fast electrode processes when such rates are not accessible by conventional means.

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Tricarbonyliron Complexes of Functional 1,2-Disubstituted Cyclobutadienes

Sir:

The recent discovery that free cyclobutadiene can be generated and intercepted as a transient intermediate by oxidative degradation of the corresponding tricarbonyliron complex[1] has presented the possibility that the chemistry of cyclobutadienes and cyclobutadienoid systems may at last be vulnerable to systematic development.[2] A major barrier to full elaboration of this approach is the scarcity of general methods for synthesizing metal complexes of specifically substituted cyclobutadienes possessing functional groups. Most current methods suffer from either lack of generality or difficultly accessible precursors for the complexation step,[3] with the result that at the present time only tricarbonyliron complexes of a series of monosubstituted cyclobutadienes, which have been prepared by electrophilic substitution reactions on the parent complex in conjunction with conventional manipulation of functionality,[4] are available *via* a general route. We have initiated a program directed toward preparation and study of a variety of cyclobutadiene-related systems by the metal complex route and describe the first results herein. Initial effort has been directed toward functional 1,2-disubstituted cyclobutadienes and this report is concerned with the synthesis of a series of tricarbonyliron complexes of this type. The availability of complexes with this particular substitution pattern is of special interest since it will not only permit potential experimental studies of a large number of theoretically interesting 1,2-disubstituted cyclobutadienes,[5] but also provide possible access to complexes of many equally interesting cyclobutadienoid systems through cyclization reactions involving adjacent substituents.

Irradiation of a dioxane solution of dichloromaleic anhydride, a threefold excess of *trans*-1,2-dichloroethylene, and benzophenone as sensitizer under nitrogen with a Hanovia 450-W high-pressure lamp through Pyrex afforded, after aqueous work-up and esterification of the resulting diacid with diazomethane, tetrachloro diester **1**[6,7] [mp 92–93°; $\nu_{\text{max}}^{\text{CCl}}$ 1765 (sh), 1755, and 1725 cm^{-1}; $\delta_{\text{TMS}}^{\text{acetone-}d_6}$[8] 3.85 (s, 3 H, -OC$H_3$), 3.95 (s, 3 H, -OC$H_3$), and 5.10 (AB quartet, 2 H, $\Delta\nu_{\text{AB}} = 25.5$ cps, $J_{\text{AB}} = 9.0$ cps, -CHClCHCl-)] in 32% yield. Treatment of the latter with activated zinc and recently prepared diiron nonacarbonyl[9] in refluxing 10% (v/v) acetic acid in ether under nitrogen led in 7–9% yield to 1,2-bis(carbomethoxy)cyclobutadieneiron tricarbonyl (**2a**)[10] [yellow needles, mp 105–106.5°; *m*/*e* 308, 280, 252, and 224; $\nu_{\text{max}}^{\text{KBr}}$ 1723, 1985, and 2063 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.77 (s, 6 H, -OCH_3) and 4.77 (s, 2 H, ring protons)].

From this key intermediate a series of complexes was prepared by standard methods. Thus hydrolysis (KOH–CH_3OH) could be effected either completely to diacid **2b**[11] [yellow amorphous powder, 208–214° dec; $\nu_{\text{max}}^{\text{dioxane}}$ 1705 (sh), 1723 (sh), 1740, 1990, 2060, and 2500–3400 cm^{-1} (br); $\delta_{\text{TMS}}^{\text{acetone-}d}$ 5.20 (s, 2 H, ring protons) and 5.85 (bs, 2 H, $CO_2$$H$)] or partially to half-ester **2c**[13] [yellow needles, mp 130–137°; $\nu_{\text{max}}^{\text{CHCl}_3}$ 1670, 1735, 2010, 2075, and 2500–3400 cm^{-1} (br); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.86 (s, 3 H, -OCH_3), 4.78 (s, 1 H, ring proton), 4.94 (s, 1 H, ring proton), and 10.06 (bs, 1 H, -$CO_2$$H$)], a cyclobutadiene complex which is unique in this series in being potentially resolvable. Treatment of diacid **2b** with thionyl chloride and pyridine at room temperature yielded bis(acid chloride) **2d** [orange needles, mp 153–156°; $\nu_{\text{max}}^{\text{CHCl}_3}$ 1775, 2020, and 2080 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.13 (s)], a highly versatile intermediate in this series. In one sequence **2d** was converted to bis(amide) **2e** [yellow microcrystals, mp 297–298° (dec, sealed tube); $\nu_{\text{max}}^{\text{KBr}}$ 1606, 1625, 1660, 1674 (sh), 2000, 2080, 3170, and 3360 cm^{-1}; $\delta_{\text{TMS}}^{\text{DMSO-}d_6}$ 5.08 (s, 2 H, ring protons), 7.40 (bs, 2 H, NH),

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(1) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965).

