

PHOTOLYTIC PREPARATION AND SOME PROPERTIES OF (SORBIC ACID) $\text{Fe}(\text{CO})_2\text{L}$  COMPLEXES, WITH  $\text{L} = \text{CO}$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_3$  AND  $\text{PEt}_3$

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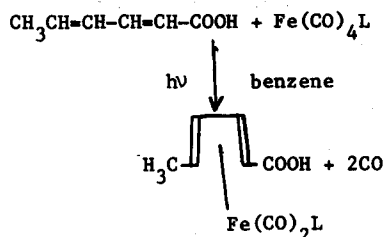
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**Abstract:** Irradiation of benzene solutions of  $\text{Fe}(\text{CO})_4\text{L}$  ( $\text{L} = \text{CO}$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_3$ ,  $\text{PEt}_3$ ) in the presence of sorbic acid (SBA), produced the complexes  $(\text{SBA})\text{Fe}(\text{CO})_2\text{L}$ . Infrared and mass spectral data of the complexes are reported.

The preparation of (sorbic acid)tricarbonyl iron (0),  $(\text{SBA})\text{Fe}(\text{CO})_3$ , was first reported by Stone *et al.*<sup>1</sup>. A mixture of  $\text{Fe}_3(\text{CO})_{12}$  and sorbic acid was refluxed in benzene for several hours, and the product formed was identified in the reaction mixture by infrared. However, the authors had failed to isolate the compound. Later, Cais and Maoz<sup>2</sup> succeeded in isolating the complex, in poor yield, after refluxing  $\text{Fe}_3(\text{CO})_{12}$  and sorbic acid for 8 h in di-n-butylether. The main limitation of these thermal methods is that the free sorbic acid undergoes extensive polymerization at temperatures higher than c.a. 50°C.

In previous papers<sup>3,4</sup>, we reported the photolytic preparation of (benzylideneacetone)dicarbonylphosphine iron(0) complexes. The method showed to be very efficient, giving the products in high yields. Here we describe the extension of this method to the preparation of  $(\text{SBA})\text{Fe}(\text{CO})_2\text{L}$  complexes, with  $\text{L} = \text{CO}$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_3$  and  $\text{PEt}_3$ . The main advantage of this method is that the sorbic acid reacts at room temperature, in a short reaction time.

Irradiation of benzene solutions of  $\text{Fe}(\text{CO})_4\text{L}$  in the presence of sorbic acid gave the products, after 2-3 h, according to the reaction



The photolysis were carried out under dry nitrogen, in a glass annular reactor, using a 125 W medium-pressure mercury lamp. After removing the solvent by distillation in vacuum, at 25°C, the crude reaction products were purified by recrystallization from methanol, giving the complexes:

$(\text{SBA})\text{Fe}(\text{CO})_3$ : yellow crystals; 25% yield; m.p.: 141-2°C. Found: C, 42.79; H, 3.14; Fe, 22.38. Calc. for  $\text{C}_9\text{H}_8\text{FeO}_5$ : C, 42.89; H, 3.19; Fe, 22.16%. Mol. mass: 252 (found in mass spectrum); calc., 252.01.

$(\text{SBA})\text{Fe}(\text{CO})_2\text{P}(\text{OPh})_3$ : yellow crystals; 36% yield; m.p.: 173-4°C. Found: C, 64.09; H, 4.71; Fe, 12.01. Calc. for  $\text{C}_{26}\text{H}_{23}\text{FeO}_7\text{P}$ : C, 64.22; H, 4.76; Fe, 11.48%. Mol. mass: 534 (found in mass spectrum); calc., 534.18.

$(\text{SBA})\text{Fe}(\text{CO})_2\text{PPh}_3$ : yellow crystals; 45% yield; m.p.: 152-3°C. Found: C, 58.27; H, 4.19; Fe, 10.75. Calc. for  $\text{C}_{26}\text{H}_{23}\text{FeO}_4\text{P}$ : C, 58.44; H, 4.33; Fe, 10.45%. Mol. mass: 486 (found in mass spectrum); calc., 486.18.

$(\text{SBA})\text{Fe}(\text{CO})_2\text{PEt}_3$ : yellow crystals; 39% yield; m.p.: 183-4. Found: C, 48.89; H, 6.61; Fe, 17.01. Calc. for  $\text{C}_{14}\text{H}_{23}\text{FeO}_4\text{P}$ : C, 49.14; H, 6.87; Fe, 16.37%.

The table shows some infrared and mass spectral data for the complexes prepared.

