Preliminary communication

A MILD PHASE TRANSFER SYNTHESIS OF THE μ-METHYLENEBIS-(TETRACARBONYLIRON) COMPLEX μ-CH₂Fe₂(CO)₈ FROM IRON PENTACARBONYL AND DIBROMOMETHANE

GUY TANGUY,

Laboratoire de Chimie des Organométalliques (UA CNRS No. 415), Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex (France)

JEAN-CLAUDE CLEMENT and HERVÉ DES ABBAYES*

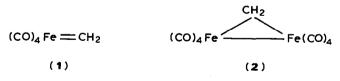
Laboratoire de Chimie Organique des Eléments de Transition (UA CNRS No. 322), Université de Bretagne Occidentale, Faculté des Sciences et Techniques, 6, avenue le Gorgeu, 29287 Brest Cedex (France)

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Summary

The bridged methylene complex μ -CH₂Fe₂(CO)₈ (2) can be readily generated by slowly introducing iron pentacarbonyl into a CH₂Br₂; H₂O/NaOH (1 *M*); Bu₄N⁺₂ SO₄²⁻ phase transfer system under a carbon monoxide atmosphere. The formation of 2 involves transient generation of the tetracarbonyl ferrate dianion Fe(CO)₄²⁻, followed by a fast reaction of this with dibromomethane.

Mononuclear and binuclear transition metal methylene complexes (such as 1 or 2) are of importance as models for the interaction of methylene groups with the metal surfaces which is thought to be involved in important heterogeneous catalytic reactions such as the Fischer-Tropsch process [1].



Complex 1, although theoretically capable of existence [2] is still unknown. Recently, Pettit and coworkers proposed a route to complex 2 involving reaction 1 [3,4].

$$(\operatorname{Et}_{4}\operatorname{N}^{+})_{2}\operatorname{Fe}_{2}(\operatorname{CO})_{8}^{2-} + \operatorname{CH}_{2}\operatorname{I}_{2} \xrightarrow{\operatorname{acetone}}_{0^{\circ}\operatorname{C}} 2 (60\% \text{ yield})$$
(1)

We report here a very simple and inexpensive synthesis of complex 2 involving

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reaction 2, which provides a further example of the application of phase transfer catalysis in metal carbonyl chemistry [5].

$$\operatorname{Fe}(\operatorname{CO})_{5} \xrightarrow[\operatorname{CH_2Br_2, 0^{\circ}C}]{\operatorname{CH_2Br_2, 0^{\circ}C}} 2 (76\% \text{ yield})$$

$$(2)$$

Iron pentacarbonyl (1 mmol) was added slowly (2 h) under CO atmosphere with vigorous stirring (1200 r.p.m.) to a mixture of CH_2Br_2 (10 ml) and a solution of NaOH (10 mmol) and $Bu_4N^+HSO_4^-$ (1 mmol) in H_2O (10 ml) maintained at 0°C. After 10 h further stirring, some of the formed 2 which is insoluble in the aqueous phase and sparingly soluble in dibromomethane, was separated from the liquid-liquid interface, and the remainder recovered from the dibromomethane solution by evaporation and subsequent extraction of the residue with hexane (overall yield 76% vs. Fe(CO)₅) [6].

The nature of the actual reactive species generated from iron pentacarbonyl in reaction 2 was deduced from the following experiments. When $HFe(CO)_4^-$ or $Fe_2(CO)_8^{2-}$ anions (generated as described in ref. 7 and 8) was used in reaction 2 in place of $Fe(CO)_5$, no complex 2 was formed. In contrast, use of $Na_2Fe(CO)_4$ [9] in place of $Fe(CO)_5$ led to transient production of complex 2, which disappeared after half an hour (detection by IR spectroscopy). Furthermore, a separate experiment carried out in homogeneous conditions revealed a conversion of the $Fe(CO)_4^{2-}$ anion to complex 2. Furthermore, a 1/1 ratio of carbonate anion to $Fe(CO)_5$ was found in the aqueous phase of reaction 2, in agreement with the stoichiometry of reaction 3, and this leads us to conclude that a mononuclear and not a binuclear anion is generated:

$$Fe(CO)_5 + 4OH^- \rightarrow Fe(CO)_4^{2-} + CO_3^{2-}$$
(3)

It appears that the very reactive anion $Fe(CO)_4^{2-}$ (3) is transiently generated from iron pentacarbonyl under the phase transfer conditions of reaction 2 [10]. Its reaction with dibromomethane is faster than its protonation (which would give the

SCHEME 1

 $HFe(CO)_4^{-}$ anion) or its coupling with unchanged $Fe(CO)_5$ (which would give the $Fe_2(CO)_8^{2-}$ anion [8]). Thus we believe (Scheme 1) that the anionic species 4 spontaneously loses a bromide anion to give the still unknown, and probably very reactive carbene complex 1. Support for the transient formation of this carbene comes from the fact that introduction of triphenylphosphine into reaction 2 leads to a 53% yield of the ylide adduct $(CO)_4Fe^ CH_2P(C_6H_5)_3$. Subsequent dimerization of the carbene would give the methylene complex 2 along with ethylene. In agreement with reaction 6 (Scheme 1), a significant amount of ethylene (14% yield based on Fe(CO)_5 used; detected by high resolution mass spectroscopy and analyzed by GC) was found in the atmosphere above reaction 2. Such dimerization of a methylene carbene complex to give a bridged methylene complex and an olefin, although unusual, is not unprecedented [11].

The success of the procedure represented by reaction 2 is due: (1) to the transient phase transfer production of the $Fe(CO)_4^{2-}$ anion which reacts rapidly with dibromomethane, (2) to the low transient concentration of this anion and the low solubility of complex 2 in dibromomethane, which prevent loss of 2 by reaction with the anion.

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