

Preliminary communication

New σ -allylic and ($\sigma + \pi$)-allylic complexes formed from
 π -(2-Cl-allyl)Fe(CO)₂NO and phosphonic ligands

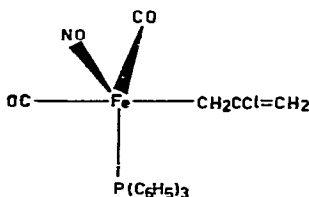
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Several examples are known of σ -allylic complexes which by chelation are transformed into π -allylic¹ or ($\sigma + \pi$)-allylic² complexes.

We have found that the reaction of π -(2-Cl-allyl)Fe(CO)₂NO with P(C₆H₅)₃ in benzene proceeds in two steps: the analysis and molecular weight of the product of the first step agree with formula (I). The reaction path suggests that the P(C₆H₅)₃ ligand lies in the trigonal plane of the bipyramid, but it is not possible to exclude substitution in the apical position.



I

The evidence for the σ -structure is as follows:

(a) No CO is evolved during the reaction, and no CO stretching frequencies attributable to a CO group inserted between the metal and the allylic group are observed.

(b) The complex shows two CO and one NO stretching frequencies at ν 2021, 1952 and 1750 cm⁻¹, respectively, in benzene. Further, a band at 1598 cm⁻¹ is observed in fluorolube mull, which is assigned to a C=C stretch.

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(c) The NMR Spectrum (Fig. 1a) shows three singlet peaks of 1/1/2 relative intensities, at τ 4.84, 5.10 and 6.57 ppm, respectively. The peaks at 4.84 and 5.10 ppm are attributable to olefinic protons, and that at 6.57 ppm to aliphatic CH_2 .

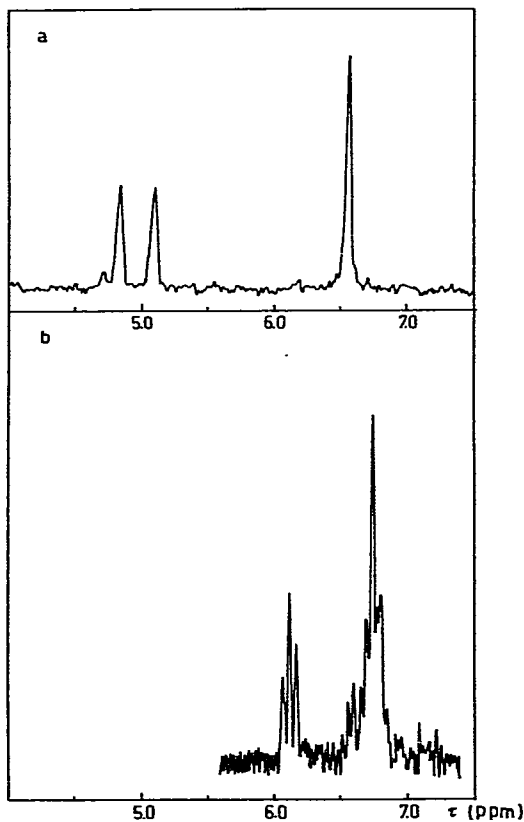


Fig. 1

Fig. 1. (a) NMR spectrum of σ -(2-Cl-allyl) $\text{Fe}(\text{CO})_2\text{NOP}(\text{C}_6\text{H}_5)_3$ in CS_2 solvent. (b) NMR spectrum of $(\sigma+\pi)$ -(2-Cl-allyl) $\text{Fe}(\text{CO})(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3$ in CS_2 solvent.

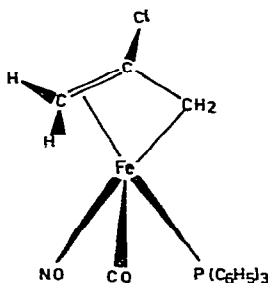
The σ allylic complex reacts further, yielding a complex for which the analysis and molecular weight are in agreement with formula (II). The mass spectrum shows a parent ion at the expected position.

Structure II is supported by the following evidence:

(a) One mole of CO gas is evolved for each mole of σ -allylic complex taken.
 (b) CO and NO stretching frequencies are observed at ν 1950 and 1708 cm^{-1} , respectively, in benzene. The band of the σ -allylic complex at 1598 cm^{-1} disappears.

(c) The NMR spectrum (Fig. 1b) is complicated by superimposition of a band of relative intensity 2 to a band of intensity 1, as shown the 3/1 ratio of band intensity. The band at τ 6.75 ppm can be attributed to a CH_2 group and the two complex multiplets at τ 6.75 ppm and τ 6.11 ppm to olefinic protons; their shape is similar to that of the

NMR spectrum of 2-bromo-1-propene³, but with a chemical shift lower by about 2 ppm, as observed for protons of ethylenic bonds involved in π -bonding with transition metals⁴. This suggests that the complex II contains a partially localized double bond, as has been observed for other complexes^{2,5} and theoretically supported⁶. Another explanation is that the π -allylic group is strongly distorted in such a way as to make the CH₂ groups asymmetric⁷.



II

In order to clarify the situation an X-ray structural analysis of II is being carried out.

The same course of reaction has been observed with other phosphinic ligands and other π -(X-allyl)Fe(CO)₂NO complexes (X = Br, CN).

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