the CO stretching frequencies, and it will be seen that there are significant variations in the set of compounds examined. For example, significant differences in the isomer shift are observed on going from the metal–carbon bonded parent complex to the CO or SO_2 insertion product. It appears from the results that the electron density on the iron nucleus for the examined complexes decreases in the sequence $-COR \approx SO_2R > R$, and that this order is independent of the nature of the other ligand coordinated to the metal.

The CO stretching frequency for complexes $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)X$ ($X = CH_3$, $COCH_3$, SO_2CH_3) decreases in the order: $SO_2CH_3[\nu(CO)\,1956] > COCH_3[\nu(CO)\,1920] > CH_3[\nu(CO)\,1905]$ which probably parallels the decrease

TABLE 1

Complexes	*I.S.*	*Q.S.*	*ν(CO), cm⁻¹*
$(\pi\text{-}C_5H_5)Fe(CO)_2COCH_3$	0.27[a]	1.66[a]	2018, 1963[f]
$(\pi\text{-}C_5H_5)Fe(CO)_2SO_2CH_3$	0.29	1.68	2063, 2015[e] 2053, 2009
$(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C_6H_5$	0.31	1.71	2008, 1951[b]
$(\pi\text{-}C_5H_5)Fe(CO_2)SO_2CH_2C_6H_5$	0.23	1.64	2060, 2010[b]
$(\pi\text{-}C_5H_5)Fe(CO)_2SO_2(p\text{-}FCH_2C_6H_4)$	0.21	1.60	2033, 1990[e]
$(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$	0.37	1.83	1905[c]
$(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3$	0.31	1.83	1920[d]
$(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)SO_2CH_3$	0.32	1.74	1956[a]
$(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2C_6H_5$	0.34	1.74	1905[d]

[a] From ref. 5; [b] From ref. 6; [c] From ref. 3; [d] From ref. 1; [e] CH_2Cl_2 solution; [f] From ref. 8.

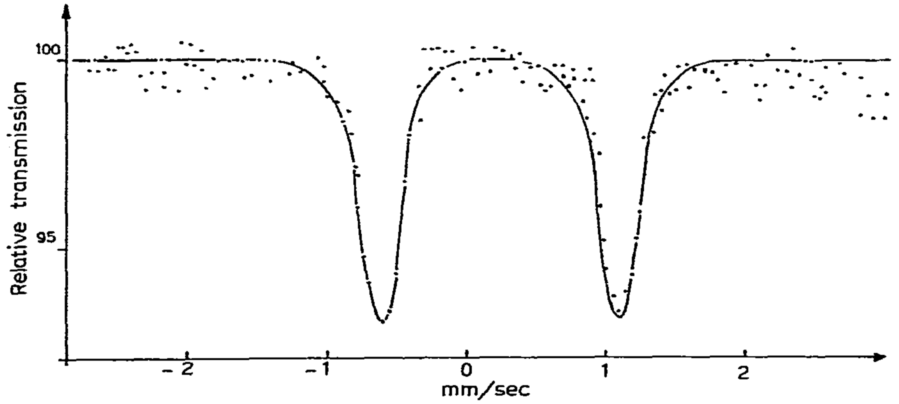

Fig. 1. Mössbauer absorption spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2SO_2CH_3$.

in the π-bonding acceptor ability of X. Although the existence of strong π-bonding between the RSO_2 group and the metal in iridium(III) and palladium(II) complexes has been questioned[7], π-bonding does seem to be important in iron sulfinato carbonyl complexes[1]. This sequence in ν(CO) is not completely reflected in our Mössbauer measurements which, although sensitive, do not reveal any appreciable difference in the electronic density on the iron atom in the sulfinato- and the acyl-carbonyl complexes (Table 1).

The combined IR ν(CO) and Mössbauer *I.S.* results indicate that the σ-donor ability of RCO is greater than that of RSO_2. This follows directly from the observation that the former ligand shows a lower CO stretching frequency, indicating smaller M–X π-bonding, and a comparable *I.S.* which indicates a similar electron density at the iron nucleus. Thus the greater π-bonding ability of RSO_2 than of RCO parallels its weaker σ-bonding ability.

REFERENCES

1 M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, 4 (1970) 347.
2 S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, 93 (1971) 2535.
3 P. M. Treichel, R. L. Shubkin, K. W. Barbiett and D. Reichard, *Inorg. Chem.*, 5 (1966) 1177.
4 E. Fluck, in V. I. Goldanski and R. H. Herber (Ed.), *Chemical Application of Mössbauer Spectroscopy*, Academic Press, New York N.Y. 1968, p. 268.
5 R. H. Herber, R. B. King and G. H. Wertheim, *Inorg. Chem.*, 3 (1964) 101.
6 J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, 88 (1966) 4862.
7 J. Chatt and D. M. P. Mingos, *J. Chem. Soc. A*, (1969) 1770.
8 R. B. King, *J. Amer. Chem. Soc.*, 85 (1963) 1918.