Dehydro-*NN′N″*-tricyclohexylguanidinohexacarbonyldi-iron(0), a Novel Carbene Generator

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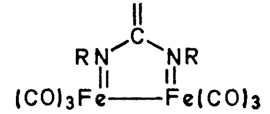
Summary The complex $Fe_2(dtg)(CO)_6$ reacts with $CHCl_3$ in the presence of EtOH to give products with olefins which show that dichlorocarbene has been added across the C–C double bond and/or inserted in C–H bonds.

WE report the synthesis and some reactions of dehydro-*NN′N″*-tricyclohexylguanidinohexacarbonyldi-iron(0), $Fe_2(dtg)(CO)_6$ (I), which is unexpectedly obtained as red crystals after refluxing $Fe(CO)_5$ with dicyclohexylcarbodiimide (DCC) in heptane for three days, followed by chromatography on a Florisil column.

Prime evidence for the formulation of the ligand as a dehydroguanidine is obtained from several sources. In the mass spectrum of (I) [*m/e* 583, $Fe_2C(NC_6H_{11})_3(CO)_6^+$; 415, $Fe_2C(NC_4H_{11})_3^+$; 303, $C(NC_6H_{11})_3^+$; 280, $Fe_2(CO)_6^+$; 112, Fe–Fe], all peaks corresponding to Fe-containing fragments show the correct isotopic distribution for Fe. Hydrolysis of (I) produces $C(NHC_6H_{11})_3^+Cl^-$, which upon conversion to the picrate is identical to an authentic sample of guanidinium picrate.[1] The i.r. spectrum of (I) shows $\nu(C{=}N)$ at 1676 cm^{-1}, whereas that of the corresponding guanidinium ion occurs at 1604 cm^{-1}, clearly showing reduction of the C=N bond order upon protonation. The above evidence, coupled with elemental analytical, molecular weight, and n.m.r. data, is consistent with the following structure for (I):



(I)

The N-atoms bonded to Fe must be three-electron donors in order to account for the observed diamagnetism of (I). The formation of (I) probably proceeds through a five-member ring intermediate, $Fe_2C(NC_6H_{11})_2$, where the C atom is a carbene. The intermediate then would attack a free DCC molecule to give (I), with liberation of cyclohexylisonitrile from DCC.

Complex (I) reacts with $CHCl_3$ containing 0·75% EtOH to evolve quantitatively and rapidly all six CO groups, giving the compound of empirical formula $[C(NHC_6H_{11})_3][FeCl_4]$ (II). Accompanying production of (II) is a mixture of a large amount of generally insoluble material which contains a relatively high ($>30\%$) amount of chlorine. This precipitate presumably contains the CCl_2 moiety after abstraction of HCl by (I).

It has been established that (I) reacts with EtOH first before generation of the carbene (or carbenoid). There is no reaction of (I) with pure $CHCl_3$, but (I) reacts with pure EtOH to produce a relatively unstable, EtOH-containing, iron carbonyl compound (III). When (III) is dissolved in EtOH-free $CHCl_3$, (II) is produced along with the insoluble precipitate.

The dichlorocarbene generated in the reaction may be trapped by olefins. Thus, when the above reaction with $CHCl_3$ is carried out in the presence of cyclohexene, three isomers of P^+ 164 (*i.e.* $C_7H_{10}Cl_2$) are obtained in about equal amounts. One of these has been identified as dichloronorcarane, where the expected addition across the double bond has occurred. However, the other two isomers apparently are the result of CCl_2 insertion into the C–H bonds of C-2 and C-3. This behaviour contrasts with that usually found for dihalogenocarbenes generated in the conventional manner; insertion reactions into single bonds are generally rare.[2] The insertion into C–H bonds parallels that found for dichlorocarbene generated from bromodichloromethylphenylmercury,[3] although dichlorocarbenes may be more conveniently formed as described in this work.

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[1] J. Bartos, *Bull. Soc. chim. France*, 1965, 3694.

[2] W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964, p. 160.

[3] D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1963, 85, 2667.