Halogenobis(*N,N*-dialkyldithiocarbamato)iron(III) Complexes as Potential Catalysts for Halogen Addition Reactions to Alkenes

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In the presence of a catalytic amount of iron(III) halogenobisdithiocarbamates, the addition of molecular halogens to alkenes occurs rapidly to afford *cis*-addition products.

In the course of our investigations on the reactions of the halogenobis(*N,N*-dialkyldithiocarbamato)iron(III) complexes $[Fe(S_2CNR_2)_2X]$ with halogens, X'_2, we have demonstrated that binuclear iron(III) complexes formulated as $[Fe(S_2CNR_2)_2X]_2(\mu\text{-}X'_2)$ can be isolated.[1] The formation of these compounds is represented by the general reaction (1),

$$2[Fe(S_2CNR_2)_2X] + X'_2 \rightarrow 2[Fe(S_2CNR_2)_2X]\cdot X'_2 \quad (1)$$

where R = Me, Et, Pr^i; X = Cl, Br, I, and X' = Br, I.

According to the spectroscopic and magnetic data, as well as the thermogravimetric and conductivity measurements, the structure of these novel binuclear complexes corresponds to a loose dimeric association of two molecules of the five-co-ordinated halogenobisdithiocarbamates by means of a molecular halogen bridging unit.[1,2] In particular, the molecular halogen, X'_2, interacts weakly in an end-to-end fashion with the halide ligand, X^-, of the mononuclear complexes, forming an extended tetrameric bridging unit, $[X\text{-}X'\text{-}X'\text{-}X]^{2-}$, between the two paramagnetic centres. The structure of the binuclear complexes, depicted schematically in Figure 1, was also verified by an *X*-ray crystal structure determination of another derivative of this series containing the pyrrolidinyldithiocarbamato ligand.[3]

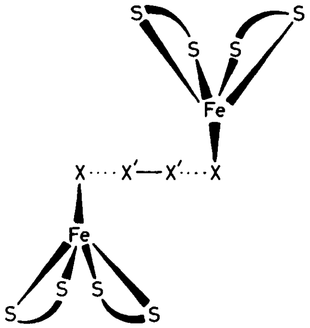


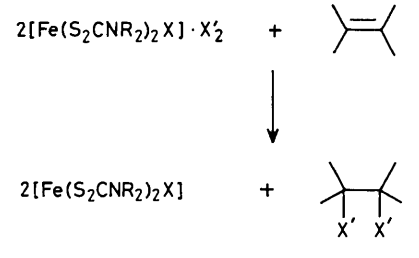
Figure 1. Structural model of the $[Fe(S_2CNR_2)_2X]_2(\mu\text{-}X'_2)$ complexes.

All the binuclear iron(III) complexes were found to react readily with alkenes such as ethylene and cyclohexene in CH_2Cl_2 solution, affording 1,2-addition products according to equation (2).

The halogenation reactions were carried out at room temperature and, in the case of ethylene, under 1 atmosphere pressure. The products of these reactions, which were obtained in almost quantitative yields, were isolated and identified by elemental analysis and spectroscopic measurements.

The halogenation of the alkenes, particularly iodination, using this method is of importance since the addition of iodine to an isolated double bond is difficult to realize. The ready addition of the iodine indicates that this molecule must be activated by association to the complexes, a necessary step in the addition reaction. In this respect the binuclear iron(III) complexes studied can be regarded as potential carriers of activated molecular halogens and hence could be the active species in homogeneous catalytic halogen addition reactions to alkenes in the presence of iron(III) halogenobisdithiocarbamates. We have found that under mild conditions (20 °C) and relatively low catalyst concentrations (10^{-2}—10^{-3} mol catalyst mol alkene^{-1}) the iron(III) halogenobisdithiocarbamates promote the ready addition of molecular halogens to alkenes in CH_2Cl_2 solutions affording the corresponding *cis*-addition products (Table 1).

Since iron(III) halogenobisdithiocarbamates readily react with molecular halogens to afford the bridging dimers,[1,4] and

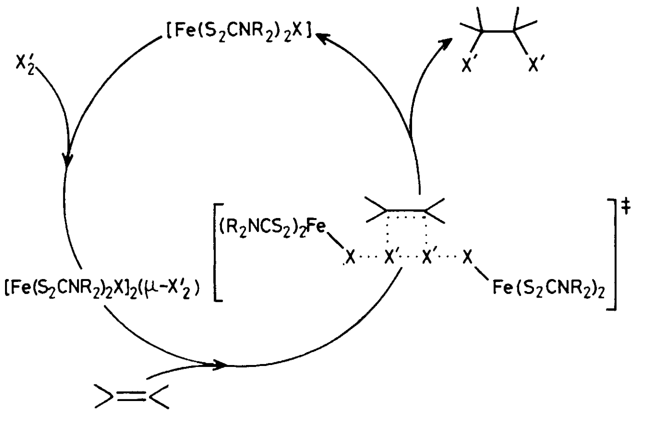


(2)

Table 1. Representative halogenation reactions of alkenes.[a]

Substrate	Halogen	Catalyst	Product (Yield)
Ethylene	I_2	$[Fe(S_2CNMe_2)_2Cl]$	CH_2ICH_2I (82%)
Ethylene	I_2	$[Fe(S_2CNMe_2)_2I]$	CH_2ICH_2I (93%)
Cyclohexene	I_2	$[Fe(S_2CNMe_2)_2I]$	1,2-cyclo-$C_6H_{10}I_2$ (79%)
Ethylene	I_2	$[Fe(S_2CNEt_2)_2Cl]$	CH_2ICH_2I (81%)
Ethylene	I_2	$[Fe(S_2CNPr^i{}_2)_2Cl]$	CH_2ICH_2I (83%)
Ethylene	Br_2	$[Fe(S_2CNPr^i{}_2)_2Cl]$	CH_2BrCH_2Br (93%)
Ethylene	I_2	$[Fe(S_2CNPr^i{}_2)_2Br]$	CH_2ICH_2I (88%)
Ethylene	Br_2	$[Fe(S_2CNPr^i{}_2)_2I]$	CH_2BrCH_2Br (98%)
Cyclohexene	Br_2	$[Fe(S_2CNPr^i{}_2)_2I]$	1,2-cyclo-$C_6H_{10}Br_2$ (80%)
Ethylene	I_2	$[Fe(S_2C\text{-}Pyrr)_2Cl]$[b]	no reaction
Ethylene	I_2	$[Fe(S_2C\text{-}Pyrr)_2Br]$[b]	no reaction
Ethylene	I_2	$[Fe(S_2C\text{-}Pyrr)_2I]$[b]	CH_2ICH_2I (82%)

[a] All reactions carried out at room temp. [b] Pyrr = Pyrrolidine.



Scheme 1

both species are catalytically active, the catalytic effect may be due to dimer formation. Therefore the catalytic cycle in Scheme 1, where the first step is the formation of the halogeno-bridged dimer, is proposed. These reactions should provide a valuable synthetic method for iodination.

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References

1 G. A. Katsoulos, C. A. Tsipis, and F. D. Vakoulis, *Can. J. Chem.*, in the press.

2 M. Lalia-Kantouri, G. A. Katsoulos, and F. D. Vakoulis, *J. Thermal Anal.*, in the press.

3 D. L. Kepert, C. L. Raston, A. H. White, and D. Petridis, *J. Chem. Soc., Dalton Trans.*, 1980, 1921.

4 F. D. Vakoulis, G. A. Katsoulos, and C. A. Tsipis, *Inorg. Chim. Acta*, in the press.