

## Preliminary communication

### An explanation of the reactivities of $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$ and $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$

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#### SUMMARY

An SCCCMO and IR study of  $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$  and  $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$  is reported, which shows that the relative reactivities depend on the electronic effects of the  $\pi$ -moiety and the geometry.

The SCCCMO results show that the M–C(O) total overlap population<sup>1</sup> of  $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$  is significantly higher than that of  $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$ . This is due to two factors: (i) the electron-donating ability of the  $\pi\text{-C}_5\text{H}_5$  group, (ii) the geometry of each molecule. The  $\pi\text{-C}_5\text{H}_5$  group is shown to be an electron-donor and  $\pi\text{-C}_3\text{H}_5$  an electron-acceptor in these compounds (see Fig.1). The  $\text{Co}(\text{CO})_2$  group is in the  $xz$ -plane, hence overlap between metal  $d_{xy}$  and  $d_{yz}$  orbitals and carbonyl  $\pi^*$  (antibonding) tangential

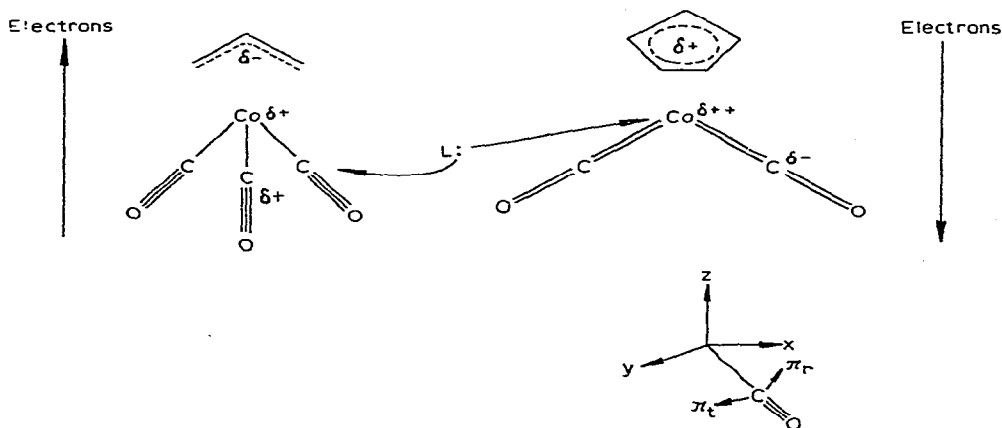


Fig.1. Qualitative representation of SCCCMO results.

orbitals is relatively high (the SCCMO calculated contribution to the total metal carbonyl  $\pi^*$  overlap population of 0.098 is 0.083). The electron-donating property of the  $\pi$ -C<sub>5</sub>H<sub>5</sub> group therefore allows the carbonyl  $\pi^*$  orbitals to accumulate electronic charge via the metal  $d_{xy}$  and  $d_{yz}$  orbitals. The Co(CO)<sub>3</sub> group of  $\pi$ -C<sub>3</sub>H<sub>5</sub>Co(CO)<sub>3</sub> is symmetrical about the z-axis, so the M( $d_{xy}$ ,  $d_{yz}$ )-C( $\pi^*$ ) overlap population is much lower.

The lower carbonyl bond order of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub> is due to the greater carbonyl anti-bonding orbital population (particularly of the  $\pi^*$  orbitals) which strengthens the M-C bond by  $d$ - $\pi^*$  overlap but weakens the C-O bond. The relatively high orbital population of the  $\pi^*$  orbitals in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub> supports the idea that such orbitals would cause an approaching nucleophile to be repulsed toward the positive metal centre giving a slow binuclear reaction,, whereas the relatively empty  $\pi^*$  orbitals of  $\pi$ -C<sub>3</sub>H<sub>5</sub>Co(CO)<sub>3</sub> would tend to act as acceptors to a nucleophile. Experimentally, it has been found that  $\pi$ -C<sub>3</sub>H<sub>5</sub>Co(CO)<sub>3</sub><sup>2</sup> reacts rapidly with triphenylphosphine with first-order kinetics, while  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub><sup>3</sup> reacts slowly with, probably, second-order kinetics. The IR results correlate with the SCCMO<sup>4</sup> calculations (Table 1).

TABLE 1

## SCCCMO AND IR RESULTS

	<i>M-C(O) overlap population</i>	$\pi^*$ orbital population	<i>C-O bond order</i>	<i>Metal charge</i>
<i>SCCCMO</i>				
$\pi$ -C <sub>3</sub> H <sub>5</sub> Co(CO) <sub>3</sub>	0.213	0.038	2.984	0.172
$\pi$ -C <sub>5</sub> H <sub>5</sub> Co(CO) <sub>2</sub>	0.245	0.157	2.888	0.217
	$\nu(M-C)(cm^{-1})$ (benzene solution)	$\nu(CO)(cm^{-1})$ (cyclohexane solution)		
<i>IR</i>				
$\pi$ -C <sub>3</sub> H <sub>5</sub> Co(CO) <sub>3</sub>	482, 458	2068, 2000		
$\pi$ -C <sub>5</sub> H <sub>5</sub> Co(CO) <sub>2</sub>	488, 475	2032, 1974		

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