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Organometallic Chemistry of the Transition Metals. V. New Iron Carbonyl Complexes of Cycloöctatriene Derivatives[1]

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Reaction of $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ with cycloöctatrienone yields a mixture of yellow $C_8H_8OFe(CO)_3$ and orange $C_8H_8OFe_2(CO)_6$. A red-orange compound $C_8H_{10}Fe_2(CO)_6$ has been isolated from the reaction between triiron dodecacarbonyl and cycloöctatriene. From the reaction between $C_8H_{10}Fe_2(CO)_6$ and salts of $(C_6H_5)_3C^+$, salts of an orange cation apparently $[C_8H_9Fe_2(CO)_6]^+$ may be isolated.

A. Cycloöctatrienone Complexes

Recently several interesting complexes have been isolated from the reaction between cycloöctatriene and various metal carbonyl derivatives. Thus the hexacarbonyls of chromium, molybdenum, and tungsten react with a mixture of 1,3,5-cycloöctatriene and 1,3,6-cycloöctatriene to give the red complexes 1,3,5-$C_8H_{10}M(CO)_3$ (M = Cr and Mo)[2,3] and the yellow complexes 1,3,6-$(C_8H_{10})_2M(CO)_2$ (M = Mo and W).[2] From the reaction between the various iron carbonyls and a mixture of the two isomeric cycloöctatrienes the following three compounds have been isolated: yellow-orange bicyclo[4,2,0]octadieneiron tricarbonyl,[2,4,5] yellow 1,3,5-cycloöctatrieneiron tricarbonyl,[5] and a red-orange compound of apparent composition $C_9H_{12}Fe_2(CO)_6$.[2] The cobalt compounds $[C_8H_{10}Co(CO)_2]_2$[6] and $C_5H_5CoC_8H_{10}$[7,7a] have also been isolated.

The existence of these metal complexes of cyclooctatriene made of interest an investigation of the reaction between 1,3,5-cycloöctatrienone[8] and various metal carbonyl derivatives in order to determine the effect on the nature of the complexes formed of the electronegative ketonic oxygen atom bonded to one of the carbon atoms of the eight-membered ring.

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 double-beam machine with NaCl optics. In addition, the metal carbonyl regions of the infrared spectra were taken in Halocarbon oil mulls and recorded on a Perkin-Elmer Model 112 single-beam machine with CaF_2 optics. Proton n.m.r. spectra were taken on a Varian Associates Model A-60 machine. Hexamethyldisiloxane was used as an internal standard. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany, and Schwarzkopf Microanalytical Laboratory, Woodside, New York. Melting points were taken in capillaries and are uncorrected.

Cycloöctatrienone was prepared from cycloöctatetraene by the procedure of Cope, *et al.*[8]

Reaction between Triiron Dodecacarbonyl and Cycloöctatrienone.—A mixture of 2.8 ml. (22 mmoles) of cycloöctatrienone, 7.2 g. (14.3 mmoles) of triiron dodecacarbonyl (or an equivalent amount of $Fe_2(CO)_9$), and 100 ml. of thiophene-free benzene was refluxed 7 hr. under nitrogen with magnetic stirring, the green color of the triiron dodecacarbonyl becoming orange. After cooling to room temperature the reaction mixture was filtered by gravity. Solvent was removed from the orange-brown filtrate at ~30 mm. The liquid residue was dissolved in ~50 ml. of thiophene-free benzene and chromatographed on a 2 × 60 cm. alumina column. The chromatogram was developed with benzene. Two principal bands were observed: a yellow-orange band due to $C_8H_8OFe(CO)_3$ and an orange band due to $C_8H_8OFe_2(CO)_6$. These were eluted with benzene.

The eluate from the yellow-orange band of $C_8H_8OFe(CO)_3$ left a yellow-orange oil on evaporation at 30 mm. A crystalline product was isolated by treating this oil with ~15 ml. of methanol and cooling overnight in a −78° bath. The yellow crystals which separated were filtered and purified further by sublimation at 70–90° (0.25 mm.) to give 0.75 g. (13% yield) of yellow crystalline $C_8H_8OFe(CO)_3$, m.p. 103°.

