

REACTIONS OF FERROCENYLACETYLENES WITH METAL CARBONYLS¹

M. Rosenblum, N. Brawn, S.J., and B. King

Edison-Lecks Laboratories, Brandeis University
Waltham, Massachusetts 02154

(Received in USA 25 May 1967)

Acetylenes enter into reactions with metal carbonyls and various organometallic complexes, affording a great diversity of both organometallic and organic products, some of considerable structural and theoretical interest.² The recent development of a simple and efficient synthetic route to ferrocenylacetylenes³ prompted us to examine the analogous reactions of these substances, with a view toward preparing sterically crowded polyferrocenyl condensation products. The results of these experiments are now reported. The physical properties and relevant spectral data for new compounds isolated in these reactions are summarized in Table I.

Treatment of ferrocenylacetylene (1a) with dicobalt octacarbonyl in dioxane solution at reflux temperature for 3 hours gave 1,2,4-triferrocenylbenzene (2) in 64% yield. Its structure follows from its elemental analysis and its oxidation by permanganate to trimellitic acid. Similar results have recently been reported by Schlögl and Soukup.⁴ Attempts to convert this substance to 1,3,5-triferrocenylbenzene (3) in the presence of aluminum trichloride or toluene sulfonic acid were without success. The symmetrical benzene derivative was however isolated from preparations of β -chlorovinylferrocene, and may also be prepared by acid catalyzed trimerization of acetylferrocene.^{4,5}

When a mixture of ferrocenylacetylene and diferrocenylacetylene (1b) were treated with dicobalt octacarbonyl, trans-diferrocenylethylene, m.p. 275-276°, (lit.⁶ 265-267°), and (2) were the only isolable products.

Diferrocenylacetylene reacts readily with the carbonyl at room temperature in dioxane solution to give the green complex (4), which is very readily oxidized in solution to

give ferrocil, FcCOCOFc , (5)⁷, m.p. 192-194°, and on treatment with diferrocenylacetylene in refluxing dioxane affords the blue tetraferrocenylcyclopentadienone (6), (parent peak m/e 816) in 81% yield. Attempts to induce this substance to enter into a Diels-Alder reaction with diferrocenylacetylene at elevated temperatures have thus far been without success. However the ketone reacts with dimethyl acetylenedicarboxylate in refluxing o-dichlorobenzene to give dimethyl tetraferrocenylphthalate (7) in 55% yield. The ketone reacts readily with phenyllithium affording a good yield of the corresponding cyclopentadienol (8), but no reaction occurs under similar or more drastic reaction conditions with ferrocenyllithium. The resistance of (6) to reactions with diferrocenylacetylene and ferrocenyllithium is most plausibly attributed to the very great steric crowding which would be expected to accompany the formation of the normal products of these reactions.

The cyclopentadienone (6) is stable in the crystalline state, but its solutions rapidly undergo decomposition in air affording diferrocenylacetylene, tetraferrocenylbut-2-ene-1,4-dione (9) (parent peak m/e 820), tetraferrocenyl-2-pyrone (10) (parent peak m/e 832), and the cyclopentenone (11) (parent peak m/e 818).⁸ The latter substance is also formed in the reaction of diferrocenylacetylene with molybdenum hexacarbonyl in diglyme solution and is the major product from the reaction of the acetylene with iron pentacarbonyl at high temperatures.

Diferrocenylacetylene reacts with triiron dodecacarbonyl in refluxing benzene solution yielding at least five substances. The principal product of this reaction is (12), accompanied by small amounts of (13) and a trace of (14). The latter complex is also obtained by photolyzing a benzene solution of (6) and iron pentacarbonyl, by treatment of (12) with triphenylphosphine in refluxing xylene, or by heating (13) at 180° for 60 hours in xylene solution in a sealed tube. Similar transformation of the phenyl analogs of 6, 12 and 13 have been reported by Schrauzer⁹ and by Hübel and Braye.¹⁰ In addition, two other substances, one violet (dec. 174°, I.R. 4.92, 5.00, 5.04, 5.09 μ ; nmr τ 5.82 (singlet), 5.60, 5.23 (triplets), rel. intensities 5:2:2; mass spec. principle peak m/e 394) and a second black (I.R. 4.90, 4.99, 5.10, 5.47 μ ; nmr τ 5.68, 6.39 (singlets), 5.79 (multiplet, rel. intensities 5:5:8) were isolated in very low yield. These are tentatively assigned structures (15) and (16) on the basis of their spectral properties

