Journal of Organometallic Chemistry, 182 (1979) C61—C64
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

NOVEL REDUCTION OF η^5-CYCLOHEXADIENYL- AND η^5-CYCLOHEPTADIENYL-TRICARBONYLIRON CATION IN ACETONITRILE

B.R. REDDY and J.S. McKENNIS
Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074 (U.S.A.)
(Received August 6th, 1979)

Summary

η^5-Cyclohexadienyl- and η^5-cycloheptadienyl-tricarbonyliron tetrafluoroborate are reduced in refluxing acetonitrile to yield mixtures of 1,3-cyclohexadienetricarbonyliron and 5,5'-di-1,3-cyclohexadienehexacarbonyldiiron, and di-η^5-cycloheptadienyltetracarbonyldiiron and 5,5'-di-1,3-cycloheptadienehexacarbonyldiiron, respectively.

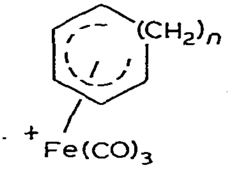
Of the numerous transition-metal π-complexed cations possessing extraordinary stability, the tricarbonyliron complex of the cyclohexadienyl cation (Ia) has been of special interest, theoretically as well as synthetically [1]. Cation Ia possesses sufficient stability towards water to be recrystallized from it, and yet on the other hand, conveniently reacts with nucleophiles stronger than water to afford addition products with attack usually occurring at carbon to give 5-substituted 1,3-cyclohexadienetricarbonyliron derivatives. Elaboration of this reaction owing to the ease of the liberation of the free ligand has proven synthetically useful. The formation of other products resulting from nucleophilic addition to the electronically deficient iron or the carbon of one of the carbonyl groups is known, but rare* (vide infra). We now report that cation Ia, as well as the η^5-cycloheptadienyl analogue (Ib), in the absence of added nucleophile is facilely reduced in acetonitrile (CH_3CN) at 90°C.

Heating solutions of Ia-BF_4 [2] (33—82 m*M*) in dry, degassed CH_3CN at reflux under nitrogen results in rapid dissipation of the IR carbonyl absorption bands of the cation Ia at 2100 and 2060 cm^{-1} and the appearance of new carbonyl absorption bands characteristic of a neutral tricarbonyliron complex at 2040 and 1970 cm^{-1}. Substantial decrease in the concentration of Ia was noticeable in ca. 10—15 minutes with complete disappearance of Ia occurring in ca. 1 h. After 1.5 h, work-up of the reaction mixture afforded a mixture of 1,3-

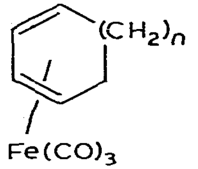
---

*Only iodide ion and phosphines have been reported [6] to ultimately give products with addition at iron and displacement of carbon monoxide. The reaction of azide ion with Ib to give addition at carbon is believed to initially involve attack at metal [16].

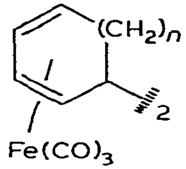
cyclohexadienetricarbonylrion (IIa) [3] and 5,5′-di-1,3-cyclohexadienehexacarbonyldiiron (IIIa) [4] in ca. 45% total yield.



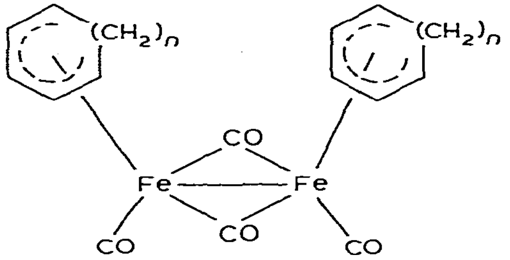
(Ia) $n = 1$
(Ib) $n = 2$



(IIa) $n = 1$
(IIb) $n = 2$



(IIIa) $n = 1$
(IIIb) $n = 2$



(IVa) $n = 1$
(IVb) $n = 2$

The ratio [IIa]/[IIIa] was concentration-dependent, ranging from a value of ca. 5.8 to ca. 2.6 over the concentration range 33 to 66 m*M*. The increase in the amount of dimer relative to parent complex with increase in concentration is consistent with the formation of parent complex by hydrogen abstraction from solvent rather than by intermolecular hydride transfer from one cation molecule to another.

