Free Radical Coupling Reactions of Organoiron Complexes: Electrochemical Studies and Preliminary Cross Coupling Experiments

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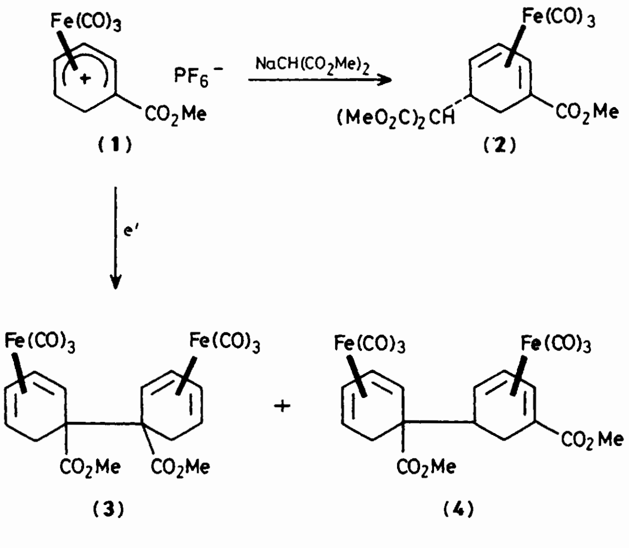
Reductive dimerization of tricarbonyl(1-methoxycarbonylcyclohexadienyl)iron hexafluorophosphate proceeds in a regioselective manner using either zinc dust or electrochemical techniques, cyclic voltammetry experiments providing evidence for a one-electron transfer process involving free radical intermediates; the first example of intramolecular cross coupling of the free radical with an alkene moiety is reported.

Free radical intermediates have previously been assumed to be present during the reductive dimerization of dienyltricarbonyliron cations,[1] based on the regiochemistry of dimerization. We are now studying this reaction and present herein chemical and electrochemical results which further characterize the dimerization process and demonstrate the feasibility of a cross-coupling reaction.

The methoxycarbonyl-substituted dienyl complex (**1**)[2] was studied. Nucleophile addition [$NaCH(CO_2Me)_2$, tetrahydrofuran (THF), 0 °C] gives exclusively the adduct (**2**), so any deviation from this regiochemistry would indicate a non-polar mechanism during reductive coupling. Treatment of complex (**1**) with zinc dust (10% MeCN in THF, 23 °C, 16 h) resulted in a high yield of a mixture of the two regioisomers (**3**) and (**4**) in a ratio 85 : 15, which were separated chromatographically and individually characterized.† Each was produced as an equimolar mixture of diastereoisomers. The formation of the major product (**3**) (78% isolated yield) is consistent with a free radical coupling process, for which further evidence was sought using electrochemical techniques.

Cyclic voltammetry experiments‡ on complex (**1**) (0.06 M in MeCN) showed a single reduction wave with a peak potential at slower sweep rates of −0.22 V *vs.* S.C.E.* (Figure 1). The maximum currents are directly proportional to the square root of the sweep rate in the range investigated (10—500 mV/s). This voltammetry curve is consistent with an E_rC_i mechanism,[3a,d] *i.e.*, heterogeneous electron transfer followed by an irreversible chemical reaction. No oxidation wave in the anodic sweep was observed, demonstrating a totally irreversible overall process,[3] as would be expected for rapid dimerization. When the electrochemical reduction was carried out at −0.20 V *vs.* S.C.E.* for 6 h,‡ isolation and characterization of the product showed an identical mixture of complexes (**3**) and (**4**) to that obtained by chemical reduction.



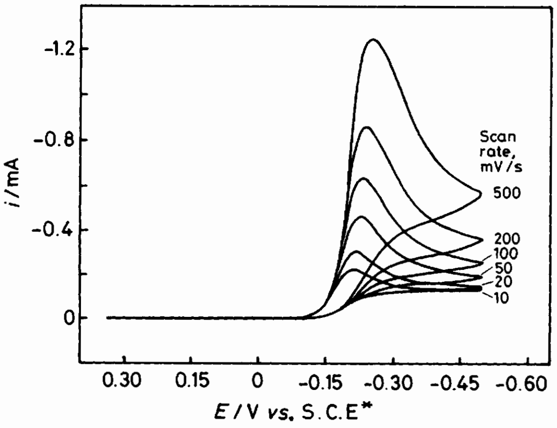


Figure 1. Cyclic voltammograms for complex (**1**) (0.06 M) in acetonitrile solution containing $Bu^n{}_4NClO_4$ (0.1 M). Sweep rates (mV/s) are as indicated.

