

## Contents

### Special Issue: One-electron Organometallic Reactivity

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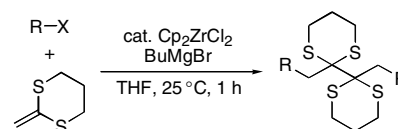
### Communications

**Suguru Yoshida, Hideki Yorimitsu,  
Koichiro Oshima**

*J. Organomet. Chem.* 692 (2007) 3110

Zirconocene-catalyzed alkylative dimerization of 2-methylene-1,3-dithiane via a single electron transfer process to provide symmetrical *vic*-bis(dithiane)s

A mixture of tertiary alkyl halide and 2-methylene-1,3-dithiane was treated with butylmagnesium bromide in the presence of a catalytic amount of zirconocene dichloride. The reaction resulted in alkylative dimerization to yield the corresponding *vic*-bis(dithiane). The reaction would proceed as follows. A single electron transfer from low-valent zirconocene to alkyl halide would generate the corresponding alkyl radical. The radical adds to 2-methylene-1,3-dithiane to afford the corresponding radical stabilized by the two sulfur atoms. A couple of the stable radicals finally undergo dimerization.

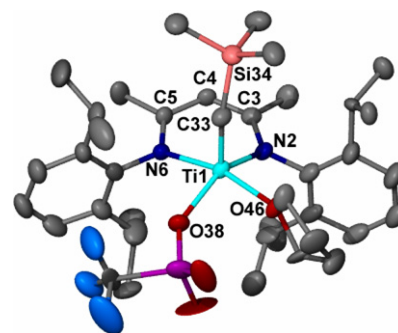


**Falguni Basuli, Debashis Adhikari,  
John C. Huffman, Daniel J. Mendiola**

*J. Organomet. Chem.* 692 (2007) 3115

Organometallic consequences of a redox reaction: Terminal trimethylsilylmethylidene titanium complexes prepared by a one-electron oxidation step

Four and five-coordinate trimethylsilylmethylidene complexes can be readily assembled via a one-electron oxidatively induced  $\alpha$ -hydrogen abstraction step. Shown is the crystal structure of a rare example of terminal trimethylsilylmethylidene complex of titanium. This complex was prepared by a general one-electron oxidation reaction of the corresponding bis-alkyl Ti(III) precursor.



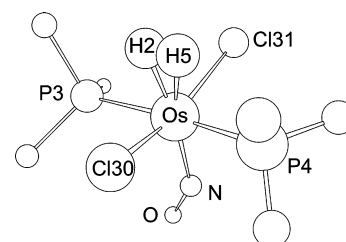
### Regular papers

**Joo-Ho Lee, Andrei N. Vedernikov, David Dye,  
Kenneth G. Caulton**

*J. Organomet. Chem.* 692 (2007) 3121

NO binds to unsaturated Os(IV) polyhydrides as a redox reagent

The fates of the hydrides in two osmium polyhydrides in reaction with NO are mapped, by experiment and DFT calculations.

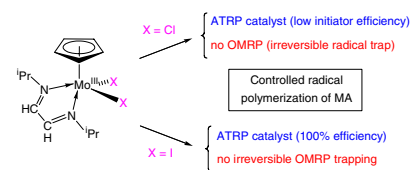


**François Stoffelbach, Rinaldo Poli,  
Sébastien Maria, Philippe Richard**

*J. Organomet. Chem.* 692 (2007) 3133

How the interplay of different control mechanisms affects the initiator efficiency factor in controlled radical polymerization: An investigation using organometallic Mo<sup>III</sup>-based catalysts

The interplay of two different mechanisms in controlled radical polymerization, both involving one-electron reactivity on a transition metal complex (one involving halogen atom transfer to a transition metal complex, ATRP; the other one involving the reversible formation of a metal–carbon bond, OMRP) may lead, in certain cases, to the irreversible trapping of the radical growing chains and to a consequent decrease of the “initiator efficiency factor”. This contribution highlights this phenomenon for this first time, on the basis of results obtained with a 17-electron half-sandwich Mo<sup>III</sup> complex.

