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C-C and C-O Coupling Reactions of Terminal Alkynes by a Water Soluble Organoiridium Electron-transfer Mediator in Thin Layer of Water on Gold Electrode

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Abstract

An electrochemical reduction process is described for the rapid and efficient conversion of terminal alkynes into useful products. Terminal alkynes (HC=CR; R = $C_{e_1}H_{s_1}$, $p-C_{e_1}H_{c_1}C_{h_2}$, $C_{H_2}C_{e_1}H_{s_2}$, $C_{e_1}H_{s_2}$) were hydrated and dimerized by cathodic reduction of catalytic amount (5 %) of [Cp1r(NCMe)₂(PAr₃)](OTf)₂. **1**, ($E_{pc} = -620$ mV vs Ag/AgCl) through an aqueous/nonaqueous interface. Thin aqueous layer containing water-soluble compound **1** was formed on gold electrode. The cathodic reduction current height of **1** increases as increasing the concentration of terminal alkynes. The electrolysis of **1** while contacting with terminal alkynes containing organic solvent produced ketones, aldehydes and dimerized enyne products from terminal alkyne/water reaction systems. A new micro-scale electrocatalysis technique is depicted.

Keywords: Electrocatalytic alkyne conversion; Enyne; Ketone; Aldehyde; Cyclic voltammetry; Water-soluble catalyst; Aqueous/ nonaqueous interface

Introduction

Electrochemical reduction and oxidation (redox) processes as a synthetic tool in chemistry are growing areas via either a direct redox reaction with electrode materials [1,2] or an electron transfer (ET) mediator [3-5]. A basic idea is that a cathodic reduction process of high oxidation state but stable organometallic compound is used to produce putative anionic radical compound. This resulting anionic radical compound could produce highly reactive species which will be used to catalyze the activation of organic substrates such as alkynes. Metal-catalyzed hydration and oligomerization of alkynes provide important processes in organic chemistry to aldehydes, ketones, and conjugated olefin compounds since they are the carbon–oxygen [6-10] and –carbon [11-19] bond forming reactions which produce a variety of new inexpensive starting materials.

Over the last few decades, there has been considerable interest in a queous and biphasic homogeneous water-soluble metal catalysis [20-26]. Among water-soluble ligands, $PAr_3 (P(m-C_6H_4SO_3Na)_3)$ is the most commonly used ligand to prepare water-soluble metal compounds [27-32]. Iridium-Cp^{*} (C₅Me₅⁻) compounds have been investigated and have drawn much attention due to their diverse and interesting reactivity with alkynes [11-18,27-37].

No electrochemical studies, however, for new water-soluble metal compounds have been explored thus far, to the best of our knowledge; therefore, we became interested in exploring the hydration and dimerization of alkynes by electrochemical reduction process mediated by the water soluble bis-acetonitrile iridium-Cp⁻ compound $[Cp^{Tr}(NCMe)_2(PAr_3)](OTf)_2$ (1) $(OTf = OSO_2CF_3)$ in two immiscible liquids (H_2O/CH_2ClCH_2Cl) by micro-scale electrochemical techniques as one of the newest experimental methods. This is the first example of combination of cathodic reduction mediated reactions and water-soluble (i.e. Green Chemistry) organoiridium catalysis. This straightforward method described in this study of thin aqueous layer containing redox active catalyst (1) on electrode is not only useful to monitor catalytic activity of water-soluble compounds with organic substrates, but also easy to separate catalyst and organic products.

During our investigation on the activation of alkynes by electroreduction of **1** in biphasic electrochemical system, we found corresponding aldehydes, ketones, and enynes from the electrochemical reactions of compound **1** (electrochemically reduced form) with alkynes via the H_2O/CH_2ClCH_2Cl interface on a gold electrode. Here we wish to report that a new method of electrochemical intermolecular C-C and C-O coupling reactions which are based on the introduction of a thin layer of water phase containing electron transfer mediator compound **1** between the surface of a gold electrode and organic phase (CH₂ClCH₂Cl). The resulting experimental setup is depicted schematically in (Figure 1). Dry and polished gold electrode (4 mm diameter, area = 0.13 cm²) exhibits sufficient hydrophilic character to adhere micro volume (3 *micro* L, thickness: *ca.* 250 *micro* meters) of water.