The red-orange eluate from the orange band of $C_8H_8OFe_2(CO)_6$ left orange crystals on evaporation. These were heated in a sublimation apparatus to 90° (0.1 mm.) to drive off oily impurities. The residue was then recrystallized once from a mixture of dichloromethane and hexane to give 0.20 g. (2.4% yield) of orange crystalline $C_8H_8OFe_2(CO)_6$, m.p. 155°.

Properties of $C_8H_8OFe(CO)_3$.—Yellow air-stable volatile crystals with a sweet odor.

Anal. Calcd. for $C_{11}H_8FeO_4$: C, 50.8; H, 3.1; Fe, 21.5; O, 24.6; mol. wt., 260. Found (duplicate values are on two independent preparations): C, 51.0, 50.8; H, 3.2, 3.4; Fe, 21.5, 21.9; O, 24.6; mol. wt., 266.

Infrared Spectrum.—Carbon–hydrogen band at 2960 (vvw) cm.$^{-1}$; metal carbonyl bands (P.E. 112 machine, Halocarbon oil mull) at 1971 (vs), 1983 (vs), and 2054 (vs) cm.$^{-1}$; ketonic carbonyl bands[9] at 1650 (m) and 1635 (m) cm.$^{-1}$; other bands at 1460 (vw), 1433 (sh), 1428 (w), 1405 (vw), 1355 (vw), 1282 (m), 1265 (m), 1245 (vw), 1165 (w), 1105 (w), 975 (w), 960 (w), 915 (w), 850 (m), 803 (w), 715 (m), and 686 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum.—Resonances observed at τ = ~3.8 (complex), τ = 4.43 (triplet), τ = 6.59 (triplet), τ = 7.10 (doublet), and τ = 7.72 (triplet) of relative intensities 2:2:1:2:1.

Properties of $C_8H_8OFe_2(CO)_6$.—Orange air-stable crystals. Sublimes at 100° (0.1 mm.) with significant decomposition.

Anal. Calcd. for $C_{14}H_8Fe_2O_6$: C, 42.0; H, 2.0; Fe, 28.0; O, 28.0; mol. wt., 400. Found (duplicate values are on two in-

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(1) For part IV of this series, see R. B. King, *Inorg. Chem.*, **2**, 642 (1963).

(2) E. O. Fischer, C. Palm, and H. P. Fritz, *Ber.*, **92**, 2645 (1959).

(3) V. S. Armstrong and C. K. Prout, *J. Chem. Soc.*, 3770 (1962).

(4) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

(5) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 6240 (1960).

(6) E. O. Fischer and C. Palm, *Z. Naturforsch.*, **14b**, 598 (1959).

(7) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).

(7a) NOTE ADDED IN PROOF.—A second isomer of $C_5H_5CoC_8H_{10}$ was recently described by W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2162 (1963).

(8) A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951); A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *ibid.*, **76**, 1096 (1954).

(9) One of these bands in the ketonic carbonyl region might arise from the carbon–carbon double bond.

dependent preparations): C, 41.5, 42.1; H, 2.2, 2.5; Fe, 28.4; O, 28.2, 27.9; mol. wt., 400.

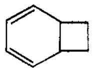
Infrared Spectrum.—Metal carbonyl bands (P.E. 112 machine, Halocarbon oil mull) at 1960 (s), 1972 (w), 1999 (s), 2012 (sh), and 2057 (s) cm.$^{-1}$; ketonic carbonyl band at 1637 (m) cm $^{-1}$; other bands at 1253 (vw) and 1233 (w) cm.$^{-1}$. Only very weak spectra of this compound were obtained.