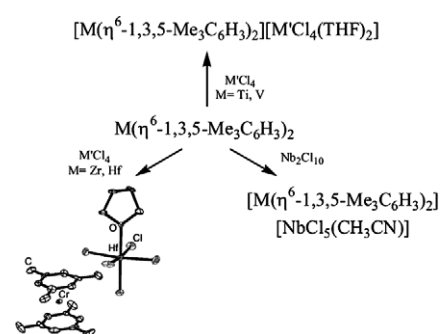


**Ulli Englert, Guido Pampaloni, Filippo Puccini,  
Manuel Volpe**

*J. Organomet. Chem.* 692 (2007) 3144

One-electron redox reactions involving chromium(0) and molybdenum(0) bis-1,3,5-trimethylbenzene derivatives

The reaction of  $M(\eta^6\text{-Me}_3\text{C}_6\text{H}_3)_2$ ,  $M = \text{Cr}, \text{Mo}$ , with the tetrachlorides of titanium(IV) and vanadium(IV) produces  $[M(\eta^6\text{-Me}_3\text{C}_6\text{H}_3)_2][M\text{Cl}_4(\text{THF})_2]$  species. In the case of the reaction of the tetrachloro complexes  $M\text{Cl}_4(\text{THF})_2$ ,  $M = \text{Zr}, \text{Hf}$ , with  $\text{Cr}(\eta^6\text{-Me}_3\text{C}_6\text{H}_3)_2$ , a Cr(I)/M(IV) derivative,  $[\text{Cr}(\eta^6\text{-Me}_3\text{C}_6\text{H}_3)_2][M\text{Cl}_5(\text{THF})]$ , has been isolated.

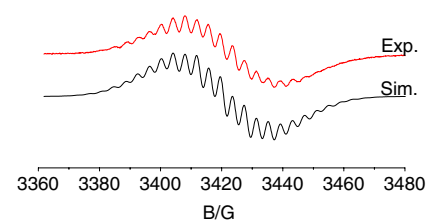


**Cüneyt Kavakli, Anders Gabriëlsson,  
Monika Sieger, Brigitte Schwederski,  
Mark Niemeyer, Wolfgang Kaim**

*J. Organomet. Chem.* 692 (2007) 3151

Reversible radical complex formation of an organometallic diplatinum(IV) compound

Despite the presence of two platinum(IV) centers and two bromide ligands as potential leaving groups the complex *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]$  accepts the first added electron in the tetrazine ring to form a spectroscopically (EPR, UV–Vis) detectable radical anion.

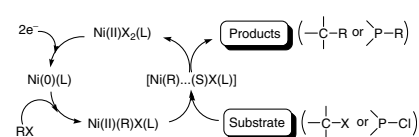


**Axel Klein, Yulia H. Budnikova,  
Oleg G. Sinyashin**

*J. Organomet. Chem.* 692 (2007) 3156

Electron transfer in organonickel complexes of  $\alpha$ -diimines: Versatile redox catalysts for C–C or C–P coupling reactions – A review

Organonickel complexes with  $\alpha$ -diimine ligands play an important role in electrocatalytic C–C or C–P cross coupling reactions. The review summarises recent insights into the reaction mechanisms of such reactions which involve nickel species with (formal) oxidation states ranging from 0 to III.

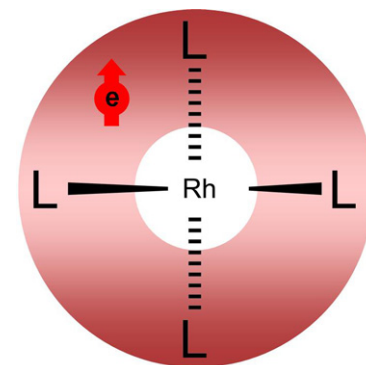


**Bas de Bruin, Jaap C. Russcher,  
Hansjörg Grützmacher**

*J. Organomet. Chem.* 692 (2007) 3167

Spin density distribution in mononuclear Rh(0) complexes: A combined experimental and DFT study

Only little spin density is localized on the rhodium center in  $RhL_4$  complexes ( $L=CO$ , phosphane, olefin) and these compounds are not adequately attributed as  $d^9$ -Rh(0) complexes but best described as highly delocalized metallo radicals.