Results and Discussion

Di-cationic water-soluble bis (acetonitrile) compound $[Cp^{+}Ir(NCMe)_{2}(PAr_{3})]^{2+}$ (1) has been prepared by replacing one MeCN of $[Cp^{+}Ir(NCMe)_{3}]^{2+}$ with PAr₃ (Equation 1) and unequivocally characterized by detailed NMR spectral (¹H, ¹³C, ³¹P NMR), IR, and elemental analysis data (see Experimental Section). Water-insoluble complex $[Cp^{+}Ir(NCMe)_{3}(PMe_{3})]^{2+}$ was previously reported [38].

Since it is well-known that terminal alkynes can be activated by organoiridium compounds [11-18], this voltammetric observation prompted us to look into details of reduced-metal catalyzed activation of alkynes in biphasic (H₂O/CH₂ClCH₂Cl) solution. The biphasic

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electrochemical experimental system was designed because terminal alkynes are insoluble in water. A water soluble electron transfer mediator stays in aqueous solution on the electrode surface while terminal alkynes are in organic solution. The cathodic reduction of 1 was investigated by cyclic voltammetry (CV) which shows a single and irreversible wave at $E_{\rm pc}$ = -620 mV vs Ag/AgCl at a gold disk electrode in H₂O (containing 0.1 M KCl)/CH₂ClCH₂Cl (containing 0.1 M [NBu₄]-[SO₃CF₃]) (Figure 2). The reduction of compound 1 in an aqueous phase is diffusion limited process since the current height is linear to the square root of the scan rate.

Observed cyclic voltammogram is proposed on the basis of the results of controlled-potential electrolysis, as discussed later. Four different terminal alkynes (R-C=CH, R = C_6H_5 , C_6H_4 -CH₃, C_6H_9 and $CH_2C_6H_5$) were examined in the absence and presence of compound 1 at the interface between water solution containing 1/KCl and dichloroethane containing alkynes [NBu,][SO,CF]. A direct reduction approach is not possible for terminal alkynes examined in this research, due to the fact that these compounds show no voltammetric response prior to the cathodic background. No redox activity of terminal alkynes was observed in the absence of compound 1 at the same potential range. The addition of alkynes, however, in organic phase affected the voltammograms of 1 in aqueous solution layer such as enhancement of the cathodic reduction current height. The voltammetic responses of this alkyne/Ir system are consistent with classic electron transfer catalysis [3-5], where Ir(II) produced at the electrode, gives an electron to alkynes, thereby returning the organo-Ir(III) compound to its oxidized form of Ir for rereduction. Compound 1 did not show the catalytic activities for the hydration and dimerization of alkynes unless it is activated by electrochemical cathodic process.

Controlled-potential electrolyses were performed to determine the nature of the product by electrochemical activation. When the 20:1 (PhC=CH:1, mol/mol) interfaced solution was bulk electrolyzed at (E_{appl}) -650 mV at an Au disk, the concentration of PhC=CH (monitored by sampling for gas chromatographic (GC) analysis) fell to nearly zero after ~30 min, with a total coulomb count of ~0.036 F/equiv of PhC=CH. Both hydrated (C-O coupling) and dimerized (C-C coupling) products of alkynes (Equation 2) in organic phase were characterized by GC-MS analysis. Product distribution of phenylacetylene reaction products was confirmed by external standard method with GC-MS calibration curves for each product. Selectivity study is under investigation because non-electrochemical dimerization of phenylacetylene to enynes catalyzed by the Pd(OAc),/Imidazolium Salt/Cs₂CO₃/dimethylacetamide solvent system has been provided of a good regio- and stereocontrolled enyne products. In which case, the product ratio of trans- and cis-1,4-diphenyl enynes was 97:3 [19]. According to GC-MS analysis, alkyne conversions to enyne isomers, ketones, aldehydes and some unknown products are ca. 60-90% (see Table 1 in experimental sections).

A very small amount of charge was passed during the electrolysis. This probably indicates that after initial reduction of 1 to form 1- in





Figure 1: Schematic depiction of the experimental setup with thin layer formation of an aqueous phase between a gold electrode and organic phase.



the aqueous phase, a radical chain mechanism is involved in the real conversion of alkynes into products through an electrocatalytic process.

The increase of steady state current during electrolysis upon addition of larger amount of terminal alkynes shows that the interaction between 1.- and alkynes is the rate limiting process. The steady state currents at 10 minutes for 1 with alkynes of 10/20 equiv (v/v) can be arranged as follows: 2.84/5.11 mA (for HC=CCH₂C₆H₅) > 1.84/3.53 mA (for HC=CC₆H₅) > 1.02/1.37 mA (for HC=CC₆H₉) > 0.64/0.94 mA (for HC=C-p-C₆H₄CH₃).

