Tetrahedron Letters,Vol.25,No.47,pp 5419-5422,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

THE SYNTHESIS OF TRICARBONYL IRON COMPLEXES OF 6,7-DIMETHYLENECYCLOHEPTADIENIUM ION AND TROPOQUINODIMETHANES

Noboru Morita, Mitsunori Oda, and Toyonobu Asao

Department of Chemistry, College of General Education
Tohonu University, Kawauchi, Sendai 980, Japan

Summary: The synthesis and spectroscopic characterization of the title complexes correspond to isoelectronic system of o-quinodimethane complex are described.

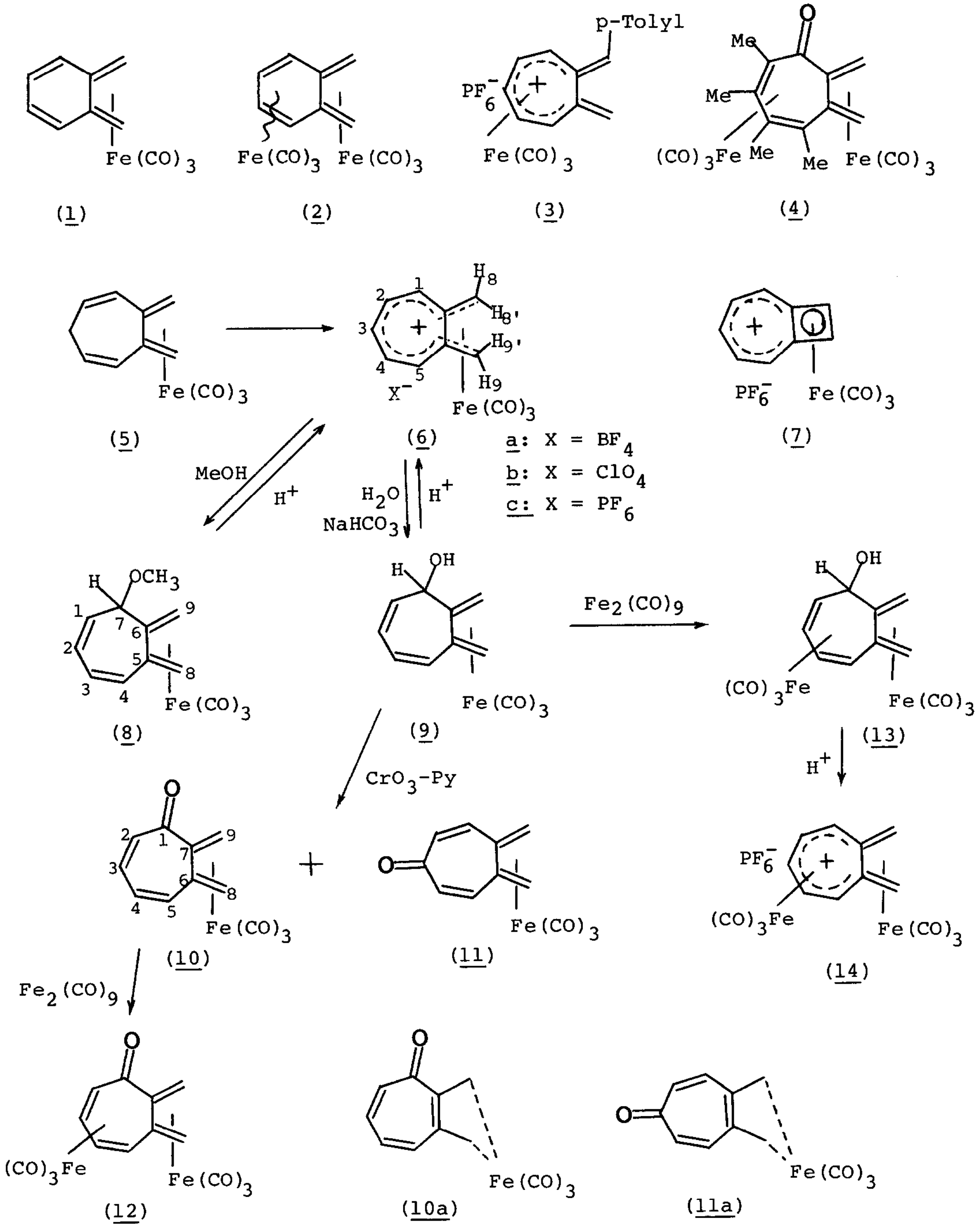
Quinodimethanes are very interesting system in theoretical and synthetic chemistry.$^{1)}$ Although o-quinodimethane is too reactive to isolate, the compound is proven to exist as reactive intermediate and can be isolated as tricarbonyl iron complexes (e.g. 1, 2).$^{2)}$ As an isoelectronic and related system of the quinodimethane complexes, 6-p-tolylmethylene-7-methylenecycloheptadienium tricarbonyl iron hexafluorophosphate (3)$^{3)}$ and 2,3,4,5-tetramethyl-6,7-dimethylenecyclohepta-2,4-dienone hexacarbonyl diiron (4)$^{4)}$ have been synthesized.