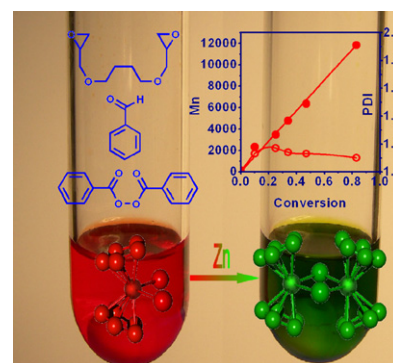


**Alexandru D. Asandei, Yanhui Chen,  
Isaac W. Moran, Gobinda Saha**

*J. Organomet. Chem.* 692 (2007) 3174

Similarities and differences of epoxide, aldehyde and peroxide initiators for  $Cp_2TiCl$ -catalyzed styrene living radical polymerizations

A comparison of epoxide, aldehyde and peroxide initiators for  $Cp_2TiCl$ -catalyzed living radical styrene polymerizations was performed by investigating the effect of reagent stoichiometry and temperature on the initiator efficiency and polydispersity. An optimum was observed for  $[Styrene]/[Initiator]/[Cp_2TiCl_2]/[Zn] = [50-200]/[1]/[2-3]/[4-6]$  at 70–90 °C.

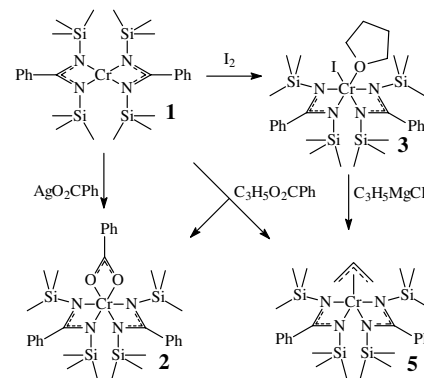


**Beth A. Dykerman, Joshua J. Smith,  
Erin M. McCarvill, Amanda J. Gallant,  
Natasha D. Doiron, Brian D. Wagner,  
Hillary A. Jenkins, Brian O. Patrick,  
Kevin M. Smith**

*J. Organomet. Chem.* 692 (2007) 3183

Synthesis of chromium(III) bis(benzamidinate) complexes via single electron oxidation

Oxidation of  $Cr[(Me_3SiN)_2CPh]_2$  (**1**) with silver benzoate or iodine provides neutral Cr(III) bis(benzamidinate) complexes, which react with  $C_3H_5MgCl$  to form the  $\eta^3$ -allyl complex. The reaction of **1** with excess allyl benzoate was monitored by UV-vis spectroscopy. The X-ray structures of **2**, **3**, and **5** are reported.

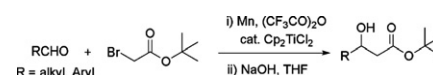


**Laura Sgreccia, Marco Bandini,  
Stefano Morganti, Arianna Quintavalla,  
Achille Umani-Ronchi, Pier Giorgio Cozzi**

*J. Organomet. Chem.* 692 (2007) 3191

Titanium-catalyzed Reformatsky-type reaction

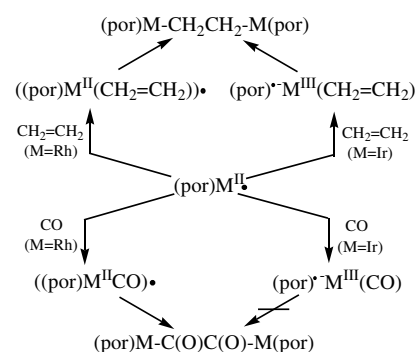
Aryl and alkyl aldehydes give moderate yields in a Reformatsky-type reaction mediated by cyclopentadienyltitaniumdichloride (10 mol%), in the presence of a stoichiometric amounts of  $(CF_3CO)_2O$  and Mn(0).



**Weihong Cui, Shan Li, Bradford B. Wayland***J. Organomet. Chem.* 692 (2007) 3198

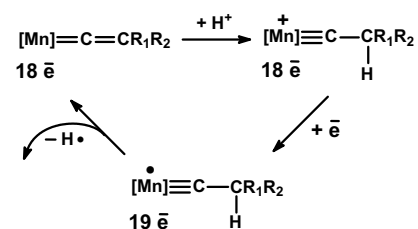
Factors contributing to one-electron metalloradical activation of ethene and carbon monoxide illustrated by reactions of Co(II), Rh(II), and Ir(II) porphyrins

Thermodynamic criteria for one electron activation of ethene and carbon monoxide are described and used as a guide to interpret the patterns of reactivity for group nine (Co(II), Rh(II), and Ir(II)) porphyrin metal-metal bonded dimers and metalloradicals.