(2) The value of this method in providing cyclobutadiene for mechanistic and synthetic studies has already been established: (a) G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965); (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 623 (1966); (c) J. C. Barborak and R. Pettit, *ibid.*, **88**, 1328 (1966); (d) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967); (e) W. Merk and R. Pettit, *ibid.*, **89**, 4787 (1967); (f) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).

(3) For recent reviews of methods of preparation of metal complexes of cyclobutadienes see: (a) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, Chapter 2; (b) P. M. Maitlis, *Advan. Organometal. Chem.*, 4, 95 (1966).

(4) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 3254 (1965).

(5) For a discussion of theoretical aspects of some of the substituted cyclobutadienes pertinent to this work, see H. E. Simmons and A. G. Anastassiou in ref 3a, Chapter 12, pp 393–395.

(6) This cyclobutane synthesis is a direct extension of the photochemical cycloaddition of cyclic dihalomaleic acid derivatives to olefins developed by Scharf and Korte: (a) H. D. Scharf and F. Korte, *Chem. Ber.*, **98**, 764 (1965); (b) H. D. Scharf and F. Korte, *Angew. Chem.*, **77**, 452 (1965).

(7) Compositional analyses of all new compounds reported herein for all elements except oxygen agreed within 0.3% of values expected of assigned structures.

(8) All nmr spectra were recorded at 60 Mcps at ambient temperatures.

(9) E. H. Braye and W. Hubel, *Inorg. Syn.*, **8**, 178 (1966).

(10) Mechanistic considerations of this complexation step are clouded by the multiply heterogeneous conditions and by limited evidence that the necessity for the presence of zinc depends on the history of the diiron nonacarbonyl used. However, details of the procedure, which will be reported in the full paper, have been developed to the point that the stated yield range is consistently attained.

While the reaction could well involve preliminary dechlorination to a dichlorocyclobutene followed by complexation of the latter with diiron nonacarbonyl, other mechanisms cannot be ruled out at this time. Consequently, work is currently in progress to define through control experiments the product-forming intermediates involved in the reaction and thus to determine whether this approach represents a new reaction type or merely a variation of the dihalocyclobutene approach.

(11) It is of historical interest that **2b** is a metal complex of Perkin's "tetrenedicarboxylic acid," the objective of one of the first attempts to synthesize a cyclobutadiene.[12] The corresponding complex of the monoacid, "tetrenecarboxylic acid,"[12] has also been synthesized.[4]

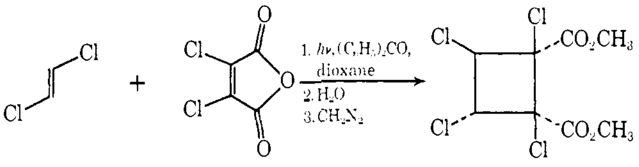
(12) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, 950 (1894); (b) W. H. Perkin, Jr., *Chem. Ber.*, **26**, 2243 (1893).

(13) We are indebted to Mr. Frank Tsantes for developing a procedure for the preparation of this compound.

and 8.12 (bs, 2 H, NH)], which in turn was dehydrated (P_2O_5) to bis(nitrile) **2f**[14] [yellow needles, mp 205–216° (dec, sealed tube); $\nu_{\max}^{\mathrm{KBr}}$ 2005, 2085, and 2225 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{acetone}\text{-}d_6}$ 5.38 (s)]. In another sequence the acid chloride was treated with diazomethane followed by hydrogen chloride to give bis(chloromethyl ketone) **2g** [yellow needles, mp 115.5–117.5°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1676, 2015, and 2075 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.26 (s, 4 H, CH_2Cl) and 5.10 (s, 2 H, ring protons)]. The latter was readily converted to bis(iodomethyl ketone) **2h** (NaI–acetone) [orange microcrystals, mp 97–99°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1667, 2010, and 2075 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.02 (AB quartet, 4 H, $\Delta\nu_{AB} = 13.8$ cps, $J_{AB} = 10.0$ cps, CH_2I) and 5.02 (s, 2 H, ring protons)] or to bis(methyl ketone) **2i** (NaI–HOAc followed by $Na_2S_2O_3$) [yellow microcrystals, mp 122.5–124.0°; $\nu_{\max}^{\mathrm{KBr}}$ 1658, 1675, 1960, 1990, and 2060 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.25 (s, 6 H, COCH_3) and 4.89 (s, 2 H, ring protons)]. In addition the acid chloride participated smoothly in Friedel–Crafts acylation ($AlCl_3$) of benzene to give bis(benzoyl) derivative **2j** [yellow plates, mp 171–173°; $\nu_{\max}^{\mathrm{KBr}}$ 1635, 1995, and 2062 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.00 (s, 2 H, cyclobutadiene ring protons), 7.23–7.65 (m, 6 H, *meta* and *para* protons), 7.65–8.00 (m, 4 H, *ortho* protons)] and esterification ($C_6H_5CH_2OH$–C_5H_5N) to give bis(benzyl ester) **2k** [yellow needles, mp 70.0–71.5°; $\nu_{\max}^{\mathrm{KBr}}$ 1730, 1977, 1998, and 2065 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.77 (s, 2 H, cyclobutadiene ring protons), 5.17 (s, 4 H, -OC$H_2C_6H_5$), and 7.32 (s, 10 H, C_6H_5)].