Figure 2 shows the polarization curves obtained using the rotating disk electrode technique. Well defined, diffusion-limited waves were observed with slight hysteresis at faster rotation rates. Control experiments (O_2 admitted) indicated that this latter effect was due to traces of oxygen in the solvent (acetonitrile) which were extremely difficult to remove. This hysteresis, together with the need to hold the potential of +0.4 V (S.C.E.*) for two minutes between sweeps in order to obtain reproducible behaviour, indicates that secondary reactions, probably involving H_2O and O_2 and/or trace impurities, may cause partial blocking of the electrode, particularly at more negative potentials, but that dissolution or desorption occurs during the rest period at +0.4 V (S.C.E.*). A linear Levich plot[3b] [rotary disk limiting current *vs.* (rotation frequency)$^{1/2}$] with zero intercept was obtained, which confirms a diffusion-limited process at potentials in the plateau region. The number of electrons (*n*) involved and the diffusion coefficient (*D*) of the reactant were estimated by combining the Levich plot with the Cottrell plot.[3c] The latter was obtained by potential step experiments from near the rest potential (+0.5 V *vs.* S.C.E.*) to the diffusion-limited region of the reduction wave (~0.4 V *vs.* S.C.E.*). This plot (i *vs.* $t^{-1/2}$) was also linear with zero intercept. From the slopes of both plots, the estimated values of *n* and *D* were 1 and $(1.1 \pm 0.1) \times 10^{-5}$ cm^2/s, respectively.

These electrochemical experiments are strongly indicative that the reductive dimerization involves free radical inter-

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† All new compounds were obtained as racemic mixtures and were fully characterized by i.r. and n.m.r. spectroscopy and gave acceptable combustion analysis and/or high resolution mass spectra. Complex (**3**): m.p. 59—61 °C; i.r. (CCl_4) $\nu_{max.}$ 2060, 1985, and 1735 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 5.45—5.22 (4H, m), 3.75 (3H, s), 3.67 (3H, s), 3.28 (2H, d, *J* 6.4 Hz), 3.02 (2H, m), 2.49 and 2.37 (1H, each, dd, J_{gem} 16.5 Hz, J_{vic} 3.9 Hz, *endo* methylene protons, diastereoisomers), 1.95 and 1.73 (1H each, br. d, J_{gem} 16.5 Hz, *exo* methylene protons, diastereoisomers). Complex (**6**): i.r. ($CHCl_3$) $\nu_{max.}$ 2050, 1995, 1970, and 1703 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 5.7 (1H, m, vinyl), 5.25 (2H, m, 3-H and 4-H), 5.2—5.0 (2H, m, vinyl), 3.87 (2H, m, allylic CH_2), 3.20 (1H, dd, *J* 9, 7 Hz, lactam), 3.16 (1H, m, obscured, 5-H), 2.85 (1H, dd, *J* 8, 2 Hz, 2-H), 2.65 (1H, t, *J* 9 Hz, lactam), 2.1 (1H, m, C*H*Me), 1.9 (2H, d, *J* 3.5 Hz, 6-CH_2), and 0.92 (3H, d, *J* 7 Hz, CH_3).

‡ For electrochemical experiments, a three-electrode configuration was used in a divided electrochemical cell of *ca.* 15 ml capacity. A gold rotating disk electrode (area *ca.* 0.03 cm^2) and gold foil (area *ca.* 2 cm^2) were used as working and counter electrodes, respectively. The counter electrode was separated from the working electrode compartment by a glass frit. A saturated calomel reference electrode was used, separated from the working compartment by a Luggin capillary and a closed wetted stopcock. The potentials reported include an uncorrected liquid junction potential, hence the designation S.C.E.*, which has a constant value for all measurements. The solvent, acetonitrile, was purified and deoxygenated as described in: H. Kiesele, *Anal. Chem.*, 1980, **52**, 2230. Tetra-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, and the cell was deaerated using purified nitrogen. The electrochemical measurements were performed with a Princeton Applied Research (PARC) Model 173 potentiostat and a PARC Model 175 universal programmer. *IR* compensation was applied. Rotation rates for the rotating disk electrode experiments were controlled by a Controvit (Tacussel Electronique) system. The reproducible curves shown were obtained by waiting at +0.4 V (S.C.E.*) for two minutes between sweeps.