Here we will describe the synthesis and characterization of new isoelectronic and related compounds of the quinodimethane complexes; tricarbonyl iron complexes of 6,7-dimethylenecycloheptadienium ion and tropoquinodimethanes (6,7-dimethylenecyclohepta-2,4-dienone and 4,5-dimethylenecyclohepta-2,6-dienone).

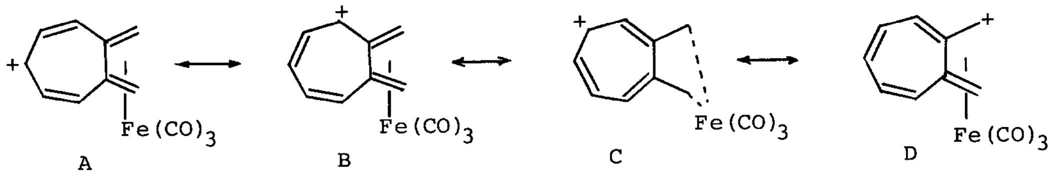
Hydrogen abstraction of 3,4-dimethylene-1,5-cycloheptadiene tricarbonyl iron (5)$^{5)}$ with trityl tetrafluoroborate and perchlorate afforded the corresponding cations (6a) [86% yield, violet crystals, mp 130°C; $\lambda_{max}^{CF_3COOH}$ nm (log ε): 522 (3.68) and 713 (2.20)] and (6b) [86% yield, violet crystals, mp 75-79°C (explosive)], respectively. There is a remarkable contrast in color of 6 with 1-5η-complex (3), yellow, but very similar with cyclobutatropylium tricarbonyl iron hexafluorophosphate (7),$^{6)}$ purple black.

^{1}H-NMR of 6a in CF_3COOD displays signals at δ 8.61 (t, J=10Hz, H-3), 8.46

(d, J=10, H-1,5), 8.12 (t, J=10, H-2,4), 3.34 (d, J=3.5, H-8,9), and 1.22 (d, J=3.5, H-8',9') which indicate that plus charge delocalizes all over the π-system, because the ring and the exomethylene protons of 6 resonate at lower field of 2.3-2.7 and 1.0-1.5 ppm, respectively, than those of 5. From these



chemical shifts, the order of deshielding of the protons is H-3 > H-1,5 > H-2,4 > H-8,9, which reflects the positive charge density at the corresponding atoms. Canonical forms A and B should contribute to a greater extent than C and D to the cation (6).



When the cation (6) was dissolved in methanol and in saturated aqueous NaHCO$_3$ solution, color changes to yellow, from which methoxy (8) and hydroxy derivatives (9) were obtained in the yields of 76.4% and 87.2%, respectively.7) On the contrary, when both compounds (8) and (9) were dissolved in CF$_3$COOH, cation (6) was immediately reformed and crystalline hexafluorophosphate (6c) was obtained by treatment of the solution with HPF$_6$ as violet crystals, mp 140-142°C (d).

Oxidation of the hydroxy compound (9) with CrO$_3$-pyridine in CH$_2$Cl$_2$ afforded a mixture of two tropoquinodimethane complexes (10) and (11) as thermally stable crystals in the yields of 59% and 16.3%, respectively. 10; Pale yellow crystals, mp 34-36°C; MS: 272(M$^+$), 244, 216, 188(100); λ_{max}^{EtOH} nm (log ε): 212^{sh}(4.43), 250^{sh}(4.04), and 395 (3.39); ^{1}H-NMR(CCl$_4$): δ 6.48-7.23 (m, 4H), 2.96 (d, J=2, H-9), 2.18 (d, J=3, H-8), 0.44 (d, J=3, H-8'), and 0.11 (d, J=2, H-9'). 11; Pale yellow crystals, mp 121-124°C; MS: 272(M$^+$), 244, 216(100), 188; λ_{max}^{EtOH}: 229 (4.37), 242^{sh}(4.35), and 378 (3.59); ^{1}H-NMR(CCl$_4$): 6.76 (d, J=12, H-3,6), 6.46 (d, J=12, H-2,7), 2.06 (d, J=3, H-8,9), and 0.26 (d, J=3, H-8',9').