Conclusive evidence that the aforementioned compounds are true cyclobutadiene complexes was obtained by chemical correlation. Treatment of bis(acid chloride) **2d** with sodium borohydride in dioxane afforded a somewhat unstable diol which was converted without characterization with concentrated hydrochloric acid to bis(chloromethyl) derivative **2l** [yellow solid, mp 73–77° (dec, HCl evolution); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1975 and 2045 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.09 (AB quartet, 4 H, $\Delta\nu_{AB} = 6.0$ cps, $J_{AB} = 13.1$ cps, -CH_2Cl) and 4.37 (s, 2 H, ring protons)]. Reductive cleavage of the latter with lithium aluminum hydride in ether then produced the known 1,2-dimethylcyclobutadieneiron tricarbonyl (**2m**),[15] which was identified by comparison of the nmr spectrum with that reported and the infrared spectrum with that of an authentic sample. In addition, a great deal of the spectral data given above points toward or is consistent with the cyclobutadiene formulation. Especially indicative were the lack of observable spin–spin coupling between ring protons in half-ester **2c**, which is consonant with previous observations that such vicinal coupling is essentially zero,[16] and the nonequivalence of geminal protons which was evident in the nmr spectra of bis(iodomethyl ketone) **2h** and bis(chloromethyl) derivative **2l** and which is in accord with the expected $m(C_s)$ molecular symmetry time averaged over rotational isomers.[17]

We are continuing to explore the potential for further development of the chemistry of cyclobutadiene now made possible by the availability of the series of complexes described herein.



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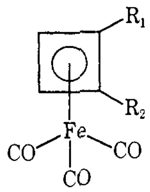

2

a, $R_1 = R_2 = CO_2CH_3$
b, $R_1 = R_2 = CO_2H$
c, $R_1 = CO_2CH_3$; $R_2 = CO_2H$
d, $R_1 = R_2 = COCl$
e, $R_1 = R_2 = CONH_2$
f, $R_1 = R_2 = CN$
g, $R_1 = R_2 = COCH_2Cl$
h, $R_1 = R_2 = COCH_2I$
i, $R_1 = R_2 = COCH_3$
j, $R_1 = R_2 = COC_6H_5$
k, $R_1 = R_2 = CO_2CH_2C_6H_5$
l, $R_1 = R_2 = CH_2Cl$
m, $R_1 = R_2 = CH_3$

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[14] For a theoretical treatment of the cyclobutadienoid portion of this complex, see ref 5.

[15] H. A. Brune, W. Eberius, and H. P. Wolf, *J. Organometal. Chem.*, **12**, 485 (1968).

[16] (a) H. G. Preston, Jr., and J. C. Davis, Jr., *J. Amer. Chem. Soc.*, **88**, 1585 (1966); (b) H. A. Brune, H. P. Wolff, and H. Huther, *Chem. Ber.*, **101**, 1485 (1968).

[17] The same effect was not observed in bis(benzyl ester) **2k**, possibly because of a distance effect, and in bis(chloromethyl ketone) **2g**, possibly because of a smaller anisotropic effect of the chlorine.

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[19] National Institutes of Health Predoctoral Fellow, 1966–1967.

Photochemical Reaction Pathways of Pentaammineruthenium(II) Complexes

Sir:

Oxidation of ruthenium(II) has recently been reported[1] to be the principal photochemical reaction pathway for the Ru(II)-molecular nitrogen complexes, $[Ru(NH_3)_5N_2]^{2+}$ and $\{[Ru(NH_3)_5]_2N_2\}^{2+}$. We have studied the photochemical reactions of several related pentaammineruthenium(II) complexes, $Ru(NH_3)_5py^{2+}$, $Ru(NH_3)_5(CH_3CN)^{2+}$, $Ru(NH_3)_5H_2O^{2+}$, and $Ru(NH_3)_6{}^{2+}$, and have found aquation of the complex as well as oxidation of Ru(II) to be a major photochemical reaction pathway in each case. Not surprisingly, preliminary studies show that the role played by the various pathways is dependent on the wavelength of the excitation radiation.

The spectrum of the pyridine complex, $Ru(NH_3)_5py^{2+}$, displays an intense metal-to-ligand charge-transfer (CT) band at 408 nm (ϵ 7800) and a ligand π–π^* band

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[1] C. Sigwart and J. Spence, *J. Am. Chem. Soc.*, **91**, 3991 (1969).