Cathodic reduction mediated reaction pathways for the formation of hydrated and dimerized products from terminal alkynes

The following steps of the reaction pathway at the interface of two immiscible liquids can be proposed: 1) reduction of 1 to form reactive radical anionic species $1 \cdot via$ electron transfer from the electrode, 2) diffusion of $1 \cdot through the aqueous thin layer to the interface, and 3) electron transfer from 1 · to alkynes through water/dichloroethane interface to initiate the alkyne activations.$

Possible pathways for the C-O coupling from alkyne hydrations

It has been known that terminal alkynes react with water in the presence of organometallic compounds to produce aldehyde, ketone and carboxylic acids [6-10]. Hahn and Wakatsuki recently carried out detailed mechanistic studies for the alkyne hydration mediated by metal compounds in homogeneous solutions [6-10,39].

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The formation of aldehyde and ketone seems to be initiated by the cathodic reduction of the water-soluble iridium compound 1, because compound 1 did not demonstrate any reactivity for the hydration of alkynes unless it is activated by cathodic reduction process. At the stage of generation of a putative 19 e⁻ Ir(II) species has to be kinetically driven either by releasing labile ligand (NCMe) or by a fast radical substrate reaction with alkyne. This reaction stage could provide a formation of either Ir-(π -alkyne), Ir-(σ -alkynyl) intermediate or equilibrium between these two forms. Terminal alkynes are known to coordinate toward metal center to give stable π -alkyne or σ -alkynyl compound [6-10]. In fact, it has been well-documented that metal vinylidene is obtained directly from the rearrangement of π -coordinated terminal alkynes [6-10,11-19,39,40]. It seems reasonable to include the direct attack of H₂O on the carbon of the Ir-(HC=CR) to produce ketones and on the α -carbon of the vinylidene moiety (Ir=C=CHR) to yield a hydroxyl carbene compounds followed by reductive elimination to give aldehydes.

Possible pathways for the C-C coupling from alkyne dimerization

The dimerization of alkynes catalyzed by a variety of transition metal compounds has been extensively studied and suggested the elaborated mechanism [11-18]. The key step of alkyne coupling reaction has been commonly proposed to involve the rearrangement of metal π -alkyne to metal vinylidene form [11-18]. In this case, the following steps of the reaction pathway for the formation of dimerized enyne products could be proposed: i) electrochemical reduction of water soluble iridium compound, ii) ligand switching from acetonitrile to alkyne, iii) rearrangement of alkyne to yinylidenyl-iridium (III), iv) oxidative addition of another alkyne to give iridium (III)-alkynyl, and v) migratory insertion of vinylidene into iridium-alkynyl bond, and vi) reductive elimination of enynyl ligand. Oligomers or higher than the dimers were not observed. Since each alkyne displayed different product distribution, in terms of mechanistic aspects and regioselectivity for product distribution, further investigation will be performed.

In summary, preliminary experiments have shown that aqueous/ nonaqueous interfaced reaction media can be utilized for electrocatalytic C-C and C-O coupling reactions. It is clear that under Ir(II)-based ET-mediator conditions in thin layer micro-scale reaction system can catalyze the dimerization and hydration reactions of terminal alkynes. Based on the data we obtained, we cannot rule out the possibility of a regioselectivity role played by an Ir(II)-alkyne intermediate in these reactions, we assume it likely that the geometries of the organic products are determined basically by the radical/substrate reaction. We will investigate this new synthetic method with internal alkynes (R-C=C-R') as well as with unactivated olefins.

Experimental Section

General Information

Deionized water from Milli Q water purification system was used for preparing aqueous solution. Solvents were reagent grade and were purged by Ar prior to use. All synthesis and product isolations were carried out under Ar using standard vacuum system, Schlenk and glovebox techniques. Phosphine oxide $(OP(m-C_6H_4SO_3Na)_3)$ seems to be produced when the water-soluble PAr₃ complexes are handled under air for a prolonged period of time. Electrochemical experiments were carried out under Ar. The experimental reference electrode was a silver/silver chloride wire separated from the working electrode compartment by a vycor glass (Bioanalytical Systems, BASi). It was prepared by deposition of AgCl onto silver. Standard three-electrode cells were used, with Pt wire counter electrodes as depicted in (Figure 1). The working electrode for voltammetry was a 4 mm diameter gold disk (BASi), which had been progressively polished with Metadi II diamond polishing compounds, rinsed with nanopure water, and dried under vacuum prior to use. Bulk electrolyses were conducted using the same setup. BAS 50W and EG&G 273 and 362 potentiostats interfaced to a personal computer were used for voltammetry and electrolysis. The supporting electrolyte was 0.1 M [NBu₄][SO₃CF₃] which was an electrochemical grade purchased from Aldrich. The NMR spectra were recorded on a Varian 500 MHz spectrometer for ¹H and 126 MHz for ¹³C, and 121.3 MHz for ³¹P. Infrared spectra were obtained on a Nicolet 205. Gas chromatography/ mass spectra were measured by Hewlett-Packard HP 5890A and VG-trio 2000 instruments or Agilent 6890 N-Agilent 5973 (MS). Elemental analysis was carried with a Carlo Erba EA1108.