Chemical shifts of seven membered ring protons of 11 are similar to those of tricarbonyl iron complex of cyclobuta[d]tropone,6) and electronic spectra of 10 and 11 show maxima at fairly longer wave lengthes. These facts may indicate contributions to a certain extent of 10a and 11a to 10 and 11, respectively, as has been observed in diene tricarbonyl iron complexes.8)

Oxidative removal of tricarbonyl iron from 10 and 11 was attempted to get parent tropoquinodimethanes, but any clear compounds could not be isolated.

Compound (10) was reacted with Fe$_2$(CO)$_9$ to give hexacarbonyl diiron complex (12) in 85.5% yield.9) It is interesting that the complex (12) is yellow in contrast to brick-red for tetramethyl derivative (4). This presumably be attributed to the difference of coordination of two irons, and the direction in 12 is considered to be trans and 4 is cis.[10)]

The reaction of 8 with $Fe_2(CO)_9$ also afforded hexacarbonyl diiron complex (13) in 64.8% yield,[11)] which was treated with HPF_6 to give 6,7-dimethylenecycloheptadienium hexacarbonyl diiron complex (14) as brown solid, mp decompose around 110°C. Since the complex (14) is not stable, the characterization is not complete at the present stage.

References and Notes

1) C. R. Flynn and J. Michl, J. Am. Chem. Soc., 96, 3280 (1974); J. J. McCullough, Acc. Chem. Res., 13, 270 (1980).
2) W. R. Roth and J. D. Meier, Tetrahedron Lett., 2053 (1967); R. Victor and R. Ben-Shoshan, J. Organometallic Chem., 80 C1 (1974).
3) B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, J. Chem. Sic., Dalton Trans, 2076 (1972).
4) E. O. Fischer, C. G. Kreiter, and W. Berngruber, J. Organometallic Chem., 12, 39 (1968).
5) M. Oda, N. Morita, and T. Asao, Chem. Lett., 397 (1981).
6) M. B. Stringer and D. Wage, Tetrahedron Lett., 65 (1977).
7) 8; Pale yellow crystals, mp 82-83°C; MS: 288(M^+), 260, 232 204, 174, 148 (100); λ_{max}^{EtOH}: 265^{sh}, 320^{sh}; ^1H-NMR($CDCl_3$): 6.58 (m, H-3,4), 6.25 (d,m, J=10, H-2), 5.87 (d,d, J=10,4, H-1), 4.00 (d,m, J=4, H-7), 3.44 (s, Me), 2.68 (d, J=2, H-9), 1.77 (d, J=3, H-8), 0.12 (d, J=2, H-9'), and -0.14 (d, J=3, H-8'). 9; Pale yellow crystals, mp 109-111°C; MS: 274(M^+), 257, 246, 229, 218, 210, 190, 173, 117(100); λ_{max}^{EtOH}: 260^{sh}(3.88), 320^{sh}(3.31); ^1H-NMR($CDCl_3$): 6.53 (m, H-3,4), 6.17 (d,m, J=10, H-2), 5.85 (d,d, J=10,4, H-1), 4.40 (bs, H-7), 2.63 (d, J=2, H-9), 2.42 (bs, OH), 1.80 (d, J=3, H-8), 0.12 (m, H-9'), and -0.11 (d, J=3, H-8').
8) E. A. K. von Gustorf, F. -W. Grevels, and I. Fischler, "The Organic Chemistry of Iron," Vol. I, Academic Press, New York (1978), p 17.
9) 12; Pale yellow crystals, mp 170-172°C (d); MS: 412(M^+), 384, 356, 328, 300 (100); λ_{max}^{EtOH}: 333 (3.73); ^1H-NMR($CDCl_3$): 6.20 (m, H-3,4), 3.51 (d,d, J=8,1, H-2), 3.17 (d,d, J=7, 1.5, H-5), 2.04 (d, J=3, H-9), 2.01 (d, J=2, H-8), 0.54 (d, J=2, H-8'), and -0.13 (d, J=3, H-9').
10) Cis oriented complex of o-quinodimethane hexacarbonyl diiron shows deeper color than trans one; see ref. 2).
11) 13; Yellow crystals, mp 101-102.5°C (d); ^1H-NMR($CDCl_3$): 5.56 (m, H-2,3), 4.27 (d,d, J=6,4, H-7), 3.85 (m, H-1), 3.22 (d, J=7, H-4), 2.18 (d, J=6, OH), 2.00 (d, J=2, H-9), 1.61, (d, J=3, H-8), 0.23 (d, J=2, H-9'), and -0.01 (d, J=3, H-8').

(Received in Japan 16 August 1984)