so-called long-lived, stable ion conditions, does not necessarily exclude the possibility that in the kinetically controlled initial protonation of anisolechromium tricarbonyl ring (or carbonyl) protonation may compete with metal protonation. The former, however, then would rapidly reverse, whereas the latter would not. Under stable conditions generally the thermodynamically most stable forms are observed, if the energy barrier of interconversion is sufficiently low at the studied temperature.

Experimental Section

Anisolechromium tricarbonyl (Strem Chemical, Inc.) was used without further purification. Protonation was carried out by adding a cold $DCCl_3$ solution of anisolechromium tricarbonyl into excess FSO_3H-SO_2 at −80° under nitrogen, to obtain an about 10% solution of protonated anisolechromium tricarbonyl in FSO_3H-SO_2. Both solutions were purged with nitrogen before mixing. FT carbon-13 spectra were obtained on Varian XL-100 NMR spectrometer using external Me_4Si capillary as reference, under experimental details described previously.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No.—Protonated anisolechromium tricarbonyl, 57444-58-3.

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Carbon–Carbon Bond Formation via Organometallic Electrochemistry

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The use of electrochemistry for organic and organometallic synthesis is well documented in the literature. However, fewer studies have been conducted in which a deliberate attempt has been exerted to exploit organometallic electrochemistry for organic synthesis or more specifically for the formation of carbon–carbon bonds.[2] Further, published results suggest that transition metals in the lower valent states are probably responsible for promotion and/or catalysis of several organic reactions.[3] As a result of these two ideas, we have embarked on an investigation of the formation of carbon–carbon bonds from the electrochemical reduction of readily available transition metal complexes in the presence of organic substrates. In this paper we wish to report our preliminary results and emphasize the macroscale synthetic utility of this technique for organic chemistry.

Although there are several stable low-valent transition metal complexes such as the metal carbonyls, π-allylnickel,[4] and bis(cyclooctadienyl)nickel[5] which are isolable and have been used for organic synthesis, they have some disadvantages. For example, they are often sensitive to air, may require reasonably sophisticated techniques to incorporate them into reaction mixtures, and may be useful only in stoichiometric amounts owing to catalyst inactivation through reaction. This reported work emphasizes an approach which generates active but nonisolable catalysts and offers some advantages over the previously mentioned complexes. For example, the acetylacetonate complexes of many transition metals are soluble in organic solvents, easily prepared,[6] have reasonable air and thermal stability, and are convenient to incorporate into a reaction medium. Another potential advantage offered by the electrochemical system for generating chemically active metal complexes is the continuous recycling of the catalyst in the event it is inactivated by oxidation. Thus, the need for stoichiometric quantities of metal complex may be alleviated. One of the limitations of this technique is that one must choose the proper metal and substrate such that the reduction potentials allow for electrochemical reduction of the desired chemical components.

Description of Electrochemical Cell and Reaction Components. Several organic halides are presently under investigation, but this article shall deal only with aliphatic, benzylic, and aromatic halides. Data resulting from these substrates are shown in Tables I, II, and III.

Nickel and iron acetylacetonate were chosen as the starting metal complex because (a) they both have reported reduction potentials below the potentials of the substrate halides; and (b) they have isolable (Ni) and nonisolable (Fe) low-valent metal complexes which could be helpful later in the detailed investigations. There have only been a few σ-bonded aliphatic iron complexes isolated.[7] Since the metal complexes are being reduced to lower oxidation states, substances such as triphenylphosphine (Ph_3P), which are referred to in this paper as stabilizing ligands, were added to (a) modify the activity and (b) perhaps aid in the solubility of the reduced metal. In reactions run without Ph_3P, the solution becomes cloudy and the cathode develops a coating. However, neither of these two conditions appeared to adversely affect the product yields or distribution (Table II).

A diagram of the electrochemical cell used in this study is shown in Figure 1. Electrodes were made from sheet metal (Al, Cu, or Ni) which was cut to the dimensions of 45 × 45 × 0.90 mm and cleaned thoroughly just prior to use. In the cell these plates were placed parallel to one another with a 6–8-mm space between them. A potential was applied across the electrodes by a constant voltage power supply, which was automaatically regulated such that the potential on the cathode relative to SCE was more cathodic than the reduction potential of the metal complex [$Fe(acac)_3$[2] −0.82 V vs. SCE in THF; $Ni(acac)_2$[2] −1.5 V vs. SCE in DMF] and less cathodic than the reported substrate reduction potentials (aliphatic bromides[8] −2.2 V vs. SCE in DMF; bromobenzene[8] −2.3 V vs. SCE in DMF; benzyl bromide[8,9] −1.22 V vs. SCE in DMF). The standard calomel electrode was periodically inserted directly behind the cathode during the reaction to obtain an approximate

