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THE IMPORTANCE OF REACTION CONDITIONS IN THE USE OF THE (η^5-CYCLOHEXADIENYL)TRICARBONYLIRON CATION IN ORGANIC SYNTHESIS

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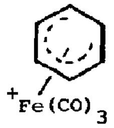
ABSTRACT:

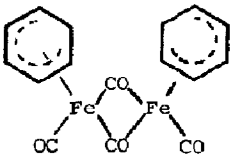
The reactions of $(\eta^5\text{-}C_6H_7)Fe(CO)_3^+BF_4^-$ with oxy anions in acetonitrile lead to variable yields of C_5-substituted (η^4-cyclohexadiene)tricarbonyliron complexes, as well as dimeric complexes, depending upon the anion and the reaction conditions.

The (η^5-cyclohexadienyl)tricarbonyliron cation I and its derivatives have found considerable use in organic synthesis owing to their extraordinary stability in polar solvents such as water and alcohols and their propensity to suffer nucleophilic attack selectively at the coordinated cyclohexadienyl ring to yield C_5-substituted (η^4-cyclohexadiene)tricarbonyliron complexes.[1] From these complexes the free organic ligand, suitable for further synthetic elaboration, can usually be oxidatively liberated in good to excellent yields. The list of nucleophiles which have been added to the coordinated cyclohexadienyl cation is extensive and includes, inter alia: alkoxides,[2a,b] dialkylcadmiums,[2c] activated aromatics,[2d] enolizable ketones,[2e,f] enamines,[2e,g] and heterocyclic amines such as adenine and guanine.[2h]

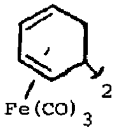
We now report that the success of nucleophilic addition of oxy anions such as alkoxides to complex I is dramatically dependent upon the choice of solvent, temperature and nucleophile. The reactions of I with the oxy anions, $^-OY, Y = H, CH_3, C(CH_3)_3, C_6H_5$, and $Si(CH_3)_3$, have been examined in acetonitrile and depending upon the temperature have afforded the 5-substituted (cyclohexadiene)tricarbonyliron complexes IVa-e in yields ranging from 95% to less than 1% (see Table).[5]



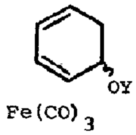
I



II



III



IV

IVa; $Y = H$
IVb; $Y = CH_3$
IVc; $Y = C(CH_3)_3$
IVd; $Y = C_6H_5$
IVe; $Y = Si(CH_3)_3$

Of special interest in these reactions is the formation of substantial amounts of the dimers, (di-η^5-cyclohexadienyl)tetracarbonyldiiron ("M-M dimer," II)[2a] and (5,5'-1,3-cyclohexadiene)hexacarbonyldiiron ("C-C dimer," III),[2b] esp. with $^-OC(CH_3)_3$ (rxn. 4). To our knowledge the formation of dimer II from the reaction of I with nucleophiles has not been previously observed.[3]

Although the formation of the C-C dimer III by the reaction of I with traditional reducing agents such Zn and Grignard reagents has been reported,[1,2b] only in a few cases,[6] and in low yields (from "trace" to a few percent), has similar reduction been observed with other nucleophiles.

TABLE

REACTIONS OF THE (η^5-CYCLOHEXADIENYL)TRICARBONYLIRON CATION (I)
WITH OXYGEN NUCLEOPHILES IN ACETONITRILE[a,b]

	$^-$Nu($^-$OY)	Temp.	II(%)	III(%)	IV(%)
1	OH	r.t.	24	15	12
2	OCH_3[c]	r.t.	25	19	1
3	OCH_3[c]	0°	9	7	--
4	$OC(CH_3)_3$	r.t.	51	6	1
5	$OC(CH_3)_3$	-45°	15	5	--
6	OC_6H_5[d]	r.t.	--	--	64
7	$OSi(CH_3)_3$	r.t.	26	11	42
8	$OSi(CH_3)_3$	-45°	5	--	95

a [I] = [Nucleophile] = 50-55 mM

b All reactions except rxn 6, were allowed to proceed to completion; reaction progress was monitored by I.R. There was no evidence for interconversion of products with time.[5]

c Sodium methoxide prepared from sodium + methanol.

d Potassium phenoxide prepared from potassium hydride and phenol. Reaction 36% complete after 8.5 h; yields based on amount of cation consumed.