**Dmitry A. Valyaev, Mikhail G. Peterleitner, Oleg V. Semeikin, Kamil I. Utegenov, Nikolai A. Ustynyuk, Alix Sournia-Saquet, Noël Lugan, Guy Lavigne***J. Organomet. Chem.* 692 (2007) 3207

Proton reduction catalysis by manganese vinylidene and allenylidene complexes

New approach for electrochemical proton reduction catalysis based on metalocumulene complexes is presented. The catalytic cycles involve the formation and reductive activation of C-H bonds in the intermediate carbyne complexes finally affording dihydrogen. The working potential for Cp(CO)<sub>2</sub>Mn=C=C=CPh<sub>2</sub> (−0.84 V vs. Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN) is the lowest reported to date.



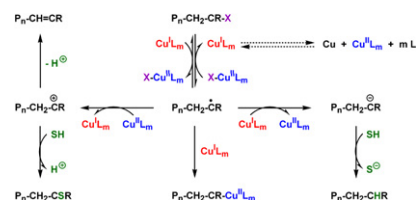
[Mn] = CpMn(CO)(PPh<sub>3</sub>); R<sub>1</sub> = H; R<sub>2</sub> = Ph − 1.60 V vs. Fc

[Mn] = CpMn(CO)<sub>2</sub>; R<sub>1</sub>, R<sub>2</sub> = (=CPh)<sub>2</sub> − 0.84 V vs. Fc

**Nicolay V. Tsarevsky, Wade A. Braunecker, Krzysztof Matyjaszewski***J. Organomet. Chem.* 692 (2007) 3212

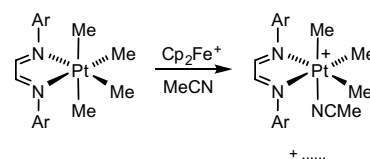
Electron transfer reactions relevant to atom transfer radical polymerization

Concurrent electron transfer reactions that can affect catalyst performance in atom transfer radical polymerization are reviewed, including disproportionation of the Cu catalyst, the reduction of organic radicals to carbanions or oxidation to carbocations, and radical coordination to the metal catalyst.

**Bror J. Wik, Mats Tilset***J. Organomet. Chem.* 692 (2007) 3223

Oxidatively induced reactions of a diimine platinum(IV) tetramethyl complex

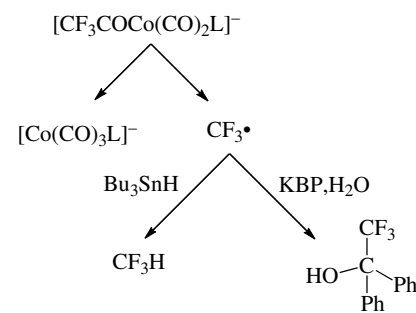
The Pt(IV) tetramethyl complex [Ar-N=CH-CH=N-Ar]PtMe<sub>4</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) is readily oxidized; its oxidatively induced reactivity has been investigated in acetonitrile and dichloromethane.



**Nanda Gunawardhana, Stephen L. Gipson***J. Organomet. Chem.* 692 (2007) 3231

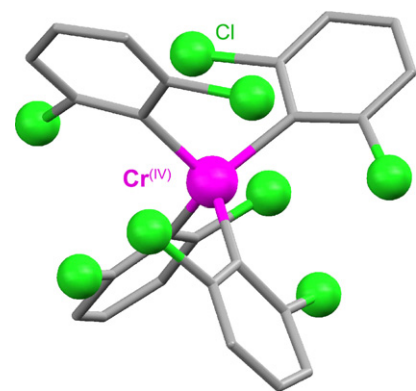
Reductively induced homolytic carbon–carbon bond cleavage in  $\text{Co}(\text{CO})_3(\text{PPh}_3)(\text{COCF}_3)$

The reduction of  $\text{Co}(\text{CO})_3(\text{PPh}_3)(\text{COCF}_3)$  produces a  $19e^-$  anion which rapidly dissociates either the  $\text{PPh}_3$  or one of the CO ligands. The resulting  $17e^-$  anion undergoes one-electron reductive elimination of  $\text{CF}_3$  to restore the metal center to an  $18e^-$  configuration as  $[\text{Co}(\text{CO})_3\text{L}]^-$ . The  $\text{CF}_3$  may be trapped by  $\text{Bu}_3\text{SnH}$  or benzophenone anion.