PAr₃, $P(m-C_6H_4SO_3Na)_3$ [27-32], $[Cp^*IrCl_2]_2$ [41] and $[Cp^*Ir(NCMe)_3](SO_3CF_3)_2$ [41] were prepared by the literature methods.

Synthesis of $[Cp^{*}Ir(NCMe)_{2}(P(m-C_{6}H_{4}SO_{3}Na)_{3})](SO_{3}CF_{3})_{2}\cdot 3H_{2}O$ (1)

A 0.11 g (0.18 mmol) of P(m-C₆H₄SO₃Na)₃)·3H₂O was added into a solution of [Cp*Ir(NCMe)₃](SO₃CF₃)₂ (0.15 g, 0.2 mmol) in H₂O (5.0 mL) under N₂ at 25°C and the reaction mixture was stirred for 3 hrs before it was distilled under vacuum to remove solvent. The yellow solid was washed with CH₂Cl₂ twice and recrystallized in H₂O/MeOH/ Me₂CO. The yield was 0.24 g and 89% based on [Cp'Ir(NCMe)₂(P(m-C₆H₄SO₃Na)₃)](SO₃CF₃)₂·3H₂O (1). ¹H NMR (D₂O): δ 1.59 (d, 15 H, J = 2.4 Hz, C₅(CH₃)₅), 2.56 (s, 6H, NCCH₃), 7.53 - 8.05 (m, 12 H, P(m-C₆H₄SO₃Na)₃). ¹³C NMR (D₂O): δ 3.17 (NCCH₃), 8.34 (C₅(CH₃)₅), 99.6 (d, J = 1.4 Hz, C₅(CH₃)₅), 126.1 (N≡CCH₃), 126.8 (d, J = 57 Hz), 130, 131.0 (d, J = 9.6 Hz), 131.1 (d, J = 16 Hz), 136. 2 (d, J = 6.3 Hz) and 144.5 (d, J = 13 Hz) P(m-C₆H₄SO₃Na)₃, ³¹P NMR (D₂O): δ 11.2 (P(m-C₆H₄SO₃Na)₃). IR (KBr, cm⁻¹): 2322, 2294 (w, v(C≡N)). Anal. Calcd for C₃₄H_{33O₁₅N₂S₅F₆PNa₃Ir·3H₂O: C, 30.70; H, 2.95; S, 12.05; N, 2.10. Found: C, 30.52; H, 2.77; S. 11.97; N, 1.99.}

Typical conditions

A 3 μ L-aqueous solution of 1 (1.0 μ mol) from 0.33 M 1/0.1 M KCl was placed on gold disk electrode prior to voltammetric analysis or electrolysis. A 2-mg (20 μ mol) of PhC=CH was added to 200 mL CH₂ClCH₂Cl/0.1 M [NBu₄][SO₃CF₃] under nitrogen; electrolyze at 293 K for 30 min. The electrolysis was then performed at -650 mV (vs. Ag/AgCl). Mass: *cis* and *trans* PhCH=CH-C=CPh, M⁺ at m/z = 204; Acetophenone, PhC(=O)CH₃, M⁺ at m/z = 120; Phenylacetaldehyde (PhCH₂C(=O)H), M⁺ at m/z = 120. The retention times of *cis*- and *trans*-PhCH=CH-C=CPh isomers are not the same. All four products were verified by running GC-MS of commercially available authentic samples. After the reaction was completed, the product yields were determined directly by GC-MS and GC calibration curves. Product distribution of alkyne reactions was provided in Table 1.



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Table 1: Observed product distributions upon electrolyses ($E_{\rm app}$ = -650 mV vs Ag/-AgCl) of each alkyne in the presence of organoiridium compound 1.

R	A (%)	B (%)	C (%)	D (%)
C_6H_5	45	20	12	10
p-C ₆ H ₄ -CH ₃	46	0	0	14
C ₆ H ₉	20	0	28	26
CH ₂ C ₆ H ₅	40	0	30	13

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