Table I
Aliphatic Bromides

Registry no.	Substrate	Metal acetylacetonate	Electrode[a]	Stabilizing ligand	Product	% yield[b]
109-65-9	1-Bromobutane[c]	Fe	Ni/Ni	Ph_3P	Octane	28
78-76-2	2-Bromobutane[c]	Fe	Ni/Ni	Ph_3P	3,4-Dimethylhexane	20
507-36-8	2-Bromo-2-methylbutane[c]	Fe	Ni/Ni	Ph_3P	No coupled product	
111-83-1	1-Octyl bromide	Fe	Al/Al	Ph_3P	Hexadecane Octene Octane	72.3
	1-Octyl bromide	Fe	Al/Al		Hexadecane Octene Octane	93.9

[a] Cathode/anode. [b] Yield is based on GLC data gathered on starting halide and the total products. [c] Products other than coupled were not investigated.

check of its potential. Since this is not an ideal method for controlling the cell potential, and since organic halides are known to react by reduction[8] directly in electrochemical cells without metal complexes present, control reactions were run at the same applied potential without the metal complex present in the reaction medium. In all control experiments, only minimal current developed or flowed (<2 mA) and at best only trace amounts of products formed from 200 hr of electrolysis. In contrast, in a typical electrolysis experiment with metal acetylacetonate present, currents as high as 40–60 mA were observed with product formation completed after 50–90 hr. A typical current profile for the reaction of $Fe(acac)_3$ and 1-octyl bromide is shown in Figure 2.[10] This curve provides a useful measure of the reaction end point. For example, at 50 hr of electrolysis there was only 10% of the starting halide remaining in the reaction medium and by 70 hr there was only 3% of the starting material remaining.

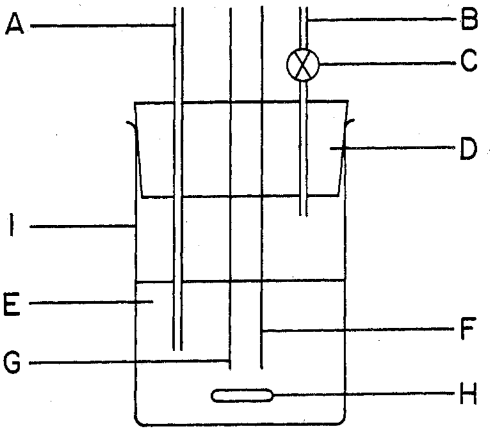

Figure 1. Electrolysis cell: (A) nitrogen inlet for purging the solution and maintaining a positive pressure; (B) gas outlet which is open during purging and closed during electrolysis; (C) stopcock for closing gas outlet; (D) rubber stopper; (E) electrolysis solution; (F) cathode; (G) anode; (H) magnetic stirring bar; (I) 100-ml Berzelius beaker.

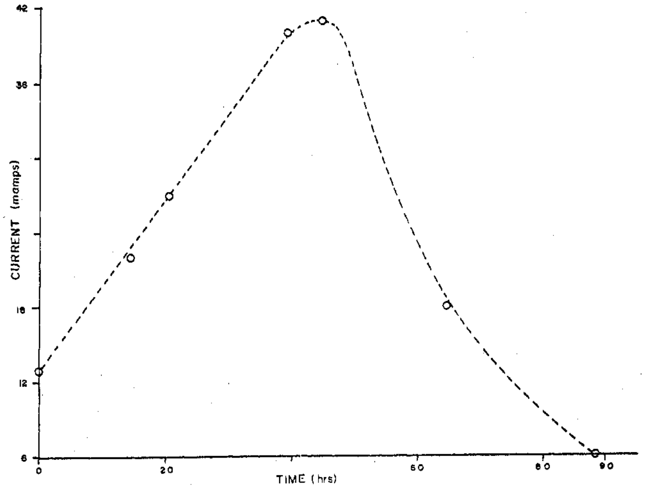

Figure 2.