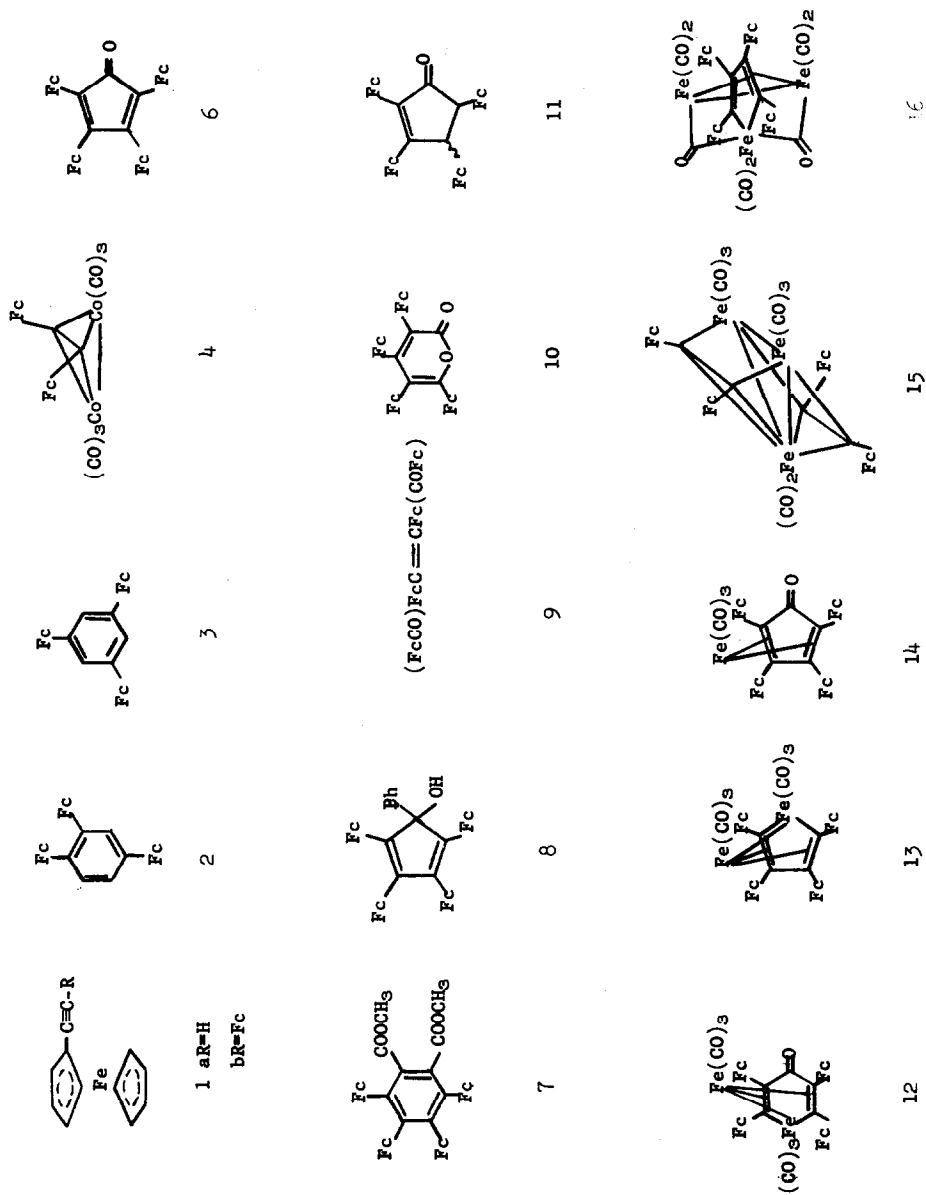
and by analogy with similar compounds obtained in the reaction of diphenylacetylene with iron carbonyls,¹⁰ the structures of which have recently been determined by x-ray diffraction studies.¹¹

Table I

Compound ^a	Color	m.p.	I.R. (μ)	N.M.R. (τ) ^b
2	orange	245-248	--	5.95(5), 5.90(5) 5.85(5)
3	orange	264-266	--	5.87(15)
4	green	151-153	4.80, 4.90, 5.00	5.76(10)
6	blue	263-265	5.90	6.00(10) 5.78(10)
7	red	258-260	5.76	6.13(10) 5.83(10)
8	orange	226-228	2.80	6.03(20)
9	blue	>300	5.75, 5.90, 6.26	5.87(10) 5.78(10)
10	maroon	262-264	5.83, 6.19	6.10(5), 6.00(5) 5.78(5), 5.67(5)
11	orange	237-239	5.91, 6.30	5.93(5), 5.83(5) 5.76(5), 5.73(5)
12	green	250(d)	4.83, 4.92, 5.00 5.97	5.81(10), 5.65(10)
13	red	215(d)	4.87, 4.98, 5.06 5.29	6.08(10), 5.75(10)
14	orange	110(d)	4.86, 4.99, 5.05 5.98	6.05(10), 5.54(10)

a. Acceptable analyses were obtained for all compounds listed

b. Chemical shifts and integrated areas of unsubstituted cyclopentadienyl ring proton absorptions. The number of these characteristic absorptions provides a very useful indication of the minimum number of structurally nonequivalent ferrocenyl substituents present in each compound. All spectra were determined in CDCl_3 solution.



Fc = ferrocenyl, C₁₀H₉Fe

References

1. This work was supported by a grant and by the award of a postdoctoral fellowship to B.K. from the National Institutes of Health, U.S. Public Health Service and by the National Science Foundation through the award of predoctoral fellowships to N.B.
2. E. O. Fischer and H. Weiner, "Metal Complexes", Elsevier Publishing Co., New York, 1966.
3. K. Schlögl and W. Steyrer, Monatsh Chem., 96, 1520 (1965). M. Rosenblum, N. Brawn, J. Papenmeier and M. Applebaum, J. Organometal Chem., 6, 173 (1966). M. O. Rausch, A. Siegel and L. P. Klemann, J. Org. Chem., 31, 2703 (1966).
4. K. Schlögl and H. Soukup, Tetrahedron Letters, 13, 1181 (1967).
5. The mass spectrum of 2 exhibits a very prominent peak at m/e 394 for Fc_2C_2 which is absent in the spectrum of 3.
6. P. L. Pauson and W. E. Watts, J. Chem. Soc., 2990 (1963).
7. K. L. Rinehart, A. F. Ellis, C. J. Michejda and P. A. Kittle, J. Am. Chem. Soc., 82, 4112 (1962).
8. Similar oxidations of arylated cyclopentadienones are known. M. A. Ogliaruso, M. G. Romanelli and E. I. Becker, Chem. Revs., 65, 261 (1965).
9. G. N. Schrauzer, J. Am. Chem. Soc., 81, 5307 (1959).
10. W. Hübel and E. H. Braye, J. Inorg. Nucl. Chem., 10, 250 (1959).
11. R. P. Dodge and V. Schomaker, J. Organometal. Chem., 3, 274 (1965).