Facile reduction of η^5-cycloheptadienyltricarbonyliron tetrafluoroborate (Ib-BF_4) [5] (31.3 m*M* in CH_3CN) also occurred in refluxing CH_3CN, but in contrast to the reaction of cation Ia, yielded the Fe—Fe dimer IVb (32%) [6] and only a small amount of C—C dimer IIIb [6] (~7%)*. The reaction of cation Ib with a reaction time of 4.5 h was dramatically slower than that of cation Ia**.

Reports of the reduction of π-complexed cations in the absence of traditional reducing agents such as sodium amalgam, zinc [3,6] and Grignard reagents [3] are few. However, the formation of small quantities (from "trace" to amounts representing 9.2% yield) of the reduction products IIa(b) and IIIa(b) has in a few cases been reported in the reactions of cation Ia and Ib with certain nucleophiles (e.g. amines) in polar solvents such as acetone or alcohols [3,6,9]. In striking contrast to these reports of low-yield reductive processes is the report

---

*A very small amount of what is probably 5,5′-di-1,3-cycloheptadienetricarbonyliron was also observed.

**Cation Ib also reacts slower than Ia with acetylacetone, the difference in rate being ascrived to predominantly a difference in $\Delta S^{\ddagger}$ [7].

of the heterogeneous reaction of cation Ib with sodium hydroxide in a mixed solvent system (acetone, ether, water, and pentane) to afford dimer IIIb in the remarkably high yield of 60% [10].

Reports of the formation of Fe—Fe dimer IVa and IVb in nucleophilic additions to Ia and Ib are rare. An 8% yield of dimer IVb has, however, been reported for the reaction of cation Ib and dicyclohexylamine [9a]. Additionally, we have observed the formation of varying amounts of dimers IVa and IVb from the reactions of cation Ia and Ib, respectively, with certain nucleophiles dependent upon the reaction conditions [11].

The mechanism(s) of the reduction of π-complexed cations in the presence of nucleophiles remains obscure, although, quite reasonably, it has been suggested that in the case of the nucleophile, hydroxide ion, nucleophilic attack might occur at the metal with ultimate oxidation of the metal and electron transfer to the complexed cation [10]. The reduction observed with other nucleophiles could be rationalized similarly, with electron transfer followed by hydrogen abstraction or dimerization. An alternative possibility would entail electron transfer directly from the nucleophile to the complex.

Similar rationalization of the reduction observed by us in the absence of added nucleophile is more difficult owing to the presence of ostensibly only two weakly nucleophilic species, $^-BF_4$ and CH_3CN. Although the equilibrium is unfavorable, the tetrafluoroborate ion ($^-BF_4$) potentially is a source of F^- which could react at metal and lead to electron transfer. Fluoride ion, however, reacts, albeit under different conditions, with cation Ia to give C-fluorination (viz., 5-fluoro-1,3-cyclohexadienetricarbonyliron) [12]. Furthermore, the tetraphenylborate salt of Ia also undergoes reduction to yield IIa and IIIa in relative amounts comparable to that obtained with Ia-BF_4.

Although a weak nucleophile, CH_3CN is known to attack the Group VI metal atom of the tropylium complexes $[C_7H_7M(CO)_3]^+ BF_4^-$ (M = Cr, Mo, W) leading to displacement of the stable species, tropylium ion [13]. Similar attack by CH_3CN at the iron atom of cation Ia could either liberate the cyclohexadienyl cation ($C_6H_7^+$) and an iron(0) species, $(CO)_3Fe(NCCH_3)_2$, or, alternatively, liberate the cyclohexadienyl radical ($C_6H_7^{\cdot}$) and a transient iron(I) species $[(CO)_3Fe(NCCH_3)_2]^+$. By analogy to the disproportionation of the iron carbonyls, $Fe_n(CO)_m$, in the presence of nitrogenous or oxygenous bases [14], either, or both, of the generated iron species could perhaps in the presence of CH_3CN undergo a similar oxidative-reductive process resulting ultimately in electron transfer to cation Ia. Similar rationalization could be offered for the reduction of Ib*.