Table II
Product Ratios and the Effect of Ph_3P

	Experiments A	Experiments B
Catalysts	$Fe(acac)_3$	$Fe(acac)_3$
Octane, %	11.08	49.21
Octene, %	3.22	17.70
Hexadecane, %	32.26	30.71
Ane/ene	3.44	2.81
% reaction	72.3	93.9
Ligand	$+Ph_3P$	$-Ph_3P$
Electrodes	Al/Al	Al/Al

Results and Discussion

From the fact that little or no product formed in absence of metal acetylacetonate, it is reasonable to conclude that direct electrolysis of the organic halides used in these studies at an applied potential of 1.3–1.8 V is negligible. Thus, it is then reasonable to suggest that the metal is being reduced first to a lower valent metal complex which then interacts with the organic halide substrate. Although somewhat indirect, the fact that metal carbonyls were generated when carbon monoxide is bubbled into the reaction medium during electrolysis strongly supports the assumption that the metal is reduced. Further, if octyl bromide is reduced in the system described in this note at an applied voltage of 2.0 V, only octane is obtained which obviously is a different product distribution than observed with metal complex present. It is also assumed without direct evidence, but with considerable literature precedence,[11] that interactions between the alkyl halide and reduced metal result in σ-bonded alkyl transition metal complex which decomposes by various pathways to products (vide infra).[12] By using a divided cell, it was ascertained that the reaction occurred only in the cathode compartment and that the anolytes are not needed for organic product formation. The anode dissolves presumably forming metallic halides or acetylacetonates which are complexed with the solvent dimethylformamide (DMF).[13]

Data in Table I show the overall yields and products

Table III

Registry no.	Substrate	Metal acetyl-acetonate	Electrode[a]	Stabilizing ligand	Product	% yield[b]
100-44-7	$PhCH_2Cl$	Ni	Cu/Ni	Ph_3P	Bibenzyl	87
100-39-0	$PhCH_2Br$	Ni	Cu/Ni	Ph_3P	Bibenzyl	85
108-86-1	PhBr	Ni	Cu/Ni	Ph_3P	Biphenyl	65

[a,b] See Table I.

using aliphatic bromides as substrates. It is apparent from these data that the butyl bromide isomers which are branched at the α carbon give lower amounts of coupled products than those that are not branched. This can be rationalized from at least two points of view. The first and most obvious rationale would be that the increased steric bulk lowers the yield of coupled product. A second explanation, which is probably complimenting the first explanation, is that more hydrogens located on the β carbons are present in tertiary butyl bromide than secondary or primary butyl bromides which may provide opportunity for additional reaction pathways to operate. The latter explanation is reasonable since σ-bonded aliphatic transition metal complexes are known to undergo a facile β-elimination of metal hydride.[12] Also from Table I, it can be seen that the overall yield from octyl bromide reactions is a function of the triphenylphosphine. The nature of this change in yield can readily be seen in Table II, which shows that in the absence of Ph_3P, both alkene and alkane production has increased. The origin of this effect will be the subject of a future publication.

Mechanistic Interpretation. At first, inspection of the data in Table II suggests that this reaction involves a free-radical mechanism which is consistent with other investigations. For example, Saito[14] had previously suggested that Et_2Ni(bipy) decomposed from thermal conditions by a free-radical process to give butane, ethane, and ethene. Further, the product analyses of experiment A agreed quite well with results published by Kochi[15] on diacyl peroxide photodecomposition. For example, in the photodecomposition of di-*n*-butyl acyl peroxide, Kochi reports alkane:alkene:coupled product ratios of 0.09:0.03:0.38 in pentane solvent. The product ratios from experiment A are 0.11:0.03:0.32. However, in experiment B, which is comparable to A except that Ph_3P is absent, the relative product yields for alkane and alkene are significantly altered and more closely agree with Kochi's results in which the diacyl peroxide was decomposed in a more viscous solvent, decalin. Since the viscosity of DMF is not appreciably altered by either the presence or absence of Ph_3P, it is not readily apparent that free-radical processes are active in our electrolysis system. However, in experiments using cumene as a free-radical trapping reagent, the yield of coupled product was reduced. For example, a 32% reduction in the yield of coupled product was observed when a 1:1 mole ratio of cumene to 1-octyl bromide was used, a 45% reduction was observed from a reaction in which the mole ratio was 4.9:1, and a 60% reduction in coupled product yield resulted in a reaction having a 10:1 mole ratio. The dilution effect resulting from added cumene is accounted for in the above percentages.[16]

Thus it appears that the formation of coupled product occurs via free-radical processes, while the alkane–alkene product forming portion of the reaction is probably not occurring by free-radical processes. These latter results suggesting a non-free-radical pathway are consistent with observations made by both Whitesides[17] and Schwartz.[18] Whitesides has shown that di-*n*-butylbis(triphenylphosphine)platinum(II) does not decompose thermally by a free-radical process to produce butene and butane. Likewise, Schwartz has made the same observation using bis(triphenylphosphine)(carbonyl)-1-octyliridium(I) in which octane and octene are produced.