Troponeiron Tricarbonyl.[10]—In order to compare its n.m.r. spectrum with that of $C_8H_8OFe(CO)_3$ troponeiron tricarbonyl was synthesized. A procedure analogous to that described above for $C_8H_8OFe(CO)_3$ rather than the less convenient previously published procedures[10] was used for the preparation of troponeiron tricarbonyl. From 3.6 g. (7.1 mmoles) of triiron dodecacarbonyl and 2.2 g. (20 mmoles) of tropone in 100 ml. of thiophene-free benzene, 0.36 g. (7.4% yield) of orange crystalline troponeiron tricarbonyl was obtained after chromatography on alumina (benzene eluent) and sublimation at 60° (0.1 mm.). No stable compound $C_7H_6OFe_2(CO)_6$ analogous to $C_8H_8OFe_2(CO)_6$ was observed in this reaction.

Proton N.m.r. Spectrum.—Resonances at $\tau = \sim 3.4$ (complex), $\tau = 5.09$ (doubled double doublet), $\tau = 6.91$ (asymmetrical quintet), and $\tau = 7.29$ (triplet) of relative intensities ~2:1:1:2.

Discussion

One of the characteristic features of the reactions between 1,3,5-cycloöctatriene and certain metal carbonyl derivatives is the tendency to form metal complexes derived from the bicyclic tautomer bicyclo-[4,2,0]octadiene (I).[5,7] In this connection it is of interest that neither of the cycloöctatrienone complexes $C_8H_8OFe(CO)_3$ and $C_8H_8OFe_2(CO)_6$ appears to be derived from the corresponding bicyclic tautomer II. In this case the decision between the two possibilities of complexes derived from cycloöctatrienone and of complexes derived from II is quite clear since in the infrared spectra of both complexes the absorption due to the ketonic carbonyl group appears at 1650 cm.$^{-1}$. If these iron complexes were derived from II, the absorption due to the ketonic carbonyl group since it is in a strained four-membered ring would be expected to appear near 1775 cm.$^{-1}$.[11] On the other hand, it is not at all unreasonable for a ketonic carbonyl group in an unsaturated eight-membered ring to appear at 1650 cm.$^{-1}$.



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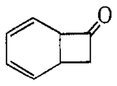

II

The yellow compound $C_8H_8OFe(CO)_3$ is apparently a diene complex involving coördination of two of the three double bonds of the cycloöctatrienone system with an iron tricarbonyl group. Its structure is probably quite similar to that of troponeiron tricarbonyl[10] except for the presence of an extra CH_2 group in the cyclic system. Attempts to prepare compounds of the type $LM(CO)_3$ (L = tropone or cycloöctatrienone, M = molybdenum or chromium) always failed to give significant quantities of any metal complexes. Apparently, tropone and cycloöctatrienone, although capable of functioning as dienes to form diene–iron tricarbonyl complexes, have only a very weak tendency to function as trienes to form triene–metal tricarbonyl complexes of chromium or molybdenum. This characteristic of tropone and cycloöctatrienone, which both contain three carbon–carbon double bonds and one carbon–oxygen double bond, may be related to the fact that cycloöctatetraene, which contains four carbon–carbon double bonds, has a strong tendency to form the diene–iron tricarbonyl complex $C_8H_8Fe(CO)_3$[4,12] but apparently no tendency to form triene complexes of the type $C_8H_8M(CO)_3$ (M = Cr, Mo).

B. The Compound $C_8H_{10}Fe_2(CO)_6$

Although the yellow compound $C_8H_8OFe(CO)_3$ appears to have a structure similar to numerous diene–iron tricarbonyl complexes described in the literature,[13] the only series of complexes corresponding to the orange derivative $C_8H_8OFe_2(CO)_6$ are some recently described fulvene derivatives of the general formula (fulvene)-$Fe_2(CO)_6$.[14] Not even a cycloöctatriene derivative $C_8H_{10}Fe_2(CO)_6$ analogous to $C_8H_8OFe_2(CO)_6$ has been described. In order to prepare such a cycloöctatriene derivative, the reaction between cycloöctatriene and triiron dodecacarbonyl[2,5] was reinvestigated on a larger scale in an attempt to isolate any $C_8H_{10}Fe_2(CO)_6$ which might be formed only in very low yield.

