Journal of Organometallic Chemistry, 49 (1973) C43–C45

Preliminary communication

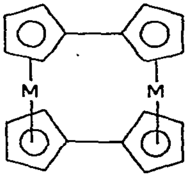
The synthesis of bis(fulvalene)dicobalt hexafluorophosphate $[(h^5:h^5\text{-}C_{10}H_8)_2Co^{III}_2][PF_6]_2$

A. DAVISON and J.C. SMART

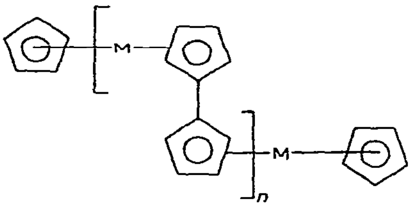
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received November 21st, 1972)

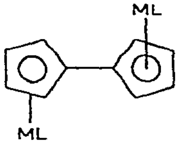
Complexes of the structural types (I), (II) and (III) have been regarded as "metallofulvalene"[1,2] derivatives. Current interest in the iron complexes of type (II) ($n = 1$), particularly the mixed valence derivatives produced by one electron oxidation[3], stems from their interesting electronic, and electrical conductivity properties[3,4]. Previous syntheses utilize either modified Ullman coupling reactions[1,5–7] or dialkyl peroxy induced polyrecombination techniques[4,8].



(I)



(II)



($L = (CO)_3$, when $M = Mn$[6])

(III)

We wish to report a facile and general route into "metallofulvalenes" of types (I), (II) and (III) which circumvents many of the inherent limitations of the previous procedures. The method is a superior route to the known iron derivatives, and has none of the ambiguities arising from cross linkage phenomena in the oligomers produced by the polyrecombination techniques[4]. We illustrate the versatility of our method by the synthesis of the isoelectronic cobalt analogue of the known bis(fulvalene)diiron.

Dihydrofulvalene[9] is produced in THF at −78° by the reaction of iodine with two equivalents of NaC_5H_5. The reaction proceeds through the formation of 5-iodocyclopentadiene[9,10] which undergoes substitution by cyclopentadienide. Deprotonation *in situ* leads to solutions of the bicyclopentadienyl dianion. Thus a convenient "one pot" synthesis of (I), (II) and (III) can be achieved. Variation in the stoichiometries and reaction conditions can be made to ensure the presence of unreacted NaC_5H_5 which increases the yield of the complexes (II) at the expense of (I). We describe a procedure which enables the isolation of $[(h^5{:}h^{5\prime}\text{-}C_{10}H_8)_2Co^{III}_2]^{2+}$ as an air stable, diamagnetic, dark orange hexafluorophosphate salt in 61% yield based on NaC_5H_5. Iodine (0.053 mol) was added to NaC_5H_5 (0.1 mol) in THF (250 ml) at –78°. The reaction was allowed to warm to room temperature and was then cooled to –78° and deprotonated by butyllithium (0.11 mols, 2.2 *M* in hexane). The addition of anhydrous cobalt chloride and stirring for 12 h at room temperature gave a blue-black solution. Oxidation was performed *in situ* by the addition of 10 ml conc. HCl to and the passage of oxygen through this solution. The dark red precipitate obtained was dissolved an aqueous HCl containing 1–2 drops of H_2O_2. The addition of NH_4PF_6 to the dark red solution caused the product to separate. Recrystallization from CH_3CN/C_2H_5OH, 1/1 v/v gave an analytically pure product. (Anal. Found: C, 36.40; H, 2.37; F, 34.55; P, 9.34. $C_{20}H_{16}Co_2F_{12}P_2$ calcd.: C, 36.17; H, 2.43; F, 34.33; P, 9.33%.) The NMR spectrum shows the characteristically large chemical shift difference found in the isoelectronic iron analogue[5] δ (60 MHz, CH_3CN, Me_4Si) 5.48t, 8H, J = 1.0 Hz; 7.48t, 8H, J 1.0 Hz. Utilizing a 4/1 molar ratio of NaC_5H_5 to I_2 gives cobaltocene, smaller amounts of (I) and complexes of the type (II). While we do not have a reproducible procedure to separate the higher oligomers of type (II), $n > 2$, NMR spectra clearly show the presence of C_5H_5 and $C_{10}H_8$ ligands in mixtures of the hexafluorophosphate salts.

The dicobalt salts $[(h^5{:}h^{5\prime}\text{-}C_{10}H_8)_2Co^{III}_2][PF_6]_2$ and $[(h^5\text{-}C_5H_5)Co^{III}(h^5{:}h^{5\prime}\text{-}C_{10}H_8)Co^{III}(h^5\text{-}C_5H_5)][PF_6]_2$ are considerably easier to reduce than $[(h^5\text{-}C_5H_5)_2Co][PF_6]$; they both show two reversible, well separated, one electron waves on polarographic reduction in CH_3CN. In the dibridged species they occur at –0.07 and –0.95 volts and in the monobridged one at –0.53 and –0.88 volts with respect to SCE. The corresponding reductive wave in $[(h^5\text{-}C_5H_5)_2Co][PF_6]$ occurs at –0.85 volts. The isolation of the mixed valent Co^{II}–Co^{III} systems together with our studies on systems containing other metals will be communicated later.

REFERENCES

1 M.D. Rausch, R.F. Kovar and C.S. Kraihanzel, *J. Amer. Chem. Soc.*, 91 (1969) 1259.

2 M.R. Churchill and J. Wormald, *Inorg. Chem.*, 8 (1971) 1970.

3 D.O. Cowan and F. Kaufman, *J. Amer. Chem. Soc.*, 92 (1970) 6198; D.O. Cowan, G.A. Candela and F. Kaufman, *J. Amer. Chem. Soc.*, 93 (1971) 3889; D.O. Cowan, R. Cullins and F. Kaufman, *J. Phys. Chem.*, 75 (1971) 2025; D.O. Cowan, J. Park, C.U. Pittman, Jr., Y. Sasaki, T.K. Mukherjee and N.A. Diamond, *J. Amer. Chem. Soc.*, 94 (1972) 5110.

4 N. Bilow, A.L. Landis and H.R. Rosenberg, *J. Polym. Sci., Part A-1*, 7 (1969) 2719.

5 F.L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, 91 (1969) 1258

6 M.D. Rausch, P.U. Roling and A. Siegel, *J. Chem. Soc., (D), Chem. Commun.*, (1970) 502.

7 M.D. Rausch and R.A. Genetti, *J. Org. Chem.*, 35 (1970) 3888.

8 H. Rosenberg and E.W. Neuse, *J. Organometal. Chem.*, 6 (1966) 76.

9 W. von E. Doering, *Theoretical Organic Chemistry – the Kekulé Symposium*, Butterworths, London, 1959, p. 35; W. von E. Doering, *U.S. Dept. Comm., Office Tech. Serv., P.B. Report, 147, 858*, 1960.
10 R. Breslow and J.M. Hoffman, Jr., *J. Amer. Chem. Soc.*, 94 (1972) 2110.