Other Substrates. In another series of experiments on different substrates designed to explore the useful breadth of this electrochemical technique, both benzylic and aromatic halides were briefly investigated (Table III).

One can readily see that the yields of coupled products from these substrates are improved over those of the aliphatic halides. While there may be some beneficial electronic factor inherently associated with the presence of the phenyl ring, we feel that one significant reason for the increased yields for the substrates listed in Table III is the lack of opportunity for alternative pathways of decomposition such as β-elimination.

Summary. This work has shown that readily available transition metal complexes such as $Ni(acac)_2$ and $Fe(acac)_3$ can be induced to react in an electrochemical system with alkyl halides to produce carbon–carbon bonds (coupled products). Presumably, low-valent metal complexes are prepared which react with alkyl halides to form σ-bonded alkyl transition metal intermediates which decompose by known pathways. The coupled products appear to arise from a free-radical pathway while the "disproportionation" products alkane and alkene may not be produced by a free-radical pathway. Organic halides having hydrogens on the carbon β to the halide atom tend to yield alkenes and alkanes in addition to coupled products.

Experimental Section

General. A Heathkit Regulated L.V. Power Supply Model IP-27 was used as a constant applied potential source for the electrochemistry. Reaction products and starting materials were analyzed via a Varian Aerograph Model 1740 gas chromatograph which was equipped with temperature program, flame detector, and a Varian CH-5 mass spectrometer. Peak areas of gas chromatographed samples were analyzed by mechanical integration which was referenced to hexane as an internal standard, and by mass spectral fragmentation patterns.

Dimethylformamide (DMF) was purchased from Baker Chemical Co. and purified by vacuum distillation at 0.50 mm and 30°C. It was stored under dried N_2 and over molecular sieves. All other reagents were purified by standard procedures. All materials used in the reaction were rigorously dried prior to electrolysis.

Tetraethylammonium Bromide (TEAB). An equal molar (1.5 *M*) mixture of triethylamine and ethyl bromide was refluxed for 24 hr. The ammonium salt which precipitated was filtered, washed with toluene, and recrystallized from a benzene–ethanol mixture. The resulting crystals were dried in a vacuum at 80°C and stored in a desiccator.

$Ni(acac)_2$ was prepared by adding an ammoniacal solution containing $NiCl_2$ (32.4 g, 0.25 mol), 150 ml of concentrated ammonia solution, and just enough H_2O to effect solution to another ammoniacal solution containing acetylacetone (55 ml, 0.535 mol) and concentrated ammonia (40 ml, 0.60 mol). The resulting thick blue mixture was vigorously stirred for 30 min, filtered, and air dried to give the diamine derivative of $Ni(acac)_2$. This derivative was boiled in toluene or, better, xylene to give the dark green solution of $Ni(acac)_2$. Hexane was added to precipitate $Ni(acac)_2$ which was filtered, washed with hexane, vacuum dried, and stored in a desiccator. An 80% yield of $Ni(acac)_2$ was obtained with mp 152–154°C.

$Fe(acac)_3$ was prepared by mixing stoichiometric amounts of

$FeCl_3$ and sodium acetylacetonate in a aqueous solution. The dark red product was extracted with $HCCl_3$. The extract was washed with H_2O three times and the solvent evaporated. The solid was then recrystallized from ethanol–water mixture which was vacuum dried. A 77% yield of Fe(acac)$_3$, mp 184°C dec, was obtained.

Electrodes. The nickel and copper electrodes were cleaned by thoroughly scouring them with steel wool and placing them in a solution of DMF and TEAB in which a potential of 5–10 V was applied across the electrodes for ≤ 1 min. After this procedure they were immediately transferred to the reaction flask. While all reactions followed a curve similar to that shown in Figure 2. cleaning the electrodes resulted in higher initial currents. Generally, currents ranged from 10 mA (initial) to as high as 80 mA (maximum) during the reaction.

The aluminum electrodes have, in more recent experiments, been cleaned by placing them in 3 *M* HCl for 15 min and rinsing thoroughly with H_2O and dried by rinsing them in organic solvents.