**Pablo J. Alonso, Juan Forniés, M<sup>a</sup> Angeles García-Monforte, Antonio Martín, Babil Menjón, Conrado Rillo***J. Organomet. Chem.* 692 (2007) 3236

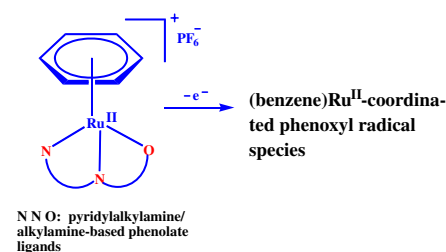
Synthesis and characterization of new paramagnetic tetraaryl derivatives of chromium and molybdenum

The highly unsaturated (10 valence electrons) organochromium(IV) derivative  $[\text{Cr}^{\text{IV}}(\text{C}_6\text{H}_3\text{Cl}_2-2,6)_4]$  (**2**) has a slightly elongated tetrahedral structure. This compound is prepared by chemical oxidation of the organochromate(III) salt  $[\text{Li}(\text{thf})_4][\text{Cr}^{\text{III}}(\text{C}_6\text{H}_3\text{Cl}_2-2,6)_4]$  (**1**). This  $[\text{Cr}^{\text{IV}}\text{R}_4]/[\text{Cr}^{\text{III}}\text{R}_4]^-$  couple is electrochemically related by a one-electron exchange process ( $E_{1/2} = 0.16$  V).

**Haritosh Mishra, Rabindranath Mukherjee***J. Organomet. Chem.* 692 (2007) 3248

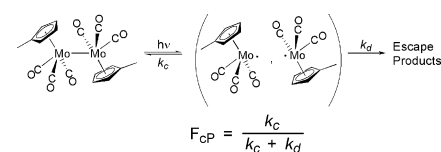
Half-sandwich  $\eta^6$ -benzene  $\text{Ru}(\text{II})$  complexes of phenolate-based pyridylalkylamine/alkylamine ligands: Synthesis, structure, and stabilization of one-electron oxidized species

Systematic comparative studies (X-ray and  $^1\text{H}$  NMR) have been made on “piano-stool” complexes of  $\text{Ru}(\text{II})$  with four tridentate ligands [4-nitro-6-(((2'-(pyridin-2-yl)ethyl)methylamino)methyl)-phenol, 2,4-di-*tert*-butyl-6-(((2'-(pyridin-2-yl)ethyl)methylamino)methyl)-phenol, 2,4-di-*tert*-butyl-6-(((2'-(pyridin-2-yl)benzyl-amino)methyl)-phenol, and 2,4-di-*tert*-butyl-6-(((2'-dimethylamino-ethyl)methylamino-methyl)-phenol)]. Structural studies reveal extensive non-covalent interactions. Coulometrically one-electron oxidized  $\text{Ru}^{\text{II}}$ -coordinated phenoxyl radical species have been characterized by cyclic voltammetry, UV–Vis, and EPR spectroscopy.

**John D. Harris, Alan B. Oelkers, David R. Tyler***J. Organomet. Chem.* 692 (2007) 3261

Microviscosity and wavelength effects on radical cage pair recombination

This study probed the reactivity of geminate radical cage pairs formed by photolysis of  $\text{Cp}'_2\text{Mo}_2(\text{CO})_6$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ). The effect of polymer additives on the relationship between bulk viscosity and the cage recombination efficiencies ( $F_{\text{cP}}$ ) and the effect of wavelength on  $F_{\text{cP}}$  were examined.