Also surprising is the failure to observe nucleophilic addition to the C_6H_7 ring with either $^-OCH_3$ or $^-OC(CH_3)_3$. In contrast to this observation with acetonitrile as solvent, with the solvents, CH_3OH and $(CH_3)_3COH$, the conjugate bases, $^-OCH_3$ and $^-OC(CH_3)_3$, afforded the C_5-substitution products IVb and c, respectively. In the $^-OCH_3/CH_3OH$ reaction neither of the two dimers, II and III, was formed.[7] On the other hand, in the $^-OC(CH_3)_3/(CH_3)_3COH$ reaction, the dimers II and III, and the C_5-substituted complex IVc, were formed in the relative amounts: 2:0.75:1, respectively.

With a reduction in the nucleophilicity of the oxy anion by replacement of the electron-donating groups, Y=alkyl, with groups capable of electron withdrawal, Y=$Si(CH_3)_3$ and C_6H_5, substitution at C_5 became competitive with dimer formation (rxn. 6,7). In fact, with phenoxid ion (Y=C_6H_5) C_5-substitution giving IVd[9] occurred exclusively.

With regard to the effect of temperature on the reaction course, the limited data in the Table indicate a decrease in dimer formation (M-M and C-C) with a decrease in temperature. In the case of Y=Si$(CH_3)_3$, the decrease in dimer production was accompanied by a concomitant incease in substitution at C_5. Strikingly, reaction at -45° (rxn. 8) led to the production of complex IVe in virtually quantitative yield.[10]

The mechanism of the formation of the M-M and C-C dimers from the reaction of I with oxy anions, although unclear at the present time, is probably a result of initial nucleophilic attack at metal or at carbonyl, followed by either homolytic or heterolytic bond cleavage.[11] Both the ruthenium and osmium analogues of I react with methoxide ion in methanol at a metal carbonyl to yield isolatable metal ester species.[12] Such esters, however, fragment to afford C_5-substituted complexes rather than dimers. As a consequence, for the formation of the dimers II and III, we presently favor a pathway involving attack at metal. Consistent with this leaning, frontier orbital calculations of I suggest that if nucleophilic addition is frontier controlled, attack should occur preferentially at metal.[13]

The operation of a free radical pathway in the formation of the dimers II and III is suggested by the ability to arrest their formation by bubbling oxygen through a solution of I and sodium methoxide in acetonitrile. Most interesting, however, is that with the introduction of copious amounts of O_2, attack at the cyclohexadienyl ring by methoxide ion now becomes the predominant, if not the exclusive, mode of attack affording (5-methoxy-1,3-cyclohexadiene)tricarbonyliron (IVb)[14,15] in 47% yield, as compared to 1% yield in the absence of appreciable amounts of oxygen.[16]

The data reported here clearly indicate the importance of the appropriate choice of reaction conditions to the success of synthetic endeavors involving the preparation of C_5-substituted cyclohexadiene complexes from the reactions of I with oxygen nucleophiles. Delineation of the dependency of the success upon factors such as the solvent, its oxygen content, the nucleophile, and the temperature is being pursued.