The standard calomel electrode which was periodically inserted into the reaction (≈ 1 min) to monitor the working electrode voltage probably led to some contamination by water. However, it did not affect product formation.

Since the anode dissolved during the reaction, current density measurements were not made. Likewise, electrochemical yields were not determined.

Electrolysis Reaction. In a typical reaction, to 60 ml of DMF in a 100-ml Berzelius beaker were added Fe(acac)$_3$ (4.4 g, 12.46 mmol), triphenylphosphine (1.5 g, 5.66 mmol), $Et_4N^+Br^-$ (0.802 g, 3.81 mmol), and 1-octyl bromide (8.6 ml, 49.78 mmol). A rubber stopper fitted with cleaned aluminum electrodes was used to seal the beaker. Nitrogen was bubbled through the stirred solution until solutes dissolved. An applied potential of 1.5 V was established and held until the current profile, as indicated in Figure 2, was completed.

Octane and octene were removed from the electrolyzed solution by vacuum distillation and analyzed by gas chromatography. An 8-ft column packed with 20% Carbowax 20M on 80–100 mesh Chromosorb W was used to separate octane from octene and a 6-ft column of 3% SE-30 80–100 mesh Chromosorb W was used to separate 1-octyl bromide from DMF.

The pot residue was treated with 100 ml of distilled H_2O and extracted with five 50-ml aliquots of ether. This ether solution was dried over anhydrous magnesium sulfate, filtered, and evaporated by rotoevaporator. Liquid chromatography on a 46 × 2 cm column of activated acidic aluminum oxide eluted with hexane was used to separate hexadecane and unreacted 1-octyl bromide from other residues contained in the ether extract. After solvent evaporation on a rotoevaporator, these products were analyzed by GLC on the same columns mentioned above.

The precent yields were based on the amount of 1-octyl bromide which had reacted and are reported in the text. The percent conversion (amount of product divided by amount of 1-octyl bromide) ranged from 70 to 98. The important factor in the percent conversion number is the concentration of starting halide or, more directly, the concentration of products. If the product concentration was too high, it began to oil out on the top of the DMF solution. This oil layer would then attract the 1-octyl bromide thereby reducing reactant in the bulk electrolysis solution. Thus it is essential for highest conversion to maintain a homogeneous solution.

Benzyl and Aryl Halides. While the general procedure for electrolysis with these substrates was identical with that described for the 1-octyl bromide, the work-up was slightly different. There was no vacuum distillation. The raw electrolysis mixture was diluted with 100 ml of water and extracted with five 50-ml aliquots of ether. The ether extract was dried, filtered, and reduced in volume by rotoevaporation. This material was then passed through an alumina column using hexane as the eluting solvent. The coupled products, bibenzyl or biphenyl, were thence isolated, sublimed, and weighed.

Divided Cell. An H cell design was used with a salt bridge mixture containing methyl cellulose (10.23 g), DMF (80 ml), and TEAB (4.4 g). Each half of the cell contained 60 ml of DMF, 0.8 g of TEAB, 1.50 g of Ph_3P, and 8.6 ml of 1-octyl bromide. The cathode compartment contained 4.4 g of Fe(acac)$_3$. After 366 hr, at an applied potential of 1.5 V and low currents (as expected), the reaction was stopped. Also the red color, due to Fe(acac)$_3$ diffusion, was hallfway across the salt bridge.

Although the yield was low owing to low currents, octane, octene, and hexadecane were isolated from the cathode compartment and analyzed by gas chromatography.

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Registry No.—Fe(acac)$_3$, 14024-18-1; Ni(acac)$_2$, 3264-82-2; $NiCl_2$, 7718-54-9; $FeCl_3$, 7705-08-0; acetylacetone, 123-54-6; sodium acetylacetonate, 15435-71-9.

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A New Stereospecific Synthesis of the *E* Isomers of 2-Phenyl-4-arylmethylene-2-oxazolin-5-ones*

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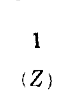
The Erlenmeyer azlactone synthesis,[1] a well-known reaction that is widely employed for the preparation of 2-aryl- (or alkyl-) 4-arylmethylene-2-oxazolin-5-ones, consists of heating aromatic aldehydes with hippuric or aceturic acids in the presence of acetic anhydride and sodium acetate and usually gives the thermodynamically stable isomers 1 (R = H).



1

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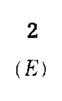

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(*E*)

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* Reactions in Polyphosphoric Acid. I.