Experimental

The cycloöctatriene required for this reaction was prepared by the reduction of cycloöctatetraene with zinc dust in a strongly alkaline medium.[15] Cycloöctatriene prepared by this reaction is reported to consist principally of the 1,3,5 isomer due to the strongly alkaline medium in which the reduction is carried out.[15]

Preparation of the Compound $C_8H_{10}Fe_2(CO)_6$.—A mixture of 50.0 g. (99 mmoles) of triiron dodecacarbonyl, 25.0 g. (212 mmoles) of cycloöctatriene, and 1 l. of thiophene-free benzene was refluxed 20 hr. under nitrogen with magnetic stirring. After cooling to room temperature, the reaction mixture was filtered first by suction and then by gravity. Solvent was removed from the reaction mixture at ~30 mm., leaving an orange liquid. This liquid was chromatographed on a 5 × 60 cm. alumina column. The chromatogram was developed with pentane. A large band appeared on the column which was yellow at the bottom, gradually becoming orange at the top. This band was eluted with pentane, the eluates (volume 1100–1700 ml.) being collected in several fractions. Evaporation of the first 50% of the eluate (yellow to yellow-orange) to be collected left behind ~35 g. of a yellow-orange liquid which appeared to consist of a mixture of $C_8H_{10}Fe(CO)_3$[5] and hydrocarbons. For the purposes of this research, this material was not investigated further.

The $C_8H_{10}Fe_2(CO)_6$ was isolated from the second 50% of the pentane eluate (orange to red-orange). This portion of the eluate was collected in two fractions, the first fraction (hereafter designated as fraction A) being of about one-third the volume of the second fraction (hereafter designated as fraction B). Evaporation of both fractions A and B at ~50 mm. left orange crystals. These were purified by dissolving in a minimum amount of pen-

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[10] E. Weiss and W. Hübel, *Ber.*, **95**, 1179 (1962).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, p. 132.

[12] M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

[13] See, for example: B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958), and R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

[14] E. Weiss and W. Hübel, *Ber.*, **95**, 1186 (1962).

[15] The procedure used was essentially that given by Brit. Pat. 773,225; *Chem. Abstr.*, **51**, 13915*c* (1957).

tane, cooling the filtered orange solution in a −78° bath, and filtering off the resulting orange crystals. The products finally were purified by single sublimations at 70° (0.1 mm.) to give orange-red air-stable crystals of pure $C_8H_{10}Fe_2(CO)_6$. Fraction A yielded 0.3 to 0.4 g. and fraction B yielded 1.3 to 1.6 g. of pure $C_8H_{10}Fe_2(CO)_6$. The total yield from a single reaction thus was 1.6 to 2.0 g. (2.6 to 3.2% based on cycloöctatriene).

Samples of $C_8H_{10}Fe_2(CO)_6$ isolated by this method melted in the range 101–103°.

Anal. Calcd. for $C_{14}H_{10}Fe_2O_6$: C, 43.6; H, 2.6; Fe, 29.0; O, 24.9; mol. wt., 386. Found (two independent samples from fraction A): C, 44.4, 43.7; H, 2.7, 2.8; Fe, 28.1, 28.2. Found (two independent samples from fraction B): C, 43.5, 43.4; H, 2.5, 2.7; Fe, 28.8, 28.9; O, 26.1; mol. wt., 413. (Note: $C_{15}H_{12}Fe_2O_6$ requires C, 45.0; H, 3.0; Fe, 28.0; O, 24.0; mol. wt., 400.)