REFERENCES AND NOTES

1. For a review, see: A. J. Birch and I. D. Jenkins, in H. Alper (Ed,) "Transition Metal Organometallics in Organic Synthesis," Academic Press, New York, 1976, Vol. 1, pp 1-82.
2. (a) M. A. Hashmi, J. D. Munro, P. L. Paulson, and J. M. Williamson, J. Chem. Soc. A, 240, (1967).
    - (b) A. J. Birch, D. E. Cross, J. Lewis, D. A. White and S. B. Wild, ibid, 332 (1968).
    - (c) A. J. Birch and A. J. Pearson, Tetrahedron Lett., 2379 (1975).
    - (d) L. A. P. Kane-Maquire and C. A. Mansfield, Chem. Commun., 540, (1973); B. R. Reddy and J. S. McKennis, J. Amer. Chem. Soc., 101, 7730 (1979).
    - (e) A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, J. Chem. Soc., Perkin Trans. 1, 1882 (1973).
    - (f) A. J. Birch, K. B. Chamberlain, and D. J. Thompson, ibid, 1900 (1973).
    - (g) R. E. Ireland, G. G. Brown, R. H. Stainford and T. C. McKenzie, J. Org. Chem., 39, 51 (1974).
    - (h) F. Franke and I. D. Jenkins, Aust. J. Chem., 31, 595 (1978).
3. The formation of the analogous η^5-cycloheptadienyl M-M dimer in 32 and 8% yield has been observed upon the reaction of the (η^5-cycloheptadienyl)tricarbonyliron cation in refluxing acetonitrile in the absence of added nucleophile,[4] and in refluxing acetone with dicyclohexylamine [F. M. Chandhari and P. L. Paulson, J. Organometal. Chem, 5, 73 (1966)].

4. B. R. Reddy and J. S. McKennis, J. Organometal. Chem., 182, C61 (1979).

5. In addition to the indicated products, varying amounts of IVa and (dicyclohexadienyl ether hexacarbonyldiiron were obtained despite the care exercised to exclude moisture (or hydroxide ion) and oxygen by the use of dried and degassed CH_3CN. No attempt was made to identify products other than organometallics.

6. *e.g.*, A. J. Birch, I. D. Jenkins and A. J. Liepa, Tetrahedron Lett., 1723 (1975).

7. Our $^-OCH_3/CH_3OH$ reaction yielded exclusively *exo* IVb, in agreement with an eariler report. The reaction of I with CH_3OH itself is reported to give a mixture of *exo* and *endo* product, as well as a small amount of (1,3-cyclohexadiene)tricarbonyliron [K. E. Hine, B. F. G. Johnson, and J. Lewis, J. Chem. Soc., Chem. Commun., 81 (1975)].

8. The stereochemistry about C_5 for IVc is not clear, but the similarity of its ^1H- and ^{13}C-nmr spectra with that of the *exo*-complex IVb, and the bulk of $(CH_3)_3CO^-$ would suggest *exo* substitution.

9. N. S. Nametkin, S. P. Gubin, V. I. Ivanov, and V. D. Tyurin, Izv, Akad. Nauk USSR, Ser. Khim. 458, (1974).

10. Reaction of IVe with $Ph_3C^+BF_4^-$ gave a 88% yield of I suggesting that the subsitution is predominately, if not exclusively *exo*.

11. In the reduction of I to (η^4-cyclohexadiene)tricarbonyliron and the C-C dimer III by heating solutions of I in acetonitrile at 90° *in the absence of added nucleophile*, we were similarly led to suggest nucleophilic attack by the solvent at the metal followed by disproportionation and ultimate electron transfer.[4]

12. E. G. Bryan, A. L. Burrows, B. F. G. Johnson, J. Lewis and G. Mario Schiavon, J. Organometal Chem., 129, C19 (1977); R. F. H. Cowles, B. F. G. Johnson, P. L. Josty, and J. Lewis , J. Chem. Soc., Chem. Commun., 392 (1969).

13. D. A. Brown, J. P. Chester and N. J. Fitzpatrick, J. Organometal. Chem., 155, C21 (1978).

14. The only other organometallic species observed was an unidentified material obtained in trace quantity.

15. The disposition of the methoxyl group was exclusively *exo*, suggestive of direct attack at the ring.

16. Similar suppression of the reductive conversion of I to III and (η^4-cyclohexadiene)tricarbonyliron in refluxing CH_3CN in the absence of added nucleophile was also achieved by a continuous introduction of O_2.

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