The infrared spectra of the dicarbonyl derivatives show two strong and sharp  $\nu_{\text{C}=\text{O}}$  bands, of same intensity, in the region 2000-1945  $\text{cm}^{-1}$ , typical of  $(\text{diene})\text{Fe}(\text{CO})_2\text{L}$  complexes<sup>3,5</sup>, and one  $\nu_{\text{C}=\text{O}}$  band in the region 1640-1660  $\text{cm}^{-1}$ , assignable to the carbonyl group of the coordinated sorbic acid (1690  $\text{cm}^{-1}$  in the free ligand). The significant decrease observed in the  $\nu_{\text{C}=\text{O}}$  frequencies of sorbic acid after coordination, is expected since the  $\text{Fe}(\text{CO})_2\text{L}$  moieties act as net electron donors to

diene ligands<sup>6</sup>. The electronic effect of the  $\text{Fe}(\text{CO})_2\text{L}$  group is transmitted through the  $\pi$ -system of the coordi-

Table. Infrared and Mass Spectral Data of (Sorbic Acid) $\text{Fe}(\text{CO})_2\text{L}$  Complexes.

L	$\nu_{\text{C}\equiv\text{O}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{C}=\text{O}}$ ( $\text{cm}^{-1}$ )	m/e (fragments)
CO	2100; 2050	1670	252( $\text{M}^+$ ); 224( $\text{M}^+ - \text{CO}$ ); 196( $\text{M}^+ - 2\text{CO}$ ); 168( $\text{M}^+ - 3\text{CO}$ )
$\text{P}(\text{OPh})_3$	2000; 1950	1660	534( $\text{M}^+$ ); 196( $\text{M}^+ - \text{CO} - \text{P}(\text{OPh})_3$ ); 168( $\text{M}^+ - 2\text{CO} - \text{P}(\text{OPh})_3$ )
$\text{PPh}_3$	2005; 1945	1655	486( $\text{M}^+$ ); 458( $\text{M}^+ - \text{CO}$ ); 168( $\text{M}^+ - 2\text{CO} - \text{PPh}_3$ )
$\text{PEt}_3$	2000; 1950	1640	286( $\text{M}^+ - 2\text{CO}$ ); 168( $\text{M}^+ - 2\text{CO} - \text{PEt}_3$ )

nated sorbic acid, increasing the electron density at the  $\pi^*$  molecular orbital of the  $\text{C}=\text{O}$  group.

The order of decrease of the frequencies  $\nu_{\text{C}=\text{O}}$  parallels the order of increase of the  $\sigma$ -donor ability of the ligand L, i.e.  $\text{CO} < \text{P}(\text{OPh})_3 < \text{PPh}_3 < \text{PEt}_3$ . This suggests that the electronic effect is transmitted via a  $\text{L} \rightarrow \text{Fe} \rightarrow \pi$  diene mechanism as previously observed in a  $^{13}\text{C}$  NMR study of (benzylideneacetone) $\text{Fe}(\text{CO})_2\text{L}$  complexes<sup>4</sup>. The frequencies  $\nu_{\text{C}\equiv\text{O}}$  are lower for the complexes with phosphorus ligands when compared to the tricarbonyl derivative. This is expected as a consequence of the increase in the electron density at the iron atom when a CO ligand is substituted by a much better  $\sigma$ -donor and poorer  $\pi$ -acceptor phosphorus ligand<sup>4</sup>.

The mass spectra show molecular peaks for the complexes with  $\text{L} = \text{CO}$ ,  $\text{P}(\text{OPh})_3$  and  $\text{PPh}_3$ . The higher m/e peak for the complex with  $\text{L} = \text{PEt}_3$ , found at m/e 286, is assignable to the  $[(\text{SBA})\text{FePEt}_3]^+$  fragment. A peak at m/e 168, assignable to the  $[(\text{SBA})\text{Fe}]^+$  fragment is observed in the spectra of all complexes. This peak is very intense for the  $(\text{SBA})\text{Fe}(\text{CO})_3$  complex, but weak for the complexes with phosphorus ligands. Peaks at m/e 196, assignable to the  $[(\text{SBA})\text{Fe}(\text{CO})]^+$  fragment,

were observed in the spectra of the complexes with  $\text{L} = \text{CO}$  and  $\text{P}(\text{OPh})_3$ . A peak at m/e 224, assignable to the  $[(\text{SBA})\text{Fe}(\text{CO})_2]^+$  fragment was observed only in the spectrum of the tricarbonyl-iron complex. The peak at m/e 458, found in the spectrum of the complex with  $\text{L} = \text{PPh}_3$ , is assignable to the  $[(\text{SBA})\text{Fe}(\text{CO})\text{PPh}_3]^+$  fragment. These results seem to indicate that the Fe-L bond strength increases in the order of L, carbon monoxide < phosphite < phosphine, which is the order of increase of the  $\sigma$ -donor ability of L.

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