Infrared Spectrum.—Carbon–hydrogen bands at 2900 (w), 2875 (sh), and 2825 (w) cm.$^{-1}$; metal carbonyl bands (P.E. 112 machine, Halocarbon oil mull) at 1967 (s), 1993 (vs), 2014 (vs), and 2066 (vs) cm.$^{-1}$; other bands at 1460 (w), 1435 (w), 1355 (w), 1325 (vw), 1305 (w), 1280 (w), 1210 (vvw), 1160 (vw), 1075 (vw), 1040 (vw), 923 (vw), 888 (vw), 870 (m), 863 (sh), 812 (vw), 789 (m), and 690 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum (See Fig. 1).—Resonances at τ = 5.47 (CS_2 solution) or τ = 5.46 ($CHCl_3$ solution) (double doublet), τ = 6.08 (CS_2 solution) or τ = 6.05 ($CHCl_3$ solution) (doubled double doublet), τ = 7.35 (CS_2 solution) or τ = 7.29 ($CHCl_3$ solution) (apparent sextet), τ = 7.96 (CS_2 solution) or 7.97 ($CHCl_3$ solution) (apparent sextet), and at τ = 8.47 (CS_2 solution) or τ = 8.50 ($CHCl_3$ solution) (complex quintet) of relative intensities 2:2:2:2:2.

1,3,5-Cycloöctatrienemolybdenum Tricarbonyl.[2]—In order to compare its n.m.r. spectrum with that of $C_8H_{10}Fe_2(CO)_6$, 1,3,5-cycloöctatrienemolybdenum tricarbonyl was synthesized. From 4.24 g. (40 mmoles) of cycloöctatriene and 10.5 g. (40 mmoles) of molybdenum hexacarbonyl in 40 ml. of refluxing ethylcyclohexane, 1.85 g. (16% yield) of orange crystalline rather unstable $C_8H_{10}Mo(CO)_3$ was isolated after a sublimation at 100–120° (0.25 mm.).

Proton N.m.r. Spectrum (See Fig. 1).—Resonances at τ = 4.15 (doubled doublet), τ = 4.86 (doubled double doublet), τ = 5.31 (apparent quintet), τ = ~7.9 (complex resonance, eight discernible peaks), and τ = 8.7 (complex resonance) of relative intensities 2:2:2:2:2.

Reaction between $C_8H_{10}Fe_2(CO)_6$ and Triphenylmethyl Hexafluorophosphate.—A mixture of 0.40 g. (1 mmole) of $C_8H_{10}Fe_2(CO)_6$, 1.0 g. (2.6 mmoles) of triphenylmethyl hexafluorophosphate,[16] and 20 ml. of dichloromethane was stirred under nitrogen at room temperature. Orange crystals soon separated from the originally clear orange solution. After 20 hr., these crystals were filtered, washed with four 10-ml. portions of dichloromethane, and dried to give 0.20 g. (38% yield) of yellow-orange $[C_8H_9Fe_2(CO)_6][PF_6]$. On heating, $[C_8H_9Fe_2(CO)_6][PF_6]$ became black at ~213°.

Anal. Calcd. for $C_{14}H_9PF_6Fe_2O_6$: C, 31.7; H, 1.7; F, 21.5; P, 5.8; Fe, 21.1. Found: C, 30.3, 30.7; H, 1.7, 1.7; F, 20.7; P, 5.7, 6.4; Fe, 19.0.

Infrared Spectrum.—Carbon–hydrogen bands at 3050 (vvw) and 2975 (vvw) cm.$^{-1}$; metal carbonyl bands (P.E. 112 machine, Halocarbon oil mull) at 2023 (s), 2034 (s), 2058 (s), and 2098 (s) cm.$^{-1}$; P–F band at 836 (s) cm.$^{-1}$.

Discussion

The complexes $C_8H_8OFe_2(CO)_6$ and $C_8H_{10}Fe_2(CO)_6$ appear to be of similar types. The proton n.m.r. spectrum of $C_8H_{10}Fe_2(CO)_6$ resembles that of the molybdenum complex $C_8H_{10}Mo(CO)_3$[2] with respect to the fine structure of the resonances of the protons which are bonded to the carbon atoms bonded to the metal atom (see Fig. 1).[17] Since $C_8H_{10}Mo(CO)_3$ is known to be derived from 1,3,5-cycloöctatriene,[2,3] this comparison of the n.m.r. spectra suggests that $C_8H_{10}Fe_2(CO)_6$ is also derived from 1,3,5-cycloöctatriene. A possible structure for $C_8H_{10}Fe_2(CO)_6$ is III which is in agreement with the experimental data and which is also suggested by its similarity in color, volatility, and solubility to the compound $C_4H_4Fe_2(CO)_6$ (IV). It is to be noted that an iron–iron bond is postulated for structure III which is similar to the iron–iron bond believed to be present in IV.

