

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*

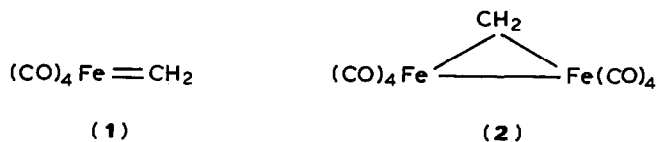
Laboratoire de Chimie Organique des Eléments de Transition (UA CNRS No. 322), Université de Bretagne Occidentale, Faculté des Sciences et Techniques, 6, avenue le Gorgeu, 29287 Brest Cedex (France)

(Received June 17th, 1986)

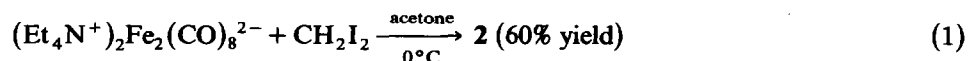
Summary

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⁺₂SO₄²⁻ 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].



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

HFe(CO)₄⁻ anion) or its coupling with unchanged Fe(CO)₅ (which would give the Fe₂(CO)₈²⁻ 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⁻CH₂P(C₆H₅)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)₄²⁻ 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.

References and notes

- 1 W.A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 21 (1982) 117.
- 2 A. Dedieu, S. Nakamura, *Nouv. J. Chim.*, 8 (1984) 317.
- 3 C.E. Summer Jr, P.E. Riley, R.D. Davies, R. Pettit, *J. Am. Chem. Soc.*, 102 (1980) 1725.
- 4 C.E. Summer Jr, J.A. Collier, R. Pettit, *Organometallics*, 1 (1982) 1350.
- 5 H. des Abbayes, Metal carbonyls in phase transfer catalysis (Review 102 ref.), *J. Israel Chemistry*, 26 (1985) 249-262.
- 6 Spectra data (IR, ¹H NMR, MS) fully consistent with those given ref. 4.
- 7 M.Y. Darensbourg, D.J. Darensbourg and H.L.C. Barros, *Inorg. Chem.*, 17 (1978) 297.
- 8 J.P. Collman, R.G. Finke, P.L. Matlock, R. Wahren, R.G. Komoto and J.I. Brauman, *J. Am. Chem. Soc.*, 100 (1978) 1119.
- 9 J.P. Collman, R.G. Finke, J.N. Cawse and J.I. Brauman, *J. Am. Chem. Soc.*, 99 (1977) 2515.
- 10 For a discussion of the phase transfer generation of the Fe(CO)₄²⁻ anion in a similar system see: B. Weinberger, G. Tanguy and H. des Abbayes, *J. Organomet. Chem.*, 280 (1985) C31.
- 11 H. Fischer, Z. Zeuner and K. Ackermann, *J. Chem. Soc. Chem. Commun.*, (1984) 684.