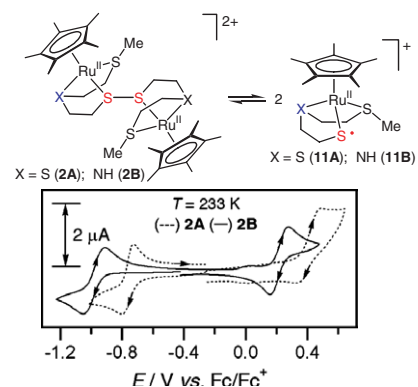


**Richard Yee Cheong Shin, Hui Shan Sim,  
Lai Yoong Goh, Richard D. Webster**

*J. Organomet. Chem.* 692 (2007) 3267

Sulfur-alkylation-initiated Cp<sup>\*</sup>Ru thiyyl radicals

The sulfur-centered chemistry of Cp<sup>\*</sup>Ru(III)L (L = [S(CH<sub>2</sub>CH<sub>2</sub>S<sup>-</sup>)<sub>2</sub>] and [HN(CH<sub>2</sub>CH<sub>2</sub>S<sup>-</sup>)<sub>2</sub>]) is dominated by redox interactions, initiated by alkylation and iodine oxidation. The Ru thiyyl radicals so generated led to S-S coupling reactions, and the facile reversible homolytic dissociation of the S-S bond, substantiated by electrochemical data, contributed significantly to the rich chemistry of these systems.

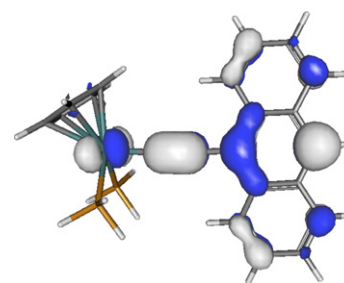


**Mark A. Fox, Rachel L. Roberts,  
Wan M. Khairul, František Hartl, Paul J. Low**

*J. Organomet. Chem.* 692 (2007) 3277

Spectroscopic properties and electronic structures of 17-electron half-sandwich ruthenium acetylide complexes, [Ru(C≡CAr)-(L<sub>2</sub>)Cp<sup>\*</sup>]<sup>+</sup> (Ar = phenyl, *p*-tolyl, 1-naphthyl, 9-anthryl; L<sub>2</sub> = (PPh<sub>3</sub>)<sub>2</sub>, Cp' = Cp; L<sub>2</sub> = dppe; Cp' = Cp<sup>\*</sup>)

One electron oxidation of [Ru(C≡CAr)-(dppe)Cp<sup>\*</sup>] affords radical cations, observable by spectroelectrochemical methods. The NIR bands observed are generally attributed to transitions between orbitals which offer significant metal and ethynyl character. In the case of 9-ethynylantracene derivatives the large anthracene character of the frontier orbitals prompts description as an anthryl radical.

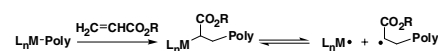


**Ayusman Sen, Sachin Borkar**

*J. Organomet. Chem.* 692 (2007) 3291

Perspective on metal-mediated polar monomer/alkene copolymerization

The preferred 2,1-insertion of acrylates into metal-carbon bonds results in the placement of the ester group on the  $\alpha$ -carbon, making the metal-alkyl species particularly prone to homolysis because of the enhanced stability of the resultant alkyl radical. We suggest ways to circumvent this problem, for example forcing 1,2-insertion by imposing steric crowding at the metal. We also discuss the danger of relying on radical traps as probes for polymerization mechanism.



## Note

**William M. Volcheck, Derek A. Tocher,  
William E. Geiger**

*J. Organomet. Chem.* 692 (2007) 3300

Electrochemical reduction of Ru( $\eta^6$ -arene)( $\kappa^3$ -tris(pyrazolyl)methane) dicationic complexes

The ruthenium hexamethylbenzene tris(pyrazolyl)methane (TPM) complex [Ru( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)( $\kappa^3$ -HCPz<sub>3</sub>)]<sup>2+</sup> undergoes a one-electron reduction ( $E_{1/2} = -1.46$  V vs. ferrocene in acetone/0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]) to a 19-electron complex which undergoes radical reactions at the arene ligand. The primary product is a dimer dication, coupled at the aryl groups, which can be anodically oxidized back to the original 18-electron complex.