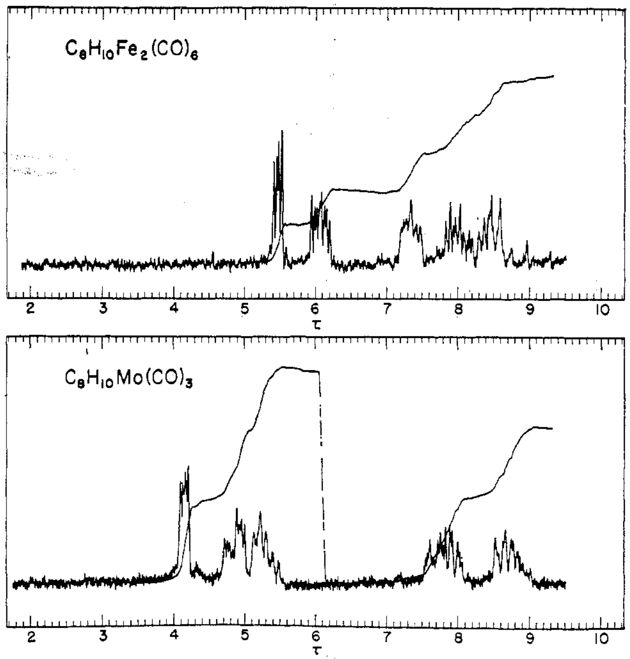
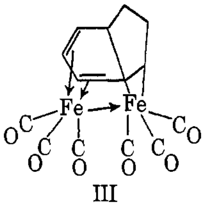
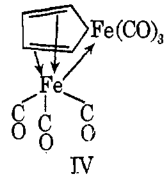


Fig. 1.—Proton n.m.r. spectra of 1,3,5-cycloöctatriene–metal carbonyl derivatives.



III



IV

It is of interest that Fischer, Palm, and Fritz[2] have reported the isolation of a compound of composition $C_9H_{12}Fe_2(CO)_6$ from the reaction between $Fe_2(CO)_9$ and cycloöctatriene. It is difficult to understand how a C_9H_{12} residue could arise from a C_8H_{10} hydrocarbon, a metal carbonyl derivative, and a saturated hydrocarbon

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[16] H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960). Triphenylmethyl hexafluorophosphate may be prepared by an analogous procedure substituting the commercial aqueous 65% hexafluorophosphoric acid solution (obtained from Ozark-Mahoning, Tulsa, Oklahoma) for the aqueous tetrafluoroboric acid in the procedure of Dauben, Honnen, and Harmon.

[17] The first three of the five resonances of the spectra of $C_8H_{10}Fe_2(CO)_6$ and $C_8H_{10}Mo(CO)$ (see Fig. 1) may be assigned to the resonances of the protons which are bonded to the carbon atoms bonded to the metal atom by analogy to the n.m.r. spectrum of $C_7H_8Mo(CO)_3$.[18,19] The wider separation between the second and third resonances of $C_8H_{10}Fe_2(CO)_6$ as compared with $C_8H_{10}Mo(CO)_3$ can account for the differences in the relative intensities of the lines of these resonances.

[18] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

[19] R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961).

solvent. "$C_9H_{12}Fe_2(CO)_6$" is reported to form orange volatile crystals, m.p. 74°, soluble in hydrocarbon solvents. The infrared spectrum reported for "$C_9H_{12}Fe_2(CO)_6$" resembles very closely that of $C_8H_{10}Fe_2(CO)_6$. We feel that "$C_9H_{12}Fe_2(CO)_6$" is actually $C_8H_{10}Fe_2(CO)_6$ contaminated with sufficient $C_8H_{10}Fe(CO)_3$ and hydrocarbons to lower its melting point from 102° to 74° and to change the composition of the mixture to approximately $C_9H_{12}Fe_2(CO)_6$. Fischer, Palm, and Fritz[2] apparently did not use recrystallization from a hydrocarbon solvent as one of the steps in the purification of their product. Our observations suggest that a recrystallization step is essential to obtain pure $C_8H_{10}Fe_2(CO)_6$ since the chromatographic separation of $C_8H_{10}Fe_2(CO)_6$ and $C_8H_{10}Fe(CO)_3$ appears to be incomplete on columns of reasonable size.