Consistent with the importance of nucleophilic attack of CH_3CN at iron, the rate of reduction of cation Ia in the more weakly nucleophilic solvent, benzonitrile, is much less than that in CH_3CN. Similar reduction in rate for attack at metal by C_6H_5CN compared to that by CH_3CN has been observed in the reaction of these nitriles with the Group VI metal carbonyls [15].

---

*An alternative rationalization obviating nucleophilic attack by nitrile and instead invoking attack by an adventitiously present nucleophile is less attractive, but cannot be ruled out. The use of reagent grade acetonitrile that had neither been dried by distillation from P_2O_5 nor degassed had no perceptible effect.

Suggestive evidence for the existence of a free radical mechanism stems from the dramatic suppression of the reduction of cation Ia or Ib in the presence of oxygen. Continuous slow bubbling of oxygen through a solution of Ia-BF_4 in CH_3CN at reflux gave an 80% recovery of Ia-BF_4 after 5 h*. In the absence of oxygen, but otherwise under identical conditions reduction is complete in ca. 1 h. Similarly, treatment of a solution of Ib-BF_4 yielded 46% recovery of Ib-BF_4 after 5 h**.

References

1 Inter alia: (a) A.J. Birch and I.D. Jenkins, in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis, Academic Press, New York, 1976, Vol. 1, p. 1—82; (b) R. Hoffmann and P. Hoffmann, J. Amer. Chem. Soc., 98 (1976) 598; (c) D.W. Clark, M. Monshi and L.A.P. Kane-Maguire, J. Organometal. Chem., 107 (1976) C40.
2 E.O. Fischer and R.D. Fischer, Angew. Chem., 72 (1960) 919.
3 A.J. Birch, D.E. Cross, J. Lewis, D.A. White and S.B. Wild, J. Chem. Soc. A, (1968) 332.
4 ref. 3; A.J. Birch, I.D. Jenkins and A.J. Liepa, Tetrahedron Lett., (1975) 1723.
5 H.J. Dauben, Jr. and D.J. Bertelli, J. Amer. Chem. Soc., 83 (1961) 497.
6 M.A. Hashmi, J.D. Munro, P.L. Paulson and J.M. Williamson, J. Chem. Soc. A, (1967) 240.
7 L.A.P. Kane-Maguire, J. Chem. Soc. A, (1971) 1602.
8 J.D. Munro and P.L. Paulson, J. Chem. Soc., (1961) 3484.
9 Inter alia: (a) F.M. Chaudhari and P.L. Paulson, J. Organometal. Chem., 5 (1966) 73; (b) A.J. Birch, K.B. Chamberlin, M.A. Haas, D.J. Thompson, J. Chem. Soc. Perkin I, (1973) 1882; (c) K.E. Hine, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Commun., (1975) 81.
10 J.E. Mahler, D.H. Gibson and R. Pettit, J. Amer. Chem. Soc., 85 (1963) 3959.
11 Unpublished results.
12 B.F.G. Johnson, K.D. Karlin, J. Lewis and D.G. Parker, J. Organometal. Chem., 157 (1978) C67.
13 K.M. Al-Kathumi and L.A.P. Kane-Maguire, J. Chem. Soc. Dalton, (1973) 1683.
14 Inter alia: H. Behrens and H. Wakamatsu, Z. Anorg. Allgem. Chem., 320 (1963) 30; W. Hieber and E.H. Schubert, ibid., 338 (1965) 37; W. Hieber and G. Brendel, ibid., 289 (1957) 338.
15 K.M. Al-Kathumi and L.A.P. Kane-Maguire, J. Inorg. Nuclear Chem., 34 (1972) 3759.
16 D.A. Brown, S.K. Chawla and W.K. Glass, Inorg. Chim. Acta, 19 (1976) L31.

---

*No neutral π-complexes were detected although presumably any IIa and IIIa could have been destroyed under the reaction conditions.

**Only a very small amount of an unidentified neutral π-complex was isolated with the starting material.