The electrochemical synthesis was carried out in a similar divided cell. Gold working (area *ca.* 1.5 cm^2) and counter electrodes were used. The average current was 0.2 mA over 6 h. The solvent was also purified acetonitrile and contained Bu_4NClO_4 (0.1 M), and the iron dienyl complex (**1**) (0.063 M). The solution was deaerated with oxygen-free N_2 (Matheson) which was bubbled continuously during the reaction. After preparative t.l.c. a yield of 11.5 and 2.7 mg of the regioisomers (**3**) and (**4**) respectively was obtained, and this corresponds to *ca.* 100% coulombic efficiency. The reaction was carried out at −0.2 V (S.C.E.*) rather than under limiting current conditions at more negative potentials because preliminary experiments indicated that the latter yielded a mixture of products, probably owing to the presence of traces of H_2O and O_2.

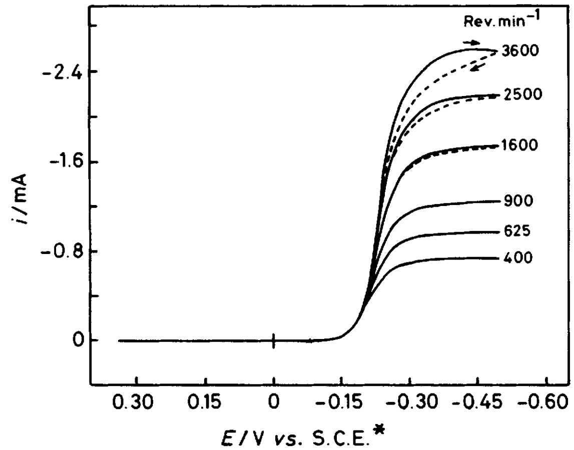
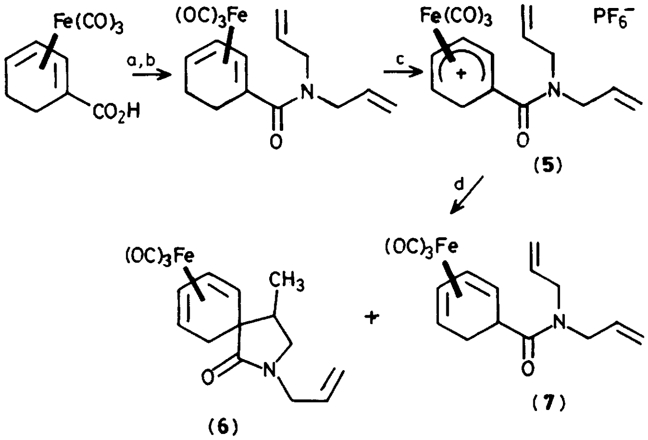


Figure 2. Current–potential curves for the reduction of complex (**1**) (0.006 M) in actonitrile solution, containing $Bu^n_4ClO_4$ (0.1 M), at a rotating disk electrode. Rotation rates are as indicated. The sweep rate was 10 mV/s.

mediates. Further evidence was sought by examining cross coupling of the free radical with unsaturated compounds. Preliminary experiments with unsaturated esters (*e.g.*, allyl, butenyl) related to (**1**) failed, owing to the stereoelectronic effects in the ester substituent[4] which disfavour the conformation required for radical cyclization.§ Accordingly, the diallylamide complex (**5**) was prepared as shown in Scheme 1. Treatment of this compound with zinc dust (20% MeCN in THF in the presence of 10 equiv. of AcOH, −10 °C, 16 h) resulted in formation of the lactam† (**6**) in 15—25% yield. Interestingly, (**6**) was obtained as a *ca.* 3:1 mixture of diastereoisomers (^{1}H n.m.r.: CH_3 doublets at δ 0.92 for major product, 0.69 for minor product) indicating a stereoselectivity not obtainable by nucleophile addition to dienyl–$Fe(CO)_3$ complexes.[5] The other product obtained during this reaction was the *monomeric* diene complex (**7**), a formal reduction product of (**5**), probably as a result of suppression of dimerization by the sterically more demanding amide group.

In conclusion, free radicals can be generated by single electron reduction of dienyl–$Fe(CO)_3$ complexes, and the first demonstration of their cross-coupling with a pendant unsaturated moiety has been described.



Scheme 1. *Reagents:* (a) $(COCl)_2$, CH_2Cl_2, room temp., 3 h; (b) diallylamine, C_6H_6, pyridine, room temp., 16 h; (c) Ph_3CPF_6, CH_2Cl_2, room temp., 1 h; (d) Zn dust, THF–MeCN (8:2), AcOH, (10 equiv.), −10 °C, 16 h.

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§ We are grateful to Professor David Hart of the Ohio State University for bringing this fact to our attention.