The molybdenum complex $C_8H_{10}Mo(CO)_3$ is reported not to form cationic species such as $[C_8H_9Mo(CO)_3]^+$ or $[C_8H_8Mo(CO)_3]^{+2}$ by hydride ion abstraction with the triphenylmethyl carbonium ion $[(C_6H_5)_3C]^+$.[2] However, when the iron complex $C_8H_{10}Fe_2(CO)_6$ was treated with dichloromethane solutions of $[(C_6H_5)_3C][BF_4]$ or $[(C_6H_5)_3C][PF_6]$, orange crystalline precipitates were obtained. These precipitates, especially the tetrafluoroborate, were hygroscopic and the analytical data were not entirely satisfactory. Nevertheless, the analytical data were in definitely the best agreement with the formulation as salts of the cation $[C_8H_9Fe_2(CO)_6]^+$. A satisfactory n.m.r. spectrum of this cation could not be obtained. The salts were insoluble in dichloromethane, chloroform, or water. They appeared to be somewhat decomposed by more powerful solvents such as dimethyl sulfoxide to give paramagnetic material which broadened the resulting spectrum to an unmanageable extent.

The fact that the $[C_8H_9Fe_2(CO)_6]^+$ ion is obtained from triiron dodecacarbonyl in an over-all yield of only ~1% for the two steps has discouraged us from investigating this potentially interesting species in greater detail.

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance. Valuable gifts of the cycloöctatetraene required in large quantities for this work were obtained from Badische Anilin- und Sodafabrik, Ludwigshafen, Germany.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS

Anodic Dissolution of Calcium in N,N-Dimethylformamide[1]

BY MAX L. RUMPEL, ARTHUR W. DAVIDSON, AND JACOB KLEINBERG

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The relationship between anodic dissolution and quantity of electricity was studied for electrolyses with a calcium anode in solutions of certain salts in N,N-dimethylformamide (DMF). For lithium chloride solutions, the weight loss of the anode was in accord with that calculated on the basis of primary oxidation to bipositive calcium ion. For sodium nitrate, lithium perchlorate, calcium perchlorate, potassium iodide, or lithium bromide solutions, the weight loss was greater than the value so calculated, even when direct chemical attack on the metal was taken into account. In each of these latter solutions, either reduction products of the electrolyte medium were produced at the anode during electrolysis, or else the anolyte, after electrolysis, was found to have reducing properties. These effects, although varying widely from one salt to another, were nearly independent of current density, concentration of salt in DMF, duration of electrolysis, or temperature in the range of conditions studied. All observations may be explained by the postulate of formation of unipositive calcium ion as the first step in anodic oxidation.

Introduction

For a number of metals under appropriate conditions of anodic oxidation, values have been found for the initial mean valence, denoted by the symbol V_i and defined as the number of faradays of electricity passed per gram-atom of metal electrolytically dissolved, which are less than the lowest familiar charge of a cation of the metal. These metals include aluminum,[2-7] titanium,[4-6] uranium,[4-6] magnesium,[4-6,8,9] beryllium,[4-6,10] zinc,[4-6,11] and cadmium.[11] The phenomenon of "abnormally" low oxidation states can plausibly be explained in terms of the hypothesis of primary anodic formation of an unstable unipositive ion which may then react with the solvent or the electrolyte to form a more stable product.

The previous observation in this Laboratory of V_i values lower than two for beryllium and magnesium[8-10] suggested the desirability of an investigation of the anodic dissolution behavior of a third group IIA element, calcium. Since calcium metal is vigorously attacked by water, its electrolytic oxidation cannot be

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